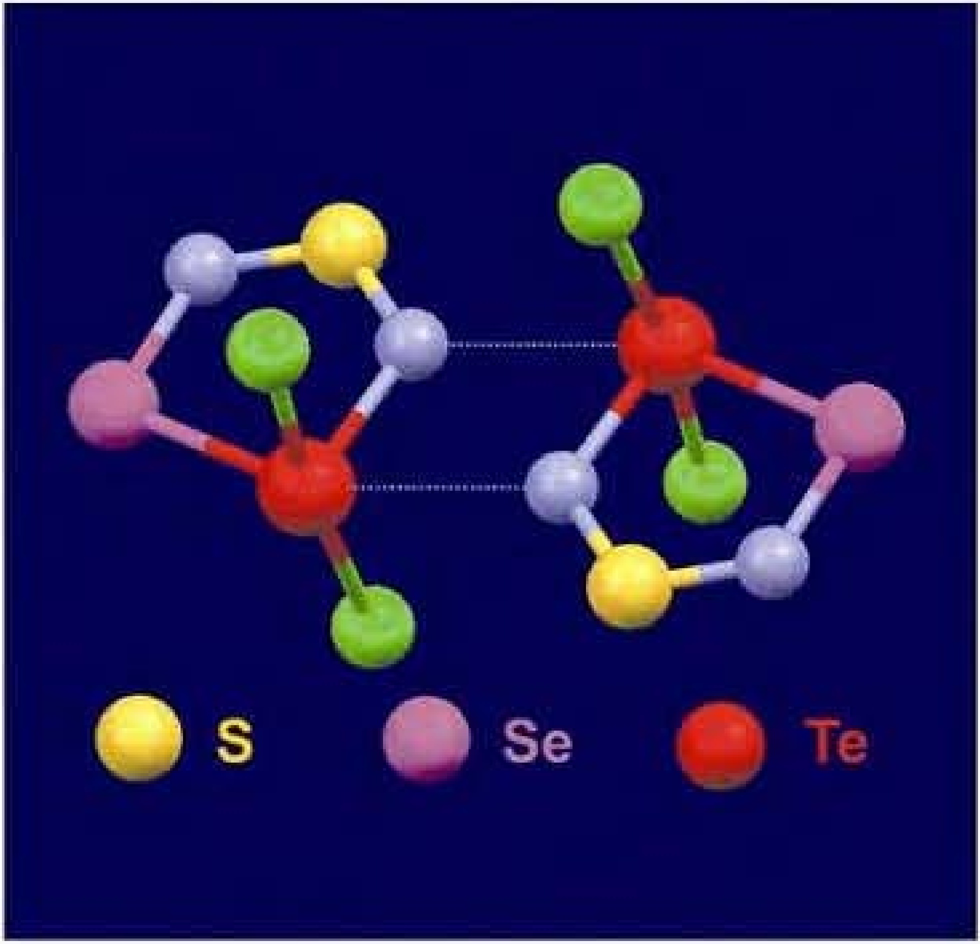
Edited by Francesco A Devillanova

Handbook of Chalcogen Chemistry

New Perspectives in Sulfur, Selenium and Tellurium



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New Perspectives in Sulfur, Selenium and Tellurium

To my delightful
grandchildren
Francesco and Silvia

Handbook of Chalcogen Chemistry

New Perspectives in Sulfur, Selenium and Tellurium

Edited by

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Preface

Up to a few decades ago, chalcogen chemistry was centred almost exclusively on sulfur, selenium being marginal compared to it and the chemistry of tellurium being practically inexistent. For many years the chemistry of Se and Te has grown rapidly: this is easily seen with an electronic search on SCIfinder comparing 1941–1950 and 1991–2000 and using as entries "sulfur/selenium/tellurium compounds". The percentage of papers on Se/Te rises from 13.4% (on a total 335 papers) for the former period to 27.7% (on a total 1905 papers) for the latter. A number of factors have contributed to this increase in the interest in the chemistry of Se and Te. One is the development of new suitable synthetic methodologies that avoid the use of obnoxious reagents (CSe_2, H_2Se, *etc.*), but most importantly the great variety of technological applications that can be found for their many compounds. To this purpose I would like to recall that compounds from the class of the charge-transfer salts of chalcogen-rich molecules, such as tetrathiafulvalene (TTF), or from that of 1,2-dichalcogenolenes, or the variegated area of metal chalcogenides are extremely important in Materials Science for their potential applications, which span from *n*-dimensional molecular conductors to magnets, to bistable switchable materials, and to NLO materials, to quote only a few. Further examples of this increasing trend, which is always of great topical interest, are the fundamental research works in the field of coordination chemistry with a large variety of ligands containing chalcogen atoms for the preparation of new precursors for metal–chalcogenide vapour deposition, of metalloenzymes containing multimetallic centres as active sites for a number of catalytic reactions, or of chalcogen-containing mixed macrocycles with signalling functional groups as sensors for heavy metal-ion recognition, and so forth.

The simplest way of organizing a handbook that contained an incredible amount of results from research on chalcogen chemistry while avoiding to omit important topics appeared to me that of considering the chemistry of chalcogen elements in combination with all other elements of the periodic table. On the other hand, an ambitious purpose of the book was to point out the increasing role of chalcogen elements in multidisciplinar fields such as biochemistry and materials science. For these reasons, the *Handbook of Chalcogen (S, Se, Te) Chemistry* was structured on a multidisciplinary approach by putting together contributions ranging from organic to inorganic and analytical chemistry, synthetic to structural and theoretical chemistry, biological to material and supramolecular chemistry. It was then divided into two parts: in the first of these the chapters are identified by the elements that are bonded to the chalcogen atoms, from boron to the halogens, including the chalcogens themselves. The overview ends with two chapters on metal–chalcogenides and metal–polychalcogenides. The second part of the book includes peculiar aspects of chalcogen chemistry that represent attractive fields of research in biological, materials and supramolecular chemistry, as well as a few miscellaneous chapters on particular topics. When different leitmotivs are considered in organizing the same subject matter, one still runs the risk of overlaps among the different chapters even though great care is devoted to avoid this negative aspect. There is one positive aspect, however, which outbalances the negative one: *i.e.*, the two parts are strictly interrelated, since the chapters in the second part are further developments of those in the first part. Thus, the chapter on the chalcogen–nitrogen bond (Chapter 4) has its counterpart in the one on stable radicals (Chapter 12.1), where it is clearly shown that fundamental research on chalcogen–nitrogen compounds can open unthinkable perspectives for the use of organic radicals in building magnetic materials. Similarly, the chapters on the chalcogenolate (Chapter 2.1) and 1,1-dichalcogenate (Chapter 10.2) ligands show that their coordination chemistry is always topical and widely exploited for potential applications in many different fields, such as that of preparing enzyme mimetic models (Chapter 11.2). The chapters on chalcogen-rich donors (Chapter 12.2) and on dithiolenes (Chapter 12.3) can be considered a continuation of those on chalcogen–carbon compounds: many compounds of both classes have found a large number of technological applications thanks to their conducting, magnetic, and optical properties. For this reason, both classes of compounds have strongly contributed to the increasing interest in chalcogen chemistry. In the same way, some important technological applications that have been found for a number of metal chalcogenides (Chapter 9.1) and polychalcogenides (Chapter 9.2) together with their remarkable diversity in their structure and properties have been the driving force of the incredible expansion of these areas of research. The ability of chalcogen elements to catenate is responsible for the great variety of molecular forms of chalcogen elements, of their cations (Chapter 7.1) and anions (Chapter 9.2), of their organic di- and poly-chalcogenides, and of their organic multication species (Chapter 7.2). Finally, the chalcogen-halogen compounds, both binary (Chapter 8.1) and those that derive from reactions of a variety of chalcogen-containing donors with halogens/interhalogens (Chapter 8.2), which are extensively dealt with in the first part of the book, appear consistently in the second part, as they provide interesting examples of hypervalency of the chalcogen elements (Chapter 10.3) and represent attractive examples of supramolecular structures (Chapter 13) built thanks to the ability of chalcogen-halogen bonds to give directional secondary bonds, in competition with other interactions (hydrogen bonding, dipole-dipole interactions, *etc.*).

Though not exhaustive, the book includes mainly the results of the last decade and illustrates the tendencies of the most appealing research work. Particular attention has been paid by the authors to update the literature almost up to the end of 2005.

The book is a candidate to become a reference book for future years. The multidisciplinary approach, with chapters reserved to biological, materials, and supramolecular chemistry, presents the book as an important source of information not only for chemists but also for physicists, biochemists, and other researchers, who in some way deal with chalcogen compounds. I hope the book may induce some curiosity in the reader and attract him towards this kind of chemistry.

I am greatly indebted to all authors for their commitment and to my collaborators for useful discussions.

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HALOGEN–CHALCOGEN X–E (X=F, Cl, Br, I; E=S, Se,Te) CHEMISTRY

METAL CHALCOGENIDES

BIOLOGICAL CHEMISTRY

MATERIAL CHEMISTRY

SUPRAMOLECULAR CHEMISTRY

CHAPTER 1

Compounds Containing the Boron–Chalcogen B–E (E=S, Se, Te) Bond

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1.1 Introduction

This chapter focusses on compounds with chalcogen (E=S, Se, Te) to B bonds and reviews the chemical literature over the period 1990–2004. Although every effort has been made to include all important advances in all sections, the review is not claimed to be comprehensive. The literature has been surveyed principally by independent keyword searches of the primary chemical journals and *ISI Web of Science* augmented by *ACS Chemical Abstracts* and RSC *Annual Reports on the Progress of chemistry, Section A (Inorganic Chemistry).* The review is structured so that relevant books, conference proceedings, and review articles that have appeared over the period are described first, and then the chemistry of specific topics are explored in more detail. Polyhedral boron hydride cluster species forms a major section of this review and this section is conveniently divided into sub-sections depending upon the nature of the B–E linkages. The remaining principal sections of this review cover two other important themes: heterocycles containing B–E linkages, and thioborate and selenoborate chemistry. The review concludes with a miscellaneous section, which includes B–E reagents.

1.2 Books and Review Articles

Sections relating to compounds with B–E bonds can be found in the authoritative review chapters found in *Comprehensive Organometallic Chemistry II* (vol 1); these chapters generally survey the literature over the period 1982–1994. In particular, Chapter 4 has a section reporting on cyclic systems with B–E

(E=S, Se) bonds,[1] and Chapter 7 surveys main group heteroboranes, with a section on thiaboranes and their metal complexes.[2] Metalloboranes, carboranes, and metallocarboranes are reviewed in Chapters 8, 6, and 9, respectively, with many such clusters containing *exo* B–E bonds.[3–5] The 'International Meeting on Boron Chemistry' (IMEBORON) has met on a number of occasions over the review period and the proceedings of these conferences have been published; these collections give an interesting perspective on the development of boron chemistry in general but with many relevant articles.[6] A review on chalcogenoboron hydrides was published in 1997 giving a historical viewpoint and covering the literature to 1997.[7] An overview of heteroboranes in which p-block elements (including S, Se, and Te) have replaced one or more vertices in parent borane cages was reported in 2002.[8] The topic of thioborate and selenoborates have been reviewed on a number of occasions,[9–11] with the most recent[12] in 2003 discussing their diverse structures, which range from rings, through clusters to 3d networks.

1.3 Polyhedral Boron Hydride Derivatives

1.3.1 Species with *Exo* B–Chalcogen Bonds

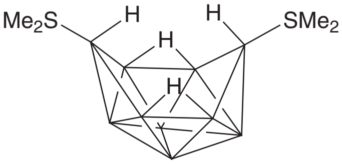
1.3.1.1 Boranes and Heteroboranes

There were a considerable number of reports over the period 1990–2004 on polyhedral boron hydride species with *exo*-chalcogen bonds and the following section is structured in terms of increasing polyhedral size. There were also a few reports on polyhedral carborane species, which are at the end of this section, but there were no reports on other heteroborane species with *exo*-chalcogen bonds.

$Na[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]$ was obtained from reaction of NaSH with BH_3.thf,[13] and $Na_2[H_3BSe_2BH_3]$, produced by the reaction of elemental Se with $Na[BH_4]$, was found to react with excess B_2H_6 to form the related salt $Na[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]$.[14] Bi-functional thiols (HSRSH, R=CH_2, CH_2CH_2, $CH_2CH_2CH_2$, 1,2-C_6H_4) were found to react with B_4H_{10} to afford *trans*-annularly bridged species *e.g. cis*- and *trans*-$[(BH_2)(\mu_2\text{-SRS})(BH)(B_2H_5)]$. Upon cooling a fully reversible rearrangement occurred and a 'butterfly'-type structure, $[(BH_2)(\mu_2\text{-SRS})(B_3H_6)]$ was obtained, again as a mixture of *cis* and *trans* isomers.[15] The adduct, $B_3H_7(SMe_2)$ (**1**) which was isolated as a liquid at room temperature, reacted slowly with additional SMe_2 to yield B_5H_9 with the mechanism of this borane framework expansion believed to involve the diborane(4) adduct, $B_2H_4(SMe_2)_2$.[16] The reaction of **1** with excess NMe_3 in Me_2S at low temperature (−80–−30 °C) led to $B_2H_4(NMe_3)_2$, but the ligand-exchanged adduct $B_3H_7(NMe_3)$ was shown not to be an intermediate in this reaction.[17] Treatment of **1** with BCl_3 yielded the chloro-substituted derivative $B_3H_6Cl(SMe_2)$.[18] Reactions of B_5H_{11} and Me_2S produced $B_4H_8(SMe_2)$ (**2**) and an unstable pentaborane adduct, $B_5H_{11}(SMe_2)$, which was shown to be a precursor to the tetraborane adduct, **2**.[19] The *closo* anion $[B_6H_6]^{2-}$ was found to react with $(SeCN)_2$ in organic media to produce $[PPh_4]_2[(SeCN)B_6H_5]$, characterized by single-crystal X-ray diffraction (XRD) studies.[20] Treatment of $[NBu_4][B_6H_7]$ with $(SCN)_2$ or $(SeCN)_2$ in dichloromethane solution in the presence of solid KOH resulted in the hexaborate species $[NBu_4]_2[B_6(ECN)_6]$ (E=S, Se).[21] The conventional preparation of 4-(L)-*arachno*-B_9H_{13} derivatives, by ligand exchange on 4-(SMe_2)-*arachno*-B_9H_{13}, was shown by NMR spectroscopy to also generate the previously unreported isomeric species 5-(L)-*arachno*-B_9H_{13}.[22]

A series of mono- and di-substituted Me_2S derivatives were obtained from the reaction of DMSO in acid with $Cs_2[B_{10}H_{10}]$, and through a modified procedure the tri-substituted 1,10-$(Me_2S)_2$-2-$(MeS)B_{10}H_7$ species was obtained.[23] The *closo* anion $[B_{10}H_{10}]^{2-}$ was found to react with $(SeCN)_2$ in organic media and produced $[PPh_4]_2[(SeCN)B_{10}H_9]$ characterized by single-crystal XRD studies.[20]

The hydroboration of alkenes with 6,9-$(SMe_2)_2B_{10}H_{12}$ (**3**) yielded 6-R-8-(SMe_2)-$B_{10}H_{11}$ (R=Pr^n, oct^n, hex^n, 3-methyl-2-butyl, 2,3-dimethyl-2-butyl), which was converted to the corresponding alkyl derivative, 6-R-$B_{10}H_{13}$, by treatment with 'super-hydride' ($LiEt_3BH$/thf).[24] Mechanistic experiments on the formation of **3** from *nido*-$B_{10}H_{14}$ and its subsequent reaction with 2,3-dimethylbut-2-ene to form *nido*-5-(Me_2S)-9-$(CMe_2CHMe_2)B_{10}H_{11}$ indicated that the movement of the Me_2S from B6 to B5 did not involve a concerted rearrangement of the boron cage, but rather a migration of H and Me_2S on an otherwise static borane cluster.[25] A high yield route to *nido*-6-alkyl decarborane(14) derivatives starting from **3** *via* a one-pot synthesis was reported with XRD results described for *nido*-6-(CMe_2CHMe_2)-8-$(SMe_2)B_{10}H_{11}$ (Scheme 1).[26]



3

Scheme 1

Compound **3** reacted with the phosphaalkyne PC^{t}Bu to form a product with two B_{10} cages linked by a HPCBu^t bridge, $[B_{10}H_{11}(SMe_2)][CBu^tPH][B_{10}H_{12}]$.[27] The mild thermolysis of **3** in inert hydrocarbon solvents gave the tridecaboranyl species, 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{10}$-1,5-(6′-*nido*-$B_{10}H_{13})_2$ (**4**) in 23% yield (Figure 1).[28] The reaction of Me_2Se_2 with *nido*-$B_{10}H_{14}$ yielded *arachno*-6,7-μ-$(MeSe)B_{10}H_{13}$, whereas Me_2S_2 failed to react under similar conditions; however, the analogous thiomethyl derivative, 6,7-μ-$(MeS)B_{10}H_{13}$, was formed by the reaction of *nido*-$B_{10}H_{14}$ with Me_2S_3.[29] The kinetics of *ortho*-$C_2B_{10}H_{12}$ formation from acetylenes (propargyl bromide, but-2-yne-1,4-diacetate, or non-1-yne) and *arachno*-6,9-$B_{10}H_{12}L_2$ [L=Me_2S (**3**), Ph_2S, $Bu^t{}_2S$, $(C_6F_5)_2S$,

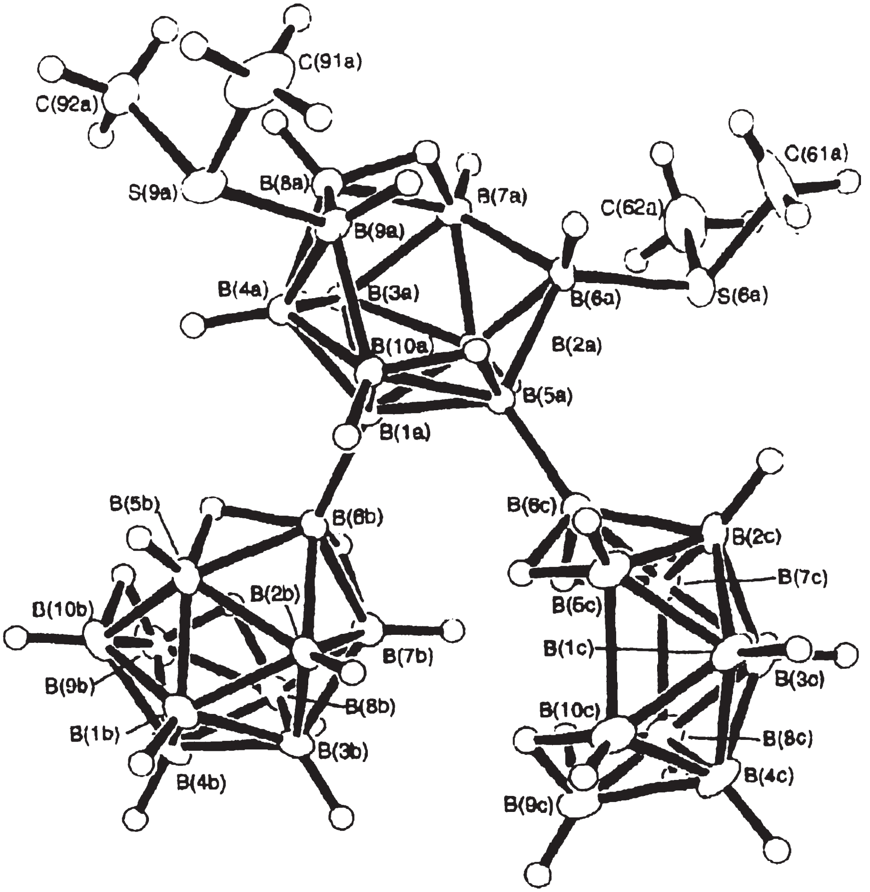
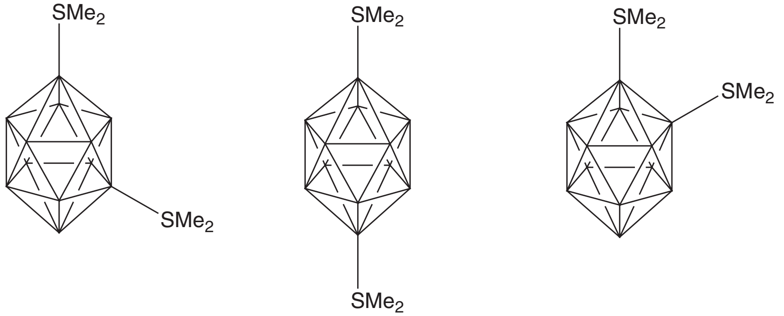


Figure 1 *Molecular structure of 6,9-*$(SMe_2)_2$*-arachno-*$B_{10}H_{10}$*-1,5-(6′-nido-*$B_{10}H_{13})_2$ *(***4***)*
(Reproduced with permission from Chem. Commun., 2001, 1788.)

MePhS, $Me(C_6F_5)S$, or $MeBu^tS$] have been investigated in detail: the rate constants decreased both with increased electronegativity and/or increased size of the substituent on S, with the yield increased as the size and/or basicity of the Lewis base increased.[30]

Excess H_2SO_4 and Me_2S were found to react with $[Me_3NH][B_{11}H_{14}]$ to yield 7-(SMe_2)-$B_{11}H_{13}$ in good yield; upon warming to 110 °C, the adduct rearranged to a mixture of 1- and 7-isomers.[31]

A one-step preparation of the Me_2S-substituted icosahedral boranes 1,7-$(SMe_2)_2B_{12}H_{10}$ (**5**), 1,12-$(SMe_2)_2B_{12}H_{10}$ (**6**), and $[SMe_3][B_{12}H_{11}(SMe_2)]$ has been reported from the self-condensation reaction of $BH_3.SMe_2$.[32] The 1,2-isomer, 1,2-$(Me_2S)_2B_{12}H_{10}$ (**7**) obtained from a mixture of products from the pyrolysis of $BH_3.SMe_2$ was characterized by XRD and multinuclear NMR, and its spectral characteristics were compared with earlier reported **5** and **6** derivatives (Scheme 2).[33] The reaction of $[PdCl_2(SMe_2)_2]$ with $Li_2[B_{12}H_{12}]$ at room temperature also resulted in **5** and **6**.[34] Two series of compounds 9-X-1,7-$(Me_2S)_2B_{12}H_9$ and 9,10-X_2-1,7-$(Me_2S)_2B_{12}H_8$ (X=Cl, Br, I) have been prepared from **5** with various halogenating reagents, and the reaction of **5** with PhSeBr and 2,4-$(NO_2)_2C_6H_3SCl$ afforded 9,10-$(PhSe)_2$-1,7-$(Me_2S)_2B_{12}H_8$ and 9-{2,4-$(NO_2)_2C_6H_3S$}-1,7-$(Me_2S)_2B_{12}H_9$, respectively.[35] The reaction of potassium phthalimide in DMF, or NaSEt in EtOH/CH_3CN, with either the **5**, **6**, or **7** produced the corresponding isomers of the anion $[(MeS)(Me_2S)B_{12}H_{10}]^-$; if excess nucleophile was used, then the dianion $[(MeS)_2B_{12}H_{10}]^{2-}$ was produced.[36] The anions $[(Me_2S)B_{12}H_{11}]^-$ and $[(MeS)B_{12}H_{11}]^{2-}$ and **5**, **6**, and **7** were reduced by excess lithium in methylamine at −15 °C to $[(HS)B_{12}H_{11}]^{2-}$ and the dithiols, $[(HS)_2B_{12}H_{10}]^{2-}$.[37] A variety of *S*-alkylated products were obtained from alkylation of the methylthioethers $[(MeS)B_{12}H_{11}]^{2-}$, [1-(MeS)-2-(or 7 or 12)-$(Me_2S)B_{12}H_{10}]^-$, and [1,2-(or 7,12)-$(MeS)_2B_{12}H_{10}]^{2-}$.[38] $[PPh_4]_2[(ECN)B_{12}H_{11}]$ (E=S, Se) have been reported[20,39] with the sulfur compound characterized by XRD.



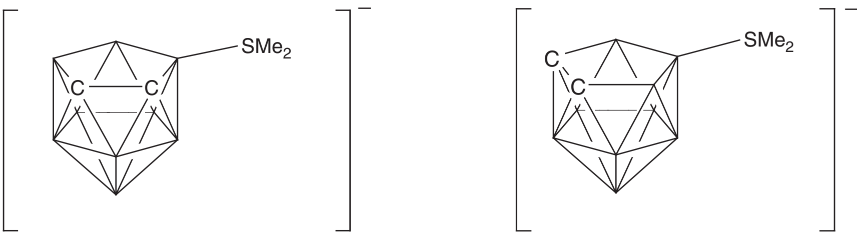
5 **6** **7**

Scheme 2

The regiospecific cluster degradation of *closo*-1,2-$C_2B_{10}H_{12}$ in the presence of SMe_2 proceeded *via* the *nido*-$[7,9\text{-}C_2B_{10}H_{13}]^-$ intermediate and afforded *exo*-6-(SMe_2)-*arachno*-4-CB_8H_{12}.[40] The synthesis and characterization of a three carborane derivatives, 10-(SEtPh)-7,8-$C_2B_9H_{11}$, 7-Me-10-(SMe_2)-7,8-$C_2B_9H_{10}$, 7-Me-10-(SEt_2)-7,8-$C_2B_9H_{10}$, along with enhanced characterization of some related compounds *e.g.* 10-(SR_2)-7,8-$C_2B_9H_{11}$ (R_2=Me_2, Et_2, $\{CH_2\}_4$) have been reported.[41]

1.3.1.2 Metalloboranes and Metalloheteroboranes

In constrast to the previous section, the literature in this area over the period of the review was dominated by metalloheteroborane (mainly metallocarborane) chemistry, narrowly focussed on 'charge-compensated' carbollide $\{C_2B_9H_{10}L\}^-$ derivatives, with relatively few examples of metalloboranes. In these charge-compensated derivatives, the *nido* 11-vertex $\{C_2B_9\}$ carbollide (1-) anion is coordinated η^5 to a metal centre and in the process forms an icosahedral *closo* 12-vertex $\{MC_2B_9\}$ cluster.



8 **9**

Scheme 3

The chemistry of monoanionic carborane ligands has been investigated by exploring the conformation adopted by formal two-orbital metal cluster bonding contributors by reactions of Tl[9-(SMe_2)-*nido*-7,8-$C_2B_9H_{10}$] (Tl**8**) with complexes of Rh(I) and Pd(II).[42] The synthesis and structure of the ferracarborane Fe**8**$_2$ and its charge transfer salt with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (**9**) has been reported with its magnetic properties discussed (Scheme 3).[43] The mixed-sandwich ferracarborane complex CpFe**8** has been synthesized and characterized by cyclic voltametry, IR, and ^{1}H and ^{11}B NMR spectroscopy; it formed stable 1:1 charge transfer salts with **9** and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane.[44] The complex [(cod)Rh**8**] has been used to prepare the halide complexes [{X_2Rh**8**}$_2$] (X=Cl, Br, I) by reaction with HX.[45] These complexes have been further used to prepare several sandwich and half-sandwich complexes containing the 'Rh**8**' fragment.[45] The reaction of **8** with [{(arene)$RuCl_2$}$_2$] (arene=C_6H_6, 1,3,5-$C_6H_3Me_3$) afforded the cationic ruthenium arene cluster complexes [(arene)Ru**8**][BF_4].[46] Reaction of [{$RuCl_2(C_6H_6)$}$_2$] with [10-(Me_2S)-7,8-*nido*-$C_2B_9H_{10}$]$^-$ (**10**) afforded the expected cationic complex [(C_6H_6)Ru**10**]$^+$ and the unexpected neutral complex [(C_6H_6)Ru{10-(HS)-7,8-*nido*-$C_2B_9H_{10}$}].[47] Ruthenacarborane clusters of the formula [3,3,3-H$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_{10}$] (L=SMe_2, SEt_2, $S(CH_2)_4$, SEtPh) and [1-Me-3,3,3-H$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_9$] (L=SMe_2, SEt_2) were prepared by the reaction of the corresponding ligands with [$RuCl_2(PPh_3)_3$].[48] A series of {$(PPh_3)_2Rh^{(I)}$} fragment half-sandwich complexes were similarly prepared by reaction of these charge-compensated ligands with [$RhCl(PPh_3)_3$].[49] Ruthenium complexes with monoanionic carborane ligands *e.g.* [$RuH(PPh_3)_3$**8**], [$RuH(PPh_3)_3${9-(SR_2)-7-Me-7,8-$C_2B_9H_9$}], have been shown to efficiently catalyze the Kharasch addition of CCl_4 across olefins.[50] The cluster substitution product, [$Mo(CO)_2(\eta^3$-$C_3H_5)${(7,8-Me_2-7,8-$C_2B_9H_8$-10-(SMe_2)}], was obtained from treatment of the salt [NEt_4][$Mo(CO)_2(\eta^3$-$C_3H_5)$(7,8-Me_2-7,8-$C_2B_9H_9$)] with [CPh_3][BF_4] and SMe_2 in CH_2Cl_2.[51] Three dialkylsulfane-substituted *nido* carboranes 7,8-Ph_2-10-(SR_2)-7,8-*nido*-$C_2B_9H_{10}$

(R_2=Me_2, Me/Et, Et_2) have been synthesized and characterized and the SMe_2-labelled B atoms gave useful stereochemical information on the course of 12-vertex MC_2B_9 isomerizations.[52] The synthesis and reactivity of the sterically encumbered charge-compensated carborane 7-Ph-11-(SMe_2)-*nido*-$C_2B_9H_{10}$ and its conversion to [1-Ph-3,3-$(CO)_2$-7-(SMe_2)-3,1,2-*closo*-$RhC_2B_9H_8$] has been described.[53]

The donor molecule Me_2S reacted with the anion $[Fe(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ in the presence of acids and hydride-abstracting reagents and gave the zwitterionic complex $[Fe(CO)_3(\eta^5\text{-}9\text{-}(SMe_2)\text{-}7\text{-}CB_{10}H_{11})]$ in which the SMe_2 was bound to a B atom lying in a β site with respect to the C.[54] Reaction of the monocarborane derivative $[Pt_2(PEt_3)_4(\eta^5{:}\eta^5\text{-}9,9\text{-}I(H)\text{-}7\text{-}CB_{10}H_{10})_2]$ with PhSeCl, Ph_2Se_2, and PhTeI yielded products with chalcogen substituents on Pt, or Pt and B.[55]

The electronically saturated chromaborane $[Cp^*_2Cr_2B_4H_8]$, when reacted with CS_2, produced in high yield the saturated cluster $[Cp^*_2Cr_2(CH_2S_2)B_4H_6]$ (**11**), which contained the intracluster bridging methanedithiolato $\{CH_2S_2\}$ ligand (Figure 2).[56] The reaction of CS_2 with the open *nido*-6-iridadecaboranes $[H(PPh_3)_2\text{-}\textit{nido}\text{-}6\text{-}IrB_9H_{13}]$ and $[H(PPh_3)(\textit{ortho}\text{-}Ph_2P\overline{C_6H_4)\text{-}\textit{nido}\text{-}6\text{-}IrB}_9H_{12}\text{-}5]$ yielded *closo* 10-vertex species with boron to metal dithioformate bridges.[57] The *isocloso* species $[1,1,1\text{-}H(PPh_3)(\textit{ortho}\text{-}Ph_2P\overline{C_6H_4)\text{-}\textit{isocloso}\text{-}1\text{-}IrB}_9H_8\text{-}2]$ reacted similarly and produced the *closo* species $[10\text{-}(PPh_3)\text{-}2,6{:}2,9\text{-}(\mu\text{-}S_2CH_2)_2\text{-}2\text{-}(\textit{ortho}\text{-}Ph_2P\overline{C_6H_4)\text{-}\textit{closo}\text{-}2\text{-}Ir\text{-}B}_9H_5\text{-}1]$ with an unusual *isocloso* → *closo* conversion.[57]

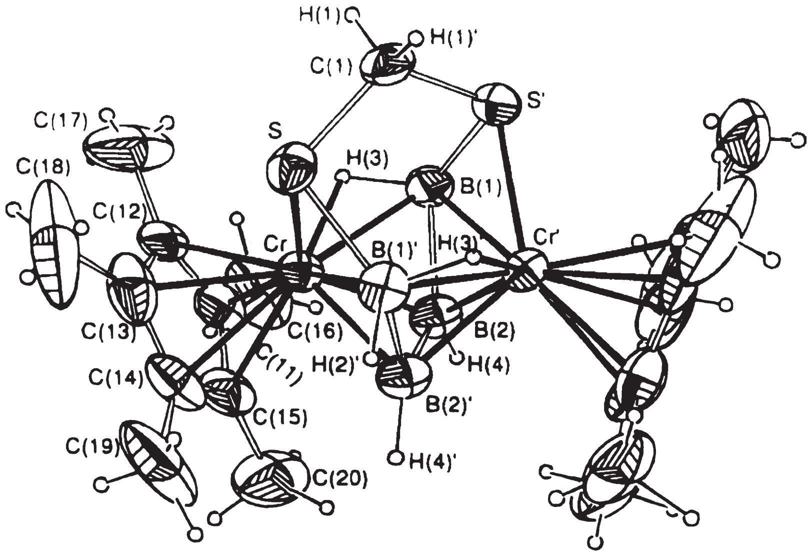


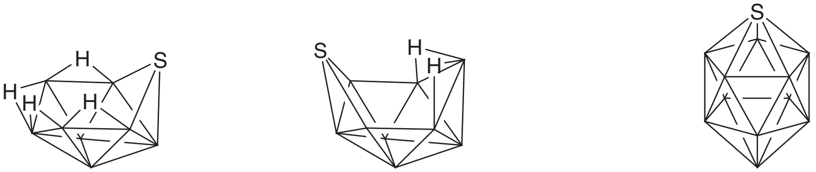
Figure 2 *Molecular structure of* $[Cp^*_2Cr_2(CH_2S_2)B_4H_6]$ (**11**)
(Reproduced with permission from Organometallics, 1996, **15**, 1964.)

1.3.2 Species with Chalcogen Atoms within the Cage

1.3.2.1 Chalcogenoboranes

This important area of boron–chalcogen chemistry has made some tremendous advances, particulary in macropolyhedral systems, in recent years. The topic was recently reviewed[7,8] in 1997 and 2002. This section is again ordered in increasing numbers of boron atoms within the cage.

A series of *exo*-6-(L)-*arachno*-4-SB_8H_{10} adducts (L=SMe_2 (**12**) PPh_3, MeCN, NMe_3, py, urotropine, MeNC, quin) have been prepared from *arachno*-4-SB_8H_{12} (**13**) and the corresponding Lewis bases with the X-ray structures of three representative examples (L=urotropine, 1/2urotropine, MeNC) reported (Scheme 4).[58] The thianonaborane anion *nido*-$[9\text{-}SB_8H_9]^-$ was prepared by deprotonation of **12** with Na metal or NaH; the reaction was reversed by treatment of the product with Me_2S and CF_3COOH.[59] Thermolysis of **13** in cyclohexane generated the 18-vertex macropolyhedral *anti*-9,9′-$S_2B_{16}H_{16}$ (**14**) in modest yield,[60] and mild thermolysis of **12** resulted in the formation of the macropolyhedral $S_2B_{17}H_{17}(SMe_2)$ (**15**) in low yield.[61] The structure of **15** is a conventional *nido*-type 11-vertex $\{SB_{10}H_9\}$ sub-cluster fused to an *arachno*-type 10-vertex $\{SB_9H_8(SMe_2)\}$ sub-cluster with two boron atoms in common.[61]



13 **16** **17**

Scheme 4

The microwave spectrum of 1-SB_9H_9 has been reported together with high-level *ab initio* and DFT calculations.[62] The reactions of *nido*-6-SB_9H_{11} (**16**) with imines and trimethylsilylazide have been investigated; the latter reagent gave the first examples of a new class of fused-ring cluster triazene-thiaborane, (μ_2-(4,*exo*-9)-1-$SiMe_3$-3-H-N_3)-*arachno*-6-SB_9H_{10}, in 42% yield.[63] *N*-^{t}butylformaldimine gave a unique zwitterionic compound, 9-($Bu^tNH_2CH_2$)-*nido*-6-SB_9H_9, which formed an adduct upon treatment with CH_3CN.[64] Reactions between **16** and Lewis bases (L) gave a series of corresponding *arachno* compounds, *exo*-9-(L)-*arachno*-6-SB_9H_{11} (L=NEt_3, quinoline, isoquinoline, urotropine, py, MeCN, MeNC, NH_3, SMe_2, PPh_3).[65] The compound *arachno*-9-(PPh_3)-6-SB_9H_{11} was obtained upon thermolytic decomposition of *arachno*-[*exo*-9-{Cl-*trans,cis*-$(PPh_3)_2H_2Ir$}-6-SB_9H_{11}].[66] The crystal structure of 9-(PCy_2Ph)-6-SB_9H_{11} has been determined and the cluster had the expected *arachno* 10-vertex $\{SB_9\}$ geometry with the phosphine substituent *exo*.[67] The structure of Cs[6-SB_9H_{12}] has been established by XRD studies.[66] Dehydrogenation of *arachno*-2-H-2,3-$S_2B_9H_{10}$

afforded the previously reported *nido*-7,9-$S_2B_9H_9$.[68] The structure of *nido*-$Se_2B_9H_9$ has been unambiguously determined as the 7,9-isomer using high-field ^{11}B NMR[69] and results from MNDO MO calculations of the $S_2B_9H_9$ thiaborane analogue have shown that all the 2c/2e bonds were localized around the $\{B_3S_2\}$ open face. The *arachno* dithiaborane cluster anion $[2,3\text{-}S_2B_9H_{10}]^-$ was obtained from the reaction of *nido*-$[6\text{-}SB_9H_{10}]^-$ anion with S_8, and reactions of this dithiaborane with MeI, CH_2I_2, and H_2SO_4 have been reported.[68] The *nido* 11-vertex thiaboranes $[7\text{-}SB_{10}H_{11}]^-$ and 7-$SB_{10}H_{12}$ were produced by synthetic sequences involving the reaction of SCl_2 with $B_{10}H_{14}$ followed by *in situ* dehydrohalogenation initiated by 'proton-sponge'.[70]

The UV–PES spectra of the thiaborane *nido*-7-$SB_{10}H_{12}$ has been reported and compared with spectra from more open thiacarboranes.[71] The previously known *nido*-$[7\text{-}SB_{10}H_{11}]^-$ anion was obtained in 45% yield from the reaction of S_8 with a solution of *anti*-$[B_{18}H_{20}]^{2-}$.[72]

The molecular structure of the *closo* 12-vertex 1-$SB_{11}H_{11}$ cluster (**17**) has been studied by electron diffraction methods augmented by *ab initio* calculations. Substantial distortions away from the regular icosahedron occurred by expansion of the pentagonal belt adjacent to sulfur.[73] The UV–PES spectra of **17** has also been reported,[71] and its microwave spectrum has been investigated and demonstrated that the molecule had C_{5v} symmetry.[74]

The18-vertex non-metallated adduct $S_2B_{16}H_{14}(PPh_3)$ was a coproduct in the reaction of $[NiBr_2(PPh_3)_2]$ with **14**.[75,76]

The reaction of metabisulfite with *syn*-$B_{18}H_{22}$ gave a good yield of the macropolyhedral thiaborane anion $[SB_{17}H_{19}]^-$, which exhibited an *arachno–nido* two-borons-in-common cluster-fusion mode.[77] The reaction of S_8 on a solution of *anti*-$[B_{18}H_{20}]^{2-}$ gave as the major product the macropolyhedral anion $[S_2B_{17}H_{18}]^-$ (**18**), isolated in 48% yield as its $[PPh_4]^+$ salt and characterized crystallographically.[72] The cluster structures of the macropolyhedral thiaborane **15** and thiaborane anion $[S_2B_{18}H_{19}]^-$ were investigated at the B3LYP/6-311 and G**//B3LYP/6-31G* density functional theory level.[78] The treatment of **18** with oxidizing acids quantitatively yielded $S_2B_{17}H_{17}$ characterized as its anion $[S_2B_{17}H_{16}]^-$.[79]

The double-cluster anion $[S_2B_{18}H_{19}]$ (**19**) (Figure 3) was prepared from the interaction of S_8 with $[syn\text{-}B_{18}H_{21}]^-$.[80]

1.3.2.2 Metallochalcogenoboranes

A series of new *arachno* and *hypho* metalladithiaborane clusters have been generated from the *hypho*-$[S_2B_6H_9]^-$ anion (**20**): reactions with $[\{(C_6Me_6)RuCl_2\}_2]$, $[Cp^*Co(CO)L]$, $[(dppe)NiCl_2]$, and $[(PMe_3)_2Rh(CO)Cl]$ have been reported and products, including *hypho*-$[1,1\text{-}(C_6Me_6)Cl\text{-}1,2,5\text{-}RuS_2B_6H_9]$ and *arachno*-$[7\text{-}(C_6Me_6)\text{-}7,6,8\text{-}RuS_2B_6H_8]$, were characterized by XRD studies.[81] A dimeric product $[\{Pd(PPh_3)(S_2B_6H_8)\}_2]$ was obtained from the attempted recrystallization of a product obtained from the reaction of $[PdCl_2(PMe_2Ph)_2]$

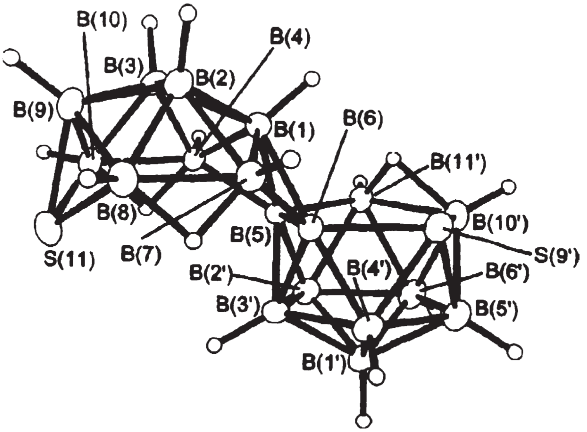


Figure 3 *Crystallographically determined structure of the anion* $[S_2B_{18}H_{19}]^-$ *(*__19__*)*
(Reproduced with permission from J. Chem. Soc., Dalton Trans., 1998, 2965.)

with **20**.[82] The molecular structure of the open 9-vertex cluster *arachno* [5,5-$(PMe_2Ph)_2$-4,6,5-$S_2PdB_6H_8$] has been established.[83]

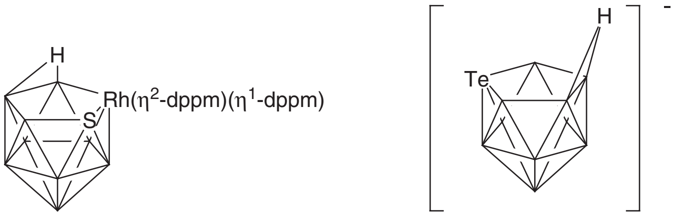
The synthesis, X-ray structure, and dynamic NMR properties of the *arachno* 10-vertex cluster [9,9-$(PMe_2Ph)_2$-9,6,8-$PtS_2B_7H_7$] has been reported; the compound was fluxional *via* a vertex flip of the {$Pt(PMe_2Ph)_2$} moiety.[84]

The formation of 9-, 10-, and 11-vertex metallathiaborane clusters, by insertion of the S atom into existing metalloborane frameworks, has been achieved for clusters containing eight boron atoms. Thus, the reaction of *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{12}$] with H_2S yielded *nido*-[2,2,2-$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$], *closo*-[2,2,2-$(PMe_3)_2$H-2,1-$IrSB_8H_8$, and *nido*-[$(PMe_3)(CO)$-$HIrS_2B_8H_8$].[85] The reaction of [$RhCl(PPh_3)_3$] with *arachno*-$[S_2B_9H_{10}]^-$ (**21**) yielded *nido*-[$(PPh_3)_2HRhS_2B_8H_8$],[86] while [{$(C_6Me_6)RuCl_2$}$_2$] reacted with *arachno*-[6-SB_9H_{12}]$^-$ (**22**) to yield *closo*-[2-(C_6Me_6)-2,1-$RuSB_8H_8$].[87] The platinathiaborane species [$(PMe_2Ph)_2PtSB_8H_{12}$] was obtained from [$PtMe_2(PMe_2Ph)_2$] with **13**.[88]

Reaction of [{(*p*-cymene)$RuCl_2$}$_2$] with **22** yielded *closo*-[2,3-(*p*-cymene)$_2$-2,3,1-$Ru_2SB_9H_9$] and [2,3-(*p*-cymene)$_2$-2,3,1-$Ru_2SB_9H_8Cl$-7], and the open *nido* species [7-(*p*-cymene)-7,8-$RuSB_9H_{10}Cl$-11].[87] The reaction of **16** with [{$IrCp^*Cl_2$}$_2$] yielded *nido*-[8-Cp*-8,7-$IrSB_9H_{11}$], whereas reaction with **22** yielded a mixture of products *e.g.* *nido*-[8-Cp*-8,7-$IrSB_9H_{10}$-Cl-9], *nido*-[8-Cp*-8,7-$IrSB_9H_{10}$-Cl-10], and *closo*-[1-Cp*-1,2-$IrSB_9H_9$].[66] The structure of *nido*-[8-Cp*-8,7-$IrSB_9H_{10}Cl$-9] was established by XRD studies.[66] Cs[6-SB_9H_{12}] reacted with Vaska's compound to afford *arachno*-[*exo*-9-{Cl-*trans,-cis*-$(PPh_3)_2H_2Ir$}-6-SB_9H_{11}][66] and with [$Rh(PPh_3)_3Cl$] at room temperature in ethanol solution to produce the orange air-stable compound [8,8-$(PPh_3)_2Cl$-8,7-$RhSB_9H_{10}$] in high yield.[89] This cluster's *nido* 11-vertex cage geometry was established by XRD studies and in solution it exhibited a fluxionality involving swinging the metal–ligand fragment from one side to the other of the {SB_9}

heteroborane cage.[89] The *nido* species [8,8,8-$(PMe_2Ph)_3$-8,7-$RhSB_9H_{10}$] was prepared in good yield by the addition of excess PMe_2Ph to [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$][90], and this crystal structure compared to that of [8,8-$(PPh_3)_2$-9-(EtO)-8,7-$RhSB_9H_9$].0.95CH_2Cl_2 showed that the addition of a third *exo* ligand on Rh had minimal effect on the cluster geometry.[91] The reaction of [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$] with CO resulted in [8,8,8-(CO)$(PPh_3)_2$-8,7-$RhSB_9H_{10}$] in quantitative yield and thermolysis of this *nido* species afforded a closed 11-vertex cluster [1,1,3-(CO)$(PPh_3)_2$-*closo*-1,2-$RhSB_9H_8$] in 46% yield.[92] The synthesis and solid-state structure of *nido*-[8,8-(dppe)-8,7-$RhSB_9H_{10}$].2CH_2Cl_2 has been reported. This 11-vertex {$RhSB_9$} polyhedron showed a gross *nido* icosahedral geometry while apparently possessing a cluster count more appropriate to a *closo* geometry; two one-electron agostic-type Rh–H–C interactions were proposed as a source of the additional electron pair.[93,94] Two new isoelectronic *nido* species [μ-9,10-(SMe)-8,8-$(PPh_3)_2$-8,7-$IrSB_9H_9$] and [μ-9,10-(SMe)-8-(η^4-Cp*H)-8,7-$IrSB_9H_9$] have been characterized by XRD studies.[95] The reactions of the unsaturated cluster [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] with bidentate phosphine ligands (dppm, dppe, dppp) have been studied and substitution of the two PPh_3 ligands occurred to give the related bidentate complexes and/or clusters with the bidentate phosphines ligands bridging.[96,97] The cluster [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-$RhSB_9H_{10}$] (**23**), containing a pendant PPh_2 group, reacted with BH_3.thf and gave the species [8,8-(η^2-dppm.BH_3)-*nido*-8,7-$RhSB_9H_{10}$] with a bidentate dppm.BH_3 ligand.[98] Compound **23** also reacted with [{MCp^*Cl_2}$_2$] (M=Rh, Ir) and gave bimetallic species.[99,100] The metal reagent [RhCl$(PPh)_3$] inserted into the quadrilateral face of the *isonido* 11-vertex cluster [1-(PPh_3)-1,3-(μ-dppm)-*isonido*-1,2-$RhSB_9H_8$] and yielded the icosahedral product [2,2,3-$(PPh_3)Cl_2$-2,3-(μ-Cl)-3,7-(μ-dppm)-*closo*-2,3,1-$Rh_2SB_9H_8$].[101] Reactions with [MCl$(PPh_3)_3$] (M=Rh, Ir) with **21** yielded *nido*-[$(PPh_3)_2HIrS_2B_9H_9$] and *nido*-[$(PPh_3)_2RhSB_9H_{11}$].[86]

A series of closed polyhedra {EMB_{10}} ((E=S, Se, or Te; M=Rh, Ru, Pd, Mo, Cu, or Pt) have been reported.[102–111] *Nido*-[7-$TeB_{10}H_{11}$]$^-$ (**24**) reacted with [{$RhCp^*Cl_2$}$_2$] in CH_2Cl_2 solution to give *closo*-[2-Cp*-1,2-$TeRhB_{10}H_{10}$] in moderate yield, and with [{Ru(η^6-arene)Cl_2}$_2$] (arene = 4-$MeC_6H_4{}^iPr$, or C_6H_6) to give *closo*-[2-(arene)-1,2-$TeRuB_{10}H_{10}$].[102] Both clusters were structurally characterized by XRD as closed {$TeMB_{10}$} polyhedra based on a distorted icosahedron with Te and M adjacent. The reaction of *closo*-[2,2,2-H$(PPh_3)_2$-1,2-$TeRhB_{10}H_{10}$] with metal carbonyl species (*e.g.* [$Os_3H_2(CO)_{10}$], [$Mo(CO)_6$]) led to the unexpected products: *closo*-[$(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}$] and [{*closo*-$(PPh_3)RhTeB_{10}H_{10}$}$_2$], which both contained two {$RhTeB_{10}$} cages.[103] The synthesis of a series of 12-vertex *closo* tellura- and selenapalladaborane cluster derivatives [2,2-$(PR_3)_2$-2,1-$PdEB_{10}H_{10}$] and [2,2-X(PPh_3)-2,1-$PdTeB_{10}H_9(PPh_3)$] (R_3 = Me_2Ph, $MePh_2$, Ph_3; E=Se, Te; X=Cl, Br, I, CN, SCN, O_2CMe) has been achieved starting from the *nido*-[7-$EB_{10}H_{11}$]$^-$ anions and appropriate Pd(II) complexes, or from [2,2-I(PPh_3)-2,1-$PdTeB_{10}H_9(PPh_3)$].[104] The reaction of [2,2-I(PPh_3)-2,1-$PdTeB_{10}H_9(PPh_3)$] with Ag[BF_4] in toluene/H_2O solution at room temperature led to a cationic cluster *closo*-[2,2-$(H_2O)(PPh_3)$-2,1-$PdTeB_{10}H_9(PPh_3)$][BF_4] in excellent yield and from which many cationic clusters were obtained by displacement of the coordinated H_2O by neutral donor ligands (CO, CN^tBu, CNC_6H_{11}, NCMe, thf, SC_4H_8).[105] An alternative route to cationic clusters *e.g.* *closo*-[2,2-$(PR_3)_2$-2,1-$PdTeB_{10}H_9(PPh_3)$]I involved the reaction of [2,2-I(PPh_3)-2,1-$PdTeB_{10}H_9(PPh_3)$] with excess phosphine ($PR_3 = PMe_2Ph$, PMe_3).[106] The synthesis and structural characterization of the rhodatelluraborane cluster *closo*-[2,2-$(PPh_3)(PhNHCS_2)$-2,1-$RhTeB_{10}H_{10}$] has been reported.[107] The fluxional behaviour of $\{M(PR_3)_2\}$ in *closo* 12-vertex $\{MZB_{10}\}$ (Z=S, Se, Te) metalloheteroboranes has been characterized and a mechanism for the rotation of the $\{M(PPh_3)_2\}$ units above the heteroborane cage was suggested.[108] The *closo* complex [2,2,2-$\{\eta^1$-SC(H)NPh$\}(PMe_2Ph)_2$-2,1-$RhTeB_{10}H_{10}$] has been characterized by XRD and was described as one of the first thioformamidate complexes to be isolated.[109] The paramagnetic *B*-fluorinated mixed-sandwich compound [2-(C_7H_7)-7,11-F_2-*closo*-2,1-$MoTeB_{10}H_8$] (**25**), formed from reaction of **24** (Scheme 5) with $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ had the 2{BF} units in adjacent positions within the *closo* 12-vertex $\{MoTeB_{10}\}$ cluster (Figure 4); the compound exhibited a reversible one-electron reduction at $E^\circ = -0.39$ V in CH_2Cl_2 solution.[110] The platinathiaborane species $[(PMe_2Ph)_2PtSB_{10}H_{10}]$ was obtained by reaction of $[PtMe_2(PMe_2Ph)_2]$ with *nido*-7-$SB_{10}H_{12}$.[88] The icosahedral *closo*-$\{CuSeB_{10}\}$cage was identified in the structure of $[(PPh_3)_2Cu_2SeB_{10}H_{10}]$, which has Cu and Se atoms adjacent; the *exo*-cage $Cu(PPh_3)$ unit was bonded to one triangular $\{CuB_2\}$ face *via* a Cu–Cu bond and two Cu–H–B interactions.[111]



23 **24**

Scheme 5

The macropolyhedral compound **14** reacted with $[PtMe_2(PMe_2Ph)_2]$ to give the $[(PMe_2Ph)_2PtS_2B_{15}H_{14}(NHCOMe)]$[88] and with $[\{RhCl_2Cp^*\}_2]$ yielded both *syn* and *anti* isomers of the macropolyhedral rhodathiaboranes $[Rh_2Cp^*_2S_2B_{15}H_{14}(OH)]$; reaction with $[NiBr_2(PPh_3)_2]$ in the presence of base afforded the 19-vertex cluster $[(PPh_3)NiS_2B_{16}H_{12}(PPh_3)]$. The latter consisted of a *nido*-shaped $\{1\text{-}NiB_8]$ sub-cluster and a *closo*-shaped $\{1,4\text{-}NiSB_{10}\}$ sub-cluster fused with a $\{NiB_2\}$ triangular face in common.[75,76] Reaction of *syn*-$[Cp^*IrB_{18}H_{20}]$, obtained from $[\{IrCl_2Cp^*\}_2]$ with *syn*-$B_{18}H_{22}$ and base, with elemental sulfur afforded, by direct heteroatom insertion of the 20-vertex cluster anion, $[Cp^*IrSB_{18}H_{19}]^-$.[112]

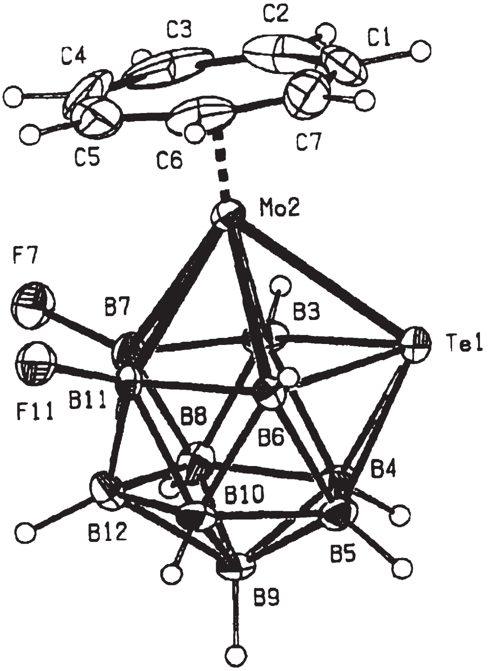


Figure 4 *View of* [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] (**25**)
(Reproduced with permission from J. Chem. Soc., Dalton Trans., 2001, 1521.)

1.3.2.3 Chalcogenoheteroboranes and Their Metallo Derivatives

Chalcogenoheteroboranes and their metallo derivatives are restricted to thio derivatives with no known examples in selena- or telluraheteroborane chemistry. The six-boron thiacarborane anion *hypho*-[7,8-CSB_6H_{11}]$^-$ (**26**) has been prepared from *arachno*-4-CB_8H_{14} (**27**).[113] The first azathiaborane clusters, *hypho*-7,8-NSB_6H_{11} and *arachno*-6,9-NSB_8H_{11}, were prepared by the reaction of *n*-butylnitrite with **13** in Et_2O or *nido*-6-SB_9H_{11} in C_6H_6.[114] The transformation of 3,4-*bis*(isopropylidene)-2,5-dichloro-1,2,5-dithiaborolane derivatives to the corresponding *nido*-4,5-diisopropyl-2,4,5-thiadicarbahexaboranes in low yield has been reported; the nine-vertex cluster *closo*-5,6-Pr^i_2-4,5,6-$SC_2B_6H_6$ was also detected by GC–MS and identified by the *ab initio*/IGLO/NMR method.[115] A 4,5-dicarba-2-thia-*nido*-hexaborane was synthesized by the hydroboration reaction of 2,5-diduryl-1-thia-3,4-diisopropylidene-2,5-diborolane by BH_3.thf, with the product characterized by MS and multinuclear NMR spectroscopy.[116] The structure of the nine-vertex *arachno*-thiadicarbaborane $C_2SB_6H_{10}$ was established by the *ab initio*/IGLO/NMR method as the 4,6,8-$C_2SB_6H_{10}$ isomer; the method also unambiguously ruled out the 4,6,5-$C_2SB_6H_{10}$ structural alternative.[117] The nine-vertex *arachno*-5-Cp*-5,4,6-$MCSB_6H_{10}$ (M=Rh, Ir) clusters were prepared from the 10-vertex *arachno*-6,9-CSB_8H_{12} (**28**) (Scheme 6) or 9-vertex *arachno*-4,6-CSB_7H_{11} (**29**) by site-specific metal centre additions with directed elimination of specific boron sites.[118] The reaction of $[\{IrCl_2Cp^*\}_2]$ with **26** afforded [2,7-Cp^*_2-*nido*-2,7,8,6-$Ir_2CSB_6H_8$] and [2,7-Cp^*_2-*nido*-2,7,8,6-$Ir_2CSB_6H_7$-9-Cl].[119]

27 **28**

Scheme 6

The seven-boron thiacarborane **29** was prepared from **28**.[113] The *arachno* cluster [9,9-$(PMe_2Ph)_2$-9,6,8-$PtCSB_7H_9$], obtained in moderate yield from **29**, $[PtCl_2(PMe_2Ph)_2]$, and proton sponge, underwent *ortho*-cycloboronation upon thermolysis to $[9,9\text{-}(PMe_2Ph)_2(PMe_2\overline{C_6H_4)\text{-}\mathit{arachno}\text{-}9,6,8\text{-}PtCSB}_7H_8\text{-}10]$.[120]

The nine-vertex monocarborane **27** reacted with S_8 in the presence of Et_3N to yield **28**.[121] The UV–PES spectra of the thiaboranes *closo*-1-$SB_{11}H_{11}$ and *nido*-7-$SB_{10}H_{12}$ have been compared with spectra from more open thiacarboranes *nido*-7,8,10-$C_2SB_8H_{10}$ and **28**, with the main conclusion being that there was a significant contribution of the bridge hydrogen atoms to the cluster-bonding HOMO and the implication that the bridge H atoms were involved in cluster bonding.[71] An extended series of thiacarborane clusters (**26**, **29**, *arachno*-[6,9-$CSB_8H_{11}]^-$, *nido*-7,9-CSB_9H_{11}, and *nido*-[6,9-$CSB_8H_9]^-$) have been prepared from **27**.[113] The thiacarborane **28** reacted with $[RhCl(PPh_3)_3]$ in ethanol solution at room temperature and produced the *nido* species [8,8,8-H$(PPh_3)_2$-8,9,7-$RhCSB_8H_{10}$] in high yield.[122] The 11-vertex thiacarborane anion [1,6,7-$C_2SB_8H_{11}]^-$, obtained from the addition of S_8 to the 10-vertex [6,9-$C_2B_8H_{10}]^{2-}$ anion, was characterized using the *ab initio*/GIAO/NMR method.[123]

Nido-7,9-CSB_9H_{11} has been prepared from **28**.[113] A *nido*-11-vertex thiacarborane, 7,10,11-$SC_2B_8H_{10}$, and the first thiaphosphaborane, *nido*-10-Ph-7,10-SPB_9H_9, were produced by synthetic sequences involving the reaction of an organophosphorus dihalide and/or sulfur dihalide with borane clusters followed by *in situ* dehydrohalogenation reactions initiated by 'proton-sponge'.[70]

1.4 Binary, Ternary, and Quarternary Chalcogenoborates

Rapid progress in recent years has been made in the understanding of ternary and quarternary chalcogenoborates due to improvements in crystallographic and solid-state preparative methods. However, the chemistry of known chalcogenoborate derivatives is limited to thio- and selenaborates with no known telluraborates. Despite this, a wide variety of compounds have been synthesized and structurally characterized over the period of this survey. As noted in Section 1.2, this topic has been reviewed recently.[12]

Two new high-pressure phases of boron sulfide, B_2S_3-II and B_2S_3-III, have been synthesized at 3.0–6.3 GPa.[124] A new method of preparing *meta*-thioboric acid (*c*-HBS_2), by reaction of H_2S with B_2S_3 in the vapour phase, has been reported.[125] The IR spectra of a series of binary K_2S/B_2S_3 glasses has been reported with spectra similar to those of the corresponding sodium thioborate system.[126] The XPS spectra of vitreous and crystalline Li_2S/B_2S_3 compounds were obtained and analyzed by theoretical calculations.[127] A structural neutron diffraction study of Li_2S/B_2S_3 glasses has also been reported.[128] $TlBS_3$ was obtained as a glassy product from $Tl_2S{\cdot}2B_2S_3$ after treatment for 7 h at 850 °C followed by annealing in a two-zone furnace for 400 h at 350–400 °C.[129] A new series of anhydrous protonated chalcogenide glasses, $(H_2S)_x(B_2S_3)_{1-x}$, analogous to alkali-modified glasses have been prepared; characterization showed that these materials were unique and did not exhibit the borate anomaly.[130] Mixing HBS_2 and B_2S_3 and GeS_2 yielded proton-containing glasses in which, except in the GeS_2-rich formulations, the borate coordination was found to be trigonal.[131]

The orthothioborates Na_3BS_3, K_3BS_3, and Rb_3BS_3 have been prepared in solid-state reactions of metal sulfide, amorphous boron, and sulfur at 600 °C and their crystal structures revealed that all three compounds contained isolated $BS_3{}^{3-}$ anions.[132] The orthothioborates Li_3BS_3, Cs_3BS_3, $Sr_3(BS_3)_2$, Li_2CsBS_3, $LiBaBS_3$, and $LiSrBS_3$ have also been prepared and their structures, determined by XRD studies, also contained isolated planar $[BS_3]^{3-}$ anions.[133–136] The crystal structure of Li_3BS_3, obtained by crystallizing the corresponding glass, exhibited higher symmetry than other $M_3B(O,S)_3$ structures and Li_3BS_3 was described as a new member of the M_3AX_3 group of compounds.[137]

The structure of $Cs_2B_2S_4$ contained isolated $B_2S_4{}^{2-}$ groups consisting of four-membered B_2S_2 rings with exocylic S atoms on each B; this was the first reported example of edge-sharing BS_3 groups in isolated thioborate anions.[138] The four-membered B_2S_2 ring was found as a building block in the polymeric thioborate anion structures observed for $TlBS_2$ and SrB_2S_4.[139] The crystal structure of the barium metathiaborate, BaB_2S_4, showed the boron atoms in both trigonal and tetrahedral coordination in a 1:1 ratio, in infinite anionic chains[140] and a new crystalline phase of EuB_2S_4 has been prepared and its crystal structure revealed polymeric $[(B_2S_4)^{2-}]_n$ anions.[141]

The synthesis, crystal structures, and properties of $LiSrB_3S_6$ and $M_3B_3S_6$ (M=Na, K, Rb) have been reported.[142] The ternary thioborate $Sr_3(B_3S_6)_2$ and the quarternary thioborate $LiBaB_3S_6$ both contained boron centres in trigonal planar coordination environments with isolated $B_3S_6{}^{3-}$ anions consisting of six-membered B_3S_3 rings with three exocyclic S atoms.[136,143]

The perthioborate, $RbBS_3$, and $Th_3B_3S_{10}$ were prepared at 600 and 850 °C, respectively, and both compounds contained tetrahedrally coordinated boron and consisted of polymeric anionic chains.[129] The perselenoborates $RbBSe_3$, $TlBSe_3$, and $CsBSe_3$ have been prepared and all three compounds contained polymeric anionic chains with spirocyclically fused five-membered B_2Se_3 rings in which the B atoms were in a tetrahedral BSe_4 coordination.[144] The lithium perselenoborate $Li_2B_2Se_5$ had a novel three-dimensional anion network with B atoms in tetrahedral BSe_4 coordination.[145] $LiBSe_3$ has been synthesized and it also possessed a novel polymeric network.[146] The perthioborates $Na_2B_2S_5$ and $Li_2B_2S_5$ had structures containing planar $B_2S_5{}^{2-}$ groups consisting of five-membered B_2S_3 rings with one additional exocyclic S atoms on each B.[139] The first alkaline earth perselenoborates BaB_2Se_6 and BaB_4Se_{13} were synthesized from appropriate amounts of barium selenide, boron, and selenium at high temperatures.[147] The synthesis of $Na_2B_2Se_7$, $K_2B_2S_7$, and $K_2B_2Se_7$ has been reported with their structures contained polymeric $B_2E_7{}^{2-}$ anion chains formed by spirocyclically connected five-membered B_2E_3 and six-membered B_2E_4 rings.[148] Heating, followed by annealing of stoichiometric quantities of Li_2S, B, and S_8, afforded the thioborates $Li_5B_9S_{13}$ (730 °C) and $Li_9B_{19}S_{33}$ (700 °C) and their crystal structures displayed interpenetrating polymeric boron–sulfur anionic networks.[149] New isotypic crystalline phases of $Sr_{4.2}Ba_{2.8}(BS_3)_4S$ and $Ba_7(BSe_3)_4Se$ were obtained through systematic studies on quarternary thioborates and selenoborates containing the heavier alkaline earth metals.[150]

The thioborate $Na_6B_{10}S_{18}$, composed of $B_{10}S_{20}$ units linked through tetrahedral corners, was shown to be a highly polymeric macrotetrahedral 3d network.[151] New polymeric-layered anion networks composed of corner-sharing super-adamantane-type $B_{10}E_{20}$ units, connected by Li and Cs cations were observed in $Li_{6-x}Cs_xB_{10}E_{18}$ ($x \sim 1$; E=S, Se) and $Na_6B_{10}Se_{18}$.[152] Lithium selenoborates such as $Li_{6-2x}Ba_{1+x}B_{10}Se_{19}$ and $Li_{3+x}Na_{5-x}B_{10}Se_{19}$, which have severely disordered cations, were reported as excellent candidates for mechanistic analysis of ionic conductivity measurements.[153,154] Similarly, $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x = 0.7$) has also been studied.[155]

The selenoborate $Cs_8[B_{12}(BSe_3)_6]$ (Cs_8**30**) was obtained from the reaction of caesium selenide, boron, and selenium by means of a high-temperature solid-state synthesis (Figure 5).[156] The retention of the icosahedral boron network during this reaction has been noted as very unusual.[157] The three selenaborates Rb_8**30**, Rb_4Hg_2**30**, and Cs_4Hg_2**30**, prepared from the metal selenides, amorphous boron, and selenium in solid-state reactions at 700 °C, also contained the B_{12} icosahedral unit saturated with six trigonal-planar BSe_3 entities.[158] Systematic studies of icosahedral-B_{12} containing selenoborates with alkali metal cations have led to a new crystalline phase for $Na_6[B_{18}Se_{17}]$, which contained neighbouring $\{B_{12}Se_{18}\}$ cluster moieties connected in one direction *via* exocyclic Se atoms in an infinite-chain anion.[159] A new crystalline phase of K_8**30** has been obtained with the selenoborato anion showing three different substitution patterns.[160] New crystalline phases of Rb_8**30** and Cs_8**30** have been reported by reaction of amorphous boron with alkali metal sulfide and sulfur at $\sim$600 °C in evacuated carbon-coated silica tubes.[161]

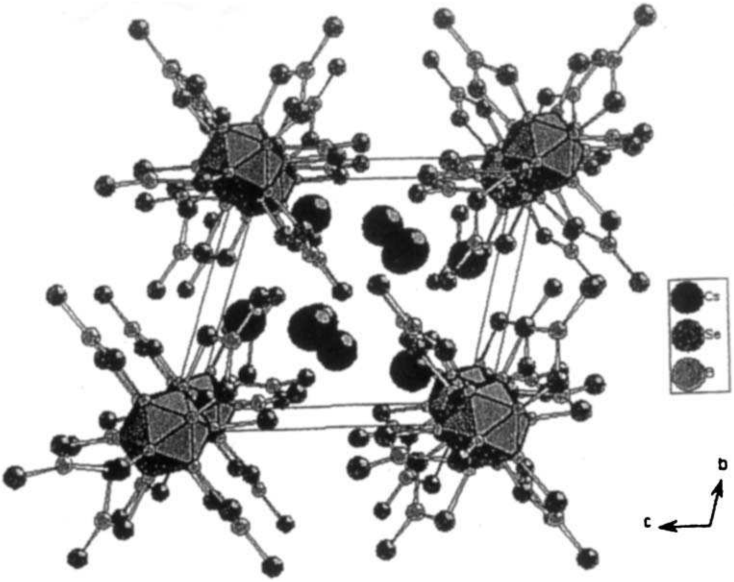


Figure 5 *Unit cell of* $Cs_8[B_{12}(BSe_3)_6]$, (Cs_8**30**)
(Reproduced with permission from Angew. Chem., Int. Ed. Engl., 1997, **36**, 1903.)

1.5 Heterocycles Containing B–E Linkages

The first stable disulfanylborane (Tbt)B$(SH)_2$ (**31**) was prepared by reaction of the overcrowded lithium hydroborate, (Tbt)$BH_3Li(thf)_3$ with S_8.[162] Dilithiation of **31** followed by treatment with electrophiles such as Cp_2TiCl_2, $(mes)_2GeBr_2$, $PhSnCl_2$, and (Tbt)$SbBr_2$ resulted in the isolation of novel four-membered 1,3-dithiaboretane rings $\overline{\mathrm{S\{B(Tbt)\}S\{E}}\mathrm{R}_n\}$ (ER_n = $TiCp_2$, $Ge(mes)_2$, $SnPh_2$ (**32**, Figure 6), or Sb{Tbt}); the structures of these ring systems were confirmed in all cases by single-crystal XRD studies.[162,163]

B_2H_6 was shown to react with H_2S_2, H_2S_3, or crude sulfane oil to form the 1,2,4,3,5-trithiadiborolane, $H_2B_2S_3$.[164] The reaction of $^tBu_2S_2$ with $ArBBr_2$ (Ar=Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-EtC_6H_4, 3,5-$Me_2C_6H_3$) in refluxing toluene gave the thermally stable, moisture-sensitive 1,2,4,3,5-trithiadiborolanes, $Ar_2B_2S_3$.[165] The reaction of $ArBBr_2$ with HgS in benzene at reflux produced a series of 1,3,5-triarylborthiins ($Ar_3B_3S_3$), which were found to be less stable than $Ph_3B_3S_3$ and were significantly decomposed to mixed B/O/S rings (*e.g.* $Ar_3B_3S_2O$, $Ar_3B_3SO_2$) within minutes in air.[166] Reaction of the $ArBBr_2$ species with $(Me_3Si)_2S$ in benzene at room temperature afforded the corresponding 1,3,5-triarylborthiins, and not the expected 1,3,2,4-dithiadiboretanes ($Ar_2B_2S_2$), while the reaction of S_8 with $PhBBr_2$ or

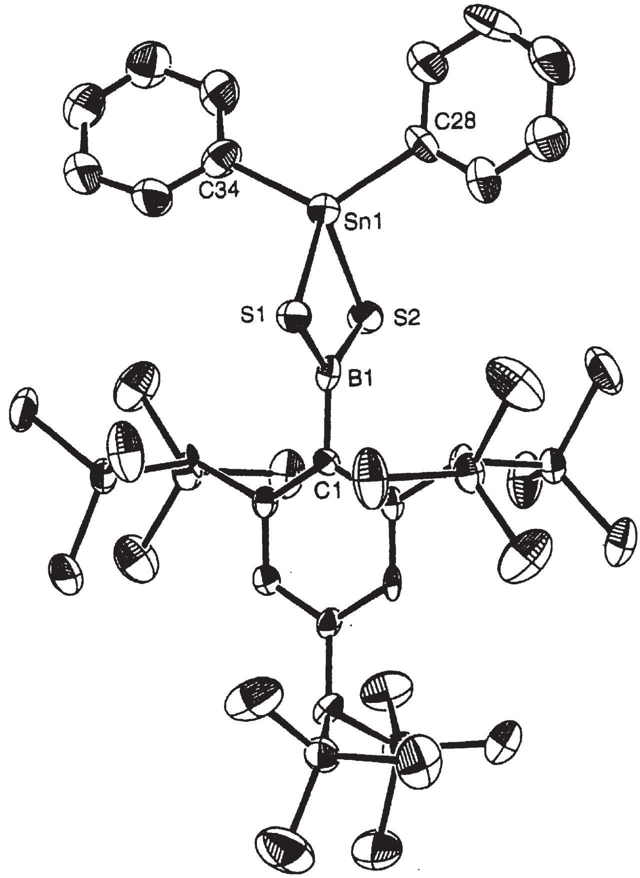
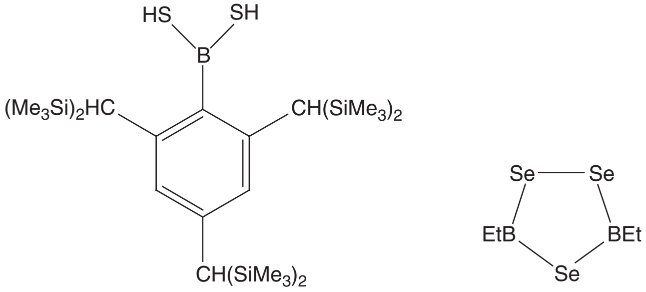


Figure 6 *ORTEP drawing of (Tbt)BS$_2$SnPh$_2$ (**32**)*
(Reproduced with permission from Organometallics, 1997, **16**, 4316.)

4-MeC$_6$H$_4$BBr$_2$ was investigated by ^{11}B NMR and mass spectrometry and cyclic RBS$_n$ species were identified.[166] A theoretical study of the structures and energetics and magnetic properties of H$_3$B$_3$E$_3$ (E=O, S, Se) has been reported with the discussion centred on the relative aromaticity of these rings compared to those of related group 15 boron heterocycles.[167]

The triselenadiborolanes 3,5-R$_2$-1,2,4,3,5-Se$_3$B$_2$ {R=Et (**33**), Pr} readily formed coordination adducts with two equivalents of pyridine, 3,5-dimethylpyridine, and 3-chloropyridine.[168] With one equivalent of base, only one of the B atoms became coordinated, and surprisingly, the system was not fluxional at room temperature.[168] The addition of two equivalents of pyrazole to **33** (Scheme 7) resulted in a brown suspension and a yellow solution. Crystals of a B$_2$N$_4$Se$_2$-bicyclo[2.2.2]octane were formed upon cooling this solution to −80 °C. With bulkier pyrazole derivatives (*e.g.* 3-methylpyrazole, 3-phenylpyrazole), the B$_2$N$_4$Se-bicyclo[2.2.1] heptanes were formed.[169]



31 **33**

Scheme 7

Elimination of hydrogen halides from dihalogenoorganylboranes by reaction with ferrocene-1,1′-dithiol resulted in 1,3-dithia-2-boryl[3]ferrocenophanes.[170] These borylferrocenophanes were air sensitive, but were characterized by NMR, MS, and elemental analysis.[170] A series of 1,3-dibora-2-X-[3]ferrocenophanes (X=S, Se, Te) were prepared and characterized and the crystal structure of $[Se\{N^iPr_2)BC_5H_4\}_2Fe]$ has been reported.[171]

The first organoborontellurium compound was prepared from the reaction of 9-Cl-9-BBN with Na_2Te_2 and Na_2Te. The product, $(9\text{-BBN})_2Te$, reacted with water to give elemental Te, $(9\text{-BBN})_2O$ and $(9\text{-H-9-BBN})_2$.[172]

The 1,2-benzothiaborolidine, a heteroaromatic analogue of indenyl, has been prepared and shown to form a η^5-complex with RuCp*.[173] The related anion, 2-(diisopropylamino)-1,2-thiaborolide(1-) has also been prepared and coordinated to Ru in $[\{(^iPr_2N)BSC_3H_3\}RuCp^*]$ (**34**, Figure 7) and Zr in $[\{(^iPr_2N)BSC_3H_3\}ZrCl_2Cp^*]$.[174]

1.6 Miscellaneous Boron–Chalcogen Compounds and Reagents

The use of bulky aryl substituents allowed the structural characterization of the monomeric B–S compounds, mes_2BSPh and $(2,4,6\text{-}Pr^i{}_3C_6H_2)$ $B(SPh)_2$, showing short B–S distances (180 pm) consistent with B–S π-interaction. Barriers to rotation of 18.4 and 12 $kcal\ mol^{-1}$ were determined by variable temperature NMR studies.[175] A thioxoborane (Tbt)BS, with a B=S bond and the very bulky aryl group on the B atom was obtained from the thermolysis of an overcrowded four-membered boracycle, 1,3,2,-dithiastannaboretane.[176] The barrier to rotation about B=E bonds of coordinatively unsaturated borates and thiaborates has also been discussed with the lower rotational barrier in the O derivatives attributed to greater stabilization of the transition state.[177] The rotational barriers did not reflect the relative strengths of the B=E π bonds.[177]

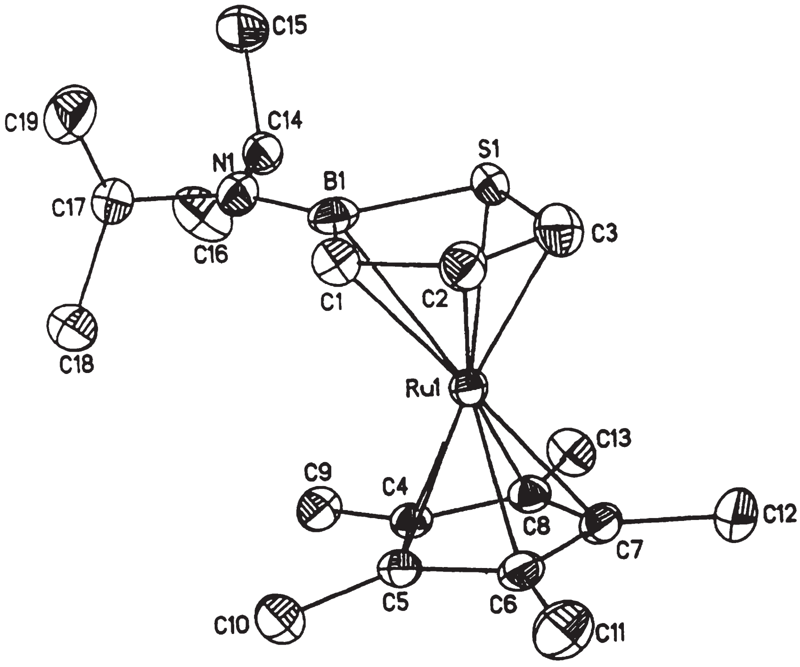


Figure 7 *Solid-state structure of* $[\{(^iPr_2N)BSC_3H_3\}RuCp^*]$ (**34**)
(Reproduced with permission from Organometallics, 2000, **19**, 4937.)

n-Octadecanethiol was found to react with $B(C_6F_5)_3$ to yield an equilibrium mixture of reactants and the 1:1 adduct, and the adduct was deprotonated by 'proton-sponge' to yield the salt $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]$.[178] Reaction with Cp^*MMe_3 (M=Ti, Hf) yielded $[Cp^*MMe_2][(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]$, which was a good initiator for the copolymerization of isobutene with isoprene in high conversions to high molecular weight copolymers.[179] The crystal structure of the tetrathiophene adduct of tris(pentafluorophenyl)borane, $(C_4H_8S)B(C_6F_5)_3$, was reported and it showed a comparatively long BS distance of 2.0843 Å.[180] Metal-catalyzed additions of B–X (X=H, B) bonds to thiocarbonyl compounds and vinyl sulfides afforded α-thioboronate esters.[181]

The reaction of $BH_3{\cdot}thf$ with NaSH or anhydrous Na_2S, or the reaction of $BH_3{\cdot}thf/Na[BH_4]$ (2:1) with excess H_2S, produced the adamantine-like compound $Na_2[(BH_2)_6S_4]$.[182] The analogous selenium compound was obtained from the reaction of elemental Se with $Na[BH_4]$ (1:1) in diglyme. The X-ray structures of both of these cage anions were determined.[182] The reaction of $Na[BH_4]/BH_3{\cdot}thf$ with S_8 proceeded with elimination of H_2 and gave $Na[(BH_2)_5S_4]$ with a noradamanatane-like $\{B_5S_4\}$ skeleton.[183] The salt $[Na(triglyme)]_2[S(BH_3)_4]$, which contained an anion isoelectronic with $[SO_4]^{2-}$, was obtained from the reaction of $Na[BH_4]$ with $Na[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]$ in triglyme.[184]

Potentially chelating $[H_2B(SPh)_2]^-$, $[HB(SPh)_3]^-$, and $[B(SPh)_4]^-$ ligands have been prepared and their reactions with 3d transition-metal complexes were investigated.[185] The synthesis, characterization, and reactivity of the S-rich tridentate ligand tetrakis(2-thienyl)borate anion was reported; unlike $[(MeS)_4B]^-$, it did not coordinate to $\{Mo(CO)_3\}$ when reacted with $[(C_7H_8)Mo(CO)_3]$.[186] Stabilization of the tetrathioborato ligand has been achieved in novel sulfido niobium clusters. Thus, the neutral diamagnetic complex, $[Nb_3Cp_3S_3(S_3BSH)]$ (**35**, Figure 8), was obtained in yields of up to 28% by reaction of S_8 with $[Nb_2Cp_2(B_2H_6)_2]$ in decane at 170 °C.[187]

Finally, this section reports on a few unusual reactions of B–E-containing compounds in which they serve as reagents, with loss of chalcogen. A novel route for the synthesis of icosahedral *closo*-$RNB_{11}H_{11}$ (R = $^tBuCH_2$, Ph) clusters involving the use of $BH_3{\cdot}SMe_2$ and *nido*-RNB_9H_{11} in decalin at 170 °C has been reported.[184] The reaction of $ClBH_2.SMe_2$ and proton sponge and NaH with *nido*-$B_{10}H_{14}$ leads to the formation of $[B_{11}H_{14}]^-$.[188] The synthesis and characterization of the first example of a three-membered borocyclopropane ring coordinated to a trimetal fragment, $[Fe_3(CO)_9(\eta^3\text{-BHCHCMe}\}]$, has been reported; it was obtained in low yield from the reaction of $BH_2Br{\cdot}SMe_2$ with $[Fepy_6][Fe_4(CO)_{13}]$.[189] The two metallaboranes $[Co_2(CO)_6B_2H_4]$ and $[Co_5(CO)_{13}(\mu\text{-CO})B_2H]$ were prepared in low yield by reaction of $[Co_2(CO)_8]$ with $BH_3{\cdot}SMe_2$; both compounds were characterized by XRD and the former compound was isoelectronic with $[Fe_2(CO)_6B_2H_6]$ and $[Co_2(CO)_6C_2H_2]$.[190]

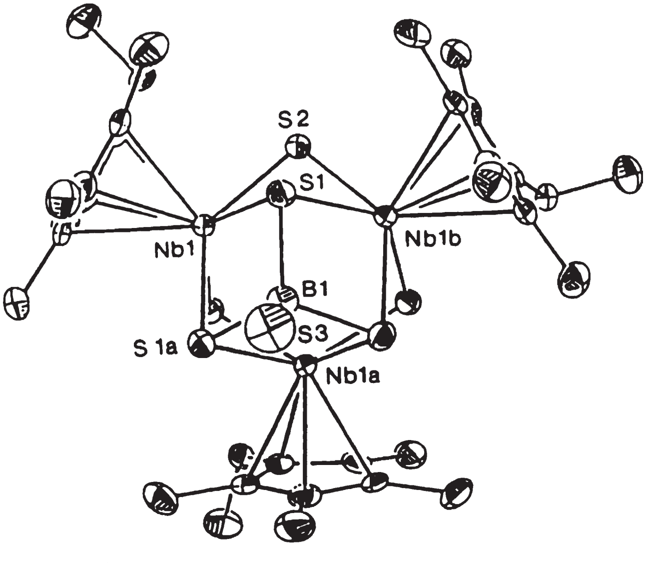


Figure 8 *Structure of* $[Nb_3Cp_3S_3(S_3BSH)]$ (**35**)
(Reproduced with permission from Angew. Chem., Int. Ed. Engl., 1992, **31**, 1022.)

$BH_3{\cdot}SMe_2$ readily reacted with P_4O_6 and formed the adduct $P_4O_6{\cdot}BH_3$, which was shown to dimerize spontaneously at −30 °C to $P_8O_{12}(BH_3)_2$.[191]

Abbreviations

Arene	any derivative of C_6H_6
Aryl	any derivative of C_6H_5
9-BBN	9-borabicyclo[3.3.1]nonane
Cp	$C_5H_5^-$
Cp*	$C_5Me_5^-$
Tbt	2,4,6-$[Me_3Si_2HC]_3C_6H_2$
Thf	tetrahydrofuran

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CHAPTER 2.1

Thiolates, Selenolates, and Tellurolates

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2.1.1 Introduction

Chalcogenolate ligands have been known since the beginning of coordination chemistry, being thiolate chemistry much more developed than the selenolate or tellurolate analogues and consequently more application-oriented work have appeared for the former. Thiolate complexes are very important in bioinorganic chemistry, mainly due to their presence in very diverse metalloproteins,[1,2] in medicine for the use of gold thiolates in the treatment of arthritis,[3,4] as precursors for chemical surface depositions of layers of metal or sulfides from vapour phase (CVD),[5–7] the chemistry relating to S–C bond cleavage reactions and desulfurization[8] or even thiolates stabilize the formation of metal nanoparticles because their outstanding capability to form self-assembled monolayers (SAMs).[9,10] Alkaline earth chalcogenolates have also importance in the production of wide band gap semiconductors,[11] and two colour IR optical windows.[12]

Metal chalcogenolate complexes are also very interesting from the structural point of view since they adopt geometries of variable nuclearity with great structural complexity. The chalcogenolate ligands tend to form bridges and polymeric species, which can be avoided by using sterically hindered or functionalized chalcogenolates and/or auxiliary ligands.

The aim of this chapter is to review the chemistry of chalcogenolates in the last 10 years. The more recent reviews in this field included chalcogenolates of the s-block elements,[13,14] early transition metal thiolates,[15] metal complexes with selenolate and tellurolate ligands,[16] copper(I), lithium and magnesium thiolates,[17] functionalized thiolate complexes,[18,19] pentafluorobenzenethiolate platinum group compounds,[20] tellurium derivatives,[21] luminescent gold compounds,[22] and complexes with lanthanide or actinide.[23]

2.1.2 Synthetic Routes of Ligands and Metal Chalcogenolates

2.1.2.1 Synthesis of the Chalcogenols

Some of the ligands discussed here can be purchased or have been obtained previously by well-established methods. Some of them are formed *in situ*, mainly through the insertion of the chalcogen in a Li–C or Mg–C bond; thiols always being more stable and abundant that selenols and those than tellurols. However, elaborate synthetic procedures are necessary for several ligands as for example, functionalized derivatives. Many of these synthesis are variations of the general procedures of Reynols *et al.*[24] (mercaptoethylation of amines with ethylene sulfide) and Harley-Manson[25] (alkaline cleavage of thiouronium salts) or hydrolysis of C–S–Li bonds.[26] The selenols are nearly always prepared by simple protonolysis of alkali metal selenolates. In contrast, few reports deal with tellurols maybe because they are thermally unstable and light sensitive. Due to the lower stability of selenols and tellurols, these chalcogenolate ligands are used *in situ*, otherwise the oxidized species REER (E=Se, Te) are formed.

2.1.2.2 Synthesis of Metal Chalcogenolates

During the last years much effort has been made in the development of reliable, reproducible, high-yielding synthetic routes for the preparation of metal chalcogenolates, enabling the synthetic chemist to choose the most appropriate for the desired compound. It is worth mentioning the high potential of alkaline and alkaline earth metal chalcogenolates in synthetic chemistry. The general strategies to achieve metal chalcogenolates will be presented and referred in other sections.

2.1.2.2.1 Protolysis of M–H, M–C, M–N, or M–O Bonds

The starting material is always the chalcogenol and, consequently, is more used for thiols than selenols and tellurols. There are several types of reactions depending if the starting materials are metal hydrides (hydrogen elimination), complexes with M–C (alkane elimination), M–N (transamination), or M–O (hydrolysis) bonds.

Hydrogen elimination is mainly used with sodium and potassium hydrides

$$\mathrm{MH} + \mathrm{HER} \rightarrow \mathrm{MER} + \mathrm{H_2} \qquad (1)$$

Alkane elimination is readily used for lithium and magnesium organometallic compounds

$$\mathrm{MBu} + \mathrm{HER} \rightarrow \mathrm{MER} + \mathrm{BuH} \qquad (2)$$

Transamination is used for alkaline earth elements and also for early transition metals when the amide complexes are available

$$\mathrm{M[N(SiMe_3)_2]}_n + \mathrm{nHER} \rightarrow \mathrm{M(ER)}n + \mathrm{nHN(SiMe_3)_2}\ (3) \qquad (3)$$

Hydrolysis is less common and always that the $M(OR)_n$ complexes are available

$$M(OR')_n + nHER \rightarrow M(ER)_n + nHOR' \qquad (4)$$

2.1.2.2.2 Metallation

The direct reaction of the metal with the chalcogenol is accessible for the heavy alkali metals, which are more reactive and also for the alkaline earth elements.

$$M + HER \rightarrow MER + \tfrac{1}{2} H_2 \qquad (5)$$

2.1.2.2.3 Salt Metathesis

This is a widely used preparation route towards metal chalcogenolates since the alkali compounds, mainly lithium and sodium derivatives, react with halogen complexes of almost any metal. The chalcogenols in the presence of a base can be used to scavenge the hydrogen halide.

$$MX_n + nLiER \rightarrow M(ER)_n + nLiX \qquad (6)$$

$$MX_n + nHER + nB \rightarrow M(ER)_n + n(HB)X \qquad (7)$$

2.1.2.2.4 Insertion of the Chalcogen in a M–C Bond

The chalcogen atoms readily insert into Li–C or Mg–C bonds and this method is widely used to prepare *in situ* these reagents for further reactions.

$$MR + E \rightarrow M(ER) \qquad (8)$$

2.1.2.2.5 Oxidation with Dichalcogenides

The oxidative addition reaction of the type shown in Equation (9) were used to prepare some of the first selenolate and tellurolate complexes still used today.

$$ML_n + RE\text{-}ER \rightarrow M(ER)_2L_n \qquad (9)$$

2.1.2.2.6 Transmetalation

Several main group metal chalcogenolates can be used as starting materials to obtain other metal chalcogenolate derivatives.

$$M + Hg(ER)_2 \rightarrow M(ER)_2 + Hg \qquad (10)$$

2.1.2.2.7 Synthesis Via Trimethylsilyl Derivatives

The formation of volatile chlorotrimethylsilane is a very clean synthetic pathway to prepare several metal complexes. Various trimethylsilyl derivatives of sulfur, selenium, and tellurium have been described.

$$MClL_n + Me_3SiER \rightarrow M(ER)L_n + ClSiMe_3 \qquad (11)$$

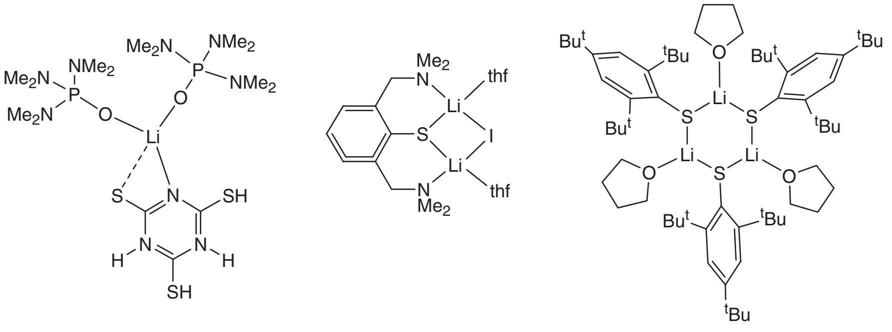
2.1.2.2.8 Electrochemical Synthesis

Complexes $M(ER)_n$ can be obtained *via* anodic oxidation of the metal in a solution containing the required chalcogenolate and also by catodic reduction of a dichalcogenide REER to the corresponding chalcogenolate and in a solution of the corresponding metal. Other auxiliary ligands may be present. This method has been used mainly with copper, silver, and gold.

2.1.3 Alkali and Alkaline Earth Derivatives

Although alkali and alkaline earth arenechalcogenolates have been known to be intermediates in the preparation of arenechalcogenols, it is only recently that structural characterization of these materials had appeared in the literature. Single crystal data on lithium chalcogenolates were first published in 1985 for lithium thiolates,[27] 1991 for lithium selenolates,[28,29] and 1992 for lithium tellurolates.[30,31] Since then a great amount of work have developed in all the alkali and alkaline earth elements. Lithium chalcogenolates are important reagents for the synthesis of a large variety of metal chalcogenolates and for this reason have been better studied.

Lithium derivatives are most conveniently prepared by reaction of the chalcogenols with ^{n}BuLi, however for sodium and potassium the use of the metal hydrides is most used and for rubidium and caesium metalation is preferred. Structural diversity depends mainly of three different factors: the metal, the size of the chalcogenol, and the auxiliary ligand used. For lithium chalcogenolates, the most common structural features observed are monomeric or dimeric species but higher degrees of aggregation have been observed. Monomeric species include the monolithiated derivative of the trithiocyanuric acid (LH_3),[32] $[Li(LH_2)(hmpa)_2]$ (hmpa=hexamethylphosphoramide) (**1**), [Li(S-py)(12-crown-4)][33] (Spy=pyridine-2-thiolate), and $[Li(SC_6H_4PMe\{CH(SiMe_3)_2\})(12\text{-crown-}4)]$,[34] which have in common the presence of functionalized chelating thiolate ligands and bulky auxiliary ligands that fulfil the cation's coordinative requirements. Also by careful ligand and donor selection monomeric species as [Li(SR)(pmdta)] ($SR=SCPh_3$, STrip; Trip = $2,4,6\text{-}{}^iPr_3C_6H_2$, pmdta = N,N,N',N'-pentamethyldiethylenetriamine) have been prepared.[35] The use of the multihapto crown ether donors such as 12-crown-4 or 15-crown-5 leads to the isolation of monomeric species whose association is governed by the thiolate ligand, and thus with $SCPh_3$ monomeric compounds are obtained, and with the cumbersome ligand SMes* (Mes* = $2,4,6\text{-}{}^tBu_3C_6H_2$) the solvent-separated ion-pair $[Li(12\text{-crown-}4)_2][SMes^*]$ is formed.[35,36] Dimeric lithium species have been reported for the alkyl, silyl, and germyl-substituted chalcogenolate $[Li\{EY(SiMe_3)_3\}L_n]_2$ (L=thf, $n = 1, 2$; L=dimetoxiethane, $n = 1$; E=S, Se, Te; Y=C, Si, Ge),[37] $[Li(SC_6H_3\text{-}2,6\text{-}Mes_2)(OEt_2)]_2$,[38] $[Li(SePh)(bipy)]_2$,[39] $[Li(Spy)(18\text{-crown-}6)]_2$,[33] $[Li(Se^nBu)(tmda)]$,[40] $[Li(SC_2N_3SiMe_3)(tmda)]_2$ (tmda=$(Me_2NCH_2)_2$),[41] and $[Li\{SC_6H_4\text{-}2\text{-}(CH_2N(Me)CH_2CH_2OMe)\}]_2$.[42] A dinuclear adduct, $[Li_2(SR)I(thf)_2]$ (**2**), with bridging thiolate and iodine ligands have been described.[42] A special case where all the alkali metals present the same donor-free homoleptic structure is with the very bulky *o*-terphenyl-substituted thiolate ligand, which imposes a dimeric structure $[A(SC_6H_3\text{-}2,6\text{-}Trip_2)]_2$ (A=Li, Na, K, Rb, Cs) even in the large cations Rb^+ and Cs^+.[43] For lithium the use of not so sterically demanding substituents or the control of the amount of donor ligand allows the synthesis of trimeric, $[\{Li(SC_6H_3\text{-}2,6\text{-}Mes_2)\}_3(C_6H_{14})]$,[43] [Li(S-Mes*)(thf)]$_3$ (**3**) (Scheme 1),[35] or tetrameric $[\{Li(SC_6H_2\text{-}2,4,6\text{-}Ph_3)\}_4(C_7H_8)]$ species.[43] Polymeric compounds have been synthesized with triazole- and tetrazole-thiolate ligands.[41,44]

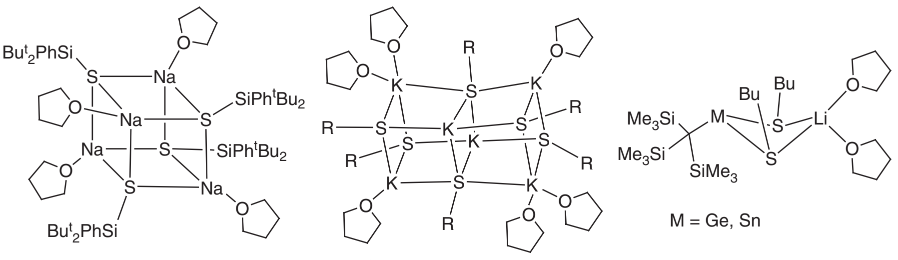


(1) **(2)** **(3)**

Scheme 1

For sodium and potassium chalcogenolates, donor influence on structural pattern has been explored with a special emphasis in donor hapticity. Thus, crown ether complexation allows the isolation of monomeric species, such as $[K(SCPh_3)(18\text{-crown-}6)L_n]$ (L=thf, C_6H_6, hmpa, $n = 0.5$; L=toluene, $n = 1$),[36] [K(SMes*)(dibenzo-18-crown-6)(thf)],[45] [K(STrip)(dibenzo-18-crown-6)(thf)],[45] and [K(SBu)(18-crown-6)].[46] With the planar 18-crown-6 ether and the more sterically demanding ligand SMes* or the bidentate pyridine-selenolate, the ion-separated species $[A(18\text{-crown-}6)(thf)_2][EMes^*]$ (A=Na, K; E=S, Se)[47] or [K(18-crown-6)][(Sepy)] have been afforded.[48] The thiolate ligand STrip and the tridentate pmdta donor ligand give the dinuclear complex $[Na(STrip)(pmdta)]_2$.[45] The use of bulky silylchalcogenolates have allowed the synthesis of several sodium salts with a cubane-like structure (**4**).[49] With monodentate donors, such as thf, or the substituted bidentate pyridinethiolate ligand the isolation of discrete hexameric compounds such as (**5**)[45,50] or $[Na(SC_5H_2N\text{-}3,6\text{-}SiMe_2{}^tBu)_2]\cdot 2OEt_2$,[51] have been isolated.[45] Polymeric compounds have been reported for small chalcogenides and/or small donor ligands, as for example $[K(STrip)(thf)]_n$,[44] $[Na(SPh)(C_6H_6N_2)]_n$,[52] or $[Na(SC_5H_4\text{-}NO)(OH_2)_2]_n$.[53]

Mixed alkali-metal chalcogenolates have been synthesized for main group elements, such as aluminium,[54,55] germanium, and tin as (**6**) (Scheme 2),[56] or transition metals such as zirconium,[57–60] iron,[61,62] vanadium,[63] nickel,[64] rhenium,[65] and cobalt,[66] or lanthanide metals.[67,68]



R = $C_6H_2{}^iPr_3$-2,4,6

(**4**) (**5**) (**6**)

Scheme 2

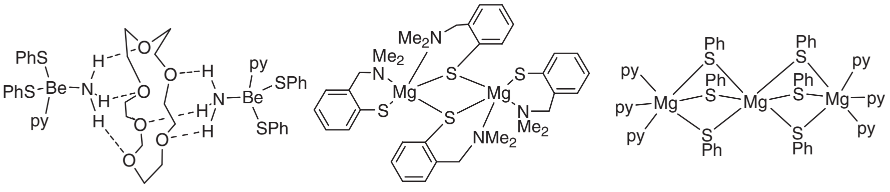
The chemistry of alkaline-earth chacogenolates have been developed from the nineties with the structural characterization of the first magnesium thiolate in 1990,[69] magnesium and calcium tellurolates in 1992,[70,71] and the first magnesium and strontium selenolates in 1994.[72]

Only three beryllium compounds have been structurally characterized, the three-coordinate monomers [Be(SMes*)$_2$(thf)][73] and [Be(SMes*)(SC$_6$H$_3$-2,6-Mes$_2$)(OEt$_2$)][74] and the four-coordinate [{Be(SPh)$_2$(py)(NH$_3$)}$_2$(18-crown-6)] (**7**).[75]

Magnesium chalcogenolate species are important starting materials for the preparation of transition metal organochalcogenides, since they are much less reducing than the corresponding alkaline derivatives. They are also very important in organic synthesis as exemplified by the selective addition of magnesium thiolates or selenolates to arynes, which provide 2-thio or 2-seleno-substituted aryl magnesium species.[76]

The magnesium–chalcogen bond has a strong ionic component as has been corroborated both by experimental and theoretical calculations. Consequently, low solubility and high tendency to polymerization are two facts that can be avoided by the use of sterically demanding or intramolecular stabilized chalcogenols and/or strong donors. Accordingly, most of the complexes known display low coordination numbers. Several tetracoordinated monomer species such as [Mg(SeMes*)$_2$L$_2$] (L=thf, OEt$_2$),[77] [Mg{E(SiMe$_3$)$_3$}$_2$L$_2$] (E=Se, Te; L=thf, py, (PMe$_2$CH$_2$)$_3$SiCMe$_3$),[72] [Mg(SCPh$_3$)(15-crown-5)],[78] [Mg(SMes*){N(SiMe$_3$)$_2$}(thf)$_2$],[79] as well as a few penta- and hexa-coordinated compounds, such as [Mg(SC$_6$F$_5$)$_2$(py)$_3$],[80] [Mg(SPh)$_2$(py)$_4$],[80] [Mg(η^2-Spy)$_2$(py)$_2$],[80] [Mg(SC$_5$H$_4$NO)(OH$_2$)$_2$],[81] and [Mg(SC$_5$H$_4$-4-R)(thf)$_2$][82] have been reported. Only one homoleptic anionic derivative has been obtained, [Mg(SC$_6$F$_5$)$_4$]$^{2-}$.[80] Base-free monomers have been prepared with the cumbersome ligand STrip.[83] With strong donors as crown ethers and sterically demanding thiolates the separated species as [Mg(15-crown-5)(thf)$_2$][SMes*] are formed.[78] Dimeric compounds as the base-free three-coordinate [Mg(SC$_6$H$_2$-2,4,6-Ph$_3$)$_2$]$_2$,[77] or penta-coordinate [Mg(SC$_6$H$_4$CH$_2$NMe$_2$)$_2$]$_2$ (**8**),[84] or the solvated four-coordinate [Mg(SR){N(SiMe$_3$)$_2$}(thf)]$_2$ (R=Ph, STrip),[79] [Mg(SMes*)(μ-SMes*)(thf)]$_2$,[79] and [Mg(S^{t}Bu)(Cp)(thf)]$_2$ have been reported.[85] The trimeric

$[Mg(SPh)_2(py)_2]_3$ (**9**)[81] (Scheme 3) and tetrameric $[Mg(S^tBu)(Cp)]_4$,[85] have also been described.



(**7**) (**8**) (**9**)

Scheme 3

For the heavier alkaline earth elements the characterized compounds are octahedral monomers, dimers, or separated-ion species. The complexes $M(SR)_2$ (M=Ca, Sr, Ba) have been obtained by aminolysis and proved to be soluble in solvents such as py; these compounds decompose rather cleanly to their metal sulfides.[86] The monomeric species include $[M(EMes^*)_2(thf)_4]$ (M=Ca, Sr, Ba; E=S, Se),[87–89] $[Ca(SC_6F_5)_2(py)_4]$,[90] $[Ca(SMes^*)_2(18\text{-crown-}6)]\cdot thf$,[90] or $[Ba(SeTrip)_2(18\text{-crown-}6)]$.[87] Only a dimeric barium derivative, $[Ba(SeTrip)(py)_3(thf)]_2$, has been described.[87] For these elements separated ion-triple species, such as $[M(18\text{-crown-}6)(hmpa)_2][EMes^*]_2$ (M=Ca, Sr, Ba; E=S, Se)[87,88,91] or contact/separated ion-triple species as $[Ba(SMes^*)(18\text{-crown-}6)(hmpa)][SMes^*]$ have been reported.[91]

2.1.4 Main Group Metal Derivatives

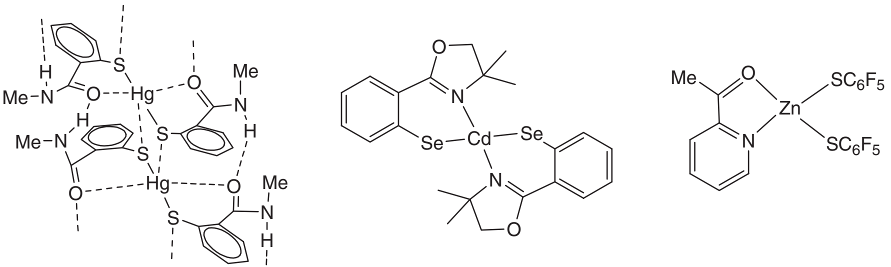
2.1.4.1 Zinc, Cadmium, and Mercury

The chemistry of group 12 metal chalcogenolates is complicated by the formation of oligomeric networks supported by bridging chalcogenolates, as exemplified by the polyadamantoid $[Cd(SPh)_2]_n$.[92,93] These compounds are interesting in order to use as precursors to group 12–16 semiconductors. However the difficulty in the characterization, low stability, and volatility of such complexes has lead to the search of new approaches to improve these precursors, as the use of sterically hindered or intramolecular stabilized chalcogenolates or auxiliary ligands.

Homoleptic derivatives of the type $[M(ER)_2]$ have been obtained for the three metals, being more numerous for the heavier element, and are usually polymeric species with the exception of bulky chalcogenolates. For Zn the only complexes which have a linear geometry are $[Zn(ER)_2]$ (E=S, Se; R=Trip, C_6H_3-2,6-Mes_2).[37,94,95] More numerous are for Cd and Hg that have been described for $SC_6H_4\text{-}2\text{-}\{C_{23}H_{36}(OH)_3\}^-$ (Hg),[96] $SePh^-$,[97,98] heterocyclic thiolate ligands,[99–102] $SC_6H_4\text{-}2\text{-}CONHMe^-$ as (**10**) (Hg),[103] $S(CH_2)_2NH_3$ (Hg),[104] 2-(acylamino)benzenethiolate (Hg),[105] $SC_nH_{2n+1}^-$ (Hg),[106] SBz^-,[107] and

$SC_6H_4NH_2^-$.[108] Many of these complexes have a polymeric structure and in the cases that the metal is linearly coordinated there are several possibilities of stabilization as M···S, Hg···Hg, M···N (in heterocyclic thiolates), intramolecular NH···S, or intermolecular CH···N interactions or π–π stacking. For mercury other type of neutral complexes of the form $[HgR(SC_6H_4NH_2)]$ (R=Me, Ph),[108] [HgCl(SR)] (R=Bz, Np (neopentyl), ^{i}Pr),[107] or $[HgMe(SC_6H_4\text{-}2\text{-}NO_2)]$ have been described.[109] Distorted trigonal planar geometry have been found in complexes $Bu_4N[Hg(SePh)_3]$ and $[K(18\text{-crown-}6)(thf)_2][Cd(SCPh_3)_3]$.[110] Homoleptic tetrahedral complexes $[Hg(SR)_4]^{2-}$ have also been prepared for the tetrazolethiolate[111] and for the carbamoilphenylthiolate ligands.[103]

The use of functionalized chalcogenolates affords mononuclear derivatives in which the chalcogenolate act as a bidentate chelating ligand, for example, with oxazoline-chalcogenolates as (**11**),[112–114] dimethylaminoalkyl-chalcogenolates,[115] butoxisilenethiolates,[116] and arenephosphinothiolate ligands.[117] Neutral tetrahedral complexes have also been achieved by the use of auxiliary ligands and have the stoichiometry $[M(ER)_2L_2]$, which have been described for zinc with butoxisilanethiolates,[116,118,119] and for mercury with heterocyclic thiolates,[120] or $[M(ER)_2(L–L)]$, where L–L represents bidentate amines for the thiolates SEt, SC_6H_4-4-X,[121–123] or the chelating N,O acetyl- or benzoilpyridine (**12**) ligands for the thiolates SC_6F_5 or STrip,[124] or the pyridine-4-thione for the thiolate pyridine 4-thiolate (Scheme 4).[125]

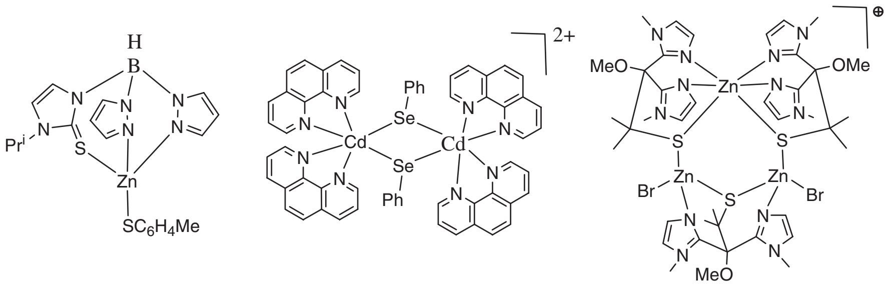


(**10**) (**11**) (**12**)

Scheme 4

Zinc is the active metal in the largest group of metalloproteins found in the nature. Recently a new class of zinc enzymes with a sulfur-rich environment has emerged the thiolate-alkylating enzimes, the most prominent of which is the cobalamine-independent methionine synthase.[126] For these reasons several monothiolate zinc complexes have been prepared for the modelling of these enzymes with different N_2S as (**13**),[127–130] N_2O,[130–132] N_3,[132,133] S_3,[134] tripod ligands, or with Cd because of the favourable spectroscopic properties with an S_3 tripod ligand.[135]

Dinuclear complexes have been reported in which the chalcogenolates act as bridging ligands between the metal centres as in $[Zn\{\mu\text{-}SSi(O^tBu)_3\}(acac)]_2$,[136] or $[Cd(\mu\text{-}ER)(L\text{–}L)_2]_2^{2+}$ ($ER{=}SC_6H_4\text{-}4\text{-}X$, $L\text{–}L{=}H_2B(C_3N_2S\text{-}3\text{-}Me)_2$, bipy, phen, tmeda; $ER{=}SePh$ (**14**) or $SeC_6H_4\text{-}4\text{-}Me$, $L\text{–}L{=}phen$).[137,139] The latters in which the cadmium adopt a rare octahedral coordination present luminescence properties. Similar complexes with mercury as $[Hg(\mu\text{-}ER)(bipy)]_n(PF_6)_n$ ($ER{=}SC_6H_4\text{-}4\text{-}OMe$, SePh) also have optical properties and a polymeric structure.[140] Trinuclear derivatives have been described with tridentate ligands like aminoalkyl-amino-alkylthiolates,[141] or the heteroscorpionate N_2S(alkylthiolate) ligand (**15**) (Scheme 5).[142] Polynuclear compounds are synthesized by the reaction of aminoalkylthiolates and MX_2 ($M{=}Cd$, Hg) salts and are of the type $[Cd_8Cl\{SCH(CH_2CH_2)_2NHMe\}_{16}]^{15+}$,[143] or $[Hg_6Cl_8(SCH_2CH_2NH_3)_8]^{4+}$ and $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9]^{3+}$.[144] Adamantane-like species as $(Me_4N)_2[Zn_4X_4(\mu\text{-}SPh)_6]$,[145] or other zinc clusters as $[Zn_6(SC_6F_5)_{10}(bppae)_2]$ (bppae = 1,2-bispyridine-2-yl-2[(pyridine-2-ylmethylene)-amino]-ethenolate,[146] or $[Zn_4(SMes^*)_4(\mu\text{-}ImCH_2O)_3(\mu\text{-}OMe)]$(Im=imidazole),[147] have also been obtained. Other compounds are clusters in which chalcogenolate and chalcogenide ligands are present, such as $[Cd_{10}S_4X_4(SR)_{12}]^{4-}$,[148] $[Zn_8S_4(\mu_4\text{-}S)(\mu\text{-}SBz)_{12}]^{2-}$,[149] $[Zn_8(\mu_4\text{-}S)(\mu\text{-}SBz)_{16}]^{2-}$,[150] and several Hg–Se and Hg–Te clusters, as for example $[Hg_{32}Se_{14}(SePh)_{36}]$ or $[Hg_{10}Te_4(TePh)_{12}(PPh^nPr_2)_4]$,[151–153] or $[Cd_{11}Zn_5Se_{13}(SePh)_6(thf)_2(tmda)_5]$,[154] which have been prepared as possible precursors of 12–16 semiconductors. Finally, heterometallic Eu/M(II) ($M{=}Zn$, Cd, Hg),[155] Ln/Hg,[156] and Hg/Re carbonyl cluster have also been synthesized.[157,158]



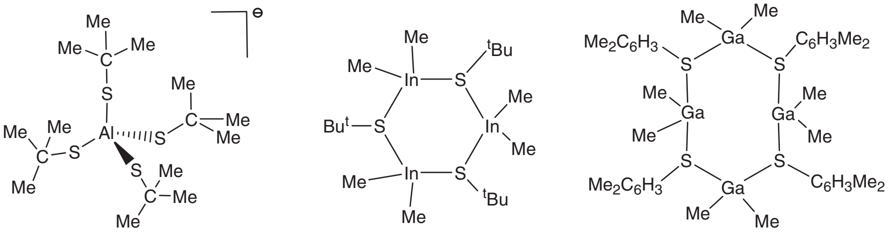
(**13**) (**14**) (**15**)

Scheme 5

2.1.4.2 Aluminium, Gallium, Indium, and Thallium

The chemistry of the chalcogenolate compounds of these elements is dominated for the seek of molecular precursors for the deposition of 13/16 chalcogenide semiconductors by MOCVD or related techniques.[159]

Mononuclear chalcogenolate complexes have the stoichiometries $[MR(ER')_2]$,[160–163] $[MR_2(SR')]$,[163] $[M(ER)_3L]$,[162,164,165] $[M(ER)_3]$,[165–171] or $[M(ER)_4]^-$ (**16**).[164–166] Usually the metals are found in a trigonal planar or tetrahedral geometry, with the exception of some $[M(ER)_3]$[168–171] complexes or $[MR(ER)_2]$[163] with functionalized chalcogenolate ligands, as for example Epy^- ($E{=}S$, Se), $SC_6H_4\text{-}2\text{-}PPh_2^-$ in which the metal is in an octahedral or a trigonal bipyramidal geometry. Other less-represented type of chalcogenolate derivatives are $[AlMe_2(SePh)(PPh_3)]$,[172] and the hydrides $[GaH(S^tBu)_2(NMe_3)]$ and $[GaH_2(S^tBu)(amine)]$.[173] Dinuclear complexes with bridging chalcogenolate ligands and terminal aryl or alkyl groups, $[MR_2(\mu\text{-}ER)]_2$, are probably the best represented mainly for thiolates but selenolates and tellurolates have also been described.[162,164,166,172–182] Other dinuclear complexes with a bridging diphosphine ligand are of the type $[\{In(SeSi(SiMe_3)_3)_3\}_2\{\mu\text{-}(PMe_2)_2CH_2CH_2)\}]$.[167] Depending of the size of the chalcogenolate and the alkyl or aryl substituents trimeric, $[MR_2(\mu\text{-}ER)]_3$ (**17**), or tetrameric species, $[MR_2(\mu\text{-}ER)]_4$ (**18**), can be isolated (Scheme 6).[175,180] Also polymeric compounds of the form $[InMe(SePh)(\mu\text{-}SePh)]$ have been described.[174] For the heaviest element of the group, less work have been done in chalcogenolates in the last years and the Tl(I) and Tl(III) complexes described tend to be polymeric as $[Tl(SCH_2C_4H_8O)_6]_n(PF_6)_n$,[183] $[TlMe_2(SC_4N_2\text{-}4\text{-}CF_3)]_n$,[184] or tetranuclear $[TlMe_2(SC_4N_2\text{-}4,\text{-}CF_3\text{-}6\text{-}Me)]_4$.[185]



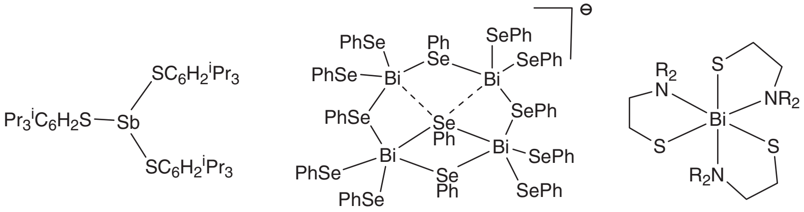
(**16**) (**17**) (**18**)

Scheme 6

2.1.4.3 Antimony and Bismuth

The work in this group has focussed mainly in antimony and bismuth because of the thermoelectric properties of the chalcogenides[186] and as low temperature single-source precursors to related semiconductor materials.[187] The use of bismuth compounds in the treatment of gastrointestinal disorders has lead to the study of several thiolate compounds as models to understand the bioactivity.

Antimony and bismuth derivatives of sterically demanding chalcogenolate ligands are mononuclear trigonal planar, $[M(EC_6H_2\text{-}2,4,6\text{-}R_3)_3]$ (M=Sb (**19**), Bi; E=S, Se; R=Me, ^{i}Pr, ^{t}Bu).[187] The compounds $[M(SR)_3]$ ($R=C_6F_5$, C_6H_4-4-Me, C_6H_3-2,6-Me_2) form loosely bound centrosymmetric dimers through M···S contacts or have Sb···arene interactions.[188,189] These compounds are Lewis acids and then several adducts of the type $[M(ER)_3L_2]$ or $[M(ER)_3L_3]$ can be formed.[190,191] Anionic complexes of the type $[Bi(SC_6F_5)_5]^{2-}$,[188] $[Bi_2(SC_6F_5)_6(\mu\text{-}SC_6F_5)_n]^{n-}$ (n = 1, 2),[192] or with halide ligands as $[Bi_2(SC_6F_5)_6(\mu\text{-}X)]^-$ or $[Bi_3(SC_6F_5)_9(\mu\text{-}Br)_2]^{2-}$ have been obtained by reaction of $[Bi(SC_6F_5)_3]$ with halide anions.[192] The reaction of $BiBr_3$ with $PhSeSiMe_3$ gives clusters, such as $[Bi_4(\mu\text{-}SePh)_5(SePh)_8]^-$ (**20**) or $[Bi_6(\mu\text{-}SePh)_6(SePh)_{10}Br_2]$.[193] The use in medicine of bismuth compounds has lead to the study of several functionalized thiolates as $S(CH_2)_2Y^-$ (Y=OH, NH_2, $NHR'_2{}^+$, NR_2) or cysteine as models for such compounds. Various complexes of stoichiometries $[BiX_3(S\text{-}Y)]^-$, $[BiX_2(S\text{-}Y)]$ (X=Cl, Br), $[Bi(S\text{-}Y)_2]^+$, $[Bi(S\text{-}Y)_3]$ (**21**) have been characterized (Scheme 7).[194–199]



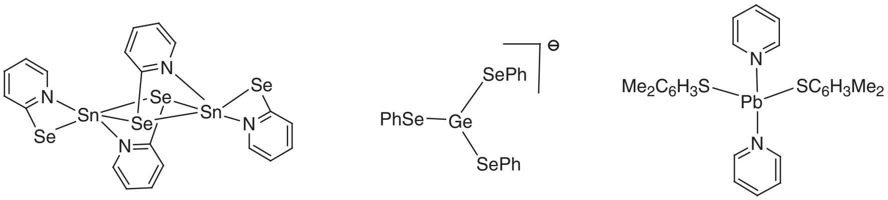
(**19**) (**20**) (**21**)

Scheme 7

2.1.4.4 Germanium, Tin, and Lead

Conformational and molecular orbital studies have been carried out in complexes $A(ER)_4$ (A=C, Si, Ge, Sn; E=O, E, Se), which reveal significant contribution of the HOMO's (based on the p-orbitals on E) to the E$\cdots$E interactions. This offers a rationale as to why certain main group species such as $Sn(SR)_4$ do not decomposes by CVD to tin sulfides as some transition metal thiolates do (p–d interactions which strengthen the M–S bond).[200] The presence of H_2S allows the deposition of tin sulfide thin films.[201,202] Tin and lead compounds with pyridineselenolates, $[Sn(Sepy)_2]_2$ (**22**), $[Sn(Sepy)_4]$ and $[Pb(Sepy)_2]$ can be used for the vapour phase deposition of MSe.[203] Germanium thiolates in oxidation states II and IV are know as $[Ge(EPh)_3]^-$ (**23**) and $[Ge(ER)_4]$ (E=S, Se).[204] Tin(IV) complexes with functionalized thiolates as $[SnMe_2(SC_6H_4\text{-}2\text{-}PPh_2)_2]$ or propionylglycinethiolate have been described.[205,206]

Lead thiolates as $[Pb(SPh)_2]$ are polymers with extensive Pb$\cdots$S interactions; the thiolate adduct $[Pb(SC_6H_4\text{-}2,6\text{-}Me_2)_2(py)_2]$ (**24**) (Scheme 8) is a monomer and $[Pb(SC_6H_4\text{-}2,6\text{-}Me_2)_2(L\text{–}L)]$ (L–L=bipy, pyrazine),[207] are polymers. Polynuclear lead thiolates are formed by oxidation of $Pb(SR)_2$ and are of the form $[Pb_5O\{SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_8]$[208] or $[Pb_{14}O_6\{SC_6H_3\text{-}2,6\text{-}Me_2\}_8]$.[209]



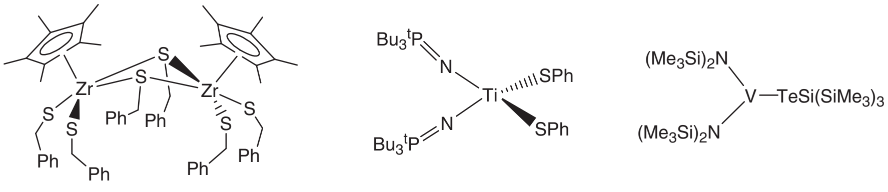
(**22**) (**23**) (**24**)

Scheme 8

2.1.5 Transition Metal Derivatives

2.1.5.1 Early Transition Metals

Homoleptic chalcogenolate complexes have been prepared for early transition metals and for vanadium in different oxidation states namely $[V^{II}(SeR)_2]_n$,[210] $[V^{III}(SeR)_3]$,[210] $[M^{IV}(ER)_4]$ (M=Ti, Zr, Hf, V; E=S, Se, Te),[210–214] and $[M^{V}(SR)_5]$ (M=Nb, Ta),[214–216] $[Ti(SC_6F_5)_5]^-$,[217] $[Zr(SC_6H_4\text{-}4\text{-}R)_6]^{2-}$,[59] or the dinuclear $[Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]^-$.[218] The metal sulfides have been produced from these complexes *via* chemical vapour deposition or sol-gel process.[213,215,216] The chemistry of these metals is dominated by the cyclopentadienyl derivatives and thus many chalcogenolate complexes bearing cyclopentadienyl or substituted cyclopentadienyl units have been described. Several stoichiometries are known with two cyclopentadienyl groups as $[MCp_2(ER')_2]$ (M=Ti, Zr, Hf), which have been used to prepare heterometallic complexes looking for early–late derivatives,[219–227] $[MCp_2(ER)X]$ (M=Ti, Zr; X=Cl, Me; E=S, Se),[228,229] or with functionalized thiolate ligands as $[TiCp_2(SC_{12}H_8)]$,[230] $[TiCp_2(SCH_2CH_2PPh_2)]^+$,[231] or $[Nb(C_5H_4SiMe_3)_2(SC_6H_7N_2)]$.[232] Complexes bearing one cyclopentadienyl ligand are of the form $[TiCp(SPh)_3]$,[233,234] $[TiCpX_2(SR)]$ (X=OR, Cl; R=Et, ^{t}Bu, Bz, Ph, $C_6H_2\text{-}2,4,6\text{-}R'_3$),[234–236] $[MCp^*(SR)_2(\mu\text{-}SR)]_2$ (M=Ti, Zr (**25**); R=^{n}Bu, Bz; Cp*=μ^5–C_5Me_5),[57,234] or $[TaCpCl_3(SC_6H_7N_2)]$.[237] Some of these CpTi-thiolate species undergo either β–C–H or C–S activation of the thiolate ligands depending on the reaction conditions. The seek of effective ethylene polymerization catalysts leads to the preparation of complexes with phosphinimide ligands because their steric and electronic analogy with cyclopendienyl and complexes such as $[Ti(N{=}P^iPr_3)_2(SR)_2]$ (R=^{i}Pr, ^{t}Bu, Ph (**26**), Bz) have been described together with the mixed Ti–Al species.[238,239] 2-Pyridine-thiolate has been widely explored in their coordination chemistry and several complexes of V(II), V(III), V(IV), or Ti(IV), as for example, $[VO(Spy)(\mu\text{-}Spy)]_2$ or $[TiCl(Spy)_3]$ with the thiolate acting as bidentate chelate or bridging ligand have been reported.[63,240] The latter shows catalytic activity for the polymerization of ethylene and styrene. Vanadium(III) selenolates or tellurolates of the form $[V\{N(SiMe_3)_2\}_2(ER)]$ (E=Se, Te (**27**); R=$Si(SiMe_3)_3$, $SiPh_3$) have been prepared and oxidazed to the vanadium(V) derivatives $[VE\{N(SiMe_3)_2\}_2(ER)]$ (E=O, S, Se) (Scheme 9).[241]



(25) **(26)** **(27)**

Scheme 9

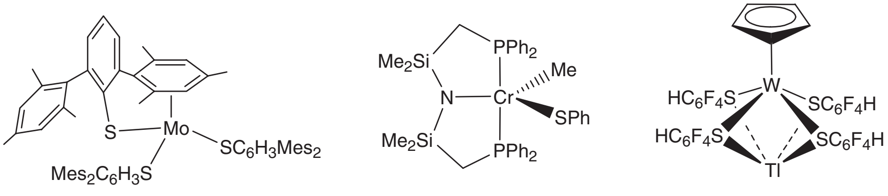
2.1.5.2 Chromium, Molybdenum, and Tungsten

Homoleptic chalcogenolate derivatives of group 6 are rare and in the last years only the complexes $[Mo\{TeSi(SiMe_3)_3\}_4]$,[212] $[W(\eta^2\text{-}Spy)_4]$,[242] or the dinuclear molybdenum complex $[Mo_2(SAd)_6]$ (Ad=adamantyl)[243] with a triple $Mo\equiv Mo$ bond have been described. The latter has been obtained from $[MoN(SAd)_3]$ by abstraction of the nitride group; this complex also produces dinuclear derivatives with the bridging nitride ligand as $[Mo_2(\mu\text{-}N)(SAd)_3(N^tBuPh)_3]$. The first homoleptic mononuclear trithiolate Mo(III) complex has been prepared from $[MoCl_3(thf)_3]$ and $LiSC_6H_3\text{-}2,6\text{-}Mes_2$, which has a strong π-interaction between the molybdenum and an *ortho*-mesityl group, $[Mo(\eta^7\text{-}SR)(\eta^1\text{-}SR)_2]$ (**28**).[244] The reactivity of the unsaturated $[MH(EC_6H_2\text{-}2,4,6\text{-}R_3)_3(PMePh_2)]$ (M=Mo, W; E=S, Se; R=Me, ^{i}Pr) with several ligands as CO, CNR, or py has been studied to give complexes such as $[Mo(SR)_2(CNR)_4]$ or with alkynes to give ylide complexes through insertion in the Mo–P bond, and also undergo facile S–C bond cleavage reactions in thf–MeOH to give complexes such as $[\{Mo(SR)(OR')(PMePh_2)\}_2(\mu\text{-}S)]$.[245–250] A comparison of the influence of alkoxide and thiolate ligands on the electronic structure and reactivity of Mo(III) and W(III) complexes has been studying in complexes, such as $[M_2(O^tBu)_2(S^tBu)_4]$, $[Mo(S^tBu)_3(NO)]_2$, or $[W(S^tBu)_3(NO)(py)]$ and has showed that the alkoxide are enthalpically favoured over the thiolate.[251] Mo(II) and W(II) complexes with the bidentate pyridine-selenolate of the type $[M(\eta^2\text{-}Sepy)_2(CO)_3]$ or with other selonolates such as $[MoCp(CO)_3(SeR)]$ have been described.[252,253] The oxidation of the chromium(II) complex $[CrMe\{N(SiMe_2CH_2PPh_2)_2\}]$ with S_2Ph_2 gives the five-coordinate Cr(III) derivative $[CrMe(SPh)\{N(SiMe_2CH_2PPh_2)_2\}]$ (**29**).[254]

Dinuclear complexes of molybdenum bearing cyclopendienyl groups and bridging thiolates have been prepared through the reaction of thiols or tritiocarbonates with the dinuclear alkyne complexes $[Mo_2Cp_2(\mu\text{-}RC_2R')(CO)_4]$, as for example, $[Mo_2Cp_2(\mu\text{-}SR)_2(\mu\text{-}S)_2]$, which further reacts with other metal compounds to give mixed metal clusters such as $[Mo_2Ru_2Cp_2(\mu_3\text{-}S)_2(\mu\text{-}SR)_2(CO)_4]$.[255–257] Similar complexes as $[Mo_2Cp^*{}_2(CO)_2(\mu\text{-}SMe)(\mu\text{-}S)]$ have been obtained by treatment of $[Mo_2Cp^*{}_2(CO)_4]$ with S_2Me_2.[258] Hydrodesulfurization processes are typically catalysed by metal sulfides deposited on a support; Mo and W are essential components, but increased catalytic activity, particularly towards thiophenes, is observed when the catalyst also comprises late transition metals. Thus mixed Rh–W systems or Mo–W with bridging thiolates have been studied.[259,260]

The reaction of thiolate molybdenum or tungsten complexes $[MCp(SR)(CF_3C\equiv CCF_3)_2]$ with alkynes gives butadienyl derivatives.[261] The reaction of $[MCpCl_3(CO)]$ (M=Mo, W) with $M'(SC_6F_4\text{-}4\text{-}H)$ gives $[MCp(SC_6F_4\text{-}4\text{-}H)_4M']$ (M′=Tl, K, Rb, Cs) (**30**) (Scheme 10).[262] Other complexes are obtained by oxidation of $[MoCp_2(SPh)_2]$ to give the mixed thiolate-diarylsulfide compound $[MoCp_2(\eta^2\text{-}SC_6H_4SPh)]$,[263] or by reaction of $[CrCp(CO)_3]_2$ with pySSpy or with $SC_4H_3N_2$ to give $[CrCp(\eta^2\text{-}SR)(CO)_2]$.[264] In the highest oxidation state VI the chromium complexes $[Cr(CNC_6H_4\text{-}2,$

6-$Me_2)_4(SC_6F_5)_2]$,[265] $[MoO_2(\eta^2\text{-}SR)_2]$ (SR=heterocyclic thiolates),[266] or $[MS_3(SR)]^-$ (M=Mo, W)[267–269] have been reported.



(28) **(29)** **(30)**

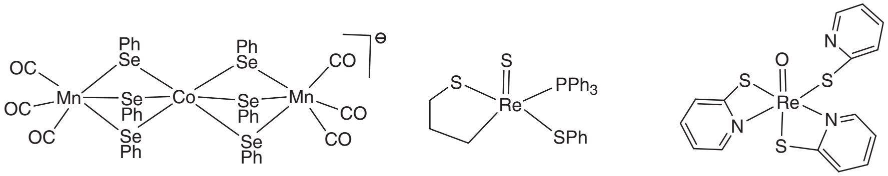
Scheme 10

2.1.5.3 Manganese, Technetium, and Rhenium

These metals form chalcogenolate complexes in several oxidation states, and from the application-oriented point of view manganese compounds have been synthesized as models for hydrodesulfurization processes and rhenium and technetium derivatives as models for radiopharmaceuticals.

Homoleptic compounds have been prepared for Mn(II) of the type $[Mn(Spy)_2]_n$, or $[Mn(EC_6H_2\text{-}2,4,6\text{-}R_3)_2]_n$ (E=Se, Te; R=Me, ^{t}Bu) and are polymeric with octahedral and tetrahedral manganese atoms, respectively.[270,271] The complex $[N(PPh_3)_2][Mn(SC_5H_4NO)_3]$ is monomeric with the thiolate acting as bidentate ligand.[272] The selenium derivatives react with bidentate ligands to give $[Mn(SeR)_2(N\text{–}N)_2]$ or $[Mn(SeR)_2(P\text{–}P)]$.[271] Manganese(II) thiolate complexes have been reported to activate the dioxygen molecule, the complex $[Mn(SC_6H_4\text{-}4\text{-}NO_2)L]$ (L=hydrotris(3,5-diisopropylpyrazol-1-yl)borate) react with oxygen to give manganese(III) oxo-complexes.[273] The reaction of PPN$[Mn(CO)_5]$ with $(ER)_2$ gives the manganese(I) derivatives *cis*-$[Mn(ER)_2(CO)_4]^-$ (E=S, Se), which has been used to form heterometallic Mn–M–Mn (M=Fe, Co, Ni) complexes with bridging chalcogenolate ligands, as for example $[Mn_2Co(\mu\text{-}SePh)_6(CO)_6]^-$ (**31**).[272,274–277] Other manganese(I) chalcogenolate complexes such as $[Mn(\mu\text{-}SeR)(CO)_4]_2$ or $[Mn(SR)(CO)_3]_4$ have been obtained by reaction of Na$[Mn(CO)_5]$ with elemental selenium followed by the treatment with RCl or by thermal reaction of $[Mn(\eta^5\text{-}C_5H_7)(CO)_3]$ with RSH, respectively.[278,279] C–S Bond cleavage reactions have been studied for benzothiophene-carbonyl-manganese compounds as models for homogeneous hydrodesulfurization giving complexes with thiolate ligands, as for example $[Mn_2(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8]$.[280–282] C–S Bond cleavage is also promoted in oxo (dithiolato)rhenium(V) by triphenylphosphine giving $[ReS(SPh)\{\eta^2\text{-}S(CH_2)_2CH_2\}(PPh_3)]$ (**32**).[283]

Technetium and rhenium coordination chemistry has actively developed in order to design materials as potential radiopharmaceuticals; diagnostic imaging agents for technetium and potential therapeutic reagents based on rhenium. Continuous efforts are still applied to find efficient chelating systems for the $[MO]^{3+}$ cores (M=Tc, Re). Thus several complexes with monodentate and functionalized thiolates have been reported. These are usually polydentate Schiff bases with S,N,O donor ligands, phosphinethiolate, pyridine- or pyrimidine-thiolates, benzimidazole-thiolates, tetrazole-thiolates as (for example, see **33** Scheme 11).[284–292]



(31) **(32)** **(33)**

Scheme 11

Rhenium(V) *oxo* or nitride complexes with fluorinated benzenethiolates such as $[ReO(SC_6H_4\text{-}2\text{-}F)_3(PPh_3)]$ or $[ReN(SC_6F_5)_2(PPh_3)_2]$ have also been obtained.[293] The reduction of the technetium or rhenium oxo complexes with phosphines leads to the trigonal bipyramidal M(III) derivatives such as $[Tc\{S(CH_2)_2O(CH_2)_2S\}(SC_6H_4\text{-}4\text{-}OMe)(PMe_2Ph)]$ or $[ReX_2(Spym)(PPh_3)_2]$ (Spym=pyrimidine-thiolale).[294–296] The reaction of the rhenium hydride $[ReH_7(PPh_3)_2]$ with 2,6-dimethylbenzenethiol gives $[Re(SC_6H_3\text{-}2,6\text{-}Me_2)_3(PPh_3)]$ with a trigonal bipyramidal geometry and a Re···H agostic interaction. Further reaction with ligands as MeCN or CN^tBu gives the corresponding pentacoordinated derivatives.[297] Rhenium(I) thiolate complexes such as $[Re_2(\mu\text{-}SC_6H_4\text{-}4\text{-}X)(CO)_6(L\text{-}L)_2]OTf$ (L–L=phen, bipy; X=Me, OMe F, Cl; $OTf=CF_3SO_3^-$) have been prepared and show luminescent properties.[298] Molecular rectangles based upon rhenium chalcogenolate dimers have been synthesized by reaction of $[Re(OTf)(CO)_4]$ with the chalcogenol to give $[Re_2(\mu\text{-}ER)_2(CO)_8]$ (E=S, Se) followed by treatment with 4,4′-bipyridines, $[Re_4(\mu\text{-}ER)_4(\mu\text{-}N\text{–}N)_2(CO)_{12}]$.[299] Chiral rhenium complexes containing functionalized thiolate ligands such as $[ReCp(SR)(NO)(PPh_3)]$, which include biological relevant molecules as cysteine or mercapto-proline derivatives, have been also synthesized.[300]

2.1.5.4 Iron, Ruthenium, and Osmium

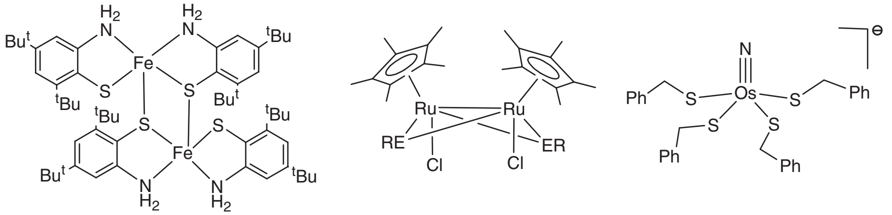
Homoleptic mononuclear thiolate complexes have been prepared for Fe(II) with sterically hindered substituents as in $[Fe(SC_6H_3\text{-}2,6\text{-}Mes)_2]$,[301] $[Fe(SMes^*)_3]^-$,[301] which is trigonal planar, or $[Fe(SC_6H_4NR_2)_4]^{2-}$ which is tetrahedral.[302] Dinuclear derivatives of the type $[Fe_2(ER)_4]$ (E=S, Se) have been obtained for several R groups.[303,304] Other stoichiometries have been reported for Fe(II) as for example $[Fe(SMes^*)_2L]$,[305] $[Fe_2(ER)_2\{N(SiMe_3)_2\}_2]$,[303,304] $[Fe(SeMe)_2(CO)_2(PMe_3)_2]$,[306] *cis*-$[Fe(Spy)_2(CO)_4]$,[307] $[Fe(Spy)_3]^-$,[307] or *fac*-$[Fe(SR)_3(CO)_3]^-$ ($R=C_7H_4SN$, C_4H_3S, $C_4H_2O\text{-}2\text{-}Me$), which form the heterometallic complex $[Fe_2Ni(\mu\text{-}SC_4H_2O\text{-}2\text{-}Me)_6(CO)_6]$.[308] The reaction of $FeCl_2$ with *o*-aminothiophenols gives the dinuclear derivatives $[Fe(SC_6H_2R_2NH_2)_2]_2$

(**34**), which are oxidized to the Fe(III) complexes $[Fe(SC_6H_2R_2NH)_2]_2$.[309] The redox electrochemistry of Fe(II), $[Fe_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$,[310] and Fe(III) thiolate complexes of the type $[FeCp(SR)(dppe)]PF_6$ (R=Me, Ph, C_6H_4-4-Br) has been studied.[311] A mixed metal thiolate complex has been synthesized by treatment of $[Fe_2(S^iPr)_6]^{2-}$ with $FeCl_2$ and CuCl to give $[Fe_3Cu(S^iPr)_6Cl_3]^{2-}$, which contains a Fe_3Cu pyramidal core.[312] Charge transfer complexes have been reported from the reaction of $[Fe_2Cp_2(\mu\text{-}SEt)_2(CO)_2]_2$ with tetracyanoquinodimethane and tetracyanoethylene.[313] Several Fe(I) dinuclear complexes with thiolate ligands as $[Fe_2(\mu\text{-}SC_6H_2\text{-}2,4,6\text{-}R_3)_2(CO)_6]$ (R=Me, ^{i}Pr) have been prepared by reaction of $[Fe_3(CO)_{12}]$ with HSR,[314] or $[Fe_2(\mu\text{-}SEt)(\mu\text{-}C{\equiv}CR)(CO)_6]$ by treatment of $[Fe_2(CO)_9]$ with R-C≡CSEt,[315] or $[Fe_2(\mu\text{-}SCH_2CH_2PPh_2)_2(CO)_4]$ obtained by photolysis of $[Fe(CO)_4]$ with $PPh_2CH_2CH_2SH$.[316]

The reaction of group 8 carbonyl clusters with thiols gives several complexes, as for example $[M_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)(CO)_9]$ (M=Ru, Os),[317] $[Os_3(\mu\text{-}H)(\mu\text{-}Spy)(\mu\text{-}dppm)(CO)_8]$,[318] or $[Os_3(\mu\text{-}H)(\mu\text{-}SR)(CO)_{10}]$ (R=CMe_3, C_6H_{11}, $C_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_4$).[319,320] The treatment of $[M_3(CO)_{12}]$ (M=Fe, Ru) with the thiophosphinite $C_6F_5SPPh_2$ gives complexes with bridging thiolate ligands such as $[Fe_2(\mu\text{-}SC_6F_5)(\mu\text{-}PPh_2)(CO)_6]$ or $[Ru_4(\mu_3\text{-}SPPh_2)_2(\mu\text{-}SC_6F_5)_2(\mu\text{-}PPh_2)_2(SC_6F_5)_2(CO)_6]$.[321] Ru(II) and Os(II) chalcogenolate complexes have been widely studied and several stoichiometries have been described as the octahedral $[Ru(\eta^2\text{-}RL)(\eta^2\text{-}Spy)(CO)(PPh_3)_2]$ (RL=imine-phenol),[322] $[MH(\eta^2\text{-}SR)(CO)(PPh_3)_2]$ (M=Ru, Os; R=quinoline, pyridine),[323] $[RuH(SR)(dppm)_2]$ (R=Ph, C_6F_5),[324] $[Ru(SPh)\{(P^iPr_2)_2CH_2CH_2\}]BPh_4$,[325] $[OsH(SC_6H_4\text{-}2\text{-}SiPh_3)(CO)(PPh_3)_3]$,[326] $[Ru(\eta^2\text{-}Spy)(bipy)_2]ClO_4$,[327] $[Os(\eta^2\text{-}Spy)_2(CO)_2]$,[328] and the trinuclear $[Ru(\eta^5\text{-}C_9H_7)(\mu\text{-}SEt)]_3$.[329] Other Ru(II) thiolate complexes have been obtained through interesting reaction pathways as the reaction of arylazopyridine complexes with dithiocarbonate, which proceed trough C–S bond cleavage and formation of the thiolate derivatives $[Ru\{SC_6H_3\text{-}2\text{-}(R)N{=}Npy\}_2]$,[330] the reaction of $PPN[Ru(SC_6H_4PPh_2)_3]$ with dichloromethane which gives the insertion of the methylene between two sulfur atoms giving the triphosphino/dithioether/thiolate complex $[Ru(SC_6H_4PPh_2)\{S_2(CH_2)(C_6H_4PPh_2)_2\}]Cl$.[331] The compound $PPN[Ru(SC_6H_4PPh_2)_3]$ oxidizes reversibly to the Ru(III) derivative.[332] Coordinatively unsaturated Ru(II) complexes such as $[Ru(ER)_2(\eta^6\text{-arene})]$ (E=S, Se, R=C_6H_2-2,4,6-R'_3)[333,334] or $[RuCp^*(SC_6H_3\text{-}2,6\text{-}Mes_2)]$, which gives the cyclotrimerization of alkynes with the thiolate acting as counteranion,[335] or $[RuCp^*(\mu\text{-}S^iPr)]_2$, which gives rutenacyclopentenyl derivatives[336] by reaction with alkynes have been reported.

Dinuclear diamagnetic Ru(III) chalcogenolate complexes of the type $[Ru_2Cp^*_2Cl_2(\mu\text{-}ER)_2]$ (E=S, Se, Te) (**35**) have been obtained by reaction of $[RuCpCl]_4$ with thiols or with the dicholgenides REER. These complexes have been thoroughly studied in catalysis, as for example, in allylation of arenes or in propargylic substitution reactions.[337–344] The reaction of $[Ru_2Cp^*_2Cl_2(\mu\text{-}SR)_2]$ (R=^{i}Pr, Bz) with Li_2S_2 gives the disulfide complexes $[Ru_2Cp^*_2(\mu\text{-}S_2)(\mu\text{-}SR)_2]$.[345] Similar complexes with fulvalene ligands as $[Ru_2(\mu_2\text{-}\eta^6\text{:}$

η^6-$C_{10}H_8$)$(SR)_2(\mu$-$SR)_2$] (R=Ph, C_6H_4-4-R) have been prepared from the fulvalene Ru(II) derivative by reaction with NaSR.[346] Cationic dinuclear Ru(III) complexes as $[Ru_2Cp_2(\mu\text{-}ER)_2(NCMe)_2]^{2+}$ (E=S, Se) or $[Ru_2Cp_2(\mu\text{-}Spy)_2]^{2+}$ have been obtained from the reaction of $[RuCp(NCMe)_3]^+$ with REER.[347] However if the starting material is [RuTpCl(cod)] (Tp=hydrotris (pyrazolyl)borate), the reaction with RSSR in dimethylformamide gives the Ru(II) derivatives as $[RuTp(\eta^2\text{-}SC_6H_4\text{-}2\text{-}SPh)$ probably *via* a Ru(IV) intermediate $[RuTpCl(SR)_2]$.[348] Paramagnetic mononuclear Os(III) thiolate complexes such as $[Os(SC_6F_5)_2(S_2C_6F_4)(PMe_2Ph)_2]$[349,350] or Os(IV) $[Os(SC_6F_5)_2(PMe_2Ph)_2]$; the latter obtained by C–F activation of $[Os(\eta^2\text{-}SC_6F_5)(SC_6F_5)_2(PMe_2Ph)_2]$[351] or Ru(III) as $[Ru(SR)_2(S_2CSR)(PMe_2Ph)_2]$ (R=C_6F_5, C_6F_4-4-H),[352] obtained by insertion of CS_2 in one thiolate ligand, have been reported. Few thiolate complexes have been prepared higher than III oxidation states and these are the M(IV) derivatives $[M(SR)_3(C{\equiv}CR)(NCMe)]$ (M=Ru, Os),[353] $[Ru(SR)_3\{SCH(Me)CH_2SR)](R{=}C_6H\text{-}2,3,5,6\text{-}Me_4)$,[354] or Os(VI) nitride derivatives $[OsN(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$ or $[OsN(SR)_4]^-$ (R=Et, Bz (**36**)) (Scheme 12).[355]

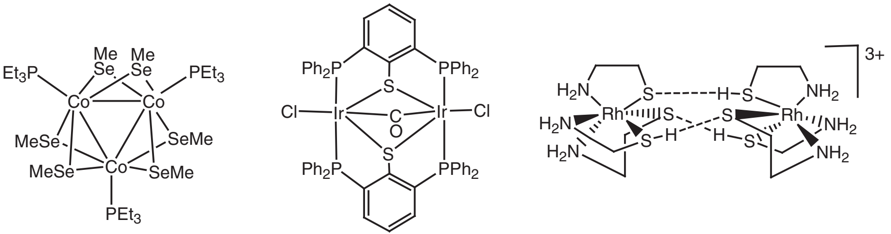


(34) **(35)** **(36)**

Scheme 12

2.1.5.5 Cobalt, Rhodium, and Iridium

Co(II) and Co(III) complexes with silanethiolates of the type $[Co(SR)_2L]$, $[Co(SR)_2L_2]$, $[Co(\mu\text{-}SR)(SR)(NH_3)]_2$, $[Co(SR)_2(NH_3)_4](SR)$ (R=$Si(O^tBu)_3$) have been prepared and structurally characterized.[356,357] The reaction of $CoCl_2$ with $NaSSi^tBu_3$ gives the complex $[CoCl(SSi^tBu_3)]_{12}$, wich has a wheel structure.[358] Other Co(II) complex with a 3-dimensional framework is obtained from the reaction of $CoCl_2$ with 6-mercaptonicotinic acid (6-mnaH$_2$), $[Co_9(6\text{-}mna)_8(\mu_3\text{-}O)_2(OH_3)_2(OH_2)_6]$.[359] Treatment of $CoAc_2$ with thiols in the presence of PEt_3 gives the trinuclear clusters $[Co_3(\mu\text{-}SR)_6(PEt_3)_3]X$ (R=Me (**37**), Et) (Scheme 13).[360] Octohedral Co(III) complexes with the heterofunctional pyridine-selenolate or phosphino-thiolate of the type $[Co(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}PPh_2)_3]$, $[Co(Sepy)(N\text{-}N)_2]^{2+}$ (N–N=en, bipy) or *fac*-$[Co(Sepy)_3]$ have been reported.[361,362] The same type of complexes have been prepared with aminothiolate, D-penicilaminate or L-cysteinate.[363] The compound $[Co(L\text{-}cys)(en)_2]$ coordinates silver ions to form a polymer with the silver atoms bonded to the sulfur atoms of the cysteine.[364] Another heteronuclear clusters is that formed by reaction of $CoCl_2$, $RuCl_3$, and the disodium salt of 2-mercaptophenol (H_2mp) and phosphine, $[Co_6Ru_2(mp)_{10}(P^nBu_3)_6]$.[365]



(**37**) (**38**) (**39**)

Scheme 13

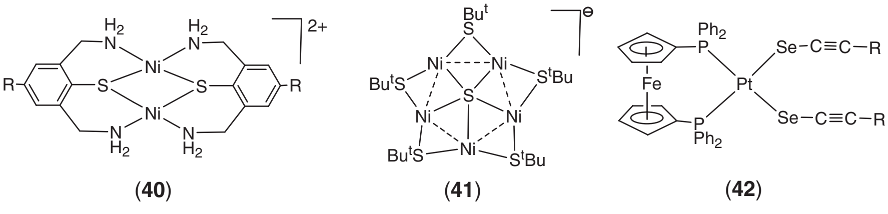
Supported Rh(I) thiolate complexes of the type $[Rh(\mu\text{-}SR)L_2]_2$ ($SR{=}S(CH_2)_2NMe_2$, $S(CH_2)_3Si(OMe)_3$, $SC_4N_2Me_2$, SC_6F_5; $L_2{=}(CO)_2$, cod) over silica or on a cationic exchange resin have been shown to catalysed hydroformylation of alkenes.[366–370] Similarly the complexes *trans*-$[Rh(SC_6F_5)(CO)(PPh_3)_2]$ and *trans*-$[Rh(\mu\text{-}SC_6F_5)(CO)(PPh_3)]_2$ or the species $[M(\mu\text{-}SR)(CO)(PPh_3)]_2$ ($M{=}Rh$, Ir; $R{=}C_6H_3\text{-}2,4,6\text{-}{}^iPr_3$, $C_6H_3\text{-}2,4,6\text{-}Me_3$) have been prepared and showed to be active hydroformylation catalysts.[371,372] The reaction of $[Rh_4(CO)_{12}]$ with *p*-thiocresol leads to the formation ot the thiolate dimer complex $[Rh(\mu\text{-}SC_6H_4\text{-}4\text{-}Me)(CO)_3]_2$ *via* elimination of dihydrogen.[373] Rh(I) and Ir(I) complexes with functionalized thiolates as pyridine-, pirimidine, or benzimidazole-thiolates of the form $[M(\eta^2\text{-}SR)(cod)]_2$ or $[M(\eta^2\text{-}SR)(CO)_2]_2$, $[M(\eta^2\text{-}SR)(CO)(PPh_3)]$, or *trans*-$[Ir(SR)(CO)(PPh_3)_2]$ have been prepared and some of them studied as good catalysts in hydroformylation reactions.[374–377] Also in the complex $[Rh(SC_4N_2Me_2)(CO)_2]$ the stacking pattern has been theoretically studied and is different from other d^8 square-planar complexes, adopting a rotated conformation by a combination of $Rh\cdots Rh$ interactions and steric factors.[378] The complex $[Rh(\mu\text{-}SR)(cod)]_2$ with benzimidazol further reacts with $[Rh(\mu\text{-}Cl)(cod)]_2$ to give the tetranuclear $[Rh_4(\mu\text{-}SR)Cl_2(cod)_4]$.[376] With phosphine-thiolate ligands, the rhodium(I) complexes $[Rh_2(SFcPPh_2)_2(CO)_2]$ ($Fc = (\eta^5\text{-}C_5H_4)_2Fe$) and $[Rh_2\{SC_6H_3\text{-}2,6\text{-}(PPh_2)_2\}Cl(CO)_2]$ or the iridium $[Ir_2\{SC_6H_3\text{-}2,6\text{-}(PPh_2)_2\}_2Cl_2(CO)]$ (**38**) (Scheme 13) with a formal oxidation state of II have been obtained.[379,380] A dinuclear rhodium(II) complex $[Rh_2(SPh)_2(\mu\text{-}SPh)_2(bipy)_2]$ have been prepared from the acetate Rh(II) complex by reaction with NaSPh.[381] Chalcogenolate M(III) complexes have been well studied and several stoichiometries were found. With cyclopentadienyl ligands several complexes such as $[MCp^*(SR)_2]$ ($M{=}Rh$, Ir; $R{=}C_6F_5$, C_6F_4H)[382] or $[RhCp(EPh)_2(PMe_3)]$ ($E{=}S$, Se, Te)[383] or $[Rh_2Cp^*_2(\mu\text{-}SR)_2(\mu\text{-}pz)]^+$ ($R{=}Ph$, C_6F_5, C_6F_4X)[384] or $[M_2Cp^*_2(\mu\text{-}S^iPr)_2(\mu\text{-}X)]^+$ ($M{=}Rh$, Ir; $X{=}Cl$)[385] have been described. The latters react with nitrobenzene to give $[M_2Cp^*_2(\mu\text{-}S^iPr)_2(\mu\text{-}PhNO)]^+$,[385] or with alkynes to give several derivatives as a result of the insertion of the alkyne.[386] Ir(III) derivatives have been synthesized by oxidative addition of the corresponding Ir(I) compounds, as in $[Ir(SR)(CO)(PPh_3)_2]$ which gives $[Ir(SR)(O_2)(CO)(PPh_3)_2]$ ($R{=}Me$, C_6F_5, benzimidazole).[387,388] Protonation with HBF_4 of $[Rh(SC_6$

H_4-2-PPh_2)(CO)(PPh_3)] gives the Rh(III) compound [Rh_2H_2(μ-SC_6H_4-2-PPh_2)$_2$(CO)$_2$(PPh_3)$_2$]$^{2+}$.[372] Oxidation of [RhTp*(NCMe)(coe)] (coe=ciclooctene) with REER gives [RhTp*(SPh)$_2$(NCMe)], [RhTp*(η^2-Spy)(Spy)], or [$Rh_2Tp^*_2$(STol)$_2$(μ-STol)$_2$].[389] The reaction of the homoleptic complex *fac*-[Rh($SCH_2CH_2NH_2$)$_3$] with HBF_4 gives the dinuclear compound with S$\cdots$H–S hydrogen bonds (**39**),[390] or with Ag(I) to give [Ag_3{Rh($SCH_2CH_2NH_2$)$_3$}$_2$]$^{3+}$ with S-Ag-S bridges (Scheme 13).[391]

2.1.5.6 Nickel, Palladium, and Platinum

Chalgogenolate complexes of group 10 metals are very well represented. Homoleptic derivatives have been obtained for nickel and are [$Ni_2(S^tBu)_6$]M_2 (M=Na, K),[392] [$Ni_4(Se^iPr)_8$],[393] the crown complex [$Ni_6(SCH_2CH_2OH)_{12}$],[394] or [$Ni_5(SCH_2CH_2N^iPr_2)_{10}$].[395] Homoleptic complexes have also been found with functionalized chalcogenolates as in [Ni(SR)$_2$] (SR=quinoline thiolate, iminopyrazole-thiolate)[396,397] [M($SC_6H_4PPh_2$)$_2$] (M=Ni, Pd, Pt),[398] or [Ni_3(SR)$_4$]$^{2+}$ (SR=bis(pyrazolyl)methane-phenylthiolate).[399] Several complexes of Ni and Pd have been prepared with the tridentate ligand 2,6-di(aminomethyl)-4-*tert*-buthyl-thiophenolate, which gives dinuclear and trinuclear derivatives as **40**.[400–402] Experimental evidences for the noninnocence of *o*-aminothiophenolates have been found for Ni(II), Pd(II), and Pt(II) [M($SC_6H_4NH_2$)$_2$] complexes in which the ligands are in three oxidation levels.[403] A new route to Ni(II) thiolate clusters occurs by insertion of elemental sulfur into Ni–C bonds.[404] Nickel clusters with chalcogenide and chalcogenolate ligands have been prepared, as for example [$Ni_{20}Se(SeMe)_{20}$]$^-$ and [$Ni_5S(S^tBu)_5$]$^-$ (**41**), the bonding has been analysed in the latter.[405–407]

M(II) complexes with bridging chalcogenolates and other auxiliary ligands are very numerous and have several stoichiometries. Mononuclear complexes of the type [M(ER)$_2L_2$] (M=Ni, Pd, Pt; E=S, Se), as for example **42** (Scheme 14), are known with several alkyl or aryl chalcogenolates and monodentate or bidentate auxiliary ligands as phosphines, diphosphines, N,C ortometalated ligands, *etc.*[408–418] The complexes [Pd(SR_F)(L–L)] (SR_F=fluorinated benzenethiolates) catalyse the Heck reaction.[419,420] The platinum diimine complexes with fluorinated thiolates [Pt(N–N)(SC_6F_4-4-X)$_2$] (N–N=bipy, phen; X=F, CN) are cromophores for which the origin of the lowest excited state have been studied.[413] Mononuclear nickel complexes with thiolates and selenolates of the form [Ni(SR)$_n$(SeR)$_{3-n}$(CO)]$^-$ (n = 0, 1, 2, 3) have been prepared and are relevant to the nickel site in CO dehydrogenases and [NiFeSe] hydrogenase.[421,422]

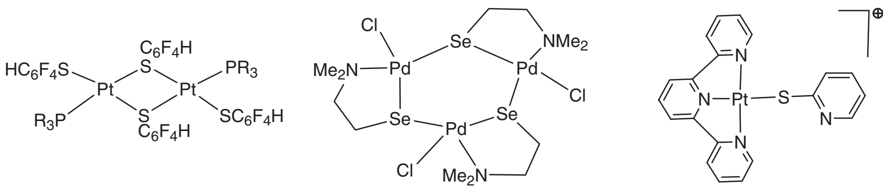


(40) **(41)** **(42)**

Scheme 14

Dinuclear complexes with bridging chalcogenolate ligands are also well represented and are mainly of the type $[MR(\mu\text{-}ER)L]_2$ as **43**, where the metal is most frequently Pd and Pt and the R ligand can be an alkyl or aryl group, halogen, *etc.*[423–431] In $[Pt(SC_6F_4H)(\mu\text{-}SC_6F_4H)(PR_3)]_2$, a C–F activation takes place to afford $[Pt(SC_6F_4H)_2(\eta^2\text{-}S(C_6F_4H)C_6F_4\text{-}2\text{-}PPh_2)]$.[423] Dinuclear palladium complexes with one bridging thiolate and chlorine ligands have mesogenic bevaviour.[432,433] Also dinuclear Pd(II)-Pt(II) compounds with only one bridging thiolate ligands as $[PdPt(C_6F_5)_2(\mu\text{-}SC_6F_5)(phen)(dppm)]^+$ have been described.[434] Anionic dinuclear and trinuclear palladium derivatives with bridging thiolate and terminal pentafluorophenyl groups as $(NBu_4)_2[Pd_3(C_6F_5)_4(\mu\text{-}SEt)_4]$ have been prepared.[435]

Complexes bearing functionalized chalcogenolates are also important and have several stoichiometries as mononuclear species as $[M(\eta^2\text{-}ER)XL]$ (ER=Spy, Sepy, Tepy, $SCH_2CH_2PPh_2$),[436–441] $[Ni(\eta^2\text{-}SR)([12]aneN_3)]^+$ (SR =heterocyclic thiolates),[442] or dinuclear species as $[M_2(\mu\text{-}\eta^2\text{-}ER)_2X_2]$ (ER=$SCH_2CH_2PPh_2$, $SCH_2CH_2pzMe_2$, $SC_6H_4\text{-}2\text{-}NCOPh$).[439,443,444] The latter complex with the carboxamido thiolate activates dioxygen to give the oxidation of the phenyl groups to phenolate in $[Ni_2(\mu\text{-}\eta^3\text{-}SC_6H_4CCOC_6H_4O)_2]$.[444] Several studies have been done in Pd(II) and Pt(II) with the ligands $Me_2N(CH_2)_nSe^-$ (n = 2, 3) in which they act as monodentate or bidentate in complexes such as $[M\{Se(CH_2)_3NMe_2\}_2(P\text{–}P)]$, $[PdCl\{\eta^2\text{-}Se(CH_2)_2NMe_2\}(PR_3)]$, $[MCl\{\mu\text{-}Se(CH_2)_3NMe_2\}(PR_3)]_2$, $[MCl\{\mu\text{-}\eta^2\text{-}Se(CH_2)_nNMe_2\}]_2$ or $[Pd\{Se(CH_2)_2NMe_2\}]_6$ and $[PdCl\{\mu\text{-}\eta^2\text{-}Se(CH_2)_2NMe_2\}]_3$ (**44**).[445–448] Other dinuclear complexes have double bridged pyridine-thiolate or related ligands, as for example $[Pt_2(\mu\text{-}Spy)_2(bipy)_2]^{2+}$,[449] or $[Pd_2(\eta^2\text{-}C_6H_4NMe_2)_2(\mu\text{-}Spy)_2]$,[450] where the platinum compounds show vapour-induced luminescence. Related complexes with terpyridine and thiolates show also luminescence properties, as for example $[Pt(SR)(terpy)]^+$ (**45**) (Scheme 15).[451,452] Heteronuclear derivatives are formed by reaction of $[Pt(HSpy)_4]Cl_2$ with chromium or vanadium to form lantern-type species as $[Pt(\mu\text{-}Spy)_4Cr(OH)]$.[453] C–S Bond cleavage of pyridinethiol have been reported in the presence of dinuclear M(II) (M=Pd, Pt) or Pt(III) complexes with bridging 5-methylpyridine-thiolate ligands.[454] Penta-coordinated Pt(II) compounds have been obtained by oxidative addition of the Pt^0 compound [Pt(dmphen)(olefin)] with RSeSeR to give $[Pt(SeR)_2(dmphen)(olefin)]$ (R=Me, Ph; dmphen = 2,9-dimethyl-1,10-phenanthroline).[455] An unprecedented insertion of isocyanide into Pd–S or Pd–Se bonds of chalcogenolate complexes have been studied.[456,457]



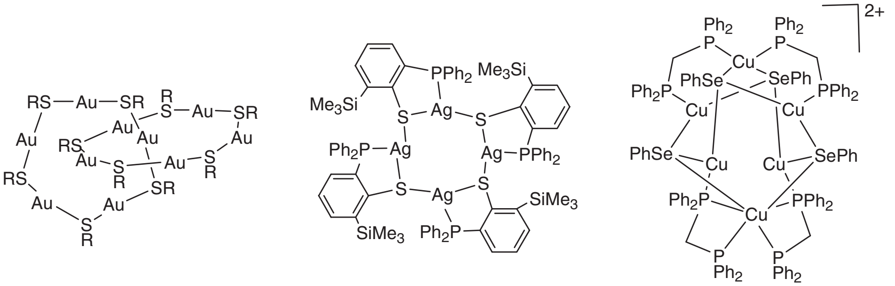
(**43**) (**44**) (**45**)

Scheme 15

Dinuclear Pd(I) complexes with bridging and terminal thiolates of the form $[Pd_2(SC_6F_5)(\mu\text{-}SC_6F_5)(\mu\text{-dppm})]$ or the tetranuclear $[\{Pd_2(\mu\text{-}SC_6F_5)(\mu\text{-dppm})\}(\mu\text{-}SC_6F_5)]_4$ have been reported.[458] Several Pd(IV) and Pt(IV) complexes with thiolates or selenolates have been described and are of the type $[PtMe_2(Bu_2bipy)L(EPh)]ClO_4$ (E=S, Se),[459] $[Pd(SeC_6H_4Cl)_2Me(C_6H_4OMe)(bipy)]$,[460] $[PtCp^*(Me)_2(STol)]$,[461] $[Pd(pz_3BH)Me_2(EPh)]$ (E=S, Se),[462] or $Na[Pt_2Me_6\{\mu\text{-}SCH(CH_2CH_2)_2NMe\}_3]$.[463]

2.1.5.7 Copper, Silver, and Gold

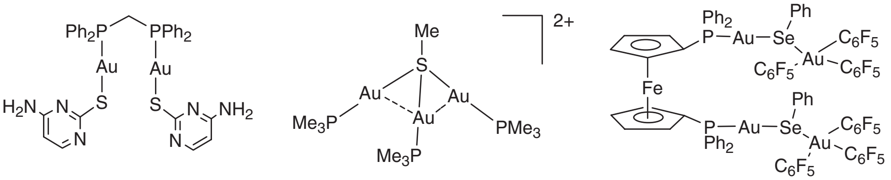
Group 11 metal chalcogenolates have been thoroughly studied because of their properties, as for example gold thiolates in medicine, silver thiolates have antimicrobial activity and many reports have dealt with the stabilization of mainly gold but also silver and copper nanoparticles by thiolates. Homoleptic complexes have been described for the three metals and are usually polymeric or oligomeric materials. Copper(I) complexes include $[Cu(SeC_6H_2\text{-}2,4,6\text{-}{}^iPr_3)]_6$, which presents a Cu_6 octahedron with bridging selenolate ligands,[464] $Et_4N[Cu_5(SAd)_6]$,[465] or $[Cu(SC_nH_{2n+1})]_n$, which show liquid crystal behaviour.[466] For silver(I), compounds such as $[Ag(SeC_6H_2\text{-}2,4,6\text{-}{}^iPr_3)]_8$,[467] $[Ag(SC_6H_2\text{-}2,4,6\text{-}{}^iPr_3)]_{10}$,[468] $[Ag(SC_6H_4COOH)]_6$, the latter present antimicrobial activity, have been described.[469] For gold the structure of the antiarthritic drug gold thiomalate (Myocrysine), $[Na_2CsAu_2(L)(LH)]$ ($L{=}O_2CCH_2CH(S)CO_2{}^{3-}$), which has a double-helical geometry,[470] and the compounds $[Au(SC_6H_4\text{-}4\text{-}CMe_3)]_{10}$ (**46**) or $[Au(SC_6H_4\text{-}2\text{-}CMe_3)]_{12}$,[471] have been reported. More abundant are the anionic linear species $[Au(SR)_2]^-$, which have been described for a large number of thiolate ligands, and for example the luminescence properties depending of the substituents in benzenethiolates, $[Au(SC_6H_4X)_2]^-$, have been studied.[472] The homoleptic gold(III) derivative $[Au(SCN_4Me)_4]^-$ has also been reported.[111] Functionalized chalcogenolate ligands have also been used to prepare several homoleptic complexes, such as $[Cu(SpySiR_3)]_6$,[473] $[Cu_3(S\text{-}pym)_3]_n$ (pym=pyrimidine),[474] $[Cu_4(SR)_4]$ (SR=picolylamine-ethylthiolate, benzimidazolthiophenolate),[475,476] or $[Cu(SC_6H_4\text{-}2\text{-}NMe_2)]_3$,[477] for copper and $[Ag(SCH_2CH_2NMe_2)]_5$,[478] $[Ag(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}PPh_2)]_4$ (**47**),[479] or several structural frameworks as graphite-like array or one-dimensional chain found for $[Ag(Spy)]_n$ for silver.[480,481] Siver(I) and copper(I) also forms chalcogenolate complexes with phosphine ligands of different nuclearities. There are mononuclear compounds, as for example $[Cu(ESiMe_3)(PR_3)_3]$ (E=S, Se, Te)[482] or $[Ag(SC_6H_4\text{-}2\text{-}COOH)(PPh_3)_3]$,[483] dinuclear as $[Cu_2(\mu\text{-}EPh)(\mu\text{-dppm})_2]BF_4$ (E=Se, Te)[484] or $[Cu_2(Spy\text{-}3\text{-}SiMe_3)_2(dppe)_3]$,[485] tetranuclear as $[Ag_4(\mu_3\text{-}SC_2B_{10}H_{11})_2(\mu\text{-}O_3SCF_3)_2(PPh_3)_4]$[486] or $[Ag_4(SPh)_4(PPh_3)_4]$,[487] $[Ag_4(\mu\text{-}SC_4N_2)_2(\mu\text{-dppm})_4]$,[488] or hexanuclear as $[M_6(\mu\text{-}ER)_4(\mu\text{-dppm})_4]^{2+}$ (M=Cu (**48**), Ag; E=S, Se) (Scheme 16).[489,490] Many of these complexes present luminescence properties. There are also three-coordinated Cu(I) derivatives with chelating amine ligands as $[Cu(SMes)(phenMe_4)]$[491] or $[Cu(S\text{-}Mes^*)(btmgp)]$ (btmgp=*bis*(tetramethylguanidine).[492] A series of cluster complexes of copper and silver with chalcogenolate or chalcogenolate/chalcogenide ligands have been reported, as for example $[\{Ag_8(\mu_4\text{-}SCH_2CH_2NH_3)_6Cl_6\}Cl_2]_n$,[493] $[Ag_9(SCH_2CH_2NMe_3)_6(NCMe)_8]_2(PF_6)_{18}$,[494] $[Ag_8Ag_{4/2}(SC_6H_4\text{-}4\text{-}{}^tBu)_{12}]_n$,[495] $[Cu_{50}Te_{17}(\mu_3\text{-}TePh)_{20}(PEtPh_2)_8]^{4+}$,[496] $[Ag_{14}(\mu\text{-}S)(SPh)_{12}(PPh_3)_8]$,[497] $[Ag_{14}(\mu\text{-}TePh)_2(\mu_3\text{-}TePh)_7(\mu_4\text{-}TePh)_3(PMe_3)_8]$,[498] $[Ag_{172}Se_{49}(Se^nBu)_{92}(dppp)_4]$,[499] or $[Cu_{13}Br_{13}(SR)_6]$.[500] The heterometallic selenolate complex $[Cu_4Fe_2Cl_2(Se^iPr)_8]^{2+}$ has also been described.[501]



(46) **(47)** **(48)**

Scheme 16

The majority of gold(I) chalcogenolate complexes are mononuclear $[Au(ER)PR_3]$ or dinuclear $[Au_2(ER)_2(\mu\text{-}P\text{–}P)]$ (**49**) with phosphine or diphosphine ligands and are known for a great variety of mainly thiolate ligands.[502–520] In the complexes $[Au(SR)PR_3]$, depending on the substituents of the thiolate, supramolecular structures are formed through Au···Au aurophilic interactions and/or hydrogen bonding.[521–524] The compounds $[Au_2(SB15C5)(\mu\text{-}P\text{-}P)]$ (SB15C5 = 4′-benzo-15-crown-5 thiolate) show specially binding abilities towards various metal cations giving luminescent species with Au···Au interactions.[525,526] Similar complexes with isocyanides of the type $[Au(SC_6H_4\text{-}4\text{-}COOH)(CNR)]$ ($R={}^tBu$, Mes) have been described and present a supramolecular assembly both through aurophilic and hydrogen bonding.[527,528] Trinuclear derivatives with triphosphine ligands and thiolates of the form $[Au_3(SR)_3\{\mu\text{-}(PPh_2)_3C_6Me_3)\}]$ (SR=quinoline thiolate) have been reported.[529] Dinuclear compounds with bridging thiolate or selenolate ligands of the type $[Au_2(\mu\text{-}ER)(PR_3)_2]^+$ or $[Au_2(\mu\text{-}ER)(\mu\text{-}P\text{–}P)]^+$ have been prepared for a large number of chalcogenolate and phosphine ligands.[504–510,530–533] Chemical or electrochemical oxidation of $[Au(SR)(PR_3)]$ gives the disulfide and the bridging thiolate complexes $[Au_2(\mu\text{-}ER)(PR_3)_2]^+$, as for example with the antiarthritic drug auranofin.[534,535] The oxidation of $[Au_2(SC_6H_4\text{-}4\text{-}Me)_2(dppm)]$ gives the thiolate cluster $[Au_9(SC_6H_4\text{-}4\text{-}Me)_6(dppm)_4](PF_6)_3$.[536] Un unexpected ring opening reaction of 2-aminothiazoline with $[Au(acac)(PPh_3)]$ gives the thiolate compound $[Au_2\{\mu\text{-}S(CH_2)_2N(CN)\}(PPh_3)_2]$.[537] Thiolate ligands can bridge more gold atoms and thus trinuclear species such as $[Au_3Cl_3(\mu_3\text{-}S^tBu)]^-$ or $[Au_3(\mu_3\text{-}SMe)(PMe_3)_3]^{2+}$ (**50**) have been reported.[506,538,539] Dinuclear complexes with bridging pyridine thiolate ligands as $[Au_2(\mu\text{-}Spy)(\mu\text{-}L\text{–}L)]^+$ can be oxidized to the gold(II) derivatives.[540] The sulfur atom can coordinate another $AuPPh_3^+$ fragment giving the compound $[Au_3(\mu_3\text{-}Spy)(PPh_3)(\mu\text{-}dppf)]^{2+}$ (dppf = 1,1′-*bis*(diphenylphosphino)ferrocene).[507] Mixed gold(I)–gold(III) compounds with bridging chalcogenolate ligands as $[Au_4(C_6F_5)_6(\mu\text{-}ER)_2(\mu\text{-}dppf)]$ ($ER{=}SC_6F_5$, SePh (**51**)) have been reported (Scheme 17).[505,509] Gold(III) complexes with thiolate ligands of the form $[Au(C_6F_5)_3(SR)]^-$, or $[Au(SR)_2\{(PPh_2)_2C_2B_9H_{10}\}]$ ($SR{=}SCB_{10}H_{10}CMe$),[508] or [Au(C–N)(cysteine)] (C–N=phenylpyridine)[541] $[Au(C_6H_4\text{-}2\text{-}CH_2NHMe_2)(SR)_3]$ (SR = 1-methyl-tetrazolethiolate),[542] have been described.

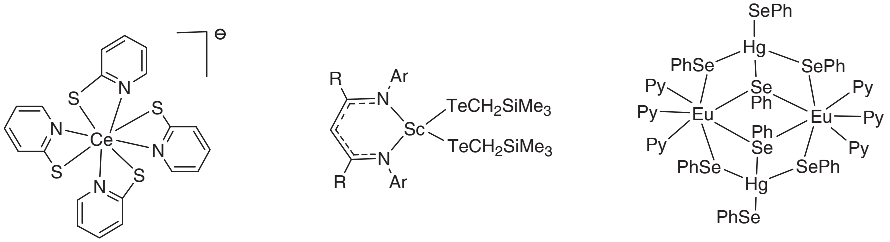


(**49**) (**50**) (**51**)

Scheme 17

2.1.6 Rare Earth Derivatives

The synthesis of lanthanide chalcogenolate complexes continues to be motivated by a fundamental interest in the nature of the Ln–E bond, and by the potential applications of Ln ions in chalcogenide-based pigments,[543] and optical fibres.[544] It is widely accepted that the bonding in lanthanide complexes is primarily ionic, with the size of the metal determining reactivity. Lanthanide metals form easily trivalent homoleptic complexes of the form $Ln(ER)_3$, obtained by reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with HER; these species usually dissolves in coordinating solvents and form the adducts $[Ln(ER)_3L_n]$. The use of sterically demanding chalcogenolates lead to the preparation of $[Ln\{SeSi(SiMe_3)_3\}_3]$ (Ln=La, Ce), which behaves as three-coordinate monomers in toluene, whereas for Y the structure is consistent with a dimer, $[Y\{SeSi(SiMe_3)_3\}_2\{\mu\text{-}SeSi(SiMe_3)_3\}]_2$. The tellurolate analogues $[Ln\{TeSi(SiMe_3)_3\}_3]$ (Ln=La, Ce) react with 1,2-*bis*(dimethylphosphino)ethane (dmpe) to give the adducts $[Ln\{TeSi(SiMe_3)_3\}_3(dmpe)_2]$.[545] The reaction of Ln with REER gives the trivalent compounds $Ln(ER)_3$ that dissolves in solvents to form $[Ln(SePh)_3(py)_3]$ (Ln=Ho, Tm, Yb),[546] $[Ln(SR)_3(py)_n(thf)_{3-n}]$ or $[Ln(SPh)_3(hmpa)]$ (Ln=Sm, Eu, Yb; hmpa=hexamethylphosphoric triamide).[547] Other adducts have been obtained with dipyridyl ligands as $[Yb(S^tBu)_2(\mu\text{-}S^tBu)(bipy)]_2$.[548] Similar compounds have been described with the pyridine-thiolate ligand as $[Ln(Spy)_2(hmpa)_3]I$ (Ln=Sm, Yb)[549] or $[Yb(Spy)_3(py)_2]$ or the homoleptic species $(PEt_4)[Ln(Spy)_4]$ (Ln=Ce (**52**), Ho, Tm).[550] In a study of the influence of metal, chalcogen, and solvent in the structure of the trivalent lanthanides, the findings were that the tendency to form oligomeric structures increases with the size of the lanthanide ion, thiolates bridge metal ions to form polymeric structures more effectively than selenolates, and pyridine displaces bridging chalcogenolates to form less extended structures more effectively than thf.[551] These lanthanide(III) thiolates of the type $[Ln(SPh)_3L_3]$ are active in the polymerization of methyl methacrylate.[552] Polymeric or oligomeric Ln(III) thiolates catalyse the ring-opening polymerization of ε-caprolactone.[553] Trivalent lanthanide with fluorinated thiolates have been obtained and they form Ln–F dative interactions that, surprisingly, remains in the presence of donor ligands as py, some examples are monomers for smaller lanthanides $[Ln(SC_6F_5)_3(py)_3]$ (Ln=Ho, Eu) and dinuclear as $[Ce(C_6F_5)_2(\mu\text{-}SC_6F_5)(thf)_3]_2$.[554,555] Chalcogen-rich lanthanide clusters have been obtained by reaction of $Ln(ER)_3$ with elemental chalcogen (E=S, Se, Te), as for example $[Ln_8S_6(SPh)_{12}(thf)_8]$ (Ln=Pr, Nd, Gd).[556–558] Also numerous complexes have been described with trivalent lanthanides and metallocene ligands, as for example with cyclooctatetraenyl $Na[Nd(cot)(S^tBu)_2]$,[559] or $[Sm(cot)(SR)L_x]$,[560] or cyclopentadienyl as $[LnCp_2(SR)(thf)]$ (Ln=Yb, Dy; SR=SC_6H_2-2,4,6-$(CF_3)_3$, benzothiazole-thiolate),[561,562] or the dinuclear $[LnCp_2(\mu\text{-}SMe)]_2$ (Ln=Yb, Y, Er, Dy) obtained by insertion of sulfur in a Ln–C bond.[563] Similarly the insertion of Te from $Te{=}P^nBu_3$ in Sc–C bonds gives the tellurolates $[Sc(\beta\text{-diketiminato})(TeCH_2SiMe_3)_2]$ (**53**).[564] Chalcogenolate complexes with the *tris*-3,5-dimethylpyrazolylborate ($Tp^{Me,Me}$) have been synthesized for samarium as $[Sm(Tp^{Me,Me})ER]$ (E=S, Se, Te; R=Ph, CH_2Ph, Ph-4-^tBu).[565] Heterometallic complexes have also been obtained with group 14 metals as $[EuPb_2(\mu\text{-}SePh)_6(thf)_2]$ or group 12 metals as $[EuHg(SePh)(\mu\text{-}SePh)_2(\mu_3\text{-}SePh)(py)_3]_2$ (**54**) (Scheme 18).[566,567] Divalent lanthanide complexes have also been reported and are homoleptic as $[Ln(STrip)_2]$ (Ln=Eu, Yb) in which the metal is bonded to two terminal thiolates but with additional η^6-π-arene interactions,[568] or $[Sm(EPh)_2]$ which stabilizes by addition of $[Zn(SePh)_2]$ giving $[SmZn(\mu\text{-}SePh)_4(thf)_3]_n$ or with py giving $[Sm(TePh)_2(py)_5]$.[569] Sm(II) complexes with Cp*/ER ligands catalyse the polymerization and block-copolymerization of styrene and ethylente.[570]



(52) **(53)** **(54)**

Scheme 18

Uranium(IV) chalcogenolate compounds have been synthesizing with several stoichiometries as the homoleptic $[U(SR)_4]$ (R = Et, ^{i}Pr, Ph) obtained by reaction of $[U(BH_4)_4]$ or $[U(NEt_2)_4]$ with thiols or by oxidation of uranium with the disulfide,[571] or those bearing cyclopentadienyl rings as $[UCp_3(ER)]$

(ER=SMe, SEt, S^iPr, S^tBu, Ph; SeMe).[572] C–S Bond cleavage in U(IV) complexes as $[UCp^*_2(SR)_2]$ gives $[UCp^*_2(SR)(S)]^+$ or the U(III) derivatives $Na[UCp^*_2(SR)_2]$.[573,574]

2.1.7 Conclusions

Chalcogenolates are a very important type of ligands whose metal complexes have been thoroughly studied because of the unique structural patterns obtained and the wide range of possible applications. The chemistry related to thiolate complexes is relevant in biological processes and with more stability than selenolate and tellurolate compounds have been better studied. In future years the expectation in this area includes the development in the poorly represented complexes, as for example alkaline and rare earth metal chalcogenolates, selenolate, and tellurolate derivatives in general and also in all the possible fields of application. Transition chalcogenolate metal complexes may be important in several chemical processes as in catalysis, were they have proved to be active in many catalytic reactions or in medicine, where the gold complexes are good antiarthritic agents or many complexes can be used as models for the bismuth antiulcer compounds or the technetium and rhenium metalopharmaceuticals. In the materials field for main group complexes, the seek of new and better precursors for chemical vapour deposition is still a work to develop, in nanomaterials these ligands have unique properties to stabilize the metal nanoparticles, or in complexes with optical properties where one can found applications in optical devices, sensors, *etc*.

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CHAPTER 2.2

Recent Developments in the Chemistry of Thio-, Seleno- and Telluro-ethers

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2.2.1 Introduction

The aim of this chapter is to provide an overview of the main developments in the synthesis and chemistry of the chalcogenoethers, ER_2 ($E = S, Se, Te$), up to the end of July 2005. A number of reviews pertaining to specific aspects of the chemistry of these compounds have appeared as follows:

- Coordination chemistry of thioethers, selenoethers and telluroethers in transition metal complexes[1]
- Chemistry of thioether macrocyclic complexes[2]
- Crown thioether chemistry[3]
- The chemistry of organoselenium and organotellurium compounds[4,5]
- Recent developments in the coordination chemistry of selenoether and telluroether ligands[6]
- Recent developments in the chemistry of selenoethers and telluroethers[7]
- Recent developments in the ligand chemistry of tellurium[8]
- Selenium-77 NMR spectroscopy[9]
- Acyclic thio-, seleno- and telluroether ligands[10]
- Macrocyclic thio-, seleno- and telluroether ligands[11]
- Early transition metal complexes of polydentate and macrocyclic thio- and seleno-ethers[12]
- Macrocyclic and polydentate thio- and seleno-ether ligand complexes of the p-block elements[13]
- The stereodynamics of metal complexes of sulphur-, selenium- and tellurium-containing ligands[14,15]

- Chiral thioether ligands: coordination chemistry and asymmetric catalysis[16]
- Model systems for Type I copper proteins: structures of copper coordination compounds with thioether and azole-containing ligands.[17]

Although thioethers have been used as ligands for many years now, research activity in this area has increased significantly over the last 20 years or so. The main impetus for in the chemistry of thioether ligands has been the development of good synthetic methods in particular for macrocyclic systems, which has permitted detailed studies with transition metal ions, with many of the resulting complexes exhibiting unexpected properties, while for selenoether and telluroether systems it is probably a combination of the availability of reliable synthetic routes to the ligands, increasing availability of FT NMR to study their solution behaviour (^{77}Se: $I = 1/2$, 7.58%, receptivity relative to ^{13}C, $D_c = 2.98$; ^{125}Te: $I = 1/2$, 6.99%, $D_c = 12.5$) and increasing evidence of enhanced ligating properties of the heavier telluroether and selenoether ligands, compared to the previously much more widely explored thioethers.

In the case of thiamacrocycles, the ligating ability is often enhanced by the *macrocyclic effect*. The coordination chemistry of macrocyclic derivatives of the heavier Group 16 elements Se and Te has been much less studied. However, new routes have become available for some derivatives (although macrocyclic telluroethers are very rare even now – see below) and both theoretical and experimental studies have shown that to low-valent metals the σ-donor capacity increases $SR_2 < SeR_2 << TeR_2$, while to medium oxidation state metals the trend is $SeR_2 > SR_2 > TeR_2$. The following discussion will concentrate on macrocycles containing only S or Se or Te donor atoms, with occasional reference to mixed-donor macrocycles containing one or more of these donor types as appropriate. The synthetic methods employed for these compounds tend to be very dependent upon the chalcogen type owing to the significant differences in their chemistry, *e.g.* the E–C and E–H bond strengths, which decrease down group 16, and the increased toxicities associated with compounds containing E–H bonds down the group.

Although acyclic thioethers have long been known, they have attracted much less interest than their phosphine analogues, probably owing to the widely held belief that they were only rather more modest σ-donors and therefore weakly coordinating ligands. There can be little doubt that the much increased interest in the coordination chemistry of thioether ligands over the last 15–20 years is a direct consequence of the availability of good synthetic routes to macrocyclic thioethers. These have been shown to impart unusual structural, spectroscopic and electrochemical properties to transition metal ions, supporting the stabilization of *e.g.* monomeric Pd(III) and Rh(II) species, and have proved effective ligands for elements from across the transition series and much of the p-block, *e.g.* $[(AlMe_3)_4([14]aneS_4)]$ and $[BiCl_3([15]aneS_5)]$.

2.2.2 Synthesis

2.2.2.1 Monodentates

A vast amount of organosulfur chemistry has been reported[18,19] and some monodentate thioethers are available commercially, *e.g.* Me_2S, Et_2S, Pr_2S, $^iPr_2S$, Ph_2S. The preparation of monodentate selenoethers R_2Se has also been reviewed.[20,21] Variants are generally obtained by modifications of standard procedures. Compounds of the type $RSeR'$ are usually prepared from treatment of RLi with elemental selenium followed by further reaction of the resultant RSeLi with $R'I$. Treatment of LiSeMe with excess MeI to give Me_3SeI, followed by dealkylation with PPh_3 gives Me_2Se in good yield.[22] Me_2Se, Et_2Se and Ph_2Se are commercially available; although air stable, the low molecular weight derivatives are highly malodorous. Methods for the preparation of monodentate telluroethers, R_2Te, are discussed in standard texts[23] and new derivatives are generally prepared by variations of these methods.[24] Disodium telluride can be obtained *in situ* from the elements in dmf at 110°C and is easily alkylated.[25] Dimethyltellurium may also be obtained from MeTeLi and excess MeI, followed by dealkylation with PPh_3.[22] The low molecular weight derivatives are air-sensitive, extremely malodorous oils.

2.2.2.2 Bi- and Polydentates

Bi- and poly-thioethers with aliphatic backbones are produced by attack of RS^- on the appropriate haloalkane. This is the method of choice for $RS(CH_2)_nSR$ (R = Me or Ph),[26] $MeC(CH_2SR)_3$,[27,28] $MeS(CH_2)_nS(CH_2)_nSMe$ ($n = 2$ or 3) and $MeS(CH_2)_nS(CH_2)_nS(CH_2)_nSMe$.[28,29] [*Caution*: Some of these syntheses involve sulfur mustard derivatives as intermediates – these are very powerful vesicants and should be handled only with extreme care.] The other tridentates $RS(CH_2)_3S(CH_2)_3SR$ (R = Et, ^iPr or Ph) may be obtained from nucleophilic attack by RS^- on the ditosylate $TsO(CH_2)_3S(CH_2)_3OTs$.[30] Tetradentate thioethers involving *o*-phenylene interdonor linkages are also known.[31] More recently the preparation and coordination chemistry of the silicon-apex derivative $MeSi(CH_2SMe)_3$ has been described.[32]

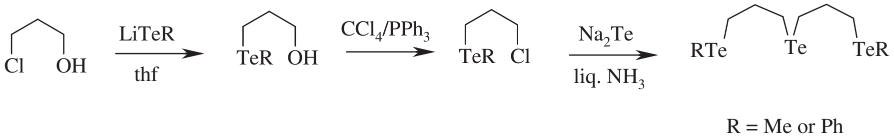
The original route to o-$C_6H_4(SR)_2$ (R = alkyl or phenyl) involved reaction of the appropriate copper thiolate with dihalobenzene in quinoline/pyridine.[33] For example, CuSPh reacts with *o*-dibromobenzene in quinoline/pyridine to give o-$C_6H_4(SPh)_2$.[26] For o-$C_6H_4(SMe)_2$, treatment of o-$C_6H_4(SMe)(SH)$ with MeI in Na/EtOH avoids the copper reagents.[26] The cleanest route to o-$C_6H_4(SMe)_2$ is *via* reaction of o-$C_6H_4Cl_2$ with NaSMe and MeI in dmf, followed by treatment of the resulting o-$C_6H_4(Cl)(SMe)$ with BuLi and Me_2S_2.[34] Testaferri and co-workers[35] have used reaction of nitrobenzenes or halobenzenes with NaSR in HMPA to give o-$C_6H_4(SR)_2$. Other aryl thioethers with different substitution patterns may be obtained similarly.[36]

The diselenoethers $RSe(CH_2)_nSeR$ (n = 1–3, 6, 12, *etc.*) are obtained in good yield by reaction of RSeLi with the appropriate dihaloalkane in thf solution,[37] or using RSeNa in liquid NH_3.[38] *Cis*-RSeCH=CHSeR requires reaction of *cis*-ClCH=CHCl and RSeNa in NaOEt/ethanol,[37] while addition of RSeSeR to HC≡CH in the presence of base or reaction of NaC≡CH, Se and RI gives RSeC≡CSeR.[39,40] The o-$C_6H_4(SeR)_2$ are less straightforward, since RSeLi does not lead to disubstitution of *o*-dihalobenzenes in ether or alcohol solutions. The R = Me or Ph derivative can be obtained from RSeSeR addition to benzyne,[37] although for R = Me, reduction of the polymeric $[o\text{-}C_6H_4(Se)_2]_n$[41] with Rongalite and treatment with MeI is more effective.[42] An alternative route to o-$C_6H_4(SeR)_2$ using electrophilic cleavage of $(\eta^5\text{-}{}^tBuC_6H_4)_2Zr(Se_2C_6H_4\text{-}o)$ with RCl has been reported.[43] The mono-substituted o-$C_6H_4Cl(SeMe)$, obtained from o-$C_6H_4Cl_2$ and LiSeMe in dmf solution, is potentially useful as a synthon for other ligands.[34]

The tripodal $MeC(CH_2SeR)_3$ (R = Me or Ph) are obtained readily from RSeLi with $MeC(CH_2Br)_3$ in thf.[37] The other tri- and tetra-dentates $MeSe(CH_2)_2Se(CH_2)_2SeMe$,[44] $MeSe(CH_2)_3Se(CH_2)_3SeMe$[37] and $MeSe(CH_2)_2Se(CH_2)_3Se(CH_2)_2SeMe$[45] require the Se to be introduced stepwise.

The development of synthetically useful routes to di- and poly-telluroether ligands is hampered by the inherent instability of Te–H bonds, the weakness of the Te–C bond which leads to Te–C cleavage occurring much more readily than for thio- or selenoethers and the accessibility of the Te(IV) oxidation state, which results in telluroethers being oxygen sensitive and providing a greater likelihood of unwanted reaction chemistry at Te during telluroether preparations.

Correspondingly, ditelluroether ligands, $RTe(CH_2)_nTeR$, are more difficult to synthesize than the thio- and seleno-ether analogues and are known only for certain values of n. For $n = 1$, successful routes include reaction of RTeTeR with diazomethane (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, *etc.*),[46] or *via* treatment of RTe^- with CH_2X_2 (for R = Me, Ph, 4-$EtOC_6H_4$).[47,48] Unlike the thio- and seleno-ether analogues, attempts to obtain $RTe(CH_2)_2TeR$ from RTe^- and $X(CH_2)_2X$ have failed, affording R_2Te_2 and eliminating ethene.[47–49] The outcomes of similar reactions with longer chain α,ω-dihaloalkanes depend significantly on the reaction conditions. Thus, while telluronium salts are obtained from reaction of $X(CH_2)_nX$ (X = Br or I; $n = 3,4$) with (4-$EtOC_6H_4$)TeNa in aqueous ethanol, similar reactions with $n = 6$–10 affords the ditelluroethers $RTe(CH_2)_nTeR$, and $X(CH_2)_5X$ affords both the products.[48,49] However, using thf solutions of RTeLi (R = Me or Ph) different reactivity occurs – while $Cl(CH_2)_3Cl$ gives R_2Te_2 and olefin at ambient temperature, using low temperatures gives high yields of $RTe(CH_2)_3TeR$.[50] The reaction of R_2Te_2 with benzyne affords o-$C_6H_4(TeR)_2$ (R = *p*-tolyl, *p*-$MeOC_6H_4$).[51,52] The o-$C_6H_4(TeR)_2$ (R = Me or Ph) are obtained by treatment of o-$C_6H_4Br_2$ with RTe^- in thf.[34] This disubstitution reaction does not occur for RSe^- or RS^- under similar conditions, indicating the much increased nucleophilicity of RTe^-. Zirconocene derivatives of *o*-ditellurophenylene may also be useful synthons for other telluroethers incorporating this rigid backbone.[53] The *o*-, *m*- and p-$C_6H_4(CH_2TeMe)_2$ are prepared similarly from MeTeLi and *o*-, *m*- or p-$C_6H_4(CH_2Br)_2$ in thf.[54,55]



Scheme 1

In general the alkyl-substituted ditelluroethers are yellow, extremely malodorous, air-sensitive oils, whereas those with phenyl substituents are low-melting solids or oils and are rather less susceptible to oxidation.

A limited range of polytelluroethers is known. Synthesis of the tripod telluroethers $MeC(CH_2TeR)_3$ utilizes reaction of $MeC(CH_2Br)_3$ with excess RTeLi in thf (R = Me or Ph).[47,56] The preparations of $RTe(CH_2)_3Te(CH_2)_3TeR$ (R = Me or Ph) are through reaction of $RTe(CH_2)_3Cl$ with Na_2Te (Scheme 1).[57] Notably, attempts to prepare these ligands *via* the tosylate $RTe(CH_2)_3OTs$ lead to decomposition, hence the conversion of $RTe(CH_2)_3OH$ to $RTe(CH_2)_3Cl$ is key and occurs in good yield.

Finally, a number of mixed donor ligands are known, *e.g.* $Te\{CH_2CH_2NR_2\}_2$[58] and $N\{CH_2CH_2TeR\}_3$.[59] Other examples are reviewed in ref. 8. Hybrid telluroethers incorporating the *o*-C_6H_4 unit are also known, *o*-$C_6H_4(TeMe)(Y)$ (Y = OMe, SMe, SeMe, NMe_2, PMe_2, $AsMe_2$, $SbMe_2$).[34]

2.2.2.3 Macrocycles

2.2.2.3.1 Thioether Macrocycles

A number of reviews describing the syntheses of thioether macrocycles[2–3,11] and seleno- and telluro-ether macrocycles have been reported.[6–7,11] The original preparation of the tetrathioether [14]aneS_4 by reaction of 1,4,8,11-tetrathiaundecane with 1,3-dibromopropane gave a yield of *ca.* 7%,[60–62] however, under high-dilution conditions the yield can be increased 55%.[63] This and other thioether macrocycles are now available in even better yields through modified routes developed by Ochrymowycz and co-workers[64] and Kellogg and co-workers[65–68] using Cs_2CO_3-promoted ring closure. It was later shown from ^{133}Cs NMR studies that the role of the Cs^+ ion is in forming a strongly solvent separated Cs^+ thiolate$^-$ ion pair in dmf solution, which reacts very readily under conditions of high dilution,[69] giving *e.g.* [14]aneS_4 in 65–70% yield.[70] The frequently used [9]aneS_3[71] and [18]aneS_6[72] are also obtained in this way.

A small number of template mediated reactions which afford thioether macrocycles are also known, *e.g.* the small trithia [9]aneS_3 is also obtained in good yield using $Mo(CO)_3$ as a template.[73,74] The crown trithioether is readily demetallated by addition of a further equivalent of $[NMe_4]_2[S(CH_2)_2S(CH_2)_2S]$. Also, dibenzo-[18]ane$S_6$ and dibenzo-[15]aneS_5 have been prepared *via* an iron dicarbonyl template.[75,76] Metal-induced cyclo-oligomerization reactions of thietane using transition metal carbonyl complexes such as $[Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2)(\mu\text{-}H)_3]$ yield [12]aneS_3, [16]aneS_4 and [24]aneS_6.[77,78]

Cyclic thioethers involving rigid linkages are also known. Examples include a range of derivatives of [14]aneS_4 incorporating 1,2-benzene and/or 1,2-cyclohexane units;[79] TTOB, TTMB;[80] tetrathia and hexathia cyclophane derivatives.[81–84]

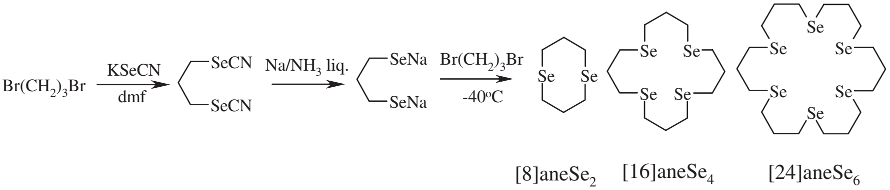
In contrast to polyaza macrocycles, which may be functionalized conveniently *via* introduction of the R substituents on the nitrogen atoms after the cyclization step, the presence of only two substituents on the sulfur atom, both of which are required for ring formation in a macrocyclic thioether, means that functionalization of these rings requires modification of the carbon backbone and is more difficult. A variety of *C*-functionalized derivatives of [9]aneS_3 have been reported in which the appropriate *C*-functionality is introduced prior to the macrocyclization step. The $Mo(CO)_3$ template route, which gives moderate yields of the *C*-functionalized rings, is preferred over the Cs_2CO_3/dmf route which gives polymeric products in some cases.[85,86] However, the presence of bulky R groups in the Mo-mediated reactions lead to unfavourable steric effects and therefore the yields are substantially lower than for [9]aneS_3 itself. A variety of other functionalities, including ketone, alcohol, amine, alkene and thiophene groups have been incorporated into the carbon framework of other thiamacrocycles.[87–93]

Sargeson and co-workers have prepared a series of thioether-containing cage ligands, typically using template reactions. Transition metal complexes of these compounds exhibit interesting properties and the extremely robust nature of the complexes is attributed to the ‘cryptate effect’.[94,95]

2.2.2.3.2 Selenoether Macrocycles

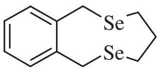
The availability of preparative routes giving a smaller range of seleno-ether macrocycles in reasonable yields has allowed their coordination to elements from across much of the transition metals and p-block elements to be explored.

The preparations of the first series of cyclic selenoethers [8]aneSe_2, [14]aneSe_4, [16]aneSe_4 and [24]aneSe_6 may be achieved *via* $Na/NH_{3\ liq}$ reduction of the appropriate $NCSe(CH_2)_nSeCN$ (n = 2 or 3) and subsequent treatment with $Br(CH_2)_3Br$ at low temperature (*e.g*. Scheme 2).[96] Modifications of this route afford the hydroxy-functionalized di- and tetra-seleno-ether macrocycles [8]aneSe_2(OH), [16]aneSe_4(OH) and [16]ane$Se_4(OH)_2$[97] and the more rigid dibenzo[14]aneSe_4.[98]

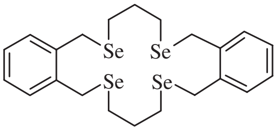


Scheme 2

Reaction of o-$C_6H_4(CH_2SeCN)_2$ with $Br(CH_2)_3Br$ under similar conditions affords the cyclic diselenoether (I) in high yield, although there was no sign of the [2 + 2] cyclization product (II) *via* this particular route.[99] An earlier report claimed yields of 55% and 18% for (I) and (II), respectively, although few experimental details were provided.[100]



(I)



(II)

A small number of macrocycles with an odd-number of Se atoms have been reported. Both [12]aneSe_3 and [20]aneSe_5 involve stepwise introduction of the Se atoms, with ring closure occurring *via* a high dilution cyclization of $NaSe(CH_2)_3SeNa$ with $TsO(CH_2)_3\{Se(CH_2)_3\}_nOTs$, $n = 1$ or 3, respectively (Scheme 3).[101]

The cyclo-oligomerization of 3,3-dimethylselenetane to give Me_4[8]aneSe_2, Me_6[12]aneSe_3, Me_8[16]aneSe_4 and Me_{12}[24]aneSe_6 can be achieved using Re carbonyl catalysts (Scheme 4).[102]

The naphthalene-derivatized seleno-ether macrocycles dinaphtho-[16]aneSe_4, naphtho-[8]aneSe_2 and naphtho-[12]aneSe_3 have also been prepared. Hydrolysis of dinaphtho-[16]aneSe_4 with sulfuric acid leads to formation of the ring contracted species naphtho-[8]aneSe_2.[103,104]

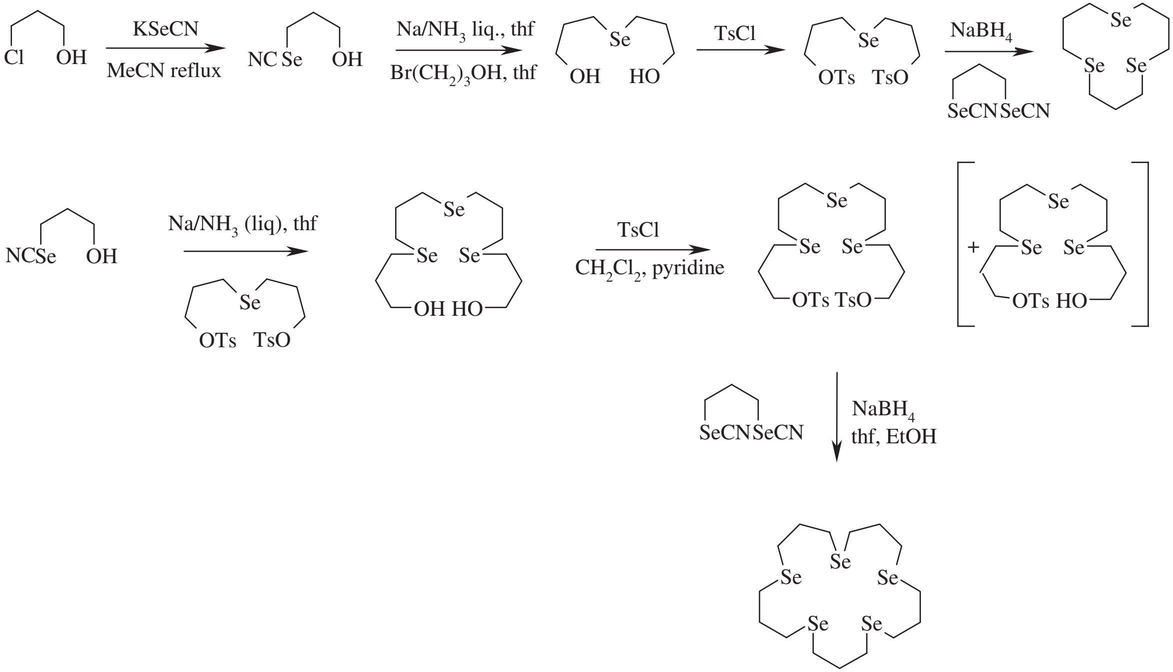
A series of mixed Se_4O_2-donor macrocycles and related Se_2O_n-donor macrocycles, have been obtained in moderate yield *via* reaction of o-$C_6H_4(SeK)_2$ with either o-$C_6H_4\{SeCH_2(CH_2OCH_2)_nCH_2X\}_2$ ($X = Cl$, $n = 1 - 3$ or $X = Br$, $n = 3, 4$) or with $X(CH_2CH_2O)_nCH_2CH_2X$ ($n = 1,2$, $X = Cl$; $n = 3$, $X = Br$) *via* [1 + 1] cyclization processes.[105,106] The yields are increased if o-$C_6H_4(SeH)_2$ is treated with the dichloroselenoether in Cs_2CO_3/dmf, utilizing the 'caesium effect'.[64] Reaction of Na_2Se with $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$ in liquid ammonia/thf at −78°C gives both [9]aneSeO_2 and [18]aneSe_2O_4 in low yield. The yield of the latter is improved when the reaction is conducted in EtOH solution under high-dilution conditions.[107] Other crown ether derivatives incorporating one Se or Te atom within the ring have been reported.[108]

Treatment of $[Co\{MeC(CH_2Se(CH_2)_2NH_2)_3\}]Cl_3$ with HCHO and $MeNO_2$ gives a rare example of a mixed N_3Se_3-donor sarcophagine ligand complex.[109]

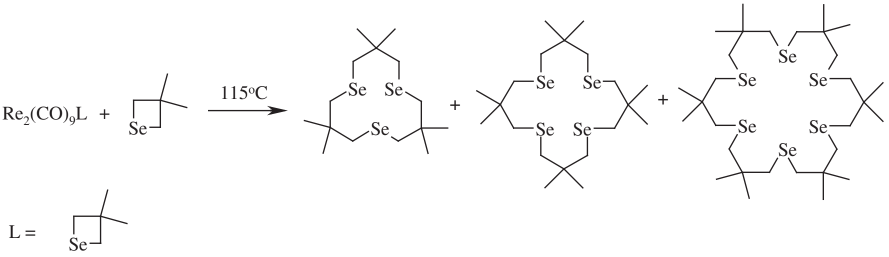
2.2.2.3.3 Telluroether Macrocycles

Synthetic routes to macrocyclic ligands containing tellurium are still very limited, mainly because of the difficulties in sequentially introducing the necessary Te centres into organic fragments, the weakness of the Te–C bonds and the unavailability or instability of many Te-containing analogues of the precursors for thio- and seleno-ether macrocycles.

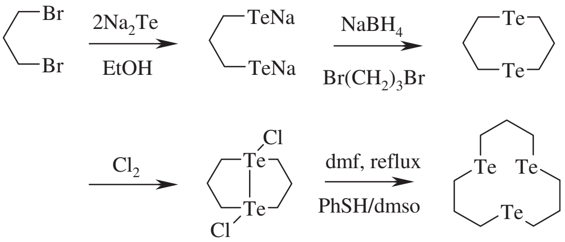
The cyclic ditelluroether [8]aneTe_2 forms upon treatment of Na_2Te with 1,3-dibromopropane in ethanol, followed by addition of $NaBH_4$ and a further


Cl
OH
KSeCN
MeCN reflux
NC Se
Na/NH3 liq., thf
Br(CH2)3OH, thf
Se
HO
TsCl
OTs
TsO
NaBH4
SeCN SeCN
NCSe
Na/NH3 (liq), thf
OH HO
CH2Cl2, pyridine
+
OTs HO
thf, EtOH

Scheme 3



Scheme 4



Scheme 5

equivalent of 1,3-dibromopropane.[110] The only known macrocyclic tritelluroether, [12]aneTe_3 has been isolated as a product from the pyrolysis of ditellurane in dmf at 160°C, followed by reduction (Scheme 5),[111] and the crystal structure of the hexachloro derivative determined (Figure 1). No coordination chemistry of this macrocycle has been reported.

A small number of mixed donor Te-containing macrocyclic ligands have been reported. The synthesis of the first series of mixed thia/tellura macrocycles, [9]aneS_2Te, [11]aneS_2Te, [12]aneS_2Te and [14]aneS_3Te occur according to Scheme 6, in which Na_2Te in liquid NH_3 is treated with the appropriate α,ϖ-dichlorothioalkane. Following work-up, the macrocyclic ligands are obtained as light yellow poorly soluble solids in moderate yields.[112] Crystal structures of both [11]aneS_2Te and [12]aneS_2Te have been determined and show that the molecules adopt approximately square conformations. The preparation of [9]aneS_2Te is accompanied by side reactions, which produce both 1,4-dithiane and 1-tellura-4-thiacyclohexane.[113] These potentially tri- or tetradentate ligands can coordinate *via* both the Te and S atoms, the coordination mode being dependent upon the transition metal centre. The crystal structure of [Ag([11]aneS_2Te)]BF_4 shows trigonal planar coordination at Ag(I) *via* two S and one Te atom from three different macrocycles, which bridge Ag atoms to give a chain polymer.[112]

The ditellurium crown, [18]aneTe_2O_4, is obtained in 50–55% yield by reaction of Na_2Te with $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$ in liquid ammonia/thf solution at −78°C without the need for high-dilution conditions. The small ring

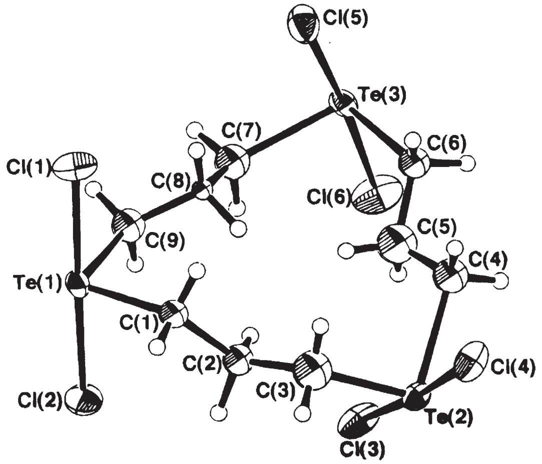
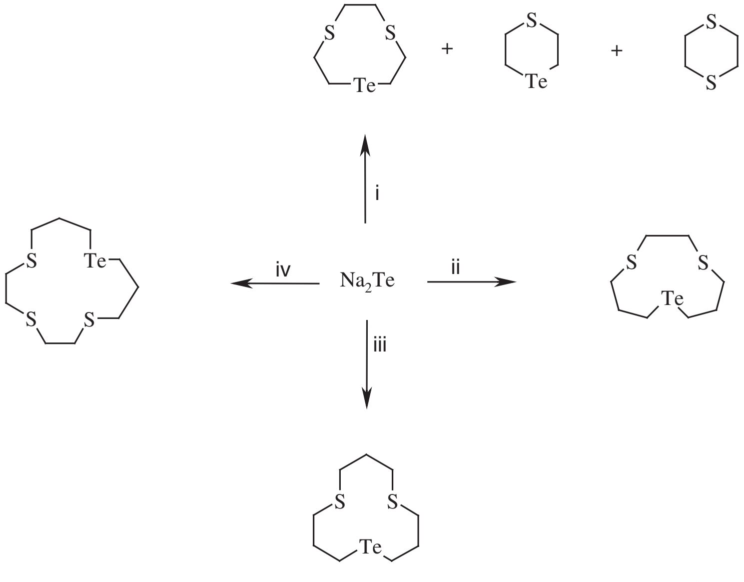


Figure 1 *Crystal structure of the hexachloride derivative of [12]aneTe*$_3$[111] (Reproduced with permission from the American Chemical Society.)



Scheme 6 *Regents and conditions: i.* $Cl(CH_2)_2\ S(CH_2)_2\ S(CH_2)_2Cl$*, thf/*$NH_3$ *(liq); ii.* $Cl(CH_2)_3\ S(CH_2)_2S(CH_2)_3Cl$*, thf/*$NH_3$ *(liq); iii.* $Cl(CH_2)_3\ S(CH_2)_3\ S(CH_2)_3\ Cl$*, thf/*$NH_3$ *(liq); iv.* $Cl(CH_2)_3\ S(CH_2)_2\ S(CH_2)_2\ S(CH_2)_3Cl$*, thf/*$NH_3$ *(liq);* $T = -78°C$.

[9]aneTeO_2 is obtained as a minor product (4%) under these conditions. The compounds may be separated by recrystallization to give the 18-membered ring, and chromatography on the residues gave the 9-membered ring.[107] These ligands coordinate readily to a range of metal ions, such as Pd(II), Pt(II), Rh(III), Cu(I) and Ag(I) *via* the Te atoms.[107]

Finally, Schiff base macrocycles incorporating telluroether functions are obtained by condensation of *bis*(2-formylphenyl)telluride with 1,2-diaminoethane (analogues with Se incorporated have also been prepared).[8,114]

2.2.3 Coordination Chemistry of Thio-, Seleno- and Telluroethers

Steric effects are much less important than in the phosphines, although the nature of the interdonor linkages and the resulting chelate ring sizes influence the coordination of polydentates and macrocycles in the usual way. The neutral chalcogenoethers R_2E, have two lone pairs per chalcogen atom, one of which may form a σ-bond to a metal acceptor. The second lone pair may form a σ-bond to a second metal, resulting in a bridging R_2E group, and examples of such behaviour are well established *via* single crystal X-ray studies for R_2E ($E =$ S, Se or Te). Alternatively, the second lone pair on the R_2E may behave as a π-donor to a suitable metal d-orbital, particularly to electron deficient metals. However, there seems to be no evidence that this is a significant component of the bonding. For R_2E, as for PR_3, the E atom can in principle behave as a π-acceptor either into the lowest empty d-orbital (as in the original Chatt model[115]), or more likely as proposed for group 15 donors,[116] into the E-C σ^* orbitals, which are of more suitable energy. It is possible that to electron rich metal centres the second lone pair will be a source of π-repulsion in M–ER_2.

Although there have been some suggestions of weak π-back-bonding, usually based upon M–E distances being slightly less than the sum of the appropriate covalent radii, these effects have been of borderline statistical significance, and consensus has been that thioethers are weak σ-donors with little or no π-component to the bonding.[1–3] However, π-acceptance may be significant for some macrocyclic thioether complexes.[117]

Within group 16, the unusually strong binding of telluroethers to low valent TM centres is considered to be due to enhanced σ-donation.[118] Studies[56,119,120] have also shown increased electron density at the metal centre $S < Se << Te$, and the data were interpreted as due to increased σ-donation down Group 16, owing to the decreased electronegativity of the donors. For low valent metals the spatial extension of the d-orbitals will be such that good overlap can occur with the large Te σ-orbital. As the metal oxidation state increases, the metal becomes harder and the orbitals contract, consistent with decreased bonding to the large, soft tellurium. This effect is clearly manifested in the poor ability of telluroethers to bond to high oxidation states of the platinum metals. The ^{77}Se and ^{125}Te NMR coordination shifts on M(I) and M(III) centres (M = Rh or Ir) have also been compared. In the M^I complexes $[M(cod)\{MeC(CH_2EMe)_3\}]^+$, the evidence is for strongest donation $Te > Se$, but for the higher oxidation state M^{III} in $[(\eta^5\text{-}C_5Me_5)M\{MeC(CH_2EMe)_3\}](PF_6)_2$ the interaction appears to be $Se > Te$.[121] Further experimental and theoretical studies are required in order to establish the factors involved and to refine the model, but it appears that within Group 16 the relative donor strength varies with the metal acceptor; to high or medium oxidation state metals it is S < Se > Te, whereas to low valent centres S < Se << Te.

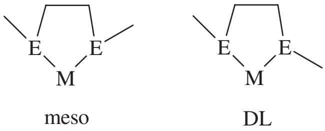
Ziegler and co-workers[122] used density functional theory to examine a series of $[(CO)_5Cr–L]$ species where $L = CO, NR_3, PR_3, SR_2, SeR_2$ and $R = H$, Me or F. They concluded that thio- and selenoethers were moderate σ-donors and weak π-acceptors. It was also concluded that SF_2 and SeF_2 (both are highly unstable in the free state) would be strong π-acceptors and, more surprisingly, good σ-donors.

2.2.4 Coordination Modes

2.2.4.1 Acyclic Ligands

The chalcogenoethers typically function as σ-donors to metal ions through one lone pair, although examples where they behave as bridging ligands by using both lone pairs are also known, *e.g.* in the chain polymer $[Ag\{MeS(CH_2)_3SMe)]_n^{n+}$,[123] $[\{(\eta^5\text{-}MeC_5H_4)Mn(CO)_2\}_2(\mu^2\text{-}Me_2Se)]$[124] and $[\{CuCl(Et_2Te)\}_n]$[125] and $[(PtMe_2)_2(\mu^2\text{-}Me_2S)_2]$.[126]

Where ER_2 carries two different R groups, coordination *via* one lone pair leads to chirality at the E donor atom. Coordination of a bi-or poly-dentate chalcogenoether also leads to chirality, *e.g.* a bidentate ligand gives rise to a *meso* form and a pair of enantiomeric *DL* isomers (III). Pyramidal inversion allows interconversion of sterreoisomers (invertomers) and often occurs on the NMR time-scale and has been studied in detail. The principal factors influencing the energy barrier to inversion include donor type (S < Se < Te), metal and oxidation state, the *trans* ligand, the substituent on E and chelate ring-size. This topic has been reviewed and hence will not be considered further in the present article.[14,15]



(III)

While bi-and poly-dentate chalcogenoethers with di- or tri-methylene or *o*-phenylene interdonor linkages often chelate, the $MeECH_2EMe$ usually behave as bridging ligands. The Sn(IV) adducts $[SnCl_4(MeSCH_2SMe)]$ and $[SnCl_4(MeSeCH_2SeMe)]$ are notable exceptions with 4-membered chelate rings (Figure 2).[127] Examples of telluroether complexes incorporating 4-membered chelate rings are $[MCl_2\{(4\text{-}MeOC_6H_4Te)_2CH_2\}]$[128,129] and $[Pd(Ph_2PCH_2CH_2PPh_2)\{(4\text{-}MeOC_6H_4Te)_2CH_2\}](ClO_4)_2$.[129]

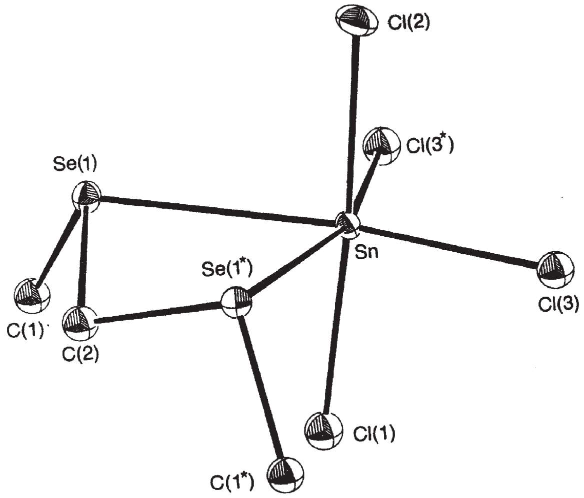


Figure 2 *Crystal structure of [$SnCl_4(MeSeCH_2SeMe)$] showing the 4-membered chelate ring*[127]
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Two- or three-carbon backboned bi- and tridentates can also bridge adjacent metal centres, *e.g.* with Cu(I), Ag(I), Sb(III) and Bi(III), giving rise to one-, two- or three-dimensional polymers.[130–133]

The majority of reported coordination complexes with thio-, seleno- and telluroethers involve low or medium oxidation states of the later d-block elements. However, while telluroethers do not stabilize high oxidation states such as Os(IV), thio- and selenoether examples are obtained straightforwardly. The versatility of the thio- and seleno-ether ligands is further demonstrated by their ability to coordinate readily to hard, early transition metal, such as Ti, Zr and Hf(IV) and Mo(VI), although to date the range of examples is limited.[134–137] The key to their preparation is the use of strictly anhydrous conditions and the avoidance of strongly coordinating solvents. The chemistry of polydentate and macrocyclic chalcogenoethers with high-oxidation state, early TM centres has been reviewed recently.[12]

There is also a growing literature describing complexes of these ligands with p-block metals/metalloids.[13] For example, the crystal structure of the first telluroether complex of a p-block element, [$BiBr_3(PhTeMe)$] has been reported, giving Br-bridged dimers with pyramidal coordination at Bi. Weak intermolecular Bi···Br interactions lead to association of the dimers into infinite chains (Figure 3).[138] The first Tl(I) seleno ether complexes involve the $MeSe(CH_2)_n$-SeMe ($n = 2$ or 3), the structures showing significant dependence upon the n value (Figure 4).[139]

A specific feature of the coordinated (heavier) chalcogenoethers is their ability to undergo E–C bond cleavage under certain conditions. For sulfur this process (S-dealkylation) has been known for many years,[1] however, Se/Te-dealkylation also occurs.[134,140] Relatively few systems have been characterized

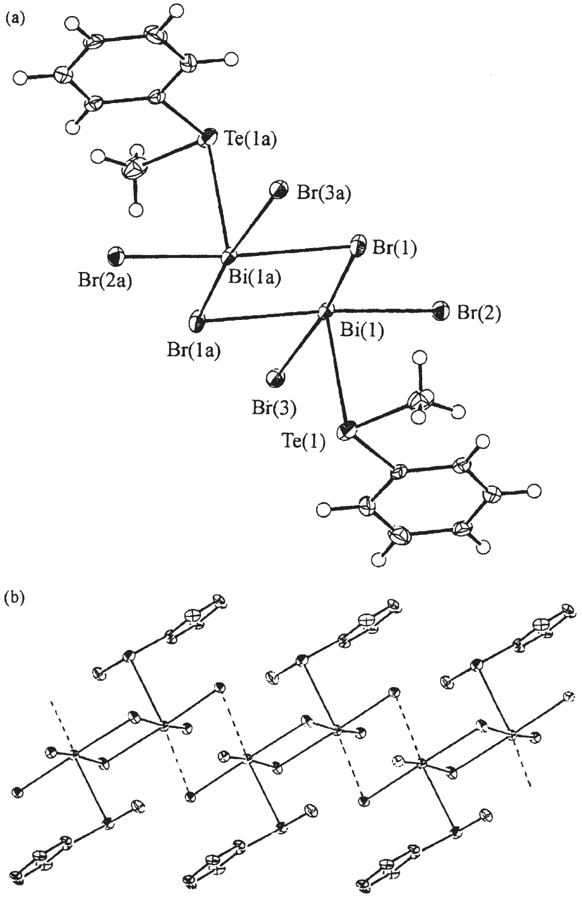

Figure 3 *Two views of the crystal structure of [$BiBr_3$(PhTeMe)]*[138]
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in detail – for tellurium the dealkylated species [{Pd(o-C_6H_4(TeMe)Te)I}$_4$] has been confirmed by X-ray crystallography.[140]

2.2.4.2 Macrocyclic Ligands

A considerable range of coordination complexes of thioether macrocycles have been reported, and although the majority involve middle and late transition metal ions in low- or medium-oxidation states, a growing number of examples with early transition metals have been described, many with structural authentication, including Ti(IV) (*e.g.* [$TiCl_2$(NBu^t)([9]aneS_3)][141] and [$TiCl_3$([9]aneS_3)]$^+$),[142] Zr(IV) (*e.g.* the 7-coordinate [$ZrCl_4$([9]aneS_3)]),[136] V(III) and (IV) (*e.g.* [VCl_3([9]aneS_3)] and [$VOCl_2$([9]aneS_3)])[143] and Cr(III) (*e.g.* *cis*-[CrX_2([n]aneS_4)]PF_6, X = Cl, Br or I; n = 12, 14 or 16[144]). The first Sc(III) example, [Sc(CH_2SiMe_3)$_3$([9]aneS_3)], has also been structurally

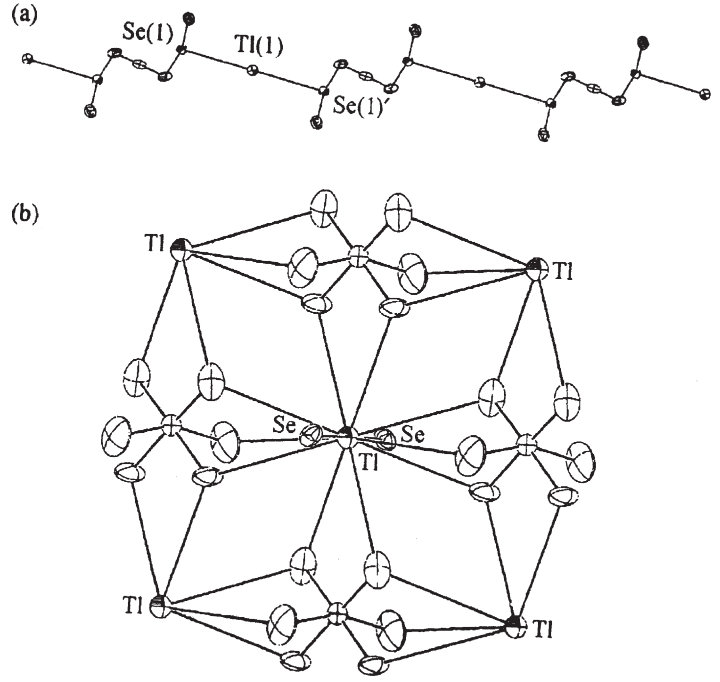

Figure 4 *Crystal structure of* $[Tl\{MeSe(CH_2)_3SeMe\}]PF_6$[139] *(a) shows the cation; (b) shows the interactions with the* PF_6^- *anions.*
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characterized (Figure 5). Activation of this compound with $BAr^F{}_3$ or $[CPh_3][BAr^F{}_4]$ affords a catalyst which is active for ethylene polymerization.[145] The extremely versatile trithiacyclononane ligand has also yielded the first authenticated examples with crown thioether coordination to f-block elements, *e.g.* in the square antiprismatic $[La([9]aneS_3)I_3(MeCN)_2]$ (formed from $LaI_3(MeCN)_3$ and $[9]aneS_3$ in diethyl ether) and the corresponding $[U([9]aneS_3)I_3(MeCN)_2]$ (Figure 6).[146] Coordination to extremely high-oxidation state metals may also be achieved as in Re(VII) (in $[ReO_3([9]aneS_3)]BF_4$[147]).

A wide range of complexes involving acceptors from the p-block, *e.g.* Tl(I), Sn(IV), As(III), Sb(III), Bi(III), Pb(II) *etc.*,[13,148] has also been characterized (Figure 7). These species display a surprisingly diverse structural chemistry, in which secondary bonding plays a significant role in determining the final structure.

The ability of thioether macrocyclic complexes (and especially those of $[9]aneS_3$) to support multi-redox behaviour at the coordinated metal centre is particularly notable. This allows a series of reversible stepwise one-electron oxidation and/or reduction processes, and stabilization of highly unusual transition metal oxidation states *e.g.* mononuclear $[Pd([9]aneS_3)_2]^{2+/3+/4+}$,[149] $[Au([9]aneS_3)_2]^{+/2+/3+}$,[150] $[Ni([9]aneS_3)_2]^{2+/3+}$,[151] and $[Rh([9]aneS_3)_2]^{+/2+/3+}$.[152] It appears to be the ability of the crown thioethers to readily adjust their

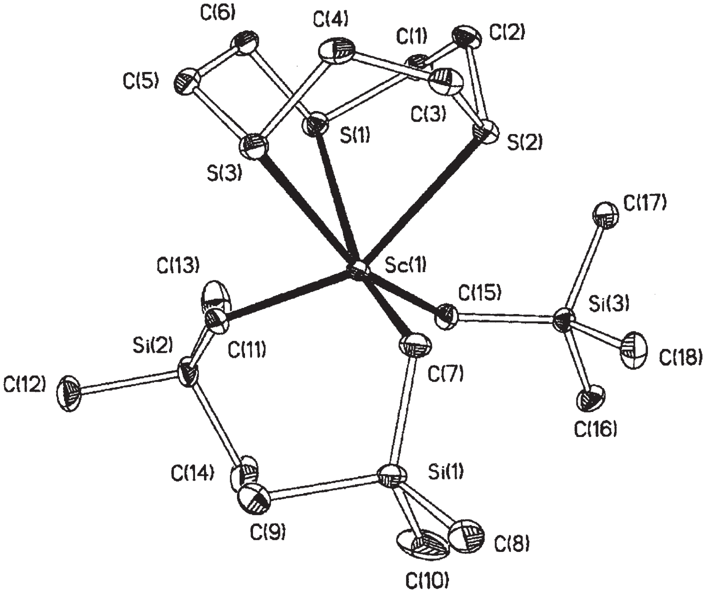

Figure 5 *Crystal structure of* $[Sc(CH_2SiMe_3)_3([9]aneS_3)]$[145]
(Reproduced with permission from the Royal Society of Chemistry.)

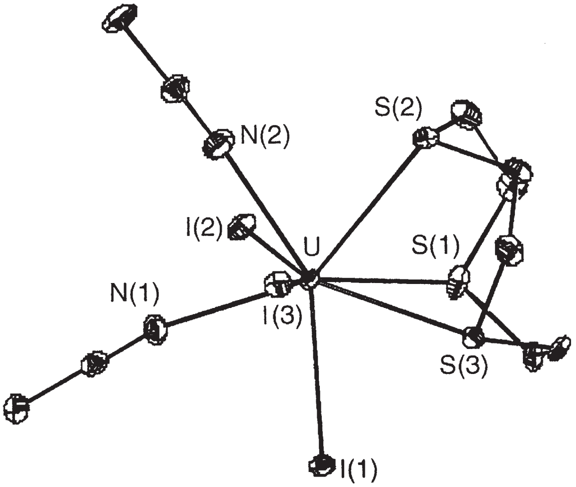

Figure 6 *Crystal structure of* $[U([9]aneS_3)I_3(MeCN)_2]$[146]
(Reproduced with permission from the Royal Society of Chemistry.)

coordination modes and conformations to accommodate the geometric preference of the particular metal oxidation state, that is of key importance in this chemistry.

In certain systems the crown thioether ligand itself may undergo some chemical transformation when coordinated to a metal ion. For example, in mildly basic conditions the Rh(III) species $[Rh([9]aneS_3)_2]^{3+}$ and $[Rh([18]aneS_6)]^{3+}$

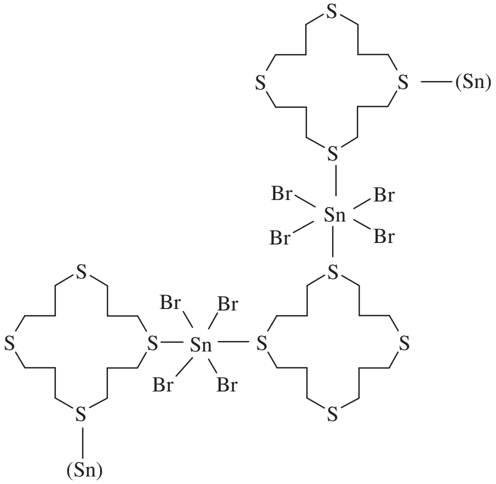

Figure 7 *Structure of a portion of the [$SnBr_4$([16]aneS_4)] coordination polymer*[148]

undergo deprotonation at an α-carbon, with subsequent ring-opening to afford vinyl thioether derivatives, *e.g.* for the former, [Rh([9]aneS_3)-{$S(CH_2)_2S(CH_2)_2SCH{=}CH_2$}]$^{2+}$, which has been structurally characterized.[153] Also, oxidation of [Fe([9]aneS_3)$_2$]$^{2+}$ with PbO_2 in 1M H_2SO_4 gives the corresponding Fe(III) complex, whereas using aqueous $Na_2S_2O_8$ gives the Fe(II)-sulfoxide derivative, [Fe([9]aneS_3){[9]aneS_2(S=O)}]$^{2+}$, through oxidation of one of the thioether sulfur atoms.[154]

The sulfimide group $R_2S = NR'$ is isoelectronic with $R_2S = O$, and recent studies have revealed the first examples of macrocyclic derivatives from reaction of the thia crown with MSH.[155,156] These compounds are of interest as ligands in their own right, and also because they provide a means of functionalizing the thiacrown at the S atom and hence the possibility of introducing pendant groups.

[9]aneS_3 has proved to be an exceptionally strongly ligating thioether. It typically functions as a tridentate, face-capping ligand, but examples exist where it behaves as a monodentate (*e.g.* in [Au([9]aneS_3)$_2$]$^{+}$[157]) or bidentate (*e.g.* in [Pd([9]aneS_3)$_2$]$^{2+}$, with additional weak Pd···S interactions[158]). The tetra- and penta-thia macrocycles may coordinate metal ions either *exo* or *endo* to the ring.[2,3] [12]aneS_4 and [14]aneS_4 (usually) prefer to adopt a folded conformations in octahedral species, leaving two mutually *cis* coordination sites for other co-ligands. However, in the square planar [Pt([12]aneS_4)]$^{2+}$ the metal is significantly displaced out of the mean S_4 plane, reflecting the mismatch between the metal ion radius and the macrocyclic hole size.[159] [16]aneS_4 comfortably accommodates many transition metals within the ring, giving *trans*-octahedral species. There are numerous examples where [18]aneS_6 promotes homoleptic hexathia coordination in an octahedral metal complex and complexes of this ligand (and [9]aneS_3) are considerably more resistent to hydrolysis/solvolysis compared to the larger ring [24]aneS_6 (and [12]aneS_3).[3] Larger ring *e.g.* octathia-macrocycles can behave as binucleating ligands.[2,3]

Studies on the coordination chemistry of seleno-ether macrocycles have focused mainly on [8]aneSe_2, [16]aneSe_4 and [24]aneSe_6. While [8]aneSe_2 behaves as either a bidentate chelate or a bridging ligand linking adjacent metal centres, a variety of coordination modes have been identified for [16]aneSe_4, including both *endocyclic* coordination, *e.g.* in the Pt(IV) species *trans*-$[PtCl_2([16]aneSe_4)]^{2+}$[160] and *exocyclic* coordination, which occurs, for example, in a variety of p block element complexes, such as $[BiBr_3([16]aneSe_4)]$ (Figure 8).[161] $[Pd([16]aneSe_4)]^{2+}$ has been identified crystallographically in two different invertomer forms; the PF_6^- salt occurs in the *up*, *up*, *down*, *down* form,[162] while the BF_4^- salt is in the *all up* form.[163] To-date there have been only two structural reports on complexes of the large ring [24]aneSe_6. In $[(PdCl)_2([24]aneSe_6)]^{2+}$[163] and $[(AsCl_3)_4([24]aneSe_6)]$,[164] the macrocycle can accommodate two Pd(II) (or As(III)) centres *endo* to the ring. In the latter, a

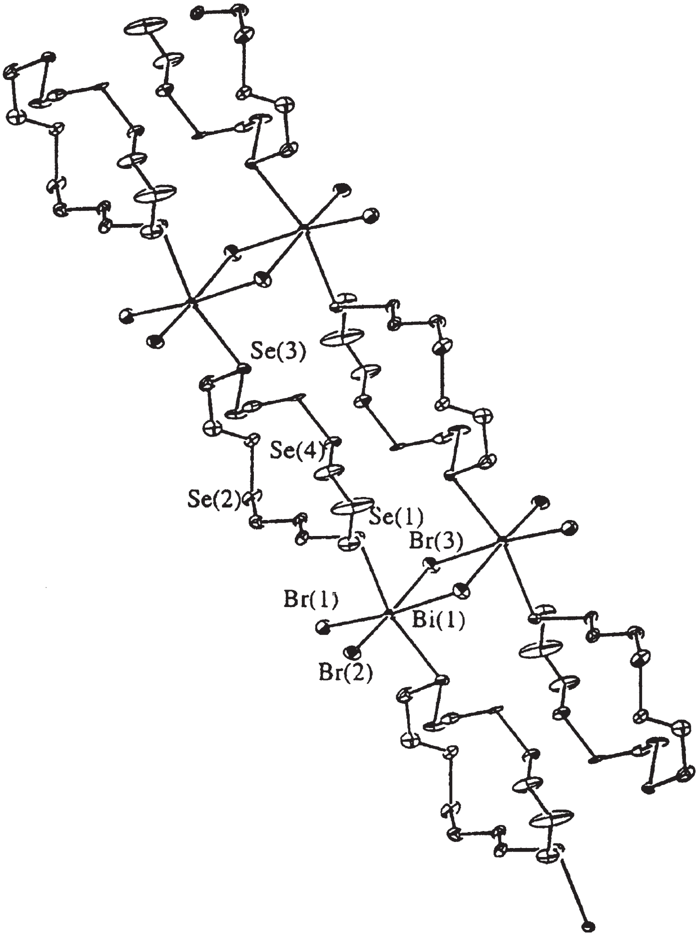

Figure 8 *Crystal structure of* $[BiBr_3([16]aneSe_4)]$ *showing the ladder-like polymer*[13] (Reproduced with permission from the Royal Society of Chemistry.)

further two As centres are coordinated *exo* to the ring, providing a very unusual example involving both *exo* and *endo* coordination in a single species. The coordination chemistry of Te-containing macrocycles is, by comparison with S and Se analogues, still a very under-developed research area, although some ligands have become available recently.

The combination of the availability of sensitive NMR probes in both ^{77}Se and ^{125}Te, together with the superior σ-donation (to low-valent metals) from SeR_2 and TeR_2 compared with SR_2 and the emergence of useful preparative methods for the Se- and Te-containing macrocycles themselves, strongly suggest that these areas will be the subject of much further research effort in the future.

2.2.5 Applications

Chalcogenoether chemistry is now a relatively mature field, as the emergence of a diverse range of applications of these species testifies.

- The use of thioether ligands as supports for transition metal organometallic species is a growing area. In particular, the soft donor set and very different electronic environment provided by thioethers (*cf*. phosphines or carbocycles) can be beneficial in the development of early transition metal catalysts such as $[Sc(CH_2CSiMe_3)_3([9]aneS_3)]$ for α-olefin polymerization.[145] Examples of co-polymerization of CO/ethene and Heck couplings based upon Pd and Pt species with mixed P/S donor ligands are also known.[165] As the early transition metal and f-block chemistry of these ligands develops, undoubtedly this area will become more prominant.
- The wide use of p-block and early transition metal chalcogenide materials for electronics applications (semiconductors, semi-metals, battery materials, *etc*.) has resulted in a large amount of work concerned with CVD using mixtures of metal halides and chalcogenoethers as dual source precursors and preformed complexes as single sources.[166]
- Multidentate and macrocyclic ligands with thioether functions in combination with N- and/or O-donor groups are of interest in the development of new series of selective metal extractants *e.g*. for Ag(I).[167]
- A range of functionalized polythioethers have been developed as carriers for radio-isotopes such as ^{99m}Tc, ^{105}Rh and ^{188}Re for diagnostic and therapeutic applications.[168,169]
- A range of metal thioether macrocyclic complexes has been used as templating agents in the preparation of extended multi-dimensional polyiodide arrays.[170] This application comes from the ability of chalcogen-containing molecules to act as donors towards halogens and interhalogens. On the other hand, cyclic thioethers have been extensively used to synthesize charge-transfer complexes with diiodine and other halogens.[171] A review on the interactions in solution between different donors (including several cyclic thioethers and trithiane) has been reported.[172]

Acknowledgements

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CHAPTER 2.3

Chalcogenone C=E compounds

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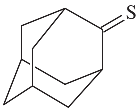
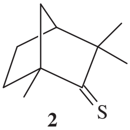
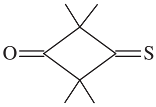
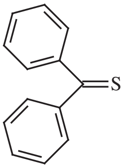
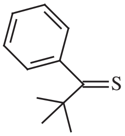
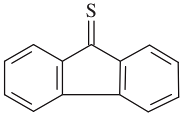
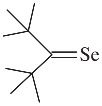
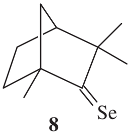
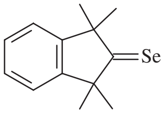
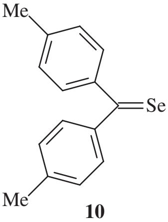
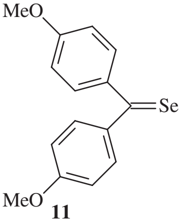
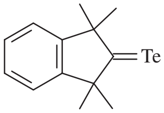
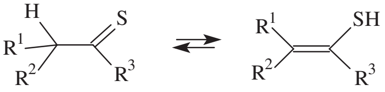
2.3.1 Introduction

Title compounds include a number of classes of substances; to limit the subject area, only chalcogenoketones will be considered here. With a few exceptions this chapter covers the thio-, seleno-, and telluro-ketone chemistry from 1994 to 2004. During these years about 80% of papers have concerned thioketones, only 16% and 4% of which selenoketones and telluroketones, respectively. Among the several groups dedicated to this chemistry, fundamental contributions have been given by Huisgen, Okuma, and Okazaki. Typical of these compounds is their high reactivity due to the low overlap of the C_{2p} orbital with those of S_{3p}, Se_{4p}, and Te_{5p}. However stable compounds can be prepared and handled when stabilized by sterical or electronic factors. In Table 1 we report some chalcogenoketones stable at the solid state. When unstable compounds are prepared, here in square parenthesis, they must be trapped as adducts by dienes *via* Diels–Alder cycloaddition, and by cycloreversion they can become the source of unstable species. In the other sections thioketones, selenoketones, and telluroketones are treated specifically, and to stimulate interest in these subjects, more space has been given to the less investigated seleno- and telluroketones. Synthesis is organized according to functional groups bonded at C=E, reactivity according to the ambidentate ability of C=E to cyclize or to the unidentate behaviour of C=E to act as an electron donor or acceptor. The terminology thione, selone, and tellone will sometimes be used alternatively to thio-, seleno-, and telluro-ketone.

Tautomeric equilibria. The presence of a hydrogen at the α carbon near the thione group induces the thione-enethiol tautomerism, Scheme 1, where C=S turns into the more stable C–S single bond.[1,2,3] Calculated enolization enthalpies[4,5] show that C=O is stronger than C=S.

Table 1 *Selected stable chalcogenoketones in the solid state*

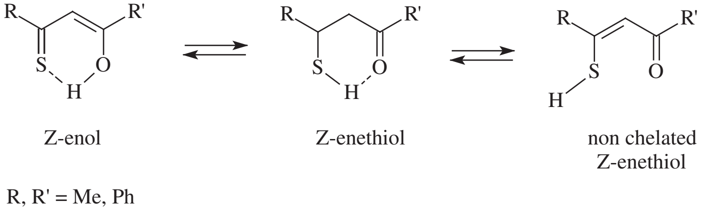
 **1** Adamantanethione	 **2** Thiofenchone	 **3** 2,2,4,4-Tetramethyl-3-thioxo cyclobutanone
 **4** Thiobenzophenone	 **5** Thiopivalophenone	 **6** Thiofluorenone
 **7** di t-Butyl-selenoketone	 **8** Selenofenchone	 **9** 1,1,3,3-Tetramethylindone-2-selone
 **10** 4,4'-Dimethylseleno benzophenone	 **11** 4,4'-Dimethoxyseleno benzophenone	 **12** 1,1,3,3-Tetramethylindantellone



Scheme 1

In contrast with the normal behaviour of aliphatic thioketones, 3-*exo*,3′-*exo*-(1R,1′R)-bithiocamphor cannot exist as enethiol, since the latter is obtained by reduction of its 1,2-dithiine, immediately stabilized by 1,5-prototropic rearrangement.[6]

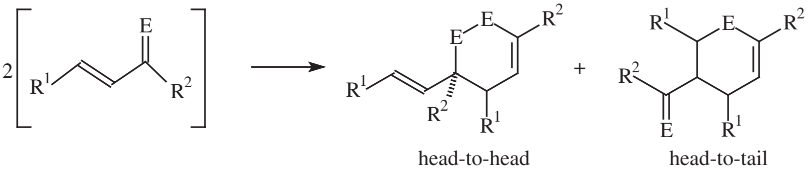
β-Thioxoketones show enol-enethiol tautomerism[7] involving the tautomers Z-enol, Z-enethiol, and non-chelated Z-enethiol, Scheme 2; however the latter form can only be observed at low temperature. For these compounds large negative primary tritium[8] and deuterium[8,9] isotope effects are observed.



Scheme 2

No data are available for compounds with C=Se and C=Te bonds and their equilibria with the seleno- and telluro-enol tautomer. For simple selenoacetone, its tautomer, and telluro-analogues, quantum mechanical calculations have been carried out using different methods.[5] These calculations have shown that on passing from O to Te, the energy difference between the tautomeric forms is reduced, a trend that parallels the calculated C=E bond energies, which decrease from O to Te.

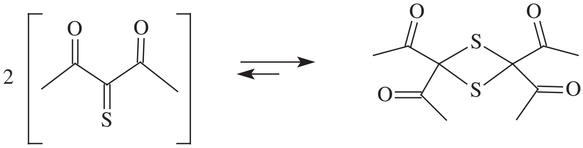
Polymerization and oligomerization reactions. 1-Halogenopropane-2-thiones give homopolycondensation,[10] in different conditions 1-chloropropane-2-thione[11] forms a polymer or a cyclic trimer. α-Oxothioketones[12–15] form dimers, by [4+2] unsymmetrical Diels–Alder cycloaddition (Scheme 7). α,β-Unsaturated thioketones,[16] Scheme 3 E = S, form dimers *via* "head-to-head" (R^1 = Ph, R^2 = Me) and "head-to-tail" ($R^1 = R^2$ = Ph), while selenoketones, E = Se, dimerize[17] *via* "head-to-head".



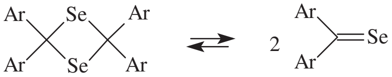
Scheme 3

α, α′-Dioxothioketones give [2+2] cycloaddition as shown for 2,4-dioxopentane-3-thione[79] in Scheme 4 to yield 1,3-dithiaetane, which undergoes a slow base-catalysed retro-dimerization.

Many selenoketones[18–20] and telluroketones[21–23] can be obtained in the solid state as stable 1,3-diselenetanes and 1,3-ditelluretanes and their formation can be assumed as proof of the existence of unstable selenoketone and telluroketone. In solution dimers of aromatic selones equilibrate with monomeric species, according to Scheme 5, where equilibrium is shifted by dilution towards the monomer.[18,24]



Scheme 4



Scheme 5

Electron donor groups (EDG) on the aromatic ring favour its displacement to the right while electron withdrawing group (EWG) favours its displacement to the left. Selenobenzophenone monomer in solution is isolated as a dimer in the solid state. Dimerization of the stable **12** to the 1,3-ditelluretane was observed in the solid state, in solution the dimer reforms **12**.[25,26] Contrary to the reaction in the solid state dimerization does not take place in solution.

2.3.2 Thioketones (Thiones)

The most investigated thioketones have found applications in the pharmaceutical, polymer, pesticide, and herbicide industries.[27] However, there is increasing interest in their photophysic[28–39] and non-linear electric properties,[40,41] which make them interesting molecules for fluorescence and phosphorescence spectroscopy, and promising building blocks for non-linear optical materials. Studies concerning the addition of a hydrogen atom to C=S,[42] the environment[43] and the ^{13}C NMR for thioketones and selenoketones[44] have been also carried out.

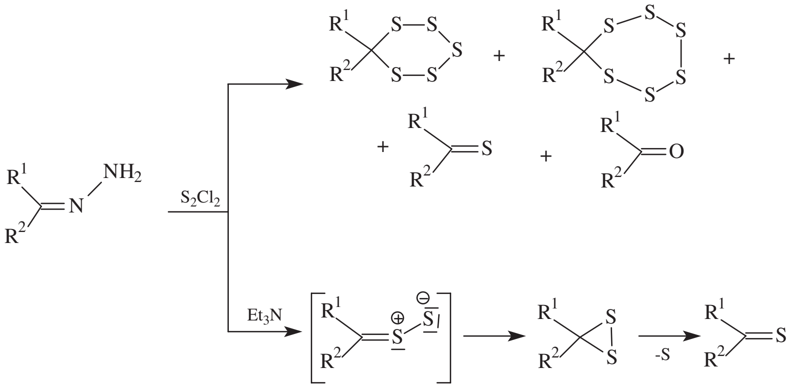
2.3.2.1 Syntheses

Syntheses and reactions of thioaldheydes and thioketones have been reviewed by Whittingham,[45] Metzner,[46] Okuma,[47] and synthesis of thioketones by McGregor and Sherrington.[48]

2.3.2.1.1 Alkyl, Aryl, and Mixed Thioketones

The conversion of a carbonyl to a thiocarbonyl group, or "thionation", is a common procedure for the synthesis of thioketones. Several methods that use P_4S_{10},[49–51] Lawesson's reagent (L.R.),[2,52–57] H_2S,[58,59] NaHS,[60] or hexamethyldisilathiane (HMDST)[61,62] are described. L.R. and P_4S_{10} have been used to sulfurate partially and entirely perfluorinated carbonyl compounds,[63] which are then trapped as anthracene adducts in a one-pot reaction. H_2S has been used as a thionating agent of aliphatic halogenated ketones[58,59] in HCl stream and absence of solvent, as well as *via* acetals[3] in the presence of Lewis acids (L.A.) Cholestan-3-one is transformed by NaHS[60] to thione, dimer, and thiol. HMDST in the presence of the highly oxophilic trimethylsilyltriflate (TfOTMS) is a good thionating agent towards ketones in solvents such as acetonitrile or methylene chloride. The very mild reaction conditions allow the synthesis of a wide variety of thioketones minimizing side reactions. Degl'Innocenti and Capperucci[64] have reviewed reactions of organothiosilanes with organic substrates, and among them the reactivity of HMDST with carbonyl compounds under $CoCl_2 \cdot 6H_2O$ or TfOTMS as a catalysts.

Hydrazones react[65] with sulfur dichloride S_2Cl_2 to yield cyclic oligosulfides, thioketones, and ketones; in the presence of triethylamine only thioketones are formed *via* thiosulfines and dithiiranes as intermediates, Scheme 6, (Okazaki reaction).



Scheme 6

Isolable dithiiranes[66–70] are rather stable under neutral or acidic conditions, they lose one sulfur atom by treatment with bases to yield thioketones. On heating they isomerize to 6-oxa-7,8-dithiabicyclo[3.2.1.] octanes *via* thiosulfine or decompose to thioketones.

Aliphatic unstable thioketones can be generated by thermolysis of their thiosulfinates in toluene.[91]

2.3.2.1.2 α,β-*Unsaturated Thioketones*

Syntheses of α,β-unsaturated thioketones, based on the hydrothiolysis of conjugated unsaturated immonium cation, have been reviewed by Timokhina and Voronkov.[71]

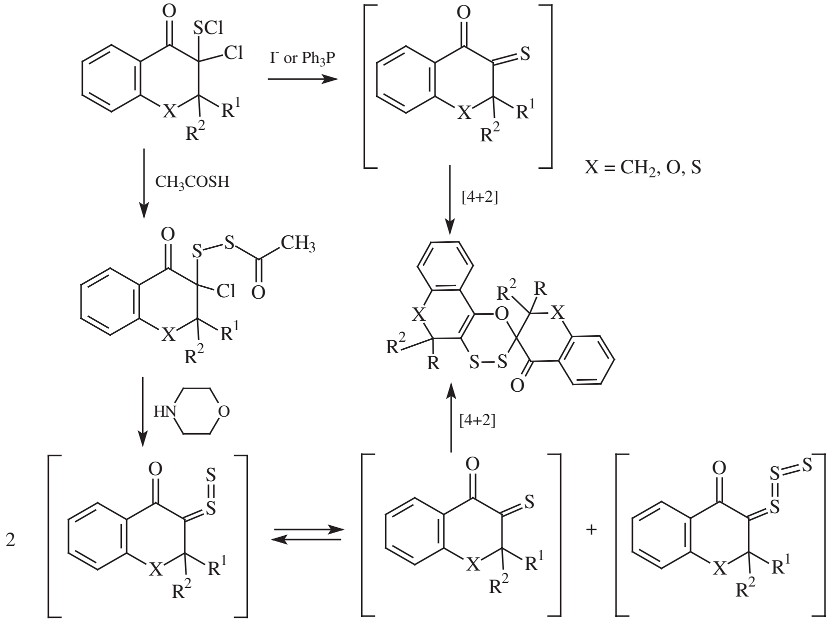
α,β-Unsaturated ketones are sulfurated with $(Me_2Al)_2S$.[16] In absence of trapping agents the obtained thioketones undergo a different [4+2] self-dimerization *in situ* (Scheme 3).

N,N′-Persubstituted *bis*(2-amino-5-thienyl)ketones and their thiazole analogues react with P_4S_{10} to yield stable 2-aminothienyl- or 2-amino-thiazolyl-substituted thioketones.[72]

3-Trimethylsilylacetylenic ketones are transformed in thioketones with HMDST,[73,74] in the presence of TfOTMS, and thioketones trapped with different dienes.

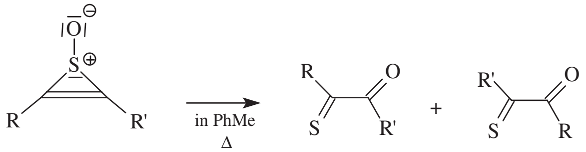
2.3.2.1.3 α-Oxo Thioketones

α-Chloro-β-oxosulfenyl chlorides can be converted by iodide ions[12] or Ph_3P[13] to the corresponding α-oxothioketones, which dimerize in an unsymmetrical Diels–Alder fashion. Alternatively they are converted to β-oxothiosulfines,[14,75] which disproportionate into β-oxothioketone and S-disulfide (Scheme 7).



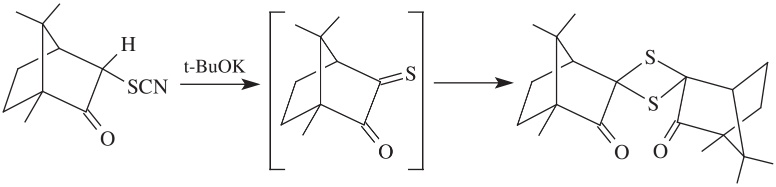
Scheme 7

Thiirene 1-oxides with bulky substituents,[76–78] R, R′ = Ph, t-Bu, Ad, isomerize to produce α-oxothioketones in high yields (Scheme 8).



Scheme 8

Phenols[79] react with phthalimidesulphenylchloride (PhthNSCl) to yield *N*-thiophthalimides. These when treated with tertiary amines afford unstable ortho-thioquinones. Base-catalysed CN-elimination from camphoryl thiocyanate yields the *anti*-1,3-dithietane as the sole stereoisomer *via* thioketone[80] (Scheme 9).



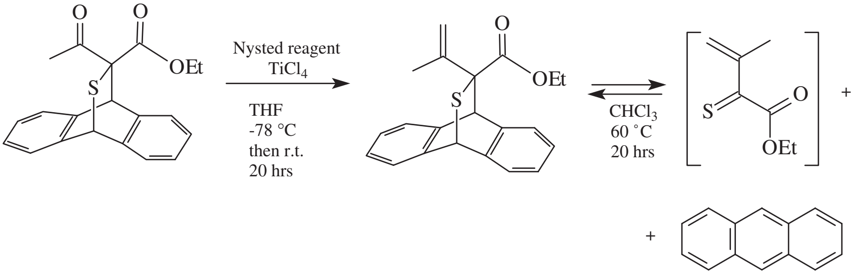
Scheme 9

Halides (X = Cl^- and Br^-) containing carbonyl groups react[81] with sodium thiosulfate in aqueous ethanol until conversion to Bunte's salt. The crude reaction mixture diluted with a trapping diene and then added with triethylamine gives the α-oxothioketone adducts.

PhthNSCl[79,82] and *N*-chlorosulphenylsuccinimide (SuccNSCl)[83] react with β-dicarbonyls in the presence of bases to afford α,α′-dioxothioketones.

2.3.2.1.4 α,β-*Unsaturated -α′-oxo-Thioketones*

The cycloadduct of an α,α′-dioxo-thioketone with antracene,[84] treated at low temperature with the Nysted reagent and $TiCl_4$, transforms a ketone group to the corresponding methylenic group. This product is thermically decomposed *via* retro Diels–Alder reaction into the unstable α, β-unsaturated-α′-oxo derivative (Scheme 10).



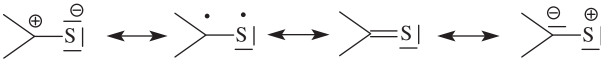
Scheme 10

2.3.2.1.5 γ-*Keto Thioketones*

Electrooxidation of 1,3,4,6-tetraaryl-2$\lambda^4\delta^2$-thieno[3,4-c]thiophenes[85] causes a thiophene ring to open with formation of γ-keto thioketones.

2.3.2.2 Reactivity

Since carbon and sulfur show close electronegativities, C=S is less polarized than the C=O bond, but it is more polarizable. EWG reduce and EDG increase the electron density on sulfur, producing polarization on C=S in the opposite sense. The weakness of C=S, its polarizability, and the attitude of sulfur to stabilize an adjacent charge or a radical centre make thioketones more reactive than ketones with reaction products that are difficult to predict. From a molecular orbital point of view the higher reactivity of thioketones is due to the lower LUMO and higher HOMO of thioketones compared to ketones. A lower LUMO shortens the gap energy with the HOMO of a nucleophile reagent while increasing the electrophilic character of thioketone. The higher HOMO of thioketones makes them more nucleophilic. Kinetic measurements[86] have shown that C=S bonds are better than CC multiple bonds to act as dipolarophiles in cycloadditions. Molecular orbital theory perturbation applied to concerted cycloaddition shows that a diminished HOMO–LUMO gap gives rise to an enhanced cycloaddition rate. Through various and complex mechanisms, the reactions of thioketones involve the following limit resonance formulae, Scheme 11, which account for the large reactivity of the thione group.



Scheme 11

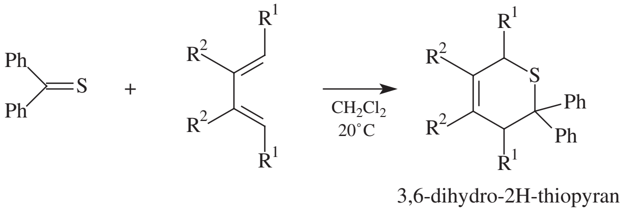
2.3.2.2.1 *Ambidentate C=S*

Cycloaddition reactions prevalently form six-, five-, four-, and three-membered rings; cycles with more than six atoms are not described.

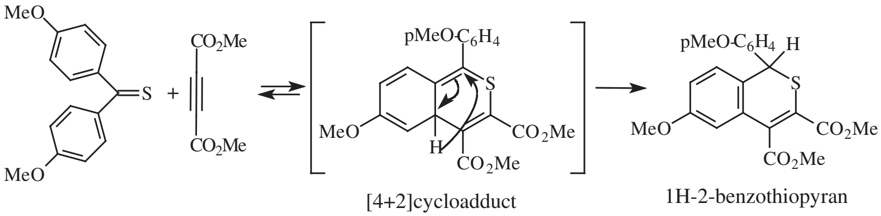
Six-membered rings. Thioketones react as dienophiles with conjugated dienes[81,87–92] in Diels–Alder [4+2] cycloadditions to form 3,6-dihydro-2H-thiopyrans regio- and stereo-selectivitely. **4** and **6** reacting with differently substituted 1,3-butadienes, Scheme 12, have shown a "*superdienophile*" activity.[87–89]

Wilker and Erker[92] have studied the stereochemistry of the [4+2] cycloaddition of diarylthioketones and corresponding diaryselenoketones with *trans, trans-* and *cis,trans*-2,4-hexadiene, (see later Scheme 30), and found an analogous behaviour between S and Se.

When the C=S bond is conjugated with double or triple bonds, thioketones can also behave as heterodienes[93–104] towards dienophiles. If thioketone contains an aromatic ring, the [4+2] cycloaddition can be followed by 1,3-prototropy to restore the ring aromaticity,[105–108] forming 1H-2-benzothiopyrans as shown in Scheme 13, where 4,4′dimethoxythiobenzophenone reacts with the dienophile dimethyl acetylenedicarboxylate (DMAD).[105]

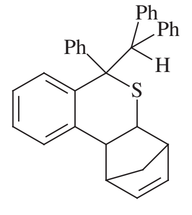


Scheme 12

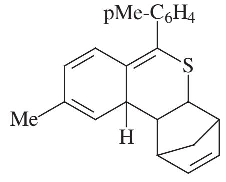


Scheme 13

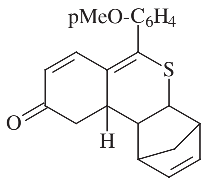
The reaction products depend on the ring substituents of the thione and the dienophile. If the dienophile is 2,5-norbornadiene,[107] **4** affords a new benzothiopyran† by reaction with a further molecule of **4**, 4,4′-dimethylthiobenzophenone yields a [4+2] cycloadduct, and 4,4′-dimethoxythiobenzophenone, a quinone derivative *via* the [4+2] cycloadduct.



1H-2-benzothiopyran



[4+2]cycloadduct



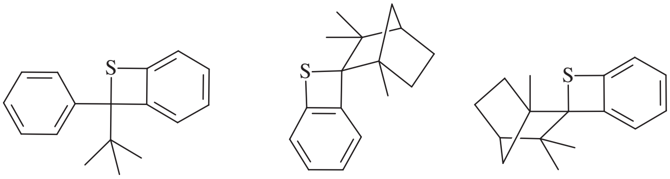
quinone

Whenever benzyne is expected to undergo a [2+2] cycloaddition as with ketones,[109] it behaves as a dienophile with aromatic thioketones. Reaction of thiobenzophenones with benzyne‡ yields the [4+2] cycloadducts and 1H-2-benzothiopyrans.[110,111] Sterically congested thiones,[111] thiopivalophenones and **2**, react with benzyne to give the [2+2] adducts, 2H-1-benzothietes.

---

† This compound was originally thought to be dihydrobenzothiepine[107] by analogy with selenobenzophenones[108] and was identified as benzothiopyran[47].

‡ Obtained both from phenyl[2-(trimethylsilyl)phenyl] iodonium trifluoromethane sulphonate and 2-trimethylsilylphenyltrifluoromethanesulfonate in the presence of tetrabutylammonium fluoride (TBAF). They are good benzyne precursors under mild conditions.

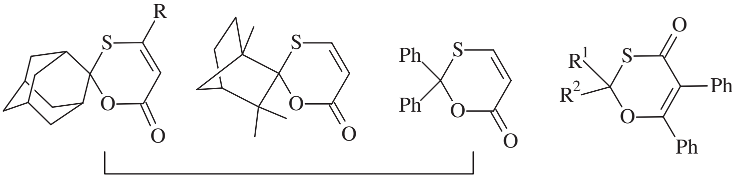


2H-1-benzothietes

In refluxing toluene, thiopivalophenones yield both 2H-1-benzothietes and 1H-2-benzothiopyrans. Using benzenediazonium-2-carboxylate, as a benzyne precursor, the reaction with **4**[111] yields a 4H-3,1-benzoxathian-4-one, and selenobenzophenone derivatives[18,111] give 4H-3,1-benzooxaselenin-4-ones (see later Scheme 34).

The heterodiene and dienophile behaviours of thioketones have been investigated by Saito in diene-trasmissive[112] and transannular[113] Diels–Alder reactions.

1 cycloadds regioselectively propiolic acid derivatives to form 2H,6H-1,3-oxathiin-6-ones,[114] **2** with propiolic acid only gives the *exo*-isomer. This reaction has been also carried out unsuccessfully with sterically crowded thioketones, whereas **4** yields a 2H,6H-1,3-oxathiin-6-one and a 1H-2-benzothiopyran derivative.[115] 2H,4H-1,3-oxathiin-4-ones have been synthesized by cycloaddition of thiones with benzoylphenylketene.[57]



2H,6H-1,3-oxathiin-6-ones 2H,4H-1,3-oxathiin-4-ones

In the presence of sodium thiophenoxide, elemental sulfur reacts with **4** or **1** to afford 1,2,4,5-tetrathianes. Huisgen[116] suggested a mechanism where the oligothiolate species PhS_x^- attacks the thione carbon as an initial step.

Five-membered rings. Most five-membered rings arise from the 1,3-dipolarophile behaviour of thioketones and studies in this field have been carried out mainly by Huisgen, Mloston, Heimgartner, and their co-workers. An exemplified thioketone reactivity to form five-membered rings with several classes of compounds is shown in Table 2.

Diazoalkanes,[117–141] azides,[142–152] partial oxiranes,[153] oxazolidinone,[154]aziridines,[155,156] trimethylsilylmethyltriflate salts (TfO^-TMSM^+),[157] and α-aminoacid ester imines[158] form pentaatomic rings through reactive intermediate ylides. Species like thiocarbonyl S-ylides,[124–141] thiocarbonyl S-imides,[151,152] thiocarbonyl S-sulfides (thiosulfines), and thiocarbonyl S-oxides (sulfines) containing a three atomic system as central unit with the sulfur atom in the middle position are known as sulfur centred 1,3-dipoles. Oxiranes[159–165] react opening the ring by L.A. Thiosulfines,[50,75,166,167] reactive intermediates in the formation of 1,2,4-trithiolanes, are not isolable species since they decompose to thione and sulfur.

Table 2 *Exemplified thioketone reactivity to form five-membered rings*

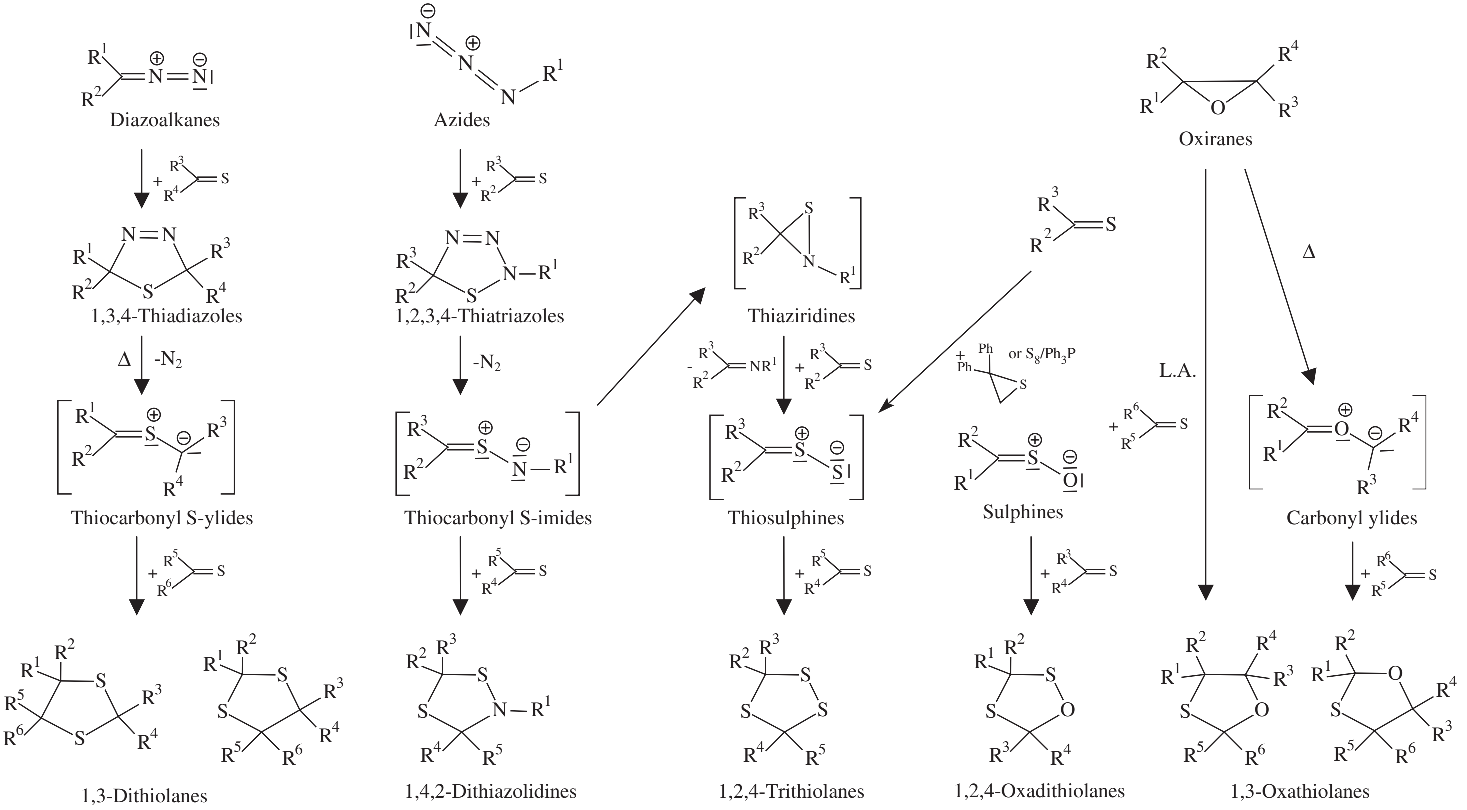
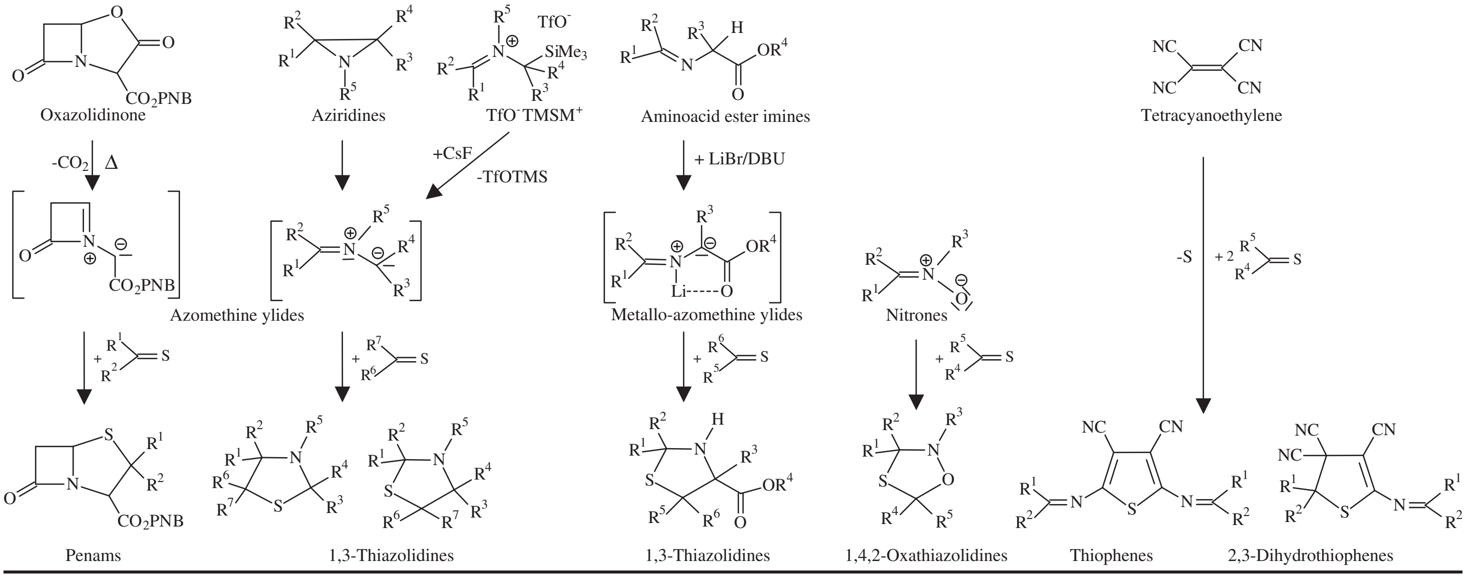


Table 2 (*continued*)



Thiaziridines,[145] thiiranes,[167] and elemental sulfur[168] (in the presence of Ph_3P) can react with a thioketone to give thiosulfines then trapped as 1,2,4-trithiolane.

In solution aliphatic and aromatic sulfines combine with aromatic and aliphatic thiones to yield 1,2,4-oxadithiolanes.[169,170] Cycloadducts with only aromatic substituents could not be obtained, since the conjugation energy of aromatic sulfine drives the equilibrium to the reactant side.[170] Thiobenzophenone- and thiofluorenone-sulfines react with **3** to afford 1,2,4-trithiolanes.[171] This is interpreted by assuming that 1,2,4-oxadithiolanes are formed in a first step, hence converted to 1,2,4-trithiolane.

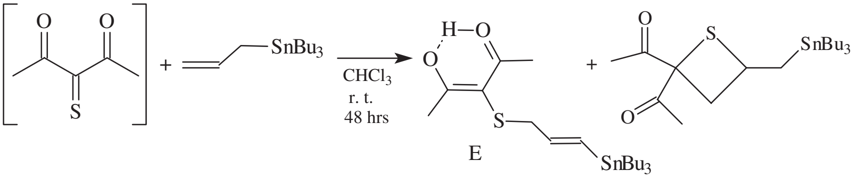
Many cycloadditions of nitrones[86,172–174] and thiones give cycloaddition-cycloreversion equilibria. *N*-Methyl-*C*,*C*-diphenyl- and *N*-methyl-*C*-phenylnitrones, react with aliphatic thiones forming 1,4,2-oxathiazolidines, while **4** does not afford a cycloadduct.[172] *N*-Methyl-*C*,*C*-2,2,4,4-tetramethyl-3-cyclobutanonenitrone reacts with alicyclic thioketones to give 1,4,2-oxathiazolidines,[174] while with **4** it enters into a metathesis reaction.

Tetracyanoethylene (TCNE)[175,176] reacts with thiobenzophenones to yield 2,3-dihydrothiophene, thiophene, and 1,2-dithiin derivatives, thus depending on temperature. Okuma suggested a mechanism[176] for the formation of 2,3-dihydrothiophenes through [2+2] and [4+2] sequential cycloadditions.

Four-membered rings. The study of the reaction between thiobenzophenone and methylenetriphenylphosphorane[177] pointed out the presence of a reactive intermediate, thiaphosphetane, which decomposed either to a thiirane and triphenylphosphine or to the Witting alkene and a phosphine sulfide, depending on the temperature.

As seen, sterically congested thiones react with benzyne to give [2+2] adducts (see page 116).

2,4-Dioxopentane-3-thione reacts[178] with allyltributylstannane, Scheme 14, to give the expected thiophilic "ene" adduct and a [2+2] cycloadduct.



Scheme 14

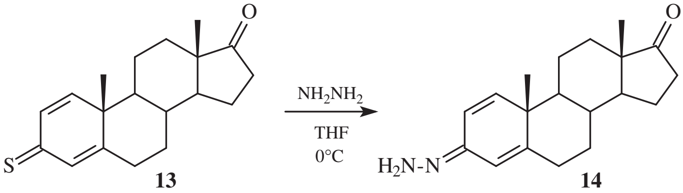
Three-membered rings. Sterically crowded cycloalkanethiones[179] react with $CHCl_3$/NaOH under phase transfer catalyst, benzyl(triethyl)ammonium chloride (TEBA), to give the corresponding gem-dichlorothiiranes, which can undergo desulfuration to give (dichloromethylidene)cycloalkanes. The reaction of sterically crowded cycloalkanethiones with Seyferth's reagent[180] and sodium iodide in boiling benzene yields gem-difluorothiiranes, while the reaction of aromatic thioketones gives gem-difluoroalkenes.

2.3.2.2.2 Unidentate C=S

Besides cyclization, thioketones give reactions where C=S behaves as a unidentate *via* sulfur or carbon.

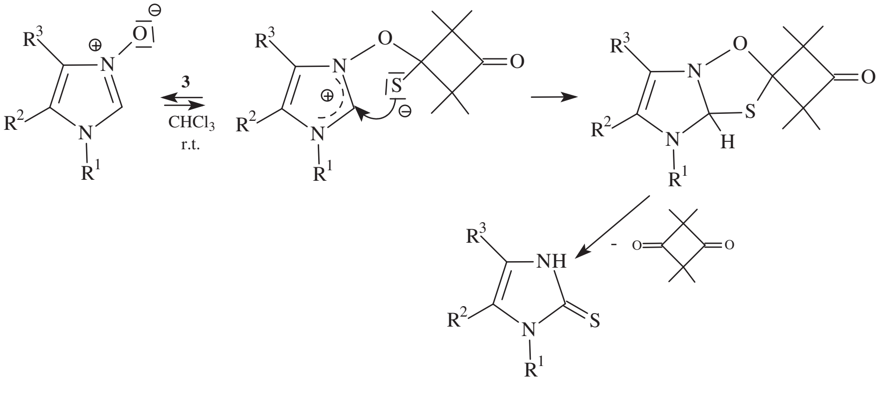
Electron donor C=S. Thionic sulfur reacts with Ag(I) ,[181–183] $SbCl_3$,[184] Yb(0), Sm(0),[185–188] and complexes such as $(Cod)_2Ni$, (Bpy)(Cod)Ni[189] $Mo(CO)_6$[190] to yield intermediates for subsequent reactions, gives oxidation reactions[191–198] to sulfine and ketone, and forms complexes with metal ions by coordinative bonds,[55,199] concerning the donor ability of the C=E group towards dihalogens (see Chapter 8.2).

Electron acceptor C=S. The thione group in **13** reacts with hydrazine hydrate (and other *N*-nucleophiles),[200] forming **14** (Scheme 15).



Scheme 15

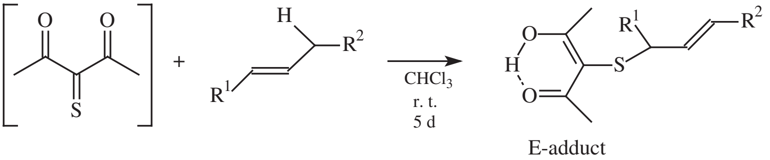
The oxygen of azole *N*-oxides produces a nucleophilic attack to C=S C-atom of a cycloalkanethione forming a zwitterion, which cyclizes and spontaneously decomposes, yielding the product of this sulfur transfer reaction[201] (Scheme 16).



Scheme 16

The presence of EWG on 2,4-dioxopentane-3-thione favours the formation of thiophilic adducts with different allyl substrates.[178] In all cases the reaction affords single thiophilic "ene" adducts and formation of C=C occurs with high E stereoselectivity (Scheme 17).

Thioketones with EWG can also give electrophile aromatic substitutions.[79] Since the CF_3S group is the most lipophilic substituent known,[202] thioketones are useful starting materials for the preparation of fluoromethylsulfides *via* the



Scheme 17

thiophilic addition to a CF_3^- anion from Rupert's compound in the presence of TBAF.[203] The course of the reaction depends on the type of thioketone. Thiobenzophenones react to give products *via* addition of CF_3^- in the thiophilic and carbophilic mode. Hexafluorothioacetone dimer behaves as a nucleophile in the reaction with methylene diphosphanes.[204] Finally thioketones are reduced to thiols by photochemical,[205,206] enzymatic,[207] and chemical catalysed reactions.[208]

2.3.3 Selenoketones (Selones)

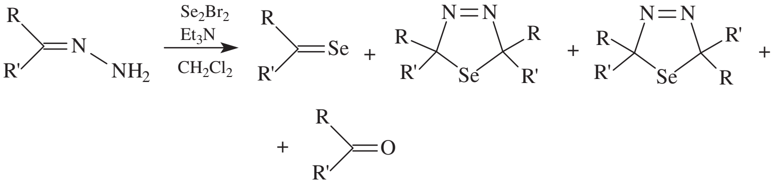
Organoselenium compounds have drawn much attention in the past years as synthons in organic synthesis[209,210] and the chemistry of selenoketones has been reported increasingly.[211–214]

2.3.3.1 Syntheses

Selenoketones are less stable than thioketones and cannot be obtained as monomers unless sterically hindered by alkyl groups or stabilized by electronic delocalization of electron rich substituents. Some stable selenoketones are reported in Table 1.

2.3.3.1.1 Alkyl Selenoketones

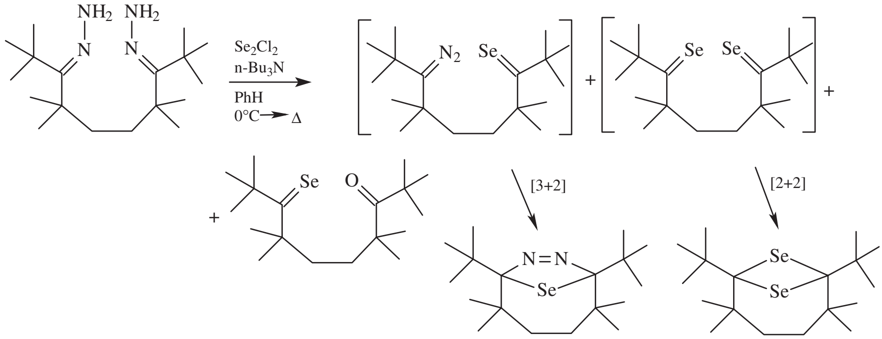
Selenoketones with R, R′ sterically crowded substituents[215,216] are obtained by reacting the corresponding hydrazones with Se_2Br_2 and Et_3N. The products of this reaction depend on temperature, Scheme 18, since the formation of *cis,trans*-1,3,4-selenadiazolines is also possible.[217]



Scheme 18

Sterically congested alkanes containing two =N-NH_2 groups at 1,6[218] and two =N_2-NH_2 groups at 1,7,[219] react with Se_2Cl_2 to form mono- and di-selones.

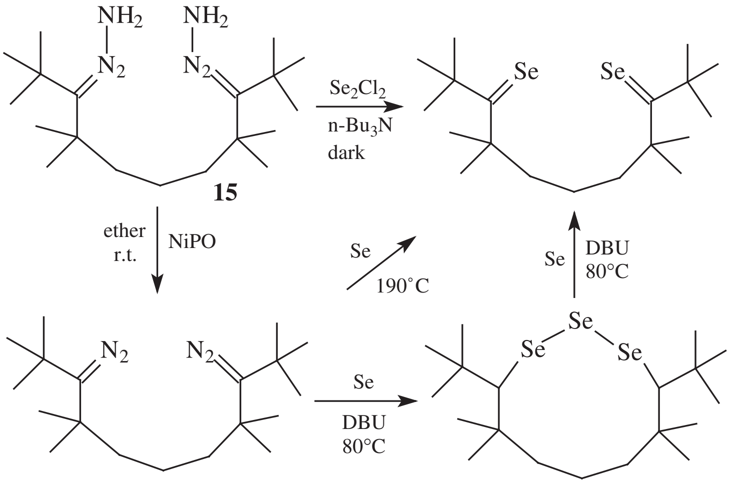
As shown in Scheme 19, dihydrazone gives a monoselenoketone, probably a diselenoketone that dimerizes, and 1,3,4-selenadiazoline.[218]



Scheme 19

A diselone derivative is prepared from **15**, Scheme 20, *via* both Se_2Cl_2 and the corresponding diazo compound and selenium.[219]

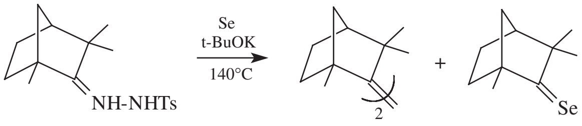
The diselone reacts with exceeding selenium in the presence of 1,8-diazabicycle-[5,4,0]-u ndec-7-ene (DBU) to give the cyclic triselenide.



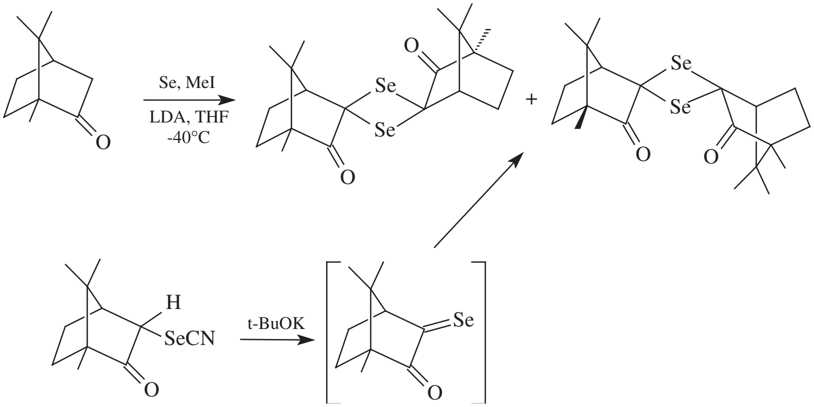
Scheme 20

Although the symmetrical olefin is the main product, Scheme 21, **8** is obtained from fenchone p-toluenesulfonyl hydrazone[220] (tosyl hydrazone) with t-BuOK and elemental selenium.

The reaction of camphor enolate with selenium in the presence of methyl iodide,[19,20] followed by areal oxidation, affords 1,3-diselenetanes formed by dimerization of the putative selenoketone intermediate (Scheme 22). These



Scheme 21



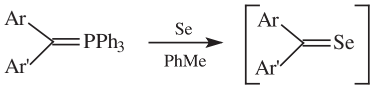
Scheme 22

products are also obtained by base-catalysed elimination of HCN from the corresponding camphoryl selenocyanate.

2.3.3.1.2 Aromatic and Mixed Selenoketones

Diferrocenylselone was obtained as an impure blue solid from the corresponding ketone and $(Me_2Al)_2Se$.[221] Aromatic and mixed selenoketones are generated by treating the corresponding ketones with *bis*(1,5-cyclooctanediylboryl) selenide.[222] This reaction produces diselenides as by products by reduction of selenoketone to selenolate and subsequent oxidation by aerial oxygen.

Methylene phosphorane derivatives, Scheme 23, react with Se to give the corresponding selenoketones.[18,24,223–225]

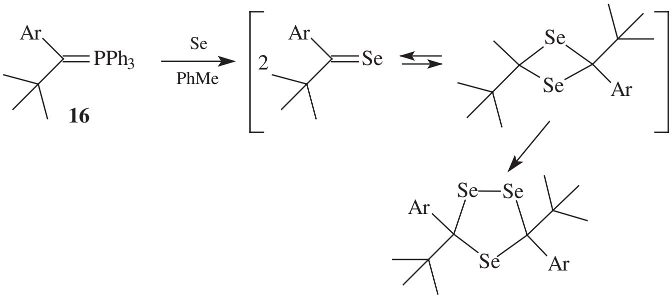


Scheme 23

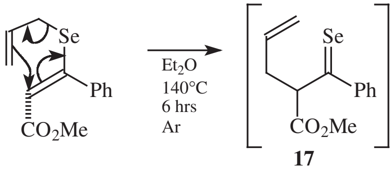
If unstable, they dimerize or, as in the reaction of **16** with Se, they also afford[225] *trans*-1,2,4-triselenolanes, Scheme 24.

In the case of 1,2,4-trithiolanes, both *cis* and *trans* isomers are obtained with a different reaction mechanism involving a molecule of thioketone and a molecule of thiosulfine.[50]

Selenoketone **17** is generated by [3,3] sigmatropic rearrangement[226] of the corresponding selenide, Scheme 25.



Scheme 24

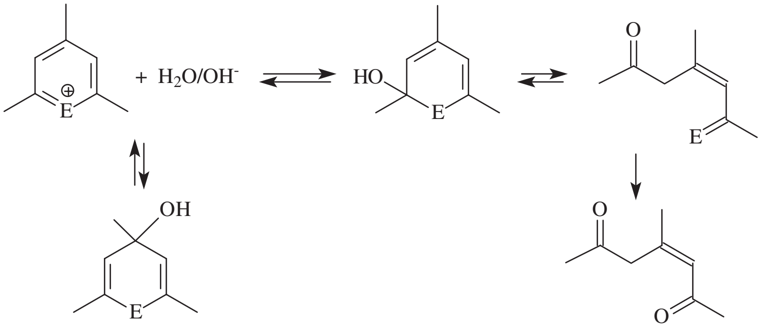


Scheme 25

2.3.3.1.3 α,β-*Unsaturated Selenoketones*

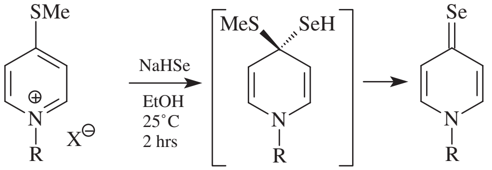
α,β-Unsaturated selones obtained[17] *in situ* from the corresponding carbonyls and $(Me_2Al)_2Se$, undergo regioselective [4+2] dimerization *via* a "head-to-head" oriented transition state to afford diselenine derivatives (*trans* and *cis* isomers) (Scheme 3). Theoretical calculations show that "head-to-head" dimerization is thermodynamically favoured over the "head-to-tail".

The initial step in chalcogenopyrylium salt hydrolysis[227] involves the addition of hydroxide/water to the ring as shown in Scheme 26. Hydrolysis of the intermediate thione, selenoketone, and telluroketone irreversibly produces a 2-pentene-1,5 dione derivative.



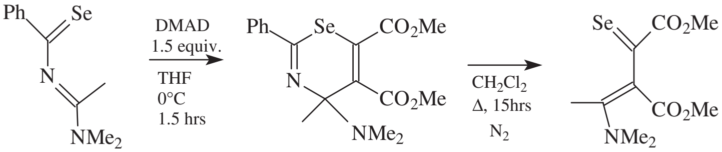
Scheme 26

N-alkyl-4-selenopyridones and 4-selenoquinolones are prepared from 4-methylsulfanylpyridinium and –quinolinium salts[228] by nucleophilic displacement with NaHSe (Scheme 27).



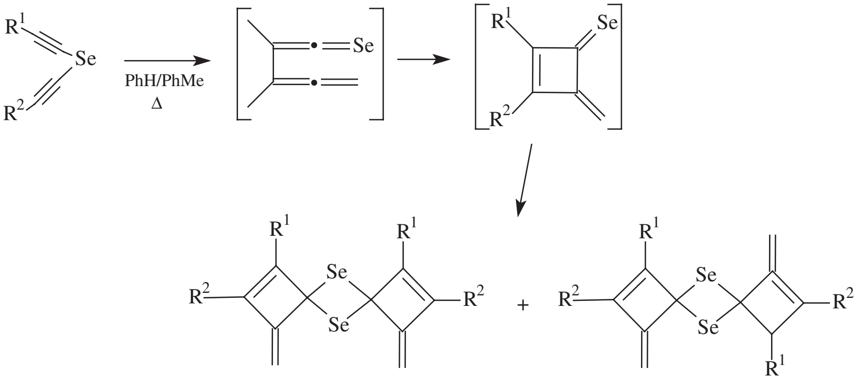
Scheme 27

N-selenoacylamidine with DMAD gives the cycloadduct 4H-1,3-selenazine,[229–231] which yields the corresponding selenoketone (Scheme 28).



Scheme 28

By heating alkynyl propargyl selenides give 2-methylene-3-cyclobutene-1-selones, Scheme 29, which dimerize giving a mixture of the corresponding 1,3-diselenetanes[232]



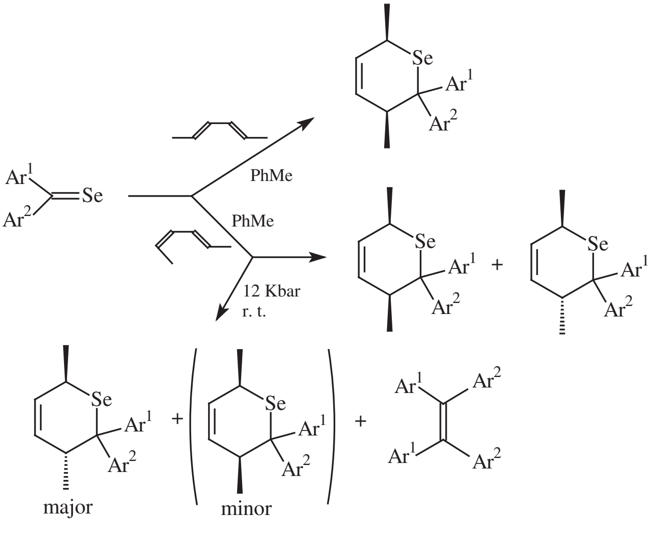
Scheme 29

2.3.3.2 Reactivity

The chemical behaviour of selenoketones is determined by the weakness and polarity of the CSe bond. Some selones eliminate selenium, and the corresponding olefins are isolated.

2.3.3.2.1 Ambidentate C=Se

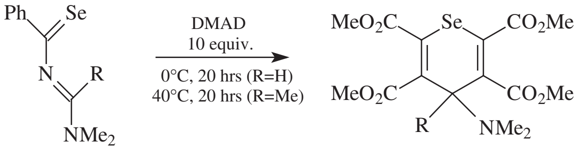
Six-membered rings. Selenoketones react as dienophiles with conjugated dienes[24,89,223,233,234] in Diels–Alder [4+2] cycloadditions to form 3,6-dihydro-2H-selenapyrans. Reaction of arylselenoketones[92]with *trans,trans*-2,4-hexadiene proceeds in a completely stereospecific way to yield the corresponding *cis*-selenapyran, while with *cis,trans*-2,4-hexadiene it proceeds stereoselectively, forming *cis*-selenapyran with small amounts of the *trans*-selenapyran isomers, Scheme 30.



Scheme 30

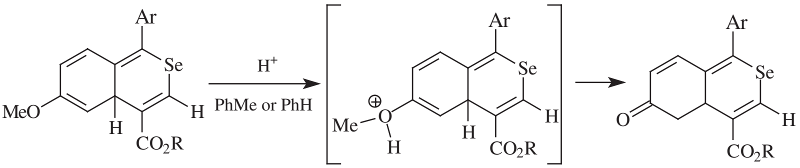
If the reaction is carried out at a pressure of 12 kbar, the mechanism changes, and cycloaddition with *cis,trans*-2,4-hexadiene proceeds stereospecifically yielding the *trans*-selenapyrans as the major products along with the corresponding tetraarylethylenes.

When C=Se is conjugated with double or triple bonds, selenoketone can also behave as a heterodiene in the presence of the dienophiles. *N*-selenoacylamidines, used as 1-selena-3-aza-1,3-dienes with 1,5 equivalents of the dienophile DMAD are converted[229,231] to 4H-1,3-selenazines, Scheme 28, with 10 equivalents being transformed into tetrasubstituted 4H-selenopyran derivatives (Scheme 31).



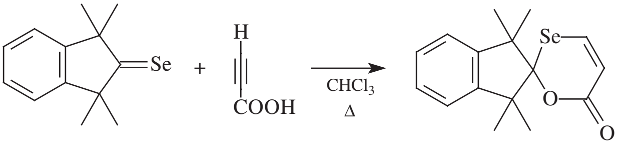
Scheme 31

The reaction between aromatic selenoketones and dienophiles proceeds regiospecifically *via* a primary [4 + 2] cycloaddition, followed by a 1,3-proton shift forming 1H-2-benzoselenopyrans.[235] Further reaction with selenobenzophenones might yield another typology of 1H-2-benzoselenopyrans thus depending on the substituent R on the ring and the dienophile[108,236] as seen for the thiobenzophenones (see page 115). Okuma[108] suggested that this reaction might proceed through carbene insertion of the primary cycloadduct. The primary [4 + 2] non aromatized cycloadduct obtained by reacting **11**[235] and a propiolic acid derivative, according to temperature, or a dienophile can be transformed to non-aromatic ketone (Scheme 32). These studies have contributed to clarify and consolidate the analogy between S and Se.

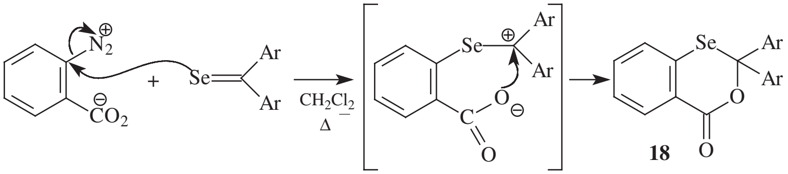


Scheme 32

Sterically crowded selones and 4′-methoxyselenopivalophenone cyclize with propiolic acid to yield 2H,6H-1,3-oxaselenin-6-one derivatives[115] (Scheme 33). With benzenediazonium-2-carboxylate or diphenyliodonium-2-carboxylate monohydrate, benzyne precursors, **11** yield **18**[18] (Scheme 34).



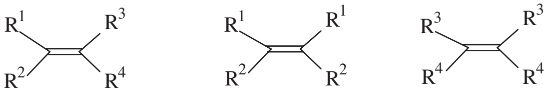
Scheme 33

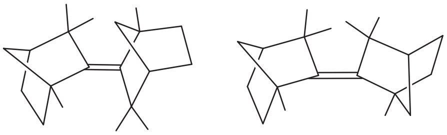


Scheme 34

Five-membered rings. An exemplified representation of selenoketones in forming pentaatomic rings is shown in Table 3.

Selenobenzophenones with cyclopentadiene afford 1:1 adducts at room temperature (r.t.), and bicyclic diselenides as by products. Using exceeding Se in refluxing toluene, the diselenides are obtained in good yields.[18] Substituted formyl selenophenes are obtained by oxidative cyclization[230] of selenabutadiene. The reaction of selenobenzophenones with TCNE affords 2,3-dihydroselenophenes,[224] only 4,4′-difluoroselenophenone and TCNE give the corresponding selenophene.[236] Selenoketones react as 1,3 dipolarophiles with azomethine ylide, obtained from an oxazolidinone, to give regiospecifically racemic selenapenams in a single step.[215] Moreover selenobenzophenones and **8** react with diazoalkane derivatives[237] and fenchone(triphenylphosphoranylidene)hydrazone,[238] respectively as 1,3-dipolarophiles to give 1,3,4-selenazolidine intermediates. They are interconverted through retrocyclization equilibria, and then lose N_2 and Se to give the corresponding olefins.





Four-membered rings. **9**, Scheme 35, and di-tert-butylselone react with benzyne,[239] derived from *o*-trimethylsilylphenyltrifluoromethanesulfonate in the presence of TBAF to give 2H- benzoselenete by a [2+2] cycloaddition. If benzyne is derived by heating benzenediazonium 2-carboxylate, also compound **19** is formed.

8 reacts with benzyne from benzenediazonium carboxylate giving a spirocyclic compound. As described in the introduction, many selenoketones are stabilized by dimerization forming 1,3- diselenetanes.

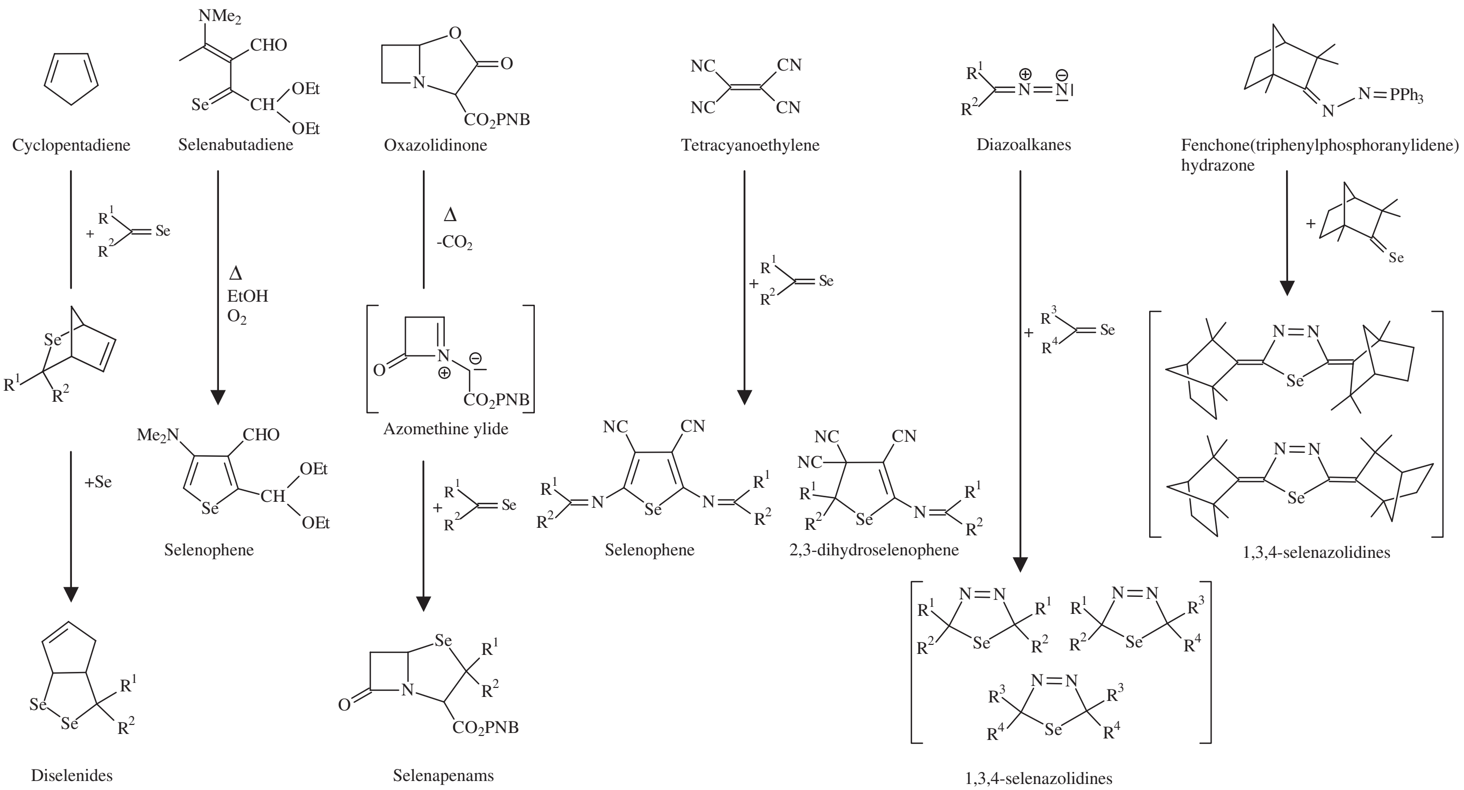
Three-membered rings. Gas-phase pyrolysis of **20** has been carried out and analysed by photoelectron spectroscopy.[216] Selenoketone eliminates molecular nitrogen to form alkylideneselenirane, which decomposes at higher temperature (Scheme 36).

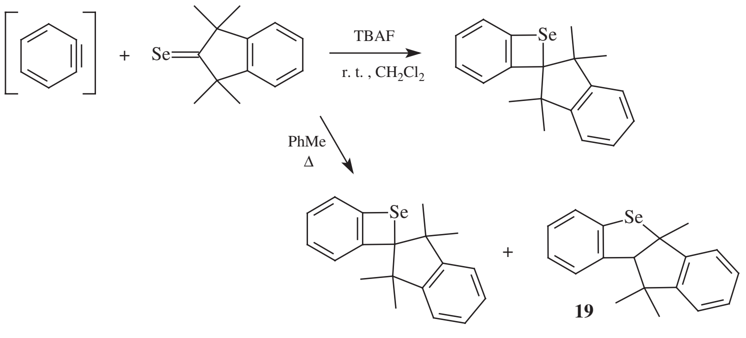
2.3.3.2.2 Unidentate C=Se

Electron donor C=Se. **11**[18] is oxidized to 4,4′-dimethoxybenzophenone, and thiated to 4,4′-dimethoxythiobenzophenone.

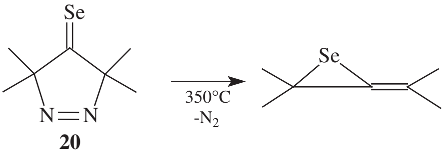
Treatment of sterically-crowded selones possessing substituted bornane skeletons with chloramine-T afford several products derived from intermediary selone Se-imides (Scheme 37). Direct observation of the intermediates was done by NMR monitoring at low temperature.[240]

Table 3 *Exemplified selenoketone reactivity to form five-membered rings*

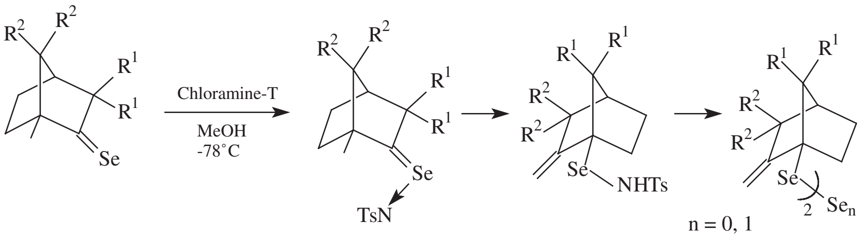




Scheme 35



Scheme 36



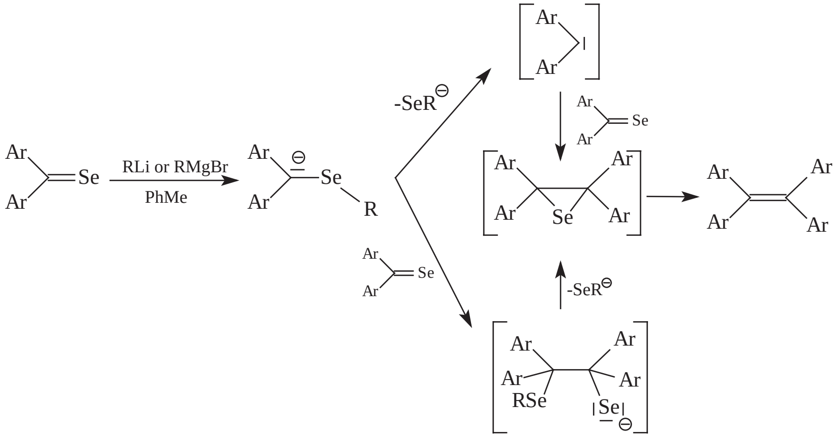
Scheme 37

Diferrocenyl selone reacts with $W(CO)_5 \cdot THF$ yielding the selone pentacarbonyl tungsten complex.[221]

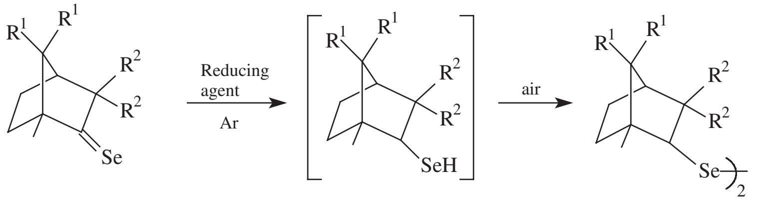
Electron acceptor C=Se. Diarylselones react with alkyllithium or Grignard reagents to give symmetrical tetraarylethylenes[241] *via* electron transfer and an episelenide intermediate (Scheme 38).

Unlike selenobenzophenone, **4** reacts with alkyllithium to afford mainly the corresponding carbophilic adducts, and with Grignard reagents, compounds resulting from addition of the organic radical to sulfur.

Stable hindered selenoketones[222] are easily reduced to give selenolate ions with various reducing agents and oxidized by air to form diselenides (Scheme 39).



Scheme 38



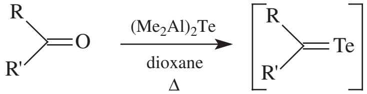
Scheme 39

2.3.4 Telluroketones (Tellones)

Maximum polarity and minimum stability in the heterocarbonyl compounds of the heavier chalcogens is reached for tellurium. It is therefore not by chance that stable telluroketones were obtained 12 years ago. Tellones are generally stabilized both by oligomerization and by coordination to transition metal centres to form rings containing C–Te bonds;[242–244] stable monomers need bulky substituents to prevent subsequent reactions. In 1993 Bildstein[221] obtained a most sensitive dark violet compound, diferrocenyltellone by treating diferrocenylketone with $(Me_2Al)_2Te$, and characterized it by subsequent reactions. Some months later, Okazaki published the preparation of stable blue solutions of **12**,[245] reporting also NMR and UV data. In the same year, the first structural evidence of the formal C=Te bond in 2-telluroimidazoline was published.[246]

2.3.4.1 Syntheses

$(Me_2Al)_2Te$ is an efficient tellurating reagent for the direct conversion of ketones to telluroketones[21] in the presence of cyclopentadiene (Scheme 40).

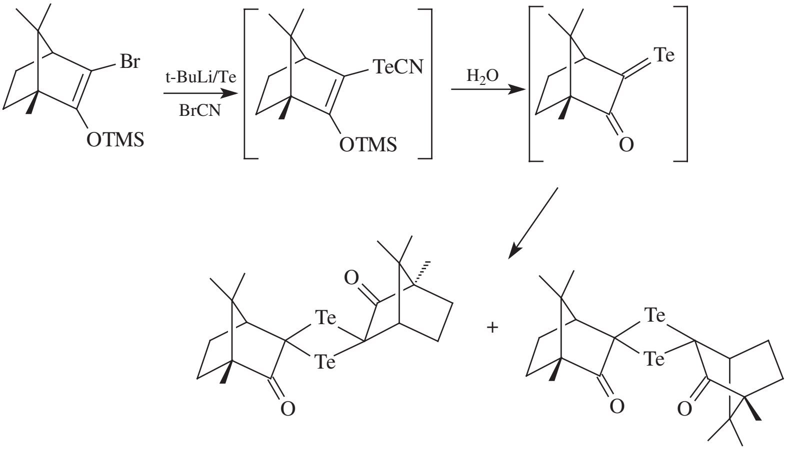


Scheme 40

Moderately sterically hindered adamantanone and bicyclo[3.3.1]nonan-9-one give the corresponding cycloadducts.

Diferrocenyltellone was reported[221] as a blue toluene solution from diferrocenylketone and (Me$_2$Al)$_2$Te. The authors recommended avoiding isolation due to its poor stability. No spectroscopic data, apart from its blue colour, or analytic data are given and its existence was deduced from chemical reactions only.

(1R)-3-telluroxocamphor was hypothesized as an intermediate obtained in the formation of the two 1,3-ditelluretane isomers[22] according to Scheme 41.

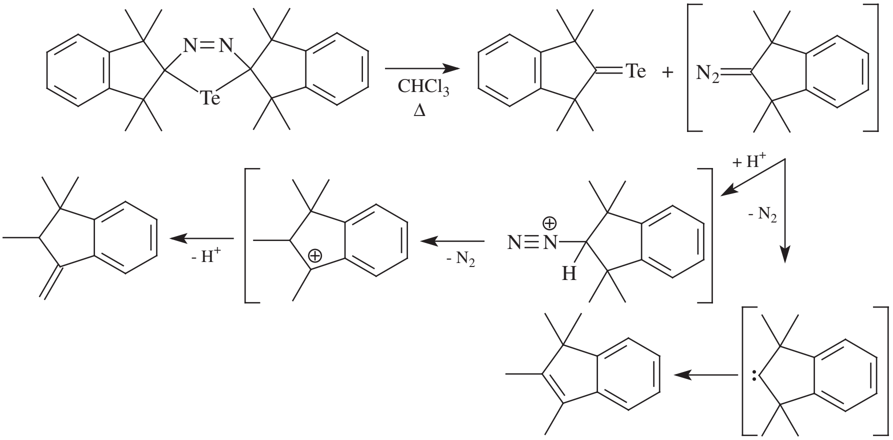


Scheme 41

12 was prepared as a blue CHCl$_3$ or benzene solution at r.t., stable up to 80°C in the absence of air and light, by thermal cycloreversion of 1,3,4-telluradiazoline (Scheme 42).[245]

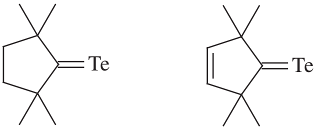
Okazaki[247] also suggested a detailed mechanism for the preparation of 1,3,4-telluradiazoline from 1,1,3,3-tetramethylindanhydrazone and tellurium halides. The reaction produces a complicated mixture of products, including **12**.

By using flash vacuum thermolysis, **12** was obtained from 1,3,4-telluradiazoline as green crystals.[25,26] The visible spectrum (CHCl$_3$ at 80°C) showed λ_{max} 825 nm assigned to the π–π^* transition of the C=Te bond. In the ^{13}C–NMR spectrum, tellurocarbonyl carbon resonates at 301 ppm, which is the most deshielded carbon observed in a neutral molecule. Similarly, the ^{125}Te-NMR shift at 2858 ppm is in the extreme downfield shift range.[245]



Scheme 42

As **12**, 2,2,5,5-tetramethylcyclopentantellone and 2,2,5,5-tetramethylcyclopententellone were synthesized from the corresponding 1,3,4-telluradiazoline and exhibit NMR and visible data in the ranges of **12**.[25]

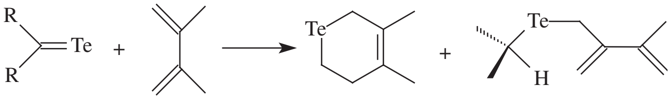


A tellone is mentioned as an intermediate, E=Te, in the base catalysed equilibrium of the tellurocycles[227] (Scheme 26).

2.3.4.2 Reactivity

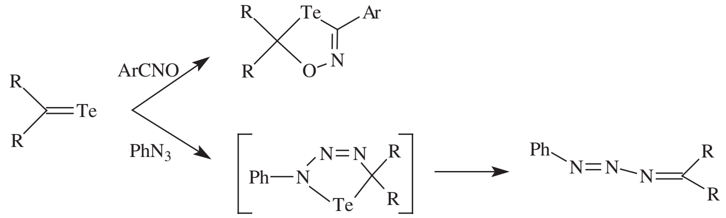
2.3.4.2.1 Ambidentate C=Te

Tellones react as dienophiles with dienes such as cyclopentadiene and 2,3-dimethylbutadiene to yield a mixture of Diels–Alder adducts and ene products (Scheme 43).[21,25,245]



Scheme 43

1,3-Dipolar cycloaddition reactions occur with mesitonitrile oxide and tellones to afford oxatellurazole in good yield,[25,245,248] while a triazene is formed with phenyl azide[25] probably *via* detelluration of a telluratriazoline ring (Scheme 44).

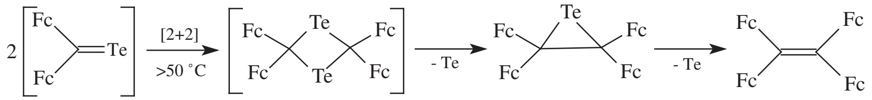


Scheme 44

2.3.4.2.2 Unidentate C=Te

12 (L) reacts with $W(CO)_5 \cdot THF$ to give a tungsten complex[249] $W(CO)_5 \cdot L$ in good yield. Both crystal structure analysis and NMR data reveal a high degree of the C=Te bond. The complex, stable in benzene or chloroform and in the solid state, is decomplexed in acetonitrile by ligand exchange.

Thermolysis of diferrocenyltellone,[250] as well as its reaction with $M(CO)_6$ (M=Cr, Mo, W),[221] yields the tetraferrocenylethylene by a twofold extrusion process from a preformed cyclic dimer of diferrocenyltelluroketone (Scheme 45).



Scheme 45

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CHAPTER 2.4

Thioamides, Thioureas and Related Selenium and Tellurium Compounds

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2.4.1 Introduction

Thioamides, selenoamides, thioureas and selenoureas are useful intermediates in many synthetic transformations. They are essential building blocks for the preparation of a number of biologically relevant peptide, heterocycles, *etc*. In present chapter, we mainly discuss the various synthetic methods of the thioamides, selenoamides, thioureas, selenoureas, telluroamides, their application in the preparation of heterocycles and their biological significances. We focus on especially recent progress of chalcogenoamides and chalcogenoureas during 1990–2005. Several review articles have been written up recently.[1–7]

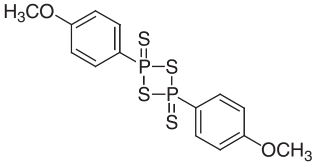
2.4.2 Thioamides

Thioamides and their use in the preparation of the heterocyclic compounds are widely reported in the literature. Also they attract considerable interests in peptide chemistry. Molecular and crystal structures of some thioamide derivatives have been confirmed by X-ray diffraction data.[8–10] Lawesson's reagent or phosphorus pentasulfide (P_4S_{10}) is actively used for the synthesis of thiocarbonyl compounds. Their preparation methods, reactions, applications in the synthesis of heterocycles and biological effects are mainly described in this section.

2.4.2.1 Synthesis of Thioamides

2.4.2.1.1 Use of Lawesson's Reagent and Phosphorus Pentasulfide (P_4S_{10})

Lawesson's reagent [2,4-*bis*(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide] **1** was first synthesized in 1956 (Scheme 1).[11]



Lawesson's reagent **1**

Scheme 1

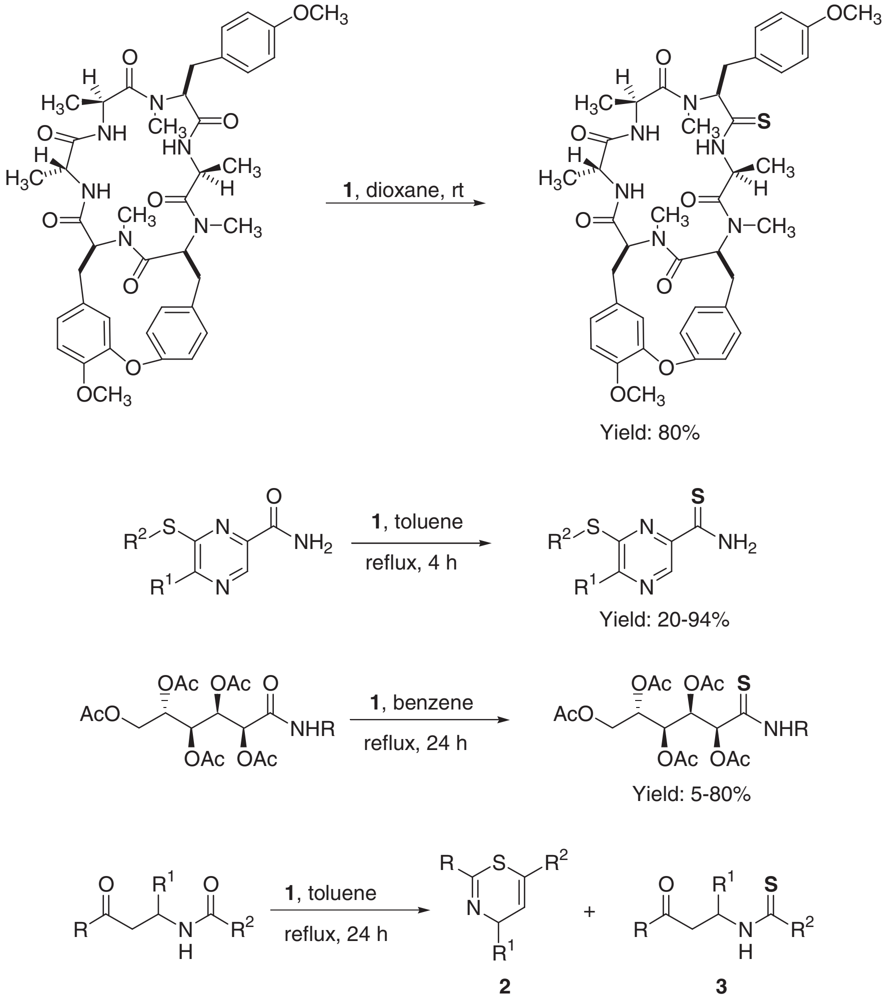
This reagent is commercially available and is presently used for many thionations of carbonyl-containing compounds. This is very versatile and efficient, thionating reagent for aromatic, aliphatic, unsaturated, and heterocyclic carboxamides. Lawesson's reagent can thionate carboxamides in the presence of many functional groups.[12–14] Treatment of 3-*N*-acylamino ketones with **1** yielded 4*H*-1,3-thiazine derivatives **2** and 3-*N*-thioacylamino ketones **3**, respectively. By changing the concentration of **1**, selective product has been obtained. The 4*H*-1,3-thiazines **2** have been produced predominantly when 1 equiv. of **1** was used, while with 0.5 equiv. of **1** the thioamides **3** have been mainly produced (Scheme 2).[15]

Synthesis and characterization of thiopeptides has been reported. Thioacylation is an alternative possible route to endothiopeptides. The following thioacylating reagents have been reported, such as thioesters, dithioesters, amino thioacids, thioacyl-benzimidazolines and nitrobenzotriazoles. Thionation of the amino acid amides with Lawesson's reagent proceeds smoothly at room temperature and provides the thioamides in high yields. These are converted to the thioacyl-*N*-phthalimides by treatment with phthaloyl dichloride at 0 °C. The thioacyl-*N*-phthalimides reacts with a selection of amino acid amides including dipeptide under mild conditions (Scheme 3).[16–18]

Direct thionation of amino acid derivatives has been achieved using P_4S_{10}. Direct thionation of anilide has been achieved with a mixture of P_4S_{10} and anhydrous Na_2CO_3 in THF.[19] Selective thionation of amide has been achieved using P_4S_{10} in THF under ultrasound irradiation. By-product is absent from the phosphorus pentasulfide thionation. Thionation of the amide with Lawesson's reagent is less selective (Scheme 4).[20]

2.4.2.1.2 Use of Elemental Sulfur

Thiomorpholides have been obtained by the reaction of nitriles or ketones and elemental sulfur with morpholine under microwave irradiation (Scheme 5).[21,22]



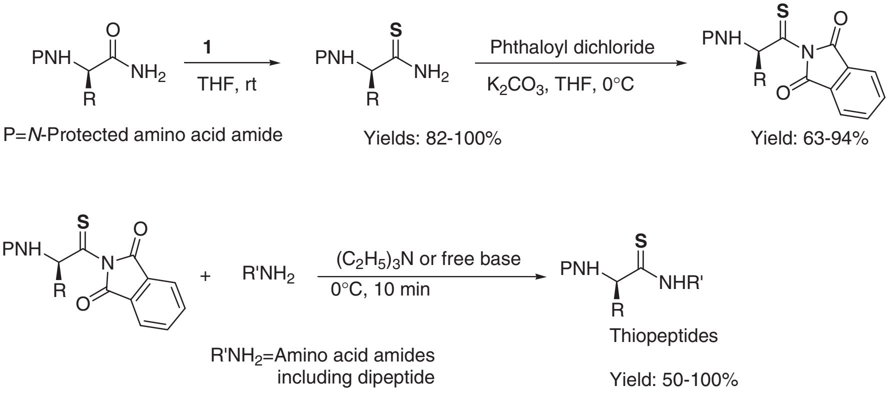
Scheme 2

The three component condensations of aldehydes, amines and elemental sulfur using 1-methyl-2-pyrrolidone as solvent employing microwave flash heating 100–180 °C for 2–20 min give the corresponding primary, secondary and tertiary thioamides (Scheme 6).[23]

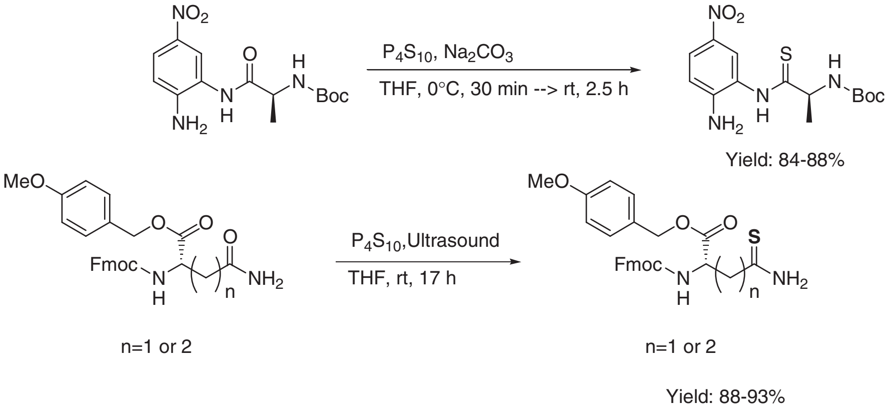
2.4.2.1.3 Use of Isothiocyanates

Reactions of isothiocyanate with nucleophiles give desired thioamides (Scheme 7).

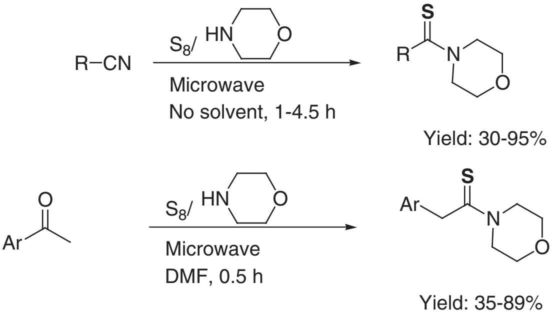
Addition of Grignard reagent to isothiocyanates provides secondary thioamides.[24]



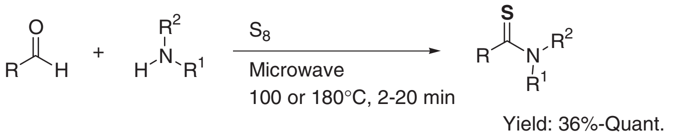
Scheme 3



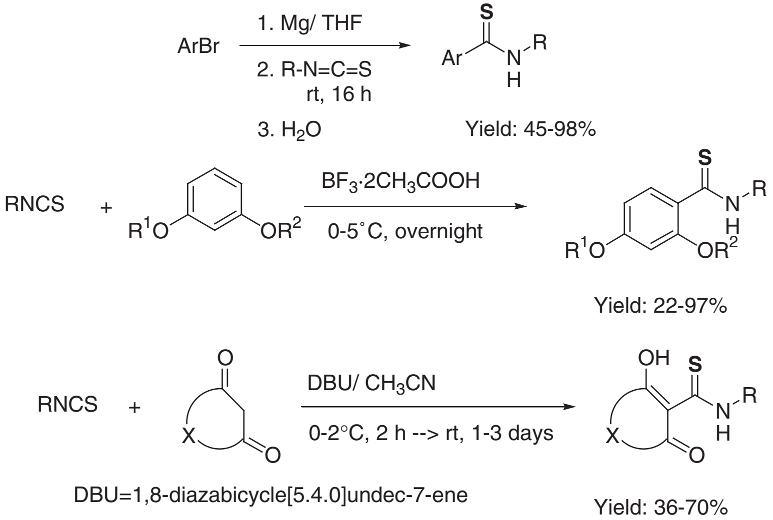
Scheme 4



Scheme 5



Scheme 6



Scheme 7

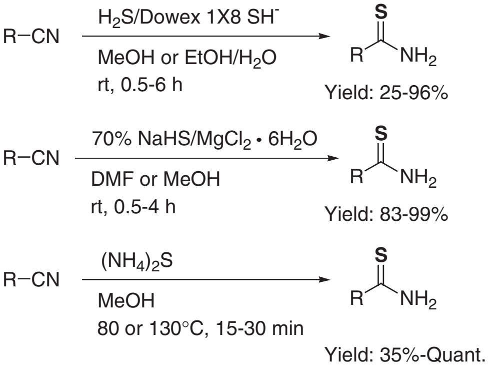
Reaction of isothiocyanates with resorcinol derivatives in the presence of boron trifluoride-acetic acid complex for overnight at 0–5 °C affords the corresponding thioamides.[25]

N-Allylthioamides have been prepared by the reaction of allyl isothiocyanate with 1,3-diketones in acetonitrile solution in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[26]

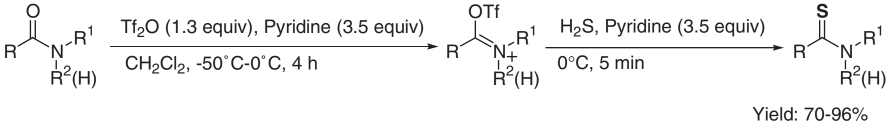
2.4.2.1.4 Conversion of Nitrile to Primary Thioamides

Conversion of nitrile using thionating reagent gives the corresponding primary thioamides (Scheme 8).

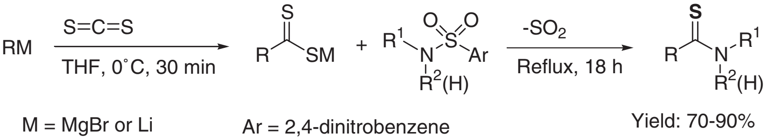
Treatment of nitriles with gaseous hydrogen sulfide in the presence of anion exchange resin (Dowex 1X8, SH^- from) at room temperature affords the corresponding primary thioamides.[27] Treatment of nitriles with 70% sodium hydrosulfide hydrate and magnesium chloride hexahydrate in DMF or methanol affords primary thioamides in high yields.[28] Primary thioamides have been



Scheme 8



Scheme 9



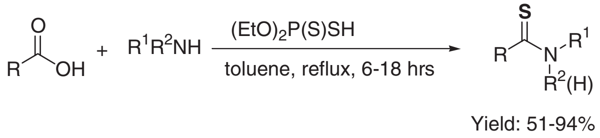
Scheme 10

obtained from the corresponding nitrile by treatment with ammonium sulfide in methanol.[29]

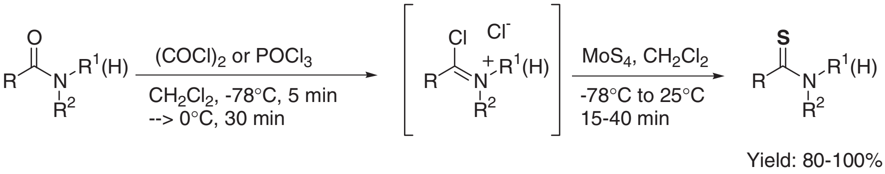
2.4.2.1.5 *Miscellaneous Thioamide Synthesis*

Imino- and iminiumtriflates could be generated from secondary or tertiary amides with trifluoromethanesulfonic anhydrate in the presence of pyridine at low temperatures. Subsequent treatment with hydrogen sulfide immediately gives rise to the corresponding secondary or tertiary thioamides at low temperature. This reaction affords both aliphatic as well as aromatic thioamides (Scheme 9).[30]

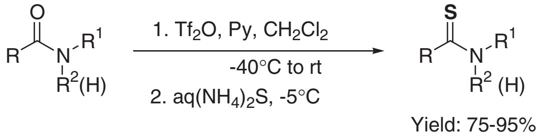
Dithioacids have been generated from carbon disulfide with Grignard reagents or alkyl lithium at 0 °C. Subsequent treatment with sulfonamide *in situ* gives the corresponding both aliphatic as well as aromatic thioamides in 70–90% yields (Scheme 10).[31]



Scheme 11



Scheme 12



Scheme 13

Carboxylic acid, amine and *O*,*O*-diethyl dithiophosphoric acid (3 equiv.) have been refluxed in toluene. This one-pot reaction yields the corresponding secondary or tertiary thioamides (Scheme 11).[32]

Chlorination of amide or lactam using oxalyl chloride gives the chloroiminium salts *in situ*. They react with tetrathiomolybdate to afford the corresponding thioamides and thiolactams in short-time and at low temperature in high yields. This method affords high yields of secondary or tertiary thioamides; on the other hand it gives low yield of primary thioamide (17% yield) (Scheme 12).[33]

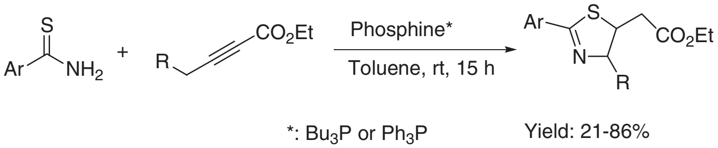
Activated amides have been generated by using trifluoromethanesulfonic anhydride in the presence of pyridine and been thionated with 20 wt% aqueous solution of ammonium sulfide to afford the desired secondary or tertiary thioamides in high yields (Scheme 13).[34]

2.4.2.2 Heterocycles Using Thioamides

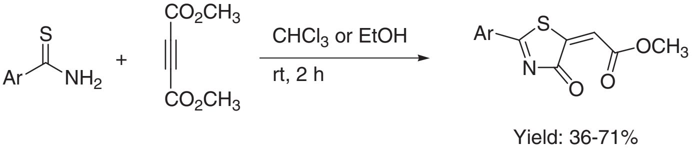
The annulation reaction of thioamides with 2-alkynoates and 2,3-dienoates under the catalysis of phosphine provides 4,5-dihydro-1,3-thiazoles, particularly those with 2-aryl substituents (Scheme 14).[35]

Reaction of arylthioamides with dimethyl acetylene dicarboxylate (DMAD) yields 2-aryl-1,3-thiazolin-4-ones at room temperature in moderate yields (Scheme 15).[36]

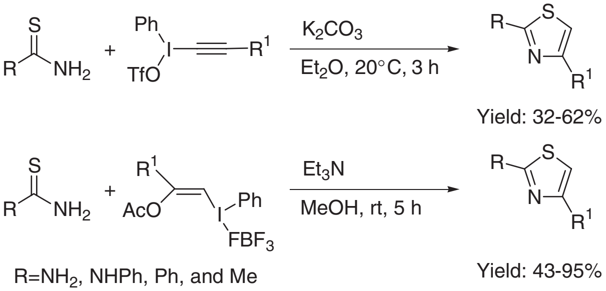
Cyclocondensation of thioamides and alkynyl(aryl)iodonium reagents affords 1,3-thiazoles in the presence of solid K_2CO_3.[37] Reaction of



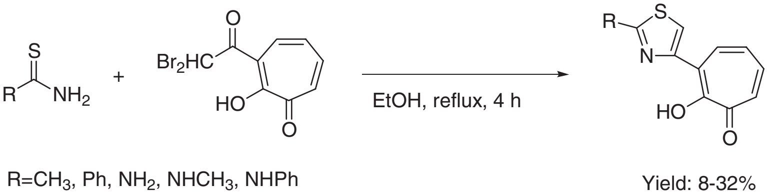
Scheme 14



Scheme 15



Scheme 16

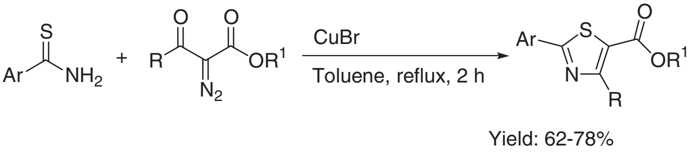


Scheme 17

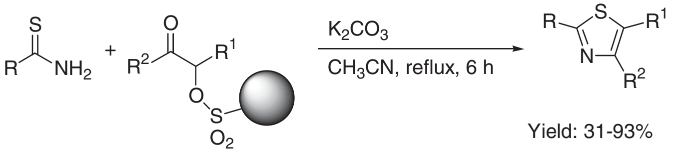
α-λ^3-iodanylketones (generated *in situ* from (*Z*)-(β-acetoxyvinyl)-(phenyl)-λ^3-iodanes) with thioamides or thioureas affords 2,4-disubstituted-1,3-thiazoles in the presence of triethylamine (Scheme 16).[38]

Reaction of dibromoacetyl derivatives with thioamides or thioureas affords the corresponding 1,3-thiazoles under reflux conditions (Scheme 17).[39]

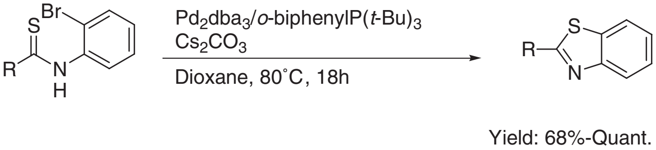
The above transformation takes place *via* the catalytic effect of copper (I), which generated the corresponding carbenoid from α-diazo-β-keto esters. These Cu-carbenoides react with the thiocarbonyl group of thioamides, after cyclocondensation to afford 2-aryl-1,3-thiazole-5-carboxylates (Scheme 18).[40]



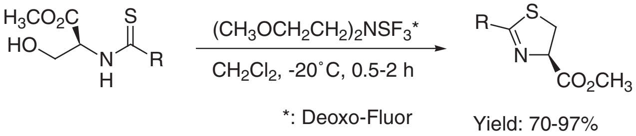
Scheme 18



Scheme 19



Scheme 20



Scheme 21

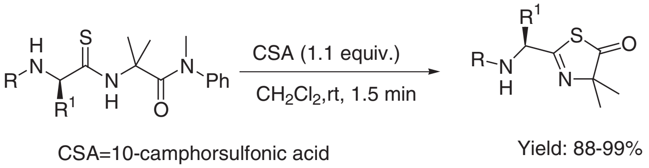
Treatment of polymer-supported α-sulfonyloxy ketones with thioamides in the presence of potassium carbonate affords 1,3-thiazoles (Scheme 19).[41]

2-Alkylbenzothiazole derivatives have been obtained by palladium-catalysed intramolecular cyclization of *N*-(*o*-bromophenyl)thioamides (Scheme 20).[42]

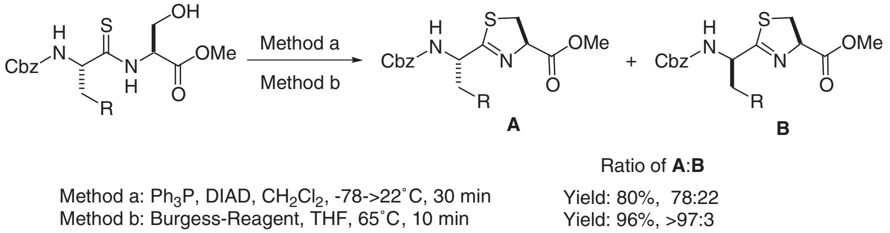
β-Hydroxythioamide cyclodehydration reaction has been carried out using Deoxo–Fluor reagent, [*bis*(2-methoxyethyl)amino]sulfur trifluoride, to afford 4,5-dihydro-1,3-thiazoles (Scheme 21).[43]

The endothiopeptide amides have been converted into the corresponding 4*H*-1,3-thiazol-5-ones or 4*H*-1,3-thiazol-5-imines in the presence of (±)- 10-camphorsulfonic acid (CSA) (Scheme 22).[44–46]

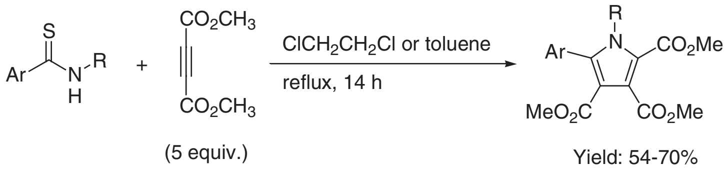
Cyclodehydration of β-hydroxythioamides under Mitsunobu conditions (Method a) has provided peptide thiazoline in 80% yield with 78:22 ratio of **A:B** and 56% de. Treatment of β-hydroxythioamides with $MeO_2CNSO_2NEt_3$,



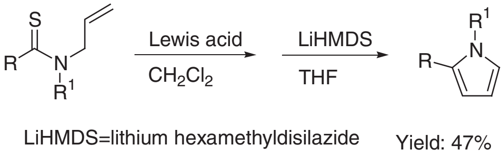
Scheme 22



Scheme 23



Scheme 24



Scheme 25

the Burgess reagent, has led to the formation of thiazoline **A** in 96% yield with less than 3% epimerization at the C(2) *exo* methane position (Scheme 23).[47–50]

The reaction of thioamides with DMAD affords the pyrrole derivatives (Scheme 24).[51]

Tertiary *N*-allylthioamides have been converted into thioamidium salts by the formation of complexes with Lewis acid. Further treatment with lithium hexamethyldisilazide (LiHMDS) affords the corresponding 1,2-disubstituted pyrroles (Scheme 25).[52]

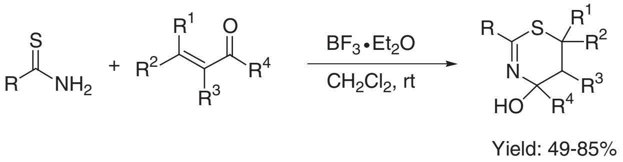
1,3-Thiazine derivatives have been obtained by reactions of primary thioamides with α,β-unsaturated ketones (Scheme 26).[53]

3,4-Dihydro-2*H*-1,3,5-thiadiazines substituted at the 2 and 5 positions have been synthesized by treatment of *N*-substituted *N*,*N*-*bis*(1*H*-1,2,3-benzotriazol-1-ylmethyl)amines with thioamides and zinc bromide in dry CH_2Cl_2 (Scheme 27).[54]

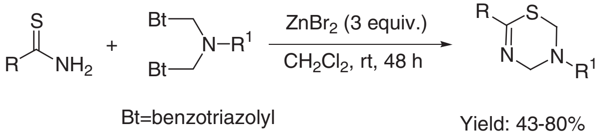
2,4-Diaryl-5,6-dihydro-4*H*-1,3-thiazines have been obtained by iodocyclization of *N*-homoallyl thioamides (Scheme 28).[55]

β-Keto thioamides react with α,β-unsaturated aldehydes to afford debenzoylated 6-hydroxypiperidine-2-thiones as major product and benzoylated 6-hydroxypiperidine-2-thiones as minor one (Scheme 29).[56]

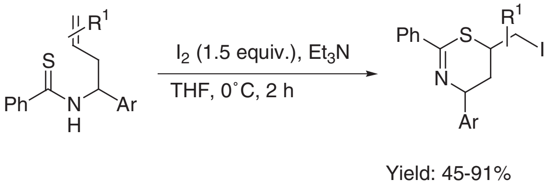
Acyl thioamides react with lithium diisopropylamide (LDA) to give β-thiolactams (Scheme 30).[57]



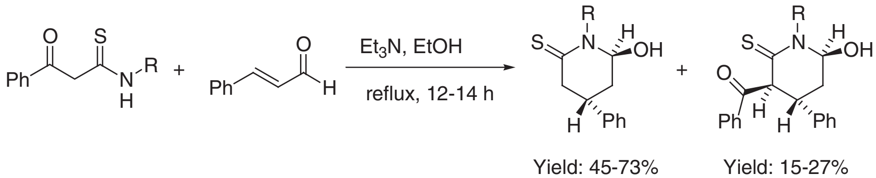
Scheme 26



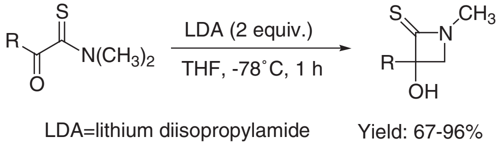
Scheme 27



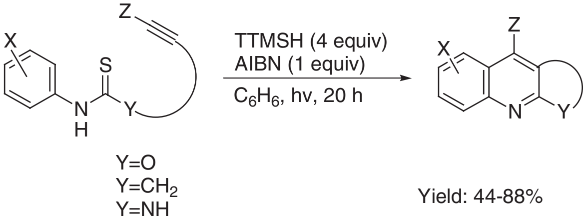
Scheme 28



Scheme 29



Scheme 30



Scheme 31

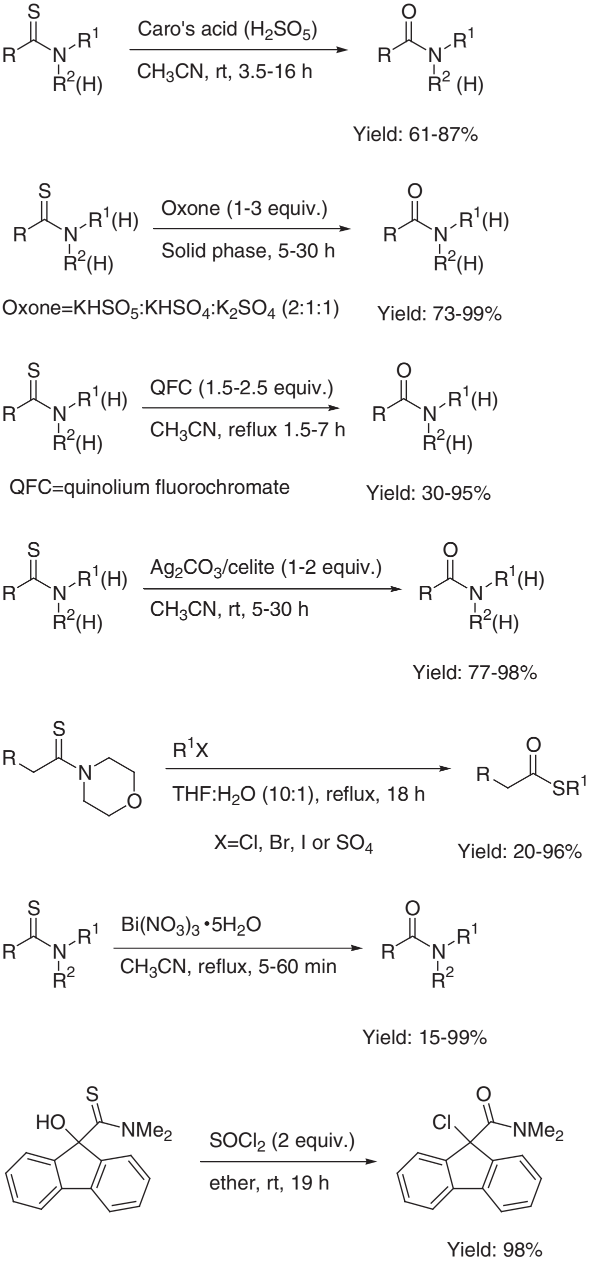
Tandem radical cyclizations of suitably substituted *N*-aryl thiocarbamates, thioamides and thioureas have been induced by exposure to 4 equiv. of *tris*(trimethylsilyl)silane (TTMSH: $(TMS)_3SiH$), 1 equiv. of 2,2′-azo-*bis*-isobutyronitrile (AIBN as a radical initiator) and UV light to provide furoquinolines, isofuroquinolines, cyclopentaquinolines, indoloquinolines and related ring systems (Scheme 31).[58]

2.4.2.3 Transformation of Thioamides

Conversion of thioamides by desulfurization into the corresponding amides has been reported (Scheme 32).

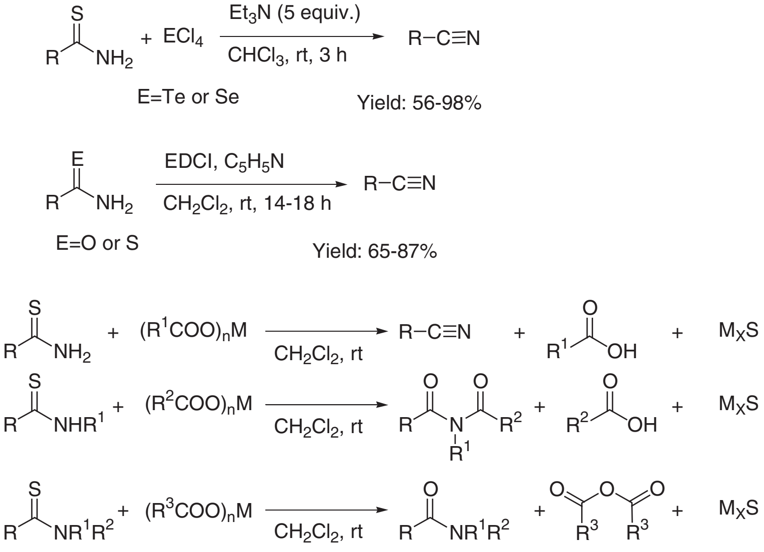
Thioamides have been converted into the corresponding amides by treatment with acids such as Caro's acid (H_2SO_5) supported on silica gel,[59] oxone,[60] quinolium fluorochromate (QFC)[61] and silver carbonate supported on celite.[62] Thioamides have been transformed into thioesters through the simple expedient of warming them in an aqueous THF solution containing an alkylating agent.[63] A variety of thioamides and thioureas have been transformed to their *oxo* derivatives with $Bi(NO_3)_3 \cdot 5H_2O$.[64] Benzylic α-hydroxythioamide has undergone an analogous transformation to the α-chloroamide derivative with 2 equiv. of thionyl chloride, and the intermediate α-chlorothioamide could be isolated only when 1 equiv. of thionyl chloride has been used.[65]

Thioamides have been transformed into the corresponding nitriles. Treatment of primary thioamides by tellurium tetrachloride or selenium tetrachloride in combination with triethylamine affords nitriles.[66] Treatment of primary amides and thioamides with 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) gives nitriles.[67] Reactions of thioamides with metal carboxylates in organic solvents enables the selective preparation of nitriles, imides or amides depending on the substitution pattern of the starting material (Scheme 33).[68]

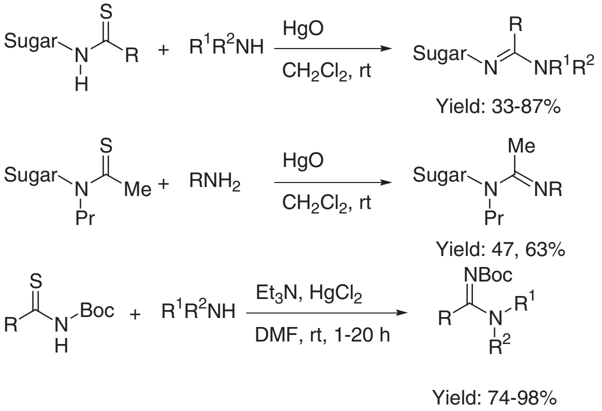


Scheme 32

Glycoamidines have been readily prepared by a mercury-promoted reaction of the corresponding thioamides with amines.[69] *N*-Boc protected amidines have been prepared from *N*-(Boc) thioamides by treatment with base and mercury(II) chloride (Scheme 34).[70]



Scheme 33

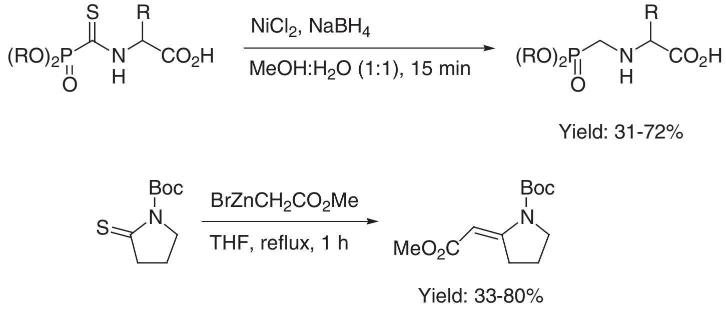


Scheme 34

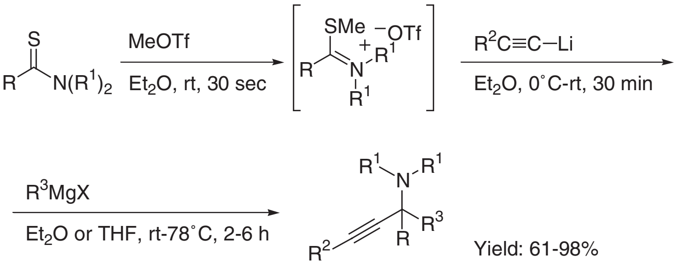
Desulfurization of phosphonylated thioamides has been achieved by nickel boride.[71–73]

Treatment of methyl bromozincacetate with *N*-(Boc)pyrrolidine-2-thione affords good yield of vinylogous carbamate (Scheme 35).[74]

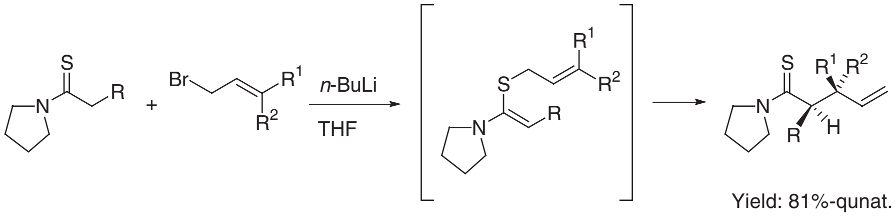
Reactions of thoiminium salts, generated *in situ* from thioamides and methyl triflate (MeOTf), with two different alkylmetals such as alkynyllithiums and alkylmagnesium bromides have been studied. The two different organometallic reagents have been nucleophilically introduced to the carbon atom of the thiocarbonyl group of thiamides to afford tertiary propargylamines in one-pot procedure (Scheme 36).[75]



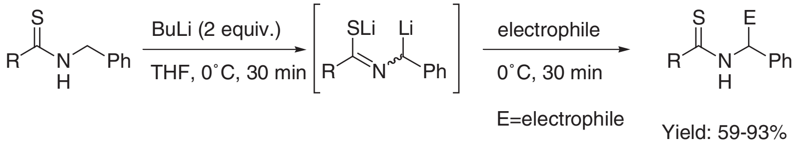
Scheme 35



Scheme 36



Scheme 37



Scheme 38

Diastereoselective asymmetric thio-Claisen rearrangement has been carried out by the reaction of thioamides with allyllic bromide (Scheme 37).[76]

Thioamide dianions (generated by the highly efficient reaction of *N*-benzyl thioamides with 2 equiv. of BuLi) take place alkylation, allylation and silylation selectively at the carbon atom adjacent to the nitrogen atom of the thioamide dianions (Scheme 38).[77]

2.4.2.4 Calculations

Conformation and stability of thiopeptides (formed by replacing the amide oxygen atom with a sp^2 sulfur atom) have been investigated by calculations. It has been confirmed that insertion of a thioamide linkage into a peptide structure is not conformationally neutral. It is predicted to be more rigid than peptide and produces substantial changes in peptide structure, primarily in the residues on the *C*-terminal side of the thioamide.[78–80]

Investigations of hydrogen bonding of several thioamides have been carried out by calculations and spectroscopy. Characterization, hydrolysis and cyclization of thioamides have been discussed by using the results of calculations and spectroscopy. Comparison of amides and thioamides has been investigated.[81–86] Rotation barriers for a series of amides and thioamides have been calculated.[87–93]

2.4.2.5 Biological Activities

Several reports are available on the biological activities of thioamide derivatives. The thioamide derivatives have shown significant activities, such as antituberculosis drug, anti-influenza virus activity, antitumor activity, anthelmintic activity, opioid receptor binding property, *etc.*[94–101]

2.4.3 Thioureas

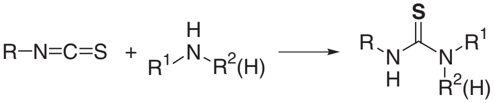
Thioureas are most commonly prepared from reaction of isothiocyanates with amines. Also there are some reports on reactions of anime or carbodiimides with several thionating reagents. *N*,*N*′-Disubstituted thioureas bearing double NH groups have been developed as sensors, and as catalysts because of their hydrogen bonding ability. *N*,*N*′-Disubstituted thiourea-linked sugar chains have been prepared by the reaction of isothiocyanate with amine.

2.4.3.1 Synthesis of Thioureas

The synthesis of thioureas has been accomplished in several manners by using isothiocyanate, carbon disulfide, hydrogen sulfide and KSCN (potassium thiocyanate).

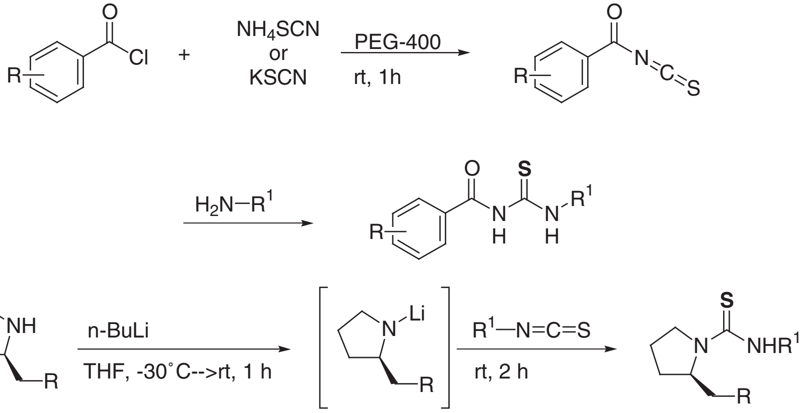
2.4.3.1.1 Reaction of Isothiocyanate with Amine

Reaction of isothiocyanate with amine gives the corresponding thioureas. Many reports are appeared.[102–111] The thiourea derivatives have been prepared by reactions of isothiocyanates with arylamines (Scheme 39) and reacted with some substrates to afford heterocyclic compounds, such as 2-amino-4*H*-benzothiazine, 1,3-thiazine, 1,3-thiazinone and 1,3-thiazolidin-4-one.[112–115]



Scheme 39

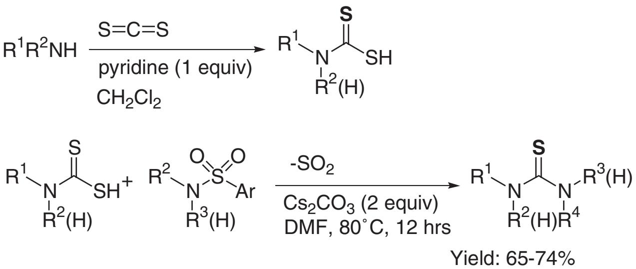
N-Aroyl-*N*′-substituted thiourea derivatives have been prepared from reaction of aroyl isothiocyanate with amines under solid–liquid phase transfer catalysis condition using polyethylene glycol-400 (PEG-400) as catalyst.[116–119] Reaction of isothiocyanates with lithiated chiral secondary amines has provided chiral thioureas (Scheme 40).[120]



Scheme 40

2.4.3.1.2 *Use of Carbon Disulfide*

Dithiocarbamates have been prepared by the reaction of carbon disulfide with primary or secondary amines. The addition of DMF, cesium carbonate and a sulfonamide to the crude dithiocarbamate, give di-, tri- and tetra-substituted thioureas in 65–76% yields (Scheme 41).[121]



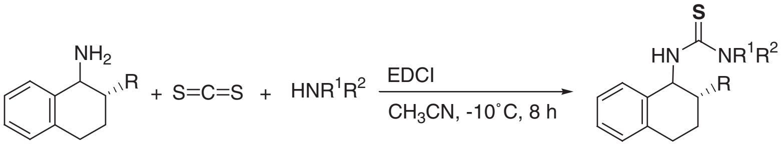
Scheme 41

1-Amino-1,2,3,4-tetrahydronaphthalene has been treated with a mixture of *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide (EDCI) and carbon disulfide in acetonitrile followed by the addition of secondary amines also affords thioureas (Scheme 42).[122]

Reaction of carbon disulfide with primary amines, using MCM-41-TBD (mesoporous MCM-41 silica, TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene) as catalyst, has given symmetrical thioureas under heterogeneous conditions. The MCM-41-TBD could be reused as a catalyst (Scheme 43).[123]

Reaction of carbon disulfide with primary amine hydrochloride in the presence of dimethyl aminopyridine (DMAP) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) affords symmetrical thioureas (Scheme 44).[124,125]

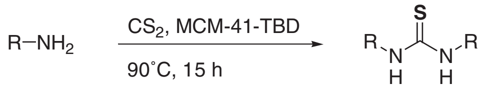
Thioureas have been also prepared in high yields by solvent-free and microwave irradiation (Scheme 45).[126]



EDCI = *N*-Ethyl-*N*-(3-dimethylaminopropyl)carbodiimide

Yield: 48-90%

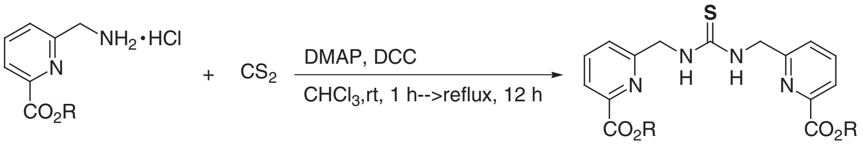
Scheme 42



MCM-41=mesoporous MCM-41 silica
TBD=1,5,7-triazabicyclo[4.4.0]dec-5-ene

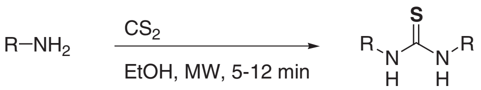
Yield: 57-91%

Scheme 43



Yield: 64%

Scheme 44



MW: Microwave irradiation

Yield: 81-97%

Scheme 45

2.4.3.1.3 Use of Hydrogen Sulfide (H_2S)

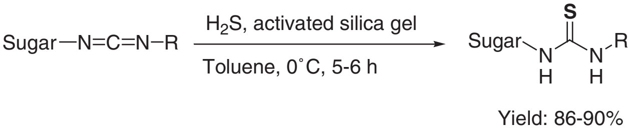
Treatment of sugar-derived carbodiimides with dry hydrogen sulfide (H_2S) in the presence of activated silica gel affords the sugar-derived thioureas (Scheme 46).[127]

Reactions of (benzotriazol-1-yl)carboximidamides and acyl- or arylaminocarbonyl(benzotriazol-1-yl)carboximidamides with hydrogen sulfide give the corresponding thioureas and *N*-acylthioureas or *N*-carbamoylthioureas, respectively (Scheme 47).[128]

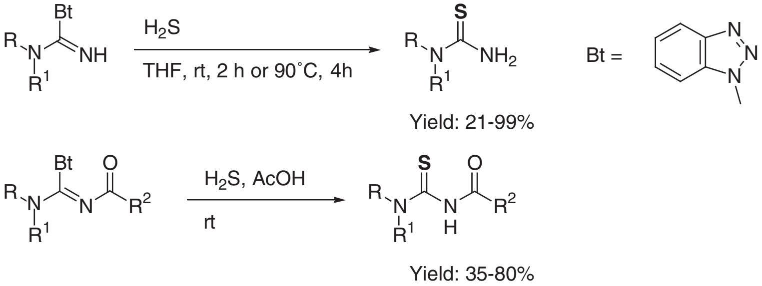
Reactions of thiocarbamoylbenzotriazole with amines in the presence of triethylamine affords the corresponding di- and trisubstituted thioureas (Scheme 48).[129]

2.4.3.1.4 Use of KSCN (Potassium Thiocyanate)

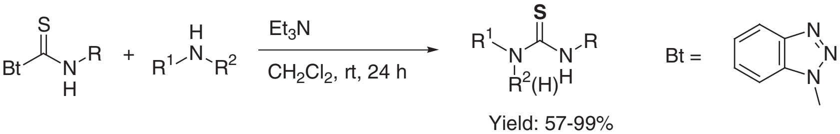
Allylic bromides reacted with $KSCN/SiO_2$ and $BnNH_3OAc/Al_2O_3$ in one-pot gives the corresponding thioureas. Reactions of crotyl bromide with a series of alkylammonium acetates, with the exception of *tert*-butylammonium acetate, results in the corresponding thioureas (Scheme 49).[130]



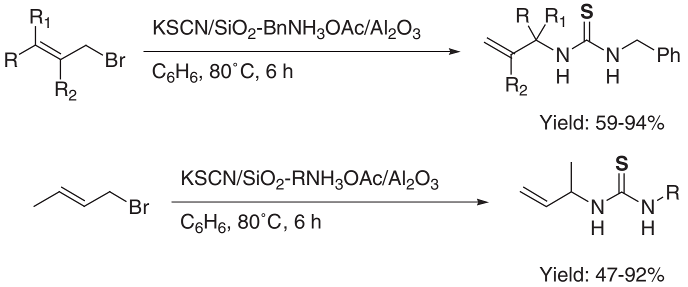
Scheme 46



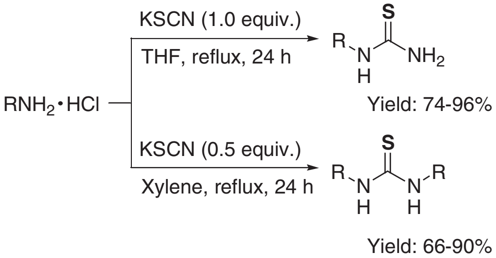
Scheme 47



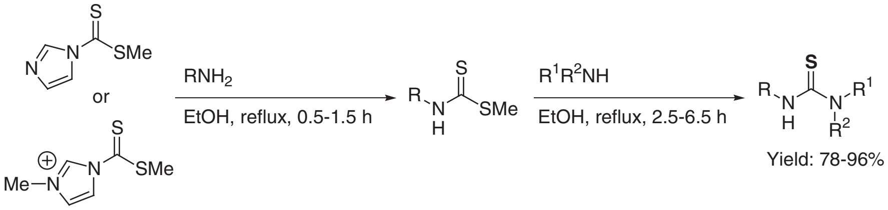
Scheme 48



Scheme 49



Scheme 50



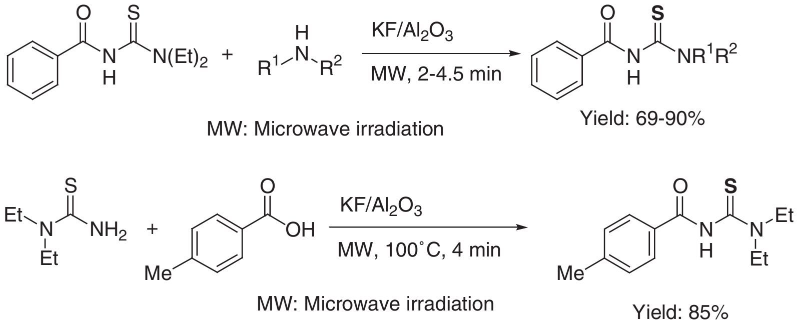
Scheme 51

Condensations of amine hydrohalides with potassium thiocyanate (KSCN) provide both the primary thioureas and symmetrical *N*,*N*′-disubstituted thioureas. Selectivity in the product was achieved by changing the concentration of KSCN as shown in the diagram (Scheme 50).[131]

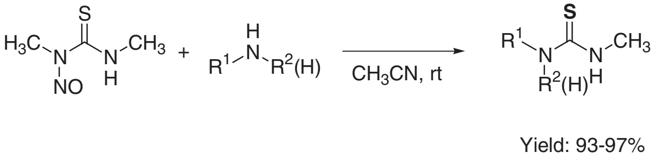
1-(Methyldithiocarbonyl)imidazole and its *N*-methyl quaternary salt have been shown to be efficient methyldithiocarbonyl and thiocarbonyl transfer reagents for the synthesis of dithiocarbamates, symmetrical and unsymmetrical mono-, di- and tri-substituted thioureas (Scheme 51).[132]

2.4.3.1.5 Transamidation

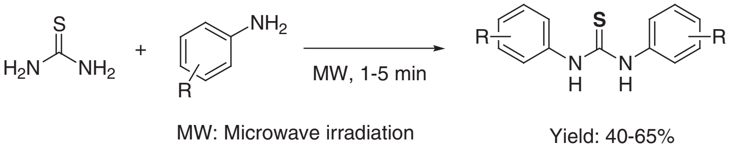
N-Benzoyl-*N*′,*N*′-dialkylthioureas have been prepared under microwave irradiation using potassium fluoride impregnated on alumina as support. Reaction



Scheme 52



Scheme 53



Scheme 54

with amine led to transamidation, whereas reaction with carboxylic acid gave acyl products (Scheme 52).[133,134]

Reaction of nitrosothioureas with alkylamines gives *N*-mono- or di-alkyl substituted thioureas (Scheme 53).[135]

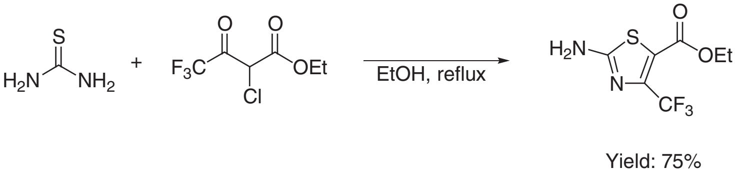
Symmetrically disubstituted thioureas have been synthesized by heating thiourea with aromatic amines or phenylhydrazine under environmentally benign conditions without solvent in a conventional microwave oven (Scheme 54).[136]

2.4.3.2 Heterocycles Using Thioureas

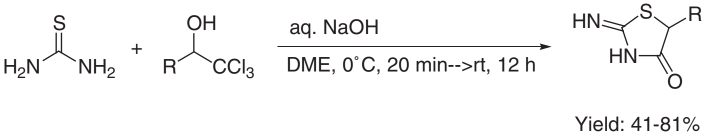
Condensation of thiourea and ethyl 2-chlorotrifluoroacetoacetate provides 2-amino-1,3-thiazole in 75% yield (Scheme 55).[137]

2-Imino-thiazolidin-4-ones have been synthesized from alkyl trichloromethylcarbinols and thiourea in the presence of base (Scheme 56).[138]

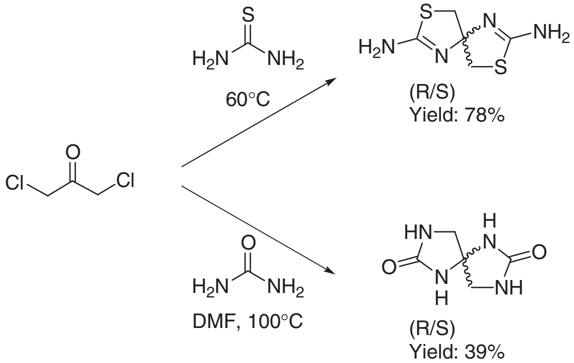
Condensation reaction of thiourea with 1,3-dichloroacetone provides 2,7-diamino-1,6-dithio-3,8-diazaspiro[4.4]nonane-2,7-diene. The use of urea



Scheme 55



Scheme 56



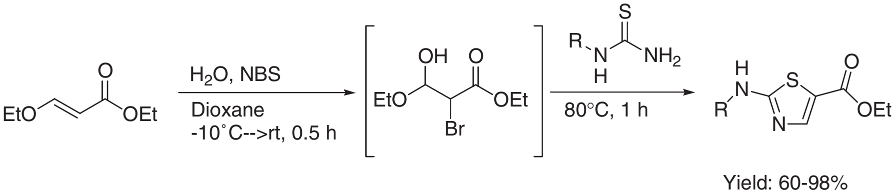
Scheme 57

instead of thiourea gives 1,3,6,8-tetraazaspiro[4.4]nonane-2,7-dione. This indicates the strong tendency of sulfur to avoid carbon–sulfur double bond in comparison to oxygen thus leading to a much higher nucleophilicity of the sulfur (Scheme 57).[139,140]

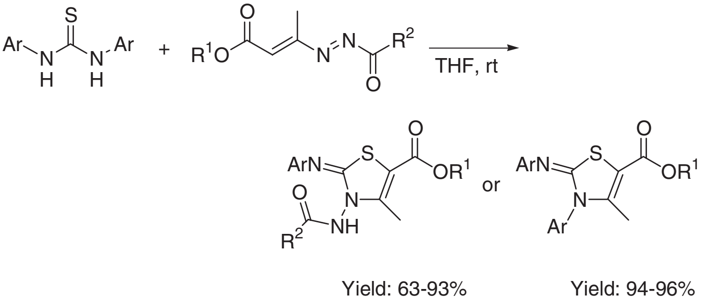
An intermediate α-bromo-α-formylacetate hemiacetal has been prepared by reaction of ethyl β-ethoxyacrylate with *N*-bromosuccinimide (NBS). Cyclization of the *in situ* formed hemiacetal with thioureas affords 2-amino-1,3-thiazole-5-carboxylates (Scheme 58).[141]

1,2-Diaza-1,3-butadienes reacts with *N*,*N*′-diarylthioureas to give 2-(arylamino)-2,3-dihydro-1,3-thiazole derivatives (Scheme 59).[142]

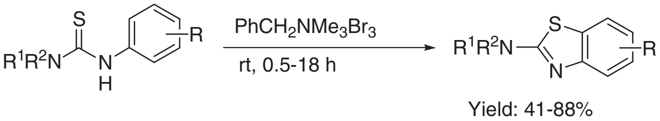
A direct procedure from isothiocyanates and amines using tetrabutylammonium thiocyanate (Bu_4NSCN) and $PhCH_2NMe_3Br_3$ affords functionalized 2-aminobenzo-1,3-thiazoles (Scheme 60).[143]



Scheme 58



Scheme 59



Scheme 60

N,N′-*Bis*(dimethylaminomethylene)thiourea (prepared by double condensation of *N,N*-dimethylformamide dimethyl acetal with thiourea) has been reacted with α-haloketones or acrylic dienophiles to give thiazolic and thiazinic diazadienes, respectively. These undergo cyclization reactions to yield imidazo[2,1-*b*][1,3] thiazoles, 5*H*-1,3-thiazolo[3,2-*a*]pyrimidines, 7*H*-imidazo[2,1-*b*][1,3]thiazines and 2*H*,6*H*-pyrimido[2,1-*b*][1,3]thiazines without any regioisomeric ambiguity (Scheme 61).[144,145]

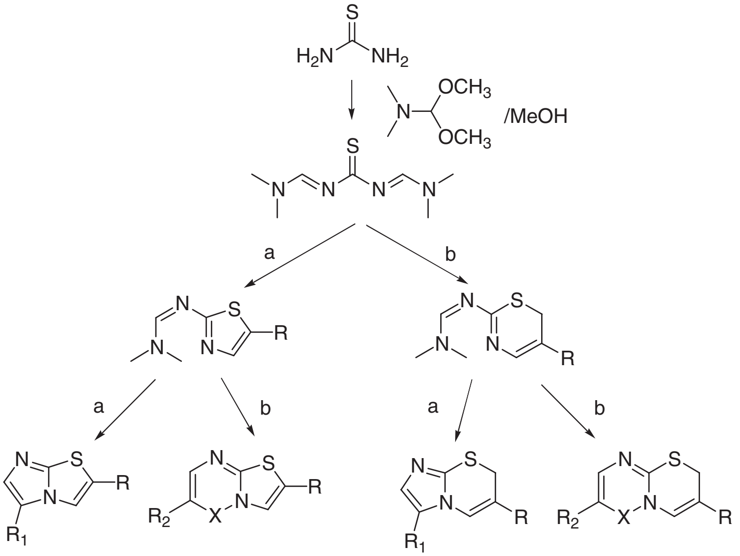
2-Phenylamino-1,3-thiazolines have been synthesized from *N*-(2-hydroxyethyl)-*N′*-alkylthioureas by a one-pot intramolecular Mitsunobu reaction.

Whereas the use of 1,3-dicyclohexylcarbodiimide affords 1,3-oxazolines from the *N*-(2-hydroxyethyl)thioureas (Scheme 62).[146–148]

Intramolecular oxidation of *N*-alkyl-*N′*-heteroarylthioureas provides a synthetic pathway to fused heterocyclic compounds (Scheme 63).[149]

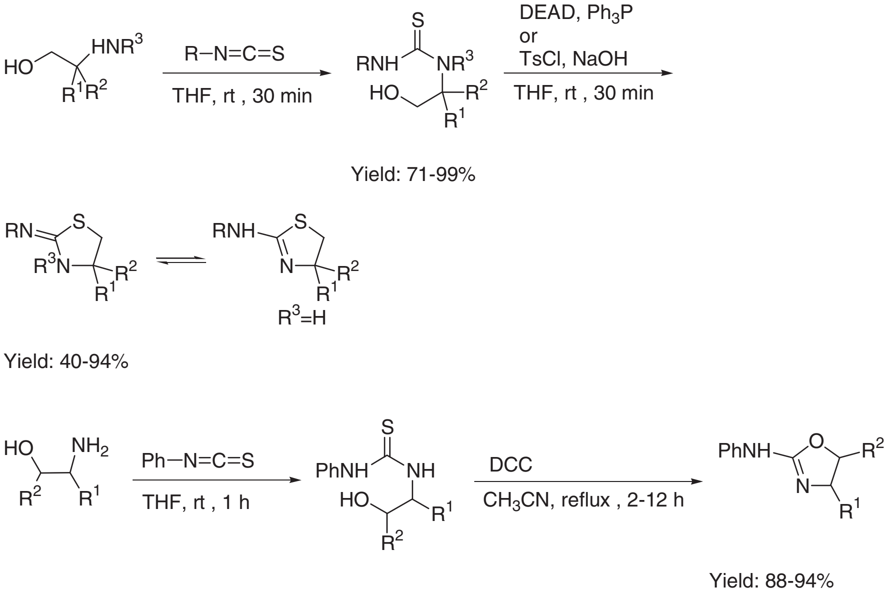
Condensation reactions of *N*-substituted thioureas in dimethyl sulfoxide or methanol in the presence of DMSO-H^+-X^- produce 1,2,4-thiadiazole derivatives (Scheme 64).[150,151]

1,2,4-thiadiazole derivatives have been obtained by the reaction of [*bis*(acyloxy)iodo]arenes with monosubstituted thioureas (Scheme 65).[152]

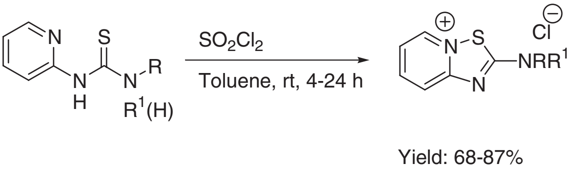


a=α-bromoketones, b=ketones (X=CO) or acrylic dienophiles (X=CH_2)

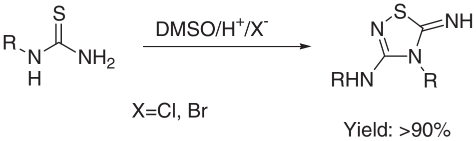
Scheme 61



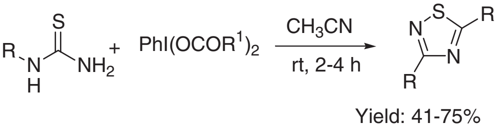
Scheme 62



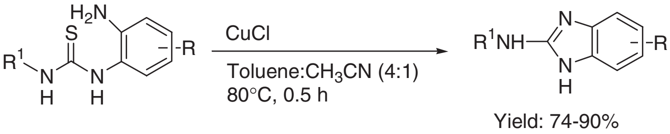
Scheme 63



Scheme 64



Scheme 65



Scheme 66

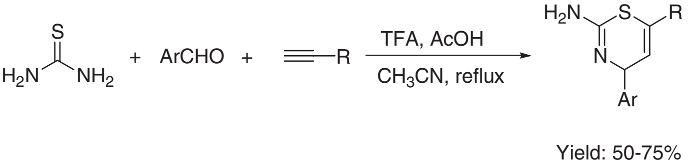
N-(2-Aminoaryl)thiourea undergoes a CuCl-promoted intramolecular cyclization to give the corresponding 2-(*N*-substituted amino)benzimidazoles in good to excellent isolated yields (Scheme 66).[153–155]

2-Amino-4*H*-1,3-thiazines have been obtained from a three-component one-pot condensation using alkynes, thiourea and aryl aldehydes (Scheme 67).[156]

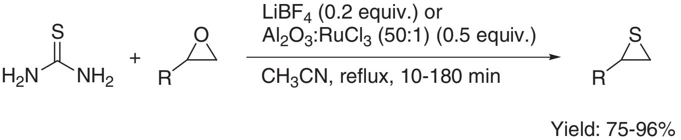
Oxiranes have been converted to the corresponding thiiranes by thiourea in the presence of catalytic amount of Ru(III) or LiBF$_4$ (Scheme 68).[157,158]

2.4.3.3 Transformation of Thioureas

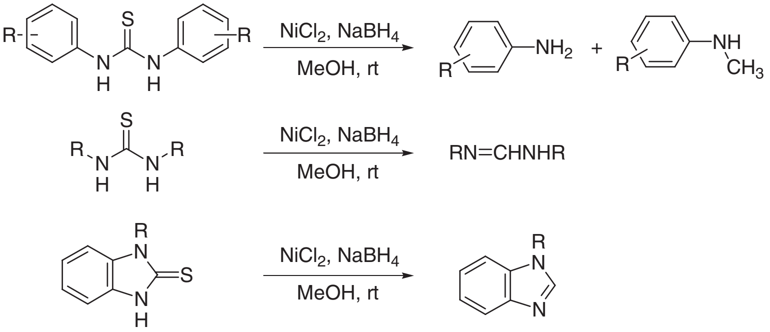
Nickel chloride promoted desulfurization and reductive cleavage of *N*,*N*′-diarylthioureas gives corresponding anilines and *N*-methylanilines (Scheme 69). While *N*,*N*′-dialkylthioureas undergo desulfurization to give formamidines, and benzimidazoline-2-thiones underwent desulfurization to benzimidazoles (Scheme 69).[159]



Scheme 67



Scheme 68



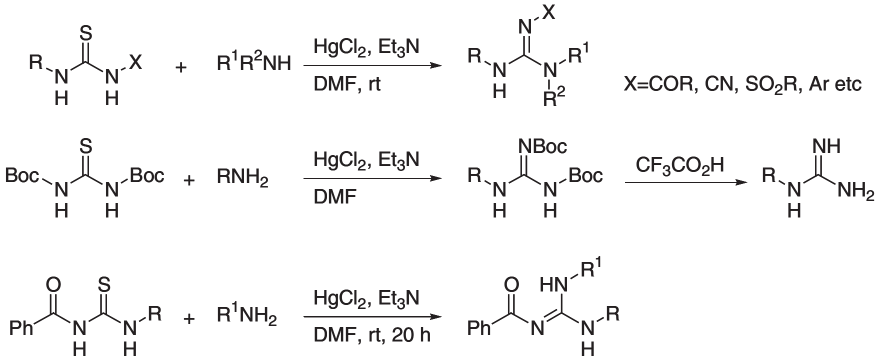
Scheme 69

Preparation of guanidine from thioureas has been carried out. There are many ways to synthesize guanidines. Converting thioures and isothiourea moieties into guanidine is one of the most popular methods.

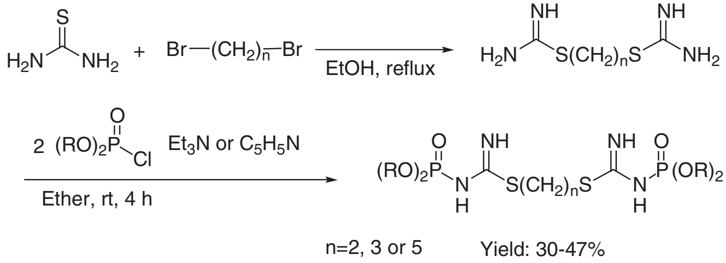
Thioureas are effectively converted into guanidine by $HgCl_2$ protocol, the thiourea is activated by a strong electron-withdrawing group and the most general approach to achieve this is by the use of *N*,*N′*-*bis*-Boc-protected thioureas. As an alternative method, the benzoyl group is used as an activating group for thioureas in the $HgCl_2$-guanylation reaction. *N*-Benzoyl-thioureas containing electronically neutral and even electron-withdrawing or electron-releasing substituents have been converted into guanidines (Scheme 70).[160–163]

Symmetric dialkylphosphoryl-*S*-alkanediyldiisothioureas have been prepared by reaction of diisothiourea derivatives with dialkyl chlorophosphate (Scheme 71).[164]

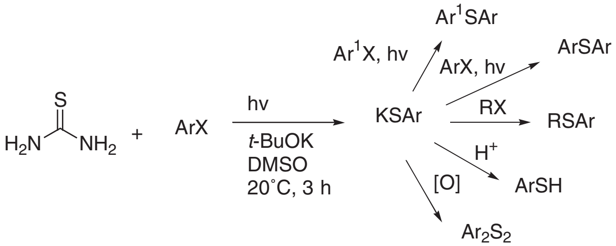
The photoinduced reactions of aryl halides with the thiourea anion afford arene thiolate ions in DMSO. These species can be used without isolation for



Scheme 70



Scheme 71



Scheme 72

subsequent aliphatic nucleophilic substitution, $S_{RN}1$ (substitution, radical-nucleophilic, unimolecular)[165] reaction, oxidation or protonation, yield aryl alkyl sulfides, diaryl sulfides, diaryl disulfides and aryl thiols in one-pot. (Scheme 72).[166]

2.4.3.4 Application as Sensor

Thioureas-binding site can be introduced to molecules like anthraquinone and is for use in various kinds of anion or fluoride sensors. Thiourea-based sensor are generally designed to recognize anion through an intermolecular hydrogen bonding.[167–171]

2.4.3.5 Application as Ligand

Application of thioureas to ligand and catalysis has been investigated in detail as significant use of thiourea in synthetic chemistry.

Thioureas have been used in palladium-catalysed reactions as ligands. Thiourea-based ligands have been quite useful for the palladium-catalysed *bis*(methoxycarbonylation) of terminal alkynes. A novel thiourea-based C_2-symmetric ligand has been used for an application in the palladium-catalysed Heck and Suzuki coupling reactions of arenediazonium salts. The corresponding arenediazonium salts have been easily generated in one step from anilines. Regiospecific carbonylate annulation mediated by palladium-thiourea complex generated benzo[*b*]furan-3-carboxylates or diversified flavones (Scheme 73).[172–176]

Bifunctional thiourea-catalysed enantioselective Michael reaction has been achieved. The thiourea moiety and an amino group of the catalyst activated a nitroolefin and a 1,3-dicarbonyl compound, respectively afford the Michael adduct with high enantioselectivity.[177,178] Thioureas work as one of the most effective and general enantioselective nitro-Mannich reaction and carbonyl cyanation catalyst.[179,180]

Chiral *bis*-thiourea-type catalysts effectively provide the Baylis–Hillman reaction with cyclohexenone and aldehydes.[181] In several reactions, thiourea derivatives have been used as significant and specific catalyst because of their intermolecular hydrogen bonding ability (Scheme 74).[182–186]

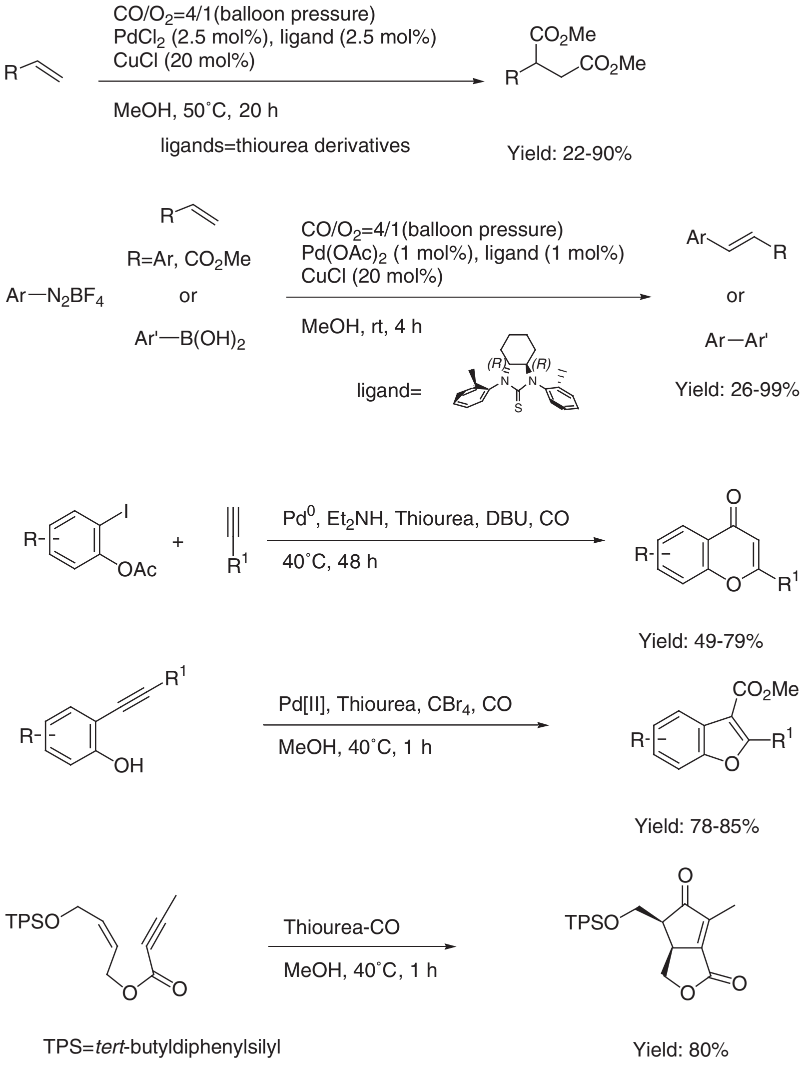
2.4.3.6 Glycosyl Thioureas

Many reports are available in the literature regarding preparation of thioureas through reactions of glycosyl isothiocyanates with amines.[187] By using the reactions of glycosyl isothiocyanates with amines, glycosyl thioures,[188] (1–6),[189] (1–1)-thiourea-linked oligosaccharides,[190] thiourea-bridged glycodendrimers,[191,192] multiple thiourea binding receptors have been prepared (Scheme 75).[193–197]

The preparation and reactions of *N*-thiocarbonyl carbohydrate derivatives, such as sugar isothiocyanates, thioamides, thioureas, thiocarbamates and their conjugates have been the subject of valuable comprehensive as well as specialized accounts, which should be consulted for details.[198]

2.4.3.7 Biological Activities

Thiourea compounds have been observed to inhibit human immunodeficiency virus (HIV) reverse transcriptase, a viral enzyme that is responsible for the reverse transcription of the retroviral RNA to proviral DNA. Phenethylthiazoylthiourea (PETT) compounds were discovered as potent inhibitors of HIV type 1 and display certain structure–activity relationships among various substituents in their structure.[199–207] Furthermore, thiourea derivatives have been found to be potent and selective viral inhibitors, antifungal and antibacterial compounds.[208–215]

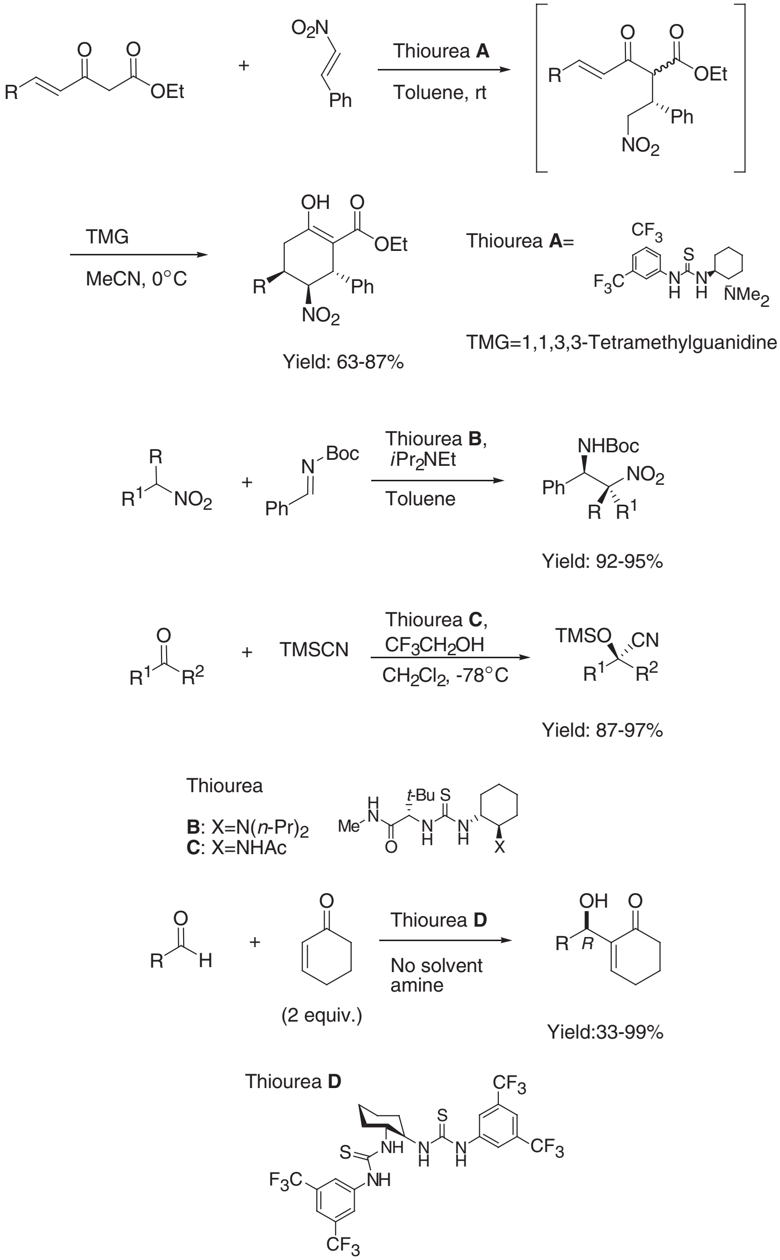


Scheme 73

The structure–activity relationships for thiourea derivatives have been investigated as vanilloid receptor antagonist,[216–220] and mast cell leukotriene release, *etc.*[221–224]

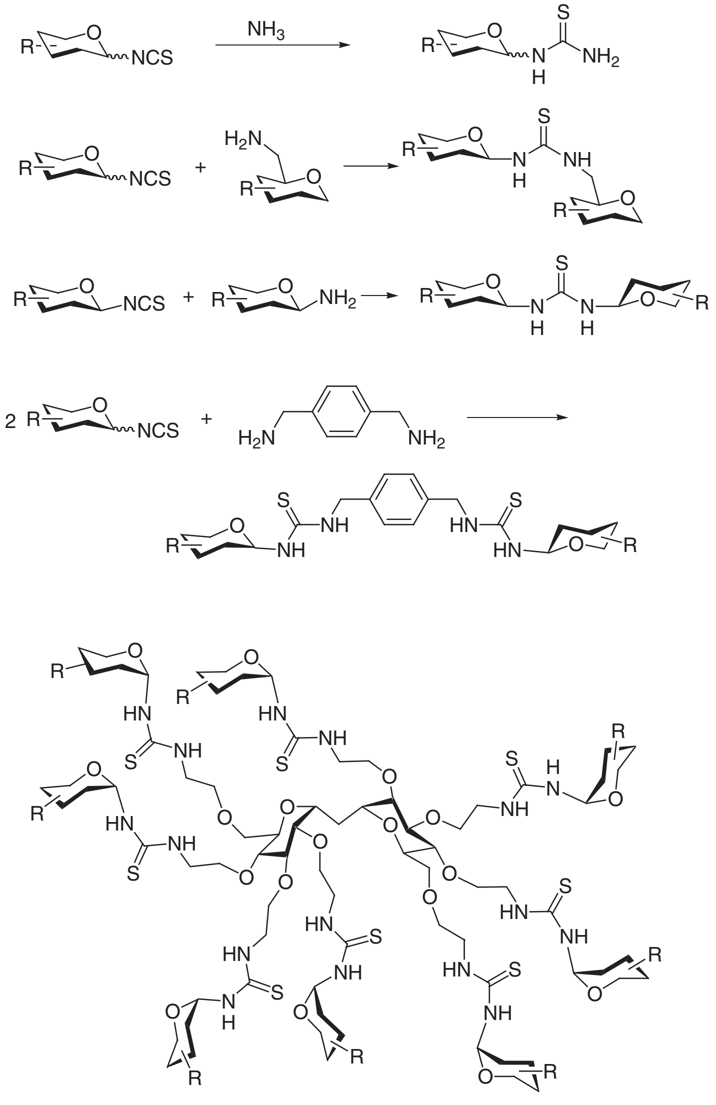
2.4.4 Cyclic Chalcogenoureas

Studies of cyclic chalcogenoureas, such as 2-thioimidazoles, 2-selenoimidazoles, thionucleosides and selenonucleosides have been reported,



Thiourea A
Toluene, rt
TMG
MeCN, 0°C
Yield: 63-87%
Thiourea A=
TMG=1,1,3,3-Tetramethylguanidine
Thiourea B, iPr2NEt
Toluene
Yield: 92-95%
Thiourea C, CF3CH2OH
CH2Cl2, -78°C
Yield: 87-97%
Thiourea
B: X=N(n-Pr)2
C: X=NHAc
Thiourea D
No solvent amine
(2 equiv.)
Yield:33-99%
Thiourea D

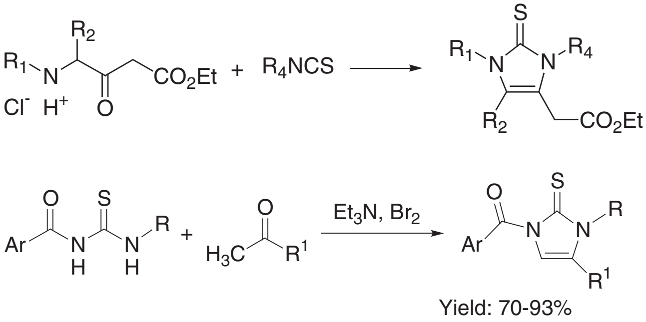
Scheme 74



Scheme 75

because of biological important roles, *e.g*. antithyroid agent,[225] stabilization of RNA complex of the HIV-1 A-loop and tRNA[226] and anticancer agents.[227]

Syntheses of cyclic chalcogenoureas have been carried out by reactions using isochalcogenocyanates, chalcogenoureas or stable carbines with elemental chalcogens. Reactions of several stable β-ketoester salts with isothiocyanates give cyclic thioureas in 68–85%.[228] 1-Aroyl-3-aryl-4-substituted imidazole-2-thiones has been prepared by the cyclization of 1-aroyl-3-arylthioureas with carbonyl compounds having methyl group in the presence of bromine and triethylamine (Scheme 76).[229]



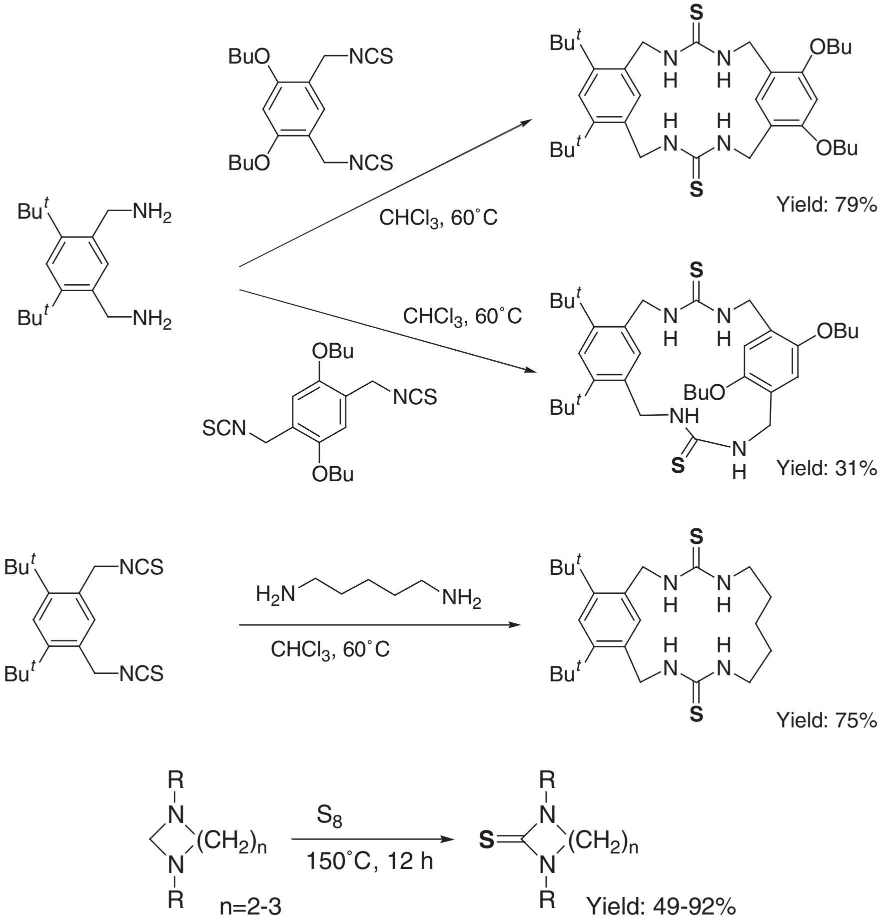
Scheme 76

Cyclic thiourea derivatives having three different types of cyclophane structure (ortho-meta, meta-meta and meta-para) and a lariat-type thiourea have been synthesized, using reaction of isothiocyanate with amine.[230] Cyclic thioureas have been obtained from formaldehyde aminals and sulfur (S_8) (Scheme 77).[231]

The cyclizations to obtain cyclic thioureas have been performed using thiocarbonyldiimidazole.[232] Reaction of methyl acetoacetate, thiourea and an aliphatic aldehyde in the presence of the zinc iodide (ZnI_2) was studied. Under the normal pressure, reaction has not been occurred whereas at high pressure (300 MPa) conditions 3,4-dihydropyrimidine-2-thione was obtained only in 10% yield.[233] The same one-pot three-component cyclocondensation reaction in the presence of iodide (I_2) provides a variety of 3,4-dihydropyrimidine-2-thione in high yields.[234] Condensation reaction of thioureas with α,β-unsaturated ketones in the presence of the sodium methoxide in methanol affords 3,4-dihydropyrimidine-2-thione derivatives.[235,236] Acylation of *N*,*N*′-disubstituted thioureas with methyl malonyl chloride followed by base-catalysed cyclization leads in the formation of 1,3-disubstituted-2-thiobarbituric acids (Scheme 78).[237]

Cyclic thioureas of carbohydrates have been studied. Methyl 2-deoxy-2-isothiocyanato-α-D-glucopyranoside, which exists in equilibrium with the corresponding 2,3-cyclic carbamate, reacts with D-glucosamine producing the pseudo-*C* and *N*-nucleoside of chiral imidazolidine-2-thione, in good yield and high stereoselectivity. Starting from the imidazolidine-2-thione, different pseudo-*C* and *N* -nucleosides of imidazoline-2-thione, are obtained.[238,239] The reaction of glycosyl 2-thioimidazoles with benzyl chloride has afforded bicyclic *S*-benzylthioimidazolines or tetrahydoxybutyl *S*-benzylthioimidazoles depending on the presence or absence of sodium hydrogencarbonate (Scheme 79).[240]

1-methyl-2-thioimidazole (MMI) has been used as an effective antithroid agent. The metabolism of MMI has been studied. In the presence of thyroid peroxidas, 1-methyl-2-thioimidazole appears initially to be oxidized to *bis*(1-methylimidazole)-2,2′-disulfide.[241,242] The reactions of MMI derivatives with halogens or borane have been exclusively reported.[243–245]

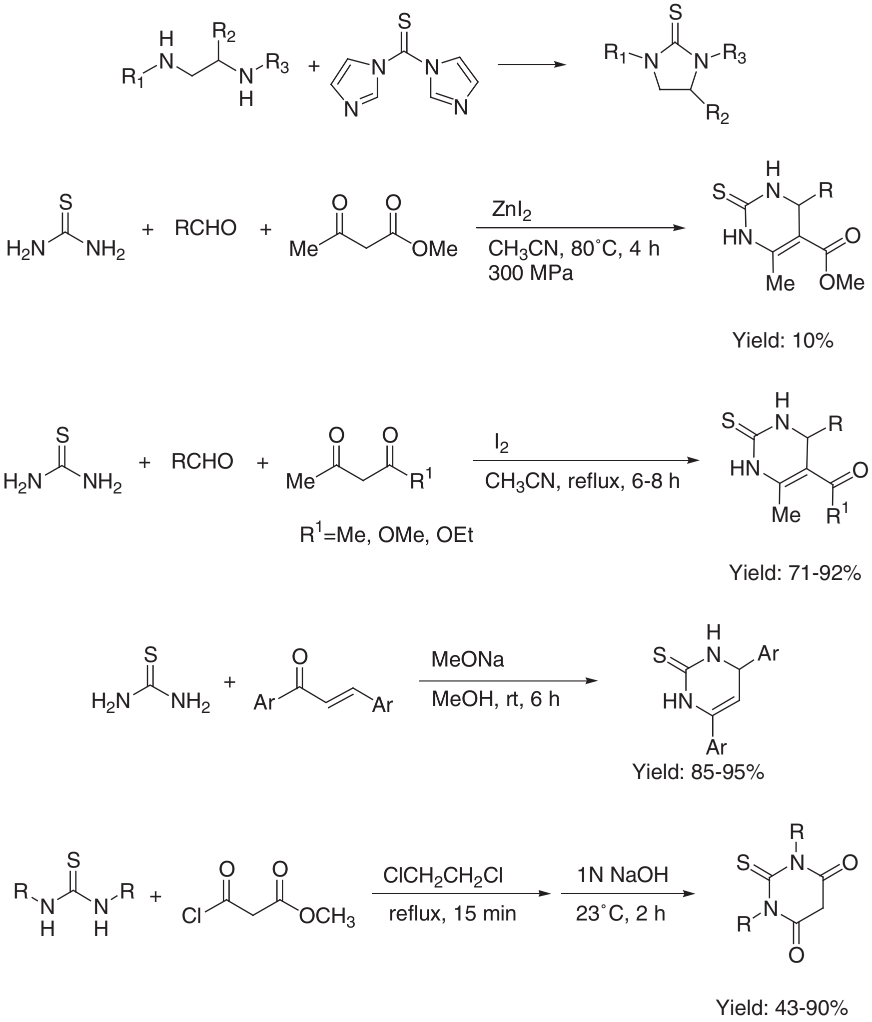


Scheme 77

Cyclic selenoureas have been investigated. The 2-selenoimidazolines have been obtained from the reaction of imidazol-2-ylidenes with elemental selenium.[246] 2-selenouracil has been synthesized by condensation of selenourea with ethyl 3-ketohexanoate (Scheme 80).[247]

2.4.5 Selenoamides and Selenoureas

Reports regarding selenoamides and selenoureas are less than the corresponding thioamides, thioureas, amides and ureas because of instability of compounds including selenium atom and their difficulty in the preparation. Recently, preparation methods to overcome some difficulties have been developed. Their reactions, preparation, application to heterocycles or biological assay systems have been actively investigated.

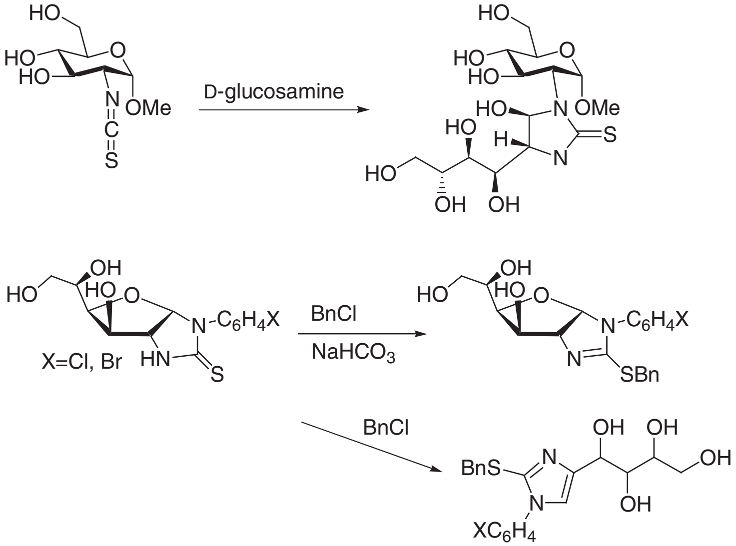


Scheme 78

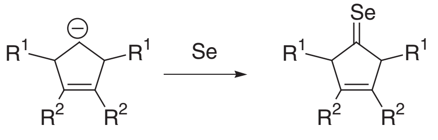
2.4.5.1 Synthesis of Selenoamides and Selenoureas

Primary selenoamides are prepared by reaction of nitriles with appropriate selenating reagent, such as phosphorus (V) selenide (P_2Se_5), hydrogen selenide (H_2Se), Al_2Se_3, NaSeH, *tris*(trimethylsilyl)monoselenophosphate or potassium selenobenzoate (Scheme 81).[248–252]

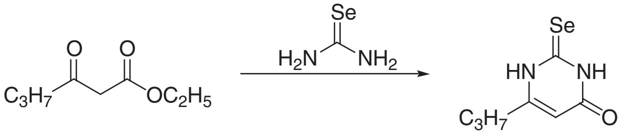
Secondary and tertiary selenoamides are obtained by several methods. A method is that reaction of amides with appropriate selenating reagents such as LiAlHSeH (prepared from $LiAlH_4$/Se), a mixture of ($^i Bu_2AlSe)_2$ and (^{i}BuAlSe)*n* (prepared from $^i Bu_2AlH$/Se), $(Me_2Al)_2Se$ (prepared from RSnSeSnR/Me_3Al), selenium-Lawesson's reagent and $(Et_4N)_2WSe_4$ (Scheme 82).[253–257]



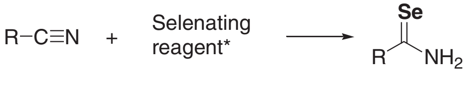
Scheme 79



R^1=CH_3, C_2H_5, *i*-Pr
R^2=CH_3



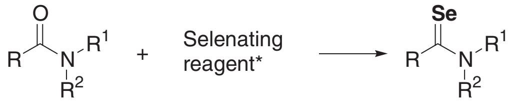
Scheme 80



*: P_2Se_5, H_2Se, Al_2Se_3, NaSeH,
tris(trimethylsilyl)monoselenophosphate
or potassium selenobenzoate.

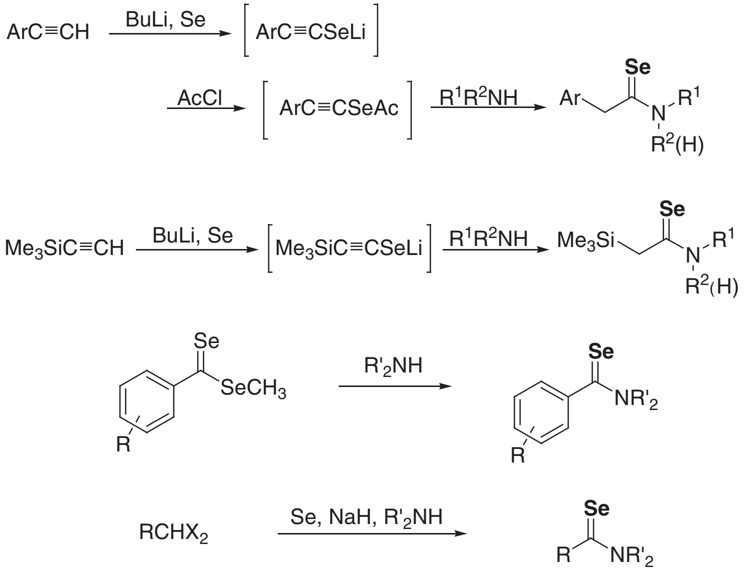
Scheme 81

For the preparation of secondary and tertiary selenoamides, several methods have been used; reaction of lithium alkyneselenolates (obtained using metallic selenium) with amines, aromatic diselenoic acid *Se*-methyl esters with amines or dihalomethane with elemental selenium, NaH and amines (Scheme 83).[258–266]



*: LiAlHSeH, $(Me_2Al)_2Se$, $(Et_4N)_2WSe_4$ or a mixture of $(iBu_2AlSe)_2$ and $(iBuAlSe)_n$.

Scheme 82



Scheme 83

Selenoureas are prepared by reaction of isoselenocyanates with amines, or by reaction of carbodiimides with a mixture of $LiAlH_4/Se$ and by reaction of cyanamides with $LiAlH_4/Se$.[267–272] The tyrosinase inhibitory activity and superoxide radical scavenger effect of selenoamides and selenoureas have been investigated (Scheme 84).[273–275]

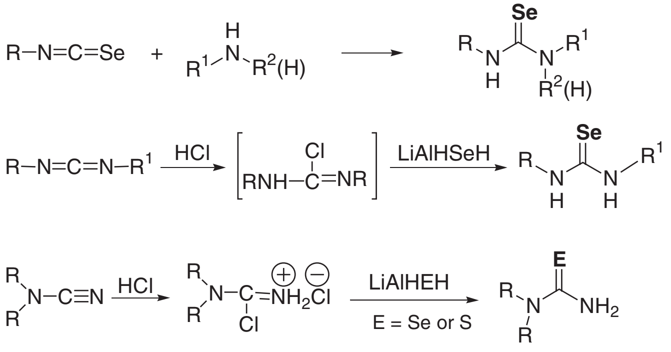
2.4.5.2 Heterocycles Using Selenoamides and Selenoureas

Selenazole and selenazine derivatives are obtained by reaction of selenoamide or selenourea with nucleophiles.[276]

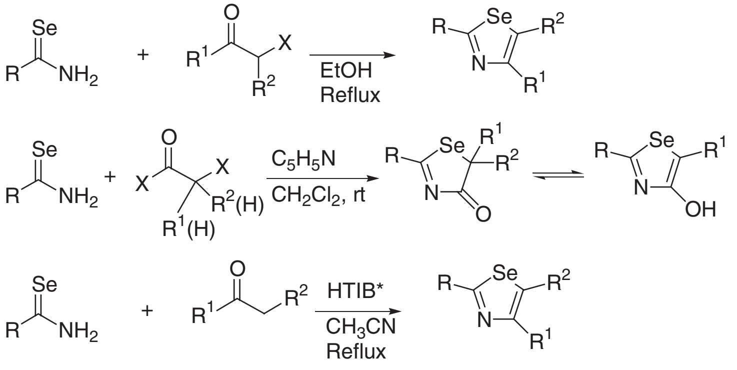
Reactions of primary selenoamides with α-haloketones, haloacyl halides or ketones provides 1,3-selenazole derivatives (Scheme 85).[277–283]

1,3-selenazine derivatives have been obtained by reactions of primary selenoamides with α,β-unsaturated ketones or malonyl chloride (Scheme 86).[284–288]

Reactions of selenoureas with ketones, haloacyl halides and chloroacetonitrile provides 1,3-selenazole derivatives,[289–295] whereas reactions with acryloyl chloride gives 1,3-selenazine derivatives (Scheme 87).[296]

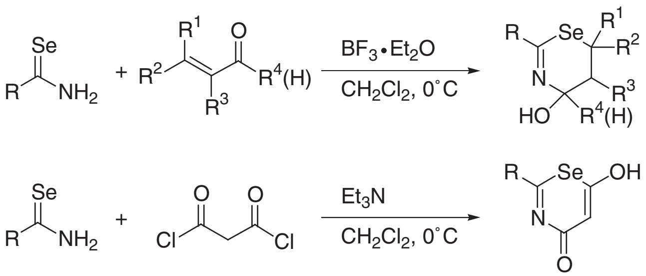


Scheme 84



*HTIB: [Hydroxy(tosyloxy)iode]benzene, PhI(OH)OTs

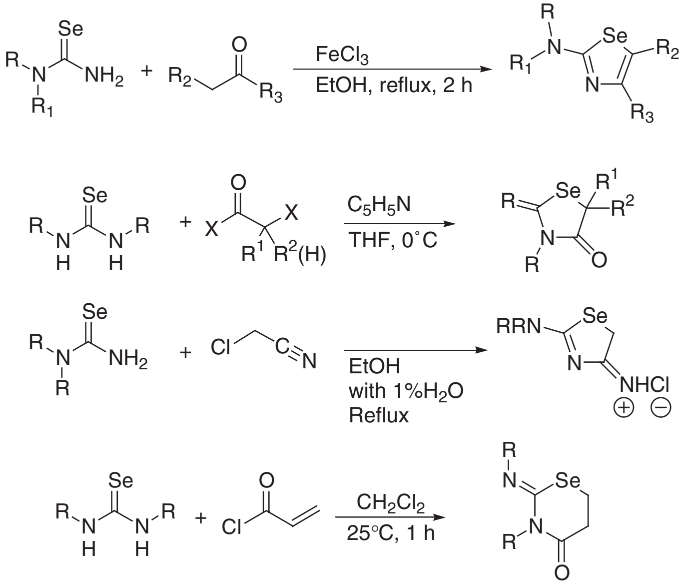
Scheme 85



Scheme 86

2.4.6 Telluroamides and Telluroureas

There are only limited reports of telluroamides and telluroureas. This is mainly due to the lability of telluroamides under air. It is thought to be the less efficient



Scheme 87

delocalization of tellurium lone-pair electrons onto carbon-containing multiple bonds.[297] Crystallographic study of telluroamides and telluroiminium salts, prepared by the reaction of telluroamides with methyl triflate, has been investigated.[255–257,298–300] Reaction of olefins (R=Me, Et) with Te in refluxing toluene gives the corresponding telluroureas (45 and 52%, respectively.) The telluroureas have been labile thermally or photochemically.[301]

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CHAPTER 3

The Compounds Between Si, Ge and Sn and Chalcogens (S, Se, and Te) Having Both a Single Bond and a Double Bond (Heavy Ketones)

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3.1 Introduction

Some reviews on the chemistry of the compounds having a single or double bond between heavier group 14 elements (Si, Ge, Sn) and chalcogens (S, Se, Te) have been reported.[1–13] Recent remarkable progress in this area is the applications of silyl chalcogenides to the synthesis of transition metal–chalcogen clusters and complexes, the synthesis of stable double-bond compounds (heavy ketones), *etc*. This chapter mainly presents the development in the chemistry of the compounds having a single and a double bond between Si, Ge, and Sn and chalcogens in recent 10 years.

3.2 The Compounds Having a Single Bond between Si, Ge, and Sn and Chalcogens

The single-bond compounds between Si, Ge, and Sn and chalcogens (S, Se, Te) are reactive and used as synthetic intermediates in the synthesis of organic compounds, organochalcogen compounds, organo-silicon, -germanium and -tin compounds, and transition metal–chalcogen complexes and clusters.

3.2.1 Structural and Spectroscopic Properties

Table 1 shows M–E single bond lengths of the cyclic group 14 metal chalcogenides, such as $(Ph_2ME)_3$ (M = Si, Ge, Sn: E = S, Se, Te) and $\{Ph(Me)SiS\}_3$[14–19] and the ^1H, ^{13}C, ^{29}Si, ^{119}Sn, ^{77}Se, and ^{125}Te NMR chemical shifts of $(Me_2ME)_3$ (M = Si, Ge, Sn: E = S, Se, Te).[20] The δ_H, δ_C, and δ_E values of the germanium compounds are shifted to lower fields compared with those of the analogous derivatives of silicon and tin. The relationship between δ_{Se} and δ_{Te} in these compounds is almost linear with a slope of about 2.5. This relationship is shown in other types of group 14 metal selenides and tellurides, such as $E(SiMe_2)_2E$, $Me_4Si_2(E)_2MMe_2$, (E=Se, Te; M=Si, Ge, Sn), *etc.*[20]

3.2.2 Formation of Single Bonds between Heavier Group 14 and 16 Elements

3.2.2.1 Reaction of Group 14 Metal Halides with Chalcogenolate Salts or Chalcogenols

The most common method for the formation of M–E (M = Si, Ge, Sn; E = S, Se, Te) bonds is the reaction of group 14 metal halides with chalcogenolate salts or chalcogenols/bases. Some recent examples are as follows.

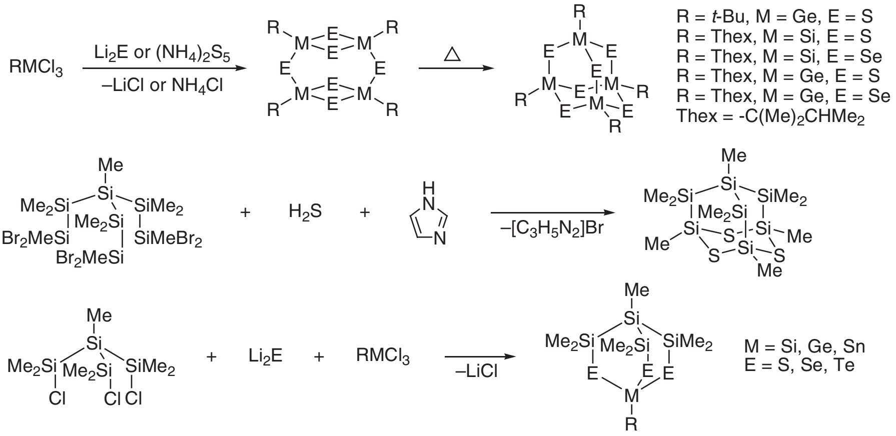
Some cage compounds such as "double decker"- and adamantane-type compounds are synthesized by bridging appropriate units containing group 14 metal halides with S^{2-} dianion as shown in Scheme 1.[21–24] The "double decker"-type compounds, $(R_2M_2E_2)_2E_2$ (M = Si, Ge, E = S, Se), isomerize to the corresponding adamantane-type compounds by thermolysis.[21,22]

Cyclic compounds containing a heavier group 14 element, chalcogens, and a boron are prepared by the reaction of boron dichalcogenolates bearing a bulky substituent with group 14 metal dichlorides (Scheme 2).[25]

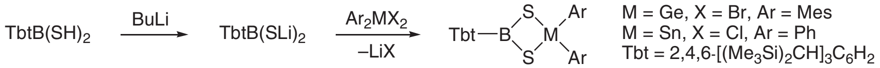
Table 1 *M–E bond lengths (Å) and multinuclear NMR chemical shifts[20] for compounds having M–E single bonds*

Compound	*M–E/Å*	δ_E/*ppm*	δ_M/*ppm*	$^1J_{ME}$/*Hz*	δ_C/*ppm*	δ_H/*ppm*
$(Me_2Si–S)_3$	2.143[a]		21.1		7.95	0.69
$(Me_2Si–Se)_3$	2.283[b]	−244	15.2	130.7	8.7	0.91
$(Me_2Si–Te)_3$	2.494[b]	−618	−23.7	344.5	8.8	1.26
$(Me_2Ge–S)_3$	2.225[b]				10.6	0.97
$(Me_2Ge–Se)_3$	2.365[c]	−182			11.1	1.15
$(Me_2Ge–Te)_3$	2.590[d]	−476			10.3	1.42
$(Me_2Sn–S)_3$	2.406[b]		133		4.8	0.86
$(Me_2Sn–Se)_3$	2.528[b]	−360	46	1217	4.4	0.99
$(Me_2Sn–Te)_3$	2.731[b]	−859	−192	3098	1.9	1.17

[a] Average value for $\{Ph(Me)SiS\}_3$.[14] [b] Average values for $(Ph_2ME)_3$.[15–17] [c] Average value for $(Ph_2Ge)_3Se_2$.[18] [d] Average value for $\{(t\text{-}Bu)_2Ge\}_3Te$.[19]

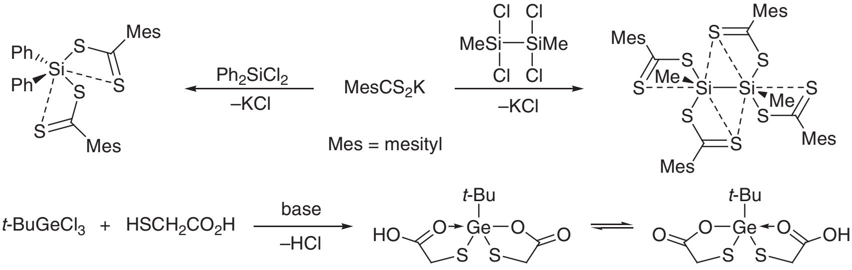


Scheme 1



Scheme 2

Compounds having highly coordinate group 14 elements such as hexa- and heptacoordinate silicon[26] and pentacoordinate germanium[27] are also synthesized by this method (Scheme 3).

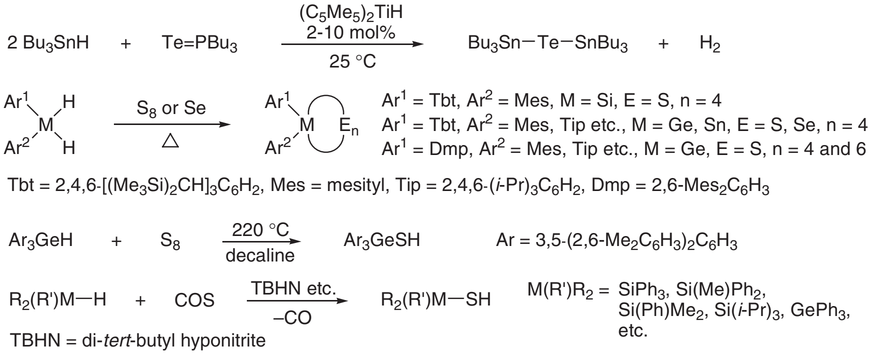


Scheme 3

3.2.2.2 Reaction of Group 14 Metal Hydrides with Chalcogen Sources

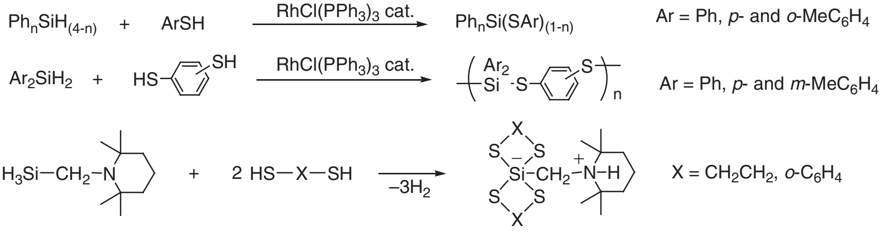
M–H (M = Si, Ge, Sn) bonds are reactive to undergo oxidative addition of transition metals, homolytic cleavage giving group 14 metal radicals, and so on. Some studies have been reported on the formation of M–E (M = Si, Ge, Sn; E = S, Se, Te) bonds by using the group 14 metal hydrides.

A tin monohydride undergoes titanium-mediated dehydrocoupling reaction with tellurium (using Te=PBu$_3$) at 25°C to give bis(tributylstannyl)telluride (Scheme 4).[28] Group 14 metal dihydrides bearing an extremely bulky substituent react with an excess amount of elemental sulfur or selenium on heating to afford the corresponding cyclic polychalcogenides.[29–32] By contrast, a bulky triarylgermanium hydride reacts with elemental sulfur to give the corresponding germanethiol *via* the insertion of the sulfur to the Ge–H bond.[33] The reaction of hydrosilanes with carbonyl sulfide in the presence of a radical initiator also gives the corresponding thiols via the elimination of carbon monoxide.[34]



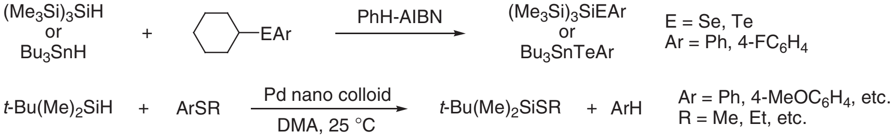
Scheme 4

Rh-catalyzed reaction of hydrosilanes with thiols results in the formation of Si–S bond compounds (Scheme 5).[35–37] The use of dihydrosilanes and dithiols as starting materials affords the corresponding polymers having Si–S bonds. The reaction of a trihydrosilane with 2 equivalent of dithiols in the absence of a catalyst gives zwitterionic pentacoordinate silicates.[38]



Scheme 5

The reaction of a hydrosilane or a hydrostannane with alkyl(aryl)chalcogenoethers in the presence of AIBN (2,2′-azobisisobutyronitrile) gives the corresponding arylchalcogenosilane or -stannane, respectively (Scheme 6).[39–41]

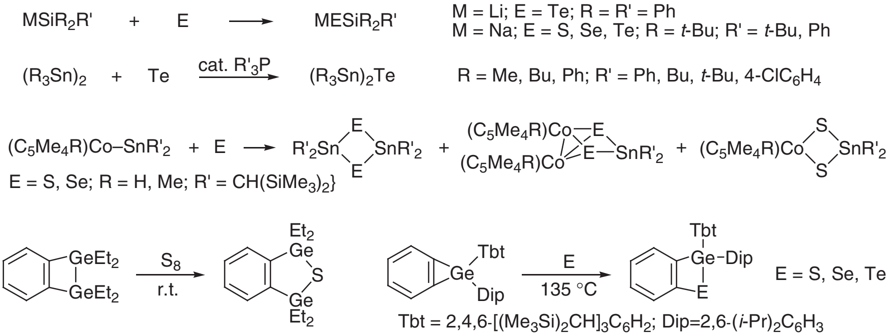


Scheme 6

It is considered that the stannyl or silyl radical and the alkyl radical are reactive intermediates in these reactions. In contrast to the selective formation of the arylchalcogenosilanes in the above radical reactions, the cross-coupling reaction of a hydrosilane with alkyl(aryl)sulfides catalyzed by palladium nanoparticles results in the selective formation of the corresponding alkylthiosilanes.[42]

3.2.2.3 Insertion of Chalcogens to Single Bonds of Group 14 Elements

A chalcogen atom inserts into the M–Si (M = Li, Na),[43,44] Sn–Sn,[45] and Co–Sn[46] bonds to give the corresponding products having a bond between the group 14 element and chalcogen atoms (Scheme 7). The Ge–Ge[47] and Ge–C[48] bonds of strained germacycles also undergo the insertion of a chalcogen atom to afford the corresponding ring-expanded products.

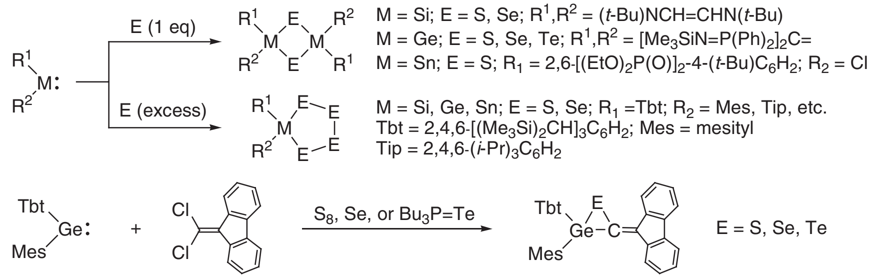


Scheme 7

3.2.2.4 Reaction of Divalent Compounds of Group 14 Metals with Chalcogen Sources

Divalent compounds of group 14 metals, *i.e.*, heavier analogs of carbenes, are highly reactive and readily insert into various bonds. Therefore, these species are useful for the formation of M–E (M = Si, Ge, Sn; E = S, Se, Te) bonds.

A stable diaminosilylene,[49] a bisgermavinylidene[50] and an electronically stabilized chlorostannylene[51] react with an equimolar amount of elemental chalcogens to afford the corresponding dichalcogenadimetallanes (Scheme 8). On the other hand, the reaction of metallylenes bearing bulky substituents with



Scheme 8

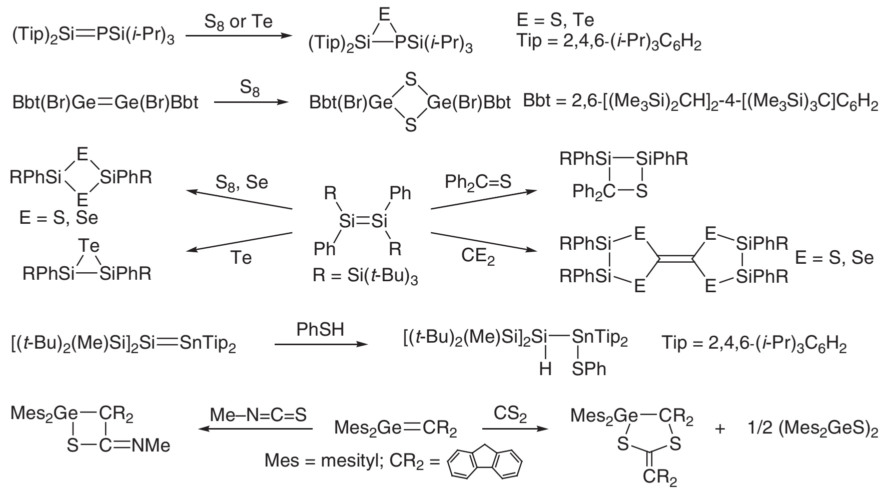
an excess amount of elemental chalcogens gives the corresponding tetrachalcogenides.[52–55] The reaction of a bulky germylene with chalcogen sources in the presence of 1.1 molar amount of 9-(dichloromethylene)fluorene results in the formation of an alkylidenechalcogenagermirane.[56]

3.2.2.5 Addition to Double-Bond Compounds

Double-bond compounds containing heavier main group elements are highly reactive to undergo ready addition reactions with various reagents.

Hydrosilanes, $R_2(R')Si–H$ ($R = Me, Et$; $R' = Me, H$), undergo almost quantitative 1,2-addition to the Ti=S double bond of $(C_5Me_5)_2Ti{=}S$ to give $(C_5Me_5)_2Ti(H)S–Si(R')R_2$.[57] Hydrosilylation of $Ph_2C{=}S$ with $R_2(R')Si–H$ (R, $R' = Me, Et, Ph$) in the presence of a catalytic amount of $B(C_6F_5)_3$ proceeds cleanly to afford the adducts, $Ph_2CHS–Si(R')R_2$.[58]

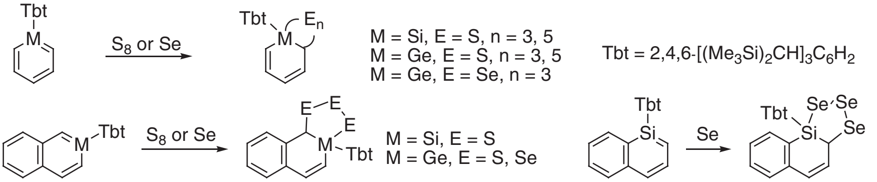
Addition of elemental chalcogens to the double bonds between silicon and phosphorus gives three-membered ring compounds (Scheme 9).[59] A 1,2-dibromodigermene reacts with S_8 to give the four-membered ring compound,[60] in



Scheme 9

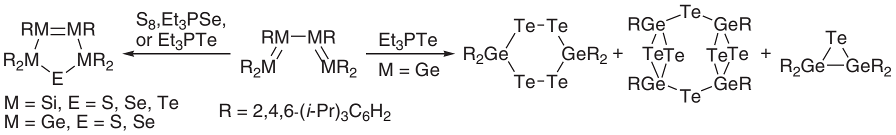
contrast to the addition of elemental chalcogens to $Mes_2M{=}MMes_2$ (M=Si,[61,62] Ge[63]) giving the corresponding chalcogenadimetalliranes. It is proposed that the 1,3,2,4-dithiadigermetane is formed *via* the sulfurization of the germylene dissociated from the digermene followed by its dimerization. A disilene bearing bulky silyl substituents reacts with chalcogens, a thioketone, CS_2, and CSe_2 to give the corresponding adducts having single bonds between silicon and chalcogens.[64] In addition, the reaction of a stable silastannene with a thiol[65] and that of a stable germene with MeNCS and CS_2[66] give the corresponding adducts.

Sila- and germaaromatic compounds react with elemental chalcogens to give the corresponding 5- and/or 7-membered-ring compounds *via* 1,2-addition to the M=C double bonds (Scheme 10).[67–72]



Scheme 10

Tetrametallabutadienes react with chalcogens to give the corresponding chalcogenametallacyclopentenes, although the reaction of the Ge analog with a phosphine telluride leads to the cleavage of all the Ge–Ge bonds without the formation of a telluragermacyclopentene derivative (Scheme 11).[73–75]



Scheme 11

Double-bond compounds between heavier group 14 and 16 elements (heavy ketones) undergo ready addition reactions with various reagents to give the corresponding single-bond compounds. The details of the reactivities are described in the next section (Schemes 20 and 21).

3.2.2.6 Miscellaneous Methods

The reaction of $NaSiR(t\text{-}Bu)_2$ (R = *t*-Bu, Ph) with S_2Cl_2 gives the corresponding bis(silyl)disulfide, $(t\text{-}Bu)_2RSiS{-}SSiR(t\text{-}Bu)_2$.[44]

Disproportionation between distannanes, RSn–SnR (R = Me, Ph), and dichalcogenides, R′E–ER′ (E = S, Se, Te; R′ = Ph, 2-pyridyl, Bu, *etc.*), is efficiently promoted by room light to give the corresponding chalcogenostannanes, RSn–ER′, quantitatively.[76]

3.2.3 Reactions

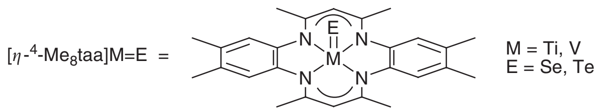
Characteristic reactivities of M–E (M = Si, Ge, Sn; E = S, Se, Te) single bonds are (i) cleavage of the M–E bonds by the reaction with halide, alkoxide, oxide, *etc.* resulting in the formation of the energetically favored bonds between the heavier group 14 element and oxygen or halogen atom, (ii) homolytic cleavage of the M–E bonds giving the M and/or E radicals, (iii) oxidative addition of the M–E bonds to transition metals. There are many reports on the applications of these reactivities to the synthesis of metal–chalcogen clusters, chalcogen-containing metal complexes, organochalcogen compounds, group 14 metal compounds, organic compounds, *etc.*

3.2.3.1 Application to the Controlled Synthesis of Chalcogen–Metal Complexes and Clusters

The reaction of silicon–chalcogen bonds, R_3Si–ER′ (E = S, Se, Te), with L_nMX (L = ligand, M = metal, X = halide, alkoxide, acetate, oxide, *etc.*) gives R′E–M and R_3SiX. The driving force in this reaction is the formation of the energetically favorable Si–X bonds. The application of chalcogenosilanes to the synthesis of chalcogen–metal clusters and metal complexes containing chalcogens have been extensively studied in recent decades.

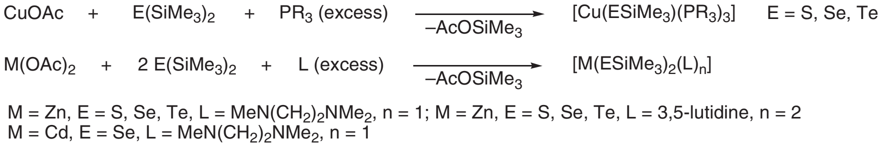
Bis(silyl)chalcogenides, $(R_3Si)_2E$ (E = S, Se, Te), act as E^{2-} equivalents. For example, bis(trimethylsilyl)chalcogenides, $(Me_3Si)_2E$ (E = S, Se, Te), react with copper(I) acetate or chloride in the presence of a phosphine ligand to give a wide variety of cluster compounds,[77] such as $[Cu_{32}Se_{16}(PPh_3)_{12}]$, $[Cu_{52}Se_{26}(PPh_3)_{16}]$, $[Cu_{72}Se_{36}(PPh_3)_{20}]$,[78] $[Cu_{146}Se_{73}(PPh_3)_{30}]$,[79] $[Cu_{12}Se_6(PCy_3)_6]$ (Cy = cyclohexyl), $[Cu_{26}Se_{13}(PCy_3)_{10}]$, $[Cu_{59}Se_{30}(PCy_3)_{15}]$,[80] *etc.* The structure types of the produced clusters depend on the reaction conditions such as the ratio of the reagents, and the types of phosphines and chalcogens, *etc.* In addition, the reaction of $(Me_3Si)_2E$ (E = S, Se, Te) with $RGaCl_2$ (R = C_5Me_5,[81] $(Me_3Si)_2C(Ph)C(Me_3Si)N$[82]) gives the cubane-type complex, $[RGa(\mu_3\text{-}E)]_4$, and the four-membered ring compound, $[RGa(\mu_2\text{-}E)]_2$, respectively, depending on the ligand types. The reactions of $(Me_3Si)_2S$ with $AlH_3(NMe_3)$ gives two types of compounds, the bicyclo-type compound $Al_4S_5(H)_2(NMe_3)_4$ and the adamantane-type compound $Al_4S_6(NMe_3)_4$, depending on the ratio of the reagents, together with Me_3SiH.[83] On the other hand, $PW_{11}O_{39}MO$ (M = Nb, Ta)[84] and $[\eta^4\text{-}Me_8taa]MCl_2$ (M = Ti, V),[85] in which the coordination sites around the central metals are protected by the ligands, react with $(RMe_2Si)_2E$ (E = S, Se, Te) to give the corresponding terminal chalcogenides (Scheme 12).

Although $(Me_3Si)_2E$ normally acts as an E^{2-} equivalent, it acts as a Me_3SiE^- unit to give the corresponding mononuclear silanechalcogenolato complexes in



Scheme 12

the reaction of $(Me_3Si)_2E$ with metal salts in the presence of excess ligand (Scheme 13).[86–88] In these reactions, it is considered that the use of an equimolar amount of $(Me_3Si)_2E$ against the AcO^- groups on the metal and the presence of excess ligands lead to the formation of monomeric complexes retaining the Si–E bonds.



Scheme 13

Organochalcogenosilanes, $RESiR'_3$ (E = S, Se, Te), normally act as RE^- equivalents, although they, can act as E^{2-} units under severe reaction conditions. Reactions of $RESiR'_3$ or $(R_3Si)_2E$ with metal salts (AgOCOR,[89–94] AgCl,[95] AgSCN,[90] CuCl,[96–98] CuOAc,[99,100] $ZnCl_2$,[101] $CdCl_2$,[102,103] $CdCl_2(PR_3)_2$,[104,105] $HgCl_2$,[106–108] *etc.*) in the presence of a ligand result in the formation of a wide variety of transition metal clusters depending on the reaction conditions. A main group metal complex $[Bi_6(\mu\text{-}SePh)_6(SePh)_{10}Br_2]$ is also synthesized by the reaction of $PhSeSiMe_3$ with $BiCl_3$.[109]

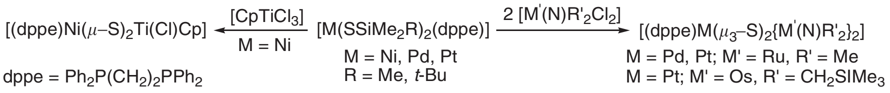
Cyclotrisilathiane, $(Me_2SiS)_3$, acts as $Me_2SiS_2{}^{2-}$ or $S(SiMe_2S)_2{}^{2-}$ unit. The reaction of cyclotrisilane with $M(OAc)_2$ (M = Fe, Co, Pd) in the presence of a ligand (L) gives the corresponding silanedithiolato complexes, $L_nM(\mu\text{-}S)_2SiMe_2$ (M = Fe, Co, Pd).[110,111] On the other hand, cyclotrisilane acts as $S(SiMe_2S)_2{}^{2-}$ equivalent in the reaction with MOAc (M = Cu, Ag)/PEt_3 to afford binuclear complexes, $[M_2\{(SSiMe_2)_2S\}(PEt_3)_3]$.[112]

3.2.3.2 Application to the Controlled Synthesis of Binary Metal–Chalcogenido Complexes and Clusters

Silanechalcogenolato metal complexes $M(ESiR_3)_nL_m$ (E = S, Se, Te) are considered to be good precursors for the synthesis of binary metal chalcogenido complexes and clusters. The reactions of silanechalcogenolato complexes of Cu, Zn, and Cd shown in Scheme 13 with metal salts or metal complexes give binary metal–chalcogen clusters, such as $[Hg_{15}Cu_{20}E_{25}(PPr_3)_{18}]$ (E = S, Se),[113,114] $[Cu_6In_8S_{13}Cl_4(PEt_3)_{12}]$,[114] $[(Me_2N(CH_2)_2NMe_2)_5Zn_5Cd_{11}Se_{19}(SePh)_6(thf)_2]$,[115] $[Zn_xCd_{10\text{-}x}E_4(EPh)_{12}(PPr_3)_4]$ (E = Se, Te),[88,116] and $[Cd_xHg_{10-x}Se_4(SePh)_{12}(PPr_3)_4]$.[88]

A silanedithiolato complex of palladium, $[(Et_3P)_2Pd(\mu\text{-}S)_2SiMe_2]$, reacts with $CpTiCl_3$ to afford the expected dimetallic complex, $[(Et_3P)_2Pd(\mu\text{-}S)_2Ti(Cl)Cp]$, while the reaction with 0.5 molar amount of $[TiCl_4(thf)_2]$ results in the formation of a different type of complex, $[\{(Et_3P)_2Pd\}_2(\mu_3\text{-}S)_2Ti(S)Cl_2]$.[111] On the other hand, a binuclear Cu(I) complex having a $S(SiMe_2S)_2^{2-}$ ligand $[Cu_2\{(S\text{-}SiMe_2)_2S\}(PEt_3)_3]$ reacts with $[TiCl_4(thf)_2]$ to afford a heterometallic sulfido complex $[ClTiCu_3S_3(PEt_3)_4]$, while it reacts with $[CpTiCl_3]$ to give a heterometallic sulfido cluster $[Cp_2Ti_2Cu_6S_6(PEt_3)_6]$.[112]

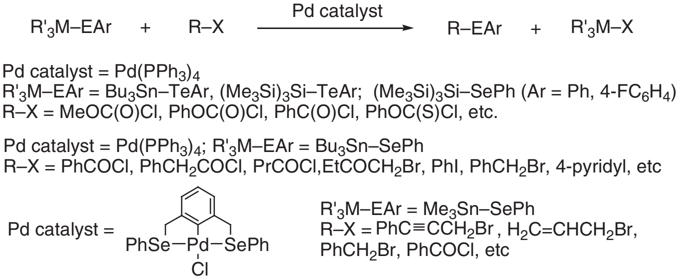
The reaction of bis(silanethiolato) complexes of group 10 metals with transition metal complexes gives the corresponding multinuclear complexes accompanied by the elimination of the silyl chloride (Scheme 14).[117,118]



Scheme 14

3.2.3.3 Application to Organic Synthesis

The reaction of $Bu_3SnTeAr$ or $(Me_3Si)_3SiEAr$ (E = Se, Te) with a variety of chloroformates, in the presence of a catalytic amount of $Pd(PPh_3)_4$ gives the corresponding arylchalcogenoformates (Scheme 15).[40,41] In addition, the application of this reaction to benzoyl chloride and *O*-phenyl chlorothioformate gives the coupling products. The Pd-catalyzed reactions of $Bu_3SnSePh$ with aroyl and acryl chlorides and aryl and alkyl halides also give the corresponding organoselenium compounds.[119–121] These reactions are considered to proceed *via* the oxidative addition of the R–X bond to the Pd(0) atom, followed by the ligand exchange reaction accompanied by the formation of the stannyl halide or the silyl halide and the subsequent reductive elimination giving the product and the Pd(0) complex. In addition, the selenation of propargyl-, allyl-, benzyl-, and benzoyl halides with $Me_3SnSePh$ catalyzed by a palladium pincer complex proceeds under mild conditions.[122] It is considered that the mechanism for this reaction is different from that in the reactions using $Pd(PPh_3)_4$, *i.e.*, the transfer of the SePh group to the Pd(II) center of the pincer complex, followed by the



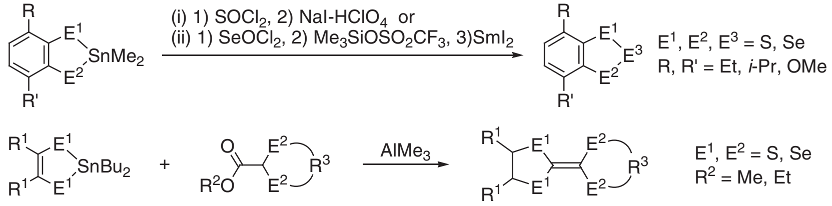
Scheme 15

S_N2-type of displacement of the halide by the lone-pair electrons of the selenium leading to the regeneration of the catalyst.

Selenenyl fluorides RSeF (R = Me, Ph, $C_6H_4CO_2Et$, *etc.*), which are reactive species used in fluoroselenylation of olefins, *etc.*, are synthesized by the reaction of $RSeMMe_3$ (M = Si, Ge, Sn) with XeF_2.[123,124]

Pyrolysis of $Me_3SnTeCFR^1R^2$ ($R^1 = R^2 = CF_5$; $R^1 = F$, $R^2 = CF_5$; $R^1 = F$, $R^2 = C_2F_5$) results in the elimination of Me_3SnF giving the corresponding telluroketones in $R^1R^2C{=}Te$, which undergo ready head-to-tail-type dimerization.[125]

A wide variety of benzotrichalcogenoles are selectively synthesized in good yields by the reactions of the corresponding benzodichalcogenastannoles with an S or Se source (Scheme 16).[126–128] Unsymmetrical tetrathiafulvalenes and diselenadithiafulvalenes are prepared by the reaction of dichalcogenastannoles with esters in the presence of $AlMe_3$.[129–131]

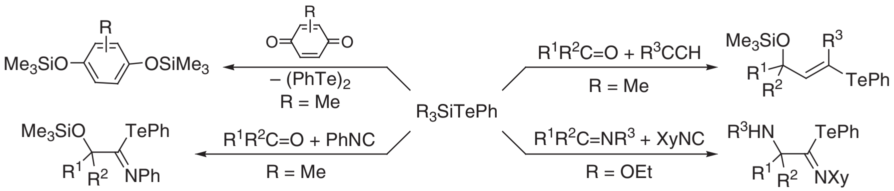


Scheme 16

3.2.3.4 Application to Organic Synthesis (Radical Reaction)

The reaction of carbonyl compounds, $R(R')C{=}O$, with $PhSeSiMe_3$ and Bu_3SnH in the presence of a catalytic amount of AIBN as a radical initiator results in the hydrosilylation of carbonyl compounds giving the corresponding silyl ethers, $R(R')CH–OSiMe_3$.[132,133]

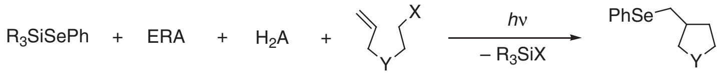
Some radical reactions using silyltellurides have been reported. The reaction of $Me_3SiTePh$ with quinones gives the corresponding *bis*-silylated hydroquinones (Scheme 17).[134] Three-component coupling among the silyl tellurides, carbonyl compounds and isocyanides proceeds on heating at 100°C to give the corresponding coupling products.[135] It is considered that the key intermediates of this reaction are the siloxymethyl radicals, $Me_3SiO(R^1)(R^2)C\cdot$, and the phenyltelluro radical, $PhTe\cdot$, which are generated by the reaction of silyl tellurides with carbonyl compounds. In addition, the use of alkynes instead of isocyanides[136] and the use of imines instead of carbonyl compounds[137] result in



Scheme 17

the formation of the corresponding three-component adducts, respectively, although the reaction using imines requires the use of $(EtO)_3SiTePh$ as a silyl telluride.

PET (photosensitized electron transfer) reduction of $PhSeSiR_3$ and the subsequent radical chain group transfer reaction have been reported (Scheme 18).[138,139] The radical anion $[PhSeSiR_3]^{\cdot -}$, generated by electron transfer from photo-excited states of ERA (electron-rich aromatic), dissociates to $PhSe^-$ and $R_3Si\cdot$ and the silyl radical initiates the cyclization reaction accompanied with the formation of R_3SiX. In the case of X = SePh, $PhSeSiR_3$-catalyzed group transfer radical reaction is achieved.[140]



ERA= 1,5-dimethoxynaphthalene or 9,10-dimethoxyanthracene; H_2A = ascorbic acid

Scheme 18

3.2.3.5 *Oxidative Addition to Transition Metals*

The reaction of RTe–MMe_3 (M = Si, Ge, Sn) with $Pt(PEt_3)_3$ results in the oxidative addition of the M–Te bonds to the Pt(0) metal giving *trans*-$[Pt(MMe_3)(TeR)(PEt_3)_2]$.[141]

On the other hand, $(R_2SnE)_3$ (R = Me, Ph; E = S, Se, Te) and $(Me_2GeTe)_3$ react with a platinum(II) complex $[PtMe_2(bu_2bpy)]$ (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) to give the corresponding platinum(IV) complexes $[PtMe_2(R_2ME)_2(bu_2bpy)]$ having a five-membered PtMEME ring.[142,143]

3.2.3.6 *Reactions without the Cleavage of the M–E bonds*

The reaction of $R_3M^1EM^2$ (M^1 = Si, Ge, Sn; E = S, Se, Te; M^2 = Li, Na, H, *etc.*) with M^3X (M^3 = transition metal, *etc.*; X = halogen, *etc.*) giving $R_3M^1EM^3$ is an effective method for the synthesis of metallachalcogenolato complexes of metals. For example, $(t\text{-Bu})_3SiSNa(thf)_n$ reacts with $FeX_2(thf)_2$ (X = Cl, Br) to give $[(X_2Fe)\{\mu\text{-SSi(t-Bu)}_3\}_2\{FeX(thf)\}]Na(thf)_4$,[144] while the reaction of $(t\text{-Bu})_3SiSH$ with $[Fe\{N(SiMe_3)_2\}_2]$ affords $[\{[(t\text{-Bu})_3SiS]_2Fe\}_2\{\mu\text{-SSi}(t\text{-Bu})_3\}_2]$.[145]

Reduction of hexathiagermepanes and tetrathiagermolanes, $Dmp(Ar)GeS_n$ (Dmp = 2,6-$Mes_2C_6H_3$; n = 6, 4), with $NaBH_4$ gives the corresponding germandithiol $Dmp(Ar)Ge(SH)_2$.[146]

3.2.3.7 *Miscellaneous Reactions*

The reaction of R_3SnSAr (R = Bu, Me) with benzyne results in the insertion of the triple bond to the Sn–S bond to give the corresponding 2-(arylthio)-arylstannnanes, 2-$(ArS)C_6H_4SnR_3$.[147] The insertion of alkyne to the Sn–E (E = S, Se, Te) bonds occurs in the reaction of $[PtMe_2(Me_2SnE)_2(bu_2bpy)]$ with $RC{\equiv}CR$ ($R = CO_2Me$).[148] The obtained seven-membered PtECCSnESn ring compounds [$PtMe_2\{EC(R)C(R)Sn(Me)_2ESn(Me)_2\}(bu_2bpy)$] slowly dissociates into the five-membered PtECCSn ring compounds [$PtMe_2\{EC(R)C(R)Sn(Me)_2\}(bu_2bpy)$] and 1/3 molar amount of $(Me_2SnE)_3$.

Silylation of styrene with Me_3SiEPh (E = S, Se, Te) in the presence of BuMgCl and a catalytic amount of [$(C_5H_5)_2ZrCl_2$] proceeds to give $PhCH{=}CHSiMe_3$. In this reaction, the phenylchalcogeno groups act as leaving groups.[149]

Thermolysis of 1,3,2,4-diselenastannaboretane $Ph_2Sn(\mu\text{-}Se)_2BTbt$, which is synthesized by the deselenation of $Ph_2Sn(\mu\text{-}Se)(\mu\text{-}Se_2)BTbt$ with PPh_3, results in the dissociation into TbtB=Se and $Ph_2Sn{=}Se$ giving $(Ph_2SnSe)_3$ *via* the trimerization.[150]

3.3 The Compounds Having a Double Bond between Si, Ge, and Sn and Chalcogens (Heavy Ketones)

Carbonyl compounds are one of the most important species in organic chemistry, and their heavier congeners are also interesting from the standpoint of their structure, reactivities, and functions. The chemistry of double-bond compounds between carbon and heavier group 16 elements (S, Se, Te) has been studied extensively, and most of their structures and properties have been systematically elucidated so far.[151–160] By contrast, the chemistry of compounds having a double bond between heavier group 14 and 16 elements, which are called "heavy ketones", has been much less explored until recently due to the difficulty in the stabilization of the highly reactive double bonds. Since the synthesis of the first kinetically stabilized heavy ketones in 1993, *i.e.*, the synthesis of a stable germanethione by taking advantage of the steric effect of extremely bulky substituents,[161] heavy ketones with various combinations between heavier group 14 and 16 elements have been synthesized as stable compounds by taking advantage of the kinetic stabilization using bulky substituents as well as the electronic stabilization by the attachment of electron-donating substituents or the coordination of heteroatoms such as a nitrogen atom.[10–12] This section summarizes the progress on the chemistry of heavy ketones in recent about 10 years.

3.3.1 Theoretical Aspects

The bond lengths and stretching frequencies as well as the σ and π bond energies for $H_2M{=}E$ (M = C, Si, Ge, Sn; E = O, S, Se, Te) have been calculated at the B3LYP level (Table 2).[11–13,52] The theoretical calculations show the 8–10% shortening of the M=E double bonds of $H_2M{=}E$ compared with the corresponding single bonds. The calculated stretching frequencies of the M=E bonds shift to the smaller wavenumbers with the increase of the atomic number of the group 14 and 16 elements. In addition, the σ bond energies in heavy ketones are much greater than the corresponding π bond energies, while the σ and π bond energies of the ketones are almost equal to each other. This

Table 2 *M=E bond lengths (Å), energies (kcal mol^{-1}), and stretching frequencies (cm^{-1}) for H_2M=E calculated at the B3LYP/TZ(d, p) level*

H_2M=E		*E*			
		O	*S*	*Se*	*Te*
H_2C=E	d^a	1.200	1.617	1.758	1.949
	Δ^b	15.5	11.9	11.1	10.1
	ν^c	1826	1087	882	755
	σ^d	93.6	73	65.1	57.5
	π^e	95.3	54.6	43.2	32
H_2Si=E	d^a	1.514	1.945	2.082	2.288
	Δ^b	8.1	9.4	9.3	8.7
	ν^c	1227	723	554	461
	σ^d	119.7	81.6	73.7	63.2
	π^e	58.5	47.0	40.7	32.9
H_2Ge=E	d^a	1.634	2.042	2.174	2.373
	Δ^b	8.6	9.5	9.2	8.6
	ν^c	942	553	387	310
	σ^d	101.5	74.1	67.8	59.1
	π^e	45.9	41.1	36.3	30.3
H_2Sn=E	d^a	1.802	2.222	2.346	2.543
	Δ^b	7.6	8.9	8.5	8.1
	ν^c	797	470	319	251
	σ^d	94.8	69.3	64.3	56.4
	π^e	32.8	33.5	30.6	26.3

[a] M=E bond lengths. [b] Values of % reduction in a bond length defined as [{(single bond length)–(double bond length)}/(single bond length)] × 100. [c] M=E stretching frequencies. [d] σ bond energies. [e] π bond energies.

indicates that heavy ketones readily undergo any kind of addition reactions, dimerization, and polymerization, because the formation of new σ bonds on the M and E atoms with the concurrent cleavage of the π bond results in substantial overall energy gain.

3.3.2 Structural and Spectroscopic Properties

3.3.2.1 Tricoordinate Heavy Ketones

Various combinations of tricoordinate heavy ketones have been synthesized as stable compounds by taking advantage of extremely bulky aryl substituents.[52–54,161–167] Table 3 shows their selected structural parameters and spectroscopic properties.

The X-ray structural analyses reveal the planar structures around the heavier group 14 elements of all the heavy ketones as well as the case of the carbon analog, ketones. This is in sharp contrast to the *trans*-bent structure in

Table 3 *Tri-coordinate heavy ketones*

$Tbt(Ar)M{=}E^{a}$			$M–E/\text{Å}$	$\Delta^{b}/\%$	$\Sigma(\angle M)^{c}/\text{deg}$	δ_M/ppm	δ_E/ppm	$\lambda_{max}/nm\ (\varepsilon)$	Raman shift/cm^{-1}	Synthetic method	References
Ar	*M*	*E*									
Tip[d]	Si	S	1.948(4)	9	360	167		396 (100)	724	(iii)	52,162
Dip[e]	Si	Se				174	635	456		(i) (iv)	163
Dip[e]	Si	Te				171	731	593		(iv)	163
Tip[d]	Ge	S	2.049(3)	9	359			450 (100)	521	(iii)	53,161
Dis[f]	Ge	S						432	512	(i) (iii)	53
Tip[d]	Ge	Se	2.180(2)	9	359		941	519 (140)	381	(iii)	53,164
Dis[f]	Ge	Se	2.173(3)	9	360		873	492	386	(i)	53
Tip[d]	Ge	Te	2.398(1)	8	360		1143	640 (180)		(i)	165
Dis[f]	Ge	Te	2.384(3)	8	360		1009	604 (119)		(i)	165
Dip	Ge	Te					1194			(iv)	163
Ditp[g]	Sn	S				531		491		(iii)	54
Dmtp[h]	Sn	S				467		486		(iii)	54
Tcp[i]	Sn	S				643		488		(iii)	54
Ditp[g]	Sn	Se	2.375(3)	7	360	440		531		(iii)	54,166
Tcp[i]	Sn	Se				556	839	544		(iii)	54
Titp[j]	Sn	Te	2.5702(6)	7	360	282	1007	436 (1400) 646 (80)		(i)	167

[a] Tbt = 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$. [b] The bond shortening (%) compared to the calculated bond lengths of the corresponding $H_3M–EH$.[52] [c] Summation of the bond angles around the M atom. [d] Tip = 2,4,6-$(i\text{-}Pr)_3C_6H_2$. [e] Dip = 2,6-$(i\text{-}Pr)_2C_6H_3$. [f] Dis = $CH(SiMe_3)_2$. [g] Ditp = 2,6-$[2\text{-}(i\text{-}Pr)C_6H_4]_2C_6H_3$. [h] Dmtp = 2,6-$[2\text{-}MeC_6H_4]_2C_6H_3$. [i] Tcp = 2,4,6-$(C_6H_{11})_3C_6H_2$. [j] Ditp = 2,6-$[2,4\text{-}(i\text{-}Pr)_2C_6H_3]_2C_6H_3$.

double-bond compounds between heavier group 14 elements, such as disilenes (>Si=Si<), digermenes (>Ge=Ge<), and distannenes (>Sn=Sn<). The 7–9% shortenings of the M–E bonds compared with those of the corresponding M–E single bonds are almost consistent with the results of the calculations (Table 2), although these shortenings are smaller than those of ketones. These structural properties indicate the double-bond character of the heavy ketones.

The ^{29}Si, ^{119}Sn, ^{77}Se, and ^{125}Te NMR signals of these heavy ketones are observed in the lower field, which is characteristic to double-bond compounds. In addition, the absorption maxima assigned to the n–π* transitions are red-shifted with the increase of the atomic number of the group 14 and 16 elements as well as the case of $R_2C=E$ (E = O, S, Se, Te). Interestingly, the λ_{max} values (n–π* of $R_2C=S$, $R_2C=Se$, and $R_2C=Te$) are greatly red-shifted compared with those of the corresponding silicon analogs. The values of the Raman shifts are well consistent with those of the calculated stretching frequencies of $H_2M=E$ (Table 2) and move to the smaller wavenumber with the increase of the atomic number of the group 14 and 16 elements.

3.3.2.2 Tetra- and Pentacoordinate Heavy Ketones

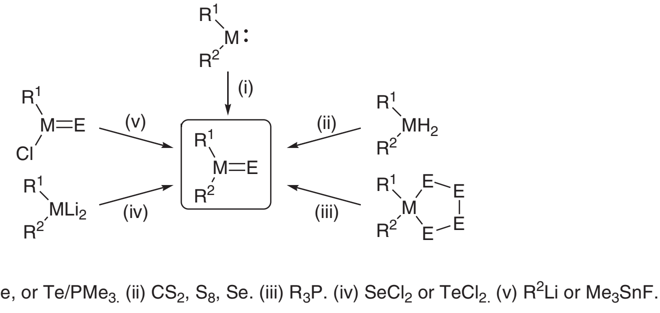
Table 4 shows the structural and spectral data of tetra- and pentacoordinate heavy ketones stabilized by the intramolecular coordination of nitrogen atoms.[168–171] Compared with the values in the tricoordinate heavy ketones (Table 3), thermodynamically stabilized systems have larger M–E bond lengths. The chemical shifts in the ^{29}Si, ^{119}Sn, ^{77}Se, and ^{125}Te NMR spectra are observed in extremely higher fields except for the ^{77}Se NMR chemical shift of a pentacoordinate germaneselone (1097 ppm), and the λ_{max} values assigned to the n–π* transitions are shifted to the shorter region. The X-ray structural analysis of a tetracoordinate silanethione shows that the silicon center has the intermediate structure between $sp^2 + p$ and sp^3 ($\Sigma(\angle M) = 345°$).[168] In the pentacoordinate heavy ketones, the GeC_2E units are almost planar ($\Sigma(\angle M) = 360°$). These results indicate the reduction of the double-bond character of the M=E bonds by the coordination of the one or two nitrogen atoms, that is, some extent of the contribution of the $N \rightarrow M^+–E^-$ or $N^+–M–E^-$ structure.

3.3.2.3 Tetra- and Pentacoordinate N-substituted Heavy Ketones

Table 5 shows the structural and spectral data of tetra- and pentacoordinate double-bond compounds between germanium or tin and group 16 elements bearing nitrogen substituents.[172–182] The M–E bond lengths are longer or almost the same compared with those of the tricoordinate heavy ketones (Table 3). The NMR spectra show the signals in the higher field except for some examples. These results suggest some extent of contribution of $M^+–E^-$ structure. In the series of $[\{ArNC(Me)\}_2CH]Ge(R)=E$, the Ge=E bond lengths are longer with the order of R = alkyl > R = Cl > R = F, which suggests that the electron-withdrawing group on the germanium atom results in the short Ge=E bond lengths.

3.3.3 Syntheses

Heavy ketones have been synthesized by several synthetic methods shown in Scheme 19; (i) the reaction of divalent group 14 element species with chalcogen sources, (ii) the reaction of dihydrometallanes with chalcogen sources, (iii) the dechalcogenation of metal polychalcogenides, (iv) the reaction of dilithiometallanes with dihalochalcogenides, and (v) substitution of the chloro group of heavy acyl chlorides. The methods used for the synthesis of heavy ketones are summarized in Tables 3–5.



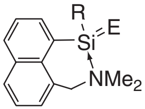
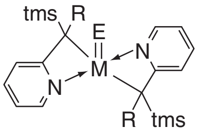
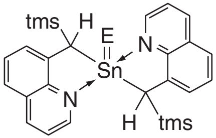
Scheme 19

The method (i) can be applied to the synthesis of almost all heavy ketones (Tables 3–5). Silanethiones and a silaneselone stabilized by the coordination of a nitrogen group have been synthesized by the method (ii) (Table 4). The method (iii) is effective to the synthesis of kinetically stabilized tricoordinate heavy ketones, although it cannot be applied to the synthesis of double-bond compounds between heavier group 14 elements and tellurium due to the instability of polytellurides (Table 3). The method (iv) can be used only when the unique dilithiometallanes can be generated (Table 3). The synthesis of heavy ketones by the method (v) demands the isolation of the corresponding heavy acyl chlorides as stable compounds (Table 5).

3.3.4 Reactivities

As reported in the theoretical aspects section, heavy ketones readily undergo addition reaction, dimerization, and polymerization, when their kinetic or electronic stabilizations are insufficient. For example, Tbt(Mes)M=E (M = Si, Ge, Sn; E = S, Se) undergo head-to-tail dimerization at ambient temperature because of their insufficient bulkiness to suppress their high reactivity. Kinetically stabilized tricoordinate heavy ketones, Tbt(R)M=E, show high reactivities to small molecules to give the corresponding adducts, although they have enough bulkiness to suppress dimerization and polymerization (Scheme 20). They react with water and methanol to give the corresponding tetracoordinate adducts *via* 1,2-addition. Moreover, they undergo cycloaddition

Table 4 *Tetra- and penta-coordinate carbon-substituted heavy ketones stabilized by the coordination of nitrogen atoms*

Compounds				*M–E/Å*	Δ[a]/%	Σ(∠*M*)[b]/deg	δ_M/*ppm*	δ_E/*ppm*	$^1J_{ME}$/*Hz*	λ_{max}/*nm* (ε)	*Synthetic method*	*References*
	R	*M*	*E*									
	Np[c]		S				22				(ii)	168
	Ph		S	2.013(3)	6	345					(ii)	168
	Ph		Se				29				(ii)	168
	tms[d]	Ge	Se	2.2472(7)	6	360		−98			(i)	169
	Ph	Ge	Se	2.426(2)	−1	360		1097		294 (1910) 372 (1330)	(i)	170
	tms[d]	Ge	Te	2.4795(5)	4	360		−461			(i)	169
	Ph	Sn	S				−55			354 (5510)	(i)	170
	Ph	Sn	Se	2.418(1)	6	360	−179	−532	2567[e] 2682	324 (14750) 366 (7320)	(i)	170
			Se	2.398(1)	7	360	−112	−735	2818[e] 2966	310 (5920) 340 (5780) 414 (850)	(i)	170,171
			Te	2.618(1)	5	360	−350	−2031	7641[e] 7808	344 (8100) 416 (820)	(i)	170,171

[a] The bond shortening (%) compared to the calculated bond lengths of the corresponding H_3M–EH.[52] [b] Summation of the bond angles around the M atom. [c] Np = 1-naphthyl. [d] tms = $SiMe_3$. [e] the coupling between ^{117}Sn and E

Table 5 *Tetra- and penta-coordinate double-bond compounds between heavier group 14 and 16 elements bearing nitrogen substituents*

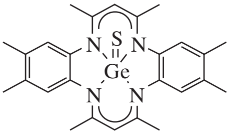
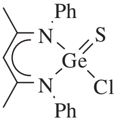
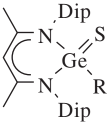
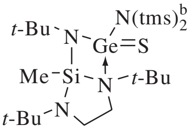
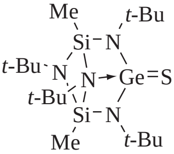
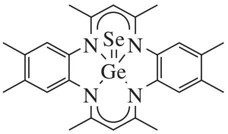
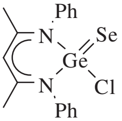
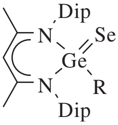
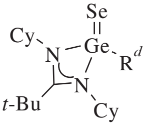
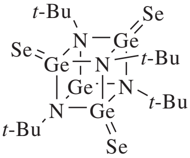
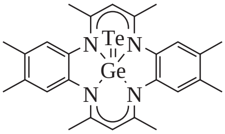
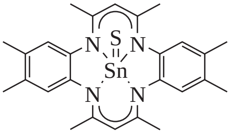
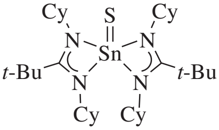
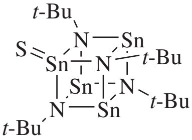
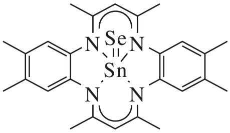
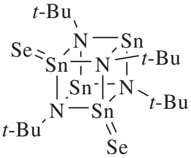
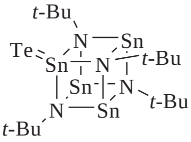
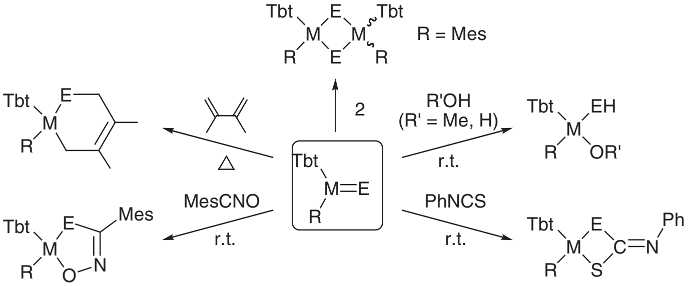
	R	*M–E/Å*	Δ^a/%	*Other data*	*Synthetic method*	*References*
		2.110(2)	6		(i)	172
		2.074(1)	8		(i)	173
	Cl	2.053(6)	9		(i)	174,175
	F	2.050(9)	9		(i) (v)	174,175
	Me	2.104(7)	7		(v)	174,175
		2.090(2)	7	$\Sigma(\angle \mathrm{M})^c = 349°$	(i)	176
		2.063(3)	9	$\Sigma(\angle \mathrm{M})^c = 355°$	(i)	177
		2.247(1)	6		(i)	172
		2.210(1)	8		(i)	173
	Cl	2.197(6)	8	$\delta_{\mathrm{se}} = -288$ ppm	(i)	175
	F	2.176(7)	9	$\delta_{\mathrm{se}} = -465$ ppm	(i) (v)	175
	Me	2.1992(5)	8	$\delta_{\mathrm{se}} = -349$ ppm	(i) (v)	175, 178
	Bu	2.219(6)	7	$\delta_{\mathrm{se}} = -297$ ppm	(v)	175
	$\mathrm{N(tms)}_2^b$	2.2212(3)	7	$\delta_{\mathrm{se}} = 1116$ ppm	(i)	179
	^{e}	2.196(4)	8	$\delta_{\mathrm{se}} = 1024$ ppm	(i)	179

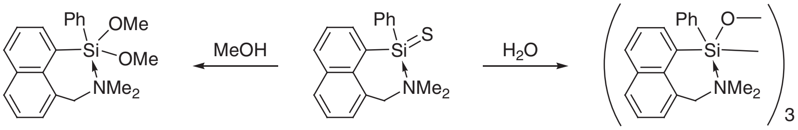
Table 5 (*continued*)

	R	*M–E/Å*	Δ^a/%	*Other data*	*Synthetic method*	*References*
		2.185(1) 2.187(1) 2.187(1)	9 9 9		(i)	180
		2.466(1)	5		(i)	172
		2.274(3)	7	$\delta_{\mathrm{Sn}} = -301$ ppm	(i)	181
	[d]	2.280(5)	6	$\delta_{\mathrm{Sn}} = -236$ ppm	(i)	182
		2.262(3)	7		(i)	180
		2.394(1)	7	$\delta_{\mathrm{Sn}} = -444$ ppm $^{1}J_{\mathrm{SnSe}} = 3450$ Hz	(i)	181
		2.372(1) 2.363(1)	8 8	$\delta_{\mathrm{Sn}} = -111$ ppm	(i)	180
		2.589(1)	6		(i)	180

[a] The bond shortening (%) compared to the calculated bond lengths of the corresponding H_3M–EH.[52] [b] tms = $SiMe_3$. [c] Summation of the bond angles around the M atom. [d] Cy = cyclohexyl. [e] N(Cy)–C(*t*-Bu)=NCy.



Scheme 20



Scheme 21

reactions with phenyl isothiocyanate, mesitonitrile oxide, and 2,3-dimethyl-1,3-butadiene to give the corresponding [2 + 2], [2 + 3], and [2 + 4] cycloadducts.

On the other hand, an electronically stabilized heavy ketone by the coordination of the nitrogen atom shows extremely low reactivity. It does not react with phosphanes, phosphates, ketones, epoxides, MeI, HCl, *etc*., although it undergoes methanolysis and hydrolysis (Scheme 21).[168]

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CHAPTER 4

Chalcogen–Nitrogen Chemistry

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4.1 Introduction

The discovery in 1973 that polysulfur nitride $(SN)_x$, a polymer comprised only of non-metallic elements, behaves as a superconductor at 0.26 K sparked widespread interest in sulfur–nitrogen (S–N) chemistry. In the past 30 years, the field of inorganic S–N chemistry has reached maturity and interfaces with other areas of chemistry, *e.g.*, theoretical chemistry, materials chemistry, organic synthesis, polymer chemistry and biochemistry, have been established and are under active development. This interest has been extended to Se–N and, to a lesser extent, Te–N systems.

Materials with unique magnetic and conducting properties that depend on intermolecular chalcogen–nitrogen interactions have been designed, and some C–N–S heterocycles exhibit magnetic behaviour that is of potential significance in the construction of organic data recording devices. Hybrid S–N/P–N macromolecules have been evaluated for use as components of matrices for oxygen sensors in the aerospace industry.

S-nitrosothiols (RSNO) have emerged as important species in the storage and transport of nitric oxide. As NO donors these S–N compounds have potential medical applications in the treatment of blood circulation problems.

Although progress in the chemistry of Se–N and Te–N compounds has been slower, there have been impressive developments in the last 10 years. Significant differences are apparent in the structures, reactivities and properties of these heavier chalcogen derivatives, especially in the case of tellurium. In addition, the lability of Se–N and Te–N bonds has led to applications of reagents containing these reactive functionalities in organic synthesis and, as a source of elemental chalcogen, in the production of metal chalcogenide semiconductors.

A book on chalcogen–nitrogen chemistry has been published recently.[1] Reviews on specific aspects of chalcogen–nitrogen chemistry that have appeared in the last 10 years are listed in reverse chronological order in refs. 2–18.

4.2 General Considerations

Some of the fundamental properties of sulfur, selenium and tellurium differ significantly from those of oxygen, giving rise to disparities between the structures and properties of heavier chalcogen–nitrogen molecules and ions compared to those of their N–O counterparts. The major contributors to these differences include the following:

(a) The Pauling electronegativities for N, O, S, Se and Te are 3.04, 3.44, 2.58, 2.55 and 2.10, respectively. As a result an E–N (E=S, Se, Te) bond will be polarized in the opposite direction to an N–O bond.

(b) There is an increasing reluctance to form multiple bonds to nitrogen for the heavier chalcogens.

(c) Sulfur can adopt a variety of oxidation states ranging from –2 to +6 in the formation of molecules or ions. The ability to achieve oxidation states +4 and +6 gives rise to sulfur–nitrogen species that have no N–O analogues.

(d) The size of chalcogens increases down the series $O < S < Se < Te$. The covalent radii are 0.73, 1.03, 1.17 and 1.35 Å, respectively.

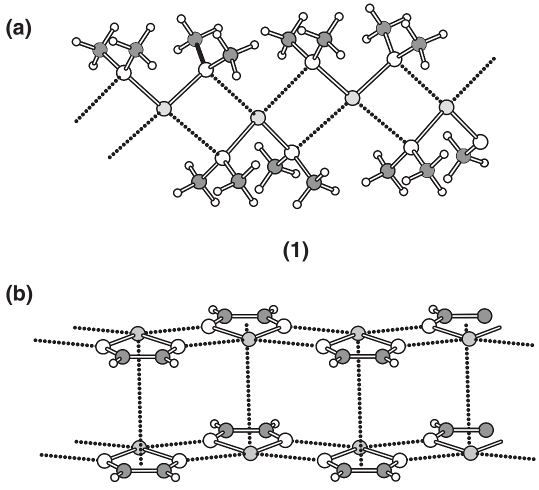
4.3 Characterization of Chalcogen–Nitrogen Compounds

A variety of physical techniques are used for the characterization of chalcogen–nitrogen compounds.

4.3.1 Diffraction Techniques

The reactions of heterocyclic chalcogen–nitrogen systems often result in substantial reorganization of their structural frameworks. Spectroscopic techniques alone are rarely sufficient to provide decisive structural information, and X-ray crystallography has been of paramount importance in the development of chalcogen–nitrogen chemistry. The structural chemistry of Se–N and Te–N compounds has been reviewed.[19]

Details of intermolecular interactions are important for understanding the physical properties, *e.g.*, conductivity and magnetic behaviour of chalcogen–nitrogen compounds. In general, these intermolecular interactions become stronger along the series $S\cdots N < Se\cdots N < Te\cdots N$. For example, $E(NMe_2)_2$ (E=S, Se) are liquids, whereas $Te(NMe_2)_2$ (**1**) is a polymeric solid (Figure 1).[20]



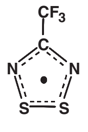
(2)

Figure 1 *Crystal packing of (a) $(Me_2N)_2Te$ (**1**) (redrawn from crystal data given in ref. 20); (b) TeN_2CH_2 (**2**) (redrawn from crystal data given in ref. 21)*

The Te–N distances in the monomer units of **1** are 2.05 Å, while the intermolecular Te···N distances are 2.96 Å, *cf.* 2.76 Å for 1,2,5-telluradiazole (**2**).[21] The sum of the van der Waals radii for Te and N is 3.61 Å.

Electron diffraction studies have also provided structural information for chalcogen–nitrogen compounds that are liquids or gases at room temperature, *e.g.*, the 1,2,3,5-dithiadiazolyl radical $[CF_3CNSSN]^{\bullet}$ (**3**)[22] and the 1,3,2-dithiazolyl $[CF_3CSNSCCF_3]^{\bullet}$ (**4**).[23] The structure of the trithiatriazine $(NSF)_3$ (**5**) has also been determined in the gas phase by a combination of electron diffraction and microwave spectroscopy, which shows that all three fluorine atoms are axial.[24]

The gas-phase structures of the 12 π-electron systems 1,3,2,4-benzodithiadiazines $X_4C_6S_2N_2$ (**6a**, X=H; **6b**, X=F) were determined by electron diffraction.[25] The parent system **6a** is non-planar in the gas phase, whereas the tetrafluoro derivative **6b** is planar. Conversely, the solid-state structure of **6a** is planar,[26] while that of **6b** is non-planar, presumably as a result of packing forces.[27]



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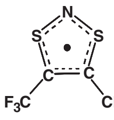

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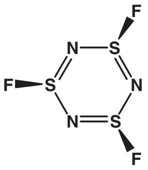

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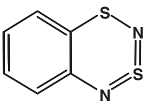
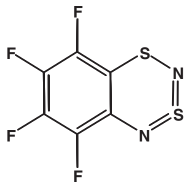


6a



6b

4.3.2 ^{14}N and ^{15}N NMR Spectroscopy

Nitrogen has two isotopes, ^{14}N ($I = 1$, 99.6%) and ^{15}N ($I = 1/2$, 0.4%), which are amenable to NMR studies. ^{15}N NMR spectra show narrow, well-resolved lines, but the acquisition times are lengthy due to long spin-lattice relaxation times. Isotopically enriched materials are needed in order to observe the effects of spin–spin coupling. On the other hand, the ^{14}N nucleus gives rise to relatively broad lines, poorer resolution and loss of coupling information. However, because of short spin-lattice relaxation times, good signal-to-noise ratios can be achieved in relatively short acquisition times.

Some illustrative examples of the application of ^{14}N NMR spectroscopy in sulfur–nitrogen chemistry include (a) studies of the $(NSCl)_3 \leftrightarrow 3NSCl$ equilibrium in solution[28] and (b) identification of the S–N species present in solutions of sulfur in liquid ammonia.[29]

4.3.3 ^{33}S, ^{77}Se and ^{125}Te NMR Spectroscopy

The ^{33}S isotope is quadrupolar ($I = 3/2$) and has low natural abundance (0.76%). Therefore, ^{33}S NMR spectroscopy has found very limited application in S–N chemistry. On the other hand, both selenium and tellurium have isotopes with $I = 1/2$ (^{77}Se, 7.6% and ^{125}Te, 7.0%), and NMR studies using these nuclei can provide useful information for Se–N and Te–N systems.

The ^{77}Se NMR spectra can be used to analyse the composition of a complex mixture of Se–N compounds. For example, ^{77}Se NMR provides a convenient probe for analysing the decomposition of selenium(IV) diimides RN=Se=NR (*e.g.*, R=^tBu).[30] An elegant application of ^{77}Se NMR spectroscopy, in conjunction with ^{15}N NMR spectroscopy, involved the detection of the thermally unstable eight-membered rings $(RSeN)_4$.[31]

4.3.4 ESR Spectroscopy

ESR studies have been used extensively to characterize S–N radicals that are persistent in solution at room temperature.[32] Typical radicals are cyclic C–N–S systems in which the unpaired electron occupies a delocalized π-orbital. In conjunction with molecular orbital calculations, ESR spectra can provide unique information about the electronic structures of these ring systems.

Exceptionally persistent acyclic S–N radicals, *e.g.*, *N*-arylthio-2,4,6-triphenylanilino (**7**), exhibit a characteristic 1:1:1 triplet in the ESR spectrum.[33] The ESR spectrum of $[(CF_3S)_2N]^{\bullet}$ (**8**) exhibits a 1:1:1 triplet of septets as a result of well-resolved coupling to the six equivalent fluorine atoms (Figure 2).[34]

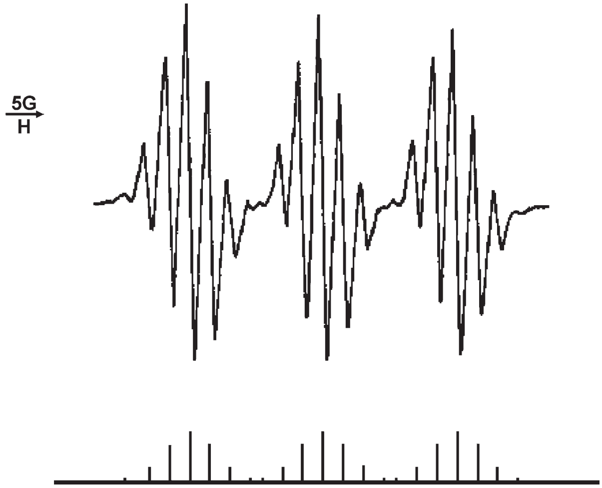


Figure 2 *ESR spectrum of a solution containing 1 mM* $(CF_3S)_4N_2$ (**8**) *in* CCl_3F *at 298 K:* $a(^{14}N) = 13.20$ *G,* $a(^{19}F) = 1.95$ *G*[34]

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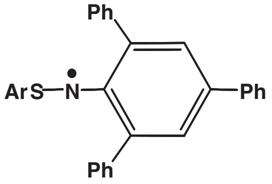

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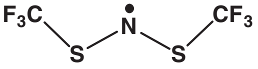

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4.3.5 Infrared and Raman Spectroscopy

Vibrational spectra have been used to identify matrix-isolated chalcogen–nitrogen species, which are unstable under ambient conditions.[35,36] In this way the species NS, SNS (and the less stable isomer NSS), NNS, NSe, SeNSe and $[SeNSe]^+$ have been identified. The technique of ^{15}N-enrichment has been used in several cases to distinguish S–N from S–S vibrations.

Raman spectroscopy is a useful probe for detecting transannular S···S interactions in bicyclic or cage S–N molecules or ions. The strongly Raman active vibrations occur at frequencies in the range 180–300 cm^{-1}, and for S···S distances in the range 2.4–2.7 Å. On the basis of symmetry considerations, the Raman spectrum of the mixed sulfur–selenium nitride $S_2Se_2N_4$ was assigned to the 1,5- rather than the 1,3- isomer.[37]

The explosive and insoluble black solid $Se_3N_2Cl_2$ was shown to contain the five-membered cyclic cation $[Se_3N_2Cl]^+$ by comparing the calculated fundamental vibrations with the experimental IR spectrum.[38]

4.4 Binary Chalcogen–Nitrogen Systems

4.4.1 Neutral Molecules

The most common binary systems are the tetramers S_4N_4 and Se_4N_4. Sulfur or selenium analogues of the monomeric species NO or NO_2 are thermally unstable.

4.4.1.1 Thiazyl and Selenazyl Monomer, NS and NSe

Thiazyl monomer is a radical with one unpaired electron. It exhibits an IR band at 1209 cm^{-1}. The experimental dipole moment is 1.83 ± 0.03 D in the opposite direction to that in NO ($\mu = 0.16$ D). Much less is known about selenazyl monomer, SeN, but it has been characterized by infrared spectroscopy.[36] The structure of a transition-metal complex $[OsTp(NSe)Cl_2]$ (Tp=hydrotris(1-pyrazolyl)borate) has been determined.[39]

4.4.1.2 Dinitrogen Sulfide, N_2S

A variety of acyclic and cyclic S–N compounds decompose at moderate temperatures (100–150 °C) with the formal loss of a symmetrical NSN fragment, but this molecule has never been detected. The lowest energy isomer, linear NNS, is generated by flash vacuum pyrolysis of 5-phenyl-1,2,3,4-thiatriazole.[40] *Ab initio* molecular orbital calculations indicate that the resonance structure $N{\equiv}N^+{-}S^-$ is dominant.[41]

4.4.1.3 Disulfur and Diselenium Dinitride, S_2N_2 and Se_2N_2

Disulfur dinitride is prepared by the thermolysis of S_4N_4 (over silver wool at 220 °C), $[S_4N_3]Cl$ or $Ph_3AsNS_3N_3$ at *ca.* 130 °C.[42] It has a square planar structure with S–N bond distances of 1.654 Å. S_2N_2 is a six π-electron system, but four of these electrons occupy non-bonding orbitals. Consequently, it has been suggested that S_2N_2 should be regarded as a two π-electron system.[43] *Ab initio* calculations reveal that the four-membered rings E_2N_2 (E=S, Se, Te) exhibit significant singlet diradical character, which increase along the series $S < Se < Te$.[44] S_2N_2 forms *N*-bonded mono- and di-adducts, $S_2N_2{\cdot}$ L and $S_2N_2{\cdot}$ 2L, respectively, with Lewis acids such as $AlCl_3$, BCl_3 and $SbCl_5$, and with a variety of transition-metal halides.[45] Coordination has very little effect on the geometry of the four-membered ring. Although the selenium analogue Se_2N_2 is unknown as the free species, the *bis*-adduct $Se_2N_2.2AlBr_3$ and the dianion $[Cl_3Pd(\mu\text{-}Se_2N_2)PdCl_3]^{2-}$ have been structurally characterized.[46,47]

4.4.1.4 Tetrasulfur Dinitride, S_4N_2

Tetrasulfur dinitride can be prepared by (a) treatment of $[(Me_3Si)_2N]_2S$ with equimolar amounts of SCl_2 and S_2Cl_2,[48] (b) the reaction of the trisulfane $S_3[N(SiMe_3)_2]_2$ with a mixture of S_2Cl_2 and $SOCl_2$,[49] (c) the decomposition of

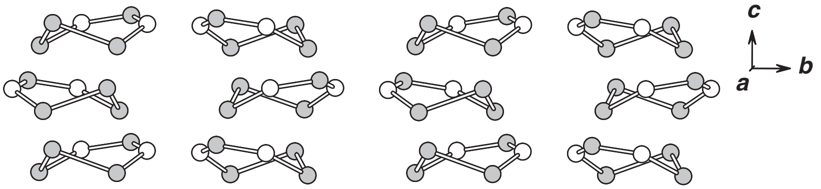


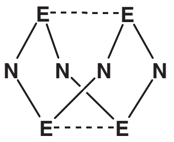
Figure 3 *The crystal structure of S_4N_2. Sulfur atoms are shown in grey and nitrogen atoms in white (redrawn from crystal data given in ref. 50)*

$Hg(S_7N)_2$, or (d) the reaction of S_2Cl_2 with aqueous ammonia. The S_4N_2 molecule consists of a six-membered ring in a half-chair conformation (Figure 3).[50] There are long S–N bonds (1.68 Å) connecting the –SSS– and –N=S=N– units, which have S–N distances of 1.56 Å. The selenium analogue Se_4N_2 is unknown.

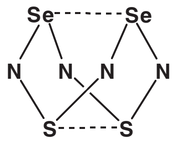
4.4.1.5 *Tetrasulfur and Tetraselenium Tetranitride, S_4N_4 and Se_4N_4*

The standard synthesis of S_4N_4 involves the treatment of S_2Cl_2 with chlorine, followed by ammonia gas in carbon tetrachloride at 20–50 °C. Alternatively, S_4N_4 can be prepared by the reaction of $[(Me_3Si)_2N]_2S$ with an equimolar mixture of SCl_2 and SO_2Cl_2.[51] The synthesis of Se_4N_4 involves the reaction of $(EtO)_2SeO$ or SeX_4 (X=Br, Cl) with ammonia under high pressure, and this method has been adapted in the preparation of $Se_4{}^{15}N_4$.[52] Other alternatives involve (a) the treatment of $[(Me_3Si)_2N]_2Se$ with $SeCl_4$[53a] or (b) the reaction of $Ph_2S{=}NBr$ with elemental selenium.[53b] Se_4N_4 is even more endothermic than S_4N_4.

Tetrasulfur tetranitride (**9a**) adopts a cage structure with equal S–N bond lengths (1.62 Å) and two weak transannular S···S interactions of *ca.* 2.60 Å at room temperature. Tetraselenium tetranitride and the hybrid 1,5-$Se_2S_2N_4$ also have similar structures (**9b**, **10**).[54] Rietveld analysis indicates that S_4N_4 undergoes a transition to a new orthorhombic phase at 397 K.[55]



9a (E = S)
9b (E = Se)



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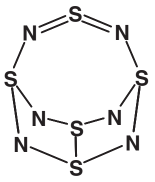

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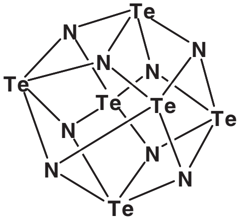

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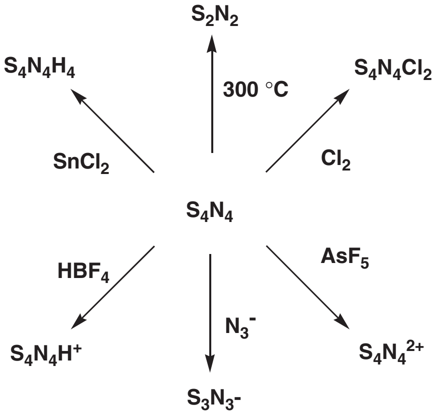
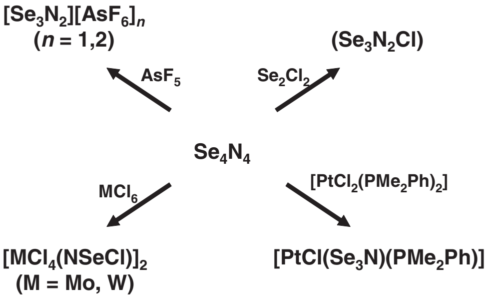
The sulfur nitride S_4N_4 is a very important source of many other S–N compounds (Scheme 1).[42] The synthesis of other S–N rings from S_4N_4 can be classified as follows: reactions with (a) halogens or other oxidizing agents (b) nucleophiles or reducing agents, and (c) metal halides or organometallic reagents. The eight-membered ring is retained in 1,5-$S_4N_4Cl_2$ and $[S_4N_4]^{2+}$, the initial products of chlorination or oxidation of S_4N_4, respectively. Further



Scheme 1 *Preparation of S–N rings from S_4N_4*



Scheme 2 *Preparation of Se–N compounds from Se_4N_4*

chlorination or oxidation results in ring contraction to give $(NSCl)_3$ or the $[S_6N_4]^{2+}$ cation.

In spite of its hazardous nature, Se_4N_4 has been used for the synthesis of other Se–N compounds (Scheme 2). However, selenium–nitrogen halides and silicon–nitrogen–selenium reagents are safer alternatives for the development of Se–N chemistry.[56]

4.4.1.6 Pentasulfur Hexanitride, S_5N_6

Pentasulfur hexanitride (**11**) is an explosive, air-sensitive orange solid, which is best prepared from $S_4N_4Cl_2$ and $(Me_3SiN)_2S$.[42] The reaction of S_5N_6 with $[Ph_4P]_2[Pd_2Cl_6]$ gives $[Ph_4P]_2[Pd_2Cl_4(S_2N_3)]$.[57]

4.4.1.7 Tellurium Nitrides

Tellurium nitride is obtained by the reaction of $TeBr_4$ with liquid ammonia. Analytical data indicated the composition is Te_3N_4 rather than Te_4N_4. This conclusion is supported by the recent structural determination of $Te_6N_8(TeCl_4)_4$ (**12**) from tellurium tetrachloride and tris(trimethylsilyl)amine.[58]

4.4.1.8 Tellurium Azides

Several explosive species in which three or more azido groups are bonded to tellurium have been well characterized.[59] The salt $[Te(N_3)_3][SbF_6]$ is formed from the reaction of $Te_4[SbF_6]_2$ with potassium azide in liquid sulfur dioxide. The neutral binary tellurium azide $Te(N_3)_4$ is prepared by the reaction of TeF_4 (in $CFCl_3$)[60] or TeF_6 (in CH_3CN)[61] with trimethylsilyl azide.

In a similar fashion, $[Me_4N][TeF_5]$ reacts with trimethylsilyl azide to produce $[Me_4N][Te(N_3)_5]$.[60] The reaction of $Te(N_3)_4$ with ionic azides generates the $[Te(N_3)_6]^{2-}$ anion, which has distorted octahedral geometry.[61]

4.4.2 Cations

4.4.2.1 The Thiazyl Cation, $[SN]^+$

Thiazyl salts are prepared by the reaction of NSF with AsF_5 or SbF_5 or from $(NSCl)_3$ by reaction with $Ag[AsF_6]$ in liquid SO_2.

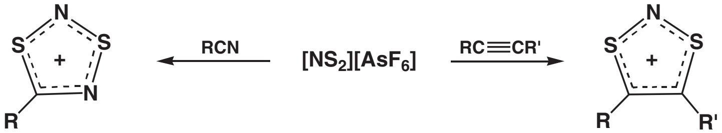
The thiazyl cation is used for the preparation of other important S–N compounds. For example, the insertion reactions with S_4N_4 or SCl_2 produce $[S_5N_5]^+$ or the acyclic $[ClSNSCl]^+$ cation,[62] respectively, and the reaction with sulfur gives $[S_2N]^+$ salts.

4.4.2.2 The Dithianitronium Cation, $[S_2N]^+$

The $[S_2N]^+$ cation is an important reagent in S–N chemistry,[63] especially in thermally allowed cycloaddition reactions with organic nitriles and alkynes, which give quantitative yields of heterocyclic cations (Scheme 3). It is conveniently prepared by reaction of $S_3N_2Cl_2$ with AsF_5 and S_8 in liquid SO_2.[63b] The $[SNS]^+$ cation is linear with S–N bond distances in the range indicating a bond order of two, *i.e.*, $S{=}N^+{=}S$.

4.4.2.3 The Dithiatriazyl Cation, $[S_2N_3]^+$

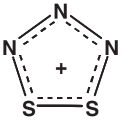
The cyclic six π-electron $[S_2N_3]^+$ cation (**13**) is the only example of a nitrogen-rich, binary S–N cation. The thermally stable salt $[S_2N_3]_2[Hg_2Cl_6]$ is obtained from the reaction of $(NSCl)_3$ with $HgCl_2$ in CH_2Cl_2.[64]



Scheme 3 *Some cycloaddition reactions of $[NS_2][AsF_6]$*

4.4.2.4 *The Trithia and Triselena-Diazyl Cations $[E_3N_2]^{+\bullet}$, $[E_6N_4]^{2+}$ and $[E_3N_2]^{2+}$ (E=S, Se)*

The $[E_3N_2]^{+\bullet}$ radical cations (**14**, E=S, Se) are prepared by oxidation of E_4N_4 with reagents such as AsF_5 or HSO_3F.[65] $[S_3N_2]^{+\bullet}$ has been well characterized in solution by its five-line (1:2:3:2:1) EPR signal. All the possible selenathiadiazolyl radicals $[Se_{(3-n)}S_nN_2]^{+\bullet}$ (n = 0–3) have also been identified by their EPR spectra.[32] In the solid state these five-membered rings form dimers of the type **15** (E=S, Se).



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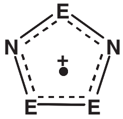

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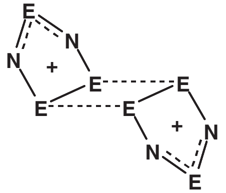

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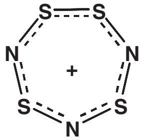

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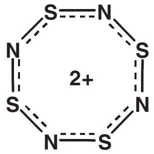

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The lattice-stabilization effects allow the isolation of $[MF_6]^-$ salts (M=As, Sb) of $[S_3N_2]^{2+}$ in the solid state from the cycloaddition of $[SN]^+$ and $[S_2N]^+$ cations in SO_2.[66] The S–S and S–N bond distances in the planar, monomeric dication are shorter than those in the dimeric radical cation dimer, as anticipated for the removal of an electron from a π^* orbital.

The selenium analogue $[Se_3N_2]^{2+}$ is prepared by the oxidation of Se_4N_4 with an excess of AsF_5 (Scheme 2).[65] In contrast to $[S_3N_2]^{2+}$, it does not dissociate significantly to $[SeN]^+$ and $[Se_2N]^+$ in solution.

4.4.2.5 *The Thiotrithiazyl Cation, $[S_4N_3]^+$*

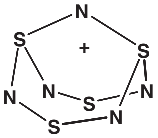
The salt $[S_4N_3]Cl$ is obtained as a yellow solid by the reaction of S_4N_4 or $[S_3N_2Cl]Cl$ with S_2Cl_2 in CCl_4.[42] The 10 π-electron $[S_4N_3]^+$ cation (**16**) is a planar seven-membered ring with approximately equal S–N bond lengths and an S–S bond. A deformation density study of $[S_4N_3]Cl$ indicates significant charge transfer as a result of the close contacts (2.81–2.82 Å) between Cl^- and the two sulfur atoms of the S–S bond.[67a] In addition, there are π-facial interactions between Cl^- and the $[S_4N_3]^+$ ring involving primarily the other two sulfur atoms.[67b]

4.4.2.6 *The Cyclotetrathiazyl Dication, $[S_4N_4]^{2+}$*

The 10 π-electron $[S_4N_4]^{2+}$ cation is prepared by the oxidation of S_4N_4 with an excess of a Lewis acid, such as $SbCl_5$ or AsF_5, or with $S_2O_6F_2$ (Scheme 1).[42] The $[S_4N_4]^{2+}$ cation (**17**) is a planar eight-membered ring with equal S–N bond lengths.

4.4.2.7 The Tetrasulfur Pentanitride Cation, $[S_4N_5]^+$

The nitrogen-rich $[S_4N_5]Cl$ is a yellow-orange, hygroscopic solid which decomposes violently on heating. It is readily prepared from $(NSCl)_3$ and bis(trimethylsilyl)sulfur diimide.[42] $[S_4N_5]Cl$ has a polymeric, predominantly ionic, structure in which bicyclic $[S_4N_5]^+$ cations (**18**) are bridged by Cl^- anions. A covalent modification has also been characterized.[68]



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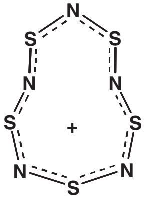

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4.4.2.8 The Cyclopentathiazyl Cation, $[S_5N_5]^+$

The 14 π-electron $[S_5N_5]^+$ cation is formed by the reaction of S_4N_4 with the $[SN]^+$ cation.[42] The planar, 10-membered ring usually has an azulene shape (**19**), with alternating sulfur and nitrogen atoms. Electrochemical reduction of $S_5N_5{}^+$ salts in acetonitrile produces the polymer $(SN)_x$.

4.4.3 Anions

Sulfur and nitrogen form a variety of binary anions with acyclic, cyclic and cage structures.[69,70] The Se–N anions are only known in metal complexes. S–N anions play an important role in the formation of cyclic sulfur imides and as constituents of solutions of sulfur in liquid ammonia.

4.4.3.1 The Sulfur Diimide Dianion, $[SN_2]^{2-}$

The pale yellow salt $K_2[SN_2]$ is prepared from $(Me_3SiN)_2S$ and $K(O^tBu)$.[70] The dilithium salt is generated from $(Me_3SnN)_2S$ and MeLi.[71] The S=N bond distances in the [K(18-crown-6)]$^+$ salt are *ca.* 0.05 Å longer than the S=O bonds in SO_2.[72]

$K_2[SN_2]$ is an important reagent for the preparation of other sulfur diimide derivatives when $(Me_3SiN)_2S$ is not sufficiently reactive. For example, both acyclic and cyclic arsenic(III) compounds, $(^tBu_2AsN)_2S$ and $(^tBuAsNSN)_2$, respectively, have been obtained in this way.[70] Protonation of the anion $[SN_2]^{2-}$ by acetic acid in diethyl ether produces the thermally unstable sulfur diimide $S(NH)_2$. Salts of mono-alkylated or arylated sulfur diimide anion $[RNSN]^-$ (R=aryl, ^tBu, $SiMe_3$) in *cis* configurations with very short-terminal S–N bond lengths are prepared by Si–N cleavage of $RNSNSiMe_3$ with $[(Me_2N)_3S][Me_3SiF_2]$.[73,74]

4.4.3.2 The [SSNS]$^-$ Anion

The orange-red $[S_3N]^-$ anion is obtained by the addition of triphenylphosphine to a solution of an $[S_4N]^-$ salt in acetonitrile.[69] It can be isolated as a salt in combination with a $[Ph_4As]^+$ or $[N(PPh_3)_2]^+$ cation. The vibrational spectra suggest an unbranched $[SNSS]^-$ arrangement of atoms (**20**). Mass spectrometry experiments support the SNSS connectivity in the gas phase.[75]

4.4.3.3 The [SSNSS]$^-$ Anion

The dark blue $[S_4N]^-$ anion is best prepared by the thermolysis of salts of the $[S_3N_3]^-$ ion in boiling acetonitrile.[69] The $[S_4N]^-$ ion (**21**) is a planar (*cis,trans*) chain with nitrogen as the central atom and short, terminal S–S bonds.

4.4.3.4 Sulfur–-Liquid Ammonia Solutions

Sulfur dissolves in liquid ammonia to give intensely coloured solutions. The colour is concentration-dependent and the solutions are photosensitive. Several S–N anions are present in such solutions.[76,77] The primary reduction products are polysulfides S_x^{2-}, which dissociate to polysulfur radical anions, notably the deep blue $S_3^{-\bullet}$ ion. In a 1M solution, the major S–N anion is *cyclo*-$[S_7N]^-$ with smaller amounts of **21** and a trace of **20**.[76]

4.4.3.5 The [S$_2$N$_2$H]$^-$ Anion

The $[S_2N_2H]^-$ anion (**22**) is formed by the treatment of $S_4N_4H_4$ with potassium amide in liquid ammonia.[76] Although the $[S_2N_2H]^-$ anion has not been isolated as an ionic salt, numerous metal complexes in which **22** acts as a bidentate (*S*,*N*) ligand are known.

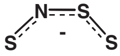
4.4.3.6 The [S$_3$N$_3$]$^-$ Anion

The 10 π-electron $[S_3N_3]^-$ anion (**23**) is produced, together with $[S_4N_5]^-$, from the reaction of S_4N_4 with a variety of nucleophilic reagents. The best preparation involves the reaction of S_4N_4 with an azide of a large cation, *e.g.*, $[(Ph_3P)_2N]^+$.[69] Alkali metal salts of $[S_3N_3]^-$ are explosive in the solid state.The cyclic $[S_3N_3]^-$ anion is essentially planar with almost equal S–N bond lengths.

4.4.3.7 The Tetrasulfur Pentanitride Anion, [S$_4$N$_5$]$^-$

The yellow $[S_4N_5]^-$ anion (**24**) was first obtained from the methanolysis of $(Me_3SiN)_2S$. It can also be prepared by the treatment of S_4N_4 with nucleophiles.[69] The structure of **24** is closely related to that of S_4N_4. In $[S_4N_5]^-$, five of the six edges of the S_4 tetrahedron are bridged by nitrogen atoms. The unbridged S$\cdots$S distance is *ca.* 2.70 Å. Alkali metal salts of $[S_4N_5]^-$ are explosive when subjected to heat or mechanical shock, but salts with large counterions, *e.g.*, $[Ph_4As]^+$ or $[(Ph_3P)_2N]^+$, are safe to handle in the solid state.

The carefully controlled thermolysis of solutions of $[S_4N_5]^-$ in boiling acetonitrile generates $[S_3N_3]^-$ and, subsequently, the $[S_4N]^-$ anion.[69] The reaction of $[S_4N_5]^-$ with bromine or iodine produces pentasulfur hexanitride, S_5N_6, whereas oxidation with chlorine yields $[S_4N_5]Cl$.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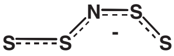
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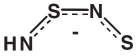
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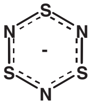
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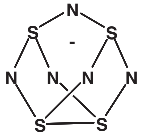
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4.5 Metal Complexes of Binary Chalcogen–Nitrogen Ligands

Important aspects of the coordination chemistry of binary chalcogen–nitrogen ligands include (a) the ability of metals to stabilize labile neutral and anionic binary S–N ligands, (b) the applications of metal complexes as reagents for the preparation of other S–N compounds, and (c) the possible incorporation of metals into sulfur–nitrogen chains to produce conducting materials.

4.5.1 Thionitrosyl and Selenonitrosyl Complexes

The NS molecule is stabilized by coordination to a transition metal and a large number of complexes, primarily with metals from groups 6–9, are known.[62,78] The most common preparative routes are reactions of (a) nitride complexes with a sulfur source, *e.g.*, S_8, propylene sulfide or sulfur halides, (b) $(NSCl)_3$ with transition-metal complexes, and (c) $[SN]^+$ salts with transition-metal complexes.

The thionitrosyl ligand is generally coordinated as a terminal, linear unit in which the bond angle $<$MNS is in the range 169–180°. The characteristic NS stretching vibration in the infrared spectrum is lowered from 1437 cm^{-1} in the cation $[SN]^+$ to 1050–1400 cm^{-1} in metal complexes (*cf.* 1205 cm^{-1} in neutral NS). The charge of the complex has a marked influence on the metal–NS back donation. The NS ligand behaves as a three-electron donor. The N–S bond distances in metal complexes vary between 1.45 and 1.59 Å (*cf.* 1.44 and 1.495 Å for $[SN]^+$ and NS, respectively). Comparison of the photoelectron spectra and electronic structures of M–NS and M–NO complexes indicates that NS is a better σ-donor and a stronger π-acceptor ligand than NO.

Reactions of metal–NS complexes include the conversion of the NS ligand in the dication $[Re(CO)_5(NS)]^{2+}$ to a thiazyl halide NSX (X=Cl, Br) by cesium halides. Oxygen transfer from an NO_2 to an NS ligand on the same metal centre to give a thiazate (NSO) complex occurs in ruthenium porphyrin complexes.[79] The treatment of an osmium thionitrosyl complex with triphenylphosphine converts the NS ligand to an $NPPh_3$ group and Ph_3PS.[80]

4.5.2 Cyclometallathiazenes

The term cyclometallathiazene refers to ring systems that contain only sulfur, nitrogen and one (or more) metal atoms. These heterocycles can formally be considered as complexes between cationic metal fragments and binary S–N anions in which, with the exception of the $[S_2N_2H]^-$ and $[S_4N_4]^{2-}$ ions, both the sulfur and nitrogen atoms are two-coordinate.[81,82] The synthesis of cyclometallathiazenes usually employs S_4N_4 as a source of the S–N fragment. The explosive regent Se_4N_4 has also been used to generate complexes of the $[Se_3N]^-$ and $[Se_2N_2H]^-$ anions. A safer route for the *in situ* generation of the anions $[Se_2N_2]^{2-}$ and $[Se_2N_2H]^-$ involves the use of $SeCl_4$ or, preferably, $SeOCl_2$, in liquid ammonia.[52,83]

Complexes containing the $[S_2N_2H]^-$ ion comprise the best-studied group of cyclometallathiazenes. The dark green nickel(II) derivative is readily obtained in good yields from the reaction of S_4N_4 with anhydrous $NiCl_2$ in methanol. The NH groups in $[M(S_2N_2H)_2]$ complexes are readily deprotonated to give mono- or di-anions, which can be converted to organic derivatives by treatment with alkyl halides.[82]

In addition to S_4N_4, a variety of S–N reagents, including $[S_3N_3]^-$, $S_4N_4H_4$/diazobicycloundecene, $[SnR_2(S_2N_2)]_2$ (R=Me, ^{n}Bu), and solutions of $[S_4N_3]Cl$ in liquid ammonia, provide a source of $[S_2N_2]^{2-}$ for metal complexes. DFT calculations for $[CoCpS_2N_2]$ indicate complete electron delocalization in the metallathiazene ring.[84a]

Complexes of the $[S_3N]^-$ anion are obtained in good yields *via* deprotonation of *cyclo*-S_7NH in the presence of metal halides or by using mercury(II) complexes $[Hg(S_7N)_2]$ or $[HgPh(S_7N)]$ as a source of $[S_3N]^-$. The $[SSNS]^-$ ligand is invariably chelated to the metal *via* the two terminal sulfur atoms.

The chelating $[S_2N_3]^{3-}$ ligand stabilizes early transition metals in high oxidation states [*e.g.*, V(V), Mo(VI) and W(VI)]. The thiazene segment of the ring is usually planar but, in some cases, the metal is tilted out of this plane. The electronic structures of six-membered cyclometallathiazenes $[MS_2N_3]$ have been investigated by DFT calculations.[84b] Charge transfer from the ligand to the M(VI) centre results in a strengthening of the S–N bonds compared to those in $[S_3N_3]^-$. Complexes of the monoanion $[S_2N_3]^-$ are obtained by the reactions of $[PPh_4][Pd_2Cl_6]$ with S_5N_6[57] or, preferably, $(Me_3SiNSN)_2S$.[85]

The only example of the eight-membered $[MS_3N_4]$ ring system is $[TiCp_2S_3N_4]$, obtained in low yield by reaction of S_4N_4 with $[TiCp_2(CO)_2]$. There is also only a single representative of the $[MS_4N_3]$ ring system, $[PtCl(S_4N_3)]$, in which the hypothetical $[S_4N_3]^-$ ligand acts as a tridentate (*S,N,S′*) ligand. In $[IrCl(CO)(S_4N_4)PPh_3]$ and $[PtCl_3(S_4N_4)]^-$, the $[S_4N_4]^{2-}$ anion acts as a tridentate ligand coordinating *facially* to the metal through two sulfur and one nitrogen atoms.[86] By contrast, $[S_4N_4]^{2-}$ adopts a *meridional* (*S,S,N*) geometry in the platinum(IV) complex $[PtCl_2(S_4N_4)(PMe_2Ph)]$, which is converted to a *facial S,N,N* isomer in boiling chloroform.[87]

4.6 Chalcogen–Nitrogen Halides

4.6.1 Thiazyl Halides NSX (X=F, Cl, Br) and the $[NSX_2]^-$ Anions (X=F, Cl)

Thiazyl fluoride is a moisture-sensitive, thermally unstable gas.[88] It is conveniently generated by decomposition $FC(O)NSF_2$ or $Hg(NSF_2)_2$. It forms the cyclic trimer $(NSF)_3$ at room temperature.

Monomeric NSCl is formed as a greenish-yellow gas by pyrolysis of $(NSCl)_3$ under vacuum or $[S_4N_3]Cl$ in an inert gas stream. NSCl may also be generated in solutions of $(NSCl)_3$ in liquid SO_2 at room temperature or in CCl_4 at 70 °C.[89] NSF and NSCl are bent molecules ($<NSF = 117°$, $<NSCl = 118°$)) with sulfur–nitrogen bond lengths of 1.448 and 1.450 Å, respectively, consistent with substantial triple-bond character. The sulfur–halogen distances are 1.643 Å (X=F) and 2.161 Å (X=Cl).

Monomeric thiazyl halides can be stabilized by coordination to transition metals.[90] The NSF complexes are conveniently prepared in SO_2. The most general route to M–NSCl complexes involves the reactions of the cyclic trimer $(NSCl)_3$ with anhydrous metal chorides in solvents such as CH_2Cl_2 or CCl_4. For example, 1:1 complexes $[MCl_5(NSCl)]$ (M=Nb, Ta) are formed from MCl_5 and $(NSCl)_3$, whereas VCl_4 yields a dimeric structure $[VCl_3(NSCl)_2]$. However, these reactions are markedly dependent on reaction conditions.

The conversion of coordinated NSCl into a nitrido ligand provides a useful synthesis of transition-metal nitrides. For example, treatment of $[ReCl_4(NSCl)(POCl_3)]$ with triphenylphosphine generates the nitrido complex $[ReNCl_2(PPh_3)_2]$. By contrast, the reduction of two juxtaposed NSCl ligands in $[ReCl_3(NSCl)_2(POCl_3)]$ with triphenylphosphine generates the novel cyclometallathiazene $[Ph_3PCl][ReCl_4(S_2N_2)]$.[91]

Thiazyl halide monomers undergo a variety of reactions that can be classified under the general headings (a) reactions involving the π–system of the N≡S triple bond, (b) nucleophilic substitution, (c) halide abstraction, and (d) halide addition. The cycloaddition of NSF with hexafluoro-1,3-butadiene provides an example of a type (a) reaction.

Nucleophilic replacement of the fluoride substituent in NSF usually results in a rearrangement with loss of the formal N≡S triple bond. The reaction of NSF with strong fluoride ion acceptors, *e.g.*, MF_5 (M=As, Sb) in liquid SO_2 was the first synthesis of $[SN]^+$ salts.[88] Thiazyl halide monomers NSX also undergo nucleophilic addition with halide ions to give ternary anions of the type $[NSX_2]^-$, *e.g.*, $Cs[NSF_2]$ and $[(Me_2N)_3S][NSF_2]$ that have been characterized by vibrational spectra.[92] The $[NSCl_2]^-$ anion has been isolated in salts with large counter-anions.[93] The $[NSCl_2]^-$ anion has a slightly distorted C_s structure with a very short S–N bond (1.44 Å) and two loosely bound chlorine atoms [d(S–Cl)=2.42 Å].

Selenazyl halides NSeX have not been characterized either as monomers or cyclic oligomers. However, the monomeric ligand is stabilized in metal complexes of the type $[MCl_4(NSeCl)]_2$ (M=Mo, W).[94]

4.6.2 Thiazyl Trifluoride, NSF_3, and Haloiminosulfur Difluorides, $XNSF_2$ (X=F, Cl)

Thiazyl trifluoride, a colourless gas, is prepared by the oxidative decomposition of $FC(O)NSF_2$ with AgF_2.[95] The chemical inertness of NSF_3 resembles that of SF_6. For example, it does not react with sodium metal below 200 °C.

Gaseous NSF_3 is a distorted tetrahedron with C_{3v} geometry and an $S{\equiv}N$ triple bond length of 1.416 Å, consistent with triple-bond character. The bond angle <FSF is *ca.* 94° and the S–F distance is 1.55 Å. The mixed halide derivatives $XNSF_2$ (X=Cl, Br, I) are obtained by the reaction of $Hg(NSF_2)_2$ with halogens. This reaction also gives rise to $FNSF_2$, a structural isomer of NSF_3. The chloro derivative $ClNSF_2$ has a *cis* arrangement of the lone pairs on the sulfur and nitrogen atoms.

The reactions of NSF_3 can be classified under the following categories: (a) reactions with electrophiles, (b) addition to the SN triple bond, and (c) reactions with nucleophiles. Metal complexes with up to four NSF_3 ligands coordinated to the M^{2+} centre have been characterized. NSF_3 is introduced into transition-metal complexes by SO_2 displacement reactions, and forms *N*-bonded adducts with fluoro Lewis acids, *e.g.*, $F_5As \cdot NSF_3$.[88] With BCl_3, however, halogen exchange occurs to produce the acyclic cation $[N(SCl)_2][BCl_4]$. The oxidative addition of an S–F bond of NSF_3 to an Ir(I) centre gives a complex of the thiazyl difluoride anion $[NSF_2]^-$.[96] In metal complexes and in the adducts with fluoro Lewis acids, the S–N and S–F bonds are both shortened significantly compared to their values in free NSF_3.

Protonation of NSF_3 by the superacid HSO_3F/SbF_5 produces the thermally unstable $[HNSF_3]^+$ cation.[88] Similarly, alkylation of NSF_3 with $[RSO_2][AsF_6]$ (R=Me, Et) gives $[RNSF_3]^+$ and $[MF_6]^-$ (M=As, Sb) cations.[97] The reaction of $[MeNSF_3]^+$ with sodium fluoride at elevated temperatures yields $MeN{=}SF_4$.[88] Treatment of NSF_3 with an excess of HF results in a double addition to give the stable pentafluorosulfur amine H_2NSF_5.[88]

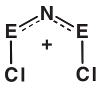
Nucleophilic reagents such as secondary amines, alcohols or organolithium reagents convert NSF_3 into monosubstituted derivatives NSF_2R (R=R'_2N, $R'O$, Ar) with retention of the $N{\equiv}S$ bond.[162]

4.6.3 Acyclic Chalcogen–Nitrogen–Halogen Cations $[N(ECl)_2]^+$ (E=S, Se) and $[N(SeCl_2)_2]^+$

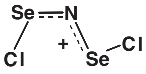
The most straightforward route to the acyclic cation $[N(SCl)_2]^+$ (**25a**) is the reaction of $[NS]^+$ with SCl_2. Other preparative methods include the reactions of (a) $(NSCl)_3$ with SCl_2 in the presence of a metal chloride (*e.g.*, $AlCl_3$ or $SbCl_5$)[98] or (b) an $[SCl_3]^+$ salt with $N(SiMe_3)_3$ in CCl_4.[99]

The treatment of $N(SiMe_3)_3$ with $SeCl_4$ yields Se_2NCl_3 (**26a**), which reacts with $GaCl_3$ to produce $[N(SeCl)_2][GaCl_4]$ containing the selenium analogue **25b**.[100] The bromo derivative **26b** is prepared from $SeBr_4$ and $N(SiMe_3)_3$.[101] Equimolar quantities of $[SeCl_3][AsF_6]$ with $N(SiMe_3)_3$ in $CFCl_3$ produce the novel cation $[N(SeCl_2)_2]^+$ (**27**).[102] Surprisingly, $[SeCl_3][SbCl_6]$ reacts with

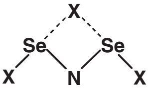
$N(SiMe_3)_3$ in a different way to give the cation **25b** as the *cis*,*cis* isomer.[103a] The reagent $[SeCl_3][FeCl_4]$ produces $[N(SeCl)_2]_2[FeCl_4]$ in which the cation **25b′** has a *cis*,*trans* geometry.[103b]



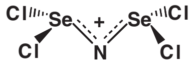
25a (E =S)
25b (E = Se)



25b'



26a (X = Cl)
26b (X = Br)



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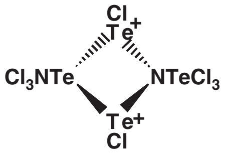
4.6.4 Tellurium–Nitrogen–Chlorides $[Te_4N_2Cl_8]^{2+}$ and $Te_{11}N_6Cl_{26}$

The $[AsF_6]^-$ salt of the $[Te_4N_2Cl_8]^{2+}$ dication (**28**) is obtained from the reaction of $TeCl_4$ with $N(SiMe_3)_3$ in a 2:1 molar ratio in acetonitrile.[104] In boiling toluene this reaction generates $[Te_{11}N_6Cl_{26}] \cdot C_7H_8$, comprised of a $[Te_5N_3Cl_{10}]^+$ cation (**29**) and a $[Te_5N_3Cl_{12}]^-$ anion linked to a $TeCl_4$ molecule.[105]



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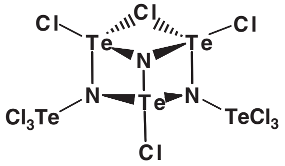

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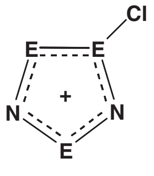
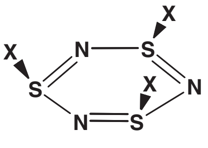
4.6.5 Thiodithiazyl and Selenadiselenazyl Dichloride $[E_3N_2Cl]Cl$ (E=S, Se)

The $[S_3N_2Cl]^+$ cation (**30a**) is an important intermediate in the synthesis of other S–N compounds such as $(NSCl)_3$, $[S_4N_3]^+$, S_4N_4 and S_3N_2O.[106] It is conveniently prepared by refluxing S_2Cl_2 with dry, finely ground ammonium chloride. The selenium analogue $[Se_3N_2Cl]^+$ (**30b**) is obtained as the $[GaCl_4]^-$ salt by the reduction of the acyclic cation **25b** with Ph_3Sb.[107] The explosive and insoluble compound $Se_3N_2Cl_2$, which also contains the cyclic cation **30b**, is formed in the reaction of Se_2Cl_2 with trimethylsilyl azide.[108]



30a (E = S)
30b (E = Se)



31a (X = Cl)
31b (X = F)

4.6.6 Cyclotrithiazyl Halides $(NSX)_3$ (X=Cl, F)

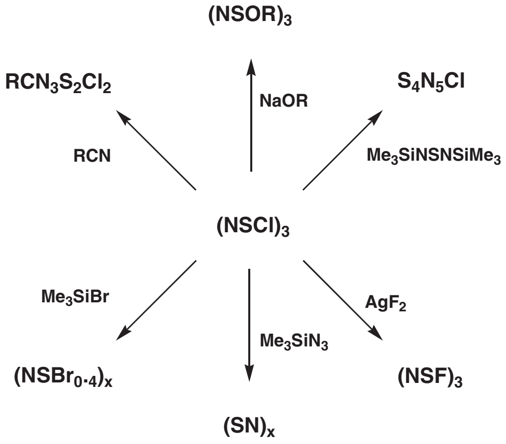
A safe and convenient procedure for the preparation of $(NSCl)_3$ (**31a**) is the chlorination of $[S_3N_2Cl]Cl$ with either Cl_2 or SO_2Cl_2.[106] The fluoride $(NSF)_3$ (**31b**) is obtained in high yield by stirring **31a** with AgF_2 in CCl_4 at room temperature.[88] The six-membered rings **31a** and **31b** adopt chair conformations with all three halogen atoms in axial positions. This arrangement is stabilized by the anomeric effect.[24]

The cyclic trimer **31a** is a versatile reagent in S–N chemistry (Scheme 4). It dissociates readily into monomeric NSCl in solution[89] and, hence, provides a source of the $[SN]^+$ cation. The S_3N_3 ring in the fluoride **31b** is more robust than that in **31a**. For example, the salts $[N_3S_3F_2][MF_6]$ are isolated from the reaction of **31b** with MF_5 (M=As, Sb), but they decompose to give the bicyclic cation $[S_4N_5]^+$.

Cyclotrithiazyl chloride is also a useful reagent in organic chemistry in the fusion of 1,2,5-thiadiazoles to quinones as well as for the synthesis of (a) isothiazoles from 2,5-disubstituted furans and (b) *bis*-1,2,5-thiadiazoles from *N*-alkylpyrroles.[10] Alkenes and alkynes react readily with $(NSCl)_3$ to give 1,2,5-thiadiazoles, while 1,4-diphenyl-1,3-butadiene gives a variety of heterocyclic products including a *bis*(1,2,5-thiadiazole).[10]

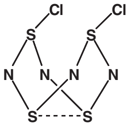
4.6.7 Dihalocyclotetrathiazenes $S_4N_4X_2$ (X=Cl, F) and Cyclotetrathiazyl Fluoride $(NSF)_4$

The oxidative addition of one equivalent of X_2 (X=Cl, F) to S_4N_4 under mild conditions produces 1,5-$S_4N_4X_2$.[106] The structure of 1,5-$S_4N_4Cl_2$ (**32**) consists of a folded eight-membered ring [d(S···S) = 2.45 Å] with the exocyclic substituents in *exo,endo* positions. The reaction of **32** with $(Me_3SiN)_2S$ is the best route to the binary sulfur nitride S_5N_6 (**11**).[42]



Scheme 4 *Some reactions of* $(NSCl)_3$

The fluorination of S_4N_4 with an excess of AgF_2 in CCl_4 under reflux gives $(NSF)_4$ (**33**).[88] It is a boat-shaped ring with juxtaposed long (1.66 Å) and short (1.54 Å) S–N bonds as a result of Jahn–Teller distortion.[109]



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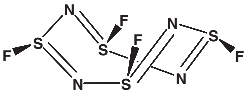

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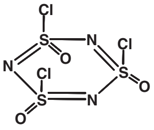
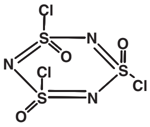
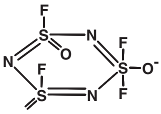


34a



34b



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4.6.8 Sulfanuric Halides $[NS(O)X]_3$ (X=Cl, F)

Sulfanuric halides contain the characteristic group –N=S(O)X– (X=Cl, F). Sulfanuric chloride $[NS(O)Cl]_3$ (**34**) is best prepared by the treatment of $SOCl_2$ with sodium azide in acetonitrile at −35 °C. It may also be obtained as a mixture of α- and β-isomers (**34a**, **34b**) in a two-stage reaction from H_2NSO_3H and PCl_5.[106] The fluoride $[NS(O)F]_3$ is formed as a mixture of isomers by the fluorination of $[NS(O)Cl]_3$ with SbF_3.

The isomer α-$[NS(O)Cl]_3$ (**34a**) is a six-membered ring in the chair form with equal S–N bond lengths (1.57 Å). The three chlorine atoms are in axial positions on the same side of the ring. The β-isomer **34b** has two axial and one equatorial chlorine atoms.[110]

The fluoride $[NS(O)F]_3$ is more stable thermally and towards nucleophilic reagents than the corresponding chloride. In warm water, however, hydrolysis occurs to give the $[N_3S_3O_4F_2]^-$ anion.[106] All three fluorine atoms in $[NS(O)F]_3$ can be replaced by primary or secondary amines at 80–90 °C in the absence of a solvent. The Friedel–Crafts reaction with benzene at reflux in the presence of $AlCl_3$ gives two isomers of $[NS(O)Ph]_3$.

Fluoride addition to $[NS(O)F]_3$ to give the anion $[N_3S_3O_3F_4]^-$ (**35**) is accomplished quantitatively by reaction with $[(Me_2N)_3S][Me_3SiF_2]$.[111]

4.7 Chalcogen–Nitrogen Oxides

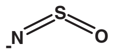
4.7.1 The Thionyl Imide Anion, $[NSO]^-$

Alkali-metal thionylimides are prepared by the reaction of Me_3SiNSO with the appropriate alkali-metal *tert*-butoxide in THF.[112] The more soluble salt $[(Me_2N)_3S][NSO]$ has also been reported.[113]

The bent $[NSO]^-$ anion (**36**) in the tetramethylammonium salt $[Me_4N][NSO]$ has approximately equal S–N and S–O bond lengths of 1.43 and 1.44 Å, respectively, and a bond angle <NSO of *ca.* 127°.[114] Salts of the $[NSO]^-$ anion can be used for the synthesis of both transition-metal and main group element thionyl imides by metathetical reactions.[70]

4.7.2 The Thionitrite and Perthionitrite Anions, $[SNO]^-$ and $[SSNO]^-$

The red $[SSNO]^-$ anion (**37**) is produced by the reaction of an ionic nitrite with elemental sulfur or a polysulfide in acetone, DMF or DMSO.[115] The $[SSNO]^-$ anion has a planar *cis* structure with a short S–S distance (1.99 Å), and S–N and N–O distances of 1.67 and 1.22 Å, respectively. The treatment of $[SSNO]^-$ with triphenylphosphine produces the thionitrite anion $[SNO]^-$ (**38**) with a bond angle of *ca.* 120° at nitrogen and S–N and N–O bond lengths of 1.69 and 1.21 Å, respectively.



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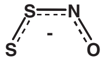

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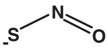

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4.7.3 The $[SO_xN_3]^-$ (x = 2, 3) Anions

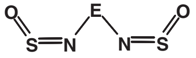
Yellow $[(SO_2)_2N_3]^-$ salts, obtained from SO_2 solutions of CsN_3 or $[Me_4N]N_3$, lose SO_2 to give the corresponding $[SO_2N_3]^-$ salts.[116] The $[SO_3N_3]^-$ anion is prepared by the reaction of $Cs[SO_3Cl]$ with trimethylsilyl azide. The weaker Lewis acidity of SO_2 compared to that of SO_3 is reflected in an increase in the S–N bond distance of 0.23 Å for $[SO_2N_3]^-$ compared to $[SO_3N_3]^-$ in the Cs^+ salts.

4.7.4 *Bis*(Sulfinylamino)Chalcogenanes $E(NSO)_2$ (E=S, Se, Te)

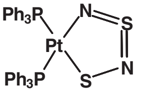
Bis(sulfinylamino)chalcogenanes $E(NSO)_2$ (E=S, Se, Te) are useful reagents for the synthesis of chalcogen–nitrogen ring systems.[15] The best method to prepare $S(NSO)_2$ is by the treatment of Me_3SiNSO with SCl_2 at reflux in the absence of solvent. This method can be adapted to the synthesis of $Se(NSO)_2$.[117] The recommended procedure for preparing the tellurium analogue involves the metathesis reaction of *bis*(trifluoromethylthio)tellurium with $[Hg(NSO)_2]$ at 50 °C.[15]

The series $E(NSO)_2$ (**39a–c**; E=S, Se, Te) exhibit planar, acyclic structures with a *cis* arrangement about the two S=N bonds. The central E–N bonds are essentially single bonds. The S=N bond distances fall in the double bond range with a significant shortening of this bond along the series.

The thermal or base-promoted elimination of SO_2 from $E(NSO)_2$ gives rise to chalcogen–nitrogen ring systems. For example, the reactions of **39a** or **39b** with $TiCl_4$ produce the polymeric adducts $[ESN_2 \cdot TiCl_4]_n$ (E=S, Se).[15] The cyclometallathiazene **40** is formed upon the treatment of **39a** with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$.[81]



39a (E = S)
39b (E = Se)
39c (E = Te)



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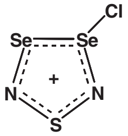

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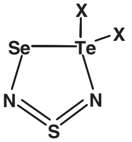
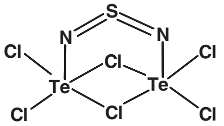


42a (X = Cl)
42b (X = Br)



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The reactions of **39b** with Lewis acids MF_5 (M=As, Sb) in liquid SO_2 produce the dimeric dication $[Se_2SN_2]_2^{2+}$ as $[MF_6]^-$ salts,[117] whereas PCl_5 or $SeCl_4$ give rise to the cation $[ClSe_2SN_2]^+$ (**41**) as the chloride salt. The corresponding reactions with tellurium tetrahalides TeX_4 (X=Cl, Br) generate $X_2TeSeSN_2$ (**42**), a five-membered ring that contains all three chalcogens.[118]

In contrast to the behaviour of **39a**, the acyclic Te(IV) compound $Cl_2Te(NSO)_2$ can be isolated from the reaction of **39c** with Cl_2 under mild conditions.[119] Subsequent reaction of $Cl_2Te(NSO)_2$ with Cl_2 generates the tricyclic compound $Cl_6Te_2N_2S$ (**43**).

4.7.5 Cyclic Chalcogen–Nitrogen Oxides

The sulfur–nitrogen oxide S_3N_2O (thiodithiazyl oxide) is a red liquid, which was first synthesized by the reaction of $(Me_2SnS_2N_2)_2$ with SOF_2, but it is more conveniently prepared from $[S_3N_2Cl]Cl$ (Equation 1).[120]

$$[S_3N_2Cl]Cl + HCOOH \rightarrow S_3N_2O + 2HCl + CO \qquad (1)$$

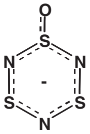
The ^{15}N NMR spectrum of S_3N_2O indicates a five-membered ring structure. Lewis acids such as $SnCl_4$ form *O*-bonded *cis*-adducts with two molecules of S_3N_2O. The neutral, six-membered ring compound $S_3N_2O_5$ is obtained when S_4N_4 or $S(NSO)_2$ is treated with an excess of SO_2.[106]

Cyclotetrathiazene dioxide $S_4N_4O_2$ is obtained as orange-yellow needles by the condensation of $[S_3N_2Cl]Cl$ with sulfamide $SO_2(NH_2)_2$.[106] Two –N=S=N– units bridge a sulfur atom and an SO_2 group to form a boat-shaped eight-membered ring.

Controlled air oxidation of $[S_3N_3]^-$ (28) generates red $[S_3N_3O]^-$ (**44**) and purple $[S_3N_3O_2]^-$ (**45**), sequentially.[69] The $[S_3N_3O_2]^-$ anion is also formed by ring contraction of $S_4N_4O_2$ under the influence of azide anion. The yellow anion $[S_3N_3O_4]^-$ (**46**) is produced as the $[S_6N_4]^{2+}$ salt from the treatment of $S_4N_4O_2$ with SO_3.[106]

The reaction of $SO_2(NH_2)_2$ with sulfuryl chloride followed by the treatment with ammonia produce the ammonium salt of cyclic, chair-shaped $[N_3S_3O_6]^{3-}$ (**47a**) anion.[121] The selenium analogue $[N_3Se_3O_6]^{3-}$ (**47b**) adopts a similar conformation.

The yellow $[S_4N_5O]^-$ anion (**48**) is obtained as the water-soluble ammonium salt from the reaction of $SOCl_2$ with liquid ammonia.[69] Its structure is related to that of the binary anion $[S_4N_5]^-$ (**24**). The $[S_4N_5O_2]^-$ ion (**49**) is prepared from **45** by oxidative-addition with $PhICl_2$, followed by the treatment with $(Me_3SiN)_2S$.[122]



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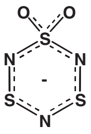

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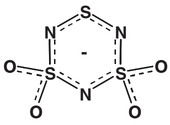

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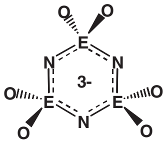
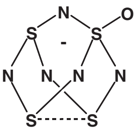


47a (E = S)
47b (E = Se)



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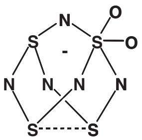

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4.8 Acyclic Organic Chalcogen–Nitrogen Compounds

Acyclic organic compounds containing an E–N (E=S, Se, Te) functional group are conveniently divided into those in which the organic group is attached to (a) nitrogen or (b) sulfur.

4.8.1 Chalcogenonitrosyls, RNE (E=S, Se)

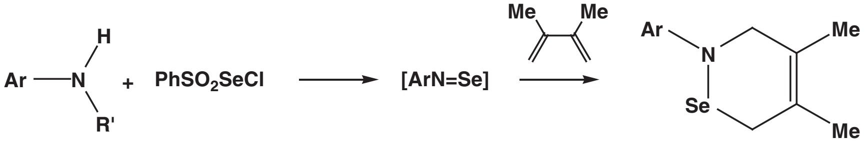
The thionitrosyl group may be stabilized either by a dimethylamino substituent or by the use of highly bulky *ortho*-substituted aryl groups. *N*,*N*′-Dimethylthionitrosoamine M_2NNS is obtained as a deep purple solid from the reaction of 1,1-dimethylhydrazine with sulfur or by the reduction of Me_2NNSO with $LiAlH_4$. 2,4-Di-*tert*-butyl-6-cyanothionitrosobenzene, produced by thermal or photochemical reactions, has been detected in argon or undecane matrices at 12 K.[123] An alternative approach to thionitrosoarenes involves the reaction of amines with SCl_2.[124] This method also produces selenonitrosoarenes ArN=Se.[125] The Diels–Alder cycloaddition of ArN=Se species with dimethylbutadiene gives 1,2-selenazine derivatives in low yields (Scheme 5).

4.8.2 Organic Chalcogenylamines RNEO (E=S, Se, Te)

Organic sulfinylamines RNSO are typically prepared by the reaction of a primary amine or, preferably, a silylated amine with thionyl chloride. A recent example is the preparation of FcNSO (Fc=ferrocenyl).[126] The important reagent Me_3SiNSO is obtained by the reaction of thionyl chloride with tris(trimethylsilyl)amine at 70 °C in the presence of $AlCl_3$.[127]

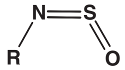
Organic sulfinylamines, *e.g.*, Ph_3CNSO, have planar, *cis* structures (**50**).[128] In the gas phase, MeNSO has S=N and S=O bond lengths of 1.51–1.52 and 1.45–1.47 Å, respectively, and the bond angle <NSO is *ca.* 117°.

The seleninylamine $(^tBuNSeO)_2$, prepared by the reaction of *tert*-butylamine with $SeOCl_2$, has a dimeric structure (**51**) in which the two exocyclic oxo substituents are in a *cis* configuration with respect to the Se_2N_2 ring.[129] The Se–N bonds are slightly longer than single bonds and the Se=O bonds are



Scheme 5 *Generation and trapping of selenonitrosoarenes*

indicative of double bonds. The tellurium analogue ($(^tBuNTeO)_n$) has not been isolated, but the tetramer **52** has been obtained as an *O*-bonded di-adduct with $B(C_6F_5)_3$.[130]



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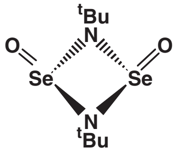

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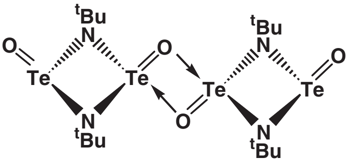


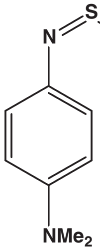
52

A variety of transition-metal complexes of RNSO ligands have been structurally characterized.[131] Three bonding modes, π(*N*,*S*), σ(*S*)-trigonal and σ(*S*)-pyramidal, are observed. Side-on (*N*,*S*) coordination is favoured by electron-rich (d^8 or d^{10}) metal centres, while the σ(*S*)-trigonal mode is preferred for less electron-rich metal centres (or those with competitive strong π-acid co-ligands).

A characteristic reaction of sulfinylimines RNSO is the quantitative addition of R′Li reagents to form complexes of the type Li[RNS(R′)NR].[132] RNSO derivatives react with two equivalents of lithium *tert*-butylamide to give diazasulfite anions $[OS(NR)(N^tBu)]^{2-}$, which as their dilithium derivatives exist as hexameric 36 atom ($Li_{12}N_{12}O_6S_6$) clusters.[133] Monoazasulfite anions $[O_2SNR]^{2-}$ are obtained from the reaction of SO_2 with lithium derivatives of primary amines.[134] The treatment of magnesium anilide $[(thf)MgNPh]_6$ with SO_2 results in 12-fold insertion of SO_2 into the Mg–N bonds to form a 48 atom ($Mg_6S_{12}N_6O_{24}$) cluster that contains the azadisulfite dianion $[O_2S(\mu\text{-}NPh)SO_2]^{2-}$, which acts as a *bis*-chelating ligand towards the Mg^{2+} centres.[135]

4.8.3 *N*-Thiosulfinylamines, RNSS

The first *N*-thiosulfinylamine $4\text{-}Me_2NC_6H_4N{=}S{=}S$ (**53**) was obtained as a deep violet solid in low yield by the reaction of phosphorus pentasulfide with *N*,*N*′-dimethyl-4-nitrosoaniline. It has much higher thermal stability than the corresponding thionitrosoarenes.



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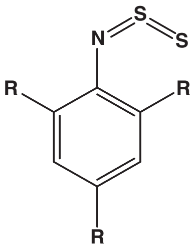
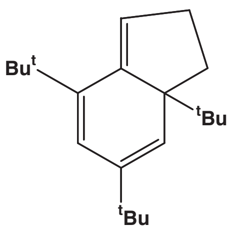


54a (R = Me)
54b(R = ^{t}Bu)



54b'

Thermally stable *N*-thiosulfinyl anilines may also be obtained by attaching an aryl group with bulky *ortho* substituents to the nitrogen atom. The derivatives **54a** and **54b** are obtained in high yields from the reaction of the corresponding aniline with S_2Cl_2 in diethyl ether in the presence of NEt_3. The derivative **54a** is purple, whereas **54b** is yellow in the solid state. The latter forms red solutions containing two isomers **54b** and **54b′**.[136,137] Compound **54a** has an acyclic NSS unit and does not form the cyclic isomer in solution.

Several compounds containing the SNSS functionality have been prepared and structurally characterized.[138]

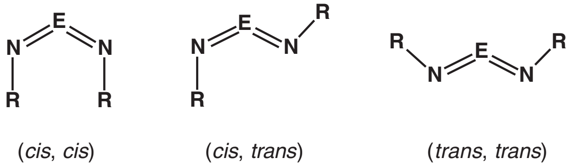
4.8.4 Chalcogen Diimides RN=E=NR (E=S, Se, Te)

The first sulfur(IV) diimide ^{t}BuN=S=N^{t}Bu was prepared *ca.* 50 years ago by the reaction of *tert*-butylamine with SCl_4 generated *in situ*. A similar approach can be used to generate ^{t}BuN=Se=N^{t}Bu,[139] which decomposes at room temperature to give a mixture of cyclic selenium imides and ^{t}BuN=N^{t}Bu.[30] The corresponding tellurium diimide ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu is obtained in good yields as a thermally stable, orange solid from the reaction of lithium *tert*-butylamide with $TeCl_4$ in THF.[140]

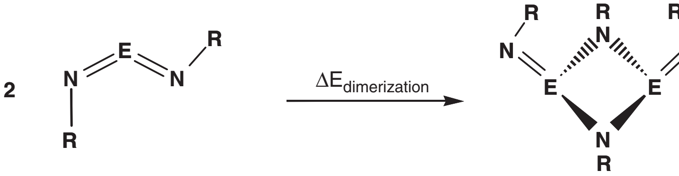
Several methods for the preparation of unsymmetrical sulfur diimides RN=S=NR′ have been developed. One approach involves the addition of a catalytic amount of an alkali metal to a mixture of two symmetrical sulfur diimides, RN=S=NR and R′N=S=NR′.[141] A second method makes use of alkali-metal derivatives of $[RNSN]^-$ anions.[142] Sulfur diimides of the type RN=S=NH (R = 2,4,6-^{t}Bu$_3$C$_6$H$_2$S) have also been prepared.[143]

Three different conformations are possible for monomeric chalcogen diimides (Scheme 6). *Cis*,*trans* or *cis*,*cis* isomers may exist in the solid state depending on the organic substituent R.[144,145] Although the former is more common, the *cis*,*cis* conformation is found for R=C_6F_5, 2,6-$Me_2C_6H_3$, 2,4,6-$C_6H_2Br_3$ and 2,6-$C_6H_3Me_2$.[144] In the gas phase $(Me_3SiN)_2S$ also adopts a *cis*,*cis* conformation.[146]

The only selenium diimide to be structurally characterized in the solid state, $Se(NAd)_2$ (Ad=adamantyl),[129] adopts the *cis*,*trans* conformation. By using *ab initio* and DFT molecular orbital methods, the *cis*,*trans* conformation is predicted to be most stable for $E(NR)_2$ (E=S, Se; R=H, Me, ^{t}Bu and $SiMe_3$) with the exception of the parent molecules $E(NH)_2$ [147] and the unsymmetrical



Scheme 6 *Conformational isomers of chalcogen diimides*



55 (E = Te, R = ^{t}Bu)

Scheme 7 *Dimerization of chalcogen diimides*

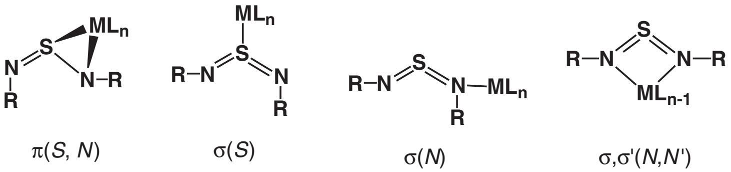
systems RNSNH,[148] for which the *cis,cis* conformation is slightly more stable than the *cis,trans* isomer. Electron density studies for ^{t}BuN=S=N^{t}Bu have shown that the bonding is predominantly electrostatic (S^+–N^-) rather than a covalent double bond (S=N).[149]

Tellurium diimides adopt dimeric structures. The *tert*-butyl derivative **55** has a *cis,endo,endo* arrangement of terminal ^{t}Bu groups with respect to the Te_2N_2 ring,[150] whereas a *trans,exo,exo* arrangement of the exocyclic groups is observed for the unsymmetrical derivatives RTeN(μ-NR$'$)$_2$TeNR (R=PPh$_2$ NSiMe$_3$; R$'$=^{t}Bu, ^{t}Oct) in the solid state.[151] The calculated dimerization energies for the [2+2] cycloaddition of two E(NR)$_2$ (E=S, Se, Te; R=H, Me, ^{t}Bu, SiMe$_3$) (Scheme 7) reveal that this process is strongly endothermic for sulfur diimides, approximately thermoneutral for selenium diimides and strongly exothermic for tellurium diimides, consistent with experimental observations.[152]

Monomeric sulfur diimides have an extensive coordination chemistry, as might be anticipated from the availability of three potential donor sites and two π-bonds.[131] Under mild conditions with suitable coordinatively unsaturated metal complexes, sulfur diimides may coordinate without rupture of the –N=S=N– unit. Four modes of coordination have been identified or invoked as intermediates in fluxional processes (Scheme 8).

The bonding mode is dependent on the nature of the metal centre as well as the steric or electronic properties of the imido substituent. For example, the M(CO)$_5$ unit in the σ(*N*)-trigonal complex [W(CO)$_5${S(NMe)$_2$}] undergoes a 1,3-shift between the two nitrogen donors, whereas the *tert*-butyl forms a *N,N$'$*-chelated [W(CO)$_4${S(N^{t}Bu)$_2$}] complex, as is also observed with main-group metal halides, *e.g*., [SnCl$_4$ {E(N^{t}Bu)$_2$}] (E=S, Se).[153]

The dimeric tellurium diimides can act as chelating or bridging ligands. In the *cis,exo,exo* conformation, the formation of *N,N$'$*-chelated complexes is



Scheme 8 *Coordination modes for monomeric chalcogen diimides*

observed, *e.g.*,with $HgCl_2$[154] or with an Ag_2^{2+} unit.[155] The interaction of **55** with copper(I) trifluoromethanesulfonate brings about a *cis*→*trans* isomerization of the ligand to give a complex in which two Cu^+ ions form linear bridges between three tellurium diimide ligands. The central ligand is in the *trans* conformation, while the terminal ligands are *trans*,*exo*,*endo*.

Sulfur diimides are prone to fragmentation to produce thionitroso and, subsequently, sulfido and imido ligands.[70,131] They are reduced chemically or electrochemically to the corresponding radical anions $[S(NR)_2]^{-\bullet}$, which exhibit five-line (1:2:3:2:1) ESR spectra.

Sulfur diimides react quantitatively with organolithium reagents at the sulfur centre to produce lithium sulfinimidinates of the type $\{Li[RS(NR')_2]\}_x$. The lithium derivatives may be hydrolysed by water to R′NS(R)NHR′ which, upon treatment with MH (M=Na, K) or the metal (M=Rb, Cs) in THF, produces the heavier alkali-metal derivatives.[132] The structures of these complexes are influenced by (a) the size and electronic properties of the R′ group, (b) the size of the alkali metal cation, and (c) solvation of the alkali-metal cation.

Selenium diimides react with unsaturated organic compounds. $(^tBuN)_2Se$ is an *in situ* reagent for allylic amination of olefins and acetylenes. Improved procedures for the diamination of 1,3-dienes have been developed using $(RN)_2Se$ (R = *para*-toluenesulfonyl, *ortho*-nitrobenzenesulfonyl).[156] The reaction of *N*,*N*′-dialkyl selenium diimides with *bis*(amino)stannylenes produces four-membered SnNSeN ring systems.[157]

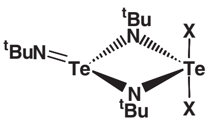
The dimeric tellurium diimide **55** undergoes a cycloaddition reaction with ^tBuNCO to generate the *N*,*N*′-ureatotellurium imide, which is converted to the corresponding telluroxide by reaction with excess ^tBuNCO.[158]

4.8.5 Imido Chalcogen Halides

Imido chalcogen halides of the type $RNECl_2$ (E=S, Se, Te) provide an interesting illustration of the reluctance of the heavier chalcogens to form –N=E< double bonds. The sulfur derivatives $RNSX_2$ (X=F, Cl) are stable, monomeric compounds.

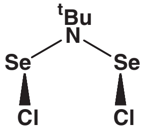
Selenium analogues $RN{=}SeCl_2$ are unknown for R=aryl or alkyl, and thermally unstable when $R{=}CF_3$ or C_2F_5. By contrast, *tert*-butylimidotellurium dihalides $(^tBuNTeX_2)_n$ (X=Cl, Br) are thermally stable in the solid state.[159] The structure of *tert*-butylimidotellurium dichloride **56a** consists of a layered arrangement of hexameric units formed by linking three $(^tBuNTeCl_2)_2$ dimers by chloride bridges.

The acyclic imidoselenium(II) dihalides $ClSe[N(^tBu)Se]_nCl$ (**57**, $n = 1$; **58**, $n = 2$) are obtained from the reaction of $SeCl_2$ with *tert*-butylamine in a 2:3 molar ratio in THF.[160] There are no sulfur or tellurium analogues of this class of imido chalcogen halide.



56a X =Cl

56b X =Br



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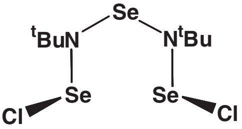

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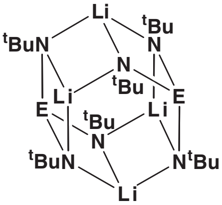
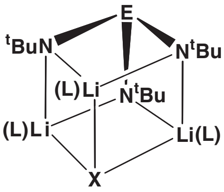
4.8.6 Triimidochalcogenites, $[E(NR)_3]^{2-}$ (E=S, Se, Te), and Sulfur Triimides, $S(NR)_3$

Dianions of the type $[E(N^tBu)_3]^{2-}$ (E=S,[161] Se,[162] Te[163]) are made by the nucleophilic addition of $LiNH^tBu$ to the appropriate chalcogen diimide followed by deprotonation with a second equivalent of $LiNH^tBu$.

The dilithium triimidochalcogenites $[Li_2\{E(N^tBu)_3\}]_2$ form dimeric structures in which two pyramidal $[E(N^tBu)_3]^{2-}$ dianions are bridged by four lithium cations to form distorted, hexagonal prisms of the type **59**.



59a (E = S)
59b (E = Se)
59c (E = Te)



60 (E = S, Se)
(X = Cl, Br, I)
(L = THF)

Lithium halides disrupt the dimeric structures of **59a** or **59c** to give distorted cubes of the type **60**, in which a molecule of the lithium halide is entrapped by a $Li_2[E(N^tBu)_3]$ monomer.[164,165] Similar structures are found for the MeLi, LiN_3 and $LiOCH{=}CH_2$ adducts of **59a**.[166–168] The pyramidal dianion $[Te(N^tBu)_3]^{2-}$ has a rich coordination chemistry,[169–171] although redox processes are sometimes observed in metathetical reactions with metal halides. For example, reaction with $PhPCl_2$ gives a spirocyclic Te(IV) complex of the $[PhP(N^tBu)_3]^{2-}$ dianion,[163] while treatment with Sn(II) salts generates a complex with a four-coordinate Sn(IV) = Te functionality.[172]

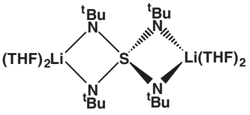
The first sulfur triimide $S(NSiMe_3)_3$ was prepared by the reaction of NSF_3 with $LiN(SiMe_3)_2$.[173] The *tert*-butyl derivative $S(N^tBu)_3$ is obtained by oxidation of the corresponding dianion with halogens.[164] The triimides $S(NR)_3$ ($R{=}SiMe_3$, ^tBu) have trigonal planar structures with S–N bond lengths in the range 1.50–1.52 Å and an NSN bond angle of 120°.[173] The SN vibrations in the Raman spectrum of $S(N^tBu)_3$ occur at much lower wave numbers (640–920 cm^{-1}) than expected for a covalent S=N bond, indicating that the bonding is predominantly electrostatic ($S^+–N^-$).[174] This conclusion is supported by electron density measurements.[149]

4.8.7 Tetraimidosulfate, $[S(N^tBu)_4]^{2-}$, and Methylenetrimidosulfate, $[H_2CS(N^tBu)_3]^{2-}$

The tetraimidosulfate anion $[S(NtBu)_4]^{2-}$ is obtained, as the dilithium derivative **61**, by the reaction of $S(N^tBu)_3$ with two equivalents of $LiNH^tBu$.[175] The nucleophilic addition of sterically undemanding alkyl-lithium reagents, *e.g.*, MeLi, to $S(N^tBu)_3$ produces the dimeric complex $[(thf)_2Li_2\{(N^tBu)_3SMe\}_2]$ (**62**).[174] *N*,*N*′-chelated complexes of the $[MeS(N^tBu)_3]^-$ anion are obtained by the nucleophilic addition of Me_2Zn or Me_3Al to $S(N^tBu)_3$.[176]

The methylenetriimido sulfite dianion $[CH_2S(N^tBu)_3]^{2-}$ is prepared by the treatment of $[CH_3S(N^tBu)_3]^-$ with methyllithium in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine).[177] The structure of $[(TMEDA)_2Li_2\{H_2CS(N^tBu)_3\}]$ (**63**) resembles that of **61** with the TMEDA ligands replacing the two THF ligands on each Li centre.

Reaction of **63** with $S(N^tBu)_3$ followed by protonation with $[^tBuNH_3]Cl$ yields $H_2C[S(N^tBu)_2(NH^tBu)]_2$, an imido analogue of methane disulfonic acid.[178]



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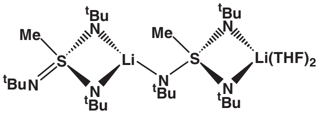

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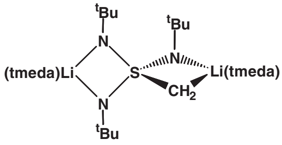

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4.8.8 Chalcogen Diamides $E_x(NR_2)_2$, (E=S, Se, Te; $x = 1–4$)

Sulfur and selenium diamides are obtained by the reaction of sulfur or selenium chlorides with an aliphatic secondary amine. Polyselanes $Se_x(NR_2)_2$ ($x = 2–4$, NR_2=morpholinyl; $x = 4$, NR_2=piperidinyl) are formed in the reaction of elemental selenium with the boiling amine in the presence of Pb_3O_4.[19] The acyclic tellurium(II) diamide $[Te(NMe_2)_2]_\infty$ (see Figure 1) is prepared by the reaction of $TeCl_4$ with $LiNMe_2$.[20]

Silylated amino derivatives of the type $E[(N(SiMe_3)_2]_2$ (E=S, Se, Te) are useful for the synthesis of other chalcogen–nitrogen compounds *via* reactions with element halides and elimination of Me_3SiCl. These reagents are made by the treatment of $LiN(SiMe_3)_2$ with SCl_2, Se_2Cl_2 or $TeCl_4$, respectively.[179] The series $E[N(SiMe_3)_2]_2$ (E=S, Se, Te) displays E–N single bond lengths. The trend in $<$NEN bond angles of 109.6°, 108.0° and 105.8°, respectively, reflect the increasing π-character in the bonding orbitals. In contrast to the monomeric structure of $Te[N(SiMe_3)_2]_2$, the dimethylamino derivative $[Te(NMe_2)_2]_\infty$ (**1**) has a polymeric structure with intermolecular Te···N contacts of 2.96 Å that give rise to trapezoidal Te_2N_2 rings.[20]

The polar tellurium(II)–nitrogen bond is readily susceptible to protolysis by weakly acidic reagents. For example, the reaction of $[Te(NMe_2)_2]_\infty$ with two equivalents of Ph_3CSH produces the monomeric thiolato derivative $Te(SCPh_3)_2$.[20]

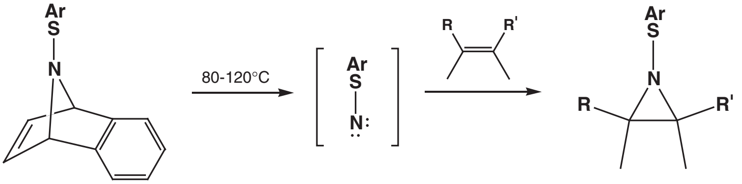
Dialkynyl tellurides are obtained in moderate yield by the one-pot reaction of $TeCl_4$ with $LiN(SiMe_3)_2$, followed by the addition of a terminal acetylene. Alkenyl tellurium(II) derivatives may also be prepared by the addition of arenetellurenamides or $Te[N(SiMe_3)_2]_2$ to the –C≡C– bond of dimethylacetylene dicarboxylate.[180]

The intriguing radical cation $[Te\{N(SiMe_3)_2\}_2]^{+\bullet}$ is formed (as the blue AsF_6^- salt) by oxidation of $Te[N(SiMe_3)_2]_2$ with AsF_5. This deep blue salt is monomeric in the solid state with d(Te–N) = 1.97 Å, consistent with multiple bonding. The broad singlet in the ESR spectrum indicates that the unpaired electron is located primarily on the tellurium atom.[181]

4.8.9 Organochalcogenyl Azides and Nitrenes

Organosulfenyl azides RSN_3 are of interest as sources of the corresponding sulfenyl nitrenes RSN, which may be used in the construction of S–N heterocycles.[182] Sulfenyl nitrenes are accessible by the oxidation of sulfenamides $RSNH_2$ with lead tetraacetate. An alternative approach involves the thermal extrusion of bridging nitrogen from 1,4-dihydro-1,4-iminonaphthalenes followed by trapping with an alkene to give an aziridine (Scheme 9).[183] Monomeric CF_3SN may be trapped by hexachlorocyclopentadiene to give $C_5Cl_6{=}NSCF_3$; NSCl reacts in a similar manner to give $C_5Cl_6{=}NSCl$.[184] Benzenesulfinyl azides $ArS(O)N_3$ (Ar=Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$), obtained by the reaction of the arylsulfinyl chloride and sodium azide in acetonitrile, can be stored in the solid state at low temperatures.[185] Selenenyl azides, $RSeN_3$, are stabilized by intramolecular coordination, *e.g.*, in 2-$Me_2NC_6H_4SeN_3$.[186]

A similar approach has been used to stabilize the organotellurenyl azide 2-$Me_2NCH_2C_6H_4TeN_3$.[187] Organotellurium(II) azides with extremely bulky alkyl or aryl groups attached to Te have also been structurally characterized.[187]



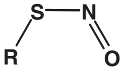
Scheme 9 *Formation and trapping of an arenesulfenylnitrene (Ar = Ph, 2,4-$(NO_2)_2C_6H_3$)*

Organotellurium(IV) azides with two or three azido groups attached to tellurium, $R_2Te(N_3)_2$ (R=alkyl, Ph, C_6F_5) and $RTe(N_3)_3$ (R=alkyl, 2,4,6-$Me_3C_6H_2$), are prepared by the reaction of organotellurium(IV) fluorides with trimethylsilyl azide.[188]

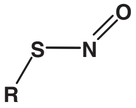
4.8.10 *S*-Nitrosothiols RSNO

S-nitrosothiols, several of which occur naturally, *e.g.*, *S*-nitrosocysteine and *S*-nitrosoglutathione, have an important role in NO transport and regulation in biological systems. Potential applications of RSNO compounds include their use as vasodilators in the treatment of angina and in the search for a cure for male impotence.[11] The most convenient route to *S*-nitrosothiol formation is the nitrosation of thiols.

S-nitrosothiols may adopt either *cis* (**64a**) or *trans* (**64b**) conformations with respect to the S–N bond. *S*-nitrosocaptopril[189] assumes a *cis* arrangement, while the *trans* isomer pertains in the solid state for *S*-nitroso-*N*-acetylpenicillamine and Ph_3CSNO.[190] The S–N bond lengths are typical for a single bond. Nevertheless, there is a significant barrier to rotation about the S–N bond.[189–192] In solution the *cis* and *trans* isomers may co-exist.



64a (*cis*)



64b (*trans*)

Stable *S*-nitrosothiols and *S*-nitrososelenols have also been generated by attaching bowl-shaped aryl substituents to the nitrogen centre.[193,194] The alkyl derivative $(Me_3Si)_3CSeNO$ is prepared by nitrosation of $(Me_3Si)_3CSeH$ with *tert*-butylnitrite.[195]

The ability of *S*-nitrosothiols to mimic many of the biological properties of NO itself may emanate from *in vivo* decomposition to generate NO. This decomposition is catalysed by Cu^{2+},[11] and may be important in the development of thrombo-resistant devices used in kidney dialysis or coronary by-pass surgery.[196] It is also possible that direct transfer of NO from RSNO occurs in biological systems.[197]

4.8.11 Trisulfenamides, $(RS)_3N$, and the Radical $[(PhS)_2N]^\bullet$

Tribenzenesulfenamide $(PhS)_3N$ is obtained as a pale yellow solid by the treatment of the sodium salt of dibenzenesulfenamide, generated *in situ*, with acetic anhydride. The perfluorinated analogue $(C_6F_5S)_3N$ is prepared by the reaction of $(C_6F_5S)_2NH$ and C_6F_5SCl in diethyl ether.[198]

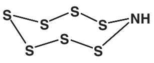
The solid-state structures of $(PhS)_3N$ and $(C_6F_5S)_3N$ and the gas-phase structure of $(CF_3S)_3N$ all show nearly planar S_3N units with the S–N bond lengths longer than typical single-bond values. Tribenzenesulfenamide decomposes at *ca.* 80 °C to give the purple radical $[(PhS)_2N]^\bullet$, which is also generated by the oxidation of $(PhS)_2NH$ with lead dioxide.

4.9 Cyclic Chalcogen Imides

The best-known examples of cyclic sulfur imides are eight-membered rings in which one or more of the sulfur atoms in *cyclo*-S_8 are replaced by an imido (NH) group.[199] Ring systems involving either fewer or more than eight atoms have been synthesized recently. For the heavier chalcogens, six-membered rings of the type $(ENR)_3$ ($R={}^tBu$; $E=Se$, Te) have been characterized. Cyclic selenium imides with five, eight or fifteen ring atoms and Se–Se linkages are also known.

4.9.1 Cyclic Sulfur Imides

The series of cyclic sulfur imides includes S_7NH (**65**); the three diimides 1,3-, 1,4- and 1,5-$S_6(NH)_2$ (**66–68**); two triimides 1,3,5- and 1,3,6-$S_5(NH)_3$; and the tetraimide $S_4N_4H_4$ (**69**).



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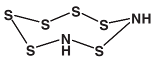

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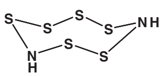

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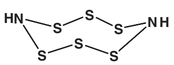

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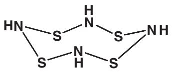

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The reaction of S_2Cl_2 with gaseous ammonia in DMF at *ca.* –10 °C, followed by hydrolysis with cold dilute hydrochloric acid, is a standard preparation of these cyclic sulfur imides.[199] The reaction of sodium azide with elemental sulfur in $(Me_2N)_3PO$ is an excellent source of S_7NH. The tetraimide **69** is prepared by reduction of S_4N_4 with methanolic $SnCl_2.2H_2O$.

These ring systems all adopt the crown configuration of *cyclo*-S_8 with S–S bond lengths in the range 2.04–2.06 Å. The short S–N bond distances and the planar geometry around nitrogen indicate three-centre π-bonding in the S–N(H)–S units. Electron deformation density measurements of S_7NH[200] and $S_4N_4H_4$[201] reveal bent S–N bonds with endocyclic maxima.

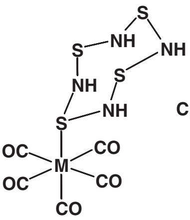
The vibrational assignments and force constants have been determined from the IR and Raman spectra of S_7NH, $S_4{}^{15}N_4H_4$ and $S_4{}^{15}N_4D_4$. The ^1H and ^{15}N NMR chemical shifts of all the cyclic sulfur imides have been determined by inverse detection methods.[202]

Deprotonation of S_7NH produces the thermally unstable, yellow $[S_7N]^-$ anion, which decomposes to the deep blue $[S_4N]^-$ anion.[69] The oxidation of S_7NH with trifluoroperoxyacetic acid yields $S_7NH(O)$, while oxidation with $SbCl_5$ in liquid sulfur dioxide generates the $[NS_2]^+$ cation.

The interaction of cyclic sulfur imides with metal centres involves adduct formation or oxidative addition.[106] Examples of the former include the formation of $[M(S_4N_4H_4)(CO)_5]$ (**70**, M=Cr, W) and $(S_4N_4H_4)_2\cdot AgClO_4$. By contrast, the reaction of **69** with $[Pt(PPh_3)_4]$ gives $[Pt(PPh_3)_2(S_2N_2)]$. Monomeric sulfur imide is stabilized as a bridging ligand in the dinuclear complex $Fe_2(CO)_6(\mu\text{-SNH})$. [203]

The six-membered rings 1,4-$S_4(NR)_2$ (R=Et, Bz, Cy, CH_2CH_2Ph) are prepared from the reactions of the appropriate primary amine with S_2Cl_2 in diethyl ether under high dilution conditions.[204] These rings adopt chair conformations, and the bond angles at the nitrogen atoms reveal a pyramidal (*sp*^{3}) geometry.

Cyclic sulfur imides containing S–S bonds undergo oxidative-addition reactions with $[TiCp_2(CO)_2]$. In the reaction with S_7NR (R=H, Me), the metal inserts into an S–S bond to give $[TiCp_2(S_7NR)]$ (**71**, R=H; **72**, R=Me)[205], whereas with 1,4-$S_4(NR)_2$ (R=Me, Oct) the metallo fragment replaces one of the NR units to yield $[TiCp_2S_4NR]$ (**73**).[206]



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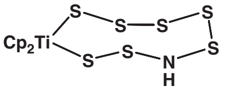

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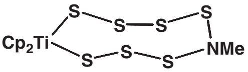

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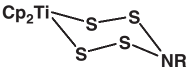

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Sulfur imides with a single NR functionality, S_5NR, S_6NR (R=Oct), S_8NH and S_9NH are obtained by the metathesis reaction between the *bis*(cyclopentadienyl)titanium complexes **71–73** and the appropriate dichlorosulfane.[206,207]

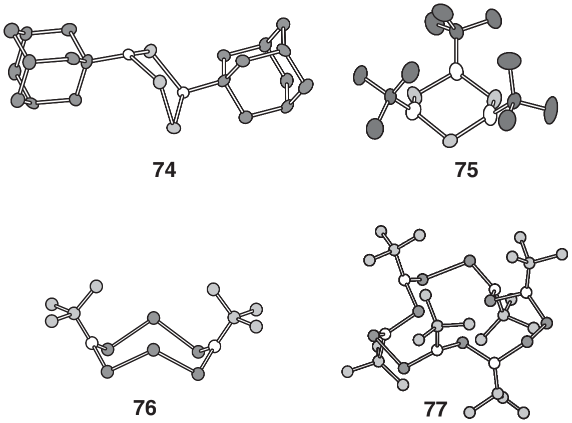
The six- and seven-membered rings S_5NR and S_6NR are yellow oils that exhibit molecular ions in their electron-impact mass spectra. The nine- and ten-membered rings S_8NH and S_9NH form photosensitive, pale yellow crystals that are soluble in CS_2. The 12-membered ring $S_{11}NH$ has only been characterized by spectroscopic methods.[207]

4.9.2 Cyclic Selenium and Tellurium Imides

The discovery of cyclic imides of the heavier chalcogens is a relatively recent development. The ring systems that have been structurally characterized all have bulky substituents attached to the nitrogen atoms, *viz*., $Se_3(NR)_2$ (**74**, R=^{t}Bu, Ad),[30,152] $Se_3(N^tBu)_3$ (**75**),[160] $Se_6(N^tBu)_2$ (**76**)[208] and $Se_9(N^tBu)_6$ (**77**).[208] The only known cyclic tellurium imide is $Te_3(N^tBu)_3$.[150]

$Se_6(N^tBu)_2$ (**76**) and $Se_9(N^tBu)_6$ (**77**) were obtained in low yields by the reaction of $LiN(^tBu)SiMe_3$ with Se_2Cl_2 or $SeOCl_2$.[208] The reaction of *tert*-butylamine with $SeCl_2$ in THF in a 1:3 molar ratio yields the smaller ring systems **74** and **75**, in addition to **76** and **77**.[30] A better preparation of **75** involves the decomposition of $^tBuN{=}Se{=}N^tBu$ in toluene at 20 °C, which also generates **74** and **76**.[30]

The ^{77}Se NMR spectra provide an informative analysis of the components of the reaction mixtures in these syntheses of cyclic selenium imides. The five- and



74 **75**

76 **77**

Figure 4 *Crystal structures of* $Se_3(NAd)_2$ (**74**), $Se_3(N^tBu)_3$ (**75**), $Se_6(N^tBu)_2$ (**76**) *and* $Se_9(N^tBu)_6$ (**77**) *(redrawn from data in refs. 30, 160 and 208).*

fifteen-membered rings, **74** and **77**, show two resonances with relative intensities of 2:1 corresponding to the –SeSe– and –Se– bridging units, respectively. The eight-membered ring **76** also exhibits two ^{77}Se resonances attributable to the two different selenium environments.[30]

The cyclic chalcogen imides **74** (R=Ad), **75** (Se and Te derivatives), **76** and **77** have been structurally characterized by X-ray crystallography (Figure 4). The metrical parameters for the puckered five-membered ring **74** are significantly different from those of the larger rings as a result of ring strain.

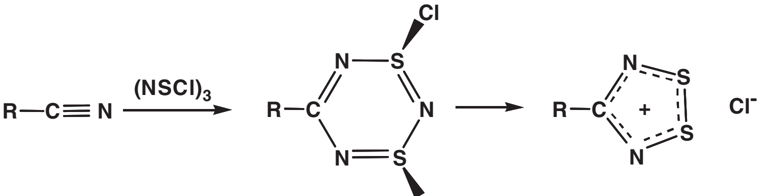
4.10 Carbon–Nitrogen–Chalcogen Ring Systems

Interest in carbon–nitrogen–sulfur ring systems was stimulated in the 1980s by the theoretical prediction that polymers of the type $(RCNSN)_x$ will have conducting properties similar to those of $(SN)_x$.[209] Although this goal has not been realized, a new area of radical chemistry based on $[RCN_2S_2]^\bullet$ (dithiadiazolyl) and related radical systems has emerged.[6,18] These heterocycles and their selenium analogues exhibit considerable potential for the development of novel one-dimensional metals or materials with unique magnetic properties.

4.10.1 Five-Membered Rings

4.10.1.1 1,2,3,5-Dichalcogenadiazolium $[RCNEEN]^+$ *and Dichalcogenadiazolyl* $[RCNEEN]^\bullet$ *Rings (E=S, Se)*

The 1,2,3,5-dithiadiazolium cation (**78**) is obtained by the reaction of organic nitriles with $(NSCl)_3$, which proceeds by the intermediate formation of six-membered ring systems of the type $RCN_3S_2Cl_2$ (Equation 2).[210]



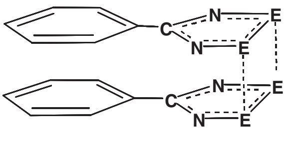
78 (2)

A more versatile synthesis of **78** and its selenium analogue involves the cyclocondensation of trisilylated amidines with SCl_2 or $SeCl_2$.[18] This route can be used to prepare the prototypal systems $[HCNEEN]^+$ (E=S, Se).[211,212] It is also readily extended to the synthesis of multi-dichalcogenadiazolium cations such as 1,3- or 1,4-$C_6H_4(CNEEN)_2]^{2+}$ (E=S, Se),[213] $[1,3,5\text{-}C_6H_3(CNSSN)_3]^{3+}$,[214] 1,3,5-$C_3N_3(CNSSN)]^{3+}$.[215] The chloro derivative (**78**, R=Cl) is prepared from the reaction of $Me_3SiN{=}C{=}NSiMe_3$ and S_2Cl_2.[18] The dication $[NSSNC\text{–}CNSSN]^{2+}$ is obtained by treatment of *N*,*N′*-diaminooxamidine with SCl_2.[216]

The six π-electron $[RCN_2S_2]^+$ ring is readily reduced to the corresponding seven π-electron radical $[RCN_2S_2]^\bullet$.[8] The structures and properties (conductivity, magnetic behaviour) of the radicals are discussed in Section 10.1.

Electrochemical reduction of **79** (E=S) generates the corresponding monoanion $[PhCNSSN]^-$, which was isolated as the [Na(18-crown-6)]$^+$ salt.[217] Dithiadiazolyls may also act as a source of chelating ligands in oxidative-addition reactions with metal complexes.[9] For example, $[PhCNSSN]_2$ produces with $[Pt(PPh_3)_3]$ the square planar complex **80**.[218] The dithiadiazolyl ring may also act as a bridging ligand, *e.g.*, in the binuclear nickel complex **81**[219] and the trinuclear palladium complex **82**.[9] In some cases, *e.g.*, the di-iron complex **83**, the heterocyclic ligand becomes protonated.[220]

The neutral radical **84** is an interesting heterocyclic analogue of 2,2′-bipyridyl. This paramagnetic ligand forms an *N*,*N′*-chelated complex with *bis*(hexafluoroacetylacetonato)cobalt(II).[221]



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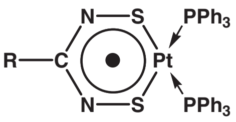

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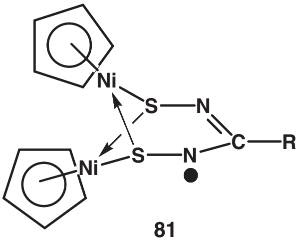

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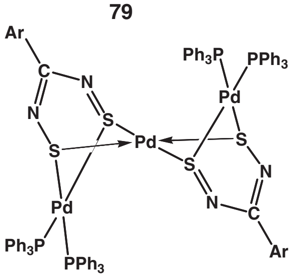

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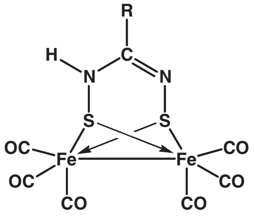

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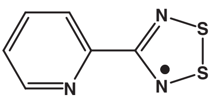

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4.10.1.2 1,3,2,4-Dithiadiazolium, $[RCNSNS]^+$, and Dithiadiazolyl, $[RCNSNS]^\bullet$ Rings

The 1,3,2,4-dithiadiazolium cation is prepared by the cycloaddition of the $[S_2N]^+$ cation to the C$\equiv$N triple bond of organic nitriles (Scheme 3).[63] This methodology may also be applied to the synthesis of molecules containing more than one 1,3,2,4- dithiadiazolyl ring, *e.g.*, by the reaction of 1,3-, 1,4- or 1,5-$C_6H_4(CN)_2$ with two equivalents of $[S_2N][AsF_6]$ to give the corresponding dications 1,3-, 1,4- or 1,5-$[C_6H_4(CNSNS)_2]^{2+}$.[222] The double addition of $[S_2N]^+$ to cyanogen produces the dication $[(SNSNC)–(CNSNS)]^{2+}$ (see ref. 223) and the triple addition of $[S_2N]^+$ to the tricyanomethide anion $[C(CN)_3]^-$ proceeds in a stepwise fashion to give the dication $[C(CNSNS)_3]^{2+}$.[224] The versatility of this approach is further illustrated by the cycloaddition of $[S_2N]^+$ to SF_5CN[225] and $Hg(CN)_2$[226] to give the corresponding 1,3,2,4-dithiadiazolium mono- and di-cations, respectively. A mixed 1,3,2,4-/1,2,3,5-dithiadiazolium dication is produced by the reaction of $[4\text{-}CNC_6H_4CNSSN]AsF_6$ with $[S_2N]AsF_6$[227]

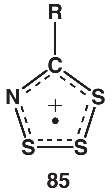
1,2,3,4-Dithiadiazolyl radicals are discussed in Section 10.1.

4.10.1.3 5-Oxo-1,3,2,4-dithiadiazole

The cyclic ketone 5-oxo-1,3,2,4-dithiadiazole, S_2N_2CO, may be prepared by two methods.[106] This neutral, diamagnetic dithiadiazole is an aromatic six π-electron ring system.[228]

4.10.1.4 1,2,3,4-Trithiazolium $[RCNSSS]^{+\bullet}$ Rings

The 1,2,3,4-trithiazolium radical cation $[RCNSSS]^{+\bullet}$ (**85**, R=CF_3) is prepared by the reaction of an equimolar mixture of $S_4[AsF_6]_2$ and $S_8[AsF_6]_2$ (an *in situ* source of S_3^+) with CF_3CN in SO_2[229] The dication diradical $[SSSNC–CNSSS]^{2+2\bullet}$ (**86**) is obtained by applying similar methodology with cyanogen $(CN)_2$ as the reagent.[230]



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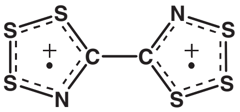

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4.10.1.5 1,2,5-Chalcogenadiazoles

1,2,5-Thiadiazole systems $(RC)_2N_2S$ are prepared by condensation reactions of sulfur halides with 1,2-diaminobenzenes or by the reaction of S_4N_4 with acetylenes. The parent 1,2,5-selenadiazole has been employed to make the tellurium analogue *via* treatment with ethylmagnesium bromide followed by the addition of tellurium tetrachloride. Tetrafluorobenzo-1,2,5-telluradiazole is obtained by the condensation of tellurium tetrachloride with 1,2-diaminobenzene upon heating in a high boiling solvent.[231a] While $[{}^{t}Bu_2C_6H_2N_2Te]_2$ is dimeric,[231b] the parent telluradiazole (**2**) has a polymeric structure (see Figure 1).

Current interest in benzo-1,2,5-thiadiazoles is focused on their possible uses in light-emitting diodes [232a] or field-effect transistors.[232b] Benzo-1,2,5-selenadiazole acts as a structure-directing agent for supramolecular aggregates *via* intermolecular Se···N interactions in silver complexes.[233a] Such interactions are strongest for telluradiazoles, which are thought to be promising candidates for the construction of conducting materials on the basis of computational results.[233b]

Cycloocteno-1,2,3-selenadiazole is an effective source of selenium for the production of semi-conductors such as cadmium selenide.[234]

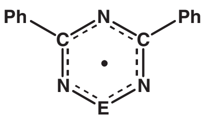
4.10.2 Six-Membered Rings

4.10.2.1 Chalcogenatriazinyl Rings, $[(RC)_2N_3E]^{\bullet}$ (E=S, Se)

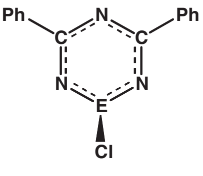
The chalcogenatriazinyl systems (**87**) are prepared by reduction of the corresponding S–Cl or Se–Cl derivatives (**88**) with triphenylantimony.[235] These six-membered rings form cofacial diamagnetic dimers in the solid state. The monohalogenated derivatives **88** (E=S, Se) are best prepared by the condensation of imidoyl amidines with SCl_2 or $SeCl_4$, respectively.

The related cyanuric–thiazyl system $(ClC)_2N_3SCl$ (**89**, X=Cl) is obtained by the reaction of sodium dicyanamide with thionyl chloride in DMF. This trihalogenated heterocycle reacts with sodium alkoxides or aryloxides with preferential substitution at sulfur.[236] Trisubstitution can be achieved without ring degradation to give $[(RO)C]_2N_3S(OR)$ (R=Me, Et, CH_2CF_3, Ph). The reaction of **89** (X=Cl) with trialkylamines results in cleavage of a C–N bond of the tertiary amine and regiospecific substitution of the dialkylamino group on the carbon atoms of the heterocycle.[237]

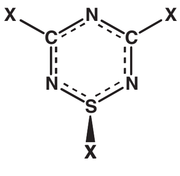
The oxidation of **89** (X=Cl) with a mixture of $KMnO_4$ and $CuSO_4 \cdot xH_2O$ ($x = 4$–6) produces the hybrid cyanuric–sulfanuric system **90**, which displays a relatively short S–Cl bond length.[238] The structure of the corresponding trifluoro derivative **89** (X=F) has been determined by electron diffraction.[239] The reaction of **90** with $NaOCH_2CF_3$ in a 1:3 molar ratio produces the trialkoxy derivative, which undergoes isomerization at 175 °C to give the corresponding sulfone.[236]



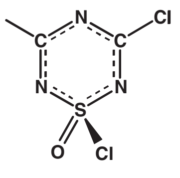
87 (E = S, Se)



88 (E = S, Se)



89 (X = Cl, F)



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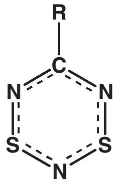
4.10.2.2 Dithiatriazines, RCN_3S_2

Aryl derivatives of the dithiatriazine ring (**91**) are prepared by the reduction of the corresponding *S,S′*-dichloro derivative **92** (R=aryl).[240] The six-membered rings **91** exist as cofacial dimers in the solid state. The dimeric structure is preserved in solution.[241] The dithiatriazine **91** (R=Ph) is also formed by insertion of excited nitrogen atoms into the S–S bond of the corresponding dithiadiazolyl ring.[242] The derivatives **91** (R=CF_3, NMe_2) are obtained as red solids by reduction of the corresponding *S,S′*-dichloro derivatives **92** using Zn or $SbPh_3$ (R=CF_3) and $Hg(SiMe_3)_2$ (R=NMe_2).[243] They undergo *S,S′*-cycloaddition with norbornadiene to give the 1,3-norbornenyl adducts **93** (R=Ph, CF_3, NMe_2).



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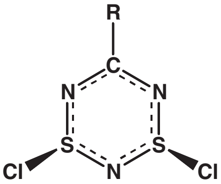

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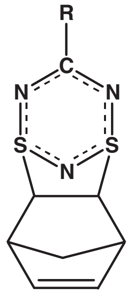
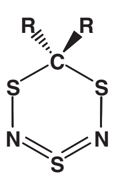


93 (R = Ph, CF_3, NMe_2)

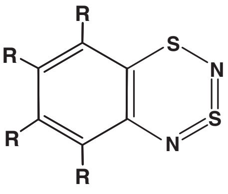
The *S,S′*-dichloro derivatives **92** (R=Ar) are prepared by chlorination of the bicyclic systems $ArCN_5S_3$ with gaseous chlorine.[240] The treatment of $(NSCl)_3$ with dialkylcyanamides R_2NCN produces **92** (R=NMe_2, NEt_2, N^iPr_2) efficiently upon mild heating in CCl_4.[210] The chlorinated derivative **92** (R=Cl) is obtained from ClCN and $(NSCl)_3$.[239] The X-ray structures of various derivatives of **92** reveal a *cis* arrangement of the two chlorine substituents.[244]

4.10.2.3 Trithiadiazines, $R_2CN_2S_3$

1,3,5,2,4-Trithiadiazines (**94**) were first obtained from the reaction of S_4N_4 with diazoalkanes.[245] This ring system is more conveniently synthesized from 1,1-*bis*(sulfenyl chlorides) and $Me_3SiNSNSiMe_3$.[246] The six-membered ring in **94** adopts a half-chair conformation with long S–N bonds connecting the –SCH_2S– and –N=S=N– units.



94
(R = H, alkyl, aryl)



95
(R = H, F)

4.10.2.4 Benzodithiadiazines, $C_6R_4S_2N_2$ (R=H, F)

The antiaromatic 12 π-electron benzodithiadiazine **95** (R=H) is obtained as a volatile deep blue solid by the reaction of $PhNSNSiMe_3$ with SCl_2, followed by an intramolecular ring closure with elimination of HCl.[247] The tetrafluoro derivative **95** (R=F) is prepared by treatment of $C_6F_5SNSNSiMe_3$ with CsF in acetonitrile.[248] Several difluoro- and trifluoro-benzodithiadiazines have also been prepared by these methods.[249] In contrast to essentially planar **95** (R=H),[247] the dithiadiazine ring in the tetrafluoro derivative is somewhat twisted.[248] In the gas phase, on the other hand, **95** (R=F) is planar, whereas **95** (R=H) is non-planar.[25,249]

4.10.3 Seven-Membered Rings

4.10.3.1 Trithiadiazepines, $(RC)_2N_2S_3$

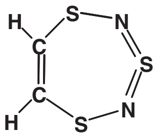
1,3,5,2,4-Benzotrithiadiazepine (**96**, R=H) is obtained as bright-yellow crystals by the reaction of benzo-1,2-*bis*(sulfenyl chloride) with $Me_3SiNSNSiMe_3$ (Equation 3).[247] The tetrafluoro derivative **96** (R=F) has been prepared by a similar procedure.[250] The isomeric 1,2,4,3,5-benzotrithiadiazepine is formed in the reaction of $PhNSNSiMe_3$ and S_2Cl_2, followed by intramolecular cyclization.[251]

(R = H,F)

96

(3)

The parent trithiadiazepine $(HC)_2N_2S_3$ (**97**) is synthesized by chlorination of ethanedithiol to the trichloro derivative $Cl(SCl)CHCH_2SCl$, followed by cyclocondensation with $(Me_3SiN)_2S$.[252] The seven-membered ring in **97** is planar and the bond lengths indicate complete delocalization. It undergoes electrophilic aromatic substitution reactions at carbon to give **98** (X=Br, NO_2, HgOAc). The heterocyclic aryne (trithiadiazepyne) **99** can be trapped as a Diels–Alder adduct with furan.[253]



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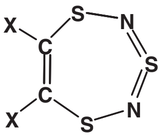

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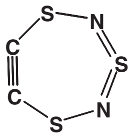

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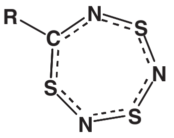


100

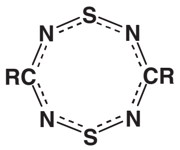
4.10.3.2 Trithiatriazepines, RCN_3S_3

The planar seven-membered CN_3S_3 ring was first obtained as the ester **100** (R=CO_2Me), which is a minor product of the reaction of S_4N_4 with dimethylacetylene dicarboxylate.[252] The parent 1,3,5,2,4,6-trithiatriazepine **100** (R=H) is obtained by carefully heating the ester with aqueous HCl followed by decarboxylation.

4.10.4 Eight-Membered Rings

4.10.4.1 Dithiatetrazocines, $(RC)_2N_4S_2$

1,5-Dithiatetrazocines, **101** (R=Ph) and **102**, were first prepared by the cyclocondensation of benzamidine or dimethylguanidine, respectively, with SCl_2 in the presence of a base. Air oxidation of the corresponding dithiadiazolium salts $[ArCN_2S_2]X$ in the presence of $SbPh_3$ is a better alternative for the synthesis of aryl derivatives of **101**.[254] This method can be adapted to generate unsymmetrically substituted dithiatetrazocines.[255] Cyclophanes containing one or two $C_2N_4S_2$ rings have also been synthesized.[256]



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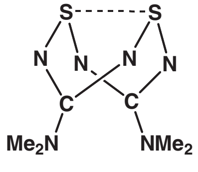

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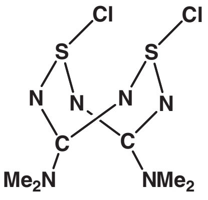
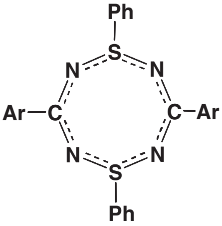


103

Aryl derivatives of **101** (R=Ar) are planar, and the bond lengths indicate a fully delocalized 10 π-electron aromatic system. By contrast, the *bis*(dimethylamino) derivative **102** adopts a folded structure. Dithiatetrazocines with exocyclic N(Me)Bu groups exhibit both *cis*/*trans* and ring inversion isomerism.[257]

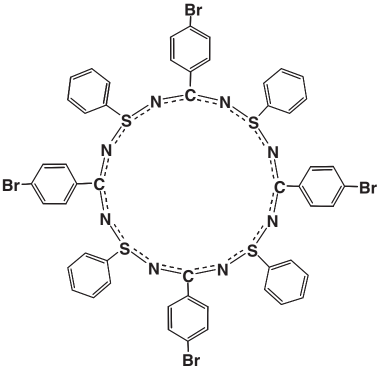
The planar ring **101** (R=Ph) does not react with *n*-butyllithium, *m*-chloroperbenzoic acid, N_2O_4 or $HClO_4$. By contrast, the folded ring **102** is readily oxidized by halogens. Reaction with Cl_2 produces $(Me_2NC)_2N_4(SCl)_2$ (**103**) as the *exo*,*endo* isomer, whereas fluorination or reaction with the radical $[(CF_3)_2NO]^{\cdot}$ results in an *exo*,*exo* substitution pattern.[258] The folded ring system **102** acts as a *S*,*S*′-bidentate ligand towards platinum upon reaction with $[Pt(PPh_3)_4]$.[259]

Eight-membered CNS heterocycles of the type $Ar_2C_2N_4S_2Ph_2$ (**104**) are generated by the cyclocondensation of trisilylated benzamidines $(4\text{-}XC_6H_4)CN_2(SiMe)_3$ (X=Br, CF_3) with PhSCl in a 1:3 molar ratio at very low temperatures.[260] The 16-membered ring $(4\text{-}BrC_6H_4)_4C_4N_8S_4Ph_4$ (**105**) is obtained as a minor product.



104

(Ar = 4-XC_6H_4;X = Br, CF_3)

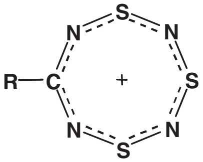


105

The eight-membered rings **104** undergo thermally symmetry-forbidden photoisomerization in the solid state to give the purple diazenes PhSN=C(Ar)N=NC(Ar)=NSPh.[261] The 16-membered ring **105** has a cradle-like structure with S_4 symmetry. Oxidation of **104** or **105** with *m*-chloroperbenzoic acid gives the corresponding cyanuric–sulfanuric ring systems.[262] The 16-membered ring retains the cradle conformation upon oxidation.

4.10.4.2 The Trithiatetrazocine Cation, $[RCN_4S_3]^+$

The trithiatetrazocine cation $[CF_3CN_4S_3]^+$ (**106**, R=CF_3) was isolated in very low yield from the reaction of $(NSCl)_3$ with CF_3CN in sulfur dioxide.[263] This eight-membered ring has an almost planar structure. The *S*-chloro derivative $Me_2NCN_4S_3Cl$ (**107**) is obtained as a minor product from the reaction of **103** (R=NMe_2) and Me_3SiNSO in carbon tetrachloride.[264] This heterocycle has a folded structure.



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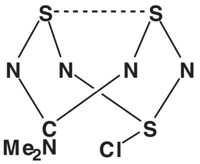
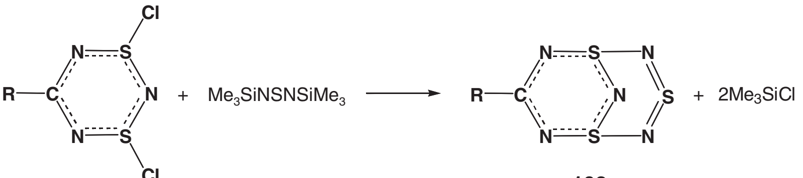


107

4.10.5 Bicyclic Ring Systems, RCN_5S_3

A wide range of derivatives of the bicylic ring systems RCN_5S_3 (**108**, R=alkyl, aryl, CF_3, NR'_2, Cl) have been prepared and structurally characterized.[265] Two synthetic routes are available: (a) reaction of *S*,*S*′-dichlorodithiatriazines with $(Me_3SiN)_2S$ (Equation 4) and (b) reactions of trisilylated benzamidines with $(NSCl)_3$.



108

(4)

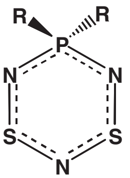
The molecular structure of the bicyclic framework in **108** is best described as a dithiatriazine bridged by an –N=S=N– group. The aryl-substituted derivatives **108** (R=aryl) form 2:1 inclusion complexes with aromatic fluorocarbons or hydrocarbons.[266] In solution, the phenyl derivative **108** (R=Ph) is fluxional.[258]

4.11 Chalcogen–Nitrogen–Phosphorus Ring Systems

4.11.1 Chalcogen–Nitrogen–Phosphorus(V) Rings

The first derivative of the six-membered ring $R_2PS_2N_3$ (**109**, R=Me_3SiNH) was obtained in 1976 from the reaction of S_4N_4 with $(Me_3Si)_2NP(NSiMe_3)_2$. The reaction of the diphosphines R_2PPR_2 (R=Me, Ph) or Ph_2PH with S_4N_4 in boiling toluene provides a source of alkyl and aryl derivatives **109** (R=Me, Ph) [267] together with the eight-membered rings 1,3-$R_4P_2N_4S_2$ (**110**, E=S) and 1,5-$R_4P_2N_4S_2$ (**111**, E=S).[268] The best route to **109** (R=Ph) is shown in Equation 5.

$$Ph_2P(NSiMe_3)(NHSiMe_3) + 1/2S_4N_4 \rightarrow Ph_2PN_3S_2 + (Me_3Si)_2NH \qquad (5)$$



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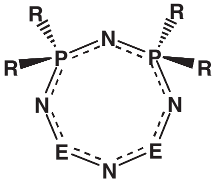

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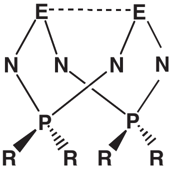
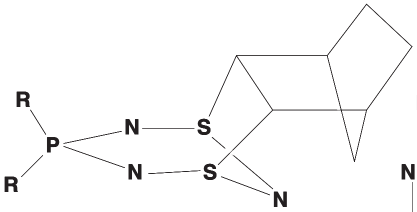


111

The phosphorus atom in **109** (R=Ph) lies out of the S_2N_3 plane. By contrast, the electron-donating substituents in **109** (R=Me_3SiNH) give rise to localized π-bonding in the NSNSN fragment of the ring. The six-membered rings **109** form white crystalline adducts with norbornadiene to give the *exo* adduct **112**. The bicyclic compound $R_2PN_5S_3$ (**113**) is obtained by oxidative addition of Cl_2 (SO_2Cl_2 or $PhICl_2$) to **109**, followed by reaction with $(Me_3SiN)_2S$.

The diphosphadithiatetrazocines **110** (E=S) and **111** (E=S) contain one more R_2PN unit in the ring than **109**. The structure of the orange-red 1,3-isomer (**110**, E=S, R=Ph) consists of an essentially planar N_3S_2 unit with the two phosphorus atoms located on opposite sides of the plane. The 1,5-isomers **111**

(E=S) are colourless, air-stable solids, which are prepared by the cyclocondensation reaction of $R_2PN_2(SiMe_3)_3$ with sulfur dichloride or thionyl chloride.[269] A similar cyclocondensation process, using a mixture of $SeCl_4$ and Se_2Cl_2 as a source of selenium, produces a mixture of the isomers **110** and **111** (E=Se, R=Ph).[270] The structures of **111** (E=S, R=alkyl, aryl) are folded eight-membered rings as a result of an intramolecular π^*–π^* interaction.[271] The ^{31}P NMR chemical shifts of **111** are *ca.* 80–100 ppm downfield compared to other P–N–S rings or cyclophosphazenes.[272]



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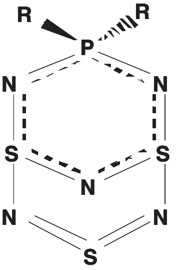

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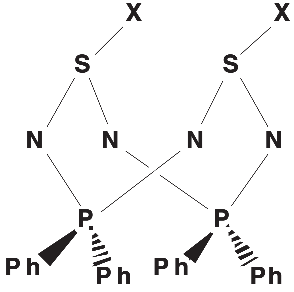

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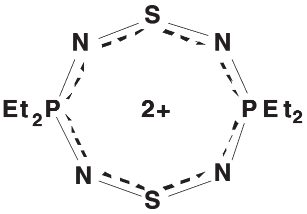

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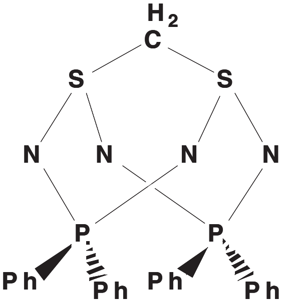


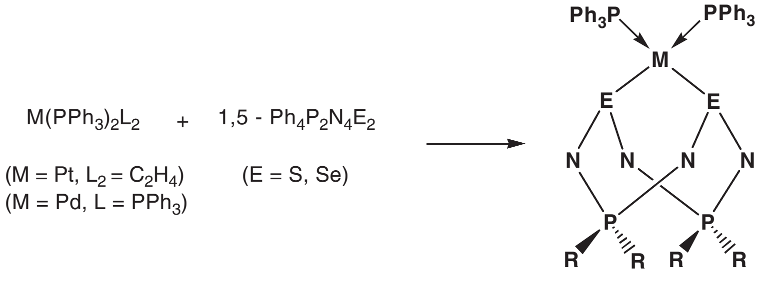
116

The integrity of the eight-membered ring in **111** (E=S) is retained in reactions with either electrophiles or nucleophiles. For example, the oxidative addition of halogens gives *exo*,*endo* dihalogenated derivatives 1,5-$Ph_4P_2N_4S_2X_2$ (**114**, X=Cl, Br). The dication $[Et_4P_2N_4S_2]^{2+}$ (**115**), prepared by the reaction of the *S*,*S*′-dichloro derivative 1,5-$Et_4P_2N_4S_2Cl_2$ with $AlCl_3$, is planar.[273]

The $P_2N_4S_2$ ring in **111** is readily susceptible to nucleophilic attack at sulfur. Reactions with organolithium reagents give monolithium derivatives

Li[$Ph_4P_2N_4S_2R$].[274] Alkali-metal derivatives of the dianion [$Ph_4P_2N_4S_2$]$^{2-}$ are prepared by treatment of **111** (E=S, R=Ph) with alkali-metal superhydrides M[Et_3BH] (M=Li, Na).[275] The methylene bridge between the two sulfur atoms in **116** is introduced by the addition of diiodomethane to $Li_2[Ph_4P_2N_4S_2]$.[276]

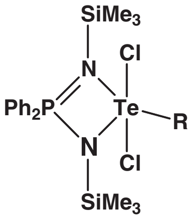
The combination of hard (*N*) and soft (*S* or *Se*) donor sites in the 1,5-$P_2N_4E_2$ ring system leads to a diversity of coordination modes in complexes with transition metals.[277] A versatile approach is the oxidative addition of the neutral ligand **111** to the metal centre (Equation 6).[278,279]



(6)

117

The planar four-membered ring **118** is obtained by the cyclocondensation of Li[$Ph_2P(NSiMe_3)_2$] with $ArTeCl_3$ or $TeCl_4$.[280]



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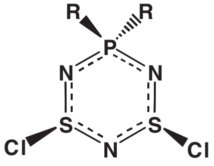

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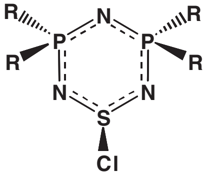
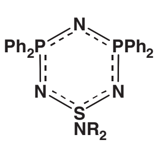


120

The ring systems **119** and **120** are hybrids of cyclophosphazenes and $(NSCl)_3$. The *S*,*S′*-dichloro derivative **119** is prepared by oxidative addition of Cl_2 to **109**, using SO_2Cl_2 or $PhICl_2$. The *S*-monochloro derivative **120** (R=Ph) is obtained from the reaction of Ph_2PCl with S_4N_4 in a 3:1 molar ratio in boiling acetonitrile.[281] The sulfur atom lies out of the NPNPN plane and the S–Cl bond distance is longer than that in $(NSCl)_3$ indicating partial ionic character. Halide ion acceptors, *e.g.*, $SbCl_5$, react readily with **120** (R=Cl, Ph) to give the corresponding cations. The tetrachlorinated cation $[(Cl_2PN)_2(NS)]^+$ is a planar six-membered ring.[282]



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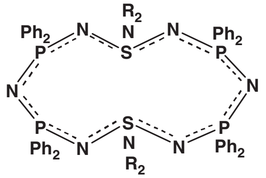

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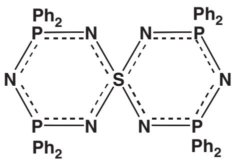

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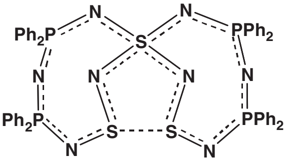

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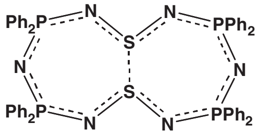

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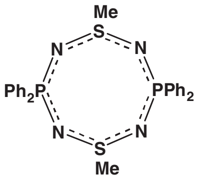
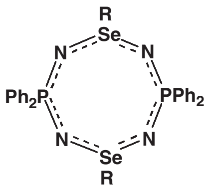


126

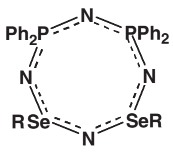
The treatment of **120** ($R{=}Ph$) with secondary amines produces the corresponding dialkylamino derivatives **121**, which undergo dimerization to form the 12-membered ring **122** in acetonitrile solution.[106] The thermally robust spirocyclic sulfur(VI) system **123** is produced by heating **122**. A related spirocyclic system **124** ($R{=}Ph$) is formed when **120** is treated with $(Me_3SiN)_2S$. The two eight-membered rings in **124** are linked by a weak S···S bond. Treatment of **120** ($R{=}Ph$) with $SbPh_3$ in acetonitrile produces the 12-membered ring **125**.[106]

Eight-membered rings of the type $(R_2PN)_2(NSR)_2$, *e.g.*, **126**, are synthesized by the reaction of $Li[Ph_4P_2N_4S_2Me]$ with methyl iodide[283a] or by treatment of $R_2PN_2(SiMe_3)_3$ with three equivalents of PhSCl.[283b] Selenium analogues **127** are prepared by the cyclocondensation reaction of $Ph_2PN_2(SiMe_3)_3$ with organoselenium trichlorides $RSeCl_3$ in acetonitile.[284] The selenium-containing derivatives undergo a solid-state transformation at room temperature to give the 1,3-isomers **128** ($R{=}Me$, Et).

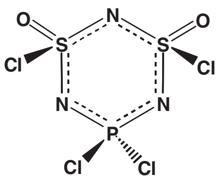
Ring systems of the type $[NS(O)Cl]_x(NPCl_2)_y$ are formally hybrids of the sulfanuric ring $[NS(O)Cl]_3$ and cyclophosphazenes $(NPCl_2)_n$[285] The best known of these heterocycles are the six-membered rings **129** and **130**. Small amounts of larger macrocycles (12- and 24-membered rings) have been isolated in the thermal ring-opening polymerization of **130**.[286]



127
(R = Me, Et, Ph)



128
(R = Me, Et)



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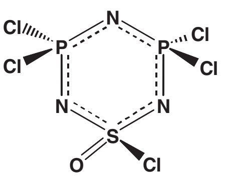
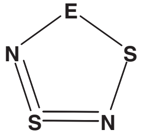


130

The best preparation of **130** involves the reaction of sulfamide with PCl_5 followed by a [5+1] cyclocondensation reaction between the *bis*(phosphazo)sulfone $Cl_3P{=}N{-}SO_2{-}N{=}PCl_3$ and hexamethyldisilazane. The reactions of **129** and **130** with nucleophilic reagents have been studied in considerable detail, with emphasis on the regiochemistry.[285]

4.11.2 Chalcogen–Nitrogen Rings Containing Phosphorus(III) or Other p-Block Elements

A few examples of five-membered rings of the type EN_2S_2 (**131**, E=AsMe, SnR_2) are known. The arsenic derivative $MeAsN_2S_2$ is obtained as a red liquid from the reaction of $MeAsCl_2$ with $(Me_3SiN)_2S$ in a 2:1 molar ratio. Organotin derivatives $R_2SnN_2S_2$ (R=Me, ^{n}Bu) are prepared by the reactions of (a) S_4N_4 with $N(SnMe_3)_3$ or (b) diorganotin dichlorides with $[S_4N_3]Cl$ in liquid ammonia.[287] These organotin reagents may be used to prepare the cyclic ketone OCN_2S_2, or cyclometallathiazenes MN_2S_2 (M=Rh, Ir).



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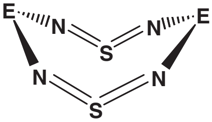


132

Eight-membered rings of the type $E(NSN)_2E$ (**132**) are known for $E{=}BNR_2$ (R=^{n}Pr, ^{i}Pr, ^{n}Bu), SiR_2 (R=Me, ^{t}Bu), AsR (R=Me, ^{t}Bu, Ph, Fc) and Sb (R=^{t}Bu).[288,289] These ring systems are obtained by the reaction of the appropriate organoelement halide [*e.g.*, R_2NBCl_2, Me_2SiCl_2, $RECl_2$ (E=As, Sb)] with $(Me_3SiN)_2S$ or $K_2[NSN]$ in a 1:1 molar ratio. The reagent $KNSNSiMe_3$ has also been used to prepare the antimony system. The heterocycles **132** generally adopt boat conformations in the solid state with short S=N bond distances.

4.12 Chains and Polymers

4.12.1 Poly(Sulfur Nitride), $(SN)_x$, and Related Polymers

The discovery of the metal-like behaviour and superconducting properties of the non-metallic polymer $(SN)_x$ in 1973 sparked interest in the area of sulfur–nitrogen chemistry.[14] Polymeric sulfur nitride is prepared by the solid-state polymerization of S_2N_2 at 0 °C over several days.[290a] The polymerization process is thought to involve the intermediate formation of a diradical generated by cleavage of one S–N bond (Figure 5). This topochemical process is nondiffusive in nature and produces monoclinic β-$(SN)_x$ (90%) and orthorhombic α-$(SN)_x$ (10%).[290b] A recent proposal for the polymerization mechanism involves excitation of the square planar singlet S_2N_2 molecule to the triplet surface, followed by puckering of the triplet species and polymerization in a direction approximately perpendicular to the S_2N_2 plane.[291] In order to

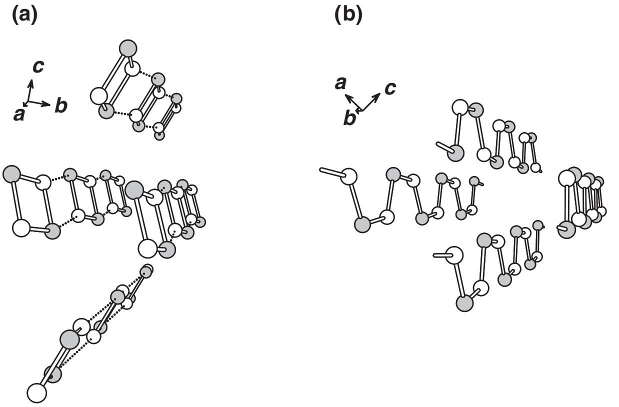


Figure 5 *Crystal structures of (a) S_2N_2 (redrawn from crystal data in ref. 290a) and (b) $(SN)_x$ (redrawn from crystal data in ref. 290b).*

prepare thin films of $(SN)_x$ on plastic or metal surfaces, several processing techniques have been investigated, *e.g.*, the electroreduction of $[S_5N_5]^+$ salts.[292]

Poly(sulfur nitride) is a shiny metallic solid consisting of highly oriented parallel fibres. The crystal structure reveals an almost planar *cis*,*trans* polymer.[14] Poly(sulfur nitride) is a conducting material along the fibres at room temperature. It becomes superconducting below liquid helium temperature. The conductivity across the fibres is much smaller. The polymer may be regarded as a one-dimensional chain of sulfur atoms. The single electron at each sulfur site gives rise to a half-filled band and, hence, metallic character.[293]

$(SN)_x$ can act as an efficient barrier electrode in ZnS junctions, increasing the quantum efficiency of the blue emission by a factor of 100 over gold.[14] It can also be used to increase the efficiency of GaAs solar cells by up to 35%. Metal ions interact more strongly with a poly(sulfur nitride) surface than with other metal electrodes. This property has stimulated investigations of possible applications of $(SN)_x$ as an electrode material.

$(SN)_x$ slowly decomposes in alkaline solutions and is readily oxidized. Partial bromination of $(SN)_x$ with bromine vapour yields the blue-black conducting polymer $(SNBr_{0.4})_x$.[14] The sulfur–nitrogen chain in this polymer is partially oxidized and the bromine is present as Br_3^- ions and intercalated Br_2 molecules. The polymer $(SNBr_{0.4})_x$ is also produced by the reaction of $(NSCl)_3$ with Me_3SiBr in CH_2Cl_2 at –60 °C.

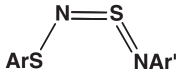
Conducting polymers with *p*-phenylene groups in the backbone are generated by metathesis (Equation 7). Doping of these polymers with acceptors such as I_2, Br_2 or AsF_5 increases the conductivity. Similar polymers have been prepared from 1,3- and 1,4-$ClSC_6H_4SCl$.[294]

$$Me_3SiNSNC_6H_4NSNSiMe_3 + SCl_2 \rightarrow 1/x[\text{-}C_6H_4NSNSNSN\text{-}]_x + 2Me_3SiCl \quad (7)$$

4.12.2 Sulfur–Nitrogen Chains

The chain compounds of the type RS_xN_yR can be conveniently classified as sulfur-rich, nitrogen-rich or even-chain species. Most of the known S–N chains contain an even number of N atoms and are neutral.[17] The exceptions are the cations $[RSNSR]^+$ (R=Cl, Br) and $[RS_4N_3R]^+$. The cationic systems are stabilized by (a) removal of an antibonding electron from the π-system, (b) lowering of the energies of the filled molecular orbitals induced by the positive charge, and (c) the ionic contribution to the lattice energy in the solid state. Early examples of the synthesis of S–N chains frequently involved the reaction of S_4N_4 with nucleophilic reagents. Subsequently, rational syntheses have been developed for chain lengths up to ArS_5N_4Ar *via* condensation reactions involving the elimination of Me_3SiCl or $(Me_3Si)_2O$.[295] The *in situ* reagent $[NS]^+$ has been used to extend chain length, *e.g.*, in the conversion of ArS_3N_2Ar into $[ArS_4N_3Ar][AsF_6]$ (Ar=Ph, 4-$O_2NC_6H_4$).[296]

The S–N chains ArS_2N_2Ar' (**133**, Ar=4-$O_2NC_6H_4$, Ar′=4-$MeOC_6H_4$), PhN_4S_3Ph (**134**) and $ArS_4N_4SiMe_3$ (**135**, Ar=4-$O_2NC_6H_4$) adopt alternating *cis*,*trans* conformations similar to $(SN)_x$.[295,297] However, there is a distinct alternation of short and long sulfur–nitrogen bonds in the oligomeric chains, consistent with a more localized [–S–N=S=N–] structure. Other chain conformations are also observed, as illustrated by the structures of ArS_3N_2Ar (**136**, Ar=4-ClC_6H_4), $[ArS_4N_3Ar]^+$ (**137**, Ar=4-MeC_6H_4), ArS_5N_4Ar (**138**, Ar=4MeC_6H_4), and ${}^tBuN_4S_3{}^tBu$ (**139**).[17] The small energy difference between various isomers is indicated by the subtle conformational change that occurs upon the replacement of the Ph groups in **134** by ^{t}Bu substituents to give **139**. The selenium-containing chain $(Me_3SiNSN)_2Se$ adopts the same conformation as **139**.[298] The *cis*,*cis* conformation adopted by **136** and the selenium derivative PhSeN=S=NSePh in the solid state is attributed to crystal packing forces.[299]



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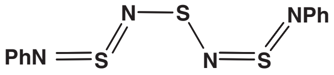

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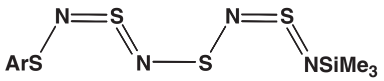

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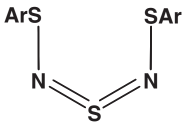

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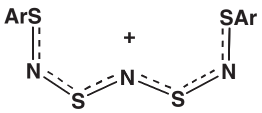

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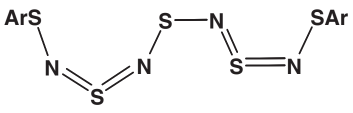

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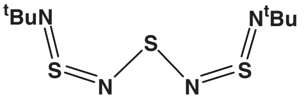
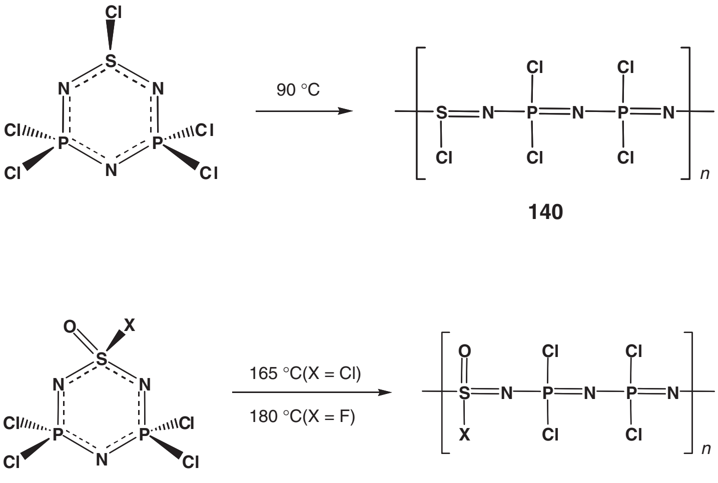


139

4.12.3 Sulfur–Nitrogen Polymers Containing Three-Coordinate Sulfur(IV)

The hybrid polymer **140** is generated by a thermal ring-opening polymerization (ROP) process (Scheme 10).[300,301] Polymers containing three-coordinate sulfur(IV) are generally hydrolytically sensitive even when the chloro substituents are replaced by phenoxy groups.[302]



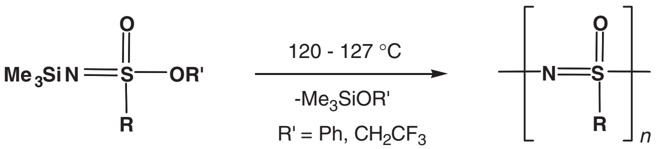
140

141a (X = Cl)
141b (X = F)

Scheme 10 *Synthesis of poly(thiophosphazene) and poly(thionyl-phosphazenes)*

4.12.4 Sulfur–Nitrogen Polymers Containing Four-Coordinate Sulfur(VI)

Sulfanuric halides $[NS(O)X]_3$ (X=Cl, F) do not undergo ring-opening polymerization. High molecular weight polymers containing repeating [–N=S(O)R–] (R=Me, Ph) units (**142**) are generated from an acyclic precursor by a condensation process (Scheme 11).[303,304]



142
(R = Me, Et, Ph)

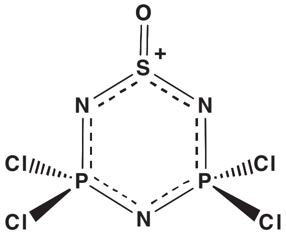
Scheme 11 *Synthesis of sulfanuric polymers*

The sulfanuric polymers **142** are thermoplastics with glass transition temperatures (T_g) in the range 30–85 °C, *cf.*, poly(phosphazenes) $(NPX_2)_n$ ($T_g = -96$ °C, X=F; –84 °C, X=OEt; –66 °C, X=Cl; –6 °C, X=OPh). The higher T_gs of the sulfanuric systems are attributed to (a) increased intermolecular interactions as a result of the polar S=O groups and (b) greater side group–main chain interactions as a result of the smaller $<$NSN bond angle (calculated value 103°) compared to *ca.* 120° for $<$NPN in poly(phosphazenes).[304]

The first example of a hybrid polymer that contains both [NS(O)Cl] and $[NPCl_2]$ units, **141a**, was obtained as a pale yellow elastomer by ring-opening polymerization (Scheme 10).[305] In the presence of $GaCl_3$, this polymerization process proceeds quantitatively at room temperature in CH_2Cl_2.[306]

The cation $[NSO(NPCl_2)_2]^+$ (**143**) is the reactive intermediate in this process, as illustrated by the isolation of the solvent-derived product **144** *via* halide abstraction by $AlCl_3$ in 1,2-dichloroethane.[306]

In order to obtain hydrolytically stable materials, the chlorine substituents in the polymer **141a** are replaced by phenoxy or *tert*-butylamino groups.[307,308] The reaction of **141a** with sodium phenoxide in dioxane produces the polymer $\{[NS(O)Cl][NP(OPh)_2]_2\}_n$ (**145**), which is a colourless elastomer, stable towards moisture with an average molecular weight of *ca.* 3×10^4. The chlorine substituents on phosphorus and sulfur are all replaced upon treatment of **141a** with an excess of *tert*-butylamine in dichloromethane to give the polymer $\{[NS(O)NH^tBu][NP(NH^tBu)_2]_2\}_n$ (**146**), which has an average molecular weight of *ca.* 2.5×10^4.



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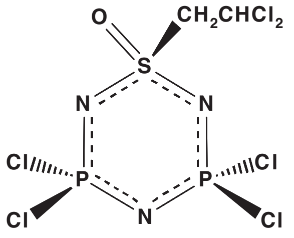

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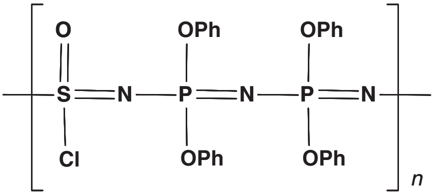

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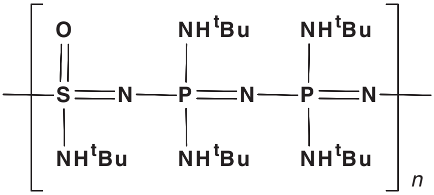


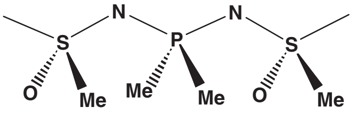
147

The T_g:s of the hybrid sulfanuric–phosphazene polymers are much closer to the values reported for poly(phosphazenes) than those of sulfanuric polymers. The values for the polymers **141a** and **141b** are –46 and –56 °C, respectively. The

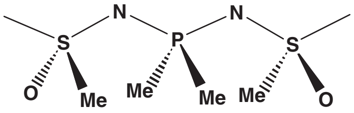
T_g of –16 °C for the butylamino-substituted hybrid polymer **146** is significantly lower than the value of +8 °C reported for the corresponding poly(phosphazene) $[NP(NH^tBu)_2]_n$ as a result of the presence of the small S=O group.

Polythionylphosphazenes have considerable potential as components of the matrices for phosphorescent oxygen sensors.[309] These sensors contain transition-metal-based dyes with oxygen-quenchable excited states dispersed in a polymer matrix. They can be used, for example, to determine the air pressure distribution on the wings of an aircraft in wind tunnel experiments. The high solubility and high diffusion coefficient for oxygen of these hybrid polymers are crucial properties in this application.[310] Although **146** forms sticky films, the block co-polymer polythionylphosphazene-*b*-polytetrahydrofuran, prepared from the reaction of the cation of **141a** with THF, forms free-standing films.[311]

Hybrid polymers containing an equal number of alternating [NS(O)Me] and $[NPMe_2]$ units in the backbone are prepared by sequential condensation processes.[312] Molecular weight determinations indicate that the hybrid polymer **147** produced in this way consists of *ca.* 30 repeat units. Multinuclear NMR spectra reveal that this polymer is comprised of approximately equal amounts of isotactic (**147a**) and syndiotactic (**147b**) forms.



147a



147b

4.13 Outlook

In the past 15 years interest in sulfur–nitrogen compounds has moved from a focus on fundamental concepts of structure and bonding and the development of an understanding of their unusual reactivity to an emphasis on applications in the design of materials with novel conducting or magnetic properties. At the same time increasing attention has been accorded to selenium- and tellurium-containing systems, since compounds containing the heavier chalcogens show promise as (a) components of useful devices, (b) reagents in organic synthesis, and (c) precursors for semi-conducting materials. These trends are expected to continue with accelerated vigour in the coming years. Investigations of chalcogen–nitrogen compounds will continue to lead to unexpected advances in the light of the unpredictable behaviour of tellurium compared to that of the other chalcogens.

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CHAPTER 5

Chalcogen–Phosphorus (and Heavier Congeners) Chemistry

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5.1 Introduction

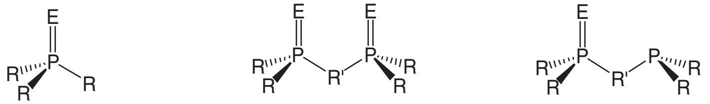
Research into chalcogen–phosphorus chemistry dates back over 200 years and covers a wide variety of compounds ranging from simple phosphorus chalcogenides containing exclusively chalcogen and phosphorus, to large biological macromolecules and nanometre-sized metal-based clusters. Over the last century, compounds containing chalcogen–phosphorus bonds have found applications in areas as diverse as the heads of "strike anywhere" matches, pesticides, lubricant and plastic additives, organic reagents and precursors for metal chalcogenide thin film and quantum dot growth.

There are currently over 130,000 different molecular species reported in the literature which contain either single or multiple sulfur to phosphorus bonds, approximately 6000 containing selenium-phosphorus bonds, and just 350 containing tellurium-phosphorus bonds.[†] The decreasing number of known chalcogen–phosphorus compounds as group 16 is descended is predominately due to weakening chalcogen–phosphorus bond strengths down group 16 [E(P-S) $>$ E(P-Se) $>$ E(P-Te)], which gives rise to increasing thermal and hydrolytic instability. This has made the synthesis and handling of phosphorus compounds containing the heavier chalcogens particularly challenging, although in recent years advances in synthetic methodology have led to much progress in this area. Another focus of recent research effort in synthetic chalcogen–phosphorus chemistry has been the move away from the use noxious and toxic reagents, such as hydrogen chalcogenides (H_2E; $E = S$, Se, Te) and sodium hydrochalcogenides (NaHE), to easier to handle and more environmentally benign reagents such as the elemental chalcogens themselves.

[†] Source: Chemical Abstracts, American Chemical Society (Scifinder Scholar, Version: 2004).

This chapter seeks to provide an overview of the main classes of phosphorus–chalcogen containing compounds, their coordination chemistry with metallic and semi-metallic elements and some of their main applications. The analogous compounds containing the heavier congeners of phosphorus (arsenic, antimony and bismuth) will also be discussed where appropriate, and compared to their phosphorus analogues. Given the huge amount of published material on chalcogen–phosphorus compounds this chapter is inevitably selective and will focus in particular on recent advances in these areas. More comprehensive reference works focussing solely or predominately on phosphorus–chalcogen compounds are available elsewhere.[1–4]

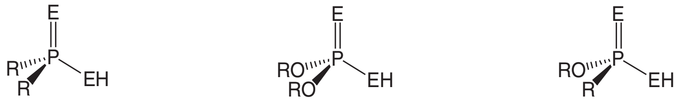
The nomenclature used for phosphorus–chalcogen containing molecules is often inconsistent in the literature, with several different naming schemes in current use. Hence for clarity, the naming system employed for the main chalcogen–phosphorus compounds in this chapter is detailed in Figure 1.



Tertiary phosphine chalcogenide

Diphosphine dichalcogenide

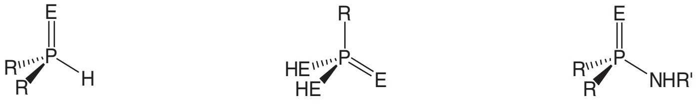
Diphosphine monochalcogenide



Dichalcogenophosphinic acid (dichalcogenophosphinate)

Dichalcogenophosphoric acid (dichalcogenophosphate)

Dichalcogenophosphonic acid (dichalcogenophosphonate)



Secondary phosphine chalcogenide (chalcogenophosphinite)

Trichalcogenophosphonic acid (trichalcogenophosphonate)

Chalcogenoamidophosphinic acid (chalcogenoimidophosphinate)

Iminobis(diorganophosphine chalcogenide) (dichalcogenoimidodiphosphinate)

Dichalcogenadiphosphetane dichalcogenide

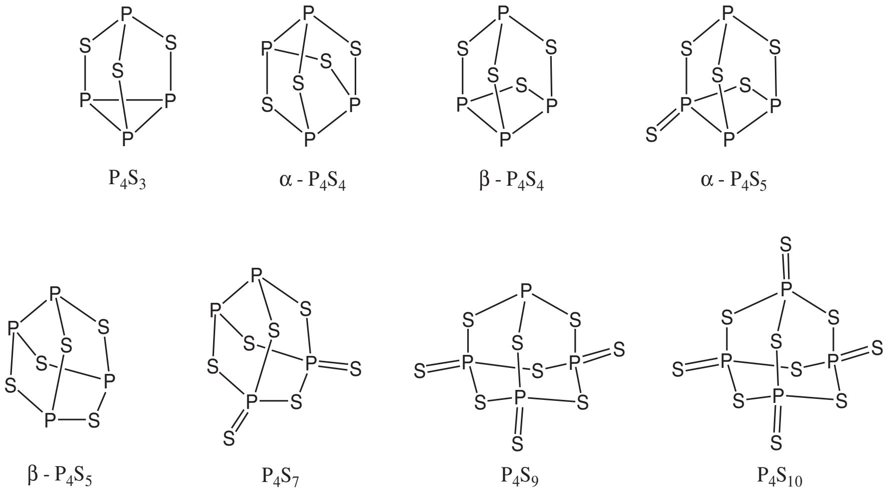
Figure 1 *Nomenclature of phosphorus-chalcogen compounds (names in brackets refer to the anionic deprotonated form). R = alkyl, aryl; E = S, Se, Te*

5.2 Preparation, Characterisation and Properties of Compounds Containing Phosphorus–Chalcogen Bonds

5.2.1. Phosphorus Chalcogenides [P_nE_m] and Chalcogeno–Phosphate Anions [P_nE_m]$^{z-}$

Many phosphorus sulfides are known to exist as discrete molecules of general formula P_4S_n. The first of these compounds were initially prepared by heating together mixtures of red phosphorus and sulfur in the appropriate stoichiometries under an inert atmosphere, or by reacting white phosphorus and sulfur in a high boiling point solvent. Since then many different synthetic approaches have been applied and high yielding routes to P_4S_3, α-P_4S_4, β-P_4S_4, α-P_4S_5, β-P_4S_5, P_4S_7, P_4S_9 and P_4S_{10} are now known.[1] In addition, a handful of other phosphorus sulfides (including γ-P_4S_4, γ-P_4S_5, δ-P_4S_6, and ε-P_4S_6) have been discovered and characterised with the aid of ^{31}P NMR spectroscopy, often existing in small quantities in mixtures with other phosphorus sulfides which cannot be efficiently separated.[5–7]

All known structures of these molecular phosphorus sulfides are based on P_4 tetrahedral cages with replacement of one or more of the P–P edges with a P–S–P unit, and in some cases by addition of terminal sulfur atoms on one or more of the phosphorus centres (Figure 2). These structures therefore differ considerably from those found for phosphorus oxides (with the exception of P_4S_9 and P_4S_{10} which are analogous to the oxides) and are often unique to group 15 – chalcogen chemistry.



P_4S_3 α - P_4S_4 β - P_4S_4 α - P_4S_5

β - P_4S_5 P_4S_7 P_4S_9 P_4S_{10}

Figure 2 *Structures of some phosphorus sulfide molecules*

Table 1 *Phosphorus sulfides and structurally analogous group 15 chalcogenides*

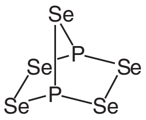
P_4S_3	α-P_4S_4	β-P_4S_4	α-P_4S_5	P_4S_7	P_4S_{10}
P_4Se_3	P_4Se_4		P_4Se_5	P_4Se_7	P_4Se_{10}
As_4S_3	α-,β-As_4S_4	γ-As_4S_4	As_4S_5		As_4S_{10}
As_4Se_3	As_4Se_4				
As_3S_4					
As_3Se_4					

All of the P_4S_n molecules are stable in CS_2 solution, with the exception of P_4S_4 which disproportionates slowly to give P_4S_3 and P_4S_5. The hydrolytic stability differs somewhat between the sulfides; P_4S_3 is the most stable and does not react with either cold or hot water, but does react with acid solutions. The other sulfides are all hydrolysed in water to give H_3PO_4, or other oxo-acids, and evolve H_2S.

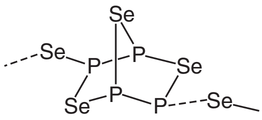
Several of these phosphorus sulfides are produced commercially for industrial applications. P_4S_3 is one of the key chemical constituents of "strike-anywhere" matches and has been used industrially for this purpose ever since 1898. P_4S_{10} is the most widely industrially used of the phosphorus sulfides with applications in the preparation of lubricant additives and pesticides and in organic chemistry to convert carbonyl or alcohol groups into their sulfur analogues (see Section 5.4).

The heavier chalcogen and pnictogen analogues of many of these phosphine sulfides are also known (Table 1).

In general, phosphorus selenides are more difficult to handle than their sulfur analogues and therefore there are fewer well-characterised examples of these species. Although many of the known phosphorus selenides are isostructural to their lighter sulfur analogues (Table 1), there are some specific examples where the structures differ considerably. For example, P_2Se_5 forms a norbornane-like structure (**1**)[8] and P_4Se_4 can exist with P_4Se_3 norbornane-like units which connect together into chains *via* bridging Se atoms (**2**).[8,9] Neither of these structural motifs has yet been observed in phosphorus-sulfur chemistry. To date, no molecular phosphorus tellurides (P_nTe_m) have been reported in the literature.



1



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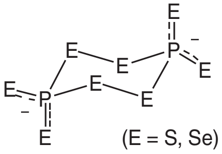
Antimony and bismuth sulfides and selenides (Sb_2S_3, Bi_2S_3 and Sb_2Se_3) are also known although these do not exist as discrete molecular compounds, but instead form ribbon-like polymeric structures where each group 15 atom is bound to three group 16 atoms and vice-versa to give an array of interlocking pyramids.

In addition to these neutral binary compounds, many ternary group 15 chalcogenides are known. These include species with one or more of the chalcogens replaced with an oxygen such as P_4O_6Se (which is a P_4O_6 cage with a terminal doubly bonded Se atom),[10] and those containing mixed group 15 elements such as P_3SbS_3 (which is a P_4S_3 cage with the apical phosphorus replaced with antimony).[11]

Reaction of binary group 15 chalcogenides with reducing agents, and in particular with chalcogenide sources such as Na_2S and K_2Se_4, gives group 15/16 anionic salts $[Q_nE_m]^{z-}$ (Q = P, As, Sb; E = S, Se).[12] These anions are also accessible from the reaction of binary group 15 chalcogenides with a basic aqueous solution saturated with H_2E and elemental E (E = S, Se). Such binary chalcogenophosphate anions can exist as ion-separate species, as ligands on discrete metal complexes or in extended lattices (these latter two classes are discussed in more detail in Section 5.3.1). Of these anions the simplest are the tetrahedral $[QS_4]^{3-}$ salts (Q = P, As, Sb), although the bismuth analogue (Q = Bi) has yet to be reported in solution – presumably due to a combination of the weak Bi=S double bond and the preference of bismuth to adopt a + 3 over a + 5 oxidation state. The tetraseleno analogues, $[QSe_4]^{3-}$, are known for Q = P, As, Sb although they suffer from increased hydrolytic and thermal instability compared to their sulfur analogues, and consequently far less is known about these species. At the moment no analogous group 15 tetratelluro anions are known.

Larger binary chalcogeno–phosphate anions are almost exclusively based on similar tetrahedral $[PE_4]^{3-}$ phosphorus (V) building blocks, which can condense to form rings or clusters. This is well illustrated by the isostructural $[1,4\text{-}P_2E_8]^{2-}$ anions (E = S^{13}, Se^{14}) (**3**) which contain chair-like six membered P_2E_4 rings formally built from two connected $[PE_4]^{3-}$ units, and the trianionic $[P_3S_9]^{3-}$ (**4**) which contains a P_3S_3 six-membered ring and can be considered as three condensed $[PS_4]^{3-}$ units.[15]



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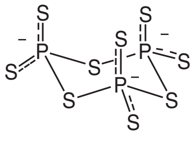

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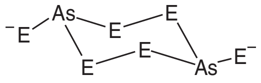
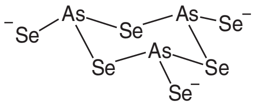
In contrast to the phosphorus-based anions, those of the heavier group 15 elements are predominately based on $[QE_3]^{3-}$ pyramidal anions (Q = As, Sb; E = S, S, Te) with Q in oxidation state + 3. These pyramidal subunits can then join together to form condensed ring structures. Recent examples include $[As_2Se_6]^{3-}$ (**5**)[16] and its isostructural Te analogue,[17] formed from two connected $[AsE_3]^{3-}$ pyramids to give six-membered As_2E_4 rings similar to the P_2E_4 rings in **3**, and $[As_3Se_6]^{3-}$ (**6**) made from three condensed $[AsE_3]^{3-}$ pyramids and containing an As_3Se_3 six-membered ring analogous to the P_3S_3 ring in **4**.[18] Larger ring sizes have also been reported such as the eight membered Sb_4S_4 cyclic in $[Sb_4S_8]^{4-}$ (**7**).[19] Binary group 15/16 anions with much larger ratios of chalcogen to pnictogen are also known containing long chains or rings of chalcogen atoms, *e.g.*, $[Bi_2S_{34}]^{3}$[20] and $[AsSe_8]^-$.[16]


(E = Se, Te)

5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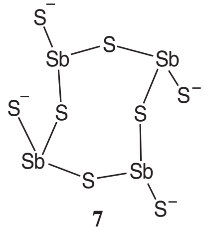
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5.2.2. Tertiary Phosphine Chalcogenides [R_3PE]

The easiest and most simple route to tertiary phosphine sulfides (R_3PS) is from the direct reaction of a tertiary phosphine with elemental sulfur in an inert solvent (Equation 1). Other high yielding routes to tertiary phosphine sulfides include the reaction of $PSCl_3$ with organolithium, Grignard or organoaluminium reagents (Equations 2–4). In addition, they can be prepared from heating the corresponding phosphine oxide with P_4S_{10}.

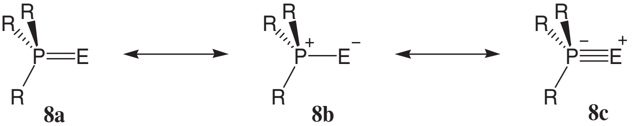
$$R_3P + E_n \xrightarrow{(E_n = S, Se \text{ or } Te)} R_3PE \tag{1}$$

$$Cl_3PS + 3\,RLi \longrightarrow R_3PS + 3\,LiCl \tag{2}$$

$$Cl_3PS + 3\,RMgX \longrightarrow R_3PS + 3\,MgXCl \tag{3}$$

$$Cl_3PS + R_3Al \longrightarrow R_3PS + AlCl_3 \tag{4}$$

Tertiary phosphine sulfides are generally stable compounds and are not easily oxidised by air, although they can be oxidised by hydrogen peroxide or dilute nitric acid. The analogous tertiary phosphine selenides and tellurides are however, more reactive to oxidation. Similar to the sulfides they can be prepared from the direct reaction of elemental chalcogen with a tertiary phosphine (Equation 1). Tertiary phosphine selenides are also accessible from tertiary phosphines using KSeCN as the selenium source instead of the element itself.


8a **8b** **8c**

Studies on the solid-state structures, vibrational frequencies and dipole moments of tertiary phosphine chalcogenides have shown the phosphorus to be in an approximately tetrahedral environment with phosphorus–chalcogen bond lengths in-between those expected for single and double bonds.[21] There has been much debate on the nature of the phosphorus–chalcogen bond in these

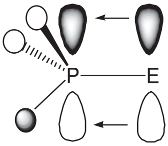


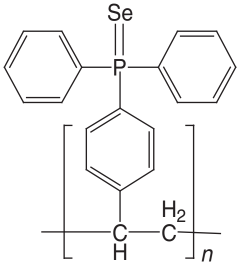
Figure 3 *Schematic view of one of the π-back bonds in an R_3PE molecule, from a filled p-orbital of E to one of the empty σ* orbital combinations of e-symmetry (C_{3v} point group) on the R_3P fragment*

species, especially concerning the degree of π-character in the bond. It was initially assumed that two resonance structures were in play: **8a**, consisting of a σ-component and a π-component which arises from the overlap of phosphorus 3d and chalcogen p orbitals and **8b** consisting solely of a σ-donor phosphorus to chalcogen bond. NMR studies suggested a large contribution of the dipolar resonance form **8b**, as evidenced by the negative value (compared to Me_2Se) of the selenium chemical shift in the ^{77}Se NMR spectra of tertiary phosphine selenides, attributable to the increased negative charge on the chalcogen atom in this resonance form. However, theoretical studies have since shown the phosphorus d-orbitals to be unavailable for bonding in these compounds, and hence there is no contribution from resonance structure **8a**.[21] Instead, the resonance structure **8c** has been proposed to make a significant contribution, containing one σ bond and two π bonds from back donation from the chalcogen p orbitals to σ* orbitals on the R_3P fragment (Figure 3). Therefore it is perhaps more correct to consider the phosphorus–chalcogen bond in these compounds as a partial triple rather than partial double bond. The π-bond order of the phosphorus–chalcogen bond in Me_3PE has been calculated, using density functional theory (DFT), to decrease down the group 16 elements from 0.7 for $E = O$ to 0.5 for $E = Te$.[22] Increasing the size of the group 15 element also leads to a weakening of the π component of the bond in the order $R_3PE > R_3AsE > R_3SbE$.

Tertiary phosphine chalcogenides can undergo an exchange reaction, whereby the chalcogen atom is transferred from the tertiary phosphine chalcogenide to another more basic tertiary phosphine or phosphorus(III) compound (Equation 5). The propensity for R_3PE to undergo this reaction increases in the order $E = S < Se < Te$ with decreasing phosphorus–chalcogen bond strength.

$$R_3PE + R'_3P \longrightarrow R_3P + R'_3PE \tag{5}$$

The lability of the phosphorus–chalcogen bond means that tertiary phosphine selenides and tellurides are often a more reactive source of selenium or tellurium than the chalcogen metal itself. It therefore follows that they have been used as chalcogen transfer reagents for organic, inorganic and nanomaterial synthesis (see Section 5.4), and polymer supported tertiary phosphine chalcogenides such as **9**[23] have been developed as convenient sources of reactive chalcogen.



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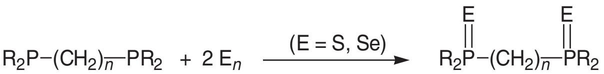
5.2.3. Diphosphine Di- and Mono-Chalcogenides [$R_2P(E)$-R'-$P(E)R_2$ and $R_2P(E)$-R'-PR_2]

Diphosphine dichalcogenides of general formula $R_2P(E)(CH_2)_nP(E)R_2$ (R = alkyl, aryl, alkoxy, aryloxy; E = S, Se) can be readily prepared by reaction of two equivalents of elemental chalcogen (or alternatively KSeCN for the diselenides) with a *bis*phosphine (Equation 6). The diphosphine mono-sulfides and –selenides are more difficult to prepare, requiring carefully controlled addition of one equivalent of elemental chalcogen to the *bis*phosphine to avoid too much contamination by dichalcogenide by-products. However, the monosulfide of *bis*(diphenylphosphino)methane (dppm) can be conveniently prepared from triphenylphosphine sulfide giving no contamination from the disulfide (Equation 7).[24] An analogous route to the monoselenide was also investigated, but found to be too low yielding for practical use.[24] Diphosphine mono- and di-tellurides are currently inaccessible by either of these synthetic routes.

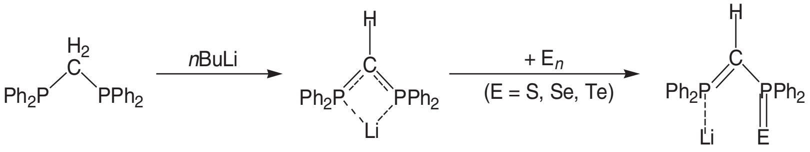


$$R_2P{-}(CH_2)_n{-}PR_2 + 2\,E_n \xrightarrow{(E = S,\ Se)} R_2\overset{\overset{E}{\|}}{P}{-}(CH_2)_n{-}\overset{\overset{E}{\|}}{P}R_2 \quad (6)$$

$$Ph_3PS + CH_3Li \xrightarrow[-PhH]{} Ph_2P(S)CH_2Li \xrightarrow[-LiCl]{+\,Ph_2PCl} Ph_2P(S)CH_2PPh_2 \quad (7)$$

Diphosphine monoselenides have been shown to undergo solution equilibria with their *bis*phosphine and diphosphine diselenide counterparts, making their application as reagents or ligands difficult and unpredictable.[25] In order to overcome this problem, mono-chalcogenides of general formula $Ph_2AsCH_2CH_2P(E)Ph_2$ (E = S, Se) have be prepared from the reaction of elemental sulfur or selenium with $Ph_2AsCH_2CH_2PPh_2$ in thf.[26] This mixed group 15 mono-chalcogenide, unlike its diphosphine analogue, does not suffer from contamination from the dichalcogenide since the phosphorus(III) centre is oxidised far more readily than the arsenic(III) centre. Mixed group 16 ligands are also known, including $Ph_2P(E)CH_2P(O)Ph_2$ (E = S, Se) which can be synthesised by gentle oxidation of the monochalcogenide $Ph_2P(E)CH_2PPh_2$ with H_2O_2.[24]

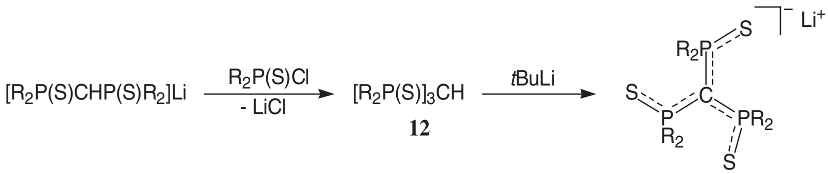
The mono- and di-chalcogenides of dppm contain an acidic methylene carbon which can undergo deprotonation. NMR spectroscopic studies on the relative acidities of these methylene groups show an increase in acidity for the series $R_2PCH_2PR_2$ < $R_2P(O)CH_2P(O)R_2$ < $R_2P(S)CH_2P(S)R_2$ < $R_2P(Se)CH_2P(Se)R_2$;[24] this can be attributed to the increasing stability of the dipolar canonical form P^+-E^- of the phosphorus–chalcogen bonds on descending the group 16 elements. Diphosphine mono- and di-sulfides can be readily deprotonated at the methylene carbon by direct reaction with *n*BuLi.[27] Coordination of the diphosphine mono- or di-sulfide to a metal centre renders the methylene carbon more acidic allowing deprotonation with milder reagents such as NaH or even organic amines.[28] Although diphosphine mono- and di-selenides can also be deprotonated with *n*BuLi, side reactions lead to considerable contamination from *n*BuSe$_n$Li and the parent *bis*phosphine.[29] Instead, these anions (**11**) are better prepared from the reaction of $[(R_2P)_2CH]Li$ with elemental chalcogen according to Equation 8.[29] Structural studies on the lithiated *bis*phosphine intermediate (**10**) in this reaction have revealed why no carbon–chalcogen bonds are formed on addition of elemental chalcogen as perhaps would first be expected, since chalcogen insertion into a C–Li bond is clearly not possible with the lithium binding exclusively to the phosphorus centres in preference to the carbanion centre.[29–31]



(8)

10 **11**

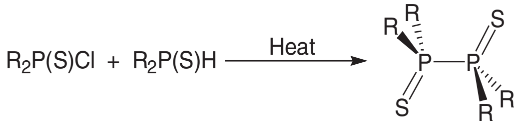
Related to these diphosphine dichalcogenides are the triphosphine trisulfides $[R_2P(S)]_3CH$ (**12**) which can be prepared from lithiated methylene diphosphine disulfides upon treatment with thiophosphinic chlorides (Equation 9). Deprotonation of **12** with *t*BuLi gives a resonance-stabilised anion **13** containing a planar central carbanion whose charge is delocalised onto the three neighbouring phosphorus and sulfur atoms.[32]



(9)

12 **13**

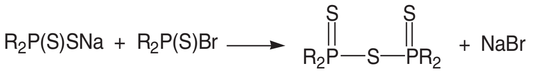
Other related compounds are the diphosphine disulfides $R_2P(S)P(S)R_2$ **14**, which contain a direct phosphorus–phosphorus bond, and polysulfur *bis*(diorganophosphine sulfides) $R_2P(S)$-S_n-$P(S)R_2$ in which the two phosphorus centres are connected by a chain of one of more sulfur atoms. $R_2P(S)P(S)R_2$ compounds are accessible from heating secondary phosphine sulfides with thiophosphinic chlorides (Equation 10) or by reaction of *bis*phosphines with elemental sulfur.[1] X-ray crystallographic, ^{31}P NMR spectroscopic and theoretical studies have all shown **14** to preferentially adopt a *trans* conformation of the P=S units.[33]



14

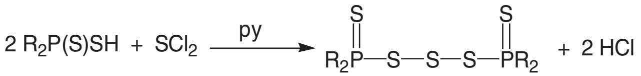
(10)

Numerous methods have been used for the synthesis of $R_2P(S)$-S_n-$P(S)R_2$ compounds. However, probably the most convenient and generally applicable for a range of alkyl, aryl, alkoxy and aryloxy R substituents is the reaction of alkali metal dithiophosphinates with thiophosphinic bromides for $n = 1$ (Equation 11), or the oxidation of dithiophosphinic acids or their alkali metal salts with I_2, SCl_2 or S_2Cl_2 for $n = 2$, 3 or 4 respectively (Equations 12–14).[1,34]

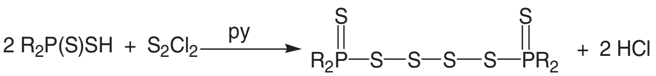


$$R_2P(S)SNa + R_2P(S)Br \longrightarrow R_2\overset{S}{\overset{\|}{P}}-S-\overset{S}{\overset{\|}{P}}R_2 + NaBr \tag{11}$$

$$2\,R_2P(S)SH + I_2 \xrightarrow{H_2O} R_2\overset{S}{\overset{\|}{P}}-S-S-\overset{S}{\overset{\|}{P}}R_2 + 2\,HI \tag{12}$$



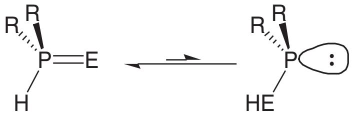
$$2\,R_2P(S)SH + SCl_2 \xrightarrow{py} R_2\overset{S}{\overset{\|}{P}}-S-S-S-\overset{S}{\overset{\|}{P}}R_2 + 2\,HCl \tag{13}$$



$$2\,R_2P(S)SH + S_2Cl_2 \xrightarrow{py} R_2\overset{S}{\overset{\|}{P}}-S-S-S-S-\overset{S}{\overset{\|}{P}}R_2 + 2\,HCl \tag{14}$$

5.2.4. Secondary Phosphine Chalcogenides [$R_2P(E)H$]

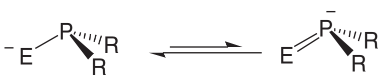
Secondary phosphine chalcogenides (**15a**) can be readily prepared from oxidation of secondary phosphines (R_2PH) with elemental sulfur, selenium or tellurium, although care must be taken to avoid over-oxidation to give the dichalcogenophosphinic acids (see Section 5.2.5).



15a **15b**

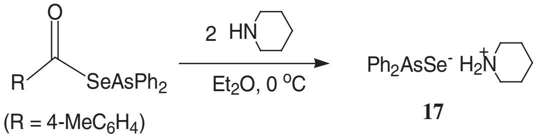
Secondary phosphine chalcogenides (**15a**) exist in equilibrium with their chalcogenophosphinous acid tautomers (**15b**). This equilibrium sits far on the side of the chalcogenide tautomer **15a** for virtually all organo R groups, to such an extent that it is difficult to even detect the presence of the acid tautomer **15b** using spectroscopic or other means. However, with very strongly electron withdrawing CF_3 substituents and E = S the equilibrium has been shown to be shifted in favour of tautomer **15b**, although in this case the resultant acid $(CF_3)_2PSH$ is unstable towards condensation to give $(CF_3)_2PSP(CF_3)_2$ and H_2S.[35]

Secondary phosphine chalcogenides are weak acids and can be deprotonated by alkali metals or organic bases. They can also be prepared directly as their alkali-metal chalcogenophosphinite salts $R_2PE^-M^+$ *via* reaction of an alkali-metal phosphide $(R_2P^-M^+)$ with elemental chalcogen.[36,37] Chalcogenophosphinites favour tautomeric form **16a** which possesses a chalcogen–phosphorus single bond with the negative charge sited primarily on the chalcogen atom, although in some cases tautomeric form **16b**, containing formally a chalcogen–phosphorus double bond, can be stabilised by coordination of the resultant phosphorus anion to a metal centre (see Section 5.3.4).



16a **16b**

Chalcogenoarsinites (R_2AsE^-; E = S, Se, Te) can be prepared analogously to chalcogenophosphinites from reaction of alkali-metal diorganoarsanides $(R_2As^-M^+)$ with one equivalent of elemental chalcogen. In addition, a selenoarsinite piperidinium salt (**17**) has been prepared from the nucleophilic cleavage of the chalcogen-carbon bond in a diphenylarsanyl selenoester by piperidine (Equation 15).[38] Similar reactions with the analogous thiocarboxylic acid diphenylarsanyl derivatives for the preparation of thioarsinites have proven unsuccessful.[39]



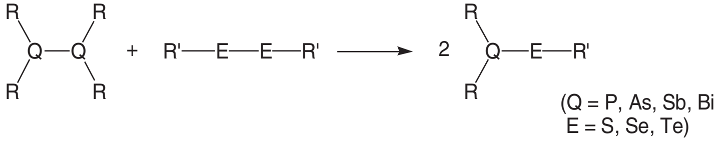
17

(15)

Chalcogenophosphinous acid esters, R_2PER' (E = S, Se, Te) can be prepared from reaction of alkali-metal chalcogenophosphinites with alkyl or aryl halides (Equation 16) among other routes.[1,2] On heating, thiophosphinous acid esters undergo rearrangement to form tertiary phosphine sulfides (Equation 16). Seleno- and telluro-phosphinous acid esters also undergo thermal decomposition reactions, but the products of these reactions are far more unpredictable and vary depending upon the R substituents.[2]

$$R_2PSLi + R'Cl \xrightarrow[-LiCl]{} R_2P{-}S{-}R' \xrightarrow{Heat} R'R_2P{=}S \qquad (16)$$

An alternative preparative route to R_2QER' acid esters (Q = P, As, Sb, Bi; E = S, Se, Te) of interest due to its generally applicability to all the heavier group 15 and 16 elements, is the dismutation reaction between diorganodichalcogenides and tetraorgano-diphosphines, -diarsines, -distibines or -dibismuthines (Equation 17).[2]



(Q = P, As, Sb, Bi
E = S, Se, Te)

(17)

5.2.5. Dichalcogenophosphinic Acids (R_2PE_2H) and their Derivatives

One of the most studied classes of chalcogeno–phosphorus compounds are the dichalcogenophosphinic, dichalcogenophosphonic and dichalcogenophosphoric acids [R_2PE_2H, $R(R'O)PE_2H$ and $(RO)_2PE_2H$, respectively]. This is due to their ease of preparation (and in some cases commercial availability) and their many applications including as pesticides, lubricant and petrol additives, reagents for organic synthesis, extraction agents and vulcanisation accelerators (see Section 5.4). In addition, their conjugate bases – the dichalcogenophosphinates $[R_2PE_2]^-$, dichalcogenophosphates $[(RO)_2PE_2]^-$ and dichalcogenophosphonates $[R(R'O)PE_2]^-$ – as well as their mixed chalcogen analogues $[R_2P(E)E']^-$ ($E = S, Se, Te$; $E' = O, S, Se$), have been shown to be very versatile ligands with a wide range of coordination chemistries (see Section 5.3.5).

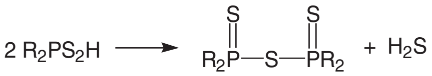
Numerous preparative methods have been reported for these acids and their salts and ester derivatives.[1–4] Dithiophosphoric acids are accessible from the reaction of phosphorus pentasulfide with alcohols or phenols (Equation 18). Dithiophosphinic acids can be prepared from thiophosphinic chlorides and sodium hydrosulfide (Equation 19), although the phenyl derivative is better prepared using a modified Friedel-Crafts reaction in which phosphorus pentasulfide is reacted with benzene in the presence of anhydrous aluminium trichloride (Equation 20).

$$P_4S_{10} + 8\,ROH \longrightarrow 4\,(RO)_2PS_2H + 2\,H_2S \tag{18}$$

$$R_2P(S)Cl + NaSH \longrightarrow R_2PS_2H + NaCl \tag{19}$$

$$P_4S_{10} + 8\,C_6H_6 \xrightarrow{AlCl_3} 4\,Ph_2PS_2H + 2\,H_2S \tag{20}$$

Dithiophosphoric and dithiophosphinic acids are strong acids, with pKa values typically in the range 1–2 (in water or alcohol solutions).[1] Dithiophosphinic acids are predominately thermally unstable compounds, and tend to undergo a condensation reaction with elimination of H_2S on storage at room temperature (Equation 21). Although dithiophosphoric acids can also undergo a similar decomposition reaction, higher temperatures are usually required ($>120°C$).



$$2\,R_2PS_2H \longrightarrow R_2P(=S)\text{—}S\text{—}P(=S)R_2 + H_2S \qquad (21)$$

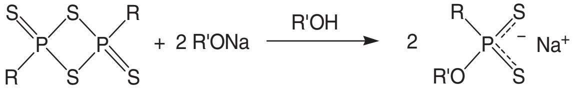
The metal and ammonium salts of dithiophosphinic acids tend to exhibit far greater stability with respect to this thermal decomposition reaction, and consequently these acids are often prepared directly in their salt form for convenience and ease of handling. Alkali-metal dithiophosphinates are accessible from the reaction of diphosphine disulfides with alkali-metal sulfides (Equation 22) or from the reaction of alkali-metal diorganophosphides with two equivalents of elemental sulfur (Equation 23). Alternatively, they can be prepared directly from the parent dithiophosphinic acid on treatment with an alkali-metal hydroxide or alkali-metal organo reagent. Reaction of secondary phosphines with elemental sulfur in dilute ammonia solution gives the dithiophosphinic acid ammonium salts (Equation 24).

$$R_2P(S)P(S)R_2 + 2\,NaS_n \longrightarrow 2\,R_2PS_2^-\,Na^+ \qquad (22)$$

$$R_2PH + n\text{BuLi} \longrightarrow R_2PLi \xrightarrow{2/8\,S_8} R_2PS_2^-\,Li^+ \qquad (23)$$

$$R_2PH + 2\,S + NH_4OH \longrightarrow R_2PS_2^-\,NH_4^+ + H_2O \qquad (24)$$

Fewer routes are known for the preparation of dithiophosphonic acids. Nevertheless sodium dithiophosphophonates have been prepared in high yields from reaction of dithiadiphosphetane disulfides with a sodium alkoxide or aryloxide in the corresponding alcohol solution (Equation 25).[40,41]



(25)

$$R_2PS_2H + R'OH \longrightarrow R_2P(S)SR' + H_2O \qquad (26)$$

$$R_2PS_2^-\,M^+ + R'X \longrightarrow R_2P(S)SR' + MX \qquad (27)$$

$$(M = Li, Na, K;\ X = Cl, Br)$$

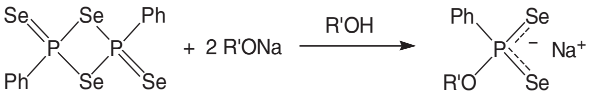
In all cases, dithio-phosphorus acids can be liberated from their alkali-metal salts by reacting them with acids such as HCl. Thio-ester derivatives of the dithio-phosphorus acids can be synthesised *via* reaction of the acids themselves with an alcohol or phenol (Equation 26) or from reaction of their alkali-metal salt with an alkyl halide (Equation 27).

The analogous selenium and tellurium species are best formed directly as their alkali-metal or ammonium salts, since the acids themselves tend to be much more unstable towards decomposition than the dithio-phosphorus acids, and are hence difficult to store and handle. Diselenophosphates can be prepared from refluxing a suspension of phosphorus(V) selenide in alcohol followed by treatment with potassium hydroxide or ammonia gas to give the potassium or ammonium salt respectively (Equation 28).[42] Diselenophosphinates are accessible from R_2PCl in a two step procedure: first the chlorophosphine is oxidised to the selenophosphinic chloride using elemental selenium, then addition of sodium hydroselenide gives the sodium diselenophosphinate salt (Equation 29).[43] A more recent route to diselenophosphinates which benefits from not emitting any noxious hydrogen selenide by-products, involves metallation of a secondary phosphine using an alkali-metal reagent, such as *n*BuLi, followed by addition of two equivalents of elemental selenium to give the alkali-metal diselenophosphinate salt (Equation 30).[37] Diselenophosphonates are accessible from $[PhP(Se)(\mu\text{-}Se)]_2$ (see Section 5.2.9) and a sodium alkoxide or aryloxide in the corresponding alcohol solution (Equation 31).[44]

$$P_2Se_5 + 2\,ROH \xrightarrow{2\,KOH} 2\,(RO)_2PSe_2K + H_2O + H_2Se \qquad (28)$$

$$R_2PCl + Se \longrightarrow R_2P(Se)Cl \xrightarrow{+\,2\,NaSeH} R_2PSe_2^-\,Na^+ + NaCl + H_2Se \qquad (29)$$

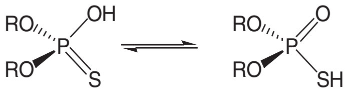
$$R_2PH + n\text{BuLi} \longrightarrow R_2PLi \xrightarrow{2\,Se} R_2PSe_2^-\,Li^+ \qquad (30)$$



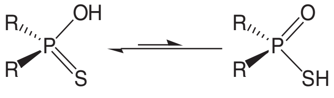
(31)

The only ditelluro-phosphorus acid reported to date is lithium diphenylditellurophosphinate, $[Ph_2PTe_2]^-Li^+$, prepared from the reaction of lithium diphenylphosphide with elemental tellurium (analogous to Equation 30).[36,45]

Mixed chalcogen derivatives of phosphinic and phosphoric acids are also known, the most studied being the mixed sulfur–oxygen species. Thiophosphoric acids exist in two different isomeric forms – the thiono form (**18a**) and the thiolo form (**18b**). The equilibria usually sits somewhere in between these two species, being dependent upon the nature of the R substituents, the solvent and in some cases the concentration. Thiophosphinic acids are also able to interconvert between the thiono (**19a**) and thiolo (**19b**) tautomers, although the equilibrium position usually sits well on the side of the thiono tautomer.[1]

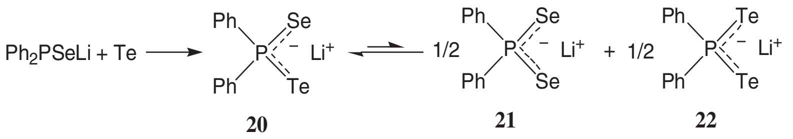


18a **18b**

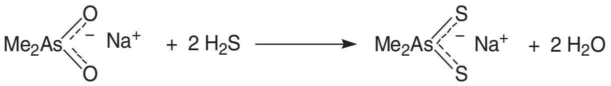


19a **19b**

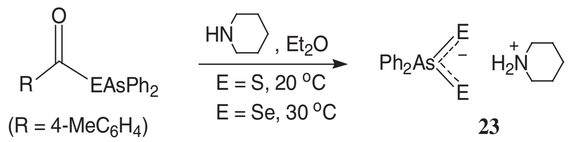
Mixed chalcogen species of the form $[R_2P(E)E']^-$ (E, E′ = S, Se, Te) are accessible from the reaction of the appropriate lithium chalcogenophosphinite with elemental chalcogen; for example the mixed seleno-telluro-diphenylphosphinate (**20**) has been prepared from elemental tellurium and lithium selenodiphenylphosphinite (Equation 32). As already seen (Section 5.2.2), on descending the group 16 elements the phosphorus–chalcogen bond becomes weaker and more susceptible to cleavage, which in this case leads to the asymmetric mixed dichalcogenophosphinate complex **20** being in equilibria in solution with the two symmetric species **21** and **22**. ^{31}P NMR spectroscopic studies have shown the equilibrium to strongly favour the asymmetric species (**20**) in thf at room temperature and above, with the equilibrium being shifted more towards the symmetric species (**21** and **22**) at lower temperatures.[36,45]



(32)



(33)

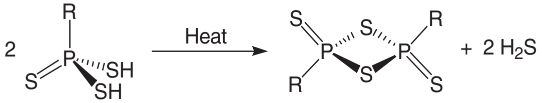


(34)

Very few examples of analogous dichalcogeno-arsenic acids are known, although the sodium salt of dimethyldithioarsinate has been prepared from the reaction of dimethylarsinate with hydrogen sulfide (Equation 33).[46] In addition, dimethyldiselenoarsinate, $[Me_2AsSe_2]^-Na^+$, has been prepared in high yield and purity from the reaction of equimolar amounts of sodium dimethylarsinic acid $[Me_2AsO_2]^-Na^+$ and sodium selenate (Na_2SeO_4) in the presence of 10 mol equivalent of glutathione.[47] The diphenyldichalcogenoarsinate piperidinium salts **23** (E = S, Se) are accessible from the diphenylarsanyl thio- or seleno-esters (Equation 34) *via* a similar reaction to that used in the preparation of selenoarsinites (Equation 15), the only difference being the higher reaction temperatures.[38,39]

5.2.6. Trichalcogenophosphonic Acids (RPE_3H_2) and their Derivatives

Trithiophosphonic acids (RPS_3H_2) are thermally unstable compounds, undergoing decomposition reactions at temperatures sometimes as low as -10°C depending upon the electronic and steric properties of the R substituent. Decomposition usually occurs *via* a condensation reaction (similar to that observed for dithiophosphinic acids – Equation 21) to give the dithiadiphosphatene disulfide and eliminate H_2S (Equation 35).[48] Similar to dithiophosphinic acids, their metal and ammonium salts are far more thermally stable and are therefore the preferred synthetic target in most cases.



(35)

Trithiophosphonic acid salts have been prepared from the reaction of dithiadiphosphatene disulfides with either ammonia,[49,50] sodium hydrosulfide[50] or dilithium sulfide (itself prepared from the reaction of $LiHBEt_3$ and S_8 in thf solution)[51] (Equations 36–38). In addition, a number of metal complexes have been shown to react with dithiadiphosphatene disulfides to give asymmetric cleavage and generate metal trithiophosphonate complexes (see Section 5.3.6), although these are often in low yields due to competition with symmetric cleavage reactions and are usually present as one of a number of products. An alternative route not requiring the preparation of dithiadiphosphatene disulfide starting materials is the reaction of primary phosphines with two equivalents of *n*BuLi (or alternatively one equivalent of $n\mathrm{Bu_2Mg}$) and three equivalents of elemental sulfur in a one pot process (Equation 39).[52]

$$[\mathrm{R_2P(S)}(\mu\text{–}\mathrm{S})]_2 + 4\,\mathrm{NH_3} \longrightarrow \mathrm{RPS_3}^{2-}.2\mathrm{NH_4}^+ + \mathrm{RP(S)(NH_2)_2} \tag{36}$$

$$[\mathrm{R_2P(S)}(\mu\text{–}\mathrm{S})]_2 + 2\,\mathrm{NaSH} \longrightarrow \mathrm{RPS_3}^{2-}.2\mathrm{Na}^+ + \mathrm{H_2S} \tag{37}$$

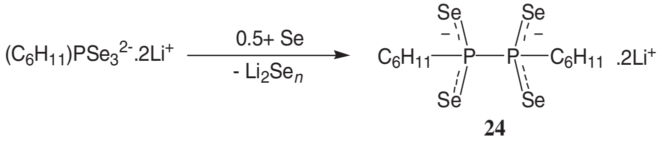
$$[\mathrm{R_2P(S)}(\mu\text{–}\mathrm{S})]_2 + \mathrm{Li_2S} \longrightarrow \mathrm{RPS_3}^{2-}.2\mathrm{Li}^+ \tag{38}$$

$$\mathrm{RPH_2} + 2\,n\mathrm{BuLi} + 2\,\mathrm{E}_n \xrightarrow{(\mathrm{E = S, Se})} \mathrm{RPE_3}^{2-}.2\mathrm{Li}^+ \tag{39}$$

The *bis*-ester derivatives of trithiophosphinic acids, $RP(S)(SR')_2$, have also been studied and, similar to the metal and ammonium salts, show enhanced thermal stability compared to their parent acids. Trithiophosphonic acid *bis*(trimethylsilyl) esters have been synthesised from organo-*bis*(trimethylsilyl)phosphanes with elemental sulfur in toluene (Equation 40).[53] These *bis*(silyl esters) can be readily converted into the parent trithiophosphinic acid by a very slow, controlled reaction with water or methanol.[53]

$$\mathrm{RP(SiMe_3)_2} + 3\,\mathrm{E}_n \xrightarrow{(\mathrm{E = S, Se})} \mathrm{RP(E)(ESiMe_3)_2} \tag{40}$$

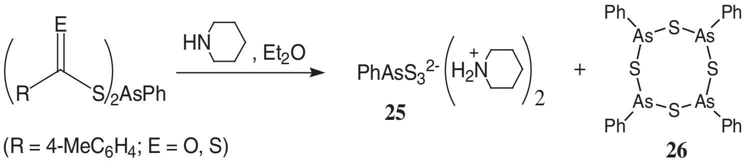
At the time of writing there are no reports in the literature of any isolated triselenophosphonic acids, presumably due to their high thermal instability. However, the alkali-metal salts of these diacids have been prepared both from primary phosphines (Equation 39)[52] and from the reaction of $RPCl_2$ with Na_2Se and Na_2Se_2 in a 1:1:1 ratio.[54] The *bis*(silyl esters) of triselenophosphonates have also been prepared in an analogous fashion to the trithiophosphonate *bis*(silyl esters) (Equation 40).[55] However, even the metal salts of triselenophosphonic acids suffer from thermal and hydrolytical instability, although their decomposition routes are often different from those observed for the trithiophosphonic acids and usually involve the deposition of elemental selenium. Initial studies on triselenophosphonates indicate them to be very reactive with a range of inorganic and organic reagents, and the dilithium complex [$(C_6H_{11})PSe_3Li_2$] has been shown to react with elemental selenium to eliminate lithium selenide and give the tetraselenohypodiphosphonate dianion **24** *via* an unusual phosphorus–phosphorus bond coupling reaction (Equation 41).[36]



(41)

Attempts to synthesise tritellurophosphonic acids or their salts have so far proved unsuccessful, and synthetic routes from primary phosphines analogous to Equation 39 with E = Te give just cyclic polyphosphanes $(RP)_n$ and lithium telluride with no observed tritellurophosphonate formation.[45]

Examples of the heavier group 15 congeners of the trichalcogenophosphonates are much rarer. The only solid-state structural determination of a trithioarsanate species is of the di(piperidinium) salt of $[PhAsS_3]^{2-}$ (**25**), which was synthesised in low yields from either phenyl*bis*(dithiocarboxy)arsine or phenyl*bis*(thiocarboxy)arsine (Equation 42) using a similar procedure to that used for the synthesis of chalcogenoarsinites and dichalogenoarsinates **17** and **23** (*vide supra*).[39] Also formed in this reaction is the cyclic tetramer $(PhAsS)_4$ **26**. Although the full mechanism for this reaction is unknown it is presumed to proceed *via* a dithioarsenate dianionic intermediate $[PhAsS_2]^{2-}$, which then undergoes disproportionation to give **25** and **26**.[39]



(42)

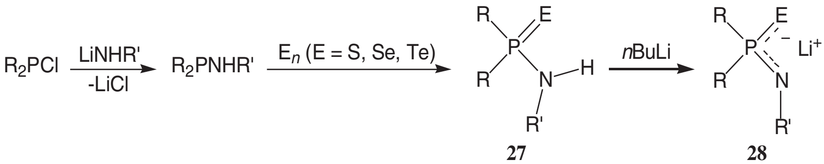
5.2.7. Amido and Imido Derivatives of Chalcogeno–Phosphorus Acids

Replacement of one or more of the chalcogen atoms with an isoelectronic imido (NR′) group in $PE_2(EH)$, $PE(EH)_3$, $R_2PE(EH)$, $RPE(EH)_2$ or in their anionic conjugate bases PE_3^-, PE_4^{3-}, $R_2PE_2^-$, RPE_3^{2-} (E = S, Se, Te) gives rise to a new range of chalcogeno–phosphorus amides and imides.[56]

Hence, chalcogenoamidophosphinic acids of general formula $R_2P(E)NHR'$ (**27**) can be considered as dichalcogenophosphinic acids with one of the chalcogen atoms replaced by an amido group. These amido species are still normally referred to as acids due to their acidic amide protons. They are accessible from reaction of thiophosphinic chlorides and primary amines (Equation 43) or from reaction of aminophosphines with elemental chalcogen

(Equation 44).[57] The amide hydrogen is acidic in these compounds and can be deprotonated with standard organometallic bases such as *n*BuLi to give the imido complex **28** (Equation 44).

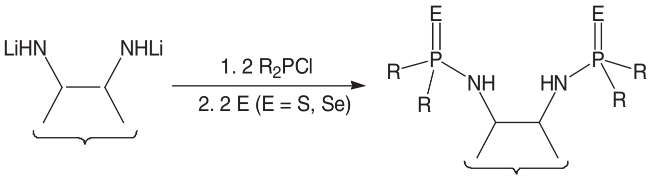
$$R_2P(S)Cl + R'NH_2 \xrightarrow[-\,HCl]{Heat} R_2P(S)NHR' \qquad (43)$$



27 **28**

(44)

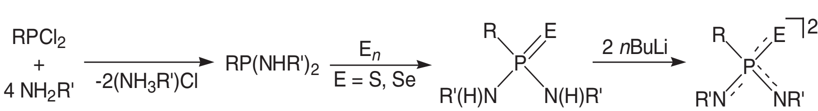
Bis(chalcogenoamidophosphinic acids) (**29**) are also well documented, mainly due to their application in coordination chemistry (see Section 5.3.7), and are accessible *via* similar synthetic routes to those used for chalcogenoamidophosphinic acids. Thus, reaction of a dilithiated diamide with two equivalents of a dialkyl or diaryl-chlorophosphine, followed by addition of elemental sulfur or selenium gives **29** (Equation 45).[58] These compounds contain two acidic amide protons and can therefore undergo double deprotonation with organometallic bases.



29

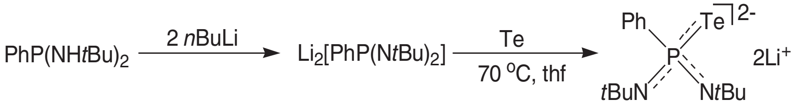
(45)

Dichalcogenoamidophosphonic acids RP(E)(EH)(NHR′) and chalcogeno*bis*amidophosphonic acids RP(E)(NHR′)$_2$ are the amide derivatives of trichalcogenophosphonic acids with one or two of the chalcogenol (EH) groups replaced by an amido (NHR′) group, respectively. Chalcogeno*bis*amidophosphonic acids (**30**) are accessible from the oxidation of the parent *bis*aminophosphine RP(NHR′)$_2$ (which can be prepared from the aminolysis of an organodichlorophosphine)[59] with elemental chalcogen (Equation 46).[60] Both of the amide protons are acidic and deprotonation using two equivalents of *n*BuLi gives the dianionic chalcogeno*bis*imidophosphonate complex **31** (Equation 46). Telluro*bis*amidophosphonic acids (**30**; E = Te) are, however, not accessible using this route since RP(NHR′)$_2$ fails to react with elemental tellurium even in boiling toluene. Nevertheless, a telluro*bis*imidophosphonate (**32**) has been prepared by first metallating the *bis*aminophosphine to give Li$_2$[PhP(N*t*Bu′)$_2$], followed by treatment with elemental tellurium to yield the dilithium salt **32** (Equation 47).[60]



30 **31**

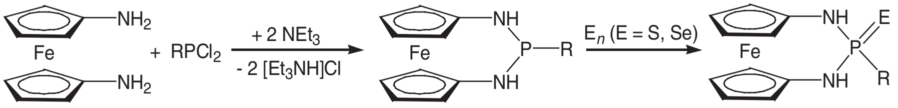
(46)



(47)

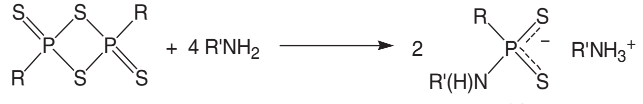
32

Use of diamines in the preparation of chalcogeno*bis*amidophosphonic acids gives heterocyclic products: for example, reaction of 1,1′-diaminoferrocene with $RPCl_2$ (R = *t*Bu, Ph) and elemental sulfur or selenium gives the thio/seleno-*bis*amidophosphonic acid **33** (Equation 48).[61]



33

(48)



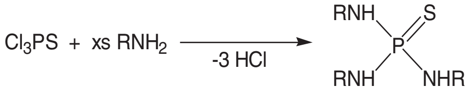
(R = *p*-C_6H_4OMe)

34

(49)

Dithioamidophosphonic acids (**34**) have been prepared for R = *p*-C_6H_4OMe from Lawesson's reagent (**43**), $[(p\text{-}MeOC_6H_4)P(S)(\mu\text{-}S)]_2$, using a ring opening reaction with a primary amine (Equation 49).[40] This reaction is comparable to the ring opening reaction of dithiadiphosphetane disulfides with metal alkoxides (Equation 25).

Thio*tris*amidophosphoric acids (**35**) are isoelectronic with phosphoric acids and were initially reported from the reaction of phosphorus pentasulfide with primary amines at high temperatures.[62] Subsequently, an improved synthesis for **35** with increased yields and milder conditions has been reported involving the room temperature reaction of thiophosphoryl chloride and primary amines (Equation 50).[63] The most convenient route to the analogous selenium derivatives $SeP(NHPh)_3$ is from the oxidation of $P(NHPh)_3$ with elemental selenium (Equation 51).[63] Also isoelectronic with phosphoric acids are dithio*bis*amidophosphoric acids (**36**), which can be prepared from the reaction of phosphorus pentasulfide with an excess of primary amine at 30°C in toluene (Equation 52).[62] The selenium derivatives of **36** can be prepared in a similar reaction from phosphorus (V) selenide, although due to their increased acidity compared to the sulfur analogues the reaction product is the ammonium salt rather than the acid itself (Equation 53).[64]



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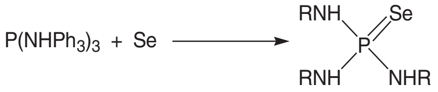
(50)



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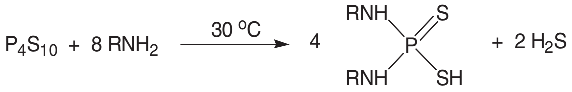
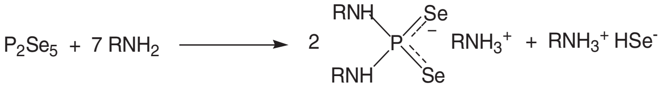


36

(52)

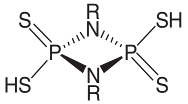


(53)

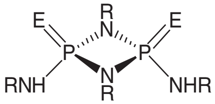
Although the trisamido species **35** are resistant to hydrolysis in both acidic and alkali solutions, the *bis*amido species **36** are hydrolysed immediately by refluxing in water, dilute acids or bases.[62]

Both chalcogeno*tris*amidophosphoric and dichalcogeno*bis*amidophosphoric acids (**35** and **36**) can potentially be deprotonated up to three times, and are therefore prospective starting materials for the preparation of polyimido analogues of the orthophosphate anion $[PO_4]^{3-}$. The mono and di-anions of chalcogeno*tris*amidophosphoric acid, $[EP(NHR)_2(NR)]^-$ and $[EP(NHR)(NR)_2]^{2-}$ (E = S, Se; R = alkyl, aryl), can be prepared *via* the correct stoichiometric addition of *n*BuLi to the acid, although competing reactions involving phosphorus–chalcogen bond cleavage have been observed to lead to the formation of Li_2E_n and other by-products for some amide substituents (*e.g.*, R = *t*Bu).[63] In contrast, $[EP(NR)_3]^{3-}$ trianions are only accessible with R = aryl as a result of the increased acidity of the NH protons in these compounds.[63] The structures of all these lithium salts are discussed in Section 5.3.7.

The final class of compounds considered here are the amido and imido derivatives of metaphosphoric acid, PE_3H (E = S, Se, Te), and its conjugate base the metaphosphate anion $[PE_3]^-$. Replacement of one the chalcogen atoms in PE_3H with an amido or imido group gives the hypothetical $[PE_2(NHR)]$ or $[P(E)(EH)(NR)]$ species, while replacement of two of the chalcogen atoms gives either $[PE(NR)(NHR)]$ or $[P(EH)(NR)_2]$. Similar to their oxygen-containing analogues, these hypothetical species can be assumed to aggregate together to form larger ring structures and are therefore only known in their dimeric or higher aggregate forms. Hence the cyclodiphosph(V,V)azanes **37** and **38** are both well known and can be considered as the cycloaddition product of two $[P(S)(SH)(NR)]$ or two $[PE(NR)(NHR)]$ units respectively (note that *cis* and *trans* isomerism of the exocyclic substituents in both **37** and **38** is possible).[56,65]

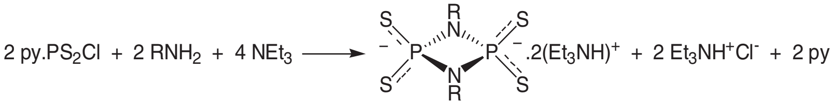


37



(E = S, Se, Te)

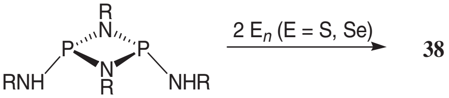
38



(54)

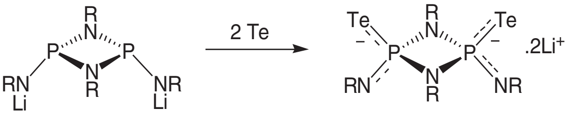
The least studied of these two cycles are the tetra-chalcogen compounds $[P(E)(EH)(\mu\text{-}NR)]_2$ for which only the sulfur analogue (E = S) **37** has been reported. It can be prepared as its ammonium salt from reaction of dithiophosphonic acid chloride betaine (py.PS_2Cl; py = pyridine) and one equivalent of primary amine in the presence of NEt_3 (Equation 54).[66,67]

The *bis*amidocyclodiphosphazane dichalcogenides **38** are accessible from the parent *bis*amidocyclodiphosphazanes *via* their oxidative addition reaction with elemental chalcogen (Equation 55), or alternatively from the thermolysis of *tris*amidochalcogenophosphates (Equation 56).[65] However, in both cases the yield of the tellurium analogues is very low and instead the ditellurides are better prepared in much higher yields as their dianionic lithium complexes (**39**) from reaction of the appropriate dilithio *bis*(imido)cyclodiphosphazane with elemental tellurium (Equation 57).[68] The alkali-metal derivatives of the disulfide and diselenide dianions $[(RN)(E)P(\mu\text{-}NR)]_2^{2-}$ (E = S, Se) can be prepared analogously to the ditellurides (Equation 57) or from treatment of **38** with two equivalents of *t*BuLi or $MN(SiMe_3)_2$ (M = Na, K).[56,69]



(55)

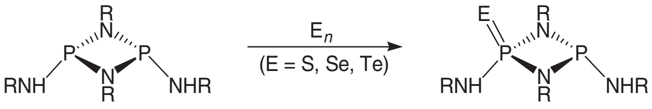
$$2\ (RNH)_3PE \xrightarrow[-2\ RNH_2]{heat} \mathbf{38} \qquad (56)$$
$$(E = S, Se)$$



39

(57)

Asymmetric *bis*amidocyclodiphosph(V,III)azane monochalcogenides (**40**), containing a phosphorus (V) and a phosphorus (III) centre, are accessible from stoichiometric oxidation of the parent *bis*amidocyclodiphosphazane with the appropriate elemental chalcogen (Equation 58) or from the conproportionation reaction between the corresponding *bis*amidocyclodiphosphazane and *bis*amidocyclodiphosphazane dichalcogenide (Equation 59).[65]



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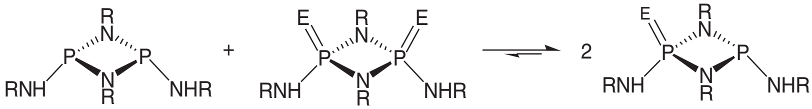
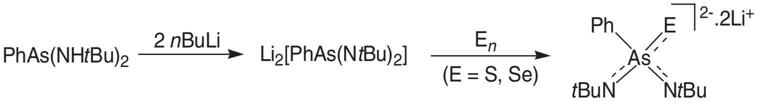
(58)



40

(59)



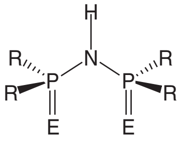
(60)

Far fewer chalcogeno- imido or amido compounds are known involving the heavier group 15 congeners although thioamidoarsininic acids of general formula $Ph_2As(S)NHR$ (R = aryl) have been prepared from heating Ph_2As-NHR with elemental sulfur in an comparable procedure to Equation 44,[70] and thio- and seleno-*bis*imidoarsonate complexes have been prepared from PhAs(NH*t*Bu)$_2$ (Equation 60).[71]

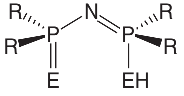
5.2.8. Dichalcogenoimido-diphosphinates [$R_2P(E)NP(E)R_2$]

Imino-*bis*(diorganophosphine chalcogenide)s and imino-*bis*(dialkoxy-/diaryloxy-phosphine chalcogenide)s, $R_2P(E)NHP(E)R_2$ (R = alkyl, aryl, alkoxy, aryloxy; E = S, Se, Te) and their N–H deprotonated anionic forms, the dichalcogenoimidodiphosph(in)ates $[R_2P(E)NP(E)R_2]^-$, have been extensively studied in the literature, mainly due to their wide-ranging coordination chemistry which has spanned almost all the metallic and semi-metallic members of the periodic table (see Section 5.3.8).[72–78]

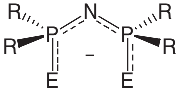
Imino-*bis*(phosphine chalcogenide)s can in theory exist in two different tautomeric states; an N–H tautomer **41a** and a E-H tautomer **41b**. However, extensive studies in both solution and the solid state have shown that in all cases (with the exception of some dioxo E = O species) the N–H tautomer predominates.[75] Structural studies have revealed the $N(PE)_2$ group in **41a** to be planar or close to planar, with P–N–P bond angles in the range 122–133°, indicative of substantial sp^2 character at the nitrogen centre. Planarity of the nitrogen is also observed in the anionic dichalcogenoimidodiphosph(in)ates **42**.



41a



41b



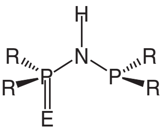
42

One of the most convenient and high yielding routes for the preparation of symmetric $R_2P(E)NHP(E)R_2$ systems (E = S, Se) is from reaction of diorganochlorophosphines with hexamethyldisilazane to give the imino*bis*(diorganophosphine), followed by oxidative addition of two equivalents of elemental sulfur or selenium (Equation 61). This oxidation can also be carried out in two steps to give first the monochalcogenide **43**, followed by further oxidative addition with a different chalcogen to give the asymmetric mixed dichalcogenide **44** (Equation 62). Asymmetric species containing oxygen (E′ = O) are also accessible by using hydrogen peroxide 30% as the oxidising agent.[72]

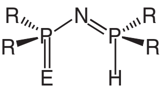
$$2\,R_2PCl + HN(SiMe_3)_2 \xrightarrow[-\,2\,Me_3SiCl]{} R_2PNHPR_2 \xrightarrow[(E\,=\,S,\,Se)]{2\,E_n} R_2P(E)NHP(E)R_2 \qquad (61)$$

$$R_2PNHPR_2 \xrightarrow[(E\,=\,S,\,Se,\,Te)]{E_n} \underset{\mathbf{43}}{R_2P(E)NHPR_2} \xrightarrow[(E'\,=\,S,\,Se)]{E'_n} \underset{\mathbf{44}}{R_2P(E)NHP(E')R_2} \qquad (62)$$

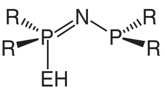
The monochalcogenides **43** can also theoretically exist in more than one tautomeric form: an N–H tautomer **43a**, a P–H tautomer **43b** or an E–H tautomer **43c**. Solution and solid-state studies on these compounds show that, depending upon the nature of the R substituents, either the N–H or the P–H tautomer predominates. Substituents which lead to increased basicity of the phosphorus lone-pair (*e.g.*, R = NMe_2[79], *i*Pr[80]) have been shown to favour the formation of the P–H tautomer, whereas in systems where the phosphorus lone pair is less basic (*e.g.*, R = Ph[81]) the N-H tautomers are favoured.



43a



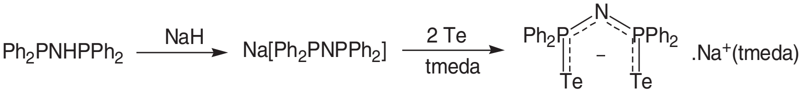
43b



43c

Asymmetrically (R ≠ R′) or symmetrically (R = R′) substituted imino*bis*(diorganophosphine chalcogenide)s $R_2P(E)NHP(E')R'_2$ can be prepared from coupling chalcogenoamidophosphinic acids with chalcogenophosphinic chlorides using sodium hydride (Equation 63). Alternatively *n*BuLi or KO*t*Bu can be employed in place of NaH. Mixed chalcogen species (E ≠ E′) are also accessible by this route.[72]

$$R_2P(E)NH_2 + NaH \longrightarrow R_2P(E)NHNa \xrightarrow[-NaCl]{R'_2P(E')Cl} R_2P(E)NHP(E')R'_2 \qquad (63)$$



(64)

Although the oxidative addition of elemental tellurium to an imino*bis*(diorganophosphine) yields the monotelluride **43** (Equation 62), further oxidation to give the imino*bis*(diorganophosphine telluride) **41** has not proved possible. However, a ditelluroimidodiphosphinate has been prepared by first deprotonating the imino*bis*(diorganophosphine) with sodium hydride, before addition of two molar equivalents of elemental tellurium in the presence of tmeda [tmeda = $(Me_2NCH_2)_2$] at 80°C (Equation 64).[68] This deprotonation step renders the imino*bis*(diorganophosphine) more susceptible to reaction with tellurium in a comparable procedure to that used in the synthesis of diphosphine monotellurides (Equation 8), telluro*bis*amidophosphinic acids (Equation 47) and *bis*-amidocyclodiphosphazane ditellurides (Equation 57).

The analogous dithio- and diseleno-imidodiphosph(in)ates are also accessible as their alkali-metal salts *via* reaction of the imino-*bis*(phosphine chalcogenide) **41** with *n*BuLi, NaH, NaOMe or KO*t*Bu. However, the most commonly used of these metallating agents is KO*t*Bu since it gives near quantitative yields and the resultant potassium salt is a good starting material for metathesis reactions (see Section 5.3.8).

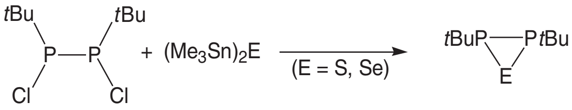
Very few examples of the heavier group 15 analogues of **41** or **42** have been reported, although the arsenic containing disulfide $i\mathrm{Pr}_2\mathrm{As(S)NHAs(S)}i\mathrm{Pr}_2$ has been prepared from the oxidative addition of elemental sulfur to $i\mathrm{Pr}_2\mathrm{AsNHAs}i\mathrm{Pr}_2$.[82]

5.2.9. Phosphorus–Chalcogen Containing Heterocycles

A very large number of heterocyclic compounds are known consisting solely of phosphorus and chalcogen atoms, as well as those containing phosphorus, chalcogen and carbon or other hetero atoms. Such heterocycles have been the subject of several reviews[2,83,84] and the discussion here will be limited to some representative examples of these compounds.

Perhaps the simplest phosphorus–chalcogen heterocycles are those based on three membered P_2E rings (E = S, Se and Te). Sulfur and selenium-containing P_2E rings were first prepared from the reaction of 1,2-dichlorodiphosphane with *bis*(trimethylstannyl)chalcogenide (Equation 65).[85] They are also accessible from the reaction of a diphosphene RP=PR (where R is a bulky aryl or alkyl group) with elemental sulfur or selenium (Equation 66), although in the case of E = Se contamination from the di(seleno)metaphosphonate by-product $RP(=Se)_2$ can be problematic.[86–88] The analogous telluradiphosphirane can be formed in a substitution and redox reaction between sodium telluride and *tert*-butyldichlorophosphine in pentane (Equation 67).[89] An alternative route uses $Te(SiMe_3)_2$ as a reagent with $(R_2N)PCl_2$ (Equation 68).[90] Although the main product in this reaction is the telluradiphosphirane, $(t\mathrm{BuP})_3\mathrm{Te}$ and $(t\mathrm{BuP})_4\mathrm{Te}$ four and five-membered rings are also formed.[90] Chalcogenadiphosphiranes

$(RP)_2E$ tend to undergo dimerization and subsequent elimination reactions on heating (especially in polar solvents) to give phosphorus–chalcogen heterocycles of varying ring sizes; $(RP)_nE_m$ ($n = 2, 3, 4$; $m = 0, 1, 2, 3$).[2]



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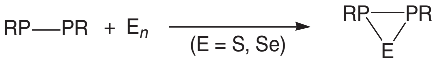

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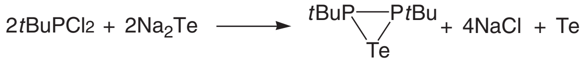

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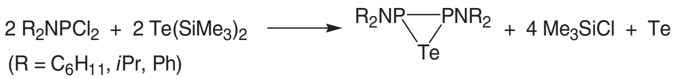
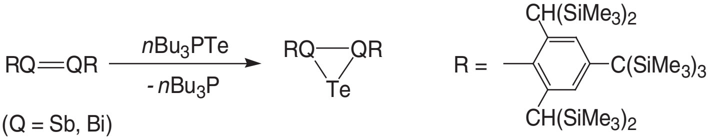


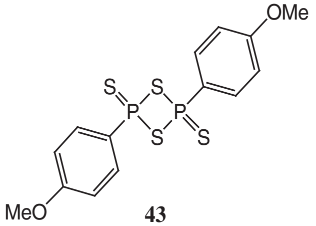
(68)

Three membered heterocycles $(RQ)_2E$ containing the heavier group 15 elements (Q = As, Sb, Bi) are accessible from the reaction of elemental chalcogen with RQ=QR, but only when very bulky R substituents are employed to kinetically stabilise the products (and reagents!). Using super-bulky R substituents has allowed the preparation of even a telluradistilbirane and a telluradibismirane from the reaction of distibene or dibismuthene with $n\text{Bu}_3\text{PTe}$ (Equation 69).[91] A tertiary phosphine telluride is used as the tellurization reagent rather than elemental tellurium itself since it is more reactive and hence permits the use of milder reaction conditions (see Section 5.2.2).



(69)

Diathiadiphosphetane disulfides are probably the most studied and the most thermally and hydrolytically stable of all the phosphorus–chalcogen heterocycles. They contain a central four membered P_2S_2 ring and can be prepared from heating phosphorus pentasulfide with aromatic compounds. The most well-known of these is Lawesson's reagent (**43**), which is made from anisole and phosphorus pentasulfide,[92] and is used extensively in organic synthesis procedures (see Section 5.4.1). Other dithiadiphosphetane disulfides of note are **44** and **45**, formed from the reaction of phosphorus pentasulfide with ferrocene or 1-bromonaphthalene respectively.[93]



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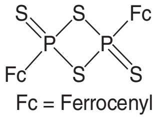

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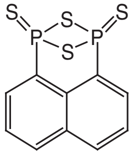
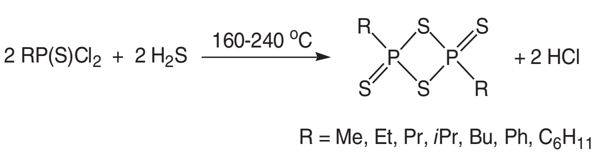


45

In contrast to **43–45** the non-aromatic dithiadiphosphetane disulfides are much more difficult to prepare, requiring the use of high temperatures and hydrogen sulfide (Equation 70).[94]



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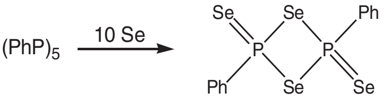

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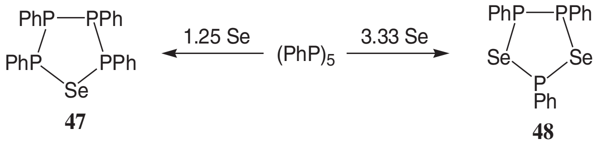


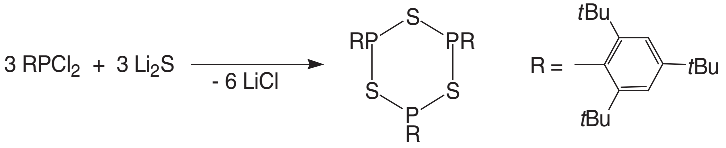
47 **48**

(72)

Although no analogous P_2Te_2 ring systems are currently known, the diselenadiphosphetane diselenide **46** (Woollins reagent), containing a four-membered P_2Se_2 heterocycle, can be prepared from treatment of the cyclophosphane $(PhP)_5$ with 10 equivalents of elemental selenium (Equation 71).[94,95] **46** has also be synthesised in larger quantities from the reaction of $PhPCl_2$ with Na_2Se and elemental Se.[95]

Treatment of $(PhP)_5$ with smaller stoichiometric amounts of elemental selenium gave the five-membered heterocycles $(PhP)_3Se_2$ (**47**) and $(PhP)_4Se$ (**48**) (Equation 72).[96] Five-membered P_4E and P_3E_2 heterocycles ($E = S^{84}$, Te^{97}) have also been prepared in a similar manner.

Larger chalcogen–phosphorus heterocycles, although less common in the literature, are accessible *via* a variety of synthetic routes.[2,83,84] For example, the cyclic trimer $(SPR)_3$ (R = 2,4,6-tri-*tert*-butylphenyl) contains a puckered six-membered P_3S_3 ring and is produced in the reaction of a phosphinic chloride with lithium sulfide (Equation 73).[98] Additionally $(R'P)_3Se_5$ (R′ = 2,4-di-*tert*-butyl-6-*iso*propoxyphenyl), synthesised from the oxidation of a primary phosphine with three equivalents of elemental selenium (Equation 74), has been shown by X-ray crystallography to contain an eight-membered P_3Se_5 ring (**49**).[99]



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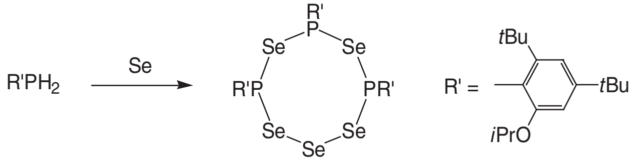
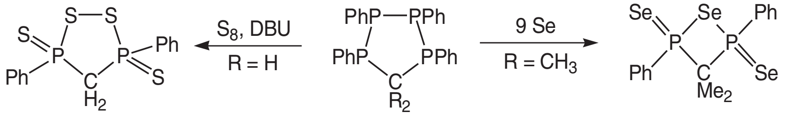


49

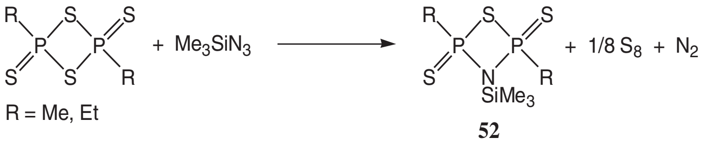
(74)

Heterocyclic rings with other atoms in addition to phosphorus and chalcogen have also been reported.[84,93] For instance, a range of carbon-containing heterocycles including **50** and **51** have been prepared from cyclocarbaphosphane $(RP)_4CR'_2$ starting materials (Equation 75).[100] Nitrogen-containing phosphorus–chalcogen heterocyclic compounds include thiazadiphosphetanes (**52**) which can be prepared from the reaction of dithiadiphosphetane disulfides with trimethylsilyl azides (Equation 76),[99] isothiocyanates, ureas, amines or imines.[93,101]



50 **51**

(75)



52

(76)

5.3 Coordination Chemistry of Ligands Containing Phosphorus–Chalcogen Bonds

5.3.1. Phosphorus Chalcogenides (P_nE_m) and Chalcogeno–Phosphate Anions $[P_nE_m]^{z-}$

Solid-state assemblies containing chalcophosphate anions, or their heavier group 15 analogues, are still relatively small in number compared to the well developed area of (oxo)phosphates. However, over the past decades there have been some significant developments in this field with some members of this class of compounds being shown to exhibit unusual or novel intercalation chemistry, ion-exchange properties and magnetic and optical phenomena.[102,103] This had led to studies on their applications in the fields of nonlinear optics, ion exchange, memory storage devices and as cathodes in lithium batteries.

The anionic polychalcophosphate building blocks $[P_mE_n]^{z-}$ present in these solid-state assemblies possess a variety of structures with differing phosphorus to chalcogen ratios (Figure 4), and are known to exhibit a wide range of denticities and bonding modes.[12,104] However, most of the reported networks to date are ternary structures based on either the ethane-like $[P_2E_6]^{2-}$ ligand (E = S, Se) with a divalent metal centre, or on a $[PE_4]^{3-}$ tetrahedron with monovalent or trivalent metal centres.[12,102,103]

Initially these compounds were prepared by heating together the metal and chalcophosphate in the correct stoichiometry at high temperatures. However, the use of salt fluxes is now more popular (prepared from the fusion of an alkali-metal monochalcogenide, a phosphine chalcogenide and an excess of elemental chalcogen) since they provide a lower temperature route (typically 200–600°C) to these solid-state assemblies, hence allowing the formation of new kinetically stable phases in preference to the thermodynamically stable ones formed at higher temperatures.[102,103] More recently even milder conditions (under 200°C) have been employed to access new phases *via* solvothermal routes in acetonitrile or amine solvents in the absence of water, hence avoiding hydrolysis of the chalcophosphate anions.[105,106]

Solid-state assemblies containing binary group 15/16 anions of the heavier pnictogens are also extremely well known, including the naturally occurring

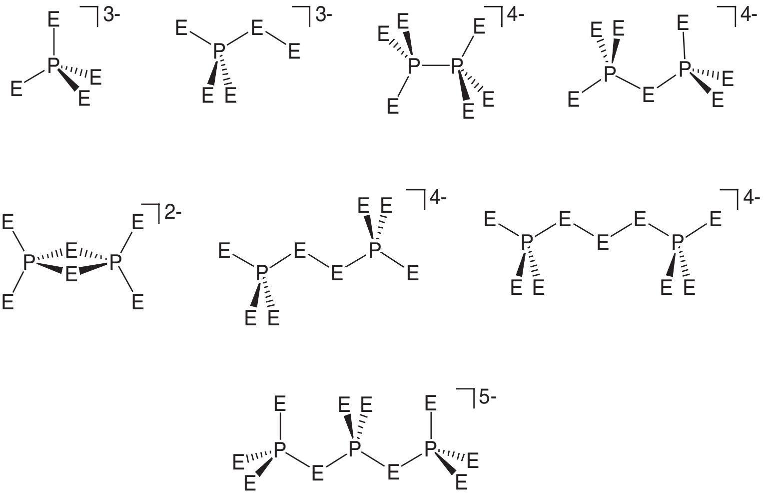
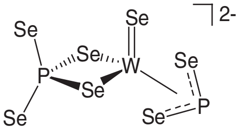


Figure 4 *Polychalcophosphate building blocks in solid-state assemblies (E = S, Se)*

sulfosalt minerals which are a large group of very stable minerals containing $[QS_3]^{3-}$ building blocks (Q = As, Sb and Bi) with heavy metals, such as silver, copper, mercury and lead. In these minerals the group 15 atom is trivalent, which therefore contrasts with the chalco-phosphate materials in which the phosphorous is usually, although not always, pentavalent. This increased preference for the heavier pnictogens to adopt trivalent forms is reflected in their range of binary group 15/16 anions, which usually consist of chains, rings or clusters of one or more fused pyramidal $[QE_3]^{3-}$ and/or tetrahedral $[QE_4]^{3-}$ fragments.[12]

In addition to their use in solid-state materials chemistry, there are many examples of chalcophosphate anions acting as ligands in discrete metal complexes. These complexes often contain binary group 15/16 anions similar to those shown in Figure 4. However, of particular interest are those complexes where unusual anions are stabilised by one of more metal centres, such as the bent $[PSe_2]^-$ unit in $[SeW(PSe_4)(PSe_2)]^{2-}$ (**53**),[107] which is isolobal to a nitrite or allyl anion, and the $[As_2Se_2]$ unit in the bi-metallic iron complex $[Cp^*{}_2Fe_2As_2Se_2]$ (**54**)[108] which acts as a four electron π-donor bridging ligand. Stabilisation of unusual tautomeric forms of chalco-phosphates in metal complexes has also been reported, with recent examples including the tri-metallic complexes $[Fe_2(CO_6)(\mu^3\text{-}E_3P)Cr(CO)_2Cp]$ (E = S, Se) (**55**) in which the constituent $[E{=}PE_2]^{3-}$ anion formally possess one double and two single chalcogen–phosphorus bonds.[109]



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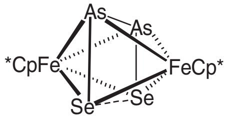

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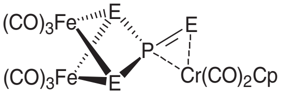


55 (E = S, Se)

5.3.2. Tertiary Phosphine Chalcogenides (R_3PE)

Many examples of *tert*-phosphine chalcogenide metal complexes are known for a wide range of main group and transition metal centers.[73,110] Tertiary phosphine chalcogenides are, in general, weak field ligands, binding to metal centres *via* the p electrons on the chalcogen in either a unidentate or bridging coordination mode. The donor properties of the ligands increase down the group 15 analogues $R_3PS < R_3AsS < R_3SbS$ as well as down the group 16 analogues $R_3PS < R_3PSe < R_3PTe$. In both cases this is likely to be due to the increased ylidic nature of the pnictogen–chalcogen bond, which leads to increased charge density on the chalcogen atom (see Section 5.2.2).

In most cases, on binding to a metal centre there is an observed lengthening and weakening of the phosphorus–chalcogen bond, which can be monitored using X-ray crystallography or IR spectroscopy. In addition, NMR spectroscopy has proved a particularly useful tool for studying this change in tertiary phosphine selenides and tellurides due to the close inverse correlation between bond length and the magnitude of the $^1J_{SeP}$ or $^1J_{TeP}$ coupling constant.[111] The weakening of an already weak P–Se or P–Te bond on coordination can result, under certain conditions, on complete cleavage of the phosphorus–chalcogen bond to yield a tertiary phosphine and a chalcogen atom, which can then be incorporated into the metal complex or cluster.[112]

As well as forming complexes with a wide range of metal centres, tertiary phosphine chalcogenides interact with dihalogens and interhalogens to give charge transfer adducts, whereby electrons are donated from a chalcogen lone pair into the dihalogen/interhalogen σ^* orbital.[113] (For more details see Chapter 8.2)

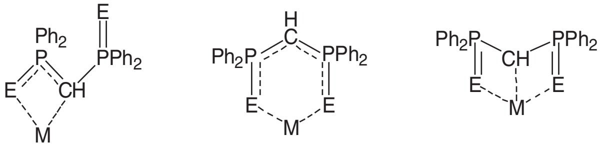
5.3.3. Diphosphine Di- and Mono-Chalcogenides [$R_2P(E)$-R'-$P(E)R_2$ and $R_2P(E)$-R'-PR_2]

Diphosphine disulfides and diselenides, $R_2P(E)$-R'-$P(E)R_2$ ($E = S, Se$), bond to metal centres from their chalcogen atoms in a similar fashion to tertiary phosphine chalcogenides (see Section 5.3.2). They can exhibit a variety of bridging and chelating bonding modes dependent upon the bridging group (R'), the chalcogen (E), the metal centre(s) and the other co-ligands present.[114]

Diphosphine mono-chalcogenides are able to bind to metal centres from either one of or both the phosphorus(III) and chalcogen donor centres. This has led to their study as hemi-labile ligands in catalyst systems, whereby one of the donor centres binds strongly to the metal centre and the other one is weakly bound and hence can be readily dissociated or reattached to reveal or protect the active site at a metal centre.[28]

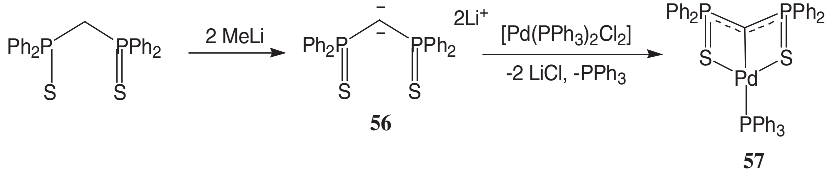
Methylene bridged diphosphine dichalcogenides $R_2P(E)$-CH_2-$P(E)R_2$, such as the dichalcogenides of dppm ($R = Ph$), can be deprotonated at the methylene position to give anionic ligands (see Section 5.2.3). These anionic ligands have been observed to coordinate to metal centres in one of three main coordination modes depending upon the metal centre present and its ancillary ligands: C,E chelation (**A**; Figure 5), E,E′ chelation (**B**) or E,C,E′ chelation (**C**).[28,110]

The methylene carbon in $Ph_2P(S)CH_2P(S)Ph_2$ can also undergo double deprotonation using two molar equivalents of methyllithium to give the dianion **56** (Equation 77). Reaction of **56** with $[Pd(PPh_3)_2Cl_2]$ gives the palladium complex **57** which can be regarded as containing a formal "carbenic" atom with two ancillary sulfide ligands.[115]

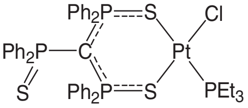


A **B** **C**

Figure 5 *Coordination modes of [$Ph_2P(E)CHP(E)Ph_2$]$^-$ ($E = S, Se$)*


(77)

The *tris*(dialkylthiophosphinyl)methanide anion $[R_2P(S)]_3C^-$ (**13**) has been observed to bind to metal centres in one of two different modes: bidentate S,S′ chelation or tridentate S,S′,S″ chelation. In the bidentate coordination mode the ligand contains a central planar methanide anion which can be considered to be sp^2 hydribised with the negative charge delocalised onto the ligand phosphorus and sulfur atoms, for example, in $[PtCl(PEt_3)(SPPh_2)_3C]$ (**58**).[31] Whereas in the tridentate mode the methanide anion is sp^3 pyramidal and supports a more localised anionic charge, for example, in $[n$Bu-$P_3Ag(SPPh_2)_3C]$ (**59**).[116]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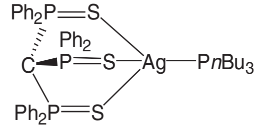
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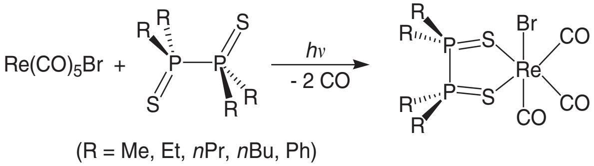
Although diphosphine disulfides of formula $R_2P(S)P(S)R_2$ take up a *trans* conformation in the solid state (see Section 5.2.3), upon coordination to a metal centre they can rearrange to adopt a *cis* conformation, hence facilitating bidentate chelation of the metal (*e.g.*, Equation 78).[117] In addition, a *cis*-bridging mode has also been proposed for these ligands in bi-metallic complexes.[117]


(78)

The final class of dichalcogenide ligands to considered in this section are the *bis*(thiophosphoryl) disulfides and *bis*(thiophosphinyl) disulfides, $R_2P(S)S_2P(S)R_2$ (R = alkyl, aryl, alkoxy, aryloxy). This class of ligand differs from the other diphosphine dichalcogenides reported in this section in that it contains a reactive sulfur–sulfur bond, so that as well as forming simple chelating adducts with metal centres similar to the other diphosphine dichalcogenides (in this case *via* a seven-membered chelate ring), in some cases it will react with a metal complex to give sulfur–sulfur bond scission. Such bond scission involves homolytic cleavage of the sulfur–sulfur bond and oxidative addition to either a single metal centre or to a metal–metal single or multiple bond.[34] This sulfur–sulfur bond breaking reaction therefore generates two new dithiophosph(in)ate ligands, $[R_2PS_2]^-$, which can themselves bind to the metal centre(s) in one of several possible coordination modes (see Section 5.3.5 and Chapter 10.2).

5.3.4. Secondary Phosphine Chalcogenides (R_2PEH)

Secondary phosphine chalcogenides and their conjugate bases (the chalcogenophosphinites) are known to adopt a range of coordination patterns with metal centres (Figure 6).[118] The large variety in their coordination modes is due to the fact that they are able to bind to one or more metal species using the phosphorus atom, chalcogen atom or through both phosphorus and chalcogen centres simultaneously.

Secondary phosphine sulfides can coordinate to transition metals either end-on from the lone pair on the chalcogen atom (**D**), or alternatively from the lone pair on the phosphorus(III) atom in its chalcogenophosphinous acid tautomeric form (**E**). Studies on these ligands in a range of metal complexes with M = Cr, Mo, W, Mn, Re have shown that in most situations coordination from the phosphorus atom (**E**) is the more thermodynamically stable of the two possible modes. This is in sharp contrast to the behaviour of the free ligand for which the secondary phosphine sulfide tautomer is highly thermodynamically favoured almost to the exclusion of the chalcogenophosphinous acid tautomer (see Section 5.2.4). Similar studies on the analogous phosphine selenides show that, in contrast, they strongly favour coordination from just the chalcogen (**D**) with the phosphorus-bonded complexes (**E**) being unstable with respect to elimination of elemental selenium.[118,119]

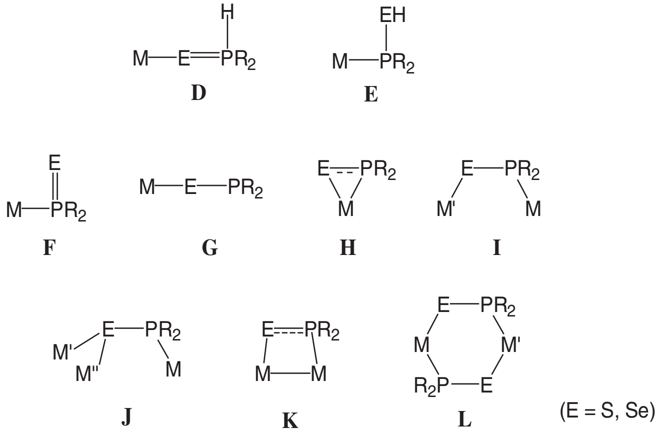
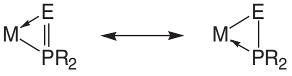


Figure 6 *Coordination modes for secondary phosphine chalcogenides and chalcogenophosphinites*

The monoanionic chalcogenophosphinite ligand $[R_2PE]^-$ can similarly bind to a metal species in a terminal fashion from either the phosphorus (**F**) or chalcogen (**G**), with coordination from the phosphorus being the most frequently observed of the two so far. However, more common in the literature than either of these terminal modes is side-on dihapto coordination from both the phosphorus and chalcogen centres (**H**). In these complexes the anionic ligand is considered to be a four-electron donor, and the phosphorus–chalcogen bond length is in between that expected for a double and a single bond. This has led to the proposal that this species is actually a resonance hybrid of two structures, **60a** and **60b**, with the negative charge either formally on the phosphorus or chalcogen centre respectively.[37,120]



60a **60b**

The chalcogenophosphinite ligand has also been observed to bridge two or more unconnected metal centres (**I**, **J**) or a metal–metal bond (**K**). In these coordination modes similar resonance hybrids to **60a** and **60b** can be drawn, and again the anionic ligands can be considered as four electron donors. In many of the type **I** structures the two metal centres are bridged by two chalcogenophosphinite ligands to give a six membered $M_2P_2S_2$ ring with the two ligands usually counter-directional to one another (**L**).

Although the majority of coordination complexes with chalcogenophosphinites are the sulfur derivatives, several selenophosphinite complexes are known, most of which contain the ligand in a bridging mode (**H, I, J**). There are very few examples of tellurophosphinites in the literature due to the instability of these compounds and their tendency to disproportionate to give elemental tellurium. The only structurally characterised tellurophosphinite is an ion-separated species, $[Ph_2PTe]^-[Li(thf)_{1.33}(tmeda)_{1.33}]^+$ (**61**).[36]

5.3.5. Dichalcogenophosphinic Acids (R_2PE_2H) and their Derivatives

The coordination chemistry of dichalcogenophosphates, dichalcogenophosphonates and dichalcogenophosphinates (see Figure 1 for structures) with transition metals, main-group metals and lanthanides and actinides has been extensively studied over the past 50 years and is the subject of several comprehensive reviews.[34,74,121–125] The ligands and their coordination compounds have found applications in many areas including as extraction agents, analytical reagents, lubricant and plastic additives, pesticides, in the regeneration of cracking catalysts and even in anti-tumour agents (see Section 5.4).

There are many documented synthetic routes to metal dichalcogenophosph(in)ates although the most common involve reaction of the alkali metal or ammonium salt of the ligand (see Section 5.2.5 for preparation of these species) with a suitable metal precursor (including metal chlorides, oxides, alkoxides and a range of other organometallic compounds). Other synthetic methods for the preparation of dithiophosph(in)ate complexes include metal insertion into the sulfur–sulfur bond of *bis*(thiophosphoryl) disulfides or *bis*(thiophosphinyl) disulfides, oxidative addition of elemental chalcogen to a metal diorganophosphide, and symmetric cleavage of dichalcogenadiphosphetane dichalcogenides with a reactive metal species.

Dichalcogenophosphinates, dichalcogenophosphates and dichalcogenophosphonates are very versatile mono-anionic ligands and display a range of coordination patterns. Monodentate coordination through just one of the chalcogen atoms (**M**; Figure 7) is known although uncommon, with bidentate chelating (**N**, **O**) or bridging (**P**–**S**) the most frequently observed coordination modes. In the chelating mode the ligand can either coordinate to the metal from the two chalcogen atoms in an isobidentate symmetrical mode (**N**) or an anisobidentate asymmetrical mode (**O**). For the isobidentate mode the negative charge on the ligand is delocalised throughout the PE_2 fragment to give P–E bond orders of close to 1.5 and equal M–E bonding distances. However, in the anisobidentate mode the negative charge is more localised on one of the chalcogen atoms giving formally one single P–E and one double P=E bond, with the chalcogen atom in the P–E single bond binding to the metal centre *via* a strong M–E interaction, and the chalcogen atom in the P=E double bond forming a weaker and much longer E···M interaction. This E···M interaction can result from either a dative bond from the chalcogen lone pair to the metal atom, or from a longer secondary "semi-bonding" interaction.[125] Similar symmetrical and asymmetrical modes have been observed for these ligands when they bridge two or more metal atoms (**P**–**S**).

One of the more recent innovations for the use of dichalcogenophosphates in coordination chemistry is in the synthesis of multi-metallic cluster compounds, in particular those involving d^{10} copper(I) or silver(I) metal centres. These clusters can be conveniently prepared from the reaction of the ammonium salt of the dichalcogenophosphate with the appropriate metal PF_6 salt. The most

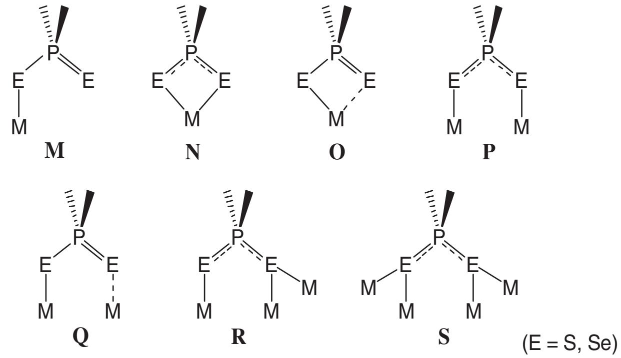


Figure 7 *Coordination patterns for dichalcogenophosphinates, dichalcogenophosphates and dichalcogenophosphonates*

common structural motif adopted by these copper and silver clusters is a cubic arrangement of eight metal centres with six dichalcogenophosphate ligands, one capping each face of the metal cube and therefore bridging four different metal centres (coordination mode **S**, Figure 7). All such cubes reported so far contain an encapsulated anion in their centre and are of general formula $[M_8(\mu_8\text{-}X)(E_2P(OR)_2)_6]^{z-}$ where M = Ag(I), Cu(I); R = Me, Et, *i*Pr; E = S, Se; X = Cl, Br, I (z = 1) S, Se (z = 0).[126–137] The structure of one such cube, $[Cu_8(\mu_8\text{-}Se)(S_2P(OEt)_2)_6]$ (**62**), is shown in Figure 8.[131] Some of these octanuclear cubes (M = Cu; X = Cl, R = Me, *i*Pr) have been studied as catalysts for the coupling of aryl iodides with alcohols to give alkyl aryl ethers, for which they show high yields under mild conditions with catalyst loadings as low as 0.4 mol% cluster.[138]

Formation of these cubic clusters is not just limited to dichalcogenophosphates, and a similar octanuclear cluster with dithiophosphinate ligands, $[Cu_8(\mu_8\text{-}S)(S_2PPh_2)_6]$, has been synthesised from the reaction of CuO*t*Bu with $Ph_2P(S)SSiMe_3$.[139] Larger metal clusters are also known, for example $[Cu_{12}(P_2Se_6)(Se_2P(OEt)_2)_6]$ which contains an ethane-like $[P_2Se_6]^{4-}$ tetra-anion at its centre.[140] Dithiophosphonates can also form multi-metallic clusters with other metals; examples include the tetranuclear zinc species $[Zn_4(\mu_4\text{-}E)(E_2P(OR)_2)_6]$

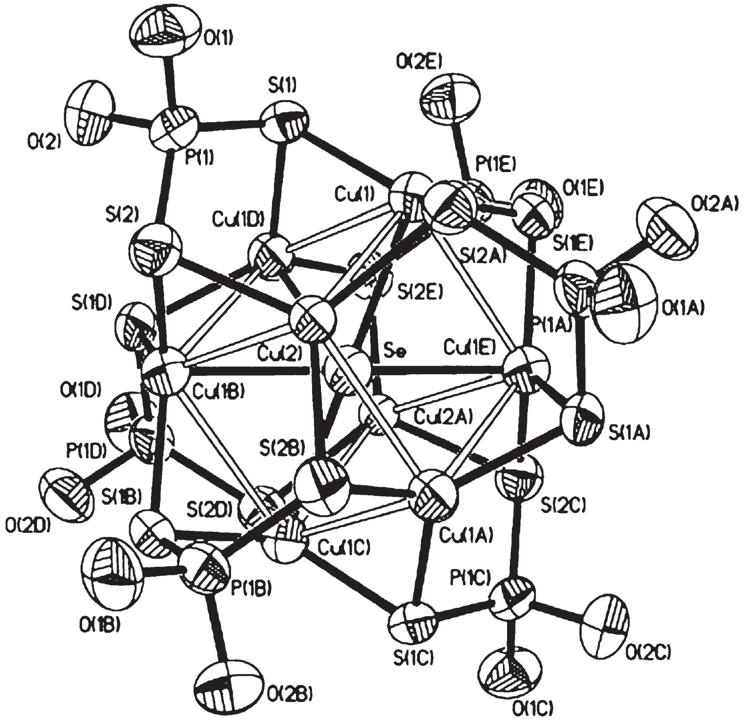


Figure 8 *Solid-state structure of $[Cu_8(\mu_8\text{-}Se)(S_2P(OEt)_2)_6]$ (**62**) with ethyl groups omitted for clarity (reprinted in part with permission from reference 131. Copyright 2003 American Chemical Society).*

($E = O$, $R = i$Bu (**63**);[141] $E = S$, $R = Et$;[142] $E = Se$, $R = n$Pr[143]) which contain a tetrahedrally coordinated group 16 dianion (Figure 9).

The majority of studies on dichalcogenophosph(in)ates, and indeed all the current commercial applications, concern the dithio species. Nevertheless the diseleno species, despite their increased thermal and hydrolytic instability compared to their dithio homologs, have been studied in some depth for their potential applications, particularly as precursors to metal selenide semi-conducting materials (see Section 5.4.3). The ditelluro homologs however, are virtually unknown. The only structurally characterised ditellurophosphinate to date is $[Ph_2PTe_2]^-[Li(thf)_{3.5}(tmeda)_{0.5}]^+$ which, similar to the tellurophosphinite **61**, is a highly moisture sensitive ion-separate species.[36]

Few examples of the heavier group 15 analogues of the dichalcogenophosph(in)ates have been reported although dithioarsinates $[R_2AsS_2]^-$ ($R = Me$, Ph) have been shown to form complexes with a variety of metal centres in an analogous fashion to the dithiophosphinates. For example, reaction of $Me_2As(S)SAsMe_2$ with $Zn(ClO_4)_2.6H_2O$ in ethanol gives $[Zn_4(\mu_4\text{-}S)(S_2AsMe_2)_6]$, a tetranuclear zinc cluster with six dimethyldithioarsinate ligands and an encapsulated sulfur atom, whose solid-state structure is directly comparable to that of the zinc dithiophosphate cluster **63** (Figure 9).[144] Additional details on the coordination chemistry of R_2PE_2H and their derivatives are reported in Chapter 12.2.

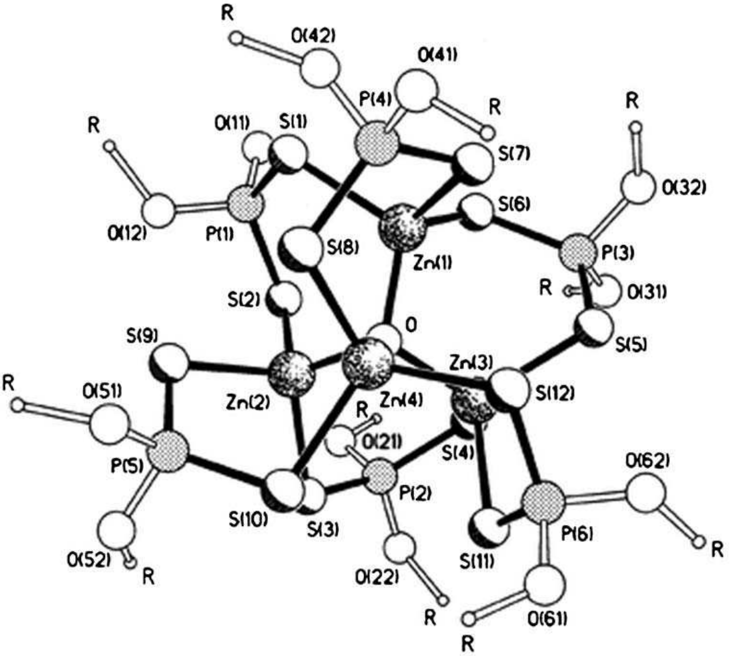
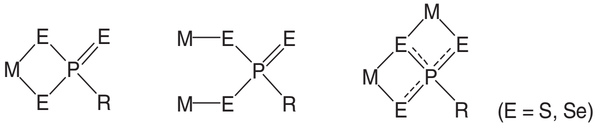


Figure 9 *Solid-state structure of $[Zn_4(O)(S_2P(OiBu)_2)_6]$ (**63**) with butyl groups represented by R for clarity (from ref.141).*



T **U** **V**

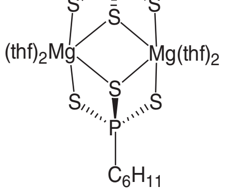
Figure 10 *Coordination patterns for trichalcogenophosphonates*

5.3.6. Trichalcogenophosphonic Acids (RPE_3H_2) and their Derivatives

The coordination chemistry of the trichalcogenophosphonates is very undeveloped when compared to the analogous metal organophosphonates (RPO_3^{2-}), which have been extensively studied owing to their potential and practical applications as ion exchangers, sorbents, sensors, proton conductors, nonlinear optical materials, photochemically active materials, catalysts and hosts for the intercalation of a broad spectrum of guests.[145]

Trichalcogenophosphonates are dianionic ligands and can coordinate to one or more metal atoms using either two (**T**, **U**; Figure 10) or three (**V**) of their chalcogen atoms.

Only a small number of metal trithiophosphonate complexes have been structurally characterised, most of which are monometallic and contain the ligand in a bidentate chelating coordination mode (**T**).[146–150] In these complexes the trithiophosphate ligand formally contains two single P–S bonds and one double thiono P=S bond, with only the two thiolato sulfurs participating in metal bonding. Several dinuclear gold complexes are also known in which the trithiophosphonate ligand bridges two gold centres, again from two thiolato sulfurs with the thiono sulfur not participating in metal bonding (**U**).[151,152] The solid-state structures of the magnesium and lithium complexes of the trithiophosphonate $[(c\text{-}C_6H_{11})PS_3]^{2-}$ (**64**, **65**) have also been reported.[52] In these complexes all three of the sulfur atoms are involved in metal binding, and the three phosphorus-sulfur bonds are all of approximately equal length indicating at least some degree of delocalisation of the negative charge over the PS_3^{2-} fragment (**V**).



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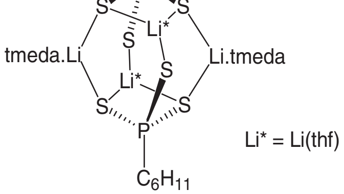


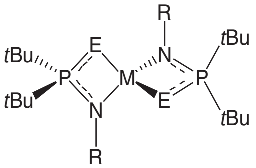
65

Hitherto, only two structurally characterised triselenophosphonate complexes have been published, $PtSe_2P(Se)PPh(dppe)$[153] and (c-C_6H_{11})PSe_3Li_2.2tmeda,[38] in which the triselenophosphonate ligand coordinates to the metal centre(s) using two (**T**) or three (**V**) selenium atoms respectively.

5.3.7. Amido and Imido Derivatives of Chalcogeno–Phosphorus Acids

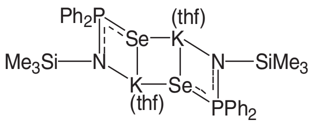
The amido and imido derivates of phosphorus–chalcogen ligands have been of much interest to coordination chemists due to the fact that they possess both hard (nitrogen) as well as soft (chalcogen) donor sites and are therefore able to act as heteroleptic ligand systems.[56]

Metal complexes of the chalcogenoimidophosphinate ligand $[R_2P(E)(NR)]^-$ are accessible from metathesis reactions of the lithium chalcogenoimidophosphinate with metal chlorides or from protolysis of a *bis*(trimethylsilyl)amide metal salt $M[N(SiMe_3)]_2$ (M = Cr, Mn, Co, Zn, Cd) with chalcogenoamidophosphinic acid.[56] In these metal complexes the chalcogenoimidophosphinate ligand has been observed to act as a N,E chelating ligand, such as in the $M[t\mathrm{Bu}_2P(E)NR]_2$ series of compounds reported by Bochmann (**66**).[154] For the potassium complex of the selenium derivative, $[(Ph_2P(Se)NSiMe_3).K(thf)]_2$ (**67**), as well as N,E chelate formation there are additional chalcogen–metal interactions resulting in dimerisation by way of a central K_2Se_2 ring.[155] In general, larger R groups on the phosphorus lead to the formation of monomers, whereas smaller R groups lead to aggregation and the formation of dimers or larger aggregates.



M = Cr, Mn, Fe, Co
E = Se, Te
R = iPr, C_6H_{11}

66



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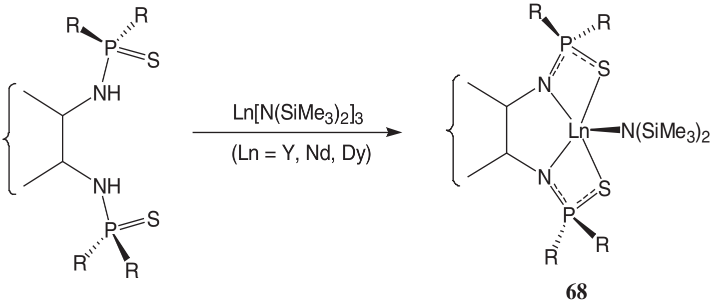
Bis(thioimidophosphinate)s are able to bind to metal centres through both of their thioimidophosphinate S,N chelating groups, and been particularly studied with the group 3 metals due to their ability to form monomeric complexes (*e.g.*, **68**). Such complexes can be prepared from the reaction of *bis*(thioamidophosphinic acid)s with group 3 metal amides (Equation 79).[58] In these complexes aggregate formation is disfavoured by the steric requirements of the pseudo-tetrahedral phosphorus centre. In addition, group 3 metals are very oxophilic and the presence of sulfur or selenium substituents leads to a lower tendency for aggregation than with oxygen-based ligands.



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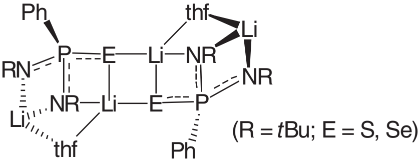
(79)

Isoelectronic to phosphonic acids are chalcogeno*bis*amidophosphonic acids $[PhP(E)(NHR')_2]$ which contain two acidic amide protons, and hence can undergo mono- or di- deprotonation to give imido-amido or *bis*-imido chalcogenophosphonates respectively. The dilithium salts of chalcogeno*bis*imidophosphonates $[PhP(E)(NtBu)_2]^{2-}$ (X = Se, Te) are all dimers in the solid state with the lithium atoms coordinated *via* N,N′ and N,E chelation within each monomer unit, and dimerisation occurring through inter-monomer Li-E interactions to give a central transoid Li_2E_2 ring (**69**).[60] The sulfide forms a very similar dimeric structure although intra-monomer S-Li interactions are not present.[60] The same parent chalcogeno*bis*amidophosphonic acids, $PhP(E)(NHtBu)_2$ (E = S, Se), can undergo mono-deprotonation on treatment with one equivalent of trimethylaluminium in boiling toluene to give the aluminium complex of the mixed imido-amido ligand, in which the ligand chelates to the aluminium centre from the imido nitrogen and chalcogen atoms (**70**).[60]



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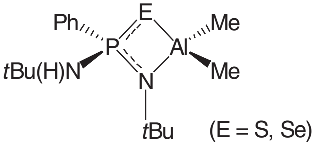

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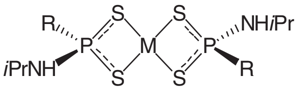
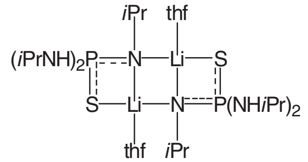
Also isoelectronic to mono-deprotonated phosphonic acid is the dichalcogenoimidophosphonate ligand, $[RP(E)_2(NR')]^-$. Group 10 metal complexes of this ligand (R = p-C_6H_4OMe; R′ = iPr; E = S), have been prepared by reaction of the ammonium salt of the ligand with $NiCl_2$, K_2PdCl_4 or K_2PtCl_4. In these complexes the ligand coordinates the metal in a S,S′ chelating fashion (**71**).[40]



(M = Ni, Pd, Pt; R = *p*-C_6H_4OMe)

71

The structures of the mono-lithio salts of thio*tris*amidophosphoric acids, $[SP(NHR)_2(NR)]^-Li^+$, depend very much on the steric requirements of the R substituents as well as on the solvent, but all involve lithium coordination from both the imido nitrogen and the chalcogen atom, with the two amido nitrogens uninvolved in metal coordination (*e.g.*, **72**).[156] Further lithiation of **72** with one equivalent of *n*BuLi in the presence of tmeda gives the dimetallated complex **73** in which the two imido nitrogens and the chalcogen atom all participate in metal coordination.[156] *Tris*-lithiated complexes $[EP(NR)_3]Li_3$ are known for R = aryl and E = S, Se and have been observed to form aggregates in the solid-state with all three imido nitrogens as well as the chalcogen atom involved in metal bonding.[63] The mono-lithiated complexes, $[SP(NHR)_2(NR)]^-Li^+$, have been used in metathesis reactions to give transition metal complexes of these ligands. One noteworthy example is the nickel complex **74** which is formed from the reaction of $NiBr_2$(dme) with $[SP(NHtBu)_2(NtBu)]^-Li^+$ and contains one of the ligands coordinated *via* a hard–soft N,S chelate mode and one coordinated *via* a hard–hard N,N′ chelate mode.[157]



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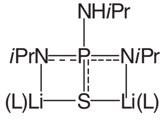
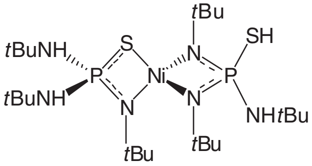


(L = tmeda)

73



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The anions of *bis*(amido)cyclodiphosphazane dichalcogenides, $[RN(E)P(\mu\text{-}NR)_2P(E)NR]^{2-}$ (E = S, Se, Te), are versatile ligand systems capable of a wide range of coordination modes involving the two chalcogen atoms as well as the two exocyclic and the two endocyclic nitrogen atoms. The most common coordination modes are shown in Figure 11 for the dianionic ligands (**W**–**Y**), as well as the mono-anionic ligand (**Z**).[56,65] The exact coordination mode adopted

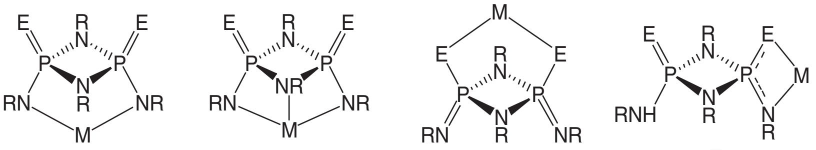


Figure 11 *Common coordination modes of bis(amido)cyclodiphosphazane dichalcogenides*

depends upon the R substituent, the metal and the chalcogen, although in general large, soft metals show a preference for E,E′ coordination mode **Y** (for example, M = $Pt(PEt_3)_2$, E = S, R = *t*Bu)[158] whereas harder metal centres prefer N,N′ coordination mode **W** (for example, M = $SnMe_2$, E = S, R = *t*Bu).[159] Alkali-metal complexes of *bis*(amido)cyclodiphosphazane dichalcogenides can be readily prepared from metallation of the neutral ligand with a reactive organometallic, metal amide or metal alkoxide reagent (see Section 5.2.7). Transition-metal complexes are then accessible from metathetical reactions between the alkali-metal complex of the ligand and a transition-metal halide. Transition-metal complexes have also been obtained *via* direct reaction of the neutral ligand with a metal halide in the presence of a weak base.[65]

5.3.8. Dichalcogenoimidodiphosphinates [$R_2P(E)NHP(E)R_2$]

The coordination chemistry of imino*bis*(diorganophosphine chalcogenide)s, imino*bis*(dialkoxy-/diaryloxy-phosphine chalcogenide)s, and in particular their mono-anionic derivatives – the dichalcogenoimidodiphosph(in)ates, has been intensively studied with almost all the metallic and semi-metallic elements.[72–77] They form inorganic (*i.e.*, carbon free) chelate rings with metals and semi-metals, and can be considered to be inorganic analogues of β-diketonates [$R_2C(O)CHC(O)R_2$]$^-$ (R = alkyl, aryl), which have also been widely employed in coordination chemistry. However, unlike β-diketonates which form planar rings, the anionic dichalcogenoimidodiphosph(in)ates are flexible around the EPNPE backbone due to the sp^3 hybridised phosphorus centres and this allows them to bind to metal centres using several possible coordination modes (Figure 12). Furthermore, metal complexes of these ligands have shown improved thermal and chemical stability over β-diketonates and other organic-based ligands, and are less susceptible to hydration, oxidation or polymerisation.

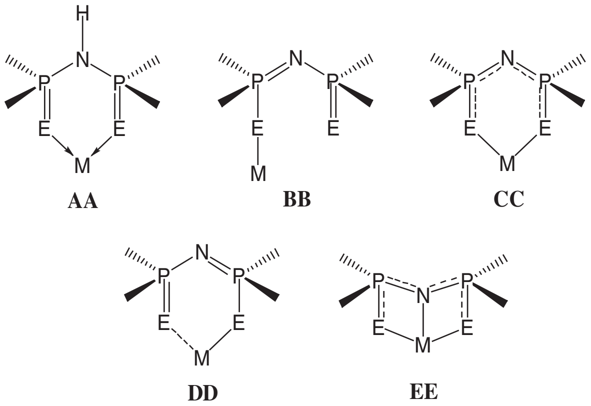


Figure 12 *Common coordination modes for iminobis(diorganophosphine chalcogenide)s and dichalcogenoimidodiphosph(in)ates*

Coordination modes observed for the neutral ligands are almost exclusively bidentate E,E′ chelating (**AA**), and these complexes are very prone to deprotonation to give the dichalcogenoimidodiphosph(in)ate complexes. Metal dichalcogenoimidodiphosph(in)ate complexes are also accessible from reaction of the potassium salt (prepared from the parent ligand and KO*t*Bu – see Section 5.2.8) and the appropriate metal halide. Alternatively the neutral ligands can be reacted directly with a reactive organometallic reagent – for example reaction of $U[N(SiMe_3)_2]_3$ with $[Ph_2P(E)NHP(E)Ph_2]$ (E = S, Se) gives the uranium(III) complex $U[Ph_2P(E)NP(E)Ph_2]_3$.[160]

Although dichalcogenoimidodiphosph(in)ates can form mono-dentate coordination patterns from just one chalcogen (**BB**), this is only regularly observed with the mixed chalcogen systems $[R_2P(E)NHP(O)R_2]$ (E = S, Se). The most commonly observed coordination mode is E,E′ chelating which gives rise to a flexible six membered chelate ring, which is able to adopt various configurations including planar, boat and chair forms. In most of these complexes the negative charge is delocalised throughout the EPNPE unit to give isobidentate chelation (**CC**). However, anisobidentate chelating modes (**DD**) are also known in which the negative charge is predominately localised on one of the chalcogen atoms resulting in unequal pairs of P–N, P–E and E–M bond distances within the complex. Some lanthanides and actinides have been reported to adopt tridentate coordination modes with dichalcogenoimidodiphosph(in)ates in which the imido nitrogen as well as the two chalcogen atoms participate in metal coordination (**EE**). Although Figure 12 shows the most frequently observed coordination patterns for these ligands, many other coordination patterns have also been observed, particularly in multi-metallic complexes.[72]

The related monochalcogenides $R_2PNHP(E)R_2$ primarily exhibit E,P coordination patterns to afford five-membered MPNPE metallacycles (**FF**, Figure 13). The anionic monochalcogenoimidodiphosph(in)ates, $[R_2PNP(E)R_2]^-$, also form similar MPNPE chelate rings (**GG**), in which the negative charge is partially delocalised throughout the PNPE π-system.[76]

5.4 Applications of Compounds and Complexes Containing Phosphorus–Chalcogen Bonds

5.4.1. Reactions with Organic Substrates

Thionation reactions have been widely used in organic syntheses, in particular for the transformation of carbonyl groups into the corresponding thiocarbonyl

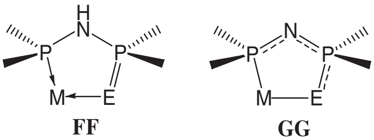
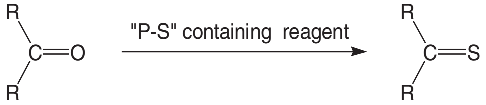


Figure 13 *Coordination modes for $R_2PNHP(E)R_2$ and $[R_2PNP(E)R_2]^-$ (E = S, Se)*

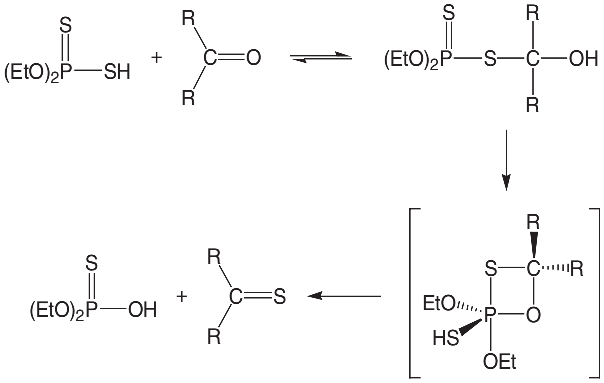
groups (*e.g.*, ketones to thioketones, Equation 80). This transformation is usually carried out with a phosphorus-sulfur containing reagent, with the driving force for reaction being the formation of strong P=O and P–O bonds in place of the weaker and more labile P=S and P–S bonds.



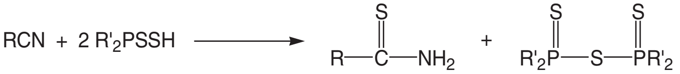
(80)

Phosphorus pentasulfide (P_4S_{10}) was one of the first reported reagents to be used in thionation reactions. However it suffers from several drawbacks, requiring a large excess of the reagent in boiling toluene, xylene or pyridine for long reaction times and the reported yields are often low. This led to phosphorus pentasulfide being superseded by other phosphorus-sulfur compounds including dithiophosphoric acids and dithiadiphosphetane disulfides, of which Lawesson's reagent (**43**) is now the most widely used example. Nevertheless there has been a recent renaissance in the use of phosphorus pentasulfide since it was reported that the addition of hexamethyldisiloxane ($Me_3SiOSiMe_3$) dramatically increased the yields to values approaching or in some cases exceeding those achieved with Lawesson's reagent.[161] Other advantages of the phosphorus pentasulfide/hexamethyldisiloxane system is that the phosphorus containing by-products can be readily removed with mild hydrolysis. Further improvements in terms of yields, selectivity and reduced reaction times with this system have been reported using microwave irradiation.[162]

Dithiophosphoric acids, $(RO)_2PS_2H$, have been used for the thionation of carbonyl groups in certain aldehydes, ketones, amides, esters, thio-carboxylates and other organics.[163] The mechanism for this reaction proceeds *via* a reversible nucleophilic attack of the thioacid on the carbonyl compound, which can then rearrange by way of a four-membered PSCO cyclic intermediate into the desired C=S containing molecule and thiophosphoric acid (Equation 81).[163]



(81)

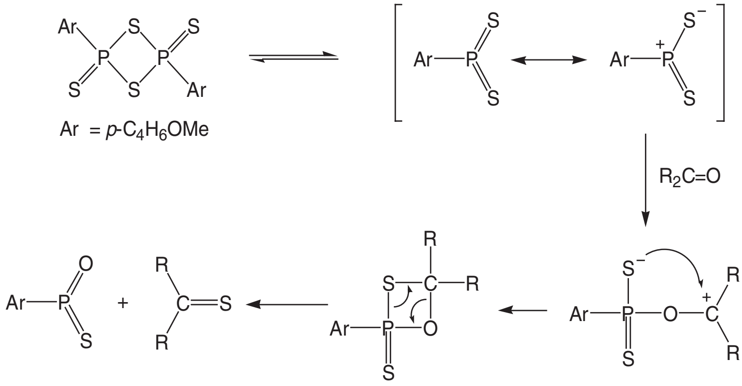


$$\mathrm{RCN} + 2\,\mathrm{R'_2PSSH} \longrightarrow \mathrm{R{-}C({=}S){-}NH_2} + \mathrm{R'_2P({=}S){-}S{-}P({=}S)R'_2} \qquad (82)$$

Dithiophosphoric and dithiophosphinic acids can also react with organic compounds containing multiple carbon–nitrogen bonds, often under very mild conditions, to give thioamides and other related compounds (*e.g.*, Equation 82).[163]

However, since Lawesson and coworkers reported the use of 2,4-*bis*(*p*-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide (**43**) for use in thionation reactions[92] this reagent (now commonly called Lawesson's reagent) has dominated the field of organic thionation reactions. This is due to its convenient handling, high yields, easy workup and use in soft thionation reactions. In addition, it is readily available from reaction of phosphorus pentasulfide with anisole (see Section 5.2.8) and is sold commercially too. Several extensive review articles have covered its use in the thionation reaction with a wide variety of substrates.[163–165] Even complicated molecules containing many functional groups, such as nucleosides, nucleotides and steroids have been shown to undergo selective and high-yielding thionations with Lawesson's reagent.

Lawesson's reagent reacts readily with both aliphatic and aromatic ketones in anhydrous toluene under reflux. The proposed mechanism for this reaction is shown in Equation 83, and reveals some similarities to the mechanism of the oxygen–sulfur exchange reaction promoted by dithiophosphates (Equation 81), with both proceeding *via* a four-membered PSCO cyclic intermediate. Again the formation of a strong phosphorus-oxygen bond is key in driving the reaction forwards.



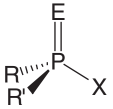
(83)

Recent advances in the use of Lawesson's reagent include its application in microwave assisted solvent-free syntheses, solid-phase synthesis and combinatorial chemistry.[165] Despite the ubiquity of Lawesson's reagent for organic thionation reactions, there are still some classes of compounds that it does not readily react with, for example, ester-containing ether functionalities. In addition, its low solubility and the high reaction temperatures often required can prove problematic in some cases. Hence the development of new thionating reagents with increased solubility, selectivity and reactivity under milder conditions is a constant challenge.[165,166]

A variety of selenium-containing compounds have been studied for the conversion of carbonyl groups into selenocarbonyl groups including ($Me_3Si)_2Se$, ($i$$Bu_2Al$)Se, NaHSe with Se_2Br_2, *bis*(1,5-cyclooctanediylboryl)selenide, tetraethylammonium tetraselenotungstate (Et_4WSe_4) and various heterocyclic phosphorus-selenium compounds. The phosphorus–selenium heterocycles do have some advantages over the other reagents due to their stability and ease of preparation and handling. Phosphorus–selenium heterocycles which have shown good conversion rates for the selenization of amides and aldehydes include [(PhP(Se)(μ-Se)]$_2$ (Woollin's reagent, **46**)[167,168] and Yoshifugi's eight membered $(RP)_3Se_5$ heterocycles (**49**).[99]

5.4.2. Pesticides and Nerve Agents

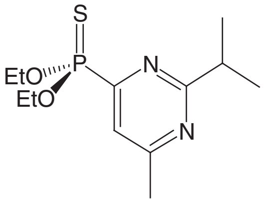
Organophosphorus compounds are one of the most widely used classes of pesticides. Although their main application has been as insecticides, they have also been used as herbicides, fungicides, acaricides, rodenticides, avicides, neamticides, molluscides and bactericides. Many of the organophosphate insecticides contain thiono or thiolo groups and conform to the general structure **75**.[1,169] Although the leaving group (X) in these compounds can be a simple acyl or acid-anion group, more frequently it is a complex organo group whose structure and properties play a key role in the biological activity of the pesticide. Organophosphorus pesticides are in general fast-acting, highly effective in small concentrations and have a low persistence being easily broken down (usually by hydrolysis) to give non toxic by-products.



E = O,S
R, R' = alkoxy, alkyl, amino
X = leaving group

75

Virtually all organophosphorus pesticides function by inhibiting the action of the ester-hydrolysing enzyme acetylcholinesterase by mimicking normal biological ester substrates and blocking the active site for prolonged periods of time. The acetylcholinesterase enzyme is needed for proper nervous system function, and this inhibition is usually fatal. Examples of commercially used organophosphorus insecticides include Diazinon (**76**) which is used to control cockroaches, silverfish, ants and fleas in residential buildings, and Malathion (**77**), which is an outdoor-use pesticide and has also been used clinically to treat head and body lice. Nerve gases also work on a similar principle by blocking the acetylcholinesterase enzyme in humans. This leads to the continuous firing of nerves since the neurotransmitter acetylcholine cannot now be broken down, resulting in contractions of all the "involuntary" muscles in the body and ultimately death. A well-known example of such a nerve gas is VX gas (**78**), which is one of the most deadly nerve agents known to date with doses of less than 10 mg being able to kill an average person.



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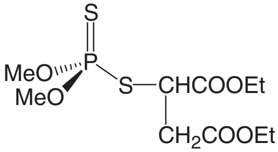

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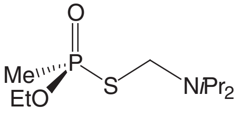
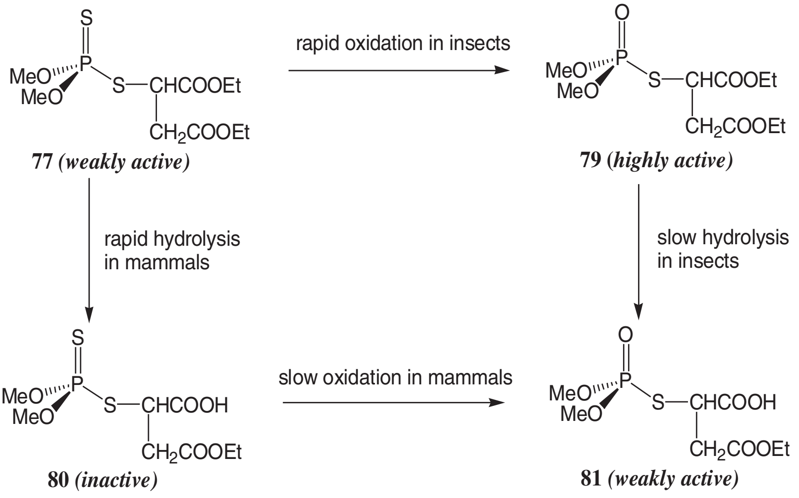


78

The toxicity of an insecticide not only depends upon its molecular structure but also the way it is metabolised. A good example of this is Malathion (**77**), which is metabolised very differently by insects and humans and is therefore only toxic to insects. The mildly active Malathion (**77**) is rapidly oxidised in insects converting it into the strongly active oxidation product **79** (Equation 84), and this is only broken down very slowly by hydrolysis to give the weakly active **81**. In contrast, oxidation of Malathion in mammals is slow, but hydrolysis of the ester group occurs very rapidly to give the inactive non-toxic compound **80** (Equation 84).[1,169]



(84)

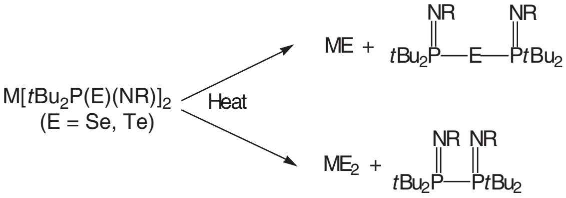
5.4.3. Precursors Towards Metal Chalcogenide Thin-Films and Quantum Dots

Metal chalcogenide semi-conducting materials have found many applications in opto-electronic, solar cell and photovoltaic devices. Deposition of these materials can be achieved by a variety of techniques of which one of the most important and widely applied is MOCVD (metal-organic chemical vapour deposition). MOCVD uses one or more element sources (precursor molecules) which are introduced into the reactor in their vapour state and undergo adsorption on a substrate surface followed by reaction to give the metal chalcogenide along with desorption of any by-products. Conventional MOCVD uses as many molecular precursors as there are elements making up the material to be deposited. However, a single molecule that comprises all the elements to be deposited (a single-source precursor) has advantages in terms of simplified reactor design and is often safer to use and more environmentally friendly than multiple-source precursors.[170] Several phosphorus–chalcogen containing compounds have found applications in this field as single-source precursor materials, their main advantages being their air stability and less noxious nature than traditionally used multiple-source precursors such as hydrogen sulfide and hydrogen selenide. The three main classes of phosphorus–chalcogen compounds studied in this area are the metal complexes of dichalcogenophosphates, dichalcogenoimidodiphosphinates and chalcogenoimidophosphinates. Volatility for these compounds is sometimes a problem but can be overcome with new techniques such as aerosol assisted CVD (AACVD).[171]

Complexes of the dichalcogenophosphinate ligand $[R_2PE_2]^-$ ($E = S, Se$) were some of the first phosphorus–chalcogen compounds to be investigated as potential single-source precursors.[170] $Cd(S_2PMe_2)_2$[172] and $Cd(S_2PEt_2)_2$[173] were studied in the early 1980s for growth of cadmium sulfide thin films. Even though these compounds contain phosphorus, there was no evidence of phosphorus incorporation into the metal chalcogenide phases grown from these precursors. Since then a number of group 12 and 13 metal complexes of dichalcogenophosphinate ligands have also been studied for deposition of group 12 or 13 chalcogenide materials.[170,171,174]

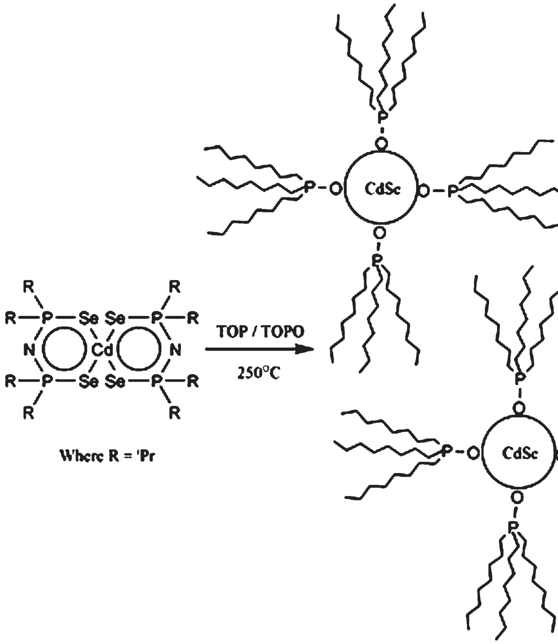
Dichalcogenoimidodiphosphinate complexes $M[(EPR_2)_2N]_xL_y$ ($R = i$Pr, Ph; $E = S, Se$; $L =$ nothing, Me, Et, Ph, Cl) have been used to deposit thin films of metal chalcogenide materials including ZnSe,[175–177] CdSe,[175–178] In_2Se_3,[179,180] In_2S_3,[181] Ga_2Se_3,[180] Bi_2Se_3,[182–184] HgE[185] and PbE[186]. In addition, $Cu[(SePiPr_2)_2N]$ and $In[(SePiPr_2)_2N]_2Cl$ have been used together under AACVD conditions to afford ternary $CuInSe_2$ solid-state materials.[187] Most of these studies have used the *iso*-propyl or phenyl derivatives of dichalcogenoimidodiphosphinates owing to their ease of preparation, and of these the *iso*-propyl derivatives have exhibited significant advantages for CVD applications owing to their increased volatility.

Far fewer single-source precursors of any kind are known for deposition of metal tellurides, although metal telluroimidophosphinates have shown some promise in this area. Complexes of general formula $[M(tBu_2P(Te)NR)_2]$ ($M =$ Zn, Cd, Cr, Mn, Fe, Co; $R = i$Pr, C_6H_{11}, tBu) are uncommonly thermally stable and are also sublimable at temperatures below 200°C.[154,188] These compounds have been evaluated for the growth of metal telluride materials and have been shown to form phases without the incorporation of nitrogen or phosphorus. Spectroscopic studies reveal the decomposition reaction to proceed with the elimination phosphorus-imide by-products (Equation 85). Similar selenium-containing complexes $[M(tBu_2P(Se)NR)_2]$ have also been used to prepare metal selenide and diselenide phases, and give similar decomposition by-products.[154,188]



(85)

More recently, similar compounds have also been used to prepare metal chalcogenide quantum dots (nanoparticles). The premise is similar in that a single molecule precursor containing both the chalcogen and the metal undergoes decomposition to give a semi-conducting metal chalcogenide. However, in this case the reaction proceeds *via* nucleation and particle growth steps in solution (often a solution of triphenylphosphine/triphenylphosphine oxide – TOP/TOPO – at temperatures up to 250°C) and hence there is not the requirement of the precursor to be volatile as is the case for MOCVD applications. The sizes of the metal chalcogenide quantum dots can be varied by the length of the reaction time and the temperature, and this control over size leads to tuneable band-gaps, which vary the resultant nanoparticles' optical response. This tuneability makes metal chalcogenide quantum dots applicable for a wide range of uses including as biomarkers, single-electron transistors, and colour display technologies. The cadmium complex $Cd[N(SeP\textit{i}Pr_2)_2]_2$ has been used successfully as a single-source precursor for the production of cadmium selenide quantum dots *via* thermolysis in TOP/TOPO solution (Equation 86).[189] The size of the quantum dots derived from this precursor could be varied accurately by increasing or decreasing the reaction time.[189]



(86)

(reprinted *from ref. 190)*

Tertiary phosphine chalcogenides are also commonly employed as a source of reactive chalcogen in multi-precursor routes to metal chalcogenide quantum dots. Hence TOPSe or TOPTe (trioctylphosphine selenide/telluride), formed from heating together TOP and the elemental chalcogen, can be reacted with a cadmium metal source such as $CdMe_2$ to give cadmium selenide or cadmium telluride quantum dots respectively.[190]

5.4.4. Metal Extraction Technologies

Thio-phophorus as well as other organo-phosphorus-based systems have found large-scale commercial uses in the field of hydrometallurgy. Some of the most important compounds for use in industrial solvent extraction procedures are the dithiophosphinic acid $(C_8H_{17})_2P(S)SH$ (commercial name CYANEX 301) and the thiophosphinic acid $(C_8H_{17})_2P(S)OH$ (CYANEX 302), which are used in the separation of cobalt from nickel or manganese, and for other rare-earth and heavy metal separations.[191] These acids, in their deprotonated forms, will ligate certain metal ions strongly, facilitating removal of the metal cation from the original aqueous phase and into an organic phase from which it can be recovered. The tertiary phosphine sulfide $(C_4H_9)_3PS$ (CYANEX 471X) also works on a similar principle and is used commercially for silver recovery from sulfate or nitrate solutions.[191]

5.4.5. Lubricant Additives

Zinc dithiophosphates, $[Zn(S_2P(OR)_2)_2]_2$ (R = alkyl or aryl), are used extensively in the formulation of anti-wear hydraulic fluids and engine oils.[192] Their role as additives in these lubricating oils is primarily as anti-oxidants, but they also play a part in protecting metals against corrosion and in improving the wear inhibition of the lubricant. A range of organo (R) substituents have been used with these zinc dithiophosphates, usually based on alkyl chains of lengths of C_3 to C_{12} or alkylated phenols. The properties of the R substituents directly influence the performance of the additive, affecting its thermal and hydrolytic stability and its function in oxidative inhibition and wear protection. Such zinc dithiophosphates are prepared on large industrial scales from phosphorus pentasulfide and the appropriate alcohol (Equation 87).

$$P_2S_5 + 4\,ROH \xrightarrow[-H_2S]{} 2\,(RO)_2PS_2H \xrightarrow[-H_2O]{ZnO} [(RO)_2PS_2]_2Zn \qquad (87)$$

Zinc dithiophosphates act as anti-oxidants by promoting the decomposition of hydroperoxides. The mechanism of this reaction is complicated involving hydroperoxides and peroxy radicals[192,193] and is also affected by the other additives present in the lubricant oil.[194] However the first step is thought to be a rapid initial reaction of the zinc dithiophosphate and hydroperoxide to give a "basic" compound $[Zn_4(\mu_4\text{-}O)(S_2P(OR)_2)_6]$ (Equation 88; Figure 9).[141]

$$4\,[(RO)_2PS_2]_2Zn + R'OOH \xrightarrow[-R'OH]{} [Zn_4O\{S_2P(OR)_2\}_6] + [(RO)_2PS_2]_2 \qquad (88)$$

5.4.6. Other Applications

Tertiary phosphine sulfides have been used as ligands for the palladium-catalysed *bis*alkoxycarbonylation of olefins;[195] secondary phosphine sulfides have been employed as ligand precursors for nickel-catalysed cross-coupling reactions of aryl chlorides with aryl Grignard reagents;[196] octanuclear copper clusters with dithiophosphate ligands $[Cu_8(\mu_8\text{-}Cl)(S_2P(OR)_2)_6]^-$, have been studied as catalysts for the coupling of aryl iodides with alcohols;[138] the *bis*(thiophosphoryl) disulfide $i\mathrm{Pr_2P(S)SSP(S)}i\mathrm{Pr_2}$ has been used as an accelerator for the vulcanisation of rubber where sulfur cross-links are promoted by heating a mixture of the accelerator, sulfur and an unsaturated polymer;[197] and antimony and tin complexes of thiophosphorus ligands, $Ph_2M(S_2PR_2)_n$ ($M =$ Sn, $n = 2$; $M =$ Sb, $n = 1$; $R =$ Ph, O*i*Pr), have been reported to display anti-tumour activity.[74]

There has also been much recent research on the substitution, with sulfur or selenium, of one or more of the oxygen atoms in the phosphonate group of biological molecules or macromolecules including phospholipids,[198] oligonucleotides,[199–202] RNA[203,204] and DNA.[205–208] The sulfur or selenium analogues of these biomolecules are of interest in elucidating the mechanism of reaction of biological transformations, in probing biomembrane structures and in modifying the reactivity of these species for new tasks such as specific gene inhibition. The seleno-derivates of phosphonates are also of interest owing to the important role they can play in the X-ray characterisation of biological macromolecules using the multi-wavelength anomalous-dispersion (MAD) technique.[206,208]

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CHAPTER 6

Chalcogen–Oxygen Chemistry

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6.1 Introduction

Owing to the high stability of bonds between oxygen and sulfur, selenium, and tellurium, respectively, a huge number of compounds containing these bonds are known. In order to be not beyond the scope of this chapter, they cannot be mentioned comprehensively and a selection has to be done. Thus, predominantly newer results will be discussed in more detail, while older and well-documented items will be only mentioned occasionally, especially in Sections 2 and 3. Furthermore, those compounds are emphasized that have been structurally characterized with high accuracy, mainly by diffraction methods. The compounds will be discussed in the text or they will at least be mentioned with appropriate referencing in the tables. The chapter starts with an overview of binary chalcogen oxides (Section 2) and moves on to mixed chalcogen oxides in Section 3. In the following section, chalcogen *oxo*-acids will be discussed, and Section 5 is devoted to the salts of these acids. This section is necessarily the most restricted one and emphasizes only very recent results.

6.2 Binary Sulfur, Selenium, and Tellurium Oxides

The simplest compounds containing a chalcogen–oxygen bond are the binary oxides. They have been investigated best for sulfur and compounds for which structural data are known are collected in Table 1. Sulfur(VI)-oxide, SO_3, is known to be trimorphic. The so-called ice-like form of sulfur trioxide, γ-SO_3, is a cyclic trimer (Figure 1a) and is obtained upon cooling SO_3 vapour below $-80\ ^\circ C$.[1] It has a melting point of $16.9\ ^\circ C$ and a boiling point of $44.5\ ^\circ C$. The asbestos-like modification α-SO_3 and β-SO_3 (Figure 1b) contains the SO_3 molecules condensed to infinites chains that are interlinked in α-SO_3 in contrast to β-SO_3.[2] Because of the stronger linkage, the melting point of α-SO_3 is

Table 1 *Chalcogen oxides and chalcogen oxygen acids investigated by X-ray diffraction*

Chalcogen	*Binary oxides*		*Mixed oxides*		*Oxygen acids*	
	Compound	*Symmetry*	*Compound*	*Symmetry*	*Compound*	*Symmetry*
S	γ-SO_3[1]	$P2_1nb$			H_2SO_4[40,41,42,43]	C2/c
	β-SO_3[2]	$P2_1/c$			$(H_3O)(HSO_4)$[44,45]	$P2_1/c$ C2/c
	SO_2[3]	Aba2			$(H_3O)_2(SO_4)$[46]	$P\bar{4}2_1c$
	S_8O[4]	$Pca2_1$			$(H_5O_2)_2(SO_4)$[47]	$P\bar{4}2_1c$
	S_7O[5]	$P2_1/n$			$(D_5O_2)_2(SO_4)$[47]	Cm
					$H_2SO_4 \cdot 6.5H_2O$[48]	$I\bar{4}2d$
					$H_2SO_4 \cdot 8H_2O$[48]	Pbca
					H_2SO_5[49]	C2/c
					$H_2S_2O_7$[50]	
Se	SeO_2[16]	$P4_2/mbc$			H_2SeO_4[51,41,52]	$P2_12_12_1$
	SeO_3[21]	$P\bar{4}2_1c$			$(H_3O)(HSeO_4)$	Pbca
	Se_2O_5[19]	$P2_1/c$			$(H_5O_2)_2(SeO_4)$[53]	Pnma
					$(H_5O_2)_2(SeO_4)$[53]	$P\bar{4}2_1c$
					H_2SeO_3[54]	$P2_12_12_1$
Te	α-TeO_2[23]	$P4_32_12$	$Te_2O_3(SO_4)$[34,35]	$Pmn2_1$	H_2TeO_4[55]	$P2_1/c$
	α-TeO_2[24,25]	$P4_12_12$	$Te(S_2O_7)_2$[33]	Cc	$Te(OH)_6$[56,57,59]	$Fd\bar{3}c$
	β-TeO_2[27]	Pbca	$Te_2O_3(SeO_4)$[39]	$Pmn2_1$	$Te(OH)_6$[57]	$F4_132$
	γ-TeO_2[28]	$P2_12_12_1$	$TeO(SeO_3)$[36,37]	Ia	$Te(OH)_6$[58]	$P2_1/n$
	β-TeO_3[32]	$R\bar{3}c$	$Te_3O_5(SeO_3)$[38]	$P\bar{1}$	$H_2Te_2O_6$[59]	$Pbn2_1$
	Te_2O_5[29]	$P2_1$				
	Te_4O_9[30]	$R\bar{3}$				

[a] Note: 41,57: neutron diffraction; 43: high pressure; 52: single crystal neutron diffraction.

remarkably higher (62.2 °C) compared to the one of β-SO_3 (32.5 °C). In both forms the terminal positions of the chains are occupied by OH^- and H, respectively, according to the formulation $H(OSO_2)_xOH$. Even if x is in fact very large, both modifications are strictly speaking polysulfuric acids.

The very toxic sulfur(IV)-oxide, SO_2, is a bent molecule (C_{2v} symmetry) that reacts as a reducing agent due to the higher stability of the oxidation state +VI for sulfur. SO_2 can be easily condensed to a colourless liquid (b.p. −10.0 °C) that has been shown to be a versatile solvent for several reactions, and below −75.5 °C a colourless molecular solid is formed. In the solid state, the SO_2 molecule shows a bond length S–O of 1.429 Å and an angle O–S–O of 119°.[3]

A number of lower sulfur oxides have been described. Most of these oxides are derived from cyclic sulfur polymorphs and were usually prepared by oxidation of these molecules by organic peroxo acids. The oxides have the general formula S_nO and n may vary from 5 to 10. For $n = 7$ even the dioxide S_7O_2 is known.[4] Not all of these phases were characterized by X-ray diffraction, but the molecular structures are certain with respect to vibrational spectroscopy. The oxygen atom is in *exo* position with respect to the sulfur ring as it has been shown by X-ray diffraction for S_8O and S_7O, respectively (Figure 2).[5,6]

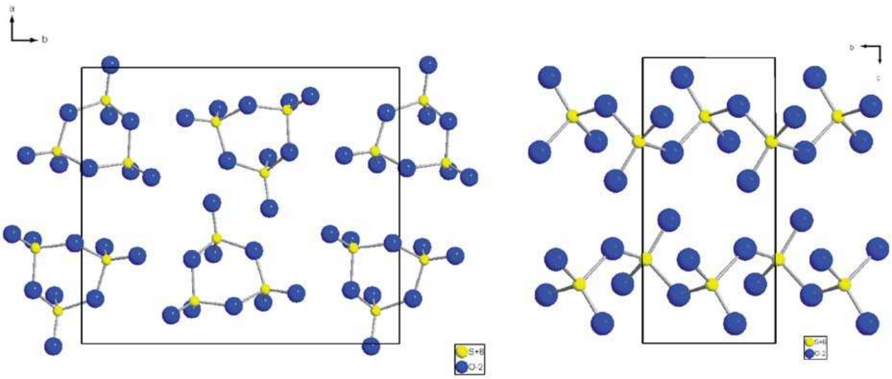

Figure 1 *Crystal structures of γ-SO_3 (left) and α-SO_3 (right)*

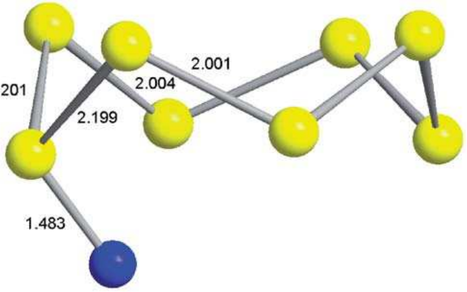

Figure 2 *Molecular structure of S_8O (distances are given in Å)*

Interestingly, it has been proved recently by computational methods that also the structure with the oxygen atom being member of the ring is a local minimum in the energy surface. The lower sulfur oxides can be stabilized by the addition of Lewis acids like $SnCl_4$ or $SbCl_5$.[7,8] For example, S_8O forms the adduct $(S_8O)_2SnCl_4$ with the oxygen atom being in *cis* position of a $[SnCl_4O_2]$ octahedron. An interesting observation is that the reaction of $SbCl_5$ and S_6O may cause dimerization of the oxide under formation of the 12-membered $S_{12}O_2$ ring bonded to two $SbCl_5$ molecules.[9] This oxide is not known without stabilization of $SbCl_5$. Another important lower sulfur oxide is S_2O. This molecule is isoelectronic with ozone and SO_2 and has also a bent structure.[10] Furthermore, it has been shown that a ring-type arrangement of the atoms with an angle SOS of 75° can be a likely structural alternative,[11] and even vibrational spectra in an argon matrix have been measured[12] as well as microwave spectra.[13]

Several structures have been considered for the neutral SO_4 species that have been said to occur in a low-temperature argon matrix. The lowest-energy structure is predicted to have a three-membered SOO ring and C_{2v} symmetry. Vibrational frequencies at the MP2/6-31+G* level of theory and isotope shifts for this structure are in good agreement with the experiment.[14] Disulfur trioxide, S_2O_3, is predicted to have a three-membered SSO ring (rather than an SOO ring) and to be 12.7 kcal mol^{-1} more stable than SO_3+S.[14] The molecular structures of SO_2, S_2O, and S_2O_2 and their harmonic force fields have been also derived from spectroscopic data and computational methods.[15]

Three binary selenium oxides are well characterized, SeO_2, Se_2O_5, and SeO_3. SeO_2 is a solid under ambient conditions. It sublimes at 315 °C and forms a liquid when heated to 340 °C in a closed tube. In contrast to SO_2, selenium dioxide shows a chain structure with $[SeO_3]$ units sharing two common oxygen atoms.[16] The distances Se–O within the chain are 1.79 Å, while the *exo*-oxygen atoms are at a distance of 1.62 Å in accordance with the description as a double bond. Recently, it has been shown by Raman scattering and synchrotron angle-dispersive X-ray powder diffraction in a diamond anvil cell that SeO_2 undergoes a pressure-induced phase transition from the tetragonal low-pressure phase to an orthorhombic high-pressure phase above 7.0 GPa.[17] The transformation occurs without major changes of the crystal lattice dimensions and the coordination around the selenium atoms. Further structural transitions above 17 GPa occur with additional distortions leading to monoclinic phases. All transformations are reversible with little hysteresis.[17]

Molecular and dimeric SeO_2 have been isolated in a low-temperature argon matrix and studied by Raman and vibrational spectroscopy.[18] The data provide convincing evidence that the centrosymmetric chair (C_{2h}) configuration for $(SeO_2)_2$ is strongly favoured.

The structure of Se_2O_5 is related to the one of SeO_2, but the chains consist of alternate pyramidal $[SeO_3]$ and tetrahedral $[SeO_4]$ units, connected *via* common vertices.[19] Within the $[SeO_4]$ tetrahedra the distances Se–O are 1.69 and 1.73 Å for bridging and 1.62 and 1.57 Å for terminal oxygen atoms. Within the $[SeO_3]$ pyramid they are 1.88, 1.92, and 1.60 Å, respectively. Another mixed valent selenium oxide, Se_3O_7, has been obtained as the nitromethane solvate $Se_3O_7 \cdot CH_3NO_2$ by the reaction of $MeNO_2$ with $(SeO_3)_4$. Se_3O_7 is a cyclic molecule consisting of two $[SeO_3]$ pyramids and one $[SeO_4]$ tetrahedron.[20] The solvating CH_3NO_2 molecule is removable in vacuo. If the reaction temperature does not exceed 10 °C, $(Se_2O_5)_n$ is formed instead of $Se_3O_7 \cdot CH_3NO_2$. Dinitrosyl triselenate $(NO)_2Se_3O_{10}$, nitrosyl hydrogendiselenate $NOHSe_2O_7$, nitrosyl hydrogenselenate $NOHSeO_4$, nitrosyl hydrogenselenatoselenite $NOHSe_2O_6$ and $(SeO_2)_n$ were further identified in the solid reaction products.[20]

Like γ-SO_3 the solid form of SeO_3 is a cyclic polymer, but contrastingly to the sulfur oxide four SeO_3 molecules are linked *via* common corners (Figure 3).[21] The Se–O bond lengths to the bridging oxygen atoms are remarkably longer (1.75 and 1.81 Å) than the distances to the *exo*-oxygen atoms (1.56 and 1.54 Å). SeO_3 has a melting point of 118 °C and above 185 °C it decomposes yielding SeO_2 and O_2. The donor–acceptor complexes $SeO_3 \cdot (C_2H_5)_2O$ and $SeO_3 \cdot [(CH_3)_2O]_2$ with diethyl and dimethyl ether, respectively, have been described. Both compounds contain trigonal planar SeO_3 molecules with one or two ether molecules acting as donor ligands *via* the oxygen atoms.[22]

Tellurium dioxide, TeO_2, exhibits three different crystal structures. α-TeO_2 is a three-dimensional network, in which the Te^{4+} ions are coordinated by four bridging oxygen atoms, two at shorter, 1.88 Å, and two at longer, 2.12 Å, distances.[23] The coordination polyhedron clearly shows the stereochemical activity of the lone electron pair at the tellurium atom, and if the latter is treated as a non-visible ligand, the polyhedron is a *pseudo*-trigonal bipyramid. α-TeO_2 crystallizes with a non-centrosymmetric chiral space group and both enantiomorphs have been gained in single-crystalline form.[23–25] Because of the lack of an inversion centre, the compound shows the non-linear second harmonic generation (SHG) effect.[26] In the β-modification of TeO_2, the coordination polyhedron around Te^{4+} remains nearly unchanged compared to α-TeO_2 and also the Te–O distances (1.88, 1.93, and 2.20 Å) are comparable.[27] However,

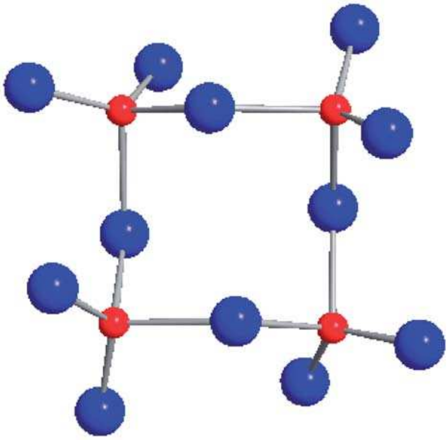

Figure 3 *The tetrameric structure of* SeO_3

the linkage of the polyhedra occurs in a way that a two-dimensional layer structure is formed. γ-TeO_2 exhibits again a three-dimensional linkage of [TeO_4] polyhedra. In this high-pressure modification, however, three of the four Te–O distances are quite short (1.86–2.02 Å), while only one is at 2.20 Å.[28]

The mixed valent oxide Te_2O_5 = $Te^{VI}Te^{IV}O_5$ shows Te^{6+} in octahedral environment of oxygen atoms (Te^{VI}–O distances from 1.85 up to 1.97 Å) and the octahedra are linked *via* two common edges to infinite chains (Figure 4).[29] The chains are connected further by dimers formed by two edge-connected [$Te^{IV}O_4$] units. The second mixed valent tellurium oxide that has been characterized is Te_4O_9 = $Te^{VI}(Te^{IV})_3O_9$.[30] In the crystal structure, [$Te^{VI}O_6$] octahedra and [$Te^{IV}O_4$] units are connected to layers that are stacked along the *c*-axis of the trigonal unit cell. Another mixed valent tellurium oxide, Te_4O_{11}, has been said to occur as intermediate in the decomposition of $Te(OH)_6$, but it is still in need of a proper characterization.[31]

Although three forms of TeO_3 can be found in the literature, only one, the so-called β-TeO_3, is a real Te(VI) compound, while α- and γ-TeO_3 contain substantial amounts of Te^{4+} as it has been shown by Mössbauer spectroscopy in the case of α-TeO_3 and by vibrational spectroscopy proving the presence of

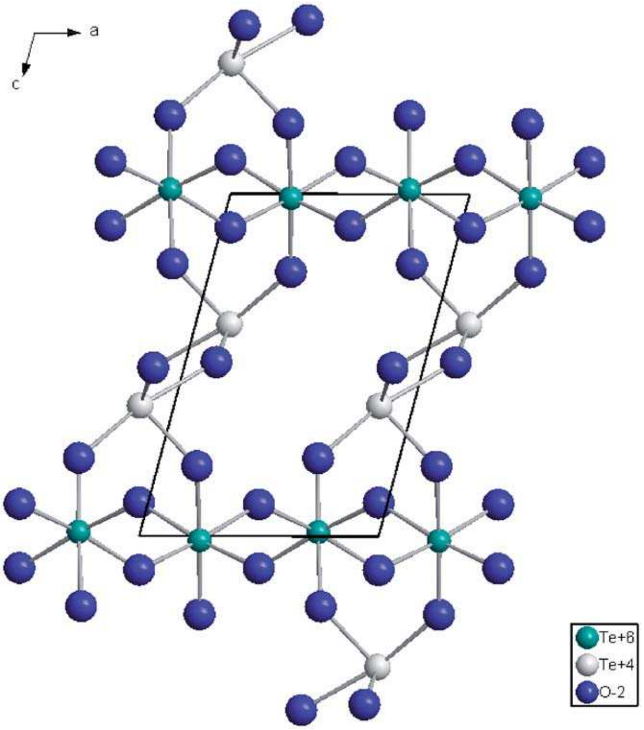

Figure 4 *Crystal structure of the mixed valent oxide* Te_2O_5. *The [Te(VI)*O_6*] octahedra are linked to chains via common edges, and the chains are connected by [Te(IV)*O_4*]*$_2$ *dimers.*

OH^- and O_2^- for γ-TeO_3.[31] β-TeO_3 has been prepared for the first time by hydrothermal decomposition of $Te(OH)_6$, but also heating of α-TeO_3 with water in a sealed glass tube has been shown to be successful. In the crystal structure of β-TeO_3, the Te^{6+} ions are in octahedral coordination of oxygen atoms and the [TeO_6] octahedra are linked *via* all vertices to a three-dimensional network of the FeF_3 type.[32]

6.3 Mixed Sulfur, Selenium, and Tellurium Oxides

Structurally characterized mixed oxides of sulfur, selenium, and tellurium are included in Table 1. The selenium sulfur compounds $Se_{10}(SO_3F)_2$ and $Se_4(HS_2O_7)_2$ contain polyatomic selenium cations and will be part of Chapter 7 of this handbook. The other mixed oxides known so far contain tellurium and sulfur or tellurium and selenium, respectively. Strictly speaking, they are not oxides but *oxo*-sulfates and *oxo*-selenates of tellurium. Thus, tellurium behaves like a typical metal in these compounds and is coordinated by complex *oxo*-anions. With respect to this, TeS_4O_{14} should be formulated as a disulfate $Te(S_2O_7)_2$ as it contains Te^{4+} ions coordinated by two chelating $S_2O_7^{2-}$ groups.[33] The bond distances Te–O fall in the range from 1.96 to 2.07 Å and the coordination polyhedron can again be regarded as a trigonal bipyramid with the lone electron pair at the tellurium atom being the fifth ligand. Te_2SO_7 is an oxide–sulfate according to the formulation $Te_2O_3(SO_4)$. The Te^{4+} ions are connected by oxide ions to form corrugated layers of the composition [Te_2O_3] that are linked by the sulfate groups (Figure 5) in [010] direction.[34,35] The stereochemical activity of the lone electron pair in within the [TeO_4] polyhedron is obvious.

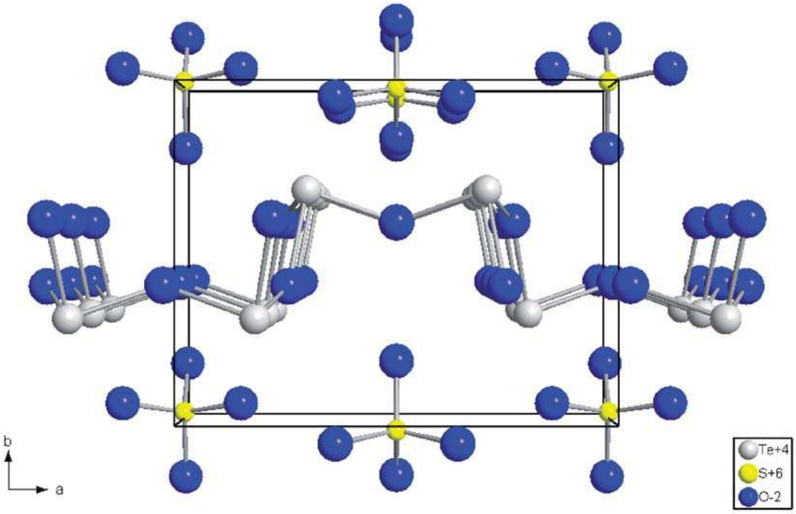

Figure 5 *Structure of $Te_2SO_7 = Te_2O_3(SO_4)$. The oxide ions connect the Te^{4+} ions to corrugated layers.*

Especially the selenites of Te(IV) have attracted considerably attention because they contain two species with lone electron pairs giving rise for the occurrence of non-centrosymmetric crystal structures exhibiting non-linear optical (NLO) effects. Two compositions are well characterized, $TeSeO_4$ and Te_3SeO_8, which should be formulated according $TeO(SeO_3)$ and $Te_3O_5(SeO_3)$ to account for the presence of selenite anions.[36–38] A third oxide, Te_2SeO_7, turned out to be isotypic with Te_2SO_7 and has therefore to be written as $Te_2O_3(SeO_4)$.[39] Interestingly, in the crystal structure of $TeO(SeO_3)$ the Te^{4+} ion is not four coordinated, but surrounded by five oxygen atoms in form of a distorted square pyramid. One of the distances Te–O is remarkably short (1.90 Å) compared to the remaining five (2.03–2.22 Å) so that the naming of the compound as telluryl selenite may be justified. The $[TeO_5]$ polyhedra are connected to zigzag chains running along the [100] direction and the chains are linked by the selenite ions. The formation of $[TeO_5]$ polyhedra is also found in the oxide-rich selenite $Te_3O_5(SeO_3)$, where one very short (1.88 Å) and four longer Te–O distances (2.02–2.22 Å) are found. The higher content of oxide ions causes a stronger linkage of the $[TeO_5]$ polyhedra and double layers are found that are coordinated by the selenite groups (Figure 6). The SHG properties of $TeO(SeO_3)$ and $Te_2O_3(SeO_4)$ have been investigated in more detail in comparison with those of the also non-centrosymmetric TeO_2 and Te_2O_5.[39]

6.4 Oxygen Acids of Sulfur, Selenium, and Tellurium

Sulfur forms three oxygen acids of the general formula H_2SO_n ($n = 3-5$), six acids of the composition $H_2S_2O_n$ ($n = 3$–8), and several compounds containing three sulfur atoms or more. Only five of the sulfur oxygen acids, namely, H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$, and $H_2S_2O_3$, can be gained as pure substance, the remaining are known in solution or in form of their salts. Among the acids

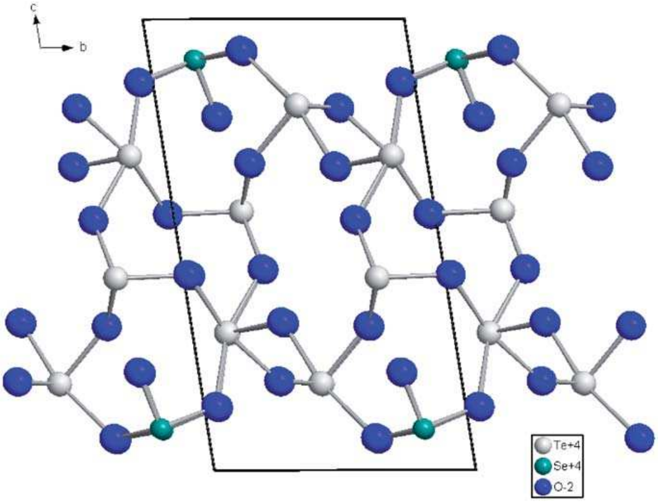

Figure 6 *Crystal structure of* $Te_3O_5(SeO_3)$.

that have been structurally characterized, H_2SO_4 and its hydrates are of vital importance. For sulfuric acid several structure determinations at different temperatures have been performed, including neutron diffraction experiments for the elucidation of the hydrogen-bonding system in the solid (Table 1).[40–42] The hydrogen bonds were found to be very strong with O–H···O distances of only 2.47 Å, with the connection of the H_2SO_4 molecules to form to layers (Figure 7). Recent investigations have shown that the hydrogen-bonding system changes when pressure is applied and the crystal structure at a pressure of 0.7 GPa has been reported. Under pressure, the H_2SO_4 molecules are connected into ribbons and the distances O–H···O are 2.67 and 2.77 Å, respectively, *i.e.* remarkably longer than found for the low-pressure modification.[43]

The monohydrate of sulfuric acid has to be formulated according to $(H_3O)(HSO_4)$, *i.e.* it is in fact an oxonium hydrogensulfate. The crystal structure exhibits a three-dimensional hydrogen-bonding system involving the H_3O^+ ions as donors and the HSO_4^- ions as both acceptors and donors. According to the donor–acceptor distances that are found to be below 2.6 Å, the hydrogen bond can be classified as strong.[42,44,45] Also, the dihydrate $H_2SO_4 \cdot 2H_2O$ has to be seen as a salt and contains H_3O^+ as well as SO_4^{2-} ions. Again, strong hydrogen bonding can be assumed with respect to the observed O–O distances.[46] The tetrahydrate of sulfuric acid has been also studied in form of its deuterated analogue and contains $H_5O_2^+$ and SO_4^{2-} anions.[47,48] Within the $H_5O_2^+$ ion one hydrogen atom is located at equivalent distances between two symmetry related oxygen atoms giving evidence for a symmetric hydrogen bond. Even higher hydrates of sulfuric acid have been prepared and characterized: $H_2SO_4 \cdot 6.5H_2O$ has to be formulated as $(H_5O_2)(H_7O_3)(SO_4) \cdot 1.5H_2O$ and shows a complicated system of hydrogen-bonded oxonium ions and H_2O molecules arranged to layers that alternate with the sulfate groups.[48]

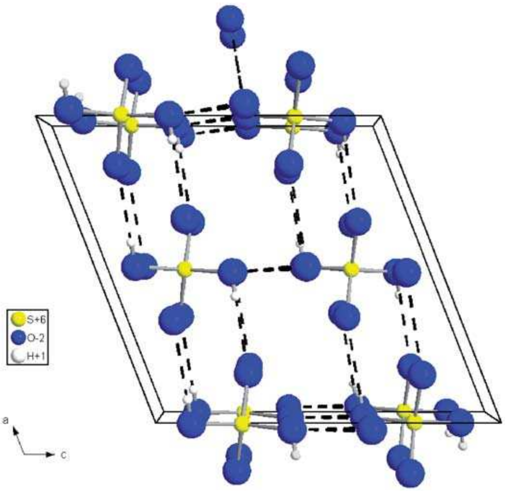

Figure 7 *Crystal structure of solid H_2SO_4 (hydrogen bonds are emphasized as black hatched lines).*

$H_2SO_4 \cdot 8H_2O$ contains also $H_5O_2{}^+$ ions and H_2O molecules according to the formulation $(H_5O_2)_2(SO_4) \cdot 4H_2O$.[48]

Single crystals of peroxomonosulfuric acid, H_2SO_5 (also known as Caro's acid) have been prepared by the reaction of fuming sulfuric acid and H_2O_2. In the crystal structure, the molecules are connected *via* hydrogen bonds.[49] The distance within the peroxo group of the anion is 1.46 Å.

For the series $H_2S_2O_n$ only the acid with $n = 7$, namely, disulfuric acid, has been structurally characterized.[50] $H_2S_2O_7$ consists of two vertex-sharing tetrahedra with the angle S–O–S being 121.8°. In crystal structure, the molecules are linked to layers by strong hydrogen bonds, while weaker hydrogen bonds connect these layers.

Selenic acid, H_2SeO_4, has been investigated in detail, including neutron diffraction for the elucidation of the hydrogen-bonding system. Interestingly, H_2SeO_4 is not isotypic with one of the different modifications of H_2SO_4, but adopts another structure with orthorhombic symmetry.[41,51,52] In the solid, the molecules are connected to layers by hydrogen bonds. One hydrate of H_2SeO_4 is known. It contains four molecules of crystal water and has to be formulated according to $(H_5O_2)_2(SeO_4)$, in analogy to the findings for the respective sulfur compound. However, in contrast to the latter $(H_5O_2)_2(SeO_4)$ is dimorphic.[53] The tetragonal modification is isotypic with $(H_5O_2)_2(SO_4)$, while a slightly different orientation of $H_5O_2{}^+$ ions and selenate groups is found in the orthorhombic modification.

In contrast to sulfurous acid, H_2SO_3, which is not known as pure substance, the respective selenium compound can be obtained in crystalline form. H_2SeO_3 crystallizes with the non-centrosymmetric space group $P2_12_12_1$ and contains pyramidal H_2SeO_3 molecules.[54] Within the molecules the bond lengths Se–O and SeOH differ by about 10 pm and the molecules are connected to puckered layers by strong hydrogen bonds.

Telluric acid contains no H_2TeO_4 molecules, but shows $[TeO_4(OH)_2]$ octahedra that are connected *via* the oxygen atoms to infinite corrugated sheets, which are stacked in the [100] direction of the monoclinic unit cell.[55] The so-called orthotelluric acid, H_6TeO_6, can be seen as the dihydrate of H_2TeO_4. In its structure, the tellurium atoms are surrounded by six OH groups. The $Te(OH)_6$ molecules can be arranged in two different ways leading to a monoclinic and a cubic crystal structure[56–58]. The acid $H_2Te_2O_6$ contains both Te^{4+} and Te^{6+} ions and is thus a mixed valent tellurium compound.[59] Te^{6+} is coordinated by six oxygen atoms and the $[TeO_6]$ octahedra are connected *via* two vertices to zigzag chains. The chains are further connected by dimers of vertex-connected $[Te(IV)O_4]$ units (Figure 8).

6.5 Selected Oxo-Chalcogenates

As mentioned in the introduction, there are a large number of salts of the chalcogen oxygen acids that have been prepared and characterized, and it is far beyond the scope of this chapter to take care of all of them. Therefore, only a

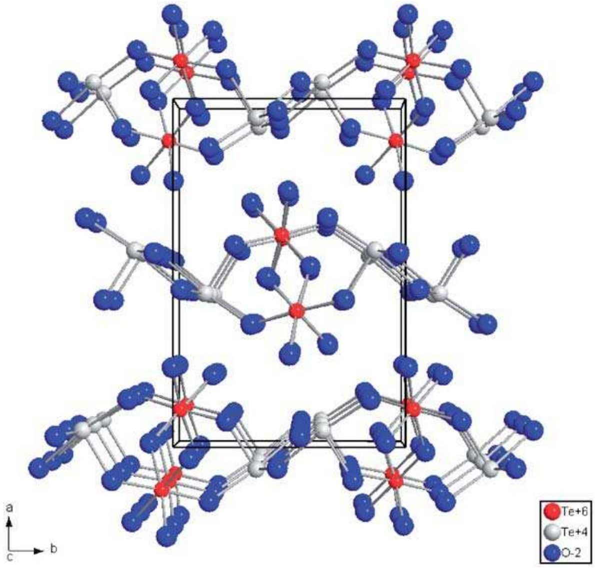

Figure 8 *Structure of the mixed valent tellurium acid $H_2Te_2O_6$.*

selection can be given here and especially recent results will be emphasized. The section is divided according to the positions of the respective metals in the periodic table, *i.e.* main group metals, transition metals, and finally lanthanides. Each subdivision starts with the sulfates and moves on to selenates and tellurates. Among the selenates and tellurates the oxidation state +IV plays a more important role compared to the sulfur species, because the tetravalent state is much more stable for selenium and tellurium. For example, the reduction potential of the couple SeO_4^{2-}/SeO_3^{2-} is only 0.03 V in alkaline solution, while the respective value is 0.12 V for the couple SO_4^{2-}/SO_3^{2-}. Therefore, the selenite ion is much less reducing than the sulfite ions and, in turn, selenates are strong oxidizers.

Generally, *oxo*-selenates can be classified according to the oxidation state of the selenium atom as *oxo*-selenates(IV), and *oxo*-selenates(VI). The same applies for the respective tellurates. Besides this systematically correct naming, chemists usually use the terms *selenites* and *tellurites* instead of *oxo*-selenates(IV) and *oxo*-tellurates(IV), and *selenates* and *tellurates* instead of *oxo*-selenates(VI) and *oxo*-tellurates(VI). Therefore, both nomenclatures will be used in parallel throughout this chapter. Compared to the respective sulfur species, the *oxo*-selenate(IV) and *oxo*-tellurates(IV) ions are very stable so that numerous compounds with these anions have been prepared.

The free selenite ion has a pyramidal shape (C_{3v} symmetry) owing to the lone electron pair at the selenium atom. Thus, the SeO_3^{2-} ion can be treated as a *pseudo*-tetrahedral anion and the lone electron pair often acts as an invisible ligand within the crystal structures of selenites. This observation is called the stereochemical activity of the lone electron pair and it will turn out as one of the most striking structural features of *oxo*-selenates(IV). In contrast, TeO_3^{2-} ions are not observed so frequently because expansion of the coordination sphere of Te^{4+} is common and often achieved *via* aggregation of the anions under formation of higher dimensional networks.

Common routes for the synthesis of selenates and tellurates(IV and VI) are the reactions of metal oxides or carbonates with the repsective acids (see Section 4). The disadvantage of this procedure is, that one usually obtains hydrates or, at higher acid concentrations, acidic compounds. Because the oxides EO_3 and EO_2 (E=Se, Te) are solids under ambient conditions, solid-state reactions with the respective metal oxides are an alternative route to prepare the anhydrous compounds.

6.5.1 Main Group Metals

Selected main group chalcogenates that have been structurally investigated are collected in Table 2. Recent results on alkali metal compounds are mainly reported for acidic species, and they have attracted considerable interest with respect to their hydrogen-bonding systems or, in relation to the latter, to their proton-conduction properties. Within the group of simple hydrogen sulfates, $M(HSO_4)$, the structure of $Li(HSO_4)$ has been determined recently and shows double tetrahedra $[Li_2O_6]$ that are connecetd by the anions to a three-dimensional network.[60] The hydrogensulfates of the remaining alkali metals have been investigated various times and phase transitions have been shown to occur frequently. For example, for $Rb(HSO_4)$ a ferroelectric phase is known[61] besides the paraelectric room temperature phase and even a high-pressure phase has been found.[62] The proton conduction of $Cs(HSO_4)$ was studied in the low- and high-conductive phases of $CsHSO_4$ and $CsDSO_4$, and X-ray data confirm the proton-migration mechanism *via* successive proton intrabond jumps and reorientation of the O–H groups.[63] The unique proton disorder that occurs in the high-conductive phases can be classified as a dynamically disordered H bond network and is responsible for the high-proton conduction of 10^{-3}–$10^{-1}\ \Omega^{-1}\ cm^{-1}$.

The acidic alkali metal sulfates have been shown to exhibit a broad range of compositions. The compounds $M_3[H(SO_4)_2]$ have been recently investigated for M=Rb and Na, and in both cases very short hydrogen bonds have been found so that one cannot distinguish between a SO_4^- and a HSO_4^- anion but should speak of a $[H(SO_4)_2]^{3-}$ anion as building unit.[64–66] Another group of acidic alkali metal sulfates has been prepared recently by the reaction of the respective sulfates with concentrated sulfuric acid. The compounds have the composition $M(HSO_4)(H_2SO_4)$ (M=K, Rb, Cs) and contain neutral sulfuric acid molecules.[67,68] The latter are coordinated to the metal ions. In the case of the potassium compound, the cations are linked to infinite chains running along the *a*-axis that are connected *via* hydrogen bonds. For the larger cations Rb^+ and Cs^+ a stronger linkage is observed and coordination occurs even *via* the OH groups of the ligands. A remarkable new acidic sulfate is $K_5(HSO_5)_2(HSO_4)(SO_4)$.[69] Along with $K(HSO_5)\cdot H_2O$[70,71] this compound is only the second example of a salt of

Table 2 *Selected chalcogenates of main group elements investigated by X-ray diffraction*

Chalcogen	*Alkali metals*	*Earth alkaline metals*	*Al, Ga, In, Tl, Pb, Bi*
S	$Li(HSO_4)$[60]		$Al_2(SO_4)_3$[97]
	$Rb(HSO_4)$[61,62]		$Ga_2(SO_4)_3$[98]
	$Cs(HSO_4)$[63]		$In_2(SO_4)_3$[98]
	$Cs(DSO_4)$[63]		$Pb(SO_3)$[115]
	$Na_3[H(SO_4)_2]$[64,65,66]		$Pb(SO_4)$[116]
	$Rb_3[H(SO_4)_2]$[64,65,66]		$Pb(S_2O_3)$[117]
	$K(HSO_4)(H_2SO_4)$[67,68]		
	$Rb(HSO_4)(H_2SO_4)$[67,68]		
	$Cs(HSO_4)(H_2SO_4)$[67,68]		
	$K_5(HSO_5)_2(HSO_4)(SO_4)$[69]		
	$K(HSO_5) \cdot H_2O$[70,71]		
	$Na_6O(SO_4)_2$[72]		
Se	$Li_4(SeO_5)$[87]	$Mg(Se_2O_5)$[110]	$In_2(Se_2O_5)_3$[114]
	$Na_2(SeO_3)$[86]	$Ca_2(SeO_3)(Se_2O_5)$[94]	$Tl_2(SeO_4)$[113]
	$Na_4(SeO_5)$[88]	$Ba(SeO_3)$[94]	$Pb(SeO_3)$[100]
	$Na_6(Se_2O_9)$[88]	$Ba(Se_2O_5)$[94]	$Pb(Se_2O_5)$[101]
			$Bi_2(SeO_3)_3$[102]
	$K(HSeO_4)(H_2SeO_4)$[81]		$Bi_2(SeO_5)$[103]
	$Cs(HSeO_4)(H_2SeO_4)$[81]		
	$Na_3[H(HSeO_4)_2)](HSeO_4)_2$[82]		
	$Na_5H_3(SeO_4)_4 \cdot 2(H_2O)$[83]		
	$Na_2SeO_4 \cdot H_2SeO_3 \cdot H_2O$[84]		
	$KH_3(SeO_3)_2$[85]		
Te	$Na_2(Te_4O_9)$[91]	$MgTe_2O_5$[96]	$Ga_2(TeO_6)$[110]
	$Na_4(Te_4O_{10})$[93]	$Ca_4(Te_5O_{14})$[72]	$Tl_2(TeO_3)$[111]
	$K_2(Te_2O_5)$[92]	$Sr(TeO_3)$[109]	$Tl_2(Te_2O_5)$[112]
	$K_2(Te_4O_9)$[92]		$Pb_2(TeO_5)$[104]
	$Rb(Te_2O_6)$[90]		$Pb_2(Te_3O_8)$[105]
	$Rb_6(TeO_4)(TeO_5)$[89]		$Bi_2(Te_2O_7)$[106]
	$Cs_2(TeO_4)$[108]		$Bi_2(Te_2O_8)$[107]

peroxo sulfuric acid, H_2SO_5, and has to be formulated as a triple salt according to $(KHSO_5)_2 \cdot (KHSO_4) \cdot (K_2SO_4)$.

Another important recent result is the preparation of the oxide sulfate $Na_6O(SO_4)_2$ from the reaction of Na_2O and Na_2SO_4.[72] The structure of this sulfate can be seen as a variant of the fluorite-type structure: The $[ONa_6]$ octahedra are in a ccp arrangement and the sulfate tetrahedra fill all of the tetrahedral voids (Figure 9).

In general, *oxo*-selenates of the alkali metals have been investigated to a lesser extent than the respective sulfates, but on the other hand, *oxo*-selenates(IV) are better investigated than their sulfur analogues. As discussed for the acid sulfates, also acidic selenates are of interest with respect to their hydrogen-bonding systems and the properties associated with them. Therefore, often neutron diffraction studies have been applied to locate hydrogen atoms.

For *oxo*-selenates(VI) the compositions $M(HSeO_4)$ and $M_3[H(SeO_4)_2]$ are well established and parallel essentially the findings for the respective

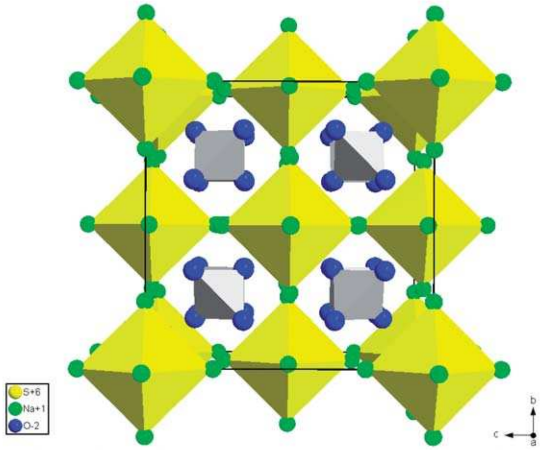

Figure 9 *Crystal structure of the oxide sulfate* $Na_6O(SO_4)_2$*. The* $[ONa_6]$ *octahedra and* SO_4^{2-} *tetrahedra are arranged like* Ca^{2+} *and* F^- *ions in the* CaF_2 *structure type.*

sulfates.[73–80] Also for the *oxo*-selenates(VI) further compositions are known. Besides $K(HSeO_4)(H_2SeO_4)$ and $Cs(HSeO_4)(H_2SeO_4)$ that contain selenic acid molecules as ligands,[81] new composition have been found. In the structure of $Na_3[H(HSeO_4)_2)](HSeO_4)_2$ two hydrogenselenate groups are connected to unique $[H(HSeO_4)_2]^-$ anions.[82] Structural characterization and vibrational spectroscopy has been performed for $Na_5H_3(SeO_4)_4 \cdot 2H_2O$.[83]

A compound containing both Se^{6+} and Se^{4+} species is $Na_2SeO_4 \cdot H_2SeO_3 \cdot H_2O$. It has been investigated by X-ray methods and vibrational spectroscopy.[84] More recently, the acidic *oxo*-selenate(IV) $KH_3(SeO_3)_2$ has been reported.[85]

Single crystals of $Na_2(SeO_3)$ have been gained for the first time from the reaction of Na_2O and SeO_2 in sealed glass tubes.[86] The crystal structure contains two crystallographically different Na^+ ions exhibiting coordination numbers of seven and six, respectively.

The *oxo*-selenates(IV) $Li_4(SeO_5)$, $Na_4(SeO_5)$, and $Na_{12}(SeO_4)_3(SeO_6)$ have been prepared from the respective binary oxides under high-oxygen pressure.[87,88] They contain the unique anions SeO_5^{4-} and SeO_6^{6-}. The latter has octahedral shape, while two different forms have been found for SeO_5.[4] In the lithium compound, the anion exhibit trigonal bipyramidal shape, and in the sodium compound the anions have square pyramidal shape (Figure 10).

Several tellurates of the alkali metal have been reported throughout the last few years, and some important compounds should be mentioned in the following. $Rb_6(TeO_4)(TeO_5)$ contains two different *oxo*-tellurate(VI) anions exhibiting tetrahedra and trigonal bipyramidal shape,[89] respectively, while $Rb(Te_2O_6)$ is a mixed valent compound showing both, Te^{4+} and Te^{6+} in a 1:3 ratio in octahedral environment of oxygen atoms.[90] The tellurates(IV) $Na_2(Te_4O_9)$[91] and $K_2(Te_4O_9)$[92] show the Te^{4+} ions in two different environments of oxygen atoms forming square pyramidal and *pseudo*-trigonal bipyramidal coordination

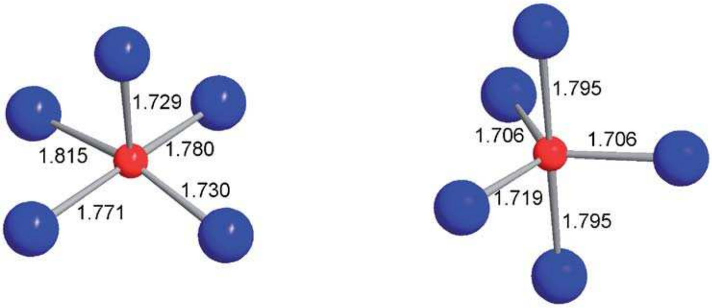

Figure 10 *The two different types of* SeO_5^{4-} *anions.*

polyhedra, which are linked to complex frameworks incorporating the alkali ions. A similar three-dimensional network is observed in $Na_4(Te_4O_{10})$, but all of the Te^{4+} ions are in *pseudo*-trigonal bipyramidal coordination in this compound.[93]

Concerning earth alkaline metals, especially the knowledge on selenites has been improved remarkably in recent years. Most of the selenites were prepared by hydrothermal methods. It turned out that depending on the specific conditions selenites or diselenites may form, and even mixed anionic compounds have been prepared. As examples, $Ba(SeO_3)$, $Ba(Se_2O_5)$, and $Ca_2(SeO_3)(Se_2O_5)$ may serve.[94] In $Ba(SeO_3)$ nine-coordinate Ba^{2+} ions are connected by the selenite ions to a three-dimensional structure and the anions act as chelating and monodentate ligands. Similarly, in $Ba(Se_2O_5)$ the anions link 10-fold coordinated barium ions to a three-dimensional structure. The anions have the typical shape and the bridging oxygen atom show distances of 1.8 Å, about 0.15 Å longer compared to the distances found in a selenite ion. The same anion is found in the calcium compound. Two new tellurites, $Ca_4(Te_5O_{14})$[95] and $MgTe_2O_5$,[96] were prepared recently. While the latter contains the ditellurite anion $Te_2O_5^{2-}$, the crystal structure of $Ca_4(Te_5O_{14})$ shows both, TeO_3^{2-} and $Te_2O_5^{2-}$ ions.

Compounds of the higher valent main group elements are investigated to a lesser extent compared to alkali and earth alkali metals. A remarkable recent result is the preparation of single crystals of the anhydrous sulfates $Al_2(SO_4)_3$,[97] $Ga_2(SO_4)_3$,[98] and $In_2(SO_4)_3$[98] by chemical transport reactions. The crystal structures of these sulfates show the metal ions in octahedral coordination of oxygen atoms, and each sulfate group is attached to four metal ions. Selenites of the later main group metals that have been investigated are $In_2(Se_2O_5)_3$, which is non-centrosymmetric and shows NLO properties,[99] $Pb(SeO_3)$[100] and $Pb(Se_2O_5)$,[101] and the bismuth selenites $Bi_2(SeO_3)_3$[102] and $Bi_2(SeO_3)O_2$.[103] The compounds of lead(II) and bismuth(III) are of special interest because they contain both a cation and an anion with a stereochemical active electron pair. Thus, for these elements also the tellurites are currently under investigation and the compounds $Pb_2(TeO_5)$,[104] $Pb_2(Te_3O_8)$,[105] $Bi_2(Te_2O_7)$,[106] $Bi_2(Te_2O_8)$[107] have been reported rather recently.

6.5.2 Transition Metals

A large number of new transition metal chalcogenates have been reported in the last few years. Table 3 gives a broad selection of structurally investigated phases and shows that especially chalcogenates of the precious metals and also of mercury have attracted considerable attention. These compounds shall be briefly discussed here.

One of the most remarkable compounds, which have been recently described is the gold(II)sulfate, $Au(SO_4)$.[118] Red single crystals of this phase have been obtained by evaporating a solution of $Au(OH)_3$ in concentrated sulfuric acid. In contrast to the assumed mixed valent character of the compound, the crystal structure exhibits the dumbbell-shaped Au_2^{4+} cation (bond length Au–Au: 249 pm), which is coordinated by two chelating and two monodentate SO_4^{2-} groups (Figure 11). The monodentate sulfate anions act as chelating ligand to another Au_2^{4+} ion leading to infinite sheets, which are stacked in [001] direction. The first Au(III)sulfates have been prepared by the evaporation of a solution of $Au(OH)_3$ and alkali metal sulfates in concentrated sulfuric acid led to yellow single crystals $MAu(SO_4)_2$ (M=Na, K, Rb, Cs)[119,120]. Although the crystal structures of the four sulfates are not isotypic, they show similar structural features: the gold atoms are coordinated by four oxygen atoms in a square planar manner. These oxygen atoms belong to four SO_4^{2-} ions, which link the $[AuO_4]$ units to infinite chains. These chains are connected *via* the monovalent cations, which show coordination numbers of 6 (Na^+), 10 (K^+), 12 (Rb^+), and 13 (Cs^+), respectively.

Other new sulfates have been reported for the platinum group metals. The unique oxide–sulfate $(NH_4)Pt_3O_2(SO_4)_3$ has been obtained as dark red single crystals in the reaction of $Pt(NO_3)_2$ with concentrated sulfuric acid at 350 °C in sealed glass ampoules. $(NH_4)Pt_3O_2(SO_4)_3$ contains as the characteristically structural feature the unprecedented cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$.[121] In order to emphasize this building unit of the oxide—sulfate, we henceforth rewrite its formula according to $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$. Within the anion the 12 Pt^{III} ions are arranged in form of an icosahedron, which is remarkably distorted owing to the formation of Pt_2 dumbbells (Figure 12). The six Pt_2 dumbbells of the icosahedron are connected by eight O^{2-} ions leading to an almost perfect trigonal-planar coordination of the oxide ions by three platinum atoms. Above the remaining 12 triangular faces tridentate coordinating SO_4^{2} groups are situated. Each sulfate ion acts as chelating ligand to one Pt_2 dumbbell and as monodentate ligand to the next. The $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ clusters are arranged in the trigonal body-centred unit cell and charge compensation is achieved by NH_4^+ ions.

Single crystals of $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$ were obtained by the reaction of Cs_2PtCl_4, K_2PtCl_4, and concentrated sulfuric acid at 400 °C in a sealed glass ampoule. The compound contains also the cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$, but now the voids within the arrangement of the cluster anions are filled by both Cs^+ and K^+ ions.[122] Red single crystals of $K_3[Pt_2(SO_4)_4H(HSO_4)_2]$ were obtained from the reaction of $K_2[Pt_2(SO_4)_4(H_2O)_2]$ with concentrated sulfuric

Table 3 *Selected transition metal chalcogenates investigated by X-ray diffraction*

	Ti/Zr	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni/Pd/Pt*	*Cu/Ag/Au*	*Zn/Cd/Hg*
S	$TiO(SO_4)$[196] $Zr(Te_3O_8)$[195]	$(VO)(SO_4)$[194] $Li_2V_2(SO_4)_3$[193] $Na_8(VO)_2(SO_4)_6$[192] $Na_2K_6(VO)_2(SO_4)_7$[191]	$Cr_2(SO_4)_3$[186]	$Mn(HSO_4)_2$[183] $Mn(HSO_4)_2(H_2SO_4)_2$[183] $Li_2Mn_2(SO_4)_3$[182]		$Co(SO_4)$[171]	$Ni(SO_4)$[171] $Li_2Ni(SO_4)_2$[197] $Pd(SO_4)$[198] $Pt_2(SO_4)_2(HSO_4)_2$[125] $K_4[Pt_2(SO_4)_5]$[124] $K_3[Pt_2(SO_4)_3H(HSO_4)]$[123] $Rb[Pt_2(SO_4)_3(HSO_4)]$[124] $Cs[Pt_2(SO_4)_3(HSO_4)]$[122] $(NH_4)_4[Pt_{12}(SO_4)_{12}O_8]$[121] $Rb_4[Pt_{12}(SO_4)_{12}O_8]$[122] $K_2Cs_2[Pt_{12}(SO_4)_{12}O_8]$[122] $K_2(NH_4)_2[Pt_{12}(SO_4)_{12}O_8]$[122] $Gd(HSO_4)_2[Pt_2(SO_4)_4(HSO_4)_2]$[127]	$Cu_3(OH)_4(SO_4)$[162] $Rb_2Cu_3(SO_4)_3(OH)_2$[161] $Ag_2(SO_4)$[160] $Au(SO_4)$[118] $NaAu(SO_4)_2$[119] $KAu(SO_4)_2$[119] $RbAu(SO_4)_2$[119] $CsAu(SO_4)_2$[120] $Ag(HSO_4)$[158,159] $Ag_2(HSO_4)_2(H_2SO_4)$[158]	$(Zn(HSO_4)_2)(H_2(SO_4))_2$[149] $Cd(HSO_4)_2$[149] $Rb_2Cd_2(SO_4)_3$[148] $CdSO_4 \cdot 2HgO$[131] $Hg_2(HSO_4)_2$[147]
Se		$V_2(Se_2O_9)$[190] $(VO)_2(SeO_3)_3$[189]	$Cr_2(Se_2O_5)_3$[185]	$Mn(SeO_3)$[180,181] $Mn(Se_2O_5)$[179] $Mn(HSeO_4)_2$[178]	$Fe_2(SeO_4)_3$[170] $BaFe_2(SeO_3)_4$[169] $RbFe(SeO_3)(SeO_4)$[169]	$Co(Se_2O_5)$[168] $Li_2Co_3(SeO_3)_4$[167]	$Pd(SeO_3)$[126]	$Cu(SeO_3)$[157] $Cu_3(SeO_4)(OH)_4$[156] $Tl_2Cu_3(SeO_3)_6$[155] $Ag_2(SeO_3)$[154] $Ag_2(UO_2)(SeO_3)_2$[153] $Au_2(SeO_3)_2(SeO_4)$[129] $Rb(Au(SeO_4)_2)$[128]	$Zn(SeO_3)$[146] $Zn(HSeO_4)_2$[145] $SrZn(SeO_3)_2$[144] $CdSeO_4 \cdot 2HgO$[131] $Cd(SeO_3)$[143] $Cd(SeO_3)_2(SeO_4)$[142] $Cd_3(HSeO_3)(SeO_3)_2$[141] $Cd(Se_2O_5)$[141] β-$Hg(SeO_3)$[134] γ-$Hg(SeO_3)$[134] α-Hg_2SeO_3[133] β-Hg_2SeO_3[133] γ-Hg_2SeO_3[133] $Hg_3Se_3O_{10}$[139] $Hg_3(HSeO_3)_2(SeO_3)_2$[140] $Ag_2Hg(SeO_3)_2$[137] $HgSeO_4$[132] $HgSeO_4 \cdot HgO$[132] $HgSeO_4 \cdot 2HgO$[132]
Te		$Cs(VO)(TeO_4)$[188] $Cs(VO_2)_3(TeO_3)_2$[187]	$Cr_2(TeO_6)$[184]	$SrMn(SeO_3)_2$[177] $Mn(Te_2O_5)$[176] $Mn_2(Te_2O_5)_2$[175] $Mn_2(Te_3O_8)$[174] $Sr_2Mn(TeO_6)$[173] $Ba_2Mn(TeO_6)$[172]	$Fe_2(TeO_6)$[163]	$Co(TeO_4)$[166]	$Ni(TeO_4)$[166] $Sr_2Ni(TeO_6)$[165] $Cu_2Ni(TeO_6)$[164]	$Cu_2(OH)_2(TeO_4)$[152] $Sr_2Cu(TeO_6)$[151] $Ba_2Cu(TeO_6)$[151] Ag_2TeO_4[150]	$CuZn_4(TeO_6)_3$[73] $Cd_2Te_2O_7$[130] $Cd_2Te_3O_9$[130] Hg_3TeO_5[135] Hg_3TeO_6[135] α-$Hg_2Te_2O_7$[136] β-$Hg_2Te_2O_7$[136] $Ag_2Hg_2(TeO_4)_3$[138]

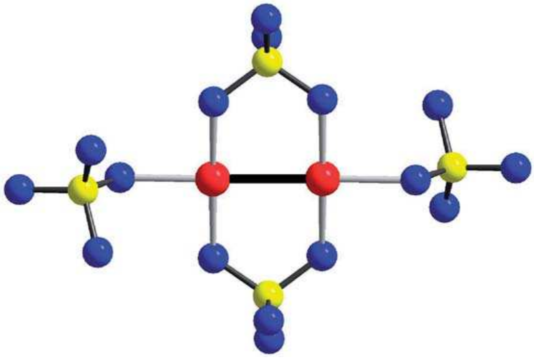

Figure 11 *The dumbbell shaped* Au_2^{4+} *ion surrounded by sulfate groups in the crystal structure of* $AuSO_4$.

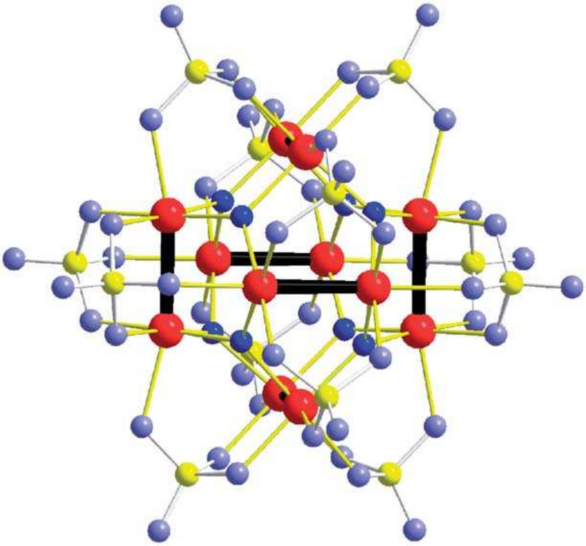

Figure 12 $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ *cluster anion formed by the linkage of six* Pt_2^{6+} *dumbbells.*

acid at 400 °C in evacuated glass ampoules.[123] In the crystal structure, $[Pt_2(SO_4)_4]$ cores are connected to infinite chains by $[H(HSO_4)_2]^-$ units, built by the linkage of two hydrogensulfate ions *via* a hydrogen atom. The sulfate groups within the $[Pt_2(SO_4)_4]$ core act as chelating ligands for the Pt_2 dumbbell, while the two hydrogensulfate groups are monodentate and occupy the terminal positions of the Pt_2^{6+} ions.

Besides the oxide sulfate described above, $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ is obtained in the reaction of $Pt(NO_3)_2$ with concentrated sulfuric acid in sealed glass ampoules at 400 °C.[124] In the crystal structure, Pt_2 dumbbells are coordinated by four bidentate-bridging sulfate ions and two axial H_2O molecules. The replacement of the axial H_2O molecules for $SO_4{}^{2-}$ ions is observed in the crystal structure of $K_4[Pt_2(SO_4)_5]$ and causes a connection of the dumbbells to chains. $K_4[Pt_2(SO_4)_5]$ has been obtained from the reaction of $K_2[PtCl_4]$ and concentrated H_2SO_4 at 400 °C in sealed glass tubes.[124] The same reaction with $Cs_2[PtCl_4]$ replacing $K_2[PtCl_4]$ leads to $Cs[Pt_2(SO_4)_3(HSO_4)]$.[124] In the crystal structure, part of the bidentate-bridging sulfate ions of the $[Pt_2(SO_4)_4]$ core act as monodentate ligands to further Pt_2 dumbbells leading to anionic layers and neutral sheets. The two types of layers are stacked alternating with the Cs^+ ions, which exhibit coordination number 10. Red single crystals of $Pt_2(HSO_4)_2(SO_4)_2$ were obtained by the reaction of elemental platinum with concentrated sulfuric acid at 350 °C in sealed glass ampoules.[125] The crystal structure shows dumbbell-shaped $Pt_2{}^{6+}$ cations, which are coordinated by four $SO_4{}^{2-}$ and two $HSO_4{}^{-}$ ions.

Yellow single crystals of $RbAu(SeO_4)_2$ were obtained upon evaporation of a solution prepared from the reaction of elemental gold and Rb_2CO_3 with concentrated selenic acid.[128] In the crystal structure, Au^{3+} is in square planar coordination of oxygen atoms, which belong to four $SeO_4{}^{2-}$ ions. Anionic chains are formed, which are connected by the Rb^+ ions. The latter are surrounded by two chelating and six monodentate selenate groups leading to a coordination number of 10.

The reaction of elemental gold and selenic acid in teflon-lined steel autoclaves leads to orange-yellow single crystals of $Au_2(SeO_3)_2(SeO_4)$. In the crystal structure, Au^{3+} is surrounded by four oxygen atoms of just as many monodentate anions in a square planar manner.[129] The linkage of the polyhedra leads to double chains in the [001] direction, which are connected to puckered layers by $SeO_4{}^{2-}$ groups. The non-centrosymmetric space group could be proved by the observation of an SHG effect that shows an efficiency of about 43% compared to a KDP reference. Upon heating, $Au_2(SeO_3)_2(SeO_4)$ decomposes at about 370 °C in one step yielding elemental gold. The presence of selenite and selenate groups in the compounds is also obvious from the IR and Raman spectra, which show the characteristic bands of both species. Furthermore, solid-state NMR spectra reveal the different surroundings of the selenium atoms in the compound.

Red single crystals $PdSeO_3$ were prepared by oxidation of elemental palladium with H_2SeO_4 in a sealed glass tube at 350 °C.[126] The X-ray single crystal diffraction shows that the monoclinic compound consists of layer that are formed by square planar-coordinated Pd^{2+} ions and pyramidal $SeO_3{}^{2-}$ groups. The layers are held together by weak interactions involving the lone electron pairs of the selenium atoms (Figure 13). The distances Se–O within the selenite ion are different (1.69 and 1.76 Å), in accordance with the different attachment of the oxygen atoms to Pd^{2+} ions.

A series of papers on mercury and cadmium chalcogenates has been published throughout the last few years. The cadmium tellurates $Cd_2Te_3O_9$ and $Cd_2Te_2O_7$ were obtained from the respective binary oxides by chemical transport experiments.[130] $Cd_2Te_3O_9$ consists of $[CdO_7]$ polyhedra and $Te(IV)O_3$ and $Te(VI)O_6$ groups. The same anionic groups are found in $Cd_2Te_2O_7$, but the

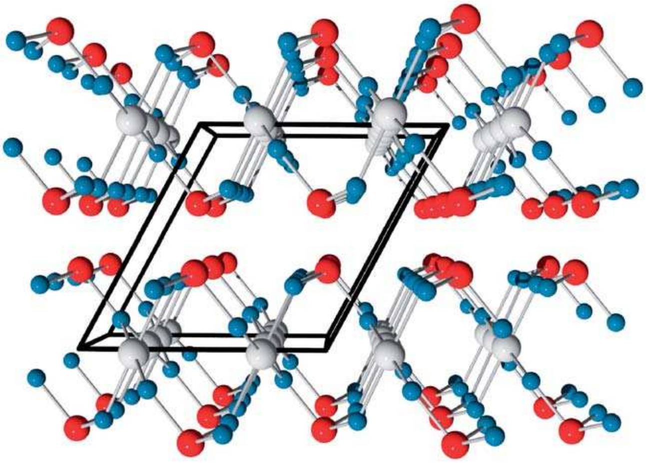

Figure 13 *Layer structure of Pd(SeO$_3$). Note, that the layers are only connected by weak interactions between the selenium atoms.*

Cd^{2+} ions are in different coordination of oxygen atoms with coordination numbers between six and eight.

Colourless single crystals of the isotypic double salts $CdEO_4 \cdot 2HgO$ (E=S, Se) were obtained from HgO and cadmium sulfate and selenate, respectively.[131] The crystal structures exhibit [O–Hg–O] chains consisting of linear [HgO_2] units, tetrahedral EO_4^{2-} anions, and distorted [CdO_6] octahedra. Similar [HgO_2] units occur in the related compounds $HgEO_4 \cdot 2HgO$ (E=S, Se), but in contrast to the cadmium compounds the linear units are linked to honey-comb-like networks incorporating the tetrahedral anions.[132]

For Hg_2SeO_3 three modifications have been described.[133] They all contain dumbbell-shaped Hg_2^{2+} ions that are linked by the selenite ions. A common feature of all crystal structures is the formation of channels, which obviously incorporate the lone electron pairs of the selenite ions.

Also mercury(II) selenite is polymorphic and two new modifications, β-$HgSeO_3$ and γ-$HgSeO_3$, have been recently described.[134] They show the mercury atoms in sevenfold coordination of oxygen atoms, and the [HgO_7] polyhedra are linked by the pyramidal selenite ions. A remarkable and unusual mercury selenite is the mixed valent compound $(HgSeO_3)_3HgSe$.[134] As a characteristic feature, the crystal structure contains [Hg_3Se] pyramids with distances Hg–Se of 2.489 Å.

Dark red single crystals of Hg_2TeO_5 were obtained hydrothermally from mercury nitrate and $Te(OH)_6$ and show chains of corner-sharing [TeO_6] octahedra that are linked by the mercury atoms.[135] Contrastingly, in the crystal structure of Hg_3TeO_6 isolated [TeO_6] octahedra are present, which are arranged in form of a body-centred packing, and the Hg^{2+} ions are located in the interstices of this packing.[135]

The tellurate $Hg_2Te_2O_7$ is dimorphic. Both forms have been prepared from HgO, TeO_2, and TeO_3 by chemical transport reactions with $HgCl_2$ as transport agent.[136] In both modifications [Te(VI)O_6] octahedra are connected to infinite chains, which are further linked to layers by tetrahedral [Te(IV)O_4] groups. In between the layers the mercury atoms are located exhibiting coordination numbers between six and eight with distances ranging from 2.0 to 3.0 Å.

A new structure type is found for $Ag_2Hg(SeO_3)_2$. Both Ag^+ and Hg^{2+} ions are in octahedral coordination in this compound.[137] The polyhedra are linked by the pyramidal shaped selenite anions.[138] In the crystal structure of the red tellurate $Ag_2Hg_2(TeO_4)_3$, the tellurium atoms are in octahedral coordination of oxygen atoms, and the octahedra are linked to infinite chains running along the *a*-axis.

6.5.3 Lanthanides

Owing to their former usage in the separation of rare earth elements, the lanthanide sulfates have been intensively studied. Thus, a great number of complexes and salts were described in the literature as might be seen from comprehensive overviews.[199,200] Even newer results have been compiled in two recent reviews,[201,202] and a limited selection should be sufficient here (Table 4). It will be restricted to anhydrous compounds, because the preparation of these phases in single-crystalline form is one of the main challenges and remarkable progress has been made throughout the last few years.

More than 20 years ago Sirotinkin *et al.*[203,204] reported the synthesis of $Nd_2(SO_4)_3$ and $Er_2(SO_4)_3$ in single-crystalline form by peritectic decomposition of $LiNd(SO_4)_2$ and $LiEr(SO_4)_2$, respectively. The crystals obtained, however, were of poor quality especially for the erbium compound. On the other hand, it has been shown that single crystals of anhydrous sulfates can be grown from alkali metal halide melts, favourably LiF and NaCl, respectively.[205,206] In the crystal structure of $Nd_2(SO_4)_3$ Nd^{3+} is surrounded by seven sulfate groups. Two of the latter are chelating ligands yielding a coordination number of nine for Nd^{3+}, and the linkage of the [NdO_9] polyhedra leads to a three-dimensional structure. For the crystal structures of the sulfates $M_2(SO_4)_3$ with M=Ho-Lu,Y a coordination number of six with octahedral coordination of the M^{3+} ions is found. The sulfate groups are attached to four M^{3+} ions. Thus, the [MO_6] octahedra and the $SO_4{}^{2-}$ tetrahedra are linked *via* all vertices (Figure 14). With respect to X-ray powder diffraction investigations there is strong evidence that the anhydrous rare earth sulfates of Gd and La have a different crystal structure than those known so far. For $Gd_2(SO_4)_3$ a monoclinic cell with space group C2/*c* and the lattice parameters $a = 9.097$ Å, $b = 14.345$ Å, $c = 6.234$ Å, and $\beta = 97.75°$ was given.[207]

The group of acidic sulfates includes hydrogensulfates as well as oxonium compounds where the proton is attached to a H_2O molecule to form H_3O^+ ions or their hydrated species $H_5O_2{}^+$. It was only in 1994 when the crystal structure of a lanthanide hydrogensulfate, namely, $Gd(HSO_4)_3$, has been determined for the first time.[208] The orthorhombic structure has subsequently been shown to be adopted with the rare earth elements Eu–Lu and Y.[205,209] It is a typical layer structure with the M^{3+} ions being in eightfold coordination of oxygen atoms. The layers are held together by strong hydrogen bonds with donor–acceptor

Table 4 *Selected lanthanide chalcogenates investigated by X-ray diffraction*

	Anhydrous chalcogenates		*Acidic chalcogenates*		*Oxide–chalcogenates*	*Halide–chalcogenates*
S	$Nd_2(SO_4)_3$[203]		$Ce(HSO_4)_3$[210]	$Gd(HSO_4)_3$[238]	$Eu_2O_2(SO_4)$[239]	
	$Er_2(SO_4)_3$[205]		$La(HSO_4)_3$[210]	$Er(HSO_4)_3$[205]		
	$Y_2(SO_4)_3$[206]		$Nd(HSO_4)_3$[210]	$Tm(HSO_4)_3$[238]		
	$Yb_2(SO_4)_3$[238]		$Pr(HSO_4)_3$[210]	$Yb(HSO_4)_3$[238]		
	$Lu_2(SO_4)_3$[238]		$Sm(HSO_4)_3$[210]	$Lu(HSO_4)_3$[238]		
	$Sc_2(SO_4)_3$[206]		$Eu(HSO_4)_3$[238]	$Er(HSO_4)(SO_4)$[205]		
			$Gd(HSO_4)_3$[208]	$(H_5O_2)Gd(SO_4)_2$[211]		
			$Tb(HSO_4)_3$[238]	$(H_5O_2)Ho(SO_4)_2$[211]		
			$Dy(HSO_4)_3$[238]	$(H_5O_2)Er(SO_4)_2$[211]		
			$Ho(HSO_4)_3$[238]	$(H_5O_2)Y(SO_4)_2$[211]		
			$Y(HSO_4)_3$[238]	$Nd(HSO_4)(S_2O_7)$[212]		
			$Er(HSO_4)_3$[238]			
Se	$Sc_2(SeO_4)_3$[240]	$Tb_2(SeO_3)_3$[218,221]	$La(HSeO_4)_3$[243]		$Sm_2O(SeO_3)_2$[218]	$LaF(SeO_3)$[219]
	$Yb_2(SeO_4)_3$[241]	$Dy_2(SeO_3)_3$[218,221]	$Gd(HSeO_4)(SeO_4)$[243]		$Eu_2O(SeO_3)_2$[218]	$Gd_3F(SeO_3)_4$[236]
	$Ce(SeO_4)_2$[242]	$Ho_2(SeO_3)_3$[218,221]	$Eu(HSeO_4)(SeO_4)$[244]		$Gd_2O(SeO_3)_2$[218]	$Dy_3F(SeO_3)_4$[217]
	$La_2(SeO_3)_3$[219]	$Er_2(SeO_3)_3$[217]	$Nd(HSeO_4)(Se_2O_7)$[245]		$Tb_2O(SeO_3)_2$[218,224]	$Nd_3F(SeO_3)_4$[221]
	$Ce_2(SeO_3)_3$[218]	$Tm_2(SeO_3)_3$[218,221]			$Dy_2O(SeO_3)_2$[218]	$Sm_3F(SeO_3)_4$[221]
	$Pr_2(SeO_3)_3$[218,221]	$Yb_2(SeO_3)_3$[218,221]			$Ho_2O(SeO_3)_2$[218]	$NdCl(SeO_3)$[247]
	$Nd_2(SeO_3)_3$[218,221]	$Lu_2(SeO_3)_3$[218,221]			$Er_2O(SeO_3)_2$[218]	$HoCl(SeO_3)$[246]
	$Sm_2(SeO_3)_3$[220]	$Y_2(SeO_3)_3$[218,221]			$Tm_2O(SeO_3)_2$[218]	$ErCl(SeO_3)$[247]
	$Eu_2(SeO_3)_3$[218,221]	$Sc_2(SeO_3)_3$[222]				
	$Gd_2(SeO_3)_3$[218,221]	$Ce(SeO_3)_2$[223]				
Te	La_2TeO_6[248]	$Ho_2(Te_4O_{11})$[253]				
	$Gd_2(TeO_6)$[249]	$Ho_2(Te_5O_{13})$[253]				
	Yb_2TeO_6[248]	$CeTe_2O_6$[254,255]				
	$Pr_2Te_4O_{11}$[250]	$Pr_2O(TeO_3)_2$[256]				
	$Nd_2Te_4O_{11}$[251]					
	$Lu_2Te_4O_{11}$[252]					

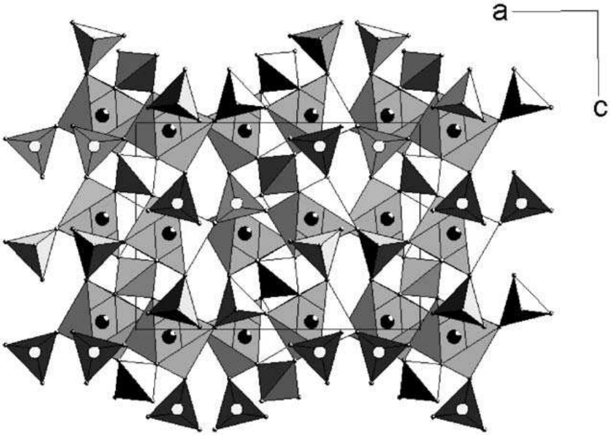

Figure 14 *Crystal structure of $Er_2(SO_4)_3$. The $[ErO_6]$ octahedra and SO_4^{2-} tetrahedra are linked via all of the oxygen vertices.*

distances of about 2.7 Å. For $Er(HSO_4)_3$ a second modification has been characterized by single crystal investigations.[205] The structure shows the same coordination of the Er^{3+} ions, but the linkage of the polyhedra now leads to a three-dimensional structure. The hydrogensulfates of the larger lanthanides La–Sm crystallize with another crystal structure.[210] The M^{3+} ions are ninefold coordinated by oxygen atoms in the form of tricapped trigonal prism. The oxygen atoms belong to nine monodentate HSO_4^- ions, which are attached to three M^{3+} ions. The OH groups of the ions remain uncoordinated and point towards channels, which are formed in the hexagonal structure along the crystallographic *c*-axis. For $Eu(HSO_4)_3$ both modifications, the hexagonal and the orthorhombic one, are found. The crystal structure of $Er(HSO_4)(SO_4)$ contains Er^{3+} ions surrounded by four monodentate SO_4^{2-} and three monodentate HSO_4^- ions, and the linkage of the tetrahedra and the $[ErO_7]$ polyhedra leads to a three-dimensional structure.[205]

Single crystals of $H_5O_2Er(SO_4)_2$ and the isotypic compounds with Gd, Ho, and Y grow from sulfuric acid (80% H_2SO_4).[211] In $H_5O_2Er(SO_4)_2$ the H_3O^+ ion and the water molecule are joined to a $H_5O_2^+$ ion with a very short hydrogen bond. The Er^{3+} ions are in a dodecahedral surrounding of oxygen atoms. Upon heating, $H_5O_2Er(SO_4)_2$ looses two molecules of water in a first step yielding $Er(HSO_4)(SO_4)$, which finally decomposes to $Er_2(SO_4)_3$.

An interesting hydrogensulfate of neodymium is $Nd(HSO_4)(S_2O_7)$, which has been obtained by treating Nd_2O_3 with fuming sulfuric acid.[212] This compound is interesting because it is the first disulfate of a rare earth element. In the crystal structure the $S_2O_7^{2-}$ ion acts as a chelating ligand to a Nd^{3+} ion and as a monodentate ligand to three further Nd^{3+} ions. One oxygen atom of the disulfate group remains uncoordinated and acts as acceptor in a hydrogen bridge.

$Sc(HSeO_3)_3$ is the only neat hydrogenselenite of which the structure is known.[213] A three-dimensional network of $[ScO_6]$ octahedra and selenite groups is formed in the crystal structure. Another interesting acidic selenite, which can be obtained from selenious acid (57% H_2SeO_3) is $Nd_2(Se_2O_5)_3(H_2SeO_3)\cdot 2H_2O$.[214] It contains two crystallographically different Nd^{3+} ions, both in ninefold coordination of oxygen atoms. One of the latter is surrounded by seven $Se_2O_5{}^{2-}$ groups of which two are attached in a chelating way. The second one has two chelating and two monodentate $Se_2O_5{}^{2-}$ neighbours and, furthermore, two H_2O and one H_2SeO_3 ligands. The coordination polyhedra are linked to sheets, which are stacked in [001] direction and held together by hydrogen bonds with the acid and the water molecules as donors. A diselenite group is also observed in $Pr(Se_2O_5)(HSeO_3)(H_2SeO_3)$[215] and $Y(Se_2O_5)(NO_3)\cdot 3H_2O$.[216] The distinct anions in $Pr(Se_2O_5)(HSeO_3)(H_2SeO_3)$ have different functionalities in the structure: the diselenite and hydrogenselenite groups link the Pr^{3+} ions to double chains, which are connected *via* hydrogen bonds of the H_2SeO_3 molecules. These are only monodentate to the Pr^{3+} ions, which are in ninefold coordination of oxygen atoms. A structure with double layers has also been determined for $Y(Se_2O_5)(NO_3)\cdot 3H_2O$. In this case, the layers are connected by hydrogen bonds involving the nitrate ions and the water molecules. The Y^{3+} ions are surrounded by two monodentate and one chelating $Se_2O_5{}^{2-}$ group, three H_2O molecules and one nitrate ion.

The anhydrous selenites, $M_2(SeO_3)_3$, were prepared in single-crystalline form either by fusion of the binary oxides in the presence of an alkali halide flux, or by decomposition of the respective selenates in a LiF melt.[217–220] The smaller selenites with M=Tb–Lu crystallize with a triclinic crystal structure. The compounds contain two crystallographically different M^{3+} ions with coordination numbers of seven and eight, respectively. An important characteristic of the crystal structure is the stereochemical activity of the lone pairs of the selenium atoms. A very similar influence of the lone pairs on the crystal structure has been observed for $La_2(SeO_3)_3$[219] and $Ce_2(SeO_3)_3$.[218] The anhydrous selenites of the other larger lanthanides M=Pr, Nd have essentially the same crystal structure as the lanthanum and the cerium compound but with a small monoclinic distortion.[218,221] For samarium another structure type emerges, which is closely related to that of the smaller lanthanides Tb–Lu.[220] For scandium as the smallest rare earth element, however, a crystal structure with octahedral coordination of the metal ions occurs.[222] For cerium also the structure of the tetravalent compound, $Ce(SeO_3)_2$, is known. In the crystal structure the Ce^{4+} ions are coordinated by eight oxygen atoms, which belong to seven $SeO_3{}^{2-}$ groups with one of them being a chelating ligand.[223]

The reaction of lanthanide oxides with SeO_2 may also lead to oxide-selenites. With M_2SeO_5 (= $M_2(SeO_3)O_2$) one possible composition has been observed as intermediate during the decomposition of selenites.[225–229] Another composition, $M_2O(SeO_3)_2$, was obtained in single-crystalline form for M=Tb.[218,224] The tetragonal structure consists of oxide-centred tetrahedra, which are linked to chains oriented along [001] and connected by the $SeO_3{}^{2-}$ ions.

The crystal structures of a handful of ternary anhydrous selenites are known, and $NaLa(SeO_3)_2$ and $NaY(SeO_3)_2$,[230] containing additional Na^+ ions, the copper phases $M_2Cu(SeO_3)_4$ (M=La–Tb)[231,232] and the lithium selenite $Li_3Lu_5(SeO_3)_9$[233] should be mentioned. The copper selenites show the M^{3+} ions in

10-fold coordination of oxygen atoms. The connection by the selenite ions leads to a three-dimensional anionic network that incorporates the Na^+ ions for charge balance. A three-dimensional anionic substructure is also found for the yttrium compound, but because of the smaller ionic radius of Y^{3+} compared to La^{3+}, the CN is lowered to seven. The CN of 10 for the M^{3+} ions in $La_2Cu(SeO_3)_4$ is achieved by the attachment of seven $SeO_3{}^{2-}$ ions, part of them being chelating ligands.

The usage of a flux for the crystal growth of rare earth selenites sometimes leads to unexpected compounds. For example, $Tb_3O_2Cl(SeO_3)_2$ was obtained when the reaction of SeO_2, Tb_4O_7, and Tb was carried out using $TbCl_3$ as a flux.[234] Characteristic features of the crystal structure are double chains of oxide-centred Tb tetrahedra and *pseudo*-hexagonal channels, which incorporate the lone pairs of the selenite ions. Further examples of the flux participation in the reaction are $Tb_5O_4Cl_3(SeO_3)_2$, $Gd_5O_4Br_3(SeO_3)_3$, and $Sm_9O_8Cl_3(SeO_3)_4$.[218,234,235] In these crystal structures double chains of vertex-connected double chains of $[OM_4]$ tetrahedra occur.

Attempts to grow single crystal of $La_2(SeO_3)_3$ from a LiF melt led to the fluoride selenite $LaFSeO_3$.[219] The crystal structure contains three crystallographically different La^{3+} and $SeO_3{}^{2-}$ ions, respectively. The coordination numbers of the cations are 11 and 10. Fluoride-selenites with a lower F^- content were obtained for M=Nd, Sm, Gd, and Dy and have the composition $M_3(SeO_3)_4F$.[217,221,236] The crystal structure of the isotypic compounds contains M^{3+} ions in triangular formation caused by one selenite group $SeO_3{}^{2-}$, which acts as a μ_3-ligand as well as by a μ_3-F^- ion capping the triangle on the opposite side. Each edge of the ring is bridged by one oxygen atom of a crystallographically different selenite group. The coordination sphere of the three M^{3+} ions is completed by further selenite ligands, so that the building unit $[M_3F(Se(1)O_3)_4(Se(2)O_3)_9]^{18-}$ results. These fragments are stacked with the same orientation along the *c*-axis, leading to the acentricity of the crystal structure (space group $P6_3mc$). The stereochemical activity of the lone electron pairs is obvious in the crystal structure (Figure 15).

Light green single crystals of $Pr_4(SeO_3)_2(SeO_4)F_6$ were obtained from the decomposition of $Pr_2(SeO_4)_3$ in the presence of LiF in a gold ampoule.[237] The compound contains two crystallographically different Pr^{3+} ions. One is attached by six fluoride ions and two chelating $SeO_3{}^{2-}$ groups, leading to a coordination number of 10, while the second is surrounded by four fluoride ions, three monodentate $SeO_3{}^{2-}$, and two $SeO_4{}^{2-}$ groups. One of the latter acts as a chelating ligand, so the coordination number is also 10. The anions F^- and $SeO_3{}^{2-}$ connect the Pr^{3+} ions into layers parallel (100), which are linked along [100] *via* $SeO_4{}^{2-}$ groups. The linkage of the coordination polyhedra leads to cavities in the crystal structure, which incorporate the lone pairs of the selenite ions. The reaction of $Sm_2(SeO_4)_3$ and NaCl in gold ampoules yielded light-yellow single crystals of $NaSm(SeO_3)(SeO_4)$.[237] The crystal structure contains 10-fold oxygen-coordinated Sm^{3+} ions. The oxygen atoms belong to five $SeO_3{}^{2-}$ and two $SeO_4{}^{2-}$ ions. Two of the $SeO_3{}^{2-}$ groups as well as one of the $SeO_4{}^{2-}$ groups act as a chelating ligand.

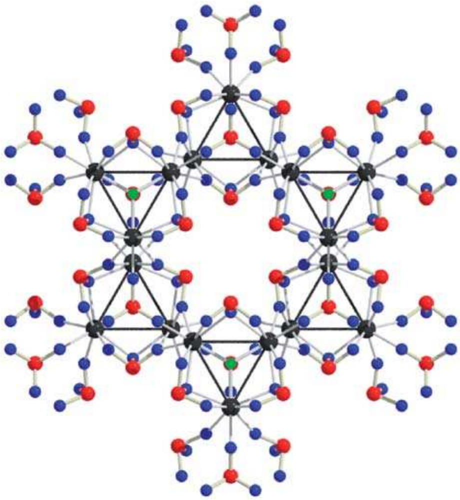

Figure 15 *Structure of the fluoride-selenite* $Gd_3F(SeO_3)_4$. *The* Gd^{3+} *ions are linked to triangles by both selenite and fluoride ions. The connection of the triangles provides channels that incorporate the lone electron pairs of the selenium atoms.*

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CHAPTER 7.1

Structure and Bonding of the Neutral Chalcogens and their Polyatomic Cations

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7.1.1 Introduction

The group of the chalcogens sulfur, selenium and tellurium is a typical triad of the more electronegative nonmetals with relatively high-ionization energies, relatively strong element–element bonds and a clear tendency to form mono- and polyatomic anions (Table 1).

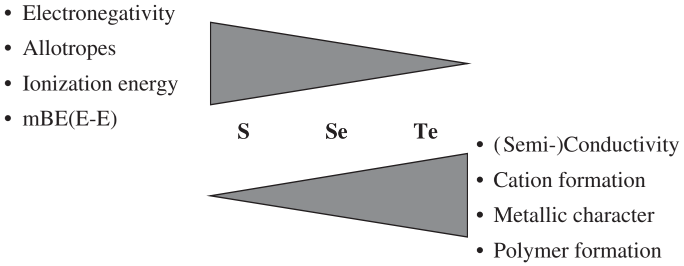
There is a clear trend to form small molecular entities; however, for sulfur those are predominantly noncharged allotropes or negatively charged polysulfides, but for selenium and more so for tellurium only the formation of charged but not neutral polyatomic entities prevails (see Scheme 1).

Thus, sulfur is the element richest in allotropes,[1] while tellurium holds the record for the number of positively charged polyatomic cations. Moreover, tellurium (and to a lesser extent Se) is at the border between a nonmetal and a metal; thus, solid grey Se and Te are semiconductors and especially

Table 1 *Fundamental properties of the chalcogen elements*

Property	*S*	*Se*	*Te*
χ(Allred–Rochow)	2.44	2.48	2.01
d(E–E) (pm)	205 (in S_8)	234 (in Se_8)	284 (in grey Te)
d(E = E) (in E_2) (pm)	188.7	215.2	255.7
mBE(E–E)^a (kJ mol^{-1})	265 (in S_8)	206 (in Se_8)	–
mBE(E = E)^a (kJ mol^{-1})	423 (in S_2)	329 (in Se_2)	255 (in Te_2)

^{a} mBE = mean bond enthalpy.



Scheme 1 *Trends in neutral and cationic chalcogen chemistry.*

Te also has a huge chemistry of polymeric structures. From these few facts one already notes that within the chemistry of S, Se and Te clear distinctions exist.

This book's chapter shall provide the interested reader with information regarding to the structure and bonding that govern the chemistry of the neutral chalcogen allotropes as well as their polyatomic cations. When X-ray structures have been redetermined with higher accuracy, only the latest references are given. Because of space limitations, we do not cover synthetic aspects as well as the extensive experimental and computational chemistry of the gas-phase chalcogen molecules. At this point other recent review articles that also cover such aspects should be acknowledged.[2–11]

7.1.2 Standard Enthalpies of Formation of the Small Chalcogen Clusters E_n (n = 1–8)

Important thermodynamic properties that relate to the structure and stability of the chalcogen allotropes and their polyatomic cations are the formation enthalpies listed in Table 2. Only reliable experimentally or quantum chemically established numbers have been included. From Table 2 it is evident that tellurium is the least investigated with respect to the entries; thus, there is clearly space for more thorough experimental or quantum chemical work in this direction. Therefore, we have assessed the missing Te data from the IP determination in ref. 12 (PE spectroscopy) and ref. 13 (quantum chemical calculations) and have put them in the table in parentheses, although it is clear that the associated error bars are relatively high. The data in ref. 14 were not considered.

7.1.3 Structure and Bonding

The material collected in the following pages is organized as follows: we distinguish between molecular and polymeric structures. In the molecular section we first use the increasing number of chalcogen atoms in the structure and second the increasing positive charges of the species as the ordering

Table 2 *Fundamental properties of the small chalcogen clusters E_n ($E = S, Se, Te$; $n = 1$–8) (in kJ mol^{-1})*

Property	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
$\Delta_f H^\circ(S_{n,\ (g)})$	**277**	**129**	133	137	124	103	114	106
$\Delta_f H^\circ(Se_{n,\ (g)})$	227	139			149	139	153	170
$\Delta_f H^\circ(Te_{n,\ (g)})$	197	139	(266)	(319)	(279)	(335)	—	—
Property	E_1^+	E_2^+	E_3^+	E_4^+	E_5^+	E_6^+	E_7^+	E_8^+
$\Delta_f H^\circ(S_n^+,\ _{(g)})$	**1277**	1032	1076	972	939	971	951	976
$\Delta_f H^\circ(S_n^+[AsF_6]^-,\ _{(c)})$	—	−1433	−1361	−1457	−1471	−1427	−1437	—
$\Delta_f H^\circ(Se_n^+,\ _{(g)})$	1168	1004	1083	960	982	996	962	1035
$\Delta_f H^\circ(Se_n^+[AsF_6]^-,\ _{(c)})$	—	−1447	−1331	−1447	−1402	−1380	−1402	—
$\Delta_f H^\circ(Te_n^+,\ _{(g)})$	1066	970 (899)	(972)	(1027)	(978)	(1044)	(IP: 7.24 eV)	(IP: 7.30 eV)
Property	E_1^{2+}	E_2^{2+}	E_3^{2+}	E_4^{2+}	E_5^{2+}	E_6^{2+}	E_7^{2+}	$E_{8>}^{2+}$
$\Delta_f H^\circ(S_n^{2+},\ _{(g)})^a$	3528	—	2538	2318	—	2238		2151
$\Delta_f H^\circ(S_n^{2+}([AsF_6]^-)_2,\ _{(c)})$	—	—	—	-3104^b		−3103	—	−3122
$\Delta_f H^\circ(Se_n^{2+},\ _{(g)})$	3212	—	—	2207	—	—	—	2071
$\Delta_f H^\circ(Se_n^{2+}([AsF_6]^-)_2,\ _{(c)})$	—	—	—	−3182	—	—	—	−3197
$\Delta_f H^\circ(Te_n^{2+},\ _{(g)})$	2861	—	—	2077	—	—	—	—
$\Delta_f H^\circ(Te_n^{2+}([AsF_6]^-)_2,\ _{(c)})$	—	—	—	−3354	—	—	—	—

Note: Values in bold are from the NIST,[15] values in parentheses have been put together by the author from PE-spectroscopy data[12] of Te_n and Te_n calculations ($n =$ 1–6).[13]

[a] $\Delta_f H^\circ(S_{10}^{2+},\ _{(g)}) = 2146$;

[b] $\Delta_f H^\circ(S_4^{2+}([AsF_6]^-)_2(AsF_3),\ _{(c)}) = -4050$.

principle. Structural curiosities that need extra explanation from the bonding side are included right after the structural discussion. However, we start with a brief bonding introduction on regularly observed interactions that lead to the features observed in the solid-state structures.

It should be noted that, due to space limitations, we restrict ourselves to the species that have been characterized in the condensed phase. Experimental or quantum chemical gas-phase investigations will be cited when appropriate; however, their literature coverage is not complete.

7.1.4 Brief Bonding Introduction

7.1.4.1 General Remarks

In the classical picture each dicoordinate chalcogen atoms bears two lone pair orbitals. It has been shown that a marked s–p separation is observed and that the nature of these two lone pair orbitals is mainly ns^2 and np^2 ($n = 3$–5). The ns^2-type orbital is usually not involved in the stereochemistry and it is clear that the structures of the species described in this chapter are determined by the repulsion between the adjacent occupied np^2 lone pair orbitals. Thus, usually the systems try to minimize coulombic repulsion by adopting E–E–E–E torsion angles of about 90 ± 20° (Figure 1).

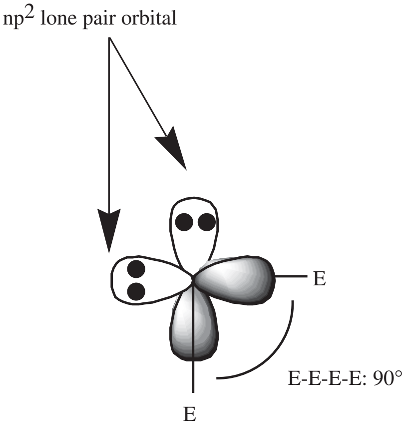


Figure 1 *Repulsion of the np^2 lone pair orbitals on adjacent E atoms leads to a preference for an orthogonal arrangement*

7.1.4.2 $np^2 \rightarrow n\sigma^*$ Interactions

If it is impossible for steric reasons to adopt torsion angles in the desired range (*i.e.* in S_7), the systems try to minimize the occupation of the neighboring np^2 lone pair orbitals with low torsion angles. This is achieved by

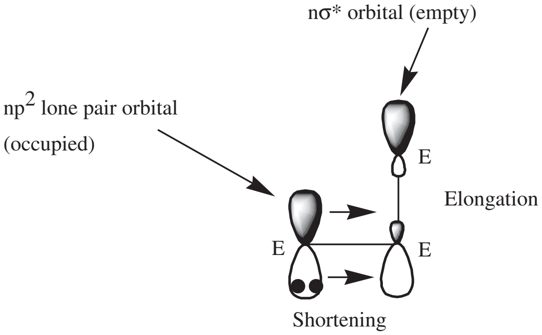


Figure 2 *Relief of the repulsion of coplanar np^2 lone pair orbitals by np^2 → nσ* interactions*

an interaction with empty orbitals in the vicinity. Usually, empty E–E σ^* orbitals have the right orientation and suitable orbital energies to achieve this (Figure 2).

This kind of an $n\text{p}^2 \rightarrow n\sigma^*$ interaction may lead to a marked bond lengths alternation; the extreme structural effect of such an interaction is certainly found for S_7, but also other neutral and cationic polychalcogen compounds frequently exhibit this interaction.

7.1.4.3 π and π*–π* Bonding

The last set of interactions is due to π bonding that may either occur in the Hückel sense and according to the $(4n + 2)$ π electron rule (E_4^{2+}; S_6^{2+}) or through an interaction of partially depleted $n\text{p}^2$ lone pair orbitals that now contain less than two electrons (Figure 3); this depletion may either proceed through an $n\text{p}^2 \rightarrow n\sigma^*$ interaction as shown above or through oxidation and cation formation.

This means that upon oxidation of neutral chalcogens giving the polychalcogen cations, electron density is removed from the occupied $n\text{p}^2$ lone pair orbitals.[15,16] From a molecular orbital (MO) view of such interactions

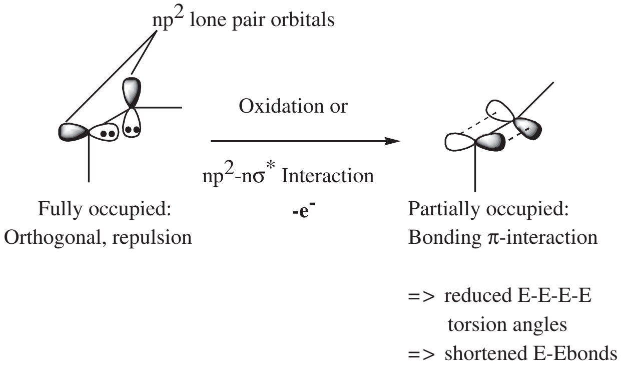


Figure 3 *Partial π bonding of the depleted np^2 lone pair orbitals*

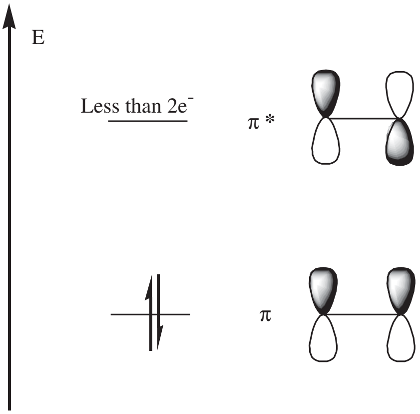


Figure 4 *MO view of the depleted adjacent np^2 lone pair orbitals*

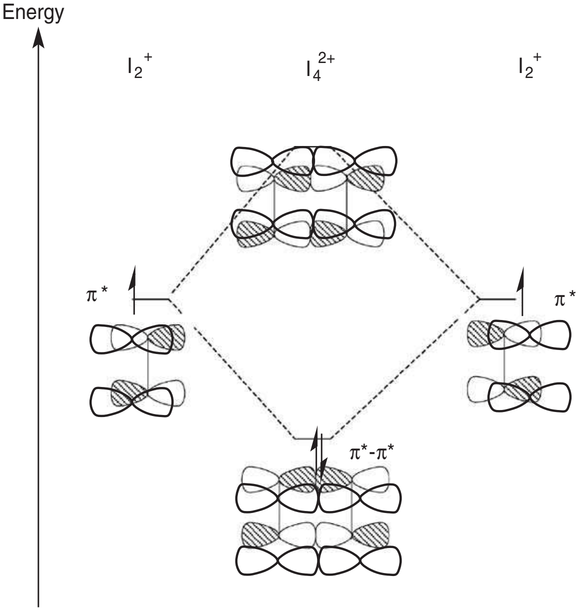


Figure 5 *Prototypical π*–π* bonding in I_4^{2+}*

it becomes evident that the antibonding π* orbitals are partially occupied (Figure 4).

Thus, an interaction of two individual and partially occupied π* orbitals may lead to weak but significant bonding; such an interaction has first been found for the I_4^{2+} dication[5] and is called a π*–π* bond (Figure 5).

For example, such π*–π* bonds are observed in the structures of Te_6^{4+} and the exo–endo structure of E_8^{2+} (see below).

7.1.5 Polyatomic Chalcogen Molecules or Molecular Cations

7.1.5.1 Molecular E_4 Moieties

The only isolated E_4 moieties that are known in condensed phases are those in the planar 6π Hückel aromatic E_4^{2+} dications. Moreover, the structures of several polymeric Te cations contain Te_4 squares (see a later section). It should be noted though that the long-standing debate on the ground state of gaseous S_4 could recently be solved by very high-level MRCI and CCSD(T) *ab initio* calculations:[17] the ground state is *cis* planar C_{2v} symmetric (green absorbing), followed by a *trans* planar C_{2h} structure (red absorbing).

Historically, Te_4^{2+} was the first of the dications to be observed already in 1798 (red solution of Te in concentrated sulfuric acid),[18] yet the E_4^{2+} structure was only assigned in the 1960s. The number of known structures increases with increasing weight of the chalcogen: thus, while only two S_4^{2+} structures[19–24] are known, more than 25 compounds containing Se_4^{2+} [25–29] and Te_4^{2+} [28,30–39] have been prepared (Figure 6).

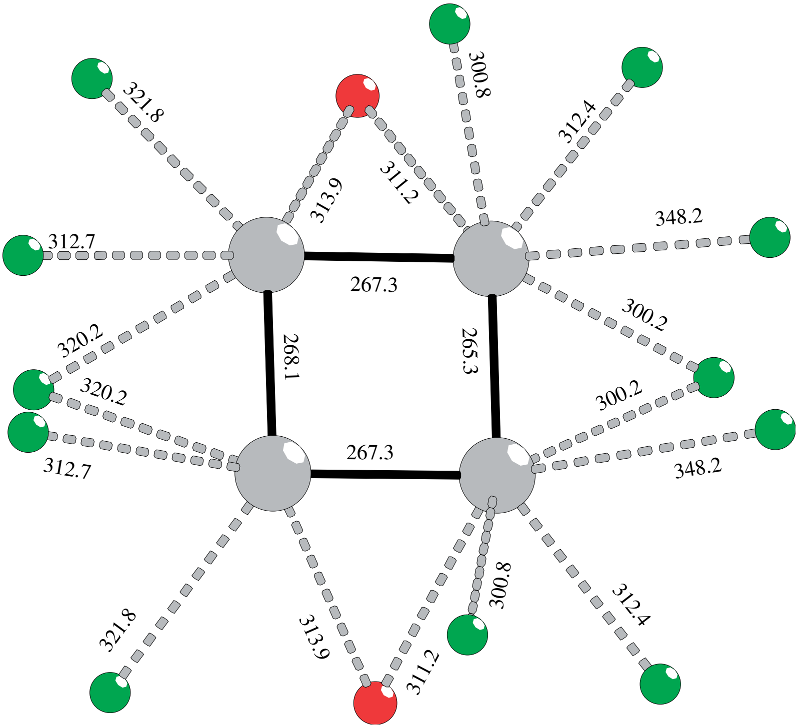


Figure 6 *Solid-state structure with contacts below 350 pm of the cation* Te_4^{2+} *in* $Te_4[AsF_6]_2(SO_2)$ *(see ref. 31)*

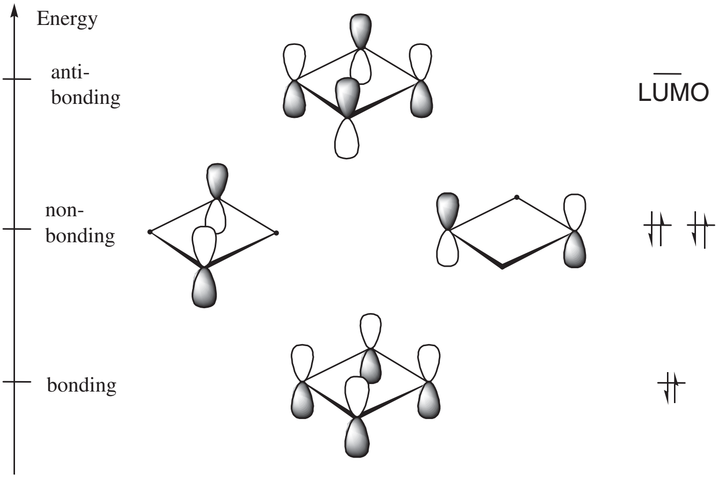


Figure 7 *MOs of π symmetry in* E_4^{2+} *(see refs. 39 and 40)*

As may be seen from the solid-state contacts in Figure 6, the positive charge in E_4^{2+} is evenly distributed and the E–E bond lengths are by about 5–10 pm shorter than expected for a conventional single bond. This is due to the additional π bonding, which increases the E–E bond order to 1.25.[40] The MOs of π symmetry[41] are shown in Figure 7.

7.1.5.2 Molecular E_5 Moieties

Only one compound containing an E_5 moiety has previously been reported; this is the S_5^+ radical cation, which is always observed upon oxidation of sulfur with MF_5 (M = As, Sb) or oleum (H_2SO_4/SO_3 mixture). No isolated S_5^+ compound is known and the existence of S_5^+ was deduced from an ESR spectroscopic study of a solution that contained 92.4% ^{33}S.[42] It is believed that S_5^+ is formed in equilibrium over $S_8[AsF_6]_2$ in solution in SO_2, *i.e.* Equation (1):[43]

$$S_8[AsF_6]_2 \rightleftharpoons 0.5\,S_6[AsF_6]_2 + S_5[AsF_6] \qquad (7.1)$$

The lowest energy calculated S_5^+ structure has C_s symmetry[43] and is best described as a five-membered ring in the envelope conformation.

7.1.5.3 Molecular E_6 Moieties

Six atomic isolated E_6 entities are common and were observed in neutral S_6 and Se_6 as well as cationic S_6^{2+}, Te_6^{2+} and Te_6^{4+}. Moreover, the structures of several polymeric Te cations contain six-membered rings (see later section).

The X-ray structures of both neutral S_6[44] and Se_6[45,46] molecules were determined (Figure 8).

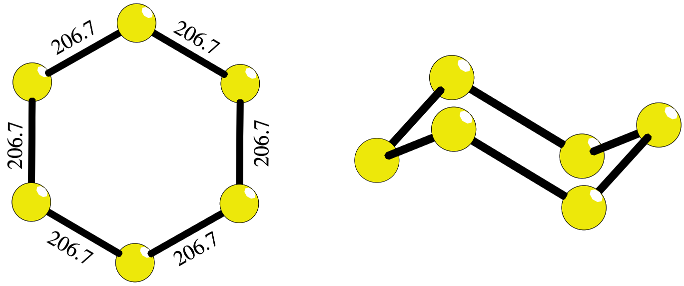


Figure 8 *Solid-state structure of S_6; S–S–S = 102.6° and S–S–S–S = 73.8°. Se_6 adopts the same structure with d(Se–Se) = 235.6 pm, Se–Se–Se = 101.1° and Se–Se–Se–Se = 76.2°*

Other isomers of S_6 were assessed by quantum chemistry.[47] For the existence of S_6^{2+} indirect yet convincing evidence[43] could be presented and $S_6[AsF_6]_2$ is part of equilibrium (1) above.[48] The structures of S_6, Se_6 and S_6^{2+} are related: all are six-membered rings in the chair conformation. However, the neutrals are strongly puckered, but the ring in S_6^{2+} was calculated[43] to be greatly flattened as may be seen from the increasing S–S–S bond and decreasing S–S–S–S torsion angles of 102.6°/73.8° (S_6) with respect to 113.7°/47.6° (S_6^{2+}). This flattening may be attributed to π bonding on removal of electrons from the $3p^2$ lone pair orbitals of S_6 with six $3p^2$ lone pair orbitals (=> 12 π electrons). In the oxidized S_6^{2+}, only 10 π electrons are present and the bonding is related to a planar 10 π Hückel system.[43] This is also reflected in the short S–S bond lengths of 202.8 pm.

By contrast, the solid-state structures of several isolated Te_6^{2+} salts[49,50] have been determined and all were shown to possess a Te_6 homocycle in the boat conformation (Figure 9).

However, in this structure the two positive charges are also completely delocalized and Te_6^{2+} uses the complete set of bonding interactions described

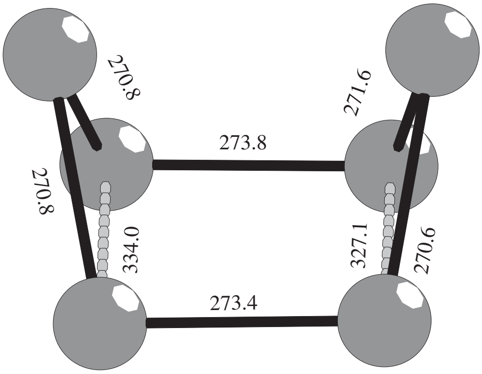


Figure 9 *Solid-state structure of the cation Te_6^{2+} in $Te_6[NbOCl_4]_2$ (see ref. 49)*

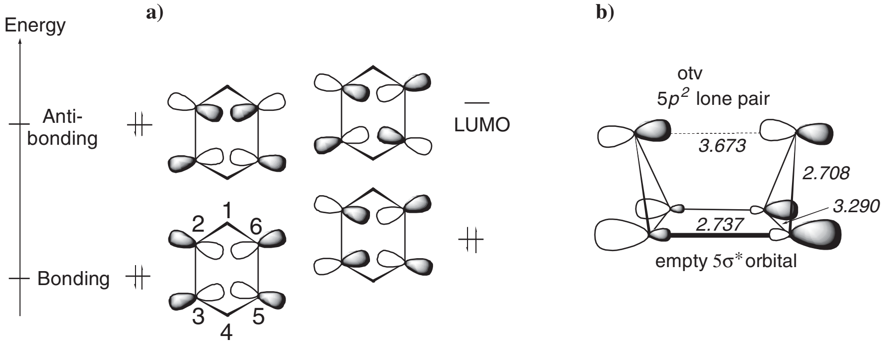


Figure 10 *Annular π bonding, transannular π*–π* bonding (a) and additional charge delocalization through an $np^2 \rightarrow n\sigma^*$ interaction (b)*

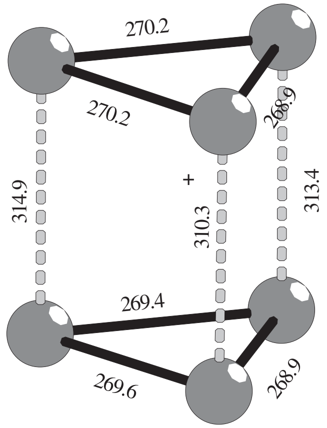


Figure 11 *Solid-state structure of the cation Te_6^{4+} in $Te_6[AsF_6]_4(SO_2)_2$ (see refs. 50 and 51)*

above: π bonding, π*–π* bonding as well as $np^2 \rightarrow n\sigma^*$ interactions have to be invoked to account for the structural features of this ion (Figure 10).[5]

On further oxidation of Te_6^{2+} the next species that was isolated is the prism-shaped Te_6^{4+} ion found in the solid-state structures of $Te_6[AsF_6]_4(SO_2)_2$[51,52] and $(Te_6)(Se_8)[AsF_6]_6(SO_2)$[53] (Figure 11).

This unusual and almost D_{3h} symmetric structure with three long edges at 310–314 pm needs some further explanation.[54] Its structure is best derived from two triangular Te_3^{2+} units. The ground state of Te_3^{2+} has D_{3h} symmetry and is a triplet with the two unpaired electrons residing in orbitals that have π* symmetry (Figure 12).

Through an interaction of the two singly occupied π* orbitals, a transannular six-center four-electron π*–π* bond with a formal bond order of 0.67 results

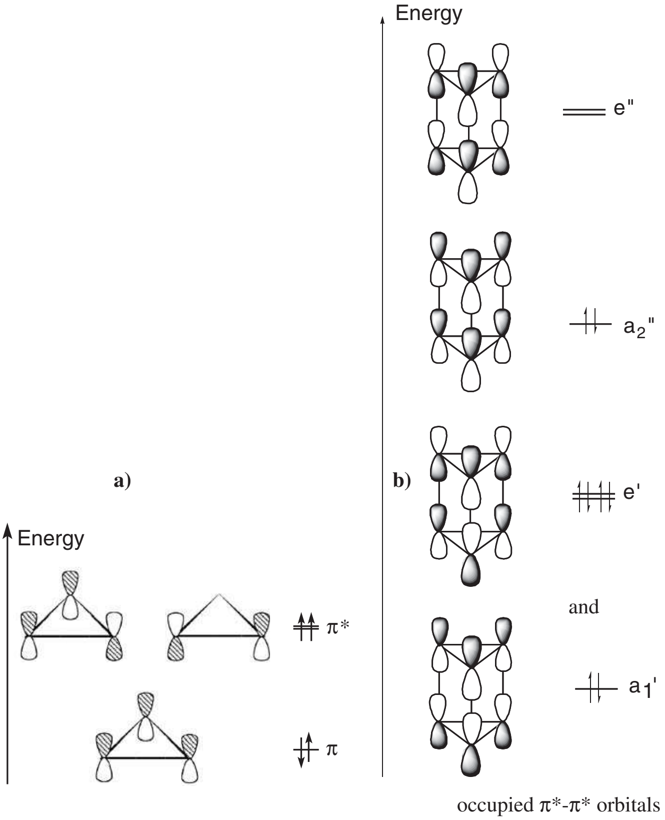


Figure 12 *(a) The three MOs of π symmetry in* Te_3^{2+}*; (b) π*–π* bonding in* Te_6^{4+} *(see ref. 53)*

and thus accounts for the observed longer separations between the two triangles in Te_6^{4+}.

7.1.5.4 Molecular E_7 Moieties

Only molecular S_7 and Se_7 are firmly known, yet only the former has been characterized by X-ray analysis. However, Re complexes of Se_7 are known[55,56] and the neutral Se_7 homocycle cocrystallized with salts of polyselenides.[57,58] S_7^+ is thought to be present in SO_2 solutions of sulfur cations; however, this is an unproven but likely hypothesis. Other than that, only the structures of S_{19}^{2+} and Se_{17}^{2+} contain E_7 homocycles (see there).

The structure of S_7 is clearly the most intriguing[59–61] of all known structures of neutral sulfur homocycles. Several modifications are known (sometimes only by powder or Raman data); however, the structural features are always the same and show a large bond length alternation and a range of S–S distances from 199 pm (bond order $>>1.0$) to 218 pm (bond order $<<1.0$; Figure 13). Other isomers were assessed by quantum chemistry.[61]

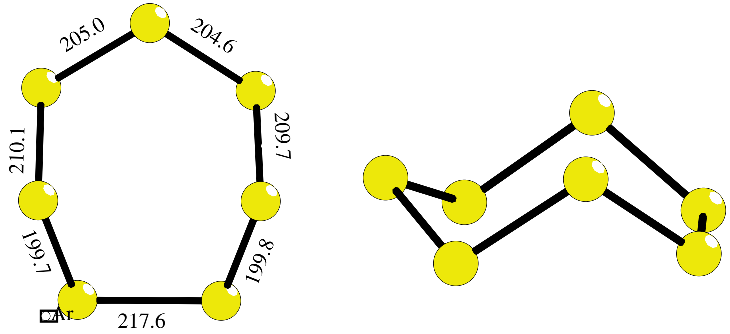


Figure 13 *Solid-state structure of one molecule of* δ S_7; $(S–S–S)_{av.} = 105°$ *and* $(S–S–S–S) = 0.3°–108.9°$, *av.:* $76°$ *(see refs. 58 and 59)*

From Figure 13 it is clear that two adjacent S atoms are forced into a structure in which their $3p^2$ lone pair orbitals are in the same plane (0.3° torsion). This leads to a strong coulombic repulsion or, in the MO picture, to an occupied π^* orbital and therefore the S–S distance between these two atoms is as long as 218 pm (*cf.* 205 pm for an S–S single bond). To reduce this repulsion, the $3p^2$ lone pair orbitals are depleted by a series of further $np^2 \rightarrow n\sigma^*$ interactions that lead to the observed bond length alternation (Figures 13 and 14) and a shortening of the adjacent bond to about 199 pm, but a lengthening of the next bond to 210 pm.[62]

The only structural data available for S_7^+ comes from quantum chemical calculations[43] and suggests that S_7^+ is a C_2 symmetric S_7 homocycle in the chair conformation and exhibits a much less pronounced bond lengths alternation

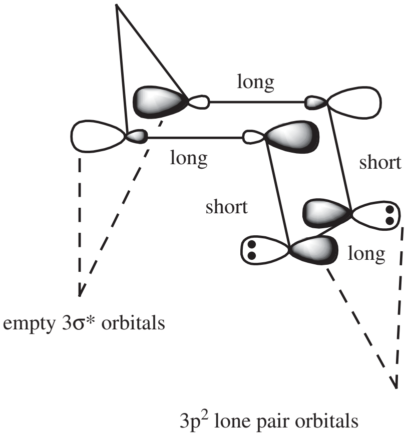


Figure 14 $np^2 \rightarrow n\sigma^*$ *interaction responsible for the bond lengths alternation in* S_7.*(see ref. 61)*

than neutral S_7. Thus, it is clear that upon oxidation, the electron is removed from the lone pair orbitals and thereby the unfavorable repulsion of the adjacent lone pair orbitals, as in Figures 13 and 14, is relieved.

7.1.5.5 Molecular E_8 Moieties

Eight-membered homocycles are a common structural motif of the chalcogens; the ground state of elemental sulfur contains such almost D_{4d} symmetric S_8 rings (several modifications),[63–65] and for Se the structure of Se_8[66,67] has also been determined. Free neutral Te_8 remains unknown, but has been observed in the structure of the large Cs telluride Cs_3Te_{22}.[68] On oxidation the connectivity of the homocycle remains the same, but the conformation changes from exo–exo in D_{4d}-E_8 into exo–endo in the most common E_8^{2+} structure. For S and Se only this E_8^{2+} structure is known, but for Te several new variants appeared recently, the structures of which range from homocycles to bicycles and cages.

The solid-state structures of orthorhombic S_8[64] and monoclinic Se_8[66] are shown in Figure 15. As may be seen from the average E–E–E bond and E–E–E–E torsion angles, this structure is almost completely relaxed and consequently lone pair repulsion and ring strain are lowest in this arrangement. Other S_8 structures were assessed by quantum chemical calculations.[69]

It should be noted that the Se_8 ring in α Se_8 becomes more distorted at lower temperatures (299 K: d(Se–Se) = 232.6(5)–234.6(5) pm; 123 K: d(Se–Se) = 226.9(1)–232.7(1) pm).[66,67] This is not the case in β Se_8.

7.1.5.5.1 Exo–Endo E_8^{2+}

On oxidation of E_8 the, exo–exo conformation of the neutrals changes and an exo–endo conformer is formed in several E_8^{2+} salts (refs.: S,[16,70] Se,[53,71,72] Te[72,73]). Very puzzling features of these structures are the three transannular

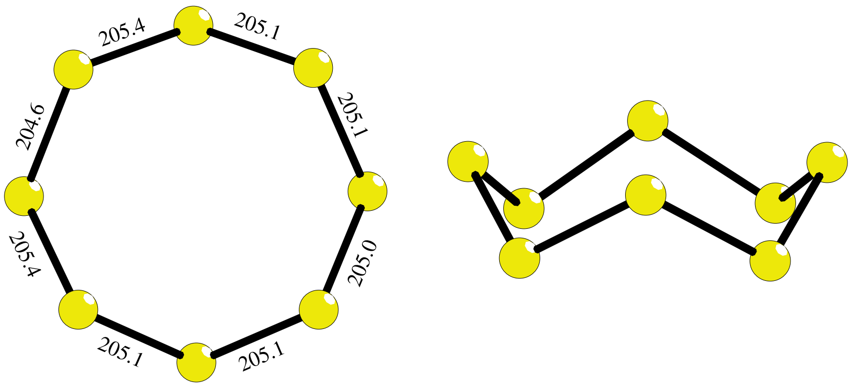


Figure 15 *Solid-state structure of orthorhombic* S_8 *(see ref. 63)* $(S–S–S)_{av.} = 108°$ *and* $(S–S–S–S) = 98.5°$*. Monoclinic α-*Se_8 *has the same structure*[65] *with d(Se–Se)*$_{av.}$*= 230.1 pm, Se–Se–Se = 105.6° and Se–Se–Se–Se = 101.3°*

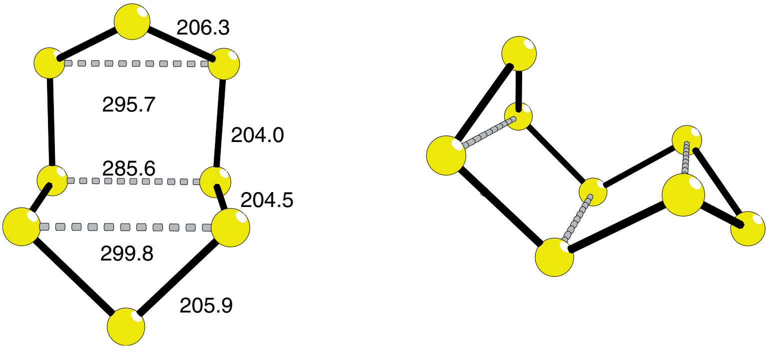


Figure 16 *Solid-state structue of the cation* S_6^{2+} *in* $S_8[AsF_6]_2$ *(see ref. 16)*

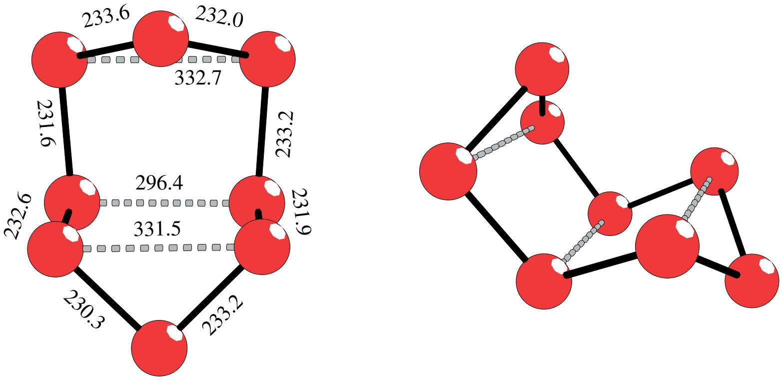


Figure 17 *Solid-state structure of the cation* Se_8^{2+} *in* $Se_8[Bi_4Cl_{14}]$ *(see ref. 71)*

interactions, which are weak, but still about 60–115 pm shorter than the sum of the van der Waals radii of the elements. The heavier the element, the shorter becomes the central bond of these three weak bonds. Such interactions are not found for the neutral molecules (Figures 16–18).

It appears that Te is more flexible in the possible arrangements (Figure 18);[72,73] it should be noted though that the counterions of these Te cations are more basic than the fluorinated anions used for S and Se cations. Thus, it may well be that the structural flexibility of the Te cations is a result of the increased cation–anion interactions in these salts.

The complete understanding of the bonding of E_8^{2+} was difficult to accomplish, since for a long time it remained impossible to optimize their structures by quantum chemistry.[74] However, in the year 2000 a full account of the successful modeling of all E_8^{2+} structures appeared[16] and the bonding may be described as follows (Figures 19 and 20).

In the classical Zintl picture, one would expect a pronounced bicyclic E_8^{2+} structure as shown in Figure 19 on the left. Here, the two tricoordinate E atoms bear the positive charge. However, the oxidation represents a depletion of the

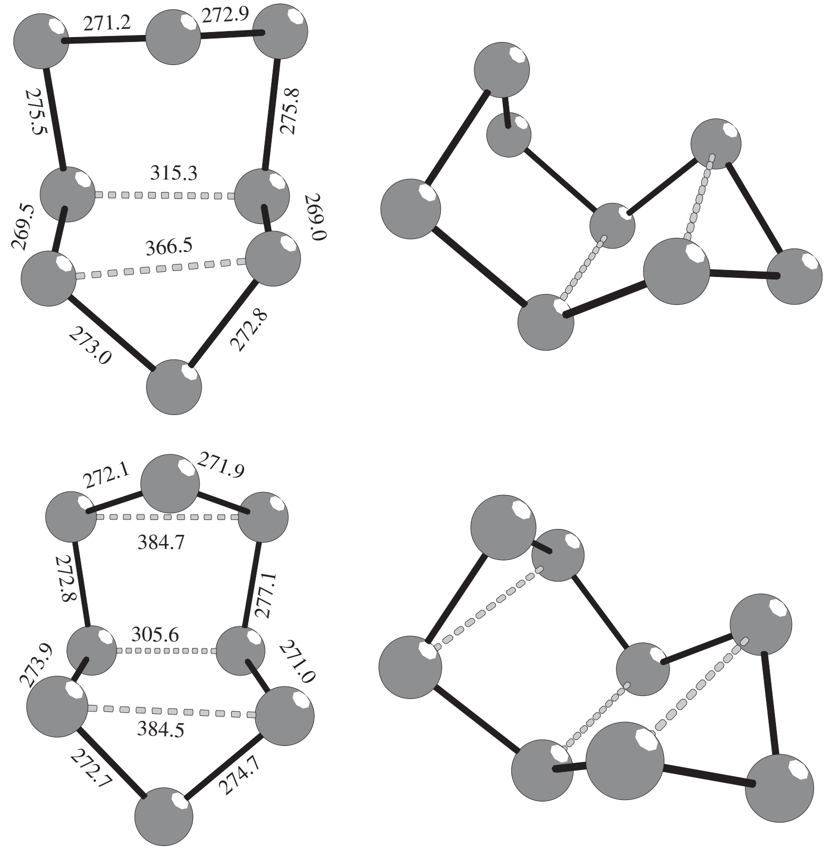


Figure 18 *Solid-state structure of the cation* Te_8^{2+} *in* $Te_8[ReCl_6]$ *(see ref. 72) (top) and* $Te_8[HfCl_6]$ *(see ref. 71) (down)*

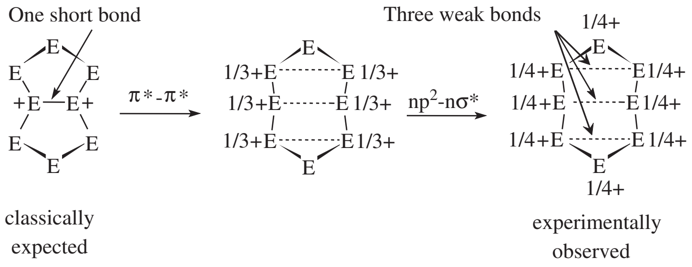


Figure 19 *Bonding in exo–endo* E_8^{2+}*: structural changes upon delocalizing the localized positive charges of the classical Zinti structure (left) by* π *and* π*–π* *bonding (middle) as well as additional* $np^2 \rightarrow n\sigma^*$ *interactions*[16]

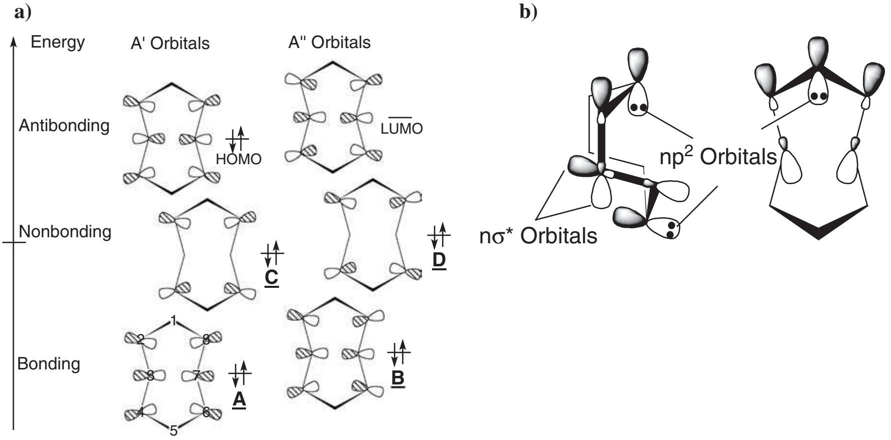


Figure 20 (*a*) π *and* π*–π* *bonding; (b)* $np^2 \rightarrow n\sigma^*$ *interactions in exo–endo* E_8^{2+} *(see ref. 16)*

$n\text{p}^2$ lone pair orbitals that can now π bond with each other (Figure 19, middle). The MOs responsible for such interactions are shown in Figure 20a and it can be seen that one noncanceled π bond is delocalized over the central six atoms of the cation, which in turn have slightly shorter E–E distances (see Figures 16–18 above). Moreover, a noncanceled transannular two-electron six-center π*–π* bond is formed that accounts for the observed transannular contacts (HOMO in Figure 20a). With further $n\text{p}^2 \rightarrow n\sigma^*$ interactions the positive charges are finally delocalized over all atoms (Figure 19, right and Figure 20b) – just as it was observed in the experiment.[16]

7.1.5.5.2 Other Te_8^{2+} Structures

According to its more electropositive nature and the longer E–E bond separations, Te is much better suited to bear more localized positive charges in the classical Zintl sense. Thus, the following Te_8^{2+} bicycle in Figure 21 may be understood in by assigning Te^+ charges to the two bridgehead atoms (tricoordinate).

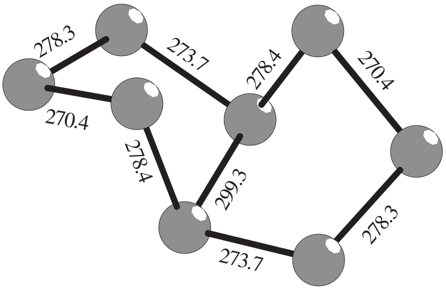


Figure 21 *Solid-state structure of the cation* Te_8^{2+} *in* $Te_8[WCl_6]_2$

Additional charge delocalization by a series of $np^2 \rightarrow n\sigma^*$ interactions is also likely to occur in this structure (see ref. 5 for more details).

A preliminary report of another Te_8^{2+} in a cage-like bicyclo[2.2.2]octane structure appeared in 1997.[4] This structure is best understood as a Zintl structure in which the two bridgehead Te atoms bear the positive charge and three noncharged Te_2 bridges are formed. However, no full structural report on this compound has been published and therefore we resist further analysis.

7.1.5.5.3 A Te_8^{4+} Structure

The structural relationships between E_8, E_8^{2+} and E_8^{4+} have already been postulated in the 1970s, a time at which only the structures of E_8 and E_8^{2+} were known (Figure 22).[16]

However, as may be seen from Figure 23 that shows the only characterized E_8^{4+} structure so far, $Te_8[VOCl_4]_2$,[75,76] the prediction was slightly wrong and the structure is more related to a cube in which two edges are not connected.

The structure of this Te_8^{4+} cation is best rationalized as a dimer of two square planar Te_4^{2+} units linked by two long and weak Te–Te bonds at 301 pm. It may be viewed as the starting point for the polymerization giving $(Te_4^{2+})_\infty$, which is described below in the polymer section. The long bonds in Te_8^{4+} may be understood as the result of a series of $np^2 \rightarrow n\sigma^*$ interactions that considerably lengthen the central Te–Te bond, but delocalize the positive charges onto all eight atoms (Figure 23, right).

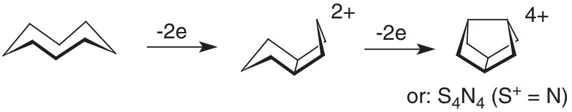


Figure 22 *Structural relationships between E_8, E_8^{2+} and E_8^{4+}. The structure of E_8^{4+} was postulated on the basis of the known structure of D_{2d} symmetric E_4M_4 ($M =$ N, P, As) that is isoelectronic to E_8^{4+} ($M = E^+$) (see ref. 16)*

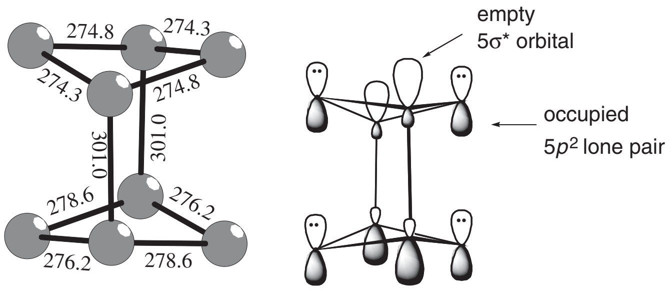


Figure 23 *Left: solid-state structure of the Te_8^{4+} in $Te_8[VOCl_4]_2$; right: charge delocalization in Te_8^{4+} (see ref. 74)*

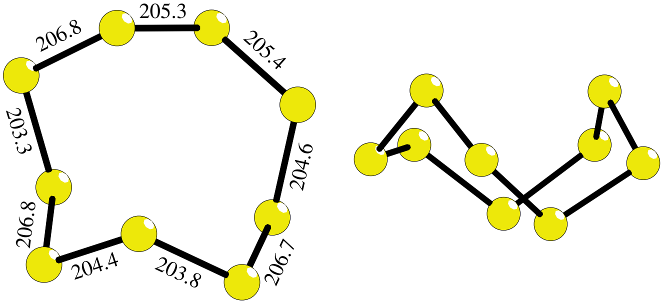


Figure 24 *Solid-state structure of S_9 (see ref. 75), $(S–S–S)_{av.}$= 107° and (S–S–S–S) = 59.7°–115.6°, av.:100°*

7.1.5.6 Molecular E_9 Moieties

The only compound known that contains nine chalcogen atoms so far is S_9 (Figure 24).[77] Because of the larger size of the ring, it appears to be easier to adopt a conformation in which the coplanarity of two adjacent lone pair orbitals is avoided and the atoms are all connected by rather normal S–S single bonds. It should be noted though that the shortest bond (203.3 pm) is neighbored by the two longest bonds (206.8 pm) and that the enclosed torsion angle is smallest (59.7°). Thus, this shows a faint resemblance to the situation discussed for S_7 above.

7.1.5.7 Molecular E_{10} Moieties

There are two types of compounds known that contain 10 chalcogen atoms: a neutral S_{10} homocycle and several isostructural bicyclic $Se_{10}{}^{2+}$ salts.

In analogy to the D_{3d} and D_{4d} structures of S_6 and S_{10} a D_{5d} structure was initially expected for S_{10}. However, the crystal structure determination showed that the compound has only D_2 symmetry (Figure 25).[78] *Ab initio* calculations[79] suggest that the D_{5d} isomer is 29 kJ mol^{-1} higher in energy than the D_2

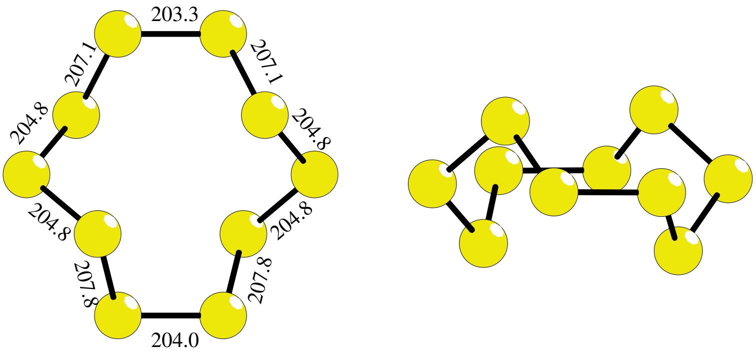


Figure 25 *Solid-state structure of S_{10}; $(S–S–S)_{av.}$= 106° and (S–S–S–S) = 75.4°–123.7°, av.: 95.7°*

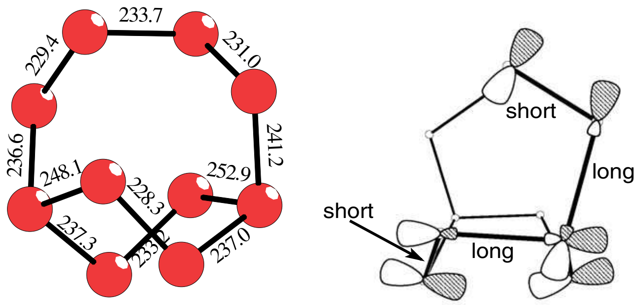


Figure 26 *Left: solid-state structure of the cation* Se_{10}^{2+} *in* $Se_{10}[Bi_5Cl_{17}]$ *(see ref. 27); right:* $np^2 \rightarrow n\sigma^*$ *interactions that delocalize the positive charges and are responsible for the bond length alternation*

form. This may be rationalized by the fact that according to the calculation the S–S–S–S torsion angles in D_{5d} S_{10} are rather strained at 116.6°. By contrast, in D_2 S_{10} they are only at 95.7° (av.) and thus almost unstrained.

Reminiscent of the situation for S_9 above, the shortest bonds (203.3, 204.0 pm) are neighbored by the four longest bonds (207.1–2078 pm) and the enclosed torsion angles are the smallest.

Upon formal oxidation of E_{10} to Se_{10}^{2+}, a completely new structural type is formed that is not related to the structure of the neutral allotrope S_{10}. Several salts of this cation are now known: $Se_{10}[SbF_6]_2$,[80] $Se_{10}[SO_3F]_2$ [81] and $Se_{10}[Bi_5Cl_{17}]$ (Figure 26).[27] The cation is built from a central Se_6 ring in the boat conformation, which is capped at the backside by a Se_4 chain; thus, two of the Se atoms are tricoordinate and thus positively charged in the Zintl sense. However, a very pronounced bond length alternation suggests that there is considerable charge delocalization through the formation of several $np^2 \rightarrow n\sigma^*$ interactions, as shown in Figure 26 on the left. Since the tricoordinate Se atoms are the only atoms that have a $4s^2$ but no $4p^2$ lone pair orbital, the structural effect of the delocalization of electron density into the $4\sigma^*$ orbitals around the tricoordinate atoms is drastic and very long bonds up to 252.9 pm result.

7.1.5.8 Molecular E_{11}–E_{15} Moieties

For this larger size of isolated polychalcogen entities only the respective neutral S_{11}–S_{14} homocycles are known; no evidence for other neutral or cationic species in this size has been given. S_{15} was not structurally characterized.[82,83]

The S_{11} structure[84–87] again contains at least one long bond (208–211 pm) that is flanked by two short bonds (203–204 pm) with large enclosed torsion angles of 137 and 141° – reminiscent of S_7 (Figure 27).

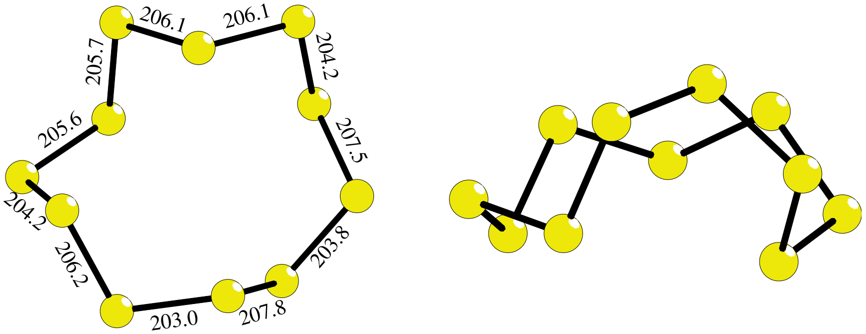


Figure 27 *Solid-state structure of S_{11} (one of the two independent molecules shown);*[82–85] *molecule 1: (S–S) = 203.7–211.0 pm, $(S–S–S)_{av.}$= 106.0° and (S–S–S–S) = 70.5°–140.5°, av.: 97.1°, molecule 2 (shown): $(S–S–S)_{av.}$= 106.3° and (S–S–S–S)= 69.3°–137.1°, av.: 96.9°*

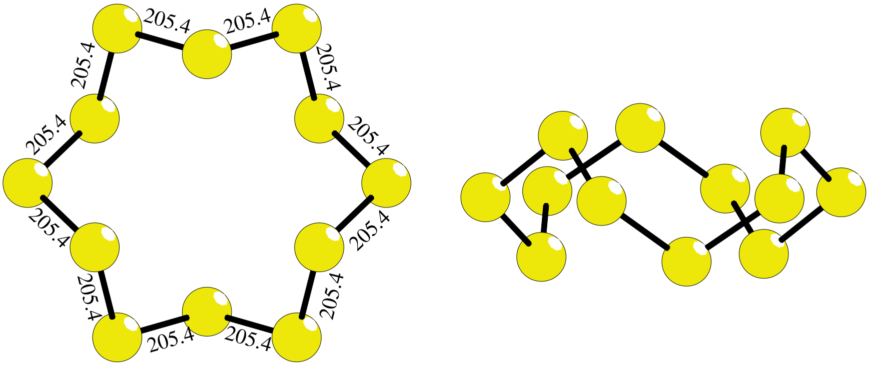


Figure 28 *Solid-state structure of $S_{12}{\cdot}CS_2$; $(S–S–S)_{av.}$= 106.2° and (S–S–S–S) = 87.9° (see ref. 87)*

The structure of S_{12} and its CS_2 solvate has been determined[86,88–90] and this revealed that the structure is an almost perfectly D_{3d}-symmetric ring (Figure 28). As seen by the only S–S–S–S torsion angle of 87.2°, the structure is unstrained and accordingly only one S–S bond lengths of 205.4 pm, prototypical for a single bond, was observed. This unstrained structure of S_{12} is also reflected in its thermodynamic stability that ranks second after the ground-state S_8 and is seen in the high-melting point of 148°C.

By contrast, the uneven-membered S_{13} homocycle[84,87] is strained and contains one long bond (207–211 pm) that is accompanied by two short bonds (198–199 pm) that enclose small torsion angles of 30–31° – again reminiscent of S_7 (Figure 29).

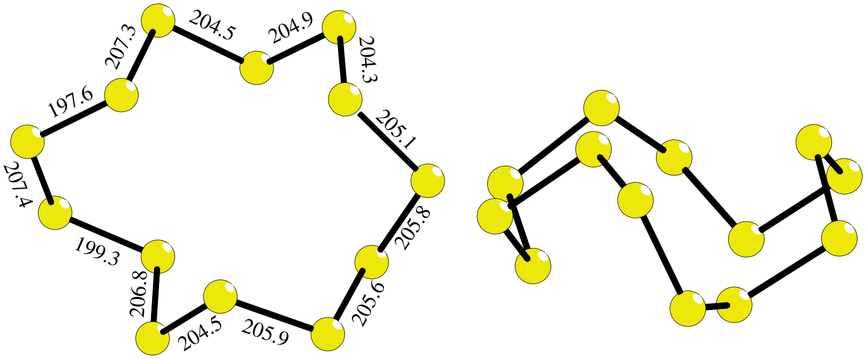


Figure 29 *Solid-state structure of one of the two independent S_{13} molecules in the structure; molecule 1 (shown): $(S–S–S)_{av.} = 106.4°$ and $(S–S–S–S) = 30.9°–116.3°$, av.: 85.3°, molecule 2: $(S–S) = 199.5–211.3$ pm, $(S–S–S)_{av.} = 106.1°$ and $(S–S–S–S) = 29.5°–114.1°$, av.: 96.9° (see ref. 85)*

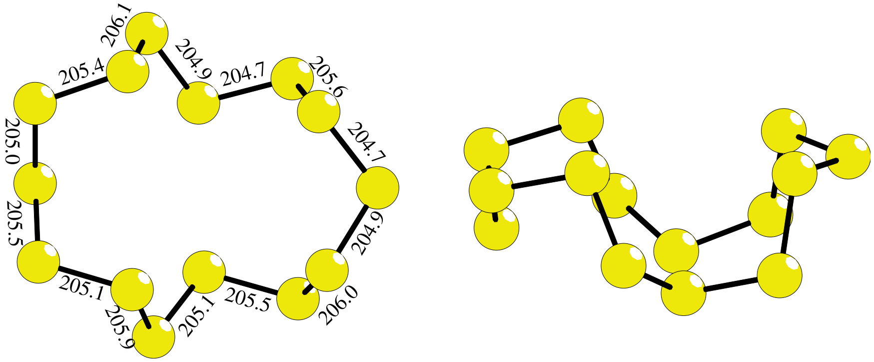


Figure 30 *Solid-state structure of S_{14}, $(S–S–S)_{av.} = 106.3°$ and $(S–S–S) = 72.5°–101.7°$, av.: 93.1° (see ref. 89)*

Upon addition of another S atom to give S_{14},[91] one reaches again a very stable even-membered homocycle that has little strain, as indicated by the range of torsion angles of 72.5–101.7 and therefore only a very narrow span of bond lengths of 204.7–206.1 pm, well in the range of normal single bonds (Figure 30).

7.1.5.9 Molecular E_{17}–E_{20} moieties

Astonishingly, in this large range at least one entry for each number 17–20 could be made. However, even entries only exist for S homocycles (18, 20), while uneven entries are only observed as cations (17, 19).

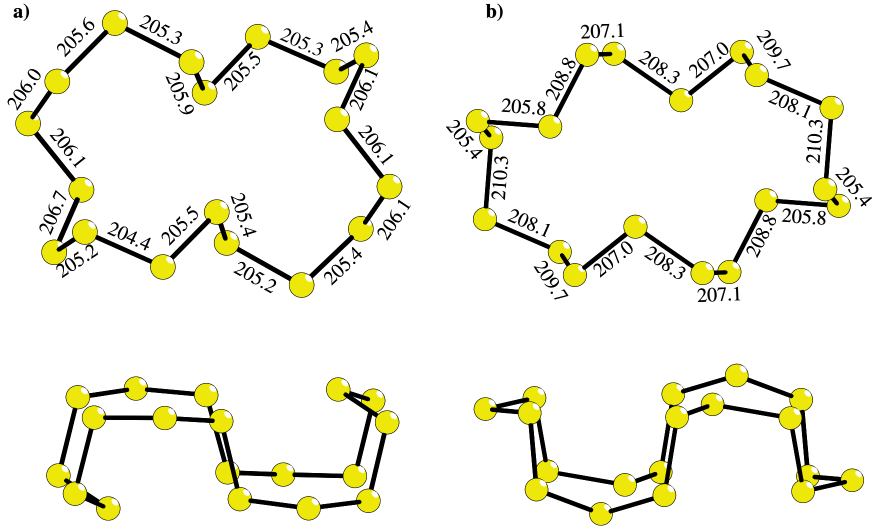


Figure 31 *Solid-state structure of α and β S_{18}. (a) α S_{18} (endo): $(S–S–S)_{av.}= 106.3°$ and $(S–S–S) = 79.5°–89.0°$, av.: 84.4°; (b) β S_{18} (exo): $(S–S–S)_{av.}= 106.3°$ and $(S–S–S–S) = 66.5°–87.8°$, av.: 80.0° (see refs. 90 and 91)*

Two forms of S_{18} were prepared:[88,90,92,93] α S_{18}[93] with an endoconformation of the ring (*cf.* Figure 31a) and β S_{18}[92] with an exoconformation (*cf.* Figure 31b).

By contrast to the homocyclic nature of all neutral E_n molecules with n up to 20, the largest known S and Se cations include two seven-membered rings in the chair conformation linked by a S_5 or Se_3 bridge. Their structures may be viewed as being electron precise in the Zintl sense with the two tricoordinate E atoms formally bearing the positive charge. Initially, the isolated S_{19}^{2+} structures in $S_{19}[MF_6]_2$ (M = As, Sb)[70,94] were viewed as rather esoteric outsiders, yet in recent years a number of closely related Se_{17}^{2+} structures[95,96] were determined which proves that such an $E_7–E_n–E_7^+$ ($n = 3, 5$) arrangement is likely and stable (Figure 32).

The presence of a very pronounced bond length alternation in both structures suggests that extensive charge delocalization occurs in these structures. This is likely achieved through a series of $n\mathrm{p}^2 \rightarrow n\sigma^*$ interactions that is related to those shown above for S_7 and Se_{10}^{2+}.

The largest of all isolated E_n moieties characterized by an X-ray structure is S_{20}, which contains the unique ring structure shown in Figure 33.[83,88,90,93] Unexpectedly, for an even-membered homocycle this S_{20} contains two long bonds at 210 pm that are flanked by short bonds (202 pm) and smaller enclosed torsion angles of 66° (see before: S_7, S_9, S_{11} and S_{13}). The long bond may also be responsible for the low-thermodynamic stability of dissolved S_{20}.

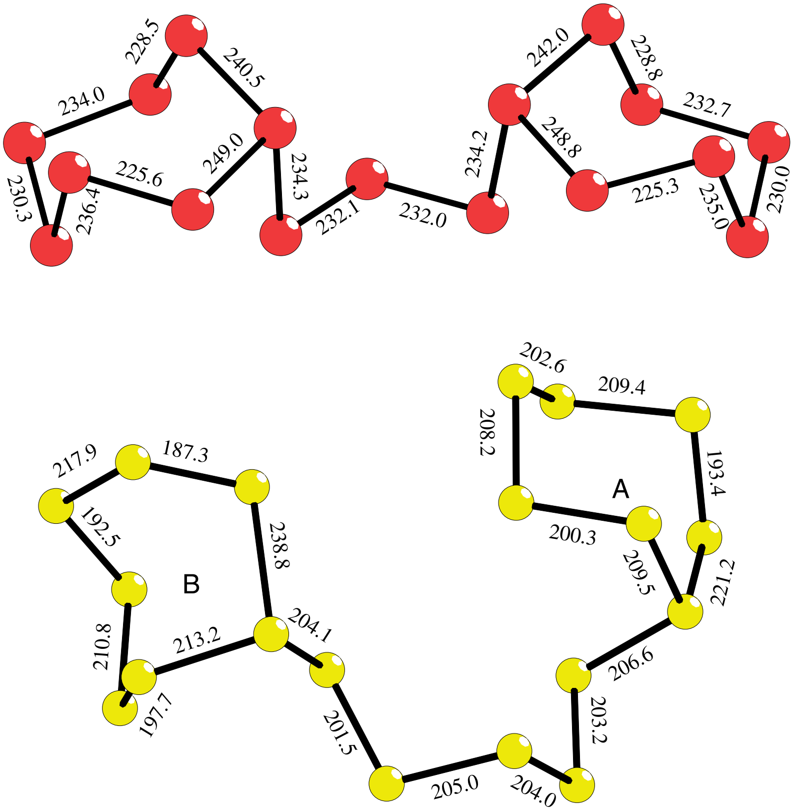


Figure 32 *Solid-state structure of the cation* Se_{17}^{2+} *in* $Se_{17}[NbCl_6]_2$ *(top)*[94] *and* S_{19}^{2+} *in* $S_{19}[AsF_6]_2$ *(see ref. 92) (down; ring B is disordered. Bond lengths are unreliable)*

7.1.6 Polyatomic Chalcogen Polymers and Polymeric Tellurium Cations

The ordering principle of this section is different to the preceding section on the isolated molecules or molecular ions. We start with the structures of the elements and then classify the polymeric Te structures by the number of atoms in the constituting homocycles, *i.e.* four-, five- and six-membered rings.

7.1.6.1 Fibrous ψ-S, grey Se and Te

Infinite helices are the building blocks of all polymeric neutral chalcogen structures. For Se and Te these semimetallic grey forms are the ground states;[97–101] for S the structure[102,103] is stable in the solid state at ambient conditions, but decomposes upon irradiation or heating with S homocycle formation. As expected from the trigonal crystal structures, the arrangement of

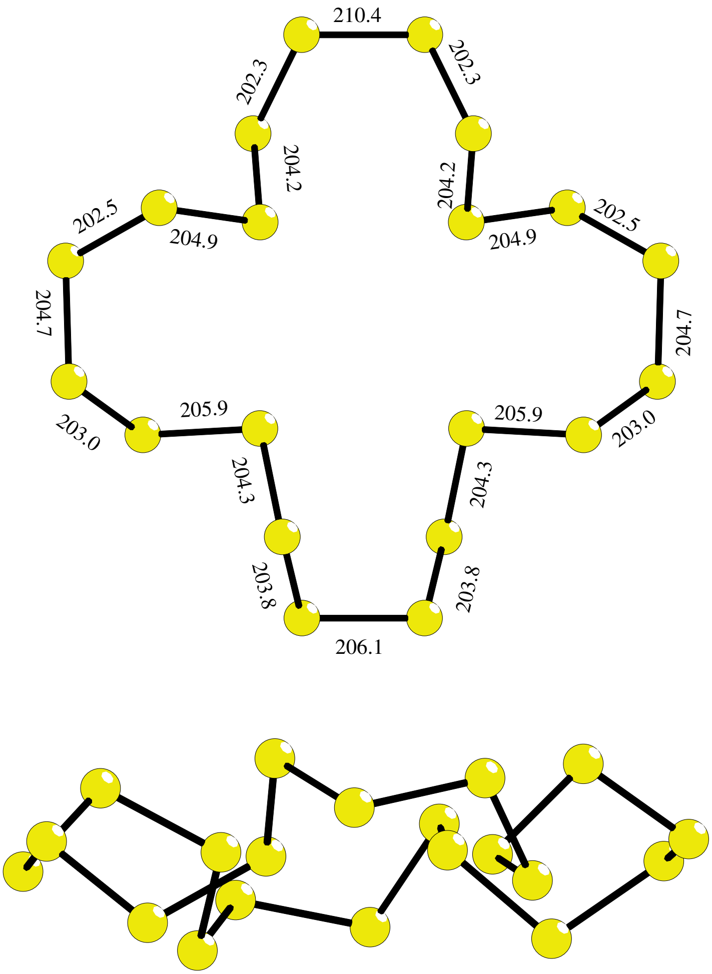


Figure 33 *Solid-state structure of orthorhombic* S_{20} *(see ref. 91)*

the individual helical chains is such that one central chain is neighbored by six parallel aligned chains (Figure 34b).

Overall one realizes from Figure 34 that the helical E structures also obey the simple rules sketched in the bonding section at the beginning of this chapter. Each of the heavier E atoms in the helices exhibits four stronger and two weaker secondary E–E interactions to E atoms of the neighboring chains (Se: 343.8 (4x) and 371.9 pm (2x), Te: 349.1 (4x) and 444.1 pm (2x)) and that are lower or at the sum of their van der Waals radii of 380 (Se) and 420 pm (Te). An (local) MO interpretation of these contacts would be the delocalization of electron density of the occupied $n\mathrm{p}^2$ lone pairs into suitable empty orbitals, which are E–E antibonding. Thus, the E–E separations in the polymeric helical forms are increased by 1.5–5 pm if compared to completely isolated singly

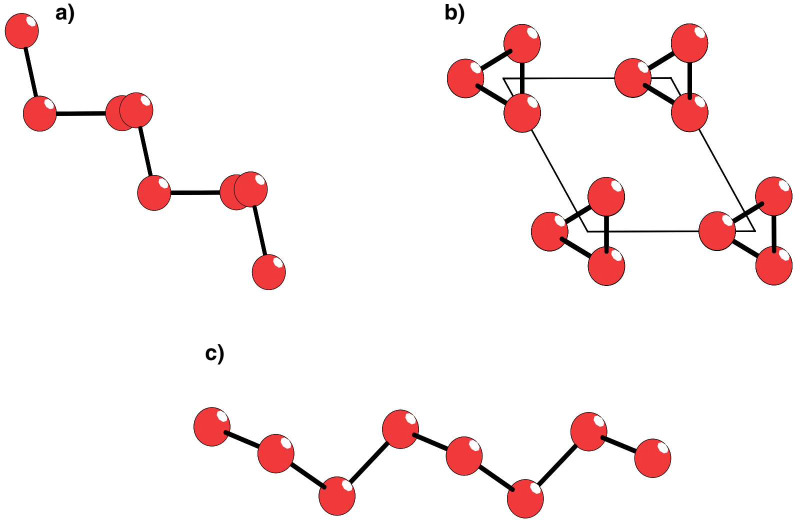


Figure 34 *Solid-state structure of grey Se. (see ref. 96) The structure of polymeric S (see refs. 100 and 101) and grey Te (see ref. 95) is similar (Se and Te are trigonal space group* $P3_121$*, that of S is monoclinic and slightly distorted). E–E distances: 206.6 pm (S), 237.5 pm (Te). (a) A view that shows the orientation of the chains with respect to the* np^2*–*np^2 *lone pair repulsion. The E–E–E–E torsion angles are: 85.3° (S), 100.6° (Se), 100.7° (Te); (b, c) views showing the helical arrangements of the chains. The E–E–E bond angles are: 106.0° (S), 103.1° (Se) and 103.1° (Te)*

bonded E–E units without secondary interactions. From the extended solid-state point of view, this is the molecular origin of the semiconducting properties of Se and Te, *i.e.* the delocalization of electrons from the valence band (built from the $n\mathrm{p}^2$ lone pair orbitals) into the charge band (formed by empty antibonding orbitals). The pressure dependence of the structures of Se and Te was studied.[98,100,101]

7.1.6.2 Polymers that Contain Te_4 Squares: Te_4^{2+}, Te_7^{2+} and Te_{10}^{2+}

Polymeric Te cations that contain Te_4 squares are abundant. It appears that some knowledge of these cations being once isolated, 6π Hückel aromatic squares is preserved in the structures of the polymeric compounds. They may formally be derived from a dimerization of Te_4^{2+} giving the isolated Te_8^{4+} cation shown in Figure 23 above. Opening of one long edge and polymerization then leads to the structure shown in Figure 35 below ((Te_4)(Te_{10})[Bi_4Cl_{16}]).

This polymeric structure may be understood in the classical Zintl sense with the tricoordinate Te atoms bearing the positive charges. However, the structural parameters with long Te–Te bonds connecting the squares and relatively short bonds within the squares suggest that the charges are delocalized through the $n\mathrm{p}^2 \rightarrow n\sigma^*$ interactions as shown in Figure 35c.

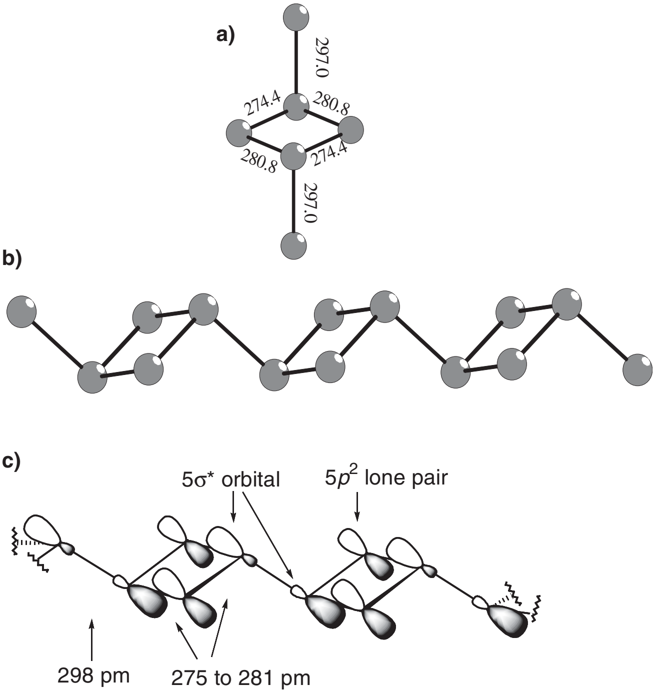


Figure 35 *Solid-state structure of polymeric* Te_4^{2+} *in* $(Te_4)(Te_{10})[Bi_4Cl_{16}]$*. (a, b) Structural parameters and orientation; (c) charge delocalization*

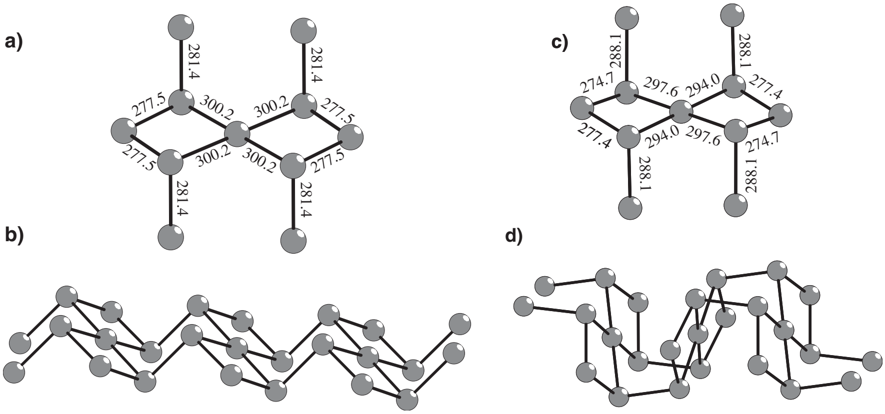


Figure 36 *Solid-state structure of polymeric* Te_7^{2+} *in* $(Te_7)[Be_2Cl_6]$ *(a, b, left) and* $(Te_7)[WOBr_4][Br]$ *(c, d, right)*

A variant of this structure, which may be rationalized by adding a Te_3 unit to each Te_4 square in Figure 35 above is shown in Figure 36, the polymeric Te_7^{2+} cations.

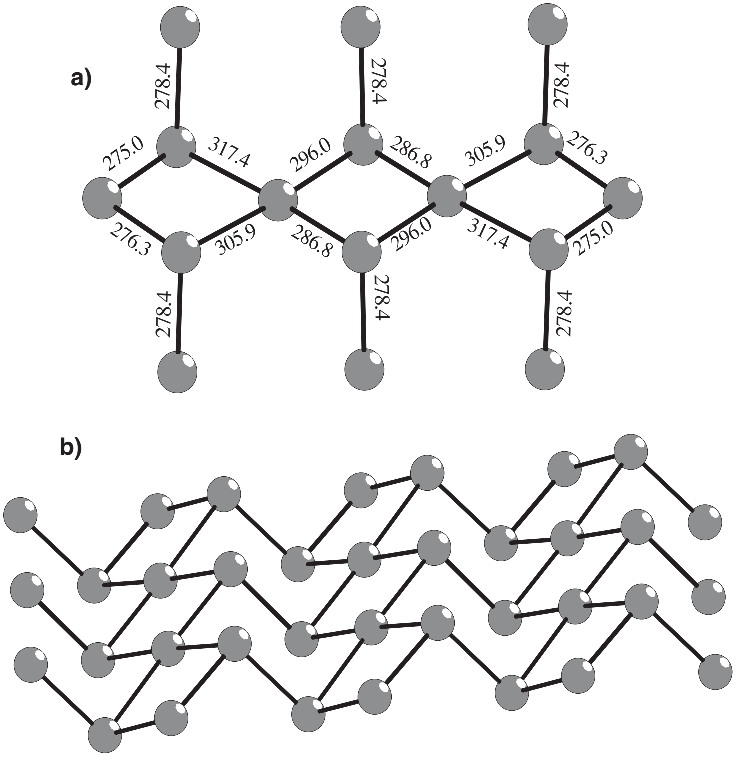


Figure 37 *Solid-state structure of polymeric* Te_{10}^{2+} *in* $(Te_4)(Te_{10})[Bi_4Cl_{16}]$

The polymeric Te_{10}^{2+} structure is again very closely related and may be rationalized by addition of another Te_3 unit to one of the squares in the Te_7^{2+} structure. It is shown in Figure 37.

The structures of these polymeric Te_4^{2+}, Te_7^{2+} and Te_{10}^{2+} cations exhibit the same basic structural features:

(i) Elongated Te–Te bonds connecting the squares (278–297 pm).
(ii) Normal Te–Te bonds along the outmost edges of the planar sheets of anellated squares (275–281 pm).
(iii) Long bonds around the central, square planar tetracoordinated Te atoms (286–317 pm, only Te_7^{2+} and Te_{10}^{2+}).

Two likely rationals have been discussed to account for this bonding situation (Figure 38a and b).

The electron precise bonding, as sketched in Figure 38a, was based on the structural analogy between the Te_7^{2+} structure and those of the Te_7^{2-} and Te_6^{5-} anions that contain similar square planar coordinated Te atoms. However, it is unlikely to invoke the presence of a dianionic Te site within the

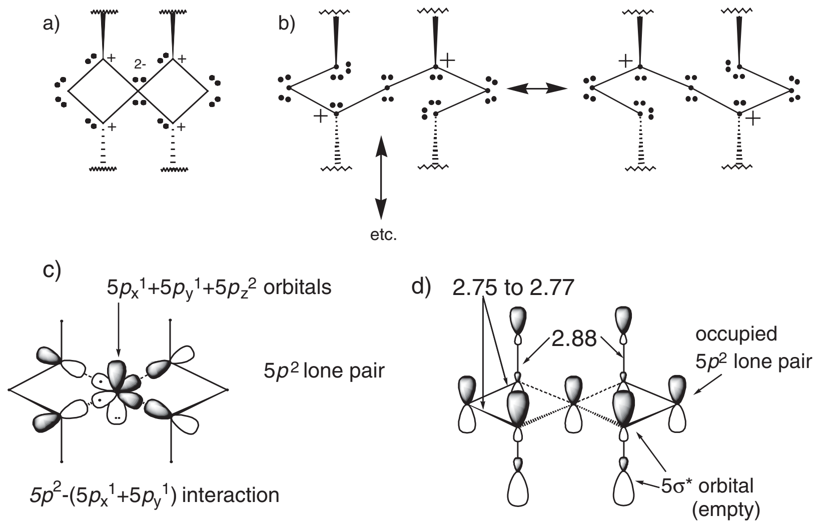


Figure 38 *Bonding within the structures of* Te_7^{2+} *as well as the closely related structure of* Te_{10}^{2+}*: (a, b) two possible Lewis structures; (c) MO rationalization of the more likely bonding as in (b); (d) positive charge delocalization within the structure by* $np^2 \rightarrow n\sigma^*$ *interactions that lead to the observed structural parameters*

framework of a Te dication. Therefore, the situation sketched in Figure 38b that assigns a bond order 0.5 to the four bonds around the central planar Te atom appears more likely. Moreover, this arrangement may easily be converted into the MO picture (Figure 38c) and one should note the relation of the MOs to those in XeF_4 (Rundle model). In such a scheme, the positive charges are delocalized over four atoms. The structural parameters suggest that an additional $n\mathrm{p}^2 \rightarrow n\sigma^*$ interaction delocalizes the positive charges onto all atoms (Figure 38d) and accounts for the long separations of the Te atoms connecting the planar sheets.

7.1.6.3 A Polymer that Contains Te_5 Homocycles: Te_6^{2+}

The structure of Te_6^{2+} in $Te_6[MCl_6]$ (M = Zr, Hf)[104] is the only structurally characterized polychalcogen compound that contains an E_5 homocycle (Figure 39). Its structure and bonding is very closely related to the situation found in $Te_7[AsF_6]_2$ (shown in, Figure 40a–d).

7.1.6.4 Polymers that Contain Te_6 Homocycles: Te_7^{2+} and Te_8^{2+}

Another series of polymeric Te cations is built from Te_6 rings that are connected by $-Te_n-$ chains with $n = 1, 2$. In one of the known structures, the Te_6 ring exhibits the chair conformation, while in all remaining structures it exhibits the boat conformation as in the structure of the isolated Te_6^{2+} cation shown above in Figure 9.

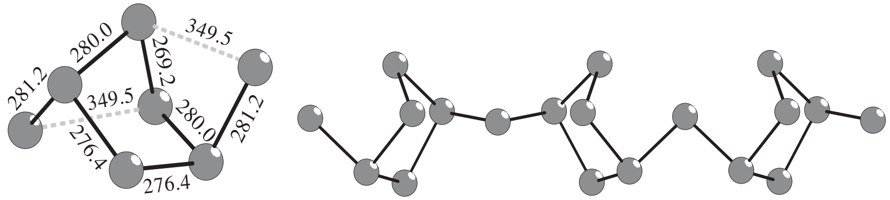


Figure 39 *Solid-state structure of polymeric* Te_6^{2+} *in* $Te_6[ZrCl_6]$

The first of those polymeric structures to be observed was that of $Te_7[AsF_6]_2$.[105] Its structure is related to that of polymeric Se_6I^+[106,107] such that the Te atoms that connect the Te_6 homocycles take the place of the I atoms in Se_6I^+. However, the bridging of I atom in the latter structure has two electrons more than the Te atom in Te_7^{2+} and therefore the Se_6–I–Se_6 bridge is almost linear, but the Te_6–Te–Te_6 linkage is bent (Figure 40a and b). The structure of this Te_7^{2+} cation is electron precise according to the Zintl concept and the two tricoordinate Te atoms formally bear the positive charges. However, according to the analysis of the Te–F cation anion contacts, extensive charge delocalization occurs. Thus, the additional bonding interactions, as in

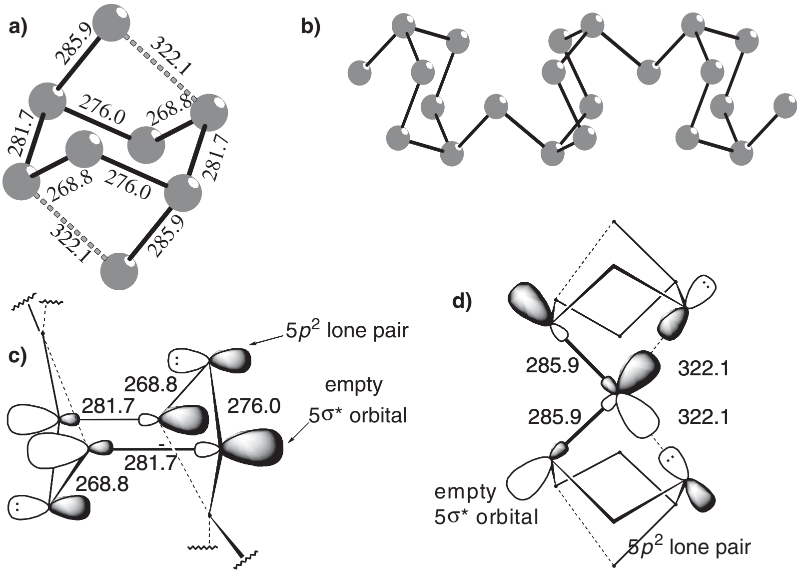


Figure 40 *(a, b) Solid-state structure of polymeric* Te_7^{2+} *in* $Te_7[AsF_6]_2$ *(see ref. 103). (c, d) Additional* $np^2 \rightarrow n\sigma^*$ *interactions that delocalize the positive charges and account for the range of the observed bond distances*

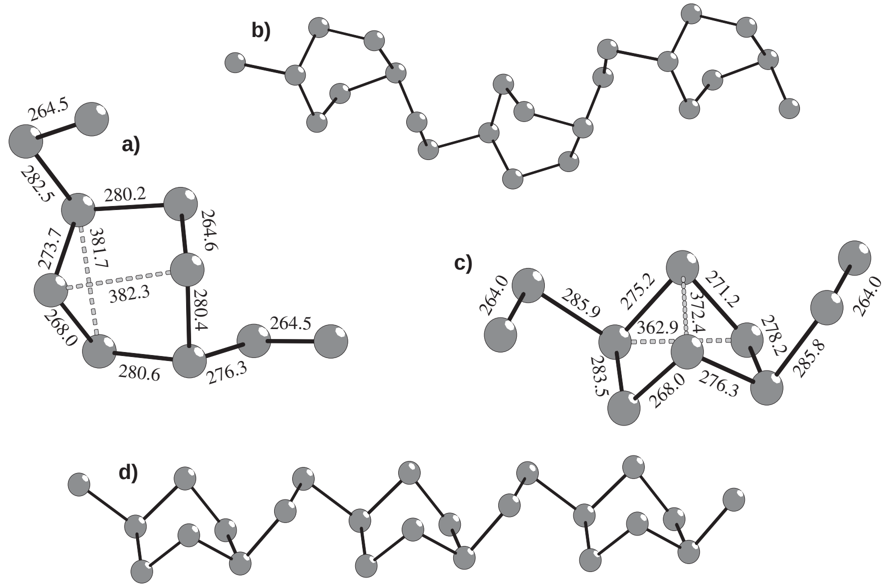


Figure 41 *(a, b) Solid-state structure of polymeric* Te_8^{2+} *in* $Te_8[Bi_4Cl_{14}]$ *(see ref. 107); (c, d) solid-state structure of polymeric* Te_8^{2+} *in* $Te_8[U_2Br_{10}]$ *(see ref. 106)*

Figure 40c and d, account for the observed bond length distribution and serve to delocalize the positive charges onto all Te atoms.

The structures of the two polymeric Te_8^{2+} cations known[108,109] are very similar and differ from the Te_7^{2+} structure in Figure 40 in that they have the Te_6 homocycle, in the (distorted) boat conformation, and that the Te_6 rings are connected by a Te_2 chain (Figure 41). A noteworthy feature of this Te_2 chain is the very short central Te–Te bond lengths of 264.0–264.5 pm. Again the structure may be understood as being Zintl precise with the two tricoordinate Te atoms formally bearing the positive charges. However, as inspection of the Te–Te bond distances in Figure 41 clearly suggests, there are additional interactions that delocalize the positive charges and thereby lead to the observed pronounced bond length alternation.

Within the Te_6 homocycle similar $n\text{p}^2 \rightarrow n\sigma^*$ interactions to the isolated Te_6^{2+} structure probably take place (Figure 10, see there). The unusually short Te–Te separation in the Te_2 bridge may also be accounted for by such an interaction (Figure 42).

With an interaction as in Figure 42, the two $5\sigma^*$(Te–Te) orbitals that include the formally positively charged tricoordinate Te atoms accept electron density from the occupied 5p^2 lone pair orbitals of the two central Te atoms. In this way the central Te–Te bond is shortened to about 264 pm through the two

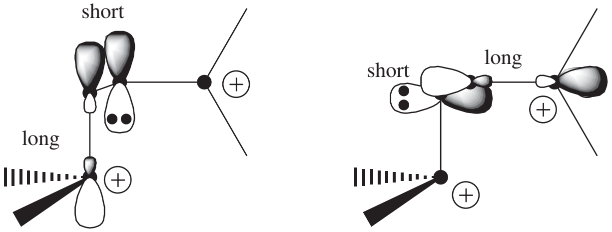


Figure 42 *The two $np^2 \rightarrow n\sigma^*$ interactions that account for the short central, but long adjacent Te–Te bonds within the Te_2 bridge that connects the Te_6 homocycles in polymeric Te_8^{2+}*

independent $n\mathrm{p}^2 \rightarrow n\sigma^*$ interactions, while the two Te–Te bonds to the tricoordinate Te atoms are lengthened to about 276–286 pm.

At this place one should note that a Te = Te double bond, as in gaseous Te_2, has a distance of about 255 pm. Thus, the short Te–Te bonds of 264 pm in the Te_2 bridge are closer to the Te–Te separation of a double (255 pm) rather than a single bond (284 pm).

7.1.7 Conclusion

In this chapter, we demonstrated that the restriction of building a compound with only one type of an element is not a restriction at all and a multitude of neutral, cationic as well as anionic polychalcogen structures is currently known. As expected for the more electronegative nonmetal (S) and meta metals (Se, Te), the bonding within these moieties is covalent and a small number of interactions, namely, $n\mathrm{p}^2$–$n\mathrm{p}^2$ lone pair repulsion, π- and π*–π* bonding as well as $n\mathrm{p}^2 \rightarrow n\sigma^*$ interactions, are sufficient to rationalize the structures and account for the bond lengths alternations or weak transannular interactions that are often found.

In the cationic systems, the positive charges are delocalized over almost all atoms, even if the individual structures may be described by the Zintl concept that assigns localized positive charges to tricoordinate E atoms. It appears that the Zintl concept is better suited, yet not sufficient, to describe the structures of the heavier chalcogen elements.

The history of polychalcogen cations is long standing and started in the end of the 18th century. However, the area is still vivid and recent additions to the chemistry of the polychalcogen cations mainly include the use of solid-state chemistry to arrive at new Se and Te structures as well as the extensive use of quantum chemical calculations to understand the structures and bonding within the compounds described in this chapter. It looks as though both areas of greatest activity are far from being mature and one can expect a further fruitful development of this delicate but very interesting area of fundamental chemistry.

Acknowledgement

This chapter is dedicated to Ralf Steudel for all the beautiful compounds he and his co-workers synthesized during his career. Thank you!

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CHAPTER 7.2

Organochalcogen Multication Species

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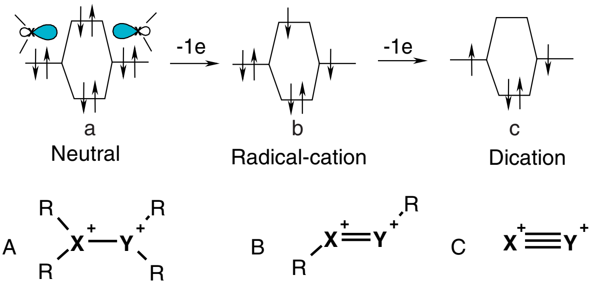
7.2.1 Introduction

1,2-dications – unique compounds with *two* cationic centers located at two *directly connected* atoms have unusual structure and reactivity. Despite the extremely strong electrostatic repulsion of the two positive charges, these compounds often possess remarkable kinetic stability.[1] The rapid development of chemistry of 1,2-dications[2,3] was facilitated by several excellent reviews[4–8] and features articles[9] dealing with small gas phase 1,2-dications as well as with certain types of organic dications containing C^+–C^+(see ref. 10), N^+–N^+ (see ref. 11) and S^+–S^+ (see refs. 12–14) moieties.

On the very basic level, kinetic stability of 1,2-dications can be explained by molecular orbital (MO) theory. When loss of two electrons leading to the formation of a dication (double oxidation) occurs from an antibonding MO, it results in the formation of a normal (two-electron/two-center) chemical bond (Scheme 1).

Depending on the initial connectivity, removal of two electrons from two chalcogen atoms may lead to the formation of a single (A), a double (B) or a triple (C) bond. Surprisingly, there are no experimental examples that correspond to case B although such species are possible intermediates in monooxygenation of disulfides. The parent chalcogen dications such as O_2^{2+}, SO^{2+}, S_2^{2+} correspond to case C.[15–18] The results of computational study at the CAS/CEP-N11G(2d) level show that O_2^{2+} possesses the largest thermodynamic instability together with a large kinetic stability.[19] Since O_2^{2+} is isoelectronic to



Scheme 1

N_2 and the oxygen atoms are connected through a formal triple bond, the O–O distance in the O_2^{2+} dication, 1.073 Å[20–22] is the shortest known O–O distance,[23] which is 0.134 Å shorter than the bond in molecular oxygen and is considered to be the shortest bond between any two heavy atoms.[21] For heavy chalcogens π-overlap of a triple bond becomes less efficient with longer bond distances.

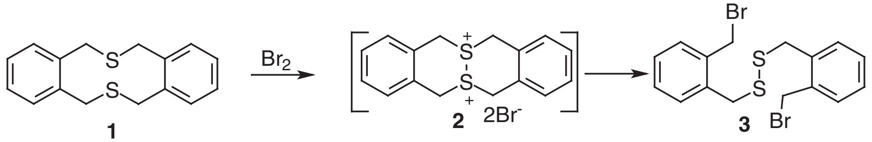
The most important of organic chalcogen dications are disulfonium dications (also called dithioether dications) – compounds with two positively charged sulfonium atoms connected by a single bond.

7.2.2 S–S Dications

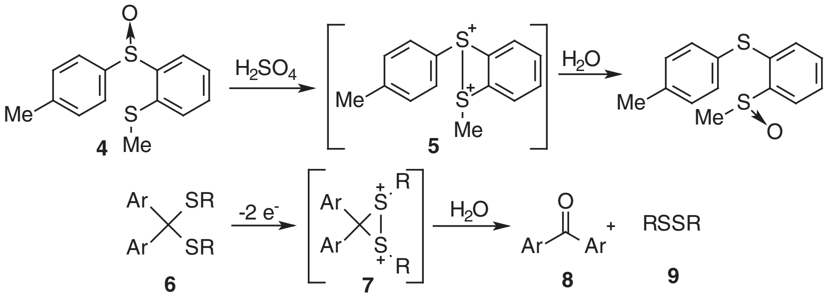
7.2.2.1 Discovery of Disulfonium Dications

At the beginning of the last century, Bruning and Autenrieth[24] suggested for the first time that the reaction of cyclic sulfide **1** with bromine results in formation of a disulfonium dication **2**. It was shown later that the actual reaction product is dibromodisulfide **3** (Scheme 2).[25]

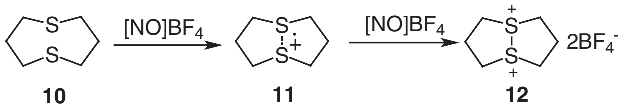
Oae and Numata[26] proposed intermediate formation of a S–S dication **5** in order to explain migration of the oxygen occurred when **4** was treated with concentrated sulfuric acid. Similarly, Ruffato and Miotti[27] proposed formation of a disulfonium dication as a result of intramolecular interaction during the oxygen atom transfer from arylmethylsulfoxide to dialkyl disulfide. In 1974, Simonet *et al.*[28] suggested transient formation of an extremely unstable S–S dication **7** (Scheme 3) during electrochemical oxidation of thioketals **6** to afford disulfides **9** and carbonyl compounds **8** after hydrolysis.



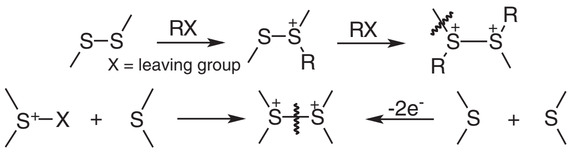
Scheme 2



Scheme 3



Scheme 4



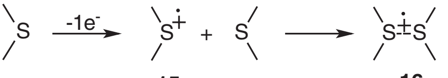
Scheme 5

The turning point in the understanding of the chemical nature of S–S dications came in 1976 when Musker reported synthesis, isolation and characterization of disulfonium dication **12** formed by the two-electron oxidation of 1,5-dithiacyclooctane **10** (Scheme 4).[29,30]

The unusually facile formation of a disulfonium dication from sulfide **10** is the result of stereochemical features of the eight-membered ring, which favor the formation of a transannular bond.[31] According to X-ray data (see in Chapter 7.1 Table 1), the distance between the two sulfur atoms in 1,5-dithiacyclooctane **10** is smaller than the sum of their van der Waals radii (3.75 Å), which results in a strong non-bonded interaction between the atoms confirmed by photoelectron spectroscopy and mass spectrometry.[32,33] This interaction and the sulfur–sulfur distance can be decreased as a result of bond formation with an electronegative substituent as in sulfoxide **13** or sulfoximine **14**.[34,35]

7.2.2.2 Synthesis of Disulfonium Dications

Retrosynthetic analysis provides two main approaches to the disulfonium-dication functionality. The first approach involves double alkylation of disulfides so far has been unsuccessful (Scheme 5).[36] All currently known methods


15 **16**

Scheme 6

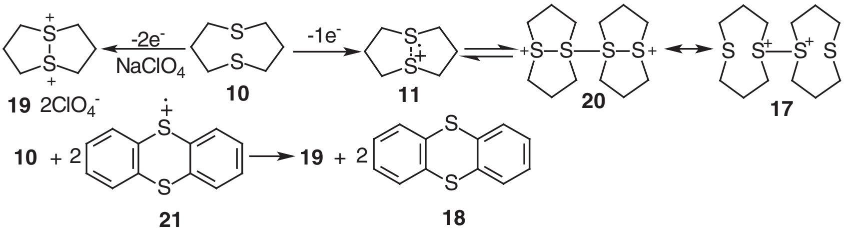
for synthesis of disulfonium dications involve formation of a S–S bond either by oxidative coupling of two sulfide moieties or by nucleophilic substitution at a sulfonium sulfur atom by a sulfide.

7.2.2.2.1 Oxidation of bis-Sulfides

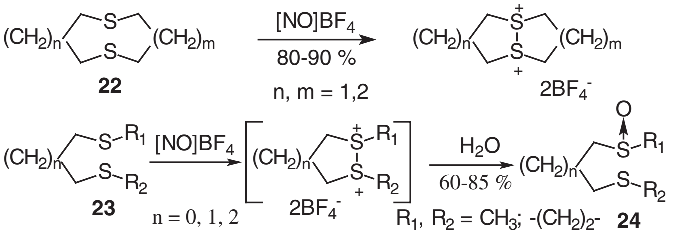
Mann and Cottrell[37] have established that electrochemical oxidation of aliphatic sulfides proceeds through a relatively stable radical-cation **15** localized on the sulfur atom. However, the more stable configuration corresponds to a molecular complex **16** derived from two sulfide molecules[38] according to ESR data.[39,40] The weak bond that is formed between the interacting sulfur atoms is a two-center three-electron (2c, 3e) bond.[41–43] Further oxidation results in formation of an ordinary single bond between the two positively charged onium ions. Similar observations were made recently for electrochemical behavior of thianthrene where the ratio of radical-cation to dimer could be easily controlled by concentration and temperature and studied quantitatively using *in situ* UV/Vis-NIR- and ESR-spectroelectrochemical measurements (Scheme 6).[44]

Musker and co-workers[45] were the first to study *intra*molecular generation of S–S dications through oxidation of aliphatic bis-sulfides. The most easily oxidized 1,5-dithiacyclooctane **10** was investigated in detail by cyclic voltammetry.[46] At low concentrations (0.05 mM), oxidation of bis-sulfide **10** occurs at 0.34 V giving disulfonium dication **19**.[45] At high concentrations, the only observed anodic wave (0.34 V) corresponds to one-electron oxidation of **10** to radical cation **11**. The latter undergoes reversible dimerization to give dication **20**.[45] A more detailed study[47] has shown that this oxidation occurs as a stepwise process with the second oxidation potential 20 mV lower than the first. Such anomalous electrochemical behavior of **10** presents more evidence for the formation of a S–S dication.[48] The first evidence that **10** can be oxidized chemically to a stable disulfonium dication was obtained by Shine and Piette.[49] While investigating the oxidative properties of the thianthrene radical cation **21**, they found that addition of 0.5 eq of sulfide **10** to **21** results in complete disappearance of the radical cation absorbance (Scheme 7).

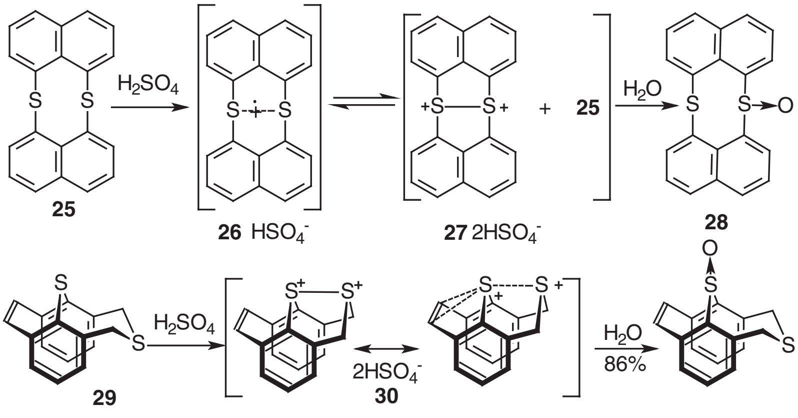
Musker[29] carried out a systematic study of the oxidation of several cyclic **22** and acyclic **23** bis-sulfides using nitrosonium salts. Several unstable dications were characterized as sulfoxides **24**. These oxidations proceed through stepwise transfer of two electrons from a bis-sulfide to the nitrosonium cation and the intermediate formation of the corresponding radical cation. Radical cations of 1,5-dithiacyclooctane **11** and 1,5-dithiacyclononane are sufficiently stable to be isolated as individual compounds (Scheme 8).[50]



Scheme 7



Scheme 8



Scheme 9

Addition of 1,5-dithiacyclooctane to zeolite CaY in the presence of molecular oxygen results in spontaneous oxidation to mono- and bis-sulfoxides through formation of the corresponding radical cation characterized by ESR and diffuse reflectance of UV–Vis spectroscopy.[51]

Most easily oxidized bis-sulfides can be transformed to S–S dications by concentrated sulfuric acid. According to the ESR data,[52] dissolving **25** in sulfuric acid establishes equilibrium between the starting sulfide **25**, dication **27** and radical cation **26**.[52] Oxidation of sulfide **29** to a dication **30** by sulfuric acid is facilitated by transannular interaction of the positively charged sulfur atom with the double bond (Scheme 9).[53]

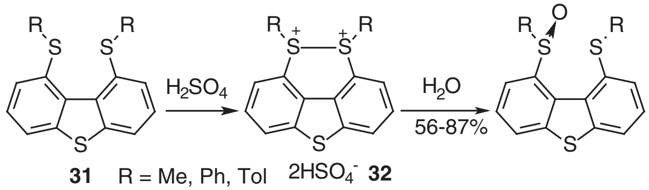
Sterically strained 1,9-dithiosubstituted dibenzothiophenes **31** are destabilized by repulsion of the lone pairs at the transannular sulfur atoms and can be also transformed to S–S dications by concentrated sulfuric acid (Scheme 10).[54–56]

Direct oxidation of bis-sulfides by trifluoromethanesulfonic anhydride was suggested only recently.[57] For example, treatment of **10** with triflic anhydride affords the corresponding dication salt **34** in high yield *via* intermediate formation of a sulfonyl sulfonium salt **33**.[58] A number of other cyclic and acyclic bis-sulfides **35** undergo facile oxidation to dications under these conditions (Scheme 11).[57]

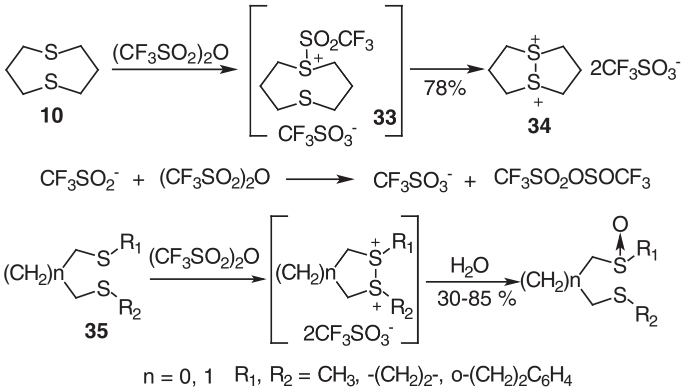
7.2.2.2.2 Interaction of H_2SO_4 with Mono-S-Oxides of bis-Sulfides

The second main approach to disulfonium dications is based on nucleophilic substitution at sulfonium sulfur atom by a sulfide. This approach is much more efficient and versatile than the direct oxidation of sulfides.[59–61]

Oae and Numata[26] were the first to postulate formation of a disulfonium dication in reaction of concentrated sulfuric acid with monosulfoxide of a bis-sulfide. Later Furukawa *et al.*[62] found that the crystalline hydrosulfate **36** can be prepared by reaction of the corresponding monosulfoxide **13** (or *N*-tosylimide **14**) with concentrated sulfuric acid. Formation of a symmetric dication **38** was confirmed by isolation of 1:1 mixture of deuterated sulfoxides **37** and **39**



Scheme 10



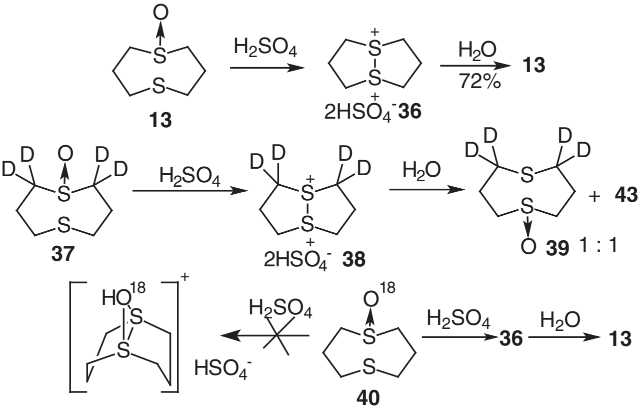
Scheme 11

after hydrolysis.[62] An alternative explanation for the equivalency of the sulfur atoms by assuming the formation of symmetric oxadisulfonium dication was eliminated by an experiment with O^{18}-labeled sulfoxide **40** (Scheme 12).[63]

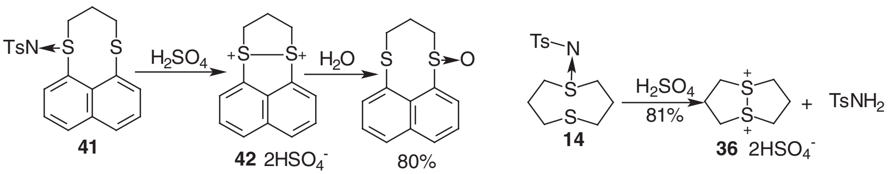
N-tosylimines can be used instead of sulfoxides. For example, treatment of sulfinilimines **14** and **41** with sulfuric acid yields dications **36** and **42** (Scheme 13).[64]

Use of concentrated sulfuric acid has certain disadvantages such as the relatively low stability of many of the resulting dications. In addition, the reaction mechanism is sometimes more complex than double protonation of sulfoxide oxygen followed by an S_N2-like nucleophilic substitution of water by the second sulfur atom.[65,66] Results with diastereomerically pure monodeuterated naphtho[1,8-b,c]-1,5-dithiocin-1-oxide **43** indicated that both formation of S–S dication **45** in concentrated sulfuric acid and subsequent hydrolysis of the dication proceeded with retention of configuration at the sulfoxide sulfur. Thus, the mechanism[67] involves double inversion, which proceeds through intermediate formation of sulfonyloxysulfonium salt **44** followed by a subsequent replacement of hydrosulfate anion by the second sulfur atom and overall retention of the configuration on sulfur (Scheme 14).[68]

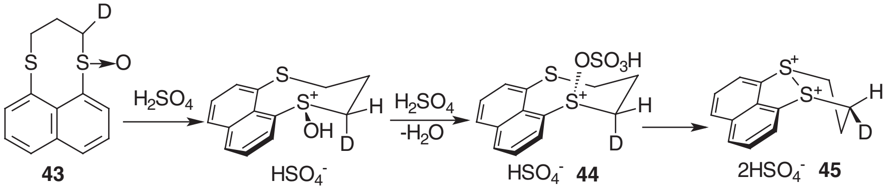
In agreement with this relatively complicated picture, the ^1H and ^{13}C NMR spectra of a S–S dication formed from 1,4-dithiane by this method are more complex than expected for such a symmetric molecule.[65] This observation can also be explained by equilibrium of dications with intramolecular and



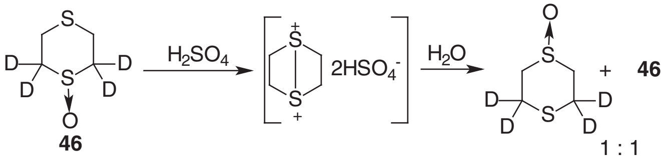
Scheme 12



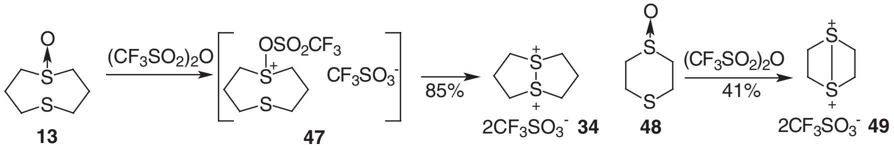
Scheme 13



Scheme 14



Scheme 15



Scheme 16

intermolecular S–S bonds.[69] Still, hydrolysis of the tetradeuterated derivative **46** results in regeneration of the starting monosulfoxide with the isotopic label equally distributed between the α and β positions (Scheme 15).[70]

7.2.2.2.3 Interaction of Triflic Anhydride with Monosulfoxides of bis-Sulfides

Many of these complications can be avoided when monosulfoxides are converted to the dications using triflic anhydride instead of concentrated sulfuric acid. This method was suggested by Furukawa *et al.*[71] in 1987. Reaction of triflic anhydride with a monosulfoxide[72] transforms it into trifluoromethanesulfonyloxysulfonium salt **47**, which undergoes clean intramolecular nucleophilic substitution of trifluoromethylsulfonate anion by the other sulfur atom with formation of the disulfonium dication **34** in a high yield (Scheme 16).[73]

Monosulfoxide **48** where the transannular interaction of the sulfur atoms is minimal also reacts with triflic anhydride to give a white precipitate of highly strained disulfonium dication **49**, which is extremely difficult to isolate.[71] Dication **49** exhibits only one ^{1}H NMR signal as a singlet at 3.80 ppm in agreement with a symmetric monomeric structure.[71]

Counterion plays an important role in the stability and structure of dications.[74] The length of the S–S bond in dication **34** is 2.13 Å, which is slightly larger than the S–S bond length in disulfides (2.08 Å), but considerably less than the S–S distance in **10** – 3.27 Å.[75] Computational data show reasonable agreement with the experimental structure.[76,77]

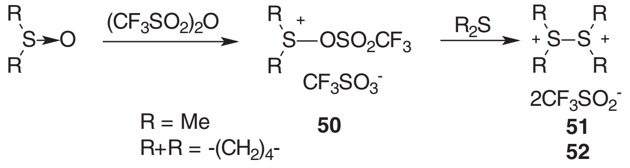
More recently, this method has been extended to preparation of a variety of disulfonium dications from both acyclic and cyclic bis-sulfides, including very labile dications not observed when other methods were used.[78] Thus, simple acyclic S–S dications were prepared by an *intermolecular* reaction of a monosulfide, a monosulfoxide and triflic anhydride.[79] In the first step, reaction of triflic anhydride with dimethylsulfoxide generates a highly electrophilic[80] complex **50** (dimethyl sulfide ditriflate).[81] The latter reacts with dimethyl sulfide to give labile tetramethyldisulfonium dication **51** identified by NMR spectroscopy.[79] In a similar manner, bis-(tetramethylene)disulfonium dication **52** is obtained from tetrahydrothiophene and its S-oxide (Scheme 17).

7.2.2.2.4 Reactions Involving Intermediate Formation of Disulfonium Dications

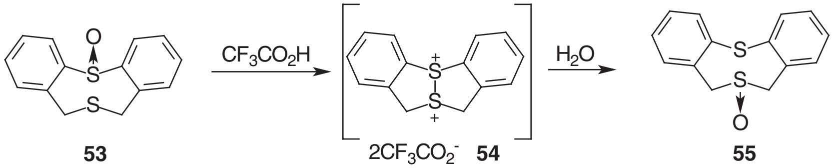
Acid-catalyzed migration of an oxygen atom from a sulfoxide to sulfide is one of the first examples where an intermediate formation of a S–S dication was proposed.[26] Recently, such intermediates were observed by physical methods. Kinetic studies suggested that an intramolecularly formed S–S dication **54** was involved in isomerization of sulfoxide **53** to **55** under influence of trifluoroacetic acid (Scheme 18).[82]

Reaction of S-oxide of 1,4-dimethylthiobenzene **56** with trifluoroacetic acid provides another example of an oxygen atom migration that proceeds through a dication. The dication is in rapid equilibrium with the protonated sulfoxide **57** (Scheme 19).[83]

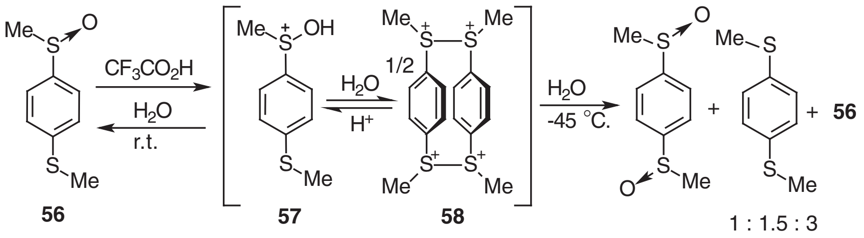
Musker and Doi[84] reported convincing kinetic evidence for the intervention of a disulfonium dication during reduction of sulfoxide **13** with iodide in



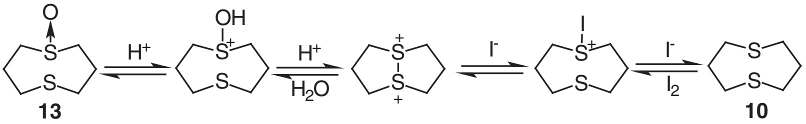
Scheme 17



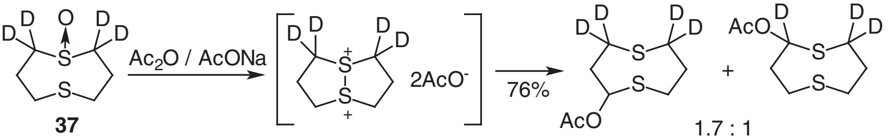
Scheme 18



Scheme 19



Scheme 20



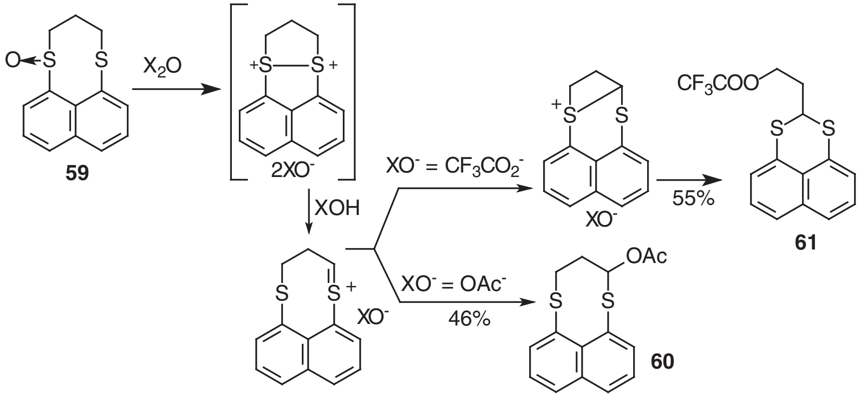
Scheme 21

aqueous acid. The reaction proceeds a 10^6 times faster than reduction of dimethylsulfoxide under the same conditions. The rate of the reaction was essentially independent of the iodine concentration, but displays a second-order dependence on the acid concentration. These experiments strongly suggested formation of a disulfonium dication as the rate-limiting step (Scheme 20).[84]

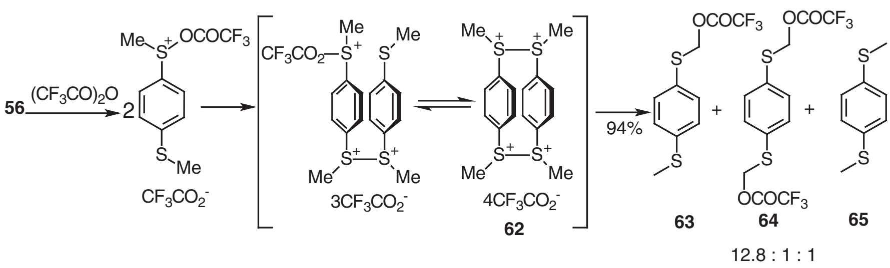
Monosulfoxide **13** undergoes the Pummerer rearrangement when treated with acetic anhydride in the presence of sodium acetate.[85] The experiments with tetradeuterated and ^{18}O-labeled sulfoxide confirm intermediate formation of a dication.[86] The ratio of 2,8,8-trideuteriated to 4,4,6,6-tetradeuteriated product **37** is equal to the intramolecular isotope effect k_H:k_D = 1.7 (Scheme 21).[85]

The differing nucleophilicity of acetate and trifluoroacetate anion determines the direction in which naphtho[1,8-b,c]-1,5-dithiocine-1-oxide **59** rearranges on treatment with acetic and trifluoroacetic anhydrides. In both cases the reaction proceeds through formation of a disulfonium dication, but the final products are different. When acetic anhydride is used, the reaction affords the corresponding α-acetylsulfide **60** – a normal product of the Pummerer rearrangement, while trifluoroacetic anhydride causes isomerization with formation of dithioacetal **61** (Scheme 22).[87]

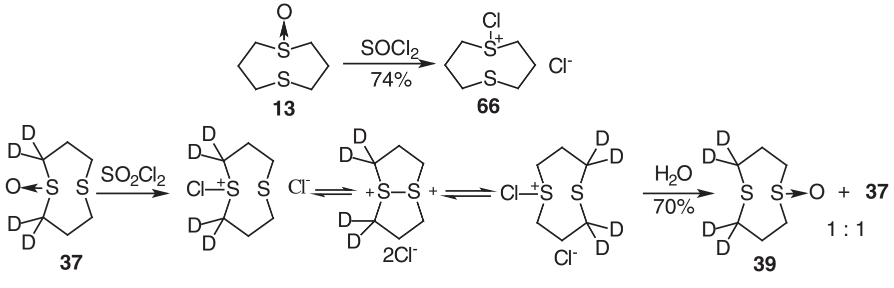
Reaction of *p*-dimethylthiobenzene sulfoxide **56** with trifluoroacetic anhydride results in a mixture of sulfide **65** and the corresponding mono- and disubstituted products of the Pummerer rearrangement **63**, **64** *via* intermediate disulfonium dication **62** (Scheme 23).[88]



Scheme 22



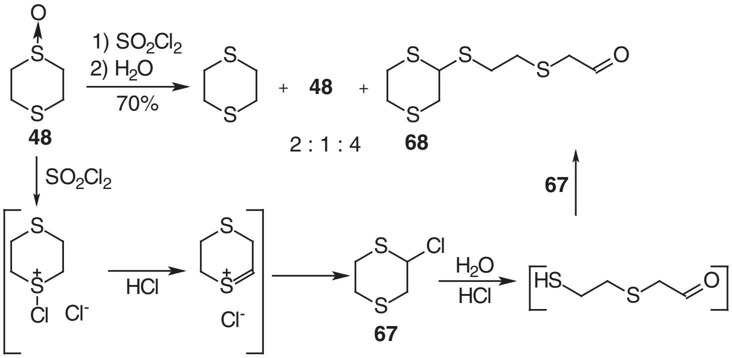
Scheme 23



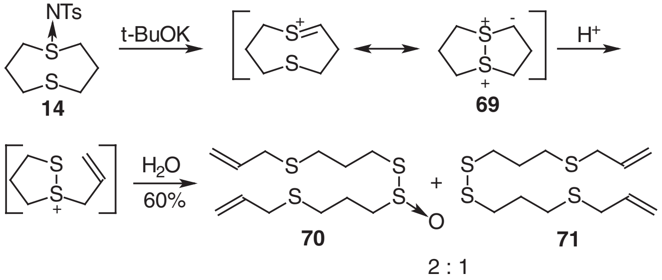
Scheme 24

Another example that illustrates formation of a disulfonium dication as an intermediate was found in the reaction of sulfoxide **13** and thionyl chloride. Instead of the normal α-chlorosulfide Pummerer product, the reaction leads to a stable chlorosulfonium salt **66**.[89] Hydrolysis of the salt obtained from 2,2,8,8-tetradeuteriated sulfoxide **37** results in a 1:1 mixture of the two possible isomers, thus indicating that the chlorosulfonium salt does exist in rapid equilibrium with a symmetric S–S dication (Scheme 24).

On the other hand, 1,4-dithiane monosulfoxide **48** reacts under the same conditions like a simple aliphatic sulfide. It is suggested that formation of the



Scheme 25



Scheme 26

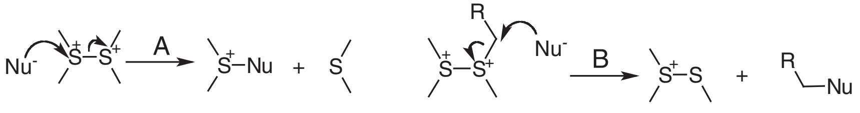
aldehyde **68** proceeds through α-chlorosulfide **67** – the product of the Pummerer rearrangement (Scheme 25).[89]

While reaction of strong bases with ordinary sulfinylimines gives Pummerer products such as *gem*-thioacetals and vinylsulfides,[90] sulfinylimines of certain bis-sulfides are converted by strong bases to ylides of the corresponding S–S dications, which undergo further transformations.[64] Thus, reaction of 1,5-dithianecyclooctane monosulfylimine **14** with potassium *tert*-butoxide affords a mixture of thiosulfinate **70** and disulfide **71**. Formation of the ring-opened products in this case is explained by α-deprotonation of the disulfonium dications to give the corresponding ylide **69**, which undergoes β-elimination (Scheme 26).[64,91]

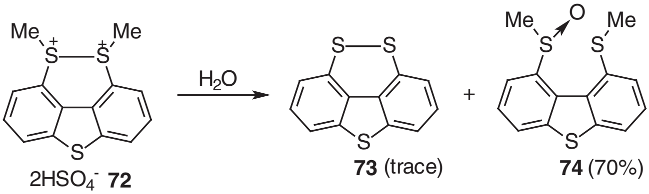
7.2.2.3 Chemical Properties of Disulfonium Dications

7.2.2.3.1 Interaction of Disulfonium Dications with Nucleophiles

Reactions of disulfonium dications with nucleophiles can follow two pathways in which, depending on the nature of the dication and nucleophile, nucleophilic substitution can occur at either the onium sulfur atom or at the α-carbon atom (Scheme 27).



Scheme 27



Scheme 28

The most typical and well-represented reactions involve nucleophilic substitution at the sulfonium atom (for example, hydrolysis to give monosulfoxides). This direction of attack is preferred because of the lower energy of S–S bonds and the decreased sterical hindrance at a trisubstituted sulfur atom compared with the hindrance at a tetracoordinated carbon atom.

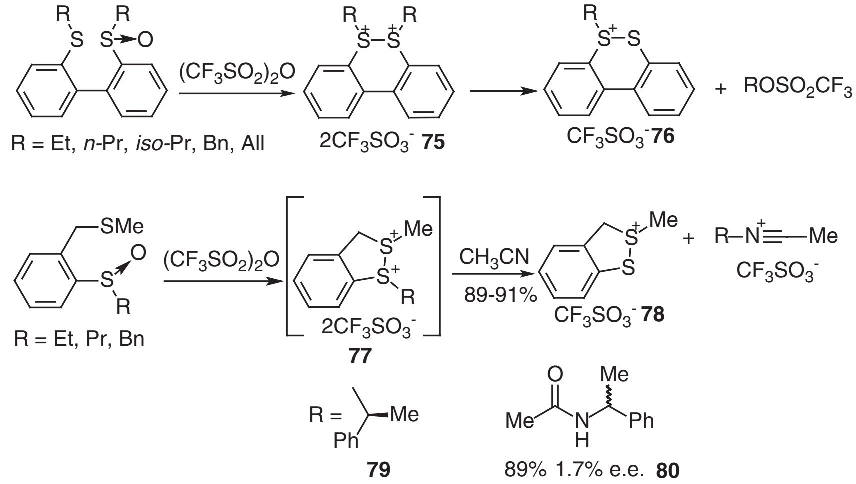
On the other hand, cleavage of the S–C bond is facile in nucleophilic substitutions involving sulfonium salts[92] and the leaving ability of the dialkylsulfide group compares with that of a bromide ion. As a result, there are several examples of type **B** substitutions in the literature.

Decomposition of highly reactive disulfonium dications in sufficiently nucleophilic medium is accompanied by formation of disulfides. Even hydrolysis of disulfonium dications generated from sterically rigid bis-sulfides often affords some disulfide as a by-product in addition to the monosulfoxide main product. For example, hydrolysis of dication **72** yields sulfoxide **74** and trace amounts of heterocycle **73** (Scheme 28).[56]

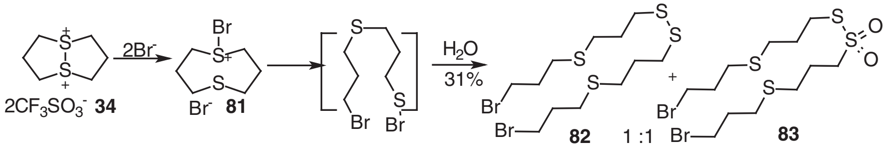
Dealkylation of labile disulfonium dications **75** derived from 2,2′-bis(alkylthio)-biphenyls gives rise to thiosulfonium salt **76**. This reaction can also be classified as nucleophilic substitution at the α-carbon atom. The intermediate dication **75** is highly reactive, but can be detected spectroscopically (Scheme 29).[93]

The propensity of S–S dications to undergo dealkylation was found to decrease in the order of methyl > ethyl > benzyl. This order of reactivity parallels the increase in the stability of the corresponding carbocations.[94] Dealkylation of dication **77** affords thiosulfonium salt **78** in quantitative yield.[95] Kinetic studies suggest S_N1 mechanism of dealkylation. In addition, reaction of sulfoxide **79** with a substituent chiral at the α-carbon results in racemic amide **80** after hydrolysis.

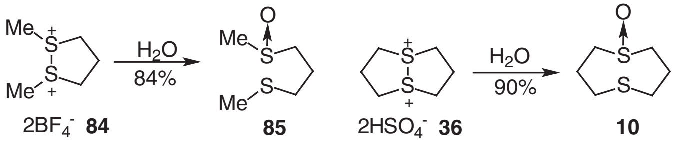
Nucleophilic substitution at the α-carbon atom does not occur in the case of the most studied and stable bicyclic disulfonium dications.[96] Although the reaction of dication **34** with bromide ions formally leads to the S–C bond cleavage, the reaction mechanism involves initial nucleophilic attack at the sulfonium atom by the bromide anion. The bromosulfonium salt intermediate



Scheme 29



Scheme 30



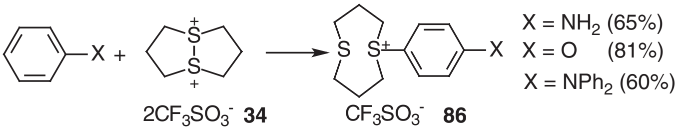
Scheme 31

81 undergoes further transformations yielding disulfide **82** and thiosulfonate **83** after hydrolysis of the reaction mixture (Scheme 30).

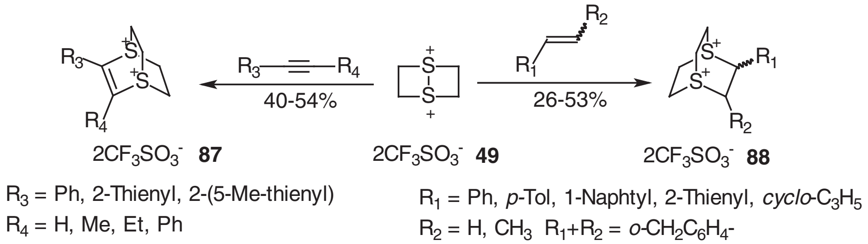
Regardless of their structure, all disulfonium dications are easily hydrolyzed to form the corresponding monosulfoxides in quantitative yield. The mechanism involves direct nucleophilic substitution at sulfonium sulfur.[29] For example, hydrolysis of monocyclic **84** and bicyclic **36** dications leads to sulfoxides **85** and **10** in high yield (Scheme 31).[62]

Reaction of disulfonium dication **34** with electron donor aromatic compounds also affords products of substitution at the sulfonium atom. For example, reaction of dication **34** with aniline, phenol and triphenylamine leads to the corresponding *para*-substituted sulfonium salts **86** (Scheme 32).[97]

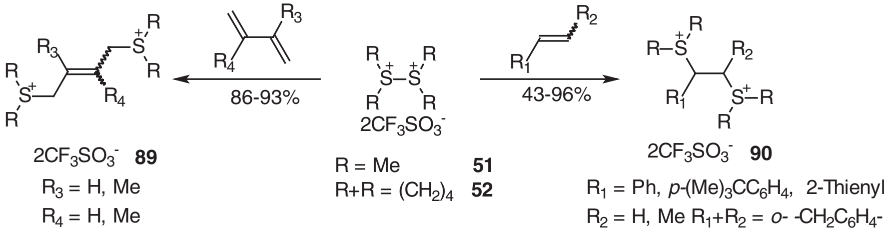
Disulfonium dications also interact with non-aromatic π-bonds. This reaction is the only known example in which a 1,2-dication adds to alkenes and



Scheme 32



Scheme 33



Scheme 34

alkynes. The reaction proceeds under mild conditions and leads to products having the simultaneous addition of two sulfonium groups – disulfonium salts bicyclo[2.2.2]octane skeleton **87** and **88** (Scheme 33).[98]

Reaction with alkenes is sensitive to steric factors – in the case of dication **49**, only reaction with mono- and 1,2-disubstituted ethylenes afforded identifiable reaction products. Only alkenes conjugated with aromatic or cyclopropane moiety undergo this reaction. In the case of 1,2-disubstituted alkenes, the relative configuration of substitutents at the double bond is preserved and only one diastereomer is formed.

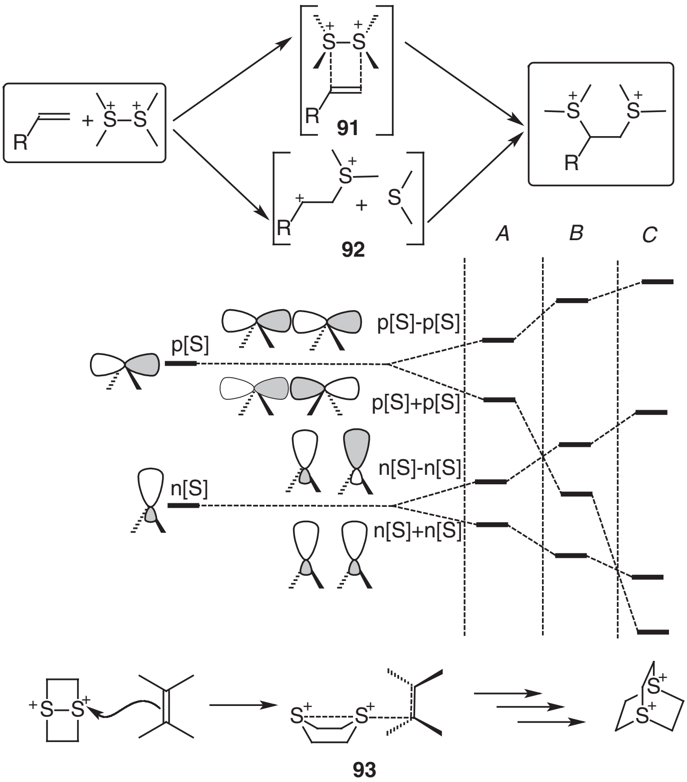
Acyclic S–S dications **51** and **52** also give 1,2-disulfonium salts **90** in reactions with olefins.[79] Formation of a mixture of diastereomers is observed in the case of 1,2-disubstituted alkenes. Reaction with conjugated dienes leads exclusively to the product of 1,4-addition **89** as mixtures of E- and Z-products whose ratio depends on steric factors (Scheme 34).[79]

Two alternative mechanisms were considered for the reaction: (a) synchronous mechanism involving a cyclic transition state **91**, and (b) stepwise electrophilic addition proceeding through formation of a carbocation **92** (Scheme 35).

Further insight into the mechanism of this reaction was obtained with the help of MO theory and quantum mechanical calculations.[99] The following orbital diagram (Scheme 35)[100,101] describes the interaction of two sulfide moieties, which results in dication formation after a two-electron oxidation (cases ***A***, ***B*** and ***C*** correspond to progressive increase in orbital perturbation and interaction between the sulfur atoms).

Theoretical calculation at the HF/6-31G* level[99,102] on some S–S dications and their precursors have shown that the electronic structure of 1,4-dithioniabicyclo[2.2.0]hexane and the *sp–sp* conformation of the tetramethyldisulfonium dication, the difference in the energy levels of *n*[S] − *n*[S] and *n*[S] + n[S][103] is decreased owing to steric strain and the order of orbitals thus corresponds to case **B**. In the less strained systems (1,5-dithioniabicyclo[3.3.0]octane, 1,4-dithioniabicyclo[3.2.0]heptane), the order of orbitals corresponds to case **C**. Interestingly, *ap–ap* conformer of tetramethyldisulfonium dication was reported to correspond to case **A**.

Restricted Hartree–Fock calculations of the suprafacial addition of ethylene to 1,4-dithioniabicyclo[2.2.0]hexane with the 6-31G* basis failed to locate the transition state for this process. Synchronous suprafacial addition should

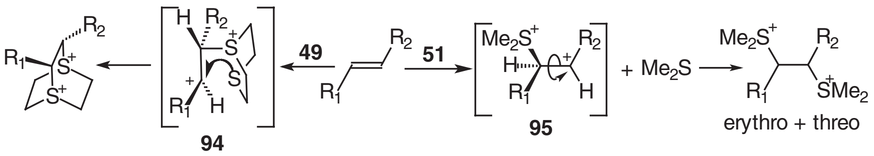


Scheme 35

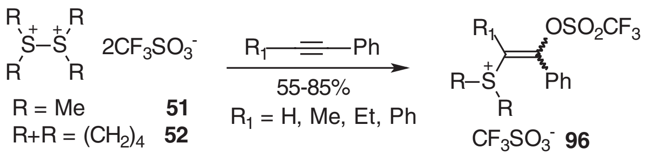
proceed through an antiaromatic transition state, which is thermally forbidden according to the Woodward–Hoffmann rules.[104,105] At the same time, during the stepwise addition the orbital factors favor nucleophilic attack of the alkene π-system on one of the sulfur atoms of disulfonium dication. This process can be described as an S_N2-like substitution at the sulfur atom ($S_N2(S)$) or as electrophilic addition to a double bond. The transition state was readily located at this geometry of the intermediate π-complex **93**.[99] The distances between the reaction centers in complex **93** (the ethylene carbon atoms and the closest of the sulfur atoms of the dication in the episulfonium ion-type geometry) were 2.74 and 2.96 Å.

According to the stepwise electrophilic reaction mechanism, the differences in the stereochemistries of the products from the reactions of alkenes with cyclic **49** and acyclic **51** disulfonium dications can be explained by the larger rates of the intramolecular reactions. In the case of a cyclic dication, the carbocationic center in intermediate **94**, which is formed as the result of initial attack by a S–S dication on a double C=C bond reacts with nucleophile intramolecularly, thus conserving the configuration of the substituents at the double bond. On the other hand, an acyclic dication undergoes transformation to two separate particles (**95** and dimethylsulfide) with a consequent loss of stereoselectivity. Additional experiments with deuteretad alkenes confirm that reaction is not stereoselective, lending further support to the stepwise mechanism (Scheme 36).[106]

Interaction of simple acyclic dications with acetylenes proceeds anomalously. Instead of unsaturated disulfonium salts, the reaction leads to the corresponding vinyltriflates **96**.[107] It was shown earlier[108] that interaction of trifluoromethylsulfonyloxysulfonium triflate (the ‘‘dimethylsulfide–ditriflate’’ complex) with certain acetylenes leads to analogous vinyl triflates. The drastic differences between the reactivity of cyclic and acyclic dications toward acetylenes provide another evidence for a stepwise mechanism of this process (Scheme 37).



Scheme 36



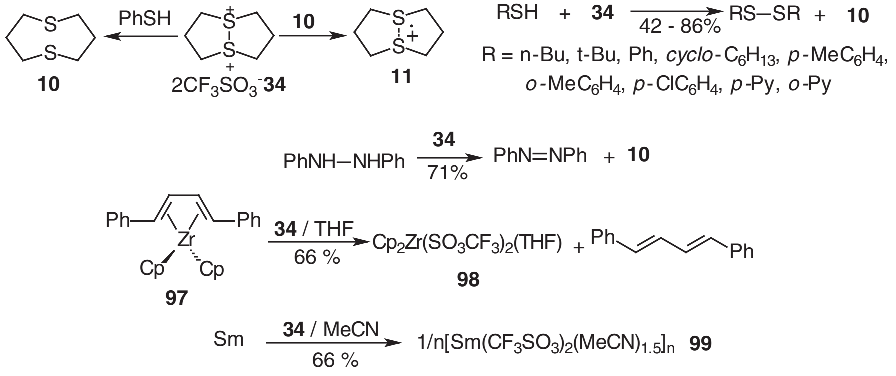
Scheme 37

7.2.2.3.2 Reduction of Disulfonium Dications. Reactions with Bases

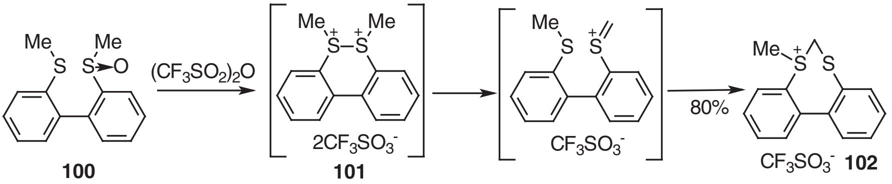
Reduction of bicyclic disulfonium dication **34** can lead either to a bis-sulfide **10** or to a stable radical cation **11** depending on the redox potential of the reducing agent. For example, reaction of dication **34** with sulfide **10** leads to the corresponding radical cation **11**, whereas treatment with thiophenol[50] or 1,2-diphenylhydrazine[97] affords bis-sulfide **10**. Disulfonium dication **34** oxidizes mercaptans to disulfides under mild conditions.[109] Dication **34** is also a mild and selective reagent for synthesis of transition metals trifluoromethanesulfonates. For example, diene complexes of zirconium **97** are transformed into corresponding bis-trifluoromethanesulfonate complexes **98** in good yields.[110] Another promising application of this reaction is oxidation of samarium metal to samarium ditriflate **99**, which is an active and highly diastereoselective catalyst for pinacol coupling (Scheme 38).[111]

In analogy to the properties of ordinary sulfonium salts, reaction of disulfonium dications with bases may lead to either α- or β-deprotonation. Deprotonation of the S–S dication formed during the Pummerer rearrangement of monosulfoxides of certain bis-sulfides **13**, **59**, **56** is a key step of the overall process.[85,86] Furukawa and co-workers[64] also suggested that direct formation of disulfonium dication ylides occurred upon treatment of sulfinylimines of **14** and **41** with potassium *tert*-butoxide. Reaction of triflic anhydride with sulfoxide **100** affords sulfonium salt **102** through deprotonation of the corresponding S–S dication **101** (Scheme 39).[78]

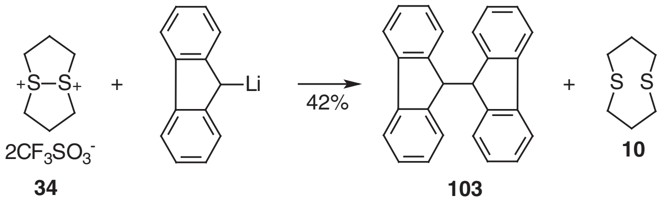
Even more interesting observation is that a number of strong bases failed to deprotonate stable dication **34** directly. Instead, all of the investigated bases (Grignard reagents, organolithium compounds and alkoxides) acted as one-electron electron donors toward the dication, thus leading to the formation of the corresponding sulfide **10**.[112] One-electron oxidation transforms carbanionic reagents into radicals, which undergo dimerization. For example, reaction of fluorenyl lithium with dication **34** afforded fluorenyl dimer **103** (Scheme 40).[96]



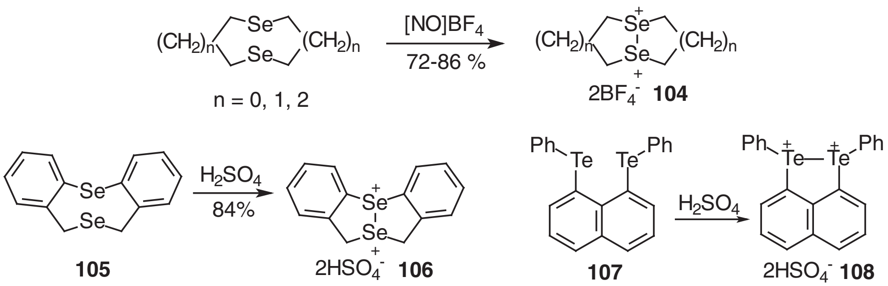
Scheme 38



Scheme 39



Scheme 40



Scheme 41

7.2.3 Se–Se, Te–Te and Mixed Dications

The larger atomic radius and larger polarizability of selenium and tellurium together with the lesser electronegativity of these elements results in increased stability of the corresponding dications. Similarities in chemical properties and electronic structure allow for formation of mixed dichalcogen dications as well.

Synthetic approaches to selenium, tellurium and mixed dications are similar to the methods used for disulfonium dications. Oxidation of bis-selenides to diselenonium dications **104** with two equivalents of nitrosonium salts – $NOBF_4$, $NOPF_6$[113] occurs more readily than the oxidation of sulfides and affords the corresponding dications in better yields (Scheme 41).[96,114]

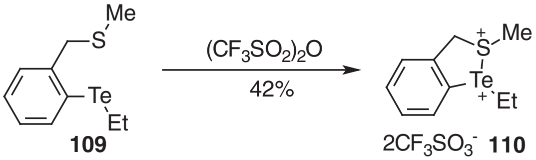
Because the redox potential of selenides is sufficiently low, oxidative generation of Se–Se and S–Se dications on treatment with sulfuric acid is more general than in the case of disulfonium dications. For example, formation of dications **106** and **108** occurs readily when the corresponding bis-selenide **105** and bis-telluride **107** are dissolved in sulfuric acid.[115–117] The only limitation of this method is the low stability of some substrates in concentrated sulfuric acid.[118]

The possibility of preparation of selenium and tellurium containing dications by direct oxidation with triflic anhydride was investigated only recently.[119] An example is provided by the synthesis of dication **110** from mixed bis-chalcogenide **109** (Scheme 42).

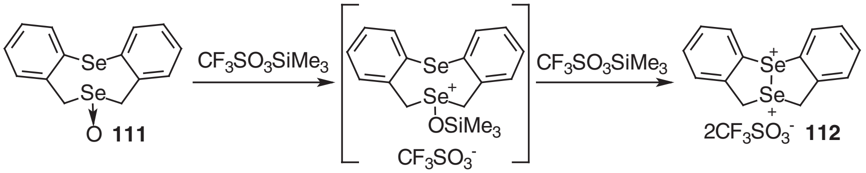
The most versatile approach to disulfonium dications – reaction of triflic anhydride with monosulfoxides of bis-sulfides – has certain limitations in the case of selenium. Most importantly, selenoxides that contain β-hydrogen atoms are labile.[120–122] Trimethylsilyl triflate was used instead of triflic anhydride for synthesis of dication **112** from a selenoxide **111** (Scheme 43).[123]

Although diselenonium-, ditelluronium- and mixed sulfonium–selenonium dications can exhibit either oxidative or electrophilic properties in reactions with nucleophiles, substitution at the onium chalcogen atom is more typical.[96] Owing to the increased stability of heavier dichalcogenium-dications, they react only with highly activated substrates such as aniline and *N*,*N*-dimethylaniline, while no reaction is observed with phenol and diphenylamine.[113] Reactions of ditelluronium dications with activated aromatics are also not known (Scheme 44).[114]

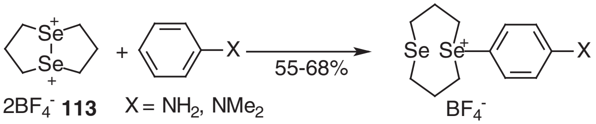
The lesser electrophilicity of the selenium and tellurium derivatives is also displayed in their hydrolytic stability. In general, all diselenonium dications are more stable toward hydrolysis than the corresponding disulfonium dications. 1,5-Diselenoniabicyclo[3.3.0]octane **113**, which is expected to be hydrolyzed to an unstable selenoxide, is stable in water.[124] On the other hand, dication **112** is



Scheme 42



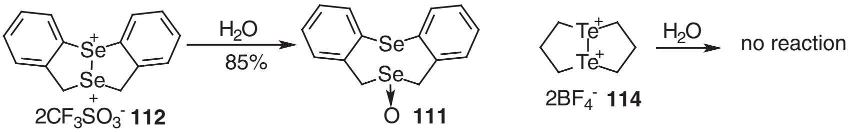
Scheme 43



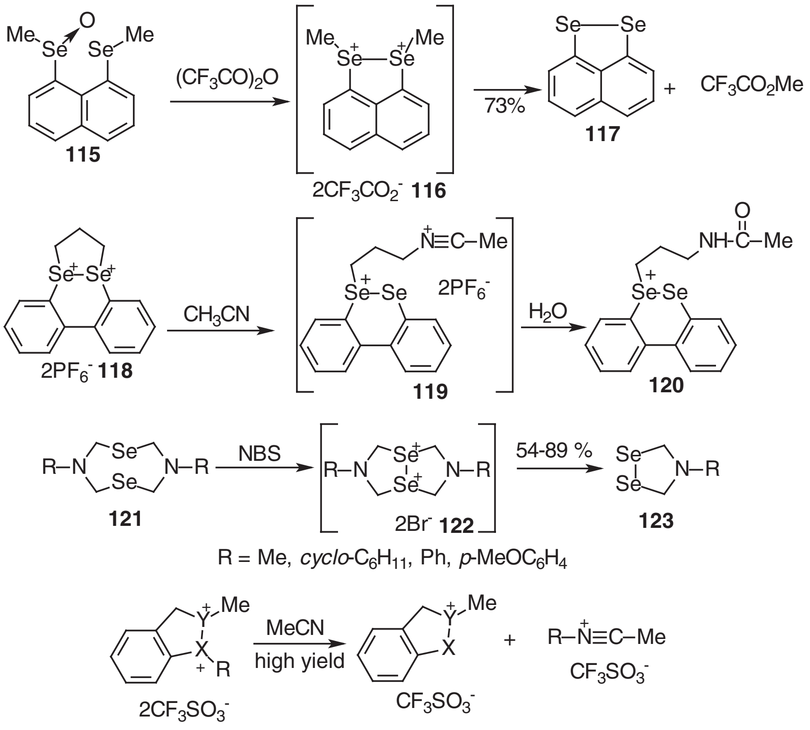
Scheme 44

hydrolyzed by aqueous carbonate solution at a moderate rate to give selenoxide **111**.[123,125] The Te–Te dication **114** is sufficiently stable toward hydrolysis and its oxidative properties can be studied in aqueous solution (Scheme 45).[114]

In the case of the most reactive compounds, substitution at the carbon atom of diselenonium and ditelluronium dications is also a possible pathway. For example, formation of diselenide **117** from selenoxide **115** was explained by demethylation of intermediate dication **116** with trifluoroacetate anion.[126] Dealkylation of salt **118**, which is stable up to −20°C, leads to formation of nitrilium salt **119**. The latter is transformed to amide **120** upon hydrolysis.[64] Dealkylation of intermediate diselenonium dication **122** was suggested as the key step in the oxidative synthesis of 1,2,4-diselenazolidines **123** from eight-membered heterocycles **121** (Scheme 46).[127]



Scheme 45



R = Me, *cyclo*-C_6H_{11}, Ph, *p*-$MeOC_6H_4$

X = Se, Y = S, R = Et **124** X = Te, Y = S, R = *i*-Pr **125** X = Te, Y = Se, R = *i*-Pr **126**

Scheme 46

Dealkylation is the main direction in the decomposition of mixed dications **124–126**. Stability of these dications strongly depends on the nature of the chalcogen and substituents.[119] In general, the order of stability is consistent with the difference in electronegativities and changes as follows: Te > > Se > S (Scheme 46).[95,119]

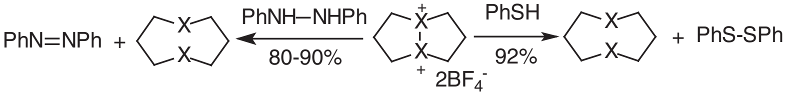
The oxidative properties of ditelluronium and diselenonium dications are similar to S–S dications. For instance, interaction of thiophenol or 1,2-diphenylhydrazine with either the diselenonium dication **113** or the ditelluronium dication **114** leads to almost quantitative formation of diphenyldisulfide or azobenzene and reduced bis-chalcogenides.[113,114,124] Reduction of **113** and **114** with $NaBH_4$ gives the same products as above but proceeds quantitatively *via* direct electron transfer (Scheme 47).[128]

Just as disulfonium dication **34**, diselenonium **113** and ditelluronium dication **114** do not undergo deprotonation. Instead, reaction of dication **113** with fluorenyllithium affords bis-selenide and fluorene dimer **103**.[96] Softer Lewis base such as *n*-tolyl magnesium bromide reacts with diselenonium-dication **113** to give **127**, a product of nucleophilic substitution at the onium atom (Scheme 48).[129]

7.2.4 Trichalcogen–Dications

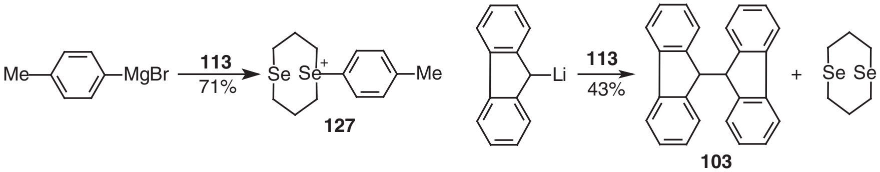
Generation of disulfonium dications involves stabilization of the cationic centers on the sulfur atoms through formation of a new S–S bond between the two sulfonium centers. When such an interaction involves more than two chalogen atoms, it leads to formation of new interesting types of dications, which contain hypervalent central atoms, such as sulfurane, selenurane or tellururane.[94]

One can use the same methods for generation of trithiodications as for synthesis of disulfonium dications, *i.e.* oxidation of suitable trisulfides with concentrated sulfuric acid or with nitrosonium salts as well as reaction of a



X = Te **114,** X = Se **113**

Scheme 47



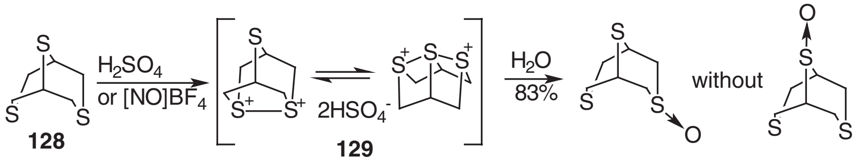
Scheme 48

corresponding monosulfoxide with either triflic anhydride or sulfuric acid.[130] Treatment of **128** with concentrated sulfuric acid or two equivalents of a nitrosonium salt leads to formation of a dication **129** (Scheme 49).[131]

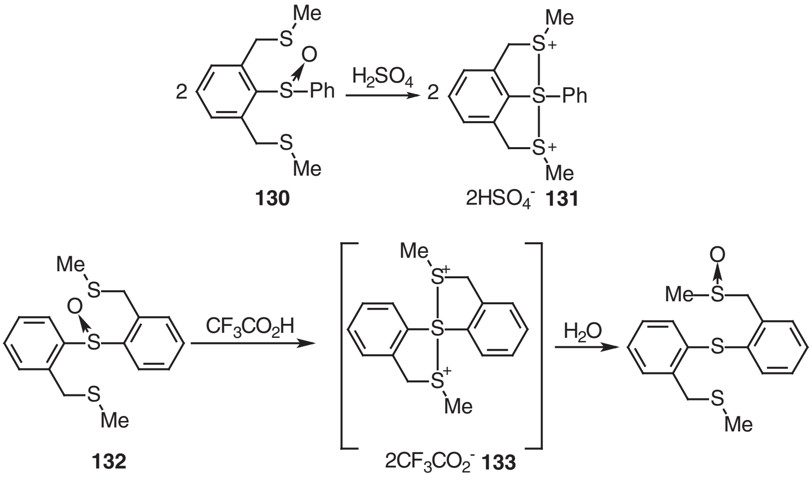
Stereochemical features of **130** favor formation of a sulfurane dication **131** by treatment with concentrated sulfuric acid.[132,133] The sulfuranyl dication **133** is postulated to be involved in the 1,5-oxygen migration observed in the reaction of monosulfoxide **132** with trifluoroacetic acid (Scheme 50).[82]

Crystalline dication **135** (X = Y = S) prepared by reaction of cyclic monosulfoxide **136** with triflic anhydride is sufficiently stable to be isolated and studied spectroscopically.[134] Other trichalcogen dications containing either one or two different chalcogen atoms were prepared and investigated starting from similar structures. Selenurane dications **135** (X = S or Se, Y = Se) were obtained either by oxidation of a trichalcogenide **134**, or by reaction of concentrated sulfuric acid or triflic anhydride with a corresponding oxide **135**.[135] Tellururane dications **138** and **139** were obtained by oxidation of the corresponding trichalcogenides **137** with nitrosonium tetrafluoborate or by reaction of triflic anhydride with a telluroxide **140** (Scheme 51).[136]

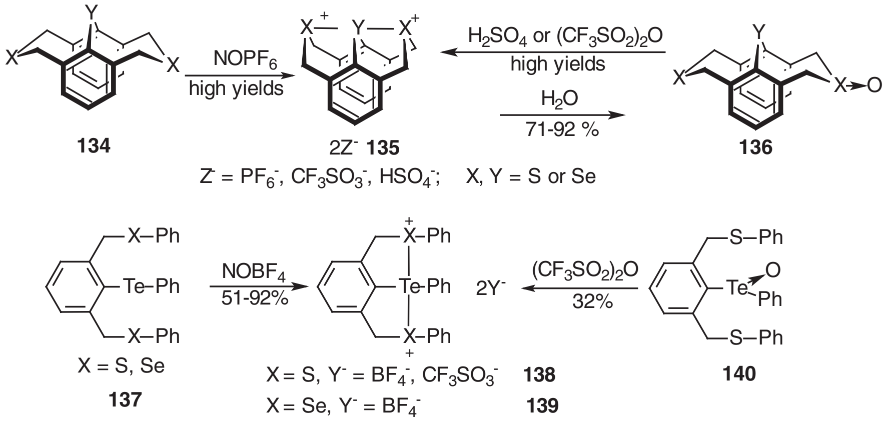
The structure of compounds **135** was established by NMR spectroscopy and by X-ray analysis. According to the X-ray data,[137] triselenium dication **135** (X = Y = Se) has a bent structure with the C(Ar)–Se–C(Ar) angle equal to 95.6°.



Scheme 49



Scheme 50



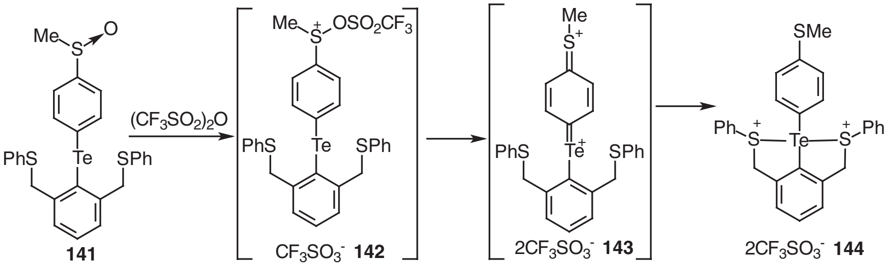
Scheme 51

The Se···Se distances, which are 2.65 and 2.56 Å longer than a normal Se···Se bond in diselenide (2.34 Å) and the Se–Se–Se angle (170°) corresponds to the angle agree with a two-electron three-center bond. A large spin–spin coupling constant (210 Hz) between the selenonium and selenurane atoms observed in ^{77}Se NMR indicates formation of a chemical bond between these atoms.[138] Similarly, X-ray data agree well with the tellurane structure of the dication **139**: the central tellurium atom has the trigonal bipyramidal configuration, the Se···Te distance (2.78 Å) and the S···Te distance (2.67 Å) are slightly longer than the normal single Se···Te and S···Te bond lengths (2.52 and 2.36 Å respectively). The X···Te···X angle is close to 160°.[136]

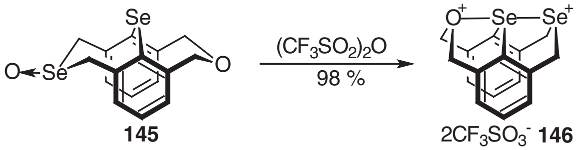
The charge distributions in triselenium dications **135** (X = Y = Se) were characterized[137] by *ab initio* calculations at the RHF/3-21G* level using the "Natural Population Analysis" method.[139,140] The positive charge is delocalized exclusively at the three selenium atoms without involvement of the phenyl rings. The natural charge at the central atom is +1.02, while at the end atoms it is +0.70. The Mulliken Se···Se bond order is 0.59.[141] The tellurium atom of **138** has the charge of +1.60. For **139**, in the selenonium environment the charge is slightly lower (+1.42). The charges at the sulfur and selenium atoms are equal to +0.49 and +0.61, respectively.[142]

An interesting way to generate telluronium dications involves electron transfer through a π-conjugated system to a spatially remote sulfoxide sulfur atom in a "domino" manner. Treatment of substrate **141** with triflic anhydride results in reduction of the terminal sulfoxide group with simultaneous oxidation of the tellurium atom in the para-position and formation of a trichalcogen dicationic moiety **144**[143] through the intermediate sulfonium salt **142** and quinoid structure **143** (Scheme 52).

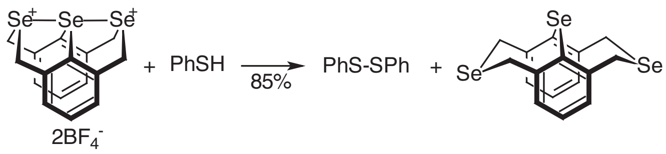
The only example of an organic dicationic system with participation of oxygen was described for the selenuranium dication **145** prepared by reaction of selenoxide **146** with triflic anhydride.[144] X-ray analysis of this dication confirmed formation of a hypervalent structure with an almost collinear



Scheme 52



Scheme 53



Scheme 54

geometry of the O–Se–Se moiety (165°) and a Se–Se bond (2.39 Å), which is only marginally longer than a Se–Se bond in diselenides (2.34 Å) (Scheme 53).[144,145]

The chemical properties of trichalcogen dications are, in many ways, analogous to the properties of dichalcogen dications, but are considerably less studied. Hydrolysis of chalcogenurane dications occurs preferentially at the onium chalcogen atom. Similar to the usual dichalcogen dications, trichalcogen dications also display oxidative properties. For example, reduction of selenurane dication **135** (X = Y = Se) is observed in reactions with Sm(II) salts, triphenylphosphine or thiophenol (Scheme 54).[135]

7.2.5 1,4-Dication with Dichalcogen Fragment

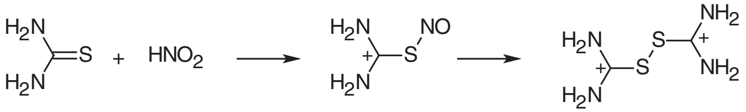
Common synthesis of disulfonium dications involves formation of a S–S bond by oxidative coupling of two sulfide moieties. Involving for oxidative generation of S–S bond, thiocarbonyl compounds can lead to new-type dications containing disulfide moieties between two positively charged fragments. There are several disulfide dications of this type derived from thioureas, thiocarbonates and thioketones as well as selenium derivatives.[137–148]

In pioneering work Werner[149] showed that in acidic media thiourea **147** is oxidized by nitrous acid to dication **149**. The principle step in this reaction is decomposition of the thionitrite **148** (Scheme 55).[150]

Nitrosonium tetrafluorobprate was used later as oxidant for convertion of dithiolanthione **150** to dication **151**.[151] This technique was found to be general for oxidation of number of thiocarbonyl compounds (Scheme 56).[146]

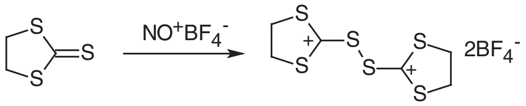
Application of free halogens such as Br_2, ICl, IBr, I_2 is also useful for synthesis of these dications.[152] Interaction of the drug methimazole **152** with I_2 gives dication disulfide **153** and monocation **154** depending on acidity of reaction media (Scheme 57).[153]

Direct oxidation of thiocarbonyl compound by triflic anhydride results in stable dication salts containing disulfide framework. For example, reaction of thiocarbonate **155** with Tf_2O yields the dication salt **156** (Scheme 58).[154]



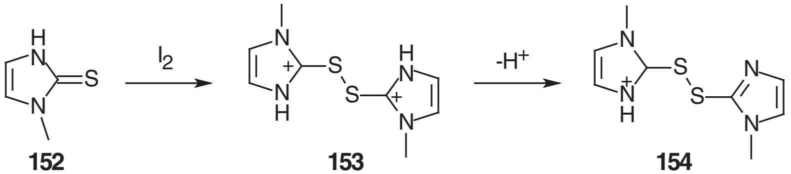
147 **148** **149**

Scheme 55



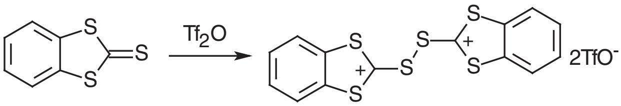
150 **151**

Scheme 56



152 **153** **154**

Scheme 57



155 **156**

Scheme 58

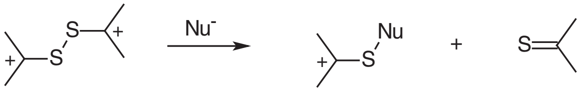
Chemical properties of disulfide dications are almost similar to the properties of disulfonium dications. Nucleophilic exchange is characteristic transformation of disulfide dications. Substitution occurs at sulfur atom with cleavage of disulfide moieties because of the lower energy of S–S bonds (Scheme 59).

Disulfide dications are remarkably stable to water, in contrast to disulfonium dications. However, all they can be hydrolyzed by alkali water solution to give starting thiocarbonyl compound or more hydrolyzed product. For example, exposition of salt **157** to the aqueous NaOH gives formamidinium salt **158** and thiourea (Scheme 60).[154]

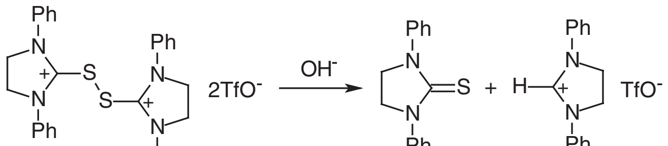
The oxidative properties of disulfide dications are similar to S–S dications but are less expressive. For example, addition of triethylsilane to **151** results in the immediate and quantitative production of dithiolanthion **150** and triethylsilylfluoride (Scheme 61).

7.2.6 Polyatomic Chalcogen Dications

Polyatomic dications of sulfur, selenium and tellurium were discovered at the end of the 1960s during the investigation of intensively colored solutions known for almost a century. These solutions are formed when chalcogens are dissolved in concentrated sulfuric acid or oleum.[155] The first dications studied by X-ray crystallography were a hydrosulfate of tetraatomic selenium dication (Se_4^{2+})[156] and tetrachloroaluminates of octaatomic selenium dication (Se_8^{2+})[157] and tetraatomic tellurium dication (Te_4^{2+}).[158] Up to now, a large volume of reliable

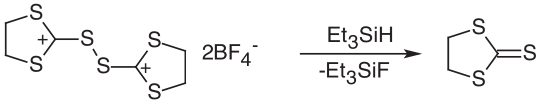


Scheme 59



157 **158**

Scheme 60



151 **150**

Scheme 61

data on synthesis and structure of a number of homo- and hetero-polyatomic chalcogen dications has been accumulated (see in Chapter 7.1 Table 2).[159] The main results of such studies have been presented in several reviews,[160–162] including some published recently.[159,163]

There are two main approaches to polyatomic chalcogen dications. The use of suitable one-electron (WCl_6, WF_6, PtF_6, $SO_3F^{\bullet}$ radical) or two-electron oxidizing agents (SbF_5, AsF_5)[164] and synproportionation between an elementary chalcogen and the corresponding chalcogen halogenide activated with a Lewis acid ($AlCl_3$, $Ag[Sb(OTeF_5)_6]$, $BiCl_3$, $NbOCl_3$) (Scheme 62).[165,166]

The principal differences in the structures of organic and inorganic chalcogen dications are well illustrated by the tetraatomic cations Te_4^{2+}, Se_4^{2+} and S_4^{2+}. According to X-ray analyses of such salts, all of the chalcogen atoms are equivalent. These atoms are located in the corners of a square and equally participate in delocalization of the positive charge.[167–169] According to a number of quantum-mechanical studies, such a dication can be represented as a typical 6π-aromatic system with equal contributions from four Lewis structures.[170–172] This bond order explains why the distance between the adjacent chalcogen atoms, which is equal to 2.66 Å for Te_4^{2+}, 2.28 Å for Se_4^{2+} and 1.98 Å for S_4^{2+} is slightly less than the length of the corresponding single bonds (Scheme 63).[161]

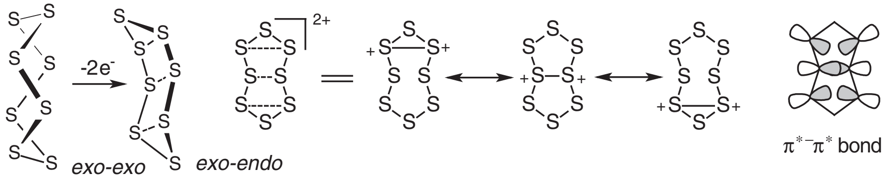
Polyatomic chalcogen dications are typical cluster compounds.[173] Current interpretation of chemical bonding in the S_8^{2+} dication invokes formation of a weak delocalized π*–π* bond as a result of overlap of six 3p orbitals of the sulfur atoms located at the opposite sides of the eight-membered ring.[163,174–176] Such salts as $Se_8[AlCl_4]_2$ and $Te_8[ReCl_6]$ are, according to X-ray crystallography data, analogous in structure to the S_8^{2+} dication (Scheme 64).[177,178]

$$4Se + S_2O_6F_2 \xrightarrow{HSO_3F} Se_4[SO_3F]_2 \qquad S_8 + 3AsF_5 \xrightarrow{SO_2} S_8[AsF_6]_2 + AsF_3$$

$$7Te + TeBr_4 + 4Ag[Sb(OTeF_5)_6] \xrightarrow{SO_2} 2Te_4[Sb(OTeF_5)_6]_2 + 4AgBr \qquad 15Se + SeCl_4 + 4AlCl_3 \xrightarrow{Na[AlCl]_4} 2Se_8[AlCl_4]_2$$

Scheme 62

Scheme 63



Scheme 64

Such dications as $S_2I_4^{2+}$ and $Se_2I_4^{2+}$ can also be formally classified as belonging to the general class of dications containing two directly bonded positively charged chalcogen atoms.[179] The first dication was isolated as the only characterized product from the reaction of S_4^{2+} with an excess of iodine. Alternatively, it can be prepared in quantitative yield by direct reaction of SbF_5, iodine and elementary sulfur (Scheme 65).[180]

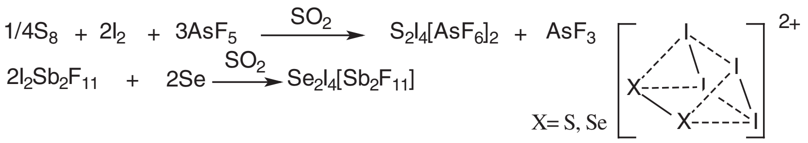
The X-ray data indicate a cluster-like character of the dication containing separate $S_2I_4^{2+}$ groups with a distorted triangular prismatic geometry. The S–S bond length is equal to 1.83 Å, which is the shortest S–S distance in all known compounds of sulfur.[181] Recently, the X-ray structure of $S_2I_4(AsF_6)_2$ was redetermined at low temperature. This data along with the vibrational spectra of $S_2I_4(MF_6)_2$, (M = As, Sb) in solid state and a normal coordinate analysis of $S_2I_4^{2+}$ confirmed the earlier suggested S–S bond order of 2.2–2.4.[182] Dication $Se_2I_4^{2+}$ was synthesized similarly to its sulfur analogue by reaction of $I_2Sb_2F_{11}$ with Se and has properties of a typical cluster compound.[183,184]

The inorganic dications display electrophilic and oxidative properties, but are much more reactive. For example, all cluster chalcogen dications are rapidly hydrolyzed even by the traces of water.[159]

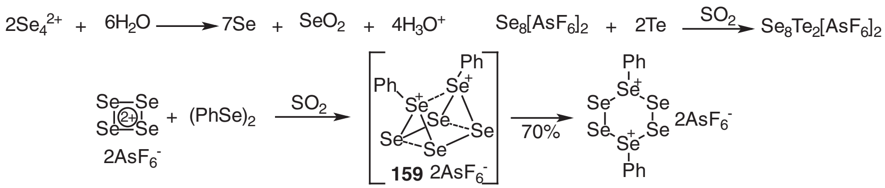
The interaction of polycations with free chalcogens leads, in some cases, to new cluster compounds.[185] Reaction of the aromatic tetraatomic selenium dication with diphenyldiselenide affords $Ph_2Se_6^{2+}$ – compound **159** with a six-membered selenium ring (Scheme 66).[186]

Reactions of S_8^{2+}, S_4^{2+}, Se_8^{2+}, Se_4^{2+} and Te_4^{2+} dications with tetrafluoroethylene and hexafluoropropylene usually result in formation of a mixture of products, mainly perfluoropolychalcogenides.[187–189] The authors[190] suggest a reaction mechanism that involves cyclic key intermediate **160**. Alternatively, this transformation can be explained in terms of a free-radical mechanism (Scheme 67).

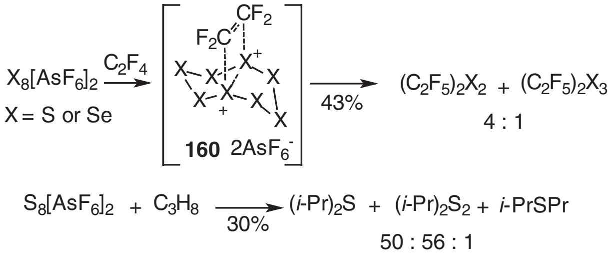
The presence of free radicals in solutions of the S_8^{2+} dication has been known for a long time. Initially, $S_4^{+\cdot}$ was detected by ESR, and its formation



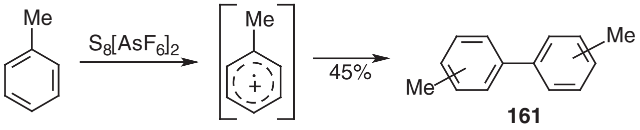
Scheme 65



Scheme 66



Scheme 67



Scheme 68

was explained by coulombic explosion of the dication into two analogous monocations.[191] In general, radical transformations are typical for reactions of polyatomic chalcogen dications.[192] For example, reaction of $S_8[AsF_6]_2$ with propane and *n*-butane leads to a mixture of isomeric sulfides and a disulfide in a total yield of 30%. Toluene was oxidized with S_8^{2+} to form a mixture of isomeric biphenyls **161** (Scheme 68).

In summary, the combination of experimental results and theoretical advances described in this work suggests that chalcogen dications, which have been considered for a long time as hypothetical or ephemeral intermediates can be used in a variety of chemical transformations. Unusual structures of these compounds impart them with reactivities that are remarkably different from other organic intermediates. Harnessing this reactivity should lead to interesting practical applications and we foresee rapid development of this field in the future.

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CHAPTER 8.1

Recent Developments in Binary Halogen–Chalcogen Compounds, Polyanions and Polycations

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8.1.1 Introduction

This chapter covers recent developments of binary halogen–chalcogen systems, including neutral compounds as well as halochalcogenate anions and cations. Most of binary chalcogen halides (see Table 1 for a summary of known examples) are well-known and commonly used as standard chemical reagents. Preparation and structural features of most of these systems would therefore be presented briefly, while recent applications in molecular and materials synthesis would be included with substantial details, so as to highlight the broader implications of the relatively well-established compounds (*e.g.*, SF_4, S_2Cl_2, Se_2Cl_2) in the area of modern materials synthesis. However, no extensive coverage of organo derivatives of the chalcogen halides or of the various branches of the chemistry of sulfenyl, thionyl, and sulfuryl halides, including the technical relevance in organic synthesis, would be given. In addition, special attention would be placed on compounds of the heavier elements (Se, Te, Br, I), since these

Table 1 *Binary chalcogen halide compounds*

	F	*Cl*	*Br*	*I*
S	FSSF, SSF_2, SF_2, SF_4, S_2F_{10}, SF_6	S_2Cl_2, SCl_2, SCl_4	S_2Br_2, SBr_2	S_2I_2, SI_2
Se	SeF, Se_2F_2, SeF_2, SeF_4, SeF_6	Se_2Cl_2, $SeCl_2$, $SeCl_4$	α-Se_2Br_2, β-Se_2Br_2, $SeBr_4$, $SeBr_2$	
Te	TeF_4, TeF_6	Te_3Cl_2, Te_2Cl_2, $TeCl_4$	Te_2Br_2, $TeBr_4$	Te_2I, α-TeI, β-TeI, TeI_4

systems often display significant intermolecular interactions that result in rich and variable structural chemistry, and could effectively modify solid-state electronic properties to form novel crystalline materials. While only developments in the past 10–15 years will be emphasized in the main text, extensive references would be made to relevant systems reported or reviewed earlier.

8.1.2 Chalcogen Fluorides

Low-valence sulfur fluorides (*e.g.*, SF_2, FS–SF, and $S = SF_2$) are generally unstable under ambient conditions, and their chemistry is not widely studied. SF_2 is highly reactive, and has been made only in gaseous phase. It can be prepared in high yield from SCl_2 and HgF_2 at low-vapor pressure.[1] It was also prepared by the UV photolysis of F_3CSF_3 and F_3CSeF_3 in an Ar matrix.[2] FS–SF and $S = SF_2$ were prepared by fluorination of S_2Cl_2 by AgF and HgF_2, respectively, and their structures were studied by IR and Raman matrix spectra for both pure ^{32}S and ^{34}S analogues.[3] By contrast, SF_6 is a well-known compound and is chemically very inert, undergoing reactions only under quite harsh conditions.

Most chemistry of sulfur fluorides concentrate on sulfur tetrafluoride (SF_4), which is widely used in chemical preparation, especially as a strong and selective fluorinating reagent.[4,5] It is an extremely reactive gaseous compound with a melting point of $-121°C$ and boiling point of $-38°C$, and it can be made by reaction of SCl_2 with a 70/30 mixture of HF/pyridine, or by the addition of SCl_2 over a period of 1–5 h into a mixture of an excess of a metal fluoride (*e.g.*, NaF, KF, CuF_2, or ZnF_2) and MeCN, tetramethylene sulfone, or PhCN at 50–80°C.[6] Among the various uses as a fluorinating reagent, the synthesis of organic fluorides for liquid crystals and electronic materials is particularly noteworthy. One recent example is the synthesis of perfluoropentacene using SF_4 as an effective fluorinating agent.[7] In two of the key steps (Figure 1), 6,13-pentacenedione **1** was fluorinated with sulfur tetrafluoride in hydrogen fluoride at 150°C to afford perfluoro-(5,6,7,12,13,14-hexahydropentacene) (**2**) in 40% yield. Defluorination of **2** with zinc at 280°C gave perfluoropentacene in 65% yield. Perfluoropentacene is a planar and crystalline material that adopts a herringbone structure as observed for pentacene, and was found to be an n-type semiconductor for organic field-effect transistors (OFETs). The OFETs showed an electron mobility of 0.11 $cm^2\ V^{-1}\ s^{-1}$, and bipolar OFETs with perfluoropentacene and pentacene were fabricated that functioned at both negative and positive gate voltages.

Chemistry of selenium and tellurium fluorides is well summarized in the literature.[8,9] SeF_2, FSeSeF, and $Se = SeF_2$ have been prepared in minute

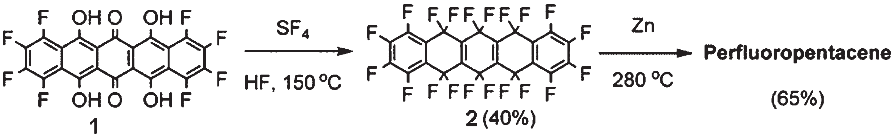


Figure 1 *Two key steps in the synthesis of perfluoropentacene*

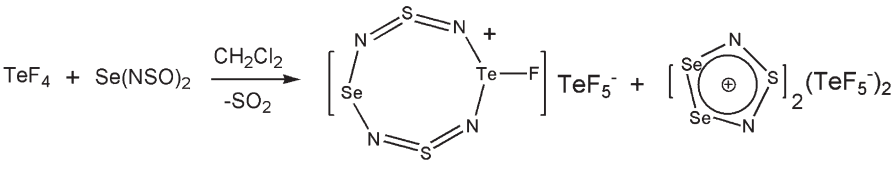
amounts, and their structures were studied by IR and Raman matrix spectra, but their chemistry is little known.[10] The chemistry of selenium fluorides is heavily concentrated in SeF_4 and SeF_6. SeF_4 (mp ~ −39°C, bp 106°C) resembles SF_4, but being a liquid and somewhat easier to handle, it has some advantage as a fluorinating agent.[11] Crystal structures of both SeF_4 and TeF_4 were reported.[12,13] In SeF_4, the Se atom is in a ψ-trigonal bipyramidal coordination with four bridging F atoms, while in TeF_4, the Te atom is in a distorted tetragonal pyramidal (ψ-octahedral) coordination with two *cis*-bridging F atoms. The Se–F bonding was described as sp^3d and the Te–F bonding sp^3d^2.

One interesting area of chemistry that TeF_4 as a reagent touches upon is that of chalcogen nitrogen heterocyclic compounds, an important class of compounds that have sparked strong interest in their electronic structures as well as the chemical and physical properties.[14] The incorporation of Se and Te atoms into the cyclic systems has enriched the chemistry (the reader should refer to Chapter 4 by Chivers and Laitinen for more on nitrogen–chalcogen compounds). For example, reaction of equimolar amounts of $Se(NSO)_2$ and TeF_4 (2.01 mmol) in CH_2C1_2 (10 cm^3) after a period of seven days and heating up to 60°C yielded a mixture of the fluorinated cationic eight-membered cation of **3** (0.63 mmol) and the well-known cyclic $SeSeNSN^+$ cation of **4** (0.31 mmol), as is also shown in Figure 2.[15] Both substances are extremely air-sensitive and insoluble in CH_2C1_2 as well as in SO_2, but they do not explode on mechanical shock or heating and melt under decomposition at 145°C (**3**) and 173–180°C (**4**). The crystal structure of **3** revealed the cation as a non-planar, partially open cage-like species featuring a short Se···Te contact of 2.902 Å (Figure 3). In a broader perspective, the chalcogen as well as the nitrogen atoms on these and other related heterocycles provide versatile coordinating sites to various metal ions,[16,17] and could serve as potential building blocks for coordination networks with interesting materials properties such as semiconductivity and magnetism in the solid state.

8.1.3 Chalcogen Chlorides and Bromides

8.1.3.1 Selenium and Sulfur Dichlorides

Selenium (and sulfur) dichlorides are useful reagents for the synthesis of organoselenium compounds,[18] nitrogen selenium heterocycles[19–21] and other selenium compounds. The key steps in these reactions usually involve a



3 **4**

Figure 2 *The synthesis of the chalcogen nitrogen heterocycles of* **3** *and* **4** *by using* TeF_4 *as a reactant*

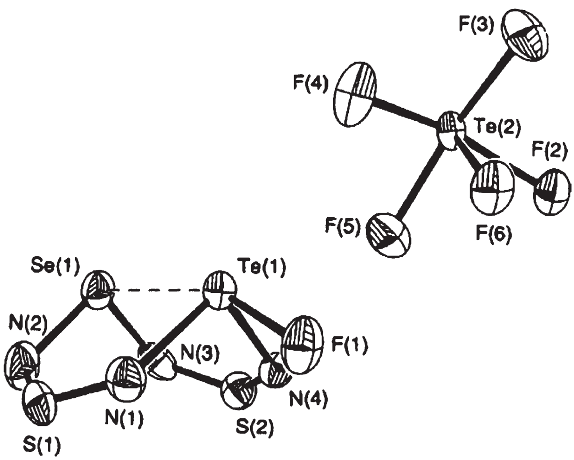


Figure 3 *Crystal structure of* **3**. *Selected bond distances (Å): Te(1)–Se(1) 2.902(2), Te(1)–F(l) 1.926(8), Te(1)–N(l) 2.04(1), Te(1)–N(4) 2.03(1), Se(1)–N(2) 1.87(1), Se(1)–N(3) 1.89(1), S(1)–N(1) 1.53(1), S(1)–N(2) 1.56(1), S(2)–N(3) 1.56(1), S(2)–N(4) 1.54(1)*
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nucleophilic species attacking the positively charged selenium atoms on $SeCl_2$. For example, the treatment of $SeCl_2$ with Grignard reagents (1:2) prepared from bromobenzene, *o*-tolyl bromide, 2,6-dimethyl-5-*t*-butyl-1-bromobenzene, and 1-bromo-2-methylnaphthalene afforded the corresponding monoselenides in good yields.[18] In a second example, a series of double-butterfly μ_4-Se-containing complexes $[(\mu\text{-RTe})Fe_2(CO)_6]_2$ (μ_4-Se) (R = Et, Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-BrC_6H_4) could be produced *via* a simple and new synthetic route involving a doubly nucleophilic reaction of the anion $[(\mu\text{-RTe})(\mu\text{-CO})Fe_2(CO)_6]^-$ with $SeCl_2$ as an electrophile (see Figure 4).[22]

Despite its importance as a reagent in the development of selenium chemistry, synthesis of pure $SeCl_2$ was achieved only recently.[23] The method was simple and efficient, and entailed treating elemental selenium with an equimolar amount of SO_2Cl_2 in THF or dioxane. It was reported to be stable in THF for one day at 23°C, and forms a crystalline *bis*-adduct with THT (tetrahydrothiophene) that may be stored in the solid state at –20°C for weeks without decomposition (see Figure 5). The THF solutions of $SeCl_2$ and the adduct $SeCl_2(THT)_2$ constitute potentially valuable Se(II) synthons for the development of selenium chemistry. In the reaction with triphenylphosphine sulfide ($Ph_3P = S$), $SeCl_2$ acted as a chlorinating agent leading to the generation of selenium sulfide rings under mild conditions (the other product is Ph_3PCl_2). In the same paper, it was also reported that halogen exchange between $SeCl_2$ and Me_3SiBr in THF yields thermally unstable $SeBr_2$ (*ca.* 0.4 M) that was characterized by ^{77}Se NMR and Raman spectra. Notice that prior to this development, $SeCl_2$ was usually generated *in situ* (*e.g.*, from $SeCl_4$ and Ph_3Sb to

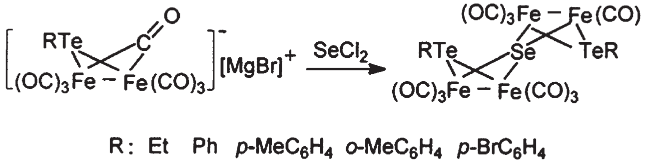

Figure 4 *A reaction of $[(\mu\text{-}RTe)(\mu\text{-}CO)Fe_2(CO)_6]^-$ with $SeCl_2$*
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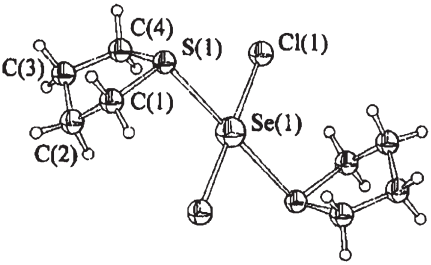

Figure 5 *ORTEP drawing (50% probability ellipsoids) and atomic numbering scheme for $SeCl_2(THT)_2$*
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form $SeCl_2$ and Ph_3SbCl_2)[21] or some other "masked" form of $SeCl_2$ equivalent (*e.g.*, $PhSO_2SeCl$)[24] had to be used.

8.1.3.2. Disulfur and Diselenium Dihalides

Selenium chlorides and bromides SeX_4 and Se_2X_2 (X = Cl, Br) are well-characterized compounds and form a useful class of reagents for many synthetic applications.[25,26] For example, disulfur and diselenium dihalides, S_2X_2 and Se_2X_2 (X = Cl, Br) have been extensively studied.[27] The crystal structures for the four compounds are known all of which contain X–E–E–X (E = S, Se) molecular chains with dihedral angles of 83.9–87.4°. In spite of being a class of familiar reagents, the ^{77}Se NMR spectra of the Se_2X_2 (X = Cl, Br)[28] indicate that disproportionation takes place in the liquid state, resulting in small amounts of SeX_2 and higher homologues, Se_nX_2 ($n = 3, 4$) in equilibrium with Se_2X_2 (*i.e.*, as in $2Se_2X_2 = SeX_2 + Se_3X_2$ and $3Se_2X_2 = 2SeX_2 + Se_4X_2$). Such information thus helped to clarify the origin of the "spurious" peaks in the reported vibrational spectra of Se_2Br_2 and Se_2Cl_2, which variously have been assigned to overtone and combination bands and impurities. In the same paper, it was also reported that mixtures of Se_2Br_2 and Se_2Cl_2 contained Se_2BrCl in equilibrium according to $Se_2Br_2 + Se_2Cl_2 = 2Se_2BrCl$.

Recently, the first structural characterization of mixed sulfur selenium dihalides, $SeSX_2$ (X = Br, Cl), has been reported in mixtures of S_2Cl_2 and Se_2X_2 (X = Br, Cl).[29,30] In addition, two-dimensional NMR exchange spectroscopy (2D-EXSY) was applied to the study of ^{77}Se exchange kinetics in mixtures of S_2Cl_2 and Se_2Br_2 (containing disulfur, diselenium, and selenium sulfur dihalides), and indicated that ^{77}Se magnetization transfer takes place predominantly by an exchange process.[31] With additional chemical evidence, an ionic process involving the breaking of the Se–X bonds was proposed as a favorable mechanism for the exchange reactions.

Disulfur and diselenium dihalides (chlorides and bromides) constitute a useful class of reagents for many synthetic applications. In the field of solid-state materials, it is a useful reagent for making metal chalcogenide halides and nitrogen chalcogenide heterocycles as stable and persistent free radicals.[32–34] The metal chalcogenide halides thus generated are usually soluble in organic solvents and provide handy starting materials for making more sophisticated products. For example, reaction of Mo powder and S_2Cl_2 at 200°C formed in high yields the product MoS_2Cl_3, which was then reacted with PPh_4Cl in MeCN to yield crystals of $(PPh_4)_2[Mo_2(S_2)_2Cl_8] \cdot 2MeCN$.[35] Notably, the acetonitrile molecules could be removed without degrading the crystals. X-ray crystallographic studies revealed that both structures (before and after loss of the solvent molecules) contain the same $[Cl_4Mo(\mu\text{-}S_2)_2MoCl_4]^{2-}$ ions in which the Mo atoms are joined by two disulfido groups and a Mo–Mo bond (see Figure 6).

In another example, the four ternary gallium(III) chalcogenide halides GaEX with E = S, Se and X = Cl, Br can be conveniently prepared from Ga metal and the dichalcogen dihalides E_2X_2.[36] Interestingly, the products are readily soluble in pyridine to give trinuclear molecular complexes $[GaEX \cdot Py]_3$, which can be purified by crystallization. In the crystal structures, the two chlorides are

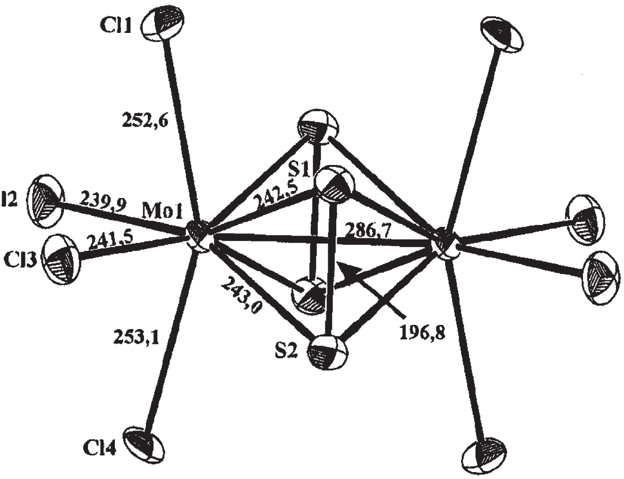

Figure 6 *The $Mo_2(S_2)_2MoCl_8^{2-}$ ion in compound $(PPh_4)_2[Mo_2(S_2)_2Cl_8] \cdot 2MeCN$ (thermal ellipsoids plotted at the 50% level, and bond lengths in pm, with standard deviation of 0.2 pm)*

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isostructural and show twisted tub-form six-membered ring molecules with the pyridine donors in axial positions. The two bromides are also isostructural, but with the pyridine ligands in two axial and one equatorial positions.

8.1.4 Chalcogen Iodides and Tellurium Subhalides

In contrast to the chlorides and bromides, it has not been possible to isolate and characterize SeI_4, Se_2I_2, and other electrically neutral selenium–iodine compounds,[25] though there is certain evidence of the presence of SeI_2 and Se_2I_2 in CS_2 solution.[37] In particular, analysis of Se solubilities in solutions of I_2 in CS_2 showed that various selenium iodide species are formed, according to the equilibrium $\mathrm{nSe} + I_2 = Se_nI_2$. Furthermore, ^{77}Se NMR spectra of the solutions exhibited four principal peaks, which were assigned to Se_3I_2 (α-Se and β-Se of the molecule), Se_2I_2, and SeI_2, as supported by their concentration dependence, chemical shifts, and half-height line widths. The main Se iodide formed is Se_2I_2, the concentration of which is 5% of that of the total I_2 in a solution saturated in Se. In addition, selenium and iodine forms a eutectic melt (51 atom% Se) at 65.5°C in which the chemical shift and half-height line width indicate that Se iodides are formed, although ^{77}Se magic-angle spinning NMR spectra and X-ray powder diffraction give evidence only for crystalline Se and I_2 in the solid formed from the melt.

Unlike its lighter congeners, tellurium displays richer chemistry regarding subhalides in low valence. Such tellurium halides include the recently reported molecular Te_2Cl_2 and Te_2Br_2,[38,39] together with Te_2Cl, Te_2Br, Te_2I, Te_3Cl_2, α-TeI, and β-TeI, which generally exhibit polymeric structures in the solid state. Earlier reviews were available on tellurium subhalides,[25,40] therefore only some major features and subsequent developments are covered here.

Te_2Cl_2 and Te_2Br_2 were prepared by reducing elemental tellurium with superhydride and treating the resultant telluride with appropriate tellurium tetrahalogenide (see Equation (1)), and the products were characterized by mass spectroscopy and ^{125}Te NMR spectroscopy.[38,39] Ditellurium dichloride was thus obtained as a yellow liquid, and ditellurium dibromide as an orange–red liquid. Both Te_2Cl_2 and Te_2Br_2 should be stored under an inert atmosphere: Te_2Br_2 is stable for hours at room temperature, while Te_2Cl_2 is less stable, but it can still be stored for hours in organic solutions (solvents prone to chlorination, however, should be avoided). Both Te_2Cl_2 and Te_2Br_2 exhibit one major ^{125}Te resonance in their respective NMR spectra. The ^{125}Te chemical shift of Te_2Cl_2 in CS_2 is at 1336 ppm and that of Te_2Br_2 at 1253 ppm. By comparison, the chemical shift of Te_2Cl_2 in toluene was earlier on determined to be 1297 ppm.[39]

$$\begin{aligned} &\mathrm{Te} \xrightarrow{\mathrm{LiBHEt_3}} \tfrac{1}{x}\mathrm{Te}_x^{2-} \\ &\mathrm{Te}_x^{2-} + x\mathrm{TeX_4} \rightarrow x\mathrm{Te_2X_2} + 2x\mathrm{X^-}\ (\mathrm{X} = \mathrm{Cl},\ \mathrm{Br}) \end{aligned} \tag{1}$$

Similar to S_2Cl_2 or Se_2Cl_2, which react with $[Ti(C_5H_5)_2S_5]$ and $[Ti(C_5H_5)_2Se_5]$ to produce cyclic seven-membered chalcogen compounds (S_7, 1,2-Se_2S_5, and

1,2,3,4,5-Se_5S_2, Se_7, respectively),[41] Te_2Cl_2 and Te_2Br_2 react with these titanocene reagents to form 1,2-Te_2S_5 and 1,2-Te_2Se_5, further verifying the identities of Te_2Cl_2 and Te_2Br_2. Only one ^{125}Te NMR resonance was observed in spectra of both 1,2-Te_2S_5 (1732 ppm) and 1,2-Te_2Se_5 (1724 ppm) thus synthesized.

Te_2Cl, Te_2Br, and Te_2I are isotypic compounds, consisting of infinite double chains condensed to ribbons of Te_6 rings with boat conformation and bridging halogen atoms at the edges (see Figure 7). Te_2Br is a stable subhalide, and can be prepared from one equivalent of Br_2 and two equivalents of Te in a sealed evacuated glass ampoule at 215°C.[42] Te_2Cl and Te_2I are metastable. Crystals of Te_2Cl were obtained from slowly cooling a Te/Cl melt of 1:1 composition from 300°C to room temperature at 3°C min^{-1}. The condensation of the vapor in this process led to the formation of small plate-like crystallites of the metastable Te_2Cl (with dark metallic luster) on the surface of the solidified cake. The bulk of the cake remained in the more stable phases of Te_3Cl_2 and $TeCl_4$, and methods for making Te_2Cl in larger amounts were not found.

Te_2I was obtained as dark-metallic needles by hydrothermal syntheses with a temperature gradient maintained between 256 and 280°C for 10 days. The mixture of tellurium and iodine (2.5:1) was first fused and annealed at 150°C for three days, before being placed in an ampoule containing 10 M HI. The ampoule was sealed under evacuation and placed into an autoclave filled with CO_2 for balancing the internal pressure of the ampoule during the reaction process. With a temperature gradient between 192 and 198°C, the similar reaction setup yielded another metastable subiodide β-TeI during a period of seven days, while the stable phase of α-TeI was obtained with the same setup under isothermal condition (195°C). The thermodynamically stable Te_3Cl_2 (together with the above-mentioned Te_2Br and α-TeI) can be crystallized from

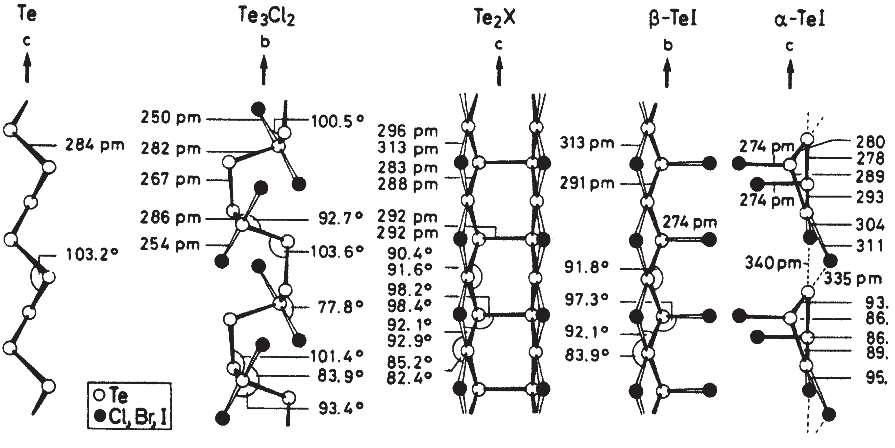

Figure 7 *Structural units of tellurium and the tellurium subhalides Te_3Cl_2, Te_2X, β-TeI, and α-TeI with bond lengths and bond angles. The upper numbers in Te_2X refer to X = Br, the numbers below refer to X = I*

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the melt of the corresponding elements by the Bridgman technique under conditions controlled by the phase diagram.[40]

As can be seen from Figure 7, the crystal structure of β-TeI is related to that of Te_2I, namely, the chains of β-TeI would be formed if the double chains of Te_2I are cleaved along the central Te–Te bonds, and the terminal iodine atoms are attached to the resulting free valences. The crystal structure of α-TeI consists of molecular Te_4I_4 units with a central four-membered tellurium ring. There are three different types of coordination around the tellurium atoms, and the Te_4I_4 units are linked *via* short intermolecular Te···I contacts (see Figure 7).

The homonuclear linkage of tellurium atoms in the tellurium subhalides may be related to the structure of elemental tellurium. The 3_1-chain of the element is modified to varying degrees, ranging from the 2_1 chain of Te_3Cl_2 to a ribbon of condensed planar zigzag chains in Te_2X and a separated planar zigzag chain in β-TeI, and then to the four-membered tellurium ring in α-TeI.

Because of the extended structures in the solid state, tellurium subhalides are of particular interest as potential solid-state materials, and their solid-state physical properties are well investigated. Optical absorption spectra of single crystals of Te_3Cl_2 and α-TeI indicated the direct band gap energies at 300 K to be $E_{\text{gap}} = 1.52$ and 1.32 eV, respectively, which are significantly larger than that of Te with 0.34 eV. Electrical conductivity of the tellurium halides has also been studied, where electrical conductivity *versus* temperature plots indicated widths of the band gaps consistent with values derived from optical measurements. With the highly polarizable heavy main group elements of Te and I, electrical conductivity in tellurium subhalides might be influenced by the degree of condensation of the tellurium framework (covalent interactions), as well as the overlapping of the non-bonding orbitals (*e.g.*, secondary Te···I contacts as in α-TeI).

8.1.5 Halochalcogenate Anions

Halochalcogenate anions can be considered as adducts of the neutral chalcogen halides (*e.g.*, TeX_4, X = Cl, Br, I) and the halogen anions X^-, and are often related to a formal disintegration of the cubane-like tetrameric molecular units (*e.g.*, Te_4X_{16}) in the neutral halide compounds (Figure 8). Depending on the stoichiometric ratios of the reactants and other conditions, a series of mononuclear, dinuclear, trinuclear, and polymeric anionic structures could be formed. A review covering the halochalcogenate anions is available.[25] Here we mainly focus on some subsequent development in this area of chalcogen halide chemistry.

The mononuclear hexahalochalcogenate anion EX_6^{2-} (E = Se, Te; X = Cl, Br, I) usually adopts a nearly ideal octahedral geometry, and has been widely reported (formally it can be considered as the end product of the nucleophilic disintegration of the tetrameric units of $(EX_4)_4$, see Figure 8). Also commonly studied are the dinuclear and trinuclear chloro- and bromo-chalcogenates(IV). Attention here will therefore be focused on the relatively rare multinuclear

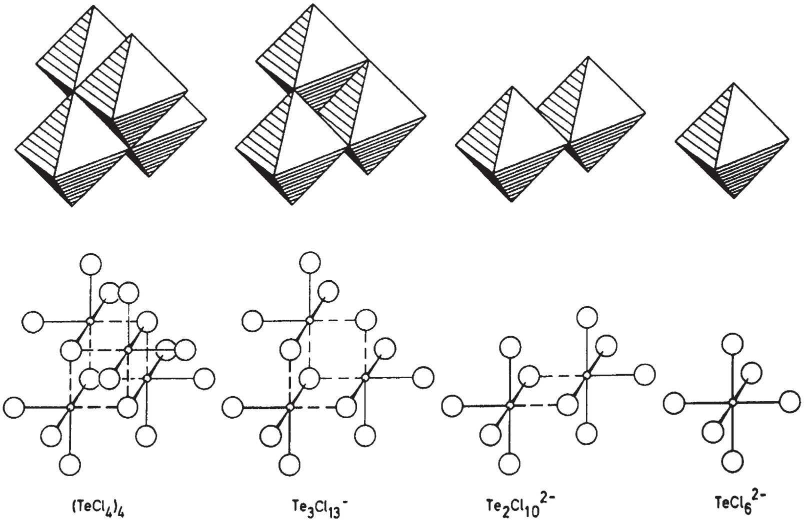

Figure 8 *A formal disintegration of the cubane-like tetrameric chalcogen(IV) halides exemplified by the formation of* $Te_3Cl_{13}^-$, $Te_2Cl_{10}^{2-}$, *and* $TeCl_6^{2-}$ *from* Te_4Cl_{16}

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iodochalcogenate(IV) compounds, which, owing to the more polarizable iodine and tellurium atoms, usually present intense electronic and photophysical properties (*e.g.*, stronger light absorption at longer wavelength) both in solution and in the solid state.

Early examples of multinuclear iodochalcogenate(IV) compounds featuring the binuclear $Te_2I_{10}^{2-}$ anion are represented by the compounds $[(C_7H_7)(C_2H_5)_3N]_2[Te_2I_{10}]$ and $[(C_2H_5)_4N]_2[Te_2I_{10}]$, which were reported by Krebs and co-workers.[25,43] Additionally, compounds, $\{C_4H_8TeI^+\}_2[Te_2I_{10}^{2-}]$ and $\{C_4H_8TeI^+\}_2(TeI_3^+)_2(I^-)_4$, which also featured the $Te_2I_{10}^{2-}$ unit,[44] were recently found as minor products in a reaction between TeI_4 and Ph_3P in THF. The bond lengths and angles in the $[Te_2I_{10}]^{2-}$ anion are virtually identical to those found in $\{(C_7H_7)(C_2H_5)_3N^+\}_2[Te_2I_{10}^{2-}]$, with relatively small variation of the Te–I bonds within the $[Te_2I_{10}]^{2-}$ unit. The cations and anions in $\{C_4H_8TeI^+\}_2[Te_2I_{10}^{2-}]$ are further linked together by weaker Te(1)···I(21) and Te(1)···I(24) contacts of 3.937(1) and 3.887(1) Å, respectively (see Figure 9). There are also several I···I contacts between the $[Te_2I_{10}]^{2-}$ anions in the range 3.609(1)–3.900(1) Å, further expanding the dimensionality of the network that results from the intermolecular contacts. The $[Te_2I_{10}]^{2-}$ portion in compound $\{C_4H_8TeI^+\}_2(TeI_3^+)_2(I^-)_4$ is, however, highly distorted, and could therefore be viewed as consisting of fragments of TeI_3^+ and the I^- ions interacting through elongated Te···I contacts (Figure 10).

By comparison, the recently reported compound *bis*(*N*,*N*-dimethylanilinium) ditellurium decaiodide $[C_6H_5NH(CH_3)_2]_2Te_2I_{10}$ provides improved synthetic

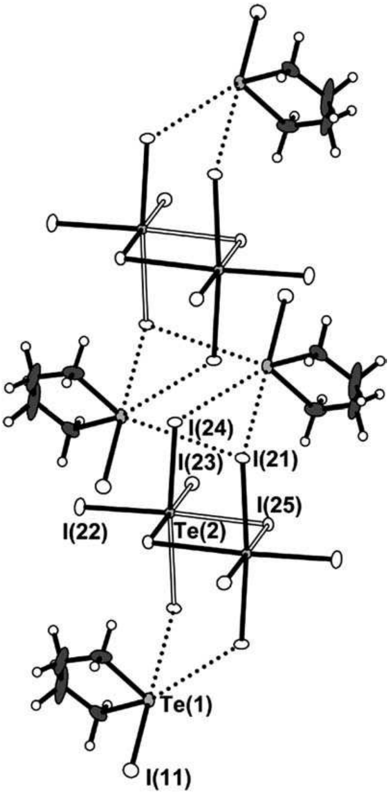

Figure 9 *The crystal structure of* $[C_4H_8TeI^+]_2[Te_2I_{10}{}^{2-}]$. *The thermal ellipsoids have been drawn at the 50% probability level. Selected bond distances (Å): Te(1)–I(11), 2.7338(8); Te(2)–I(22), 2.7982(8); Te(1)–C(11), 2.141(8); Te(2)–I(23), 2.7982(8); Te(1)–C(14), 2.152(9); Te(2)–I(24), 2.8743(8); Te(1)–I(21), 3.3270(9); Te(2)–I(21), 3.0270(8); Te(2)–I(25), 3.1579(9), 3.1514(9)*

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accessibility and higher product purity.[45] It was obtained as a single-phase crystalline solid from diffusing pentane vapor into a mixture of compound *bis*(dimethylaminophenyl) tellurodiiodide and tin(II) iodide dissolved in ethanol and 1,2-dichlorobenzene. Similar to the above $Te_2I_{10}{}^{2-}$ dianions, the $Te_2I_{10}{}^{2-}$ unit is based on two edge-sharing $TeI_6{}^{2-}$ octahedral with relatively small variation in the Te–I bond distances. Interestingly, a three-dimensional Te(IV)–I open framework was formed through extensive interconnecting I···I contacts across the $Te_2I_{10}{}^{2-}$ dianions (the I···I contacts range between 3.66 and 3.80 Å, and are significantly shorter than the corresponding sum of van der Waals radii of 4.0 Å, see Figure 11). It was suggested that such intermolecular contacts could potentially enhance electronic interactions in the solid state, although further work is still needed to test such a hypothesis. The synthetic accessibility facilitated the study of materials. Thus, solid-state reflectance

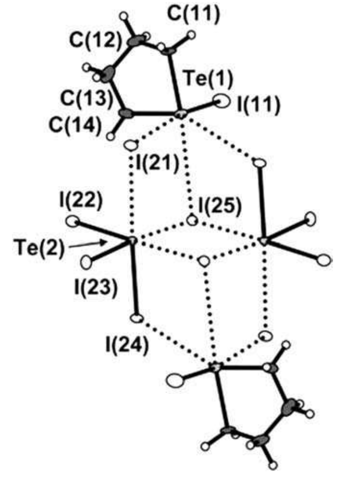

Figure 10 *The crystal structure of* $(C_4H_8TeI^+)_2(TeI_3^+)_2(I^-)_4$. *The thermal ellipsoids have been drawn at the 50% probability level. Selected bond distances (Å): Te(1)–I(21), 3.261(2); Te(1)–I(24), 3.900(2); Te(1)–I(25), 3.676(2); Te(2)–I(21), 3.328(1); Te(2)–I(22), 2.767(1); Te(2)–I(23), 2.777(1); Te(2)–I(24), 2.783(1); Te(2)–I(25), 3.197(1), 3.249(1)*

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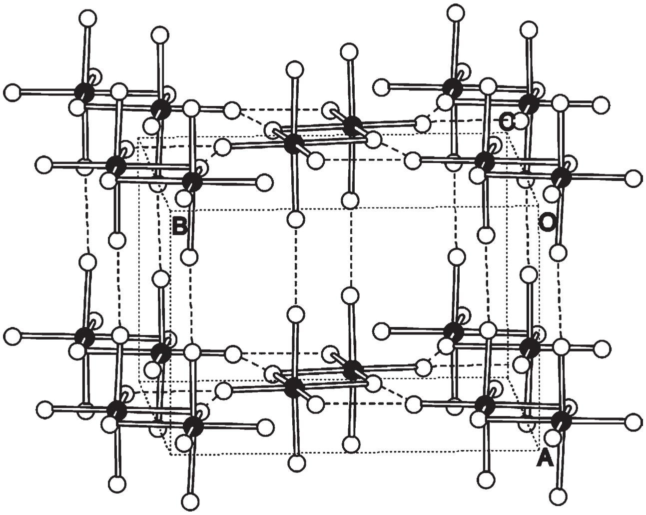

Figure 11 *Packing of the* TeI_6^{2-} *anions in the crystal structure of* $[C_6H_5NH(CH_3)_2]_2Te_2I_{10}$. *Black spheres: Te; white spheres: I; dashed lines: I···I contacts*

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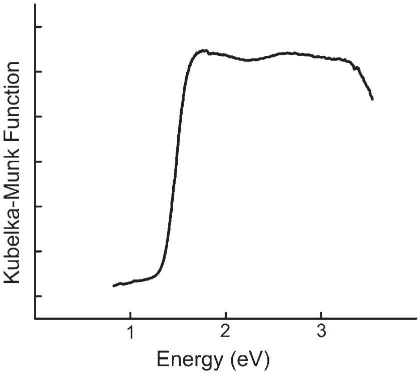

Figure 12 *A room-temperature diffuse reflectance spectrum of compound* $[C_6H_5NH(CH_3)_2]_2Te_2I_{10}$

measurement of the crystalline sample was conducted and indicated a sharp absorption edge at about 1.2 eV (see Figure 12), and thin film samples of the compound were obtained by drop-casting from a heated solution in DMF.

Other polynuclear iodochalcogenate(IV) systems include the compounds $[Cu(CH_3CN)_4{}^+][Te_2I_9{}^-]$ and $[(CH_3)_3NH^+]_2[TeI_7{}^{2-}]$. The former was reported by Krebs and co-workers,[43] and it contains the nonaiododichalcogenate(IV) anion $Te_2I_9{}^-$, which is based on face-sharing of two TeI_6 octahedra. The latter features chains of *trans*-corner-sharing distorted TeI_6 octahedra with the composition of $[TeI_5{}^-]_n$.[46] In addition, the crystal structure contains a remarkable type of almost equidistant $[I_2{}^-]_n$ polyiodide chains (I···I 3.091 and 3.133 Å), so that the structural formula of the compound is expressed as $[(CH_3)_3NH^+]_2[TeI_5{}^-]_n[I_2{}^-]_n$.

8.1.6 Halochalcogenate Polycations

In contrast with the rarity of neutral sulfur or selenium iodides, sulfur and selenium halogen (iodine included) cations are more common, and have been previously reviewed by Passmore (see Table 2 for the known examples).[47] The simplest solid selenium–iodine cation that has been characterized in the solid state by X-ray crystallography is the pyramidal $SeI_3{}^+$ cation.[48] Its chlorine[49] and bromine[50,51] analogues are also known. Other well-characterized selenium–iodine cations include $Se_2I_4{}^{2+}$,[52] $Se_4I_4{}^{2+}$,[53] $(Se_6I^+)_n$,[54,55] and $Se_6I_2{}^{2+}$.[55,56] In the solid state they adopt polymeric, ring, and cage structures.[6]

In particular, $Se_2I_4{}^{2+}$ was quantitatively prepared in the form of $Se_2I_4(AsF_6)_2 \cdot SO_2$ and $Se_2I_4(Sb_2F_{11})_2$ by reacting stoichiometric amounts of Se, I_2, and AsF_5, and by reacting Se and $I_2Sb_2F_{11}$ in liquid SO_2, respectively. The crystal packing of $Se_2I_4(AsF_6)_2 \cdot SO_2$ and $Se_2I_4(Sb_2F_{11})_2$ consists of columns of $Se_2I_4{}^{2+}$, $AsF_6{}^-$, and SO_2 and columns of $Se_2I_4{}^{2+}$ and $Sb_2F_{11}{}^-$, respectively. The $Se_2I_4{}^{2+}$ cations in both salts are similar and adopt the eclipsed configuration with long Se–Se bonds (average 2.481 Å). There are significant intraionic interactions between the syn iodine atoms (average 3.673 Å) that give

Table 2 *Characterized examples of binary sulfur, selenium, and tellurium halogen cations*

	F	*Cl*	*Br*	*I*
S	SF_3^+	SCl_3^+	SBr_3^+ S_7Br^+ Br_2S^+SSBr	$S_2I_4^{2+}$ S_7I^+ $[(S_7I)_2I]^{3+}$
Se	SeF_3^+	$SeCl_3^+$ $Se_7{}^+SeSeCl$	$SeBr_3^+$ $Se_2Br_6^+$ $Br_2Se^+SeSeBr$	SeI_3^+ $Se_2I_4^{2+}$ $I_2Se^+SeSeSe^+I_2$ $(Se_6I^+)_n$ $Se_6I_2^{2+}$
Te	TeF_3^+	$TeCl_3^+$ $[Te_{15}Cl_4^{2+}]_n$	$TeBr_3^+$ $[Te_{15}Br_4^{2+}]_n$	TeI_3^+ $Te_6I_2^{2+}$

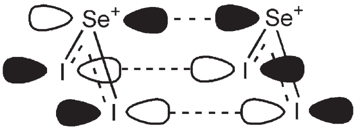

Figure 13 *Two SeI_2^+ radical cations joined via weak π*–π* interactions to give $Se_2I_4^{2+}$*

the cation a distorted trigonal-prism-like shape (see Figure 13). The Se–I bonds (average 2.451 Å) are shorter than those in SeI^{3+} (average: 2.510 Å), implying $4p_\pi$–$5p_\pi$ bonding, with a formal bond order of 1.25 per Se–I bond. The $Se_2I_4^{2+}$ ion can thus be considered as consisting of two SeI_2^+ radical cations joined by a 6-center, 2-electron π*–π* bond.

The $Se_4I_4^{2+}$ cation was prepared by reaction of Se_4^{2+} [*i.e.*, $Se_4(AsF_6)_2$] and iodine in SO_2 solution, and characterized by ^{77}Se NMR spectra.[53] The ^{77}Se NMR spectrum of the $Se_4I_4^{2+}$ solution is consistent with an $I_2Se^+SeSeSe^+I_2$ structure for the cation, and with an equilibrium of $Se_4I_4^{2+}$ with lesser amount of SeI^{3+} and $Se_6I_2^{2+}$.

Compound $[Se_6I^+]_n \cdot n[AsF_6^-]$ can be prepared quantitatively from Se, I_2, and AsF_5 in liquid SO_2 solution, and its structure was determined by single-crystal X-ray diffraction.[54] The crystal structure consists of AsF_6^- anions and polymeric strands of $[Se_6I^+]_n$ cations with some cation–cation and cation–anion interactions. The hexaselenium rings have a chair conformation, and are joined to two neighboring hexaselenium rings by two weak (2.736 Å) exocyclic 1,4-axial Se–I bonds (Figure 14).

Compound $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ can be prepared in 79% yield by condensing AsF_5 onto Se and iodine over liquid SO_2 (cooling the solution to −80°C for 10 min, and then warming to room temperature).[55,56] The crystal structure was determined by single-crystal X-ray diffraction, in which the discrete centrosymmetric cation of $Se_6I_2^{2+}$ contained a Se_6 ring of chair conformation with 1,4-axial iodine substituents (see Figure 15). The tricoordinate selenium atoms in the $Se_6I_2^{2+}$ cation are positively charged but there is some delocalization of

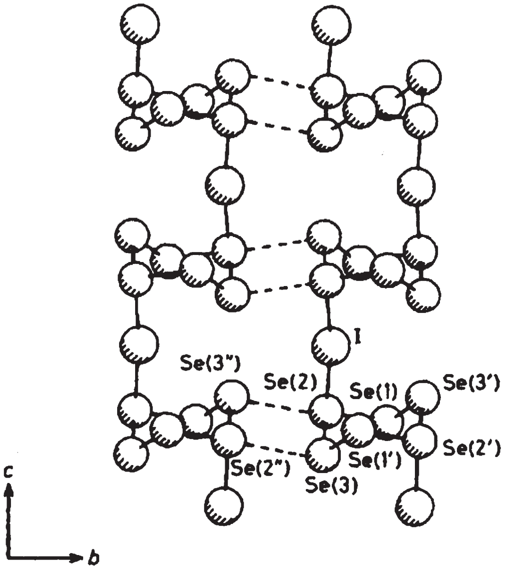

Figure 14 *View of the polymeric cations in* $[Se_6I^+]_n \cdot n[AsF_6^-]$ *(*AsF_6^- *omitted) showing the close contacts between chains. Bond lengths (Å): I–Se(2), 2.736(3); Se(1)–Se(2), 2.365(3); Se(1)–Se(3′), 2.292(4); Se(2)–Se(3), 2.370(4). Contacts (Å): I–Se(1), 4.030(3); I–Se(1′), 3.839(3); I–Se(3), 3.998(3); I–Se(3′), 3.865(3); I–Se(3″), 4.062(3); Se(2)–Se(3″), 3.591(3)*

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charge into the ring, giving rise to the observed Se–Se bond alternation. Each of the two iodine atoms makes two intra-ionic contacts [3.719(2) and 3.709(2) Å] with both the dicoordinate, but partially charged selenium atoms within the ring. The contacts are substantially shorter than the sum of the van der Waals radii of selenium and iodine (4.15 Å). The overall conformation of $Se_6I_2^{2+}$ is therefore that of a distorted cube.

Trihalotelluronium cations TeX_3^+ (X = F, Cl, Br, I) can be considered as being resulted from the reaction of Lewis acidic metal halides with tellurium tetrahalides, and have been reported in a number of systems. For example, reaction between $TeCl_4$ and Au_2Cl_6 formed the compound $[TeCl_3][AuCl_4]$,[57] and depending on the reaction conditions, different polymorphs of $[TeCl_3][NbCl_6]$ and $[TeCl_3][TaCl_6]$ could be obtained from reacting $NbCl_5$/$TaCl_5$ with $TeCl_4$.[58] As another example, $[TeBr_3][AsF_6]$ were prepared from tellurium and an excess of Br_2 and AsF_5, or by reacting $Te_4(AsF_6)_2$ with excess bromine.[51] Although the distinct trigonal-pyramidal TeX_3^+ unit can be identified in the crystal structures of these compounds, secondary interactions between the TeX_3^+ unit and the anions (*e.g.*, Te···X contacts) usually resulted in higher-order molecular or even extended structures, which suggests that this type of compounds may be useful for the construction of functional solid-state networks.

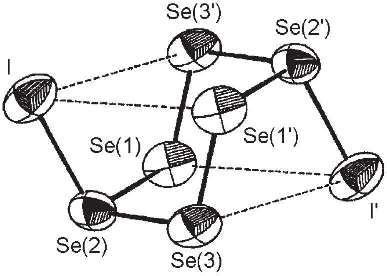

Figure 15 *The $Se_6I_2^{2+}$ cation in the crystal structure of $Se_6I_2(AsF_6)_2 \cdot 2SO_2$. Bond lengths: I–Se(2), 2.454(2); Se(1)–Se(2), 2.482(2); Se(2)–Se(3), 2.468(2); Se(1)–Se(3′), 2.227(2) Å. Bond angles: I–Se(2)–Se(l), 102.0(1)°; I–Se(2)–Se(3), 102.9(1)°; Se(1)–Se(2)–Se(3), 95.7(1)°; Se(2)–Se(1)–Se(3′), 103.5(l)°; Se(2)–Se(3)–Se(1′), 103.4(1)°. Contacts: I–Se(1′), 3.719(2) Å; I–Se(3′), 3.709(2) Å*

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The TeI_3^+ cation was reported in the compound TeI_3AsF_6, which was prepared by the reaction of I_2, Te, and AsF_5 in an SO_2 solution.[59] The single crystal structure consisted of essentially discrete TeI_3^+ cations and AsF_6^- anions with some cation–anion interaction, and the TeI_3^+ cation therein had approximately C_{3v} symmetry with an average Te–I distance of 2.667 Å and I–Te–I angle of 99.90°. In addition, the isostructural compound TeI_3SbF_6 was also prepared in a similar procedure.[48] Other systems featuring the TeI_3^+ cation include the solvated $TeI_3[AsF_6] \cdot 0.5SO_2$[60] and $TeI_3[AlI_4]$ (made from Te, two equivalent of I_2, and AlI_3, and was reported to be dark red, moisture-sensitive crystals.[61]

The Lewis acid–base reactions of Te_2Br with $MoOBr_3$, $TeCl_4$ with $MoNCl_2$/$MoOCl_3$, and Te with WBr_5/$WOBr_3$ yielded black, needle-like crystals of $[Te_{15}X_4][MOX_4]_2$ (M = Mo, X = Cl, Br; M = W, X = Br).[62] The crystal structure determinations showed that all three compounds are isotypic and consisted of one-dimensional $([Te_{15}X_4]^{2+})_n$ and $([MOX_4]^-)_n$ strands. The structures of the cationic strands (*e.g.*, see Figure 16) are closely related to the above-mentioned tellurium subhalides Te_2X (X = Br, I). One of the two rows of halogen atoms that bridge the band of condensed Te_6 rings is stripped off, and additionally, one Te position has only 75% occupancy which leads to the formula $([Te_{15}X_4]^{2+})_n$ (X = Cl, Br) for the cation. The anionic substructures consist of tetrahalogenooxometalate ions $[MOX_4]^-$ that are linked by linear oxygen bridges to polymeric strands. The compounds are paramagnetic with one unpaired electron per metal atom indicating oxidation state M(V), and are considered weak semiconductors.

In the reaction of WCl_6, I_2, and Te in a 2:1:6 ratio $Te_6I_2(WCl_6)_2$ is formed quantitatively by annealing at 150°C.[63] The crystal structure consists of $Te_6I_2^{2+}$ cations and slightly distorted octahedral WCl_6^- anions. The $Te_6I_2^{2+}$ ions are isostructural with the above $Se_6I_2^{2+}$ and consist of a six-membered ring of Te

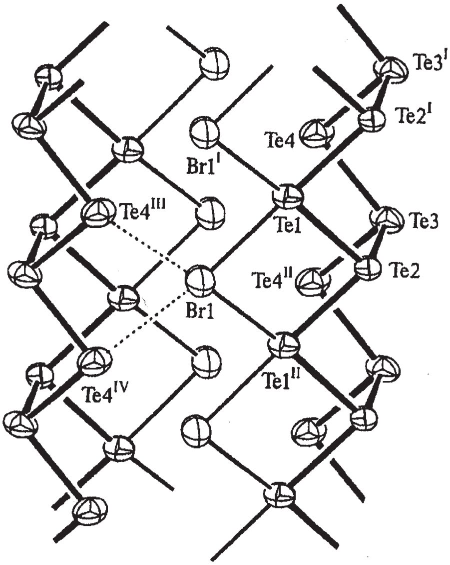

Figure 16 *A section of the two directly neighboring* $[Te_{15}Br_4^{2+}]_n$ *polycations in the structure of* $[Te_{15}Br_4][MOBr_4]_2$*. The Te(4) positions are only 75% occupied; the dotted lines indicate the weak interionic Te···Br contacts (3.29 Å, 90% probability ellipsoids); the superscript roman numerals indicate symmetry-related atoms*

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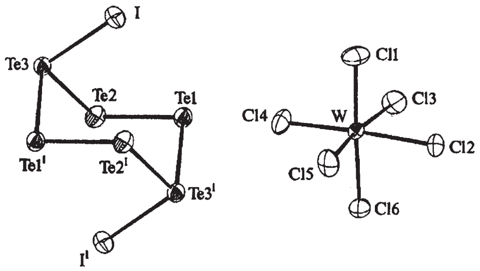

Figure 17 *The* $Te_6I_2^{2+}$ *and* WCl_6^- *ions in the structure of* $Te_6I_2(WCl_6)_2$ *(shown in 70% probability of the thermal ellipsoids). Selected distances (Å) and angles (°): W–Cl, 2.269(1)–2.387(1); Te(1)–Te(2), 2.670(1); Te(2)–Te(3), 2.861(1); Te(1)–Te(3′), 2.842(1); Te(3)–I, 2.670(1); Te–Te–Te and Te–Te–I, 97.5(1)–102.8(1)*

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atoms in the chair conformation with two I atoms bound in the 1,4-positions (see Figures 14 and 17). Like the above $Se_6I_2^{2+}$, the bond length in $Te_6I_2^{2+}$ shows distinct alternations. For example, the bonds Te(3)–Te(2) (2.86 Å) and Te(3)–Te(1′) (2.84 Å) are relatively long, while the remaining bonds Te(2)–Te(1) and Te(1′)-Te(2′) with an average of 2.67 Å are significantly shorter than a Te–Te single bond (2.75 Å). Some degree of double bonding could be assigned to the shortened bonds, and the positive charge was considered as being delocalized over all atoms of the cation, including the iodine atoms. This interpretation appeared to be consistent with the short contacts of the chlorine atoms of the surrounding WCl_6^- anions to the Te and I atoms of the cation. The shortest contact is formed by Te(3) with a Te···Cl distance of 3.174(1) Å, while the shortest I···Cl distances range from 3.500(1) to 3.727(1) Å.

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CHAPTER 8.2

Charge-Transfer (C.-T.) Adducts and Related Compounds

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8.2.1 Introduction

Reactions of di-halogens (I_2, Br_2) and inter-halogens (IBr, ICl) with organic molecules containing Group 16-donor atoms (LE; L = organic framework, E = S, Se, Te) have been the subject of renewed interest in the past few years both for their intrinsic interest and for their implications in different fields of research which span from synthetic to biological, material, and industrial chemistry.[1–11]

These reactions can follow a variety of pathways depending both on the acid/base nature of the reactants and on the experimental conditions used, the most important being the formation of neutral charge-transfer (C.-T.) "spoke" adducts featuring an almost linear E–X–Y moiety (X = Y = I, Br; X = I, Y = Br, Cl)[1,2,12,13] or insertion adducts containing a "T-shaped" X–E–Y fragment (X = Y = I, Br, Cl; X = I, Y = Br, see Chapter 10.3).[1,2,4–6,8] Other different structural archetypes have also been established by X-ray diffraction analysis and vibrational spectroscopy (especially FT-Raman) for the products of these reactions; they include donor oxidation ionic products having chalcogen–halogen terminal bonds ($[LE–X]^+$),[1,2,14,15] two-chalcogen-coordinated halogen(I) complexes ($[LE–X–EL]^+$),[1,2,16–18] and dications containing a chalcogen–chalcogen single bond ($[LE–EL]^{2+}$, see Chapter 7.2).[1–3,6,7,9,14,19] Polyhalides of exciting structural complexity are generally found as counter-anions of these ionic compounds.[9,15,16]

Predicting the outcome of the reactions between LE chalcogen-donor molecules and di- and inter-halogens is still a challenge, and attempts have been made in this direction by judging whether all the different products could be formed from a common intermediate species following a general pattern of reactivity. In particular, S. Husebye proposed that this species was the $[LE–X]^+$

(E = S, Se; X = I, Br) cation.[20] Whether this cation really forms in solutions, especially in low-polar solvents, is difficult to prove. It has been shown, however, that the calculated NBO charge distribution on $[LE–X]^+$ can be of great help in predicting the most likely product, at least among $[LE–EL]^{2+}$ dications, C.-T. "spoke", and "T-shaped" hypervalent adducts.[21,22] In fact, these three types of products can formally derive from a nucleophilic attack of the appropriate nucleophile on the $[LE–X]^+$ cation at the chalcogen or the halogen site.

A general broad qualitative observation is that on decreasing the electronegativity difference between the halogen and the chalcogen, C.-T. "spoke" adducts are more likely to be formed than "T-shaped" hypervalent adducts. Indeed, the number of structurally characterised "T-shaped" adducts decreases on passing from chlorine to iodine for S- and Se-donor molecules, and hypervalent sulfur compounds with iodine are unknown. On the other hand, no C.-T. XY-adducts are known for organic compounds containing tellurium as the donor atom.

In this chapter we will not attempt to give an overview of all of the knowledge on the reactivity of chalcogen-donor molecules towards di- and inter-halogens, since some aspects of this are discussed in other chapters. Instead, this chapter is dedicated exclusively to the analysis of the chemical bond and structural features of C.-T. adducts between LE chalcogen-donor molecules (E = S, Se) and di- and inter-halogens, and their reactivity towards metal powders.

Information on the thermodynamic properties (complexation constants, enthalpies of complexation, Gibbs energy of formation, and their relationships with structural and spectroscopic parameters) can be found in refs. 12, 23, and 24.

8.2.2 General Aspects of C.-T. Adducts between Chalcogen-Containing Molecules and Di- and Inter-Halogens

The reason why the interaction between LE chalcogen-donor molecules and XY di- and inter-halogens (X = Y = I, Br; X = I, Y = Br, Cl) to afford adducts containing an almost linear E–X–Y fragment is termed C.T. or electron-donor–acceptor is that it occurs, simplistically speaking, *via* the transfer of electron density from the non-bonding orbitals of the donor atom into the LUMO (Lowest Unoccupied Molecular Orbital) of the di-/inter-halogen acceptor molecule, which is a $\sigma_u{}^*$ orbital lying along its main axis, with consequent lowering of the X–Y bond order. The consequent increase of the X–Y bond length can be finely modulated by using donors of different strength, which means changing either the chalcogen-donor atom or its chemical environment.

Based on structural, vibrational, and electronic features, C.-T. adducts of S-donor molecules with I_2 (the most numerous) were classified in three categories:[25–28] (i) Weak or medium weak characterised by a mutual perturbation effect between the donor and the I_2 molecules. The I–I bond order [*n*(I–I)]† in these systems ranges from values slightly lower than 1 (unperturbed I_2 molecule), to not less than 0.6. These adducts show peculiar vibrational and electronic spectra; in particular they are characterised by only one Raman peak due to the ν(I–I) stretching vibration at wavenumbers lower than 180 cm^{-1} observed for solid I_2. (ii) Strong adducts characterised by *n*(I–I) ranging between 0.4 and 0.6. The vibrational and electronic spectra are determined by the nature of the S–I–I three-body fragment. (iii) Very strong adducts in which the donor–acceptor interaction is so strong that *n*(I–I) becomes lower than 0.4. The nature of the vibrational and electronic spectra of these systems reflects the properties of an LS–I$^{\rceil +}$ cation interacting with an I^- anion (LS–I$^{\rceil +}\cdots I^-$).

A different simplified description of the bond in C.-T. adducts between chalcogen-donor molecules and di-/inter-halogens can be derived from the one normally used for the bond in triatomic anions, such as I_3^-, Br_3^-, IBr_2^-, and ICl_2^- (XY_2^-), which can be considered hypervalent complexes of halogen(I).[20] The empty p_z orbital (σ_u^+ in $D_{\infty h}$) of a 16-electron low-spin central X^+ cation (X = I, Br) interacts with the out-of-phase terminal atom symmetry orbital (TASO) of adapted symmetry deriving from the linear combination of the lone-pairs of the two terminal Y^- anions, to produce a bonding and an antibonding Molecular Orbital (M.O.), the other TASO (σ_g^+ in $D_{\infty h}$) becoming a non-bonding orbital. This description is referred to as a three-centres, four-electrons (3c, 4e) bonding scheme, and accounts for the 0.5 bond order observed in these symmetrical trihalides. It can easily be adapted to other related compounds such as two-chalcogen-coordinated halogen(I) complexes ($[LE–X–EL]^+$), "T-shaped" hypervalent adducts (X–E(L)–Y, see Chapter 10.3), asymmetric trihalides, and also C.-T. "spoke" adducts. Both M.O. descriptions consider all these compounds strictly related to each other, particularly trihalides and C.T. adducts. Furthermore, both descriptions justify the presence of a partial negative charge on the terminal Y atom on the LE–X–Y system. In this way, Y itself can behave as a donor towards another XY acceptor molecule to give adducts of higher structural complexity (see Section 4 in this Chapter).

8.2.3 C.-T. "Spoke" Adducts

Most of the reported structurally characterised neutral "spoke" C.-T. adducts have sulfur as the donor atom and di-iodine as the acceptor molecule.[1,2,10,12,13,18,28–38] Those obtained from molecules containing selenium and di-iodine are less numerous,[1,2,39,40]

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† The *n*(I–I) bond order was calculated according to the empirical logarithmic function (1) proposed by Pauling and adapted by Burgi:[25]

$$n(\text{I–I}) = \exp[(d_0(\text{I–I}) - d(\text{I–I})/\text{b}] \qquad (1)$$

where *d*(I–I) and d_0(I–I) (2.67 Å, the gas phase value for the I–I single bond) are the bond distances of coordinated and free I_2, b (0.85 Å) is an empirical constant evaluated by Burgi from the analysis of experimental inter-atomic distances in tri-iodides.

while few adducts of S- and Se-donors with IBr[1,2,11,22,36,37,41–43] and ICl[1,2,37,43,44] have been reported and structurally characterised in the literature. Three Br_2-adducts of S-donors have been characterised by X-Ray diffraction analysis,[1,45] and no C.-T. adducts of Te-donors are known with any di- or inter-halogen. In some cases, I_2-adducts have been obtained from the reaction with IBr and ICl, demonstrating the tendency of these inter-halogens to disproportionate in solution.[26,27] In these compounds, the 1:1 stoichiometry in the asymmetric unit characteristic of a "spoke" C.-T. adduct may also correspond to extended 1D or 2D structures, in which LE and XY (E = S, Se; X = Y = I, Br; X = I, Y = Br, Cl) molecules alternate regularly (*m*:*m* adducts). Furthermore, chalcogen-containing molecules with several donor sites may give "spoke" adducts with a higher di-/inter-halogen content (*1*:*m* "spoke" adducts). Lastly, XY chains of varying length and structural complexity may be attached to the donor molecule (*1*:*m* "extended spoke" adducts).

The structural parameters describing the geometry of di-/inter-halogens binding to chalcogen-containing molecules (thioethers, selenoethers, thiocarbonyl, and selenocarbonyl compounds) are defined in Figure 1.

The directional parameters θ and φ are calculated with respect to the plane that contains the two electron-pairs of the chalcogen donor atom in a local tetrahedral sp^3 (Figure 1a) or trigonal sp^2 (Figure 1b) geometry. θ is the dihedral angle between this plane and the E–X vector, φ is the rotational angle from the bisector of the $(L)_2(C)E$ angle of the projection of the E–X vector onto the plane containing the two electron-pairs of the chalcogen-donor atom (Figure 1). An analysis of a large number of structural data of C.-T. "spoke" adducts having E–XY distances between 2.4 and 3.0 Å suggests a strong tendency of di-/inter-halogens to lie in the plane ($|\theta|$ statistically close to 0°) of the putative lone-pair of thioethers, selenoethers, and of most thiocarbonyl and selenocarbonyl compounds.[12,13] In some C.-T. "spoke" adducts of thiocarbonyl and selenocarbonyl donors the di-/inter-halogen molecule lies *quasi*-perpendicular to the $(L)_2(C)E$ plane ($|\theta|$ *ca.* 80°). These complexes are termed "perpendicular" and are formed with donor molecules having sterically crowded lone-pairs on the chalcogen atom.[12,13] Mean $|\varphi|$ values are statistically found 15–21° lower than

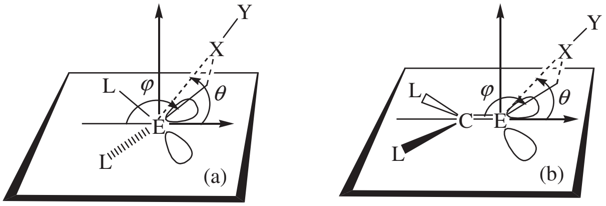
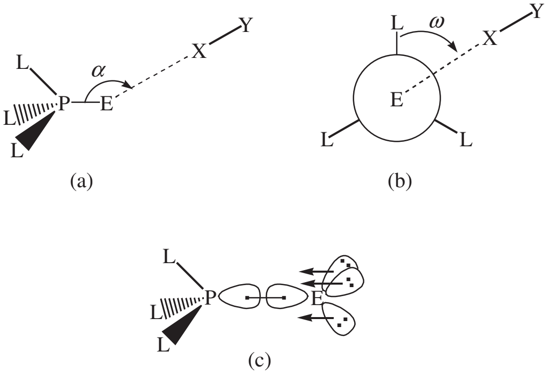


Figure 1 *Directional structural parameters describing the geometry of di-/inter-halogens binding to chalcogen-containing molecules in the cases of an sp^3 (a), and an sp^2 (b) hybridised chalcogen-donor atom. θ is the dihedral angle between the plane containing the chalcogen electron-pairs and the E–X vector; φ is the rotational angle between the E–X vector projected onto the plane containing the electron-pairs of the chalcogen-donor atom and the $(L)_2(C)E$ angle bisector*

the $|\varphi|=125.5°$ or $|\varphi|=120°$ values corresponding to the position of an idealised S(Se) sp^3 or sp^2 lone-pair, respectively. This observation has been explained in terms of a larger size of the valence shell of elements of the third and subsequent periods (sulfur and selenium), which allows lone-pairs to repel each other more strongly than in the valence shell of elements belonging to the second period (oxygen).[12] The directional parameters θ and φ cannot be used to parameterise the interaction of di-/inter-halogens with phosphine sulfides and selenides ($(L)_3PE$; E = S, Se), on account of the fact that the nature of the P–E bond, and therefore of the lone-pair(s) on the chalcogen atom, is still a matter of debate among theoreticians and experimenters.[12] To characterise the position of the XY molecule relative to the PE bond, the PE–X angle and the LPE–X torsion angle around the PE bond (α and ω, respectively, in Figure 2a–2b) are used instead.

The observed average values for these two angles are 105 and 57°, respectively, which agree with a staggered distribution of the electron pairs on the chalcogen relative to the P-substituents and support a one σ–bond, three π back-bonds description of the P–E bonding (Figure 2c).[12] These results, together with an average value very close to 180° generally observed for the E–X–Y angle indicate a strong directionality at short E–X distances (2.4–3.0 Å) in the formation of LE–XY C.-T. "spoke" adducts, which agrees very well with a C.T. or donor–acceptor bonding scheme for these compounds.

Under such circumstances, the E–X and X–Y bond distances should be strongly correlated in C.-T. "spoke" adducts. In fact, it is well known that for C.-T. "spoke" I_2-adducts with S-donors a reciprocal correlation exists between d(I–I) and d(S–I), which was initially proposed by F.H. Herbstein and W. Schwotzer as a hyperbola.[46] Assuming a valence (bond order) model for the description of the S–I–I system within C.-T. adducts, with $n(\text{I–I}) + n(\text{E–I}) = 1$



(a) (b)

(c)

Figure 2 *Directionality parameters describing the E–XY interaction (a and b) for phosphine-chalcogenide donors in the case of a one σ-bond, and three π back-bonds description of the P–E bond (c). For an alternative description of the P–E bond (see Chapter 5)*

(E = S, Se; n = bond order), and with n given by Equation (1), S. Husebye and co-workers,[20] proposed the following expression for the dependence of d(I–I) on the d(E–I) distance:

$$d(\text{I–I}) = d_0(\text{I–I}) - b(\text{I–I}) \ln\{1 - \exp[(d_0(\text{E–I}) - d(\text{E–I}))/b(\text{E–I})]\} \qquad (2)$$

where d_0(I–I) = 2.67 Å (the gas phase value for the I–I single bond), d_0(S–I) = 2.37 Å and d_0(Se–I) = 2.50 Å (the sum of Pauling's covalent radii), and b(I–I) = b(E–I) was assumed and calculated to be 0.362(E = S) and 0.357(E = Se), respectively. More recently, Laurence and co-workers[12] have extended Equation (2) to C.-T-. IBr- and ICl-adducts of N-, S-, and Se-donors trying to obtain d_0(E–I) and b(E–I) by fitting Equation (2) for the appropriate E–I–Y (E = N, S, Se; Y = I, Br, Cl) system against experimental data. They assumed b(I–Y) ≠ b(E–I), and starting from the average of structural data available for symmetrical $[\text{Y–I–Y}]^-$ fragments, by using Equation (1) with $n = 0.5$, they calculated the b(I–Y) constants to be 0.346, 0.326, and 0.340 for X = I, Br, and Cl, respectively.[12] By considering the experimental structural data of C.-T. I_2-adducts with S- and Se-donors (which are sufficiently numerous and diversified), the fitted values for d_0(E–I) and b(E–I) resulted 2.370 and 0.373 Å (E = S), and 2.495 and 0.389 Å (E = Se), respectively. The fitted values for d_0(E–I) agreed within 0.04 Å with the experimental values of 2.396 Å (E = S) and 2.528 Å (E = Se).[12] From the closeness of the calculated b(I–Y) values (see above) and from the nature of Equation (2), Lawrence and co-workers[12] already predicted that C.-T. "spoke" I_2-, IBr-, and ICl-adducts should have very close curves of Δd(I–Y) [$\Delta d(\text{I–Y}) = d(\text{I–Y})_{\text{adduct}} - d_0(\text{I–Y})_{\text{gas phase}}$(Y = I, Br, Cl)] *versus* d(E–I) for the same donor atom E(S, Se). Very recently, Lippolis and co-workers[22] pushed the latter consideration to extremes by putting together the crystal data of 94 I_2-, 14 IBr-, and 3 ICl-adducts with S-donors, and fitting them as a unique data-set to the following generalised form of Equation (2):

$$d(\text{I–Y}) = d_0(\text{I–Y}) - b(\text{I–Y}) \ln\{1 - \exp[(d_0(\text{S–I}) - d(\text{S–I}))/b(\text{S–I})]\} \qquad (3)$$

with d_0(S–I) = 2.396 Å (experimental value),[12] and b(I–Y) and b(S–I) as parameters. A good fitting could only be obtained if the 15 data for I_2-adducts characterised by bridging I_2 molecules (S–I distances lying between 3.01 and 3.25 Å and I–I distances between 2.74 and 2.79 Å) and the data for the "spoke" adduct benzimidazole-2(3*H*)-thione · I_2 were excluded from the data-set.[22] The remaining experimental data could be fitted very well (correlation coefficient R = 0.967) by a unique curve corresponding to Equation (3) with generalised coefficient parameters b(I–Y) and b(S–I) of 0.363 ± 0.020 and 0.366 ± 0.020, respectively. The exclusion of the experimental data for C.-T. I_2-adducts characterised by I_2 bridging two donor molecules from the fitting procedure was justified on grounds that these systems are very different from the C.-T. "spoke" adducts in terms of M.O. description.[22] In fact, the result of extending the simple $n \rightarrow \sigma^*$ description for the donor/acceptor interaction in "spoke"

I_2-adducts (M.O. combination of a lone-pair from the donor with the empty σ*orbital of I_2) to a system in which an I_2 molecule bridges two donor molecules ($n \rightarrow \sigma^* \leftarrow n$), is that only two electrons have a bonding nature, since the other two occupy a non-bonding orbital. However, these two bonding electrons are distributed over three bonds instead of over two, as in "spoke" I_2-adducts (much longer S···I and shorter I–I bond distances are expected). On the other hand, the fact that the structural data for the adduct benzimidazole-2(3*H*)-thione · I_2 do not fit the generalised Δd(I–Y) *versus* d(S–I) correlation was accounted on grounds that in this compound the terminal iodine atom is strongly H-bonded to an adjacent and symmetry related adduct unit.[18,22] This interaction lengthens both the S–I and the I–I bonds with respect to the values generally observed in "spoke" I_2-adducts with S-donors. In fact, in this adduct the sum of S–I and I–I distances is 5.81 Å, which is quite different from the value of 5.60 Å obtained by averaging the values for the other "spoke" I_2-adducts reported in the literature. The possibility of fitting all experimental data for I_2-, IBr-, and ICl-adducts with a given E-donor molecule (E = S, Se) with only one curve therefore seems real. This could be a consequence of the fact that the crystallographic data available have not been determined with the same accuracy, and also that they are differently affected by solid state interactions involving the S–I–Y moiety within the crystal lattice. Figure 3 shows the scatter plot Δd(I–Y) *versus* d(S–I) for an updated crystal data-set of neutral C.-T. I_2-, IBr-, and ICl-adducts with S-donors (125 points).

It also includes the structural data for adducts in which the coordinated IY molecule interacts with further IY molecules (14 points, Y = I, Br, Cl). Not all of these were considered by Lippolis and co-workers[22] in their attempt to fit a smaller data-set of this type (111 points) with a unique generalised curve (these systems are characterised by shorter S–I, 2.44–2.87 Å, and longer I–Y distances, 2.76-3.17 Å, see below). All the data except those for I_2-adducts featuring I_2 bridging two donor molecules (Δ in Figure 3) and the data for the adduct benzimidazole-2(3*H*)-thione · I_2 (○ in Figure 3) are fitted very well (correlation coefficient $R = 0.967$) by a unique curve corresponding to Equation (3) with fitting parameters b(I–Y) and b(S–I) of 0.306 ± 0.012 and 0.426 ± 0.017, respectively. A similar scatter plot and fitting of the available structural data (29 points) against Equation (3) can be obtained for IY-adducts with Se-donor molecules (Figure 4). These results clearly indicate that for both S- and Se-donor molecules, the d(E–I) and d(I–Y) bond distances (E = S, Se; Y = I, Br, Cl) observed within C.-T. adducts with IY acceptor molecules, are correlated and show the same degree of variability.

Δd(I–Y) was used as a generalised parameter, "independent" of the acceptor IY (Y = I, Br, Cl), to extend the classification of I_2-adducts with S-donor molecules (see above), based on the value of n(I–I) in weak or medium weak, strong, and very strong adducts also to IBr-, and ICl-adducts. Roughly, values of Δd(I–Y) lower than about 0.18 Å indicate formation of weak or medium weak adducts; values higher than about 0.34 indicate a very strong donor/acceptor interaction, the resulting compounds being described as an $\mathrm{LS{-}I]^{+}\cdots Y^{-}}$ ion-pair; and intermediate values of Δd(I–Y) ranging from 0.18

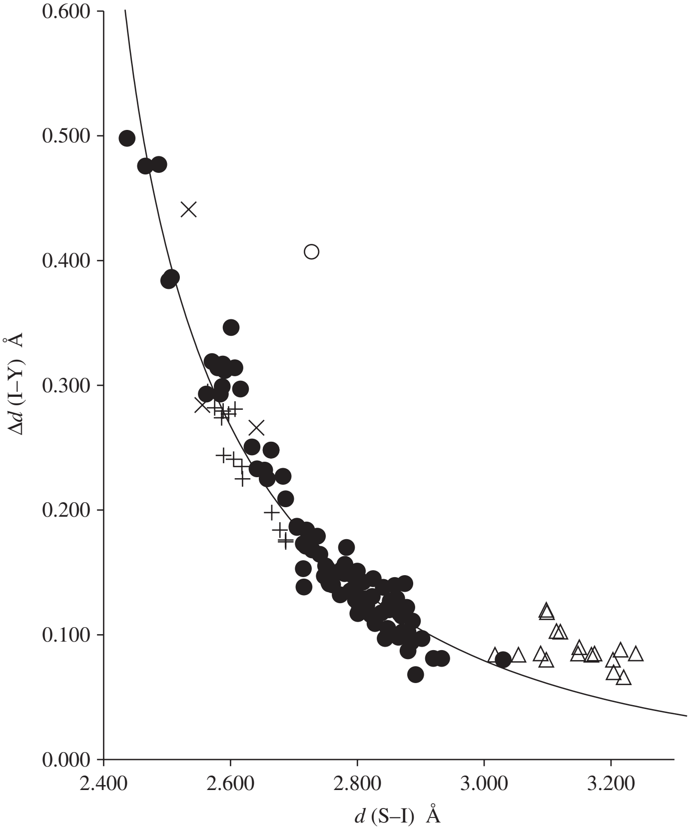


Figure 3 *Scatter plot of* $\Delta d(\mathrm{I–Y})$ [$\Delta d(\mathrm{I–Y}) = d(\mathrm{I–Y})_{adduct} – d_0(\mathrm{I–Y})_{gas\ phase}$ *(Y = I, Br, Cl)] versus* $d(\mathrm{S–I})$ *[Y = I(●, 90 points), Br(+, 14 points), Cl(×, 3 points)], and non-linear least-square curve fitting against Equation (3)* [$d_0(\mathrm{S–I}) = 2.396$ Å,[12] $d_0(\mathrm{I–I})_{gas\ phase} = 2.67$ Å, $d_0(\mathrm{I–Br})_{gas\ phase} = 2.47$ Å, $d_0(\mathrm{I–Cl})_{gas\ phase} = 2.32$ Å, $b(\mathrm{I–Y}) = 0.306 \pm 0.012$, *and* $b(\mathrm{S–I}) = 0.426 \pm 0.017$, $R = 0.967$]. *(Δ, 17 points) C.-T.* I_2*-adducts characterised by* I_2 *bridging two S-donor molecules, (○) benzimidazole-2(3H)-thione ·* I_2[18]

to 0.34 Å correspond to strong adducts with S–I and I–Y of similar strength (these ranges of variability for Δd(I–Y) were evaluated by Equation (1) and considering the empirical constant $b = 0.85$ Å for I_2-, IBr-, and ICl-adducts).[47] A similar classification can also apply to C.-T. "spoke" adducts of Se-donor molecules, and from Figure 4 it is evident that most of the known adducts with Se-donors can be classified as strong adducts in agreement with a "softer" character of selenium compared to sulfur, which implies better donor properties of Se-donors towards "soft" acceptor IY molecules (Y = I, Br, Cl). Significantly a linear correlation has been found between the observed FT-Raman stretching frequencies, ν(I–Y), and Δd(I–Y) (Y = I, Br) for C.-T. "spoke" adducts with S-donor molecules.[27]

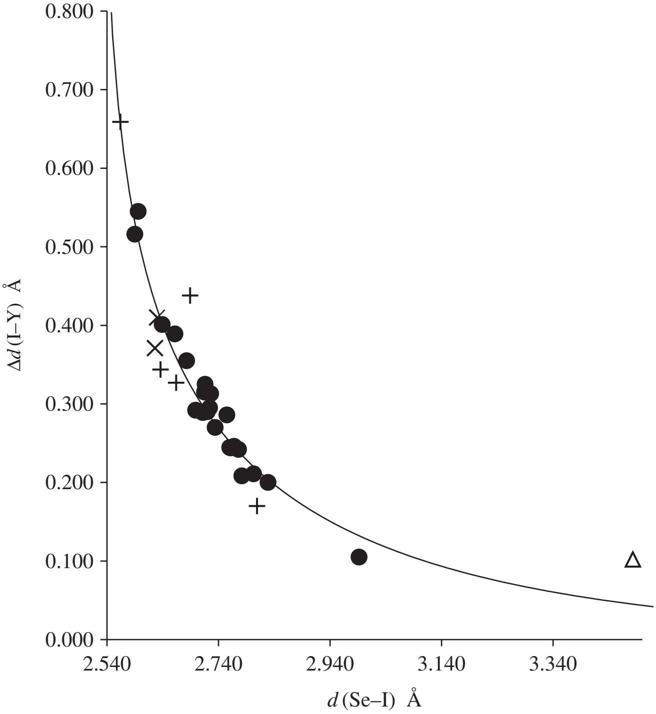


Figure 4 *Scatter plot of* $\Delta d(I\text{–}Y)$ [$\Delta d(I\text{–}Y) = d(I\text{–}Y)_{adduct}\text{–}d_0(I\text{–}Y)_{gas\ phase}$ *(Y = I, Br, Cl)] versus d(Se–I) [Y = I(●, 22 points), Br(+, 5 points), Cl(×, 2 points)], and non-linear least-square curve fitting against Equation (3)* [$d_0(Se\text{–}I) = 2.528$ Å,[12] $d_0(I\text{–}I)_{gas\ phase} = 2.67$ Å, $d_0\ (I\text{–}Br)_{gas\ phase} = 2.47$ Å, $d_0(I\text{–}Cl)_{gas\ phase} = 2.32$ Å, $b(I\text{–}Y) = 0.238 \pm 0.017$, *and* $b(Se\text{–}I) = 0.543 \pm 0.069$, *R=0.957]. (Δ) C.-T.* I_2*-adducts characterised by* I_2 *bridging two donor molecules. Six points in the plot correspond to C.-T.* I_2*-adducts characterised by* I_2 *interacting with further* I_2 *molecules*

8.2.4 C.-T. "Extended Spoke" Adducts

As already mentioned, a C.-T. "spoke" adduct of the type LE–XY (E = S, Se; X = Y = I, Br; X = I, Y = Br, Cl) can behave as an acceptor towards another LE donor molecule to form an LE–X–Y–EL system, in which XY bridges two donor units and *d*(X–Y) is shorter than that observed in the "spoke" 1:1 (LE/XY) system (see Section 3). Furthermore, an adduct of the type LE–XY can also behave as a donor towards an acceptor (A) to give the system LE–X–Y···A (A is normally another XY molecule). The interaction between the terminal halogen atom Y and the acceptor A will contribute to delocalise the negative charge on Y (see Section 2), leading to a strengthening of the E–X bond. The stronger the Y···A interaction, the stronger the E–X bond, so that in the extreme case we can see the whole system as being made up of two $LE\text{–}X^{\rceil+}$ and $Y\text{–}A^{\rceil-}$ ions interacting with each other ($LE\text{–}X^{\rceil+}\cdots Y\text{–}A^{\rceil-}$). The XY–A angle is generally very close to 90° owing to the fact that the π^*-donor HOMOs of the XY molecule are generated by combination of the wave functions of the p_x and p_y orbitals on the atoms X and Y, with the main axis lying along the direction of the X–Y bond. Therefore, a C.-T. type LE–X–Y···XY interaction takes place in "extended spoke" adducts, with donation from one of the two filled π^* orbitals of the XY molecule coordinated to the chalcogen atom towards the empty σ^* orbital of the second XY molecule.

A very illustrative example of this is represented by the 1:2 adduct between *N*-methylbenzothiazole-2(*3H*)-selone (btseMe) with IBr (Figure 5).[26]

The interaction between the Se-atom and the first IBr molecule (*d*(Se–I) = 2.564(1) Å) is so strong that the I–Br bond lengthens to 3.129(1) Å; at the same time the terminal bromine atom (Br(1) in Figure 5) interacts with a second IBr molecule to form an asymmetric IBr_2^- species (*d*(Br–I) = 2.803(1) and 2.645(1) Å); the whole system can therefore be described with the ionic formulation $(LE–I]^+\cdots Br–IBr]^-)$ (LE = btseMe). Another complex of the type $LE(XY)_2$ describable as a $(LE–X]^+\cdots Y–XY]^-)$ ionic-pair is obtained from the reaction of bromine with the adduct between the carbene 1,3-di-isopropylimidazol-2-ylidene and CS_2.[7] The crystal structure shows the ionic-pair being formed by a bromosulfane cation and a Br_3^- anion interacting each other through a Br···Br contact of 3.217(3) Å.

The donor behaviour of the terminal halide atom of numerous "spoke"-like XY-adducts of chalcogen-donor molecules towards additional XY molecules (XY is mainly I_2) has been demonstrated by carrying out the reactions with an excess of XY with respect to the 1:1 molar ratio between the reagents.[17,18,20,26,30,37,46,48,49] The structural features of adducts having a 1:2 (LE/XY) stoichiometry do not always conform to the general LE–XY···XY bent-shaped or $(LE–X]^+\cdots Y–XY]^-)$ ionic description adopted for btseMe · 2IBr.[26] For example, in btseMe · $2I_2$[26] and $(Me_2N)_3PSe \cdot 2I_2$ (Figure 6),[20] the strong interaction with the selenium atom (*d*(Se–I) = 2.67(2) (mean value) and 2.596(1) Å for the two compounds, respectively) lengthens the I–I bond of

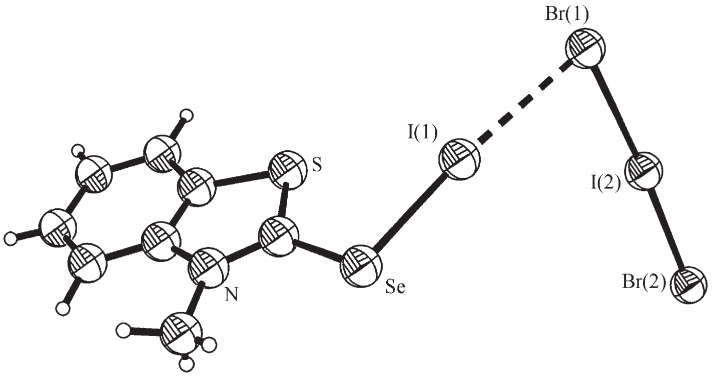


Figure 5 *Asymmetric unit in the 1:2 adduct btseMe · 2IBr (btseMe = N-methylbenzothiazole-2(3H)-selone):*[26] *Se–I(1) 2.564(1), I(1)–Br(1) 3.129(1), Br(1)–I(2) 2.803(1), I(2)–Br(2) 2.645(1) Å; I(1)–Br(1)–I(2) 89.27(3)°*

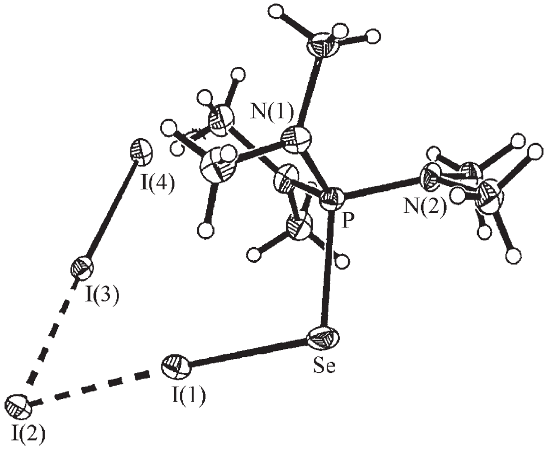


Figure 6 *ORTEP view of the compound* $(Me_2N)_3PSe\cdot 2I_2$*:*[20] *Se–I(1) 2.596(1), I(1)–I(2) 3.215(1), I(2)–I(3) 3.175(1), I(3)–I(4) 2.778(1) Å; I(1)–I(2)–I(3) 80.59(2)°*

the I_2 molecule interacting with the chalcogen atom to 3.03(4) (mean value) and 3.215(1) Å, respectively.

However, the interaction of the terminal iodine atom of the Se–I_2 system with the second I_2 molecule ($d(I\cdots I_2) = 3.29(7)$ (mean value) and 3.175(1) Å for btseMe · $2I_2$ and $(Me_2N)_3PSe\cdot 2I_2$, respectively) is not strong enough to form a triiodide ion. For these systems a bent-shaped $[LE–I]^{+}\cdots I^{-}\cdots I_2$ sequence, resembling a "V"-shaped pentaiodide ($I_2\cdots I^{-}\cdots I_2$), would be a better general description. An analogous situation was observed by M.E. Noble and co-workers[50] in the products of halogenation of the neutral bridge sulfur sites within M_2S_2 cores of various binuclear complexes of Mo(V) and W(V). These compounds are polymeric and feature bent-shaped $[S–I\cdots I\cdots I–S]^{3-}$ inter-M_2S_2 dimer links.

According to its structural features, the compound $(R_2'N)_3PSe\cdot 2.5I_2$ ($R_2'N$ = *N*-morpholyl),[20] having higher di-iodine content, can be described, as in the case of $(Me_2N)_3PSe\cdot 2I_2$, as an ionic compound of the type $[LE–I]^{+}\cdots I^{-}\cdots I_2$, in which an I^- ion interacts with an I_2 molecule and with a $[(R_2'N)_3PSe–I]^{+}$ cation through the iodine atom. An additional di-iodine molecule occupies a special position on an inversion centre and bridges the above-mentioned ionic aggregates pairwise by short contacts (Figure 7).

The local environment of I^- in this system is structurally reminiscent of some I_7^- ions that feature a central I^- interacting with three di-iodine molecules with an approximate local C_{3v} symmetry.[16]

Structurally characterised XY-adducts with a di-halogen content higher than 1:1 are still quite rare and so we cannot generalise about their structural archetypes. Apart from the cases already discussed, the adduct of triphenylphosphine sulphide (TPPS) with I_2 reported by E.A. Mayers and co-workers and having a 2:3 donor/acceptor stoichiometry,[30] is characterised by

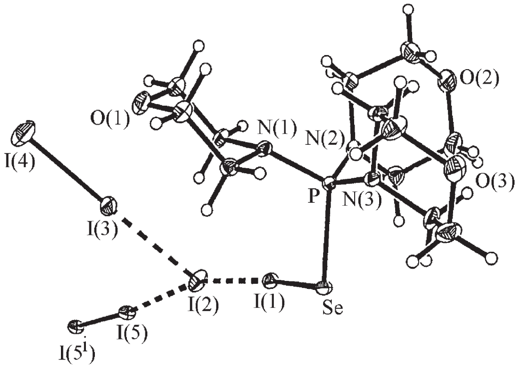


Figure 7 *ORTEP view of the compound* $(R_2'N)_3PSe \cdot 2.5I_2$ *(*$R_2'N$ *= N-morpholyl):*[20] *Se–I(1) 2.590(1), I(1)–I(2) 3.186(1), I(2)–I(5) 3.338(1), I(2)–I(3) 3.100(1), I(3)–I(4) 2.786(1), I(5)–I(5*^{i}*) 2.754(1) Å; I(1)–I(2)–I(3) 89.29(3), I(1)–I(2)–I(5) 165.87(2), I(3)–I(2)–I(5) 95.95(3)°; i = −1 − x, −y, 1 − z*

"soft–soft" I···I interactions between two TPPS–I_2 weak "spoke"-like adduct units and a bridging I_2 molecule. On the whole, the compound can be described as a discrete "Z"-shaped LE–I_2···I_2···I_2–EL system (LE = TPPS), in which the terminal iodine atom of each adduct unit behaves as a donor towards the same bridging di-iodine molecule. A similar structural motif is observed in the compound having the stoichiometry $(tu)_2 \cdot 3I_2$ (tu = thiourea, Figure 8),[17] and in the adducts corresponding to the formulation LE · IBr · 1/2IBr[41] and LE · ICl · $1/2I_2$[37] (LE = dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate and 4,5-*bis*(bromomethyl)-1,3-dithiole-2-thione, respectively) in which two LE–IBr and LE–ICl "spoke"-like C.-T. adduct units are bridged by an IBr and I_2 molecule, respectively.

All these "extended spoke" adducts structurally resemble "Z"-shaped X_8^{2-} polyhalides (X = I, Br) in which two asymmetric X_3^- trihalides are bridged by an X_2 molecule.[15] This further supports the above-mentioned similarity in the chemical nature of asymmetric X_3^- trihalides and linear E–X–Y systems in C.-T. adducts.

A different structural motif is observed in the compound with the stoichiometry $(tu)_3(I_2)_5$ (tu = thiourea) which according to the authors, consists of a tu–I_2 "spoke"-like strong C.-T. adduct, a $(tu)_2(I_3)]^{1+}$ cation counter-balanced by an I_3^-, and a perturbed di-iodine molecule.[17] The strong tu–I_2 adduct and the "V"-shaped planar tu–I···I···I–tu$]^{1+}$ cation are bridged at their terminal an central iodide atoms, respectively, by a di-iodine molecule (Figure 9).

More complicated structural situations are observed in di-halogen-rich adducts of chalcogen-donor molecules when further "soft–soft" halogen··· halogen interactions intervene, thus generating multidimensional networks (see Chapter 13.1). A clear example is represented by the structure of the compound $(dithizone)_2 \cdot 7I_2$.[46] Based on structural data the authors have described the repeating unit in this polymeric compound as a

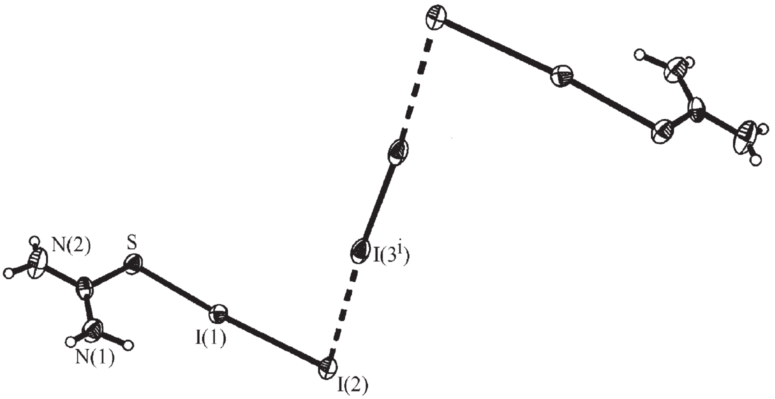


Figure 8 *ORTEP view of the compound* $(\mathrm{tu})_2\cdot 3\mathrm{I}_2$ *(tu = thiourea).*[17] *Two symmetry-related tu–*I_2 *"spoke"-like adducts are joined by a neutral* I_2 *molecule: S–I(1) 2.5028(13), I(1)–I(2) 3.0538(2), I(2)–I(3*^{i}*) 3.407(5) Å; I(1)–I(2)–I(3*^{i}*) 84.64°; i = −x, +y, 1/2 − z*

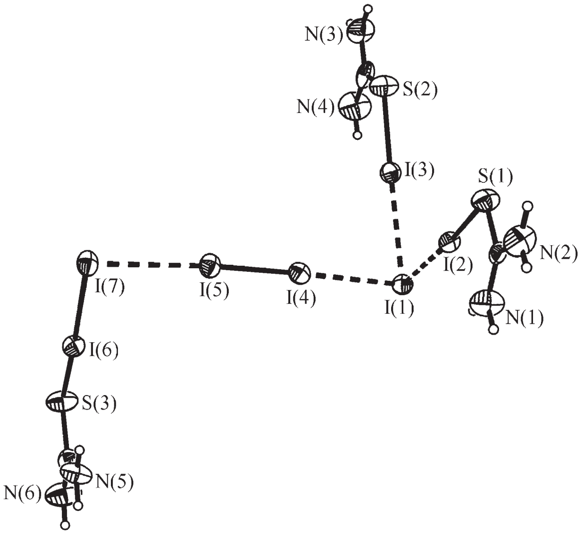


Figure 9 *A* $(\mathrm{tu})_2(\mathrm{I}_3)\rceil^{1+}$ *cation and a tu–*I_2 *"spoke"-like adduct joined by a neutral* I_2 *molecule in* $(\mathrm{tu})_3(\mathrm{I}_2)_5$ *(tu = thiourea); the counter* I_3^- *anion is not shown for clarity:*[17] *S(1)–I(2) 2.466(2), S(2)–I(3) 2.437(3), S(3)–I(6) 2.507(3), I(1)–I(2) 3.1457(9), I(1)–I(3) 3.168(1), I(1)–I(4) 3.247(1), I(4)–I(5) 2.756(1), I(5)–I(7) 3.491(1), I(6)–I(7) 3.0565(9) Å, I(6)–I(7)–I(5) 81.38, I(3)–I(1)–I(4) 82.48, I(2)–I(1)–I(4) 83.97°*

$\mathrm{LE{-}I}\rceil^{1+}\cdots\mathrm{I}_5\rceil^{1-}\cdots\mathrm{I}_2\cdots\mathrm{I}_5\rceil^{1-}\cdots\mathrm{I{-}EL}\rceil^{1+}$ sequence (LE = dithizone) and not as a chain of neutral di-iodine molecules. I···I contacts of 3.714 Å between "V"-shaped centrosymmetrically related I_5^- units form an approximately planar array of $\mathrm{I}_5\rceil^{1-}\cdots\mathrm{I}_2\cdots\mathrm{I}_5\rceil^{1-}$ fragments with $\mathrm{LE{-}I}\rceil^{1+}$ units alternatively arranged as perpendicular appendages on both sides of the plane containing the infinite poly-($I_5{}^{]1-}\cdots I_2\cdots I_5{}^{]1-}$) chains.

A polymeric structure is also observed in the adduct $LE \cdot 2I_2$ (LE = 4,5-*bis*(bromomethyl)1,3-dithiole-2-thione). $LE–I_2\cdots I_2$ bent-shaped units, which are typical in discrete "extended spoke" adducts with 1:2 (LE/I_2) stoichiometry, are joined head-to-tail by "soft–soft" $I\cdots I$ interactions involving the terminal iodide atom of the $LE–I_2$ moiety and the terminal iodide atom of the second coordinated di-iodine molecule.[37]

Surprisingly, the IY-adducts of chalcogen-donor molecules with a higher IY (Y = I, Br, Cl) content than the 1:1 (LE/XY) stoichiometry do not feature extended networks of weakly perturbed IY molecules. In this respect, the only example is represented by the I_2-adduct of TPPS with the formulation $TPPS \cdot 3I_2$.[30] In this compound a $TPPS–I_2$ weak C.-T. adduct unit interacts with a second di-iodine molecule, which in turn behaves as donor towards a third di-iodine molecule, to give, all together, a unique bent-shaped $TPPS–I_2\cdots I_2\cdots I_2$ system in the asymmetric unit. Infinite polycyclic ribbons are built in the crystal lattice *via* $I\cdots I$ "soft–soft" interactions between $TPPS–I_2\cdots I_2\cdots I_2$ units, as described in Chapter 13.1. To the best of our knowledge, this compound represents the only example of a di-halogen-rich adduct, in which an extended network of weakly perturbed di-halogen molecules is achieved. Compounds of this type can be considered stoichiometric reservoirs for di-halogen storage or as starting materials for halogenation reactions.[15]

8.2.5 Reactivity of C.-T. Adducts Towards Metal Powders

8.2.5.1 C.-T. Adducts as New Oxidising Reagents

The use of C.-T. adducts of chalcogen-donor molecules with di- and inter-halogens as oxidising reagents is thanks to the pioneering work by C.A McAuliffe's group starting from the year 1991. Together with his co-workers, he developed di- and inter-halogen adducts of molecules containing Group 15-donor atoms as new oxidising agents in mild conditions towards elemental metals, thus opening new perspectives to the synthesis of unusual transition-metal and main-group metal phosphine, arsine, and stibine complexes.[51–53] This synthetic route has made it possible to isolate a great number of metal complexes with unusual stoichiometries, geometries, and oxidation numbers at the metal centre. Some of these metal complexes, as the authors have reported, would not have been expected to exist according to the "hard–soft" acid–base theory (*e.g.* the ion $FeI_4{}^-$ in $[Ph_4Sb][FeI_4] \cdot Ph_3Sb \cdot I_2$ obtained by reacting $Fe_2(CO)_9$ with $Ph_3Sb \cdot I_2$).[54] Interestingly, in many cases (especially with noble metals) it was proved that the oxidation process of the metal as a powder was not possible if performed with free di- or inter-halogens. However, in spite of the validity of the results obtained, C.-T. adducts of phosphine, arsine, and stibine donors with di- and inter-halogens are unsuitable for practical applications, since their handling requires controlled anhydrous and inert conditions. Moreover, they are quite unattractive to use.

8.2.5.2 Oxidation of Metals by C.-T. Adducts of Sulfur-Donors

Given the interest aroused by this synthetic route to unusual metal complexes proposed by McAuliffe and co-workers, and given its potential industrial applications in the fields of electronics and the recovery of precious metals from waste materials, some efforts have been devoted to finding alternative classes of C.-T. adducts as oxidising reagents towards metal powders, which might avoid the drawbacks of handling molecules that contain Group 15-donor atoms. In this respect, C.-T. adducts of chalcogen-donor molecules with di- and inter-halogens appear to represent a good alternative thanks to their stability and easy handling. The S-donor molecules, whose C.-T. adducts with I_2 or IBr have been used so far as oxidising reagents towards metal powders, are shown in Figure 10.

Up to now, the scientific community agrees on considering the overall reaction as being made up of two distinct processes: oxidation of the metal by the ‘‘activated’’/perturbed di-/inter-halogen moiety in the C.-T. adduct, and complexation of the metal ion formed *in situ* by the molecule containing Group 15-, or 16-donor atoms, initially coordinated to the di-/inter-halogen molecule in the adduct. What still puzzles researchers is the higher oxidising ability of C.-T. adducts towards noble metal powders as compared to free di-/inter-halogens in solvents such as diethylether (Et_2O) and tetrahydrofuran (THF). In this respect, the electrochemical behaviour of some C.-T. adducts of S-donor molecules with I_2 and IBr has been investigated by cyclic voltammetry in Et_2O or THF.[11,55] Surprisingly, with the adducts in these solvents no significant increase in the oxidation potentials of the perturbed di-/inter-halogen molecules is observed compared to free di-/inter-halogen molecules.

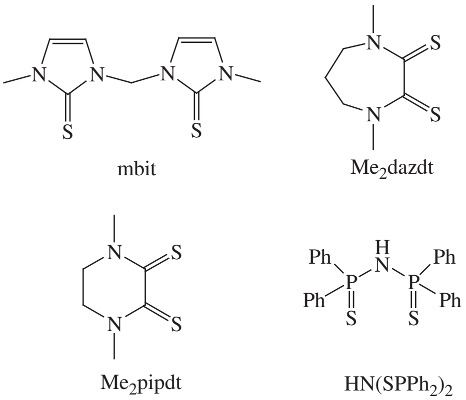


Figure 10 *Sulfur-donor molecules whose C.-T. adducts with I_2 or IBr have been used as oxidising reagents towards metal powders*

Therefore, other factors that have not yet been studied and are not easily quantifiable, such as the absorption properties of the C.-T. adduct at the surface of the metal powder and the solubility of the formed species should be important in determining the oxidation properties of C.-T. adducts towards metal powders. Furthermore, some extrinsic factors inherent to the experimental conditions, such as reaction temperature, reagent concentration, and nature of the solvent have been reported to affect the overall yield or the course of the reaction, and led to separation of different products in some cases.[55–59] In any case, it appears that the simultaneous presence of the donor molecule and the di-/inter-halogen lowers the oxidation potentials of the metals, allowing their oxidation, dissolution, and complexation.

The adduct mbit · $2I_2$ (mbit = 1,1′-*bis*(3-methyl-4-imidazoline-2-thione)methane, Figure 10) was found to oxidise tin(0) metal powder in Et_2O at room temperature to afford an air-stable Sn(IV) dicationic complex of formula $[Sn^{IV}(mbit)_2I_2]^{2+}$ counter-balanced by two asymmetric I_3^-.[60] In the cation, the Sn(IV) atom lying on a symmetry centre shows a slightly distorted octahedral coordination, with the iodides at the apices in *trans* position, and the two mbit molecules acting as bidentate-chelating ligands through the sulfur atoms.

The C.-T. adduct $Me_2dazdt \cdot 2I_2$ (Me_2dazdt = *N*,*N*′-dimethylperhydrodiazepine-2,3-dithione, see Figure 10), which proved to be air-stable, was successfully reacted in THF at room temperature with gold(0)[61] and palladium(0)[62] in powder, and with liquid mercury;[63] conversely, no reactivity of this adduct with platinum(0) and rhodium(0) was observed, even on refluxing the solvent.

From the reaction of $Me_2dazdt \cdot 2I_2$ with gold(0), the square-planar complex cation $[Au(Me_2dazdt)I_2]^+$ having a triiodide counterion was separated and its crystal structure solved.[61] The reaction of the corresponding IBr-adduct, $Me_2dazdt \cdot 2IBr$, with gold(0) as powder, wires, and thin films afforded the complex $[Au(Me_2dazdt)_2Br_2]IBr_2$,[11] which is structurally analogous to $[Au(Me_2dazdt)I_2]I_3$. Applications of this reaction to the dissolution of gold(0) contained in microelectronic devices were reported.[64]

The almost quantitative oxidation/complexation of palladium(0) in powder or foils by $Me_2dazdt \cdot 2I_2$ in THF, acetone, acetonitrile, and methylethylketone (MEK) to afford $[Pd(Me_2dazdt)_2](I_3)_2$ makes this synthetic route appealing for practical industrial applications. A selective process for Pd-recovery from model three-way car converters was simulated obtaining a Pd-extraction yield $\geq$ 90%, and was proposed as an alternative to hydrometallurgical processes.[62]

Liquid mercury is also quantitatively dissolved with production of the neutral complex $[Hg(Me_2dazdt)I_2]$ in which the metal ion resides in a severely distorted tetrahedral coordination environment.[63]

Although the salt *N*,*N*′-dimethylpiperazinium-2,3-dithione triiodide $[(Me_2pipdt)I_3]$ is not a C.-T. adduct, it is interesting to report its reactivity towards platinum in powder, with formation of the platinum(II) complex $[Pt(Me_2pipdt)_2](I_3)_2$.[65]

The choice of the I_2-adduct of tetraphenyldithioimidodiphosphinic acid, $HN(SPPh_2)_2$ (Figure 10), for the oxidation of metal powders by Isaia and co-workers, represents a successful attempt to bring together the donor ability of the phosphine-sulfide group towards I_2 and the well-known intrinsic ability of $HN(SPPh_2)_2$, and its deprotonated form $(N(SPPh_2)_2)^-$, to give *S,S′* metal chelation, while adapting to the preferred coordination geometry required by the metal ion.

The reaction in Et_2O of $HN(SPPh_2)_2 \cdot I_2$ (prepared *in situ* by mixing $HN(SPPh_2)_2$ and I_2 in a 1:1 molar ratio) with a variety of metals as powders – Sb,[66] Co,[67] Pd,[55] In,[56] Hg,[57] Au,[58] Cu,[59] – allowed their oxidation and the formation of complexes of the resulting metal ions with the ligand in its neutral or deprotonated form.

In particular, the reaction between $HN(SPPh_2)_2 \cdot I_2$ and antimony(0) metal powder in anhydrous Et_2O afforded a yellow-orange insoluble product, whose re-crystallisation from hot MeCN gave air stable yellow crystals of the unique binuclear $[(N(SPPh_2)_2)Sb(\mu\text{-}S)(\mu\text{-}I)_2Sb(N(SPPh_2)_2)]$ neutral complex.[66] In this complex, two five-coordinate antimony(III) ions are bridged by a sulfide and two iodide ions. Two bidentate $(N(SPPh_2)_2)^-$ ligands complete the coordination sphere at each metal ion through the two sulfur atoms, leading to a slightly distorted square pyramidal coordination geometry.

After re-crystallisation from hot MeCN, the reaction among $HN(SPPh_2)_2$, I_2, and cobalt(0) metal powder in anhydrous Et_2O or CH_2Cl_2 using a reaction molar ratio ranging from 1/1/1 to 1/3/3 always afforded crystals of the neutral complex $[Co(N(SPPh_2)_2)_2]$ in which a distorted tetrahedral coordination geometry is achieved at the metal centre by two bidentate monoanionic $(N(SPPh_2)_2)^-$ ligands.[67]

Interestingly, using either $HN(SPPh_2)_2 \cdot I_2$ or $HN(SPPh_2)_2 \cdot IBr$ as oxidising agents generated *in situ*, the same reaction with palladium(0) afforded the complexes $[Pd(HN(SPPh_2)_2)X_2]$ ($X = I, Br$) as air stable brownish microcrystals.[55] Re-crystallisation of $[Pd(HN(SPPh_2)_2)I_2]$ in hot MeCN afforded crystals of the neutral square-planar complex $[Pd(N(SPPh_2)_2)_2]$ featuring two $(N(SPPh_2)_2)^-$ anions acting as bidentate ligands.

Metal complexes of the neutral ligand $HN(SPPh_2)_2$ are very rare, since the imido-proton dissociation to afford the anionic species $(N(SPPh_2)_2)^-$ can occur very easily (see Chapters 5). However, after re-crystallisation from anhydrous CH_2Cl_2, the reaction of liquid mercury with one molar equivalent of $HN(SPPh_2)_2 \cdot I_2$ in anhydrous Et_2O afforded stable colourless crystals of $[Hg(HN(SPPh_2)_2)I_2]$ in which a distorted tetrahedral coordination geometry is achieved at the metal ion by two iodide ions and the sulfur atoms of a bidentate neutral $HN(SPPh_2)_2$ ligand. Besides the main product $[Hg(HN(SPPh_2)_2)I_2]$,[57] on performing the same reaction with a $Hg/HN(SPPh_2)_2/I_2$ molar ration of 1/2/2, a small amount of white crystals of the neutral complex $[Hg(N(SPPh_2)_2)_2]$, structurally analogous to $[Co(N(SPPh_2)_2)_2]$,[67] was isolated.[57]

The simultaneous formation of two different complexes was also observed in the reaction of copper(0) metal powder with one molar equivalent of $HN(SPPh_2)_2 \cdot I_2$ in anhydrous Et_2O.[59] They proved to be $[Cu_4(N(SPPh_2)_2)_3]I_3$ and $[Cu(HN(SPPh_2)_2)_2]I_3 \cdot MeCN$: the former features a tetrahedron cluster of copper(I) atoms surrounded by three bidentate $(N(SPPh_2)_2)^-$ ligands coordinated to the metal ions through the sulfur atoms; the latter is characterised by two bidentate neutral $HN(SPPh_2)_2$ ligands imposing a distorted tetrahedral coordination geometry at the copper(I) centre.

Crystals of $[In(N(SPPh_2)_2)I_2]$[56] and $[Au(N(SPPh_2)_2)I_2]$[58] were obtained directly from the reaction mixture made up of $HN(SPPh_2)_2 \cdot I_2$ and one molar equivalent of indium(0) and gold(0), respectively, in anhydrous Et_2O. In both complexes the metal ions feature a +3 oxidation state. In the case of indium(0) it was observed that the reaction with $HN(SPPh_2)_2 \cdot I_2$ in Et_2O occurs in two steps:[56] the first leads to the formation of In_2I_6; the second consists of the reaction of this species with $HN(SPPh_2)_2$ to give the final complex $[In(N(SPPh_2)_2)I_2]$ and InI_4^-. The optimum $HN(SPPh_2)_2/I_2/In$ reaction molar ratio was 1/3/2.

The complexes, $[Co(N(SPPh_2)_2)_2]$, $[Pd(N(SPPh_2)_2)_2]$, $[Hg(N(SPPh_2)_2)_2]$, $[In(N(SPPh_2)_2)I_2]$, and $[Au(N(SPPh_2)_2)I_2]$, can also be prepared by using the appropriate metal salt and $KN(SPPh_2)_2$.[68]

The reactivity of the complexes $[In(N(SPPh_2)_2)I_2]$ and $[Hg(HN(SPPh_2)_2)I_2]$ dissolved in CH_2Cl_2 towards excess HI_{aq} was investigated to design a chemical process aimed at the recovery of the two metals from industrial waste materials. In both cases the formation of MI_4^{n-} ($M = Hg$, $n = 2$; $M = In$, $n = 1$) was observed together with the release of $HN(SPPh_2)_2$, which could be recycled in a cyclic recovery process as shown in Figure 11.

All the metal complexes obtained using C.-T. adducts of S-donor molecules with halogens and inter-halogens as oxidising reagents towards metal powders are summarised in Table 1.

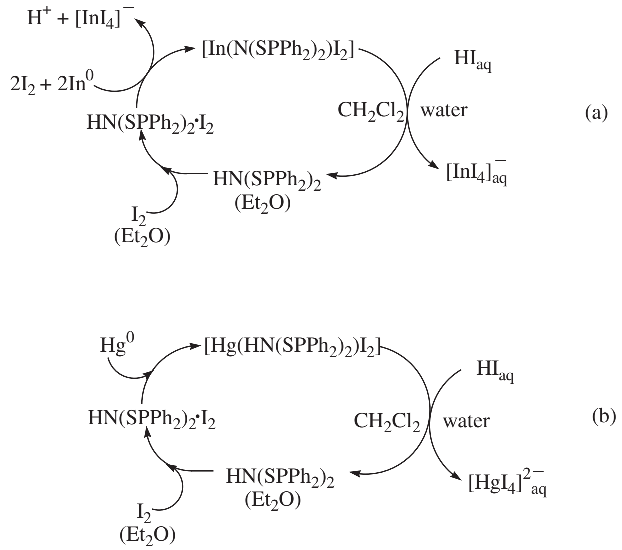


Figure 11 *Proposed reaction schemes for the recovery of indium (a) and mercury (b) from waste materials using* $HN(SPPh_2)_2 \cdot I_2$ *as oxidising reagent*[56,57]

Table 1 *Structurally characterised metal complexes obtained using C.-T. adducts of S-donor molecules as oxidising reagents towards metal powders*

Adduct[a]	*Metal*	*Solvent*[b]	*Main product/s*	*Yield (%)*	*References*
mbit $\cdot$ $2I_2$	Tin	Et_2O	$[Sn(mbit)_2I_2](I_3)_2 \cdot 2/3I_2$[c]	—	60
Me_2dazdt $\cdot$ $2I_2$	Gold	THF	$[Au(Me_2dazdt)I_2]I_3$[d]	—	61
Me_2dazdt $\cdot$ 2IBr	Gold	THF	$[Au(Me_2dazdt)Br_2]IBr_2$[d]	100	11
Me_2dazdt $\cdot$ $2I_2$	Mercury	THF	$[Hg(Me_2dazdt)I_2]$[d]	100	63
Me_2dazdt $\cdot$ $2I_2$	Palladium	THF	$[Pd(Me_2dazdt)_2](I_3)_2$	100	62
$HN(SPPh_2)_2 \cdot I_2$	Antimony	Et_2O	$[(N(SPPh_2)_2)Sb(\mu\text{–}S)\text{-}(\mu\text{–}I)_2Sb(N(SPPh_2)_2)]$[c]	45	66
$HN(SPPh_2)_2 \cdot I_2$	Cobalt	Et_2O	$[Co(N(SPPh_2)_2)_2]$[c]	75	67
$HN(SPPh_2)_2 \cdot I_2$	Copper	Et_2O	$[Cu(HN(SPPh_2)_2)_2]I_3 \cdot MeCN$ $[Cu_4(N(SPPh_2)_2)_3]I_3$	10 89	59
$HN(SPPh_2)_2 \cdot I_2$	Gold	Et_2O	$[Au(N(SPPh_2)_2)I_2]$	20	58
$HN(SPPh_2)_2 \cdot I_2$	Indium	Et_2O	$[In(N(SPPh_2)_2)I_2]$	23	55
$HN(SPPh_2)_2 \cdot I_2$	Mercury	Et_2O	$[Hg(HN(SPPh_2)_2)I_2]$ $[Hg(N(SPPh_2)_2)_2]$	95 —	57
$HN(SPPh_2)_2 \cdot I_2$	Palladium	Et_2O	$[Pd(HN(SPPh_2)_2)I_2]$ $[Pd(N(SPPh_2)_2)_2]$[c]	95 40	55
$HN(SPPh_2)_2 \cdot IBr$	Palladium	Et_2O	$[Pd(HN(SPPh_2)_2)Br_2]$	35	55

[a] See Figure 10. [b] Reaction conditions: stirring at room temperature under nitrogen atmosphere or in air for several hours or days. [c] Obtained after re-crystallisation from MeCN of the product isolated from the reaction mixture. [d] Obtained from the reaction mixture by diffusion of Et_2O vapour.

8.2.5.3 Oxidation of Metals by C.-T. Adducts of Selenium-Donors

To date no published reports of this novel synthetic route applied to C.-T. adducts between Se-donor molecules and di- and inter-halogens have been reported. In 2001, S.M. Godfrey and co-workers[2] announced the reaction of the adduct $Me_2Se \cdot I_2$ with unactivated cobalt metal powder to give the complex $[(Me_2Se)_2CoI_2]$, which would be the first cobalt(II) selenoether complex and the first tetrahedral cobalt(II) selenium complex to be characterised crystallographically.

8.2.6 Conclusions

The structural diversity shown by the products of the reactions between chalcogen-donor molecules and di- and inter-halogens clearly explains the considerable renewed interest in these systems. Among all products, C.-T. adducts are the most studied. However, although much is now known concerning the solid-state structure of "spoke" adducts, more complicated systems (*e.g.* "extended spoke" adducts with the coordinated di-/inter-halogen molecule (XY) interacting with other XY molecules) require further investigation. Moreover, a larger number of "spoke" adducts with IBr and ICl for S-donor molecules, and with I_2, IBr and ICl for Se-donor molecules need to be synthesised and structurally characterised to completely elucidate the structural relationships within these systems. C.-T. adducts with Te-donor molecules still represent a challenge. All this, together with several potential applications for these compounds (*e.g.* oxidation reagents for unactivated metal powders for their recovery from waste material, reservoirs of di- and inter-halogens for organic and inorganic synthesis, and synthetic drugs for metabolic and autoimmune disorders) is certain to keep our interest awake for long time.

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CHAPTER 9.1

Metal Chalcogenides: Clusters, Layers, Nanotubes

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9.1.1 Introduction

The metal chalcogenides form a vast, almost infinite area of research. It is practically impossible in a single review to cover all the aspects of this chemistry, including synthesis, crystal and electronic structure, physical properties of the solids, chemical properties and applications. The task is made easier since reviews devoted to different aspects of the metal chalcogenide chemistry have been appearing continuously, trying to keep up with the new compounds, while the synthesis and characterization of chalcogenides continues unabated.[1–16] For example, only quite recently pure Rb_2Te was prepared (for the first time!) and the structures of its polymorphs determined.[17] The efforts in this area are constantly driven by important technological applications found for many of these materials as well as their remarkable diversity in structure and properties. With increased access to sophisticated structural tools and solution methods, more and more complicated compounds are prepared and characterized. A vast amount of research was dedicated also to the intercalation of innumerable guests into the chalcogenide hosts. The chalcogenides-host lattices are conducting: it means that the concentration of the guest species (which are ionic) can be altered by oxidation or reduction of the host lattice. Group 4–6 transition metal (TM) dichalcogenides (M=Ti, Zr, Hf, Nb, Ta, Mo, W) and ternary 3d chalcogenides AMQ_2 (A=alkali metal; M=Ti, V, Cr, Mn, Fe, Co, Ni) all have 2D-layered structures capable of intercalating various guests. The notion of intercalation has been expanded to include 3D lattices – the Chevrel phases $M_xMo_6Q_8$ (intercalation into intersecting channels), Nb_3Q_4 (Q=S, Se) $A_xTi_3S_4$, $Tl_xV_3S_4$ (intercalation into the tunnels) and 1D structures – MQ_3 (M=Ti, Zr, Hf; Q=S, Se), $AFeS_2$ (A=Na–Cs), AMo_3Q_3 (A=alkali metal; Q=S, Se).[18–29]

The present review is thus not intended to give the comprehensive coverage of all sides of metal chalcogenide chemistry and material science. The preparation methods mostly include high-temperature synthesis from the elements, and the structures of many binary metal chalcogenides belong to the very basic structural types, found in inorganic crystallography textbooks and earlier reviews. Not being a physicist, the author prefers to leave detailed discussion of physical properties to the specialists. Instead, he chooses selected important topics for the review. These are cluster formation and metal–metal bonding in the chalcogenide structures and new nanostructures (nanotubes and inorganic fullerens based on metal chalcogenides). To the best of our knowledge, no comprehensive coverage of metal–metal bonding situations for all the metal chalcogenides has appeared to date.

9.1.2 Metal Clusters, Chains, Layers

9.1.2.1. General Remarks

The metal chalcogenides tend to form covalent, often low-dimensional structures in contrast to the ionic, 3D-type structures of the oxides. Only in single cases, the oxide and chalcogenide phases are isostructural, as in $BaMX_3$ ($M=Zr$, Hf; $X=O$, S) perovskites.[30] The greater covalency of the metal–chalcogen interactions reduces the relative charge on the metal ion thus enhancing metal orbital diffuseness and favors M–M bonding. Above all, the 4d and 5d elements are capable of using the remaining valence electrons to form metal–metal bonds. The occurrence of the latter often rationalizes the stoichiometry of chalcogenides and has resulted in the replacement of the old scheme of classification of simple compounds, by one based on structural elements.[31] M–M bonding can be restricted to a few directly coupled atoms, which then leads to clearly defined cluster units. Frequently, however, infinitely extended regions of bonded metal atoms result. The basic principle is that when the number of non-metal atoms in a compound is not sufficient to isolate the metal cluster, the latter will condense, will link up *via* direct M–M bonds. The structures of metal-rich compounds of the TMs with 13–16 group elements are often analyzed only in terms of characteristic coordination polyhedra of the non-TM atoms and the way in which they link together, and the significance of the M–M interaction has been recognized much later than for the metal-rich halides. Of course, every structural classification is based on idealized structures, and involves a considerable amount of interpretation. It should also be noted that no generally valid relationship exists between interatomic distance and bond order. For example, in metal-rich alkali metal oxides and alkaline earth nitrides, the bonding M–M distances are considerably larger than the non-bonding M–M distances. In the review, a broad approach is taken. For 3d elements, M–M distances shorter than 3 Å were taken into account, for early TMs and lanthanides this margin was even larger. Even if two metals being close do not necessarily means strong direct orbital overlap, this often is very important for magnetic interactions and for other bulk properties of the solid.

In many cases, M–M bonding is propagated along linear or zigzag chains. Finally, in very metal-rich compositions, one arrives at the situation where the whole domains of the metal crystal lattice incorporate chalcogen atoms. A striking example here is offered by Lu_7Te and Lu_8Te, which can be simply regarded as products of *regular substitution* of Te atoms in a rather distorted h.c.p. of Lu metal, specifically for every 4th atom in every 3rd horizontal row of Lu in Lu_8Te, and for every 2nd atom in every 4th row for Lu_7Te. What is quite remarkable is that the analogous products have not been found for La, Pr, Gd, Ho, Tm, Yb instead of Lu.[33]

9.1.2.2. Isolated Clusters

Isolated clusters are not too frequently encountered in the chalcogenide structures. The M_2^{4+} units (M=Al, Ga, In) are found in M_7Te_{10}, GaQ (Q=S, Se, Te), In_6Q_7 (Q=S, Se), In_4Q_3), $InGaQ_2$ (Q=Se, Te). Their formation is easily explained by simple valence rules.[33–38] Isolated dimeric units Fe_2^{6+} were found in antiferromagnetic Na_3FeS_3 (edge-sharing tetrahedral anion with Fe–Fe distance of 2.877(2) Å.[39] The dimeric Cr_2^{6+} units (Cr–Cr 2.9 Å) are formed by face-sharing octahedra in MCr_3S_5 (M=Tl, Rb, Cs).[40] Dimerization of two Ti^{3+} (Ti–Ti 3.14 Å) occurs in $TlTi_5Se_8$.[41] In the structures of Rh_2Q_3 (Q=S, Se) and Ir_2S_3, similar face-sharing of two octahedra is not able to bring two M^{3+} centers closer than at 3.2 Å with hardly any M–M interaction.[42] M_2 dimers can also be discerned in the structures of lower tellurides of Zr_5Te_6 (Zr–Zr 3.26 Å) and $Hf_{1.35}Se_2$ (Hf–Hf 3.38 Å).[43,44] An interesting situation is observed in the structures of M_3SiTe_6 (M=Nb, Ta): the M and Si atoms form planar five-membered rings M_2SiMSi, which thus include M–M dimers (Nb–Nb 2.95; Ta–Ta 2.90 Å). Nb_3GeTe_6 is isostructural.[45] The rings are fused together into flat ribbons *via* opposite (NbSi) sides. The chalcogen-rich selenides M_2Se_9 (M=V, Nb) can be regarded as $\{M_2(\mu_2\text{-}Se_2)_2\}^{4+}\{Se_5^{4-}\}$. The cluster units are completely separated from each other by unusual "superreduced" Se_5^{4-} anions in the chains.[46] Sometimes M_2 and M_3 units result from distortions in the infinite metal chains (*vide infra*).

The trimeric units are quite rare. A linear Rh_3 chain is observed in *prassolite*, $Rh_{17}S_{15}$ (Rh–Rh 2.59 Å). Each Rh atom has four S atoms in the square plane perpendicular to the chain axis. The short Rh–Rh distance implies a strong interaction.[47] In the structure of a thiospinel, $FeRh_2S_4$, linear triplets M–Rh–M (here M denotes mixed Fe/Rh occupancy) are found (M–Rh 2.91 Å).[48] Linear trinuclear Nb_3 groups (Nb–Nb 3.07–3.25 Å) can also be discerned in the structure of $NbTe_4$=$Nb(Te_2)_2$. They are connected through ditellurido bridges acting simultaneously both as inter- and intracluster links to give a 3D-structure. The Nb–Nb bonding is electron-deficient (bond order 0.75).[49] An intriguing example is found in U_2PdS_4, where V-shaped units ($\angle$ UPdU 147°, U–Pd 3.10 Å) are observed. This seems to be the only example of U–M bonding in chalcogenides (the chalcogenides with U–U bonding are completely lacking).[50] M_3 triangles are present in the trigonal modifications of NiQ (Q=S (*millerite*), Ni–Ni 2.53 Å; Q=Se, 2.64 Å).[51]

Open M_4 units are also quite rare. In the selenobromides $M_4Se_{16}Br_2$ (M=Nb, Ta) there are tetranuclear units $\{M_4(\mu\text{-}Se_2)_6\}$, which result from condensation of three $\{M_2(\mu\text{-}Se_2)_2\}$ clusters. The M–M distances within them are about 3.1 Å.[52] Single crystal structure determination of V_5S_8 revealed the presence of rhombic vanadium clusters in the structure with hinge V–V bond of 2.88 Å, peripheral bonds of 3.04 Å and strong intercluster bonding (V–V 2.92 Å).[53]

Tetrahedral M_4 clusters are more common. As a part of cuboidal units $M_4(\mu_3\text{-}Q)_4{}^{5+}$ they are present in ternary chalcogenides GaM_4Q_8 (M=Nb, Ta; Q=S, Se) and $GaTa_4Se_8$. Mo can substitute for Nb in solid solutions $GaNb_{4-x}Mo_xS_8$. The magnetic properties of these compounds indicate a semimetal behavior. The Nb–Nb bonds in the tetrahedron are 2.975(1) Å in $GaNb_4S_8$, 3.026 Å in $GaNb_4Se_8$ and 3.002(2) in $GaTa_4Se_8$.[54,55] The Nb and Ta compounds are Mott insulators, but at high pressure they become superconductors; the pressure do not affect much the intracluster M–M bonding but rather the intercluster M–M contacts. The isostructural vanadium chalcogeniudes AV_4Q_8 (A=Ga, Ge; Q=S, Se) are magnetic Mott insulators.[56,57] For Mo, MMo_4S_8 (M=Al, Ga), $GaMo_4Se_8$ and $GaMo_4(S_xSe_{8-x})$ are known.[58–61] Formation of mixed cation $GaE_{0.5}Mo_4S_8$ (E=Ge, Si and even C) was also claimed.[62] $GaMo_4S_8$ shows ferromagnetic ordering at low temperatures.[63] To this type also belong $MMo_2Re_2S_8$ (M=Zn, Fe, Co, Ni).[64] This structure type is alternatively derived from distorted thioshpinel structure, where the 4d and 5d TMs are no longer in the centers of the chalcogenide octahedra, the M-Q distances split into three longer and three shorter bonds, they join into tetrahedral clusters, while M remains in the tetrahedral positions. In $Re_4S_4Te_4$, obtained from the elements or from Re_6Te_{15} and S, the cuboidal units $Re_4(\mu_3\text{-}S)_4{}^{8+}$ (Re–Re 2.785 Å) are connected into a 3D network *via* telluride bridges.[65] This is in sharp contrast to ReS_2, $ReSe_2$, and ReSSe which all feature flat rhombic Re_4 clusters, connected into chains (*vide infra*). In fact, these chains can be regarded as originating from opening up of one of the M–M bonds in the Re_4 tetrahedron, and polymerization of the resulting flattened "biradicals." This last example also shows which potentially rich possibilities, still largely unexplored, the preparation of chalcogen-mixed phases (in particular with S/Te combination) might offer. Partially substituted quarternary chalcogenides $Re_{4-x}Mo_xS_4Te_4$ $(0<x<2)$ and $Re_3MoS_{4-y}Se_yTe_4$ $(0<y<1)$ with modified $Re_{4-x}Mo_xS_4{}^{8+}$ and $Re_3MoS_{4-y}Se_y{}^{8+}$ cores were also prepared, and their electronic structures were investigated by X-ray electron spectroscopy and theoretical calculations. The formal oxidation state of Re remains +4 upon substitution, which means that the clusters become more electron-deficient when x increases. The $Re_{4-x}Mo_xS_4Te_4$ $(0<x<1)$ phases are metallic with a maximum conductivity at x=0.33. The conductivity is due to the mixing of Te AO with partially empty cluster d-based orbitals.[66] Cations can be incorporated, as in

$(Cu_{0.83}Fe_{0.15})(Re_{2.74}Mo_{1.26})S_8$.[67] The adaptability of the cuboidal cores to different electron counts is remarkable, ranging from highly electron-deficient $M_4Q_4^{5+}$ (7e in the tetrahedral cluster MO) in the Group 5 phases up the electron-precise 12e $Re_4S_4^{8+}$ in $Re_4S_4Te_4$. Isolated cuboidal anionic clusters $[Co_4(\mu_3\text{-}Se)_4Se^a{}_4]^{7-}$ and $[Fe_4(\mu_3\text{-}Te)_4Te^a{}_4]^{7-}$ are found in $Cs_7M_4Q_8$ (Figure 1).[68] $Cu_3Pd_{13}S_7$ possesses a unique structure with the $(Cu_xPd_{1-x})_4(\mu_3\text{-}S)_4$ cuboidal units (M–M 2.932(3) Å) embedded into a 3D framework of the Pd–Pd bonds.[69]

Pentanuclear units are extremely rare. Open tetrahedral $PdPd_4$ (Pd–Pd 2.74 Å) are found in $Pd_{3.5}Te$.[70] The similar $SnIn_4^{8+}$ core is present in $SnIn_4S_4$, initially formulated as In_5S_4.[71]

Isolated octahedral $M_6(\mu_3\text{-}Q)_8^{2+}$ (Q=S, Se) clusters are found in a big family of Tc and Re ternary sulfides and selenides of general formula $A_xM_6Q_{11+y}$, where A is an alkali, Tl^+, Cu^+ (x=4); alkaline earth, Eu^{2+} or Pb^{2+} (x=2) ion, and y = 0, 1 or 2. These phases were discovered and thoroughly studied by Prof. W. Bronger's group. The cluster units contain regular M_6 octahedra with M–M bond lengths of 2.60–2.65 Å for Tc and

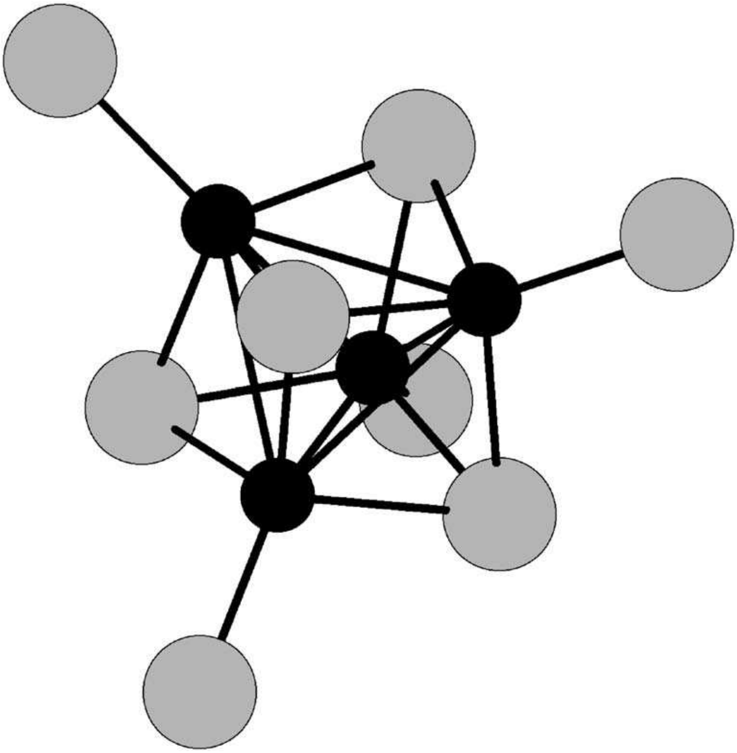

Figure 1 *View of the $Co_4(\mu_3\text{–}Se)_4Se^a{}_4{}^{7-}$ cluster anion in the structure of $Cs_7Co_4Se_8$. Small circles – Co, big circles – Se*

2.59–2.62 Å for Re, interconnected *via* S^{2-} or S_2^{2-} bridges. The value of y determines both the ratio of S_2^{2-} to S^{2-} in the structure and its connectivity. Thus, the $A_x[M_6S_{11}]$ compounds all contain S^{2-} and are best described as $A_x[M_6S^i_8S^a_{6/2}]$ with the metal–chalcogen framework corresponding to the Nb_6I_{11} type ($Eu_2Re_6S_{11}$ and $Ba_2Re_6S_{11}$).[72] The sulfur-richer compounds are to be formulated as $A_x[M_6S^i_8S^a_{4/2}(S^a_2)_{2/2}]$ and $A_x[M_6S^i_8S^a_{2/2}(S^a_2)_{4/2}]$.[73] Topotactic oxidation of $Na_4[Re_6S^i_8S^a_{2/2}(S^a_2)_{4/2}]$ at ambient temperature gives 3D-modification of ReS_2.[74] In $Cs_6Re_6S_{15}$, the Re_6S_8 units are bound into a 3D framework *via* six $S^a{}_2^{2-}$ bridges, so that this compound may be regarded as highest perthio homologue of 3D-$A_4Re_6S_{11}$.[75] The dimensionality is lowered to 2D in $A_6Re_6S_{12}$ (A=Rb, Cs), *i.e.*, $A_6[Re_6S^i_8(S^a)_2(S^a)_{4/2}]$ with no S_2-bridges between the octahedral units.[76] The isolated anions $[M_6S^i_8S^a_6]^{10-}$ are found in $A_{10}M_6S_{14}$ (A=Rb, Cs; M=Re, Tc).[77] The Tc family is also represented by $A_4Tc_6S_{12}$ and $A_4Tc_6Se_{12}$ (A=K–Cs).[78] It is interesting to note that in the mixed compound $Cs_4Re_6S_{9.45}Se_{3.55}$ the μ_3-Q^i positions in the cluster core are occupied exclusively by the sulfur atoms, while Se prefers the intercluster $Q^a{}_2^{2-}$ bridges.[79] There are no direct tellurium analogues to the Bronger's compounds, but the same octahedral clusters are found in the structure of Re_6Te_{15}, in which they are interconnected *via* butterfly-like *spiro*-Te_7^{2-} ions, giving a simple stoichiometric ratio $[Re_6Te_8(Te_7)]$.[80] Selenium enters the cluster core, but apparently not the *spiro*-anion, up to the composition $[Re_6Se^a_8(Te_7)]$.[81] A heterometallic cluster sulfide, $Cs_3[Re_5OsS_{11}]$, was also prepared.[82]

A very important class of the octahedral chalcogenide clusters with the $M_6(\mu_3\text{-}Q)_8$ core (Figure 2, left) is represented by the Mo_6Q_8 and $A_xMo_6Q_8$ (Q=S, Se, Te) phases, currently known as Chevrel phases, after one of their discoverers. This large family counts more then 100 compounds. Element A can be Pb, Sn, Ln, Ca, Cu, Li, *etc.* – altogether 40 elements including Np, Pu and Am, and even Mo itself (in $Mo_{1.7}Mo_6S_8$) can be incorporated; x varies from 0 to 4.[83–86] Neither Cr nor W are able to replace Mo.

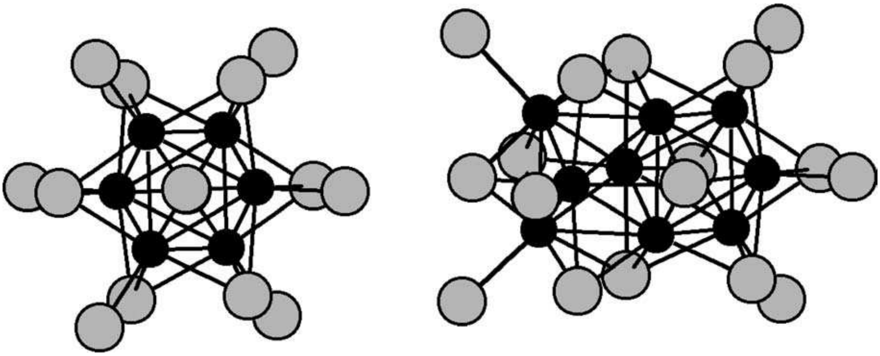

Figure 2 *Right: the $Mo_6Q^i{}_8Q^a{}_6$ cluster unit; Left-the $Mo_9Q^i{}_{11}Q^a{}_6$ cluster unit. Small black circles – Mo, large gray circles – chalcogen*

The only Mo-free Chevrel phase is $Nb_{6-x}Ru_xTe_8$ with a narrow range of existence ($2.50<x<3.17$).[87] Re, Ru, Nb, Rh can partially substituted for Mo.[88–90] It is possible to prepare chalcogen-mixed solid solutions like $Mo_6S_{8-x}Se_x$ and $PbMo_6S_{8-x}Se_x$ (x = 0–8).[91] Mixed cationic part is present in $PbCu_xMo_6S_8$, $SnZn_xMo_6S_8$ and $SnFe_xMo_6S_8$.[92] Ternary chalcohalogenides $Mo_6Q_{8-x}X_x$ (Q=S, X=I, Br, x = 2; Q=Se, X=Cl, Br, I, x = 3; X=Br, I, x = 1; Q=Te, X=Cl, I, x = 2, 3 are also related to this family.[93] Partial oxygen substitution is possible and oxosulfides $Mo_6S_6O_2$, $A_2Mo_6S_6O_2$ (A=Cu, Ni, Co) and $PbMo_6S_6O_2$ were reported.[94] Strictly speaking (and in contrast to the Re and Tc clusters discussed above), the Mo_6 clusters are not isolated from each other, they interact to give a net of *quasi*linear chains roughly in the three perpendicular directions along the rhombic axes. The intracluster Mo–Mo distances range from 2.65 to 2.80 Å, the intercluster bonding is weaker, with the Mo–Mo contacts of 3.10–3.60 Å. The Chevrel phases have attracted much attention because of their superconducting properties (with T_c as high at 15 K) coupled with very high critical fields (H_{c2} is about 60 T for $PbMo_6S_8$). The lanthanide phases $LnMo_6S_8$ show long-range antiferromagnetic ordering. Although superconductivity has remained chief driving force behind the studies of the Chevrel phases, other possible applications are hinted at by the discovery of catalytic activity of $Ru_2Mo_4Se_8$ in the water oxidation reaction.[95] The electronic structure of the Chevrel phases can be described in terms of the MO of the $Mo_6Q_8{}^{n-}$ fragments and compared to that of their Re_6Q_8 analogues. The latter always have 24 electrons for M–M bonding (though in the molecular clusters one or two electrons can be removed from the cluster core without much affecting the M–M bonding). The most Chevrel phases are electron deficient (the "pure" binaries Mo_6Q_8 have only 20 electrons), but they can be reduced by accepting one, two, three or four electrons (as in $Cu_4Mo_6S_8$), and the mixed-metal $Mo_2Re_4S_8$ and $Mo_4Ru_2Se_8$ have "electron-precise" 24 e-cluster cores. The flexibility of the Chevrel phases to the electron population is due to the fact that the e_g orbital (which has primarily $d_z{}^2$ character) is also sensitive to the axial ligand coordination (the axial position is occupied by a chalcogen atom from another Mo_6Q_8 group) and is pushed up in energy. From the other side, the M_6Q_8 arrangement itself corresponds to a section of close packing, so that the occurrence of this structural unit not only in isolated but also in condensed clusters (*vide infra*) is hardly surprising.

The only non-octahedral hexanuclear cluster units are six-membered ring Rh_6 (chair conformation, Figure 3), and open, non-planar zigzag chain Zr_6, which are found respectively in Rh_3S_4 and Zr_3Te (Rh–Rh 2.70 and 2.87 Å; Zr–Zr 3.01–3.15 Å). In addition there are strong transannular interactions in the Rh_6 ring (3.09 Å), and weak contacts between the Zr_6 chains.[96,97]

The largest isolated (*i.e.*, not connected to other structural fragments *via* M–M bonds) clusters are cubes Co_8, found as cluster units $Co_8(\mu_4\text{-}Q^i)_6$ in the Co_9Q_8 (Q=S, Co–Co 2.51 Å (*pentlandite*), Q=Se (Co–Co 2.66 Å), and in $Ba_6Co_{25}S_{27}$ (Co–Co 2.65–2.76 Å, Figure 4). They are interconnected *via*

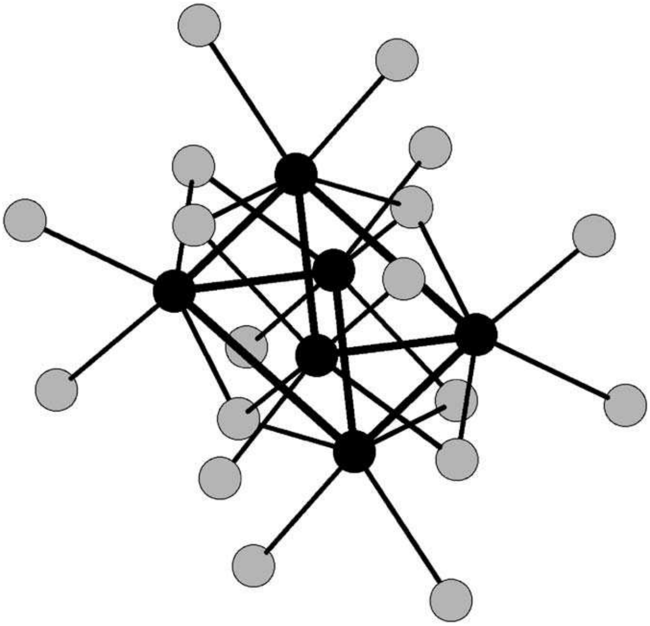

Figure 3 *The Rh_6 cluster in its chalcogen environment in Rh_3S_4. Black circles – Rh, gray circles – S*

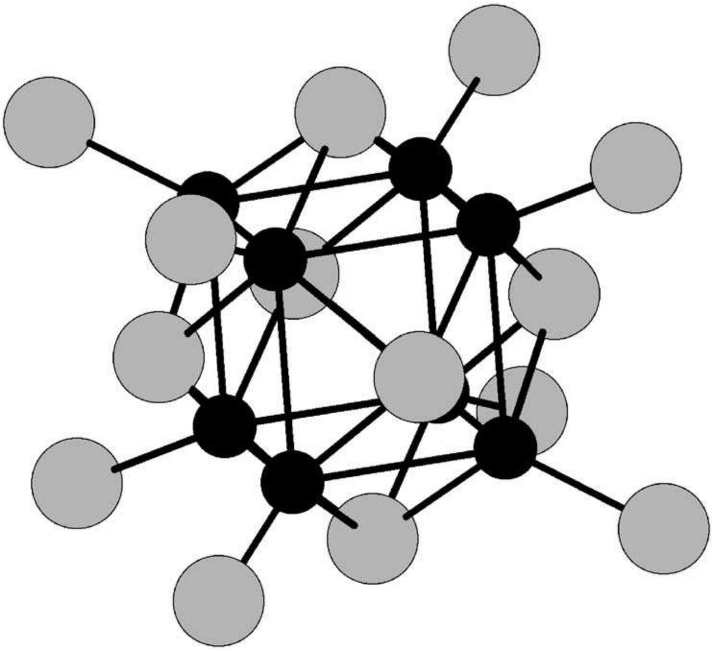

Figure 4 *The $Co_8(\mu_4\text{-}S)_6$ cluster in its chalcogen environment in the structure of $Ba_6Co_{25}S_{27}$. Small black circles – Co, large gray circles – S*

bridging sulfides (S^a) (which complete the CoS_4 tetrahedral environment around each Co atom) into 3D-framework.[98–100] In the *goddlevskite* Ni_9S_8, despite the same stoichiometry as pentlandite, the Ni atoms form a puckered ring Ni_8, rather S_4N_4-like in conformation with bond lengths of 2.51–2.53 Å, and with transannular contacts of 2.88 Å (the four Ni atoms of the same plane). The Ni_8 units may interact with each other *via* longer Ni–Ni contacts.[101] A peculiar M_8 unit is found in *pyrrhotine* Fe_7S_8, where six-membered Fe rectangles have two "dangling" Fe atoms in 1,4-positions (Fe–Fe 2.89–2.96 Å).[102]

9.1.2.3. Connected and Condensed Clusters

Connecting metal clusters *via* significant chemical bonding *between* the vertices (as opposed to condensation where the clusters *share* common vertices, edges or faces) is rare among the chalcogenides. In the structure of Pd_3Te_2, the triangles Pd_3 (Pd–Pd 2.88 Å) are joined into zigzag ribbons with the intercluster distance of 3.0 Å. In *hazelwoodite* Ni_3S_2, the Ni_3 triangles (Ni–Ni 2.51 Å) are connected into 3D frameworks instead.[104] In TcS_2[105] and ReQ_2 (Q=S, Se; including ReSSe)[106–109] and MMo_2S_4 (M=V, Cr, Fe, Co) rhombic M_4 clusters (M–M 2.6–2.9 Å) are joined together *via* opposite vertices into chains (Figure 5).[110]

Various ways of condensation of the octahedral clusters give rise to a great variety of chalcogenides. The condensation of M_6Q_8 clusters *via* opposite metal atoms leads to a 1D column $M_4M_{2/2}Q_{8/2} = M_5Q_4$. The structure of tetragonal Ti_5Te_4 consists of such columns running parallel to each other. The octahedra are compressed along the column direction (8(Ti–Ti) 2.84 Å, 4(Ti–Ti) 3.22 Å). Like in the Chevrel binaries, there is also a strong interchain interaction

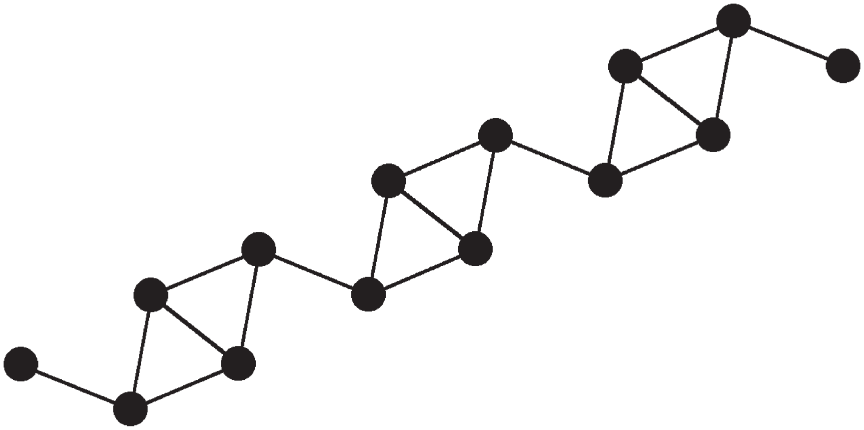

Figure 5 *The chain of rhombic clusters in TcS_2. Only metal atoms are shown*

(2.94 Å). V_5Q_4 (Q=S, Se), Nb_5Q_4 (Q=Se, Te) and $V_{4.64}Te_4$ (V–V 2.66–2.83 Å)[111–114] also belong to this structure type. There are two possible ways of connecting two M_5Q_4 chains *via* edges, either by making each octahedron to share one edge with a neighboring octahedron ($M_{4/2}M_2Q_{6/2} = M_4Q_3$), or by making it to share two *cis*-edges with neighboring octahedra ($M_{3/3}M_3Q_{4/2} = M_2Q$). The first type is observed in M_2Q (M=Ti, Zr; Q=S, Se).[115] In these four isostructural compounds the M_4Q_3 chains run parallel, and extra Ti or Zr atoms occupy the space between them. The second type is exemplified by Nb_2Se.[116] In all cases, the octahedra are strongly distorted with some edges being shorter, and some longer than 3.0 Å. Of the four possible ways of linking three M_5Q_4 chains together *via* common edges, one is observed in the structure of $Nb_{14}S_5$, where the network of the condensed clusters contains triple chains united, however, to the double chains known from the Nb_2Se structure. These two building units are linked to each other by vertex atoms with additional metal atoms occupying the spaces between the triple chains.[117] The structure of $M_{21}S_8$ (M=Zr, Nb) consists of two kinds of building block, which are not mutually connected, namely, from the isolated Nb_5S_4 chains, and from four condensed Nb_5S_4 chains which have the composition $Nb_{12/2}Nb_6S_{4/2}S_2 = Nb_{12}S_4$. Together with additional Nb atoms which are located in the voids between these chains, and the stoichiometry is accounted for by the formula $(Nb_5S_4)(Nb_{12}S_4)(Nb_4)$.[116,118] In the structure of Ti_8S_3, the units built of two Ti_5S_4 chains (in the same way as in Ti_2S) are linked *via* vertices to form aggregates of four Ti_5S_4 chains.[119]

Simple *trans*-edge-linkage of cluster octahedra is observed in Ta_4BTe_4, where the B-centered BTa_6 octahedral units are linked into linear, 1D chains.[120] The distorted octahedra sharing *trans*-edges and some of the side edges are found in Sc_2Te and Dy_2Te. The resulting fused double octahedra are decorated at the extremes with trigonal prisms of the metal atoms, leading to the constructions, termed "blades" by the authors. This structure type contains also zigzag chains as separate units. Typical Sc–Sc distances are 3.05–3.49 Å; in the chain, 3.48 Å. The isostructural β-Ti_2Se and Zr_2Te were subsequently also shown to exist. Higher concentration of d-electrons strengthens M–M bonding in the Group 4 chalcogenides.[121] The structures of Sc_6MTe_2 (M=Pd, Ag, Cu, Cd) and Y_6MTe_2 (M=Ru, Os, Rh, Ir, Pt, Ag, Cu) are based on the same units, but now the "blades" and zigzag chains are fused together *via* the heterometal into rumpled sheets. The heterometal is surrounded by a tricapped trigonal prism of the Sc (Y) atoms, and its incorporation causes significant strengthening of the M–M bonding in general.[122–124]

The *trans*-face-linkage of the M_6Q_8 clusters would lead to a chain with the composition $M_{6/2}Q_{6/2}$ (=MQ). Finite numbers of the face-linked octahedra would give rise to the compositions $M_{3n+3}Q_{3n+5}$, where n is the number of fused octahedra. Thus the first member is Mo_9Q_{11} unit, encountered in metastable superconductor Mo_9Se_{11} (Figure 2, right),[125] in $Ag_{3.6}Mo_9Se_{11}$, $Ag_{2.3}CsMo_9Se_{11}$[126] and in $M_2Mo_9S_{11}$ (M=K, Rb).[127] Both Mo_6Q_8 and

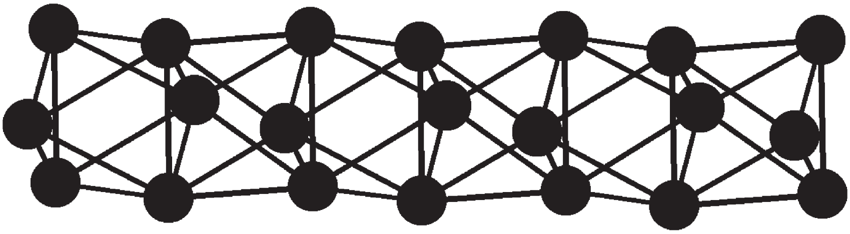

Figure 6 *Fused octahedral cluster core in $Cs_5Mo_{21}S_{23}$. Only Mo atoms are shown*

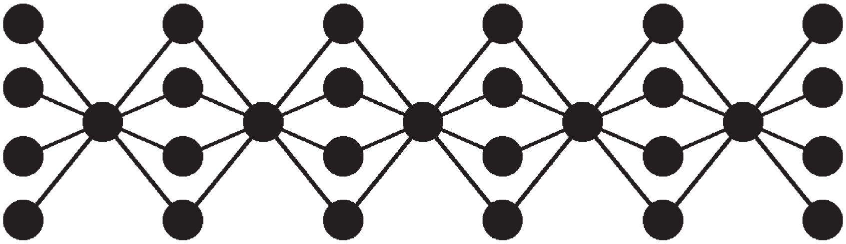

Figure 7 *Metal cluster chain in Zr_5Te_4. Only Zr atoms are shown*

Mo_9Q_{11} units are present in 1:1 molar ratio in the structures of $M_3Mo_{15}S_{19}$ (M=In, K, Rb)[128] and in cation-free $Mo_{15}Se_{19}$.[129] The next member of the series, the $Mo_{12}Q_{14}$ cluster, is found paradoxically in $Tl_2Mo_9S_{11}$, where there are no Mo_9S_{11} units, but Mo_6S_8 and $Mo_{12}S_{14}$ clusters coexist in equimolar ratio.[130] $M_2Mo_{12}Se_{14}$ (M=Rb, Cs) contain only the $Mo_{12}Se_{14}$ units.[131] The $Mo_{15}Se_{17}$ clusters exist in $M_3Mo_{15}Se_{17}$.[132] Condensation of five octahedra leads to the $Mo_{18}Se_{20}$ cluster, discovered in $Rb_4Mo_{18}Se_{20}$[133] and six-fused octahedra form the $Mo_{21}S_{23}$ clusters in $Cs_5Mo_{21}Q_{23}$ (Q=S, Se, Figure 6).[134] The next member, the $Mo_{24}S_{26}$ cluster, is found in the structure of $Rb_8(Mo_6S_8)(Mo_{24}S_{26})$.[135] The present-day limit of the isolated cluster size in these systems is reached in $Rb_{10}Mo_{36}S_{38}$ with 11-fused octahedra in the $Mo_{36}S_{38}$ cluster.[136] Further, work on the $A_2Mo_6Q_8$–Mo_6Q_8 systems (A=Rb, Cs; Q=S, Se, Te) has led to the discovery of other fused clusters within the Mo_{12}–Mo_{30} limits.[137] The limiting case – the 1D chain of fused octahedra – is reached in the quasi1D compounds $A_2Mo_6Se_6$,[138] in $K_2Mo_6S_6$,[139] in $A_2Mo_6Q_6$ (A=In, Tl; Q=Se, Te)[140] and $AgMo_6Te_6$.[141] Curiously, $Tl_2Fe_6Te_6$ (the only non-Mo cluster of the whole family!) belongs to the same type (Fe–Fe 2.60 Å).[142]

Fusion of larger clusters also occurs. In Zr_5Te_4 centered cubes $ZrZr_8$ share two opposite faces, so that the cluster bonding can be described as $^1_\infty ZrZr_{8/4}$ (Zr_c–Zr 3.16 Å, Figure 7).[143] The structure of Hf_3Te_2 is based on the extension

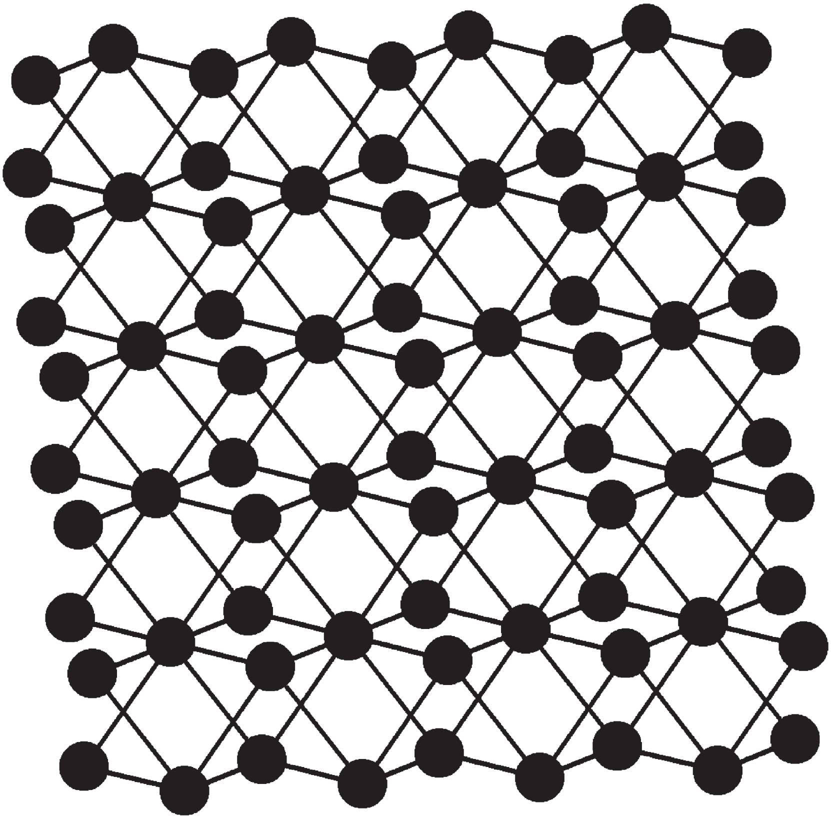

Figure 8 *Metal atoms arrangement in* Hf_3Te_2

of the same principle, involving fusion of the $HfHf_8$ cubes (Hf–Hf 3.12 Å) trough the four lateral faces to give layers (Figure 8).[144] Somewhat more complicated layers built of $TaTa_8$ centered cubes (Ta_c–Ta 2.80–2.83 Å) are observed in the structures of Ta_2Se and $Ta_2S_{0.65}Se_{0.35}$.[145] Square antiprisms MTa_8 (M=Fe, Si) fused trough the opposite Ta_4 faces into 1D chains dominate the crystal structure of ternary tellurides Ta_4ZTe_4 (Z=Al, Si, Cr–Ni, Figure 9). In fact, the encapsulated central atoms are strongly bound together to form linear chains, thus embedded into the outer layer of fused Ta_8 square prisms (*e.g.*, very short Fe–Fe distances, 2.39–2.41 Å, Fe–Ta 2.6 Å, Ta–Ta 2.99 Å in Ta_4FeTe_4).[146] Theoretical treatment of the bonding in these structures was given.[147] In the structure of $Sc_{14}M_3Te_8$ (M=Ru, Os), the Sc atoms define infinite chains of alternate *trans*-face-sharing cubes and pairs of square antiprisms in which each polyhedron is centered by a Ru (Os) atom. The Ru–Sc distances are 2.69–2.79 Å, while the Sc–Sc distances are 3.28–3.41 Å.[148]

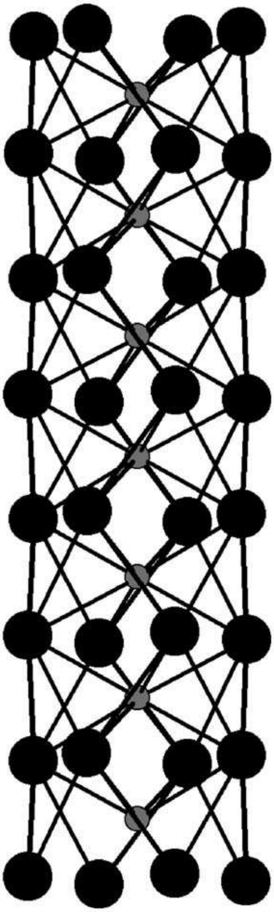

Figure 9 *Fused square antiprisms chain in Ta_4FeTe_4. Only metal atoms are shown. Small gray circles – Fe, large black circles – Ta*

A decanuclear cluster unit, centered tetrakaidekahedron (or tricapped trigonal prism), has emerged in the last decade as important building block in a number of ternary early-late TM chalcogenides. It is found in $M_2Ta_9S_6$ (M=Fe, Co, Ni),[149] $M_2Ta_{11}Se_8$ (M=Fe, Co, Ni),[150] $NiSe_8Ta_8$ (Figure 10),[151] Zr_6MTe_2 (M=Mn, Fe, Co, Ni, Ru, Pt) and $Zr_6Fe_{0.6}Se_{2.4}$,[152] $Ta_{11}Si_2Se_8$,[153] Hf_8MnTe_4,[154] $Er_7Ni_2Te_2$.[155] A common motif in all these structures is condensed tricapped trigonal prisms with the heterometal in the center, arrayed into columns $M'M_3M_{3/2}M_{3/2}$ (M′ is a 3d metal, M is early TM) *via* common opposite trigonal faces. Additional interactions between the building blocks involving the capping atoms create a wealth of two- or three-dimensional structures. Recently, the list of the compounds belonging

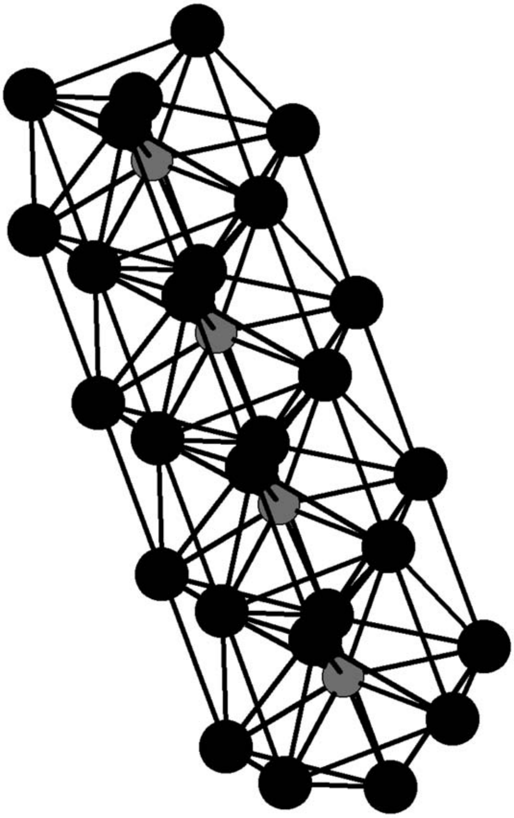

Figure 10 *Fused trigonal bipiramides chain in $NiTa_8Se_8$. Only metal atoms are shown. Small gray circles – Ni, large black circles – Ta*

to this class was extended by including rare-earth ternary tellurides: Sc_6MTe_2 (M=Fe, Co, Ni, Ru, Os, Rh, Ir), $Y(La)_6CoTe_2$, Dy_6MTe_2 (M=Fe, Co, Ni), Gd_6MTe_2 (M=Co, Ni), Er_6RuTe_2.[156–159] From the crystallographic point of view, these structures can be regarded as an extension of the well-known Fe_2P type, or, more specifically, as analogues of the Zr_6CoAl_2 type.

Ta-centered pentagonal antiprisms fused *via* common pentagonal faces to chains $^1_\infty[TaTa_{10}]$ occur in the Ta-rich phases Ta_6S_3, Ta_6S_4 and Ta_6S. By varying the sulfur content, the chains can be fused into 2D and 3D networks, but 1D network (which would have the formula Ta_6S_5) has not been observed.[160]

A family of ternary early-late tellurides of Y and Sc features columns of Y (Sc) puckered hexagons, with zigzag TM chains inside, arranged in different ways. In $Y_5M_2Te_2$ (M=Fe, Co, Ni), hexagons are condensed into sheets at *trans*-vertices, while in $Sc_5Ni_2Te_2$ and $Y_5Cu_2Te_2$ they are condensed into pairs by side-to-side fusion. In $Y_5Ni_2Te_2$, pairing of two columns is achieved *via* common vertices.[161]

9.1.2.4. Metal Chains

These can be already discerned in many common structural types. For the simplest 1:1 M/Q ratio, they are observed in TM monochalcogenides (NiAs type). In this case, the face-sharing MQ_6 octahedra form columns $MQ_{6/2}$, in which the central metal atoms interact to give a chain running in the same direction. To this type belong FeSe, FeTe, CoQ, NiQ (Q=S, Se, Te), RhSe, RhTe, and IrTe.[162–171] The M–M distances are quite short and must be essential for stability of this structural type (2.67 Å in α-NiS, 2.60 Å in CoS (*jaipurite*), 2.69 Å in IrTe, in RhSe 2.74, and 2.83 Å in RhTe).[171] $Nb_{0.92}S$ does not belong to the NiAs type and exists in two modifications. The high-temperature modification contains 1D chains of Nb atoms, slightly ondulating (∠Nb–Nb–Nb 5–7°, Nb–Nb 3.01 Å). In the low-temperature modification, there are isolated Nb_3 triangles (Nb–Nb 2.92 Å).[172] In TaS the building blocks for 1D chains are no longer octahedral, but trigonal prisms, stacked on their trigonal faces (Ta–Ta 3.125 Å).[174] The same 1D strings of $[MS_{6/2}]$ face-sharing octahedra that run parallel to the *c* axis of the hexagonal cell are found in the ternary chalcogenides (the $CsNiCl_3$ structure type). This arrangement also results in short M–M separations (2.8–3.0 Å) that involve some degree of direct M–M bonding ($BaVS_3$, $BaVSe_3$).[175] Even if insulating $BaTiS_3$ contains d^0–Ti^{4+} and no Ti–Ti bonding is possible despite reasonably short Ti–Ti separation of 2.90 Å,[176] solid solutions $Ba(V_{1-x}Ti_x)S_3$ ($x = 0.99, 0.8, 0.5, 0.2, 0.06$) which pass from insulator to metal, or of $Sr_{1.14}(Ti_{0.86}Fe_{0.14})S_3$ with desired concentration of valence electrons can be prepared.[177] In the structure of $Ba_9Fe_3S_{11}(S_2)_2$, infinite columns of face-sharing FeS_6 octahedra with alternating Fe–Fe distances of 2.94 and 3.14 Å are found.[178]

An extensive class of binary M_3Q_4 and structurally related ternary $A_xM_3Q_4$ chalcogenides (M=Ti, V, Nb, Ta, Cr; A is a A^+ or A^{2+}, Q=S, Se, Te) exists. They are often formulated as $A_xM_6Q_8$, but this is better to be avoided, since they contain no specific M_6 cluster units.[16,21] In their structures the MQ_6 octahedra share both faces and edges, to give infinite rutile-like columns with zigzag metal chains inside. The degree of M–M interaction varies with M and Q. Niobium forms cation-free binaries Nb_3Q_4, which are low-temperature superconductors with the following T_c: Q=S, 4.0 K (Nb–Nb 2.88 Å); Q=Se, 2.0 K (Nb–Nb 2.89 Å); Q=Te, 1.8 K (Nb–Nb 2.97 Å).[178–180] Another example is $Tl_{0.22}Nb_3Te_4$, and even up to one As atoms can further substitute for Te in this structure.[181] Theoretical treatment of the bonding in Nb_3Q_4 was given.[182] In fact, the structure of Nb_3Q_4 also involves weak M–M interactions between the chains (Nb···Nb 3.37, 3.47 and 3.65 Å for the sulfide, selenide and telluride.[178–180] Zigzag chains (Nb–Nb 3.0–3.1 Å) are found also in $Nb_2Te(Te_2)$.[183] In V_3Q_4 (Q=S, Se, Te) similar zigzag chains (V–V 2.85 Å (S), 3.01 Å (Se) and 3.29 Å (Te) are united with each other *via* extra V atoms. Each member of this vanadium family differ in structure details from its homologues. The importance of the chalcogenide matrix is obvious: large Te atoms bring V centers in V_3Te_4 too far apart for any significant M–M interaction to arise.[184–186] Examples for ternary compounds are many: for Ti–A=K, Tl; Q=S, Se; for V–A=K, Rb, In, Tl; Q=S, Se; for Nb–A=Na, K, Rb, Ag, Zn, Pb, In, Tl, Cu ...; Q=S, Se, Te; for Cr–A=K, Rb; Q=S.[16] The cations are accommodated in the hexagonal channels between the chains. The structures of Ti chalcogenides Ti_3Q_4 are stabilized only in the presence of cations. In $K_{0.3}Ti_3S_4$ Ti–Ti 3.152(3) Å is close to the Ti–Ti distance in metallic Ti itself.[187]

In $Eu_{0.59}Nb_5Se_8$, the $NbSe_6$ octahedra are connected *via* joint faces into double chains, so that again zigzag chains of Nb atoms (Nb–Nb 2.95–2.96 Å) result.[188]

All the structures derived from NiAs and $CsNiCl_3$ contain metal atoms in octahedral environments. In $MQ_3 = M^{4+}(Q^{2-})(Q_2{}^{2-})$ (M=Ti, Zr, Hf, Nb, Ta; Q=S, Se, Te) and some ternaries like $M_{1+x}Nb_{3-x}Se_{10}$ (M=Fe, Cr, V, Nb, Ta) the chains are formed by the metals in trigonal-prismatic environment. The M–M interaction appears only when the d-orbitals become populated. The situation with the Nb and Ta derivatives is complicated. In NbS_3, there are Nb_2 pairs in the chain (3.04 Å), separated from each other by much larger distance – 3.69 Å, as results from pairing of two d^1 centers with the formation of localized two-center bonding. In $TaSe_3$, there are two types of columns with two different Se–Se distances 2.58 and 2.90 Å. In monoclinic $NbSe_3$, three types of chains with three different Se–Se bond lengths are observed: 2.37 Å ("normal" Se–Se ordinary bond), 2.49 and 2.91 Å, respectively. Depending on their lengths, the Se–Se pairs have different electron population, and only the first case corresponds to the $M^{4+}(Q^{2-})(Q_2{}^{2-})$ description. Larger values of Se–Se bonding correspond to increasing depletion of the d-electron density, probably approaching the $M^{5+}(Se^{2-})(Se_2{}^{3-})$ state for the largest Se–Se distance. However, the M–M distances for all these different types of chains are still the same, 3.48 Å in $NbSe_3$ and 3.50 Å for $TaSe_3$. Under higher pressure (2 GPa), NbS_3 and TaS_3 crystallize in the same monoclinic $NbSe_3$ type.[189] The ternaries $M_{1+x}Nb_{3-x}Se_{10}$ can be viewed as intercalation products of "MSe" (M in the octahedral coordination) into the parent $NbSe_3$ structure, and in addition to (or rather instead of) the linear Nb–Nb chains, they also contain heterometallic zigzag M–Nb chains. Their structures are better represented by the formulation $(MM')Nb_2Se_{10}$, where MM′ are in the octahedral sites; known combinations of MM′ are (FeNb), $(Fe_{1.2}Nb_{0.8})$, $(Fe_{1+x}Nb_{1-x})$, $(Cr_{1.45}Nb_{0.55})$, $Cr_{1.6}Nb_{0.4})$, $(FeV_{0.5}Nb_{0.5})$, $(Fe_{1.3}Ta_{0.7})$.[191] Similarly, the structures of the Ni- and Pd-containing ternaries $Nb_2Pd_3Se_8$ (very long non-bonding Nb $\cdots$ Nb distance of 3.55 Å, but much shorter, bonding Nb–Pd distance of 2.92 Å), Nb_2PdSe_6, $Nb_2Pd_{0.71}Se_5$, $Nb_3Pd_{0.72}Se_7$, Nb_8PtSe_{20}, $Ta_2Pt_3Se_8$, $Ta_2Ni_3Q_8$

(Q=S, Se, always Q^{2-}), $Nb_2Pd_{3-x}Ni_xSe_8$, $x \leq 1$, can be understood from the same structural principles.[191,192] Similarly, in $Pd_3Ta_4Te_{16}$ the only important M–M interaction is found in zigzag heterometal chains … Pd–Ta–Pd–Ta (Pd–Ta 3.07 Å).[193] Ni and Ta alternate in zigzag chains present in the structure of $Ni_3Ta_2Se_8$.[194] In $Co_2Nb_4PdSe_{12}$, two chains of weakly interacting Nb atoms (Nb–Nb 3.4 Å) are held together by Co atoms (Co–Nb 2.9–3.0 Å) so that the cluster units are better described as Co_2Nb_2 rhombuses united into a ribbon *via* opposite Co vertices.[195] In $Fe_{1.25}TaTe_3$, there are zigzag chains of Fe atoms (Fe–Fe 2.49 Å), lying close to each other (Fe···Fe 2.6–2.7 Å) and decorated with Ta atoms in a way to form $TaFe_3$ units (Ta–Fe 2.86 Å).[196]

Linear chains with tetragonal-antiprismatic coordination of metal atoms by chalcogens are found in $V(S_2)_2$ (*patronite*), $Nb(Te_2)_2$, $Ta(Te_2)_2$, and in ternary chalcohalides $[M(Q_2)]_nX_m$ (M=Nb, Ta; Q=S, Se, Te; X=Br, I).[189,197,198] In the latter, the halide (or a larger anion such as $TaBr_6^-$) occupies the space between the columns of the stacked square antiprisms of the "parent" $M(Q_2)_2$ structure, which is thus partially oxidized. Contrary to the situation observed for the "trichalcogenides" MQ_3, the Q–Q distances have their usual value and correspond to the Q_2^{2-} formulation. The real picture is almost always more complicated and involves various degrees of M–M bonding alternation in the chain. Isolated $V_2(S_2)_2^{4+}$ clusters are encountered in a mineral *patronite* (VS_4), whose crystallographic formula is $V_2(S^i{}_2)_2(S^a{}_2)_{4/2}$. The V–V distances alternate between 2.84 and 3.21 Å. Accordingly, it is diamagnetic and a semiconductor.[199] At the other side are $[Ta(Se_2)_2]_2I$, where all the Ta–Ta distances are equal (3.206 Å).[200] In $[Nb(Se_2)_2]_3I$ the $Nb_2(Se_2)_2^{4+}$ clusters (Nb–Nb 3.06 Å) are separated from each other in the chain by single Nb^{5+} centers (Nb^{4+}–Nb^{5+} 3.25 Å); some electron delocalization, however, must account for the respective lengthening and shortening of the Nb^{4+}–Nb^{4+} and Nb^{4+}–Nb^{5+} distances.[201] In $[Ta(Se_2)_2]_2TaBr_6$[202] and $[Nb(Se_2)_2]_{3.33}I$[203], the situation is more complicated, with three different M–M distances in the range of 3.15–3.23 Å. In $[Te(Se_2)_2]_4Br_2$, the chain distorts from linear to zigzag, with alternation of shorter and longer M–M distances, to form quasiisolated Ta_4 groups: Ta(1)–Ta(2) 3.187(1) Å, Ta(2)–Ta(3) 3.055(1) Å, Ta(3)–Ta(4) 3.153(1) Å, Ta(4)–Ta(1) 3.683(1) Å.[204] The tellurides[205] are also known $[M(Te_2)_2]I$ (M=Nb, Ta), $[Ta(Te_2)_2]_4I_2(TaI_6)$, $[Ta(Te_2)_2]_6I_4[TaI_6]$, $[Ta(Te_2)_2][PtI_6]I_2$, but no chloride phases could be obtained so far. Anionic, not neutral or cationic, chains are possibly present in $In_{1/3}[Nb(Se_2)_2]$ (Nb–Nb···Nb···Nb–Nb; Nb–Nb 3.03 Å, Nb···Nb 3.24 Å).[206] These peculiarities in the M–M distances can be (at least partially) explained by ascribing localized d^0 (M^{5+}) and d^1 (M^{4+}) states. These can lead to short localized d^1–d^1 bonding (as in patronite), longer delocalized d^1–d^1 bonding, and to very electron deficient d^0–d^1 interactions (localized or delocalized), together with non-bonding very long distances between two d^0 centers in the halogenated ternaries.

The alkali metal thioferrates $AFeS_2$ (A=K, Rb, Cs), first prepared as early as in 1869, crystallize in 1D chain structure types with tetrahedral

FeQ_4 environment. The ${}^1{}_\infty[FeS_2]$ framework corresponds to the SiS_2 structure. The Fe–Fe intrachain contacts average 2.7 Å and the compounds are linear chain antiferromagnetics with 3D ordering temperature.[16] It is possible to make a reduced compound $Na_3Fe_2S_4$, with slightly longer Fe–Fe distances (2.75 Å). Further increase in the d-electron population in the Co compound $Na_5Co_2S_5$ weakens the M–M interaction (Co–Co 3.11 Å). The band structures calculations show that the M–M elongation is only a secondary effect.[207] The M–M bonding is not the determining factor in the realization of this particular structure type, as the existence of SiS_2 itself or $CsGaS_2$ (Ga^{3+}), isotypic with $RbFeS_2$, shows.[208] 1D chains of double FeS_4 tetrahedra (composed of two chains of edge-sharing tetrahedra bound together *via* common edges) are found in $BaFe_2Q_3$ (Q=S, Se).[209] In mixed-valence $Ba_7Fe_6S_{14}$ ($2Fe^{3+}$ and $4Fe^{2+}$) the ideal $[FeS_2]$ framework distorts in a way to form 1D zigzag $[Fe_3S_6S_{2/2}]$ chains (Fe–Fe 2.747 and 2.849 Å).[210] A more complicated 1D chain, which also incorporates edge-sharing FeS_4 units with short Fe–Fe distances is found in $Ba_6Fe_8S_{15}$ ($2Fe^{3+}$; $6Fe^{2+}$).[209]

There is a large family of metal dichalcogenides MQ_2, which feature M–M chains in their structures (distorted CdI_2 or $CdCl_2$ type). Here belong $NbTe_2$, $TaTe_2$, β-$MoTe_2$, WTe_2. The distortion arises from the formation of zigzag infinite metal chains; for this to appear, the metal atoms are moved away from the central positions in the octahedra, which they would occupy in the perfect CdI_2-type structure. Apparently, the heavier chalcogens favor distortion: for TaS_2 (and for Group 4 chalcogenides), undistorted CdI_2-type structure is preferred. The most symmetrical zig-zag chains are found in β-$MoTe_2$ (Mo–Mo 2.90 Å) and WTe_2 (W–W 2.86 Å).[211] In Nb and Ta ditellurides the chains are more complicated and involve three rows of metal atoms each ("double" zigzag chains).[212] In $IrTaTe_4$ alternating Ir and Ta atoms form zigzag chains with Ir–Ta distances of 3.04–3.06 Å.[213] The sesquichalcogenides Nb_2Se_3, Ta_2Se_3 and Mo_2S_3 crystallize in their own structure type, in which the M atoms in a distorted octahedral environment form zigzag chains, which are in turn distorted to permit the formation of planar rhombic clusters with the M–M distances about 2.9 Å.[214,215]

A peculiar class is formed by ternary metal chalcogenides M'_xMQ_2 (M' is a 3d TM, M=Group 4–6 metal; Q=S, Se, Te, $x \leq 1$). They formally can be regarded as intercalates of 3d metal between the chalcogen layers of parent MQ_2.[216–222] The resulting structure features linear chains of alternating M and M' atoms, running perpendicular to the layers, with M–M distances short enough to permit some direct interaction. For example, in $Mn_{0.25}TaS_2$ the Mn–Nb distances in the Mn–Nb–Mn–Nb chain are only 3.13 Å,[223] in $Fe_{0.47}NbS_2$ the Fe–Nb distances – 3.06–3.13 Å,[224] in $V_{0.33}NbS_2$ – 3.08 Å.[223]

In the structure of $Bi_2Ni_3Se_2$, there are Ni–Ni chains (Ni–Ni 2.813 Å), joined together *via* Bi atoms into a 3D framework (so that planar $NiBi_4$ units result, Ni–Bi 2.75 Å) The corresponding sulfide (*parkerite*) also exists.[225] The structure of *rhodplumsite* $Pb_2Rh_3S_2$ features linear chains of alternating Pb and Rh atoms with the M–M distance of 2.85 Å.[226]

9.1.2.5. Metal Layers

The dimensionality of M–M interactions is increased to 2D in some layered chalcogenides, which have enough d-electrons for significant M–M bonding in two dimensions. In MoS_2 and WS_2, each metal atom has six metal neighbors in the same plane, at only 3.15 Å distance, so that triangular nets result (in the electron-poor Group 4 and 5 disulfides the M–M distances are much larger, > 3.3 Å). Different order of stacking the M and S layers in the 3R and 2H polytypes hardly influence the M–M distance. The matrix effect is however strong, and the W–W distance in WSe_2 is increased to 3.28 Å.[227–229]

Square metal nets are found in the tetragonal modifications of FeQ (Q=S, Se, Te); the Fe–Fe distances in the *mackinawite* modification of FeS are only 2.60 Å.[230] There are also metallic phases TlM_2Q_2 (M=Co, Cu; Q=S, Se) and $TlFe_2Se_2$ that all adopt the $ThCr_2Si_2$ structure type, where the TM atoms form flat square nets with short M–M distances (2.65–2.75 Å).[232]

The structure of Ta_2Se can be alternatively described as four square-net Ta layers (spacing 3.375 Å) inserted between two square-net Se layers. It is therefore quite simply related to the bcc-Ta. A considerable amount of sulfur can be incorporated into the Ta_2Se structure.[145] Isostructural $Ta_{2-x}Nb_xS$ phases can be prepared, while in $Ta_{2.5-x}Nb_xS_2$ five (Nb, Ta) square net layers are sandwiched between the sulfide layers.[233,234] In Ta_2Te_3, there is a puckered net of hexagons and rhombuses with Ta–Ta distances in the 2.98–3.10 Å range (Figure 11).[235]

Ternary Nb and Ta tellurides, $TaCoTe_2$, $TaNiTe_2$, $NiNbTe_2$, $CoNbTe_2$, $FeNbTe_2$ (Figure 12) all possess corrugated honeycomb layers built of elongated Nb hexagons, which host Co_2, Ni_2 or Fe_2 dimeric units. The Nb–Nb and Ta–Ta distances are rather long, > 3.2 Å, but the 3d metals in the dimeric units are strongly bound (Co–Co 2.52 Å; Fe–Fe 2.49 Å), and there are also strong interactions between the dimeric units and surrounding Nb (Ta) atoms.[235–237] M_2TaTe_2 (M=Co, Ni) have another type of layered structure, where the Ta atoms form a slightly corrugated square net with μ_4-Co (Ni) atoms located below and above each square, and they further connected to each other to create another non-planar net based on the Co_4 (Ni_4) squares (in Co_2TaTe_2 Ta–Ta > 3.3 Å, Co–Ta 2.71 Å and Co–Co 2.55 Å (Figure 13).[238] A certain variation in the composition is possible, as the preparation of TaNiCoTeSe shows.[239] Another type of metal layers can be found in $Ni_{2.05}TaTe_3$ (Figure 14),[240] where Ta atoms connect zigzag chains of Ni atoms into layers. Complicated five-fold (Ni, Ta) layers are present in the structure of $Ni_2Ta_{11}Se_8$ (Figure 15).[241] The ribbons of the rhombic Mo_4 clusters in MMo_2S_4 (M=V, Cr, Fe, Co) run parallel to chains

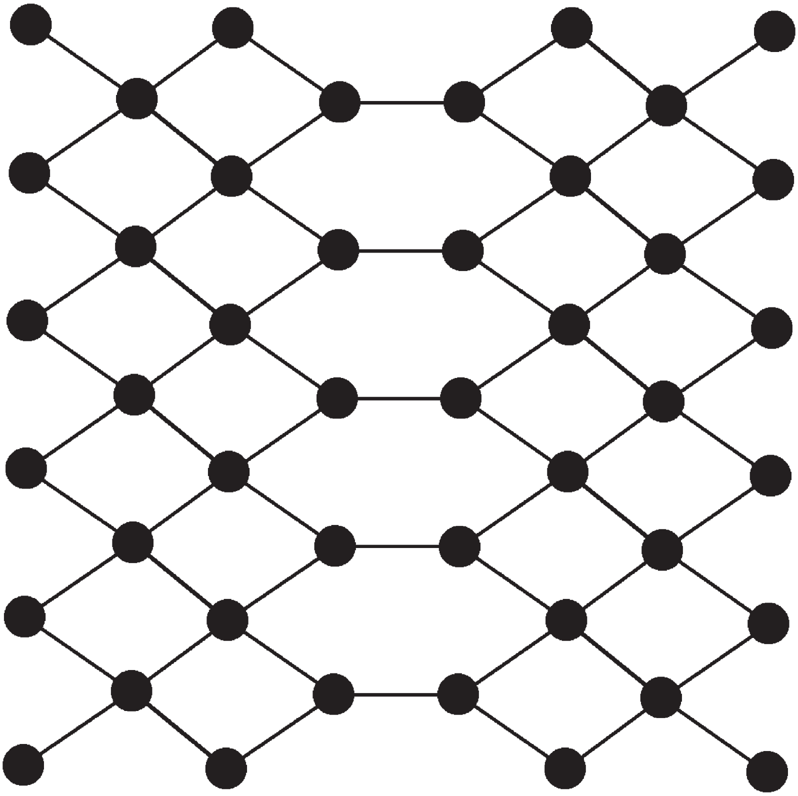

Figure 11 *Metal layer in the structure of* Ta_2Te_3. *Te atoms are omitted*

of the 3d M atoms, and both these building blocks are joined together to form a layer structure (Figure 16).[110]

9.1.2.6. Three-Dimensional Metal Frameworks

These group include the cases when the cluster framework is best regarded as a piece of metal packing. Of course, in most of the structures discussed above there occur secondary bonding between chains or sheets, so that strictly speaking, DOS and COOP analysis is required to evaluate real importance of such interactions. For example, there are considerable contrasts between the largely 2D-bonding in Sc_8Te_3 or Y_8Te_3 (puckered sheets) and the much more 3D-bonded metal arrays of the isotypic Ti_8S_3 and Ti_8Se_3.[242–244] There is a family of lower Ni, Pd and Rh chalcogenides ($Ni_{22.52}S_{15.44}$, Pd_7Se_2 (superconducting), Pd_7Se_4, $Pd_{34}Se_{11}$, $Pd_{20}Te_7$ and Pd_9Te_4, Rh_3Te_2 (Figure 17); as well as $Ti_{45}Se_{16}$) which belong to this group.[245–250] The essentially metal-based

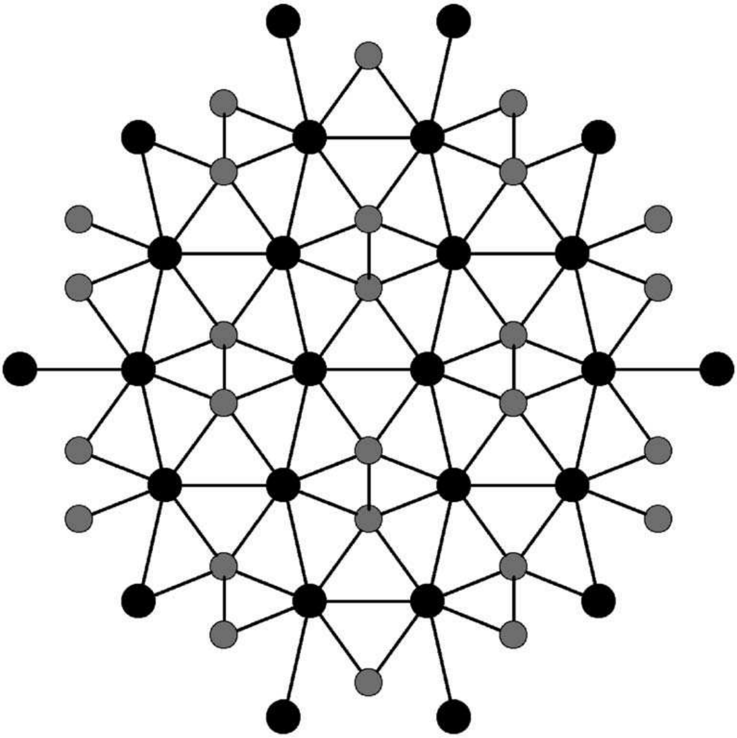

Figure 12 *Metal layer in $CoNbTe_2$. Gray circles – Co atoms, black circles – Nb atoms. Te atoms not shown*

structures of Lu_7Te and Lu_8Te have already been cited.[33] Quite complicated networks are found in Sc_9Te_2 and Ti_9Se_2.[251]

Quite unusual, but very simple is the metal framework in MnPdTe, where alternating Mn and Pd atoms form a ZnS-like network, so that $MnPd_4$ and $PdMn_4$ units result (Mn–Pd 2.71 Å, Figure 18).[252] A Cu_3Au-type of 3D bimetallic network is found in ternary chalcogenides of Ni with the Group 14 metals – Ni_6SnS_2, $Ni_9Sn_2S_2$, Ni_xSnQ_2 (Q=Se, Te; $x = 5.6$–5.7).[253]

9.1.3 Nanotubes

The formation of closed polyhedra and nanotubes is expected to be a common property of materials with anisotropic 2D-layered structures, when their dimensions diminish to the nanometer range (thousands of atoms). This is due to the increasing instability of the planar structure on this scale, since too many "dangling" bonds would result. In fact, if the crystallites are not

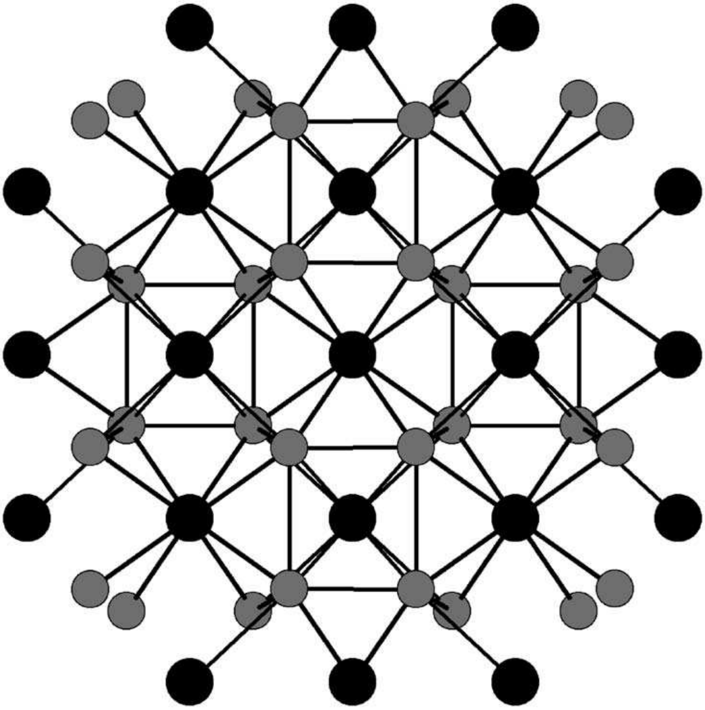

Figure 13 *Metal sublattice in Co_2TaTe_2. Large black circles – Ta, small gray circles – Co. Te atoms not shown*

allowed to grow beyond the size of some hundreds of nanometers, the hollow and closed nanostructures are thermodynamically preferred. The formation of perfectly crystalline structures by layers bending is possible by adding elements of lower symmetry (squares, pentagons or heptagon) to the essentially hexagone-based structure.[254] These materials must be regarded as a genuine part of the phase diagram of the respective constituents. However, there exist an activation barrier for bending the layers and sufficient thermal energy is needed to overcome it. This bending leads in the case of carbon to the fullerenes, multilayer "onions" and carbon nanotubes. The inorganic analogues of the fullerenes are notated as inorganic fullerene (IF) modifications.[255] In fact nanotubes and microtubes of a semicrystalline nature can be formed by almost any compound by a templated growth. After the fullerenes and carbon nanotubes, MoS_2 and WS_2 were the first compounds which were shown to exist as multiwall fullerene-like particles (IF-MoS_2, IF-WS_2) and nanotubes (NT-modifications).[256–258] The selenides followed suit.[259–261] The nanotubes can be open-ended (open-tipped) or capped, and they can be multi- or single-walled. For example, single-walled NT-WSe_2 can be made by decomposition of WSe_3 or $(NH_4)_2WS_4$ under H_2.[261] A typical multiwall nanotube is NT-$NbSe_2$, with the outer diameter of 57 nm,

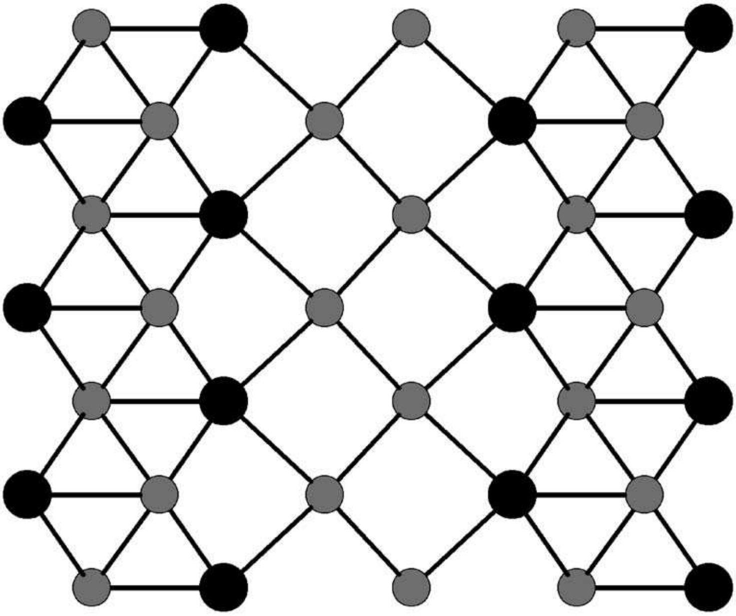

Figure 14 *Metal sublattice in $Ni_2Ta_{11}Se_8$. Large black circles – Ta, small gray circles – Ni. Se atoms not shown*

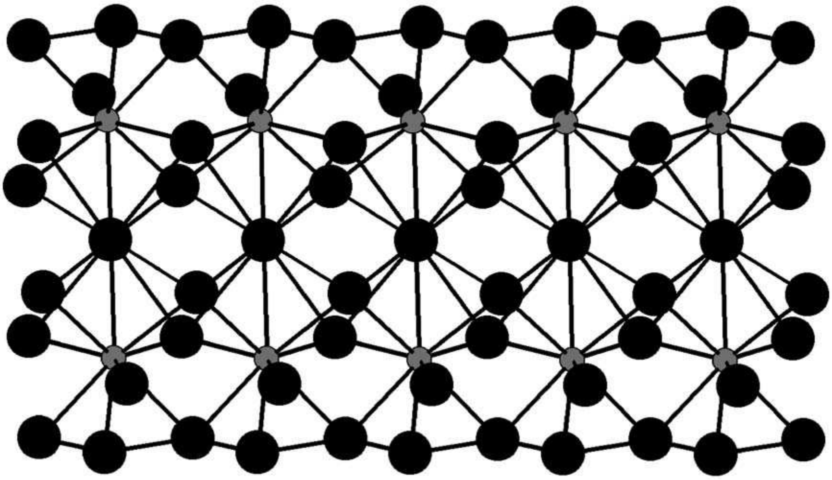

Figure 15 *Metal layer in Ni_2TaTe_3. Large black circles – Ta, small gray circles – Ni. Te atoms not shown*

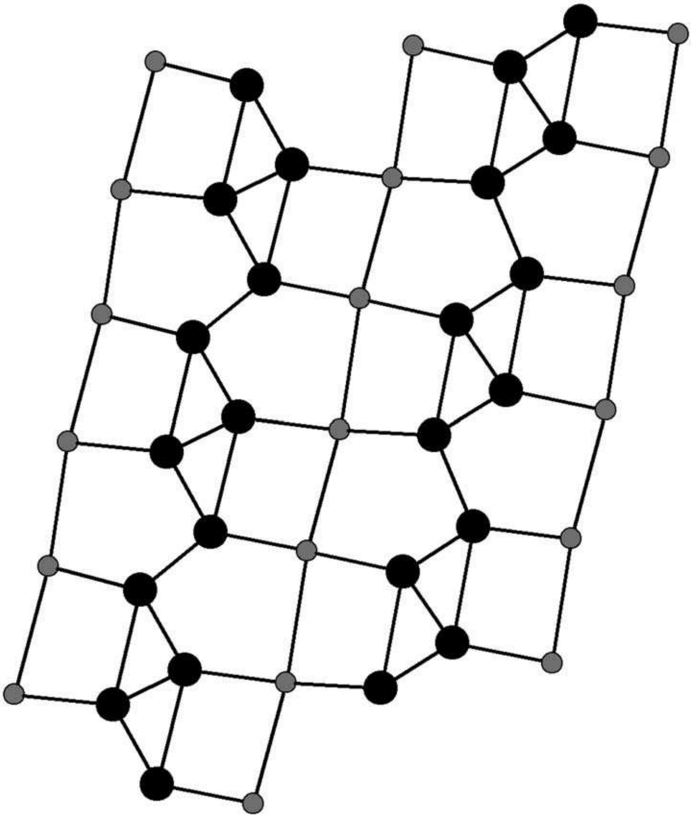

Figure 16 *Building the metal layer in* $FeMo_2S_4$. *Large black circles – Mo, small gray circles – Fe. S atoms not shown*

and the wall consisting of 16 layers.[262,263] The interlayer distances in the NT are somewhat (by 1–3%) expanded from their values in bulk 2D MQ_2 dichalcogenides, because the weaker interlayer Q ... Q contacts can easily be adapted to the inevitable distortions which accompany the bending. The layer sequences in the NT correspond to those of the bulk MQ_2 polymorhps, and often depend on the mode of preparation and size: in the case of NT-MoS_2, chemical transport gives 2H-NT-MoS_2, while larger nanotubes (more than 1 μm in diameter and several hundreds μm seem to prefer the 3R polytype layer sequence.[264–266] The capped end of the nanotube is not exactly spherical, and polygonal caps or rectangular tips are frequently observed.[267] Various types of open ends are observed flat, conical and with more complicated arrangements of the layers close to the tip.[268] Depending on the way in which the layers fold they can be classified as armchair, zigzag or chiral. The outer layers are almost always complete, but the inner layers show defects, dislocations and terminated growth. The NT can exhibit both

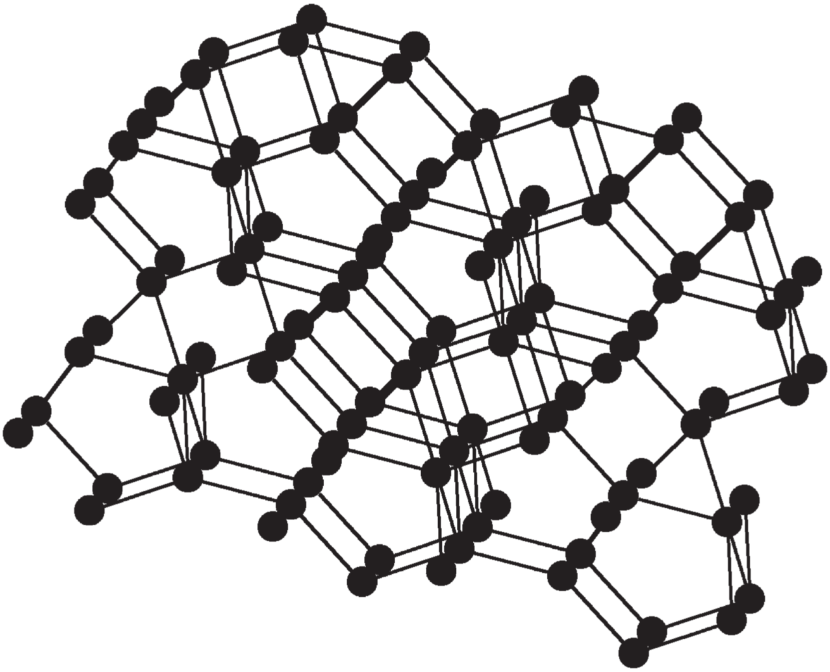

Figure 17 *The metal framework in the structure of Rh_3Te_2. Te atoms are omitted for clarity*

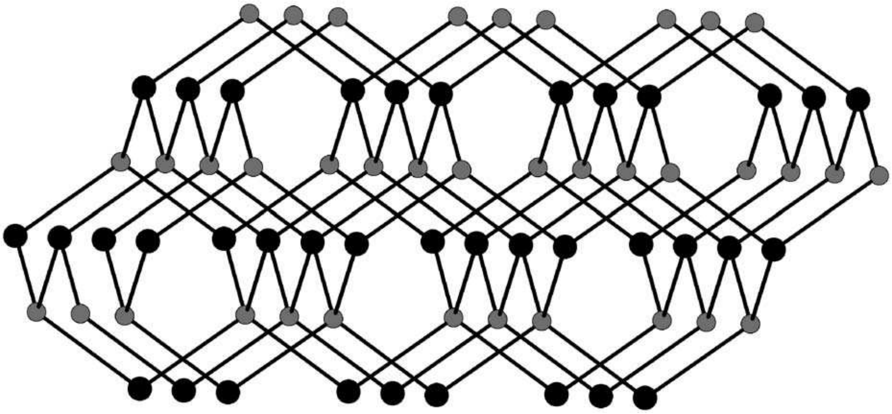

Figure 18 *The metal framework in MnPdTe. Black circles – Pd, gray circles – Mn. Te atoms not shown*

positive and negative curvature, when the absence of a central M or Q atom can give rise to triangular or rombohedral point defects. Theses point defects lead to topological defects like the square and octagonal-like defects, and the topological defects can cause the tube closure.[269,270] Besides, the dichalcogenide structures can form concentrically nested fullerene cylinders ("onions"), with however a less regular structure than in the carbon nanotubes. An example is given by IF-NbQ_2 (Q=S, Se),[262] TiS_2 and ReS_2.[272–276] The preparation of VS_2 nanotubes[271,277] is especially worth mentioning since bulk VS_2 (and VSe_2) exist only as A_xVQ_2 (A=alkali metal, Cu).[278] In all these compounds, the MQ_2 layers are analogous to the single graphene sheets in the carbon materials. They all are already accessible in large amounts by different synthetic strategies, which generally do not require a catalyst.[278–290] For example, pure phase of NT-WS_2 2–10 mμ long and of 20–30 nm in diameter is available by reacting tungsten oxide nanowhiskers with H_2S under mild reducing conditions.[291] Group IV NT-MQ_2 are also represented by ZrS_2 and HfS_2, both obtainable *via* decomposition of the trisulfides.[292]

Several routes to the NT dichalcogenide phases have been identified. They all usually involve sulfidization of the oxides or thermal decomposition of the trichalcogenides. By the first method, the growth of the NT-MoS_2 can even be achieved from the vapor phase, since MoO_3 is sublimable. On the other hand, the growth of NT-WS_2 takes place at the vapor–solid interface. The growth mechanism for the NT-MS_2 (M=Mo, W) materials has been studied in detail. Once the first sulfide layer enfolds the oxide nanoparticle its surface is completely passivated, and their sintering into larger aggregates, unfavorable for folding, is prevented.[289] Arc discharge and laser ablation, sonochemical and electrochemical approaches are also useful.[293–295]

Recently it has been recognized that other, non-graphene-like chalcogenides can also form nanotubes. Nanotubes and nanowires of semiconducting CdS and CdSe have been obtained by a soft chemical route involving surfactant-assisted synthesis. These NT are polycrystalline formed by aggregates of nanoparticles.[296] ZnS nanotubes have been prepared by sulfidizing ZnO columnar templates with H_2S. At first stage, this method gives the ZnS coated ZnO columns, and the subsequent etching leaves hollow NT-ZnS.[297] Layer-rolled structures of NiS have been obtained by hydrothermal reaction between $[Ni(NH_3)_6]^{2+}$ and CS_2.[298] Thick-walled, mostly open-ended nanotubes of $Cu_{5.5}FeS_{6.5}$ were also prepared hydrothermally. The bulk $Cu_{5.5}FeS_{6.5}$ has a layered structure based on MS_4 tetrahedra. Rolling the basal planes leads to the NT-structure.[299]

NT-VS_2 is not the only example of stabilization of particular compositions in IF and NT phases. Enhanced stability is shown by Na-intercalated IF-MoS_2,[300] Ag- and Au-intercalated coaxial nanotubes MoS_2 and WS_2.[301] The reason of the stability enhancement is probably related to the fact that the IF and NT structures are always closed and no reactive edges are exposed to the "hostile" environment.

Multicomponent nanotubes can also be prepared. Iodine intercalation into NT-MoS_2 has been achieved.[302] Heating Nb_2O_5 coated $W_{18}O_{49}$ nanorods in H_2S gives NT-$Nb_xW_{1-x}S_2$, and pyrolysis of H_2S/N_2 mixture over Ti–Mo alloy leads to NT-$Ti_xW_{1-x}S_2$.[303] It was shown that in the NT-$Mo_xW_{1-x}S_2$ tungsten occurs in the MoS_2 layers, rather than having a structure with alternate layers of MoS_2 and WS_2.[304] A composite nanotube Mo–W–C–S_2 was prepared by pyrolysis of H_2S over carbon-containing W and Mo-oxide complexes.[305]

Possible applications of the NT and IF materials can take advantage from their mechanical, electrical, electrochemical and catalytical properies. Nearly defect-free nanotubes are rigid as a consequence of their structure and do not permit plastic deformations. NT-MoS_2 and WS_2 are semiconductors, while NT-$NbSe_2$ shows metallic behavior and becomes superconducting at 8.3 K (for the bulk $NbSe_2$ $Tc = 8.6$ K).[306] NT-MoS_2 can be electrochemically charged (with the hydrogen uptake up to the composition $H_{1.24}MoS_2$, and discharged, thus showing a remarkable ability for storing hydrogen.[307] As solid lubricants, NT-MoS_2 and WS_2 have clear advantages over conventional powders of these dichalcogenides. Their supertribological properties arise from the rolling friction, allowed by the round shape of the nanoparticules.[308] Open-tipped NT-MoS_2 were used as a catalyst for the conversion of CO with H_2 into CH_4, with the characteristics superior to the conventional polycrystalline MoS_2 particles.[309]

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CHAPTER 9.2

Polychalcogenides

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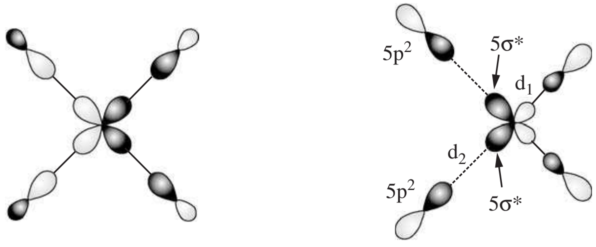
9.2.1 Introduction

In contrast to oxygen, for which only the di- and tri-nuclear homopolyatomic anions O_2^{2-}, $O_2^{\cdot-}$ and O_3^{2-} are known, the characteristic strong tendency of sulfur and its higher Group 16 congeners to catenate is reflected in the wide range of polychalcogenide ions E_n^{2-} (E = S, Se, Te), that have been isolated as salts from polar solvents in the presence of suitable counter cations. Although, for instance, unbranched chain-like dianions in the range $n = 2$–6 are the only significant stable species in alkali metal polysulfide solutions,[1,2] S_n^{2-} anions with $n = 7$ and 8 can be crystallized by employing bulky alkylammonium cations.[3,4] Polyselenides Se_n^{2-} with $n = 2$–11 and polytellurides Te_n^{2-} with $n = 2$–6, 8, 12 and 13 have likewise been structurally characterized in the solid state.[5,6]

Despite its more limited ability to form large homocyclic rings in comparison to selenium and particularly sulfur, tellurium does, in fact, exhibit a much richer homopolyatomic anion chemistry than its lighter homologues. This is due to the increasing importance of both hypervalent bonding and weak $n\mathrm{p}^2 \rightarrow n\sigma^*$ ($n \geq 3$) interactions on going down Group 16. As a result, tellurium can form not only the classical bent $TeTe_2^{2-}$ units of unbranched polytelluride chains but also linear $TeTe_2^{4-}$, T-shaped $TeTe_3^{4-}$ and square-planar $TeTe_4^{6-}$ units by participating in linear 3-centre 4-electron bonds with a formal bond order of 0.5 (Figure 1a). On applying the Gillespie–Nyholm concept,[7] the coordination spheres of the central Te atom in the latter two units can be described as respectively ψ-trigonal bipyramidal and ψ-octahedral. This versatility in the adoption of $TeTe_x^{y-}$ building units is complemented in many polytellurides by weak secondary Te···Te bonding between neighbouring tellurium atoms to afford polymeric 1- to 3-dimensional networks. The energy difference between occupied $n\mathrm{p}^2$ lone pair orbitals and antibonding $n\sigma^*$



(a) 3-centre 4-electron (b) 5p^2 ⟶ 5σ*

Figure 1 *(a) Hypervalent bonding in a square-planar* $TeTe_4^{6-}$ *unit and (b)* $5p^2 \rightarrow 5\sigma^*$ *secondary bonding between two Te atoms and the central atom of a* $TeTe_2^{2-}$ *unit*

orbitals decreases with increasing *n*, thereby making such intra- or intermolecular $n\text{p}^2 \rightarrow n\sigma^*$ bonding more favourable, in particular for the relatively diffuse Te 5p^2 and 5σ* orbitals (Figure 1b). As the total order for E–E bonds and their complementary secondary E···E interactions must remain constant at 1.0, a distance such as d$_1$ in Figure 1b will increase in logarithmic dependence on its individual bond order as the opposite distance (d$_2$) decreases. The relatively flat energy hypersurface for this type of 3-centre 4-electron bonding leads to the observation of a wide range of E···E distances [*e.g.*, d(Te···Te) = 304–360 pm] and the possibility of network distortions in which E_x^{y-} substructures temporarily adopt a more isolated character by strengthening "intramolecular" and weaking "intermolecular" bonds. Such rapid structural modulations can favour the development of charge density waves and are typical for low-dimensional metals.[8]

The preparation, structure and properties of polychalcogenide anions in their salts with alkali/alkaline earth metal or organic counter cations will be considered in the following Section. Polychalcogenides E_n^{2-} retain the typical terminal or bridging coordination modes of the simple chalcogenide ions and augment this bonding versatility by their ability to participate in 3- to 8-membered chelate rings. The conformational flexibility and variable nuclearity of E_n^{2-} chains also means that they are highly suitable bridging ligands for the construction of solid-state polychalcogenidometalate networks in the presence of structure-directing counter cations. Synthetic access to this class of polymeric anions is provided by reactions both in molten alkali metal polychalcogenide fluxes[9,10] at 200–600°C and under mild solvothermal conditions[11] in superheated polar fluids (*e.g.*, H_2O, CH_3OH, CH_3CN, en) at 120–200°C. A survey of the possible binding modes for the polychalcogenide ligands E_2^{2-} to E_7^{2-} (E = S, Se, Te) in both molecular complexes and polychalcogenidometalate networks is given in Section 2.3, with particular emphasis being placed on more recent examples. For a comprehensive literature coverage of the coordination chemistry of polyselenides and polytellurides up to 1994, the reader is referred to a number of excellent review articles.[10,12–15]

9.2.2 Polychalcogenide Anions

9.2.2.1 Synthesis and Speciation

Three general methods are available for the preparation of polychalcogenides:

(i) Intermediate temperature fusion (200–600°C) of alkali or alkaline earth metals with the appropriate chalcogen.[9,10]
(ii) Reaction of alkali metals with chalcogens in liquid ammonia at temperatures between −78 and 220°C. NH_3 is supercritical at 220°C and 100 bar.
(iii) Extraction of alkali/alkaline earth binary polychalcogenides in a basic solvent (*e.g.*, DMF, en) in the presence of an encapsulating agent or a large non-coordinating organic cation, *e.g.*, $[Na(15\text{-crown-}5)]_2S_6$, $[Sr(15\text{-crown-}5)_2]Se_9$, $[Ph_3PNPPh_3]_2Te_5 \cdot 2DMF$.

A convenient method of generating polysulfide anions is to pass a stream of gaseous H_2S through an aqueous ammonia solution in the presence of elemental sulfur. Oligonuclear polysulfides can be crystallized as salts from the resulting solution through addition of suitable alkylammonium or phosphonium cations. Primary to ternary alkylammonium cations can also be generated *in situ* by treating selected amines with sulfur and an H_2S gas stream in protic solvents. This synthetic approach is generally impractical for the heavier polychalcogenides owing to the highly poisonous nature of H_2Se and the instability of H_2Te.

Aqueous or methanolic solutions of alkali metal carbonates induce disproportionation of chalcogens to oxoanions and polychalcogenides E_n^{2-} under solvothermal conditions.[11] Potential redox equilibria such as (1) are driven to the right at 120–200°C by the development of CO_2.

$$3CO_3^{2-} + 2(n+1)S \rightleftharpoons 2S_n^{2-} + S_2O_3^{2-} + 3CO_2(g) \tag{1}$$

The generation of thiosulfates in alkaline S/H_2O systems is well documented.[16] An example for the preparative application of such a disproportionation in the case of selenium is provided by the methanolothermal synthesis[17] of Cs_4Se_{16} on treatment of Cs_2CO_3 with Se at 160°C. The lamellar tellurium-rich tellurides $RbTe_6$,[18] Cs_3Te_{22}[19] and Cs_4Te_{28}[20] can be prepared under similar mild methanolothermal conditions (160–195°C) by reaction of A_2CO_3 (A = Rb, Cs) with a suitable tellurium source such as Ge/Te for $RbTe_6$ or As_2Te_3 for the cesium tellurides.

Polychalcogenides form chain fragments E_n^{2-} that are in dynamic equilibrium with one another both in solution and in molten alkali metal fluxes. Longer chains ($n = 3$–6) can exist in significant concentrations at the relatively low temperatures employed for mild solvothermal syntheses (120–200°C), but are unstable with respect to disproportionation reactions of type (2) at higher temperatures.

$$E_n^{2-} \rightleftharpoons E_{n-x}^{2-} + xE \tag{2}$$

This means that addition of elemental E to alkali metal polychalcogenide fluxes (200–600°C) will promote the formation of longer chains as potential ligands, when such molten salts are employed as reaction media for the preparation of polychalcogenide complexes. Speciation analysis for polychalcogenides in solution has been performed by a variety of physical methods including UV/vis absorption spectroscopy, Raman spectroscopy, ^{77}Se, ^{123}Te and ^{125}Te NMR, electron spin resonance and electrospray mass spectrometry.

9.2.2.2 Polysulfides

Although polysulfide chains with 2–8 members have been structurally characterized in the solid state, those with five or more sulfur atoms can only be isolated as salts of large monocations such as Cs^+ and $[Na(15\text{-crown-}5)]^+$ ($n = 6$),[21,22] $[PPh_4]^+$ ($n = 7$)[23] and $[NR_{4-x}H_x]^+$ ($n = 6$–8, R = alkyl or aryl substituent).[4,24,25] For the alkali metals A = K–Cs, crystal structures are also known for A_2S_2, A_2S_3 and A_2S_5 (see refs. 26–28 for A = Cs); for Na_2S_n, this is the case for $n = 2, 4, 5$.[29–31] In the presence of highly symmetrical counter cations, long-chain polysulfides ($n \geq 6$) generally adopt a helical *all-trans* conformation, in which all torsion angles are *gauche* and of the same sign. In contrast, packing forces can often lead to the adoption of alternative chain conformations in the presence of cations of lower symmetry. Of the six theoretically possible conformations for heptasulfide anions, both *trans–cis–trans* (++−− sequence of *gauche* torsion angles) as in $[H_2N(C_6H_{11})_2]_2S_7$ (C_6H_{11} = cyclohexyl)[32] and *cis–trans–cis* (+−−+ sequence) as in $[H_3N(C_6H_{11})]_2S_7 \cdot C_6H_{11}NH_2$[3] have been stabilized in addition to *all-trans* (++++) in this manner. A *trans–cis–cis–trans* (++−++) conformation is adopted by the S_8^{2-} chain in the only known octasulfide $[HN(C_2H_5)_3]_2S_8$.[4] Although *gauche* torsion angles close to ±90° will be expected to minimize the repulsion of non-bonding electron pairs on neighbouring sulfur atoms, a much wider range of values [±(59–98)°] has, in fact, been observed in polysulfides. S–S–S bond angles of 106–111° and S–S distances of 201–208 pm are typical for S_n^{2-} chains,[24,25] in which, due to charge localization at the first and last chain member, the shortest distances are generally found for the terminal bonds. Short intermolecular secondary S···S bonds have not been observed in polysulfides (Figure 2).

Solutions of alkali metal polysulfides have been investigated by UV/vis and Raman spectroscopy.[1–2,33] All species S_n^{2-} in the range $n = 2$–5 are present in

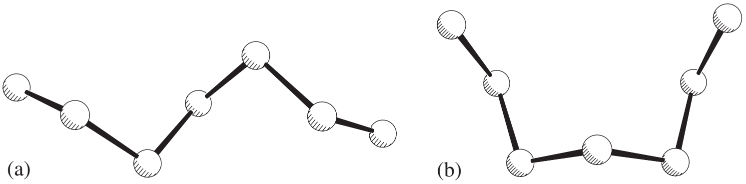


Figure 2 *Conformations of heptasulfide chains: (a) all-trans (++++) in* $[PPh_4]_2 S_7$[23] *and (b) trans-cis-trans (++−−) in* $[H_2N(C_6H_{11})_2]_2S_7$[32]

aqueous solution[1] and Lelieur *et al.*[2] have also identified the S_6^{2-} ion in a solution of Li_2S_n in liquid ammonia. Particular interest has been placed on the blue species with an absorbance maximum at 610 nm that is formed in ammonia and other electron-pair donor solvents. The responsible species is the radical anion $S_3^{\cdot-}$, which is present in equilibrium with S_6^{2-}. The temperature-dependence of S_6^{2-} dissociation ($K_d = 4.3 \cdot 10^{-3}$ M at 298 K in ammonia) is illustrated in Figure 3a by the vis absorption spectra taken for an ammonia solution of Li_2S_6 at temperatures between 215 and 292 K. As may be seen, the characteristic band at 610 nm for $S_3^{\cdot-}$ disappears completely at the lower temperature, while the S_6^{2-} absorbance maximum at 450 nm increases. $S_3^{\cdot-}$ radical anions are responsible for the characteristic bright blue colour of the precious mineral *Lapis lazuli*, which was already known in the Sumerian civilisation some 5500 years ago.[34] The underlying pigment is an ultramarine with the mineral sodalite, $Na_8[Al_6Si_6O_{24}]Cl_2$ as its zeolitic host framework. Partial or complete substitution of the chloride ions by $S_3^{\cdot-}$ and $S_2^{\cdot-}$ radical ions, which are generated simultaneously with the formation of zeolitic cages during mineral synthesis, leads to the characteristic blue hue. The extraordinary stability of the di- and trisulfur radical ions as colour centres in *Lapis lazuli* is due to the impermeability of the resulting sodalite cages. In synthetic ultramarines, it is possible to increase the $S_2^{\cdot-}/S_3^{\cdot-}$ ratio (Figure 3b) to generate steel blue, turquoise and eventually green colours.

Radical anions are also present in solutions of sulfur in oleum and in various polychalcogenide fluxes. However, only one radical ion $S_6^{\cdot-}$ has been successfully characterized in the solid state, namely in $[Ph_4P]S_6$, which can be prepared according to Equation (3) by treating $[Ph_4P]N_3$ with H_2S in the presence of trimethylsilyl azide.[35]

$$2[Ph_4P]N_3 + 20Me_3SiN_3 + 22H_2S \rightarrow 2[Ph_4P]S_6 + 10(Me_3Si)_2S + 11NH_4N_3 + 11N_2 \qquad (3)$$

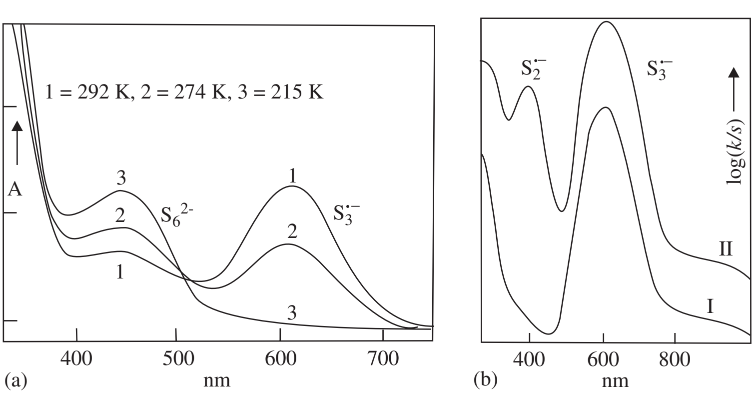


Figure 3 *(a) Vis-absorption spectra of an ammonia solution of Li_2S_6 ($4.5 \cdot 10^{-3}$ M) taken at different temperatures[2] and (b) powder reflection spectra[34] of ultramarines with trapped $S_3^{\cdot-}$ radical anions, either alone (I) or in the presence of $S_2^{\cdot-}$ (II)*

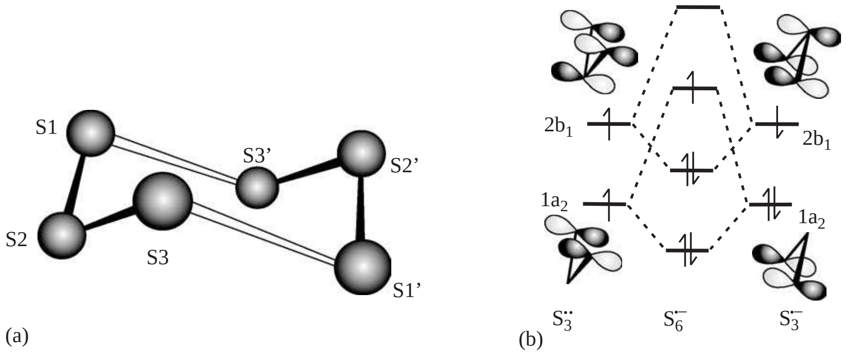


Figure 4 *(a) Structure of the $S_6^{\cdot-}$ radical anion in $[Ph_4P]S_6$ and (b) a schematic molecular orbital scheme based on the interaction of S_3 and $S_3^{\cdot-}$ fragments*[35]

The discrete six-membered rings of $S_6^{\cdot-}$ exhibit a chair conformation (Figure 4a), in which two bent S_3 units with typical S–S single bonds (d = 206 pm) are connected by two very long S–S interactions (263 pm). Molecular orbital calculations[35] indicate that the observed structure can be rationalized as resulting from the net bonding interaction between an $S_3^{\cdot-}$ radical ion and an $S_3^{\cdot\cdot}$ diradical, one of whose valence electrons has been promoted from $1a_2$ to $2b_1$. The $2b_1$ SOMOs of these three atom fragments combine to an electron pair bond, the $1a_2$ HOMO of $S_3^{\cdot-}$ and the $1a_2$ SOMO of $S_3^{\cdot\cdot}$ to a 3-electron bond (Figure 4b).

9.2.2.3 Polyselenides

Discrete polyselenide chains Se_n^{2-} without significant secondary intra- or intermolecular Se···Se contacts have been structurally characterized for $n = 2$–8.[36] Crystal structures are known in addition to K_5Se_3[37] for the following binary alkali metal selenides A_2Se_n in the range $n = 2$–5: A_2Se_2 for A = Na, K, Rb,[38,39] A_2Se_3 for A = Rb, Cs,[27] Na_2Se_4[40] and A_2Se_5 for A = Rb, Cs.[41,42] Longer Se_n^{2-} chains with $n = 6$–8 have only been isolated as salts of encapsulated alkali metal cations or large non-coordinating organic monocations.[36] Two heptaselenides, $[K(2.2.2\text{-crypt})]_2Se_7 \cdot H_2O$[43] and $[Na(12\text{-crown-}4)_2]_2Se_7$,[44] with respectively *all-trans* and *cis–trans–cis* chain conformations have been studied. The only known octaselenide, $[Na(12\text{-crown-}4)_2]_2Se_8 \cdot Se_6, Se_7$[45] exhibits the *all-trans* conformation generally expected for a highly symmetrical counter cation. Terminal Se–Se distances in the polyselenide chains are, in general, shorter than those observed for the other interchain bonds. For instance, the former distances exhibit an average value of 228 pm in the heptaselenide anion of $[K(2.2.2\text{-crypt})]_2Se_7 \cdot H_2O$, the latter 233 pm.[43] The Se–Se–Se angles lie in the range 104–111°, the torsion angles in the *all-trans* chain between 66 and 84°.

The increasing importance of hypervalent 3-centre 4-electron bonding on going down Group 16 is reflected in the structures of Se_n^{2-} anions with $n = 9$–11, which are without parallel for the polysulfides. Although a chain structure is still apparent for the nonaselenide anion of $[Sr(15\text{-crown-}5)_2]Se_9$[36] (Figure 5a),

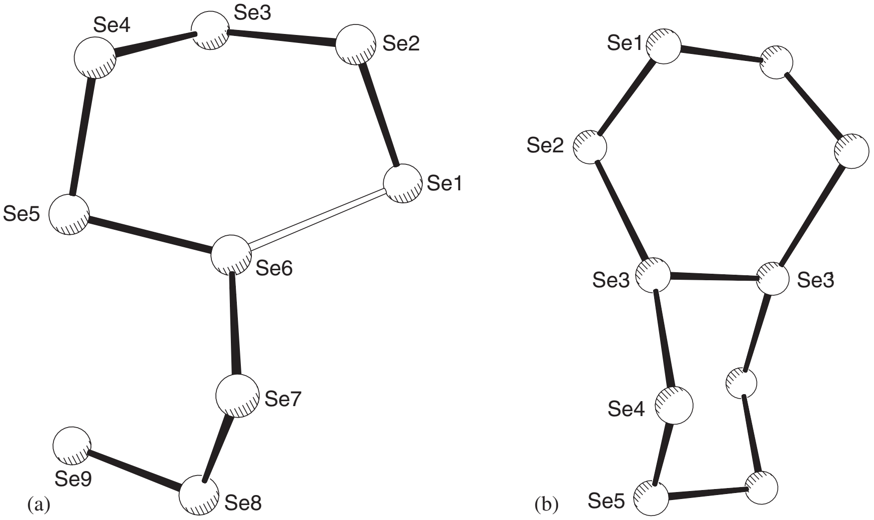


Figure 5 *Structures of (a) the* Se_9^{2-} *anion in [Sr(15-crown-5)*$_2$*]Se*$_9$[36] *and (b) the* Se_{10}^{2-} *anion in [Ph*$_3$*PNPPh*$_3$*]*$_2$*Se*$_{10}$[46]

its observed conformation clearly results from the additional stabilization that can be achieved through the weak secondary Se1···Se6 interaction of length 295.3(4) pm. This leads to a significant lengthening of the opposite Se5–Se6 distance to 247.3(4) pm and a narrowing of the Se4–Se5–Se6 angle to 93.0(1)°. A similar transannular Se3–Se3′ distance of 246.0(2) pm is observed in the C_2 symmetric bicyclic Se_{10}^{2-} anion of $[Ph_3PNPPh_3]_2Se_{10}\cdot DMF$,[46] in which the participating Se3 atoms exhibit distorted ψ-trigonal bipyramidal coordination geometries and axial Se3–Se2/Se3–Se4 distances of 275.9(3) and 257.2(3) pm.

The observed solid-state structures of Se_9^{2-} and Se_{10}^{2-} anions suggest that internal bonding interactions will lead to cyclization and a resulting stabilization of all polyselenides Se_n^{2-} with $n > 8$. This conclusion is further underlined by the bicyclic structure $[Se(Se5)_2]^{2-}$ adopted by the Se_{11}^{2-} anion in both of its known salts, $[PPh_4]_2Se_{11}$[47] and $[NPr_4]_2Se_{11}$[48] (Figure 6a). In this spirobicyclic polyanion, the central four-coordinate Se1 atom extends its coordination sphere to square planar by participating in two hypervalent 3-centre 4-electron bonds (see Figure 1a). These interactions are once again strongly asymmetric in the dianion of $[NPr_4]_2Se_{11}$ as evidenced by opposite d_1/d_2 distances of 255.7(5)/277.2(6) pm at the central ψ-octahedral Se1 atom, which can formally be assigned an oxidation state of +2. The fact that almost identical opposite bond lengths of 265.9(2)/268.0(3) are found in $[PPh_4]_2Se_{11}$ indicates, however, that the energy hypersurface for the distortion of the Se–Se–Se 3-centre 4-electron bonds must indeed be very flat. Packing factors involving the structure-directing counter cations will, therefore, play an important role in determining the extent of any coordination sphere distortion. This is presumably also the case for the Se_{16}^{4-} anion of Cs_4Se_{16}[17] (Figure 6b), which can also be regarded as being composed of an Se_6 ring and two weakly associated

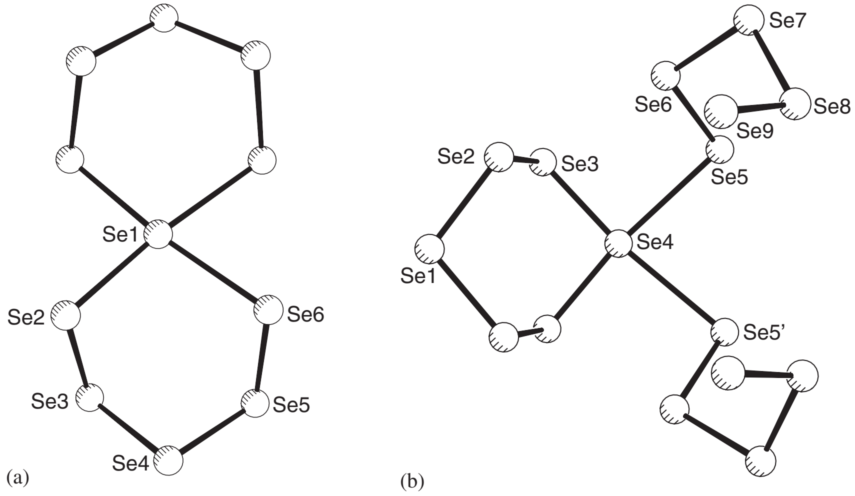


Figure 6 *Structures of (a) the* Se_{11}^{2-} *anion in* $[NPr_4]_2Se_{11}$[48] *and (b) the* Se_{16}^{4-} *anion in* Cs_4Se_{16}[17]

Se_5^{2-} anions. Highly asymmetric opposite Se4–Se3/Se4–Se5′ distances of 242.5(4)/298.9(4) pm are observed in the square-planar coordination sphere of the central Se4 atom.

Aqueous polyselenide solutions are often employed as electrolytes in high-efficiency photoelectrochemical cells[49] with photoanodes made of cadmium chalcogenides or gallium arsenide. UV/vis spectrophotometric structures[50–52] have confirmed successive formation of Se_2^{2-}, Se_3^{2-} and Se_4^{2-} anions on progressive oxidation of alkali metal polyselenide A_2Se_n solutions. Whereas the 430 nm absorption band of the diselenide Se_2^{2-} is dominant for a mean value of $n = 2$, three bands at 330, 380 and 530 nm belonging to Se_3^{2-} become prominent as n increases to 3 (Figure 7a). Finally, bands at 380 and 470 nm for $n = 4$ can be assigned to Se_4^{2-}, the longest polyselenide ion present in such aqueous solutions. A Raman spectroscopic study by Saboungi and co-workers[52] revealed only two characteristic peaks at 269 and 324 cm^{-1}. Whereas the former feature can readily be assigned to Se_4^{2-}, the 324 cm^{-1} bond is attributed to the radical anion $Se_2^{\cdot-}$, whose formation is ascribed to a photolytic process in the electrolyte. This radical anion can also be trapped in the sodalite cages of synthetic ultramarines to generate minerals with a range of red-brown hues.[34] Both electrospray mass spectrometry[53] and ^{77}Se NMR[54] have also been employed for speciation analysis of polyselenide solutions. The former technique indicates the presence of Se_5^{2-} anions in aqueous sodium polyselenide solutions and reveals that Se_4^{2-} is predominant at pH > 9, regardless of the nature of the alkali metal cation ($A = Na^+, K^+, Cs^+$). ^{77}Se NMR is well suited to probe individual selenium atoms of an Se_n^{2-} chain, as the chemical shift δ_{Se} is dependent on the distance from the chain end α [$\delta_{Se}(\gamma) > \delta_{Se}(\beta) > \delta_{Se}(\alpha)$] and lies in the range $\delta = 192$–860 relative to $\delta(Me_2Se) = 0$. All polyselenides Se_n^{2-} with $n = 3$–6 were detected by Cusick and Dance[54] in DMF, but

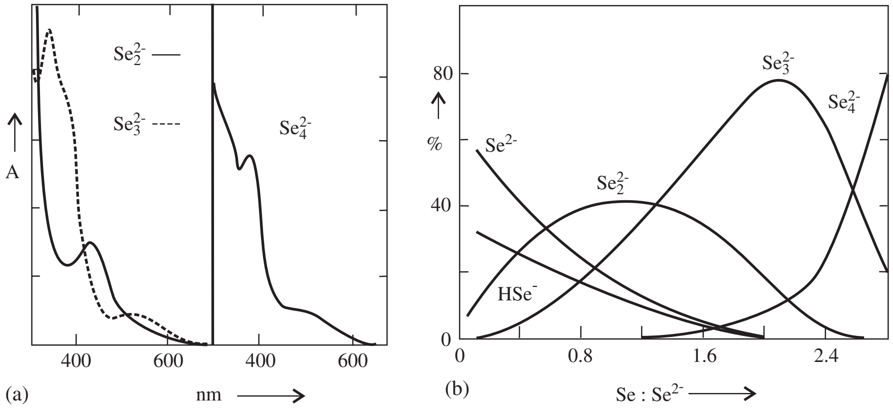


Figure 7 *(a) UV/vis absorption spectra*[52] *of potassium selenide solutions* K_2Se_n *with increasing mean value n; (b) species dependence*[51] *for a 1 M* K_2Se/KOH *solution on the amount of added Se. The solution is saturated at an Se:*Se^{2-} *ratio of 2.8:1*

interestingly no NMR evidence was obtained for the presence of Se_2^{2-} in this or other solutions (H_2O, C_2H_5OH).

9.2.2.4 Polytellurides

The increased tendency of tellurium to participate in intra- and intermolecular $n\mathrm{p}^2 \rightarrow \mathrm{n}\sigma^*$ bonding leads to the presence of distorted linear Te–Te···Te units in many polytellurides. As a consequence, their classification as discrete or as polymeric chains, sheets or 3D frameworks may often be relatively arbitrary. When only strong Te–Te bonds are taken into account (*i.e.*, $d < 313$ pm), isolated chains Te_n^{2-} can, however, be clearly recognized for dianions with $n =$ 2–6, 8, 12 and 13. In similarity to Se, discrete bicyclic dianions are also known, in the case of Te for $n = 7, 8$. $[Re_6Te_8]Te_7$ features a butterfly-like Te_7^{2-} dianion[55] (Figure 8a) and $[K(15\text{-crown-}5)_2]_2Te_8$ a likewise bicyclic anion[56] (Figure 8b), both of which contain a central square-planar $TeTe_4$ unit. The crystal structures of salt-like polytellurides have been comprehensively covered up to 1999 in a review article by Smith and Ibers.[6]

In contrast to the polysulfides and almost all the polyselenides (exception Cs_4Se_{16}[17]), a number of polytelluride anions are also known with total negative charges greater than 2, as, for instance, in NaTe[57] with discrete $[Te_5]^{4-}$ ions and in Cs_3Te_{22} with polymeric sheet-like ${}^2_\infty[Te_6^{3-}]$ ions.[19] These are examples for the striking variety of structural motifs and formula types (x/y = 5/3, 1/1, 2/3, 2/5, 1/3, 1/4, 1/6, 2/13, 1/7 and 3/22) that are known for the alkali metal polytellurides A_xTe_y and which reflect the propensity of tellurium both to catenate and to participate in hypervalent coordination polyhedra. Whereas discrete anions are observed for $x/y \geq 2/3$, polymeric chain and lamellar anionic networks are present in such tellurides when $x/y \leq 2/5$.[58,59]

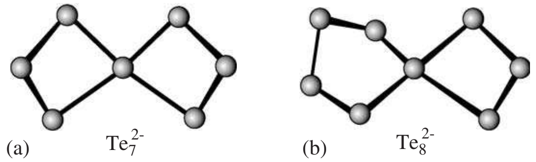


Figure 8 *Structures of (a) the* Te_7^{2-} *anion in* $[Re_6Te_8]Te_7$[55] *and (b) the* Te_8^{2-} *anion in* $[K(15\text{-crown-}5)_2]_2Te_8$[56]

Phases of the type A_5Te_3 (A = K, Cs), α and β-A_2Te_2 (A = K, Rb), Cs_2Te_2, $MgTe_2$ and $BaTe_2$ all contain simple dumbbell-shaped Te_2^{2-} units. The A_5Te_3 compounds are better formulated as $A_{10}Te_6$ and contain four Te^{2-} anions together with a Te_2^{2-} anion, whose dumbbells stack end to end to generate a linear chain of tellurium atoms. In K_5Te_3, for instance, respective Te–Te distances of 283.9(2) and 352.5(2) pm are observed for the ditelluride anions and their very weak interchain contacts.[60] The bent Te_3^{2-} anions in A_2Te_3 (A = K, Rb, Cs) and Ba_2Te_3 exhibit Te–Te bond lengths in the range 277–280 pm and Te–Te–Te angles between 104 and 109°. For comparison, the infinite helical chains of elemental tellurium[61] exhibit analogous dimensions of 283.5(2) pm and 103.2°. Much shorter Te–Te distances and wider Te–Te–Te angles are found for tritelluride chains in the presence of encapsulated or chelated counter cations such as $[K(2.2.2\text{-crypt})]^+$ or $[Ba(en)_{4.5}]^{2+}$, for which significant electrostatic interactions between the alkali/alkaline earth metal and Te atoms are not possible. $[K(2.2.2\text{-crypt})]_2Te_3$, for instance,[62] exhibits Te–Te distances of 269.2(3) and 272.0(4) pm and a large anion angle of 113.1(2)°. Similar short-terminal bond lengths are also observed for Te_4^{2-} and Te_5^{2-} in the presence of analogous encapsulated cations, $[PPh_4]^+$ or alkylammonium cations. There are no known binary alkali or alkaline earth polytellurides that contain discrete chain anions with $n = 4$ or 5.

As discussed previously, isolated polytelluride anions are only observed for binary alkali metal salts A_xTe_y with $x/y \geq 2/3$. Hypervalent bonding leading to linear $TeTe_2^{4-}$, T-Shaped $TeTe_3^{4-}$ and square-planar $TeTe_4^{6-}$ building units is characteristic for the polymeric anions in phases with $x/y \leq 2/5$. Examples of the former and latter coordination spheres are illustrated respectively by the central linear Te unit of the discrete Z-shaped Te_5^{4-} anion of NaTe and by the structurally related 1D chains of Cs_2Te_5[63(a)] and Rb_2Te_5[63(b)] depicted in Figure 9. The Te–Te distances of respectively 308(1) and 305(1) pm to the central Te atoms of these units in NaTe and Cs_2Te_5 are typical for 3-centre 4-electron bonds. Although Te_6^{2-} anions can be identified as building units in $LiTe_3$ and $NaTe_3$, their chains are linked by strong secondary Te···Te bonds into infinite helical strings. Interchain distances range from 276.7(1) to 297.9(1) pm for the Te_6^{2-} units of $NaTe_3$,[64] which are connected by Te···Te interactions of length 316.4(1) pm. On ignoring such secondary bonding with the given bond distances d_2 or greater (see Figure 1b), respectively Te_8^{2-} (d_2 = 314 pm), Te_{12}^{2-} (d_2 = 314 pm) and Te_{13}^{2-} (d_2 = 318 pm) moieties can be recognized within the anionic sheets of $CsTe_4$[65] (see Figure 14 for the isostructural phase $Cs_2Te_2Se_6$),

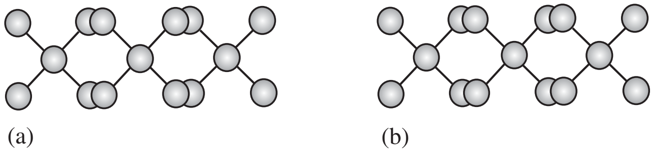


Figure 9 *Structures of (a) the* $^{1}_{\infty}[(TeTe_4)^{2-}]$ *chain anion in* Cs_2Te_5[63(a)] *and (b) the* $^{1}_{\infty}[(TeTe_4)^{2-}]$ *chain in* Rb_2Te_5[63(b)]

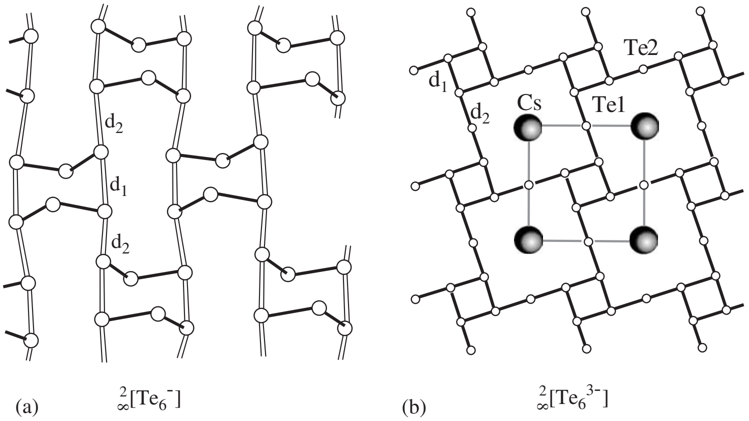
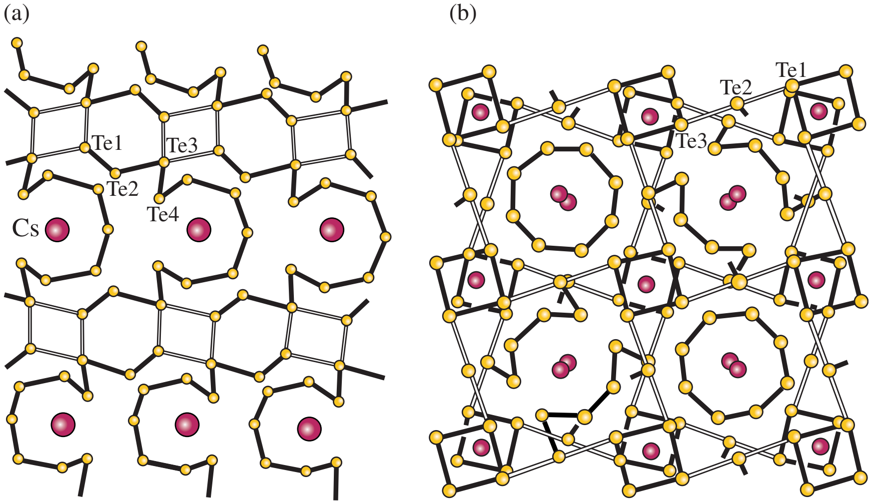


Figure 10 *The polytelluride nets: (a)* $^{2}_{\infty}[Te_6^-]$ *in* $RbTe_6$[18] *and (b)* $^{2}_{\infty}[Te_6^{3-}]$ *in* Cs_3Te_{22}.[19] *The unit cell of* Cs_3Te_{22} *is depicted by the grey lines*

$[N(C_2H_5)_4]_2Te_{12}$[66] and Cs_2Te_{13}[20] (Figure 11). In an analogous manner, $[Cr(en)_3]Te_6$[67] can be described as containing Te_4^{2-} units, whose terminal Te atoms each link to two further tetratelluride anions ($d_2 = 314$ pm) to generate a puckered $^{2}_{\infty}[Te_6^{3-}]$ sheet with open 24-membered rings.

The very tellurium-rich alkali metal polytellurides $RbTe_6$[18] and Cs_3Te_{22},[19] whose unique lamellar nets $^{2}_{\infty}[Te_6^-]$ and $^{2}_{\infty}[Te_6^{3-}]$ are depicted in Figure 10 can be isolated under methanolothermal reaction conditions as discussed in Section 2.1. For instance, the $^{2}_{\infty}[Te_6^-]$ layers of $RbTe_6$ are generated by treatment of a methanol solution of Rb_2CO_3 with Te in the presence of Ge (as a reducing agent) at 160°C. On ignoring Te···Te interactions greater than 318 pm, it is possible to recognize bent individual Te_3 chains with internal bond lengths of 277.7(3) and 278.9(2) pm and a formal charge of −0.5. These moieties are connected by two much longer Te···Te interactions of length 319.5(3) pm (d_1) into chair shaped six-membered rings, whose structure is strikingly reminiscent of that adopted by the discrete $S_6^{\cdot -}$ radical anions (Figure 4a) of $[Ph_4P]S_6$.[35] A similar 3-electron 4-centre bonding scheme (see Figure 4b) can, therefore, be proposed for such $Te_6^{\cdot -}$ units, which link through secondary Te···Te bonds (d_2) of length 321.4(3) pm into the corrugated $^{2}_{\infty}[Te_6^-]$ sheets of Figure 10a.

The pronounced bond length alternation within the anion sheets of $RbTe_6$ is in stark contrast to the modest difference between the Te–Te distances (d_1 = 300.3(1), d_2=307.7(1) pm) belonging to the planar thinned 4^4 nets



$$Cs_2Te_{13} \xrightarrow[180°C]{+Te} Cs_4Te_{28}$$

Figure 11 *The structural relationship between the metastable phases Cs_2Te_{13} and Cs_4Te_{28} on the reaction pathway to Cs_3Te_{22}*

(4^4 = network of Te_4 squares with 4-coordinated Te-nodes and shared sides) of Cs_3Te_{22} (Figure 10b). This cesium polytelluride can be prepared by methanolothermal reaction of Cs_2CO_3 with As_2Te_3 at 195°C and contains, in addition, effectively neutral crown-shaped Te_8 rings, which separate the ${}^{2}_{\infty}[Te_6^{3-}]$ sheets and coordinate the Cs^+ counter cations in a sandwich-like manner. UV/vis[68] and $^{123}Te/^{125}Te$ NMR[69] spectroscopic studies on solutions of alkali metal tellurides in ethylenediamine or liquid ammonia solution have confirmed the presence of short telluride chains Te_n^{2-} ($n = 2$ or 3) but provide no evidence for neutral cyclic species Te_n or anions with $n > 4$. It is, therefore, reasonable to assume that the strikingly different tellurium substructures in Cs_3Te_{22} must reflect a specific templating role of the alkali metal cation during a multiple-step reaction pathway. Indeed, the construction of neutral Te_8 crowns and defective square planar ${}^{2}_{\infty}[Te_6^{3-}]$ nets can readily be explained mechanistically[59] on the basis of the structures of two intermediate polytellurides Cs_2Te_{13} and Cs_4Te_{28} (Figure 11), isolated at respectively 150 and 180°C. Initial cesium templation generates the valence precise Te_{13}^{2-} chains of Cs_2Te_{13}, whose Te1 and Te3 atoms participate in secondary bonds of length 318.1(2) and 326.1(2) pm to afford the sheet anions of Figure 11a. Following cleavage of the symmetry-related Te3–Te4 bonds in Cs_2Te_{13}, addition of a Te atom to the liberated Te_7 fragment could generate the isolated Te_8 crowns of Cs_3Te_{22}. Rearrangement of the remaining weakly bonded ${}^{1}_{\infty}[Te_6^{2-}]$ ladders into the thinned 4^4 net of ${}^{2}_{\infty}[Te_6^{3-}]$ can be achieved by $1e^-$ reduction and concomitant cleavage of the old Te1–Te2 bonds with associated formation of new Te1–Te2 contacts between the Te_4 rings of previously adjacent ladders. Cs_4Te_{28} represents an intermediate product in which $^{2}_{\infty}[\mathrm{Te}_6^{4-}]$ sheets are linked by Te_6 chains and only half of the Cs^+ cations are coordinated by neutral Te_8 crowns. On ignoring the longer Te1···Te2 [315.3(2) pm] and Te2···Te3 [319.4(2) pm] bonds, both isolated Te_4 squares [Te1–Te1′ distances 291.1(2), 295.5(2) pm] and Te_6^{2-} chains can be identified in addition to Te_8 rings in a formally valence precise polytelluride $[\mathrm{Te}_{28}]^{4-}$.

The resulting count of 40 electrons per Te_6 units (i.e., 4×6 electrons for the Te_4^0 squares and 2 × 8 electrons for the two terminal Te atoms of the Te_6^{2-} chains) corresponds to the observed $^{2}_{\infty}[\mathrm{Te}_6^{4-}]$ formulation for the component polytelluride sheets of $\mathrm{Cs}_4\mathrm{Te}_{28}$. An alternative way of deriving the preferred electron count for networks of heavy main group elements consisting of finite-length linear chains is to employ an electron-rich multicentre bonding scheme proposed by Hoffmann *et al.*[70] The respectively $^{2}_{\infty}[\mathrm{Te}_6^{3-}]$ and $^{2}_{\infty}[\mathrm{Te}_6^{4-}]$ sheets of $\mathrm{Cs}_3\mathrm{Te}_{22}$ and $\mathrm{Cs}_4\mathrm{Te}_{28}$ can be regarded as being comprised of Te_5 linear units crossing each other at right angles. Bonding analysis is facilitated by the absence of significant s–p mixing for tellurium and the relative unimportance of π-bonding. According to the hypervalent bonding scheme, five p_x orbitals (Figure 12a) split into bonding (*x*2), non-bonding (*x*1) and antibonding molecular orbitals of which only the former three are filled. In $\mathrm{Cs}_3\mathrm{Te}_{22}$, four five-centre bonds emanate from each unit cell, so that two multicentre bonds corresponding to 2 × 6 electrons must be taken into account per Te_6 unit. These are then added to the s and p_z lone pair electrons of the six Te atoms (6 × 4) and the additional four in-plane p_y lone pair electrons of the two central Te atoms (2 × 2) to afford the required total count of 40 electrons for a $^{2}_{\infty}[\mathrm{Te}_6^{4-}]$ formulation. Extended Hückel calculations[71] indicate that the Te_4 rings of $\mathrm{Cs}_4\mathrm{Te}_{28}$ should, in fact, be described as Te_4^- (charge −0.94) and the Te_6 chains as Te_6^- (charge −1.06).

The $^{2}_{\infty}[\mathrm{Te}_6^{3-}]$ sheets of $\mathrm{Cs}_3\mathrm{Te}_{22}$ contain one electron less than the expected count of 40 e^- and it is reasonable to assume that this missing electron must be removed from a band originating from the non-bonding σ-orbital of Figure 12a. Actually, these orbitals are somewhat antibonding due to mixing with lower-lying

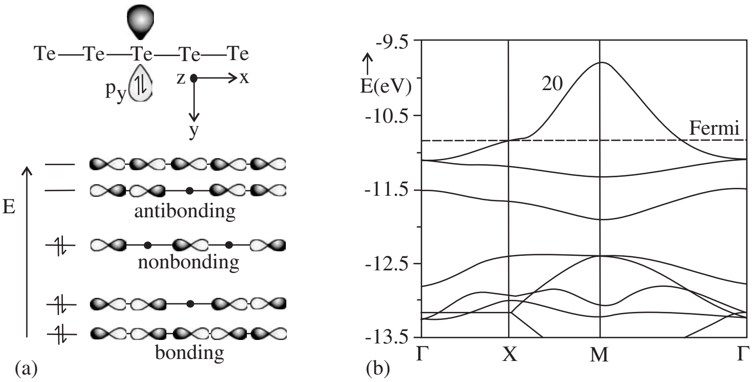


Figure 12 *(a) Simple bonding scheme[70] for a five-centre bond in Cs_3Te_{22} and (b) bond structure for the $^{2}_{\infty}[Te_6^{3-}]$ sheet close to the Fermi level[72]*

s-bands, and extended Hückel calculations[72] have indicated that the Fermi level crosses through the middle of the apposite band 20 (Figure 12b). A wide gap of about 2 eV is found above this band and as a consequence of its being half-filled, the phase Cs_3Te_{22} could be metallic. The Fermi surface of the ${}^{2}_{\infty}[Te_6^{3-}]$ layer is almost perfectly nested according to these calculations, with the result that there could be an associated charge density wave instability (CDW), which would be responsible for a metal-to-insulator transition. However, *ab initio* tight-binding linear muffin-tin orbital calculations (TB-LMTO)[73] have suggested that Cs_3Te_{22} may, in fact, be an insulator owing to weak secondary interactions (341, 344 pm) between the Te_8 rings and the ${}^{2}_{\infty}[Te_6^{3-}]$ sheets. Experimental magnetic and conductivity data are, unfortunately, not available for this material.

The quaternary polytelluride $K_{0.33}Ba_{0.67}AgTe_2$ contains alternating formally ${}^{2}_{\infty}[(Te_2)^{4/3-}]$ square nets (Figure 13a) and puckered ${}^{2}_{\infty}[(Ag_2Te_2)^{2-}]$ layers that are separated by K^+ and Ba^{2+} cations.[74] While extended Hückel band theory predicts that the polytelluride network should exhibit metallic properties, experimental measurements indicate that the compound is a semi-conductor at room temperature with an electrical conductivity of *ca.* $0.2\ S \cdot cm^{-1}$. Electron diffraction studies reveal the presence of two different but related superstructures, whose observation can be rationalized by a network distortion to allow the formation of discrete Te_3^{2-} units linked by weaker secondary bonds (Figure 13b). This means that the material already exists in a CDW state at room temperature, which destroys metallic conductivity. CDW states have also been observed for transition metal polychalcogenides such as $NbSe_3$ and $ZrTe_3$, whose structures will be discussed in Section 3.

Solvothermal treatment of a mixture of *n*-propylamine, aqueous KOH, tellurium and antimony affords the black microporous semiconductor $K_6Te_{12} \cdot Sb_{12}O_{18} \cdot 6H_2O$ (SBC-1),[75] in which 24-membered Te tubular units host discrete $Sb_{12}O_{18}$ rings, which in turn host K^+ cations and water molecules. Each tellurium tube within the honeycomb-like 3D polytelluride network consists of six parallel *dreier* single chains (Te–Te: 288 pm) running along the *c* axis connected to one another via secondary bonds (Te–Te: 318 pm) to Te_2^{2-} dumbbells (Te–Te: 278 pm) in the *ab* plane. Its narrow band gap of 0.25 eV, highly anisotropic conductivity ($5.9 \cdot 10^{-3}\ S \cdot cm^{-1}$ in *c* direction, $2.6 \cdot 10^{-6}\ S \cdot cm^{-1}$ in the *ab* plane) and microporous structure suggests that SBC-1

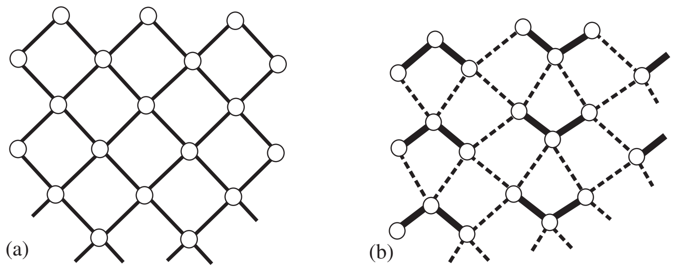


Figure 13 *(a) Undistorted square 4^4 net and (b) observed distortion of the ${}^{2}_{\infty}[(Te_2)^{4/3-}]$ net in $K_{0.33}Ba_{0.67}AgTe_2$*[74]

and other potential compounds of this type may be suitable for a range of technological applications, for example, in the fields of chemical sensors, thermoelectronics and low-dimensional electronics.

9.2.2.5 Thio- and Selenidotellurates

A number of mixed Te/S and Te/Se polychalcogenide anions have been prepared by intermediate temperature fusion reactions or solvothermal/solution techniques and contain Te(II) or Te(IV) centres bonded to E_n^{2-} species (E = S, Se). As for the polysulphides S_n^{2-}, only discrete thiotellurate anions are known and these are limited[76,77] to the pyramidal thiotellurate(IV) TeS_3^{2-} and the thiotellurates(II), $[Te(S_5)_2]^{2-}$, $[Te(S_5)(S_7)]^{2-}$ and $[Te(S_7)_2]^{2-}$. The central tellurium atoms in the latter anions of the salts $[PPh_4]_2[Te(S_5)_2]$, $[NEt_4]_2[Te(S_5)(S_7)]$ and $[NEt_4]_4[Te(S_5)_2][Te(S_7)_2]$ exhibit square planar coordination spheres and are coordinated by S_5^{2-} and/or S_7^{2-} chains in a chelate manner. Their bicyclic structures can, therefore, be compared with those of the $[Te(Te_3)(Te_4)]^{2-}$ anion of $[K(15\text{-crown-}5)_2]_2Te_8$[56] (Figure 8b) and the $[Se(Se_5)_2]^{2-}$ anions of $[PPh_4]_2Se_{11}$[47] or $[NPr_4]_2Se_{11}$[48] (Figure 6a). The TeS_3^{2-} anion has not only been characterized as a discrete moiety in salts such as $[PPh_4]_2[TeS_3]\cdot 2CH_3CN$[76] and $[NEt_4]_2[TeS_3]$[77] but also as a complex ligand (*e.g.*, in $[Me_4N]_2[Au_2(TeS_3)_2]$[78]) and a building unit in solid state structures (*e.g.*, in $(CuI)_3Cu_2TeS_3$[79]). ESR evidence has been presented for the presence of bent $TeS_2^{\cdot-}$ radical anion ligands in addition to TeS_2^{2-} ligands in the phase $(CuBr)_5Cu_6[TeS_2^{\cdot-}]_4[TeS_2^{2-}]$.[80]

The $[K(2.2.2\text{-crypt})]^+$ cation has been employed to extract both the bent $TeSe_2^{2-}$ anion with a central Te atom (Te–Se: 250.1 and 250.4 pm; Se–Te–Se: 111.3°) and the pyramidal $TeSe_3^{2-}$ anion (Te–Se: 245.4–246.5 pm; Se–Te–Se: 104.8–108.9°) from ethylenediamine solution.[69] Whereas $[K(2.2.2\text{-crypt})]_2TeSe_2\cdot en$ and $[K(2.2.2\text{-crypt})]_2TeSe_3\cdot en$ could be crystallized at room temperature by employing K_2Te and Se as starting materials, reaction of the elements K, Te and Se (molar ratio 1:1:5) in refluxing ethylenediamine in the presence of 2.2.2-crypt leads to formation of $[K(2.2.2\text{-crypt})]_2TeSe_{10}$.[81] $[Ba(2.2.2\text{-crypt})(en)]TeSe_{10}\cdot 0.5en$ with an analogous bicyclic $[Te(Se_5)_2]^{2-}$ anion can also be prepared under similar conditions. The bent $TeSe_2^{2-}$ anion has also been characterized in $[Mn(en)_3]TeSe_2$[82] and an Se–Te–Te–Se chain anion, $Te_2Se_2^{2-}$, has been isolated in $[PPh_4]_2[Te_2Se_2]$.[83] $[Te(TeSe_3)_2]^{4-}$ participates as a hexadentate ligand in the cage anions of $[N(Ph_3P)_2]_2[Ag_2\{Te(TeSe_3)_2\}]\cdot DMF$[78] for which the sulfur analogue is also known. Methanolothermal reaction of Se with Cs_2CO_3 in the presence of solid Bi_2Te_3 leads to formation of the selenium-rich selenidotellurates $Cs_2Te_2Se_6$ and Cs_4TeSe_{15},[84] owing to the very slow release velocity of tellurium from the Group 15 telluride. $Cs_2Te_2Se_6$ is isostructural to $CsTe_4$[65] and contains $[\{Te(Se_2)\}_2(\mu\text{-}Se_2)]^{2-}$ chains on ignoring weaker Te . . . Se interactions greater than 291 pm. Inspection of Figure 14 indicates, however, that these dianions are linked into sheets and that the coordination number of Te is increased to four when the longer Te1 · · · Se1 secondary bonds are taken into account. Cs_4TeSe_{15} is isostructural to Cs_4Se_{16}[7] (Figure 6b) and exhibits

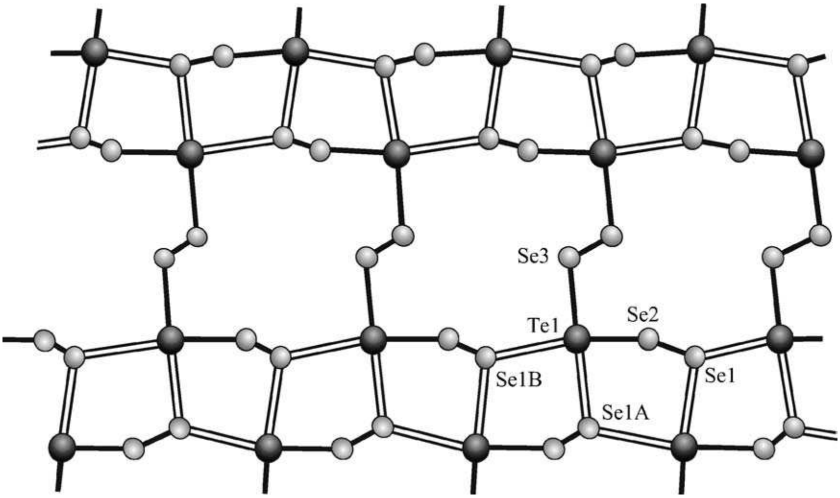


Figure 14 *Structure of the* $^{2}_{\infty}[Te_2Se_6^{2-}]$ *anion in* $Cs_2Te_2Se_6$[84] *with long Te . . . Se interactions (> 291 pm) depicted as open bonds. Selected bond lengths: Te1–Se1A 292.2(2), Te1–Se2 260.3(1), Te1–Se3 271.8(2), Te1–Se1B 324.4(1) pm*

asymmetrical Te4–Se3/Te4–Se5′ distances of 260.2(3)/296.2(4) pm in the central square-planar coordination sphere of Te4. The $TeSe_{15}^{4-}$ anion can be described as $[Te(Se_5)_3]^{4-}$ and the lessening of the difference (36.0 pm) between opposite distances to its central atom in comparison to Se_{16}^{4-} (56.4 pm) reflects the increased tendency of tellurium to participate in $n\text{p}^2 \rightarrow n\sigma^*$ secondary bonding.

The selenidotellurates $[NEt_4]_2[Te_3Se_6]$ and $[NEt_4]_2[Te_3Se_7]$ were synthesized at 293 K by reactions between Te_n^{2-} and Se_n^{2-} anions in DMF in the presence of $[NEt_4]Cl$.[83] Both contain infinite anionic chains separated by $[NEt_4]^+$ cations. In the former compound, each $^{1}_{\infty}[Te_3Se_6^{2-}]$ polyanion comprises of open-book shaped Te_3Se_5 rings bridged by Se atoms (Figure 15a). The $^{1}_{\infty}[Te_3Se_7^{2-}]$ chains of the second compound are depicted in Figure 15b and consist of fused five- and six-membered rings bridged by Se atoms. The component Te_3Se_6 ring can be regarded as an inorganic analogue of bicyclononane.

9.2.3 Complexes of Polychalcogenide Ligands

9.2.3.1 Synthesis

Metal sulfides and polysulfides have been extensively studied because of their key role in important catalytic processes such as the hydrodesulfurization of crude oil or the biosynthesis of metalloproteins. The coordination chemistry of polysulfides[85,86] has been comprehensively reviewed similar to that of the heavier polychalcogenides.[10,12–15] Polysulfido complexes are themselves reactive and their exothermic desulfurization can be exploited as a means of

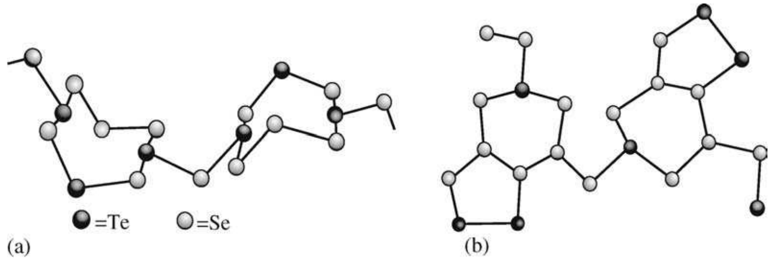


Figure 15 *Structure of (a) the* $^{1}_{\infty}[Te_3Se_6^{2-}]$ *chain anion in* $[NEt_4]_2[Te_3Se_7]$ *and (b) the* $^{2}_{\infty}[Te_3Se_7^{2-}]$ *chain anion in* $[NEt_4]_2[Te_3Se_7]$[83]

generating new clusters and rings.[87] A number of general routes are available for the synthesis of polychalcogenido complexes.

(i) Reaction of metal complexes or salts with alkali metal polychalcogenides

This is the most common method for preparing chalcogen-rich complexes and is carried out in polar organic solvents such as en, DMF, CH_3CN or alcohols at room or higher temperature (*e.g.*, solvothermal conditions). The required alkali metal polychalcogenides can be prepared by intermediate temperature fusion or liquid ammonia reactions of alkali metals and chalcogens. As demonstrated by the following examples, the approach is suitable for both simple metal salts and organometallic complexes.[15,88]

$$ZnCl_2 + 2Na_2Se_4 + 2Ph_4PCl \xrightarrow{DMF} [PPh_4]_2[Zn(Se_4)_2] + 4NaCl \qquad (4)$$

$$Mo(CO)_6 + K_2Te_4 + 2Ph_4PBr \xrightarrow{DMF/THF} [PPh_4]_2[Mo(Te_4)(CO)_4] + 2CO + 2KBr \qquad (5)$$

Alternatively, the polychalcogenide may be generated *in situ* and then allowed to react immediately with the appropriate metal compound.[89]

$$2FeCl_2 + 6Na + 12Se \xrightarrow{DMF} Na_2[Fe_2Se_2(Se_5)_2] + 4NaCl \qquad (6)$$

(ii) Reaction of metal complexes with chalcogens

Elemental sulfur or selenium can react with coordinatively unsaturated metal complexes or compounds containing metal–metal bonds to afford polychalcogenido complexes.[90,91]

$$[Os(CO)_2(PPh_3)_2] + 2Se \xrightarrow{benzene} [Os(Se_2)(CO)_2(PPh_3)_2] \qquad (7)$$

$$[Cp^*_2Rh_2(CO)_2] + 5Se \rightarrow [Cp^*_2Rh_2(\mu\text{-}Se)(\mu\text{-}Se_4)] + 2CO \qquad (8)$$

Treatment of thio- or selenidometalates with the respective element affords chelate rings *via* a simple redox process.

$$MoS_4^{2-} + 5S \xrightarrow{DMF} [MoS(S_4)_2]^{2-} \qquad (9)$$

The lower reactivity of elemental tellurium has prevented the general exploitation of this approach for polytellurido complexes.

(iii) Treatment of oxometalates and metal complexes with H_2E ($E = S, Se$)

This traditional method for preparing thiometalates (*e.g.*, MoS_4^{2-}) can also afford polysulfido complexes, due to generation of S_n^{2-}, when H_2S is bubbled into an alkaline aqueous solution.

$$MoO_4^{2-} + 4H_2S \rightarrow MoS_4^{2-} + 4H_2O \tag{10}$$

Although its use as a routine reagent is less convenient, H_2Se has been employed for the synthesis of selenidometalates such as $MoSe_4^{2-}$ and polyselenido complexes, *e.g.*, $Cp_2V_2Se_5$.[92]

(iv) Treatment of metal complexes with chalcogen transfer reagents

Trialkylsilyl derivatives $(R'R_2Si)_2E$ ($R = CH_3$; $R' = CH_3$, ${}^tBu$, $CH_3(CH_2)_7$; $E = S, Se, Te$) exploit the strength of the Si–O or Si–Cl bond to generate a stable leaving group (*e.g.*, $(Me_3Si)_2O$ or Me_3SiCl) under mild conditions. For instance, an improved method of preparing $MoSe_4^{2-}$ is to react MoO_4^{2-} with $[Me_2(Me(CH_2)_7)Si]_2Se$.[93a]

$$\begin{aligned} MoO_4^{2-} &+ 4\left[Me_2(Me(CH_2)_7)Si\right]_2Se \\ &\rightarrow MoSe_4^{2-} + 4\left[Me_2(Me(CH_2)_7)Si\right]_2O \end{aligned} \tag{11}$$

Metal-rich chalcogen clusters have also been prepared with such trialkylsilyl derivatives, *e.g.*, reaction of $[NiCl_2(PPh_3)_2]$ with $(Me_3Si)_2Se$ generates the large cluster $[Ni_{34}Se_{22}(PPh_3)_{10}]$.[93b] In a number of cases, diselenide fragments have been incorporated into metal complexes on treating these with reagents such as CoSe, CSe_2, Se_2Cl_2 or SeO_3^{2-}.

(v) Molten alkali metal polychalcogenide fluxes

Metal powders can readily react with alkali metal polychalcogenide melts at typical temperatures in the range 200–600°C to afford chalcogen-rich complexes. As discussed in an excellent review article,[10] the highly ionic nature of the melt greatly enhances the solubility of the chosen metal and often facilitates the growth of single crystals.

$$2K_2S + 12S + 3Ti \xrightarrow{375^\circ C} K_4[Ti_3S_{14}] \tag{12}$$

$$2K_2Te + 9Te + 8Cu \xrightarrow{350^\circ C} K_4[Cu_8Te_{11}] \tag{13}$$

The use of large organic cations (*e.g.*, PPh_4^+) instead of alkali metals not only lowers the metal point of the flux but also often directs the formation of novel structures, *e.g.*, $[Ph_4P][Ga(Se_6)_2]$.[94]

9.2.3.2 Terminal and Bridging Modes

Owing to their conformational flexibility, bridging and/or chelating coordination modes are typical for polychalcogenide ligands. As a result, very few

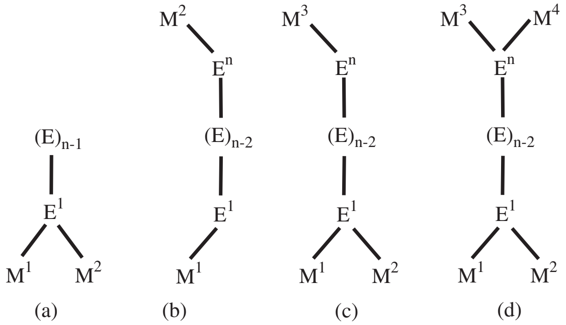


Figure 16 *Selected bridging coordination modes for polychalcogenide ligands: (a)* μ-$1\kappa E^1{:}2\kappa E^1$*; (b)* μ-$1\kappa E^1{:}2\kappa E^n$*; (c)* μ_3-$1\kappa E^1{:}2\kappa E^1{:}3\kappa E^n$*; (d)* μ_4-$1\kappa E^1{:}2\kappa E^1{:}3$-$\kappa E^n{:}4\kappa E^n$.

examples are known for the simple terminal κE^1 mode or the μ-$1\kappa E^1{:}2\kappa E^1$ (Figure 16a) binding pattern and these appear to be restricted to E = Se, Te.

The discrete $[AuTe_7]^{3-}$ anions of $[NEt_4]_3[AuTe_7]$ comprise of a central Au(III) atom coordinated in a square planar fashion by two monodentate Te_2^{2-} dumbbells (κTe^1 mode) and a bidentate Te_3^{2-} ligand.[95] Weak secondary interactions of length 312.0(2) and 337.4(2) pm are observed between the non-coordinating Te2 atoms of the Te_2^{2-} ligands and the neighbouring coordinating Te1 and Te3 atoms of the chelating Te_3^{2-} anion. Terminally bonded Te_n^{2-} ligands have been structurally characterized in $[K(2.2.2\text{-crypt})]_2[Cr(Te_3)(CO)_5] \cdot 0.5en$[96] (Figure 17a) and $[Fe(en)_3]_2[Hg_2Te_9]$.[97] The dinuclear $[Hg_2Te_9]^{4-}$ anions of the latter compound can be formulated as $[Hg_2(\mu\text{-}Te)(\mu\text{-}Te_2)(Te_3\text{-}\kappa Te)_2]^{4-}$ and are connected into polymeric chains through weak intermolecular Te···Te contacts of length 348.8(2) pm between coordinating Te1 atoms of the Te_3^{2-} ligands.

In contrast to these shorter Te_2^{2-} and Te_3^{2-} ligands, in the case of the polyselenides, end-on coordination has, somewhat surprisingly, only been reported for the longer E_5^{2-} and E_6^{2-} chains, which typically adopt chelating or bridging modes. Both the discrete $[Mo_6Se_{42}]^{6-}$ anions of $[NEt_4]_6[Mo_6Se_{42}]$[98] and the infinite $^1_\infty[AuSe_{13}^{3-}]$ chains of K_3AuSe_{13}[99] exhibit terminally coordinating Se_5^{2-} ligands. K_3AuSe_{13} was isolated by reacting gold powder with a molten potassium polyselenide flux at 250°C. Each Au(I) atom in the $^1_\infty[AuSe_{13}^{3-}]$ chains is coordinated by two terminal Se_5^{2-} ligands and bridged by shorter Se_3^{2-} anions. In addition to these examples of κSe^1 coordination for Se_5^{2-}, a unique terminal hexaselenide ligand Se_6^{2-} (Figure 17b) has been found in the compound $[K(2.2.2\text{-crypt})]_3[Ag(Se_6)\{Se_2C_2(CN)_2\}]$.[100]

A rare example of the μ-$1\kappa E^1{:}2\kappa E^1$ bridging mode (Figure 16a) is observed for the Te_2^{2-} ligand in the dinuclear anion of $[PPh_4]_2[\{Fe(CO)_3\}_2(\mu\text{-}Te)(\mu\text{-}Te_2)]$.[101] More complexes are known in which polychalcogenide ligands connect four metal centres by employing this coordination pattern for both of the terminal chalcogen atoms (Figure 16d). For instance, dichalcogenide anions E_2^{2-} (E = S, Se, Te) bridge the four iron atoms in this manner in the octanuclear

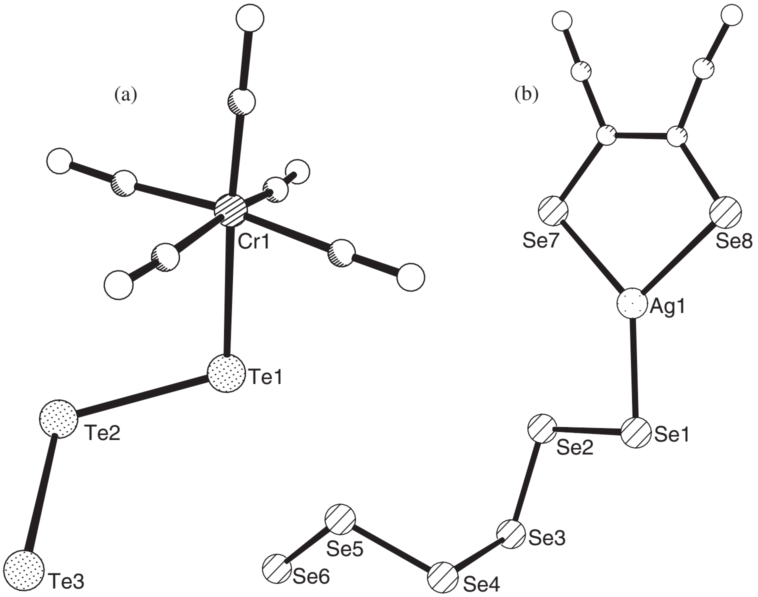


Figure 17 *(a) Terminal κTe¹ coordination of a* Te_3^{2-} *ligand in [K(2.2.2-crypt)]₂[Cr(Te₃)(CO)₅]*[96] *and (b) terminal κSe¹ coordination of an* Se_6^{2-} *chain in [K(2.2.2-crypt)]₃[Ag(Se₆){Se₂C₂(CN)₂}]*[100]

complexes $[\{(CO)_8(\mu\text{-}PCy_2)Re_2(\mu_4\text{-}E)Fe_2(CO)_6\}_2(\mu_4\text{-}E_2)]$.[102] Treatment of $W(CO)_6$ with $[Ph_4P]_2Te_4$ at 100°C in DMF affords the oxidative decarbonylation product $[Ph_4P]_2[W_6(Te_2)_4(CO)_{18}]\cdot CH_2Cl_2$[103] whose hexanuclear anion is depicted in Figure 18a. A central Te_2^{2-} dumbbell connects six tungsten atoms in this attractive cluster, whose trigonal prismatic faces are bridged by three additional Te_2^{2-} dimers in an ecliptic μ_4 manner. A contrasting staggered conformation[104] is observed for the bulky $Cr(CO)_5$ fragments of the $[Cr_4(Te_2)(CO)_{20}]^{2-}$ anion prepared by treatment of $Cr(CO)_6$ with K_2Te_2. When K_2Te_3 is employed as the tellurium source, an analogous $[Cr_4(Te_3)(CO)_{20}]^{2-}$ anion (Figure 18b) with a μ_4 bridging tritelluride ligand is obtained. This coordination pattern has also been characterized for the S_4^{2-} ligand in the tetrarhenium complex[105] $[\{Re_2(\mu\text{-}S)(S_2CN^iBu_2)\}_2(\mu_4\text{-}S_4)][PF_6]_2$. A rare example of unsymmetrical μ_3 bridging by a polychalcogenide ligand is provided by the $[\{\eta^5\text{-}C_5H_5)Fe(CO)_2\}_3(Se_2)]^+$ cation,[106] in which the Se_2^{2-} dumbbell connects three iron atoms in the manner depicted in Figure 16c.

Although simple μ-1κE¹:1κEⁿ bridging (Figure 16b) is far more common for E_n^{2-} anions in polymeric compounds, a number of interesting exceptions are known. The solvothermally prepared compound $Rb_4Hg_5Te_{13}$,[107] for instance, contains Hg_5 square pyramids, where one $\mu_3\text{-}Te_3^{2-}$ and two monotelluride $\mu_3\text{-}Te^{2-}$ units cap three triangular faces of the pyramid and a single $\mu_4\text{-}Te_2^{2-}$ dumbbell caps its basal plane (Figure 19a). A second tritelluride Te_3^{2-} ligand bridges the two upper basal mercury atoms in a μ-1κTe¹:2κTe³ manner. The μ₃-1κTe¹:2κTe²:3κTe³ coordination mode of the capping Te_3^{2-} unit

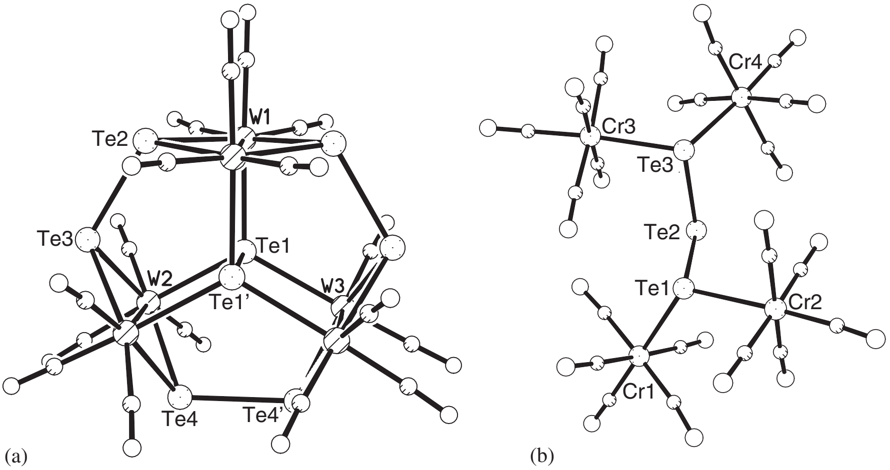


Figure 18 *Structure of the anions of (a)* $[Ph_4P]_2[W_6(Te_2)_4(CO)_{18}]\cdot CH_2Cl_2$[103] *and (b)* $[Ph_4P]_2[Cr_4(Te_3)(CO)_{20}]$[104]

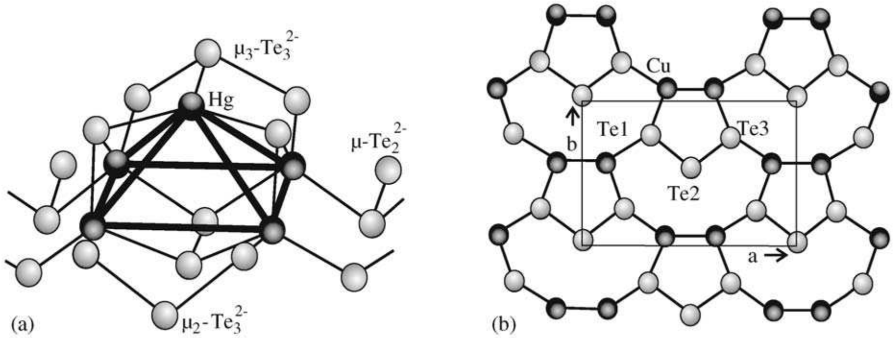


Figure 19 *(a) Fragment of the* $^{1}_{\infty}[\{Hg_5(Te)_3(Te_2)_2(Te_3)_2\}^{4-}]$ *anionic chain in* $Rb_4Hg_5Te_{13}$;[107] *(b) projection of the component* Cu_2Te_3 *layer of* $K_2Cu_2Te_5$[107]

appears to be unique, whereas μ_4 bridging by Te_2^{2-} dumbbells was discussed above for molecular complexes and has also been observed in other solid-state phases such as $K_2Cu_2Te_5$[107] and $Cs_3Cu_8Te_{10}$.[108] Individual Hg_5 clusters in $Rb_4Hg_5Te_{13}$ are joined into polymeric anionic chains $^{1}_{\infty}[\{Hg_5(Te)_3(Te_2)_2(Te_3)_2\}^{4-}]$ by Te atoms and dangling Te_2^{2-} moieties. Contrasting telluride binding modes are also present in the $^{2}_{\infty}[\{In_{16}(Te)_{22}(Te_2)_4(Te_3)\}^{8-}]$ layers of $[Zn(en)_3]_4In_{16}Te_{33}$,[107] in which In_4Te_{10} supertetrahedra are connected by μ-Te^{2-}, μ-Te_2^{2-} and μ_6-Te_3^{2-} units. Each of the Te atoms in the latter tritelluride anions coordinates two indium atoms in a binding mode also found in the phase $[NEt_4]_4[Au(Ag_{1-x}Au_x)_2Sn_2Te_9]$ ($x = 0.32$) synthesized by solvent extraction of an intermetallic alloy.[109] A further example for the versatility of polytelluride bridging is provided by $K_2Cu_2Te_5$, in which Cu atoms are linked by intralayer

μ_4-Te_3^{2-} units into the Cu_2Te_3 nets depicted in Figure 19b. μ_4-Te_2^{2-} dumbbells connect Cu_2 pairs from adjacent layers into an open 3D framework, with K^+ cations located in the resulting cavities.[107]

Whereas simple μ-1κE^1:2κE^n bridging is known for chain lengths in the ranges $n = 2$–7 and $n = 2$–6 for respectively S and Se, the bonding versatility of the polytellurides appears to restrict this coordination mode to Te_n^{2-} with $n = 2, 3, 4$. Figure 20a depicts the dinuclear $[In_2S_{27}]^{4-}$ anion of $[Ph_4P]_4[In_2S_{27}]$, which contains the longest known bridging polysulfide unit.[110] It is interesting to note that the analogous selenidoindate(III) $[Ph_4P]_4[In_2Se_{21}]$[111] contains an Se_5^{2-} anion as its bridging ligand together with four chelating tetraselenide units Se_4^{2-}. However μ-1κSe^1:2κSe^6 coordinating Se_6^{2-} chains have been successfully incorporated into the ${}^2_\infty[\{Pd(\mu\text{-}Se_6)_2\}^{2-}]$ layers of $[(CH_3N(CH_2CH_2)_3N]_2PdSe_{12}$.[112] Analogous ${}^2_\infty[\{Pd(\mu\text{-}Se_n)_2\}^{2-}]$ polyanions can be prepared for $n = 4, 5$ under similar methanolothermal conditions by employing suitable structure-directing cations.[112] Tetratelluride bridging units are found in the isostructural phases $[PPh_4]_4[M_2Te_{12}]$ (M = Cu, Ag),[113] where the Group 11 metal atoms are also chelated by Te_4^{2-} anions (Figure 20b). Many molecular and polymeric complexes are known in which metal centres are bridged by E_n^{2-} chains with $n \leq 4$, as for instance for $n = 2$ in the ${}^1_\infty[SnTe_4^{2-}]$ ribbons of Cs_2SnTe_4[114] or the ${}^2_\infty[Sn_2Se_6^{2-}]$ sheets of $Cs_2Sn_2Se_6$.[115]

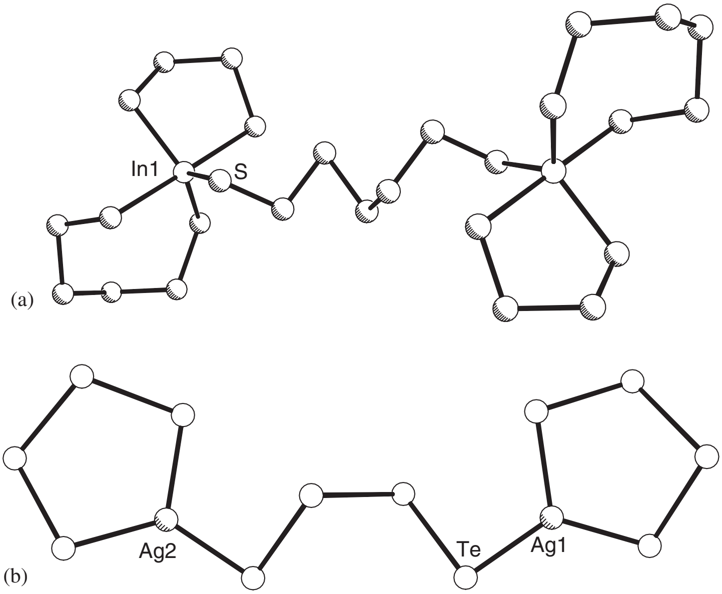


Figure 20 *(a) Bridging* Se_7^{2-} *chains in* $[Ph_4P]_4[In_2S_{27}]$;[110] *(b) bridging* Te_4^{2-} *chains in* $[Ph_4P]_4[Ag_2Te_{12}]$[113]

9.2.3.3 Side-On and Chelating Modes

Possible side-on coordination modes for dichalcogenide ligands E_2^{2-} (E = S, Se, Te) are depicted in Figure 21. Both the κ^2E^1,E^2 and $\mu\text{-}1\kappa^2E^1,E^2{:}2\kappa^2E^1,E^2$ binding patterns are characteristic for sulfur and selenium. In contrast analogous complexes containing Te_n^{2-} units are generally unstable and, therefore, more limited in number. Bulky chelating ligands such as triphos and ppp [*bis*(2-diphenylphosphinoethyl)phenylphosphane] have been employed to stabilize complexes such as [(triphos)Ni(Te_2)] and [(ppp)Ni(Te_2)][116] with the κ^2E^1,E^2 coordination mode and [{(triphos)Ni}$_2$(μ-Te_2)][117] with a planar bridging side-on pattern. The alternative folded butterfly arrangement of Figure 21b is typical for S_2^{2-} and Se_2^{2-} dumbbells.

Side-on coordinated dichalcogenide ligands E_2^{2-} are also capable of participating in κE binding to one or two additional metal atoms as depicted in Figures 21c and d. For instance, two iron atoms are linked in the $\mu\text{-}1\kappa^2Se^1,Se^2{:}2\kappa Se^1$ fashion in [{(η^5-C_5H_5)Fe(CO)$_2$}(μ-Se_2){Cr(CO)$_2$(η^5-C_5H_5)}][118] (Figure 22a) and three manganese atoms in the $\mu_3\text{-}1\kappa^2Te^1,Te^2{:}2\kappa Te^1{:}3\kappa Te^2$ mode in [$PhCH_2N(CH_3)_3$][{(CO)$_3$Mn(μ_3-Te_2)}$_2$Mn(CO)$_4$][119] (Figure 22b). An analogous binding pattern is observed for the side-on coordinated μ_3-S_2^{2-} ligands of

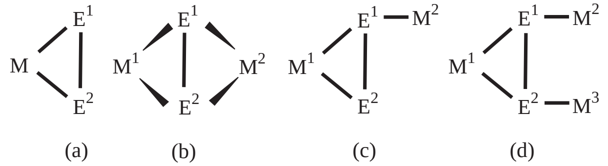


Figure 21 *Side-on coordination modes for dichalcogenide ligands* E_2^{2-}*: (a)* κ^2E^1,E^2*; (b)* $\mu\text{-}1\kappa^2E^1,E^2{:}2\kappa^2E^1,E^2$*; (c)* $\mu\text{-}1\kappa^2E^1,E^2{:}2\kappa E^1$*; (d)* $\mu_3\text{-}1\kappa^2E^1,E^2{:}2\kappa E^1{:}3\kappa E^2$

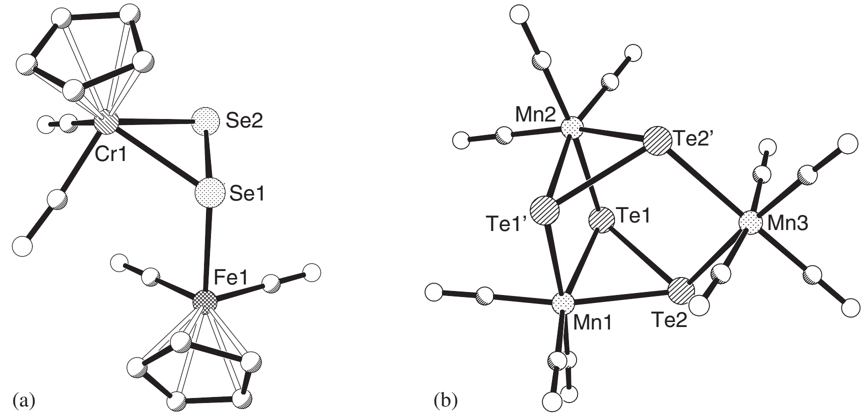


Figure 22 *(a)* $\mu\text{-}1\kappa^2Se^1,Se^2{:}2\kappa Se^1$ *bridging of the* Se_2^{2-} *ligand in [{(*η^5*-*C_5H_5*)Fe (CO)*$_2$*}(*μ*-*Se_2*){Cr(CO)*$_2$*(*η^5*-*C_5H_5*)}]*[118] *and (b)* $\mu_3\text{-}1\kappa^2Te^1,Te^2{:}2\kappa Te^1{:}3\kappa Te^2$ *bridging of two* Te_2^{2-} *ligands in [*$PhCH_2N(CH_3)_3$*][{(CO)*$_3$*Mn(*μ_3*-*Te_2*)}*$_2$ *Mn(CO)*$_4$*]*[119]

$[(CO)_{15}Mn_4(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)]$[120] and $[(CO)_{14}Mn_4(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)(SCH_2CH_2)]$,[121] in which, however, the second S_2^{2-} dumbbell extends its bridging to μ_4 by coordinating a fourth Mn atom of respectively an $[Mn(CO)_5]$ or an $[Mn(CO)_4(SCH_2CH_2)]$ fragment.

As previously mentioned, polychalcogenide anions E_n^{2-} exhibit a strong tendency to participate in chelate rings involving κ^2E^1,E^n coordination of the formally negatively charged terminal chalcogen atoms. Although cases are known in which an internal E atom coordinates a metal atom, this is comparatively rare. Examples of κ^2E^1,E^n chelation are illustrated in Figure 20a for S_4^{2-} and S_6^{2-} chains in the $[In_2S_{27}]^{4-}$ anion[110] and in Figure 20b for the Te_4^{2-} chain[113] in $[Ag_2Te_{12}]^{4-}$. On taking side-on coordination into account, chelate rings with 3–8 atoms are known for polysulfide and polyselenide ligands E_n^{2-} ($n = 2$–7) but only 3–5 atoms for Te_n^{2-} ($n = 2$–4). For instance, rhenium(V) atoms are chelated by S_3^{2-} chains in the organometallic half-sandwich complex $[(\eta^5\text{-}EtMe_4C_5)ReCl_2(S_3)]$,[122] tellurium(II) atoms by S_5^{2-} and S_7^{2-} chains in $[NEt_4]_2[Te(S_5)(S_7)]$.[77] The analogous Re(V) compound $[(\eta^5\text{-}Me_5C_5)ReCl_2(Se_3)]$[123] contains Se_3^{2-} ligands, the octaselenidoarsenate(III) anions of $[NEt_4][As(Se)(Se_7)]$[124] chelating Se_7^{2-} anions. κ^2Te^1,Te^3 coordination of Te_3^{2-} chains has already been discussed for the $[Te(Te_3)(Te_4)]^{2-}$ anion in $[K(15\text{-crown-}5)_2]_2Te_8$[56] and for the $[Au(Te_2)_2(Te_3)]^{3-}$ anion in $[NEt_4]_3[AuTe_7]$.[95]

When a secondary Te···Te bond of length 312.0(2) between one of the terminal Te_2^{2-} ligands and the chelating Te_3^{2-} unit is taken into consideration, the latter anion can also be formulated as $[Au(Te_2)(Te_5)]^{3-}$ with a κ^3Te^1,Te^3,Te^5 *bis*-chelating pentatelluride Te_5^{2-} chain. The structure of this remarkable $[AuTe_7]^{3-}$ anion contrasts with those[95,125] of $[CuTe_7]^{3-}$, $[AgTe_7]^{3-}$ and $[HgTe_7]^{2-}$, which contain a central metal atom coordinated in a trigonal planar fashion (Figure 23a) by a κ^3Te^1,Te^4,Te^7 tridentate Te_7^{2-} ligand. Whereas the essentially linear central Te3–Te4–Te5 interaction is strongly asymmetric for M = Cu [322.5(1), 289.4(1) pm] and M = Ag [323.0(2), 286.6(2) pm] in $[PPh_4]_2[NEt_4][MTe_7]$,[95,125] closely similar Te3–Te4 and Te4–Te5 distances are observed for $[HgTe_7]^{3-}$ with respectively $[PPh_4]^+$ [305.0(2), 299.7(2) pm] and $[NEt_4]^+$ [303.9(2), 300.8(2) pm] as counter cations.[125] These findings and

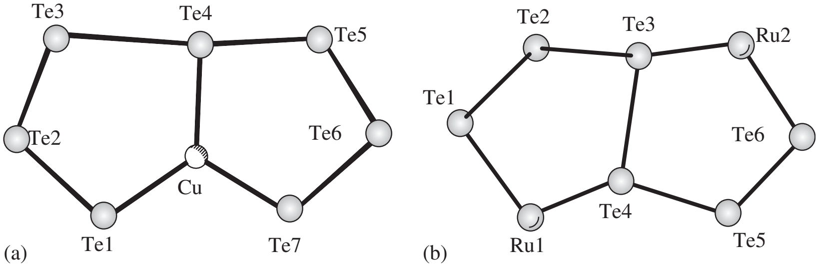


Figure 23 *(a) Molecular structure of the* $[CuTe_7]^{3-}$ *anion in* $[PPh_4]_2[NEt_4][CuTe_7]$[125]; *(b)* $\mu\text{-}1\kappa^2Te^1,Te^4:2\kappa^2Te^3,Te^6$ *bridging by the* Te_6^{2-} *ligand in* $[\{CpRu(PPh_3)\}_2(\mu\text{-}Te_6)]$[128]. *The Cp and* PPh_3 *ligands have been omitted for clarity*

ab initio calculations for $[CuTe_7]^{3-}$ indicate that such telluridometalate anions can be regarded as resulting from secondary $5p^2 \rightarrow 5\sigma^*$ interactions between Te5 of a terminally coordinated Te_3^{2-} chain and Te4 of a chelating Te_4^{2-} ligand.

Through relatively uncommon, examples are also known in which an internal chalcogen of a chelate ring coordinates to a second metal atom, as for instance Se2 of the first μ-1κ^2Se^1,Se^4:2κSe^2 bridging Se_4^{2-} ligand in the complex $[\{(\eta^5\text{-}C_5H_5)Ir\}_2(Se_4)_2]$.[126] The second chelating tetraselenide anion bridges in a μ-1κ^2Se^1,Se^4:2κSe^1 manner through its terminal Se1 atom. Both terminal sulfur atoms S1 and S6 exhibit this type of μ-1κE:2κE bridging for the S_6^{2-} ligand in $[(Ph_3Te)_2(\mu\text{-}S_6)] \cdot CHCl_3$,[127] which chelates both Te atoms. A unique example of μ-1κ^2Te^1,Te^4:2κ^2Te^3,Te^6 bridging by a Te_6^{2-} ligand has recently been reported for the bicyclic complex $[\{CpRu(PPh_3)\}_2(\mu\text{-}Te_6)]$,[128] where ring fusion occurs along the central Te3–Te4 bond (Figure 23b). The hexasulfide dianion exhibits an analogous binding mode in the related compounds $[(CpRu\{P(OMe)_3\})_2(\mu\text{-}S_6)]$[129] and $[\{MeCpRu(PPh_3)\}_2(\mu\text{-}S_6)]$.[130] Combined chelating and bridging modes have also been reported for polychalcogenide anions in solid-state compounds, for instance the μ_3-1κ^2Te^1,Te^4:2κTe^1:3κTe^3 coordination pattern in $[NMe_4][MTe_4]$ (M = Cu, Ag).[131] Three Au(I) atoms are connected in respectively μ_3-1κ^2Se^1,Se^4:2κSe^1:3κSe^4 and μ_3-1κ^2Se^1,Se^4:2κSe^1:κSe^5 fashion by Se_4^{2-} in $[NPr_4]_2[Ag_4Se_{12}]$ and Se_5^{2-} in $[Me_4N][AgSe_5]$.[10]

9.2.3.4 Polymeric Ligands

As discussed in detail in Section 2.4, the pronounced tendency of tellurium to participate in both hypervalent bonding and secondary $5p^2 \rightarrow 5\sigma^*$ interactions can lead to the construction of polymeric telluride networks.

The phenomenon of charge density waves was already discussed for $K_{0.33}Ba_{0.67}AgTe_2$,[74] whose $^2_\infty[(Te_2)^{4/3-}]$ square nets (Figure 13) are responsible for the material existing in a CDW state at room temperature. In this case, the telluride layers are separated from Ag(I) atoms by K^+ and Ba^{2+} cations, but CDWs are also possible in solid state phases in which the chalcogen atom participates in transition metal coordination. For instance, the metallic conductor $ZrTe_3$, whose structure[132] is depicted in Figure 24a, undergoes a transition to a CDW state at 63 K and displays superconductivity below 2 K.[133] The zirconium atoms are formally coordinated in a two-fold capped trigonal prismatic fashion with Zr–Te distances in the range 294.1–315.5 pm by Te^{2-} ions and Te_2^{2-} dumbbells with a Te2–Te3 distance (d_1) of 279.4(1) pm. However, these Te_2^{2-} units interact with one another through Te3 . . . Te2 secondary bonds of length 310.5(1) pm to generate infinite Te chains in the [100] direction, that are responsible for the CDWs.

Two extreme formulations can be considered for such metal chalcogenides ME_3 with linear E chains: (i) $[M^{4+}E^{2-}(E_2^{2-})]$ implying E_2^{2-} dumbbells as structural fragments ($d_2 >> d_1$) and semiconducting behaviour or (ii) $\{M^{4+}E^{2-}\,{}^1_\infty[E^-]_2\}$, implying chains of equidistant E^- ions ($d_1 = d_2$) and metallic properties. The former description clearly applies to $ZrSe_3$[134] (d_1 = 234.4 pm, d_2=306.8 pm) and UTe_3[135] (d_1 = 275.1 pm, d_2 = 335.0 pm) and both

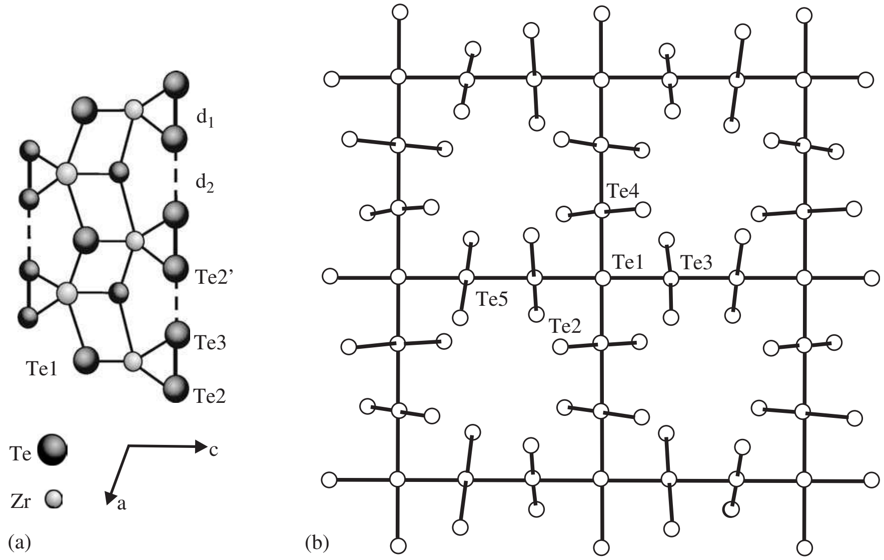


Figure 24 *(a) Projection of the* $ZrTe_3$ *structure*[132] *perpendicular to the [010] axis; (b) the* ${}^{2}_{\infty}[Te_5^{4-}]$ *nets of* $Rb_4Sn_4Te_{17}$[71] *for which the terminal Te atoms of bridging ditetrahedral* Sn_2Te_6 *units are also shown*

are semiconductors. UTe_2 contains analogous infinite Te chains with closely similar values of d_1 (305.7 pm) and d_2 (307.6 pm) and is metallic.[136] Despite distinct chain alternation, $ZrTe_3$ ($d_1 = 279.4$ pm, $d_2 = 310.5$ pm) also displays metallic conductivity and its antibonding p_x bands (σ^*) intersect the Fermi level E_F (Figure 25c). In comparison to UTe_3 (Figure 25b), the gap between d_1 and d_2 is some 25 pm shorter in $ZrTe_3$ and this leads to more dispersive bands and a smaller gap between the p_x σ and σ^* bands in the chain direction. In contrast to $ZrTe_3$, linear chains of equidistant Nb^{4+} ions within the trigonal rods in the [010] direction are considered to be primarily responsible for CDW formation at 145 and 29 K in the metallic compound $NbSe_3$, whose structure is similar.[137]

Band structure calculations have suggested that the defective square-planar ${}^{2}_{\infty}[Te_5^{4-}]$ nets (Figure 24b) of $Rb_4Sn_4Te_{17}$[71] may also display the properties of a low-dimensional metal. This polytelluridostannate(IV) can be isolated by methanolothermal reaction of Rb_2CO_3 with elemental Sn and Te and exhibits a unique 3D network in which parallel ${}^{2}_{\infty}[Te_5^{4-}]$ layers are linked through ditetrahedral $Sn_2Te_6^{4-}$ spacer ligands.

9.2.4 Note Added in Proof

Cs_3Se_{22} has recently been prepared under methanolothermal conditions[138] and is isostructural to Cs_3Te_{22}[19]. In contrast to the ${}^{2}_{\infty}[Te_6^{3-}]$ sheets (Figure 10b) of the polytelluride, the anionic sheets in Cs_3Se_{22} are best described as ${}^{2}_{\infty}[(Se_3^{\cdot-})(Se_3^{2-})]$, in which disordered pairs of bent $Se_3^{\cdot-}$ radical anions and Se_3^{2-} anions are linked through secondary interactions.

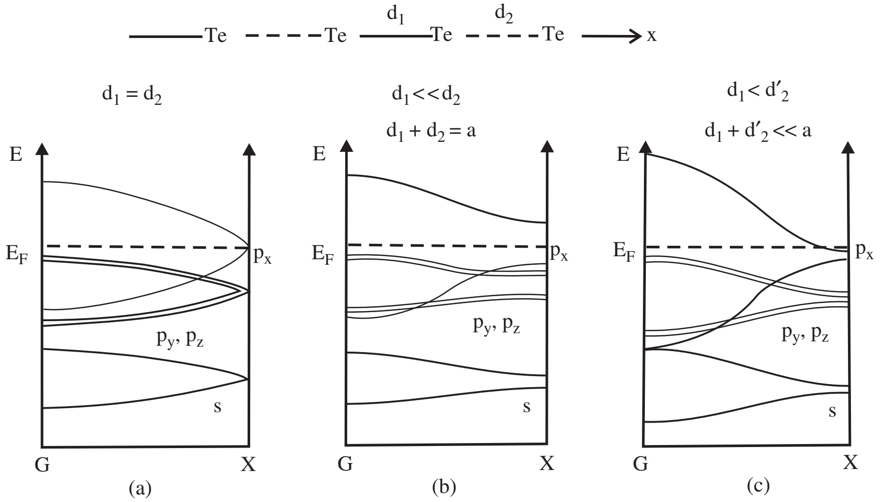


Figure 25 *Schematic dispersion relationships of the bands of an infinite linear Te chain: (a) for an equidistant chain, (b) for an alternating chain with the repeating distance a and (c) for an alternating chain with a much smaller repeating distance a′. The dotted line at E_F represents the Fermi level*

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CHAPTER 10.1

Synthesis and Stereochemistry of Optically Active Chalcogen Compounds

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10.1.1 Introduction

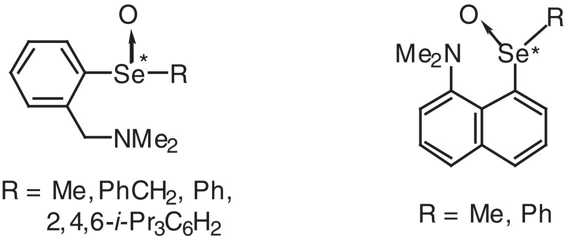
A number of optically active organosulfur compounds, such as sulfoxides, sulfonium salts, sulfonium ylides, sulfilimines, sulfoximines, and sulfuranes, have been synthesized, and their stereochemistry, properties, and reactivities have been widely studied with results included in numerous books.[1] Moreover, numerous papers dealing with asymmetric synthesis utilizing these optically active organosulfur compounds have also been published. On the other hand, the number of optically active selenium or tellurium compounds isolated so far is limited, although chiral organoselenium and tellurium compounds are felt to be important key intermediates for asymmetric syntheses.[2–4] Studies on the isolation and stereochemistry of optically active selenium and tellurium compounds have been addressed in some reviews.[3,5] Optically active selenium and tellurium compounds, such as telluroxides, chalcogenic acids, and seleninate esters, were isolated for the first time during the last decade.

In this chapter, recent development on the synthesis and stereochemistry of optically active chalcogen compounds over the last 10 years will be described, focusing mainly on chiral selenium and tellurium compounds.

10.1.2 Chalcogen-oxides

Optically active sulfoxides are well known and several synthetic methods have been developed, with numerous papers published on asymmetric synthesis utilizing optically active sulfoxides as chiral sources.[1,6]

Optically active selenoxides are known to be unstable toward racemization. An optically active selenoxide having a steroidal frame was obtained for the first time by Jones and co-workers in 1970.[7] Enantiomeric selenoxides were prepared by Davis *et al.* in 1983,[8] and an enantiomerically pure selenoxide was isolated for the first time by us in 1989.[9] Many optically active selenoxides, which are kinetically stabilized by bulky substituents, were synthesized over the last two decades, and their stereochemistry and stability toward racemization were studied.[3,5,10] Recently, some optically active selenoxides, which were thermodynamically stabilized by the intramolecular coordination of a Lewis base to the selenium atom, have been isolated. Optically active selenoxides **1** and **2** were obtained by optical resolution on chiral columns, and their stereochemistry and stability toward racemization under various conditions were clarified (Scheme 1).[11,12]



R = Me, PhCH$_2$, Ph, 2,4,6-*i*-Pr$_3$C$_6$H$_2$

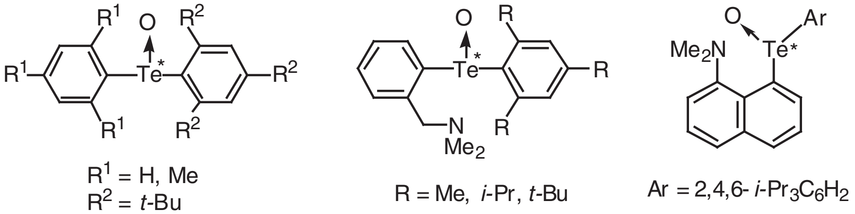
1

R = Me, Ph

2

Scheme 1

On the other hand, optically active telluroxides have not been isolated until recently, although it has been surmised that they are key intermediates in asymmetric synthesis.[3,4] In 1997, optically active telluroxides **3**, stabilized by bulky substituents toward racemization, were isolated for the first time by liquid chromatography on optically active columns.[13,14] The stereochemistry was determined by comparing their chiroptical properties with those of chiral selenoxides with known absolute configurations. The stability of the chiral telluroxides toward racemization was found to be lower than that of the corresponding selenoxides, and the racemization mechanism that involved formation of the achiral hydrate by reaction of water was also clarified. Telluroxides **4** and **5**, which were thermodynamically stabilized by nitrogen–tellurium interactions, were also optically resolved and their absolute configurations and stability were studied (Scheme 2).[12,14]



R^1 = H, Me
R^2 = *t*-Bu
3

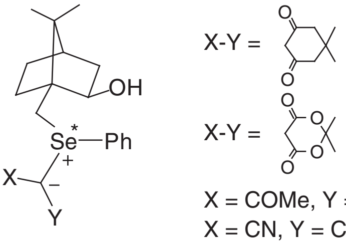
R = Me, *i*-Pr, *t*-Bu
4

Ar = 2,4,6-*i*-Pr$_3$C$_6$H$_2$
5

Scheme 2

10.1.3 Chalcogen-onium Ylides

Chiral sulfonium ylides have been known for some 30 years, and their stereochemistry and properties have been studied.[15] Optically active selenonium ylides were obtained by reacting selenoxides with 1,3-cyclohexanedione under asymmetric conditions by Sakaki and Oae in 1976 for the first time,[16] and also optically resolved by fractional recrystallization of the diastereomeric mixtures in the early 1990s.[17] In 1995, optically active selenonium ylides **6** were obtained in over 99% de by nucleophilic substitution of optically active chloroselenurane or selenoxide with active methylene compounds with retention of configuration.[18] The absolute configurations were determined by X-ray analysis of one isomer of the ylides (Scheme 3).

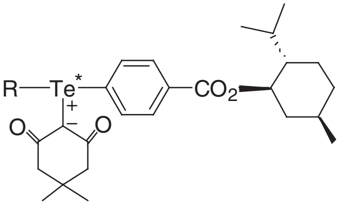


X = COMe, Y = CO_2Me
X = CN, Y = CO_2Et
X = Y = COMe

6

Scheme 3

Optically active telluronium ylides were not obtained for a long time. Optically active diastereomeric telluronium ylides **7** were obtained for the first time in 1995 by fractional recrystallization of the diastereomeric mixture.[19] The absolute configurations of the chiral telluronium ylides were determined by comparing their specific rotations and circular dichroism spectra with those of the corresponding selenonium ylide with known absolute configuration. The telluronium ylides were found to be much more stable toward racemization than the sulfonium and selenonium ylides (Scheme 4).



R = Me, 2,4,6-i-$Pr_3C_6H_2$

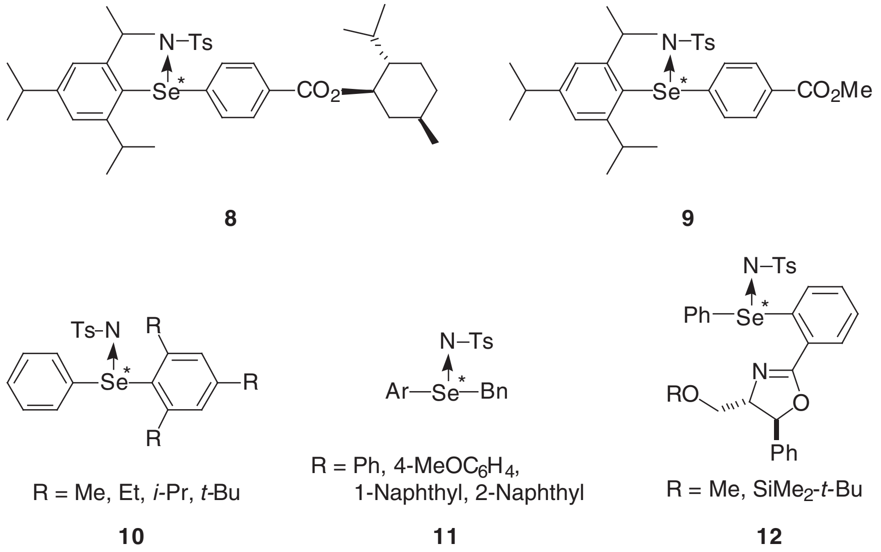
7

Scheme 4

The increasing stability toward racemization was supported by theoretical calculations carried out on the dimethyl chalcogen-onium ylides.[20] In fact, the activation energies for the pyramidal inversion of chalcogen-onium ylides, which is one of the possible pathways for racemization, were estimated to be 27, 33, and 42 kcal mol^{-1} for S, Se, and Te, respectively, in agreement with experimental results.

10.1.4 Chalcogen-onium Imides

Some optically active sulfonium imides have been synthesized.[21] Optically active selenonium imides were reported for the first time by Krasnov and co-workers in 1981 although their optical purities were unknown.[22] Diastereomerically pure selenonium imide **8** was obtained for the first time in 1994 by fractional recrystallization of the diastereomeric mixture, and the absolute configuration was assigned based on the circular dichroism spectrum.[23] Enantiomeric selenonium imide **9** was also obtained in 80% optical purity by stereoselective transformation of the corresponding optically active selenoxide with retention of stereochemistry, and an hypothesis was put forward as to the mechanism of the transformation.[24] Enantiomerically pure selenonium imides **10** were isolated by optical resolution using liquid chromatography on an optically active column in 1999.[25] The absolute configurations were determined by X-ray crystallographic analysis of one isomer, and the activation energies for the racemization of the optically active selenonium imides were found experimentally to be greater than those for sulfonium imides. In 2000, optically active selenonium imides **11** and **12** were synthesized by Uemura *et al.* by enantioselective imidation of prochiral selenides using optically active *bis*(oxazoline) or diastereoselective imidation of corresponding selenides in up to 36% ee and 76% de, respectively.[26] Enantioselective imidation was also utilized in the asymmetric synthesis of chiral allylic *N*-tosylamides (Scheme 5).



8

9

R = Me, Et, *i*-Pr, *t*-Bu

10

R = Ph, 4-$MeOC_6H_4$,
1-Naphthyl, 2-Naphthyl

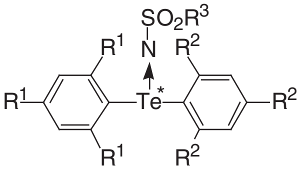
11

R = Me, $SiMe_2$-*t*-Bu

12

Scheme 5

On the other hand, telluronium imides **13** were isolated for the first time in 2002 by optical resolution of their racemic samples on an optically active column by medium-pressure column chromatography.[27] The relationship between the absolute configurations and the chiroptical properties was clarified on the basis of their specific rotations and circular dichroism spectra. The racemization mechanism of the optically active telluronium imides, which involved the formation of corresponding telluroxides by hydrolysis of the telluronium imides, was proposed (Scheme 6).



R^1 = H, Me, Et
R^2 = *i*-Pr, *t*-Bu
R^3 = *p*-tolyl, CF_3

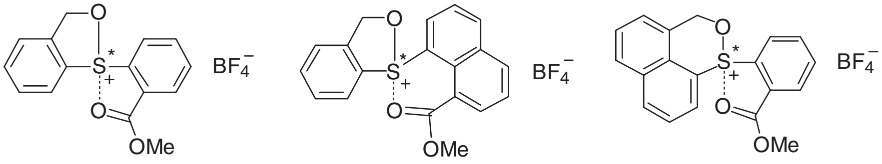
13

Scheme 6

The pyramidal inversion energies of chalcogen-onium imides were estimated by MO calculations.[28] The values for model compounds, dimethyl chalcogen-onium imides, were evaluated to be 34, 44, and 54 kcal mol^{-1} for S, Se, and Te, respectively, indicating that among the chalcogen-onium imides, telluronium imides are those that are most stable toward pyramidal inversion.

10.1.5 Chalcogen-onium Salts

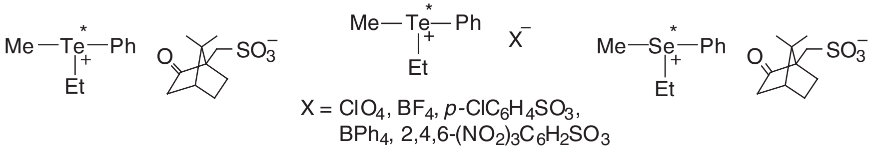
Optically active sulfonium and selenonium salts are well known and the stereochemistry of the isomers has been studied.[1–3] Optically active cyclic diaryl(alkoxy)-sulfonium salts **14**, **15**, and **16**, stabilized by intramolecular sulfur–oxygen interaction, were synthesized in 2000 by reacting optically active spirosulfuranes with trimethyloxonium tetrafluoroborate.[29] The absolute configurations were assigned on the basis of the reaction mechanism. The sulfonium salts were hydrolyzed in $KHCO_3$aq. to yield optically active sulfoxides in over 86% ee (Scheme 7).



14 **15** **16**

Scheme 7

Although two papers addressing the synthesis of telluronium salts were published several decades ago,[30] their optical purities and absolute configurations remained unknown. Only recently, (*R*)- and (*S*)-diastereomerically pure ethylmethylphenyltelluronium salts **17** have been isolated by fractional recrystallization of the diastereomeric mixture,[31] and their absolute configurations been determined by X-ray crystallographic analysis. Enantiomerically pure telluronium salts **18** have been prepared by anion-exchange reaction of the diastereomerically pure telluronium salts without loss of optical purities. The optically active telluronium salts have been found to show peculiar optical properties in terms of specific rotations and circular dichroism spectra in solution compared with those of the corresponding sulfonium and selenonium salts. In the first two papers reporting chiral telluronium salts,[30] it was mentioned that mutarotation was observed in solutions; however, telluronium salts **17** and **18** are stable toward racemization even in solutions. The stereochemistry of diastereomerically pure ethylmethylphenylselenonium salt **19** has also been clarified by X-ray diffraction analysis (Scheme 8).[32]



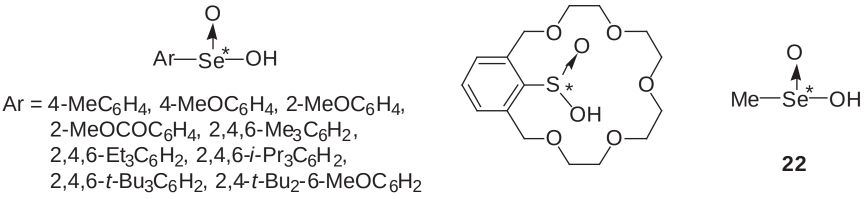
17 **18** **19**

Scheme 8

10.1.6 Chalcogenic Acids

Chalcogenic acids, R–E(O)OH, are also tricoordinate and considered to have pyramidal structures. However, no studies on their optical activity have been reported since facile racemization of chalcogenic acids may occur *via* achiral chalcogenate anions, which are formed by the extrusion of a proton and/or by an intra- or intermolecular proton transfer reaction.

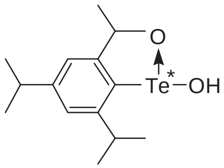
In 2001, optically active areneseleninic acids **20** were obtained for the first time as solution by optical resolution on a chiral column using liquid chromatography.[33] Bulky substituents and electron-donating groups on the aromatic ring were effective in retarding racemization. The absolute configurations of the optically active seleninic acids were assigned by comparing their circular dichroism spectra with that of optically active sulfinic acid **21**, the absolute configuration of which was determined by X-ray crystallographic analysis. Sulfinic acid **21** represents the first example of a chiral sulfinic acid showing a relationship between absolute configuration and optical properties.[34] Optically active methaneseleninic acid **22** was isolated as stable crystals for the first time by chiral crystallization.[35] The relationship between the absolute configuration and the circular dichroism spectra of the enantiomers was determined by X-ray crystallographic analysis. The optically active methaneseleninic acid was stable toward racemization in the solid state, although it racemized immediately in solution. Each enantiomer of methaneseleninic acid was also obtained in bulk by chiral crystallization in the presence of a seed crystal or from chiral solvents.[36] The absolute configuration of optically active methanesulfinic acid was assigned for the first time by comparing its circular dichroism spectrum in the solid state with that of methaneseleninic acid (Scheme 9).[36]



20 **21** **22**

Scheme 9

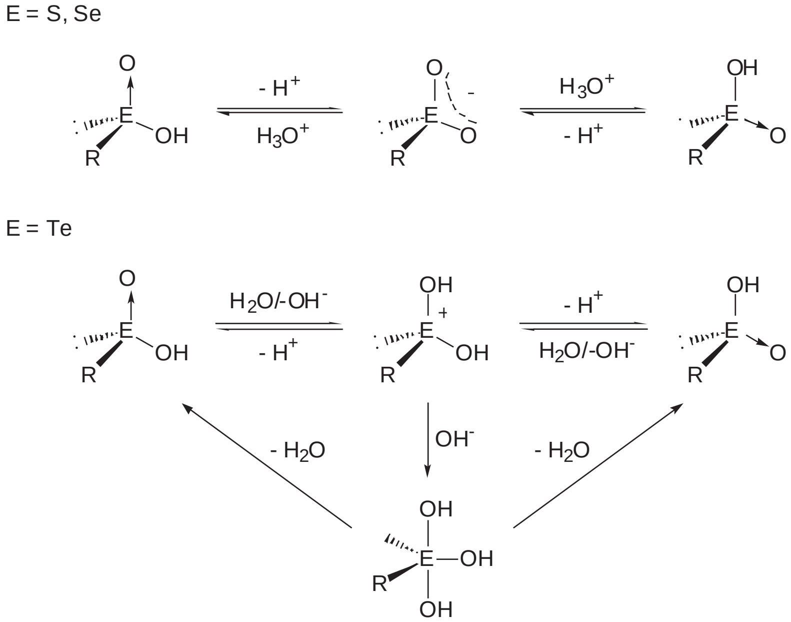
Optically active arenetellurinic acid **23** was obtained for the first time by chromatographic resolution of the racemic sample on a chiral column in 2004.[37] It is stable toward racemization in solution, whereas the corresponding seleninic acids racemize in solution under similar conditions. Its absolute configuration was assigned by comparing the circular dichroism spectra with that of an optically active seleninic acid (Scheme 10).



23

Scheme 10

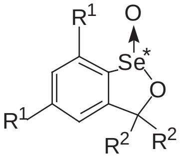
Kinetic studies on racemization, oxygen exchange reaction using $H_2{}^{18}O$, and theoretical studies clarified the mechanism for racemization of optically active chalcogenic acids.[34,37] The mechanism of racemization of tellurinic acids is different from that of the corresponding seleninic acids. In fact, the mechanism for racemization of optically active tellurinic acids was found to involve an achiral tellurane that is formed by the addition of water to the tellurinic acid, whereas the racemization of the optically active sulfinic and seleninic acids involves a sulfinate or selenate anion that is formed by the extrusion of a proton (Scheme 11).



Scheme 11

10.1.7 Chalcogenate Esters

Chiral sulfinate esters, such as *l*-menthyl *p*-toluenesulfinate, are well known and utilized as precursors of chiral sulfoxides.[38–40] However, no studies on the corresponding chiral seleninate esters were reported until 2005. The reason for this lack is mainly due to the fact that acyclic seleninate esters are unstable toward hydrolysis. Optically active cyclic seleninate esters **24** were obtained for the first time by Nakashima *et al.* in 2005 by chromatographic resolution on an optically active column.[41] Their absolute configurations were determined by comparing their chiroptical properties with those of an analogous sulfinate ester, the absolute configuration of which was determined by X-ray analysis. The optically active seleninate esters were found to racemize in solution. Kinetic studies of racemization, oxygen exchange reaction with $H_2{}^{18}O$, and theoretical studies have clarified that the racemization of the optically active seleninate esters in solution proceeds *via* an achiral hypervalent selenurane intermediate (hydrate), which is formed by the addition of water to the selenium atom. The optically active areneseleninate esters and arenesulfinate esters, which have bulky substituents at the *ortho* position of the benzene ring, react with Grignard reagents with retention of stereochemistry to give optically active selenoxides and sulfoxides, respectively (Scheme 12).



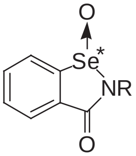
R^1 = H, *t*-Bu
R^2 = H, Bu

24

Scheme 12

10.1.8 Chalcogeninamides

Many reports on the isolation and properties of optically active sulfinamides have been published.[38] However, there have been no reports on the chiral selenium analogues, probably because of the instability of the seleninamides toward hydrolysis. Very recently, optically active seleninamides **25** were obtained for the first time by chromatographic resolution on an optically active column.[42] Their absolute configurations were determined by comparing their chiroptical properties with those of analogous sulfinamides, the configuration of one of which is known whereas that of the other was determined based on the reaction with Grignard reagent to form chiral sulfoxide with inversion of stereochemistry. The optically active seleninamides were found to racemize in solution. Kinetic studies of racemization and theoretical studies have clarified that also in this case, racemization in solution proceeds *via* an achiral hypervalent hydrate formed by reaction with water (Scheme 13).



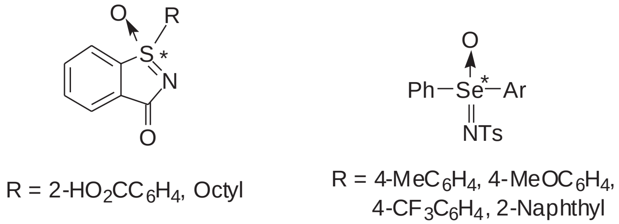
R = *t*-Bu, 1-Ad, 2,4,6-$Me_3C_6H_2$,
2,4,6-*i*-$Pr_3C_6H_2$

25

Scheme 13

10.1.9 Chalcogen-oximines

Sulfoximines are an example of a tetracoordinated chiral compound, and their optical isomers have been isolated. Their stereochemistry was also studied approximately 30 years ago.[43] Endocyclic sulfoximines are an example of chiral heteroaromatics. Endocyclic sulfoximines **26** were optically resolved on a chiral column for the first time by Allenmark and co-workers in 1995.[44] The stereoisomers were obtained by amination and subsequent cyclodehydration of optically active *o*-carboxyphenyl sulfoxide with hydrazoic acid or O-(mesitylenesulfonyl) hydroxylamine (Scheme 14).



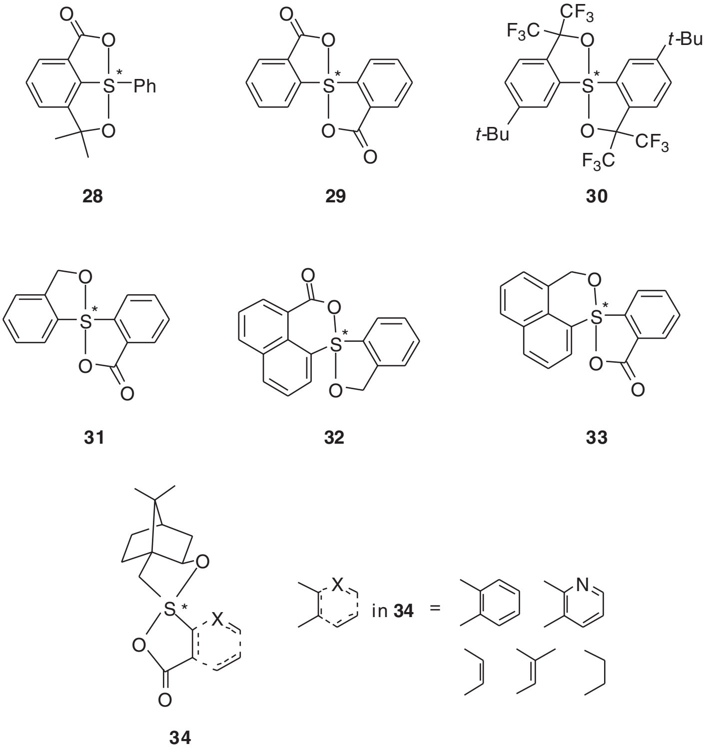
26 **27**

Scheme 14

The corresponding optically active selenium compounds, selenoximines, have not been prepared. Recently, optically active selenoximines **27** were isolated for the first time by optical resolution using chromatography on a chiral column.[45] The absolute configurations were determined by comparing their specific rotations and circular dichroism spectra with those of the corresponding sulfur analogues with known absolute configurations. No racemization of the chiral selenoximines took place under several neutral, acidic, and basic conditions, and only decomposition was observed under aqueous acidic and basic conditions to give the corresponding selenone and *p*-toluenesulfonamide.

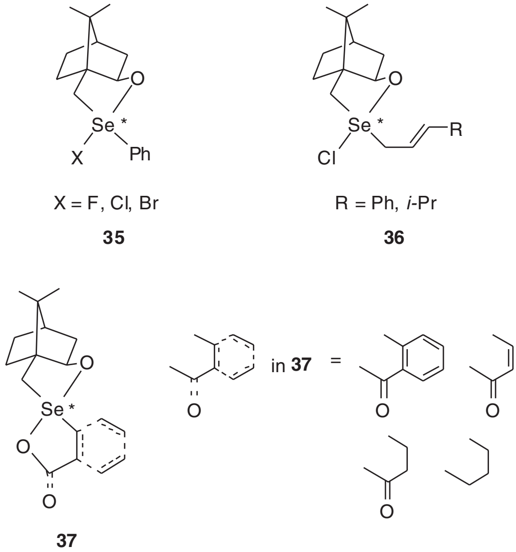
10.1.10 Chalcogenuranes

Many optically active hypervalent chalcogen compounds, particularly sulfur compounds, have been synthesized and proposed as important key intermediates in various reactions of the chalcogen compounds.[46] Since the synthesis of spirosulfurane by Kapovits and Kálmán,[47] many optically active spirosulfuranes were isolated in the last decade. Spirosulfurane **28** was separated into enantiomers by kinetic resolution using a chiral host molecule and found to be optically stable by Drabowicz and Martin.[48] Spirosulfurane **29** was separated into enantiomers by chromatographic method by Allenmark and Claeson, and characterized by chiroptical methods.[49] Optically active compound **30** was obtained by dehydration of prochiral sulfoxide diol under asymmetric conditions.[50] The dehydration of optically active diaryl sulfoxides also yielded optically active spirosulfuranes **31**, **32**, and **33**.[51] The molecular structures including absolute configurations were determined by the X-ray diffraction method. Optically active spirosulfuranes **34** were obtained as single diastereomers from chiral sulfides by Koizumi *et al.*, and were found to have a slightly distorted TBP structure by X-ray analysis (Scheme 15).[52]



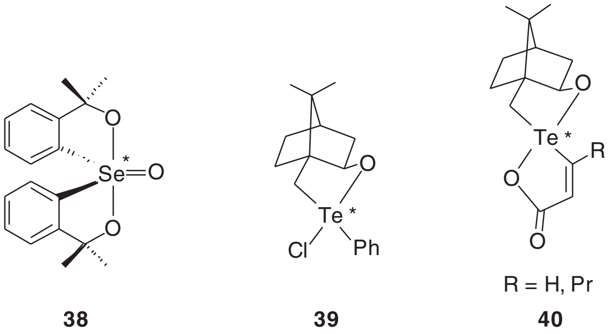
Scheme 15

In the case of selenuranes, optically pure haloselenuranes **35** were synthesized by treatment of optically active selenoxide with HX.[53] Chloroselenuranes **36** were also obtained by treatment of the corresponding allylic selenides with *tert*-butyl hypochlorite.[54] Optically active spiroselenurane was obtained by Lindgren in 1972, although the stereochemistry and the enantiopurity were not clear.[55] Optically pure spiroselenuranes **37** with 2-*exo*-hydroxy-10-bornyl group as the chiral ligand were obtained by treatment of selenides with *tert*-butylhypochlorite, followed by the addition of triethylamine (Scheme 16).[56]



Scheme 16

Selenurane oxides are also one of the hypervalent selenium compounds. Recently, the enantiomers of chiral selenurane oxide **38** were isolated for the first time by enantioselective liquid chromatography of the racemate or by spontaneous resolution occurring during slow evaporation of its acetonitrile solution or slow crystallization from the same solvent.[57] The absolute configurations of the enantiomers were determined by X-ray crystallographic analysis (Scheme 17).



Scheme 17

In the case of telluranes, treatment of telluride with *tert*-butylhypochlorite yielded optically active chlorotellurane **39**.[58] Optically active fluoro-, bromo-, and iodo-telluranes were obtained from the chlorotellurane by treatment with AgF, NaBr, and NaI, respectively. Optically active spirotelluranes **40** were obtained by Koizumi *et al.*, and the stereochemistry was determined by X-ray crystallographic analysis.[56,58]

10.1.11 Dichalcogenides

Acyclic dichalcogenides are well known to show skewed structures in the crystalline state or in the gas phase,[59] except for dichalcogenides with congested substituents, and many theoretical studies have indicated that such skewed geometries are global minima. Therefore, dichalcogenides are thought to exist in chiral *P*- and *M*-helical forms. However, the rotation barriers of chalcogen–chalcogen bonds for racemization are not sufficiently high to enable isolation of the optical isomers. The disulfide linked to the 2- and 2′-positions of a chiral 1,1′-binaphthyl group is considered to be a chiral disulfide.[60] However, this compound is configurationally restricted by atropisomerism of the binaphthyl group. Optically active simple dichalcogenides **41**, diphenyl disulfide, diphenyl diselenide, and diphenyl ditelluride, were isolated in bulk for the first time by chiral crystallization in 2001.[61] The relationship between the absolute configurations and the chiroptical properties in the solid state was clarified by X-ray crystallography of one isomer of the disulfide. Furthermore, the stereochemistry of chiral crystallization can be controlled by using an optically active crystal as seed crystal.

10.1.12 Conclusions

Recent studies on the synthesis and stereochemistry of chalcogen compounds focused on higher periodic chalcogen compounds, such as selenium and tellurium compounds. In the chemistry of chiral sulfur compounds, asymmetric synthesis utilizing the chiral compounds is of interest. Many optically active selenium and tellurium compounds were obtained, and their stereochemistry and properties were clarified in the last decade. Various applications of optically active chalcogen compounds to asymmetric synthesis have also been developed. In the next decade, further development leading to the application of chiral higher periodic chalcogen compounds is expected.

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CHAPTER 10.2

1,1-Dithiolato Ligands and Related Selenium and Tellurium Compounds

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10.2.1 Introduction

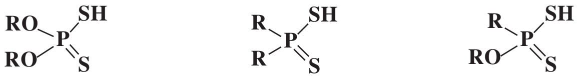
1,1-Dithiolato moieties are versatile ligands, which enjoy continuous interest. There is a remarkable diversity of compounds in which two sulfur atoms are attached to the same non-metal element (phosphorus, arsenic, carbon, silicon) in mononegative anions.[1] More recently some dinegative silane-1,1-dithiolato ligands have been described, but few if any, successful attempts to prepare similar boron, germanium, or other element-dithiolato ligands have been made. Similar selenium-containing ligands are also known, but the tellurium analogues are very scarce.

The 1,1-dithiolato ligands and their complexes have been reviewed rather extensively in earlier publications. Reviews on various aspects of dithiophosphato,[2] dithiophosphinato,[3] xanthato,[4] dithiocarboxylato,[5] and dithiocarbamato[6] ligands are available. In this section, only the more recent literature (basically after 1990) will be considered because of space limitations.

10.2.2 Phosphor-1,1-dithiolates

Phosphor-1,1-dithiolates comprise ligands derived from dithiophosphoric acid *O*,*O*-dithioesters (further called simply dithiophosphates), dithiophosphinic acids (dithiophosphinates), and the hybrid dithiophosphonic acid *O*-monoesters (dithiophosphonates) (Scheme 1).

As ligands in metal complexes, the anions derived from these acids display a broad variety of coordination patterns (Scheme 2). Usually, the ligands are described as monodentate, bidentate chelating or bridging, and polydentate. We use here a description based upon the number of connections between the

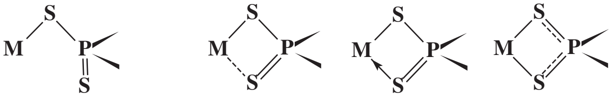


dithiophophoric (phosphorodithioic) acid O,O-diesters

dithiophosphinic (phosphinodithioic) acids

dithiophosphonic (phosphonodithioic) acid O-esters

Scheme 1



monodentate monometallic monoconnective

bidentate unsymmetric (anisobidentate)

bidentate symmetric (isobidentate)

monometallic biconnective

Scheme 2

donor atoms of the ligands and the coordinated metal atom. The "connections" can be normal covalent bonds, dative coordinate bonds, or even weaker "secondary bonds". The latter are interactions leading to interatomic distances longer than covalent bond but shorter than Van der Waals interactions.[7] Dative bonds (Lewis acid–base interactions) are characterized by interatomic distance slightly longer than covalent bonds between the same atoms.[8] Intermolecular donor–acceptor or secondary bonds may lead to supramolecular self-assembly.[9]

Monodentate (monometallic monoconnective) phosphor-1,1-dithiolato ligands are rare. Bidentate (monometallic biconnective) form chelate rings and three sub-types can be distinguished according to the degree of asymmetry (Scheme 2). The most asymmetric type (anisobidentate) occurs when a covalent bond is associated with a secondary bond; this takes place mostly in main-group metal complexes. The second type is rare and is the result of the association between a covalent and a dative coordinate bond. The symmetric bidentate bonding (isobidentate) is found mainly in transition metal complexes.

Numerous examples of isobidentate coordination can be cited. A selection of recent ones is presented. These include a chromium complex, $Cr[S_2P(OEt)_2]_3$,[10] mononuclear $Mo[S_2P(OMe)_2]_3$,[11] and dinuclear $Mo_2O_3\{S_2P(OR)_2\}_4$ ($R = Pr^i$, Ph) and $Mo_2O_2S_2(S_2P(OEt)_2\}_2$ molybdenum dithiophosphato complexes,[12] and a technetium complex, $TcCl_2[S_2P(OMe)_2](PMe_2Ph)_2$.[13] Isobidentate chelating ligands are also observed in anionic $[CoCl\{S_2P(OMe)_2\}_2]^-$,[14] and numerous Group 10 metal dithiophosphato derivatives. Nickel(II), palladium(II) and platinum(II) complexes, $M[S_2P(OR)_2]_2$, are all square planar, four coordinate complexes with isobidentate chelating ligands (see the reviews cited in the section on Introduction). The nickel(II) dithiophosphates readily form five coordinate $\mathrm{Ni[S_2P(OEt)_2 \cdot PPh_3}$,[15] six-coordinate octahedral $\mathrm{Ni[S_2P(O\text{-}Pr^{\mathit{i}})_2]_2 \cdot 2Py}$,[16] or $\mathrm{Ni[S_2P(OCH_2Ph)_2 \cdot (2,2'\text{-}bipy)}$,[17] and many other adducts.[18]

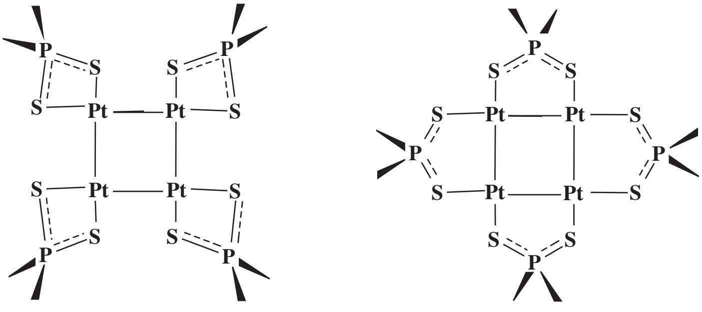
Two isomeric forms of the unique tetrameric platinum complex, $\mathrm{Pt_4(OAc)_4\{S_2P(OEt)_2\}_4}$ have been isolated and structurally characterized (Scheme 3); one contains chelating and the other contains bridging dithiophosphato ligands (acetato groups not shown for clarity).[19]

Bimetallic biconnective bridging can also be symmetric or can display a variable degree of unsymmetry (Scheme 4). This coordination mode occurs in dinuclear complexes and in supramolecular chain-like arrays. When a metal–metal bond is present five-membered rings are formed.

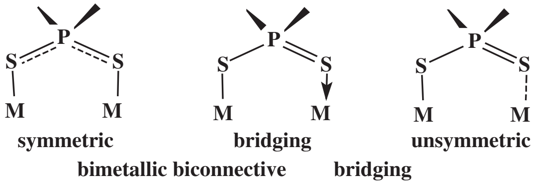
The symmetric bridging can be illustrated by silver(I), which forms eight-membered cyclic dimers $\mathrm{[AgS_2P(OPr)_2 \cdot Phen]_2}$ (R = Pr, Ph).[20] In tetrahedral $\mathrm{Zn_4(\mu_4\text{-}E)[S_2P(OEt)_2]_6}$ (E = O, S), the six ligands are bridging and span the edges of the tetrahedron.[21]

Zinc(II) dithiophosphates and their adducts, *e.g.* $\mathrm{Zn[S_2P(OR)_2]_2 \cdot L}$ [R = $\mathrm{Pr^{\mathit{i}}}$, Cy; L = 4,4′-bipy, *trans*-1,2-*bis*(4-pyridyl)ethylene, 1,2-*bis*(4-pyridyl)ethane][22] and $\mathrm{Zn[S_2P(OPr^{\mathit{i}})_2]_2(4,4'\text{-}bipy)}$[23] are self-asssembled in the solid state through bridging ligands to form supramolecular chain-like arrays. The metal is four-coordinate tetrahedral.

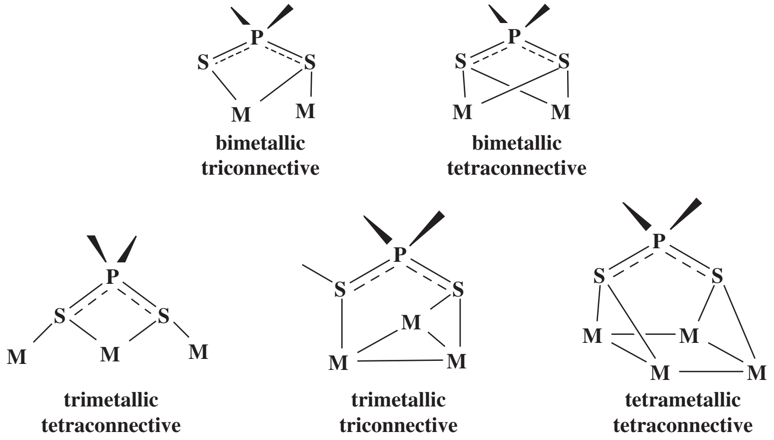
In a number of polynuclear complexes various modes of bi-, tri-, and even tetrametallic connectivity (Scheme 5) may occur and several examples are known for each one.



Scheme 3



Scheme 4



Scheme 5

10.2.2.1 Dithiophosphates (Dithiophosphoric Acid Diesters)

Dithiophosphato metal complexes are usually prepared by metathesis of metal halides with alkali metal or ammonium salts. A convenient method uses the redox reaction of *bis*(thiophosphoryl)disulfanes $(RO)_2(S)PSSP(S)(OR)_2$, with metal species in low oxidation states resulting in the insertion of the metal into the sulfur–sulfur bond.[24] Recently it was used for the synthesis of long alkyl chain, liquid platinum(II) dithiophosphates[25] and for the synthesis of $Ru(CO)_2[S_2P(OPr^i)_2]_2$ from $Ru_3(CO)_{12}$ with $(Pr^iO)_2(S)PSSP(S)(OPr_i)_2$.[26]

Group 3, 4, and 5 metal dithiophosphates are scarce, but Group 6 metal complexes are well represented by many polynuclear molybdenum and tungsten compounds. In these complexes, the coordination patterns are more diversified and in addition to bidentate chelating moieties, triconnective bridging ligands are frequently found. Thus, many trinuclear and tetranuclear (cubane-based) clusters containing molybdenum or tungsten, alone or in combination with other metals can be cited, *e.g.* $Mo_3OS_3\{S_2P(OEt)_2\}_4(H_2O)$,[27] $Mo_3Te_4\{S_2P(OPr^i)_2\}_3(PhCO_2)(PBu_3)$,[28] $W_3Te_7\{S_2P(OR)_2\}_3I$ ($R = Et, Pr^i$),[29] $WCu_3S_4\{S_2P(OCH_2Ph)_2\}(PPh_3)_3$, $WAg_3OS_3\{S_2P(OPr^i)_2\}(PPh_3)_3$,[30] and $M_4Q_4(S_2P(OR)_6$ ($M = Mo, W$; $Q = S, Se$; $R = Et, Pr^i$)[31] to name only a few. Some recent examples are spectacular. Thus, $[NBu_4]_2[(MoOS_3)_4Cu_{12}\{S_2P(OEt)_2\}_6]$, obtained from $[MoOS_3]^{2-}$ and $CuS_2P(OEt)_2$, contains monodentate and bidentate ligands; the latter bridge the copper atoms and link a closed double cubane $[Mo_2O_2S_6Cu_6]^{2+}$ core and two incomplete cubanes $[MoOS_3Cu_3]^+$ units. In $[NEt_4][(WS_4Cu_4)\{S_2P(OEt)_2\}_3]$ bidentate doubly bridging dithiophosphato groups form a chain anion.[32] The tetranuclear complex $WCu_3OS_3(PPh_3)_3[S_2P(OPr^i)_2$ is based upon a distorted tetragonal core, with triply connected dithiophosphato ligands.[33] The molybdenum and tungsten cage compounds $MOS_3Cu_3(PPh_3)_3[S_2P(OCH_2Ph)_2]$ ($M = Mo, W$) are isostructural incomplete cubane structures with triply bridging ligands and display non-linear optic properties.[34] The supramolecular architectures of $[Mo_3S_4\{S_2P(OEt)_2\}_2]_2[OOC(CH_2)_nCOO]L_2$ are also unique.[35] Several cubanes containing a $[Mo_3OS_3Sn]^{6+}$ cluster and dithiophosphato ligands have also been described,[36] and it seems that the variety of polynuclear clusters of molybdenum and tungsten with these ligands is never ending since new structures are being reported one after another in rapid succession.

There are several representatives of Group 8 dithiophosphato complexes, including octahedral iron(III) derivatives $Fe[S_2P(OR)_2]_3$ (R = Me, Pr^i),[37] and the iron(II) complex $Fe[S_2P(OEt)_2]_2 \cdot Phen$.[38] Ruthenium and osmium are represented by mononuclear, paramagnetic pseudo-octahedral $Ru^{III}[S_2P(OR)_2]_3$, dinuclear $[(RO)_2PS_2]_2Ru^{IV}(\mu\text{-}S)_2Ru^{IV}[S_2P(OR)_2]_2$ (R = Me, Et) complexes,[39] and $Os^{III}[S_2P(OR)_2]_3$ (R = Me, Et).[40]

Among the numerous nickel dithiophosphates, the chiral complexes deserve to be cited.[41] Unusual trinuclear $Pd_3(\mu_3\text{-}E)_2[S_2P(OR)_2]_2(PPh_3)_2$ with E = S, Se, R = Et, Pr, Pr^i, Bu, have been prepared and $Pd_3(\mu_3\text{-}S)_2[S_2P(OEt)_2]_2(PPh_3)_2$ revealed a structure containing three distorted square-planar Pd atoms and sharing two μ_3-S ligands.[42]

A plethora of polynuclear copper(I) complexes with bi-, tri-, and tetraconnecting dithiophosphato ligands have been discovered. These include cyclic dimers, $[CuS_2P(OEt)_2 \cdot PPh_3]_2$,[43] tetrahedral $Cu_4[S_2P(OPr^i)_2]_4$,[44] prismatic $Cu_6\{S_2P(OR)_2\}_6$, cubane $Cu_8(\mu_8\text{-}E)[S_2P(OEt)_2]_6$ (E = S, Se),[45] (also known for silver)[46] and $[Cu_8\{S_2P(OPr^i)_6(\mu_8\text{-}X)][PF_6]$ (X = Cl, Br).[47] A supramolecular chain-like array of cubane units interconnected through iodine bridges was found in $\{Cu_8(S)[S_2P(OEt)_2]_6(\mu\text{-}I)\}_x$.[48]

A unique structure is that of the tetranuclear cation in $[Ag_4\{S_2P(OEt)_2\}_3(\mu\text{-}dppm)_2]^+[X]^-$ (X = BF_4, PF_6), which contains three distinct coordination patterns of the dithiophosphato ligand, two of which are novel.[49] Another fascinating structure is that of $Ag_{10}S[S_2P(OEt)_2]_8$ based upon a distorted Ag_{10} monocapped quasi-prism, with bridging dithiophosphato ligands and an encapsulated sulfur atom in center of prism.[50]

Interesting gold dinuclear $[(RO)_2P[SAu(PR'_3)_2]^+[BF_4]^-$ and trinuclear $[(RO)_2P[SAu(PR'_3)_3]^{2+} \cdot 2[BF_4]^-$ gold compounds have been obtained from $(RO)_2P(S)SH$ with $[\{(R'_3P)Au\}_3O]^+[BF_4]^-$.[51]

Group 12 metals tend to form supramolecular self-assembled dithiophosphato complexes. Thus, cadmium dithiophosphates are polymeric, *e.g.* $Cd[S_2P(OBu^i)_2]_2$, which forms chains made of eight-membered rings resulted from doubly bridging dithiophosphato ligands.[52] The complexes $Cd[S_2P(OR)_2]_2$ (R = Pr^i, Et) form 1:1 adducts with 4,4′-bipy, *trans*-1,2-*bis*(4-pyridyl)ethylene, 1,2-*bis*(4-pyridyl)ethane, *etc.*, which are polymers with linear, zig-zag or arched topology and *cis*- or *trans*-N_2S_4 coordination at cadmium, depending on the nature of the bridging ligand and their steric influence. Increasing the steric bulk precludes polymer formation and only a dimer is formed with 1,3-*bis*(4-pyridyl)propane.[53,54] Mononuclear complexes are also known, *e.g.* octahedral cadmium $Cd(phen)[S_2P(OPr^i)_2]_2$ with chelating ligands.[55] Supramolecular self-assembly occurs in mercury(II) dithiophosphates, through unsymmetrical anisobidentate ligands and $Hg\cdots S$ secondary bonds, *e.g.* in $Hg[S_2P(OPr^i)_2]_2$.[56]

The tin(II) derivative $Sn[S_2P(OPh)_2]_2$ is a dimeric supermolecule formed through intermolecular $Sn\cdots S$ secondary bonds and Sn–π–aryl interactions.[57] Lead(II) dithiophosphates, $Pb[S_2P(OR)_2]_2$, *e.g.* R = Me,[58] Pr^n and Cy,[59] all form supramolecular chain-like arrays. The ligands are unsymmetrically bridging and form $Pb\cdots S$ secondary bonds.

Organometallic derivatives of dithiophosphato ligands have focused considerable attention. Dicyclopentadienyl-titanium and -zirconium alkylenedithiophosphates, $Cp_2M(ORO)$, (M = Ti, Zr, R = $CMeCH_2CHMe$, $CH_2CMe_2CH_2$, CMe_2CMe_2) are among the few Group 4 metal dithiophosphates.[60]

Organochromium compounds with various coordination modes of the ligand, namely $CpCr(CO)_2S_2P(OPr^i)_2$ (bidentate), $CpCr[S_2P(OPr^i)_2]_2$ (one bidentate and one unidentate) and $Cr[S_2P(OPr^i)_2]_3$ (bidentate) are formed in reactions of $[CpCr(CO)_3]_2$ with $(Pr^iO)_2(S)PSSP(S)(OPr^i)_2$. Variable temperature NMR shows rapid interchange between bi- and unidentate ligands in solutions of $CpCr[S_2P(OPr^i)_2]_2$.[61]

Heptacoordinate molybdenum and tungsten carbonyl complexes $M(CO)_3[S_2P(OEt)_2]_2$ (M = Mo,W) in which carbon monoxide can be replaced by PPh_3, dppe, or dppm, to give $M(CO)_2(PPh_3)[S_2P(OEt)_2]_2$, $\{M(CO)_2[S_2P(OEt)_2]_2\}_2$(μ-dppe), $M(CO)(dppm)[S_2P(OEt)_2]_2$ (M = Mo, W), $Mo(CO)(dppe)[S_2P(OEt)_2]_2$, $Mo(O)(I)(dppe)[S_2P(OEt)_2]$ and $W(CO)_2(dppe)[S_2P(OEt)_2]_2$ have been reported.[62] The anion $[W(CO)_4S_2P(OEt)_2]^-$ is the first $W^{[0]}$ tungsten dithiophosphate.[63]

Other reported organometallic derivatives include $Mo(\eta^3\text{-allyl})(MeCN)[S_2P(OEt)_2]$ and $[NEt_4][Mo(CO)_4S_2P(OEt)_2]$,[64] $[NEt_4][(CO)_4WS_2P(OEt)_2]$ (bidentate ligand),[65] *endo*-$[Mo(\eta^3\text{-allyl})(CO)[S_2P(OEt)_2(\eta^2\text{-dppe})$,[66] $Cp^*MCl_3[S_2P(OEt)_2]$ (M = Mo, W), [67] $(\eta^6\text{-arene})RuCl\{S_2P(OR)_2\}$ (arene = benzene, *p*-cymene; R = Et, Pr, Pr^i, Bu, Bu^s) and $(\eta^6\text{-}p\text{-cymene})RuS_2P(OEt)_2$,[68] $Cp^*RhCl\{S_2P(OR)_2\}$ (R = Et, Pr, Pr^i) and $Cp^*Rh[S_2P(OEt)_2]_2$.[69]

Several main group metal organometallics have been studied with some interesting results. Organotin dithiophosphates $Ph_2Sn[S_2P((OEt)_2]_2$,[70] and $Ph_2Sn(OPr^i)_2]_2$ are structurally different: in the ethyl derivative the ligands are anisobidentate whereas in the iso-propyl derivative the ligands are symmetrical, isobidentate.[71] This situation was called "heterogeometrism".[72] The triphenyltin derivative, $Ph_3SnS(S)P(OEt)_2$ displays a rare monodentate coordination.[73]

Several organoarsenic(III), organoantimony(III), and organobismuth(III) derivatives have been investigated. Interesting examples include the self-assembled supramolecular chain-like compound $\{Ph_2Sb[S_2P(OPr^i)_2\}_x$, formed through secondary $Sb\cdots S$ bonds of the anisobidentate ligands[74] and $RBi\{S_2P(OR')_2\}_2$ and $R_2Bi\{S_2P(OR')_2\}$ (R = Me, Ph, *p*-Tol; R′ = Me, OEt, Pr^i, Ph),[75]

Organotellurium(II) derivatives, $ArTeS_2P(OR)_2$ (Ar = 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$, R = Me or Et; Ar = mesityl, R = Pr^i) are supramolecular chain-like compounds, self-assembled through $Te\cdots S$ secondary bonds and bridging unsymmetrical ligands.[76,77] Monomeric organotellurium(IV) derivatives, *e.g.* pentagonal bipyramidal $PhTe[S_2P(OPh)_2]_3$,[78] ψ-trigonal bipyramidal $Ph_2Te[S_2P(OR)_2]_2$ (R = Me, Et)[79] with anisobidentate ligands and $Ph_3TeS_2P(OEt)_2$ with an anionic ligand[80] have been reported in addition to several others.[81]

10.2.2.2 Dithiophosphoric Acid *O*-monoesters $(RO)P(O)(SH)_2$

The *O*-monoesters of dithiophosphoric acids can generate dinegative anions $[(RO)P(O)S_2]$,$^{2-}$ which can act as ligands. Their coordination chemistry is practically unexplored and it seems that all known compounds are the result of serendipity. A dimeric nitrido rhenium complex $ReN[S_2P(O)(OEt)](PMe_2Ph)_2$ is formed through $P{=}O \rightarrow Re$ dative bonds.The ligand is bidentate chelating through two rhenium–sulfur bonds.[82] All other complexes of this type of ligand are nickel derivatives and contain diphosphine or isonitrile additional ligands. Examples include square planar $Ni[S_2P(O)(OEt)](PCy_3)(CNAr)$, $Ni[S_2P(O)(OEt)](CNAr)_2$, ($Ar = 2,6\text{-}Me_2C_6H_3$),[83] $Ni[S_2P(O)(OEt)](dppe)$, and $Ni[S_2P(O)(OEt)](dppb) \cdot EtOH$ [dppb = *bis*(diphenylphosphino)butane].[84]

10.2.2.3 Dithiophosphinates

Metal dithiophosphinates focused recent interest due to their potential use as single source precursors for low-pressure, metal–organic chemical vapor deposition (LP–MOCVD) of metal sulfides. Thus, zinc and cadmium dithiophosphinates and their phenanthroline and bipyridine adducts were characterized and used for deposition of ZnS and CdS.[85,86]

Metal dithiophosphinato complexes are usually prepared by metathesis of metal halides with alkali metal or ammonium dithiophoshinates, but can also be conveniently prepared by reactions of *bis*(thiophosphinyl)disulfanes, $R_2(S)PSSP(S)R_2$, with metal species.[87] The electrochemical oxidation of metals in acetonitrile solution, in the presence of diphenylphosphine and sulfur affords $M(S_2PPh_2)_2$ (M = Co, Zn, Cd),[88] but this is not a preparative method.

Some lanthanide dimethyldithiophosphinates enjoyed some attention recently.[89] Dodecahedral complexes $Ln(S_2PBu^i_2)_3L$ (Ln = Pr, Nd, Sm, Eu; L = 1,10-phen, 2,2′-bipy) were prepared and the structures of the europium complex was determined by X-ray diffraction.[90] Actinide dithiophosphinato complexes have been investigated by EXAFS and laser fluorescence spectroscopy.[91] Thorium complexes are similar. The eight-coordinate methyl derivative, $Th(S_2PMe_2)_4$ has been analyzed with the aid of synchrotron X-ray diffraction.[92] Dioxouranium dithiophosphinato complexes, *e.g.* $UO_2(S_2PPr^i_2)_2 \cdot H_2O$,[93] and the dimer $[U^{IV}(S_2PMe_2)_2(OSPMe_2)(\mu\text{-}O_2PMe_2)]_2$[94] are pentagonal bipyramidal with isobidentate chelating ligands in the equatorial plane.

There is an extensive dithiophosphinate chemistry of Group 6 metals. Chromium(III) dithiophosphinates, $Cr(S_2PR_2)_3$ (R = Me, Ph, Cy), are twisted octahedral complexes with isobidentate ligands.[95] Some mononuclear molybdenum mixed ligands complexes are known, *e.g.* $Mo(O)[H_2B(3,5\text{-}Me_2Pz)_2](S_2PPr^i_2)$, with five-coordinate molybdenum and chelating dithiophosphinate,[96] but most common are the trinuclear and tetranuclear (cubane-derived) clusters, *e.g.* $[Mo_3X(\mu\text{-}S_2)_3(\mu_3\text{-}S)(R_2PS_2)_3]$ (R = Et, Pr, Bu; X = Cl, Br, I),[97] $Mo_3SnS_4(S_2PEt_2)_6$,[98] $Mo_3S_4(S_2PR_2)_4HgI_2$ (R = Et, Pr),[99] $Mo_2WCuS_4I(S_2PR_2)_4$ (R = Et, Pr),[100] and $Mo_2W_2S_4(S_2PR_2)_6$ and $Mo_2Co_2S_4(S_2PR_2)_2(CO)_2(MeCN)_{2(4)}$ (R = Et, R=Pr),[101] to name only a few. Also of interest are the tungsten mixed ligand complexes of the type $Tp^*WS_2(S_2PPh_2)$,[102] $Tp^*W(S)(\mu_2\text{-}S)_2W(S)(S_2PPh_2)$[103] [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borato] and *syn*-$W_2S_2(\mu_2\text{-}S)_2(S_2PPh_2)_2$. The latter was obtained from $[NEt_4]_2[WS_4]$ with $Ph_2(S)PSSP(S)Ph_2$, an unconventional reaction.[104] In $Tp^*W^{VI}OS(S_2PPh_2)$ the complex is distorted octahedral with monodentate dithiophosphinato ligands, a facial tridentate Tp* ligand and mutually *cis*-terminal W=O and terminal W=S bonds.[105]

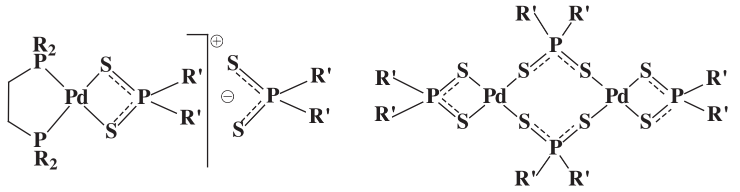
The adducts $Mn(S_2PBu^i{}_2)_2(bipy)$ and $Mn(S_2PBu^i{}_2)_2(phen)$ are octahedral and in solid state form supramolecular architectures through $\pi-\pi$ interactions between the aromatic heterocyclic ligands.[106] Technetium derivatives, important for radiological imaging, such as $^{99m}TcN(S_2PR_2)_2$ (R = Me, Et, Pr, *i*-Pr), have been described.[107]

Group 8 metal complexes of dithiophosphinato ligands include $M(S_2PAr_2)_3$ (M = Fe, Ru, Os; Ar = 2,4,5-$Me_3C_6H_2$, ESR studies)[108] and octahedral $Fe(S_2PAr_2)_2 \cdot 2L$ (Ar = 4-MeC_6H_4, L = MeOH, THF, DMF),[109] and a trigonal bipyramidal anion $[Fe(S_2PAr_2)_2Cl]^-$(Ar = 4-MeC_6H_4),[110] containing isobidentate ligands. Ruthenium dinuclear metal–metal bond species $[Ru_2(S_2PMe_2)_2(CO)_4(PPh_3)_2]$ with bridging ligands are known.[111]

Few Group 9 metal dithiophosphinates have been described and structurally characterized, including five-coordinate trigonal bipyramidal $Co(S_2PPh_2) \cdot L$ (L = nitrogen base),[112] and a surprisingly five-coordinate anion $[Co(S_2PR_2)_3]^-$ (with two bidentate chelating and one monodentate ligands),[113] and six-coordinate *cis*-octahedral cations $[Co(S_2PMe_2)_2(dmpe)]^+$.[114]

Group 10 metals are well represented by numerous nickel dithiophosphinates, $Ni(S_2PR_2)_2$, and $Ni(S_2PR_2)Cl(PR'_3)$. In all these nickel maintains square planar four-coordination and the dithiophosphinato ligand is bidentate chelating. The same coordination geometry is observed in palladium complexes with some interesting consequences. This is illustrated by $[Pd(S_2PEt_2)_2(dcpe)]^+[Et_2PS_2]^-$ [where dcpe = 1,2-*bis*(dicyclohexyl)phosphinoethane], obtained by cleavage of $Et_2(S)PSSP(S)Et_2$ with $Pd_2(\mu\text{-}dcpe)_2$ along with another unusual dinuclear compound $[(Et_2PS_2)Pd\ (\mu\text{-}S_2PEt_2)]_2$ formed in small yield. The compound contains both chelating and non-coordinated anionic dithiophosphinato ligands (Scheme 6). Variable-temperature ^{31}P NMR spectra of the salt indicate rapid interchange of the coordinated and free $R_2PS_2{}^-$ counterion in solution at room temperature.[115]

A number of nickel dithiophosphinate adducts with nitrogen donors and higher coordination numbers have been structurally characterized. Among these the following diisobutyldithiophosphinato complexes are mentioned: monomeric 2,2′-bipyridine and pyrazine adducts $Ni(S_2PBu^i{}_2)_2 \cdot (2,2'\text{-bipy})$ and $Ni(S_2PBu^i{}_2)_2 \cdot 2Py$ (with two monodentate pyrazine in *trans* positions), polymeric $[Ni(S_2PBu^i{}_2)(\mu\text{-}Py)]_n$ (with bridging pyrazine),[116] dinuclear



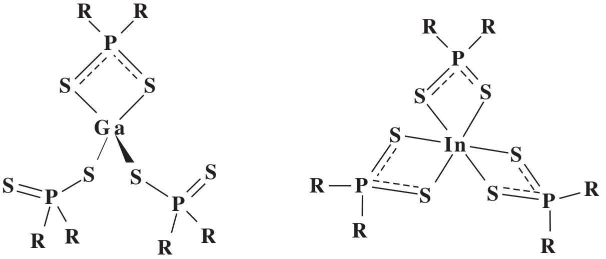
Scheme 6

hexamethylenetetramine complex $[Ni_2(S_2PBu^i_2)_4(CH_2)_6N_4]$,[117] monomeric imidazole $Ni(S_2PBu^i_2)_2 \cdot 2Im$, and 3,5-dimethylpyrrazole $Ni(S_2PBu^i_2)_2 \cdot 2(3,5\text{-}Me_2Pz)$.[118] Strong nitrogen donors, like orthophenanthroline (Phen) can displace the dithiophosphinato ligands and a series of three adducts resulted from successive displacement $Ni(S_2PBu^i_2)_2 \cdot Phen$, $[Ni(S_2PBu^i_2)(Phen)_2]^+[S_2PBu^i_2]^-$, $[Ni(Phen)_3]^{+2}[Bu^i_2PS_2]^-_2$ has been reported.[119] The copper, silver, and gold compounds are known mostly as phosphine adducts. Thus, copper(I) forms four-coordinate $CuS_2PMe_2 \cdot 2PPh_3$,[120] and $CuS_2PBu^i_2 \cdot 2PPh_3$ with bidentate chelating dithiophosphinate, and $CuS_2PBu^i_2 \cdot 3PMe_3$ with monodentate dithiophosphinate.[121] The reaction of $Ph_2P(S)SSiMe_3$ with Group 11 salts produce supramolecular $[Ag(S_2PPh_2)(dppe)]_x$, cationic cluster $[Ag_4(S_2PPh_2)_4(dppe)]^+$, large cluster $[Cu_{48}S_{20}(OBu^t)_2(S_2PPh_2)(dpme)]$ and other fascinating structures.[122] Gold dithiophosphinates, $[Au(S_2PR_2)]_2$, (R = Me, Et, Bu^i, Ph),[123,124,125] $Au_2(CH_2)_2PMe_2(S_2PPh_2)$, $Au_2Cl_2[(CH_2)_2PMe_2](S_2PPh_2)$, $\{Au_2(\mu\text{-}CH_2)[\mu\text{-}(CH_2)_2PPh_2]_2\}(S_2PPh_2)_2$[126] and other luminescent gold dithiophosphinates[127] have been structurally characterized.

Recently, zinc and cadmium dithiophosphinates focused some attention. Octahedral geometry is found in most cadmium compounds, whereas the zinc analogs are four-coordinate (distorted tehrahedral). Therefore, the molecular structures of zinc and cadmium analogues are different. Among the new compounds structurally characterized, the following deserve to be cited: monomeric tetrahedral $Zn(S_2PBu^i_2)_2 \cdot Phen$ and $Zn(S_2PBu^i_2)_2(2,2'\text{-bipy})$ with monodentate dithiophosphinato ligands,[128] octahedral $Cd(S_2PBu^i_2)_2 \cdot Phen$ and $Cd(S_2PBu^i_2)_2(2,2'\text{-Bipy})$ with isobidentate ligands,[129] polymeric $[Cd(S_2PBu^i_2)_2(4,4'\text{-Bipy})]_x$ with bridging dithiophosphinato ligands,[130] the cyclic dimers $[Cd(S_2PPh_2)_2]_2$,[131] and $[Cd(S_2PCy_2)_2]_2 \cdot CHCl_3$ with bridging and chelating ligands and the distorted trigonal bipyramidal five-coordinate tributylphosphine adduct $Cd(S_2PCy_2)_2 \cdot PBu_3$.[132]

The mercury(II) diphenyldithiophosphinate is a cyclic dimer $[Hg(S_2PPh_2)_2]_2$ with both chelating and bridging ligands.[133] Dimerization occurs through secondary bonds and the bridging ligands are unsymmetric.

Variable coordination modes in compounds of similar general formula but different compositions (heterogeometrism) has been observed in the case of gallium and indium diisobutyldithiophosphinate pair, $M(S_2PBu^i_2)_3$, M = Ga or In; the gallium compound is four-coordinate, distorted tetrahedral, whereas the indium compound is six-coordinate, distorted octahedral (Scheme 7).[134] Other



Scheme 7

alkyls reported are the methyl and ethyl derivatives $Ga(S_2PR_2)_3$, R = Me, Et.[135] The indium dithiophosphinates $In(S_2PR_2)_3$, (R = Me and Ph) are distorted octahedral, with bidentate ligands.[136]

Interesting comparisons can be made between the structures of Group 14 metal dithiophosphinates. Thus, germanium is constantly four-coordinate, whereas lead achieves higher coordination numbers and its derivatives are frequently self-assembled into supramolecular structures. Thus, $Ge(S_2PMe_2)_2$ is monomeric, with a distorted ψ-trigonal bipyramidal configuration determined by two anisobidentate $Me_2PS_2^-$ ligands and presumably a lone electron pair on germanium(II).[137] By contrast, the lead(II) analog forms cyclic dimers $[Pb(S_2PMe_2)_2]_2$, which are further self-assembled into polymeric chains through Pb···S secondary bonds.[138] Unfortunately, the structure of $Sn(S_2PMe_2)_2$ is unknown and only a tin(IV) compound, $Cl_2Sn(S_2PPh_2)_2$ (acetone solvate) has been investigated structurally.[139] Two other lead(II) dithiophosphinates whose structures were determined by X-ray diffraction are supramolecular compounds, $[Pb(S_2PR_2)_2]_x$ (R = Et, Ph),[140,141] associated through Pb···S secondary bonds and containing anisobidentate ligands.

Group 15 metal dithiophosphinates have been studied to some extent. The two antimony derivatives investigated, $Sb(S_2PR_2)_3$ with R = Et and Ph are both six-coordinate but structurally different (heterogeometric). While the ethyl compound is distorted octahedral,[142] the phenyl derivative displays a rare pentagonal pyramidal geometry.[143] In both compounds the ligands are anisobidentate. Some bismuth compounds are monomeric, *e.g.* $Bi(S_2PEt_2)_3 \cdot C_6H_6$ (distorted octahedral with isobidentate ligands) but the methyl[144] and phenyl[145] derivatives are dimeric supermolecules $[Bi(S_2PR_2)_3]_2$ (R = Me, Ph) formed by self-assembly through secondary Bi···S bonds.

The tendency of arsenic and to form additional secondary bonds has interesting consequences in the case of dialkyldithiophosphinate arsocane and stibocane derivatives, $X(CH_2CH_2S)_2MS_2PR_2$, X = O, S; R = Me, Et or Ph; M = As,[146] or Sb[147,148] The conformational trends and intermolecular association in these compounds are influenced by the competition between endocyclic, transannular As···X interactions and an exocyclic As···S secondary interaction.

Organometallic dithiophosphinates enjoyed considerable attention. Selected examples are cited below.

Cyclopentadienylchromium dithiophosphinates, $CpCr(CO)_2(S_2PPh_2)$ and $CpCr(S_2PPh_2)_2$ obtained from $[CpCr(CO)_3]_2$ with $Ph_2(S)PSSP(S)PPh_2$ have been structurally characterized. The dicarbonyl derivative $CpCr(CO)_2(S_2PPh_2)$ contains a bidentate ligand whereas in $CpCr(S_2PPh_2)$ one dithio ligand is bidentate and the second is unidentate. Variable temperature ^1H and ^{31}P NMR showed a very rapid exchange between the unidentate and bidentate ligands in the temperature range from -80 to 60°C.[149] Organometallic nitrosyl complexes of molybdenum and tungsten of the type $Cp^RM(NO)I(S_2PR'_2)$ ($R = H$, Me; M = Mo,W; $R' =$ Me, MeO have been described.[150]

The crystal structures of $Mn(CO)_4(S_2PMe_2)$[151] and $Re(CO)_4(S_2PPh_2)$[152] were reported recently; the ligand is isobidentate chelating. Ruthenium cyclopentadienyl derivatives $CpRu(S_2PR_2)(PR'_3)$ ($R =$ Ph, also OEt, OPr, OPr^i, OBu),[153] carbonyl derivatives including monomeric $Ru(S_2PMe_2)_2(CO)_2$ and dinuclear $Ru_2(\mu\text{-}S_2PR_2)_2(CO)_4L_2$ ($R =$ Me, Ph; $L =$ tertiary phosphine) have been described; the structure of $[(Ru_2(CO)_4(\mu\text{-}S_2PMe_2)_2(PPh_3)_2] \cdot 1/2CH_2Cl_2$ contains bridging dithiophosphinato groups.[154]

Mononuclear dithiophosphinato complexes of rhodium $Rh(S_2PPh_2)L_2$ ($L_2 =$ COD; $L =$ CO), $Rh(S_2PPh_2)(CO)(PPh_3)$, $[Rh(S_2PPh_2)(NO)(PPh_3)][BF_4]$, and $RhI(S_2PPh_2)(COMe)(PPh_3)$ have been reported but only the crystal structure of the latter was determined. The compound displays a square pyramidal coordination geometry with the acyl group in apical position and bidentate chelating dithiophosphinate.[155]

Some platinum dithiophosphinates are worth mentioning: dimeric $[Me_3Pt(S_2PPh_2)_2]_2$ (formed through dative S–Pt bonds of triconnective ligands) and monomeric $Me_3Pt(S_2PPh_2)Py$ with bidentate chelating dithiophosphinato ligand.[156]

Organomercury dithiophosphinates are self-assembled supramolecular species. Thus, the dimeric $[MeHgS_2PPh_2]_2$[157] and self-assembled $[PhHgS_2PEt_2)_2]_x$,[158] both are formed through intermolecular $Hg\cdots S$ secondary bonds. A cyclometallated mercury compound, $ArHg(S_2PCy_2)$ (Ar = 2-(2-pyridyl)phenyl) is monomeric owing to the formation of an internal $N \rightarrow Hg$ dative bond.[159]

Most diorganothallium dithiophosphinates display self-assembled supramolecular structures through $Tl\cdots S$ secondary bonds. Known examples include self-assembled $[Me_2TlS_2PPh_2]_x$,[160] $[Ph_2TlS_2PCy_2]_x$ and five-coordinate $PhTl(S_2PCy_2)_2$,[161] $[R_2TlS_2PEt_2]_x$ ($R =$ Me, Ph),[162] and anionic $[Ph_2Tl(S_2PPh_2)_2]^-$.[163,164]

In organogermanium dithiophosphinates the ligand is monodentate, whereas in heavier metal compounds $M\cdots S$ secondary bonds may result in supramolecular self-assembly. Examples are: monomeric $Ph_3GeS(S)PR_2$ ($R =$ Me, Ph),[165] and $Me_2Sn(S_2PR_2)_2$ ($R =$ Me,[166] Et[167]), supramolecular chain-like $[Ph_3PbS_2PMe_2]_x$ (with unsymmetrical bridging dithio ligands and secondary $Pb\cdots S$ bonds),[168] and monomeric $Ph_2Pb(S_2PPh_2)_2$ (six-coordinate lead, anisobidentate ligands).[169]

Organoarsenic dithiophosphinates are practically unknown, except phenoxarsine derivatives. The diphenyldithiophosphinate was found to dimerize through $As\cdots S$ secondary bonds.[170]

Rather numerous organoantimony derivatives are known, including dimeric $[R_2SbS_2PR'_2]_2$ (R = Ph, R′ = Me,[171] R = 4-MeC_6H_4, R′ = Et), self-assembled polymeric $[Me_2SbS_2PMe_2]_x$,[172] and monomeric antimony(V) derivatives $Me_3Sb(S_2PPh_2)_2$,[173] $(Me_3SiCH_2)_3Sb(S_2PPh_2)_2$.[174] A five-coordinate bismuth derivatives with anisobidentate ligands, $MesBi(S_2PPh_2)_2$ (Mes = mesityl) is also mentioned.[175]

Organotellurium dithiophosphinates display interesting and unusual structures owing to their strong tendency to self-assemble into supramolecular structures. An unusual monodentate biconnective coordination pattern (Scheme 8) was found in the self-assembled supramolecular $[PhTeS(S)PPh_2]_x$.[176] In this rare coordination mode one sulfur donor atom is unsymmetrically connected to two metal atoms to form a monoatomic bridge, while the other is dangling non-coordinate. Dithiolato ligands seldom form this type of bridging, which is typical for monothiolato ligands (RS^-).

monodentate
bimetallic biconnective

Scheme 8

Other structurally characterized compounds include $Ph_2Te(S_2PPh_2)_2$ (chloroform solvate),[177] iodo-hexahydrotellurophene derivatives $[C_4H_8TeI(S_2PMe_2)]$, $[C_4H_8TeI(S_2PEt_2)]$,[178] 1,3-dihydrobenzotellurole derivatives [1,2-C6H4(CH2)2TeI(S2PR2)] (R = Me, Et), all containing Te · · · S secondary bonds leading to supramolecular self-assembly.[179]

10.2.2.4 Dithiophosphonates (Dithiophosphonic Acid O-monothioesters)

The dithiophosphonic acid monoesters, RP(OR′)(S)SH can be conveniently prepared by cleavage of dimeric, cyclic diphosphetane disulfides, $[RP(S)S]_2$ with alcohols, silanols, or trialkylsilylalcohols[180] and then can be converted into metal complexes $M[SPR(OR')]_2$ without isolation.[181] The substituted ferrocenyl anion, $(N_3C_6H_4CH_2O)(CpFeC_5H_4)PS_2^-$ has been prepared in two steps from P_4S_{10}, ferrocene and hydroxymethylbenzotriazole (and its salt was used for the preparation of some nickel and rhodium complexes).[182] Zwitterionic ferrocenylditiophosphonates,

η^5-$CpFeC_5H_4P(S)(S^-)(OCH_2CH_2N^+HR'R'')$ (R′ = H, R″ = Me; R′ = R″ = Et) were obtained from $[\eta^5\text{-}CpFeC_5H_4P(S)S]_2$ with aminoethanol derivatives.[183]

A convenient preparation of dithiophosphonato metal complexes of transition metals, $M[S_2PR(OR')]_2$ (M = Ni, Pd, Pt) uses the direct reaction of the Lawesson reagent, [4-MeOC6H4P(S)S]$_2$, with metal salts in alcohols, without isolation of the acid or of an alkali metal salt intermediate. Thus, the reaction between $NiCl_2$ and Lawesson reagent in the appropriate alcohol, ROH (R = Me, Et, *iso*-Pr, Bu, benzyl) gives the *bis*-[*O*-alkyl/aryl-(4-methoxyphenyl) phosphonodithioato]Ni(II) complexes in high yields (64–91%). A similar reaction has been performed with Pd(II), Pt(II) and Co(II) salts.[184,185] The square planar nickel dithiophosphonates thus prepared form octahedral amine adducts and the crystal structures of $Ni[S_2P(OMe)(C_6H_4OMe\text{-}4)]_2 \cdot 2Py$ and $Ni[S_2P(OMe)(C_6H_4OMe\text{-}4)]_2 \cdot 2(4\text{-}MePy)$ have been reported.[186] When the reaction was carried out in the presence of chelating ethylenediamine the product was a salt containing the free, non-coordinated anion and a six-coordinate nickel-ethylenediamine complex cation, *i.e.* $[Ni(en)_3][4\text{-}MeOC_6H_4P(OEt)S_2]_2$. The square planar nickel phosphonodithioates can be used as building blocks for the construction of self-assembled supramolecular coordination polymers, by reacting them with dipyridyl donor ligands (*e.g.* 4,4′-bipyridine and similar) using the tendency of metal to become octahedral six-coordinate by nitrogen coordination.[187,188]

Alternatively, sodium dithiophosphonates $Na[S_2PR(OR')]$, can be prepared in nearly quantitative yields by reacting cyclic dimers $[RP(S)S]_2$ (R = ferrocenyl, $4\text{-}MeOC_6H_4$) with sodium alkoxides, NaOR′ (R′ = Me, Et, Pr^i).[189] The ligands thus obtained were used for the synthesis of nickel(II), palladium(II) and platinum(II) square planar complexes (all containing isobidentate chelating dithio ligands), and zinc(II), cadmium(II), mercury(II), lead(II) dimers $\{[M(S_2P(OR)C_6H_4OMe\text{-}4)]_2\}_2$.[190] The reaction of $[4\text{-}MeOC_6H_4P(S)S]_2$ with copper(I) *tert*-butoxide in the presence of triphenylphosphine, produced an unexpected dinuclear complex of pyrophosphonodithioate, $(Ph_3P)_2Cu[S_2(R)POP(R)S_2]Cu(PPh_3)_2$ where R = $4\text{-}MeOC_6H_4$. In the presence of $Ph_2PNHPPh_2$ the product was a tetracopper cage complex, $Cu_4[S_2(R)\text{-}POP(R)S_2]_2(Ph_2PNHPPh_2)_2$.[191]

Several cyclic dithiadiphosphetanes $[RP(S)S]_2$ (R = aryl, ferrocenyl) were converted to dithiophosphonic acid salts, which reacted with chlorogold(I) complexes to produce the first dinuclear gold(I) dithiophosphonato complexes $[AuS_2PR(OR')]_2$ (R = Ph, R′ = Et; R = $4\text{-}C_6H_4OMe$, R′ = $SiPh_3$) in high yield ($>70\%$).[192] A series of spectacular dinuclear gold(I) dithiophosphonato complexes with monodentate, bidentate chelating and bidentate bridging ligands and their derivatives with a variety of phosphines, PPh_3 and $Ph_2P(CH_2)_nPPh_2$ (n = 1–4) has been reported.[193] The gold complexes of dithiophosphonato ligands display luminescent properties.[194]

The cadmium derivative $Cd[S_2P(C_6H_4OMe\text{-}4)(OC_5H_9)]_2$ is a cyclic dimer based upon an eight-membered $Cd_2S_4P_2$ ring and contains both chelating and bridging ligands.[195]

Some *organometallic derivatives* of dithiophosphonato ligands have been reported. Recently, anionic *bis*(pentafluorophenyl)nickel arylphosphonates $[(C_6F_5)_2Ni[S_2PAr(OR)]^-$ (isolated as tetrabutylammoniumm salts; R = Me, Et, Pr^i) were prepared by reacting $[NBu_4][(C_6F_5)_2Ni(\mu\text{-}OH)]_2$ with either the Lawesson reagent in alcohols or with the ammonium salts of $[ArP(S)(OR)S]^-$ (Ar = ferrocenyl). The dithio ligand is isobidentate.[196]

Numerous main group organometallic derivatives, $R_nMS_2P(OMe)R$, have been prepared directly from the Lawesson reagent, $[4\text{-}MeOC_6H_4P(S)S]_2$, or homologues of Davy's reagent $[RP(S)S]_2$ (*e.g.* R = Et, *i*-Bu) with metal alkoxides or thiolates (M = Al,[197] Si, Ge, Sn,[198,199,200] Pb,[201] Sb,[202,203] Bi[204]). Organosilicon derivatives of dithiophosphonic acids, *e.g.* disilyl aryldithiophosphonates, $ArPS(S)(OSiR_3)(SSiR_3)$, *O*-silyl-S-germyl aryldithiophosphonates, $ArP(S)(OSiR_3)(SGeR_3)$, and related compounds have been reported.[205]

10.2.3 Arsen-1,1-dithiolates

Arsen-1,1-dithiolates are less popular than their phosphorus analogs, perhaps due to fear of toxicity and foul smell of the ligands.

10.2.3.1 Dithioarsenates

To the best of our knowledge only two dithioarsenate complexes containing an $[(RO)_2AsS_2]^-$ anion have been reported to date. They are $Cp_2V[S_2As(OMe)_2]$[206] and $[CrS_2As(OMe)_2(H_2O)_3(NO)]$,[207] mentioned with their ESR spectra, but no X-ray structure is available.

10.2.3.2 Dithioarsinates

Alkali metal dithioarsinates, $M[S_2AsR_2]$ can be prepared by treating arsenic acids or their salts, $M[O_2AsR_2]$ with hydrogen sulfide (M = Na, R = Me[208]; M = K, R = Ph,[209] CH_2Ph[210]). The crystal of $K[S_2AsMe_2]\cdot 2H_2O$ contains infinite sheets of $K(H_2O)_4S_2$ octahedra connected through weak O–H···S hydrogen bonds in a supramolecular structure.[211]

The coordination patterns of dithioarsinates identified so far are similar to those of phosphor-1,1-dithiolates, *i.e.* monodentate, bidentate chelating (symmetrical and unsymmetrical) and bridging.

A tetranuclear, hexa-μ-dithioarsinatotetrazinc sulfide, $Zn_4S(S_2AsMe_2)_6$, contains a central sulfur atom bonded to four zinc atoms located at the corners of a tetrahedron, with six bridging $[Me_2AsS_2]^-$ ligands on the edges.[212] The molecular and electronic structures of $M_4(\mu_4\text{-}S)(\mu\text{-}S_2AsMe_2)_6$ (M = Zn, Cd) have been investigated by a combination of physical methods and theoretical DFT calculations.[213]

The indium(III) derivatives, $In(S_2AsR_2)_3$ (R = Me, Ph) are monomeric with isobidenate ligands,[214] the bismuth dimethyldithioarsinate, $Bi(S_2AsMe_2)_3$ is a dimer formed through Bi···S secondary bonds[215] and $Cr(S_2AsMe_2)_3$ is monomeric with trigonally distorted octahedral coordination geometry.[216]

Antimony(III) and phenylantimony(III) dimethyldithioarsinates, $Ph_nSb(S_2AsMe_2)_{3-n}$ with $n = 0$–2, have been prepared and $Ph_2SbS_2AsMe_2$ was found to contain molecular units self-assembled into a chain-like supramolecular structure with $SAsMe_2S$ bridging ligands, displaying short (covalent, 2.655 Å) and long (secondary bonding, 2.830 Å) antimony–sulfur bonds.[217]

10.2.4 Xanthates (Dithiocarbonic Acid *O*-monoesters)

The anionic species $ROCS_2^-$ resulted from *O*-alkyl(aryl) esters of the hypothetical dithiocarbonic acids, ROC(S)SH, better known as xanthates, are versatile ligands and they generate an extensive coordination chemistry. The interest for metal xanthates is stimulated by their potential use as single source precursors for nanoscopic metal sulfides in photochemical or thermal vapor deposition systems under mild conditions,[218–221] *e.g.* for Zn,[222] Cd,[223] In,[224] Bi[225,226] sulfides.

Direct synthesis of xanthato complexes is possible by reacting CS_2 with an alcohol (also used as solvent) and an appropriate metal reagent. As examples can be cited, the formation of polymeric $(CuS_2COMe)_n$ from a reaction of $[NMe_4]_2[Cu_4(SePh)_6]$ with CS_2 in methanol[227] or the synthesis of $[NBu_4][(C_6F_5)_2Ni(S_2COR)]$ (R = Me, Et) from $[NBu_4][\{(C_6F_5)_2Ni(\mu\text{-}OH)\}_2]$ with CS_2 in the corresponding alcohols (MeOH, EtOH).[228] Long chain diols allow cyclization with formation of a macrocyclic dinuclear complex, $Ni_2[(S_2CO(CH_2CH_2O)_4CS_2]_2$.[229]

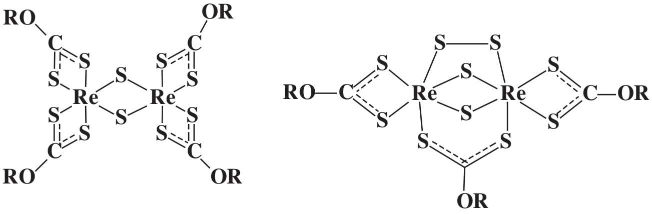
The insertion of carbon disulfide into M–OR bonds of metal alkoxides provides an alternative route to metal xanthato complexes. Thus, *fac*-$(CO)_3M(S_2COR)L$ (where M = Mn, Re; L = dppe or dppp; R = Me, Et, CF_3CH_2),[230] and $(CO)_3Re(S_2COR)(L_2)$ (where L_2 = $2PMe_3$ or diars; R = Me, *etc.*),[231]have been obtained from the corresponding alkoxides. The reaction was used for the synthesis of rare magnesium, calcium, strontium and barium xanthates.[232] The insertion of CS_2 into M–OPh bonds of phenoxides, *e.g.* $M(CO)_5OPh$ is facile and leads to $M(CO)_5(S_2COPh)$.[233]The method was used for the synthesis of a variety of substituted arylxanthato derivatives, *e.g.* $Ph_3MS_2COC_6Cl_5$ (M = Sn,[234]Ge and Pb[235]), $Cd(S_2COC_6H_3R_2\text{-}2,6)_2(base)_n$, (R = Me, *tert*-Bu, Ph, base = Py, THF, THT) and $Cp^*W(CH_2Bu^t)(NO)(S_2COBu^t)$.[236]

Carbon disulfide inserts into Zn–OH bonds of $Tp^{MePh}ZnOH$ in the presence of methanol to form the xanthate $Tp^{MePh}ZnS(S)COMe$ (with monodentate ligand and Zn···O intramolecular interactions).[237] The insertion of CS_2 into a metal–hydrogen bond, occurring with a hydrido complex (in deuteroacetone) was reported for $[Cp_2WH \cdot THF][CF_3SO_3]$ to give $[Cp_2WS_2COCH(CD_3)_2][CF_3SO_3]$,[238] thus suggesting that the reactions of metal hydrido complexes with carbon disulfide might be an interesting subject for further research.

Less obvious is the formation of dinuclear xanthato complexes, $Re^{IV}{}_2(\mu\text{-}S)_2(S_2COBu)_4$ and $[NEt_4][Re^{IV}{}_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}S_2COR)(S_2COBu^i)_2]$ (Scheme 9) in a redox reaction of a thiometalate, $[NEt_4][Re^{VII}S_4]$ with the isobutyldixanthogen, $[Bu^iOC(S)S]_2$.[239]

Nickel(III) xanthates, $Ni(S_2COR)_3$, with R = Me, Et, Pr, *i*-Pr, Bu, *i*-Bu, *sec*-Bu, can be quantitatively generated in acetonitrile solution by electrooxidation of anionic $[Ni(S_2COR)_3]^-$ or by oxidative addition of ethyldixanthogen, $[EtOC(S)S]_2$ to $Ni(S_2COEt)_2$. Solutions of $Ni(S_2COR)_3$ readily disproportionate into $Ni(S_2COEt)_2$ and $[EtOC(S)S]_2$.[240]

The lability of the xanthato moiety may sometimes result in unpredictable dealkylation. Thus, in attempted preparation of palladium(II) and platinum(II)



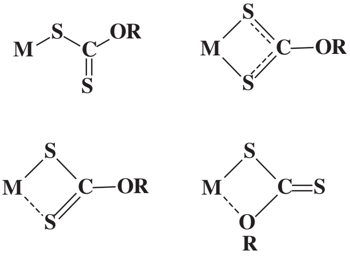
Scheme 9

tris-xanthato anionic complexes, mixed derivatives containing the dithiocarbonato ligand, $[M(S_2COR)(S_2CO)]^-$ were obtained, and $Pt(S_2CO)(Ph_2POMe)_2$ was formed when $[Pt(S_2COEt)(Ph_2POMe)_2]Cl$ reacted with NaI in acetone.[241] When a Co^{2+} salt reacted with dppe and ethylxanthate in ethanol the dithiocarbonato complex $Co^{III}(dppe)(S_2COEt)(S_2CO)$ was formed.[242]Complete dealkylation of the xanthate occurred in the reaction of $TcNCl_2(PPh_3)_2$ with KS_2COEt, with formation of a dithicarbonato complex, $K_2[TcN(S_2CO)_2]\cdot 2H_2O$.[243]

The coordination patterns observed for xanthato ligands are as diverse as those of other 1,1-dithiolato complexes discussed here. They can display monodentate (monometallic monoconnective), symmetrical or unsymmetrical bidentate chelating (monometallic biconnective) or bridging (bimetallic biconnective) coordination patterns. The crystal packing may influence the molecular geometry of some metal xanthato complexes, as revealed for diorganotin systems.[244] As a result, the rotation of the ligand may lead to a weak coordination of the oxygen[245](Scheme 10).

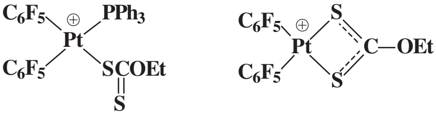
The great structural diversity of coordination patterns and supramolecular self-assembly has been analyzed in detail for nickel(II), zinc(II), mercury(II), and tellurium(II),[246]*bis*(xanthato) complexes.

An unprecedented coordination of xanthate, with one sulfur bridging three platinum centers, was observed in $[NBu_4][Pt_4(C_6F_5)_8(S_2COEt)_2]$. Small changes in the composition induce different coordination patterns; thus, the xanthato ligand is monodentate in $[NBu_4][(C_6F_5)_2Pt(S_2COEt)(PPh_3)]$ whereas the ligand



Scheme 10

is bidentate chelating in $[NBu_4][(C_6F_5)_2Pt(S_2COEt)]$ [247] (Scheme 11). In the organometallic complexes $CpCo(S_2COR)_2$ (R = Me, Et) one ligand is monodentate and the other one is bidentate, and the complexes can be described as $CpCo(\eta^1\text{-}S_2COR)(\kappa^2\text{-}S_2COR)$[248](see ref. 198). Potassium alkylxanthates react with $CpRuCl(PEt_3)_2$ to give $CpRu(S_2COR)(PEt_3)_2$ in which the xanthato ligand is monodentate, but with $Cp^*RuCl(PEt_3)_2$ it yields a complex $Cp^*Ru(S_2COR)(PEt_3)$ (R = Me, Et, *i*-Pr) containing a bidentate xanthato group.[249]



Scheme 11

Further selected examples of interesting xanthates are presented below.

A dinuclear vanadium complex, $V_2(\mu_2\text{-}S_2)_2(S_2COPr^i)_4$,[250] contains isobidentate chelating ligands. Thiocyanato anions (monodentate) can be replaced in $[NEt_4][Nb_2S_4(NCS)_8]$ by bidentate xanthato ligands to give dinuclear niobium xanthato complexes, $Nb_2S_4(S_2COR)_4$, R = Et, *i*-Pr, Cy.[251]

In the crystal structures of slightly distorted octahedral $Cr(S_2COR)_3$ with R = Me[252] and Pr^i (see ref. 253) the xanthato ligands are isobidentate. Molybdenum and tungsten form carbonyl xanthato complex anions $[M(CO)_5(\eta^1\text{-}S_2COR)]^-$ (with monodentate ligands) and $[M(CO)_4(\kappa^2\text{-}S_2COR)]^-$ (with bidentate xanthato ligands) (M = Mo, W) in the reactions of their metal hexacarbonyls with alkali metal xanthates.[254] A unique trihapto coordination of the xanthate was found in $MoO(\eta^3\text{-}S_2COPr_i)(\kappa^2\text{-}S_2COPr^i)(PMe_3)$,[255] and in the dinuclear $[Mo(\eta^3,\kappa^2\text{-}S_2COEt)(\kappa^2\text{-}S_2COEt)Br]_2$.[256] Molybdenum and tungsten tend to form sulfur-containing clusters and some xanthato derivatives, *e.g.* $MoCu_3S_3(S_2COEt)(O)(PPh_3)_3$,[257]$WCu_3S_3(S_2COEt)(O)(PPh_3)_3$,[258] have been reported.

The manganese and technetium xanthato complexes $Mn(S_2COEt)_2(2,2'\text{-bipy})$,[259,260] $Tc(S_2COBu)_3(PPh_3)$,[261] and $Tc(S_2COEt)_3(PMe_2Ph)$[262] contain featureless bidentate chelating ligands. More interesting are the structures of dimeric $[Re(\mu_2\text{-}S)_2(S_2COBu)_2]_2$ (with bidentate chelating ligands and sulfur bridges) and the anion $[Re_2(\mu_2\text{-}S)_2(\mu_2\text{-}S_2)(\mu_2\text{-}S_2COBu^i)(\kappa^2\text{-}S_2COBu^i)_2]^-$ (containing two bidentate chelating one bridging xanthato ligands).[263] The rhenium carbonyl xanthate, $Re(CO)_5(S_2COEt)$ was obtained from $Re(CO)_5Cl$ and KS_2COEt, without displacement of carbon monoxide, leaving the ligand monodentate.[264]

In the iron, ruthenium, osmium, cobalt, and rhodium complexes the xanthato ligands are isobidentate chelating. Selected examples are *trans*-$Ru(S_2COEt)_2(PMe_2Ph)_2$,[265] *cis*- and *trans*-$Os(S_2COMe)_2(PPh_3)_2$,[266] $Co(S_2\ COMe)_3$.[267]

Numerous four-coordinate, square planar nickel(II) xanthates with isobidentate ligands, $Ni(S_2COR)_2$, have been characterized structurally. Less common are the clusters $Ni_3S_2(S_2COR)_2(diphos)$,[268] and $[Ni(OCH_2C_5H_4N)(S_2COEt)]_4$,[269] both containing bidentate chelating ligands. Square planar nickel(II) xanthates are able to coordinate two nitrogen base donors and become octahedral. Several such adducts have been analyzed structurally, *e.g.* *trans*-$Ni(S_2COEt)_2$(isoquinoline)$_2$,[270] and *cis*-$Ni(S_2COCH_2CH_2OMe)_2 \cdot 2Py$.[271] The latter forms a supramolecular chain-like array through O···H–C weak hydrogen bonds. There are numerous adducts with dinitrogen bases. Those with pyrazine and 4,4′-bipyridine form supramolecular chains in the crystal, *e.g.* $[Ni(S_2COPr^i)_2(pyr)_2]_x$,[272] and $[Ni(S_2COR)_2(4,4'\text{-bipy})(\text{solvent})]_x$ (R = Et, Bu)[273,274] Six-coordinate nickel(II) *tris*(xanthate) anions $[Ni(S_2COR)_3]^-$ are also known.[275]

Among platinum complexes the neutral $Pt(S_2COEt)_2$ is four-coordinate square planar[276] with isobodentate ligands. An unusual structure is found in the dianion $[(C_6F_5)_8Pt_4(S_2COEt)_2]^{2-}$, which contains chelating-bridging xanthato ligands and a Pt_2S_2 cyclic core[277]. Copper forms a supramolecular $[Cu(S_2COMe)]_x$,[278] and tetranuclear $[Cu(S_2COAr)]_4$ (Ar = 2,6-Bu^t_2-4-MeC_6H_2),[279] with bridging xanthato ligands. Fluorinated copper xanthates, $Cu(S_2COR)_2 \cdot 2PPh_3$ (R = $C_8H_{17}CF_3$, $C_3H_6CF_3$) have been reported.[280]

In silver and gold compounds, such as $(Ph_3P)_2AgS_2COEt$,[281] $R_3P \cdot AuS_2COR'$,[282,283] the ligands are unsymmetrically chelating and in dinuclear $Au_2(\mu\text{-dppe})(\mu\text{-}S_2COR)X_2$ (R = Me, Et, Pr^i, X = Cl, Br, I) the xanthate coordinates as a bridging ligand.[284] The compounds $[AuS_2COBu]_2$[285] and $(R_3P)_2AuS_2COEt$ (R = Ph or CH_2CH_2CN)[286] are strongly luminescent.

Zinc, cadmium, and mercury form a variety of xanthato complexes, many of which form supramolecular self-assembled architectures in solid state. A unique polynuclear $[Cd_{17}S_4(SPh)_{24}(S_2COMe)_{4/2}]_n$,[287]is worth mentioning. In the *tris*(xanthato) anions, $[Zn(S_2COEt)_3]^-$ the ligands display different coordination modes.[288] Mercury(II) and organomercury xanthates are interesting due to their tendency to self-assemble through Hg···S intermolecular secondary bonds to form intricate supramolecular architectures in the solid state. Selected examples illustrate such behavior of mercury *bis*(xanthates),[289] and organomercury derivatives, including methylmercury $MeHg(S_2COR)$,[290] and phenylmercury xanthates $PhHg(S_2COR)$ (R = Me, Et, Pr^i).[291]

Xanthate ligands were less frequently used with Group 13 metals. A supramolecular organothallium xanthate, $Ph_2Tl(S_2COMe)$, is mentioned.[292]

In germanium(IV) and organogermanium derivatives the xanthato ligands are monodentate.[293] Di- and triorganotin xanthates, $R_2Sn(S_2COR')_2$ and $R_3Sn(S_2COR')$ (R = Me, Ph; R′ = Me, Ph, CH_2Ph) have been prepared,[294] and the crystal structures of $Me_2Sn(S_2COPr^i)_2$,[295] $Ph_2Sn(S_2COR)_2$ (R=Me, Et, Pr^i),[296] and $(ROCS_2)SnMe_2(OR)OSnMe_2]_2$ (R = Pr^i, CH_2Ph)[297] among others, are known. An important comparative study of the ^{119}Sn, ^{13}C, and ^{31}P NMR spectra of organotin xanthates, dithiocarbamates, and dithiophosphates has been published.[298]

The crystal structures of $M(S_2C\text{-}OR)_3$ with M = As, Sb, Bi[299–301] have been discussed comparatively and a correlation of the ^{13}C NMR spectra of $M(S_2C\text{-}OR)_3$ with their crystal structures is available.[302]

The molecular structures of $PhAs(S_2COPr^i)_2$,[303] $PhSb(S_2COEt)_2$,[304] $Bi(S_2COR)_3$ (R = Et, Bu, Cy, CH_2Ph)[305] have been established by X-ray diffraction.

Some antimony and bismuth xanthates tend to self-assemble through M···S secondary bonds into supramolecular structures.

The tellurium(II) xanthates, $Te(S_2COR)_2$,[306] mixed halide–xanthato complexes, $Me_2TeX(S_2COR)$ (X = Cl, I),[307]triorganotelluronium Me_3TeS_2COR (R = Me, Et, Pr^i, Bu^t, Ph),[308] and dimeric $[Ph_3TeS_2COEt]_2$ (with unsymmetrical bridging xanthato ligands)[309] are often self-assembled in some forms of supramolecular architectures.[310]

10.2.5 Dithiocarboxylates

The anions of dithiocarboxylic acids, RCS_2^-, have been occasionally used as ligands but their chemistry is much less investigated than that of dithiophosphates or dithiocarbonates. This may be due to their lower stability, somewhat cumbersome preparation and foul smell.

The free dithiocarboxylic acids can be isolated, but their salts are preferred. In some cases their metal complexes can be prepared directly by insertion of carbon disulfide into metal–carbon bonds. Thus, the reaction of Grignard reagents, RMgX, with CS_2, followed by acid treatment gives the dithiocarboxylic acids RCSSH and metal complexes in good yields.[311]

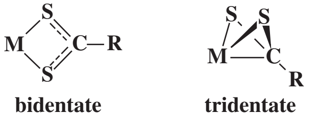
Carbon disulfide can be inserted into Li–C bonds, to form lithium salts. A recent example is the formation of $RC{\equiv}CCS_2^-$ anions (further used for the synthesis of ruthenium carbonyl complexes) by insertion of carbon disulfide into Li–C bonds of acetylides, $LiC{\equiv}CR$ (R = Ph, tert-Bu, Mes).[312] The reaction was also used for the preparation of lithium dithiocarboxylates with bulky organic groups, $Li[S_2CAr]$, where Ar = 2,6-$Mes_2C_6H_3$ and 2,6-$TripC_6H_3$, and they were used for the preparation of titanium and vanadium dithiocarboxylates.[313] In view of ready commercial availability of organolithium reagents, this method seems to be of great potential for generation of dithiocarboxylato ligands, followed by their immediate use for the synthesis of metal complexes.

Among the metal complex dithiocarboxylates prepared by insertion of CS_2 into M–R bonds, and the formation of $R'_3P \cdot CuS_2CR$ by insertion into copper(I) alkyls or aryls, $R'_3P \cdot Cu^IR$,[314] can be mentioned. Insertion of CS_2 into W–C bond of $[W(CO)_5CH_3]^-$ gave $[W(CO)_5S_2CMe]^-$, which under irradiation was converted into $[W(CO)_4(\eta^2\text{-}S_2CMe)]^-$ (isolated as PPN salt, PPN = $[Ph_3PNPPh_3]^+$ cation).[315] Iron complexes η^5-CpFe(diphos)(S_2CR) (R = Me, Ph) have been prepared by insertion of CS_2 into Fe–C bonds.[316]

The synthesis of alkali metal xanthates from trimethylsilyl dithiocarboxylates and alkali metal fluorides[317] has been described as convenient and useful for preparative purposes of metal complexes and organometallic derivatives.

The reactions of tetraethylammonium tetrathiometallates, $[NEt_4]_2[M^{VI}S_4]$ (M = Mo, W) and $[NEt_4][Re^{VII}S_4]$, with disulfides, $[RC(S)S]_2$, afford dithiocarboxylato complexes, *e.g.* $Mo^{IV}(S_2CPh)_4$, $W^{VI}S(S_2)(S_2CPh)_2$, $[NEt_4][W^{IV}O(S_2)(S_2CPh)]$ and $Re^{III}(S_2CPh)(S_3CPh)_2$.[318]

The coordination patterns of dithiocarboxylates are expected to be similar to those of other 1,1-dithiolato ligands. In addition to the common bidentate chelating and bridging coordination patterns, in the case of dithiocarboxylato ligand a rare trihapto coordination pattern η^3 (Scheme 12) has been reported. The latter differs from the basically coplanar four-membered ring pattern in bidentate coordination and displays a butterfly motif, with an approximately tetrahedral arrangement of the metal, two sulfur atoms and a participating carbon atom. This rare coordination pattern has been found in an iron complex, η^5-CpFe(η^3-S_2CMe)(κ^1-dppm),[319] and two molybdenum complexes MoO(η^3-S_2CPh){κ^2-SS(S)CPh}[320] and MoO(η^3-$S_2CC_6H_4Me$-*p*)(κ^3-$HBPz_3$).[321]



Scheme 12

A selection of metal dithiocarboxylate structures is highlighted. A full picture can be obtained from the reviews cited in Section 1.

The eight-coordinate vanadium complex $V(S_2CMe)_4$ contains both dodecahedral and square prismatic eight-coordinate molecules in the same crystal.[322] Of particular interest is the chain-like, mixed valence platinum complex $[Pt_2(S_2CMe)_4(\mu\text{-}I)]_x$, which displays unusual electrical properties: metallic conduction between 300 and 340 K and semiconducting properties below 300 K,[323] whereas the analogous nickel complex, $[Ni_2(S_2CMe)_4(\mu\text{-}I)]_x$ is a semiconductor.[324]

Sulfur-rich *bis*(perthiobenzoato)(dithiobenzoato)-technetium(III) heterocomplexes have been reported.[325] A redox reaction of $[M^{VII}OCl_4]^-$ anions (M = Re, Tc) with arylditiocarboxylato anions produce dithiocarboxylato/perthiocarboxylato mixed complexes $[M^{III}(S_2CAr)(S_3CAr)_2]$, which display six-coordinate trigonal prismatic geometry.[326] The same rare coordination geometry is observed in $(MeCS_2)_2V(\mu,\eta^2\text{-}S_2)_2V(S_2CMe)_2$ prepared from $V(\eta^6\text{-}C_6H_6)_2$ with MeC(S)SH.[327]

Dinuclear complexes $[Cp_2MoH_2AgS_2CR]_2$ (R = Me, Ph) with bridging dithiocarboxylato (also dithiophosphato, xanthato, and dithiocarbamato)[328] ligands have been described. In the copper(I) complex $(PPh_3)_2Cu(S_2CMe)$ the ligand is bidentate.[329] Gold(I) forms tetramers $Au_4(S_2CMe)_4$ with bridging ligands.[330] Square planar complexes, $Cl_2Au(S_2CC_6H_4OC_nH_{2n+1})$ display liquid crystal properties.[331]

Some organometallic derivatives of dithiocarboxylato ligands are known and the following types are cited as examples: $M(CO)_5(S_2CPh)$ (M = Cr, W),[332] and $Rh^I(CO)(PPh_3)(S_2CR)$,[333] $CpNi(S_2CPh)$.[334]

Main group organometallic derivatives include: R_3MS_2CR' and $R_2M(S_2CR')_2$ (M = Si, Ge, Sn, Pb; R = Me, Ph, R′ = Me, Pr^i, Ph, Cyh),[335–337] and $Ph_nAs(S_2CR)_{3-n}$ (R = Me, Et, Pr^i, Ph; n = 0–2).[338] In main group metal complexes the dithiocarboxylato ligand is generally anisobidentate.

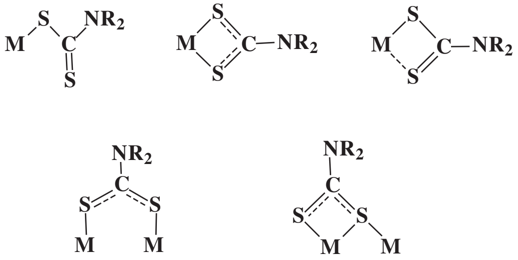
This brief presentation suggests that dithiocarboxylato anions are versatile ligands and it is believed that the field holds much promise for novel chemistry to be explored in the future.

10.2.6 Dithiocarbamates

Dithiocarbamates are subject to uninterrupted research, and interesting chemistry is frequently reported. In addition to their academic interest, dithiocarbamates have useful applications as analytical reagents for the determination of metals in foodstuff, water, and environmental samples,[339] as NO trapping agents,[340] or in the removal of heavy metals from waste waters.[341]Probably the most important reason of interest for thiocarbamates is their potential use as sulfur source for vapor deposition and nanoparticle growth of metal sulfide materials.[342] This is illustrated by the formation of crystalline antimony sulfide by thermolysis of antimony dithiocarbamates under mild conditions[343] and by the use of dithiocarbamates as single-source precursors for MOCVD (Metal Organic Chemical Vapor Deposition) of nanosized particles of tin,[344] lead,[345] bismuth,[346] palladium, and platinum[347] sulfide thin films, exploiting their favorable thermochemistry in this respect.[348] Interesting and promising results of the investigation of gold dithiocarbamato complexes as potential anti-cancer agents have been reported recently.[349] Since the extensive literature on the coordination chemistry of dithiocarbamato ligands was thoroughly reviewed (Section I) only essential information and some highlights will be presented here.

The coordination patterns of dithiocarbamato ligands (Scheme 13) are similar to those of the previous 1,1-dithiolates. In rare cases bimetallic triconnective) coordination is observed, *e.g.* in $[Co_2(\kappa^2\text{-}S_2CNMe_2)_2(\mu_3\text{-}S_2CNMe_2)_2\{PPh(OMe)_2\}_2][PF_6]$.[350] Tri- and tetraconnective coordination was found in $[Ag_{11}(\mu_5\text{-}S)(\mu_4\text{-}S_2CNEt_2)_6(\mu_3\text{-}S_2CNEt_2)]$.[351] In arsocane derivatives the molecular geometry is influenced by a competition between transannular and exocyclic As···Ssecondary bonding, the dithiocarbamato groups being coordinated as typical anisobidentate ligands.[352]

Anhydrous calcium dithiocarbamates $Ca(S_2CNR_2)_2$ (where $NR_2 = NEt_2$, $NPr^i{}_2$, NBu_2, NC_4H_8, $NHBu^t$, $NHC_2H_6NMe_2$), and a strontium



Scheme 13

dithiocarbamate, $Sr(S_2CNBu_2)_2$, were prepared from $Ca(NH_2)_2$ and $Sr(NH_2)_2$ with CS_2 and the appropriate amine.[353]

The obvious preparation of metal dithiocarbamato complexes uses the metathesis of metal halide compounds with alkali metal dithiocarbamates. An efficient alternative is the reaction of trimethylsilyl dithiocarbamates like $Me_3SiS(S)CNEt_2$ with metal halide complexes, which occurs under mild conditions. The reaction was used to prepare $M_2(\mu\text{-}N_2)(S_2CNEt_2)_6$ from $(MCl_3)_2(\mu\text{-}N_2)(THF)_4$ (M = Nb, Ta).[354] The reaction of $NbCl_5$ with $Me_3SiS(S)CNEt_2$ afforded two coordination isomers, namely $NbCl_3(S_2CNEt_2)_2$ and $[Nb(S_2CNEt_2)_4][NbCl_6]$.[355] The insertion into the Mo–N bond of $(\eta^3\text{-}C_3H_5)(CO)_2Mo(HNC_5H_{10})\{\eta^1\text{-}S_2P(OEt)_2\}$ afforded $(\eta^3\text{-}C_3H_5)(CO)_2\text{-}Mo(S_2CNC_5H_{10})$, after releasing the dithiophosphato ligand.[356]

Another convenient preparation of dithiocarbamato complexes uses thiuram disulfides, $[R_2NC(S)S]_2$, as starting materials in oxidative addition reactions. Thus, dithiocarbamato complexes of aluminum(III) and gallium(III), $M(S_2CNR_2)_3$, have been prepared by reductive cleavage of thiuram disulfides, with trimethylamine-metal hydrides, $Me_3N \cdot MH_3$ (M = Al, Ga; R = Me, Et, CH_2Ph). The same compounds can be obtained by transmetallation reactions between $Et_2O \cdot AlH_3$ and $M(S_2CNEt_2)_3$, which is a novel preparative method for metal dithiocarbamates.[357] The reaction of tetraethylthiuram disulfide, $[Et_2NC(S)S]_2$, with $[NH_4][WSe_4]$ in acetonitrile afforded seven-coordinate, $WS(Se_2)(S_2CNEt_2)_2$ and $WO(Se_2)(S_2CNEt_2)_2$.[358] The reaction of $M(CO)_6$ with elemental selenium and $[Et_2NC(S)S]_2$ gave trinuclear $[M_3(\mu_3\text{-}Se)(\mu\text{-}Se_2)_3(S_2CNEt_2)_3]_2Se$ (M = Mo, W) and other products, whereas $Cr(CO)_6$ produced only $Cr(S_2CNEt_2)_3$.[359] Cyclopentadienylchromium tricarbonyl dimer, $[CpCr(CO)_3]_2$, reacted with $[Et_2NC(S)S]_2$ to give $Cp_6Cr_8S_8(S_2CNEt_2)_2$, in addition to several unexpected C–S bond cleavage and C–C coupling products.[360]

A unique ruthenium assisted insertion of isothiocyanates into the silicon–sulfur bond provides another route to metal complex dithiocarbamates. Thus, $Cp(PPh_3)RuS_2CNRR'$ ($R = SiPr^i{}_3$, $R' = Ph$, 4-MeC_6H_4, 1-naphtyl; R = H, R′ = Ph, 1-naphtyl) and the dinuclear $Cp(PPh_3)RuS_2CNR\text{-}C_6H_4\text{-}NRCS_2Ru(PPh_3)Cp$ ($R = SiPr^i{}_3$) have been prepared by the reaction of isothiocyanates, RNCS, and 1,4-phenylene diisocyanate with $Cp(PPh_3)_2RuSSiPr^i{}_3$ and $Cp(PPh_3)_2RuSH$.[361]

Insertion into metal–nitrogen bonds is illustrated by the formation of the anion $[(C_6F_5)_2Pd(S_2CNHPh)]^-$ in the reaction of $[Pd_2(C_6F_5)_4(\mu\text{-}NHPh)_2]^{2-}$ with carbon disulfide.[362]

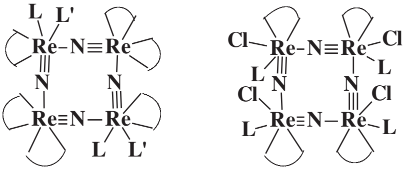
The structural chemistry of some metal dithiocarbamates, *i.e.* systematics, coordination modes, crystal packing, and supramolecular self-assembly patterns of nickel, zinc, cadmium, mercury,[363] organotin,[364] and tellurium,[365,366] complexes has been thoroughly analyzed and discussed in detail. Supramolecular self-assembly frequently occurs in non-transition heavier soft metal dithiocarbamates. Thus, lead(II),[367] bismuth(III)[368] zinc,[369] cadmium,[370] and (organo)mercury[371] dithiocarbamates are associated through M···S secondary bonds, to form either dimeric supermolecules or chain-like supramolecular arrays. The arsenic(III)[372] and antimony(III)[373] dithiocarbamates are monomeric, propeller-like molecules, with anisobidentate chelating ligands) displaying only intramolecular M···S secondary bonds).

Numerous molybdenum and tungsten clusters of the type $[M_3YS_3M']^{n+}$ (Y = O, S; M = Mo or W; M′ = Cd, Hg, Sn, Pb, Sb, Bi) with dithiocarbamato (also dithiophosphato) ligands have been structurally analyzed and their chemistry is now better understood. These compounds display non-linear optical properties.[374] An interesting family of oxo- and thio-molybdenum and tungsten with mixed *tris*(dimethylpyrazolyl)borato and dithiocarbamato ligands, $Tp^*MQ(S_2CNEt_2)$ (M = Mo, W; Q = O, S) contain bidentate chelating dithiolato and tridentate Tp* ligands in an octahedral coordination.[375] In simpler compounds like *cis*-$WO_2(S_2CNBu^i{}_2)_2$ the ligands are bidentate and the coordination geometry is also octahedral.[376]

The dithiocarbamato ligands stabilize high oxidation states, like Co^{IV} in $[Co^{IV}(S_2CNR_2)_3]^+$ (R = Et, Cy) prepared by electrochemical oxidation methods.[377] A mixed-valence copper(II)–copper(III) dithiocarbamate catenane has been described,[378] and the crystal structures of square planar $[Cu^{III}(S_2CNMe_2)_2][ClO_4]$ and $[Cu^{III}(S_2CNEt_2)_2][FeCl_4]$ have been determined.[379] A nanoarchitecture formed by metal-directed self-assembly and containing four dithiocarbamato-functionalized resorcarene ligands, assembled by eight Cu^{III} ions, has been described.[380] Copper(II) diethyldithiocarbamatec forms a molecular complex with fullerene,$[Cu(S_2CNEt)_2]_2 \cdot C_{60}$, having interesting magnetic and optical properties.[381] A nickel(IV) dithiocarbamato complex, containing three ferrocenyl building blocks linked to a central nickel(IV) core, with interesting electrochemical properties, should also be mentioned.[382] Supramolecular macrocyclic molecular boxes were obtained by metal-directed self-assembly of polyferrocenyl dithiocarbamato complexes.[383] The photochemistry of Fe(III), Fe(IV), Mo(VI), and Ni(IV) has been covered in a review.[384]

Some interesting polynuclear vanadium dithiocarbamato complexes have been structurally characterized, including $[NEt_4][V_3(\mu^3\text{-}S)(\eta^2\text{-}\mu\text{-}S_2)_3(S_2CNEt_2)_3] \cdot 3MeCN$,[385] $[NEt_4]_3[V_2S_2O_2(S_2CNEt_2)_2K]$, or $[NEt_4]_3[\{V_2S_2O_2)(S_2CNMe_2)_2\}_3Na_3(H_2O)]$[386] and the cubane-like cluster compound $[NEt_4][V_4S_4(S_2CNC_4H_8)_6]$[387] The dinuclear anion $[NEt_4][Mo_2(\mu\text{-}SPh)_2(CO)_6(S_2CNEt_2)]^-$ with a planar Mo_2S_2 core, is formed from $Mo_2(SPh)_2(CO)_8$ and NaS_2CNEt_2,[388] and metal–metal bonded cations $[Mo_2(S_2CNR_2)_6]^{2+}$ have been reported as a source of $Mo^{III}S_2CNR_2)_3$ fragments.[389] Related compounds are the dinuclear *syn*- and *anti*-isomers of $[MoO(NAr)(S_2CNR_2)]_2$ (R = Et, Pr; Ar = Ph, 4-tolyl).[390] The trinuclear cation $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2CNEt_2)_3]^+$ should also be mentioned.[391] Uncommon trinuclear palladium(II) complexes, containing both bridging and terminal dithiocarbamato ligands, have been reported.[392]

Cyclic rhenium dithiocarbamato complexes (Scheme 14), containing an eight-membered Re_4N_4 ring, with distinct single (Re–N 2·03 Å) and triple (Re–N 1·69 Å) bonds alternating, *cyclo*-$[ReN(S_2CNEt_2)Cl(PMe_2Ph)]_4$ and *cyclo*-$[Re_4N_4(S_2CNEt_2)_6(MeOH)_2(PPh_3)_2][BPh_4]_2$ and other Re_4N_4 ring derivatives have been described.[393]



Scheme 14

Unusual heterobimetallic μ-nitrido dithiocarbamato ruthenium(II) complexes, *e.g.* $(Ph_3P)(Et_2NCS_2)(CO)RuNOsO_3$ and $(Ph_3P)(Et_2NCS_2)(CO)RuNRe(S_2CNEt_2)_2$, have been structurally characterized.[394] In $[Ru^{III}(\eta^1\text{-}S_2CNMe_2)(\eta^2\text{-}S_2CNMe_2)(tacn)]^+[PF_6]^-$ (where tacn = 1,4,7-triazacyclononane) the two dithiocarbamato ligands display mono and bidentate coordination modes.[395] A nitride coupling reaction between $MoN(S_2CNEt_2)_3$ and $OsNCl_2(BPz_3)$ afforded $(Et_2NCS_2)_3Mo{=}N\text{-}OsCl_2(HBPz_3)$ and released N_2.[396]

Nickel(II) dithiocarbamates, $Ni(S_2CNRR')_2$, are monomeric, square planar complexes. A less common dinuclear complex is the thiolato bridged $[Ni(S_2CNHMe)(\mu\text{-}SMe)]_2$, in which the dimers are self-assembled into tetrameric supermolecules through weak axial Ni···S secondary bonds.[397]

Luminescent, trinuclear-mixed dithiocarbamato-xanthato gold complexes, $[Au_3Cl(S_2CNR_2)(S_2COEt)(\mu\text{-dpmp})]$ where R = Me, CH_2Ph and dpmp = *bis*(diphenylphosphinomethyl)phenylphosphine, $PhP(CH_2PPh_2)_2$ have been prepared and their optical properties were investigated.[398]

Arsenic dithiocarbamates, $As(S_2CNR_2)_3$ (R = Bu, CH_2Ph),[399] and toluene-3,4-dithiolato arsenic and bismuth dithiocarbamato derivatives, $(MeC_6H_3S_2)M(S_2CNR_2)$ (M = As, Bi; R = Me, Et, CH_2CH_2)[400] have been structurally characterized and the supramolecular self-assembly in Sb(III) dithiocarbamates has been carefully examined.[401]

Among the novel organometallic dithiocarbamates, cyclopentadienyl chromium derivatives, $CpCr(CO)_n(S_2CNR_2)$ (n = 2 and 3) with bidentate and monodentate dithiocarbamate, $Cp_6Cr_8S_8(S_2CNR_2)_2$ (R = Me, Et, Pr^i),[402] $CpMo\{\eta^4\text{–}C_4(CF_3)_4\}(S_2CNMe_2)$,[403] the nickel derivatives $(C_6F_5)_2Ni(S_2CNR_2)$,[404] dimeric trimethylplatinum compounds, *fac*-$[Me_3PtS_2CNMe_2]_2$ and *fac*-$[Me_3PtS_2CNHPh]_2$ (with both bridging and chelating ligands),[405] dimesityl gold derivatives, $Mes_2AuS_2CNR_2$ (R = Me, Et, CH_2Ph),[406] and the tetrahydrotellurophene derivatives $C_4H_8TeI(S_2CNR_2)$ with R = Et; $R_2 = C_4H_6$ (also dithiophosphinates),[407] are mentioned. Organotin dithiocarbamates display a remarkable structural diversity.[408] Several new crystal structures, including those of $Cy_3SnS_2CNBu_2$,[409] $PhSnCl(S_2CNBu^i_2)_2$, and $BuSnCl(S_2CNBu^i_2)_2$,[410] $Bu_2Sn(S_2CNEt_2)_2$ (at 153 K) containing anisobidentate dithiocarbamato ligands, are mentioned.[411]

Interesting results were reported with dithiocarbamates derived from diamines. Thus, a series of dinuclear zinc(II), cobalt(II), and nickel(II) dithiocarbamate ditopic macrocyclic receptors containing various spacer groups of different sizes has been reported.[412,413,414] Spectroscopic investigations and

X-ray diffraction analysis show that these receptors can bind neutral and anionic bidentate guests species, *e.g.* 1,4-diazabicyclo[2.2.2]octane, isonicotinate, or terephthalate to form 1:1 intramolecular inclusion complexes.[415]

10.2.7 Dithiocarbimates and Related Compounds

Closely related to dithiocarbamates are the compounds containing the dianionic ligands $[R–N{=}CS_2]^{-2}$ (carbimates), which contain a C=N double bond, both carbon–sulfur bonds being single bonds. A few illustrative examples will be cited here.

Metal cyanodithiocarbimates $M_2[S_2C{=}N\text{-}CN]$ (M=Na, K, Rb, Cs, Tl), $K_2[S_2C{=}N–CN]\cdot H_2O$, and $Ba[S_2C{=}N–CN]\cdot 2H_2O$ were prepared by reaction of cyanamide with CS_2 in alkaline medium.[416] Gold derivatives of the type $[PPN]_2[Au_2(S_2C{=}N–CN)_2]$ have been reported and the perylene salt of this anion exhibit metallic character.[417,418] Rhenium complexes $[Re(S)(S_4)(S_2C{=}N–R)]^-$ and $[Re_2S_5(S_2C{=}N–R)_2]^{2-}$ are formed by [3+1] cycloaddition of isocyanides to $[ReS_4]^-$ anions. The crystal structure of $[PPh_4][Re(S)(S_4)(S_2C{=}N\text{-}Me)]$ has been reported.[419]

The nickel *N*-cyanodithiocarbimato complex $[Ni(bipy)(S_2C{=}N–CN)]$ has been prepared and investigated by X-ray diffraction. The coordination geometry is square planar and supramolecular self-assembly through intermolecular $Ni\cdots S$ secondary interactions [3.412(2) Å] and hydrogen bonds is observed in the crystal.[420] Square planar coordination geometry occurs also in *bis*(tetra-*n*-butylammonium) *bis*[(4-cyanophenyl)dithiocarbimato(2-)-S,S′]nickelate(II) $[NBu_4]_2[Ni(S_2C{=}N–C_6H_4CN\text{-}p)_2]$.[421] Palladium(II) and platinum(II) dithiocarbimates, $M(S_2C{=}N\text{-}C_6H_4NH_2)_2$, are formed by reactions of dithiocarbamates $M(S_2C–NHC_6H_4NH_2)_2$ (M=Pd, Pt) with strong bases. The single-crystal X-ray analysis of $[Bu_4N]_2[Pd(S_2C{=}N–C_6H_4NH_2)_2]$ was the first reported for a dithiocarbimato complex and revealed a square-planar coordination geometry with an asymmetrically coordinated bidentate chelating ligand.[422]

Bis(triphenylphosphine)(*N*-ethoxycarbonyldithiocarbimato)palladium(II), $Pd(S_2C{=}N–COOEt)(PPh_3)_2$ is formed in reactions of Pd(II) complexes wiyh a large excess of EtOCO–NCS in the presence of PPh_3. The coordination geometry is slightly distorted square planar in a PdS_2P_2 environment, the dithio ligand being bidentate chelating.[423] A platinum complex $(PPh_3)_2Pt(S_2C{=}N\text{-}Me)$ was formed by loss of phenyl isocyanate from a cyclic compound $(PPh_3)_2PtS_2CNMeC(O)NPh$ formed by insertion of CS_2 into $(PPh_3)_2Pt\{NMeC(O)NPh\}$.[424]

Organometallic dithiocarbimates are also known. Thus, a diarylgermanium phenyldithiocarbimate, $Tbt(Tip)GeS_2C{=}N\text{-}Ph$, was obtained from the kinetically stabilized diarylgermylene Tbt(Tip)Ge: in a reaction with phenyl isothiocyanate, *via* [2+2] cycloaddition of a diarylgermanethione [Tbt(Tip)Ge=S] intermediate, evidenced by electronic spectroscopy.[425]

The formation of most dithiocarbaminato complexes seems to be the result of serendipity and rational synthesis of such compounds has yet to be developed. There is much novel chemistry to be expected in this area.

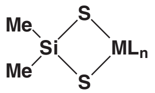
10.2.8 Silane-1,1-dithiolates and Tin Analogs

An exotic class of 1,1-dithiolato ligands is represented by a few examples of silane-1,1-dithiolates (Scheme 15). The first such compounds reported were titanium and vanadium organometallic derivatives, $Cp'_2TiS_2SiMe_2$ and $Cp'_2VS_2SiMe_2$, and the platinum triphenylphosphine complex, $(PPh_3)_2PtS_2SiMe_2$, in which the dimethyldithiosilanolate anion, $Me_2SiS_2{}^{2-}$, acts as a bidentate chelating ligand. The titanium compound was prepared from $(Me_2SiS)_3$ with Cp'_2TiCl_2 *via* $Me_2Si(SLi)_2$ (obtained from the trimer and Li_2S) and the vanadium and platinum complexes by ligand transfer from the titanium complex in reactions with L_2MCl_2 ($L = PPh_3$ or Cp'; $M = Pt$ or V).[426] A similar palladium complex, $(PEt_3)_2PdS_2SiMe_2$ has been obtained from $(Me_2SiS)_3$ and $Pd(OAc)_2$ and PEt_3.[427]

Treatment of metal acetates $M(OAc)_2$ (M = Fe, Co, Pd) with cyclotrisilthiane $(Me_2SiS)_3$ in the presence of Lewis bases gave dimethylsilaneditiolato complexes $Fe(S_2SiMe_2)$(pmdeta), $Fe(S_2SiMe_2)(Me_3TACN)$, $Co(S_2SiMe_2)$ (pmdeta) (where pmdeta = N,N,N′,N′,N″-pentamethyldiethylenetriamine; Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane) and $(PEt_3)_2Pd(S_2SiMe_2)$, all containing the bidentate chelating Me_2SiS_2 ligand. The reactions of the starting material, hexamethylcyclotrisilthiane $(Me_2SiS)_3$ with metal compounds are, however, unpredictable, since analogous reactions of $(Me_2SiS)_3$ with copper(I) and silver(I) acetates in the presence of PEt_3 produced dinuclear complexes $(PEt_3)_3M_2(SMe_2SiSSiMe_2S)$ (M = Cu, Ag) of the disilthiane dithiole ligand, $[SMe_2SiSSiMe_2S]^{2-}$. With $(PEt_3)M(OAc)$ (M = Cu, Ag) the cyclotrisilthiane gave the same complexes.[428,429]

The interest for these ligands will be probably negatively affected by the hydrolytic sensitivity of silthianes, but the cited complexes promise to be useful precursors for metal–sulfur clusters.

Similar dithio organotin ligands may be expected, as suggested by the formation of the $[PhSnS_3]^{3-}$ anion (from $Ph_4Sn_4S_6$ with $Na_2S \cdot 5H_2O$) isolated as sodium salt $Na_3[PhSnS_3]$,[430] which was used for the synthesis of a copper complex $(CuPMe_2Ph)_6(PhSnS_3)_2$, structurally characterized by X-ray diffraction.[431] This suggests that the reaction of $(R_2SnS)_3$ with Na_2S might generate $[R_2SnS_2]^{2-}$ anions, which could become interesting ligands. Some reactions of $(R_2SnE)_3$ (E = S, Se, Te) with the dimethylplatinum complex $Me_2Pt(Bu^t{}_2bipy)$ ($Bu^t{}_2bipy$ = 4,4′-di-tert-butyl-2,2′-bipyridine) gave five-membered metallacycles $PtESnR_2ESnR_2$, cotaining both Sn–Pt and Pt–E bonds, by oxidative addition of $R_2SnESnR_2E$ fragments.[432] This suggests that stanna-1,1-thiolato ligands are feasible.



$ML_n = TiCp_2', VCp_2'$

$M = Pd, Pt, L_n = 2PR_3$

Scheme 15

10.2.9 Phosphor-1,1-diselenolates

10.2.9.1 Diselenophosphates

Diselenophosphates have been much less investigated than the analogous dithiophosphates, but some interesting chemistry was revealed. The reactions of phosphorus(V) selenide, P_2Se_5, with alcohols and phenols produce diselenophosphoric acid diesters, $(RO)_2P(Se)SeH$, the parent compounds of diselenophosphato anionic ligands. The free acids are not stable and should be immediately converted to metal salts or complexes.

The trinuclear molybdenum complex $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3\{Se_2P(OCH_2CH_3)_2\}_3]Br$ was synthesized by selective substitution of the bromo ligands in $[PPh_4]_2[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]$ with bidentate ligands $[Se_2P\ (OEt)_2]^-$. The crystal structure was determined by X-ray diffraction and the ^{31}P and ^{77}Se NMR spectra confirm that the cation persists in solution.[433]

Some unusual polynuclear copper(I) clusters with diselenodithiophosphato ligands have been reported. A chlorine centered cubic Cu_8 cluster was identified in the compounds $[Cu_8(\mu_8\text{-}Cl)\{Se_2P(OR)_2\}_6][PF_6]$ (R=Et, Pr, Pr^i) prepared from $[Cu(MeCN)_4][PF_6]$ with $NH_4[Se_2P(OR)_2]$ and $[NBu_4]Cl$ in a molar ratio of 4:3:1 in diethyl ether. The structure consists of a discrete cationic cluster in which eight Cu ions are linked by six diselenophosphato ligands and a central μ_8-Cl ion with a non-coordinating $[PF_6]^-$ anion. The shape of the molecule is a chloride-centered distorted Cu_8 cube. The diselenophosphato ligand exhibits a tetrametallic tetraconnective (μ_2,μ_2) coordination pattern, and each occupies a square face of the cube. Each copper atom of the cube is coordinated by three Se atoms with a strong interaction with the central chloride ion.[434]

A selenium centered cube is found in $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr_i)_2]_6$, in which each face of the cube is bridged by a diselenophosphato ligand and a selenide ion, Se^{2-}, is encapsulated within the cube.[435,436]

A nine-membered cluster containing a non-acoordinate encapsulated selenide anion, displaying a tricapped trigonal prismatic geometry, $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr^i)_2]_6$, was isolated along with the selenide centered cube, $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$ and a bromide-centered cube $Cu_8(\mu_8\text{-}Br)[Se_2P(OPr^i)_2]_6[PF_6]$, from the reaction of $[NH_4][Se_2P(OPr^i)_2]$, $[Cu(MeCN)_4][PF_6]$, and $[NBu_4]$ Br in CH_2Br_2. The $Cu_{11}Se$ core is stabilized by three bromido and six $Se_2P(OPr^i)_2$ ligands.[437] Similarly, from the reaction of $NH_4[Se_2P(OR)_2]$ (R = Pr, Pr^i), $[Cu(MeCN)_4][PF_6]$, and $[Bu_4N]I$ in a 3:2:2 molar ratio in Et_2O two types of products were isolated: a selenide centered-cube $Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6$, and an iodine bridged capped trigonal prismatic derivative $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OR)_2]_6$. Again in the cubane complex the six diselenophosphato ligands, each capped on the square face of the cube, adopt a tetrametallic tetraconnective coordination pattern. The eleven Cu atoms in the second compound adopt the geometry of a 3,3,4,4,4-pentacapped trigonal prism with a Se atom in the center. The coordination geometry for the central Se atom is tricapped trigonal prismatic. The central $Cu_{11}Se$ core is further stabilized by three iodides and six diselenophosphato ligands.[438]

During the synthesis of the selenide-centered Cu_8 cube $Cu_8(\mu\text{-}Se)[Se_2P(OEt)_2]_6$ from $NH_4[Se_2P(OEt)_2]$ and $[Cu(CH_3CN)_4][PF_6]$, the copper cluster $Cu_{12}(P_2Se_6)[Se_2P(OEt)_2]_8$ was unexpectedly isolated. X-ray diffraction analysis shows that it contains an ethane-like hexaselenodiphosphate(IV) anion encapsulated in a dodecanuclear copper cluster stabilized by eight diselenophosphate ligands. The *i*-Pr derivative $Cu_{12}(P_2Se_6)[Se_2P(OPr^i)_2]_8$ was also structurally characterized.[439]

Two halide-centered cubane silver cluster complexes, containing discrete units, $[Ag_8X\{Se_2P(OEt)_2\}_6][PF_6]$, or unidimensional chains, $\{Ag_8X[Se_2P(OEt)_2]_6X\}_n$ ($X = Br$ and Cl) have been reported. This is an interesting case where the counter ions dictate the molecular/supramolecular architecture.[440]

Another remarkable case is the co-crystalization of two neutral clusters, a selenium-centered cubane $Ag_8(Se)\{Se_2P(OPr^i)_2\}_6$ and a hexanuclear prism $Ag_6[Se_2P(OPr^i)_2]_6$.[441] The compounds $[Ag(Se_2P(OR)_2)]_n$ ($R = Et$, $n = x$; $R = Pr^i$, $n = 6$) and $Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OR)_2]_8$ ($R = Et$, Pr^i) were formed in the reaction of $[Ag(MeCN)_4][PF_6]$ with $NH_4[Se_2P(OR)_2]$ in Et_2O at −20°C. In the hexameric cluster $Ag_6[Se_2P(OPr^i)_2]_6$ six Ag atoms are located at the corners of a pseudohexagonal prism alternating with Se atoms in two Ag_3Se_3 rings interconnected vertically by the P–Se bridges of the diselenophosphinato ligands, organized in a paddle-wheel fashion about an Ag_6Se_6 pseudohexagonal prismatic core. The decasilver cluster contains an encapsulated Se atom in a distorted, *cis*-bicapped trapezoidal-prismatic geometry, surrounded by eight diselenophosphinato ligands having three different types of coordination pattern.[442]

The structures of zinc diselenophosphates are dictated by the peripheral organic groups. Thus, the ethyl derivative is a chain polymer $\{Zn[Se_2P(OEt)_2]_2\}_x$, whereas the isopropyl derivative is a dimer $\{Zn[Se_2P(OPr^i)_2]_2\}_2$. In both compounds both chelating and bridging diselenophosphato ligands are present. Variable-temperature ^{31}P NMR spectra show that monomeric and dimeric forms of the complex are in equilibrium in solution, *via* exchange of bridging and chelating ligands. However, at temperatures $> 40°C$ the complex exists as a monomer and with lowering of the temperature the percentage of dimer increases gradually at the expense of monomer. Below −90°C the complex exists as a dimer.[443] A tetrahedral complex $Zn_4(\mu_4\text{-}Se)[Se_2P(OPr)_2]_6$ has also been described.[444]

The indium compounds $In[Se_2P(OR)_2]_3$, $R = Et$, Pr^i display distorted octahedral geometries and are self-assembled in solid state through intermolecular $Se\cdots Se$ secondary bonds.[445]

In spite of the interesting results obtained for organometallic dithiophosphates, similar studies with diselenophosphates have not been performed for comparison. Only recently some organogermanium, -tin, and -lead derivatives of the type $Ph_3MSe(Se)P(OR)_2$ ($M = Ge$, Sn, Pb; $R = Et$, Pr, Pr^i), containing monodentate ligands have been reported.[446]

10.2.9.2 Diselenophosphinates

Diselenophosphinates have been prepared several years ago and their chemistry began with the synthesis of diselenophosphinic acid (from Et_2PCl with elemental selenium). A lithium diphenyldiselenophosphinate $[Ph_2PSe_2Li \cdot THF \cdot TMEDA]$ was obtained by oxidation of $[Ph_2PSeLi \cdot TMEDA]_2$ with elemental selenium and its crystal structure was determined by X-ray diffraction.[447] More recently, some other alkali metal salts were reported, namely dimeric $[K(Se_2PPh_2)(thf)_2]_2$, and the dipotassium salt of methylene-*bis*(diselenophenylphosphinic) acid $K_2[Se_2PhPCH_2PPhSe_2]$.[448]

An unconventional preparation of nickel diphenyldiselenophosphinate, $Ni(Se_2\,PPh_2)_2$, involves oxidation by elemental selenium of $Ni(PPh_2)_2$, obtained in turn by electrochemical oxidation of nickel metal in acetonitrile solutions of Ph_2PH.[449]

The indium complexes $In(Se_2PPh_2)_3 \cdot L$ (where L = THF, MePh) are self-assembled dimers in solid state through Se···Se secondary interactions.[450]

Organometallic derivatives are represented by $Cp_2Ti(Se_2PPh_2)$, obtained from $Cp_2TiSePPh_2$ or from $LiSeP(Se)Ph_2$ with $[Cp_2TiCl]_2$,[451] η^3-allylpalladium $(\eta^3\text{-}Me_2CCMeCH_2)PdSe_2PPh_2$,[452] and a pentamethylcyclopentadienyl ruthenium complex, $[Cp^*Ru(\mu_2\text{-}Se_2PPr^i_2)(\mu_2\text{-}SePPr^i_2)][PF_6]$, which was unexpectedly formed in the reaction of $[Cp^*Ru(MeCN)_3][PF_6]$ with $HN(SePPr^i_2)_2$.[453]

10.2.9.3 Diselenophosphonates

Like the dithio analogues, diselenophosphonates have received less attention. Only recently sodium salts of the type $Na[Ph(RO)PSe_2]$ with R = Me, Et, Pr^i, have been obtained by cleaving the cyclic dimer $[PhPSe_2]_2$ (Woollins' reagent) with sodium alkoxides and several metal complexes of the anionic ligand have been investigated structurally. The cadmium complex is a dimer $\{Cd[Se_2PPh(OMe)]_2\}_2$, the nickel compound $Ni[Se_2PPh(OMe)_2]_2$ is a square planar complex as expected, and two types of dimeric lead supermolecules have been observed.[454]

10.2.10 Arsen-1,1-diselenolates (Diselenoarsinates)

The piperidinium salt of diphenyldiselenoarsinic acid was prepared in 83% yield by reacting $4\text{-}MeC_6H_4C(O)SeAsPh_2$ with piperidine at 30°C in diethyl ether. The crystal structure determination of the salt $[H_2N_2C_5H_{10}]^+[Se_2AsPh_2]^-$ reveals a supramolecular dimer formed through N–H···Se hydrogen bonding and Se···Se secondary interactions.[455] The synthesis of this compound opens the way to a coordination chemistry of diselenoarsinato ligands but so far no metal derivatives have been reported.

10.2.11 Tellurium Analogs

Ditellurium analogs of phosphor-1,1-dithiolates and arseno-1,1-dithiolates are almost unknown. The only ditellurophosphinates reported are the lithium salts $Li[R_2PTe_2]$ with R = Ph, cyclohexyl, obtained from R_2PH with RLi followed by treatment with elemental tellurium in THF,[456] but telluroiminophosphinates, containing the $[R_2P(NR')Te]^-$ anions (R = Pr^i, Cy) and some of their complexes with Group 12 metals have been described.[457] Related anions containing tellurium-phosphor bonds are the ditelluro(diimino)cyclodiphosphazanates $[Te(RN)P(\mu\text{-}NR)_2P(NR)Te]^{2-}$,[458] monotelluroimidodiphosphines, $[TeR_2PNHPR_2]$ (R = Pr^i), ditelluroimidodiphosphinates $[TeR_2PNPR_2Te]^-$, and and some of their metal complexes $M[TeR_2PNPR_2Te]_n$ (R = Pr^i, Ph; $n = 2$, M = Zn, Cd, Hg; $n = 3$, M = Sb, Bi),[459,460] are known. This raises hopes that more chemistry of metal complexes with ditellurophosphinato anions $[R_2PTe_2]^-$ and related ligands will be developed in the near future.

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CHAPTER 10.3

Hypervalent Chalcogen Compounds

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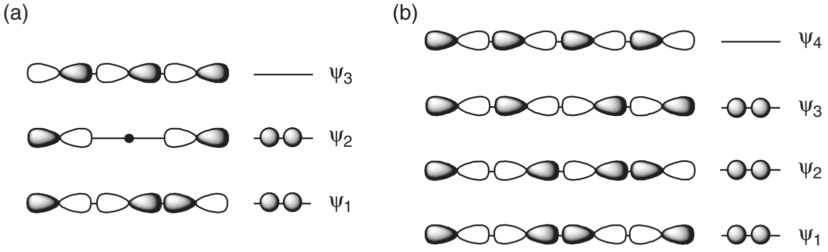
10.3.1 Introduction

A new field of chemistry has been started with the preparation of highly unstable SCl_4 in 1873[1] and it has developed rapidly in the last four decades. The structure of SCl_4 is trigonal bipyramidal (TBP) with a lone pair orbital of S (n(S)) located at the equatorial position. Three Cl, S, and Cl atoms align linearly and construct the apical bonds. The apical S–Cl bonds are longer than the equatorial ones. Randle proposed the notation of ‘‘hypervalent bonding’’ for the linear bonds.[2] Hypervalent molecules are defined as ions or molecules of group 15–18 elements bearing more electrons than the octet within the valence shell.[3a] Hypervalent bonds are analyzed as three center–four electron bonds (3c–4e) of the σ-type, as proposal by Musher and Pimentel.[3] The bonding scheme is well established:[4,5] the bonds are mainly constructed by atomic *p*-orbitals whereas *d*-orbitals play an additional role as the polarization functions and the traditional dsp^3 and d^2sp^3 hybrid orbitals do not contribute to the bonds.[4d,e] The nature of the hypervalent bonds is still discussed based on new aspects of the theory, however.[6]

Scheme 1a shows the approximate molecular orbital model for the hypervalent X–E–X 3c–4e in EX_4, such as SCl_4. Characters of the three molecular orbitals are bonding (ψ_1), nonbonding (ψ_2), and anti-bonding (ψ_3). Two electrons are in ψ_1 and two in ψ_2. Electrons in ψ_2 localize on X of X–E–X and the hypervalent bonds are mainly characterized by ψ_2. Consequently, (1) the hypervalent X–E–X bonds are usually weaker than the normal ones: bond orders of the apical E–X bonds are less than 1.0, typically around 0.5. (2) Apical bonds are stabilized by X whose electronegativity (χ(X)) is larger than χ(E): the more electronegative ligands show a trend to occupy apical



Scheme 1 *Approximate molecular orbital models for (a) 3c–4e and (b) 4c–6e*

positions (apicophilicity). The valence shell of the hypervalent atom expands formally with more than eight electrons. However, it would not do substantially, since apical bonds usually contain suitable highly polar molecular orbitals, such as ψ_2, where the electrons localize on ligands (Scheme 1a).

The hypervalent chalcogen chemistry has been developed to higher coordinated species with various ligands,[7–10] where TBP changes to square pyramidal (SP) or octahedral (Oh), *etc*. Additional atomic orbitals of E, such as an *s*-orbital, may operate to stabilize the structures.[10b] The concept is also extended over linear σ-bonds constructed by m (≥ 4) atoms with n electrons (extended hypervalent bonds; *m*c–*n*e ($m \geq 4$)).[11–14] The approximate molecular orbital model for *m*c–*n*e ($m \geq 4$) is also exhibited in Scheme 1a, exemplified by 4c–6e.

The main purpose of this chapter is to review the development of hypervalent chalcogen chemistry after the book of "*Chemistry of Hypervalent Compounds*" edited by Akiba (1999).[5] Although several types of compounds may belong to hypervalent ions or molecules by the definition,[3a] such hypervalent chalcogen compounds (E = S, Se, and Te) will be mainly discussed here that contain σ-type linear bonds.[15]

10.3.2 Bond Distances in Hypervalent Region

What is the region of bond distances for hypervalent bonds of chalcogens? Bond orders of hypervalent 3c–4e are typically around 0.5. A bond distance with a bond order of 0.5 is predicted to be 0.18 Å longer than that with a bond order of 1.0.[16]

The O–S–X 3c–4e type interactions are summarized by Kucsman and Kapovits.[17] They concluded that the S–O distance of 1.65–2.25 Å belonged to the hypervalent region, with a covalent S–O single bond region of 1.56–1.65 Å and an S···O nonbonded interaction region of 2.03–3.25 Å, where 3.25 Å[†] corresponds to the sum of van der Waals radii of S and O. du Mont *et al.* proposed that the Se–I distance of 2.60–3.00 Å was the typical 3c–4e region, with a predominantly covalent region of less than 2.60 Å and a secondary bond

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[†] The distance is 3.32 Å, if the van der Waals radii proposed by Bondi[29] are used.

region of about 3.00–3.90 Å, where 3.90 Å corresponded to the sum of van der Waals radii of Se and I.[15e] Therefore, typical 3c–4e regions must be shorter than the sum of van der Waals radii minus *ca.* 1.0 Å. The shorter limits of hypervalent regions are sometimes very close to the corresponding typical single bond distances since some bond orders of 3c–4e are very close to 1.0.[18–20] The hypervalent regions are supported by the I–I distances. The primary I–I bond region is 2.67–2.92 Å, which contains the hypervalent region.[15f] The legion is also shorter than the sum of van der Waals radii by *ca.* 1.0 Å.

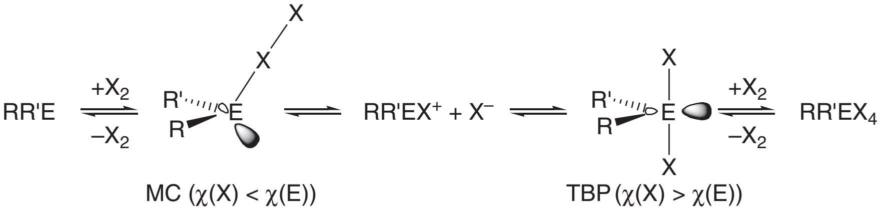
10.3.3 Factors to Stabilize Hypervalent Bonds

TBP of $RR'E \cdot X_2$ (and/or $R_2E \cdot X_2$) will be in equilibrium with molecular complexes (MC), together with the components, in solutions (Scheme 2).[20–22] Both X–E–X and E–X–X bonds are hypervalent 3c–4e.[15e,20] According to the *N–X–L* notation, proposed by Martin,[23] the hypervalent atoms in X–E–X (TBP) and E–X–X (MC) are represented by 10–E–4 and 10–X–2, respectively. The notation will be employed in this chapter.

A factor to determine the structure of $R_2E \cdot X_2$ is the magnitude of charge-transfer (CT) from $n(E)$ to $\sigma^*(X–X)$, which can be estimated by χ of elements. Table 1 shows χ of O, S, Se, and Te.[24] TBP of $R_2E \cdot X_2$ is formed if $\chi(X)$ is larger than $\chi(E)$, while MC will form when $\chi(X)$ is less than $\chi(E)$ (general rule).[21,25] This generalization explains most of the observed structures for R of usual organic groups. However, the electronegativity of E in R_2E will be modified by the electronic property of R: the effective electronegativity (χ^{eff}) of all atoms in a molecule must be equal.[26] The structure of R also affects strongly on the electronic property of R_2E, especially when R is stabilized by the cyclic 6π system:[27,28] $\chi^{eff}(E)$ will be much affected in such a case.

TBP are four-coordinated, whereas MC are three. Therefore, the bulkiness around E will be more severe for TBP than for MC. The increased bulkiness around E prefers MC to TBP.[21b–e] Namely, it is possible to prepare hypervalent chalcogen compounds other than those predicted from the general rule based on χ, by modulating electronic and/or steric conditions around chalcogens in organic chalcogen compounds.

Table 1 shows covalent radii (r_{co})[16a] and van der Waals radii (r_{vdW})[29] for O, S, Se, and Te. Differences between r_{co}(Se) and r_{co}(S) (0.13 Å) and between



Scheme 2 *Equilibrium between $RR'E \cdot X_2$ (TBP) and $RR'E \cdot X_2$ (MC), together with the components, in solution*

Table 1 *Electronegativity, covalent and van der Waals radii of group 16 elements, together with outermost maximum values and energies of s- and p-atomic orbitals*

	O	*S*	*Se*	*Te*
χ^a	3.50	2.44	2.48	2.01
r_{co}/Å	0.66	1.04	1.17	1.37
r_{vdW}/Å	1.52	1.80	1.90	2.06
$r_{max}(s)^b$/Å	0.4629	0.7491	0.8107	0.9660
$r_{max}(p)^b$/Å	0.4410	0.8551	0.9647	1.1558
$E(s)^b$/eV	−34.081	−24.146	−23.478	−20.391
$E(p)^b$/eV	−16.759	−11.586	−10.653	−9.515

[a] Ref. 24; χ(F) = 4.10, χ(Cl) = 2.83, χ(Br) = 2.74 and χ(I) = 2.21. [b] Ref. 31.

r_{co}(Te) and r_{co}(Se) (0.20 Å) are much smaller than that between r_{co}(S) and r_{co}(O) (0.38 Å). The weaker shielding effect by *d*-electrons, relative to that of *s*- and *p*-electrons, acts on Se and Te and the relativistic term becomes important in Te.[30,31] The resulting values of r_{co} essentially control the bond distances. Table 1 also contains the expectation values at the outermost maximum of the radial functions (r_{max}) and the energies for *s*- and *p*-atomic orbitals (*E*(*s*) and *E*(*p*), respectively).[31] Since $r_{max}(p)$ is larger than $r_{max}(s)$ for each of S, Se, and Te and *E*(*p*) of S, Se, and Te are much higher relative to others, *p*-atomic orbitals are mainly utilized for the bond formation of S, Se, and Te and the hybridization is not important for the atoms, in contrast to the case of O.

The crystal packing effect sometimes plays a crucial role to determine the structure in crystals. The structure of the bromine adduct of selenanthrene (**1**) (**1** · Br_2) is TBP in crystals,[14] whereas it is predicted to be MC in solutions, based on NMR.[21b] That of the tetrabromide (**1** · Br_4) is TBP for one $SeBr_2$ moiety and MC for another in crystals (TBP, MC).[14] The strong electron withdrawing ability of the $SeBr_2$ (TBP) group, together with the bulkiness, must prevent the formation of TBP for the second $SeBr_2$ group. 1-Selena-4-oxane (**2**) shows a similar crystal packing effect: **2** · ICl is MC in crystals[32] but they are mixtures of **2** · Cl_2 (TBP) and **2** · I_2 (MC) in solutions.[20] Figure 1 shows the structures of **1** · Br_2 and **1** · Br_4, where those for **1** · Br_2 (MC) are drawn based on quantum chemical (QC) calculations.

10.3.4 Hypervalent Chalcogen Compounds

10.3.4.1 10–E–3 (T-shaped)

One of the ideas to prepare T-shaped 10–E–3[5,15a] is to remove a ligand on E of 10–E–4. In this case, a pair of electrons remains on E, together with a negative charge. The negative charge is neutralized by a suitable counter cation in **3**[33] and by the pyridinium groups in **4**.[34] Since the counter ion is an anion in **5**, a formal charge of +1 develops at the central atom E.[35] Therefore, E in **5** would

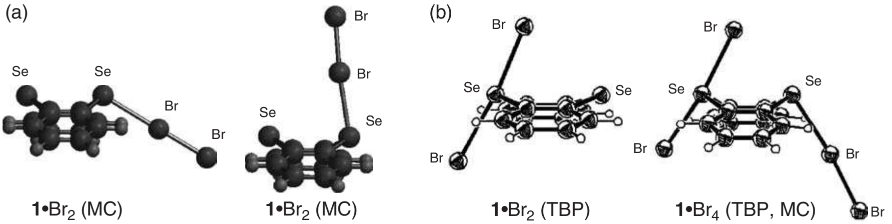
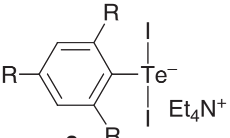


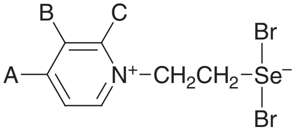
Figure 1 *Structures of* **1** · *Br_2 and* **1** · *Br_4; (a) optimized structures predicted in solutions and (b) observed ones in crystals*

be classified as 8–E–3 (onium ions) if the formal charge is really on E. However, they should be 10–E–3 if two lone pairs remain on E with the positive charge spread over the whole molecule. The 10–E–3 nature of **5** would be supported by ∠NEN of 162°–169° and by *r*(E, X) of the typical hypervalent bond region. **5** (E = Te) is also detected by NMR.



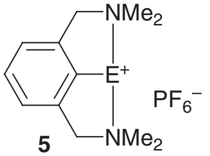
3

R	*r*(Te, I)/Å
H	2.945 2.963
i-Pr	2.959(1)



4

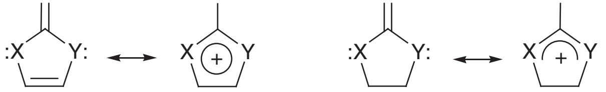
A	B	C	*r*(Se, Br)/Å
H	H	H	2.499(3)
H	Br	H	2.463(3)
CN	H	H	2.718(5)
H	$(CH)_4$		2.541(3)



5

E	*r*(E, N)/Å	∠NEN/°
S	2.063(1)	168.54(9)
Se	2.154(7) 2.180(7)	161.9(3)
Te	δ(Te) 1950 in CD_3CN	

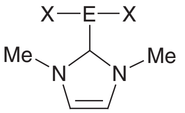
Unsaturated five membered 2-chalcogenons with two heteroatoms at 1,3-positions (**6**) will show versatile reactivities with acceptors, since E in **6** must be very electron rich with the formation of a stable cyclic 6π electron system (**6A**).[27,28] A saturated ring system **7** is expected to show similar trend due to the stabilization by the allylic X–C–Y framework with 4π electrons (**7A**). Arduengo reported the TBP formation of 1,3-dimethyl-4-imidazoline-2-thione (**8**), a typical example of **6** (X = Y = NMe and E = S), with bromine (**8** · Br_2), together with the reactions.[36]



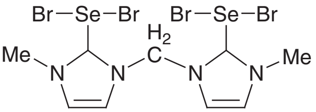
6 **6A** **7** **7A**

Devillanova and co-workers studied the structures of halogen adducts of 1,3-dimethyl-4-imidazoline-2-selone (**9**) and the methano- and ethano-bridged derivatives (**10** and **11**, respectively).[37] **9** · Br_2 is TBP and **10** · $2Br_2$ and **11** · $2Br_2$ are (TBP, TBP). While **10** · $2I_2$ is (MC, MC), **9** · I_2 is TBP and **11** · $2I_2$ is (TBP, TBP).[37a] Figure 2 shows the structures of **9** · I_2, **10** · $2I_2$, and **11** · $2I_2$.

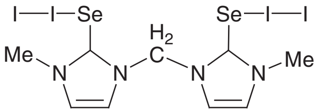
The TBP structures of **9** · I_2 and **11** · $2I_2$ are noteworthy, since iodine adducts of selenides are predicted to be MC based on the general rule (χ(Se) (=2.48) > χ(I) (=2.21)). This must be the reflection of the high ability of the imidazoline ring to donate electrons to Se by the formation of the stable cyclic 6π system. It will decrease χ^{eff} of Se in **9** and **11** to give TBP with iodine. Since the electronic conditions in **10** must not be so different from those in **9** and **11**, they should not be responsible for the different structures of the adducts. This working hypothesis is supported by DFT calculations.[38] Therefore, the crystal packing effect must play a crucial role in determining the structures of the iodine adducts of **9–11**. The reactions are followed by spectroscopic and conductometric methods.[37]



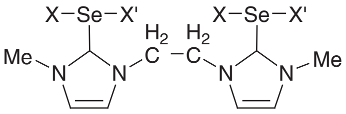
8•Br_2 (E = S)
9•X_2 (E = Se; X = Br, I)



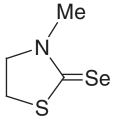
10•$2Br_2$



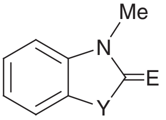
10•$2I_2$



11•2XX' (XX' = Br_2, I_2, IBr)



12



	Y	E
13	S	Se
14	NMe	S
15	NMe	Se

The structure of **11** · 2IBr is (TBP, TBP), which represents the first example of a T-shaped adduct of a selenium compound with IBr.[39a] The anomalous bond distances in **11** · 2IBr (Se–Br (Å)/Se–I (Å) 2.897(2)/2.606(2) and 2.766(2)/2.629(2) for the two Br–Se–I units, respectively) have been explained on the basis of different polarities of the two bonds and on the basis of the involvement of Br in intramolecular hydrogen bondings. Reactions and/or structures are similarly investigated for *N*-methylthiazolidine-2(3H)-selone (**12**), *N*-methylbenzothiazole-2(3H)-selone (**13**), *N,N*′-dimethylbenzoimidazole-2(3H)-thione (**14**), and -selone (**15**) with bromine,[39b,c] and more recently, for **14** and **15** with IBr.[39d] In this last case, the prediction of a 10–I–2 adduct for **14** · IBr and a 10–Se–3 adduct for **15** · IBr from the DFT calculations has been experimentally confirmed.[39d]

Trialkylphosphane chalcogenides, RR′R″P=E (**16**: E = S and Se), contain the ylide nature of the RR′R″P^+–E^- form (**16A**), similarly to the case of **6** and **7**.

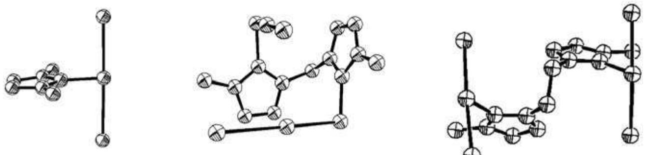
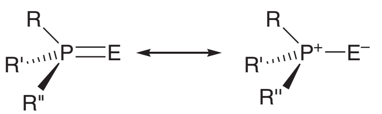
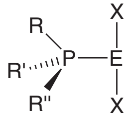

9•I_2 **10**•$2I_2$ **11**•$2I_2$

Figure 2 *Structures of* **9** · I_2, **10** · $2I_2$, *and* **11** · $2I_2$

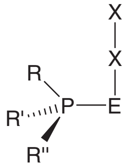
Therefore, the donor ability of E in **16** must be larger than that in usual selenides. T-shaped structures **17** are observed for the bromine adducts of **16** (E = Se), where R, R′, and R″ are NMe_2, C_6H_{11}, *i*-Pr, and *t*-Bu.[40,41] **18** (MC) are reported for $\mathbf{16}\cdot I_2$ (E = Se).[42] Some I–I bonds in $\mathbf{16}\cdot I_2$ (E = Se) are elongated.[15e,f] The secondary bonds play an important role for the elongation. The results show that the structures of $\mathbf{16}\cdot X_2$ (E = Se, X = Br and I) are essentially the same as those predicted from the general rule, while **16A** contributes to **16**.



16 **16A**

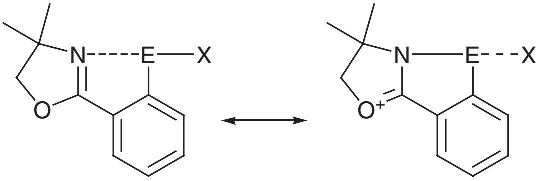


17 (E = Se, X = Br)



18 (E = Se, X = I)

T-shaped Y···E–X 3c–4e interactions occur by the attack of Y at E of polar E–X bonds. Such interactions are usually highly unsymmetric.[17,43] However, the N–E–X bonds are close to symmetric in some cases. Singh and co-workers reported such interactions. Table 2 shows the bond distances and the differences from the sum of covalent radii in **19** (E = Se), together with the angles.[44] The N–E–X (E = Se) bonds are rather typical 3c–4e for X of halogens, especially for X = I. The Y–E···X character shown in **19A** contributes to the interactions in substantial amount, although the distances are affected by the nature of the Se–X bonds. Similar interactions are reported.[45–48]



19 **19A**

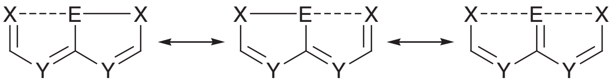
If intramolecular interactions occur in the both sides of E, the interactions lead to hypervalent X···E···X 3c–4e. Such interactions are observed typically in the framework of **20**. The X···E···X bond is recognized to be σ-type 3c–4e, although it is also stabilized by the 10π electron system. The system containing the basic structure of **20** is widely studied.[5,49–51] The structure of the C_{2v}

Table 2 *Observed r(Se, X), r(Se, N) and ∠NSeX values in* **19** *(E = Se)*

X	*r(Se, X)/Å*	*Δr/Å*[a]	*r(Se, N)/Å*	*Δr/Å*[b]	*∠NSeX/°*
Cl	2.482(8)	0.32	2.052(2)	0.18	175.06(7)
Br	2.6318(7)	0.32	2.063(3)	0.19	176.14(10)
I	2.7773(7)	0.28	2.133(4)	0.26	177.69(12)
CH_2Ph	1.966(3)	0.02	2.798(3)	0.93	175.4(3)

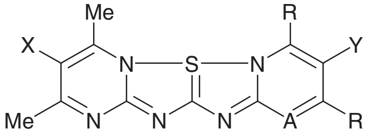
[a] $r(\mathrm{Se, X}) - [r_{\mathrm{co}}(\mathrm{Se}) + r_{\mathrm{co}}(\mathrm{X})]$. [b] $r(\mathrm{Se, N}) - [r_{\mathrm{co}}(\mathrm{Se}) + r_{\mathrm{co}}(\mathrm{N})]$.

symmetry is shown to be more stable than C_s for **20** with X = E = S and Y = CH by the MP4 calculations.[51b]



20

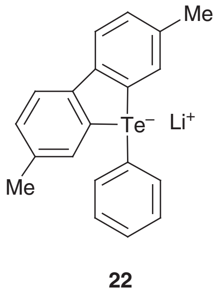
(X, Y, E) = (N, N, Se), (N, N, S), (S, C, S), (Se, N, S)



21 (A = N or CH)

The nature of the hypervalent N···S···N bonds is investigated thoroughly by Akiba and co-workers, employing **21** and the related compounds, through evaluating the dissociation energies of the N–S bonds, together with the structures.[5,49]

Hypervalent ate complexes of T-shaped 10–E–3 are presumptive intermediates in metal–halogen, metal–tellurium, and related exchange reactions. Reich and co-workers further investigated, employing *o*,*o*′-biphenyldiyl and *m*-terphenyl groups for Ph_2E with PhLi.[52] The ate complex **22** is formed predominantly in THF with excess PhLi at −112°C ($\Delta H = -10.4 \pm 0.4$ kcal mol^{-1}, $\Delta S = -36 \pm 1.6$ eu for K_{ate}). The direct Li/S exchange process is observed for **23** (E = S) in THF-Et_2O (80:20) ($\Delta H^{\ddagger} = 9.3 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9.8 \pm 2$ eu for k_d). The ate complex **24** (R = H) is detected at −135°C in THF-Et_2O (80:20). The equilibrium between **24** (R = H) and **23** (E = Se) is examined ($\Delta H = -3.1 \pm 0.3$ kcal mol^{-1}, $\Delta S = -16.7 \pm 1$ eu for K_{ate}). Contribution of a strong contact ion pair is postulated to explain the degenerate exchange related to **23** (E = Se), based on the examination of **24** (R = *i*-Pr).



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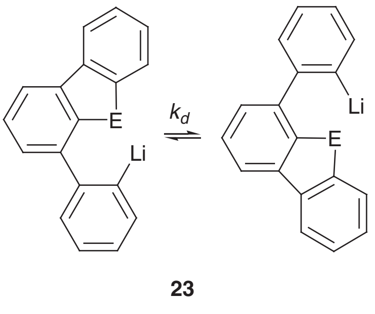

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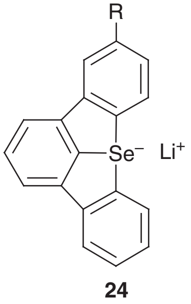
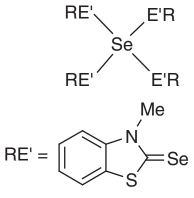


24

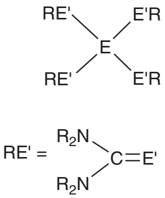
10.3.4.2 10–E–4

10.3.4.2.1 10–E–4 (X4 and CX3: X = Heteroatoms)

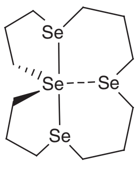
The structures and reactions have been summarized for EX_4 (X = halogens and O).[10a,b] The structures of EX_4 (X = S, Se, and Te) are also determined for **25–29** and the related compounds.[10b,53] The hypervalent nature of the E′–E–E′ bonds has been paid attention. Compounds R–EX_3 are also well known.[7c,54]



25



26
(E, E') = (Se, Se), (Te, S), (Te, Se)



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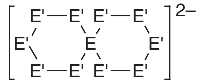
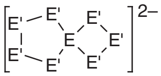


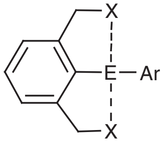
28
(E, E') = (Se, Se), (Te, S), (Te, Se)



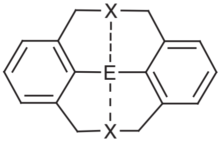
29
(E, E') = (Te, Te)

10.3.4.2.2 10–E–4 (C2X2: X = Heteroatoms)

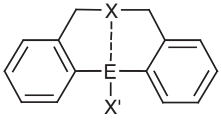
Hypervalent 10–E–4 (C2X2) compounds are widely studied.[10a,b] Furukawa and co-workers studied the 10–E–4 (C2X2) of the types **30** and **31**, together with the related compounds, such as **32**.[10b,15d,35,55] The interactions are established by the X-ray analysis and NMR.[15d,35] Adducts **33** and **34** are also detected by NMR. If the X and Te atoms in **33** and **34** align linearly, the multi-center bonds are expected to form the extended hypervalent bonds, which will be discussed later.



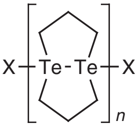
30 (E = S, Se, Te)
(X = EAr, E(O)Ar, NR_2)



31 (E = S, Se, Te)
(X = EAr, E(O)Ar, NR_2)



32 (E = S, Se, Te)
(X = EAr, E(O)Ar, NR_2)



33 (n = 1)
34 (n = 2)

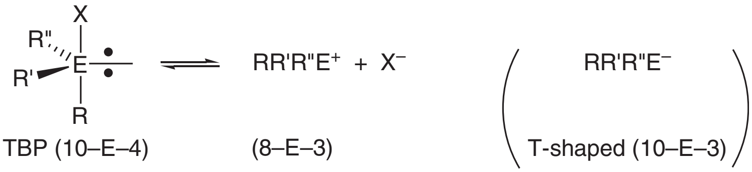
Hypervalent O–Te–O oligomers are also investigated, recently.[56]

10.3.4.2.3 10–E–4 (C3X: X = Heteroatoms)

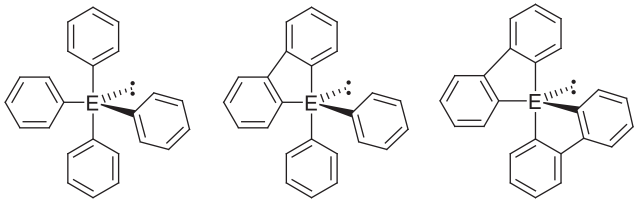
The hypervalent 10–E–4 (C3X) compounds are reported.[7c,10b,57] RR′R″EX will be in equilibrium with RR′R″E^+ (8–E–3) and X^- in solutions (Scheme 3). The related ate complexes of the RR′R″E^- type (10–E–3: T-shaped) are discussed in Section 10.3.4.1 (*cf.* **22** and **24**).

10.3.4.2.4 10–E–4 (C4)

Hypervalent compounds of **35–43**, which belong to 10–E–4 (C4) are also well investigated by the X-ray analysis and NMR. The kinetics, reactivity, and the dynamic properties of the compounds are studied. The results are summarized in Scheme 4.[10b,15b]



Scheme 3 *Equilibrium of $RR'R''EX$ (10–E–4) with $RR'R''E^+$ (8–E–3) and X^-, whereas $RR'R''E^-$ would T-shaped (10–E–3), as shown by* **22** *and* **24**



E /			
S	**35**: *a*, *b*	**36**: *a*	**37**: *c*, *d*, *e*
Se	**38**: *a*, *b*	**39**: *a*	**40**: *c*, *d*, *f*
Te	**41**: *d*, *e*, *f*	**42**: *d*	**43**: *c*, *d*, *e*, *f*

a: Detected. *b*: Kinetics of ligand coupling reactions. *c*: Reactivity. *d*: Isolation. *e*: X-ray analysis. *f*: DNMR for pseudorotation.

Scheme 4 *Hypervalent Ar_4E: How investigated?*

10.3.4.3 10–E–5 and 12–E–5

Akiba and co-workers prepared both Ph_5Te^+ of 10–Te–5 (C5) and Ph_5Te^- of 12–Te–5 (C5) ions, recently.

A stable nonclassical onium Ph_5Te^+ cation was prepared by removing X^- from Ph_5TeX (X = Cl and Br). The cation has no interaction with the counter anion in Ph_5Te^+ $(C_6F_5)_4B^-$.[9a] Figure 3 shows the structure of Ph_5Te^+. The geometry is SP with one apical phenyl group and four propeller-like basal phenyl groups. The basal Te–C bonds (2.195(5), 2.208(5), 2.196(5), and 2.205(5) Å) are longer than that of apical one (2.101(5) Å). The counter anions affect little on the structure.[9] The cation is in rapid Berry pseudo-rotation containing SP and TBP structures in solution.[9b]

The Ph_5Te^- anion is prepared in the reaction of $TeCl_4$ or $TeBr_4$ with five equivalents of PhLi at low temperature.[58–60] Ph_5TeLi reacts with halogen sources, such as SO_2Cl_2 and Br_2, to give Ph_5TeCl and Ph_5TeBr, respectively (Scheme 5). Ph_5TeF is also prepared in the reaction of Ph_5TeBr with KF.

A noncyclic sulfuranyl dioxide anion, $(CF_3)_3SO_2^-$ (**44**) of 10–S–5, was prepared in the reaction of $PhOSO_2CF_3$ with CF_3SiMe_3 and F^-.[61] The anion is analogous to the intermediate postulated for an associative *C*-nucleophilic attack at the sulfonyl sulfur.

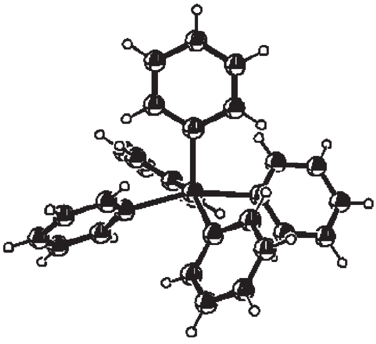
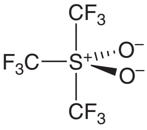


Figure 3 *Structure of Ph_5Te^+*

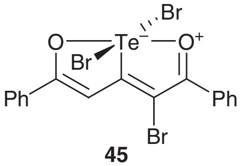
$$TeCl_4 \textit{ or } TeBr_4 \quad + \quad 5PhLi \longrightarrow Ph_5Te^-Li^+ \xrightarrow{X_2} Ph_5TeX$$

Scheme 5 *Formation of $Ph_5Te^-Li^+$, followed by the reaction with X_2*

Compounds corresponding to 12–Te–5 (**45**) are also investigated.[10b,15a]



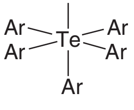
44



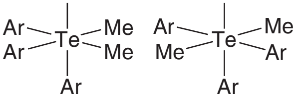
45

10.3.4.4 12–E–6

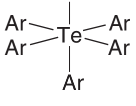
Various $Ar_{6-n}R_nTe$ ($n = 0$, 1, and 2) of 12–Te–6 (C6) are prepared *via* Ar_5TeX (X = Cl and Br) under suitable conditions.[9a,58,62] Lots of reactions are examined; reductive cleavage of $Ar_{6-n}Me_nTe$ ($n = 0$ or 2) with KC_8, nucleophilic substitution of Ar_5TeX, Ar_4MeTeX (X = Cl, Br, or OTf), or those shown in Scheme 5. Typical compounds prepared are shown below.



Ar: p-$CF_3C_6H_4$, C_6H_5, p-MeC_6H_4, p-BrC_6H_4



Ar: p-$CF_3C_6H_4$ (*cis* & *trans*), C_6H_5 (*trans*), p-MeC_6H_4 (*trans*)



R = p-$MeOC_6H_4$, $PhSCH_2$, vinyl or *n*-Bu; X = F, Cl, Br for Ar = p-$CF_3C_6H_4$, etc.

Changes from *cis*- to *trans*-isomers of some 12–S–6 (C2F4) were reported.[63]

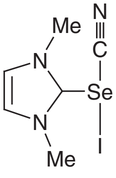
10.3.4.5 Higher Coordinated Species

Seven coordinated Te species, such as TeF_7^-,[8] $MeOTeF_6^-$,[64a] $(MeO)_2TeF_5^-$,[64a] $(R_2NCS_2)_3TeX$,[64b] and $(R_2NCS_2)_3TeR$,[64c] are reported and the structures of eight-coordinated Te dianions such as $TeF_8{}^{2-}$ and $(R_2NCS_2)_4Te^{2-}$ are also determined.[8,65] The bonding scheme of these species is of interest.

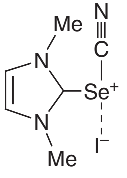
10.3.5 Weak Hypervalent Interactions

Weak hypervalent G···Se–X 3c–4e type interactions[17,43,66] are closely related to T-shaped 3c–4e interactions and often control the fine structures of the compounds.

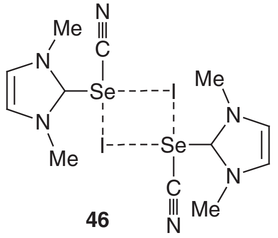
Devillanova and co-workers investigated the ICN adduct of **9** (**9**·ICN).[67] The structure is T-shaped with $r(\mathrm{Se, C_{CN}}) = 1.885(5)$ Å, $r(\mathrm{Se, I}) = 3.300(1)$ Å, and $\angle \mathrm{C_{CN}SeI} = 174.8(2)°$. **9**·ICN forms a dimer **46**. Since r(Se, I) is longer than the sum of the covalent radii by 0.88 Å, the ionic nature of the $\mathrm{I^-\cdots Se^+}$ bond was debated, in connection to the structure of **46**.



9•ICN

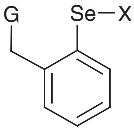


9•CN$^+$---I$^-$

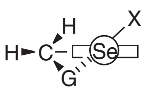


46

Tomoda and co-workers investigated weak G···Se–X interactions in benzene system **47**, where G = RR′N, RO, and halogens bonded to benzyl carbon, employing NMR and QC calculations.[68] Conformer **47A** contributes to the G···Se–X interaction, which is stabilized by the $n(\mathrm{G})\cdots\sigma^*(\mathrm{Se–X})$ interaction. The contribution of the electrostatic factor increases if the polarity of Se–X becomes higher. That for $2\text{-}\mathrm{CHOC_6H_4SeX}$ is analyzed similarly. The magnitudes of the G···Se–X interactions are in an order of G = N > O > F.[68a–f] However, they are concluded to be F > Cl > Br for G of halogens.[68g] The G···Se distances in **47A** are evaluated to be shorter than the sum of van der Waals radii for halogens by 0.58 (G = F), 0.17 (G = Cl), and 0.10 Å (G = Br) when X = CN, although the values depend on X.

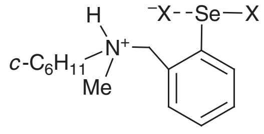


47



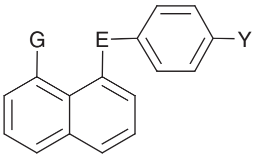
47A

(G=*i*-PrMeN, HO, MeO, *i*-PrO, F,Cl, and Br)
(X=CN, Cl, Br, SeAr (diselenide), Me, etc.)

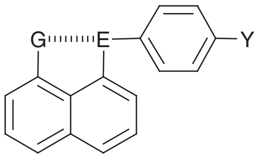


48 (X = Cl, Br)

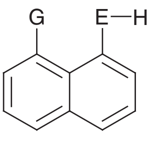
The Se–X bonds (X=Cl and Br) in **48** are examined by stabilizing through the coordination of X^-, in which the negative charge brought by X^- is neutralized by the ammonium group.[69]



49 (E = S)
50 (E = Se)
51 (E = Te)



49A (E = S)
50A (E = Se)
51A (E = Te)

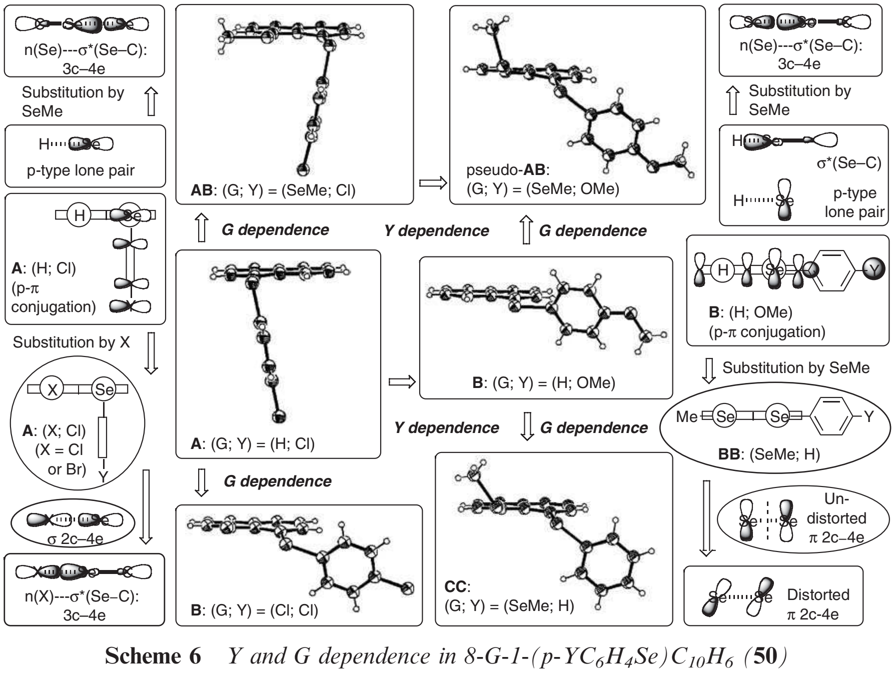


52 (E = Se)

G = H, F, Cl, Br, EMe, EAr (E = S, Se, Te)
Y = H, OMe, Me, Cl, Br, COOEt (or COOMe), NO_2

Naphthalene 1,8-positions serve as a good system to study nonbonded interactions.[12,70–73] Weak hypervalent $n(G)\cdots\sigma^*(E–C)$ 3c–4e type interactions are examined for 8-G-1-(ArE)$C_{10}H_6$ (**49–51** (Ar = *p*-YC_6H_4)) and 8-G-1-(HSe)$C_{10}H_6$ (**52**), to elucidate the factors to determine the structures.[70,71] The structures are well explained by three types, type **A** (**A**), type **B** (**B**), and type **C** (**C**),[12,70] where the E–C_{Ar} (or E–H) bond is almost perpendicular to the naphthyl plane in **A**, it is located on the plane in **B**, and it is intermediate between **A** and **B** in **C** (see the structures in Scheme 6).

Scheme 6 explains the structural change, exemplified by **50** with (G; Y) = (H, Cl, or SeMe; Cl, H, or OMe). The **A** structure of **50** (H; Cl) changes to **B** by replacing Y of Cl with OMe (Y dependence), which is affected by the n_p(E)-π(Ar) and n_p(E)-π(Nap) interactions: the structure is **A** when the former is stronger then the latter, whereas it will be **B** if not. Substitution of G of H by Cl



Scheme 6 *Y and G dependence in 8-G-1-(p-YC_6H_4Se)$C_{10}H_6$ (**50**)*

in **50** (H; Cl) also changes **A** to **B**. The change is called G dependence. The hypervalent n_p(G)···σ*(Se–C) 3c–4e interaction controls the G dependence. On the other hand, substitution of G of H in **50** (H; Cl) by SeMe gives a pure **AB** pairing (**AB**) with **A** for SeC_6H_4Cl-*p*. Indeed, the structure around SeC_6H_4Cl-*p* in **50** (MeSe; Cl) seems unchanged, but the n_p(Se)···σ*(Se–C) 3c–4e interaction must operate to stabilize it. The structure of **50** (SeMe; OMe) is pseudo **AB** with pseudo **B** for SeAn-*p*, which must be the reflection of **B** of **50** (H; OMe). The structure of **50** (SeMe; H) is **CC**, which corresponds to distorted **BB**. The disappearance of a nodal plane in **CC** must stabilize **CC**,[72] where the nodal plane appears clearly in π*(Se–Se) of **BB**. The factor is called Möbius stabilization although the π system is not cyclic.[72] If one examines the structures of **50** (SeMe; Y) carefully, one realizes a successive change on passing from Y of Cl to H and then to OMe.

The discussion is also applicable for **49** and **51**. Structures are **A** for Y of acceptors, whereas they are **B** with Y of donors (Y dependence), if G = H.[70] When G of H is replaced by Cl or Br, **A** of **49** and **51** changes to **B** (G dependence).

Table 3 shows the observed G···Se distances in **50** (G; OMe) and the calculated values in **50** (G; H) and **52** (G), together with the differences from the sum of van der Waals radii of Se and G. Table 3 also contains the calculated energy differences between **B** and **A** for **50** (G; H) and **52** (G). The results show that the magnitudes of hypervalent G···Se–C 3c–4e type interactions are in an order of $G = F < Cl \leq Br$, in naphthalene system.[71] This order is just the opposite to that observed in **47** (G = halogens). The linear alignments of the three G···Se–X atoms, together with suitable G···Se distances, are required for the effective interactions. Such favorable conditions are easier to accomplish in **50**. The conditions must be more severe in **47** (G = halogens), especially for heavier halogens, due to their decreased basicity.[68g]

10.3.6 Extended Hypervalent Bonds; *m*c–*n*e (*m* ≥ 4)

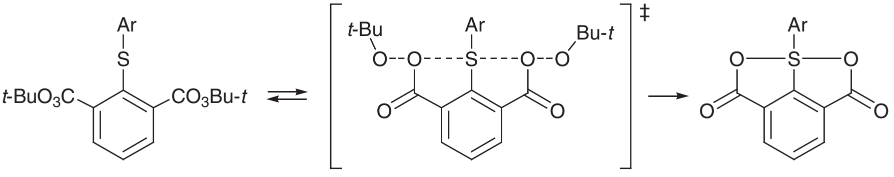
10.3.6.1 3c–4e to *m*c–*n*e (*m* ≥ 4)

If an interaction of the X···E–E 3c–4e type occurs in both sides of an E–E bond, the X···E–E···X interaction is expected to be symmetric or close to symmetric under suitable conditions. The interaction is no more treated as

Table 3 *Observed and calculated r(Se, G) and energy differences in* **50** *and* **52**[a]

Compd	**50** *(G, OMe)*		**50** *(G, H)*			**52** *(G)*		
G	*r(Se, G)*[b]	Δr^c	*r(Se, G)*[d]	Δr^c	ΔE^e	*r(Se, G)*[d]	Δr^c	ΔE^e
F	2.753(3)	0.62	2.7558	0.61	−10.5	2.7668	0.60	−8.4
Cl	3.005(1)	0.65	3.0427	0.61	−11.3	3.0475	0.60	−12.6
Br	3.103(3)[f]	0.65	3.1485	0.60	−11.0	3.1481	0.60	−12.9

[a] Distances in Å and ΔE in kJ mol^{-1}. [b] Observed. [c] Differences from the sum of van der Waals radii. [d] Calculated. [e] ΔE = E(**B**) − E(**A**). [f] Y = Cl.



53 **55** (TS) **54**

Scheme 7 *Facile thermal decomposition of* **53**, *via* **55** *(TS), with the simultaneous participation of the* $\sigma^*(O\text{–}O)\cdots n_p(S)\cdots\sigma^*(O\text{–}O)$ *5c–6e type*

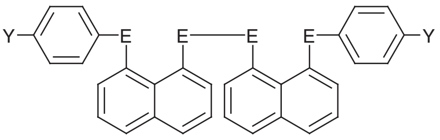
double 3c–4e. It must be analyzed by the 4c–6e model. Such σ-type linear interactions would extend over *m* atoms with *n*-electrons. Nakanishi called the hypervalent bonds higher than 3c–4e "extended hypervalent bonds; *m*c–*n*e ($m \geq 4$)".[12,13] If the extended hypervalent bonds are limited to the singlet state, $m < n < 2m$ (*n* being even) is required for *m*c–*n*e ($m \geq 4$).[14] This requirement is also satisfied in 3c–4e. Approximate molecular orbital model for *m*c–*n*e ($m \geq 4$) is shown in Scheme 1b, exemplified by 4c–6e.

Martin observed an extremely facile thermal decomposition of bisperester **53**, which gave **54** (Scheme 7).[74] The decomposition proceeds *via* a transition state **55**, with the simultaneous participation of the σ^*(O–O)---n_p(S)---σ^*(O–O) type.[74] The transition state can be draw by the 5c–6e interaction. Alvalez discussed the structure and the stability of Br_4^{2-}, together with neutral Br_4.[11a] The dianion could be analyzed by the 4c–6e model, if the four atoms align linearly with suitable distances. Farnham investigated the fluorine-bridged linear C–I···F···I–C interaction based on 5c–6e.[11b]

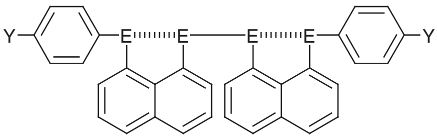
Extended hypervalent bonds containing chalcogens have been substantially discussed in the last decade, however.

10.3.6.2 4c–6e

Hypervalent *n*(E)---σ^*(E–E) 3c–4e interactions are expected to be much stronger than *n*(E)---σ^*(E–C) for E = S, Se, and Te, since σ^*(E–E) must work much more effectively as acceptors than σ^*(E–C). This idea led to design 4c–6e of four E atoms (E_4 4c–6e: E = Se and S) in naphthalene system.



56 (E = Se: Y = H, OMe, Me, Cl, Br, COOEt, NO_2)
58 (E = S: Y = H, OMe, NO_2)



56A, **58A**

Figure 4 shows the structures of *bis*[8-(phenylselanyl)naphthyl]-1,1′-diselenide (**56** (Y = H))[12a,b] and di(naphthyl)-1,1′-diselenide (**57**),[75] determined by the X-ray analysis. The structures of **56** and **57** are called linear and Z-shaped forms, respectively, here. The Se_4 atoms in **56** (Y = H) align linearly with ∠Se(3)Se(1)Se(2) = 177.10(5)°, ∠Se(1)Se(2)Se(4) = 170.45(5)°, *r*(Se(1), Se(3)) = 3.018(1) Å, and *r*(Se(2), Se(4)) = 3.087(1) Å. If the C–Se bonds

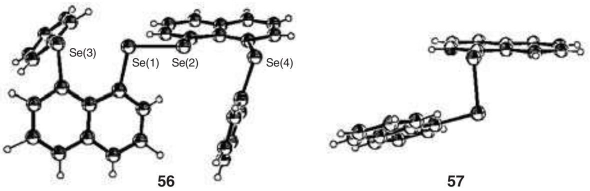


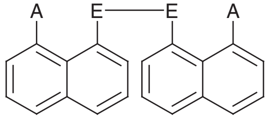
Figure 4 *Structures of* **56** *and* **57**

in **56** (Y = H) rotate freely, the Se_4 atoms must be the Z-shaped from. Such partial structure is observed in **57**,[75] although **57** does not contain arylselanyl groups at the 8,8′-positions. Those of *bis*[8-(phenylthio)naphthyl]-1,1′-disulfide and the derivatives (**58** (Y = H, OMe, and NO_2)) are also determined.[12c] They are very close to that of **56** (Y = H).

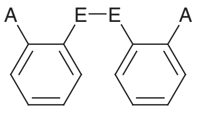
The driving force for the linear alignment of Se_4 in **56** and S_4 in **58** must be the energy lowering effect by the formation of the extended hypervalent $n_p(E) \cdots \sigma^*(E–E) \cdots n_p(E)$ 4c–6e (E = Se and S). The effect of S_4 4c–6e is not perturbed by the substituents (OMe and NO_2) at the phenyl *p,p′*-positions in **58**. The direction of CT of E_4 4c–6e (E = Se and S) is the $n_p(E) \rightarrow \sigma^*(E–E) \leftarrow n_p(E)$ type, which is just the opposite to the case of 3c–4e.

Models **a** and **b** are devised based on the structure of **56** and model **c** from **58** (Scheme 8). Magnitudes of CT are evaluated for models **a** and **c** by calculating the natural charges (*Qn*) for the components: $Qn(H_2Se_2)$ in model **a** amounts to -0.200 and $Qn(H_2S_2)$ in model **c** to -0.120. The values should be compared with $Qn(H_2S)$ of 0.821 in $H_2S \cdot Br_2$ (TB),[20] $Qn(H_2Se)$ of 0.920 in $H_2Se \cdot Br_2$ (TB),[20] and $Q(^2F)$ of 0.03 in the $[^1F–^2F–^3F]^-$ anion, where $Q(^2F)$ stands for the Mulliken charge of ^2F.[76]

The nature of $n_p(Se) \cdots \sigma^*(Se–Se) \cdots n_p(Se)$ 4c–6e is further investigated by examining the substituent effect of Y on δ(Se) in **56**.[77] Whereas a regular substituent effect (downfield shifts by Y of accepting groups) is observed for δ(Se) at the 8,8′-positions, an inverse substituent effect is observed for δ(Se) of the Se–Se atoms. Absolute shielding constants for Se in model **b**, calculated based on the gauge-independent atomic orbital (GIAO) method, demonstrate that the inverse effect is the results of the 4c–6e interaction, together with the normal effect from the p(Y)–π(C_6H_4)–p(Se) interaction.

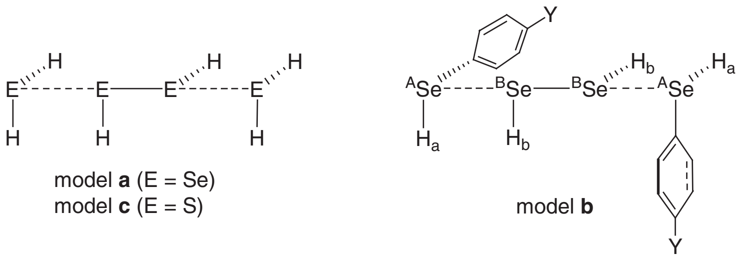


57 (E = Se; A = H), **59** (E = Se; A = SeMe)
60 (E = S; A = H), **61** (E = S; A = SMe)
66 (E = Se; A = NMe_2), **67** (E = Te; A = NMe_2)
68 (E = Te; A = H)



62 (E = Se; A = H), **63** (E = Se; A = SeMe)
64 (E = S; A = H), **65** (E = S; A = SMe)
69 (E = S; A = Cl or Br), **70** (E = Se or Te; A = CH_2NMe_2)
71 (E = S, Se, or Te; A = 4,4-dimethyl-2-oxazolinyl)

How do E_4 4c–6e stabilize the linear forms? Energies of linear and Z-shaped forms are calculated for naphthalene and benzene systems. The results are



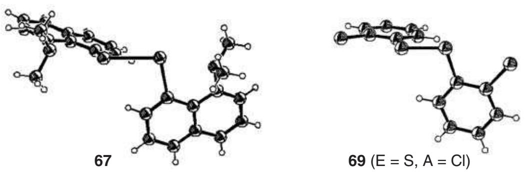
Scheme 8 *Models* **a–c**, *derived from* **56** *and* **58**

shown in Table 4.[78] While the linear form of **57** is evaluated to be less stable than the Z-shaped by 15 kJ mol^{-1}, the linear form of **59**[79] is more stable than the Z-shaped by 29 kJ mol^{-1}. Therefore, Se_4 4c–6e is estimated to stabilize the linear form by 44 kJ mol^{-1} in naphthalene system ($\Delta\Delta E$ in Table 4). The effect of S_4 4c–6e in **61** is evaluated to be 21 kJ mol^{-1}, relative to that of **60**: the value is about half of that of Se_4 4c–6e in **59**. The effects of Se_4 4c–6e in **63** is 23 kJ mol^{-1} (relative to **62**) and S_4 4c–6e in **65** 11 kJ mol^{-1} (relative to **64**). The values in the benzene system are about half of the corresponding values of the naphthalene system.

Table 4 *Energies of linear and Z-shaped conformers in naphthalene and benzene systems*[a]

Compd	ΔE^{b}/kJ mol^{-1}	$\Delta\Delta E^{c}$/kJ mol^{-1}	*Compd*	ΔE^{b}/kJ mol^{-1}	$\Delta\Delta E^{c}$/kJ mol^{-1}
57	15.0	as 0.0	**62**	8.1	as 0.0
59	−28.9	−43.9	**63**	−14.7	−22.8
60	14.7	as 0.0	**64**	7.1	as 0.0
61	−6.6	−21.3	**65**	−3.7	−10.8

[a] The 6-311+G(d) basis sets being employed for S and Se and 6-31G(d) for H and C at the B3LYP level. [b] *E*(Linear) − *E*(Z-shaped). [c] ΔE(A = A) − ΔE(A = H).



67

69 (E = S, A = Cl)

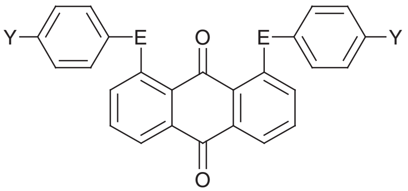
Figure 5 *Structures of* **67** *and* **69** *(E = S, A = Cl)*

Four Se_2N_2 atoms in **66** and four Te_2N_2 atoms in **67**[78] align linearly, whereas the structure of **57** is Z-shaped (Figure 4) and that of **68** is very close to that of **57**. The linear alignments of four E_2A_2 atoms are also reported, containing those of **69–71**.[45b,80,81] Figure 5 shows the structures of **67**[45b] and **69** (E = S, A

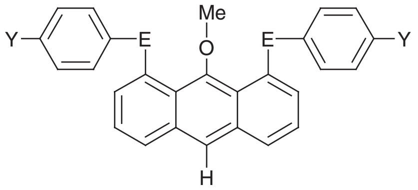
= Cl).[80] The linear alignments of E_2A_2 could be analyzed by the 4c–6e model, based on the results shown in Table 4.

10.3.6.3 5c–6e

The structures are determined for 1,8-*bis*(arylselanyl)anthraquinones (**72**) and 9-(methoxy)-1,8-*bis*(phenylselanyl)anthracene (**73**) by the X-ray analysis, together with those of 1,8-*bis*(arylselanyl)anthracenes (**74**) for convenience of comparison.[13a,b]



72 (E = Se; Y = H, Cl), **75** (E = S; Y = H, Cl)



73 (E = Se; Y = H), **76** (E = S; Y = H)

Five C_i–Se···O···Se–C_i atoms in **72** and **73** align linearly, whereas five C_i–Se···H···Se–C_i atoms in **74** never align linearly. Figure 6 shows the structures of **73** (Y = H) and **74** (Y = H). The linear alignment is analyzed by the 5c–6e model with the $\sigma^*(C_i\text{–Se})\cdots n_p(O)\cdots\sigma^*(\text{Se–}C_i)$ interaction.[13a,b] The structures of sulfur analogs, **75–77**, are very close to those of **72–74**, respectively. QC calculations well reproduce the observed structures. The energy lowering effect by the C_2S_2O 5c–6e in **75** (Y = H) is about two thirds of that of C_2Se_2O 5c–6e in **72** (Y = H), for instance.[13c]

10.3.6.4 Higher Extended Hypervalent Bonds

The linear alignments of six Se_2Br_4 and seven Se_2Br_5 atoms were detected in $\mathbf{1}_2\cdot Br_4$[82] and $\mathbf{1}_2\cdot Br_6$, respectively, where **1** stands for selenanthrene.[14] Figure 7 shows the structures of $\mathbf{1}_2\cdot Br_4$ and $\mathbf{1}_2\cdot Br_6$. $\mathbf{1}_2\cdot Br_4$ has the symmetry close to C_{2h} with r(Br(1), Br(1)*) = 3.279(1) Å and ∠Se(1)Br(1)Br(1)* = 175.50(3)°. The seven Se_2Br_5 atoms in $\mathbf{1}_2\cdot Br_6$ align almost linearly with ∠Br(1)Se(1)Br(2) = 169.79(6)°, ∠Br(2)Br(3)Br(4) = 162.90(9)°, ∠Br(3)Br(4)Se(2) = 149.85(8)°, r(Br(1), Se(1)) = 3.196(2) Å, r(Se(1), Br(2)) = 2.640(2) Å, and r(Br(3), Br(4)) = 3.161(2) Å.

The linear bond in $\mathbf{1}_2\cdot Br_4$ is analyzed by the 6c–8e model. Linear Br–Se–Br 3c–4e bonds in $\mathbf{1}\cdot Br_2$ interact mutually to give $\mathbf{1}_2\cdot Br_4$, which contains the linear alignment of the six Se_2Br_4 atoms. The linear bond in $\mathbf{1}_2\cdot Br_6$ is analyzed

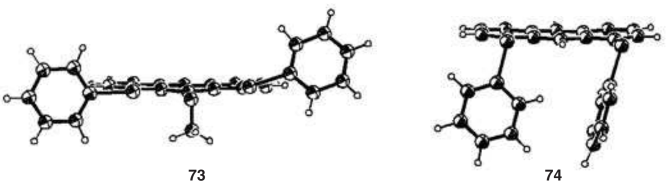


Figure 6 *Structures of* **73** *(Y = H) and* **74** *(Y = H)*

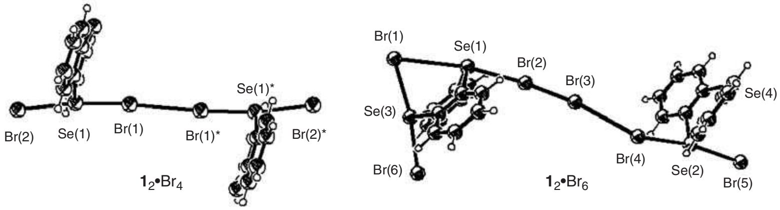


Figure 7 *Structures of* $\mathbf{1}_2 \cdot Br_4$ *and* $\mathbf{1}_2 \cdot Br_6$

based on the 7c–10e model. Ten electrons are supplied from Br–Se–Br–Br 4c–6e in $\mathbf{1} \cdot \mathrm{Br}_4$ and from Br–Se–Br 3c–4e in $\mathbf{1} \cdot \mathrm{Br}_2$ (TBP) to the linear σ-bond (*cf.* Scheme 1). The framework of $\mathbf{1}_2 \cdot \mathrm{Br}_6$ is well understood based on the nature of the linear [Br–Se–Br–Br–Br–Se–Br]$^-$ anion revealed by QC calculations. The linear anion is optimized as the C_{2h} symmetry and recognized to be a typical 7c–10e.

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CHAPTER 11.1

Chalcogens (S, Se, Te) in Microorganisms and Plants

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11.1.1 Introduction

Sulfur, the most abundant of the chalcogens in the Earth's crust, has evolved into an important bioelement, participating vigorously in the chemical processes of living organisms. The literature on the metabolism of sulfur is extensive but there is less information for selenium and tellurium. Increasing knowledge of chalcogen biochemistry is due to the use of sophisticated analytical methods.

11.1.2 Sulfur

11.1.2.1 General and Secondary Metabolism. Role of Chirality at Sulfur

Compounds present in microorganisms and plants often have unusual chemical structures that are unique in occurring only in a single, or very few, organism(s). These so-called "natural products", many of them being sulfur-containing compounds, have provided countless challenges and pleasures to the organic chemists. An example is *n*-pentenylpenicillin, only found during growth of a very limited number of fungi.

A more useful and restrictive distinction is that between general and secondary metabolites. General metabolites are those found in most living systems and are essential to growth and life. Secondary metabolites are not essential to growth and life of the producing organism and occur in restricted taxonomic groups; in some cases, secondary metabolites may impart selective advantages to the producer. Secondary metabolism represents the splendid idiosyncratic diversity of Nature.[1] Thus, the sulfur-containing amino acid, cysteine, probably a component of all living systems, is best described as a general metabolite rather than as a natural product. On the other hand, the sulfur-containing *n*-pentenylpenicillin is clearly a secondary metabolite. In their interactions with humanity, secondary metabolites are a Janus-faced tribe. Some, such as penicillin, are important in medicine as antibiotics, while others such as gliotoxin and the amatoxins are typical mycotoxins.

The general metabolism of sulfur, extensively described in many texts of biological sciences, is not considered in this article; some topics (*e.g.* metallo-enzymes) are discussed elsewhere in this volume (Chapter 11.2). Our focus is on sulfur-containing secondary metabolites in microorganisms and plants. In view of the vast literature, we can only provide an eclectic account citing recent work where possible.

Certain chalcogen structures display the phenomenon of chirality (Chapter 10.2). As with carbon,[2] chirality at sulfur can influence physiological events; there are many stereoselectivities in the interactions of chiral sulfur compounds with enzymes and receptor molecules. Sulfur chirality in secondary metabolites is most commonly observed with sulfonium salts, sulfoxides and sulfoximines.[3]

11.1.2.2 Overview of Structural Types for Sulfur-Containing Secondary Metabolites

11.1.2.2.1 Introduction

In 1977, a survey of "low molecular weight sulphur-containing compounds in Nature",[4] noted that these secondary metabolites had little more in common than the possession of one or more sulfur atoms. The reader was left with a kaleidoscopic impression of almost 80 chemical structures. A comprehensive review today would require many hundreds of sulfur-containing chemical structures.

A striking instance is provided by a 1998 study of the volatile flavor components of yellow passion fruits (*Passiflora edulis* f. *flavicarpa*) using sophisticated analytical techniques.[5] More than 100 volatiles containing sulfur were detected, (using gas chromatography) many at low concentrations. Of these, 47 compounds were specifically identified; 35 were not previously known in passion fruit and 23 were unknown in any material as food flavors. In all, 180 components were identified for the first time. The molecular masses of the sulfur-containing materials covered a range from 122 (diethyl disulfide) to 434 daltons (3-[1-butyryloxy-3-hexyldithio]hexyl hexanoate). Although most of these 47 sulfur-containing compounds were linear structures, two cyclic 1,3-oxathianes and 4-methyl-5-vinylthiazole were identified.

11.1.2.2.2 Hydrogen Sulfide, Carbon Disulfide, Carbonyl Sulfide (COS)

Although at first sight, CS_2 and COS may seem unlikely metabolites, they have been known as biogenic materials for three decades.[6] They warrant a special section since they differ profoundly from the more typical metabolites, virtually all of which contain H in addition to C and S. Also included here is the inorganic H_2S.

Hydrogen sulfide is a well known general metabolite produced on sulfate reduction by certain bacteria. Moreover, organic forms of sulfur can give rise to HS^-, hence H_2S in certain bacteria. Thus, cysteine desulfhydrase (EC 4.4.1.1, cystathionine γ-lyase) converts L-cysteine to H_2S, pyruvate, and NH_3. This enzyme shows a requirement for pyridoxal phosphate and the unstable aminoacrylic acid is an intermediate (Equation 1) in the reaction:

$$\mathrm{HS{-}CH_2{-}CH(NH_2){-}COOH \rightarrow HS^- + CH_3{-}CO{-}COOH + NH_3} \quad (1)$$

This enzyme was recently purified from *Streptococcus anginosus* and the encoding gene, *lcd*, was cloned and characterized.[7] H_2S is also produced by roots of *Acacia* x *giraffae* Willd. and *Pithecellobium elegans* Ducke and occasionally by roots of other *Acacia* species.[8]

Another enzyme, cysteine desulfurase, converts L-cysteine to L-alanine and a sulfane sulfur – a chain of divalent sulfur atoms. A protein-bound cysteine persulfide is formed on a conserved cysteine residue. Such enzymes have important roles in the biosynthesis of Fe-S clusters and sulfur-containing cofactors.[9]

CS_2 and COS occur in the atmosphere in significant amounts – CS_2, 3.8–4.7 Tg S yr^{-1}, COS, 2.7–3.5 Tg S yr^{-1}; one-fifth to one quarter of these amounts are probably anthropogenic. Biogenic CS_2 mainly originates in marine settings – anaerobic sediments (bacteria) and salt marshes with a role for *Spartina alterniflora*.[6,10] Some terrestrial plants produce CS_2 and tree roots are another source, usually after cutting or wetting. A tree of central America, *Stryphnodendron excelsum*. can be detected by its CS_2 odor.[10]

In the family *Fabaceae*,[8] CS_2 production was investigated with 40 taxa of the subfamily *Mimosoideae*; 29 produced CS_2 and 18 produced COS (the latter was not formed in absence of CS_2 production). CS_2 production was less common in the subfamilies, *Caesalpiniodeae* and *Papillonoideae*. Since CS_2 has a variety of bacteriostatic, fungicidal, nematicidal, and insecticidal properties, this production might deter soil pathogens.

To a limited extent, CS_2 is formed in *Arabidopsis* plants.[11] In a study of a regulatory role for cystathionine γ-synthase, EC 4.2.99.9 [*O*-succinylhomoserine (thiol)-lyase], in methionine biosynthesis, the enzyme was overexpressed in transgenic tobacco (*Nicotiana tabacum*) in either a complete or truncated version lacking an extended *N*-terminal sequence. Those plants with a full-length enzyme showed the same phenotype and developmental pattern as the wild type. Those with a truncated enzyme showed a very abnormal phenotype, producing substantially higher levels of dimethyl sulfide and CS_2. The *N*-terminal region of the enzyme may play a role in protecting plants from these catabolites of methionine.

L-Djenkolic acid was identified as a precursor for CS_2 formation in *Mimosa pudica*, undergoing "hydrolysis" with a *S*-alkylcysteine lyase. The actual mechanism is, presumably, an αβ elimination leading to the formation of unstable methylene dithiol, HS–CH_2–SH. This reaction has been shown with enzyme extracts from seeds of *Albizzia lophantha* and is discussed in connection with djenkolic acid (Section 11.1.2.7). A two stage oxidation of methylene dithiol *via* dithioformic acid, HS–CH=S (Equation 2), possibly with an NAD-requiring dehydrogenase, would lead to CS_2.

$$\mathrm{HS{-}CH_2{-}SH \rightarrow HS{-}CH{=}S \rightarrow S{=}C{=}S} \qquad (2)$$

Moreover, potential reactions can be written for conversion of dithioformic acid to thioformic acid (Equation 3), and hence COS.

$$\mathrm{HS{-}CH{=}S \rightarrow HO{-}CH{=}S \rightarrow O{=}C{=}S} \qquad (3)$$

It is also possible that COS might be a precursor for CS_2 in soil and vegetation; chemical analogies have been proposed.[12] The reverse reaction, $CS_2 \rightarrow COS$, occurs in our oxidative atmosphere *via* hydroxyl radical and other gas phase oxidants.

11.1.2.3 Sulfur-Containing Fungal Metabolites

11.1.2.3.1 Penicillins and Cephalosporins

While many sulfur-containing fungal secondary metabolites are known, they are found less frequently than in plants. There is a structural range from CH_2S_6, 1,2,3,4,5,6-hexathiapane, from *Lentinus edodes*, to $C_{82}H_{114}N_{20}O_{17}S$, a 13-unit peptide containing methionine from *Saccharomyces cerevesiae*.[13]

The most famous fungal metabolites are, of course, the penicillins and cephalosporins. The association of sulfur and penicillin has a curious history. Penicillin was investigated chemically in 1932 by Harold Raistrick and his colleagues.[14] The antibacterial activity could be extracted into ether from acid solution but on solvent evaporation the residue was without antibacterial activity. Clearly, penicillin was not a well-behaved natural product! If only Raistrick had carried out a back-extraction from ether into dilute alkali, penicillin might have become available in the 1930s (and Raistrick would have become a Nobel Laureate).

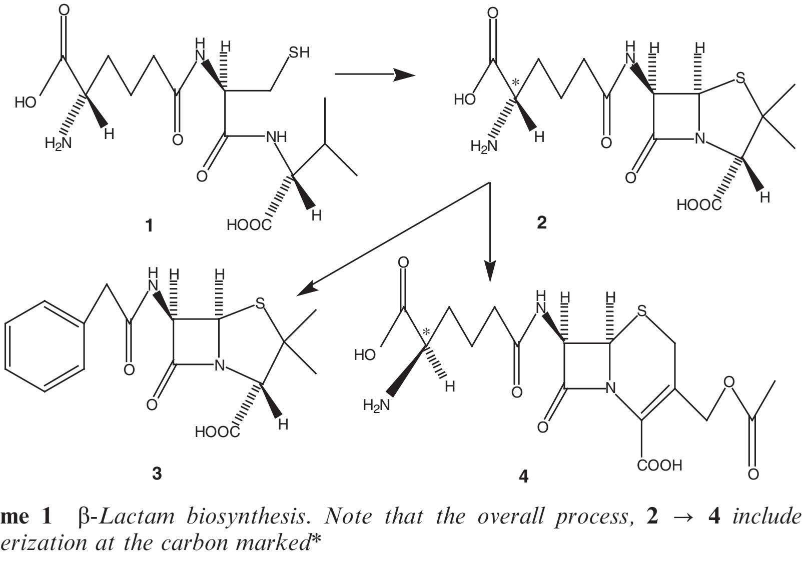
When penicillin was restudied by Howard Florey and his team at the Sir William Dunn School of Pathology, Oxford University, about 1939, a crude barium salt was hydrolyzed, forming a crystalline base, penicillamine (as a hydrochloride) possibly $C_6H_{11}NO_4 \cdot HCl$ or $C_7H_{13}NO_4 \cdot HCl$.[15] On oxidation, penicillamine gave penicillaminic acid apparently analyzing as $C_5H_{11}NO_7$. Since it was difficult to fit structures to this empirical formula, it was suggested that the oxidation was that of a thiol, *i.e.* -SH → -SO_3H. Although early tests for sulfur in crude preparations of penicillin had been negative, retesting revealed the error. Penicillaminic acid was shown to be $C_5H_{11}NO_5S$, and penicillamine became $C_5H_{11}NO_2S$. Penicillamine was a new, sulfur-containing, amino acid, ββ-dimethylcysteine. The difficulty had arisen because of the fact that the atomic mass of sulfur, 32, is twice that of oxygen, 16. Analysis of pure, crystalline penicillin preparations confirmed the presence of sulfur. Only slowly was the β-lactam formula, with the fused thiazolidine ring, accepted for penicillin.[16]

Also at Oxford, Abraham and Newton discovered the first cephalosporin, cephalosporin C, as a product of *Acremonium chrysogenum* (*Cephalosporium acremonium*).[17] This new, sulfur-containing antibiotic was also a β-lactam but the fused, sulfur-containing ring is a six-membered dihydrothiazine.

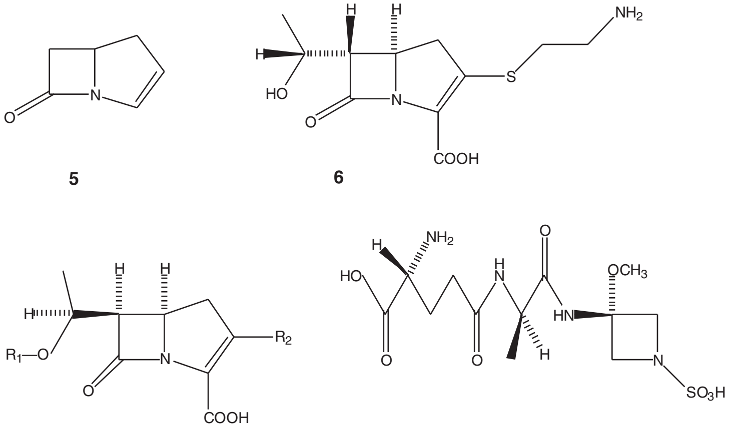
The β-lactam antibiotics are now so extensively described that we cannot attempt to summarize the literature. Since our emphasis is on sulfur, we note that the sulfur atoms of the thiazolidine or dihydrothiazine rings derive from a common tripeptide, δ-(L-α-aminoadipyl)-L-cysteinyl-D-valine **1**, "ACV" or "Arnstein tripeptide". ACV is converted to a β-lactam structure, isopenicillin N **2** and thereafter, the two pathways diverge, *i.e.* to benzylpenicillin **3** or to cephalosporin C **4** (Scheme 1). There have been extensive studies of the genes and enzymes involved in β-lactam biosynthesis.[18,19]

There are several naturally occurring variations on the lactam-thiazolidine or lactam-dihydrothiazine structures, leading to other useful antibiotics or to inhibitors of the β-lactamases, enzymes that hydrolyze the β-lactam unit. One group, termed carbapenems **5** has a five-membered ring in which the thiazolidine sulfur is replaced with CH_2. Such compounds may still contain sulfur in a thioethylamine side chain (derived from L-cysteine) as in thienamycin **6**, originally isolated from *Streptomyces cattleya* (Scheme 2).

The olivanic acids from *S. olivaceus* have side chains similar to that of thienamycin, with sulfur as either sulfide or sulfoxide; **7** R_1=H or $HOSO_3$, R_2=–SO–CH=CH–NH–CO–CH_3 or –S–CH=CH–NH–CO–CH_3 or –S–CH_2–CH_2–NH–CO–CH_3. The hydroxyethyl group (as in thienamycin) may be in a



Scheme 1 β-*Lactam biosynthesis. Note that the overall process,* **2** → **4** *includes an epimerization at the carbon marked**



5 6 7 8

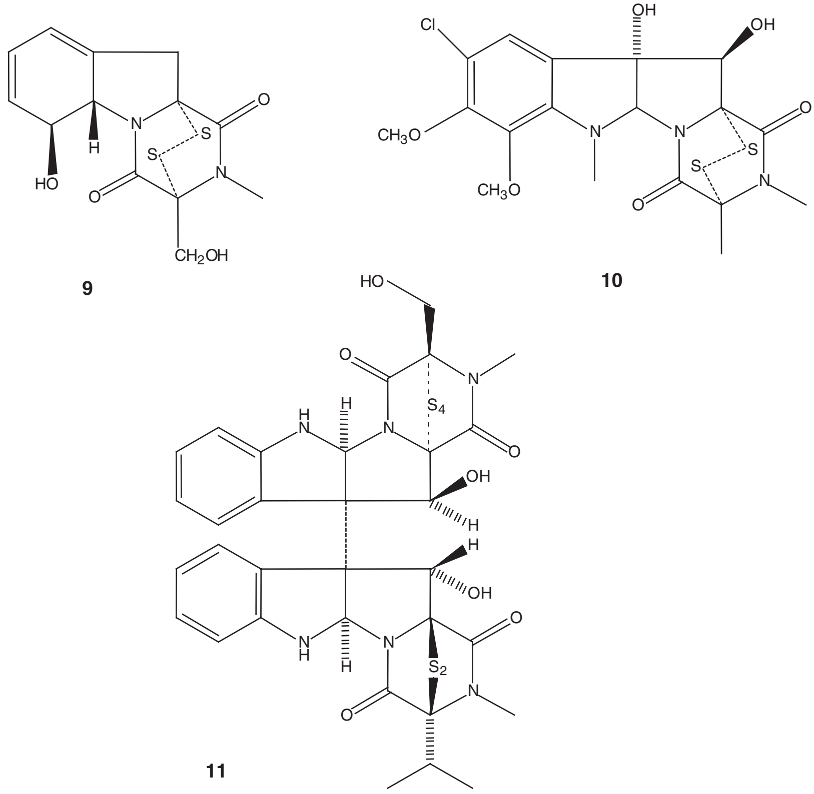
Scheme 2 *Antibiotics related to penicillin. Note that in sulfazecin,* **8**, *the dipeptide unit contains* D*-glutamate and* D*-alanine*

sulfated form depending on the sulfate content of the medium. Carpetimycins A and B, isolated from *S. griseus* subsp. *cryophilus*, have very similar structures.

A further modification is a single β-lactam ring as found in the monobactams. Characteristically, there is a sulfonate residue (derived from sulfate) on the nitrogen atom. An example is sulfazecin **8** from *Pseudomonas acidophila* and *P. mesoacidophila*. This material also contains a dipeptide unit of D-glutamate and D-alanine (Scheme 2). Pharmaceutical chemists have synthesized many variations on the β-lactam structure and have devised semi-synthetic processes. The resulting materials are not natural products and are beyond the scope of this article.

11.1.2.3.2 Toxins (Mycotoxins)

There are two major groups of sulfur-containing mycotoxins – the epipolythiodioxopiperazines (epipolythiopiperazine-3,6-diones) and the amatoxins (amanita toxins). Antagonisms between microorganisms have been known for a very long time. In 1932, a crystalline secondary metabolite that inhibited growth of other fungi, was isolated from a *Gliocladium* sp. This material, named gliotoxin **9**, was eventually shown to have a bridge of two sulfur atoms across a diketopiperazine ring (Scheme 3). It was the first of a large group of related compounds. In some cases, there are more than two sulfur atoms in the bridge. They have a variety of toxic properties; gliotoxin is toxic to mice and rats, inhibits multiplication of RNA viruses and growth of various bacteria and fungi, and is inhibitory to some mammalian cell cultures. Just as the gliotoxin structure was determined, the sporidesmins **10**, formed by *Pithomyces chartarum* (*Sporidesmium bakeri*) were investigated as materials toxic to sheep and cattle. Many of the organisms producing these epipolythiodioxopiperazines are



Scheme 3 *Gliotoxin and related materials*

found in soil and pasture and are potentially dangerous to farm animals. In sheep, sporidesmins produce characteristically a facial eczema due to a secondary photosensitization. Growth of the animals is also decreased.

The literature is extensive; for instance, a query for gliotoxin to PubMed in February, 2005, returned 289 "hits". Reviews are available.[20–22] All that can be done here is to illustrate representative types (Scheme 3).

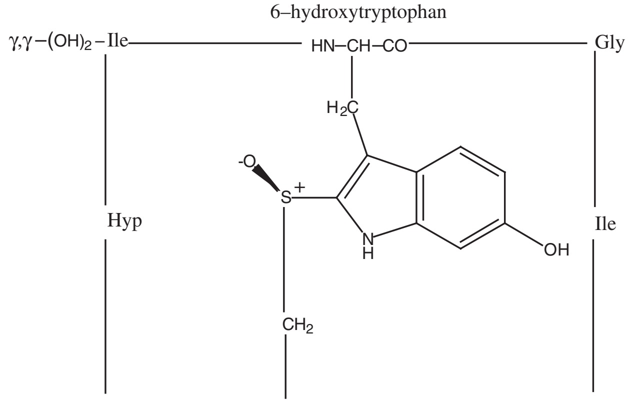
Dimeric structures are possible as exemplified by the leptosins, from a strain of *Leptosphaeria* (a fungus isolated from the marine alga *Sargassum tortile*). Some of these, *e.g.* leptosin A **11**, may have up to 4 sulfur atoms across the diketopiperazine ring system.[23] Various leptosins have antitumor and cytotoxic properties.

Poisoning and sometimes death from eating (unidentified) mushrooms is well known. In particular, *Amanita* sp. are particularly dangerous, with much emphasis on the "death cap fungus", *Amanita phalloides*.[24] The best known toxins are the amatoxins and phallotoxins, which are complex, bicyclic peptides. An unusual feature relates to sulfur; a tryptophan (or substituted tryptophan) unit is linked to a cysteine sulfur at the carbon atom next to the NH group of the pyrrole ring, forming the unit, –CH_2–S–C(NH)=C, *e.g.* in phallotoxins. In amatoxins, *e.g.* α-amanitin **12**, there is a further modification; the sulfur atom carries an oxygen as a sulfoxide function (Scheme 4). This sulfur atom therefore has the property of chirality. The highly toxic naturally occurring α- and β-amanitins both have (*R*) configuration at this sulfur; the (*S*) configured amanitins are much less toxic.[25] A precise connection between this stereochemical feature and toxicity has not been revealed.

11.1.2.3.3 Oligopeptide Antibiotics

It is convenient to consider here oligopeptides with antibiotic activity, although these are typically bacterial and not fungal metabolites. These oligopeptides often contain the usual amino acids but in the D configuration, as well as unusual amino acid structures (*e.g.* 2,4-diamino-butyric acid) and/or hydroxy fatty acids (*e.g.* 2-hydroxyisovaleric acid). As a general rule, sulfur-containing amino acids are absent in antibiotics, such as gramicidin S, tyrocidine A, and polymixin B. However, in the bacitracins, produced by *Bacillus subtilis* and *B. licheniformis*, an original L-cysteine unit has been converted to a thiazoline in a reaction with L-leucine (*e.g.* bacitracin A **13**, Scheme 5). The thiazoline structure is of interest in view of the thiazolidine and dihydrothiazine units in the β-lactam antibiotics. Bacitracins inhibit cell wall synthesis, especially for Gram positive bacteria, and are used in antibiotic creams such as Neosporin. Commercial samples of bacitracin contain at least 9 products with the best known being bacitracin A.

Bacitracin biosynthesis requires a non-ribosomal peptide synthetase with three major protein components, BacABC. This synthetase has a modular structure. There are associated regulatory and transport systems. Biosynthesis of bacitracin has been engineered in the surrogate host, *B. subtilis*, by genetic techniques. A strain, *B. subtilis* KE 350, expresses the entire 49-kb bacitracin



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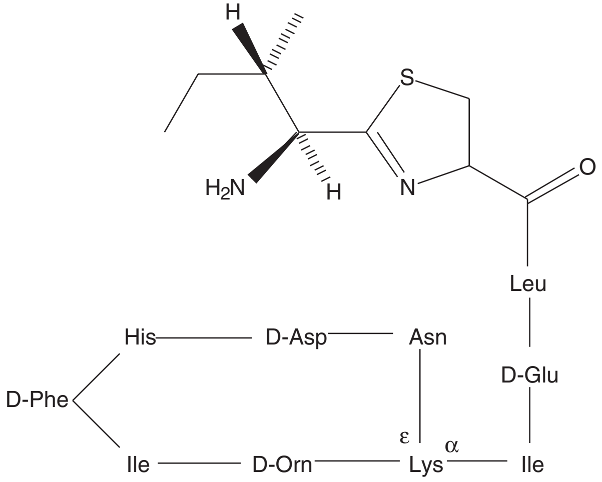
Scheme 4 *α-Amanitin. Standard three letter abbreviations are used for the amino acids*



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Scheme 5 *Bacitracin A. Standard three letter abbreviations are used for the amino acids*

biosynthetic operon of *B. licheniformis*. The BacABC protein template provides 12 modules for the 10 substrate amino acids. Four appropriate epimerization domains allow formation of the D enantiomers of aspartate, glutamate, ornithine, and phenylalanine. BacA carries a cyclization domain for thiazoline ring formation[26] (and papers cited therein).

11.1.2.4 Flavor Compounds Containing Sulfur

11.1.2.4.1 Introduction

Sulfur compounds are renowned for unpleasant odors beginning with the rotten egg smell of H_2S and many are responsible for the off-flavors of various foods. Nevertheless, some sulfur compounds provide the pleasant odors associated with many plants and are also prominent in desirable food flavors. The determination of flavor or aroma is very complex since large numbers of components may be involved both for microorganisms and plants. Many flavor compounds, of course, do not contain sulfur. Much has been and continues to be written. We can only convey an eclectic flavor of the many situations involving sulfur compounds – a tasting menu. The colorful language of experts in aroma and taste bears a close resemblance to that of enophiles.

11.1.2.4.2 Fruits

Fruits have received extensive study; one example is that of the passion fruit volatiles. Another fruit in which sulfur volatiles play an aroma role is muskmelon (*Cucumis melo* cv. Makdimon). A "musky overtone" is provided by 3-(methylthio)propanal ("stale") and *S*-(methylthio)-butanoate ("pine, earthy") while fruity odors come from 3-(methylthio)propyl acetate ("apples") and other non-sulfur esters. A minor contribution of a "garlic toast" odor is provided by *S*-(methylthio)ethanoate and *S*-(methylthio)pentanoate.[27]

11.1.2.4.3 Yeasts

A study of three commercially available extracts of yeast (*Saccharomyces cerevisiae*) identified 268 volatile components of which 67 contained sulfur (34 of these were identified for the first time as yeast extract components). The identified substances ranged from CS_2 to complex thiophenes and thiazoles.[28]

Examination of 37 basidiomycetous yeasts indicated formation of several sulfur volatiles: 3-(methylthio)-1-propanol, methanethiol (MT), *S*-methyl thioacetate, dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), allyl methyl sulfide and 4,5-dihydro-3(2*H*)-thiophenone. The component produced in the largest amounts, 40–400 mg L^{-1}, was 3-(methylthio)-1-propanol[29] Cheese-ripening yeasts are considered later (Section 11.1.2.4.5).

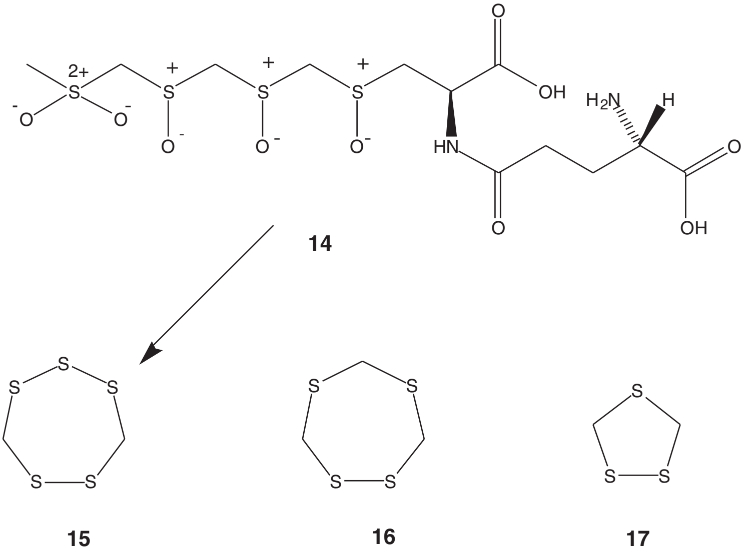
11.1.2.4.4 Cyclic Polysulfides

Mushrooms have been investigated with especial reference to shiitake, *Lentinus edodes*, the flavorful fungus widely used in Chinese and Japanese dishes. While the umami taste is attributed to guanylic acid, lentinic acid **14** (Scheme 6) is converted to lenthionine, 1,2,3,5,6-pentathiacycloheptane **15**, a compound with the characteristic shiitake flavor. This complex reaction requires a C-S lyase enzyme.[30] Other important flavor compounds are 1,2,4,6-tetrathiacycloheptane **16** (Scheme 6) and 1,2,3,4,5,6-hexathiacycloheptane (not shown).

Lenthionine has the characteristic shiitake flavor. It is formed from the precursor, lentinic acid **14** by complex reactions involving a C-S lyase enzyme.[30] Cyclic polysulfides occur in other Basidiomycete mushrooms (Genus *Micromphale* and *Collybia*), in some red alga, and in seeds of *Parkia speciosa*. The latter contain lenthionine and 1,2,4-trithiolane (1,2,4-trithiacyclopentane) **17** as well as compounds with 4, 5, or 6 sulfur atoms.[31] These seeds are valued in Indonesia for a unique, onion-like odor. Djenkolic acid and dichrostachinic acid {*S*-[(2-carboxy-2-hydroxyethylsulfonyl)-methyl]cysteine} are converted by a C-S lyase enzyme to cyclic polysulfides: djenkolic acid yields 1,2,4-trithiolane and 1,2,4,6-tetrathiepane; the latter is also formed from dichrostachinic acid.[32]

11.1.2.4.5 Cheese

Since antiquity, animal milks have been converted by empirical processes to a wide variety of cheeses. With the development of microbiology as a scientific discipline, the critical role of microorganisms – bacteria, fungi, yeasts – in cheese began to be understood. Today, more than 650 cheese types are recognized and the flavor(s) of cheese has (have) now been investigated for more than a century.[33] Typically, the situation is complex and the literature is enormous. For instance, more than 200 volatiles occur in Cheddar cheese. In a listing of 58 of these volatiles, 7 are sulfur compounds: dimethyl sulfide (DMS),



Scheme 6 *Lentinic acid and cyclic polysulfides*

DMDS, DMTS, MT, methional, hexanethiol and thiophene 2-aldehyde. H_2S and COS also make a contribution.[33]

In soft cheeses, such as Brie, Camembert, and Limburger, the following sulfur compounds were implicated: 3-(methylthio)propanol, MT, DMS, DMDS, DMTS, dimethyl tetrasulfide, methyl ethyl disulfide, diethyl disulfide, 2,4-dithiapentane, 3-methylthio-2,4-dithiapentane, methional, 2,4,5-trithiahexane, 1,1-*bis*-methylmercaptodisulfide, methyl thioacetate (=methanethiol acetate), benzothiazole, methylthiobenzothiazole, methyl ethyl sulfonate, methyl methane thiosulfonate, thiophene 2-aldehyde, and H_2S.[34] Many of these were only present in small amounts; Limburger cheese was notable for 13.2% of DMDS, 0.5% of methyl thioacetate, and 0.8% of DMTS.

Sulfur-containing amino acids, especially L-methionine, serve as precursors for MT and the many materials derived from this compound, such as DMS, DMDS, DMTS, methyl thioacetate, *etc.* The most direct route for the L-methionine · MT conversion is by "demethiolation" (Equation 4) catalyzed by methionine γ-lyase, EC 4.4.1.11:

$$\begin{gathered}\mathrm{CH_3{-}S{-}CH_2{-}CH_2{-}CH(NH_2){-}COOH \rightarrow CH_3SH} + \\ \mathrm{CH_3{-}CH_2{-}CO{-}COOH} + \mathrm{NH_3}\end{gathered} \tag{4}$$

This pyridoxal phosphate-requiring enzyme has been studied in several bacteria and X-ray crystal structures are available.[35] The coryneform bacterium, *Brevibacterium linens*, is common on the surface of several cheeses, including Limburger and those of the Trappist type. The methionine γ-lyase of this organism has been purified to homogeneity[36] and the relevant gene, *mgl* (from MGL, abbreviation for methionine γ-lyase) has been cloned and analyzed.[37]

When the *mgl* gene was disrupted, the ability of *B. linens* to produce MT was much reduced. Methionine γ-lyase clearly was an important means for production of MT and related compounds in this organism.

Two further enzymes, implicated in MT formation from L-methionine in some bacteria, are cystathionine β-lyase, EC 4.4.1.8, and cystathionine γ-lyase, EC 4.4.1.1. The "normal" (most efficient) substrate for these enzymes is cystathionine; the β-lyase forming homocysteine, pyruvate, and NH_3, the γ-lyase forming 2-oxobutanoate, cysteine, and NH_3. Both lyases can also degrade L-methionine forming MT, 2-oxobutanoate, and NH_3, although less efficiently (see Equation 4). These enzymes are present in high levels in lactococci and lactobacilli.[38] The *metC* gene, encoding the β-lyase, has been extensively studied in *Lactococcus lactis* subsp. *cremoris*, an organism involved in production of Gouda cheese.[39] Although necessary for the conversion of cystathionine to homocysteine (and hence to methionine) the β-lyase did have a role in formation of MT. However, other enzyme(s) were needed, possibly the γ-lyase or the demethiolase discussed below. For the purified γ-lyase of *Streptococcus anginosus,* see Section 11.1.2.2.2.

There is a further possibility for conversion of methionine to MT. Transaminase enzymes can convert methionine to 4-methylthio-2-oxobutanoate (also, α-keto-γ-methylthiobutyrate). One such enzyme is aromatic-amino-acid transaminase, EC 2.6.1.57, for which L-methionine is, albeit, less efficiently, a substrate (Equation 5):

$$\begin{gathered}CH_3–S–CH_2–CH_2–CH(NH_2)–COOH + 2\text{–oxoglutarate} \rightarrow \\ CH_3–S–CH_2–CH_2–CO–COOH + \text{glutamate}\end{gathered} \quad (5)$$

A demethiolation of 4-methylthio-2-oxobutanoate (Equation 6) would yield MT and possibly 2-oxobutanoate:

$$\begin{gathered}CH_3–S–CH_2–CH_2–CO–COOH \rightarrow CH_3–SH + \\ CH_3–CH_2–CH_2–CO–COOH\end{gathered} \quad (6)$$

Although not well understood, demethiolation has been noted in some fungi.[38] Moreover, evidence for a required enzyme activity was obtained for lactococci (used in cheddar cheese production)[40] and a relatively high level of demethiolase activity was present in *Kluyveromyces lactis*, a cheese-ripening yeast (see below).[41]

In addition to bacterial conversion of L-methionine to cheese aroma compounds, certain cheese-ripening yeasts have been implicated. They include *Debaromyces hansenii, Geotrichum candidum,* and *Yarrowia lipolytica*, in addition to *Kluyveromyces lactis* and *Saccharomyces cerevisiae* (previously noted). Of these yeasts, *Geotrichum candidum* was most effective at producing sulfur compounds with the major product being *S*-methyl thioacetate, with smaller amounts of MT, DMS, DMDS, and DMTS. *Kluyveromyces lactis* had a similar profile, but produced a much smaller amount of *S*-methyl thioacetate than did *G. candidum. S*-Methyl thioacetate is formed by a reaction of MT and acetyl-CoA (Equation 7):

$$CH_3–SH + CH_3–CO–S–CoA \rightarrow CH_3–S–CO–CH_3 + CoA–SH \quad (7)$$

The supply of MT may be rate-limiting in *K. lactis*. In addition to *S*-methyl thioacetate, *G. candidum* also contains *S*-methyl thiopropionate, *S*-methyl thiobutanoate, *S*-methyl thio*iso*butanoate, *S*-methyl thio*iso*valerate, and *S*-methyl thiohexanoate in smaller amounts.[42]

11.1.2.4.6 Character Impact Compounds

As these examples indicate, the characteristic flavor of a food, fruit, *etc.*, usually derives from a complex mixture of components. In a few cases, one unique sulfur compound is a "character-impact" compound, a material recognized as having the same organoleptic character as the material itself. Although some 670 compounds, of which more than 100 are sulfur-containing, have been identified in roast coffee, one material, furfurylmercaptan (2-furylmethanethiol) is considered to be a character-impact compound.[43,44] The threshold level for detection of 2-furylmethanethiol in water is 0.005 ppb, and at levels of 0.01–0.5 ppb, it has the very characteristic aroma of freshly roasted coffee. However, as in many other cases, there is a concentration effect. At levels from 1–10 ppb the aroma is that of "staled coffee with a sulfury note".[43] Hence, 2-furylmethanethiol has a two headed property – at low concentrations it is a character impact compound and at higher levels it is an off-flavor component.

11.1.2.4.7 Instrumentation

Many sophisticated analytical techniques have been used to deal with these complex mixtures.[5,45,46] A detailed description is not possible here, but it can be noted that GLC, often coupled with mass spectrometry (MS), is a major workhorse. Several other GLC detectors are available for use with sulfur compounds including flame photometer detector (FPD), sulfur chemiluminescence detector (SCD), and atomic emission detector (AED).[47] Multidimensional GLC (MDGC) with SCD detection has been used[48] as has HPLC.[49] In some cases, "sniffer ports" are provided for the human nose on GLC equipment.

There are possible difficulties when heat-labile compounds are analyzed by GLC, so that sometimes an identified compound will actually be an artifact. These problems for instance, have been extensively discussed with respect to materials from *Allium* sp. (see Section 11.1.2.5.2).[49]

11.1.2.4.8 Role of Enantiomers in Organoleptic Properties

Enantiomers of a chiral compound show many different physiological responses, including those of odor and taste[2] and it has long been known that enantiomers of some sulfur-containing compounds may have different odors. The examples discussed here are for sulfur-containing compounds where the chirality is based on carbon. While certain compounds can show sulfur-based chirality, there are apparently no known cases where enantiomers dependent on sulfur chirality exhibit different odors.

A good example is 1-*p*-menthene-8-thiol; the (*R*) enantiomer is an important flavor component of grapefruit juice, having a very low olfactory threshold of

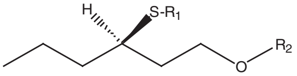
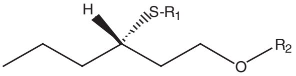
10^{-4} ppb – one of the lowest ever found. This means that 1 g of this compound in 10 million metric tons of water could be detected by odor.[50] Although the (*S*) enantiomer was originally described as having an obnoxious sulfur odor, this odor was due to the presence of small amounts of the impurity, 2,8-epithio-*cis*-*p*-menthen.[51] Highly purified (*S*) enantiomer has a weak, non-specific odor.

Possible differences are also well illustrated by 3-thio- and 3-methyl-thiohexanols and their esters (Table 1). Among these compounds, there is a tendency for the (*R*) enantiomers to have a typical, fruity aroma. However, for 3-methylthiohexanol (an aroma component of yellow passion fruit) this situation is reversed; the (*S*) enantiomer had the characteristic fruity aroma ("exotisch, fruchtig").[52] For the separation of enantiomers of odorous compounds, enantioselective GLC with chiral stationary phases, and MGDC techniques using a conventional capillary column and an enantioselective column are commonly used.[53]

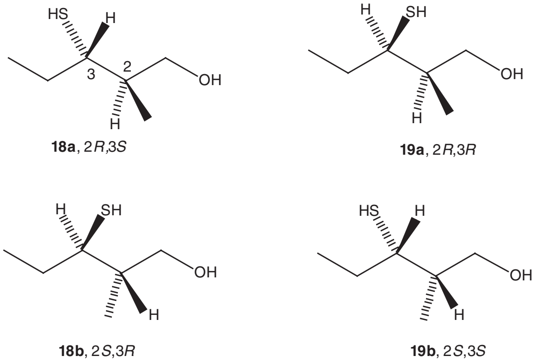
Enantiomers of the same compound may have differing threshold values. This property was observed for a new, strong and high impact, flavor compound, 3-thio-2-methylpentan-1-ol, first detected in thermally processed materials but that is actually present in raw onions.[54] First of all, there is a marked concentration effect; at 1 ppm in 5% saltwater, the odor is described as "sulfuric, burnt gum, sweaty, onion" and at 0.5 ppb as "meat broth, sweaty, onion, leek". Since there are two chiral centers (both dependent on carbon) there are four stereoisomers, all of which have been prepared: **18a**, **18b**, **19a**, **19b** (Scheme 7). For this compound, enantiomers have the following marked differences in odor thresholds (but apparently all have the same general odor).

	H_2O, µg L^{-1}	**Air, ng L^{-1}**
Compound **18a** (2*R*, 3*S*)	0.04	0.00007–0.0002
Compound **18b** (2*S*, 3*R*)	0.03	0.003–0.007

Table 1 *Odors for enantiomers of 3 substituted hexanols and their esters*

		
$R_1{=}R_2{=}H$	Intense sulfur odor	Intense sulfur odor[a]
$R_1{=}H$, $R_2{=}COCH_3$	Tropical fruit	Sulfur, herbaceous
$R_1{=}H$, $R_2{=}CO(CH_2)_2CH_3$	Tropical fruit	Sulfur, oniony
$R_1{=}H$, $R_2{=}CO(CH_2)_4CH_3$	Herbaceous, fresh sulfur	Burnt sulfur
$R_1{=}CH_3$, $R_2{=}H$	Herbaceous, weak	Exotic, fruity
$R_1{=}CH_3$, $R_2{=}COCH_3$	Fruity	Intense sulfur, herbaceous
$R_1{=}CH_3$, $R_2{=}CO(CH_2)_2CH_3$	Fruity, very weak	Oniony
$R_1{=}CH_3$, $R_2{=}CO(CH_2)_4CH_3$	Fruity, very weak	Weak oniony, roasty

[a] Note that in this case there is no enantiomeric difference.



18a, 2*R*,3*S* **19a**, 2*R*,3*R*

18b, 2*S*,3*R* **19b**, 2*S*,3*S*

Scheme 7 *Stereoisomers of 3-thio-2-methylpentan-1-ol*

For the enantiomeric pair, (2*R*, 3*R*) **19a** and (2*S*, 3*S*) **19b**, the odor thresholds are very much higher (>12 to >30 µg L^{-1} in H_2O, not determined in air). These two materials both were contaminated with small amounts of the highly potent (2*R*, 3*S*) enantiomer so these values are not too reliable. The (2*R*, 3*S*) enantiomer is one of the most powerful flavor components to be discovered.

11.1.2.5 Aroma and Medicinal Roles of Sulfur-Containing Plant Metabolites

11.1.2.5.1 Compounds from the Family Cruciferae

The family *Cruciferae* contains several economically important vegetables, such as broccoli, Brussels sprouts, cabbage, and cauliflower. There has always been some ambivalence about the use of these vegetables. While some of them have desirable, pungent flavors, cooking odors tend to deter their consumption. It is stated that cauliflowers are rarely purchased in France and there is a relatively low consumption of sauerkraut in the USA.[55]

As would be expected, the chemistry is complex. Unpleasant, off flavor odors usually derive from sulfur compounds, such as MT, DMS, DMDS, and DMTS, formed either enzymatically or non-enzymatically from sulfur-containing amino acids.[35] Enzymatic routes to MT are essentially those previously considered (Section 11.1.2.4.5). Some DMS may derive by methylation of MT (Equation 8) with the donor, *S*-adenosylmethionine, AdoMet:

$$CH_3\text{–}SH + \text{AdoMet} \rightarrow CH_3\text{–}S\text{–}CH_3 + \text{S-adenosylhomocysteine} \tag{8}$$

Another source (Equation 9) is lyase action on *S*-methylmethionine:

$$\begin{gathered}(CH_3)_2\text{–}S^+\text{–}(CH_2)_2\text{–}CH(NH_2)\text{–}COOH \rightarrow \\ CH_3\text{–}S\text{–}CH_3 + CH_3\text{–}CH_2\text{–}CO\text{–}COOH + NH_3\end{gathered} \tag{9}$$

For DMS and DMTS, *S*-methyl-L-cysteine sulfoxide is a precursor; action of a C-S lyase enzyme yields methanesulfenic acid, CH_3–S–OH, and hence methyl methanethiosulfinate, CH_3–SO–S–CH_3. Disproportionation reactions yield polysulfides such as DMS.[56]

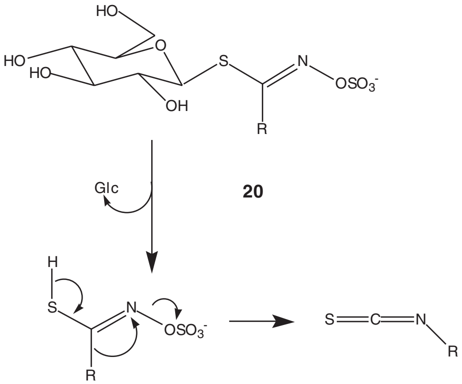
The more attractive, pungent flavors of cruciferous vegetables are due to isothiocyanates **22** formed from glucosinolates **20** (Scheme 8). These latter materials are all 1-β-D-thioglucopyranosides; they are commonly found in other plant families and occur in seeds for instance of white and black mustards. Damage to the plant or seeds releases the "mustard oils", volatile, pungent, and lachrymatory isothiocyanates. This is due to the action of a thioglucosidase, EC 3.2.3.1, forming D-glucose and a thiohydroximate sulfonate **21**.

The latter intermediate undergoes a Lössen-type rearrangement to an isothiocyanate **22**. Thus, for instance, sinigrin (allylglucosinolate) **20**, R=–CH_2–CH=CH_2, from black mustard (*Brassica nigra*) or horseradish (*Amoracia rusticana*), yields D-glucose and allylisothiocyanate **22**, R=–CH_2–CH=CH_2. The thiohydroximate sulfonate formed by action of thioglucosidase may in some cases rearrange to form a thiocyanate, R–S–C≡N or a nitrile, R–C≡N.

The many naturally occurring glucosinolates fall into three groups, aliphatic, aromatic, and indole; representative examples are given in Table 2.

Arabidopsis thaliana contains 12 glucosinolates and there is an unusual feature in several of them – a benzoate group is esterified to C-6 of the glucose moiety.[57] Cabbage contains 14 glucosinolates, 11 isothiocyanates (including goitrin, see following), and 5 sulfur-containing cyanides, as well as many non-sulfur products.[58] The sulfur-containing materials that are present depend on many factors: plant species, roots *vs.* leaves *vs.* seeds, cultivation techniques, and storage conditions for harvested vegetables.

Glucosinolates derive from amino acids by conversion to an aldoxime, R–CH=N–OH. In a not well understood process, the aldoximine is converted to a thiohydroximic acid, R–C(SH)=N–OH; the introduced sulfur is likely derived from



Scheme 8 *Formation of an isothiocyanate from a glucosinolate*

Table 2 *Representative, naturally occurring glucosinolates*

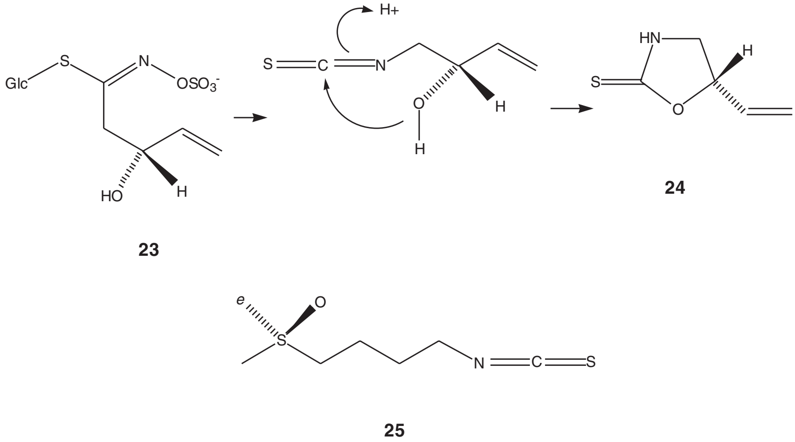
Name	*R group*	*Sources*
Aliphatic		
Sinigrin	Allyl	Black mustard (*Brassica nigra*), horseradish (*Amoracia rusticana*)
Glucoiberin	4-methyl-sulfinylpropyl	Broccoli (*Brassica oleracea botrytis asparagoides*), Brussels sprouts (*B. oleracea gemmifera*), cabbage (*B. oleracea capitata*)
Aromatic		
Gluconasturtin	Phenylethyl	Watercress (*Nasturtium officinale*), rape seed (*Brassica napus*)
Sinalbin	4-hydroxybenzyl	White or yellow mustard (*Sinapis alba*)
Indole		
Glucobrassicin	3-indolylmethyl	*Brassica* spp.
4-Hydroxyglucobrassicin	4-OH-3-indolylmethyl	*Brassica* seeds

L-cysteine. The process is completed by glucosylation and addition of SO_3^- at the nitrogen (Equation 10) by reaction with 3′–phospho–adenosine-5′-phosphosulfate.

$$\begin{gathered}\text{R–CH(NH}_2\text{)–COOH} \rightarrow \text{R–CH(NH–OH)–COOH} \rightarrow \\ \text{R–CH=N–OH} \rightarrow \text{R–C(SH)=N–OH} \rightarrow \text{R–C(S–Glc)=} \\ \text{N–OH} \rightarrow \text{R–C(S–Glc)=N–OSO}_3 \text{ (Glc=glucose)}\end{gathered} \tag{10}$$

Some foods have a tendency to induce goiter, an enlargement of the thyroid gland. A potent goitrogen, inhibiting iodine incorporation and thyroxine formation, is goitrin **24**, (*S*) (5-vinyl-2-thiooxazolidine) (Scheme 9). It is formed from progoitrin **23**, 2-hydroxy-3-butenyl-glucosinolate, found in yellow turnips and also in the oil seed from rape (*Brassica napus*). This property limits use of rape seed meal for animal feeding. The (*R*) enantiomer of goitrin, found in *Crambe abyssinica* seeds is a potent inducer of hepatic glutathione *S*-transferase and epoxide hydrolase activities in rats. It is postulated to be a modulator of chemical carcinogenesis (*e.g.* by aflatoxin).[59]

There is significant evidence that eating vegetables such as broccoli is conducive to good health. The reason lies with glucosinolates and isothiocyanates containing a second sulfur carrying an oxygen atom – *i.e.* a sulfoxide group. An example is glucoiberin (see Table 2) containing the methylsulfinylpropyl group and giving rise to the mustard oil, iberin, $CH_3SO(CH_2)_3NCS$. Of particular interest is glucophoranin, 4-methylsulfinylbutyl glucosinolate, from broccoli and other plants, that gives rise to sulforaphane, (-)-1-isothiocyanato-(4*R*)-methylsulfinylbutane **25**, $CH_3SO(CH_2)_4NCS$ (Scheme 9). Sulforaphane induces phase II enzymes for xenobiotic metabolism, such as glutathione *S*-transferase



Scheme 9 *Formation of (S)-(-)-goitrin* **24** *and structure of sulforaphane. In* **25**, *e represents a lone pair of electrons*

and quinone reductase.[60,61] Since these enzymes detoxify electrophilic carcinogens there is currently much interest in promoting vegetable use to reduce cancer risk.[62,63] Sulforaphene, $CH_3–SO–CH{=}CH–CH_2–CH_2–NCS$, is found in radish. Sulfoxides with the general structure $R_1–SO–R_2$, $R_1 \neq R_2$, are chiral at the sulfur atom. The naturally occurring mustard oils usually have the (*R*) configuration as shown for sulforaphane **25**.

4-Methylthiobutyl glucosinolate derives from L-methionine by a complex elongation process leading to dihomomethionine. Four of the five carbons of methionine are retained, one being lost in a decarboxylation. The two necessary additional carbons each derive from a methyl group of acetyl-S-CoA by a complex, multi-step condensation mechanism (Equation 11):

$$CH_3–S–(CH_2)_2–CH(NH_2)–COOH \rightarrow CH_3–S–(CH_2)_4–CH(NH_2)–COOH \tag{11}$$

These reactions to 4-methylthiobutyl glucosinolate, the precursor for sulforaphane formation, have been extensively studied in *Eruca sativa* (arugula, rocket).[64] A gene controlling variation in the glucosinolates of *Arabidopsis* is part of the methionine elongation pathway just described.[65]

11.1.2.5.2 Compounds from the Genus Allium

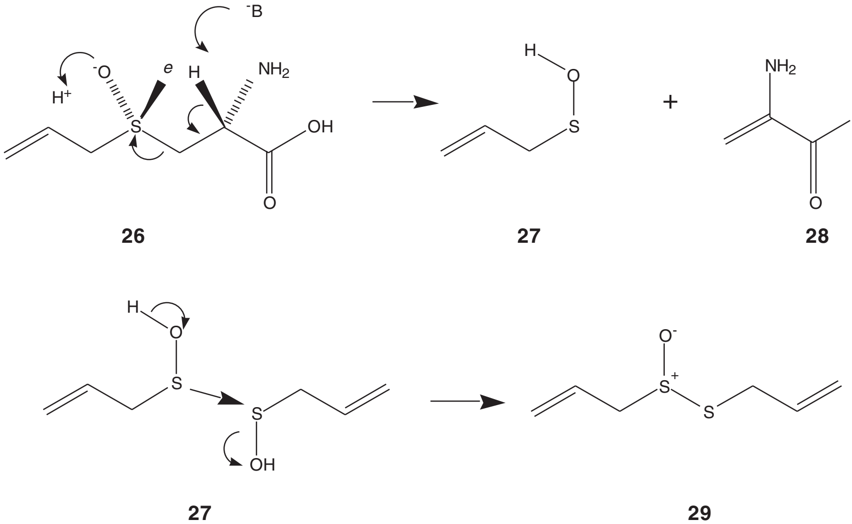
Garlic has received much use in the past by folk healers and there is continued interest in the medicinal use of garlic at the present time.

Plants of the genus *Allium*, *e.g.* garlic (*Allium sativum*), leek (*Allium ampeloprasum*), and onion (*Allium cepa*), produce a bewildering variety of sulfur compounds. Selenium analogs for some of these have also been found (Section 11.1.3.6). Much work has focused on garlic (contains more than 100 such materials) and onion.[56,66,67] Key compounds for formation of the *Allium* sulfur-containing secondary metabolites are sulfoxides of cysteine derivatives,

$HOOC–CH(NH_2)–CH_2$-SO–R. In the best known, the group R is either a one carbon unit, CH_3, or a three carbon unit. The major garlic sulfoxide, alliin, has R=–CH_2–CH=CH_2. Also present in garlic are sulfoxides with R=–CH_3, R=–CH_2–CH_2–CH_3, and R=–CH=CH–CH_3. Some *Allium* sp. contain ethiin, R=–C_2H_5, and butiin, R=–C_4H_9.[68] It is not clear how any of these sulfoxides are formed. Unspecified oxidases, either acting at the level of glutamylcysteines or cysteines, are usually invoked. For alliin formation, this would require either γ-glutamyl-*S*-2-propenyl-L-cysteine or simply *S*-2-propenyl-L-cysteine (allyl cysteine) formed from the glutamyl derivative by a glutamyl transpeptidase. Complex routes from γ-glutamylcysteine or glutathione are proposed for production of γ-glutamyl-*S*-2-propenyl-L-cysteine.[56,67] In mammalian systems, *S*-2-propenyl-L-cysteine is oxidized to alliin by flavin monooxygenases and cytochromes P 450.[69,70] Similar oxidases may be involved in plants.

Naturally occurring alliin, the major precursor to the garlic aroma, is (R_cS_s)-(+)-*S*-allyl-L-cysteine sulfoxide **26** (Scheme 10) with both a chiral carbon and chiral sulfur – probably the first such compound (note that sulforaphene – see earlier – was isolated more or less simultaneously with alliin). Hence there are four possible stereoisomers. The alliin level in garlic is significant: 5–14 mg g^{-1} fresh weight.

An intact, undamaged garlic bulb has almost no odor but a strong aroma quickly develops on cutting or crushing due to the formation of allicin, diallylthiosulfinate **29**, by action of the enzyme alliinase, EC 4.4.1.4, on alliin (Scheme 10). This enzyme is present in large amounts in garlic, up to 10% of total bulb protein.[71] Since alliinase is located in vacuoles while substrate alliin is cytosolic, reaction does not occur in absence of crushing to release the two components. The three-dimensional structure of alliinase has been determined

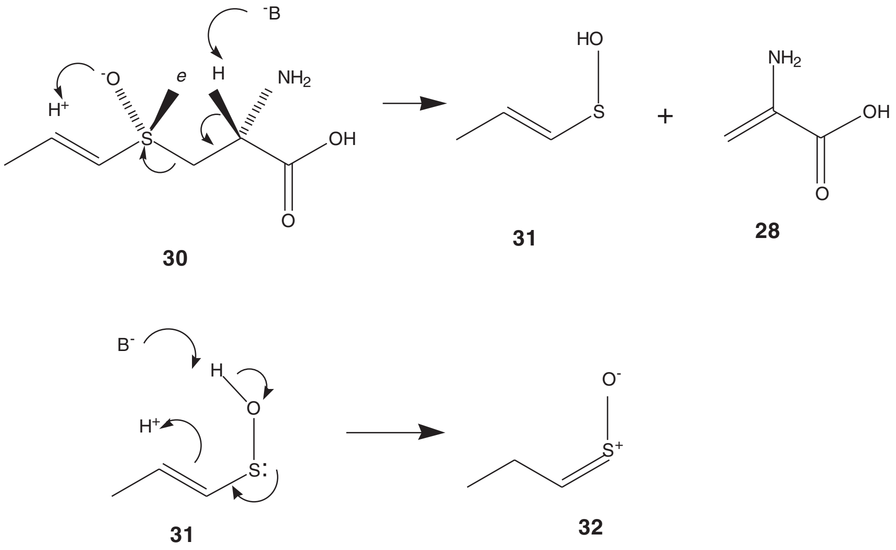


Scheme 10 *The formation of allicin from alliin by alliinase action*

by X-ray crystallography;[72] a cDNA clone encoding it was isolated and an expression vector constructed in yeast.[73]

Allicin **29**, with a strong, pungent garlic odor, is formed by an elimination of aminoacrylic acid **28** from alliin with the formation of allylsulfenic acid **27**. The unstable aminoacrylate decomposes to pyruvate and NH_3, while two molecules of allylsulfenic acid combine (Scheme 10). Although the sulfur atom of the sulfoxide is chiral, there is no information as to specific stereochemistry. Allicin is rather unstable and decomposes on gas chromatographic columns, apparently by an initial elimination of 2-propenesulfenic acid (allylsulfenic acid) and formation of thioacrolein, $S{=}CH{-}CH{=}CH_2$. The latter dimerizes to form 3-vinyl-4*H*-1,2-dithiin and 2-vinyl-4*H*-1,3-dithiin. The dithiin ring has 4 carbons and 2 sulfurs with a single double bond linked to one sulfur. Also, because of its chemical reactivity, allicin is a prodigious precursor for a multitude of secondary metabolites – too many to list all of them here. The notorious garlic breath arises when thiosulfinates, *e.g.* allicin, interact with oxygen to form materials such as allyl methyl sulfide, allyl methyl disulfide, and diallyl disulfide.

Cutting onions is a tearful proposition due to alliinase action on *iso*alliin, $(R_\mathrm{c}S_\mathrm{s})$-(+)-*S*-*trans*-1-propenyl-L-cysteine sulfoxide **30**, forming propenylsulfenic acid **31** (Scheme 11). Rearrangement of the latter by a recently discovered synthase activity leads to lachrymatory factor, LF, propanethial-*S*-oxide **32**.[74] There are *E* and *Z* isomeric possibilities for the CH=S double bond; the *Z* form is shown as **32**. Natural LF contains the isomers in the ratio, *Z*:*E*=95:5. Genetic engineering leading to the down-regulation of the synthase might lead to a flavorful, but non-lachrymatory onion.[74] This would be a major accomplishment for molecular biology!



Scheme 11 *Formation of onion lachrymatory factor*

A tree, *Scorodocarpus borneensis*, native to Borneo and the Malay peninsula, has a garlic-like smell and is known as "wood garlic". The fruit is used locally for seasoning. The major volatile flavor compounds from wood garlic are similar to those of garlic itself. Some of these materials are polysulfur compounds and have antimicrobial activity against some bacteria and fungi. These materials contain four sulfur atoms.[75] They are either 2,4,6-trithiaheptane-5-thione-2,2-dioxide (CH_3–SO_2–CH_2–S–CS–S–CH_3) or derivatives of tetrathiaoctane (CH_3–S–CH_2–S–S–CH_2–S–CH_3, CH_3–SO_2–CH_2–S–S–CH_2–S–CH_3, CH_3–S–CH_2–SO_2–S–CH_2–S–CH_3).

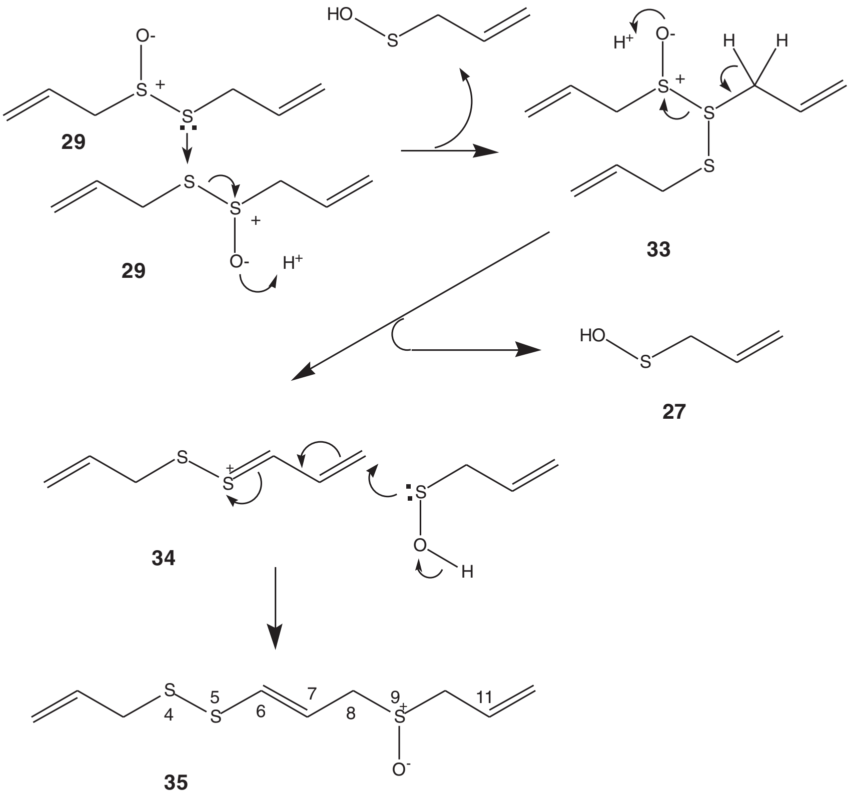
11.1.2.5.3 Medicinal Properties of Allium Secondary Metabolites

Almost 5 decades ago, the diethyl analog of allicin, C_2H_5–SO–S–C_2H_5, was prepared by action of garlic alliinase on *S*-ethyl-L-cysteine sulfoxide, and was then termed ethylthiosulfinic ethyl ester.[76] This material prevented development of sarcoma 180 ascites tumor in mice. Since similar compounds are present in *Allium* plants after crushing, there has been much interest in the use of garlic, in human nutrition, to prevent cancer.[77] An additional bonus is that garlic contains significant levels of selenium, a required human nutrient (Section 11.1.3.1). Varieties of selenium-enriched garlic are available.

Garlic supplements – powder tablets or capsules, steam-distilled oil, vegetable oil macerate extract, or extract aged in dilute alcohol – are widely available and are taken by millions. Since the active principle, allicin, is not present in garlic bulb, the supplements rely on the presence of precursor alliin and enzyme alliinase. In tests on 24 commercial brands of enteric-coated tablets, all except one gave low dissolution allicin release: 83% of the brands released less than 15% of their potential allicin.[78,79] Relevant factors were impaired enzyme activity caused by excipients and slow tablet disintegration. Caveat emptor!

The role of individual garlic components as therapeutic agents has been studied less extensively. Although Pasteur probably described the antibacterial action of garlic juice in 1858, it was not until definitive work on garlic chemistry in the1940s that allicin was specifically implicated as an antibiotic.[80] There is a close relationship between bactericidal action and allicin's ability to inhibit enzymes dependent on –SH group activity.[81] Recent work suggests that a new, stable, aqueous extract of allicin may be of value against methicillin-resistant *Staphylococcus aureus*.[82] Allicin also has antifungal and antitumor activities and decreases cholesterol biosynthesis in rat hepatocytes.[83]

Ajoene (Spanish, ajo, garlic), 4,5,9-trithiadodeca-1,6,11-triene-9-oxide **35** (Scheme 12), an antithrombotic compound with other well-defined physiological properties, is formed from allicin.[84] Like allicin, ajoene is a sulfoxide but has two further sulfur atoms in a disulfide linkage. *E* and *Z* isomeric forms are possible involving the C=C bond at positions 6 and 7. Ajoene is somewhat more stable than allicin. The formation of ajoene probably involves condensation of 2 molecules of allicin forming a sulfonium salt **33**, with elimination of propenesulfenic acid. Elimination of a second molecule of propenesulfenic acid



Scheme 12 *Formation of the E isomer of ajoene*

yields the cation **34**. The latter now reacts with propenesulfenic acid yielding ajoene shown (Scheme 12) as the *E* isomer.[84]

Ajoene has antitumor activity, inhibits cholesterol biosynthesis, modulates membrane-dependent functions of immune cells, inhibits protein prenylation[83] and is an anti-leukaemia agent for acute myeloid leukaemia.[85] In antithrombotic assays, the *Z* isomer is more active than the *E* isomer.[84]

11.1.2.6 Role of Plants and Microorganisms in Production of VOSCs

A number of volatile sulfur compounds are present in the atmosphere including the inorganic SO_2 and H_2S. There is also an important role for organic compounds, Volatile Organic Sulfur Compound, VOSCs. A major VOSC component is DMS, along with DMDS, MT, CS_2, and COS. These materials are major components of the global, biogeochemical sulfur cycle and have environmental functions being involved in acid precipitation, cloud formation, and global warming. Space limitations allow only a brief introduction to a very large topic; several books[86–88] and reviews[35,89–91] are available.

In simple terms, the global sulfur cycle has two components. One is biochemical involving the conversion of sulfate to sulfide and the formation of DMS; the other is atmospheric photochemical oxidation of DMS to sulfur oxyacids. DMS is formed mainly in the oceans by microorganisms and to a lesser extent in plants. About 38–40 Tg year^{-1} of DMS are released to the atmosphere from the oceans. The major precursor for DMS formation is the sulfonium salt, dimethylsulfoniopropionate, $(CH_3)_2–S^+–CH_2–CH_2–COOH$, DMSP. DMSP lyase enzymes catalyze an elimination of acrylic acid from DMSP (Equation 12) with the release of DMS:

$$(CH_3)_2–S^+–CH_2–CH_2–COOH \rightarrow CH_3–S–CH_3 + H_2C{=}CH–COOH \quad (12)$$

DMSP is formed from L-methionine; required processes, not necessarily in this order, are methylation, deamination, and decarboxylation. Several available pathways have been comprehensively reviewed.[35]

As already noted, MT has several sources such as lyase enzymes for L-methionine and *S*-methyl-L-cysteine. There are complex relationships between DMS, MT, and other VOSCs in the atmosphere, and in marine and terrestrial environments. The previously cited reviews should be consulted.

11.1.2.7 Miscellaneous Sulfur Compounds

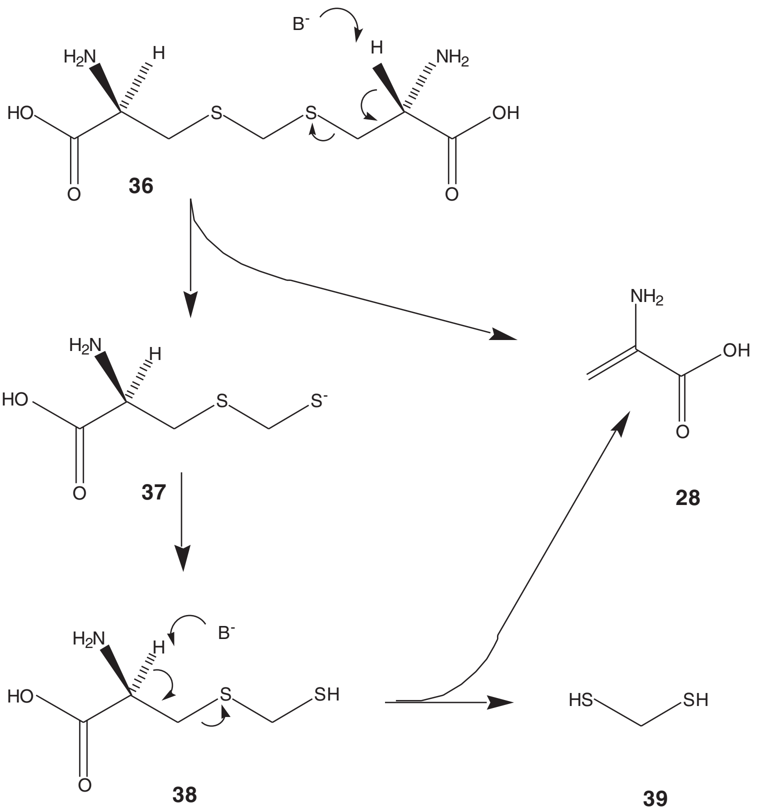
While not intended to be comprehensive, some other sulfur-containing compounds from plants and microorganisms are listed here.

The sulfur-containing amino acid, djenkolic acid **36** (Scheme 13), was mentioned earlier. It was originally isolated from djenkol beans, the seed of *Pithecolobium lobatum* or *P. bigeminum*. The broad, round, reddish beans are eaten as a delicacy in Indonesia and nearby areas, sometimes causing a poisoning (djenkolism); symptoms range from lumbar pain, vomiting and diarrhea to hematuria and proteinuria and may progress to anuria and renal failure.

In structural terms, djenkolic has two units of L-cysteine joined through a CH_2 group linked to sulfur atoms. It has also been found in seeds of *Albizzia lophanta* and *Parkia speciosa*[32] and, as noted earlier, is the source of CS_2 in *Mimosa pudica* (Section 11.1.2.2.2). An enzyme in *A. lophanta* seeds converted djenkolic acid to an unstable material with a leek-like odor, methylene dithiol **39**.[92] This was presumably an elimination of aminoacrylic acid **28** *via* intermediates **37** and **38** (Scheme 13). The methylene dithiol decomposed to H_2S and possibly, thioformaldehyde, CH_2S; the latter might be a source for polysulfides.

Ergothioneine is the betaine derived from 2-thiol histidine (*i.e.* the trimethylammonium derivative). It can be written as a thiol **40** or thione **41** ↔ **42** the latter predominating in aqueous solution (Scheme 14). It occurs widely in various actinomycetes and to a lesser extent in filamentous fungi. Its function is unclear, but is possibly that of an antioxidant.[93] β-Hydroxy-ergothioneine is present in the mushroom, *Lyophyllum connatum*.[94]

Mycothiol **43** (Scheme 14) is a complex cysteine derivative isolated from *Streptomyces clavuligerus*, *Mycobacterium bovis,* and other mycobacteria. It

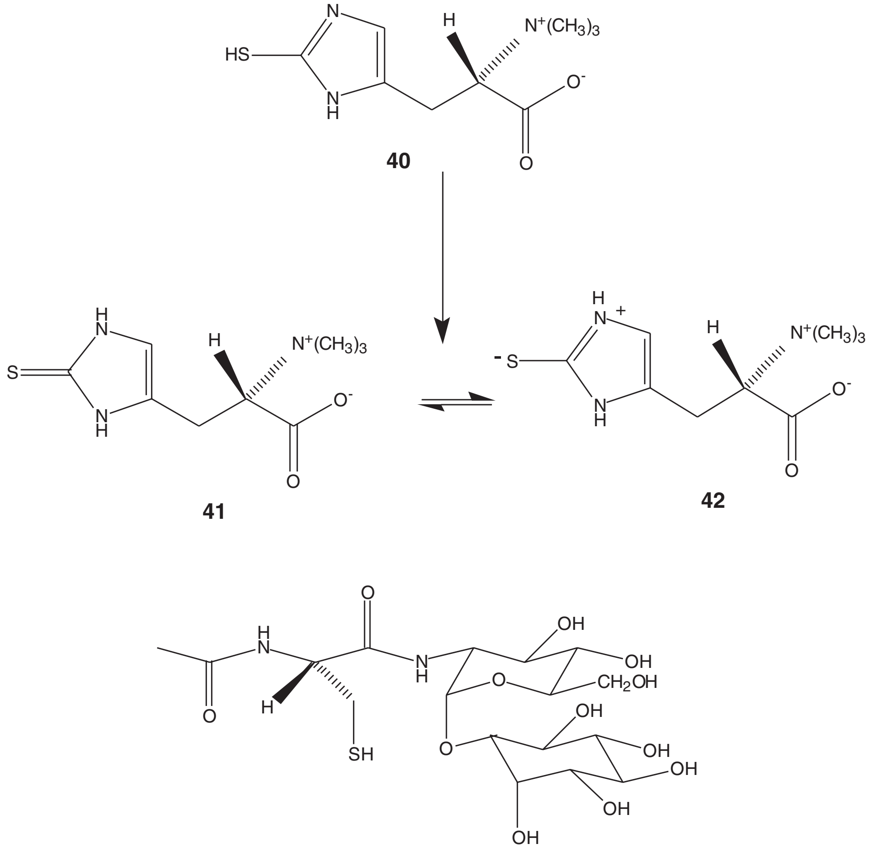


Scheme 13 *Formation of methylene dithiol from djenkolic acid*

probably plays a role in detoxification of formaldehyde peroxide, and electrophilic alkylating agents.[93]

Several secondary metabolites are dithiolanes, as for instance the allelochemicals found in the tropical weed, *Sphenoclea zeylanica*. Zeylanoxide A is present in two stereoisomeric forms depending on whether the chirality at sulfur is (*R*) or (*S*); the latter form is **44** (Scheme 15). Zeylanoxides B are similar but in these cases the oxide function is on the sulfur at the 2 position. These molecules inhibited root growth in rice seedlings as well as the germination of letuce seeds.[95]

A more complex structure is that of leinamycin **45** (Scheme 15), a material with potent cytotoxic and antitumor properties, isolated from a *Streptomyces* sp. A 1,2 dithiolane-3-one ring is spiro fused to a complex macrolactam[96] (and references therein). Leinamycin has the remarkable ability to cleave DNA. In brief, leinamycin reacts with a thiol and, after a profound rearrangement, forms an episulfonium ion. This ion alkylates the N7 position of guanosine residues in double stranded DNA; an unstable adduct is depurinated by hydrolysis of the glycosidic bond between the alkylated base and a deoxyribose residue. Some structurally less complex 1,2-dithiolane-3-one 1-oxides have a similar DNA cleaving ability.[97]



40

41

42

43

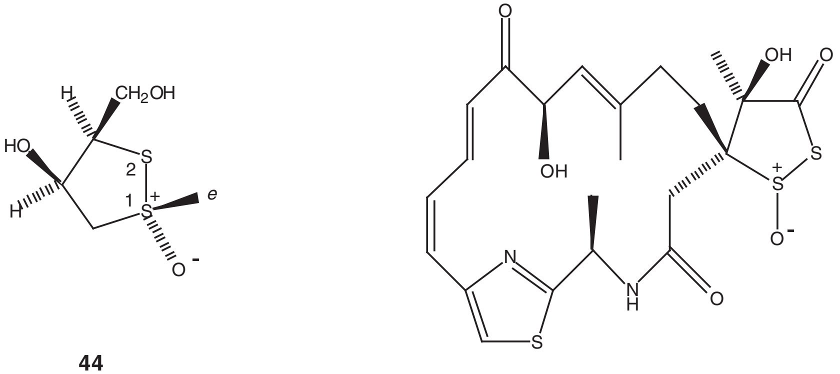
Scheme 14 *Ergothioneine and mycothiol*

A number of heteroaromatic monothiocarboxylic acids are formed by *Pseudomonas* sp. From *P. putida*, there was isolated pyridine-2,6-di-(monothiocarboxylic acid) **46** (Scheme 16). Of interest is the fact that in *P. stutzeri* KC, a copper complex of **46** is the active agent for a one electron transfer in the bacterial biodegradation of CCl_4. Methylation of *P. putida* extracts provides a number of related structures such as **47**. In addition, a *P. fluorescens* sp. contains 8-hydroxy-4-methoxy-quinoline-2-monothiocarboxylic acid **48**.[98]

11.1.3 Selenium

11.1.3.1 General Biological Role of Selenium

The toxicity of selenium (Se) belies the fact that it is a required trace-nutrient for many biological organisms. The general order of toxicity for the most



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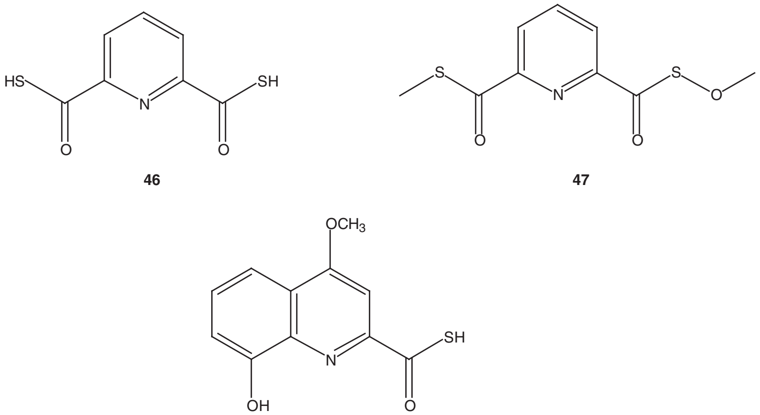
45

Scheme 15 *Dithiolane secondary metabolites.*



46

47

48

Scheme 16 *Heteroaromatic monothiocarboxylic acids from* Pseudomonas *sp.*

common environmental forms of selenium is selenite (SeO_3^{2-}) > selenate (SeO_4^{2-}) > organo-Se > > elemental selenium (Se^0).

As early as 1916 selenite was used to enrich and select for *Typhus bacillus*, quickly excluding other microorganisms.[99] Even today, the American Public Health Association describes use of selenite for enrichment for *Salmonella* ssp.[100] Initially an element thought to only be toxic and possibly carcinogenic, the biochemical and nutritional importance of Se in mammalian and bacterial enzyme systems has been established over the past 50 years[101] and due in no small part to work by Stadtman and coworkers.[102–105] While the minimum required level of Se for adult humans is approximately 40 μg per day,[106] at daily ingestion levels only ~25 times greater toxic effects begin to occur.[107] Incorporation of Se in enzymes and proteins following the analogous sulfur forms (see above in this chapter) centers around selenium-containing amino acids.

Reviews of the extensive biochemistry of selenium in bacteria are available.[108,109] US Center for Disease Control summaries for Se toxicology are also available[110] A more recent review of the processes of biomethylation of selenium and tellurium in microorganisms and plants is also available.[111]

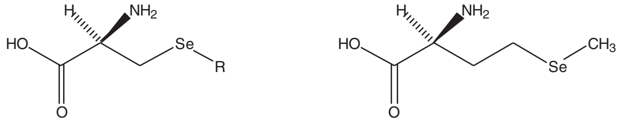
11.1.3.2 Se-Containing Amino Acids

11.1.3.2.1 Se-Cysteine

The importance of the selenium-analog of cysteine, selenocysteine (Se-cysteine), $HSeCH_2CHNH_2COOH$, and its incorporation into protein *via* a ribosomal mechanism has earned it the label of the 21st amino acid.[112–115] Assuming L configuration at the α carbon, Se-cysteine is represented by **49**, R=H (Scheme 17).

All selenium-containing proteins and enzymes in animals, microorganisms and plants incorporate selenocysteine non-specifically[105] or as part of Se-dependent antioxidant enzymes such as glutathione peroxidase, (EC 1.11.1.9) which has a Se-cysteine residue in its active site.[116–120] An active form of Se, selenophosphate, is produced by selenophosphate synthetase in several bacteria. This active form is required for the production of Secys-tRNA, a precursor for Se-cysteine.[121] In a similar vein, a Se-containing modified-tRNA nucleoside, 5-methylaminomethyl-2-selenouridine, encodes a selenouridine synthase which replaces sulfur in tRNA with selenium.[122]

In a Se-tolerant, grassland legume species (*Melilotus indica* L.) grown in Se-laden sediment from agricultural drain water, selenocysteine as well as selenomethionine (see below) and three other seleno-amino acids were detected as non-protein-bound forms in plant tissue with selenomethionine constituting more than 50% of the total Se-amino acid content. Like other accumulator plants (*e.g.* genus *Astragalus*) this sour clover could concentrate >200 mg Se/kg without growth reduction.[123] The bioconcentration of this metalloid from the environment has important toxicological implications and may affect how selenium-laden plant material can be disposed of when the plants are used in an environmentally friendly phytoremediation schemes.[124] In fact, pigs fed Se-accumulator plants (*Astragalus bisulcatus*, 300 μg Se/g dry wt.) daily (25 μg Se/g/day) developed, among other effects, neurological signs of paralysis and skin lesions. Some effects were apparent within the fifth day of the 6 week experiment.[125] These effects were more severe than with analogous diets of selenomethionine and selenite.



49

50

Scheme 17 *Selenocysteine (R=H) and selenomethionine*

11.1.3.2.2 Se-Methionine

Selenomethionine, $CH_3SeCH_2CH_2CHNH_2COOH$, **50** (Scheme 17) is also incorporated non-specifically in proteins of *Clostridium kluyveri*[126] and in yeast[127,128] apparently taking the place of methionine; however, no specific biological incorporation of Se-methionine has been found.[105]

From recent work in Poland, rye seedlings supplemented with selenite apparently incorporated 40% of added Se as selenomethionine. Enrichment measurements were approximately 60-fold over unamended seedlings, and sour dough bread made with the enriched-Se seedlings was found to be a good source of dietary selenium.[129] Enrichment of Indian mustard (*Brassica juncea*), sunflower (*Helianthus annus*) and white lupine (*Lupinus albus*) showed inorganic amendments mostly incorporated as selenomethionine in amino acid extracted and analyzed *via* high performance liquid chromatography/inductively coupled plasma/MS.[130] Se-methylselenocysteine (CH_3–$SeCH_2CHNH_2$–COOH) **49**, R=CH_3 (Scheme 17) was also found in Indian mustard extracts. Its presence was attributed by the authors to this plant's Se-detoxification mechanism, since it is a non-protein amino acid. Broccoli (*Brassica oleracea* var. *italica*) also accumulates Se as Se-methylselenocysteine.[131]

11.1.3.3 Selenocysteine Containing Se-Proteins

11.1.3.3.1 Formate Dehydrogenase

In *Escherichia coli,* a selenium-dependent formate dehydrogenase, again with a Se-cysteine residue, catalyzes the oxidation of formic acid produced during glucose formation.[132,133] Two Se-cysteine-containing enzymes can be formed: formate dehydrogenase cytochrome (EC 1.2.2.1) which interacts with the nitrate reductase complex and formate dehydrogenase H (EC 1.2.1.2), part of a system formerly called formate hydrogenlyase. During translation in *E. coli*, an in-frame UGA codon controls the insertion of Se-cysteine into the seleno-polypeptide chain and depends on the availability of selenium in the medium.[134]

11.1.3.3.2 Glycine Reduction

A mechanism of glycine reduction to acetyl-phosphate has been described involving selenoethers and selenocysteines.[135] This is a microbial energy saving process that has been evidenced in Gram-positive and Gram-negative bacteria. Though the probable glycine reduction mechanism involves genes similar to those of the thioredoxin system, Andreesen notes the difficulty of further understanding of the assumed glycine reductase mechanism because of unusual reactions involving selenoethers and redox active selenocysteines.

11.1.3.3.3 Thioredoxin Reductase

Bacteria, fungi, and plants have a thioredoxin reductase system involving Se-containing thioredoxin reductase (EC 1.8.1.9), NADPH, and thioredoxin. Effecting the intercellular redox poise, this system interacts in selenium metabolism, DNA synthesis, and cellular antioxidation.[136] Thioredoxin reductase reduces selenium and thereby acts as a source of selenide for selenium-containing proteins. Madeja *et al.*[137] recently suggested that over expression of thioredoxin reductase enhanced resistance to selenium toxicity. Gromer *et al.*[104] using the pK_a of cysteine as contrasted to the pK_a of Se-cysteine in this system suggest that the efficiency of selenoproteins is not the inherent driving force in their incorporation in biological systems, but instead may "expand the metabolic capacities in terms of activity toward a wider variety of substrates and over a broad range of pH".[138]

11.1.3.4 Manipulation of Bacterial Genes Involving Se Resistance

Metalloid resistance by bacteria has been of interest for over 70 years. Alexander Fleming examined metalloid-resistant bacteria in the 1930s.[139] Cowie and Cohen successfully substituted selenomethionine for methionine in *E. coli* in 1957 by using sulfur-free medium and amendment with Se oxyanions and concluded in part: "... some variation in the amino acid composition of a given protein may be the rule rather than the exception".[140] Summer and Jacoby noted that transferable plasmids in gram-negative bacteria could confer resistance to tellurite or tellurate.[141] A 100-fold increase in resistance was observed for modified *E. coli*. More recent work has centered on metalloid substitution in targeted enzymes or proteins. To investigate the properties of Se-containing proteins, chemical modification can be used[142,143] or genetic manipulation harnessing cells has been developed. As an investigative tool, the manipulation of the genes that confer bacterial metalloid resistance is often carried out by the isolation of genes from resistance bacteria (as measured by an evaluation of the bacterial minimal inhibitory concentration, MIC) and subsequent insertion of the isolated genes, *via* plasmids, in metalloid-sensitive microbes.[144] When subsequently grown in metalloid-amended cultures, only metalloid-resistant clones reproduce. Some genetic manipulation involves the transfer of genes between different species, even different biological kingdoms. Genes from a flatworm (*Schistosoma japonica*) were inserted *via* a plasmid into the bacterium *E. coli* strain BL21 (DE3). The expression of selenoproteins containing selenocysteine was successfully carried out at levels that allowed purification of those products when supplemented with 5 μM selenite and at levels that allowed measurement of kinetic parameters of those recombinant proteins.[118] Ranjard *et al.*[145] constructed clones of *E. coli* containing the bacterial thiopurine methyltransferase enzyme from freshwater bacteria which were selenium-resistant. The genetically modified *E. coli* produced dimethyl selenide, CH_3SeCH_3, DMSe, and dimethyl diselenide ($CH_3SeSeCH_3$, DMDSe, see below) when amended with selenite or methylselenocysteine. More recently Favre-Bonte *et al.*[146] examined five distinct, freshwater samples (containing polycultures of freshwater bacteria) which produced DMSe and DMDSe (see below) when amended with selenite or methylselenocysteine and a nutrient broth. Following bacterial screenings and DNA sequencing they determined that the genes responsible for this reduction and methylation had apparently drifted "outside regions encoding highly conserved domains" but were most closely related to methyl transferases.

Transposon integration mutagenesis can be used to allow the selection of metalloid-resistant mutants with enhanced MICs.[147] Ledgham *et al.*[148] found a transposon-disrupted gene in a mutant – with a three-fold increase in Se-resistance – that encoded a protein from a member of the DedA family of membrane proteins that was implicated in the uptake of selenite through cell membranes. This is a reasonable hypothesis for how metalloid resistance occurs in some microorganisms.

11.1.3.5 Oxidation/Reduction Processes Involving Selenium

The oxidation/reduction of selenium in molecules in biological systems can change the solubility, volatility, and probably most important, biological availability and toxicity of this element. Bacterial response to toxic metalloids often involve combinations of chemical reduction or chelation, sequestration (sometimes as elemental forms), reduced intake and "increased expression of cellular repair machinery".[149] Plant response can be concentration of metalloid-containing compounds in plant tissue or reduction and methylation to volatile forms.[150] For the strictly inorganic forms of Se the toxicity is generally $SeO_3^{2-} > SeO_4^{2-} > > Se^0$. For the organic forms the toxicity is more varied but with volatile, methylated forms much less toxic than the oxyanions.[111,151] The biological reduction of fully oxidized selenium (selenate, Se^{+6}) to the most reduced form (selenide, Se^{2-}, as DMSe), can be represented by a series of reduction and methylation steps:[111,152]

SeO_4^{2-} – reduction → SeO_3^{2-} – methylation → CH_3SeO_3H – reduction → CH_3SeO_2H – methylation → $(CH_3)_2SeO_2$ – reduction → $(CH_3)_2SeOH$ – reduction → $(CH_3)_2Se$

Also cellular thiol reduction of selenium oxyanions was suggested by Painter over 60 years ago and elemental Se was proposed as one of the products.[153] And in fact, red, elemental selenium is often seen in Se-amended cultures of Se-resistance bacteria.[154–158] Deposition of elemental Se in plants is, so far, unknown.

Obviously the redox poise in biological systems is very important and the movement of selenium through this process has been investigated for denitrifiers such as *Paracoccus denitrificans*,[159] a specialized selenate-respiring bacterium *Thauera selenatis* which used selenate as the sole electron acceptor,[160,161] and phototrophic bacteria which produced different reduced forms of selenium when amended with either selenite or selenate and even added insoluble elemental Se.[162] As noted above, Andreesen has commented on the importance of redox active selenocysteines[135] and Jacob *et al.*[136] note the importance of the thioredoxin system to redox poise.

11.1.3.6 Analytical Methods for Elemental Se and Organo-Selenium

Non-volatile elemental and inorganic selenium, biologically formed in bacterial or plant samples, can be determined *via* atomic absorption spectrometry (AAS) most often with electrothermal atomization[163] or hydride generation AAS,[164,165] inductively coupled plasma spectrometry,[130,166] and X-ray absorption spectroscopy (XAS).[154] The XAS K-edge method can be used to determine selenium in specific inorganic oxidation states[167–169] and in different organoselenium molecules such as Se-containing amino acids.[170] And most recently, XAS has been used to investigate specific coordination environments in biomolecular structures in which sulfur was replaced with selenium in the coenzyme involved in the reversible redox reaction of heterodisulfide reductase. Both quantitative data and measurements of specific bond distances in the enzymes under study were available with this method.[171]

Transmission electron microscopy energy dispersive X-ray analysis has also been used to image intracellular Se granules present from Se bioreduction in bacteria. Reduction of selenite and the deposition of elemental Se in cell cytoplasm or in the extracellular space may be lead to promising bioremediation schemes.[172]

Liquid chromatography/MS has also very recently been used for selenate and selenite determination[173] and selenomethionine.[174] And another recent liquid chromatographic hyphenated method, liquid chromatography-hydride generation atomic fluorescence spectrometry, has been used to determine selenite, selenate, selenocysteine, and selenomethionine in a single run. Reverse-phase and ion-exchange columns were used in series to accomplish the complex separation of all four of these analytes.[175] And microchip capillary electrophoresis has most recently been used for determination of various Se-amino acids with "negligible sample consumption".[176] An excellent US Center for Disease Control summary of Se analytical methods is available.[110]

Volatile organo-selenium analytes are most commonly determined using gas chromatography (GC). Flame ionization detector response falls short for trace analysis and in complex samples and so specialized GC detectors are used. GC with AAS has been used for 30 years.[177–179] To improve detection limits modern methods use solid phase microextraction (SPME) to preconcentrate volatile samples by use of a fiber to adsorb analytes prior to GC. SPME sampling of headspace of hydroponically grown *Brassica juncea* amended with selenate, selenite, selenomethionine and KSeCN followed by analysis with ICP/MS allowed for the detection of DMSe, DMDSe and dimethyl selenenyl sulfide (CH_3SeSCH_3, DMSeS).[180] SPME sampling can be from the sample's gas phase, solution phase, or simultaneously from both by partially immersing the SPME fiber through the gas phase and into a culture medium or solvent containing analytes in equilibrium with the headspace.

Methylated organo-selenium has been determined by GC/MS or fluorine-induced chemiluminescence to determine DMSe, DMDSe, and DMSeS. This last compound, dimethyl selenenyl sulfide, was mistakenly identified as dimethyl selenone ($CH_3SeO_2CH_3$) in earlier work with bacteria.[181,182] However, much recent work with many microorganisms have shown ample evidence of DMSeS production from Gram-negative bacteria,[181,183] phototrophic bacteria,[167,184] phytoplankton[185] and in *B. juncea* detailed above. SPME with microwave-induce plasma atomic emission spectrometry was recently used to determine volatile organo-selenides in the headspace of crushed garlic and growing lupine and Indian mustard plants (Section 11.1.2.5.2). These workers reported detection of DMSe, diethyl selenide, and possibly DMSeS.[186] While reported here from plant origin, diethyl selenide has not been detected in bacterial headspace. The organo-sulfur compounds detailed above, found in garlic and onion (Section 11.1.2.5.2), are often mirrored by selenium analogs. For instance, *Allium* species produce trace amounts of DMSe, DMDSe, CH_3SeSCH_3, and $CH_2{=}CHSeCH_3$ among many others.[187,188] Most recently, MS methods for determination of selenium-containing species in high-Se yeast, garlic, and onions have been reviewed.[189]

11.1.4 Tellurium

11.1.4.1 General Biological Role of Tellurium

Unlike selenium there is no required biological role for tellurium in bacteria or plants that has been determined; however, this may ultimately not be the whole story.[111] Selenium was only viewed as a toxic metalloid with no necessary role for metabolism until at least the 1950s; see above. While tellurite is less soluble than tellurate in aqueous solution, in general tellurite is probably more toxic to most organisms.[190] The non Te-resistant wild type *E. coli* bacterium (Gram-negative) has MICs of 1 to 3 ppm for tellurite and tellurate.[144,191,192] Tellurite is used to enrich and select for *Staphylococcus aureus*.[169,193,194]

Like Se^0, elemental Te from a solubility point-of-view alone is much less toxic. The volatile, methylated forms of tellurium are probably less toxic than the oxyanions or Te-containing amino acids but little data are available evaluating methylated tellurides. One report, involving human squalene monooxygenase, showed that dimethyl telluride, DMTe, acting as an inhibitor, reacted at (50%) minimal inhibitory concentrations 100 times lower than tellurite.[195] Tellurium-containing compounds in garlic have also been proposed as hypocholesterolaemic (lipid-lowering) agents.[196] In toxicity experiments on rats that compared similar doses of tellurite to DMTe, that +4 oxyanion was clearly the more toxic of the two; however, solubility is an important variable in these types of comparisons. Dimethyl sulfoxide (0.2%) was required to dissolve DMTe in aqueous solutions used in those experiments.[197] There has been a recent reversal of the long held notion that another methylated metalloid, trimethyl arsine $[(CH_3)_3As]$, is significantly toxic to humans.[198] Furthermore the widely known production of DMTe by humans exposed to tellurium salts[199–202] lends credence to the hypothesis that methylated tellurium is, in general, relative low in toxicity compared to Te oxyanions. Bacterial toxicity experiments of simple methylated tellurides are unreported.

In experiments parallel to those of Cowie and Cohen (see above), a Te-resistant fungi grown in high tellurite amendments with little available sulfur produced telluromethionine, tellurocysteine, and tellurocystine.[140,203] So like selenium, tellurium can apparently substitute for sulfur under certain conditions. Boles *et al.* were able to force incorporation of telluromethionine into cellular dihydrofolate reductase to replace methionine. This was accomplished by amending a culture in mid-log phase (and containing minimal levels of methionine) with telluromethionine and a promoter that induced the dihydrofolate reductase gene. Dihydrofolate reductase purified from the culture contained 2 moles of Te per mole of dihydrofolate reductase.[204] An improvement on this incorporation/derivatization of heavy atoms into proteins was more recently described with Te-methionine being incorporated into all 5 methionyl sites in dihydrofolate reductase.[205]

11.1.4.2 Manipulation of Bacterial Genes Involving Te Resistance

The mechanism of tellurium resistance has been investigated using genetic manipulation similar to that of Se (see above) and cellular oxidant capacity apparently plays an important role.[144,206] A few tellurite determinants – both chromosomal and plasmid encoded – have been identified in bacteria.[113,147,192,207,208] Recent studies have focused on the role of methyltransferases in Te resistance. Liu *et al.*[111] determined that the *E. coli* gene *tehB* uses *S*-adenosylmethionine and a methyltransferase in tellurite detoxification, but while no methylated tellurium compounds (see below) were observed, a loss of tellurite was observed in tellurite-amended cultures and Te complexation was inferred.[191]

More recent work by Araya *et al.*[144] has involved the insertion of genes into *E. coli* taken from a thermophilic bacterium,[209] *Geobacillus stearothermophilus* V. A bacterial clone was produced (1VH) with inserted genetic fragments involving three open reading frames (ORFs) of 780, 399, and 600 base pairs. These encode for three protein products that were most similar to the SUMT methyltransferase (ORF 780), BtuR protein of *Bacillus megaterium* (ORF 399), and the UbiE methyltransferase of *Bacillus anthracis* A2012. The unmodified *E. coli*'s MICs were 1.25 ppm for tellurite and 2.5 ppm for tellurate, and the MICs for the *E. coli* 1VH recombinant clone were 25 ppm for TeO_3^{2-} and 125 ppm for TeO_4^{2-} showing resistance had been conferred. In addition to increased Te resistance, black, elemental Te and organotellurium compounds were produced (see below). The authors suggest that the Te resistance gained by these cloning experiments – from a Gram-positive thermophile to a Gram-negative enteric bacterium – could be strongly connected to the ability of the clone to reduce and methylate tellurium. Experiments to block SAM production in the recombinant cells (using ethionine) dropped the Te resistance back to that of the wild type; this suggest that *S*-adenosylmethionine was also involved in the resistance process.[144]

11.1.4.3 Oxidation/Reduction Processes

Like selenium, the process of reduction/oxidation cycling in biological systems is important and changes in the oxidation state are often an easy means of determining bioreduction for added tellurium oxyanions. The general order of toxicity for tellurium's most common biospheric forms mimics selenium: $Te^0 << TeO_4^{2-} < TeO_3^{2-}$. Black, elemental Te ($Te^0$) formation is relatively common for Te-resistant bacteria.[144,156,190,210] In recent work with the facultative, phototrophic bacterium *Rhodobacter capsulatus*, reduction of added tellurite produced Te^0 depositions in cells undergoing photosynthetic-anaerobic growth. Electron micrographs show black Te^0 deposits in the cell cytoplasm.[210] Interesting is the report of two children who had accidentally ingested (high concentration) Te-containing solutions. They exhibited production of elemental Te on oral mucosa as well as garlic breath.[211] It is probable that to a large degree, the biological source of these Te-containing products was (enteric symbiotic) bacteria. The further reduction of Te oxyanion amendments to telluride, Te^{2-}, and methylated forms are discussed below.

11.1.4.4 Analytical Methods for Elemental Te and Organo-Tellurium

The analytical methods for Te^0 and organo-tellurium exactly mirror those for selenium (see above). Elemental and oxyanions of Te have been analyzed by ICP/MS[212,213] and X-ray absorption LI-edge spectroscopy.[169] This last method is analogous to the Se K-edge method described above and allows differentiation between different oxidation states of tellurium in biological samples. Prange *et al*. report the reduction of Se oxyanions to Se^0 by a strain of *Pseudomonas fluorescens* (DSMZ 50090^T) but that same strain did not reduce tellurium oxyanions (neither tellurite nor tellurate).[169] Work with another strain of *P. fluorescens* has detected the biological production of elemental Se and Te for the +4 oxyanion amendments to growing cultures of this bacterium.[155,190] Isotope dilution GC/MS has been used to determine Te in urine following a rather cumbersome method of sample digestion and subsequent derivatization.[214]

As with selenium analysis, HGAAS also finds a place in Te determination. Basnayake *et al*. amended cultures of *P. fluorescens* K27 with 0.1 mM tellurite and, after 92-h growth, determined that approximately 34% of added Te was present as either precipitated, elemental Te in/or on centrifuged cells; the balance of added Te remained in solution.[190] In this same study, GC/MS was used for determination of DMTe in the same facultative anaerobe amended with tellurate.[190] Earlier, GC/MS was used to analyze the headspace of a tellurium-resistant fungus amended with tellurite.[215] This last is one of the few reports of the detection of dimethyl ditelluride in microbial headspace (see below).

Beginning with Fleming and Alexander's determination of DMTe using a GC flame ionization detector,[216] gas chromatography has usually figured in the determination of this volatile, microbially produced, reduced compound. Before that microbial production of DMTe was noted as a garlic smell only.[217] More recently, volatile organo-tellurium compounds have been determined in the headspace of genetically modified Gram-negative bacteria, *E. coli* 1VH, described above. DMTe, DMDTe ($CH_3TeTeCH_3$) and most interestingly methanetellurol, CH_3TeH, and dimethyl tellurenyl sulfide CH_3TeSCH_3, were detected in anaerobic headspace above growing cultures.[218] This last sulfur/tellurium mixed compound is analogous to the aforementioned DMSeS and has never been reported in the literature before. A clone of this same organism with (only) inserted genes coding for UbiE methyltransferase produced DMTe when the cells were amended with tellurate but not with tellurite. The authors note:[144] "These results may be indicative that the two Te oxyanions could be detoxified in the cell by different metabolic pathways." Headspace analyses in these experiments involved GC with fluorine-induced chemiluminescence detection[162] and/or GC/MS.[144,218]

11.1.5 Summary

As has been indicated, there are many similarities between the secondary metabolism of sulfur in plants and microorganisms and the more general metabolic processes of selenium and tellurium. The main difference is the more dramatic and extensive involvement of sulfur in both general and secondary metabolism. Were it not for the essential nutritional role of selenium in animals and humans, the roles of selenium and tellurium might well be described as only those of secondary metabolism. Nevertheless, a nutritional role for tellurium may yet be uncovered. A striking feature for all three chalcogens has been the development of very sensitive analytical methods for both inorganic and organic forms of these elements.

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CHAPTER 11.2

Metal-Sulfur Clusters as the Model for the Active Sites of Metalloenzymes

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11.2.1 Introduction

Nitrogen is the element essential for all living things and a significant part of nitrogen needed on Earth is supplied in the form of ammonia produced from atmospheric nitrogen by biological nitrogen fixation. This highly important reaction, converting quite an inert N_2 molecule into ammonia through coupled protonation and electronation, is known to proceed under ambient conditions by the catalysis of metalloenzyme nitrogenase.[1] This presents a sharp contrast to the industrial nitrogen fixation,[2] *i.e.* Haber-Bosch process, that requires an extremely drastic condition to produce ammonia from gaseous nitrogen and hydrogen in the presence of Fe-based heterogeneous catalyst. From 1970s, certain Mo-Fe-S aggregates had been proposed as the active site structure of nitrogenase mainly on the basis of the EXAFS data,[3] and it was in 1992 that the first report appeared about the results of the single-crystal X-ray diffraction study for the most common nitrogenase, *viz.* Mo nitrogenase, which disclosed the surprising $MoFe_7S_9$ mixed-metal sulfido core present at the active site.[4] By the more recent crystallographic results at the stage of the more accurate resolution, one interstitial light atom, most probably N, was found at the center of this core as depicted in Figure 1.[5]

Owing to the remarkable progress in the techniques of the single-crystal X-ray analysis, detailed structures have recently been clarified for a number of enzymes, which include several metalloenzymes containing the cluster cores with sulfur-bridged multimetallic centers at their active sites such as hydrogenase,[6] sulfite reductase,[7] and carbon monoxide dehydrogenase[8] (Figure 2), along with nitrogenase. It is likely that high catalytic activities of these enzymes result

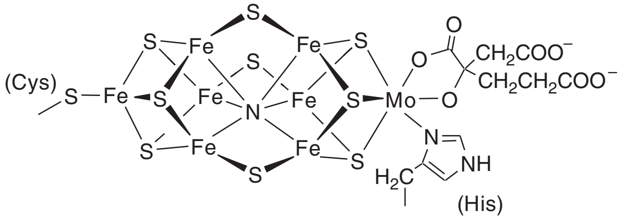


Figure 1 *Structure of the $MoFe_7S_9N$ cluster of FeMo-co in Mo nitrogenase*

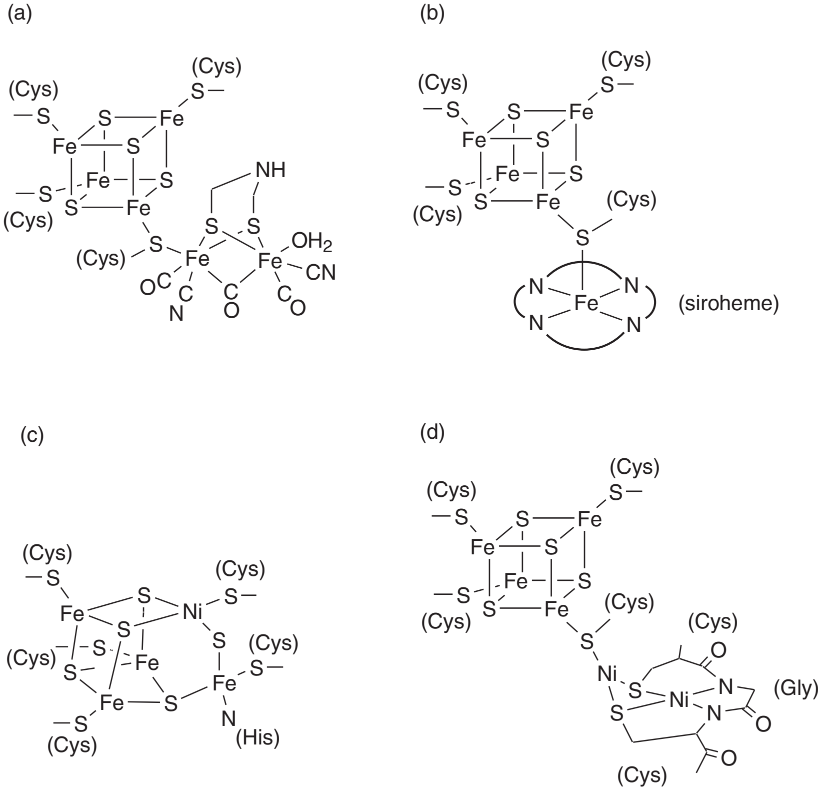


Figure 2 *Structures of the actrive sites of metalloenzymes containing metal-sulfur cluster units. (a) Fe only hydrogenase, H-cluster (H_{OX} form); (b) Sulfite reductase; (c) NiFe carbon monoxide dehydrogenase, C-cluster; and (d) NiFe carbon monoxide dehydrogenase, A-cluster, which functions as acetyl-CoA synthase*

from the co-operation of two or more metal centers in the proximity, whereby the sulfur ligands such as sulfides and thiolates are the choice as the bridges to maintain these multimetallic cores intact during catalysis. The features characteristic of the S atom, that is, the strong affinity with transition metals and the high bridging ability, are presumably the reasons of the choice of S as the bridging atom. However, although the X-ray crystallographic analyses have successfully disclosed the active site structures of these enzymes in the resting state, those in catalytic turnover may possibly be different. Furthermore, their function mechanisms are essentially unknown. Apparently it is quite difficult to observe directly what are occurring at the active sites embedded in the huge proteins, so that the studies to synthesize the model compounds and clarify their reactivities are of much importance. In this chapter, recent advances in the chemistry of the metal–sulfur clusters as the synthetic analogues to the natural enzymes will be summarized briefly.

11.2.2 Well-Defined Metal–Sulfur Clusters in Metalloenzymes and Syntheses of Their Structural Models

Iron-sulfur proteins are ubiquitous in all life forms, which contain at their active sites most commonly the Fe_2S_2, Fe_3S_4, and Fe_4S_4 cluster cores shown in Figure 3 to mediate the electron transfer as their predominant role. In the early 1970s, synthetic approach to these iron-sulfur cluster sites was initiated and the excellent analogues of these rhomboidal, incomplete cubane-type, and cubane-type Fe clusters having certain thiolato groups as ancillary ligands in place of the cysteinyl residues have already been prepared successfully.[9]

On the other hand, such approaches to the metalloenzymes described above in Figures 1 and 2 are still under way. Thus, the model clusters reproducing precisely their complex metal–sulfur assemblies in the native form have not yet been isolated. In this section, the studies aiming at the syntheses of the model compounds of two clusters in nitrogenase, FeMo cofactor and P-cluster, will be surveyed. The choice of these clusters as the representatives of the metal–sulfur clusters in metalloenzymes arises from the fact that these are the largest and most complicated metal-sulfur clusters known at present among those observed in natural enzymes.

11.2.2.1 Preparation and Reactions of the FeMo Cofactor Model Clusters

Most common nitrogenase is composed of two proteins, Mo-Fe protein and Fe protein, both of which contain metal–sulfur clusters. The former protein

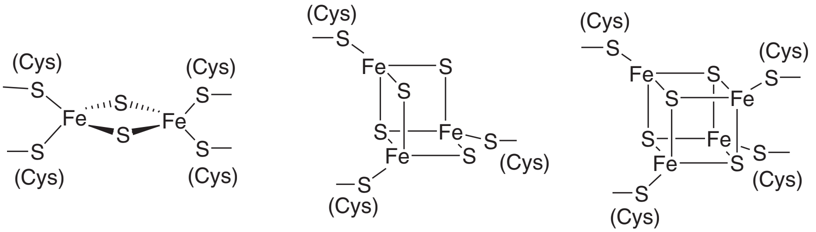


Figure 3 *Three representative Fe-S multimetallic cores observed in iron-sulfur proteins*

contains two kinds of clusters: FeMo-co, *viz*. Mo-Fe-S cluster which is believed to be the site for N_2 activation and reduction, and P-cluster, *viz*. Fe-S cluster mediating the transfer of electrons for N_2 reduction from Fe protein to FeMo-co, while the latter protein does the Fe_4S_4 cluster. Before the elucidation of the single-crystal X-ray structure for Mo nitrogenase in 1992, the structure of FeMo-co had been proposed mostly based on the EXAFS results. The cubane-type $MoFe_3S_4$ core was one of those proposed in 1978 as the partial structure of FeMo-co using the EXAFS data around Mo.[3] Synthesis of the $MoFe_3S_4$ clusters was reported in as early as 1978[10,11] and their reactivities toward nitrogenase substrates have been investigated thereafter. Importantly, this led not only to the isolation of the clusters with these substrate molecules bonded to the Mo site but also the demonstration of the reaction systems containing the $MoFe_3S_4$ clusters that can reduce nitrogenase substrates. Although it is now known that, as shown in Figure 1, the Mo-Fe-S aggregate present in FeMo-co does not have the cubane-type $MoFe_3S_4$ fragment but the incomplete cubane-type $MoFe_3(\mu_3\text{-}S)_3$ chromophore that is connected by one μ_6-N and three μ_2-S ligands with the $Fe_4(\mu_3\text{-}S)_3$ unit, it is doubtless that these studies represent one of the most successful examples of the synthetic approach mimicking the metalloenzyme system.

The cubane-type $MoFe_3S_4$ cluster was first prepared in the form of the double cubane clusters $[Mo_2Fe_6S_8(SR)_9]^{3-}$,[10] and $[Mo_2Fe_6S_9(SEt)_8]^{3-}$,[11] which contain two cubanes connected at each Mo site by three μ-SR bridges or one μ-S and two μ-SEt bridges (Figure 4). These clusters were obtained by self-assembly reactions using the elementary Mo-, Fe-, and S-containing reagents. The $[Mo_2Fe_6S_8(SR)_9]^{3-}$ cluster undergoes chemical and electrolytic, one- and two-electron reductions to give the clusters $[Mo_2Fe_6S_8(SR)_9]^{n-}$ ($n = 4$ and 5). Hydrogen evolution by treatment of the reduced clusters $[Mo_2Fe_6S_8(SPh)_9]^{n-}$ ($n = 5, 4$) with PhSH in solutions was demonstrated as the model of hydrogenase function observed for nitrogenase.[12] Reduction of acetylene into ethylene[13] and that of hydrazine[14] or N_2[15] into ammonia were also attained under electrolytic conditions in *e.g*. THF-MeOH by using $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ as catalyst precursor. However, the efficiencies were still poor and the mechanism operating in these substrate reductions is uncertain. It is worthy of note that the cluster contains only coordinatively saturated Mo and Fe centers even in the reduced form $[Mo_2Fe_6S_8(SPh)_9]^{5-}$.

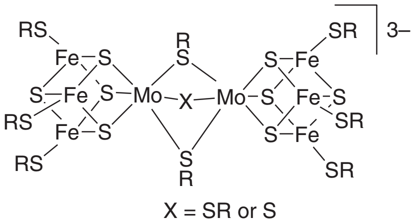


Figure 4 *Mo-Fe-S clusters containing two cubane-type $MoFe_3S_4$ cores, which are the extensively studied, synthetic models of FeMo-co*

On the other hand, the synthesis of the $MoFe_3S_4$ single cubane clusters having the potential substrate-binding site was also attempted, which provided more sophisticated models for FeMo-co than the above-mentioned, double cubane with two Mo atoms each surrounded by six sulfur ligands. By starting from $Fe(SEt)_6$-bridged double cubane cluster $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$, the desired single cubane clusters $[MoFe_3S_4(SR)_3(cat)(L)]^{n-}$ (cat = substituted catecholate; $n = 2, 3$) were able to be derivatized, in which not only the RS^- and RO^- anions but also nitrogenase substrates such as MeCN, N_2H_4, N_3^-, and CN^- can bind to the Mo site as L.[16] Hydrazine-bridged double cubane cluster $[\{MoFe_3S_4Cl_3(cat)\}_2(\mu\text{-}N_2H_4)]^{4-}$ was also isolated and fully characterized (Figure 5).[17]

Upon elucidation of the single-crystal X-ray structure of FeMo-co containing the Mo atom with homocitrato ligand, synthesis of the $MoFe_3S_4$ cubane clusters with polycarboxylato ligand was attempted subsequently, which led to the isolation of the clusters $[MoFe_3S_4Cl_3(X)(L)]^{n-}$ (X = oxalato: L = Cl, CN;[18] X/L = methyliminodiacetate,[18] thiodiglycolato[19]). Interestingly, a series of the clusters of this type consisting of the tridentate ligands at the Mo site can catalyze the reduction of hydrazine into ammonia at room temperature in the system using 2,6-lutidinium chloride and cobaltocene as external proton and electron sources, respectively, for which reduction of hydrazine is presumed to proceed on the single Mo site.[20] Under analogous conditions, reduction of acetylene into ethylene[21] and that of *cis*-dimethyldiazene into methylamine[22] were attained along with the conversion of hydrazine into ammonia[23] by the use of $[MoFe_3S_4Cl_3(Cl_4\text{-cat})(MeCN)]^{2-}$ (Cl_4-cat = tetrachlorocatecholato) as catalyst.

The Mo-Fe-S clusters containing the cores other than the $MoFe_3S_4$ cubane are also known. These include, for example, the cuboidal $MoFe_3S_3$ clusters such as $[MoFe_3S_3(Cl_4\text{-cat})(CO)_6(PEt_3)_2]$ and $[MoFe_3S_3(Cl_4\text{-cat})(CO)_4(PPr_3)_3(pyridine)]$[24] that are of much interest as the model of the $MoFe_3S_3$ fragment in FeMo-co, bicapped prismatic $Mo_2Fe_6S_6$ clusters $[Mo_2Fe_6S_6X_6(CO)_6]^{3-}$ (X = Cl, Br, OR),[25] and the $MoFe_4S_6$ cluster $[MoFe_4S_6(PEt_3)_4Cl]$ (Figure 6).[26] By treatment of the single cubane cluster $[MoFe_3S_4Cl_3(Cl_4\text{-cat})(MeCN)]^{2-}$ with

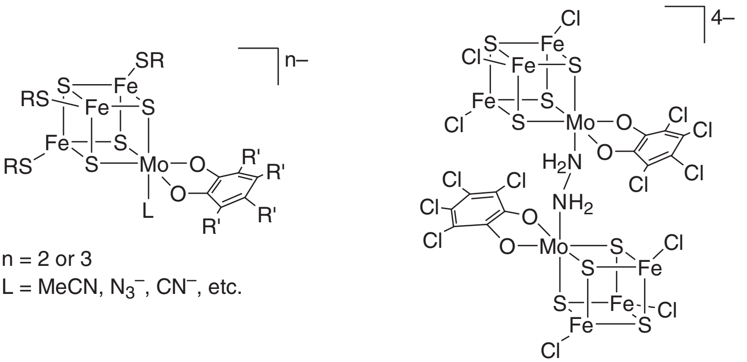


Figure 5 *$MoFe_3S_4$ clusters with the nitrogenase substrates bonded to their Mo site*

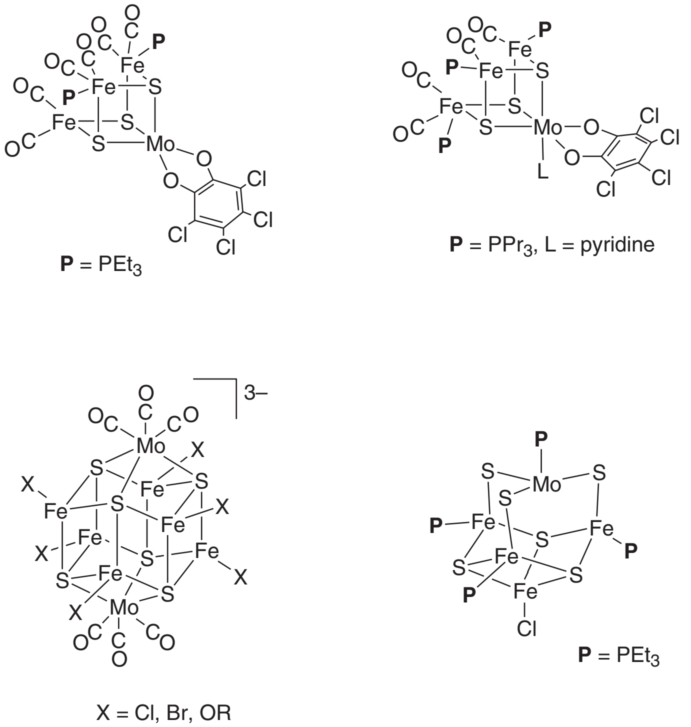


Figure 6 *Mo-Fe-S clusters prepared as the models of FeMo-co, representing the partial structures of FeMo-co*

PEt$_3$, the edge-bridged double cubane cluster [{MoFe$_3$S$_4$(PEt$_3$)$_3$(Cl$_4$-cat)}$_2$]$^{2-}$ was obtained,[27] which was converted upon reaction with [Et$_4$N]SH to the higher nuclearity cluster [Mo$_6$Fe$_{20}$S$_{30}$(PEt$_3$)$_6$(Cl$_4$-cat)$_6$]$^{8-}$ containing the Mo$_2$Fe$_6$S$_9$ fragments relating topologically to the P^N cluster core in nitrogenase described below.[28] Similar Mo$_2$Fe$_6$S$_9$ core was also found in the relating cluster [Mo$_2$Fe$_6$S$_9$(Tp)$_2$(SH)$_2$]$^{3-}$ (Tp = hydrotris(pyrazol-1-yl)borate) that is derivatized from [MoFe$_3$S$_4$Cl$_3$(Tp)]$^-$ in an analogous route, as depicted in Figure 7.[29]

11.2.2.2 Preparation of P^N-Cluster Models

The X-ray analysis recently disclosed the structures of P-cluster in the dithinite-reduced state (P^N-cluster) and the oxidized state (P^{OX}-cluster) (Figure 8).[30] The P^N-cluster core has a corner-shared double cubane structure connected further by two cysteinyl μ-S atoms. As described above, the Mo$_2$Fe$_6$S$_9$ fragments observed in [Mo$_6$Fe$_{20}$S$_{30}$(PEt$_3$)$_6$(Cl$_4$-cat)$_6$]$^{8-}$ and [Mo$_2$Fe$_6$S$_9$(Tp)$_2$(SH)$_2$]$^{3-}$ have quite resembled metal-sulfur connecting scheme. Apparently, the core structures of FeMo-co and P-cluster are mutually relating intimately: two incomplete cubane-type M$_4$S$_3$ cores are connected by either μ$_6$-N or μ$_6$-S, respectively.

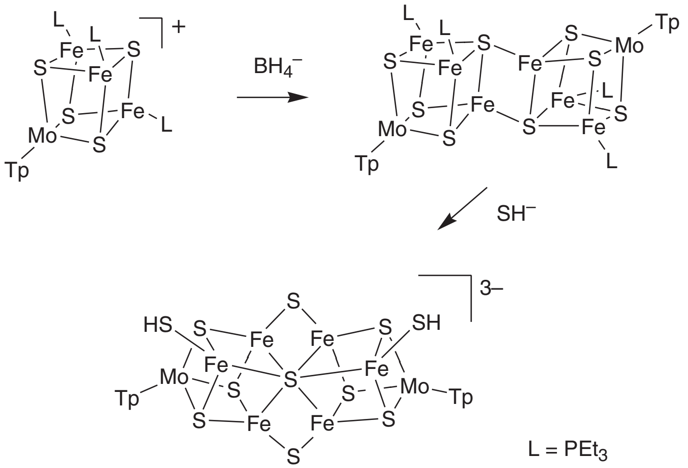


Figure 7 *Mo-Fe-S cluster consisting of the metal-sulfur connecting scheme akin to that in P^N-cluster*

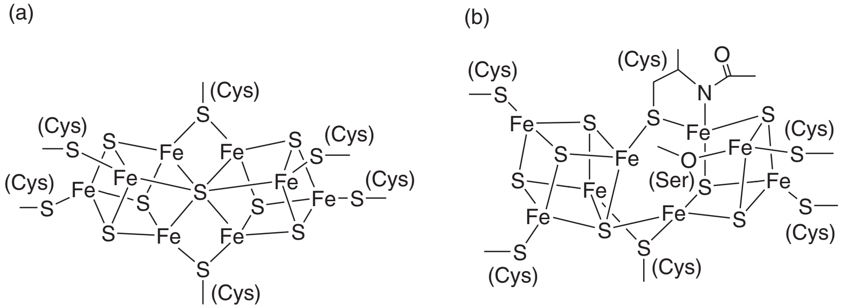


Figure 8 *Structures of P-cluster. (a) Reduced form (P^N-cluster) and (b) Oxidized form (P^{OX}-cluster)*

More recently, the corner-shared Fe_8S_7 core itself has been constructed by self-assembly reaction using $[Fe\{N(SiMe_3)_2\}_2]$, tetramethylthiourea, 2,4,6-triisopropylbenzenethiol, and elemental sulfur. The product $[Fe_8S_7\{SC(NMe_2)_2\}_2\{N(SiMe_3)_2\}_4]$ contains two cuboidal Fe_4S_3 core bridged by one μ_6-sulfide and two bis(trimethylsilyl)amides.[31] Amide-free cluster as the more sophisticated model $[\{Fe_4S_3(SR^1)\}_2(\mu_6\text{-}S)(\mu\text{-}SR^1)_2(\mu\text{-}SR^2)]$ (R^1 = 2,6-$(1',3',5'\text{-}Me_3C_6H_2)_2C_6H_3$, R^2 = 2,4,6-$^iPr_3C_6H_2$) has subsequently been isolated quite recently under modified reaction conditions (Figure 9).[32]

For further details about the progress in the syntheses of the structural models of the clusters in MoFe protein, please see the other recent reviews,[33] together with those dealing with the reactions of metal-sulfur clusters relating to the nitrogen-fixation chemistry.[34]

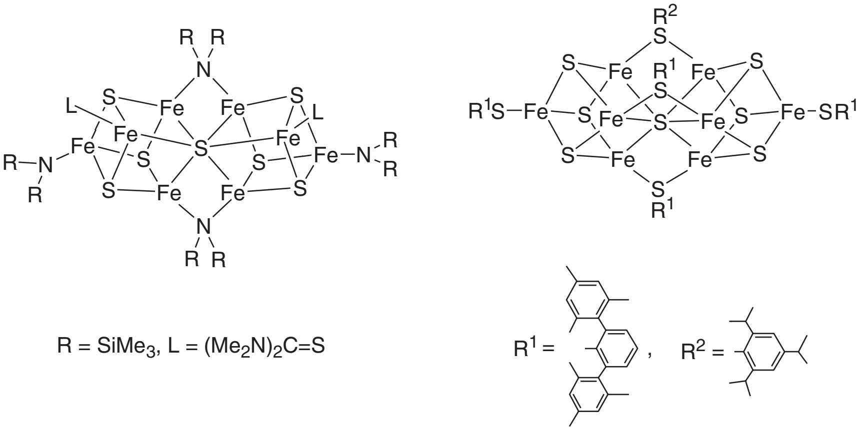


Figure 9 *Fe-S clusters containing a Fe_8S_7 core analogous to that in P^N-cluster*

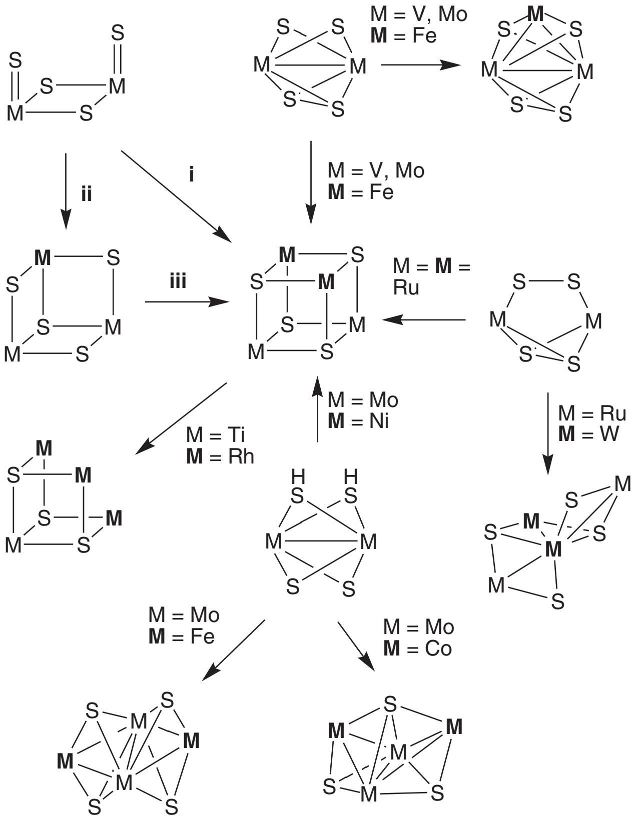
11.2.3 Metal–Sulfur Clusters as the Functional Models for Metalloenzymes

Approaches to the chemistry of metal–sulfur clusters relevant to the active sites of metalloenzymes have been done not only by attempting to synthesize their precise structural models but also by preparing their functional models. This latter approach emerges from the view that although the enzymes are presumably possessing the optimum catalytic systems that they have finally acquired after long evolution processes, these were attained under the conditions available only in the natural environment. Thus, the nature of the metals they can select is limited to those with the high natural abundance and the construction of the active sites must be carried out under ambient conditions. This means that it might be possible for us, synthetic chemists, to create more excellent man-made catalysts than the biological catalysts, natural enzymes. Indeed, in many organic reactions higher activities are found for the catalysts consisting of noble metals than those containing the 3d transition metals in the same triad, although noble metals are not the choice as the key metals of the metalloenzymes. It is therefore of much interest to synthesize the metal–sulfur clusters that contain a wide range of transition metals and survey their reactivities as the functional models of the enzyme reactions. It is to be noted that the metal–sulfur clusters have also been investigated extensively in terms of the active site models of the industrial hydrodesulfurization catalysts.[35]

A huge number of transition metal–sulfur clusters have been synthesized,[36] most of which have been obtained based on the self-assembly methods. On the other hand, to construct the cluster cores with the desired metal–sulfur compositions and connecting schemes, rational pathways leading to the high-yield syntheses of tailored metal-sulfur clusters have recently been explored. Fragment condensations have been demonstrated to be the powerful methods to obtain such clusters numerously,[37] some examples of which are shown below.

11.2.3.1 Preparation of Metal–Sulfur Clusters from Dinuclear Precursors

As the dinuclear metal–sulfur complexes that can exhibit excellent ability to serve as the precursors to the tailored metal–sulfur clusters, those with the M_2S_4 cores are known to be used for synthesizing cubane-type and relating sulfido clusters. These include the reactions that start from the complexes having Mo(μ-SH)$_2$(μ-S)$_2$Mo,[38] M(μ-S$_2$)(μ-S)$_2$M (M = V,[39] Mo[40]), Ru(μ-S$_2$)$_2$Ru,[41] and MS(μ-S)$_2$MS (M = Mo, W,[42] Re,[43] Ti[44]) cores, which are summarized in Figure 10.



i: M = Ti, **M** = Rh, Ir; M = Mo, W, **M** = Co, Rh, Ir, Pd;
M = Re, **M** = Ru, Pt, Cu
ii: M = Re, **M** = Ru, Rh, Ir
iii: M = Re, **M$_2$** = (Ru, Rh, Ir)/(Mo, W, Pd, Ru, Rh)

Figure 10 *Schematic representation of the syntheses of cubane-type and relating sulfido clusters using M_2S_4 complexes as precursors*

Versatile dinuclear precursors of the other type are those containing M_2S_2 cores. Cubane-type clusters $[(Cp^*M)_4(\mu_3\text{-}S)_4]$ are available through dimerization of the $M(\mu\text{-}S)_2M$ complexes $[Cp^*M(PMe_3)(\mu\text{-}S)_2IrCp^*]$ (M = Rh, Ir)[45] and $[\{Cp^*Ir(CO)\}_2(\mu\text{-}S)_2]$.[46] Although bridging hydrosulfido complexes are less common as compared to the bridging sulfido complexes, a series of $M(\mu\text{-}SH)_2M$ complexes $[(Cp^*MCl)_2(\mu\text{-}SH)_2]$ (M = Ru, Rh, Ir) has been isolated recently. It has been demonstrated subsequently that these μ-SH complexes readily produce not only the numerous homo- and heterometallic trinuclear $M_3(\mu_3\text{-}S)_2$ and pentanuclear $M_5(\mu_3\text{-}S)_4$ clusters by treatment with certain metal species[47] but also the cubane-type clusters *via* dimerization in the presence of NEt_3 for dehydrochlorination[48] (Figure 11).

The complexes $[(Cp^*MCl)_2(\mu\text{-}SH)_2]$ undergo the crossed condensation with $[\{MoO(DMF)_3\}_2(\mu\text{-}S)_2]I_2$ in the presence of NMe_4Cl, yielding the mixed-metal cubane-type clusters $[(Cp^*M)_2\{MoCl_2(DMF)\}(MoOCl_2)(\mu_3\text{-}S)_4]$ (M = Ir, Rh) and $[(Cp^*Ru)_2\{MoCl_2(DMF)\}_2(\mu_3\text{-}S)_4]$. Interestingly, the former oxo cubanes can catalyze the nitrogenase model reaction. Thus, reduction of the hydrazine $MePhNNH_2$ proceeds smoothly at room temperature in the presence of lutidinium chloride and cobaltocene to give MePhNH and NH_3. By treatment of $[(Cp^*Ir)_2\{MoCl_2(DMF)\}(MoOCl_2)(\mu_3\text{-}S)_4]$ with $MePhNNH_2$, the cubane cluster with the hydrazido(2−) ligand $[(Cp^*Ir)_2\{MoCl_2(DMF)\}\{MoCl_2(NNMePh)\}(\mu_3\text{-}S)_4]$ was isolated as the possible intermediate of the reductive cleavage of the hydrazine (Figure 12).[49]

Dinuclear Pt complexes of the type $[\{Pt(PR_3)\}_2(\mu\text{-}S)_2]$ are also known to serve as the good precursors to the trinuclear clusters. A series of triangular cluster cores $M'Pt_2(\mu_3\text{-}S)_2$ has been constructed therefrom (M′ = transition metals, main-group metals).[50]

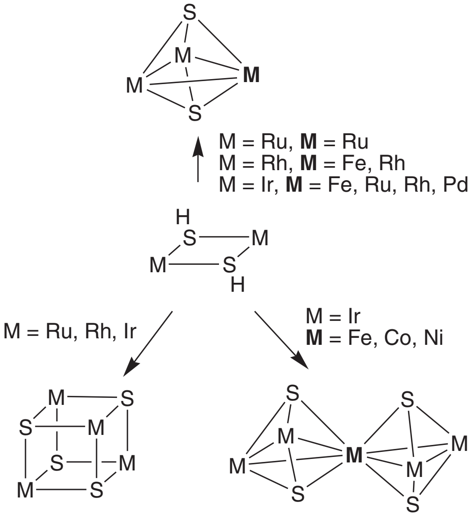


Figure 11 *Construction of metal-sulfido cores starting from hydrosulfido-bridged dinuclear complexes*

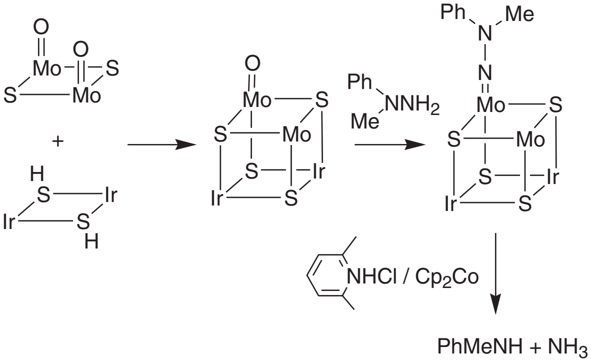


Figure 12 *Reduction of MePhNNH$_2$ into MePhNH and NH$_3$ by litidinium chloride and cobaltocene using the Mo site of cubane-type Mo$_2$Ir$_2$S$_4$ cluster via the hydrazido(2−) intermediate*

11.2.3.2 Preparation of Metal-Sulfur Clusters from Trinuclear Precursors

Construction of cubane-type clusters by incorporating the metal fragment into the void corner of the incomplete cubane-type M$_3$S$_4$ clusters (M = Mo, W) has been studied extensively. Thus, $[M_3(\mu_3\text{-S})(\mu_2\text{-S})_3(H_2O)_9]^{4+}$ was treated with elemental metals M′ in acidic aqueous solutions to give single cubane-type M$_3$M′S$_4$, corner-shared double cubane-type M$_6$M′S$_8$, and edge-fused double cubane-type M$_6$M′$_2$S$_8$ clusters, depending on the nature of the incorporated metals (Figure 13).[51] It has also been found that analogous clusters are available from $[M_3(\mu_3\text{-S})(\mu_2\text{-S})_3(H_2O)_9]^{4+}$ by treatment with the metal salt/NaBH$_4$ systems in place of elemental M′ in acidic media.[52]

Among the clusters derivatized by these methods, $[\{Mo(tacn)\}_3(PdCl)(\mu_3\text{-S})_4]^{3+}$ (tacn = 1,4,7-triazacyclononane) is noteworthy, since this cluster can bind the substrate molecules such as alkene and CO at its tetrahedral Pd site generated by dissociation of the Cl anion. More interestingly, it has turned out that addition of ROH and RCOOH to various alkynes proceeds at this Pd site to give vinyl ethers and vinyl carboxylates catalytically.[53] These reactions represent one of the yet rare examples that are catalyzed by well-defined cubane-type clusters with retention of their core structures.

Organometallic precursors containing incomplete cubane-type cores, $[(Cp'M)_3(\mu_3\text{-S})(\mu_2\text{-S})_3]^+$ (M = Mo or W, Cp′ = η^5-C$_5$H$_4$Me;[54] M = Mo, Cp′ = Cp*[55]), have been prepared more recently, from which a new series of mixed-metal cubane-type clusters with the M$_3$M′S$_4$ cores (M′ = Ni, Pd, Pt, Co, Rh, Ir, Ru, Os) have been derived.[56] With respect to these organometallic cubanes, reactions with a range of small molecules have been investigated in organic media, leading to the isolation of CO[55,57] and alkyne[58] clusters. From the reaction of (Cp*Mo)$_3$RuS$_4$ cluster with hydrazine, ammine cluster $[(Cp^*Mo)_3\{Ru(NH_3)(PPh_3)\}(\mu_3\text{-S})_4]^+$ and μ-amido-μ-hydrazido(1−) cluster $[\{(Cp^*Mo)_3(\mu_3\text{-S})_4Ru\}_2(\mu\text{-NH}_2)(\mu\text{-NHNH}_2)]^{2+}$ have been obtained (Figure 14).[59]

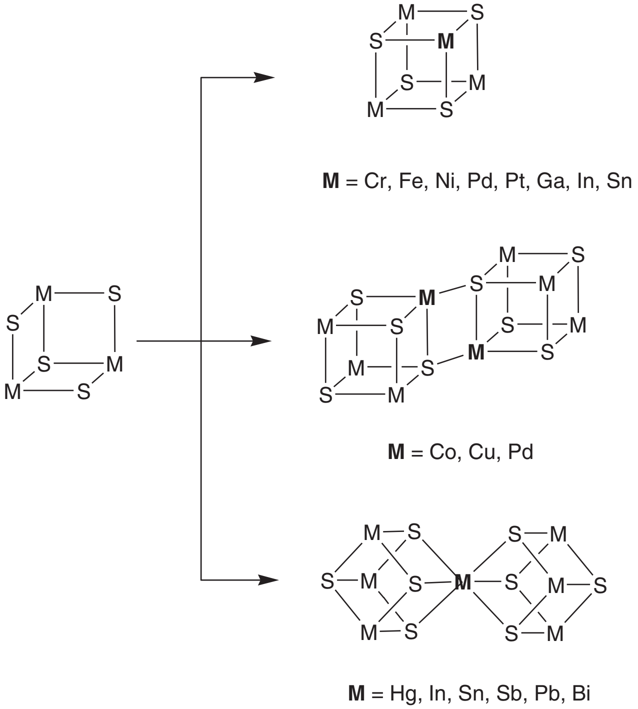


Figure 13 *Syntheses of cubane-type clusters starting from incomplete cubane-type Mo_3S_4 aqua cluster*

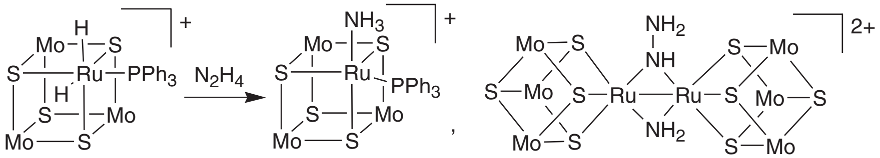


Figure 14 *Reaction of the cubane-type* $[(Cp^*Mo)_3RuH_2(PPh_3)(\mu_3\text{-}S)_4]^+$ *affording ammine cluster and* μ*-amido-*μ*-hydrazido(1−) cluster*

Rational syntheses of mixed-metal cubane-type $M_3M'S_4$ clusters starting from M_3S_4 clusters have also been attained for M = Fe with respect to the two precursors with different core structures; one is a linear $[Fe_3(\mu\text{-}S)_4(SR)_4]^{3-}$ cluster and the other is an incomplete cubane-type $[Fe_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(L)]^{3-}$ cluster where L = tris(thiolato) ligand. The former reacts with certain metal salt or complexes to give $Fe_3M'S_4$ cubanes accompanied by core rearrangement (M′ = Mo, W, Fe, Co, Ni), while incorporation of M' into the missing corner of the latter precursor gives another series of $Fe_3M'S_4$ cubanes (M′ = Mo, W, Fe, Co, Ni, Cu, Ag, Tl) (Figure 15).[9a,60]

Incomplete cubane-type μ-sulfido-μ-hydrosulfido cluster $[(Cp^*Ir)_3(\mu_3\text{-}S)(\mu_2\text{-}SH)_3]^+$ can also be used as the precursor to the mixed-metal cubane-type

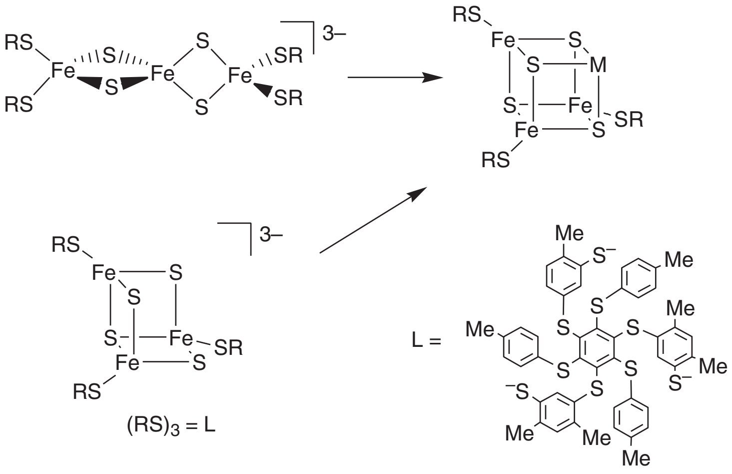


Figure 15 *Syntheses of cubane-type MFe_3S_4 clusters using a linear or incomplete cubane-type Fe_3S_4 clusters*

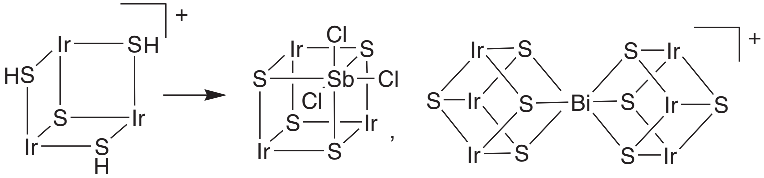


Figure 16 *Single cubane-type and corner-shared double cubane-type clusters derived from the incomplete cubane-type sulfido-hydrosulfido cluster $[(Cp^*Ir)_3(\mu_3\text{-}S)(\mu_2\text{-}SH)_3]^+$*

clusters, those derived from which are a single cubane $[(Cp^*Ir)_3(SbCl_3)(\mu_3\text{-}S)_4]$ and a corner-shared double cube $[\{(Cp^*Ir)_3(\mu_3\text{-}S)_4\}_2Bi]^+$,[61] along with the Mo or Fe containing single cubanes (Figure 16). The Ir_3MoS_4 cluster obtained here proves to catalyze the hydrazine disproportionation reaction: $3N_2H_4 \rightarrow 4NH_3 + N_2$.

11.2.4 Conclusion

Metal-sulfur aggregates are now known to occur in biological systems as the active sites of a significant number of metalloenzymes, and clarification of their detailed structures are currently progressing rapidly. In consideration of the results of these studies, many researchers are attempting to synthesize the direct structural models as well as the functional models of the active sites of natural enzymes that promote various important reactions in the biological systems under ambient conditions, which presumably leads in the near future to the development of the novel man-made catalysts that exhibit the activities exceeding those of natural enzymes.

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CHAPTER 12.1

Stable Chalcogen Radicals

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12.1.1 Introduction

The word stable is open to many different interpretations. One might think that a radical is stable only if it is persistent over a long period of time *e.g.* the sulfur-based radicals which provide the colour centres in many precious gems. The definition of 'a long period of time' itself is open to debate; it might be considered to comprise weeks, months or years, although for femtosecond spectroscopists a matter of minutes would appear an eternity! In the limit one might think a radical is stable if it can be detected at all, even if it can never be isolated. For the present chapter, we will use the term 'stable' as defined by Power[1] *i.e.* it is taken to indicate "a species that can be isolated and shows no sign of decomposition under an inert atmosphere at room temperature", whereas a "persistent" radical has "a relatively long lifetime under the conditions in which it is generated". In order to qualify one or more derivatives must have been isolated and characterised by X-ray diffraction.

The open shell nature of free radicals tends to make them extremely reactive with respect to either one-electron reduction or oxidation to generate closed-shell configurations. In order to stabilise free radicals, the structure of the molecule should provide both thermodynamic and kinetic stabilisation of the radical centre. Thermodynamic stability is afforded by lowering the energy of the SOMO (singly occupied molecular orbital) through the use of electronegative elements and/or the inclusion of some π-delocalisation. The low lying set of orbitals provided by the electronegative chalcogens (especially S and Se) is good for stabilising radicals and the most stable radicals are often those containing chalcogens in conjunction with other electronegative elements from groups 15 (N and P) as well as those containing electronegative substituents, such as CN and CF_3. We shall see in later sections that thermodynamic stabilisation must also be supported by kinetic stabilisation in order to achieve stable radicals. In the absence of such stabilising functional groups then two radicals can come together *via* covalent bond formation, whether this be conventional σ-bond formation or *via* a weaker π–π bonding interaction.

Multiple classifications can be thought of when attempting to put an order to the vast family of radicals formed by the chalcogen radicals. They can be divided into naturally occurring and synthetic ones, homo-nuclear and hetero-nuclear systems, *etc*. In this chapter, we will focus on the five-membered rings of group 15/16 elements since a substantial body of work in recent years has been devoted to them. However, some other radicals have been isolated and their chemistry and properties reviewed recently.[2,3]

In recent years, the amount of research time devoted to materials chemistry has risen almost exponentially and sulfur-based radicals, such as the charge-transfer salts based upon TTF (tetrathiafulvalene), have played an important role in these developments. These TTF derivatives will not be discussed here but are dealt with elsewhere in this book. Instead we focus on recent developments in the area of group 15/16 free radicals. Up until the latter end of the last century, these radicals posed fundamental questions regarding the structure and bonding in main group chemistry. Now, in many cases, their thermodynamic and kinetic stability allows them to be used in the construction of molecular magnets and conductors. In this overview we will focus on the synthesis and characterisation of these radicals with a particular emphasis on their physical properties.

12.1.2 Five-Membered C/N/S and C/N/Se Rings

The $S_3N_2^{+\bullet}$ radical cation (**1**) was first reported at the end of the 19th century[4] and can be considered the parent radical for a large family of five-membered heterocyclic thiazyl rings. Other members of this family can be considered to arise out of the isoelectronic substitution of S^+ by N or R–C. In these heterocycles, each S atom can be considered to contribute a p-orbital and two electrons to π-bonding, while the C and N atoms each contribute one p-orbital and one electron towards π-bonding. The π-manifold of these ring systems are effectively similar to those of $C_5H_5^-$ with the additional unpaired electron occupying either the π_4 or π_5 antibonding orbital, depending on the relative energies of π_4 and π_5. The π-delocalised character of the SOMOs (Figure 1) coupled with the electronegative nature of the S and N atoms leads to low-lying antibonding orbitals providing the thermodynamic stability. In the case of the cations **1**$^+$, **6**$^+$ and **7**$^+$ the positive charge leads to additional lowering of the orbital energies. Within this family the isomeric dithiadiazolyl (DTDA) radicals (**2** and **3**) and the dithiazolyl (DTA) radicals (**4** and **5**) have been extensively studied. In addition the radical cations **6**$^+$ and **7**$^+$ have recently been characterised in the solid state.

In all cases there is little steric hindrance and many derivatives exhibit a propensity to dimerise both in solution and in the solid state. Elegant EPR studies by Sutcliffe, Passmore and co-workers have determined the thermodynamics of the dimerisation process in solution and reveal that ΔH_{dim} is

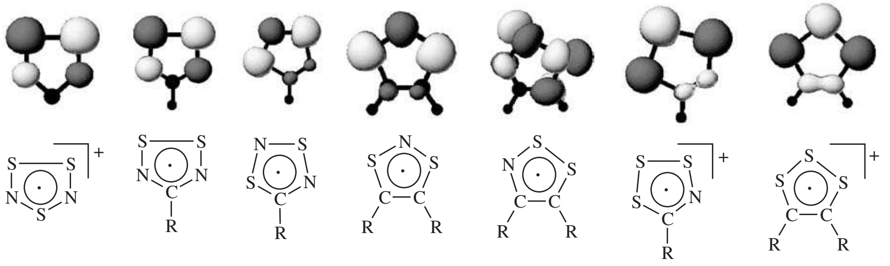
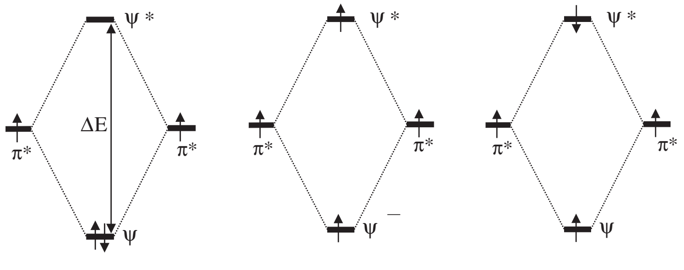


Figure 1 *Molecular structures and singly occupied molecular orbitals for radicals* **1–7**

approximately −45 kJ mol^{-1} for $\mathbf{1}^+$, −35 kJ mol^{-1} for derivatives of **2** (R=CF_3, ^{t}Bu and Ph), −19 kJ mol^{-1} for **3** (R=^{t}Bu) and ~0 for **4** (R=R′=CF_3).[5] Data are not available at the present time for derivatives of **5–7**. Gas phase calculations on dimers of dithiadiazolyl radicals **2** generally support the solution measurements, although the value of ΔH_{dim} appears very sensitive to basis set employed.[14] In the case of the TTTA (1,3,5-trithia-2,4,6-triazapentalenyl) radical **30**, a derivative of **4**, a solid-solid phase transition between dimeric and paramagnetic phases is observed in which ΔH_{dim} has been measured as 1.41 kJ mol^{-1} (of dimer) supporting the low favourable dimerisation enthalpy. The variation in ΔH_{dim} is a reflection of the strength of bonding between the two radicals and is directly comparable to high spin *vs.* low spin configurations in transition metal chemistry, *i.e.* if the energy gap between bonding and antibonding orbitals (ΔE in Figure 2) is larger than the inter-electron repulsion term, P_E, then a spin-paired diamagnetic ground state is favoured, whereas for small values of ΔE and larger inter-electron repulsion dimerisation is disfavoured. The magnitude of ΔE depends on the extent of orbital overlap between SOMOs while P_E depends on the extent of inter-electron repulsion, which is minimised in systems with more extended π-delocalisation.



(a) (b) (c)

Figure 2 *Different electronic configurations arising from the relative strengths of orbital overlap (ΔE) and pairing energy (P_E); $\Delta E > P_E$ favours a closed-shell diamagnetic singlet (a) whereas $\Delta E < P_E$ favours open shell triplet (b) and singlet (c) configurations. The configurations (b) and (c) are both $\psi^1\psi^{*1}$, which destabilises the dimeric structure*

The solid-state structures of many of these radicals comprise π*–π* bonded diamagnetic dimers indicative of the fact that $\Delta E > P_E$. The symmetry of the SOMO often permits a number of symmetry-allowed π*–π* dimerisation processes. Among these five-membered heterocyclic radicals, the 1,2,3,5-dithiadiazolyl radicals **2** are perhaps the most extensively studied and four different modes of association have been reported (Figure 3).

In all cases the dimerisation energy may be overcome by solvation effects and the diamagnetic dimers regenerate paramagnetic radicals on dissolution. This behaviour is not unique to these thiazyl rings and is reflected in other π-delocalised radicals. If $\Delta E > P_E$ but comparable to kT then the closed shell-dimers are expected with thermally accessible open-shell excited states [Figures 2 (b) and (c)]. Evidence for the triplet state has recently been observed for the first time by Passmore and co-workers through detailed EPR studies on $(\mathbf{6}^+)_2$ (R=Cl) in which the ground state is a closed shell singlet but the excited triplet state becomes thermally accessible above *ca.* 250 K. Variable temperature studies reveal a singlet-triplet separation of *ca.* 20 kJ mol^{-1}. If $\Delta E < P_E$ then the $(\psi)^1(\psi^*)^1$ configuration becomes preferred. This leads to a formally non-bonding interaction between the two radicals and dimerisation is disfavoured. Notably in the condensed phase, intermolecular effects will also contribute to the stabilisation or destabilisation of dimers.

Theoretical calculations on the dithiazolyl radical **4** (R=CF_3) have recently shown that π*–π* dimerisation was unfavourable but association of two such dimers *via* electrostatic interactions generated a thermodynamically stable tetramer consistent with single crystal X-ray studies. Thus while the value of $[\Delta E–P_E]$ may favour (or disfavour) dimer formation, the van der Waals, dipole contributions and electrostatic interactions to the lattice enthalpy should not be underestimated in assessing the thermodynamic stability or instability of these

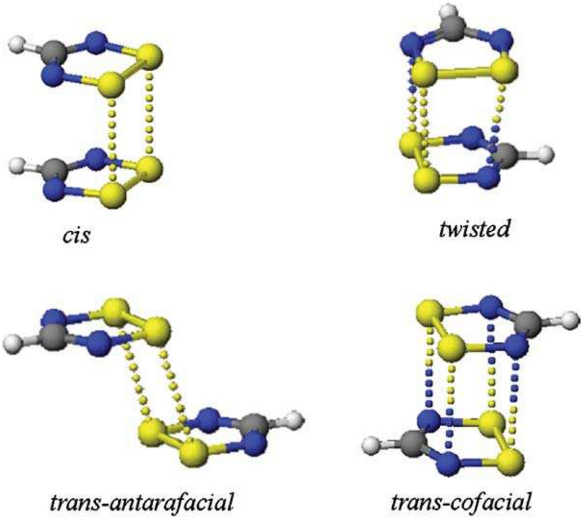


Figure 3 *Four modes of association of 1,2,3,5-dithiadiazolyl radicals (**2**)*

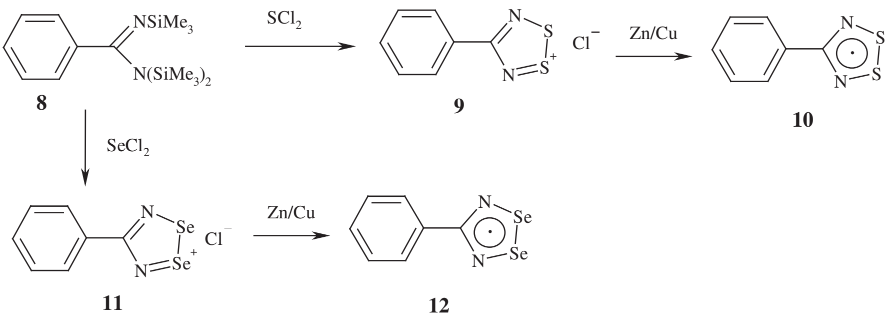
radicals in the condensed phase. This point is simply emphasised by the observation of monomeric and dimeric structures of 2-NCBDTA (**31**); below 250 K the dimeric phase is thermodynamically preferred, but it undergoes a solid-state phase transition above 250 K to a paramagnetic phase in which the increased entropy from unpairing the electron spins provides some enhanced stabilisation. This spin switching is discussed in more detail in Section 12.1.2.3.3.

In the following sub-sections we examine recent results relating to radicals **1–7**.

12.1.2.1 1,2,3,5-Dithiadiazolyl Radicals

12.1.2.1.1 Synthesis

A number of synthetic routes to **2** have been developed and have been reviewed elsewhere. Arguably the single most important advance in this area was the development of a convenient synthetic methodology of the intermediate silylated amidine (Scheme 1) by Oakley from the reaction of the corresponding benzonitrile with $Li[N(SiMe_3)_2]$.[6] This methodology provided access to a range of phenyl derivatives bearing both electron-withdrawing and electron-releasing groups. Subsequent condensation of these silylated-amidines **8** or their *N*-lithio salts with excess of sulfur dichloride in refluxing acetonitrile affords the 6π dithiadiazolylium cations **9** in good yield.[7] One electron reduction with Ag powder, Zn/Cu couple or Ph_3Sb *inter alia* yields **10**, which can be typically purified by vacuum sublimation.[8] This synthetic method can be extended towards the selenium analogues (**11**) through the use of $SeCl_4$/Se or Ph_3Sb/$SeCl_4$ as an *in situ* source of $SeCl_2$.[9] This methodology has been successfully extended to the synthesis of di- and tri-radicals.[10] A number of other routes have also been established for synthesising alkyl derivatives and their structures reported recently (R=H,Cl,F,Br,NC),[11] as well as the sterically-protected derivative (R=2,4,6-$(F_3C)_3C_6H_2$).[12] The mixed S/Se derivative has recently been identified, along with [**11**]Cl, in the reaction of [**7**] with SeO_2 in refluxing MeCN.[13] The mechanism for this reaction is not yet clear but possesses strong similarities to similar chalcogen-exchange reactions seen in derivatives of **5**



Scheme 1

(Section 12.1.2.4). The majority of derivatives of **2** and all reported derivatives of **11** tend to associate as dimers in the solid state (Figure 2). Theoretical calculations[14] and solution UV/*vis* and EPR measurements[15] all point towards greater dimerisation enthalpies for the Se analogues.

12.1.2.1.2 Physical Properties

Theoretical and EPR studies[16] coupled with recent polarised neutron diffraction studies[17] have shown that the spin density is almost entirely localised on the N_2S_2 fragment of the dithiadiazolyl ring with approximately 25% spin on each N and 28% on each S (Figure 1). The slight excess spin density is accommodated by a small accumulation of negative spin density on the heterocyclic C. The spin density distribution is not strongly influenced by the substituent;[16] variations in hyperfine coupling between 4.9 and 5.4 G for **2** ($R{=}CF_3$) and **2** ($R{=}CH_3$) correspond to *ca*. 22.4% and 25.6% spin densities at N, respectively. The minimal influence of substituent on the spin density distribution is also reflected in electrochemical studies on **2**, which reveal only minor variations in the redox behaviour of phenyl-substituted derivatives with a wide range of electron-withdrawing and releasing functional groups.[18] Notably the energy difference between the $\mathbf{2}^+/\mathbf{2}^{\cdot}$ and $\mathbf{2}^{\cdot}/\mathbf{2}^{-1}$ redox couples remains approximately constant at 1.4 eV. This has important ramifications for the transport properties of these materials (below).

12.1.2.1.3 Conductivity

Traditional approaches to the development of molecular conductors have been based on two-component systems in which charge-transfer between segregated stacks of molecules gives rise to the formation of partially occupied bands. In this context TTF and related derivatives (Chapter 1) have been explored extensively. In 1975, Haddon proposed an alternative model for conductivity based on regular stacks of closely spaced π-radicals.[19] Overlap of the singly SOMOs of these radicals should give rise to a half-filled band in which the energy gap between the bonding and antibonding orbitals is zero[19] [Figure 4(a)]. Within this context the sterically unencumbered π-delocalised radicals, such as **1–7** and other radicals presented in this chapter appear excellent building blocks.

A range of derivatives of **2** was examined as part of a systematic approach by Oakley. Planar derivatives, particularly those bearing functional groups, which favour in-plane interactions and the use of di- and tri-radical derivatives[10] to favour lateral interactions, were successfully employed to generate π-stacked structures. However in all cases the systems were subject to a spin-Peierls or charge-density-wave (CDW) distortion of the structure. This distortion of the regular π-stack opens up a band gap at the Fermi level [Figure 4(b)] and the conductivities of the pristine materials were poor, *i.e.* insulators or poor semiconductors. The inherently low conductivity observed in these π-stacked dithiadiazolyl (DTDA) dimers arises in part from the band gap, but also

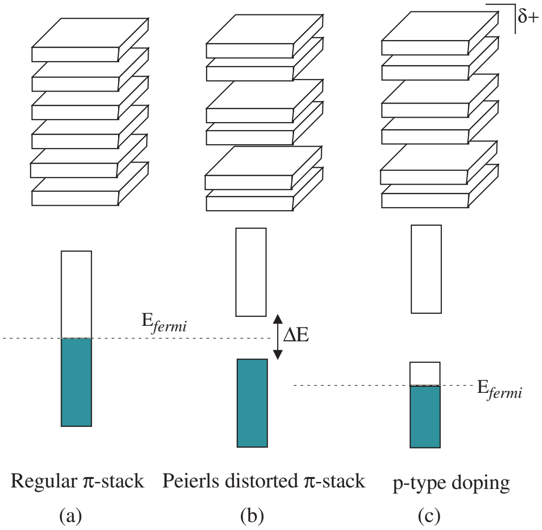


Figure 4 *Schematic band structures for (a) a regular π-stack (b) a Peierls distorted π-stack and (c) a Peierls distorted π-stack after p-type doping*

because of a large energy barrier to electron transfer. Within the Hubbard model[20] this energy barrier (U) for electron transfer is given by

$$\mathrm{U} \sim \mathrm{IE{-}EA}$$

where IE and EA are the ionisation energy and electron affinity of the neutral radical. To a first approximation, an estimate of this energy can be derived from the difference in the electrochemical potentials for the $\mathbf{2}^{+}/\mathbf{2}^{\cdot}$ and $\mathbf{2}^{\cdot}/\mathbf{2}^{-}$ couples. The electrochemical studies reveal that this energy is high and is not sensitive to chemical tuning. As a consequence, even if the Peierls distortion were suppressed this energy barrier is sufficiently large to inhibit electron transfer *i.e.* the spins are trapped on the radical sites, and the materials become Mott insulators. While this is detrimental for the itinerant nature of conducting electrons, it is extremely helpful for the development of magnetic materials in which localised electrons are desirable (see below).

Hole (p-type) doping of these band-gap insulators with acceptors such as the heavier halogens (Br_2 and I_2) leads to some electron transfer generating a partially oxidised π-stack $[\mathbf{2}]_n[\mathrm{X}]$ (X=Br, I; $n > 1$). This doping of the radical stack has been found to reduce the tendency for dimerisation along the π-stacking direction. Elegant studies by Oakley have shown that a CDW driven sinusoidal modulation of the π-stack occurs depending on the dopant level.[21] The removal of some electron charge may move the position of the Fermi level away from the band-gap region [Figure 4(c)] and may lead to enhanced conductivity depending on the distribution of the density of states. In addition the introduction of a cation defect into the π-stack reduces the Hubbard energy U for electron transfer since the electron affinity of a cation defect located within a regular stack ($\mathbf{2}^{+} \rightarrow \mathbf{2}^{\cdot}$) is equivalent to the ionisation energy of a radical ($\mathbf{2}^{\cdot} \rightarrow \mathbf{2}^{+}$) *i.e.* U ~ 0. As a consequence halogen-doping with Br_2 or I_2 has led to markedly improved conductivities,[22,23] reaching 10^2 S cm^{-1}, characteristic of metallic conductors (Figure 5).

12.1.2.1.4 Magnetism

When a magnetic field is applied to a free radical the electron tends to align with the applied field. The vast majority of free radicals show very little magnetic anisotropy, *i.e.* the interaction of the electron with the applied field shows little dependence on molecular orientation. The anisotropy in the single ion magnetism is reflected in their EPR spectra. For single crystal or frozen solution spectra the anisotropy is reflected in the observation of three principle g-tensors (g_x, g_y and g_z). For most organic radicals, $g_x \sim g_y \sim g_z \sim 2.0$ consistent with approximately isotropic ('Heisenberg'-like) spin-only behaviour. A frozen solution EPR spectrum of **2** (R=*p*-C_6F_4-CN) is shown in Figure 6. The spin-only behaviour arises since there is usually no orbital degeneracy and to a good approximation it is only the electron spin, which contributes to the magnetic behaviour. Since there is no preferred orientation of the Heisenberg spins in relation to the magnetic field, then long range magnetic order can only be achieved when there is a three dimensional set of magnetic exchange interactions propagating through the lattice. (For systems with considerable anisotropy, then this spin anisotropy may assist with the preferred orientation).[24] The first free radicals to exhibit bulk magnetic order were reported in 1991; both *p*-NPNN and DOTMDAA (Scheme 2) ordered as ferromagnets [Figure 7(a)] with magnetic ordering temperatures close to absolute zero (0.6 and 1.6 K, respectively).[25]

There has been considerable interest in the magnetic behaviour of thiazyl radicals because of the discovery of long-range magnetic order in derivatives of **2**.

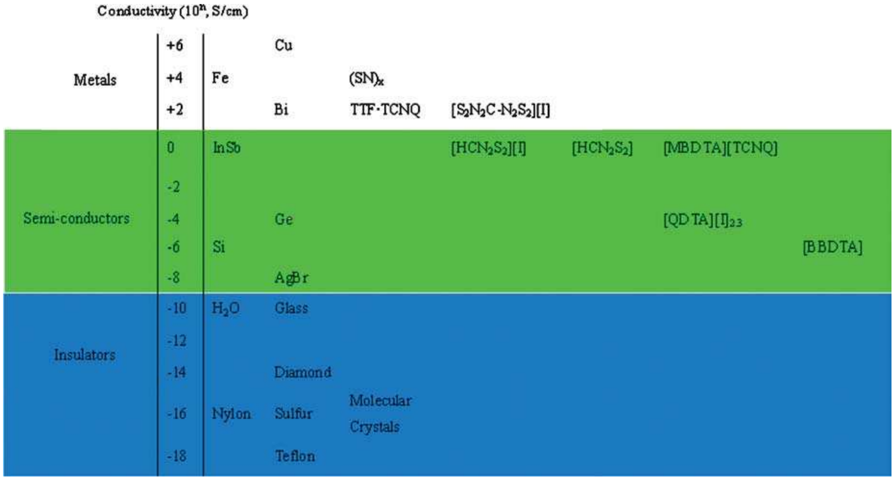


Figure 5 *Conductivities of natural, polymeric and molecular materials*

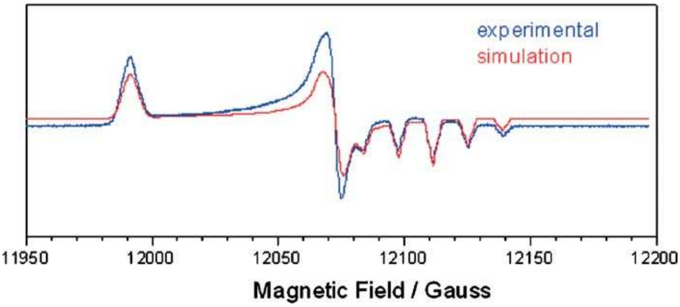
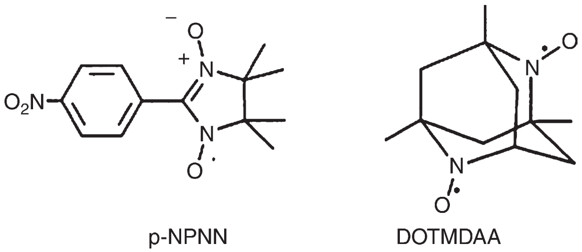


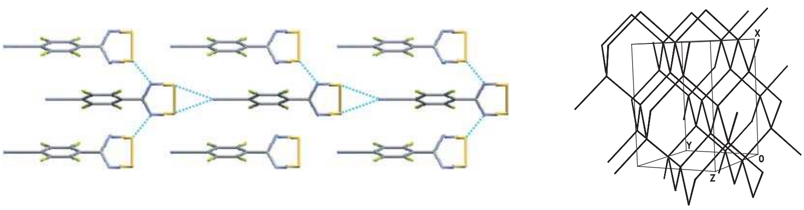
Figure 6 *Frozen solution EPR spectrum of 2 (R=p-C_6F_4-CN)*

The dimerisation energy for derivatives of **2** (*ca.* 35 kJ mol^{-1}) is considerable, particularly in relation to the strength of intermolecular forces and some persistence is required in order to isolate derivatives of **2** which do not form π*–π* dimers in the solid state. A survey of the monomeric derivatives has been published recently.[26] Since the spin density distribution in **2** is rather insensitive to chemical tuning, approaches to inhibit dimerisation rely exclusively on structural modifications, which affect the nature of the intermolecular forces. Inclusion of sterically demanding groups, such as **13**, **14** and **15** has proved partially successful (in the case of the diradical **14** one ring is involved in formation of a π*–π* dimer, while the other retains its open shell character). Another approach has been to include strongly-structure directing groups *e.g.* CN and NO_2 in **16**, **17** and **18** (Scheme 3). Here the favourable $CN^{\delta-}\ldots{}^{\delta+}S$ and $NO_2{}^{\delta-}\cdots{}^{\delta+}S$ interactions successfully compete with the favourable π*–π* dimerisation process.

Radical **16** was the first dithiadiazolyl radical to remain monomeric in the solid state and was found to be polymorphic; both the α-phase[27] and thermodynamically more stable β-phase[28] comprise chains of radicals linked by $S^{\delta+}\cdots NC^{\delta-}$ contacts (S···NC *ca.* 3.0 Å). In the α-phase the chains run antiparallel and are related *via* an inversion centre (space group P-1) whereas in the β-phase the chains align coparallel generating a macroscopically polar structure (space group *Fdd*2, Figure 7 (a)). At room temperature the effective magnetic moment of both phases are a little less than the values expected for a

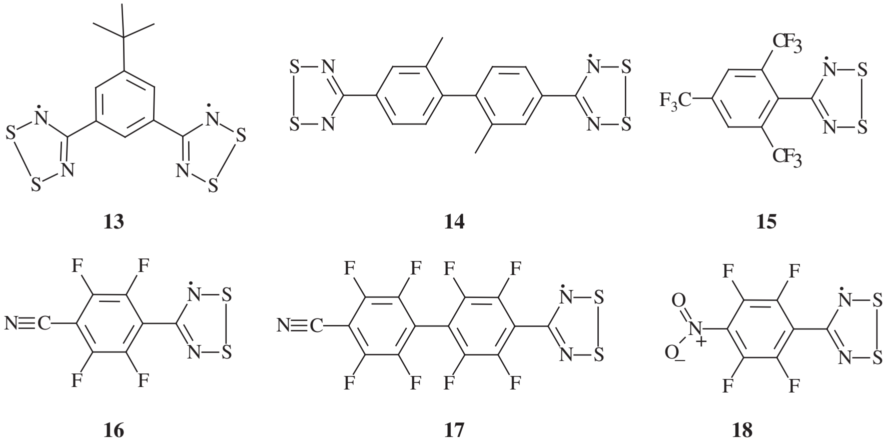


Scheme 2



(a) (b)

Figure 7 *(a) crystal structure and (b) magnetic exchange pathway in* **16**β



Scheme 3

near isotropic ('Heisenberg') S=1/2 paramagnet with g=2.0 (1.73 BM) consistent with local antiferromagnetic coupling between radical centres. While the α-phase does not exhibit any magnetic order down to 5 K, the β-phase orders as a canted antiferromagnet below 36 K. In an antiferromagnet the spins on each molecule align antiparallel throughout the lattice. However the lack of inversion centre between spins (associated with the polar space group *Fdd*2) allows the spins to tilt slightly with respect to each other, generating a small spontaneous moment. Detailed experimental[29] and theoretical[30] studies of the exchange interaction in **16**β indicate that the communication between spins occurs *via* heterocyclic S···N contacts between the supramolecular chains. In **16**β each molecule forms four symmetry equivalent S···N contacts, which generate a diamond-like three-dimensional motif in the solid state [Figure 7 (b)]. The high Tc is due to the strong communication between radicals. The magnetic ordering has been probed by an armoury of physical methods including heat capacity, neutron diffraction, muon-spin relaxation and EPR spectroscopy.[17,31] Application of pressure leads to an increase in the magnetic ordering temperature up to 70 K at 16 kbar.[32]

Dithiadiazolyl radical **18** has recently been reported to order as a ferromagnet below 1.3 K.[33] The application of pressure also leads to an increase in magnetic ordering temperature. Heat capacity and susceptibility measurements reveal magnetic order at 1.75 K at the higher pressures measured (15 kbar).[34] The related derivatives **17** and **2**(R=*p*-BrC$_6$F$_4$) do not order down to 1.8 K. This has been attributed to the low-dimensionality of the exchange pathway.[35]

12.1.2.1.5 Reactivity

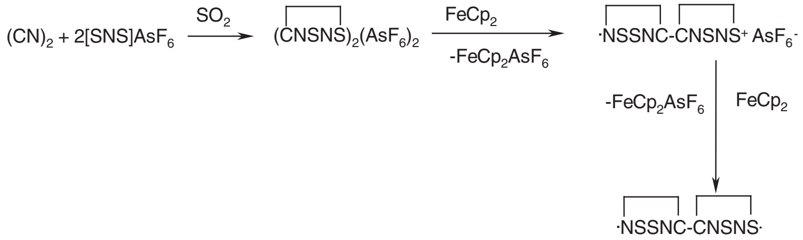
The reactivity of **2** has been reviewed recently[36] and is characterised by one-electron processes. We have already seen that small amounts of halogen lead to doped structures of composition [**2**]$_n$X. When X=Cl, the mixed-oxidation state complexes [**2**]$_3$Cl can be identified, as well as the integer oxidation state [**2**][X] and polyhalide complexes [**2**]X$_3$.[37] Conversely reaction with low-oxidation state metal complexes leads to an oxidative ring opening addition to the metal centre forming a variety of mono-, di- and tri-nuclear complexes.[38] The selenium derivative **12** exhibits a similar behaviour, although a slightly higher reactivity. Reaction of the *m*- and *p*-pyridyl derivatives of **2** with Pt(PPh$_3$)$_4$ yielded trimetallic complexes analogous to the phenyl derivative in which the thiazyl radical has oxidatively added to the metal centre.[39] Subsequent reaction showed that the pyridyl N could act as a Lewis base towards BEt$_3$. However, with careful selection of transition metal complexes, which do not undergo redox reactions, the ortho-pyridyl derivative has been found to form the first chelate coordination complexes in which the ring N is metal-bound.[40] The magnetic properties of this complex indicate that the unpaired electron on the heterocyclic ring is strongly coupled to the metal centre.

12.1.2.2 1,3,2,4-Dithiadiazolyl Radicals

12.1.2.2.1 Synthesis

The chemistry of the 1,3,2,4-dithiadiazolyl ring system became established in the 1980s after the pioneering work on the cycloaddition chemistry of [SNS][AsF$_6$] with nitriles by Passmore.[41] This reverse-electron demand cycloaddition yielded the corresponding 6π 1,3,2,4-dithiadiazolylium cations in high yield. The cycloaddition chemistry of [SNS][AsF$_6$] has been reviewed[42] and a recent synthesis of [SNS][SbF$_6$] from convenient starting materials has been reported. The cycloaddition chemistry has been successfully extended to the preparation of multi-dithiadiazolylium salts including [Hg(CNSNS)$_2$]$^{2+}$.[43] With the exception of the latter complex (which decomposes with formation of S$_4$N$_4$), other 1,3,2,4-dithiadiazolylium cations can be reduced with Ag, Na$_2$S$_2$O$_4$, [R$_4$N]Cl/Ph$_3$Sb or Cp*$_2$Fe (Scheme 4).[44]

The selenium analogues of 1,3,2,4-dithiadiazolyl(ium) ring systems have not been thoroughly explored. However Klapötke has shown[45] that [ClSeNSeCl]$^+$[MF$_6$] will undergo cycloaddition to RCN in the presence of tin(II)chloride to form [RCNSeNSe][AsF$_6$], the tin(II) chloride acting as a chlorine scavenger reducing the ClSeNSeCl$^+$ cation to SeNSe$^+$ *in situ*.



Scheme 4

12.1.2.2.2 Physical Properties

Electrochemical studies on a series of aromatic derivatives revealed a one-electron reduction to the corresponding 1,3,2,4-dithiadiazolyl radical (**3**).[18] The redox behaviour showed little variation with the electron-withdrawing/releasing properties of the substituent in an analogous fashion to the isomeric 1,2,3,5-dithiadiazolyls (Section 12.1.2.1). The 1,2,3,5-DTDA ring seems to be easier to reduce, since the phenylene analogue bearing both $\mathbf{2}^+$ and $\mathbf{3}^+$ can undergo two sequential one-electron reductions, which can be monitored by EPR spectroscopy. The EPR and theoretical studies on the 1,3,2,4-dithiadiazolyl radical showed that the spin density was predominantly localised on the SNS fragment of the dithiadiazolyl ring. While both ring N atoms formally bear some of the spin density, EPR studies normally appear as well-resolved triplets with coupling to the SNS nitrogen atom in agreement with MO calculations (Figure 1). A review of 1,3,2,4-dithiadiazolyl chemistry can be found in ref. 46.

The stability of the 1,3,2,4-dithiadiazolyl radical is extremely sensitive to substituent[5] and is susceptible to both thermal and photochemical isomerisation to the thermodynamically more stable 1,2,3,5-dithiadiazolyl radical (Section 12.1.1.1) *via* a bimolecular rearrangement.[47] In a number of other instances the radicals appear indefinitely stable in dilute solution, but decomposition appears to occur at high concentrations. As a consequence few 1,3,2,4-dithiadiazolyl radicals have been isolated in the solid state. Of these the phenylene-bridged *bis*(1,3,2,4-dithiadiazolyl) adopts a π^*–π^* dimeric structure in the solid state[48] while the mixed 1,2,3,5-/1,3,2,4-*bis*(dithiadiazolyl) has recently been reported (Figure 8).[44] This too adopts a π^*–π^* bonding mode,[44] although the dimers exhibit an unexpected behaviour with two sets of π^*–π^* interactions between **2** and **3** rather than the symmetric **2**/**2** and **3**/**3** dimer.

12.1.2.3 1,3,2-Dithiazolyl Radicals

12.1.2.3.1 Synthesis

There is not one generic route into 1,3,2-dithiazolyl/ium chemistry. For acyclic derivatives the [4+2] cycloaddition chemistry of [SNS][AsF$_6$] to alkynes has been successfully expoited by Passmore.[49] However for benzo-fused derivatives, the simplest route is *via* Wolmershauser's method in which 1,2-sulfenyl

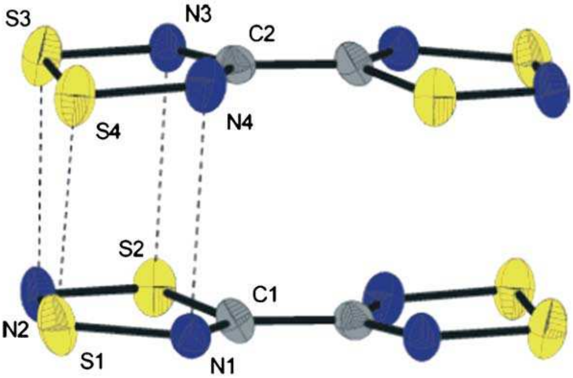
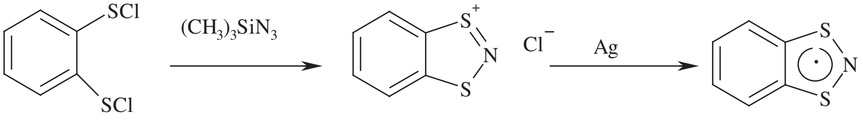


Figure 8 *π*–π* interactions between the mixed 1,2,3,5-/1,3,2,4- bis(dithiadiazolyl) radicals*



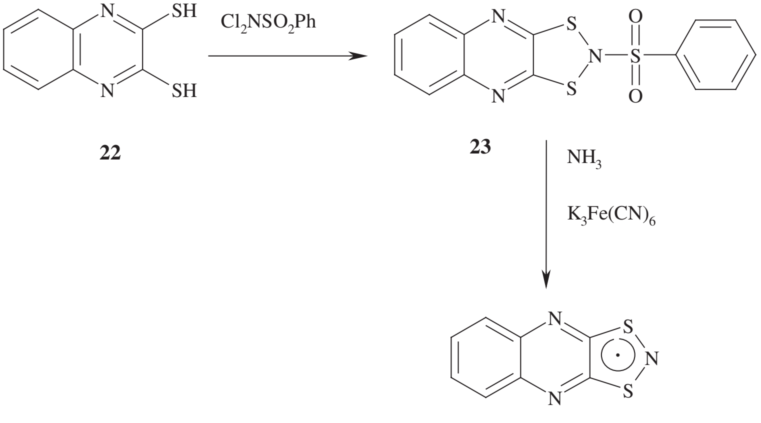
19 **20** **21**

Scheme 5

chlorides **19** are prepared *via* chlorination of a 1,2-dithiol and then condensed with Me_3SiN_3 to yield the 6π dithiazolylium ring.[50] While this approach has been successfully employed[51] for the synthesis of many other 1,3,2-dithiazolylium salts and stable radicals, it is not infallible and other methods have been identified (Schemes 5, 6 and 7).

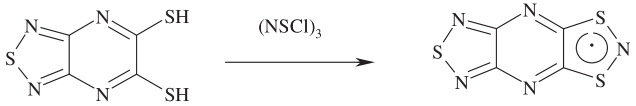
In many circumstances both cyclic and acyclic derivatives of **4** may be generated *in situ* by one-electron reduction of $\mathbf{4}^+$ using Zn/Cu couple, Ag powder or sodium dithionite. For the acyclic derivatives the free radicals can be observed in dilute solution[52] but only those derivatives bearing strongly electron-withdrawing functional groups ($R{=}R'{=}CF_3$ and R=R′=CN) have so far proved sufficiently stable to be isolated in the solid state.[49] For fused derivatives, it has often proved possible to isolate the radicals in the solid state by sublimation *in vacuo*. Alternative routes have been explored for other derivatives where this approach has had limited success, *e.g*. the reaction of *bis*(sulfenyl chlorides) and amine derivatives gives *N*-substituted 1,3,2-dithiazole derivatives that, in some instances, have been used as precursors for stable radicals.[53] Starting from 1,2-dithiol **22**, *N*-arylsulfonyl-1,3,2-dithiazole **23** was formed by reaction with *N*,*N*-dichloroarylsulfonamide. Reaction of **23** with ammonia, followed by oxidation with potassium ferricyanide, gave the quinoxaline-1,3,2-dithiazolyl radical **24** (Scheme 6).[53]

The stable heterocyclic radical 1,2,5-thiadiazolo- 1,3,2-dithiazolopyrazinyl **26** was prepared by treatment of 5,6-dithiolo-1,2,5-thiadiazolo[3,4-*b*]pyrazine



22 **23** **24**

Scheme 6



25 **26**

Scheme 7

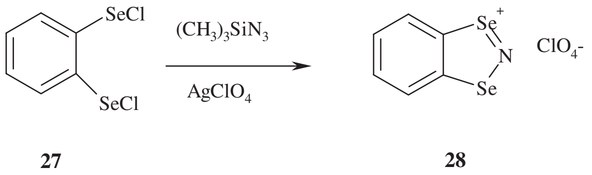
(**25**) with trithiazyl trichloride, and purified by sublimation in vacuum.[54] This method has not yet been used successfully for other 1,3,2-dithiazoles (Scheme 7).

The general synthetic methodology to benzo-fused dithiazolyl radicals has been extended to the synthesis of di- and tri-radicals. Of these the benzo-1,2:4,5- *bis*(1,3,2-dithiazole) system has been studied in its full range of oxidation states, *i.e.* **34**, **35** and **36** (Scheme 9).

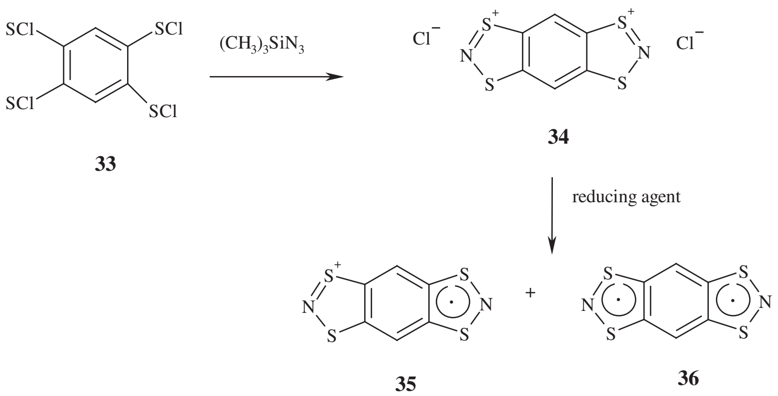
The selenium analogues of these 1,3,2-dithiazolyl radicals have not been extensively studied. Benzo-1,3,2-diselenazolium perchlorate **28** can be prepared from **27** in an analogous fashion to the corresponding sulfur compound[55] and its structure determined by X-ray structure analysis. Unlike BDTA (1,3,2-dithiazolyl radical), reduction of **28** afforded an unstable neutral radical. No stable selenium analogues have yet been isolated (Scheme 8).

12.1.2.3.2 Physical Properties

Electrochemical studies on a number of derivatives reveal a reversible one-electron reduction to the dithiazolyl radical. The greater spin density at the heterocyclic C atoms in **4** (Figure 1) facilitates greater π-delocalisation onto the fused substituents than observed for **2** and **3**. As a consequence the position of the $E_{1/2}$ for the +1/0 redox process has been found to be somewhat more



Scheme 8



Scheme 9

sensitive to the nature of the substituents.[56] Since the $\mathbf{4}^+/\mathbf{4}^\bullet$ and $\mathbf{4}^\bullet/\mathbf{4}^-$ processes involve sequential addition of electrons into the same orbital then the energy gap between the two can be considered to be primarily a reflection of the extent of inter-electron repulsion. The latter itself is dependent upon the degree of π-delocalisation. Notably the enhanced π-delocalisation in **4** (in relation to **2** and **3**) leads to a reduced 'on site coulomb potential' *e.g.* the separation of the $E_{1/2}$ values for these two $1e^-$ processes for **4** typically fall in the range 1.35–1.41 V. These values are reflected in a smaller Hubbard potential, which has implications in the physical properties of these radicals (See Section 12.1.2.1.3).

Reduction (for example with Ag or Zn/Cu in non-aqueous solvents) yields the corresponding dithiazolyl radicals, which have been observed by EPR spectroscopy. The EPR spectra of these radicals typically reveal a large hyperfine coupling to the heterocyclic N, consistent with localisation of the larger component of the spin density on the heterocyclic ring (Hyperfine coupling to S is not normally detected due to the low natural abundance of spin-active ^{33}S).[57] In some cases an analysis of the hyperfine coupling has been made, which provides a detailed picture of the spin density distribution.[65] Additional superhyperfine interactions to other spin-active nuclei has also sometimes been observed.[58] The values of the spin density distribution from solution EPR have typically been found to be in good agreement with DFT estimates of the spin density distribution in the gas phase.[59]

Solution EPR measurements on **4** ($R=R'=CF_3$) showed that the solution phase dimerisation process was essentially enthalpically neutral.[5] Unlike **2** and **3**, there is likely to be a greater tendency for the formation of derivatives with either regular π-stacked motifs or other paramagnetic structure.

12.1.2.3.3 Conductivity and Spin-Switching

Physical studies on dithiazolyl radicals in the solid state have shown wealth and diversity of magnetic and structural phenomena. We will focus initially on the electronic properties of π-stacked structures. At low temperatures ($T \leqslant T_1$, Figure 9) these π-stacked structures tend to exhibit a Peierls-type or CDW-driven distortion forming alternate long/short S···S contacts down the stack. The short contacts (typically *ca.* 3.2–3.3 Å) are a little longer than those observed in the discrete dimers of **2** (typically 3.0–3.1 Å) described in Section 12.1.1.1, although the longer inter-dimer S···S contacts (typically *ca.* 3.7–3.8 Å) are somewhat shorter than the non-bonded inter-dimer contacts observed in derivatives of **2** (3.8–3.9 Å). Thus these π-stacked 1,3,2-dithiazolyl radicals appear to undergo a less severe distortion along the π-stacking direction which may be a reflection of the lower tendency for π*–π* dimerisation identified in solution phase EPR studies.[5b]Nevertheless magnetic measurements reveal them to be diamagnetic. This can be explained either through formation of a closed-shell singlet ground state or through a large band gap precluding thermal promotion to vacant orbitals.

However at elevated temperatures ($T_2 > T_1$, Figure 9) the increased entropy ($T\Delta S$) associated with an open shell structure overcomes the π*−π* enthalpy of dimerisation associated with these distorted π-stacked structures and they undergo a solid–solid phase transition (Figure 9) The high temperature phase is typically associated with a π-stack of regularly spaced radicals which exhibit longer inter-radical S···S contacts (*ca.* 3.7 Å). This process was first observed by Oakley[60] in the DTA radical thiadiazolopyrazine-1,3,2-dithiazolyl **26**, and a number of other derivatives have subsequently been identified which exhibit similar behaviour. These are compiled in Table 1.

This bistability is favoured by structures, which will adopt π−stacked motifs, i.e. lamellar molecules. In addition the tendency to adopt the planar structure is enforced by the presence of electronegative heteroatoms (currently restricted to N), which lead to a propensity of in-plane electrostatic S···N contacts between rings. These may comprise heterocyclic S···N contacts or S···N contacts to other functional groups such as the pyrazine or cyano nitrogen atoms.

Bistability is currently thought to arise out of the presence of a substantial activation energy barrier (E_A) to interconversion. Consider a free energy phase diagram (Figure 9). Below T_1 the dimeric low-temperature phase is favoured, whereas above T_1 the regular π-stacked phase is favoured. However if E_A is higher than kT then the low-temperature phase can exist in a metastable state up to the point T_2 where kT_2 is now greater than E_A. At T_2 a phase transition occurs to the regular π-stacked entropically favoured phase. On subsequent cooling the high-temperature phase is stable down to T_1. Below T_1 the

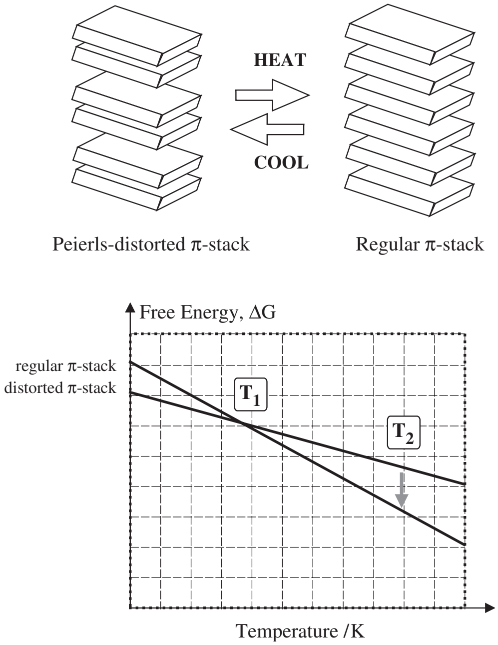


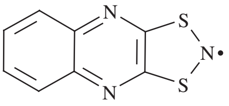
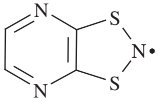
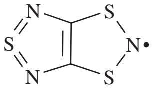
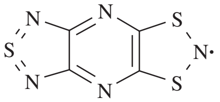
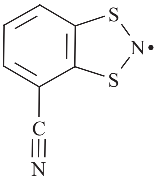
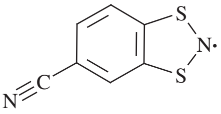
Figure 9 *(Top) schematic of bistability in 1,3,2-dithiazolyl radicals arising from a solid–solid phase transition between regular and Peierls distorted π-stacks; (bottom) free energy diagram of the two structural phases present*

low-temperature phase is more stable and the reverse process occurs. Elegant studies on the interconversion mechanism by Oakley have outlined the cooperative nature of the phase transition and indicate that the activation energy arises out of a breaking and reforming of the inter-stack contacts.[60,61]

The result is a system, which has a region of bistability in which thermal or photochemical switching between diamagnetic and paramagnetic phases can be achieved. Of these, trithiatriazapentalenyl (TTTA, **30**) has perhaps been studied in the greatest detail. It was first reported by Wölmershauser in 1989[64] but its unusual properties were not identified until 1999.[65] The phase transition in TTTA has been monitored by magnetic susceptibility, DSC, EPR, single crystal and powder X-ray diffraction.[65] All these methods confirm $T_{C\downarrow} \sim 230$ K and $T_{C\uparrow} \sim 320$ K. The temperature range of bistability (which encompasses room temperature) is truly remarkable. It is one of only a handful of (organic or inorganic) compounds, which exhibit bistability at room temperature. The relative stability of the two phases is sensitive to the free energy profile. While this is clearly a function of temperature, the phase-transition has also been shown to be promoted by both the application of pressure and irradiation. The low- and high-temperature structures of TTTA and the temperature dependence of its magnetic susceptibility are presented in Figure 10.

Pressed pellet conductivity measurements on some of these radicals (*e.g.* **24** and **29**) indicate room temperature conductivities of $<10^{-6}$ S cm^{-1}.[62] The low

Table 1 *Phase transition temperatures for π-stacked DTA derivatives.*

Radical	$T_{C\uparrow}/K$	$T_{C\downarrow}/K$	*Bistability range, $\Delta T/K$*	*Ref.*
 **24**	120	95	25	61
 **29**	343	297	46	62
 **30**	320	230	90	65
 **26**	175	92	83	60
 **31**	250 27	250 39	0 13	63
 **32**	304 27	293 37	11 10	63

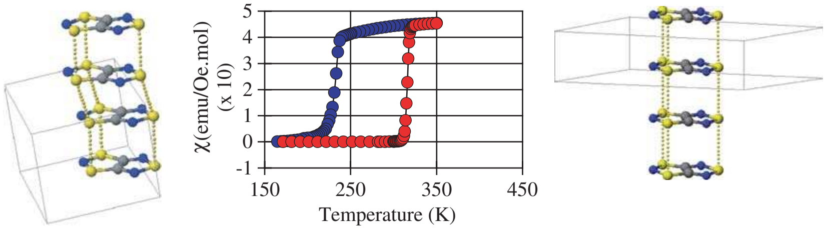


Figure 10 *LT phase (left) and HT phase (right) packing diagrams of TTTA radical; centre the temperature dependence of χ on heating and cooling*

conductivities might seem surprising given the fact that its evenly spaced π-stack structure fulfils the prescription for a neutral π-radical conductor, but the larger intermolecular separation, in relation to the stacked dithiadiazolyls, leads to a narrow bandwidth. In addition the large on-site Coulomb repulsion inhibits electron transfer, leading to a Mott insulating state.[66]

12.1.2.3.4 Magnetism

A number of 1,3,2-dithiazolyl radicals adopt structures, which are monomeric but not π-stacked. These systems have been found to be paramagnetic. EPR studies on these radicals indicate that most of the spin density is localised on the SNS fragment of the dithiazolyl ring. The presence of close S···S or S···N contacts between radicals leads to strong communication between radicals. As we saw in Section 12.1.2.1.4, long-range order will only be observed in systems exhibiting a three-dimensional network of exchange contacts. For example methyl-benzo-1,3,2-dithiazolyl (MBDTA) shows very strong antiferromagnetic coupling between radicals (evidenced by a broad maximum at 140 K) but no long-range order down to 1.8 K.

While the heterocyclic diradical *bis*-benzo dithiazolyl (BBDTA, Scheme 9) consists of associated molecules in the crystal state,[60] the radical cation $\mathbf{35}^+$ adopts a number of different motifs dependent upon both the anion and solvent of crystallisation, *e.g.* the $GaCl_4$ salt, when crystallised from acetonitrile gives a solvated product with dimerised radicals and diamagnetic behaviour in the range 2–300 K.[67] However if the salt is recrystallised in a mixture of trimethylacetonitrile and dichloromethane at −23 °C, the desolvated material can be isolated and comprises discrete monomers of $\mathbf{35}^+$ sandwiching a $GaCl_4^-$ between them. This non-solvated structure orders as a ferromagnet with T_c=7.0 K.[68] When crystallised with the paramagnetic $FeCl_4^-$ anion, it orders as an antiferromagnet at 44 K, once the solvent of crystallisation has been removed.[69]

12.1.2.3.5 Paramagnetic Liquids

The thermal stability of many 1,3,2-dithiazolyl radicals is sufficiently high for them to melt without decomposition to form stable liquids. In the case of **2**

($R{=}R'{=}CF_3$) the vapour pressure is sufficiently high enough to exist as a blue gas allowing its structure to be determined in the gas phase by electron diffraction.[49] For dithiazolyls, which adopt dimeric solid-state structures, the melting process (breakdown of intermolecular forces) is associated with the collapse of the π^*–π^* dimeric structure and a rapid increase in paramagnetism. Subsequent cooling of these paramagnetic liquids leads to re-solidification. Interestingly these radicals also exhibit thermal hysteresis around their melting points, which has been ascribed to the formation of a metastable glassy phase (*cf.* the solid–solid phase transition). Previous studies[70] have indicated that bistability at the solid/liquid boundary is usually a reflection of substantial differences in the local structures of the liquid and solid phases. In the case of these 1,3,2-dithiazolyls, this is clearly reflected in the magnetism which indicates π^*–π^* dimers in the solid state and paramagnetic monomers in the liquid phase. Reformation of the solid phase is inhibited by the substantial differences in the nature of their structures as well as substantial viscosity, which slows down the kinetics of the crystallisation process.

The benzo-derivative BDTA exhibits particularly unusual behaviour. Passmore showed that in samples prepared by sublimation *in vacuo* it formed a diamagnetic π^*–π^* dimer (but not a π-stack) with a *trans*-geometry and close S···S contacts between rings within the dimer ($d_{S\cdots S}=3.217$ Å).[71] Recently Awaga and co-workers[72] showed that on heating, BDTA melted and immediately re-solidified to form a new phase, which was paramagnetic in the solid state. In the case of BDTA there are (at least) two stable solid-state structures but their packing motifs are such that they preclude interconversion between them. As a consequence melting the π^*–π^* dimer then allows the substantial structural rearrangement necessary to obtain the paramagnetic second phase. Subsequent cooling of this second phase leads to magnetic ordering as an antiferromagnet below 11 K.

12.1.2.3.6 Charge-Transfer Salts

Dithiazolyl radicals also have potential in the formation of charge-transfer salts. Wolmershauser[50] originally reported that BDTA formed a highly conducting charge transfer complex with tetracyanoquinodimethane (TCNQ) although no structure was reported. More recently other salts have been formed; co-crystallisation of BDTA with metal dithiolenes such as $Ni(dmit)_2$ or $Cu(mnt)_2$ have led to the isolation of a novel multiband conducting system[73] and an ideal 1-D magnetic chain.[74] However the potential to optimise the conducting properties through fine-tuning the redox behaviour has not yet been investigated.

12.1.2.3.7 Coordination Chemistry

The only report of coordination of a dithiazolyl radical to date is the formation of the complex $TTTACu(hfac)_2$.[75] In it the TTTA molecules played the role of a bidentate bridging ligand, forming an alternating chain with the Cu(hfac) units.

This is expected since the nitrogen atom in the thiazyl radicals bear negative polarised charges. A magnetic study of this compound revealed a ferromagnetic exchange between the Cu and the TTTA moieties, with an antiferromagnetic coupling between chains.

12.1.2.4 1,2,3-Dithiazolyl Radicals

12.1.2.4.1 Synthesis

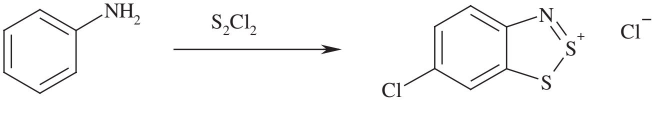
Closely related to the 1,3,2-dithiazolyl radicals are the isomeric 1,2,3-dithiazolyl radicals. The benzo-fused derivatives were originally prepared by Herz in 1922[76] from the reaction of aniline and its derivatives with an excess of S_2Cl_2 (Scheme 10). Almost invariably the aromatic ring becomes substituted by chlorine *para* to the amine N atom.

While the stoichiometry of the reaction appears simple, the reaction mechanism is not well understood, despite numerous studies,[77] and the reaction tipically gives rise to a number of by-products. Purification of Herz salts is best achieved *via* metathesis to one of a number of more soluble salts ($AlCl_4^-$, BF_4^-, $SbCl_6^-$), which can be recrystallised to a high degree of purity.[78]

While the Herz reaction provides a convenient route to many dithiazolylium salts, the propensity for chlorination of the aromatic substituent has led to the development of several other approaches to 1,2,3-dithiazolylium salts and 1,2,3-dithiazolyl radicals. A particular convenient route involves the mild condensation reaction between thionyl chloride and *ortho*-amino-thiophenols.[79] This methodology can be easily adapted to allow the preparation of all the different selenium-for-sulfur substituted derivatives with a lesser tendency for ring chlorination (see below).

Reduction of **38** leads to the formation of the corresponding 1,2,3-dithiazolyl radical. The simple benzo-derivatives have long lifetimes and have been studied extensively by EPR spectroscopy, although attempts to isolate radicals to date appear to have been broadly unsuccessful. The only 1,2,3-dithiazolyl which has been structurally characterised is the non-fused 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl.[80] Theoretical calculations indicate that the majority of the unpaired spin density resides on the heterocyclic ring, although there is considerable delocalisation onto the fused aromatic substituent. The failure to isolate any of these radicals led to the attempt to add extra stabilisation through the formation of more extended π-delocalised systems.

The methodology of Huestis[79] can be extended to the formation of both the *bis*(1,2,3-dithiazolylium) ring systems and the mixed S/Se derivatives, *e.g.*



Scheme 10

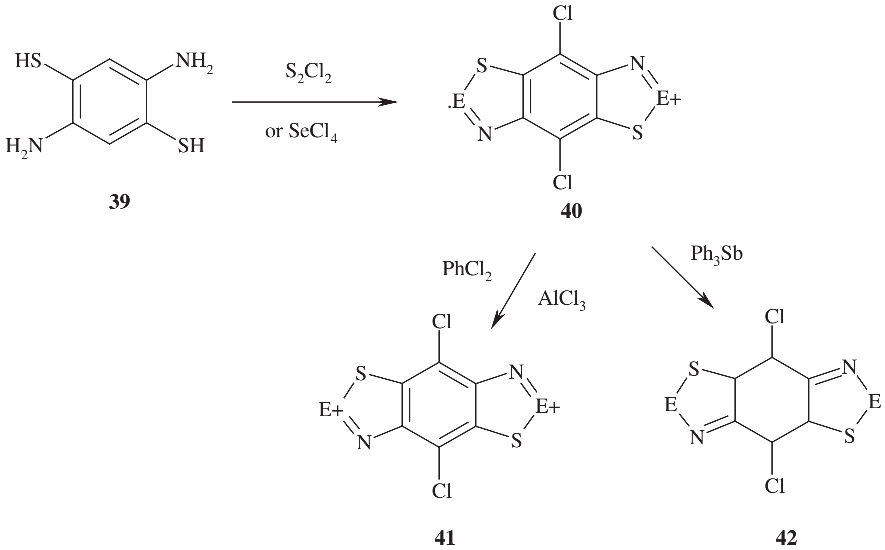
condensation of diaminobenzenedithiol **39** with disulfur dichloride afforded the chloride salt of the radical cation **40** (E=S) while similar condensation with $SeCl_4$ gave the mixed S/Se analogue **40** (E=Se). Note that even using these milder conditions there is a marked tendency for ring chlorination. The corresponding parent dications **41** (E=S,Se) were obtained by oxidation of the radical cations (Scheme 11).[81]

Reduction of **40** (E=S/Se) could be achieved with triphenylantimony to form the neutral molecules **42** (E=S/Se). Compounds **42** (E=S and E=Se), which are formally antiaromatic **16** π-systems, exhibited bond lengths consistent with a quinoid formulation.

12.1.2.4.2 Physical Properties

Electrochemical studies indicate that the redox behaviours of the different derivatives are dominated by the nature of the chalcogen at position 2, with the selenium containing cations more readily reduced (by more than 0.1 V) than the sulfur analogues.[82] The difference has been ascribed to the extent of delocalisation of the positive charge away from the heterocycle, onto the fused aromatic ring.

The EPR spectra of a large number of 1,2,3-dithiazolyl radicals have been reported[83] in a series of comprehensive studies. In all cases the *g*-value is substantially greater than that for the free electron, indicative of spin orbit coupling arising from significant amounts of spin density at sulfur, in agreement with the *g*-values observed for all the chalcogen radicals. There is some variation in the *N*-hyperfine coupling, depending on the substituents, and a good correlation has been observed between the Hammet parameter for the



Scheme 11

para substituents and the *N*-hyperfine interaction, the two being inversely proportional;[84] the more extensive the delocalisation, the smaller the *N*-hyperfine coupling constant. The disproportionation energy for these derivatives (*e.g.* separation of the $E_{1/2}$ values for the $\mathbf{5}^+/\mathbf{5}^{\cdot}$ and $\mathbf{5}^{\cdot}/\mathbf{5}^-$ processes) is much lower (by *ca.* 0.7 V) than those reported for either DTDA or 1,3,2-DTA derivatives, consistent with the further enhancement of the π delocalisation suggested by the EPR studies. However initial studies indicate that this energy barrier to electron transfer still appears inaccessible to fine tuning.[85]

12.1.2.4.3 Conductivity

Only 5 derivatives have been isolated to date. While the non-fused system forms a π*–π* dimer ($d_{S\cdots S}$=3.27 Å),[86] structural studies on the more delocalised derivatives indicate a reduced tendency to dimerise. However, rather than forming optimal π-stacked motifs, there is a clear tendency to adopt slipped π-stack structures which minimise orbital overlap. As a consequence although the Hubbard energy is low, conductivity measurements show poor conductivities (10^{-5} S cm^{-1}) similar to those observed in either the isomeric 1,3,2-dithiazolyl (**4**) or 1,2,3,4-dithiadiazolylradicals (**2**).[84]

12.1.2.4.4 Magnetism

The reduced orbital overlap between the radicals reduces the bandwidth and the electronic structures could be better considered as those of a localised rather than itinerant electron system. This poor overlap results in very small antiferromagnetic interactions being observed, and the compounds behave as nearly perfect Curie–Weiss paramagnets. In the cases when improved lateral interactions between the stacks are achieved by change of the substituents[85] the compounds behave as weak 1D ferromagnets due to the effective orthogonality of the S···C interactions.

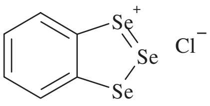
12.1.2.5 1,2,3-Trithiolium Radicals

12.1.2.5.1 Synthesis

A systematic route into non-fused derivatives appears to be from the reactivity of $[S_4][AsF_6]_2$ and $[S_8][AsF_6]_2$ with alkynes.[87] The equi-molar mixture of S_4^{2+} and S_8^{2+} appears to act as if it were S_3^+ although there is little evidence of this species in solution itself. The reactivity of this hypothetical S_3^+ radical appears to mimic that of the closed-shell SNS^+ cation but with an additional electron in a π* orbital. Using this method Passmore has isolated **7** (R=CF_3, R=CO_2Me).

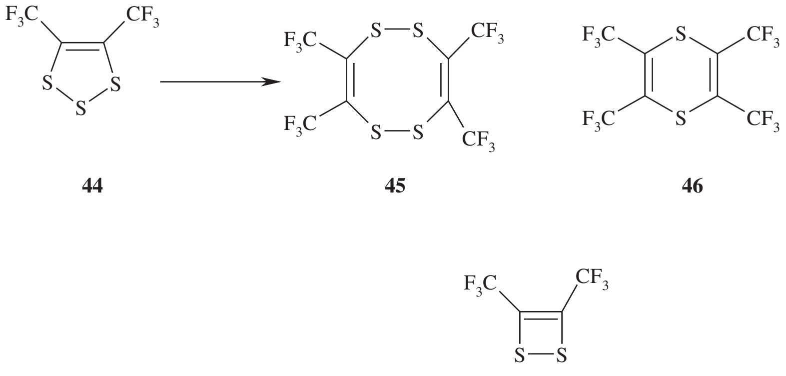
The benzo-1,2,3-triselenolylium radical cation is the only benzofused derivative to have been isolated.[88] It can be synthesised from the reaction of **27** with Se powder to yield **43** in 72% yield as the chloride salt (Scheme 12).

Conversely, no benzofused trithiolium radicals have been isolated to date. This is due to the inherent instability of the benzotrithiole molecule, which readily forms oligomeric and polymeric mixtures.[89] Further efforts to try to



43

Scheme 12



44 **45** **46**

47

Scheme 13

isolate trithiolium radicals have focused in introducing bulky substituents onto the benzene ring,[90] and although some of the parent trithioles have been isolated[91] and electrochemistry studies have proved that it is feasible to obtain the 7π radical cations, their isolation remains unreported.

12.1.2.5.2 Physical Studies

The EPR spectrum of **7** ($R{=}CF_3$) AsF_6^- salt in SO_2, consisted of a central binomial septet due to coupling of 6 equivalent F atoms with one set of weak ^{33}S satellites. Although trithiolylium cations contain two inequivalent sets of sulfur nuclei, only one set of ^{33}S satellites were observed. Further studies with **7** ($R{=}CO_2Me$) however managed to resolve the ^{33}S satellite into two components in 1:2 intensity ratio, consistent with the structure of a 1,2,3-trithiolylium radical cation.[92]

Although no electrochemical studies exist to our knowledge, the AsF_6^- salt may be reduced with potassium iodide to give the neutral species **44**, which readily decomposes into **45–47**.[92]

The crystal structure of **7**[AsF_6] ($R{=}R'{=}CF_3$) comprises monomeric radical cations separated by the diamagnetic AsF_6^- anion. The absence of a π-stacked motif mitigates against a delocalised conduction band and the variable temperature magnetic studies confirm that this salt is a paramagnet with antiferromagnetic coupling. The broad maximum in χ at *ca.* 3 K is likely to reflect short-range rather than long-range bulk antiferromagnetic order, although more measurements are required.

The benzo-1,2,3-triselenolylium radical cation was identified by X-ray diffraction[88] and it reveals the presence of dimeric units with short (3.27 Å) Se···Se contacts.

Solution EPR has been reported and consisted of a singlet of low intensity when recorded in acetonitrile. However, the signal intensity increased when the solvent used was trifluoroacetic acid, indicating a solvent-dependent dissociation equilibrium. No set of satellites due to coupling to Se were reported.

12.1.2.6 1,2,3,4-Trithiazolylium Cations

12.1.2.6.1 Synthesis

Recent studies by Passmore have extended the cycloaddition chemistry of 'S_3^{+}' (see Section 12.1.2.5) to nitriles. Reaction of CF_3CN with equimolar quantities of $[S_4][AsF_6]_2$ and $[S_8][AsF_6]_2$ produces good yields of $[CF_3CNSSS][AsF_6]$.[93] In addition reaction of dicyanogen $(CN)_2$ yields the diradical $[SSSNC–CNSSS][AsF_6]_2$.[94]

12.1.2.6.2 Physical Properties

Both the diradical and the CF_3 derivative are monomeric in the solid state,[94] affording materials in which layers of radical cations are sandwiched between layers of the corresponding counter anions.

12.1.2.6.3 Magnetic Properties

The monomeric diradical $[SSSNC–CNSSS][AsF_6]_2$, like **7**$[AsF_6]$ ($R{=}CF_3$), is paramagnetic in the solid state. A broad maximum in χ at 60 K is indicative of short-range antiferromagnetic coupling.[94]

Solid-state EPR studies of the diradical[95] shows a rhombic *g*-matrix consistent with it being a planar diradical with the two rings separated by a sp^2–sp^2 hybridised C–C single bond. The two unpaired electrons are nearly disjoint (*i.e.* non-communicating). The EPR spectrum is consistent with a triplet (S=1) ground state with a near-degenerate singlet state with an energy gap of *ca.* 0.5 kJ mol^{-1}. This value was supported by theoretical calculations which were in good agreement with the determined singlet-triplet gap between these two configurations to be around 0.88 kJ mol^{-1}.[96] Variable temperature magnetic measurements revealed the diradical to show antiferromagnetic coupling with a maximum in the magnetic susceptibility at 60 K. This is consistent with a triplet ground state but with an almost degenerate singlet state, with a gap between these two configurations around 0.5 kJ mol^{-1}.

12.1.3 Conclusions

A large family of sulfur-based radicals exist, a number of which are extremely stable. A number of derivatives have been extensively studied and have already revealed enormous potential as molecular conductors, magnets and bistable switchable materials. Yet these are not the only potential areas, other applications have been proposed in areas as diverse as paramagnetic liquid crystals and organic/inorganic hybrid magnetic materials. The first results in these areas of metallo-organic systems augur well for their future development. Yet the majority of these studies have focused on a small group of these radicals. Further fundamental research into basic synthetic methodologies is necessary to support and compliment the more technologically driven aspects of this area.

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CHAPTER 12.2

Chalcogen-Rich Compounds as Electron Donors

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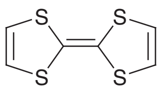
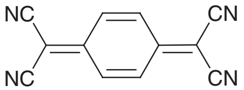
12.2.1 Introduction

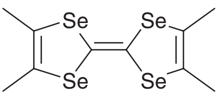
The discovery in 1973 of metallic conductivity in the charge transfer salt of tetrathiafulvalene (TTF, **1**) and tetracyano-*p*-quinodimethane (TCNQ, **2**)[1] was responsible for the subsequent explosion in interest of chalcogen-based electron rich molecular conductors. In this material, an average of 0.59 electrons are transferred from the TTF molecules to the electron deficient TCNQ units. The resulting TTF radical cations ($TTF^{+\bullet}$) and acceptor anions ($TCNQ^{-}$) form adjacent columnar stacks (Figure 1).[2] Close contacts between sulfur atoms arising from ring-over-bond overlap in the TTF stacks provide the framework for 1-dimensional intermolecular delocalisation of π-electrons. The polarisation of the sulfur atoms was also cited as helping to improve the electron transport properties of the salt. Materials of this donor–acceptor type are viable conductors because transfer of electrons from donor to acceptor generates charge carriers in the oxidised donor and reduced acceptor



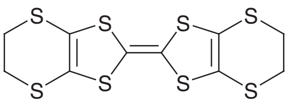
TTF **1**



TCNQ **2**



TMTSF **3**



BEDT-TTF **4**

Vast synthetic effort was subsequently employed to produce new conducting charge-transfer (CT) salts incorporating TTF-based donor structures. The first

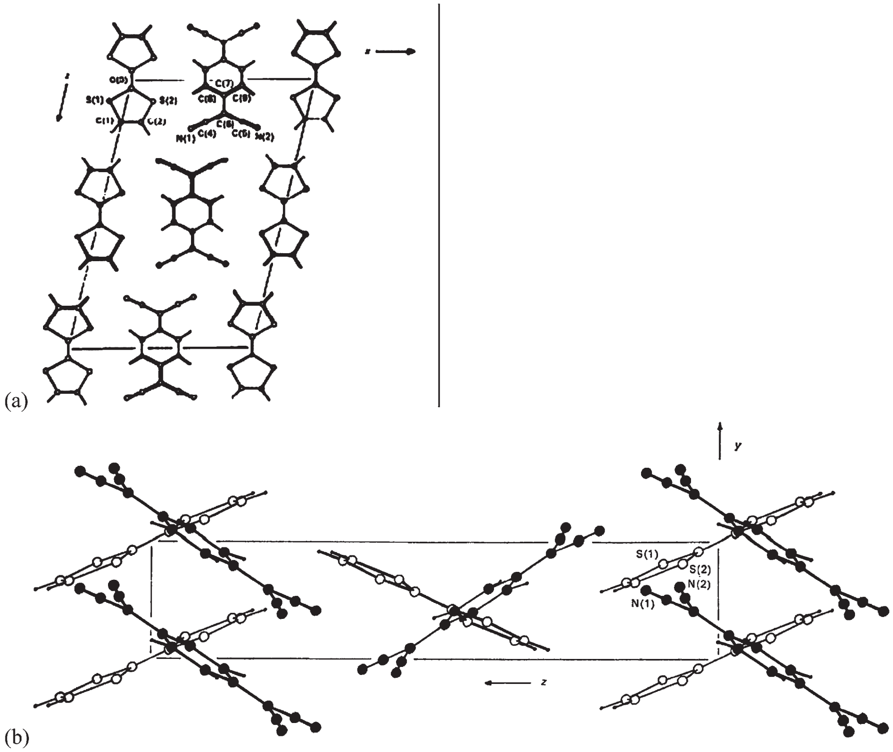


Figure 1 *(a) A view normal to the ac plane of the crystal packing in TTF–TCNQ. The shaded molecules have their centroids at y = 1/2. (b) A view along the [100] direction. The shaded molecules have their centroids at x = 1/2*
(Reproduced from Kistenmacher *et al.*[2] with IUCr's copyright permission)

superconducting complexes, known as the Bechgaard salts, employed the substituted selenium analogue tetramethyltetraselenafulvalene (TMTSF, **3**), which was electrocrystallised with a variety of counter anions.[3] The best results have originated from the donor *bis*-ethylenedithio-tetrathiafulvalene (BEDT–TTF **4**).[4] Although similar to TTF in terms of electrochemical behaviour, the presence of a different chalcogen atom (in the case of TMTSF) or more chalcogen atoms (BEDT–TTF) in the structure has a profound impact on the crystal packing. Se–Se contacts in TMTSF are remarkably close (3.8–4.0 Å, Figure 2). The increase in number of chalcogen–chalcogen contacts involving the external sulfur atoms of BEDT–TTF affords new packing modes, characterised by a 2-dimensional arrangement of BEDT–TTF dimers.[5–8]

The last three decades have seen organic chemists develop hundreds of analogues and derivatives of TTF, including the large family of linearly π-extended TTFs. A diverse range of electron acceptors, including organic, inorganic and metal-coordination species has also been studied in conjunction with this family of donors. Intrinsic physical properties of these counter ions, such as magnetism[9–18] or chirality[19,20] can be combined with the conducting

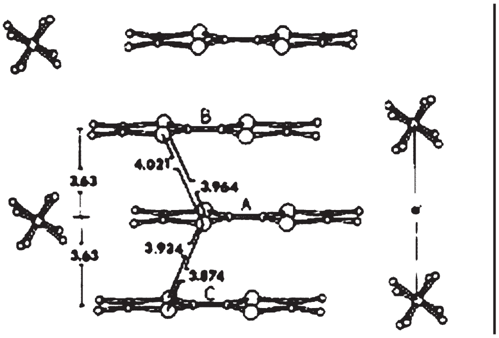


Figure 2 *Side view of the stacks in* $(TMTSF)C1O_4$
(Reproduced from Bechgaard *et al.*[3] with permission from the ACS)

nature of the TTF-derivative, to provide multifunctional nano-structured electroactive materials. Many materials with interesting electrochemical properties incorporate a tetrachalcogenafulvalene moiety or an analogue. Their unique electrochemical and structural properties find relevance in areas such as field-effect transistors (FETs),[21–24] molecular memory,[25] proton conduction for fuel cell components,[26] electrochromism,[27] non-linear optics[28] and sensors.[29,30] The supramolecular versatility of TTF has allowed for the preparation of some large, elegant assemblies such as catenanes and rotaxanes. Neutral TTF acts as a recognition site for the tetracationic cyclophane cyclobis(paraquat-*para*-phenylene) ($CBPQT^{4+}$, **5**) as a result of donor–acceptor π–π stacking interactions.[31–33] These interactions can be 'switched off' when the TTF is electrochemically oxidised causing the $CBPQT^{4+}$ ring to move to a more thermodynamically favoured location. This relatively new methodology for construction of TTF-based materials that are capable of doing mechanical work[34–37] embodies a radical approach to electronic applications[38–40] and broadens the materials chemistry horizon yet further. Simultaneous with the breakthroughs in TTF chemistry was the development of other conducting molecular and polymeric systems, and another extremely well-studied chalcogen-containing material, polythiophene (PT), has found applications in diverse settings such as polymer LEDs, photovoltaic cells, FETs and electrochromism.[41]

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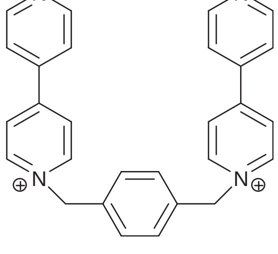


12.2.2 Structural Diversity

More than 30 years of research has produced great structural diversity in chalcogen-containing electroactive materials. From small molecules to large, elegant macrostructures, a common theme of heterocyclic π-delocalised structure is at its heart. In their excellent, recent review of TTF derivatives, Segura and Martín[42] organised these compounds into molecular, macromolecular, polymeric or supramolecular categories. Here we expand this system beyond TTF derivatives to illustrate the structural range of chalcogen-containing electroactive materials.

12.2.2.1 Molecular

Many electroactive molecular systems containing chalcogens are based on CT complexes where tetrachalcogenafulvalene (TEF, Figure 3) acts as electron donor, although the TEF framework has been altered with a variety of structural motifs, while retaining either the 1,3-dithiole ring or a similar structure. Crystal structure analysis has shown the importance of the packing modes of the donors, as the different phases observed in TEF packing allow for varying degrees of inter-stack interactions through chalcogen–chalcogen contacts. The recent observation by Laukhina *et al.*[43] of polymorphism in trihalide salts of BEDT–TTF provides a useful example of this principle. This study is the first example of a high-temperature transformation from β″ metal to β′ semiconductor and β metal in BEDT–TTF-based salts (see Figure 4). ESR indicates a reduction in dimensionality going from metallic β″ to β′ phase. X-ray data confirms there are fewer S···S close contacts in the semiconducting phase than in the metallic phase.

Extended TEFs[44] contain a conjugated spacer group between the 1,3-dithiole rings. Upon oxidation, TEF species form cations mainly localised on these heterocycles. Greater spatial separation of these charges is provided in extended analogues. Of course, increased conjugation can also lead to a reduced band gap, desirable in semiconductors.[45] Spacers of linear (Figure 5), annulated (such as **6**[46] and **7**[47]) or spiroconjugated[48] types have been prepared. Spacer design allows for influence over the extent of delocalisation of π-electrons.[49] The CT complexes of these donors, along with the relationship between solid state structure and electrochemical properties have been reviewed recently by Frère and Skabara.[50]

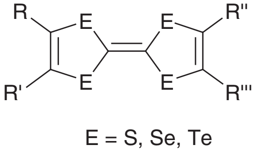


Figure 3 *General substituted tetrachalcogenafulvalene (TEF)*

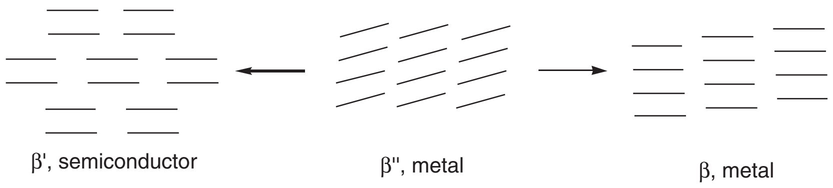


Figure 4 *Schematic representation of polymorphic transitions in trihalide salts of BEDT–TTF*[43]

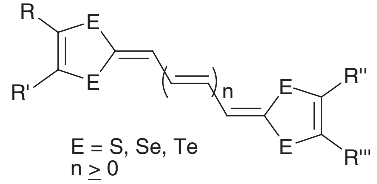
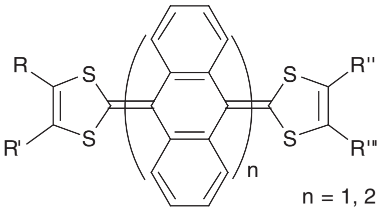


Figure 5 *General linear π-extended TEF*



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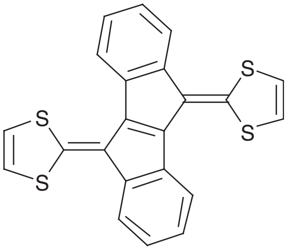

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Metal complexes based on 1,2-dithiolene ligands (M(bdt)$_2$, Figure 6) can be thought of as analogues of TEF, with the central C=C of TTF replaced by a metal ion which is coordinated to bidentate chalcogenide ligands. The conductance band structure is hence augmented by availability of the metal-ligand charge transfer band. Among these, the best studied are the M(dmit)$_2$ and M(dddt)$_2$ complexes (dmit=1,3-dithiole-2-thione-4,5-dithiolate; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, Figure 6). These groups have been reviewed by Cassoux *et al.*[51] and Yagubskii,[52] respectively. M(dmit)$_2$ complexes in the partially reduced state form conducting complexes with donor molecules such as TTF derivatives, while M(dddt)$_2$ complexes form conducting cation salts when partially oxidised, analogous with BEDT–TTF (**4**). The modes of packing in these conducting salts mirror those seen in the TEF analogues.[53] Variation of the metal and the counterion gives rise to diversity in these two groups of materials. Superconducting M(dmit)$_2$ complexes have been prepared, such as TTF[Ni(dmit)$_2$]$_2$,[54,55] [Me$_4$N][Ni(dmit)$_2$]$_2$[56] and TTF[Pd(dmit)$_2$]$_2$.[57] Many semiconducting complexes of both types are known.[51,52]

Conducting complexes using new classes of chalcogen-rich dithiolate ligands are being continuously developed with interesting results. Recent examples (see Figure 6) include the 1:1 semiconducting salt of BEDT–TTF with monomeric [Ni(tdas)$_2$]$^-$ which also exhibits weak antiferromagnetic coupling.[58] Nickel

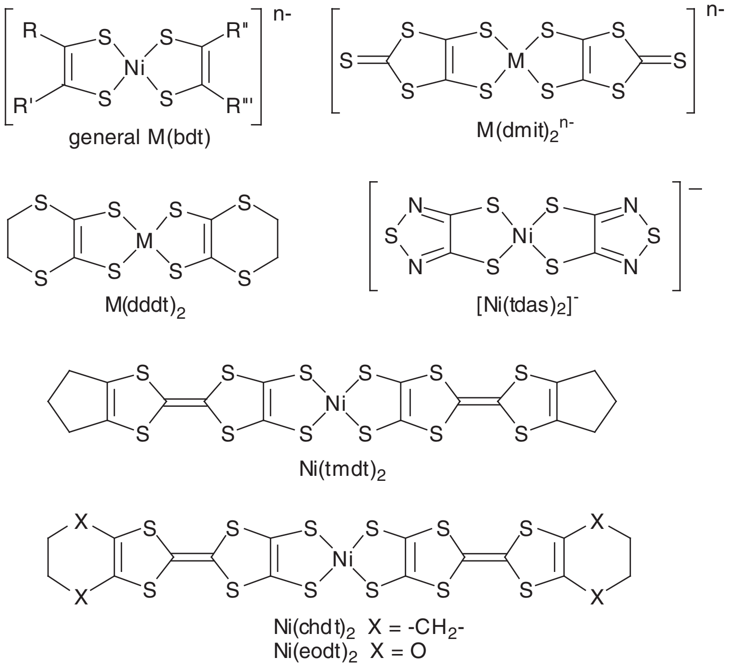
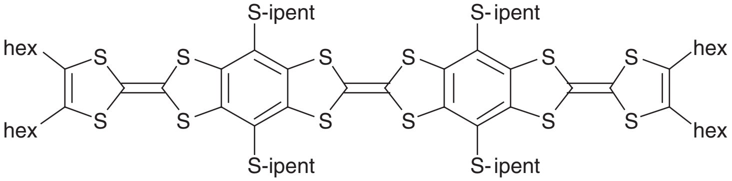


Figure 6 *Metal complexes based on 1,2-dithiolene ligands*

complexes of ligands incorporating TTF moieties (Ni(tmdt)$_2$,[59] Ni(chdt)$_2$ and Ni(eodt)$_2$[60]) have not only afforded semiconducting salts in their anionic states but have also given rise to single component molecular metals, that is complexes which exhibit metallic conductivity in the neutral state. In these cases the band gap of the neutral molecule is small enough to allow the HOMO and LUMO bands to overlap and form a partially filled conduction band.[61] In the example of Ni(tmdt)$_2$, X-ray studies account for many S···S contacts between molecules in 3-dimensions, leading to room-temperature conductivity of almost one order of magnitude higher than typical BEDT–TTF or BETS superconducting salts. Furthermore, high conductivity and metallic behaviour reported for compressed powder samples of the neutral species is consistent with a 3-dimensional chalcogen–chalcogen interaction network.

12.2.2.2 Macromolecular

Covalent combination of molecular systems outlined in 12.2.2.1 with other electroactive components affords macromolecular species that benefit from additional dimensionality and improved band filling. Large numbers of TEF-dimers, trimers and higher assemblies have been prepared.[42,62–64] Of particular interest are systems showing intramolecular electronic interactions between the TEF units, such as **8**[65] and **9**.[66,67] These interactions depend on the geometry and electronic nature of the linking spacer between the TEF units. Such compounds can be used as stoichiometrically controllable building blocks with multi-stage redox behaviour in supramolecular chemistry.



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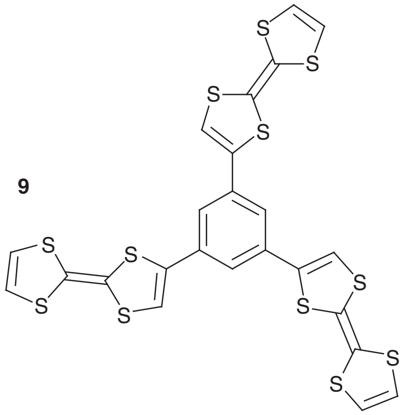
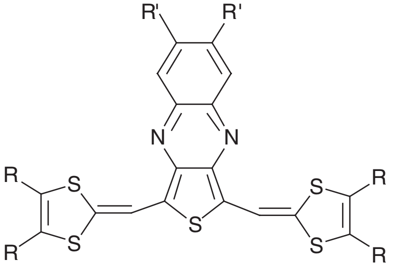


Macromolecules containing TEF-related donors linked to electron acceptors derived from molecules such as TCNQ and fullerenes have received much attention in the search for molecular rectifiers and non-linear optical and photovoltaic molecular materials. Similar to the TTF assemblies above, the spacer group between donor and acceptor units can be conjugated (D-π-A) or non-conjugated (D-σ-A), and variable in length, allowing for different intramolecular electron transfer pathways. Rectification was first observed in a D-π-A assembly by Ashwell in 1990.[68,69] Conjugated assemblies of this type continue to receive much attention.[70,71] New structural variations and use of novel acceptor moieties have been reported recently, such as the D-π-A-π-D triads, **10**.[72] **11**[73] contains a rigid σ-type spacer and an A-σ-D-σ-A structure. Bryce and co-workers[74] have recently proposed **12** as the first TTF-σ-A molecular rectifier, citing an extremely small HOMO-LUMO energy gap.



R = COOMe / SCH_3
R' = H / CH_3
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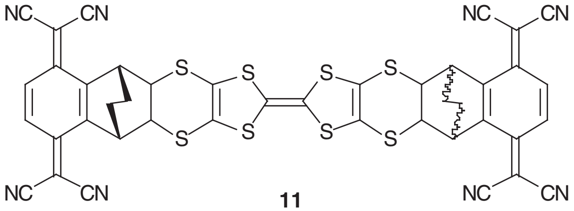

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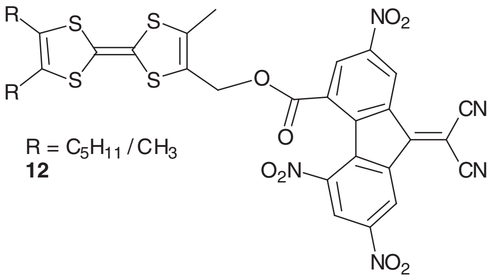

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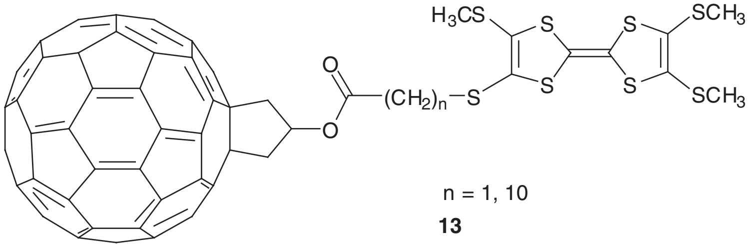
Fullerenes have shown particular promise as acceptors in molecular electronics, and numerous interesting TTF/C_{60} ensembles have been reported.[42] For example, Ordúna and co-workers[75,76] prepared the TTF/C_{60} dyad **13** and observed photoinduced electron-transfer from the TTF to the fullerene. Martín *et al.*[77] observed two separate one-electron transfer events in their conjugated dyads **14** (where $n = 2$). The TTF-porphyrin-fullerene triad **15**, prepared by Carbonera *et al.*[78] showed long-lived photoinduced charge separation.



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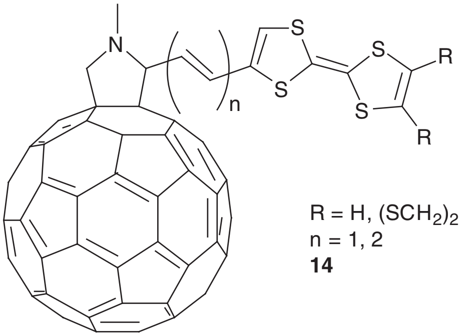

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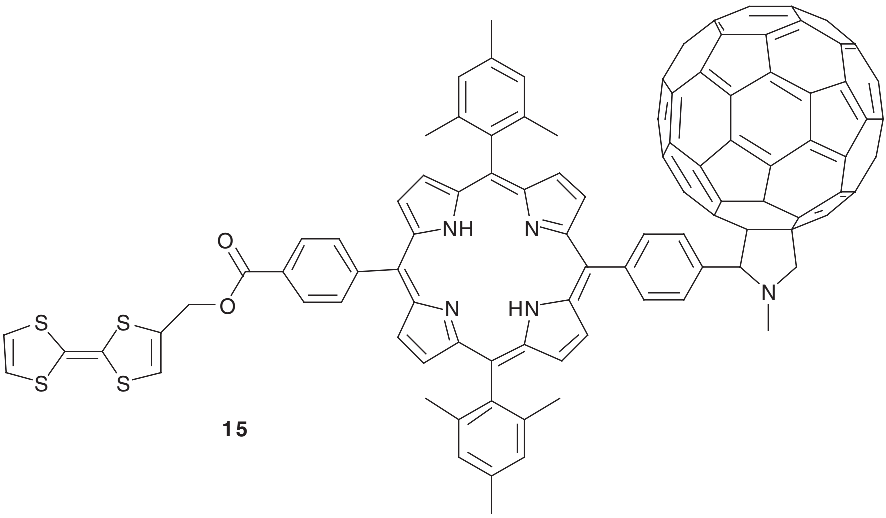

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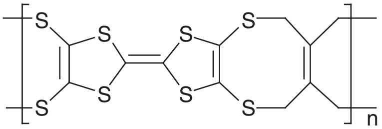
12.2.2.3 Polymeric

There is currently great commercial interest in plastic alternatives to conventional silicon-based components in electronic devices. Polymeric architectures offer flexible, low-cost, processable materials for this lucrative global market, and can be designed with more emphasis on device performance. The principal goals of improved band filling, dimensionality and new conductance mechanisms remain the same, and provide a subtly different challenge to the materials chemist.

Various TEF-containing polymers have been prepared. The incorporation of TEF units into polymer backbones (see, for example **16**, **17**, **18**[79]) was followed by polymers with pendant TEF units such as **19**[80] and **20**[81] and TEF-containing dendrimers such as **21**.[82] Segura and Martín[42] reviewed this group of compounds in detail, while Iyoda[63] reviewed the TTF dimers, trimers and oligomers.



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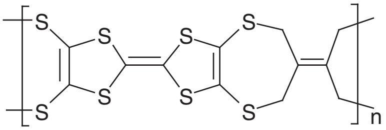

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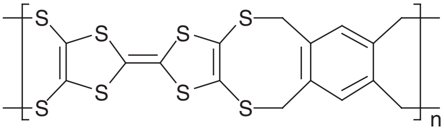

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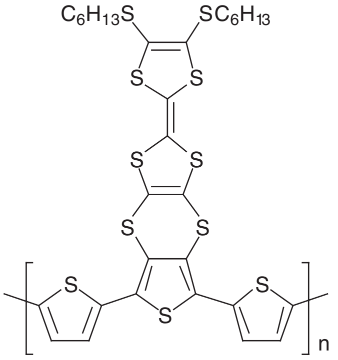

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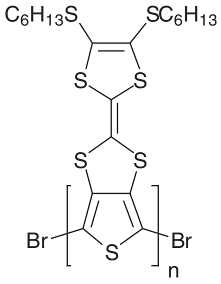

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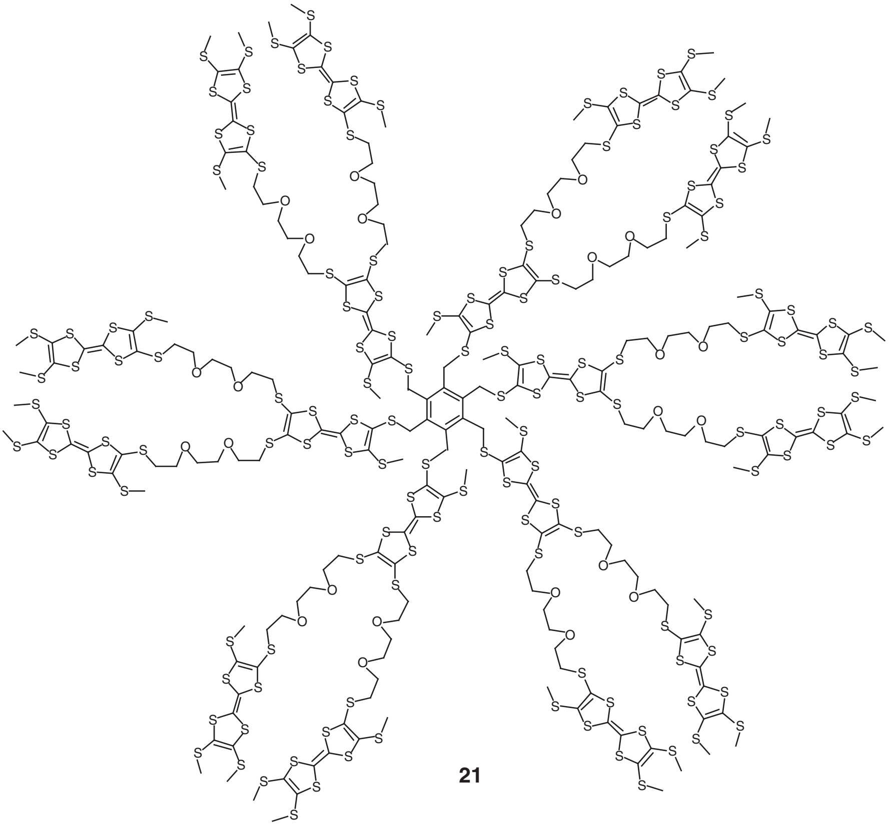

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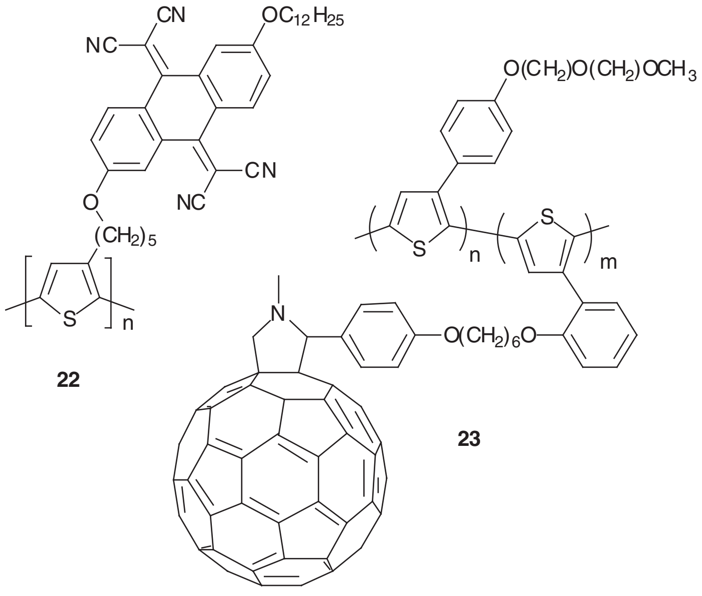
Thiophene and its derivatives, however, have become the most-studied chalcogen-containing monomers. Doped (oxidised) PT is highly conducting, and 3-alkyl-substituted PTs are soluble, easily characterised polymers,[83–85] see Figure 7. Self-assembly is an important consideration in these substituted PTs, allowing control of the degree of planarity, π-orbital overlap, and hence optical band gap.[86] This can be achieved by ensuring regioregularity within the polymer structure, imparting liquid crystalline properties or by utilising heteroatom groups to promote intrachain interactions. For instance, head-to-head polymerisation of 3-alkyl thiophene results in steric clash between alkyl groups forcing a twist in the chain between thiophene units. Regioregular (head-to-tail) polymers are not only planar but can also show long-range ordering where interdigitisation of long alkyl chains is possible. Poly(3,4-ethylenedithiothiophene) (PEDTT) and poly(3,4-ethylenedioxythiophene) (PEDOT) are examples of important PT derivatives (see Figure 7). Inclusion of the additional chalcogen atoms in the plane of the aromatic heterocycle allows for more interchain π-overlap (for PEDTT), similar to BEDT–TTF.[4] In the case of PEDOT, strong intrachain S---O interactions ensure a planar structure.[87] Poly- and oligothiophenes have been well studied as electron donors in conjunction with acceptors such as fullerene; the resulting *p*-type composite materials, such as **22**[88] and **23**,[89] show promise for plastic solar cells and non-linear optic devices.[90]



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12.2.3 The Role of the Chalcogen

In this section, we look more closely at what effect the chalcogen atom has on the properties of the molecular conductors we describe. We do not attempt to review exhaustively all the chalcogen-containing components in electroactive systems, to do so would be a colossal task. Instead, carefully chosen examples and studies illustrate how chalcogen chemistry is used in the design and manipulation of electroactive materials, and ultimately how it effects suitability for molecular device applications.

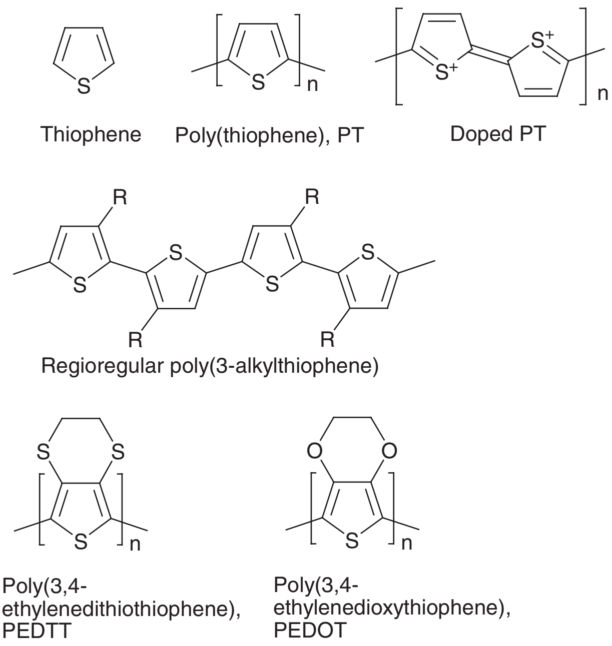


Figure 7 *Thiophene, its common derivatives and polymers*

12.2.3.1 Heterocyclic Structure

Chalcogen-containing heterocycles are ubiquitous in the electroactive structures described in the previous section. A common feature of these structures is sp^2-hybridised chalcogen atoms, which impart electron density (from their p-orbital lone pair) to delocalised or conjugated π-systems. In some cases this contributes to Hückel aromaticity ($4n + 2$ π-electrons), in thiophene for example. TEF and its derivatives also show interesting aromatic behaviour. Each 1,3-dichalcole ring in TEF can lose one electron (see Figure 8). The resulting 1,3-dichalcolium cation is 6π aromatic. Where the neutral molecule often has a puckered geometry (see for example Figure 9[91]) aromatisation causes a change from puckered to planar in the oxidised radical cation state. Aromatisation provides the thermodynamic driving force for TEF to act as an electron donor, while providing a conformational change which is often advantageous to crystal packing.

Short intramolecular contacts between chalcogens and other chalcogens or other heteroatoms have been shown to influence molecular geometry, particularly planarity, in many structures of electroactive materials. Hence the position of the chalcogen atom in the material can profoundly affect its properties. For example Crouch *et al.*[92] report the X-ray crystal structure of compound **24** (Figure 10), a candidate for an organic field-effect transistor, showing the effect of intramolecular S···F close contacts (in tandem with H···F contacts) on the planarity of the molecule in the solid state. Note also the

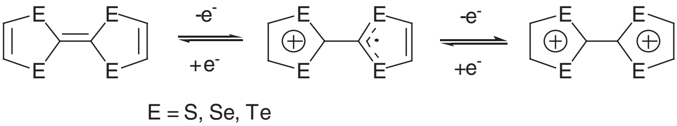


Figure 8 *Redox states of TEF compounds*

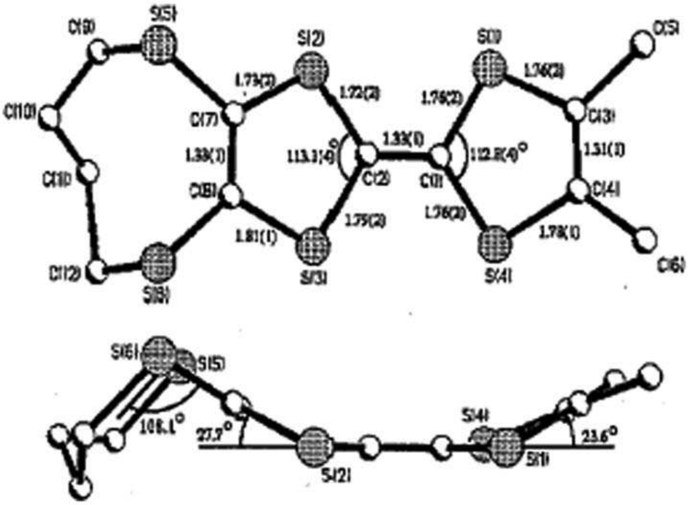
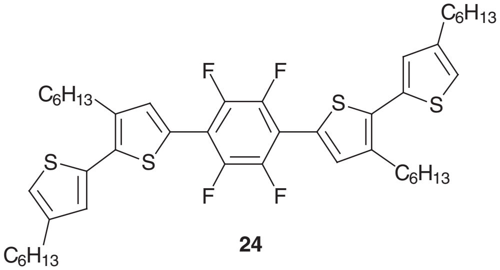


Figure 9 *Molecular structure of tetramethylenedithiodimethyltetrathiafulvalene (TMDTDM-TTF) showing puckered conformation in the neutral state*
(Reproduced from Konarev *et al.*[91] with permission from Elsevier)

intermolecular S···S contacts forming chains of molecules. Increased planarity and rigidity generally means better conjugation and π-orbital overlap between molecules, leading to a smaller HOMO-LUMO gap and lower oxidation potential. Planar radical cations benefit from better chemical stability as a result of delocalisation. Improved stacking in the crystal lattice of planar molecules also facilitates intermolecular charge transfer. The synthetic chemist who can manipulate these interactions therefore has control over some fundamental properties of the material.



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In order for a material to act as a useful bulk charge-transport medium, one molecule (be it a polymer or a small molecule in a crystal) must be able to transfer

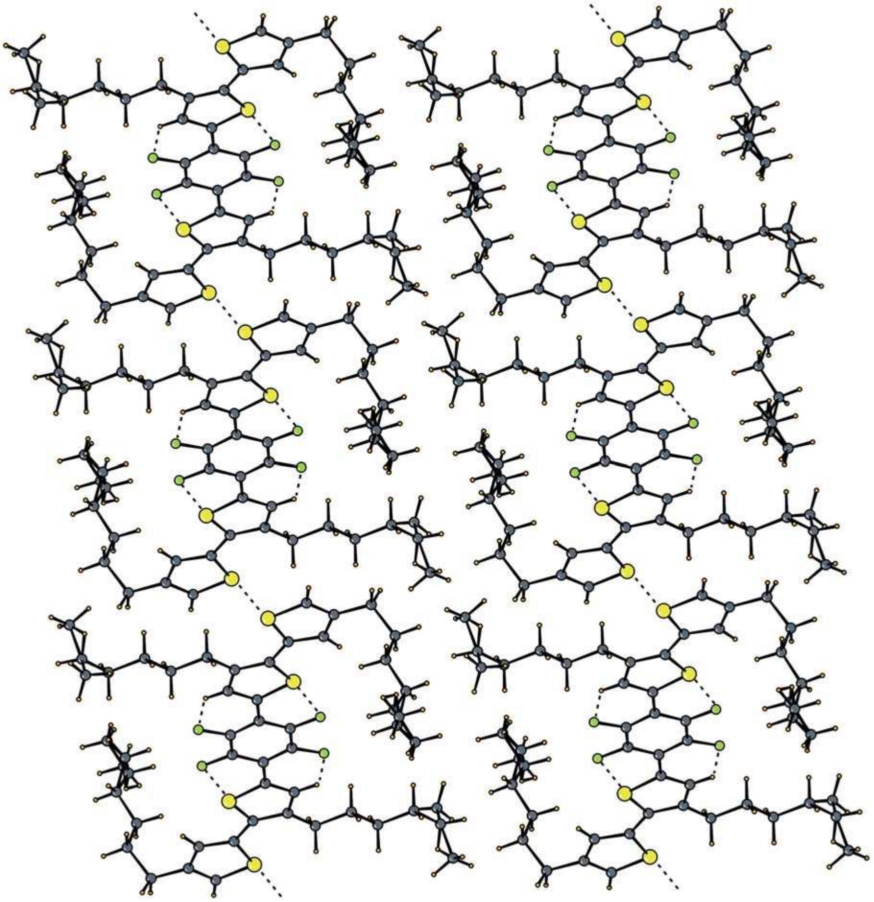
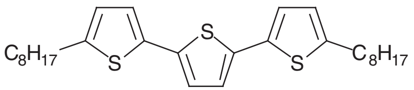


Figure 10 *Packing diagram of compound* **24***, viewed along the a axis, showing intra- and inter-molecular contacts*
(Reproduced from Crouch *et al.*[92])

charge to its neighbour, thus establishing a conductance mechanism. Usually this is achieved by intermolecular orbital overlap. The large π-orbitals resulting from the presence of chalcogen atoms provide an excellent basis for co-facial stacking and serve to hold conducting molecules into ordered, self-assembled arrays. The 1D columnar stacks of TTF units in the TTF/TCNQ crystal structure (essentially a 1:1 mixture of radical cation and neutral molecules, Figure 1) are a useful example. The dimensionality of the structure is reflected in its 1D charge-transport properties, since the only intermolecular close contacts occur between sulfur atoms in co-facial units.[44]

Conduction in these 1D metals is vulnerable to impurities, defects and thermal vibrations within each stack. Inter-stack interactions allow for increased dimensionality, and in some cases, superconductivity, by suppressing



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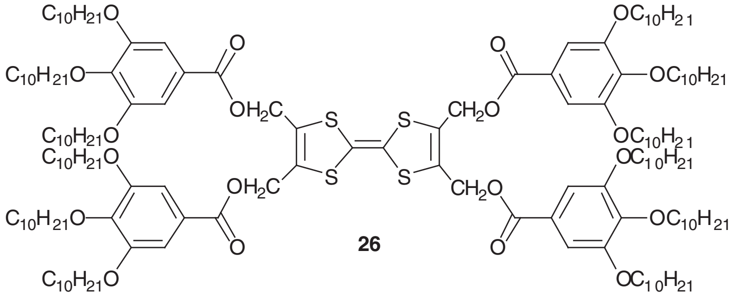

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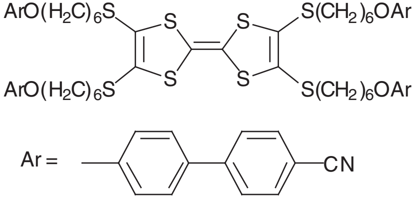

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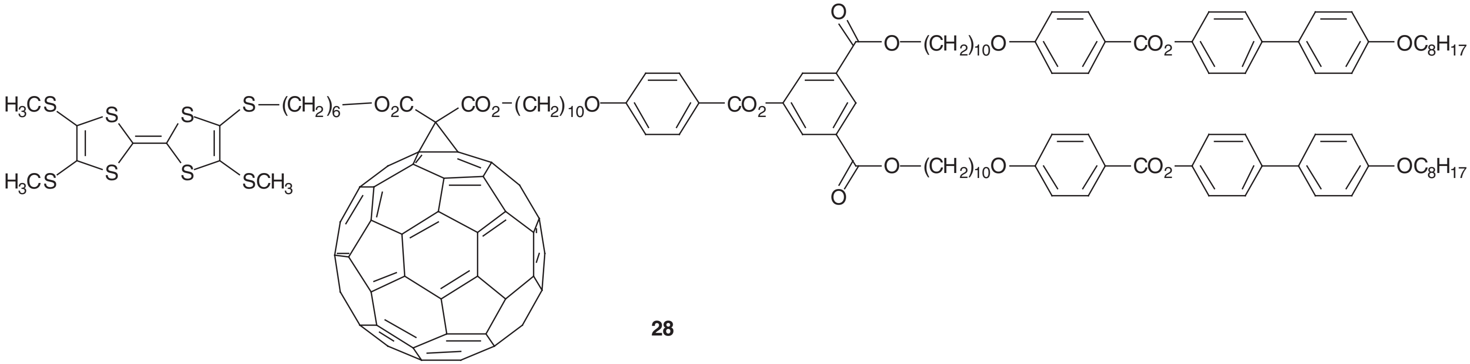

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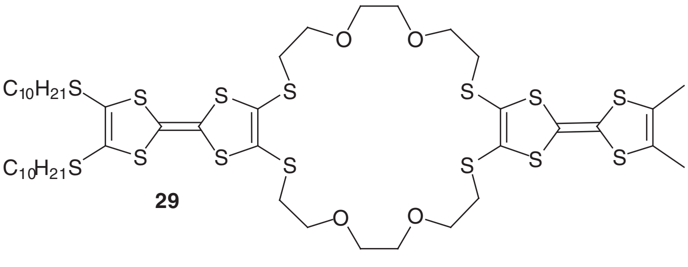
the Peierls distortion, an inherent, disruptive flaw characteristic of 1-dimensional conductors. Radical cation salts of BEDT–TTF, for example, employ chalcogen–chalcogen contacts to achieve quasi-2-dimensional conductivity. The flexible ethylene bridge also allows the radical cations to adopt a number of conformations achievable through use of different counterions. Many organic metals have been prepared from salts of BEDT–TTF; this structural family was comprehensively reviewed in 2004 by Geiser and Schlueter,[53] and by Shibaeva and Yagubskii.[8]

Inter- and intra-stack chalcogen–chalcogen interactions are important in formation of conducting supramolecular structures such as Langmuir–Blodgett films, self-assembled monolayers (SAMs) and liquid crystals. Development of this technology continues to attract attention in order to bridge the gap between promising materials properties and ease of device fabrication.[93] Terthiophene **25**[94] shows hole and electron mobilities above 1×10^{-2} cm^{2}V^{-1}s^{-1} in the smectic G phase at elevated temperatures. Garín and co-workers[95] reported the first discotic liquid crystal built around a TTF-core, namely compound **26**. The same group prepared a charge transfer salt of compound **27**[96] which showed a LC phase, a promising result in the search for new multi-property materials. The TTF units align in parallel stacks, held by interdigitisation of the aryl groups with adjacent stacks. In **28**, the fullerene unit controls the supramolecular organisation.[97]

Other common techniques have been applied to the assembly of layers or films of TTF-derived molecular conductors. Compound **29** is an example of an amphiphilic TTF derivative. It forms conducting Langmuir–Blodgett charge transfer films with the acceptor TCNQF$_4$ (**30**).[98] Self-assembly of compound **31** on gold by electrochemical methods yielded an electroactive monolayer which was remarkably stable to electrochemical cycling.[99]



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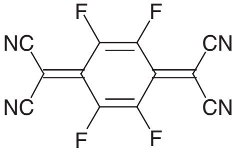

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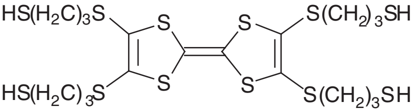

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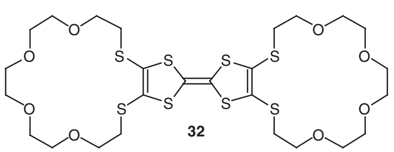
12.2.3.2 Chemical Sensors: A Case Study of Chalcogen-Metal Bonding in Electroactive Materials

The strong covalent and non-covalent interactions between chalcogens and certain metals are exploited in so-called 'host-guest' and supramolecular chemistry. Crown ethers containing either O or S atoms are known to bind alkali metal ions, for instance. When 'host' structures are linked to a redox active or electroactive moiety a change in the physical properties of the molecule is often detected when a 'guest' is bound. This is the basis of a molecular sensor. In structures such as **32**,[100] complexation of metal ions (in this case Na^+) causes a small positive change (80 mV) in the first ionisation potential of the TTF moiety. This is assigned to a through-space inductive effect caused by the presence of the cation, and can be observed by cyclic voltammetry (CV). The second ionisation potential is usually unchanged, and can be used as an internal reference. In fact, the metal ion is thought to be repelled from the crown cavity when the TTF cation is formed. Binding is therefore electrochemically switchable. Guest binding can also be detected by NMR, UV-vis spectroscopy or mass spectrometry.

Many other candidate structures for cation sensors incorporating a crown ether as the host 'antenna' and TTF as the 'transducer' have been prepared. The area has been covered by a number of recent reviews.[30,42,44,101,102] Most of the compounds studied incorporate the S- and O-containing crown ether annelated to the TTF. Variations of cavity size have been used to tune selectivity for specific metal ions,[100] while modifications to the basic TTF structure have been investigated also. Sensitivity of extended TTF derivatives such as **33**,[103] **34**[101] and **35**[101] depends on the ability of the extended TTF to delocalise cationic charge, and on the proximity of the binding position to the HOMO of the receptor.[103] Few examples exist of polythioether TTF derivatives, which are suited to bind to soft low-valent metal ions. Poor solubility often hampers cation binding studies with these systems.[104] Notable among this group is **36**[104] where the polythioether chain is tethered to the 2,7-positions of the TTF. CV showed a positive shift in the first redox potential on addition of silver triflate. Good selectivity was seen for Ag^+ ions as no response was observed for a variety of group 1, 2 and transition metal ions. Binding of Ba^{2+} ions to the similar oxo-crown structure **37**[105] was found to be highly efficient and reversible, and also redox-controllable. In these last two cases the HOMO and the binding site are very close.



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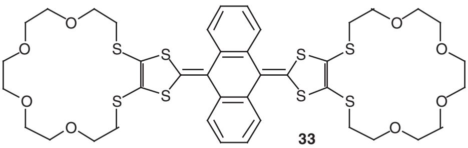

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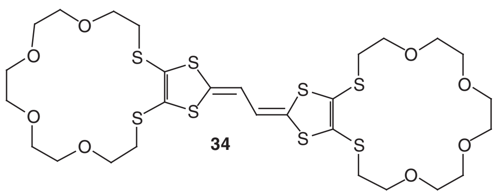

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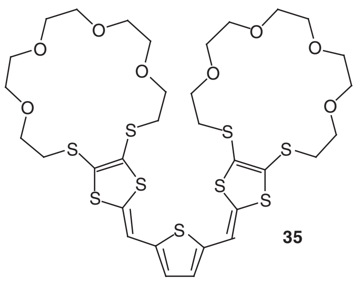

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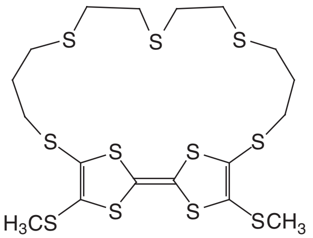

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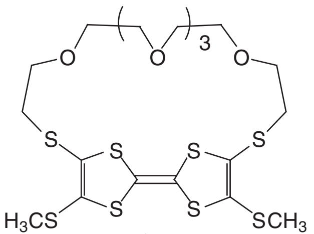

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TTF is not the only chalcogen-containing motif to be incorporated as the 'signaller' in cation sensors; PT has also been widely studied in this context. Polymer films containing groups capable of molecular recognition are desirable in terms of electrode modification and device fabrication. Roncali *et al.*[106,107] reported the first example of molecular recognition by a conjugated polymer in 1989, in a simple PT system **38** containing flexible polyether side chains. Coordination of Li^+ was detected by CV. Later studies on the related structure **39**[108,109] confirmed that cation binding caused a twist in the PT backbone, reducing the extent of conjugation. A shift to higher energy of the absorption maximum in the UV-vis absorption spectrum and an increase in the first oxidation potential was therefore diagnostic of binding. A PT system incorporating an annelated crown ether **40** has been prepared by Bäuerle *et al.*[110] Na^+ ions bound in the ether cavity caused the expected increase in oxidation potential, but slow diffusion of ions means this type of system is unlikely to yield a useful device. Bäuerle and co-workers also employed flexible spacers to separate the PT backbone and the crown ether (*e.g.* **41**[111]) and proposed a 'shielding effect' on the conjugated chain whereby bound cations form a barrier to conduction. Figure 11 shows the binding of metal ions to an electrochemically prepared fused PT derivative whereby sulfur and nitrogen atoms from different monomer units contribute to binding.[112] Ag^+ ions in aqueous $LiClO_4$ solution bound in this manner caused a very large positive shift (*ca.* 400 mV) in the oxidation potential of films of this polymer.

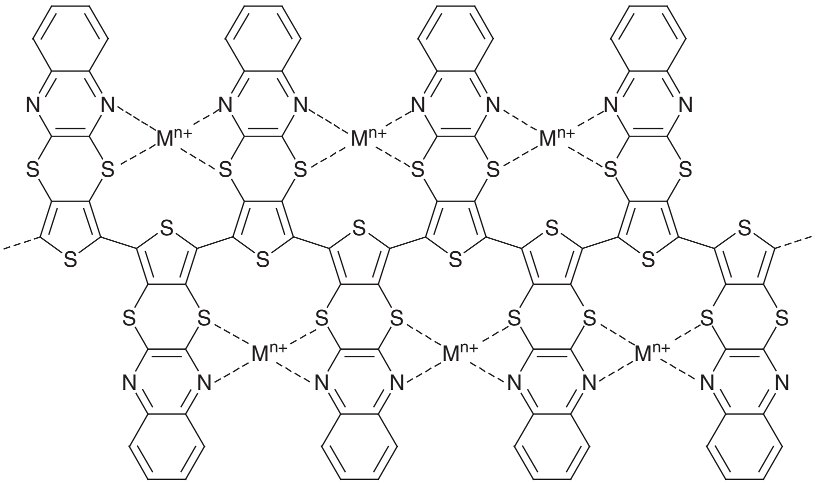
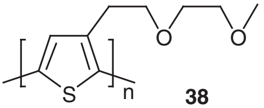


Figure 11 *Binding of metal ions to a fused PT derivative* (Reproduced from Goldenberg *et al.*[112])



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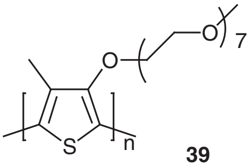

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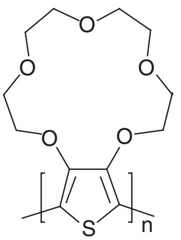

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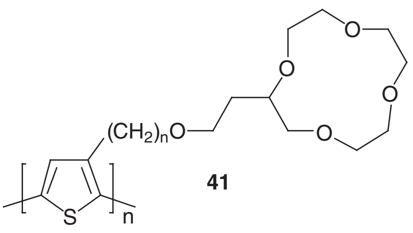

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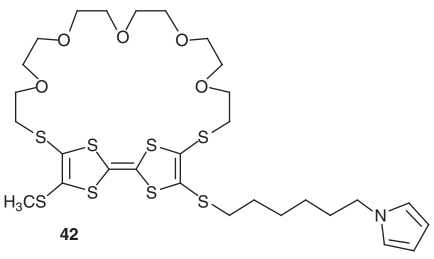
Building on the success of **37** in recognition of barium ions, this unit was incorporated into monomer units derived from pyrrole and EDOT (**42**, **43** and **44**).[113] Electrodes modified by the corresponding electrodeposited polymers showed an electrochemical response in the presence of Ba^{2+} which was similar to **37**, albeit of a lesser magnitude.



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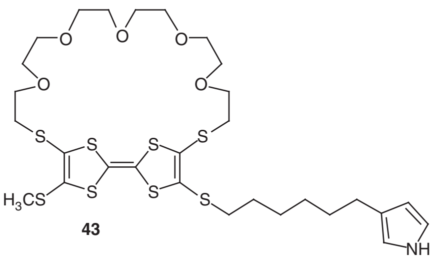

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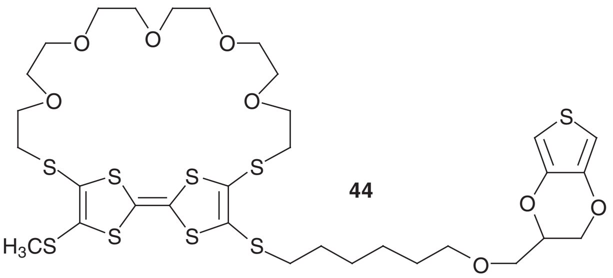

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The well-known affinity of sulfur for gold and platinum has been put to use for immobilisation of sensor monolayers on electrode surfaces, as another promising route to designing small, convenient devices. Goldenberg *et al.*[102] reviewed the progress in surface modification of electrodes in 1999. They highlight the potential benefits of a sensor monolayer, with a chemically tailored surface, achievable by Langmuir–Blodgett or self-assembly techniques, drawing particular attention to the ease of preparation and stability of SAMs.

Two examples from literature illustrate this approach nicely. Moore *et al.*[114] assembled thiol-terminated long-chain S_2O_4-crown TTF onto Au and Pt surfaces by thiolato-metal bonds (see Figure 12). In the presence of various cations, most successfully Ag^+, small differences were observed in the first oxidation potential (typically 60–80 mV). Similar responses were observed in solution state experiments with the same materials. The SAMs were stable when electrochemically cycled over the first oxidation wave but unstable when scanned beyond this point. Liu *et al.*[115,116] prepared SAMs of **45** and **46** on Au substrate. Anchored to the solid surface by four Au–S bonds per molecule, these SAMs were stable for hundreds of cycles over the full oxidation range. In response to the presence of Na^+ *both* the TTF oxidation waves were shifted anodically by 55–60 mV. This observation was ascribed to either surface aggregation or cooperativity of neighbouring crown rings.

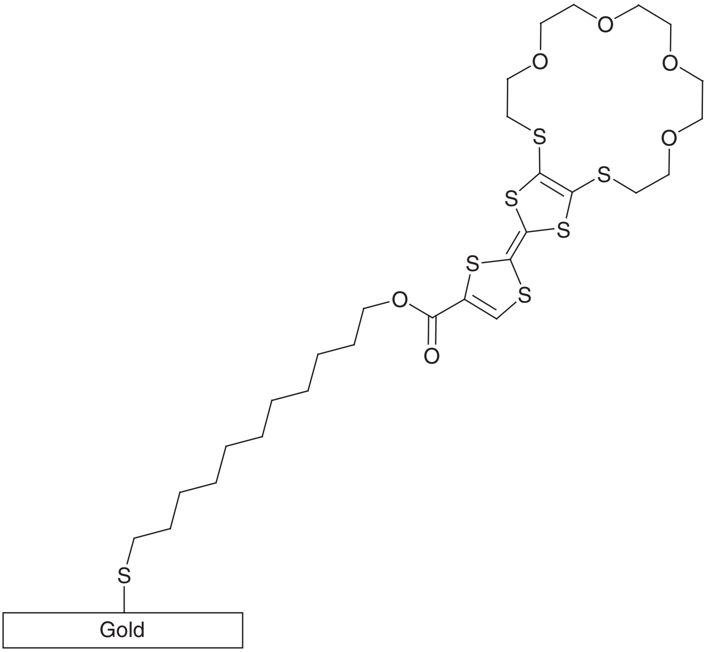
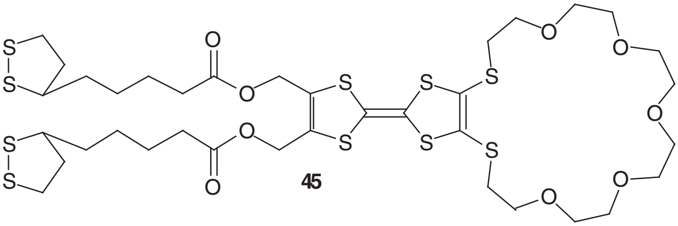


Figure 12 *Self assembled monolayer of TTF-based cation sensor on gold substrate* (Redrawn from Moore *et al.*[114])



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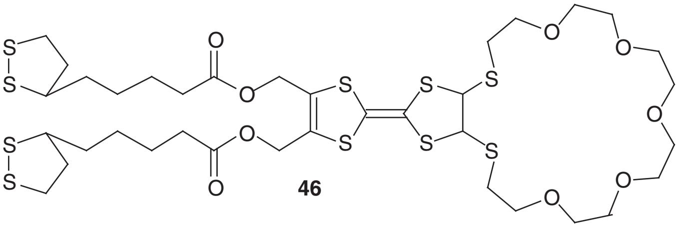

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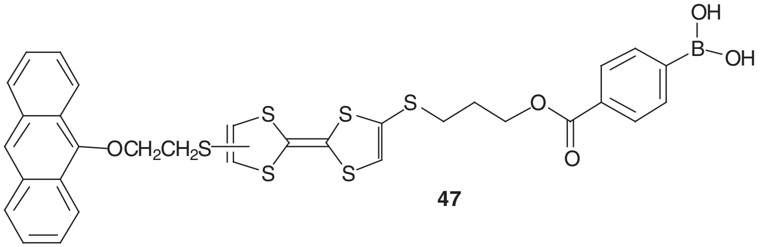
It is worth noting that TTF-based sensors for species other than metals, particularly organic species, have been well studied. The principle is, of course, the same; a 'host' group capable of recognising a 'guest' molecule is tethered to the 'signaller' TTF, which displays an altered physical response when a guest is bound and when the receptor is free. Systems of this type are of particular interest as biosensors, for example, in the detection of saccharides for disease diagnosis and for understanding of cellular processes. For instance, the anthracene unit in **47** shows a significant fluorescence enhancement in the presence of fructose.[117] When fructose is bound to the boronic acid group it becomes a better electron acceptor, and is better able to compete with the anthracene for photo-induced electron transfer from the TTF. The anthracene fluorescence is therefore quenced to a lesser extent than in the free state.



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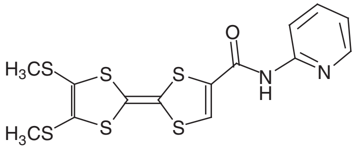

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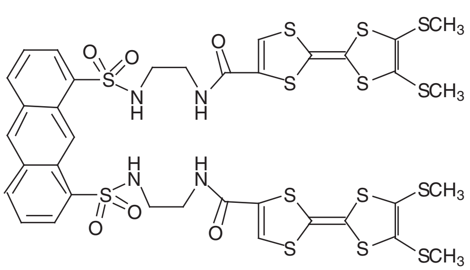

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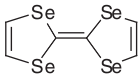
Recently, Xu and co-workers[118,119] have studied detection of $H_2PO_4^-$ using TTF derivatives **48** and **49** capable of multiple hydrogen bonding. Binding of $H_2PO_4^-$ was detected principally by significant changes in redox behaviour. Receptors tailored in this way can show improved selectivity for a specific guest over other competing species.

12.2.3.3 Use of the Chalcogens Heavier than S

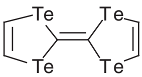
We have seen the versatility of chalcogen-containing materials in the previous sections. In most cases, materials properties have been investigated and improved through subtle changes to molecular structure. So far, however, we have not discussed the result of changing the chalcogen atom to give an otherwise isostructural material. A change in substituent group, for example, may change the solid-state structure of the material. Substituting a selenium or tellurium atom for a sulfur will, in many cases, cause no change in conformation or packing, so the electronic origins of properties may be probed more insightfully. Clever synthetic chalcogen chemistry therefore holds the key to interesting variation of physical properties.

Exactly this approach led to the discovery of the first organic superconductors, the Bechgaard CT salts of tetramethyltetraselenafulvalene (TMTSF, **3**) with various counteranions: $(TMTSF)_2PF_6$ (under pressure) in 1980[120] and

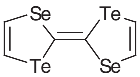
$(TMTSF)_2ClO_4$ (at ambient pressure) in 1981.[3] Tetraselenafulvalene (TSF, **50**) was first reported by Engler and Patel.[121,122] Otsubo[64] notes that of the fourteen TTF-type superconductors, nearly half are Se-containing. There are eleven tetramethyltetraselenafulvalene (TMTSF) salts with polycyano acceptor anions alone, and all show semiconducting behaviour.[53] Tetratellurafulvalene (TTeF, **51**) was reported by McCullough in 1987.[123] The CT salts of TSF and TTeF with TCNQ followed in 1990.[124] The first tellurium-hybrid TEFs (diselenaditellurafulvalene, DSDTeF, **52** and dimethyldiselenaditellurafulvalene, DMDSDTeF, **53**) were prepared in 1997.[125]



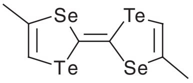
TSF, **50**



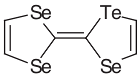
TTeF, **51**



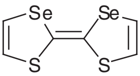
DSDTeF, **52**



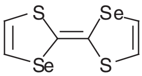
DMDSDTeF, **53**



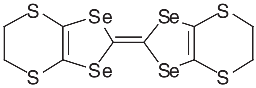
TSTeF, **54**



cis-DSDTF, **55**



trans-DSDTF, **56**



BETS, **57**

Since few examples of isostructural series of chalcogen-containing materials have been reported, this topic is afforded a more detailed treatment herein. It still does not represent, however, an exhaustive list of all reported structures incorporating the heavier chalcogens. The structures discussed here were chosen not necessarily on the basis of outstanding electrical properties but on their value as illustrative comparisons. The recent reviews by Bryce,[44] Otsubo[64] and Geiser and Schlueter[53] provide further context in this area.

12.2.3.3.1 Effect of Heavier Chalcogens on Donor Ability

Starting with the most simple material, TTF, it is possible to reveal the effect on the first oxidation potential, $E_{1/2}(1)$ (and hence on electron-donor ability), by insertion of a heavier chalcogen atom into the framework of the molecule. Table 1 shows the first oxidation potential of a variety of neutral tetrachalcogenafulvalene donors. The first observation to make is that changing the chalcogen from sulfur in TTF to selenium in TSF results in a higher oxidation potential for the neutral molecule, making it a weaker donor, thermodynamically. The Se=C π-bond is weaker than the S=C π-bond, a result of better size matching of C and S orbitals. Oxidation of the donor generates a radical cation which is stabilised by resonance forms incorporating a C=E double bond (see Figure 8). It follows that the more thermodynamically stable cation is more easily accessible.[122]

This trend in bond-strength continues with TTeF, but the more polarisable Te p- and d-orbitals allow for greater stabilisation of the cationic charge, giving the order TTF < TTeF < TSF in $E_{1/2}(1)$. The difference between the first and second ionisation potentials, $\Delta E_{1/2}$, follows the trend TTeF < TSF < TTF. Again, the superior polarisability of Te over Se and S reduces intramolecular coulombic repulsion between the dicationic charges.[123] This behaviour has also been reported in extended TTF derivatives[126] and anthracenediylidenes.[46]

12.2.3.3.2 Effect of Heavier Chalcogen on Properties of CT Salts

We saw in Section 12.2.3.1 that the presence of additional chalcogen atoms in BEDT–TTF/TCNQ promotes interstack interactions, suppressing the Peierls distortion and imparting upon the salt increased dimensionality compared to TTF/TCNQ. The result of including a different chalcogen into the TTF/TCNQ structure is shown in Table 2. Despite losing donor efficiency compared to TTF (Table 1) the TCNQ complexes of *cis*/*trans*-diselenadithiafulvalene (DSDTF, 55/56) and TSF show an improvement in conductivity when two or four selenium atoms are incorporated. The reduced metal-insulator transition suggests that this effect is also caused by a suppression of the Peierls distortion. Increased Se–Se interstack contacts add dimensionality to the structure and limit the co-facial dimerisation typical of Peierls distortion. Wider conduction bands are afforded from the improved overlap of diffuse orbitals.

Morikami[127] poses the question, 'how many Te atoms in the TSF skeleton are necessary to suppress the M-I transition altogether?' TSF[121] and triselenatellurafulvalene (TSTeF, **54**[125]) form TTF-type 1-D stacks with TCNQ in which the Peierls instability is inherent. The crystal structure of DSDTeF/TCNQ on the other hand shows a completely different relative position of the donor and acceptor columns, brought about by side-by-side Se–Te and Se–Se contacts.[125] No M-I transition is observed down to very low temperatures. This structure is analogous to TTeF, where the Peierls distortion is suppressed by Te–Te interactions. High conductivities accompany these improvements. The findings led Morikami *et al.*[127] to classify TEF/TCNQ complexes into two structural categories: 1-D organic metals of the TTF/TCNQ type, and quasi 1-D organic metals containing multiple side-by-side hetero-contacts between columns of donors.

Saito *et al.*[130] studied the salts of TMTSF and the sulfur analogue tetramethyltetrathiafulvalene, TMTTF, with a polycyano dianion. Although the conductivity of both compounds was low ($\sigma_{rt} = 10^{-5}$ Scm^{-1} for TMTSF *vs.* 10^{-7} Scm^{-1} for TMTTF) the conductivity of the Se-donor salt was improved by two orders of magnitude. Optical absorption spectroscopy was also used to assess the materials. The electronic transition between radical cations within the segregated donor columns occurred at considerably lower energy (8800 cm^{-1}) in the TMTSF salt than in the TMTTF (11500 cm^{-1}). A concurrent improvement

Table 1 *Electrochemical data for tetrathiafulvalene (TTF), tetraselenafulvalene (TSF) and tetratellurafulvalene (TTeF)*[123]

Donor	$E_{1/2}(1)$, *V*	$E_{1/2}(2)$, *V*	$\Delta E_{1/2}$, *V*
TTF, **1**	+0.47	+0.81	+0.34
TSF, **50**	+0.62	+0.90	+0.28
TTeF, **51**	+0.59	+0.84	+0.25

Table 2 *Electrochemical and structural properties of the TCNQ CT salts of some TEF donors*

Donor	*Room temperature conductivity, σ_{rt}, Scm^{-1}*	*Metal-insulator transition, K*	*Structural classification (after Morikami et al.*[127]*)*
TTF, **1**[1]	500	59	1-D organic metal
cis/trans-DSDTF, **55**/**56**[128]	550	64	1-D organic metal
TSF, **50**[121]	800	40	1-D organic metal
TSTeF, **54**[125]	2000	85	1-D organic metal
DSDTeF, **52**[125]	1400	Metallic at 4.2 K, no transition	quasi 1-D, strong interstack interactions
TTeF, **51**[124,129]	2200	Metallic at 2 K, no transition	quasi 1-D, strong interstack interactions

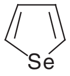
in inter- and intra-stack interactions seems to benefit the heavy chalcogen-containing material in this example.

The BEDT–TTF skeleton has been modified extensively with alternative chalcogens to sulfur. Much attention has been devoted to salts of bis(ethylenedithio)tetraselenafulvalene (BEDT–TSF, or BETS, **57**), as inclusion of larger Se atomic orbitals lead to more isotropic electronic structures, and more stable molecular metals. α-(BETS)$_2$TlHg(SeCN)$_4$ is isostructural with its BEDT–TTF analogue, but the crystal structure shows almost twice as many Se–Se, Se–S and S–S contacts. A typical unit cell volume increase of 2.8% is seen in the Se-containing structure.[131] Despite the improved inter-stack contacts, the structures of these two analogues are too similar to bring about a large change in electrical properties; both α- (BETS)$_2$TlHg(SeCN)$_4$ and α-(ET)$_2$TlHg(SeCN)$_4$ are stable metals down to very low temperatures (1.3 K).

κ-(BETS)$_2$C(CN)$_3$,[131] on the other hand, is not isostructural with κ-(ET)$_2$C(CN)$_3$,[132] and crystallises in a different space group. It benefits from 22 close chalcogen–chalcogen contacts between each BETS molecule and its six neighbours, of which four are face-to-face dimeric interactions within the stack. The all-S analogue contains only eight such contacts (S$\cdots$S) to its nearest two molecules, but interestingly has no inter-stack S$\cdots$S contacts of less than the sum of the van der Waals radii for two sulfurs. In both cases the ethylene bridge remains disordered. These structural alterations are enough to bring about a significant difference in properties between the two complexes. The BETS salt is also a stable metal down to 1.3 K but the ET complex undergoes a M-I transition at about 180 K, indicating that the S$\cdots$S contacts do not give a sufficiently rigid framework to suppress Peierls transition.

12.2.3.3.3 Higher Chalcogenophenes: Selenophene and Tellurophene and their Polymers

Thiophene and its related polymers have received the same treatment as the TEF derivatives. Selenophene, **58**,[133] and tellurophene, **59**,[134,135] are both known, but their polymers are far less well studied and understood than thiophene. Replacement of sulfur by the more polarizable, heavier chalcogens offers an interesting route to reduced monomer oxidation potential, and consequently for fine tuning of the electrochemical and optical properties of the corresponding polymer.[136] This approach should also lead to increased bandwidths, improved dimensionality and reduced on-site coulombic repulsion.[137]



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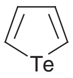

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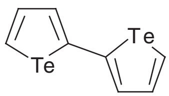

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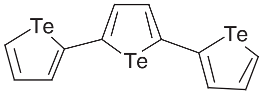

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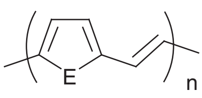
Aside from the often complicated chemistry of selenium and tellurium in comparison with that of sulfur, the principal reason behind the lack of study on polyselenophene (PSe) and polytellurophene (PTe) is the high monomer oxidation potentials in conventional solvents. Over-oxidation when attempting electropolymerisation results in damage to the polymer backbone giving a poor film, and shorter effective conjugation lengths. Poorer solubility of selenophene compared to thiophene is also blamed for a lower extent of polymerisation in selenophene systems. As a result the role of the chalcogen atom in these systems remains somewhat unclear. Glenis *et al.*[138] observe a negligible contribution to the π-electron system from the Se atom in the ground state, but an important effect on the conjugation length and conductivity. The best room temperature conductivity so far reported for a polyselenophene film is 10^{-1} Scm^{-1}.[139] This was prepared in neat boron trifluoride diethyl etherate, in which the oxidation potential of selenophene is significantly lower than in, for example, acetonitrile. This result represented an improvement of an order of magnitude over the best previously reported PSe conductivities.[138,140] Semiconductor-type temperature/conductivity dependence was seen in PSe.[138]

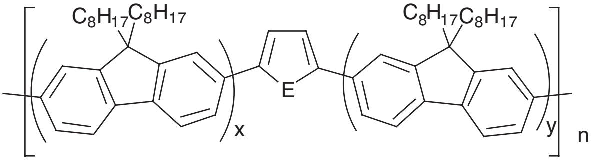
PTe has proved harder to prepare, but there are some reports[141] of successful electropolymerisation, particularly from Otsubo's group where bitellurophene **60** and tertellurophene **61** have been used as monomers.[142,143] The higher oligomers have lower oxidation potentials than tellurophene as a result of the larger conjugation, also reflected by lower energy absorption bands. Perhaps more significant is that the tellurophene oligomers have lower oxidation potentials and absorb at longer wavelengths than the corresponding oligoselenophenes and thiophenes. Electropolymerisation of the dimer or trimer can therefore be performed at lower potentials and better quality films result. Electropolymerisation of tellurophene, bitellurophene and tertellurophene yielded black films,[142] indicating that the materials are obtained in their doped states. Low stability or extensive branching of the polymers is thought to be responsible for the low conductivities; the highest conductivity so far reported for polytellurophene was 1.3×10^{-5} Scm^{-1}, in the case of electropolymerised tertellurophene.

The best conductivities achieved for PSe and PTe are still much lower than for PT (2000 Scm^{-1}).[144] However, the evidence suggests that the large difference does not originate from the inherent band gap, bandwidth or oxidation potential of the polymers. The samples of PSe so far reported may suffer from a significantly shorter effective conjugation length, resulting in charge trapping at chain ends.[145] Indeed, there are numerous other examples of the theoretical superiority of PSe and PTe over PT for electronic materials applications. Inoue *et al.*[146] prepared a series of oligoselenophenes (monomer through hexamer) and found, as expected, that the higher oligomers showed lower oxidation potentials than the shorter oligomers. Furthermore, the oligoselenophenes absorbed at longer wavelengths by about 0.2–0.3 eV compared to their corresponding oligothiophenes. A smaller band gap would hence be expected for PSe than for PT. Conductivities of the oligomers were not reported. To date, the measured band gaps of PSe samples at around 2.0 eV[138,140] are identical to the band gap of PT.[144]

A thorough theoretical comparison of PT, PSe and PTe by Salzner and co-workers[147] lends further weight to the argument that it is the quality of the samples prepared, not an intrinsic property of the materials, that results in low conductivities. The study predicts very similar values of band gap, ionisation potential, electron affinity, HOMO and conductance bandwidth for PT and PSe. PTe is predicted to have the lowest bandgap (0.34 eV lower than PT), in agreement with the work on tellurophene oligomers by the Otsubo group. It has a slightly smaller HOMO bandwidth and slightly larger conductance bandwidth than PT. Ionisation potentials increase in the trend PTe < PSe < PT, in agreement with the trend in donor strength. The authors assert that there is therefore no reason to suggest PT is superior to the higher chalcogenophenes, unless the increased heteroatom size leads to larger interchain distance and hence less favourable charge ‘hopping’ between chains. It is predicted that optimisation of PSe and PTe will result in improved conductivities; these materials, while demanding to prepare, still offer great potential.



62; E = S, Se



63; E = S
64; E = Se

In other studies, polymers **62** were prepared chemically by Ng and co-workers.[148] The selenium-containing polymer showed a higher room temperature conductivity and a smaller band gap than the corresponding thiophene polymer. A greater extent of conjugation in the selenophene derivative was also observed by UV-vis absorption studies. Copolymers of thiophene and dialkylfluorene (**63**) are very well studied systems. Yang *et al.*[149] compared these copolymers with the selenophene analogues **64**, which showed significantly red-shifted photoluminescence (PL) and electroluminescence (EL) emission. The extent of bathochromic shift increased with greater selenophene content. This is most likely the result of the increased polarisability of selenophene allowing for greater adjustment in the excited state. Increasing the heavier chalcogenophene content in such a copolymer leads to a reduced threshold concentration for quenching of the fluorene fluorescence. This concentration is higher for the selenophene-containing copolymer than the thiophene analogue. To explain this reduced PL efficiency the authors invoke the heavy atom effect, which may serve to increase intersystem crossing (singlet to triplet). The increased quenching observed in the selenophene copolymer also suggests interchain interactions are stronger where heavy chalcogens are used.

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CHAPTER 12.3

1,2-Dithiolene Ligands and Related Selenium and Tellurium Compounds

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Abbreviations:

1D	One-dimensional
2D	Two-dimensional
AcO^-	Acetate
α-tpdt^{a}	2,3-Thiophenedithiolate
AIBN	Azoisobutyrylnitrile
bddt^{2-a}	4*a*,5,6,7,8,8*a*-Hexahydro-1,4-benzodithiin-2,3-dithiolate
bds^{2-b}	Benzene-1,2-diselenolate
bdt^{2-a}	Benzene-1,2-dithiolate
BEDT-TTF	Bis(ethylenedithio)tetrathiafulvalene
BrBzPy	4-Bromobenzylpyridinium
btdt^{2-a}	Benzotetrathiafulvalenedithiolate
Bz	Benzene
cddt^{2-a}	4*a*,6,7,7*a*-5*H*-Cyclopenta[*b*]-1,4-dithiin-2,3-dithiolate
CD-ROM	Compact Disk Read Only Memory
ChSTF	2,3-Cyclohexylenedithio-1,4-dithia-5,8-diselenafulvalene
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CT	Charge-Transfer
dcit^{2-}	3,4-Dimercapto-5-cyanoisothiazole
dcmdtcroc^{2-}	4-(Dicyanomethylene)-1,2-dimercaptocyclopent-1-eme-3,5-dionato
ddds^{2-b}	5,6-Dihydro-1,4-dithiin-2,3-diselenolate
dddt^{2-a}	5,6-Dihydro-1,4-dithiin-2,3-dithiolate
ddt^{2-a}	1,4-Dithiin-2,3-dithiolate
DETHQ^{2-}	Bis(3-*N,N′*-diethyltetrahydroquinazolyl)-ethylene-1,2-dithiolate

(*continued*)

DFT	Density Functional Theory
diod^{2-a}	1,4-Dithia-6-oxa-2,3-dithiolate
DMAD	Dimethyl acetylenedicarboxylate
dmbit^{2-}	2-Thione-1,3-dithiole-benzo[*d*]-4,5-dithiolate
dmbt^{2-}	Dimethyltetrathiafulvalenedithiolate
dmdt^{2-}	Dimethyltetrathiafulvalenedithiolate
dmio^{2-a}	2-Oxo-1,3-dithiole-4,5-dithiolate
dmise^{2-a}	2-Selenoxo-1,3-dithiole-4,5-dithiolate
dmit^{2-a}	2-Thioxo-1,3-dithiole-4,5-dithiolate
dmox^{2-a}	4,5-Dimethoxybenzene-1,2-dithiolate
dmt^{2-a}	3-Thioxo-1,2-dithiole-4,5-dithiolate
dphdt^{2-a}	5,6-Diphenyl-1,4-dithiin-2,3-dithiolate
dsis^{2-b}	2-Selenoxo-1,3-diselenole-4,5-diselenolate
dsise^{2-b}	2-Selenoxo-1,3-dithiole-4,5-diselenolate
dsit^{2-b}	2-Thioxo-1,3-dithiole-4,5-diselenolate
dsitse^{2-b}	2-Selenoxo-1,3-thiaselenole-4,5-diselenolate
dssq^{2-b}	1,2-Diselenosquarate
dtcs^{2-a}	3,4,5-Trioxocyclopent-1-ene-1,2-dithiolate
dtdt^{2-a}	1,4,6-Trithia-2,3-dithiolate
dtsq^{2-a}	1,2-Dithiosquarate
DT-TTF	Dithiopheno-tetrathiafulvalene
edt^{2-a}	Ethylene-1,2-dithiolate
EDT-TTF	Ethylenedithiotetrathiafulvalene
EHT	Extended Hückel Theory
F$_2$pdt^{2-a}	2,2-Difluoro-1,3-propanediyldithioethylene-1,2-dithiolate
HMTTF	Bis(trimethylene)-tetrathiafulvalene
HOMO	Highest Occupied Molecular Orbital
JUL1^{2-}	Julolidinyl-ethylene-1,2-dithiolate
JUL2^{2-}	1,2-Bis(julolidinyl)-ethylene-1,2-dithiolate
LD-ROM	Laser Disc Read Only Memory
LLCT	Ligand to Ligand Charge Transfer
LMCT	Ligand to Metal Charge Transfer
LUMO	Lowest Unoccupied Molecular Orbital
madt^{2-a}	Maleamide-1,2-dithiolate
mdt^{2-a}	2*H*-1,3-Dithiole-4,5-dithiolate
medt^{2-a}	5,6-Dihydro-6-methyl-1,4-dithiin-2,3-dithiolate
midt^{2-a}	Maleimide-1,2-dithiolate
mns^{2-b}	1,2-Maleonitrile-1,2-diselenolate
mnt^{2-a}	1,2-Maleonitrile-1,2-dithiolate
NIOS	Non-Integral Oxidation State
NIR	Near Infrared
NLO	Nonlinear Optics
pddt^{2-a}	6,7-Dihydro-5*H*-1,4-dithiepinin-2,3-dithiolate
p-EPYNN	*p*-*N*-Pyridinium α-nitronyl nitroxide

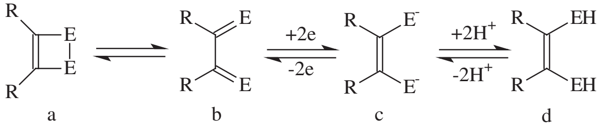
(*continued*)

pds^{2-b}	Pyrazine-2,3-diselenolate
pdt^{2-a}	Pyrazine-2,3-dithiolate
Per	Perylene
$phdt^{2-a}$	5,6-Dihydro-5-phenyl-1,4-dithiin-2,3-dithiolate
PMMA	Polymethylmethacrylate
qdt^{2-a}	Quinoxaline-2,3-dithiolate
$R\text{-}dmet^{2-a}$	Substituted 2-thioxo-thiazoline-4,5-dithiolate
$R,R'\text{-}timdt^{2-a}$	Disubstituted 2-thioxoimidazoline-4,5-dithiolate
SHG	Second Harmonic Generation
SORCI	Spectroscopy Oriented Configuration Interaction
SP	Spin-Peierls
TBA	Tetrabutylammonium
$TCNQF_4$	Tetrafluorotetracyanoquinodimethane
$tdas^{2-a}$	1,3,5-Thiadiazole-3,4-dithiolate
tds^{2-b}	1,2-Bis(trifluoromethyl)ethylenediselenolate
tdt^{2-a}	Toluene-3,4-dithiolate
tfd^{2-a}	1,2-Bis(trifluoromethyl)ethylenedithiolate
$tmdt^{2-}$	Trimethylenetetrathiafulvalenedithiolate
TMTSF	Tetramethyltetraselenafulvalene
TTeF	Tetratellurafulvalene
TTF	Tetrathiafulvalene
Vis	Visible
YAG	Yttrium Aluminium Garnet
YLF	Yttrium Lithium Fluoride
ZORA	Zeroth Order Regular Approximation

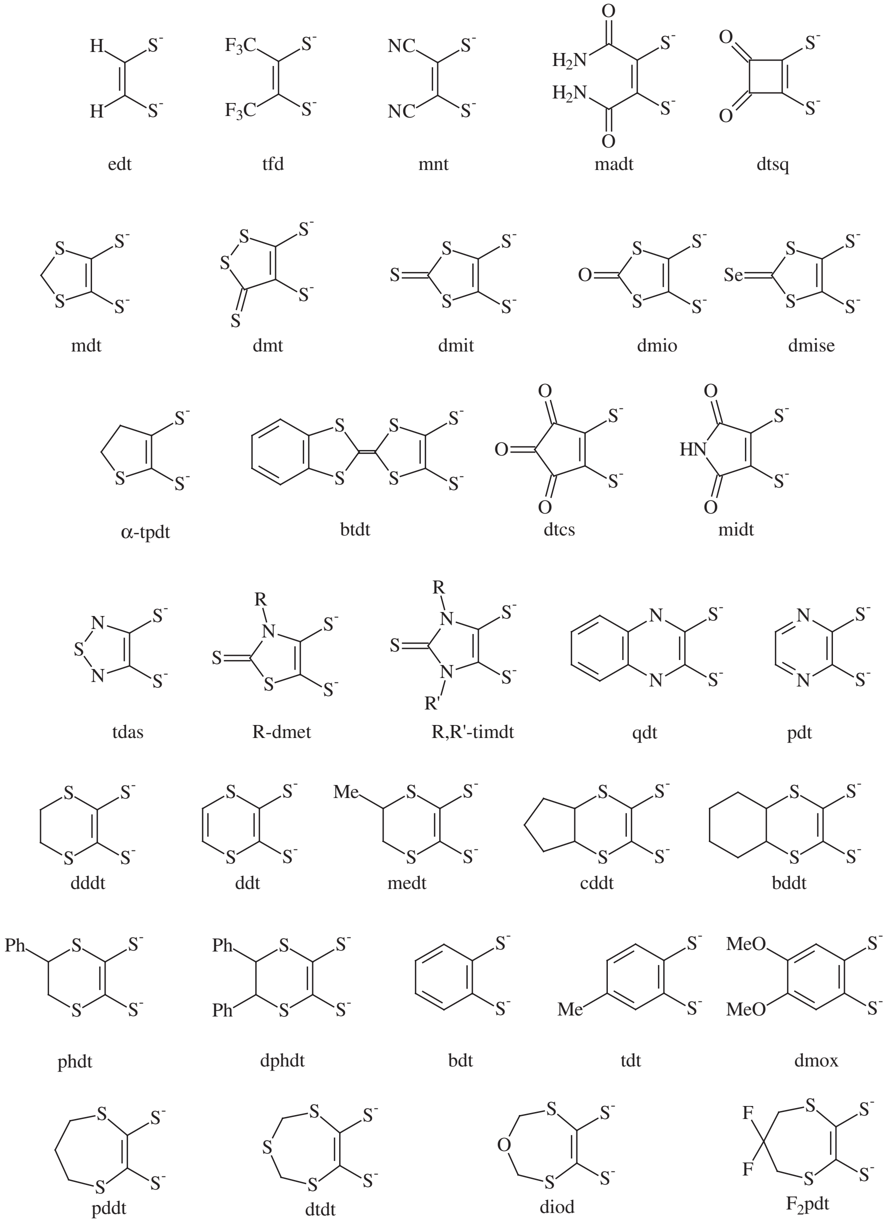
[a] Depicted in Scheme 2. [b] Depicted in Scheme 3.

12.3.1 Introduction

The chemistry of 1,2-dichalcogenolene ligands (Scheme 1) has been of increasing interest for the scientific community over the past 40 years, though 1,2-dithiolene systems, containing unsaturated 1,2-dithiolates, such as tdt^{2-} (Scheme 2), and their reactivity towards several metal ions have been the subject of study since the mid-1930s by Clarcke and co-workers.[1–3]

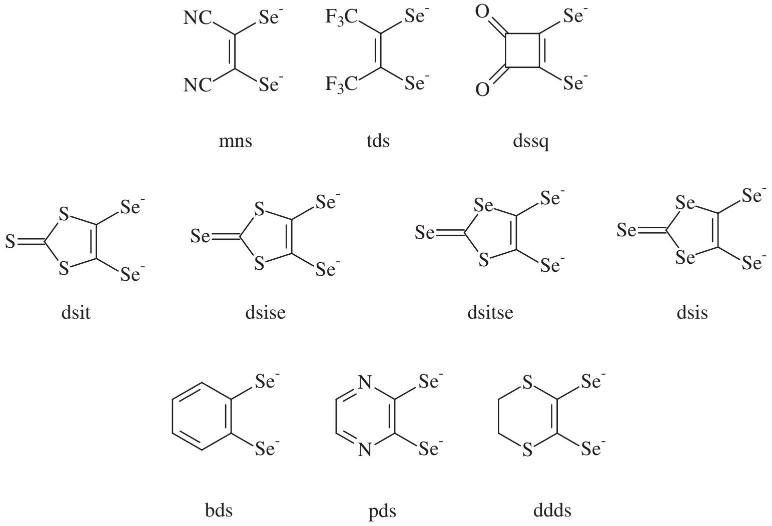


Scheme 1 *Equilibria between 1,2-dichalcogenolene precursors: dichalcogenete (a), 1,2-dichalcogenone (b), 1,2-dichalcogenolato (c), and 1,2-dichalcogenol (d). E=S, Se, Te*



Scheme 2 *Selected 1,2-dithiolene ligands and commonly used acronyms. All ligands have been drawn in their 1,2-dithiolato form*

In 1957, Bähr and Schleitzer[4] first reported a Pd complex deriving from the sodium salt of a ligand they had prepared, Na_2mnt (Scheme 2), and observed that the complex could be oxidised to an unidentified product. Two years later, Stevancevic and Drazic[5] reported some dianionic metal complexes derived from



Scheme 3 *Selected 1,2-diselenolene ligands and commonly used acronyms. All ligands have been drawn in their 1,2-diselenolato form*

H_2qdt (Scheme 2). Nevertheless, it was only in the mid-1960s with the seminal works by Schrauzer and Mayweg[6] on [$Ni(Ph_2C_2S_2)_2$], and by Gray on nickel maleonitriledithiolato complexes,[7] that the chemistry of 1,2-dithiolene complexes started to attract the interest of researchers. Since then, a very large variety of different 1,2-dithiolene ligands and their complexes with numerous metal ions have been reported. The interest in 1,2-dithiolene chemistry was further enhanced by the discovery of a large number of applications, in fields as varied as conductivity, magnetism, linear, and nonlinear optical properties, and of the role of 1,2-dithiolene systems in biology. Therefore, the number of publications have increased year by year; along with papers and communications, several reviews have appeared, dealing with single classes of 1,2-dithiolene complexes, on specific features, or on their applications,[8–22] while in 2004 an entire volume of Progress in Inorganic Chemistry was published.[23]

In 1967, in view of interest focusing on the chemistry of 1,2-dithiolene complexes, Davison and Shawl thought it was reasonable to prepare the corresponding selenium-containing complexes, and synthesised several 1,2-diselenolene transition metal complexes.[24,25] The number of scientific works addressing 1,2-diselenolene complexes is much smaller than that regarding 1,2-dithiolene complexes, both because of synthetic difficulties and because the properties of these complexes are very similar to those of the fully sulfured congeners, in contrast to what occurs in the case of dioxolenes.[26] Descending along the group, only very few publications have addressed the synthesis and characterisation of 1,2-ditellurolene complexes. In general, 1,2-dichalcogenolene ligands appear in both homoleptic and heteroleptic complexes, in which case the ligands can be wholly or partly of 1,2-dichalcogenolene types. The huge variety of metal complexes and their possible applications, taken together with the extremely large number of publications and patents on this subject do not allow us to deal in depth with any aspect of this chemistry. In this chapter, an overview on metal 1,2-dichalcogenolene complexes will be provided, mainly focused on homoleptic complexes, the aim being to illustrate to the reader the general properties and trends and perspectives of this branch of coordination chemistry.

In particular, the synthesis and the electrical, magnetic, and optical properties of the title complexes will be concisely reviewed here. Other aspects, of no less importance, such as the reactivity of 1,2-dichalcogenolene complexes[27] and the role of 1,2-dithiolene complexes in biology[28] or in analytical chemistry[29] have been recently reviewed and the reader is referred to the most recent publications for more information.[30–52]

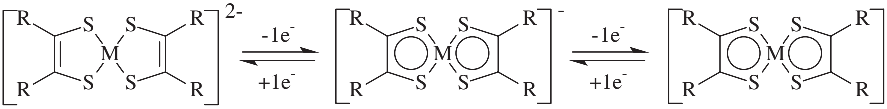
12.3.2 Nomenclature

Naming in 1,2-dithiolene chemistry has been variable in literature over the past decade. Though terms such as 1,2-alkene- or 1,2-arene-dithiolato may be useful for referring to the free ligands, they are not very meaningful when applied to the corresponding coordination metal complexes. The name of 1,2-dithiolene, originally introduced by McCleverty,[4] and the more general name of 1,2-dichalcogenolene, are conventionally assigned to metal complexes formally deriving from 1,2-disubstituted alkene-1,2-dichalcogenolates, and refer neither to a specific molecular charge nor to the oxidation state of the central metal ion.

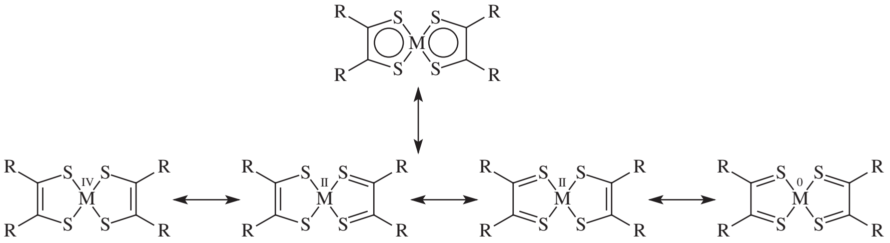
In fact, one of the peculiar properties of the title class of compounds is the ability of the molecular entity to carry a charge which can vary considerably, also assuming fractional values in non-integral oxidation state (NIOS) salts. The different molecular oxidation states are reversibly accessible by chemical or electrochemical means. A good example is the case of *bis*(1,2-dithiolene) complexes of d^8 metal ions [such as Ni(II), Pd(II), Pt(II), Au(III)], whose charge can assume values typically ranging between −2 and 0 (see Scheme 4).

This makes it difficult to assign clearly separated formal charges to the metal and to the ligand, which would not be meaningful as a consequence of the non-innocent nature of 1,2-dithiolene ligands.[53,54] In Scheme 5, the case of neutral diamagnetic square-planar *bis*(1,2-dithiolene) complexes is illustrated.

As mentioned, a very large variety of 1,2-dichalcogenolene complexes have been reported so far in literature, accompanied by many acronyms. Schemes 2 and 3 summarise some of the most commonly encountered



Scheme 4 *Redox processes involving bis(1,2-dithiolene) metal complexes*



Scheme 5 *Lewis structures for neutral bis(1,2-dithiolene) complexes of d^8 metal dications*

acronyms of 1,2-dithiolene and 1,2-diselenolene ligands, drawn in their dianionic form. The reader is referred to these Schemes and to the abbreviation list for all acronyms cited below.

12.3.3 Synthesis

12.3.3.1 Synthesis of 1,2-Dichalcogenolene Ligands or Precursors

The synthesis of metal complexes deriving from 1,2-dichalcogenolato ligands is generally complicated by the tendency of these ligands to polymerise or decompose. A plethora of different and specific synthetic routes to 1,2-dichalcogenolene ligands has been reported. Nonetheless, some general routes can be identified for the synthesis of most 1,2-dithiolene ligands,[55] often extendible to 1,2-diselenolene and 1,2-ditellurolene species.

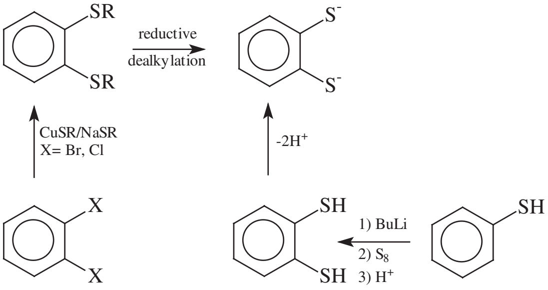
12.3.3.1.1 Synthesis of Arene-1,2-Dichalcogenolato Ligands

Arene-1,2-dichalcogenolene ligands are generally stable as 1,2-dichalcogenols or 1,2-dichalcogenolato sodium salts.[55,56] Aromatic 1,2-dithiolates can be prepared by following two different synthetic approaches, shown for bdt^{2-} in Scheme 6, which start either from dihalo-substituted arenes or from mercapto- or vicinal dimercapto- arenes.[57–62]

In the former case, the dibromo- or dichloro-substituted arene is reacted with cuprous or sodium thiolates to give vicinal thioethers, which can be reductively dealkylated, for example with Na/NH$_3$, to give the dithiols.[63] Alternatively, benzenethiol is reacted with *n*-BuLi, and the resulting lithiated product is made to react with elemental sulfur to give the 1,2-dithiolate salt.

The corresponding diselenolene ligand can be obtained by reacting 1,2-dibromobenzene with Na$_2$Se to give poly(*o*-phenylenediselenide), which can be reduced by NaBH$_4$, yielding the bds^{2-} anion, characterised by conversion to the known 4,5-benzo-1,3-diselenole-2-thione.[64,65]

Moreover, dilithium arene-1,2-dichalcogenides have been used as starting materials for the synthesis of ditellurolene, selenotellurolene, thiotellurolene, and thioselenolene complexes of the ligands having general formula (1,2-C$_6$H$_4$EE$'$)$^{2-}$ (E, E$'$=S, Se, Te).[66–70] 1,2-dithiosquarate and 1,2-diselenosquarate



Scheme 6 *Strategies for the synthesis of 1,2-arenedithiolato ligands*

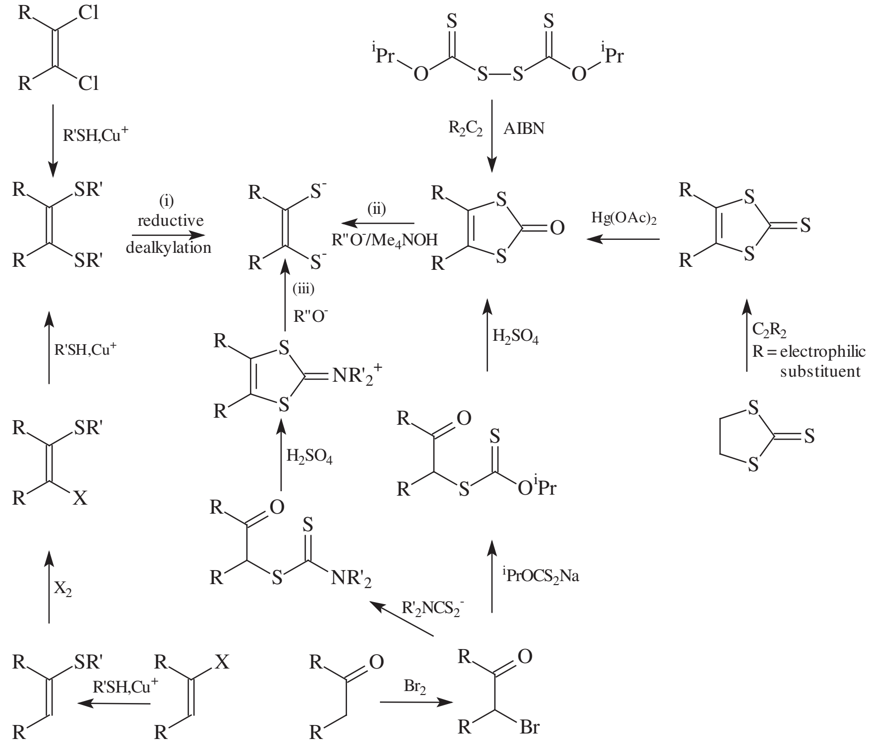
($dtsq^{2-}$ and $dssq^{2-}$) have been isolated as potassium salts, obtained by reaction of 1,2-diethoxysquarate and H_2E ($E{=}S$[71,72] and Se,[73,74] respectively), although the selenium compound is highly air and moisture sensitive.

12.3.3.1.2 Synthesis of Stable 1,2-Alkenedichalcogenolato Ligands

Compared to 1,2-arenedithiols, 1,2-alkenedithiols, and the corresponding dithiolates are generally much less stable, and must be protected until reacted with the metal salt. In fact, the sodium salts of 1,2-alkenedithiolates are strongly reducing species, highly reactive towards water or halogenated solvents. Also in this case, several synthetic routes, summarised in Scheme 7, are available.

The first method [(i) in Scheme 7], analogous to that described for arene-1,2-dithiolates, starts from dithioethers, typically *cis*-1,2-benzylthioalkenes ($R'{=}CH_2Ph$ in Scheme 7), to give the *cis*-alkene-1,2-dithiolato species by reaction with strongly reducing agents. Dithioethers can be obtained starting from mono- or 1,2-dihaloalkenes. In the second method, α-bromoketones, obtainable by halogenation of ketones, are reacted with alkylxantate or dialkyldithiocarbamate salts [typically $^iPrOCS_2Na$ and $(^iPr)_2NCS_2Na$, respectively][75] to give the corresponding α-ketoxanthate or α-ketodithiocarbammate esters, which undergo cyclisation in concentrated sulfuric acid to give the vinylene dithiocarbonate or iminiumdithiocarbonate. The reactions of both types of compounds with strong bases [reactions (ii) or (iii) in Scheme 7, respectively] lead to the desired symmetrically or unsymmetrically substituted 1,2-alkenedithiolates.[49,75,76] When the final 1,2-dithiolene ligand features acidic moieties, such in the case of $madt^{2-}$, different agents, such as NaSMe, can be used to promote the opening of the vinylene dithiocarbonate.[77]

Alternatively, 1,3-dithiol-2-ones have been obtained by reacting diisopropylxanthogen disulfide with unsaturated substrates, such as disubstituted alkynes R_2C_2, in the presence of AIBN (azoisobutyrylnitrile), a radical initiator.[78] Finally, vinylene dithiocarbonates can be obtained by reacting mercury(II) acetate with the corresponding trithiocarbonates, generated by reaction of electrophilic alkynes with ethylene trithiocarbonate.[79] Analogously,



Scheme 7 *Strategies for the synthesis of 1,2-ethylenedithiolato ligands*

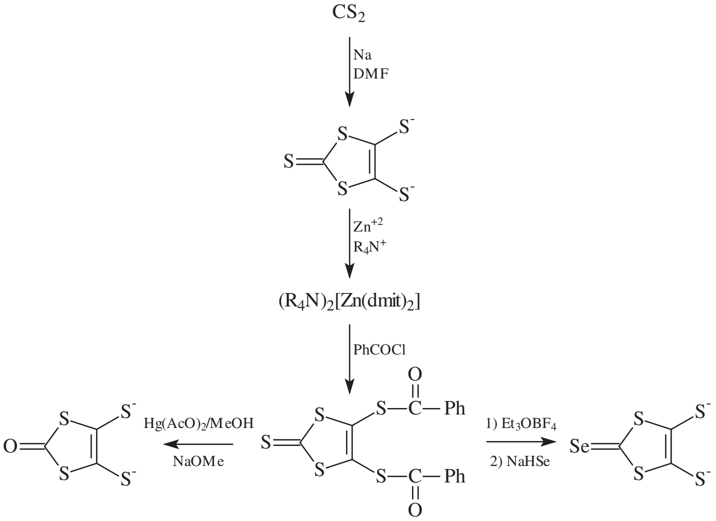
disubstituted vinylene triselenocarbonates have been obtained by reacting the corresponding ethylenetriselenocarbonates with activated alkynes R_2C_2.[80]

It should be noted that the synthetic pathway (ii) has been extended to cyclic 1,2-dithiolene and 1,2-diselenolene ligands, such as dddt^{2-}, ddds^{2-}, ddt^{2-}, phdt^{2-}, medt^{2-}, and so on.[81]

12.3.3.1.3 Synthesis of mnt^{2-}, dmit^{2-}, and Isologs

Specific procedures have been used for the synthesis of the two most commonly encountered 1,2-dithiolene ligands, mnt^{2-} and dmit^{2-} and their selenium isologs. Na$_2$mnt has been prepared by reacting NaCN with CS_2; the intermediate $[S_2CCN]^-$ species undergoes a coupling reaction accompanied by loss of sulfur.[82] The synthesis and coordination properties of dmit^{2-} and isologs were reviewed by Pullen and Olk in 1999.[11] The chemical or electrochemical reduction of CS_2 and CSe_2 gives the dmit^{2-} and dsis^{2-} ligands, along with the corresponding trichalcogenocarbonate.[83–88] Both anions can be isolated as air stable quaternary ammonium or arsonium salts of the corresponding Zn-complex, $[Zn(dmit)_2]^{2-}$ (Scheme 8) and $[Zn(dsis)_2]^{2-}$.[85,89,90]

In addition, the reactions of $[Zn(dmit)_2]^{2-}$ and $[Zn(dsis)_2]^{2-}$ with PhC(O)Cl led to the thioesters dmit[C(O)Ph]$_2$ and dsis[C(O)Ph]$_2$, whose hydrolysis with



Scheme 8 *Strategies for the synthesis of dmit^{2-}, dmid^{2-}, and dmise^{2-} ligands*

NaOMe yields Na_2dmit and Na_2dsis, respectively. Metathesis reactions starting from these salts and the desired metal salt (typically halides), followed by addition of a solution of a quaternary salt, such as Ph_4PCl, have been extensively used to obtain a large number of different salts containing dmit-dithiolene and dsis-diselenolene complexes.[91]

Replacement of the terminal sulfur of the dmit^{2-} ligand with oxygen, performed by reaction with $Hg(OAc)_2$, has been used to prepare the dmid^{2-} ligand (Scheme 8).[92] The corresponding 2-selone analogue, dmise^{2-}, can be prepared from dmit$[COPh]_2$ by alkylating the terminal thiocarbonyl group with Et_3OBF_4 and subsequently reacting the formed dithiolium salt with NaHSe (Scheme 8).[93] Lithiation of various vinylene trichalcogenocarbonates followed by reaction with elemental sulfur or selenium has been used to synthesise various dmit^{2-} isologs,[11] stabilised as Zn(II) complexes, which, similarly to $[Zn(dmit)_2]^{2-}$, are powerful starting reagents for the synthesis of a variety of 1,2-dichalcogenolene complexes. This synthetic strategy, originally proposed by Nigrey for the synthesis of dsit^{2-},[94,95] has been extended to the synthesis of dsise^{2-}, dsis^{2-}, and dsitse^{2-}.[96–102]

12.3.3.2 Synthesis of 1,2-Dichalcogenolene Complexes

1,2-Dichalcogenolene ligands form complexes with main group and *d* transition metal ions.[103] *Bis*(1,2-dithiolene) complexes have been obtained for metals, such as Cr, Mn, Ni, Cu, Zn, for the first row, Pd, Ag, and Cd for the second row, and Pt, Au, and Hg for the third row. Homoleptic *tris*(1,2-dithiolene) complexes have been obtained for Ti, V, Cr, Zr, Nb, Mo, Tc, Ru, Ta, W, Re, and Os. Fe and Co have been found both in *bis* and *tris*(1,2-dithiolene) complexes, although *tris*(1,2-dithiolene) complexes containing these metal ions are more common. Recently, lanthanide (Ce, La, Nd, Sm, Gd, Er, Y) and actinide (U) 1,2-dithiolene complexes have been reported.[102,104–107] Among these, the first example of a *tetrakis*(1,2-dithiolene) complex has been characterised in the complex $[Na_4(THF)_8U(dddt)_4]_\infty$.[106] Fewer are the reports on complexes containing 1,2-diselenolene ligands, with metals such as Ti, V, Co, Ni, Cu, Zn, Ge, Zr, Rh, Pd, Ag, Cd, In, Sb, W, Ir, Pt, Au, Hg, Tl, and Pb.

Bis and *tris*(1,2-dichalcogenolene) complexes can exist in different molecular oxidation states [Scheme 4 for *bis*(1,2-dithiolene) complexes], but with only few exceptions, they are obtained as anionic species. As far as 1,2-dithiolene complexes are concerned, it has been established that less negatively charged species can be obtained by air (for couples with approximately $E_{1/2} > 0.00$ V *vs.* SCE) or iodine oxidation ($E_{1/2} > 0.40$ V),[62] depending on the nature of the ligand and on the electronic structure of the resulting metal complex.[108] On the other hand, oxidised species can be reduced to more negatively charged complexes by several agents, spaning from weakly basic solvents (such as ketones or alcohols, when $E_{1/2} > 0.20$ V) to strong reducing agents, such as hydrazine, sodium amalgam, $NaBH_4$, or $LiAlH_4$.[108]

Stable 1,2-dichalcogenolene salts, such as those of mnt^{2-} or those of 1,2-arenedithiolates, directly yield the corresponding homoleptic *bis* or *tris*(1,2-dichalcogenolene) complexes when reacted with metal halides,[62] such as $NiCl_2$,[53,62,65,109,110], $FeCl_3$,[54] $RuCl_3$,[111] $MoCl_5$, or WCl_6.[63,112] The same reaction has been used for the synthesis of the monotellurolene complexes of types $[Pt(1,2\text{-}TeEC_6H_4)(PPh_3)_2]$ (E=S, Se, Te) and $[Pt(1,2\text{-}Te_2C_5H_6)(PPh_3)]$.[68]

The isolation of $dmit^{2-}$ and isologs in the form of quaternary ammonium salt of the Zn-complex, $(R_4N)_2[Zn(dmit)_2]$, has made it possible to obtain a large number of different anionic complexes through ligand exchange reactions,[50] the resulting complexes being counterbalanced by a large variety of organic and inorganic cations,[113,114] including cationic metal complexes of different kinds.[115–117] Moreover, Ni *bis*-complexes have been used as starting materials for the synthesis of several types of heteroleptic *mono*(1,2-dichalcogenolene) complexes, such as those of the type [CpNi(L)] (Cp=cyclopentadienyl; L=$dmit^{2-}$, $dsit^{2-}$, $dmid^{2-}$).[118]

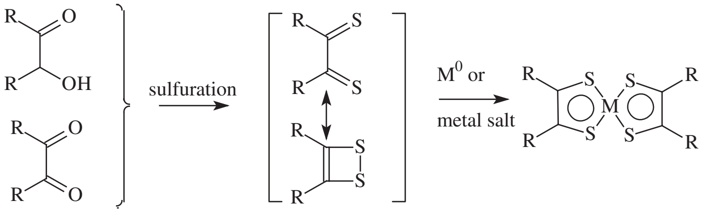
As regards 1,2-dithiolene and 1,2-diselenolene complexes, as mentioned above, commonly used precursors are vinylene di- or at times tri-chalcogenocarbonates, or iminiumdichalcogenocarbonates, which are prone to hydrolysis in alkaline media, yielding the corresponding complexes in the presence of suitable metal salts (generally halides).[80,81,119,120] This route has been very widely applied for the synthesis of almost all types of 1,2-dithiolene complexes,[75] including oxometal 1,2-dithiolene complexes, and heteroleptic *mono*(1,2-dithiolene) complexes, such as those of the type $(arene)M[S_2C_2(COOMe)_2]$ [for example arene=pentamethylcyclopentadienyl (Cp*), M=Ir;[36] arene=variously substituted benzene, M=Ru].[30,121] The same method has also been applied for the synthesis of several 1,2-diselenolene complexes, such as $[Ni(tds)_2]^{2-}$, $[Ni(Se_2C_2Me_2)_2]^{2-}$, and $[Ni(ddds)_2]^{2-}$.[80,81] The complex $[Ni(mns)_2]^{2-}$ has also been synthesised according to this route,[120,122] although an alternative synthesis, also extended to other metal ions, has been reported more recently.[123–126]

As regards to ligands tfd^{2-} or tds^{2-},[8,24,25,127,128] common use has been made of 1,2-dithietes or 1,2-diselenetes, four-membered $R_2C_2E_2$ rings formally deriving from the oxidation of the corresponding 1,2-alkenedichalcogenolates [E=S, Se; Scheme 1(a)],[129] as starting materials for the synthesis of *bis* and *tris*(1,2-dichalcogenolene) complexes (Scheme 9),[12,55] though their preparation requests severe synthetic conditions.[8,24,25] Correlated is the sulfuration of α-hydroxyketones (acyloins),[55,130,131] and of 1,2-diketones, carried out with various sulfuring reagents spanning from P_4S_{10} to Lawesson's reagent,[132] in the presence of metal salts or elemental metals (Scheme 9).[12,13,55] This method has been used to prepare several diaryl substituted 1,2-dithiolene complexes, and has been exploited more recently to synthesise neutral complexes belonging to the classes [M(R,R′-timdt)$_2$] and [M(R-dmet)$_2$] (M=Ni, Pd, Pt),[133–139]

The reactions of electrophilic alkynes, such as DMAD (dimethyl acetylenedicarboxylate), with metal per- and poly-chalcogenido complexes have been exploited for the synthesis of homoleptic and heteroleptic 1,2-dithiolene, 1,2-diselenolene, and 1,2-ditellurolene complexes.[55,140–145] For example, the reaction of $[WSe_9]^{2-}$ with DMAD afforded $[W(Se_2C_2COOMe_2)_3]^{2-}$,[144] while the reactions of DMAD with $[Cp_2TiSe_5]$[141] and $[Cp^*IrSe_4]_2$[142] yielded the corresponding heteroleptic 1,2-diselenolene complexes. Similarly, the reactions of $[Mo(O)(Te_4)_2]^{2-}$ or $[MTe_7]^{n-}$ (M=Hg, $n = 2$; M=Au, $n = 3$) anions with DMAD yielded Mo, Hg, and Au complexes containing the $Te_2C_2(COOMe)_2$ 1,2-ditellurolene ligand.[146,147] Related are the reactions between $(\mu\text{-EE}')_2Fe_2(CO)_6$ or $(\mu\text{-E})_2Fe_3(CO)_9$ clusters (E, E′=S, Se, Te) and R-C≡C-R′ alkynes [R=R′=H;[148] R=H, R′=Ph;[149] R=Ph, R′=M(CO)$_5$C(OEt), M=Cr, W;[150–152] R=H, R′=C_3H_3;[153] R=Me, R′=C≡C–H[154]], and those between the mixed-metal disulfide compounds $CpMoMn(CO)_5(\mu\text{-}S_2)$ and unsaturated hydrocarbons.[155]

Morley and co-workers demonstrated that 4,5-disubstituted 1,2,3-selenadiazoles react with sulfur or selenium in the presence of organotransition metal complexes to yield the corresponding heteroleptic 1,2-dithiolene or 1,2-diselenolene complexes.[142,156–158] In addition, mono- and di-nuclear Pd 1,2-diselenolene complexes have been obtained from *bis*(cycloalkeno)1,4-diselenins, in their turn obtained from 1,2,3-selenadiazoles.[159–161]

The synthetic pathway to TTeF (tetratellurafulvalene), starting from (*Z*)-1,2-*bis*(trimethylstannyl)ethane[162] has been exploited for synthesising heteroleptic Pt complexes containing the only examples of the Te- and Se-analogs of edt^{2-}.[163]



Scheme 9 *Synthesis of bis(1,2-dithiolene) complexes by sulfuration of acyloins or vicinal diketones and complexation in situ*

Owing to their involvement in bioinorganic processes and catalysis, much interest has been attracted by the chemistry of Mo and W 1,2-dithiolene complexes.[39,40] Molybdenum oxo-1,2-dithiolene complexes can be typically obtained through routes, recently reviewed,[164] starting from $[MoO_2(CN)_4]^{4-}$ or $[MoO(SAr)_4]^{2-}$ (by reaction with H_2bdt and related compounds)[47] or from $[MoOCl(MeCN)_4]^+$ (by reaction with Li_2bdt).[165] Tungsten monoxodithiolene complexes can be obtained through various synthetic methods,[166] for example, by reacting $[W(S_2C_2R_2)_2(CO)_2]$ with Et_4NOH.[164] *Bis*-oxo-dithiolene species of the type $[M(O)_2(S_2C_6R_4)_2]^{z-}$ have been obtained by oxidation of oxo-1,2-dithiolene complexes with Me_3NO.[49,50,164,165,167] *Mono*(1,2-dithiolene) molybdenum complexes, of biological interest,[40] have been synthesised both by following a procedure of stepwise introduction of 1,2-dithiolene ligands, and through removal of a 1,2-dithiolene ligand from *bis* or *tris*(1,2-dithiolene) complexes.[55]

Whatever the synthetic procedure adopted, the isolated mono, *bis* or *tris*(1,2-dithiolene) or (1,2-diselenolene) complexes can be further exploited as starting materials for ligand exchange reactions, involving both redox and non-redox processes.[90,141,168,169]

Charge-Transfer (CT) compounds containing 1,2-dichalcogenolene complexes and NIOS salts were generally prepared using electrocrystallisation techniques.[170]

Finally, it should be noted that tellurium can act not only as ligand donor site in 1,2-ditellurolene ligands, but can itself be bound by 1,2-dithiolene ligands, as in the case of compounds containing $[Te(mnt)_2]^{2-}$ and $[Te(dtsq)_2]^{2-}$ dianionic 1,2-dithiolene complexes.[171,172]

12.3.4 General Structural Features of 1,2-Dichalcogenolene Complexes

1,2-Dichalcogenolene complexes have been characterised by means of a large number of techniques. Nonetheless, solid-state diffraction techniques play a primary role, also in view of the importance of solid-state properties of metal 1,2-dithiolene and 1,2-diselenolene complexes. Furthermore, as previously pointed out, 1,2-dichalcogenolene ligands possess the ability to carry variable molecular charges due to the considerable electronic flexibility of the planar five-membered 1,2-dichalcogenolene rings, and in this context interatomic distances within the chelate rings have been utilised as indicators to elucidate the electronic configuration of the complexes, and to distinguish between 1,2-dichalcogenolate and 1,2-dichalcogenone forms, not only in homoleptic chalcogenolene complexes, but also in push-pull heteroleptic complexes (see Section 12.3.5.3).[173] Since the first structural reports on homoleptic complexes $[Ni(mnt)_2]^{2-}$ and $[Ni(bdt)_2]$ were published,[6,174–176] several reviews have focused on the structural features and packing effects of 1,2-dichalcogenolene complexes.[8,9,12,77,103,104,177,178] In particular, Beswick *et al.*[103] reviewed over 500 homoleptic dithiolene complexes characterised by X-ray diffraction. On the other hand, apart from metallorganic complexes containing the $Fe_2(CO)_6$ common core,[148–154] only few papers dealt with 1,2-dichalcogenolene systems containing different chalcogen donor atoms.[68–70] An examination of the structural reports has allowed to deduce some features common to the large variety of compounds examined.

(1) In *bis*(1,2-dichalcogenolene) complexes the central metal ion adopts square-planar, near tetrahedral, or square-pyramidal coordination geometries. Several structural parameters (such as the dihedral angle between the two E–M–E planes, the angle c_1–M–c_2, where c_1 and c_2 represent the midpoints between the two coordinating chalcogen atoms of the two ligand units, the bend angle between the E–M–E and E–C–C–E planes) have been used to better define the coordination geometry of the metal and quantify distortions with respect to idealised geometries (E=S, Se).

Square-planar *bis*(1,2-dithiolene) and *bis*(1,2-diselenolene) complexes exhibit a tendency to form dimeric[62,81,128,179] or trimeric[180] structures, especially when the transition metal has a formal configuration between d^5 and d^8. Within the dimers, the monomeric units maintain the structural characteristics of the deriving monomers.[181] Different dimers or trimers can interact with each other,[110,182] and the difference between interacting dimers or trimers and stacked polymeric structures can be uncertain. In the case of anionic complexes, the nature and size of the countercations can play a crucial role in the formation of the stacks.[10,183] The stacking formation becomes more common as the π-systems of the complex increase, as observed in $dmit^{2-}$ *bis*(1,2-dithiolene) complexes.[184] The stacks are often connected by neutral or charged bridging units to give rise to complex supramolecular architectures.[134,185–189]

No example of stacking motif has been reported so far for *mono* or *bis*(1,2-ditellurolene) complexes.

(2) In *tris*(1,2-dithiolene) and *tris*(1,2-diselenolene) complexes, the central metal ion adopts an octahedral or a distorted trigonal prismatic coordination geometry. [144,190,191] A number of geometrical parameters have been proposed to discriminate between these two possibilities: (i) the twist angle between E atoms in the two dimensional projection along the threefold axis, (ii) the dihedral angle between the ligand E–M–E plane and the E–E–E plane formed by three coordinating chalcogen atoms from the three units lying on the same side with respect to the metal centre, or (iii) the dihedral angle between the two E–E–E planes defined as described above (E=S, Se).[144,192,193]

(3) In general, the different ligands feature typical geometrical parameters over a wide range of 1,2-dichalcogenolene complexes.[103]

12.3.5 Applications and Properties of 1,2-Dichalcogenolene Complexes

Metal 1,2-dithiolene and 1,2-diselenolene complexes have been exploited for a large variety of diverse applications,[115,116,194–198] thanks to their unique molecular properties, exhibited both in solution and in the solid state. In the following paragraphs, attention will focus on electrical, magnetic, and optical applications, which will be briefly summarised according to the properties they are based on.

To the best of our knowledge, no applicative study on 1,2-ditellurolene complexes has been reported hitherto.

12.3.5.1 Electrical Properties

The solid-state conducting and magnetic properties of 1,2-dithiolene and 1,2-diselenolene complexes have been the subject of a vast number of publications and reviews.[13,15–18,199,200] In all cases, conducting properties (insulating, semi-conducting, metal-like, or even superconducting) have been rationalised in terms of their crystal structure, which in turn is affected by temperature and applied pressure (including *chemical* pressure).[200] For conducting molecular one-dimensional (1D) systems, some criteria have been proven to be necessarily satisfied in order to make observation of solid-state conductivity possible:[199] (i) the existence of stacking structures, (ii) a spatial extension of the electronic system so as to allow for a significant overlap between stacked units, and (iii) the partial filling of the conducting band, achieved by means of non-integral oxidation or CT processes. In order to avoid Peierls instability, predicted in 1962 by McConnell and collaborators,[201] and first reported in (TTF)[M(tfd)$_2$] CT-complexes (M=Cu, Au; TTF=tetrathiafulvalene, Chapter 12.1),[199,202,203] much effort has been devoted to enhancing the structural dimensionality beyond 1D. BEDT–TTF [*bis*(ethylenedithio)tetrathiafulvalene] has indeed provided a variety of 2D-metallic systems, thanks to the possibility of intermolecular interactions guaranteed by the peripheral sulfur atoms.[200,204] Metal 1,2-dichalcogenolene complexes are a very suitable source of open-shell stable systems (generally radical-anions, but also radical-cations, in the case, for example, of dddt^{2-} complexes) and are able to satisfy these criteria provided that a sufficiently extended planar system is present in the ligands. In particular, open-shell systems deriving from both *bis*(1,2-dithiolene) and *bis*(1,2-diselenolene) systems of d^8 metal ions feature a marked tendency to form intermolecular stack-interactions with short metal–metal distances. However, in the first 1,2-dichalcogenolene complex showing metal-like conductivity, (Per)$_2$[Pt(mnt)$_2$] (Per=perylene),[205,206] the stacking of perylene units was responsible for the conducting properties, while the first compound containing a 1,2-dichalcogenolene complex responsible for the metal-like behaviour was $(H_3O)_{0.33}Li_{0.82}[Pt(mnt)_2]\cdot 1.67H_2O$.[207] Several 1,2-dichalcogenolene complexes can behave as molecular acceptors in CT-complexes with organic donors such as TTF and related species, or can originate NIOS compounds. In principle, the possibility of forming transverse short E···E (E=S, Se) contacts between different stacks could avoid the mono-dimensionality of the stacking structure.[208] Moreover, due to the greater orbital spatial extension of Se compared to S, the replacement of sulfur with selenium has been proposed with the aim of achieving greater interanionic interactions.[127,209]

The complex $TBA_2[Ni(dmit)_2]_7 \cdot 2MeCN$ was the first reported conducting dmit^{2-} salt.[210] A 2D-structure was present in α-$(Et_2Me_2N)[Ni(dmit)_2]_2$,[211] while the first superconductor containing a dithiolene system, (TTF)[Ni(dmit)$_2$],[212] was reported in 1986. To date, nine other compounds based on 1,2-dithiolene complexes and exhibiting superconducting properties have been identified,[213–223] and the superconducting properties of three more compounds have been anticipated.[224–226] Remarkably, all of these compounds contain the dmit^{2-} ligand. More common are 1,2-dichalcogenolene-based compounds exhibiting metal-like behaviour. Even if metallic behaviour has been proven possible also in single-component 1,2-dithiolene molecular crystals,[22] such as [Ni(tmdt)$_2$] or [Ni(dmdt)$_2$],[227–230] metal-like compounds are generally either NIOS salts or CT-complexes, which contain donors of various types, such as Per or TTF (Chapter 12.1). More than one-half are again Ni-, Pd-, or Au- complexes based on the dmit^{2-} ligand,[199] but recent literature also reports many examples of *bis*(1,2-dithiolene) complexes deriving from mnt^{2-} (with metals such as Au, Co, Cu, Fe, Ni, Pd, Pt), tfd^{2-}, dddt^{2-}, dmise^{2-}, dcit^{2-}, and dmbit^{2-} (Ni and Pd).[11,18,19,199,200,231] Some examples of CT salts containing 1,2-diselenolene complexes with metal-like conductivity have also been reported, such as (TMTSF)$_2$[M(tds)$_2$] (M=Ni, Pt, Cu; TMTSF=tetramethyltetraselenafulvalene).[209,232] In addition, few examples of CT-compounds containing heteroleptic *bis*(1,2-dithiolene) complexes, such as (TTF)[Ni(dmit)(mnt)] or (EDT–TTF)[Ni(dmit)(tdas)] (EDT–TTF=ethylenedithiotetrathiafulvalene), have been reported.[233]

In the case of NIOS salts containing cationic radicals, such as [M(dddt)$_2$], the charge can be counterbalanced by inorganic anions (PF_6^-, HSO_4^-) as well as by different metal compounds, such as $AuBr_2^-$.[234–236] Nevertheless, much more common is the case of NIOS salts containing anionic 1,2-dithiolene or 1,2-diselenolene complexes counterbalanced by different cations, such as alkaline ions, *tri*- or *tetra*-alkylammonium, and cyclic saturated or unsaturated organic cations. As previously mentioned, the cation exerts a crucial role in determining the solid-state structure of the (cation)(dichalcogenolene) salt; in the context of this book, it seems important to stress the effect that chalcogen–chalcogen interactions between cations and anions can have in determining the conducting properties of the resulting salts. In some anion radical salts of [M(dmit)$_2$] the secondary bonds between Te-containing cations and the sulfur atoms of the crystalline 1,2-dithiolene complex have been reported to be determinant in increasing conductivity.[200] An interesting comparison between the solid-state properties of compounds containing [M(dmit)$_2$] anions counterbalanced by telluronium cations, such as $(Me_3Te)[Ni(dmit)_2]_2$, β-$(MeTeC_4H_8O)[Ni(dmit)_2]_2$, $(Me_3Te)[Pd(dmit)_2]_2$, and $(Et_2\text{-}MeTe)[Pd(dmit)_2]_2$, has been discussed by Kato.[200,237–239]

12.3.5.2 Magnetic Properties

As mentioned in the previous paragraph, solid-state magnetic properties of 1,2-dithiolene and 1,2-diselenolene complexes have been dealt with in several reviews.[8,12,15–18,20,199,200] The most common magnetic behaviour is antiferromagnetism, not only in compounds containing non-diamagnetic *bis*(1,2-dichalcogenolene) complexes,[81,110,117,199,240–242] but also in heteroleptic systems, such as those of the type [Cp_2M(dichalcogenolene)], [CpM(dichalcogenolene)$_2$] (M=Ti, Zr, Hf, V, Nb, Ta, Mo, W), or [CpM(dichalcogenolene)] (M=Co, Rh, Ni).[118] More unusual are the systems featuring spin-Peierls (SP) transitions, spin-ladder (SL) behaviour, or ferromagnetic properties.

SP transitions are temperature-dependent magnetoelastic transitions involving quasi 1D insulating systems, and were cited in the paragraph 12.3.5.1.[201] Typically reported systems featuring a Peierls transition are the complexes (TTF)[M(tfd)$_2$], with M=Cu and Au,[202] featuring SP transitions below 12 and 2 K, respectively, resulting in a dramatic decrease in magnetic susceptibility as a consequence of the spin "dimerisation". Among 1,2-diselenolene complexes, (TTF)[Cu(tfs)$_2$] shows an SP transition below 6 K.[243]

The definition of spin-ladder systems is related to crystalline frameworks resulting from the interactions between a finite number of $S = 1/2$ strongly magnetically coupled chains arranged each next to the other.[199] The number of coupled chains (odd or even) and the strength of their interaction produce different magnetic behaviours. Among the most important systems, it is worth recalling (*p*-EPYNN)[Ni(dmit)$_2$] (*p*-EPYNN=*p*-*N*-pyridinium α-nitronyl nitroxide, a radical cation),[244] which exhibits short-order ferromagnetic interactions below 40 K, and (DT-TTF)$_2$[Au(mnt)$_2$] (DT–TTF=dithiophenotetrathiafulvalene).[245–248] In the compound (BEDT–TTF)[Co(mnt)$_2$], recently reported, the dithiolene anion is diamagnetic and only the organic cation is responsible for the spin system.[249] Also some members belonging to the heteroleptic class [Cp_2M(L)](TCNQF$_4$), such as [Cp_2M(dmid)](TCNQF$_4$)] (M=Mo, W; TCNQF$_4$=tetrafluorotetracyanoquinodimethane)[20,250] and (AsF_6)[Cp_2W(dsit)][251] have shown spin-ladder behaviour.

Short-range order ferromagnetic interactions have been reported for several compounds containing 1,2-dithiolene and 1,2-diselenolene complexes,[252–254] with various types of ligands and metal ions, such as Ni,[244,252,255–265] Pd,[255] Pt,[255,266–268] Cu,[269] and Mo.[270]

Even more atypical are long-range ferromagnetic interactions resulting in bulk ferromagnetism,[271–276] a behaviour reported for example in the case of the two homoleptic 1,2-dithiolene complexes (NH_4)[Ni(mnt)$_2$]·H_2O,[19,274,275] and (Cp_2*Mn)[Ni(dmit)$_2$].[276]

12.3.5.3 Optical Properties

One of the most striking properties of 1,2-dithiolene[8,12,13,119,199,277] and 1,2-diselenolene[110,128,277] complexes is their intense molecular absorption in the Visible-Near Infrared (Vis-NIR) region. For *bis*(1,2-dithiolene) complexes, this falls at wavelengths (λ_{max}) ranging between 700 and roughly 1750 nm, depending on the nature of the substituents at the carbon atoms of the 1,2-dithiolene system, on the metal ion, on the coordination geometry, on the global charge of the complex (electrochromism), and on the solvent (solvatochromism). Though electronic absorption has been studied also for *mono* and *tris*(1,2-dithiolene) and (1,2-diselenolene) complexes,[49,64,158] the attention of researchers has focused mainly on *bis*(1,2-dithiolene) complexes of d^8 metal ions. For these, the absorption intensity, with ε between 15,000 and 120,000 M^{-1} cm^{-1},[136] is unmatched in any other transition metal compound, whose low energy absorptions are generally ascribed to *d–d* transitions.[12] On the contrary, Vis-NIR absorption has been interpreted as an electronic $\pi-\pi^*$ transition between the HOMO and the LUMO, and its nature has been studied at different levels of theory, ranging from EHT to DFT.[53,278–280] In a restricted approach, calculations qualitatively agree in the description of the two molecular orbitals mainly involved. Since only the LUMO has a contribution from the *d* orbitals of the central metal ion, the Vis-NIR transition can be considered as a partial LMCT process.[281]

As regards neutral 1,2-dithiolene complexes, as compared to the simplest 1,2-dithiolene nickel complex ([Ni(edt)$_2$], $\lambda_{max} = 720$ nm),[282] donor substituents cause a bathochromic shift in the λ_{max} value, while acceptor substituents do not markedly affect the energy of the Vis-NIR absorption band. The interpretation provided by Mueller-Westerhoff[13] accounts qualitatively for the effect of the substituents based on their acceptor/donor abilities. According to this model, acceptor substituents lower the energies of HOMO and LUMO by similar amounts of energy, not resulting in drastic shifts in transition energies, while donor substituents raise the energy of the filled orbital more than that of the LUMO, thus reducing the HOMO–LUMO energy gap and therefore causing a bathochromic shift of the $\pi-\pi^*$ transition towards the NIR region. Worthy of note, by inducing a lowering in the LUMO energy, acceptor substituents tend to stabilise the anionic forms of *bis*(1,2-dithiolene) complexes, while donor substituents tend to stabilise neutral or, rarely, cationic forms.[12,13]

The substituent effect has been exploited to fine-tune the position of absorption in order to lower its energy as much as possible. In particular, Mueller-Westerhoff and co-workers reckoned that in *bis*(1,2-dithiolene) Ni complexes, this aim could be achieved by introducing in the 1,2-dithiolene ligand aromatic substituents planar with the dithiolene system, in order to enhance extension of the π-system, and containing amino-donor groups: examples of such 1,2-dithiolene ligands are JUL1^{2-}, JUL2^{2-}, or DETHQ^{2-}, whose nickel complexes exhibited absorptions falling at 1180, 1270, and 1370 nm, respectively in CH_2Cl_2.[12,199] More recently, a few other neutral *bis*(1,2-dithiolene) complexes have been reported featuring low-energy NIR absorptions around 1000 nm, such as [Ni(dmit)$_2$],[137] [Ni(phdt)$_2$],[283] [Ni(medt)$_2$],[283] and [Ni(bddt)$_2$][284] [Ni(cddt)$_2$],[119] and those belonging to the classes [M(R,R′-timdt)$_2$][133–136,138–139,285,286] and [Ni(R-dmet)$_2$][137] (M=Ni, Pd, Pt). In addition, the low-energy absorption bands of neutral 1,2-dithiolene complexes containing ferrocenyl substituents have been discussed.[287] It is worth noting that with neutral *bis*(1,2-dithiolene) complexes with very narrow HOMO–LUMO gaps, such as single-component molecular conductors, electronic absorption is dramatically shifted into the IR region.[229]

Monoanionic *bis*(1,2-dithiolene) complexes of d^8 metal ions feature electronic absorptions that are generally bathochromically shifted as compared to those of the corresponding neutral species, and in the case of nickel and platinum complexes they fall between 1100 and 1450 nm.[137,283,288,289] It is interesting to note that salts formed by different 1,2-dithiolene complexes acting both as anions and as cations can present low-energy absorption bands in the solid state, attributed to intermolecular CT transitions.[290,291]

The strong NIR absorption peculiar to neutral or monoanionic *bis*(1,2-dithiolene) complexes has been exploited for several applications.

(a) *Q-Switching*. Laser emission consists of a continuous output of coherent radiation, that can be compressed into ultra-short pulses of extremely high energy[292] by using "Q-switching" dyes,[13] provided that (1) the dye has a significant absorption close to the laser emission energy; (2) the dye has no higher excitations at the same energy; (3) the excited state lifetime is long enough to allow for bleaching of the laser; and (4) the dye is thermally and photochemically stable.

Bis(1,2-dithiolene) complexes are generally thermally and photochemically very stable, and their Vis-NIR absorption can be tuned in order to reach the wavelength ranges of interest for NIR lasers, such as Nd:YAG, Nd:YLF, and Er:Glass solid-state lasers (emission wavelengths $\lambda_{em} = 1064$, 1053, and 1540 nm, respectively). In this context, many groups of researchers have devoted their efforts to synthesising 1,2-dithiolene complexes for this type of application, and indeed some of them have been patented and are commercially available, such as *bis*(4-dimethylaminodithiobenzil)nickel.[277,293,294]

(b) *Nonlinear Optics*. Metal 1,2-dithiolene complexes have been studied for applications in the field of second- and third-order nonlinear optical properties.[295] Crystalline second-order NLO materials, possessing large molecular hyperpolarisability reflected by their intense low-energy CT absorption,[296] can give rise to the phenomenon of frequency doubling, where an input wave generates another wave with twice the frequency (second-harmonic generation, SHG). Since these materials must not be centrosymmetric,[297,298] heteroleptic *bis*(1,2-dithiolene) complexes are mainly involved in this field,[199] although homoleptic *bis*(1,2-dithiolene) complexes as counterions of the hemicyanine dye have been reported to enhance its SHG properties.[299] Several heteroleptic *bis*(1,2-dithiolene) complexes of the type [M(L)(L′)], featuring both ligands L and L′ of dithiolene type, have been reported in this context along with measurements and theoretical calculations regarding their hyperpolarisability tensors.[300,301] Of particular interest are those systems where the two 1,2-dithiolene ligands have opposite donor/acceptor behaviour, the so-called push-pull systems. In these complexes, the HOMO is mainly localised on the dithiolene ligand with higher acceptor character, while the LUMO on the ligand with higher donor character, so that the peculiar low-energy transition possesses an intramolecular CT dithione-dithiolato nature, resulting in high hyperpolarisability values.[302] Several neutral complexes of this type have been reported.[169,173,199,302,303] Among heteroleptic complexes featuring ligands of different types, the systems most frequently reported are those of the type [M(diimine)(dithiolate)],[297] with different metals M, such as Ni, Pd, Pt, and Zn.[304,305]

Third-order NLO effects, of interest for potential applications, for example in optical limiting[119,295,306–309] impose no symmetry constraints. Thus, studies on this type of nonlinearity have addressed both homoleptic and heteroleptic 1,2-dithiolene complexes. Among the members of the former class, study on TBA salts of monoanionic nickel *bis*(1,2-dithiolene) complexes with ligands such as phdt^{2-}, dddt^{2-}, pddt^{2-},[283] cddt^{2-},[119] and *p*-substituted 1,2-diphenyl-1,2-ethylenedithioate[310] have been published. Underhill and co-workers[311] have reported on the nonlinear properties of unsymmetrically substituted *bis*(1,2-dithiolene) complexes, such as *bis*[1-butyl-2-phenylethene-1,2-dithiolato(2$^-$)-S,S′]nickel(II), embedded in PMMA-based composites (PMMA=polymethylmethacrylate), or in sol–gel materials.[312] As regards the latter class, some works have dealt with complexes containing mnt^{2-} and dmit^{2-} ligands.[199]

(c) *Optical Technology*. Several publications and patents have dealt with application of 1,2-dithiolene systems to the various branches of optical information technology. Thus, 1,2-dithiolene complexes have been exploited in materials used for optical data storage, such as CD-ROM or LD-ROM media, in copiers, or as optical switches. Recently, the applications of 1,2-dithiolene complexes to wavelength-sensitive NIR-photoconductivity have been investigated,[139,290,313–315] and a working prototype converting a train of impinging NIR-light pulses into electrical signals has been created.[136,314–316] In addition, only citing some recent examples, due to their linear and nonlinear optical properties, 1,2-dithiolene complexes have been investigated as components of dye-sensitised solar cells,[317,318] for photo-imaging media,[319,320] as Vis-NIR optical filters,[321–327] or as ink components.[328]

12.3.6 Conclusions

1,2-Dithiolene chemistry has been investigated in-depth over the last 40 years. The electrical, magnetic, and optical properties of 1,2-dithiolene complexes, accompanied by their general thermal and photochemical stabilities, make them useful for a great number of potential applications, thus justifying the increasing attention of more and more researchers. The intrinsic interest in their electronic structure makes this class of complexes appealing for both the experimental and the theoretical chemist.

Surprisingly, notwithstanding the general interest towards 1,2-dithiolene complexes, and the plethora of different applicative fields in which these compounds have been exploited, only a limited number of research groups have systematically investigated the chemistry of 1,2-diselenolene complexes, and only sporadic publications have reported on 1,2-ditellurolenes. In particular, while the electrical and magnetic features of compounds containing 1,2-diselenolene complexes have been studied, their optical properties have been tapped only marginally. While papers dealing with Vis-NIR absorption properties of 1,2-diselenolene generally indicate that their spectroscopic properties are very similar to those of the sulfured congeners, only few systematic explorations of their electrochromic behaviour have been reported, and investigations on NLO properties seem to be at a very early stage. This is clearly shown by simple comparison of the number of patents dealing with 1,2-diselenolene and 1,2-dithiolene ligands and complexes. The chemistry of 1,2-ditellurolene is in an even more embryonic phase, and less than ten papers deal with the synthesis of these complexes, while their spectroscopic, electrochemical, electrical, and magnetic properties are almost wholly unexplored.

It is easy to predict that during the next decade the chemistry of 1,2-diselenolene complexes, but even more that of 1,2-ditellurolenes, will be investigated in depth, achieving the richness of knowledge and applicative significance that is nowadays a hallmark of 1,2-dithiolene complexes.

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253. (HMTTF)$[Ni(mnt)_2]$ (ref. 262), (ChSTF)$[Ni(mnt)_2]$ (ref. 262), (BrBzPy)-$[Pt(mnt)_2]$ (ref. 267), $[Cr(bz)_2][Ni(dmox)_2]$ (ref. 264) have been reported recently to show strong ferromagnetic interactions in the solid-state.
254. $(Cp^*{}_2Fe)[Ni(bds)_2]\cdot MeCN$ (ref. 260), $(Cp^*{}_2Fe)[Ni(tds)_2]$ (ref. 268), and $(Cp^*{}_2Fe)[Pt(tds)_2]$ (ref. 268) have been reported to display ferromagnetic couplings.
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CHAPTER 13

Chalcogen-Halogen Secondary Bonds in Self-Assembling of Supramolecular Structures

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13.1 General Aspects of Supramolecular Chemistry with Soft–Soft Interactions

From elemental sulfur to selenium and tellurium, intermolecular interactions (*secondary bonds, soft–soft interactions*) play an increasing role. According to *N.W. Alcock*,[1] the term *"secondary bond"* describes interatomic distances longer than covalent single bonds but shorter than *van der Waals* interatomic distances.[1] In many cases secondary bonds can also be described as coordinative *Lewis base – Lewis acid* or *charge transfer* (*donor-acceptor*) types of interactions.

Such secondary bonds are formed by donation from the lone pair of a nucleophile into the σ* orbital of a covalent bond *("n → σ* attack")*. Weak covalent bonds (implying low-energy σ* levels) are easier attacked by $n \rightarrow \sigma^*$ overlap, leading to unsymmetric or symmetric 3c–4e bonds, than strong bonds; this is why supramolecular arrays, due to secondary interactions or 3c–4e bonds, play a particular role in the chemistry of the heavier main group elements.

The role of secondary bond-like intermolecular interactions in basic inorganic compounds of selenium and tellurium has been the subject of a number of reviews; classic examples like the tetrameric tellurium tetrahalides and tetravalent organotellurium halides are also covered by major textbooks. Recent books like *Haiduc/Edelmanns* "Organometallic Supramolcular Chemistry", *Patai/Rappoports* "The Chemistry of Organic Selenium and Tellurium Compounds" and *Akibas* "Chemistry of Hypervalent Compounds", describe a number of basic examples of hypervalency and self-assembly in organoselenium and in organotellurium compounds.[2–4] Classic reviews from *Bent*,[5] *Mc Cullough*,[6] *Krebs*,[7] *Klapötke/Passmore*,[8] *Husebye*[9] and *Devillanova*[10] are also covering the field of intermolecular and cation–anion interactions involving chalcogen and halogen atoms. The directed character of charge transfer and halogen bond geometry has been analysed.[11]

A recent overview comparing various compounds with Se–I bond distances from little less than the sum of the van der Waals radii (about 390 pm) to regular single bonds (about 250 pm) has illustrated the continuum of interactions from weak $n \rightarrow \sigma^*$ overlap *via* typical 3c–4e systems to 2c–2e covalent bonds.[12] The following chapter will report a selection of supramolecular structures ordered under the aspects of functional groups (like roles of halogen and chalcogen atoms in certain environments as donor or as acceptors) and geometrical implications (like T-structures, square planar structures, *etc*.).

13.2 Supramolecular Aspects of Structures from Classes of Compounds discussed in Previous Chapters

13.2.1 Binary Chalcogen Halides

Developments in chalcogen-halide chemistry were covered by a comprehensive review in 1990 (see Chapter 8.1).[7] In the solid tetrahalides E_4X_{16} (E=Se: X=Cl, Br; E=Te: X=Cl, Br, I) halogen atoms act as μ_2- and μ_3-bridging donors towards six-coordinated selenium and tellurium atoms.[7,13] The *formal* mixed valence anions $Te_4I_{14}^{2-}$ and $Se_4Br_{14}^{2-}$ can be regarded as pairs of planar dimeric anions $E_2X_6^{2-}$ (E^{II}) linked by two I^+ or Br^+ cations through 3c–4e E-X-E bridges (Figure 1).[7,14] In these compounds Se and Te atoms can be regarded as electrophiles towards terminal halogen atoms and as nucleophiles towards the bridging ones. The *true* mixed valence compound $[(C_6H_5CH_2)(C_2H_5)_3N]_4[TeI_4]$ $[TeI_6]$[7] contains layers of square planar $[TeI_4]^{2-}$ anions and of slightly distorted octahedral $[TeI_6]^{2-}$ anions (I···I contacts about 420–pm). In the anion $Se_2Br_8^{2-}$ two bromine atoms are bridging square planar Se^{II} with octahedral Se^{IV}.

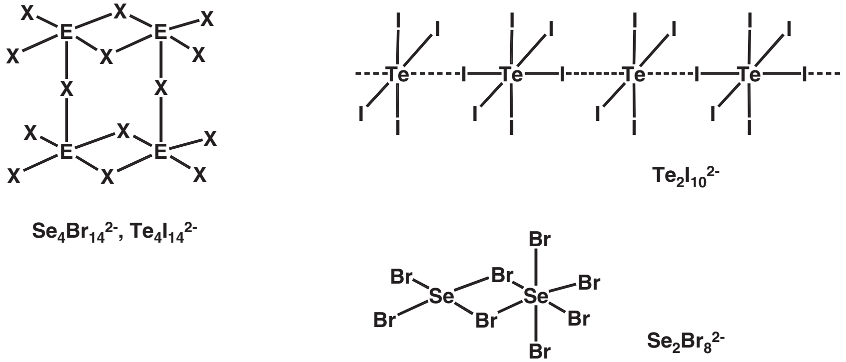


Figure 1 *Mixed valence halogenoselenates and–tellurates*

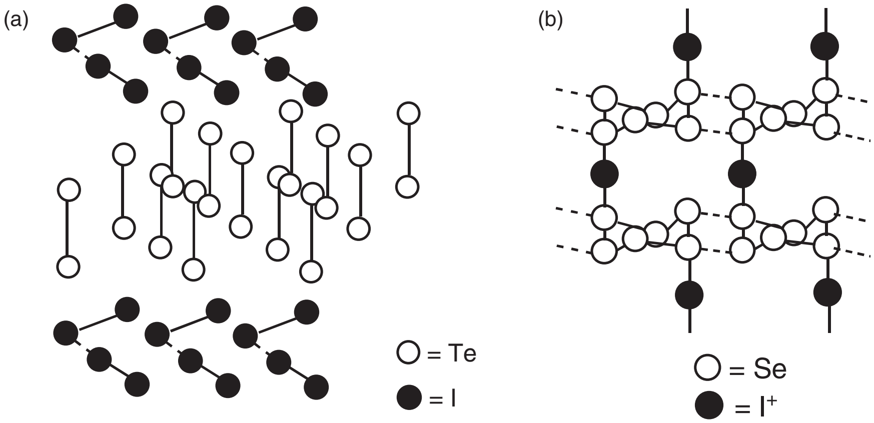


Figure 2 *(a) Layers of solid* $(Te_2)_2I_2$ *and (b) interactions between polymeric* Se_6I^+ *ions*

Solid SCl_2 at –134 °C is weakly associated by S···Cl [S(1): 342, 355; S(2): 337, 339 pm] and S···S (346 pm) contacts. α-Se_2Br_2 (*intermol.* Se···Se 345 pm) and β-Se_2Br_2 (*intermol.* Se···Br 337 pm) differ by the kind of their weak intermolecular contacts leading to layers or three-dimensional nets.[15] A common feature of tellurium subhalides Te_3Cl_2, Te_2X (X=Br, I) and β-TeI are endless tellurium chains with terminal or/and bridging halogen atoms.[16] In the strands of α-TeI two of the four iodine atoms from Te_4I_4 moieties are involved in Te-I···Te bridges. The unique compound $(Te_2)_2(I_2)$, made from GeTe and Te with excess HI, consists of alternating layers of square nets of Te_2 molecules (Te=Te 271.3 pm) and of layers of L-shaped I_4-dimers (I–I 286.6 pm) [Figure 2(a)].[13,17] A part of the I_2-molcules is replaced by HI-molecules.

13.2.2 Di- and Multichalcogen Cationic Species

Cation-containing homoatomic chalcogen rings are covered by reviews (see also Chapters 7.1 and 7.2).[7,8] Interestingly, the polymeric cation chains in $[Se_6I][AsF_6]$ (Se_6-rings bridged by I^+-cations) are connected by pairs of additional weak Se···Se contacts [Figure 2(b)].[18]

The dication $S_2I_4^{2+}$ can either be regarded as *bis*-sulfonium ion, or as adduct of the multiply bonded S_2^{2+} cation with two side-on coordinating I_2 molecules.[19] In the solid state, the AsF_6^- or SbF_6^- counteranions undergo weak bridging and chelating donor–acceptor interaction with all six atoms of the cation, leading to a three-dimensional coordination network.

The neighbourhood of onium functions (carbenium, phosphonium) to Se–Se bonds enhances the electrophilicity of the Se_2-moiety so that it becomes target of attacking nucleophilic anions.

Se–Se-bridged dications with halide or interhalide anions can be obtained under certain conditions by halogenation of 4-imidazoline-2-selones and 4-imidazolidine-2-selones. In the solid salts, Se-Se-bridged dications exhibit significant interactions with their anions, depending on the number and the

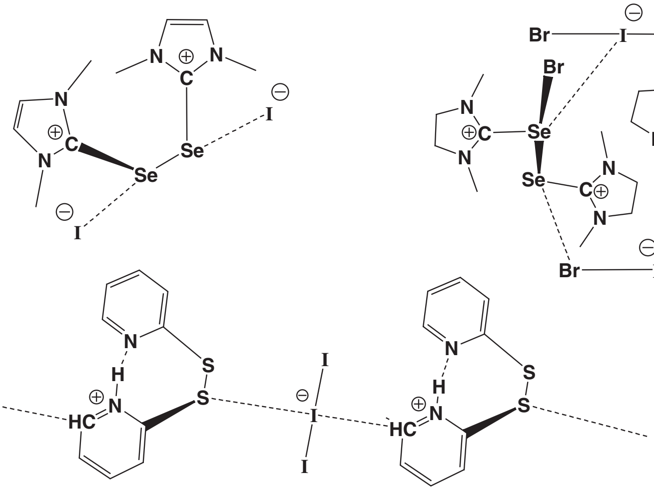


Figure 3 *Examples of cation–anion interactions*

"soft" nucleophilicity of the anions. Increasing extent of cation–anion interactions correlates fairly with Se–Se bond expansion as a consequence of population of the σ*[SeSe] orbital. The solid compound $[(C_5H_8N_2\text{-Se})_2I_2$,[20] prepared by reduction of $(C_5H_8N_2)\text{-SeI}_2$ with tellurium, contains an almost linear I···Se-Se···I fragment (< ISeSe 165.78° and 176.00°) with cation–anion Se···I contacts of 341.0 and 333.0 pm [Figure 3(a)]. Additional secondary contacts (Se···I 362.7 pm) determine a tetracoordination at the corresponding selenium atom and the formation of chains parallel to the *b* axis.

A number of related dications with different extents of cation–anion (n → σ*[SeSe]) overlap have been characterised.[21] In the solid salt $[(C_5H_8N_2\text{-Se})_2Br]^+$ IBr_2^-, obtained from the selone with IBr, one bromine atom is attached to one atom of the Se-Se moiety, and the central iodine atom of the IBr_2^- anion exhibits a weak secondary contact to the other selenium atom [Figure 3(b)].[20] In a related fashion, protonated *bis*-(2-pyridyl)disulfide exhibits a S···I contact involving the central atom of the triodide ions (Figure 4), that are adjacent to a C-H function of the next neighbour molecule [Figure 3(c)].[22]

A very particular compound containing a Se-Se-bridged dication has been obtained by reacting *N,N′*-dimethylimidazolidine-2-selone with iodine in CCl_4 in a 1:1 molar ratio.[21] The asymmetric unit contains both the molecular iodine adduct of the selenium donor molecule and the dication $[(C_5H_{10}N_2\text{-Se})_2]^{2+}$ balanced by two I_3^- ions. The crystal packing features chains of dications asymmetrically bridged by one I_3^- (see Figure 4) (Se···I 359.0 and 349.8 pm). The bridging I_3^- interacts at one end with the terminal iodine atom of the charge-transfer adduct unit by I···I long–range interactions of 419.3 pm. On the basis of structural data, the I_2-adduct unit (Se-I 268.3 and I-I 302.5 pm) can also be seen as deriving from the donor-acceptor interaction between a $[RSe\text{-}I]^+$ fragment and an iodide atom (n[I^-] → σ*[Se-I], see Section 13.2.3.5). A further

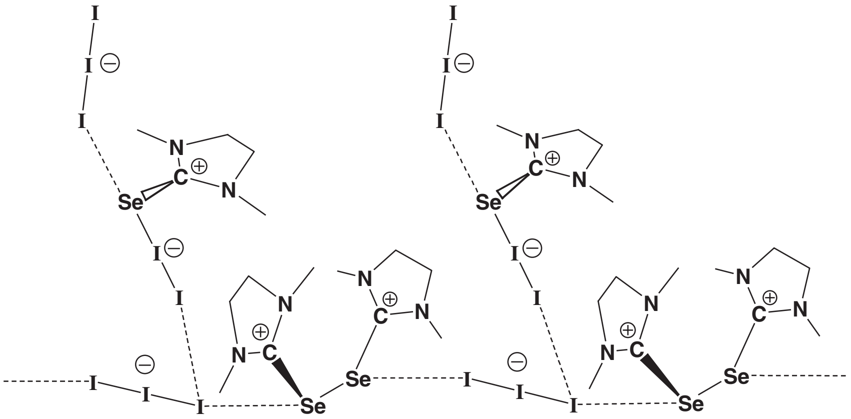


Figure 4 *Se···I and I···I interactions in solid* $[(C_5H_{10}N_2\text{-}Se)_2]^{2+}$, $2\ I_3^-$, $C_5H_{10}N_2\text{-}Se\text{-}I_2$

contact exists between the second molecule of I_3^- and the selenium atom of the adduct unit (386.7 pm), which determines the formation of an almost linear $I(I_3^-)\cdots[RSe\text{-}I]^+\cdots I^-$ system. Both Se–Se (237.2 pm) and Se–I (268.3 pm) bonds are slightly longer than those of non-coordinated diselenides (about 234 pm) and significantly longer than typical Se–I single bonds, respectively.[12]

13.2.3 Chalcogens as Donor Atoms in Molecular Adducts

13.2.3.1 Halogen Adducts of Diorganylsulfides and Selenides

With bromine, diorganosulfides tend to furnish charge transfer adducts, whereas selenides can give equilibria between C.T. adducts and products from oxidative addition, *i.e.* molecular Se(IV) compounds.[23] A particular example of such equilibria is the bromination of selenanthrene reported by *Nakanishi et al.*[24] (see Chapters 8.2 and 10.3).[24]

With molecular iodine or iodine-like electrophiles I-X, diorganylsulfides and selenides react providing molecular charge transfer complexes (see Chapter 8.2)[5,6,10,25] that may undergo intermolecular secondary interactions leading to supramolecular arrays. In the tetrahydroselenophene-diiodine adduct, the Se···I–I arrangement is essentially linear, and additional weak contacts between the "terminal" iodine atom (having acquired donor properties) and the Se atom of a neighbouring molecule (Se···I 364 pm) lead to a polymeric chain structure. The 1,4-diselenan-diiodoacetylene adduct shows a related topology (Figure 5).[26]

The crystal structure of the complexes between iodine and 1,4-diselenane ($[6]aneSe_2 \cdot 2I_2$, Se–I 282.9, I–I 287.0 pm, Se–I–I 180.0)[6] shows discrete molecular units of the adducts hold together by Se···I contacts (388.9–402.2 pm), which contribute to the crystal packing together with several I···I long-range interactions. A slightly stronger Se···I [370.8 pm] secondary interaction is also determinant for the crystal packing of $[6]aneOSe \cdot I_2$.[6] On the other hand, the related adducts of 1,4-diselenane with triiodomethane (Se···I 351.2 and 346.5 pm),

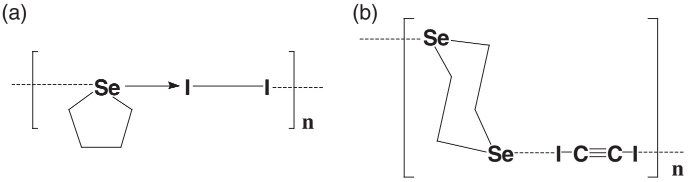


Figure 5 *Topolgy of (a) the tetrahydroselenophene-I_2 and (b) 1,4 diselenenane-diiodoacetylene chains*

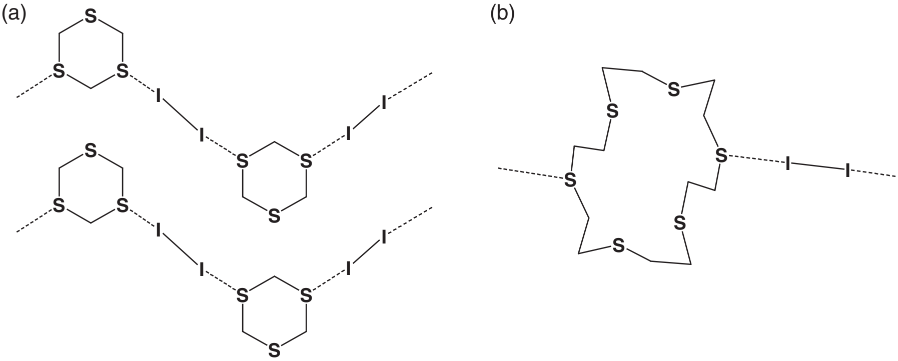


Figure 6 *1:1 Adducts of (a) 1,3,5-trithiacyclohexane ([9]aneS_3) and (b) of [18]aneS_6 with diiodine*

tetraiodoethylene (Se···I 341 pm) and diiodoacetylene (Se···I 333.6 pm) (Figure 5) are cases of weak (n[Se] → σ*[I–C]) interactions between uncharged molecules.[28–30]

13.2.3.2 Thia-and Selena-Crown Ether Complexes

1,3,5-Triselenane ([6]aneSe_3) gives a molecular 1:1 adduct with iodine, exhibiting weak intermolecular Se···I contacts (376.4–395.0 pm).[26]

Thia-crownethers tend to act as bifunctional bridging ligands towards molecular iodine, for instance the 1:1 adducts of 1,3,5-trithiacyclohexane ([9]aneS_3) or of [18]aneS_6 with diiodine (Figure 6). [15]aneS_5 gives a 2:7 adduct with iodine; one I_2-molecule bridges two equivalent [15]aneS_5 ligands that contain three terminal S–I–I functions and one non-coordinated sulfur atom. In [18]ane$S_6(I_2)_4$ the molecules interact weakly through two independent S···I contacts of similar lengths (376 and 378 pm) building up a three-dimensional network (Figure 7).

Interestingly, there is a tendency to obtain only certain stoichiometries of crownether iodine complexes in the solid state, *i.e.* product formation is governed by packing behaviour and solubility of the particular complexes. In solution, 1:1 adducts are often the predominant species.[24,31–34]

The thia-crownether [14]aneS_4 gives with IBr a 1:2 complex that exhibits intermolecular S···I and S···Br contacts, in [16]ane$S_4(IBr)_4$ all sulfur atoms are

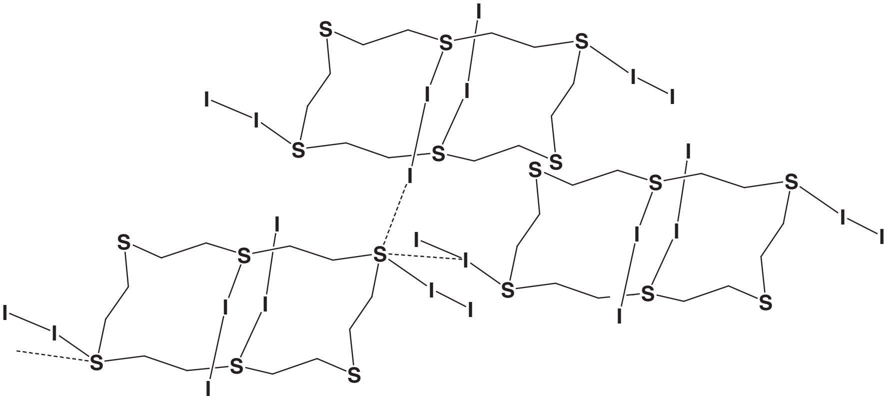


Figure 7 *1:4 Adduct of [18]aneS$_6$ with diiodine; a representative part of the intermolecular S···I contacts shown by dashed lines*

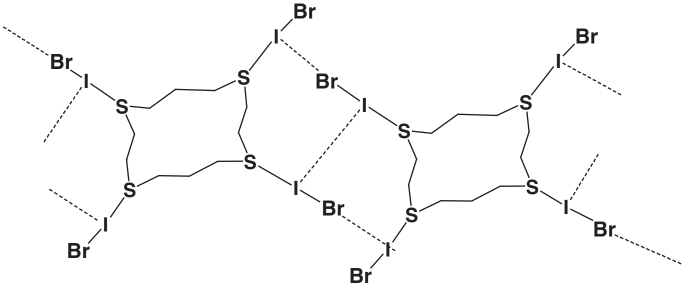


Figure 8 *1:4 Adduct of 16]aneS$_4$(IBr)$_4$; partial view of the intermolecular I···I and I···Br contact pattern within a ribbon*

involved in coordination. Soft–soft interactions, established by I···I and I···Br contacts (Figure 8), generate one-dimensional ribbons, which by additional I···Br contacts give a three-dimensional grid.[35]

13.2.3.3 Reactions of Organic Diselenides with Iodine

In mixtures of organic diselenides with iodine, the charge-transfer-like Se → I coordination is competing with Se–Se bond cleavage. Diphenyldiselenide gives a solid dimeric 1:1 adduct with molecular iodine.[36] One selenium atom of each diselenide is a donor towards molecular iodine (Se–I 299.2 pm, I–I 277.5 pm), whereas the other selenium atom behaves as a very weak acceptor (Se–I 358.8 pm) (Figure 9). Formation of the "square" dimer $(Ph_2Se_2I_2)_2$ allows donor and acceptor selenium and iodine atoms to fulfill the geometric predictions from VSEPR theory (like linear (10-I-2) "hypervalent" and bent (8-I-2) bridging iodine atoms). In the crystal, the squares of $(Ph_2Se_2I_2)_2$ are connected by I···I contacts (412.7 pm)[36,37] in the range of the van der Waals distance.

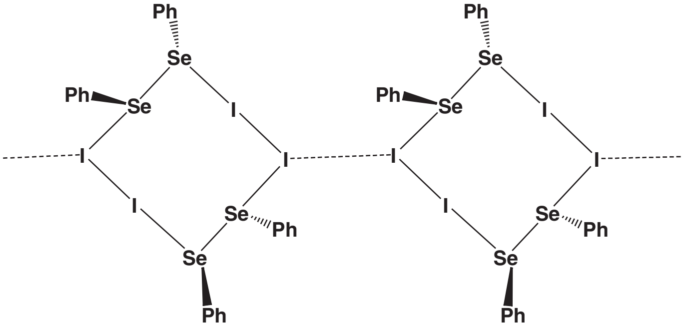


Figure 9 *Chains of rings from* $(Ph_2Se_2I_2)_2$

The same reaction using a more bulky 2,4,6-i-$Pr_3C_6H_3$ organic substituent leads to a different crystalline compound, which contains two equivalents of the diselenide starting material and one equivalent of iodine.[38] This solid may be regarded as an "inclusion compound" of 0.5 equivalent of iodine within the solid diselenide. The iodine molecule is in contact (348.3 pm) with the selenium atoms of two different diselenide molecules (related to each other by a centre of inversion). The diselenide molecules appear to be undisturbed by the weak interaction with iodine; their Se–Se bond length (235.3 pm) is only slightly longer than that of the non-coordinated diselenide (233.9 pm).[39]

13.2.3.4 Coordination Compounds of Thio- and Selenocarbonyl Derivatives with Halogens

Molecular coordination compounds of thio- and selenocarbonyl derivatives with iodine have been known since long as *charge transfer complexes* (Chapter 8.2). Equilibrium constants of the 1:1 adduct formation between selenium donors and diiodine are larger than those of related sulfur donors[39,40] and, generally, their charge transfer complexes with IX (X=I, Br, Cl) are stronger than those reported with selenides and the formation of $[RSe–I]^+$ cations is more likely to occur. Starting from a series of different pentaatomic rings all containing a C=Se group, it has been shown that slight variations in the surroundings of the C=Se function or small changes in the reaction conditions can influence the nature of the final solid products, being molecular (10-I-2) adducts $[RR'C{=}Se \rightarrow I\text{-}I]$,[41,42] ionic (10-I-2) compounds $[(RR'C{=}Se)_2I]^+$ I_n^-,[43] molecular compounds with three-coordinated selenium (10-Se-3) $[RR{-}CSeI_2]$,[37,42,44–46] or dicationic diselenides $[(RR'CSe)_2]^{2+}$ (see also Chapter 8.2). In some cases, ionic compounds with (2c–2e) Se–I bonds in cations $[RR'CSeI]^+$ can be formed, which may exhibit additional anion–cation interactions. Characteristic structural and bonding features of 3c–4e bonding systems with C=S and C=Se ligands have been covered recently by a comprehensive review.[25]

13.2.3.4.1 Intermolecular Association in Complexes $[RR'C{=}E \rightarrow I\text{–}I]$ *(E=S, Se)*. In the 1:1 complex of 4,5-ethylenedithio-1,3-dithiole-2-thione with iodine, the C=S sulfur atom binds the iodine in the usual linear S-I-I fashion (S–I 275.5 pm, I–I 281.2 pm, S–I–I 175.4°), but the packing is determined by the secondary contacts involving the sulfur atoms of the five-membered heterocycle, one of which undergoes a weak intermolecular S···I interaction and the other one exhibits a secondary S···S contact (Figure 10).[47] The reaction of the related 1,3-dithiole-2-thione-4,5-dicarboxylic ester ligand with IBr gives the usual molecular adduct, which is packed in centrosymmetric dimers by weak intermolecular S···I contacts (S···I 367 pm; Figure 11). Again, one of the two endocyclic sulfurs has valuable *intra*molecular S···I contact (336 pm) with the central iodine. In the structure, additional disordered IBr molecules bridge the dimers, so that the final stoichiometry of the adduct results to be 1:1.5. Additional C=O···HC contacts contribute to connect the dimers.[48a]

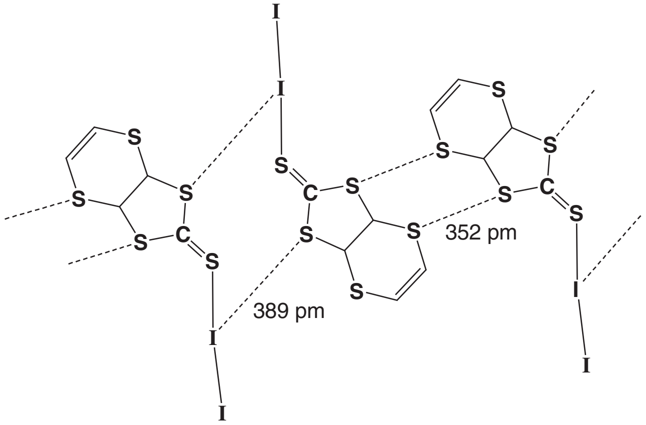


Figure 10 *4,5-Ethylenedithio-1,3-dithiole-2-thione-I$_2$*

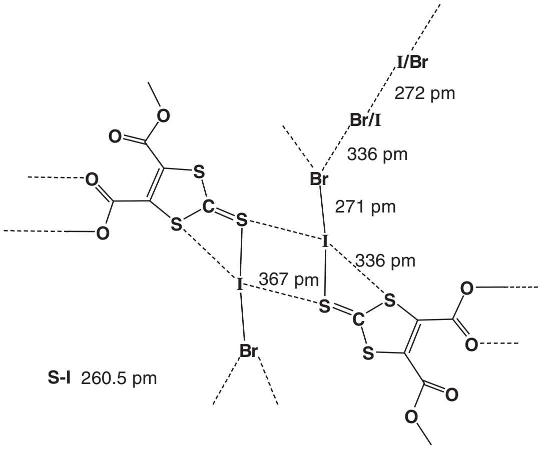


Figure 11 *The 1,3-dithiole-2-thione-4,5-dicarboxylic ester 1:1.5 adduct with IBr*

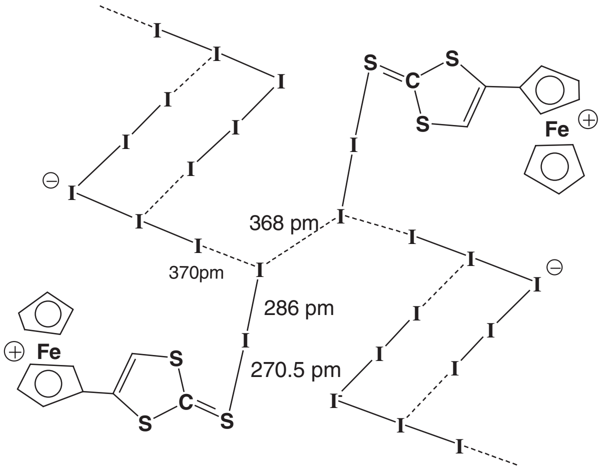


Figure 12 *The polyiodide network determined by I···I cation/anion contacts in 4-ferrocenium-ethylene-1,3-dithiole-2-thione · I_2 adducts balanced by V-shaped pentaiodides*

Attachment of a ferrocenyl substituent in 4-position of the ethylene-1, 3-dithiole-2-thione leads to a ionic product, containing oxidised ferrocenium fragments and linear S–I–I moieties, which are in weak contact with the V-shaped pentaiodide anions. The supramolecular structure is determined by a network of I···I interactions involving cation–cation, cation–anion and anion–anion in the range of 370–390 pm (Figure 12). This structure represents an interesting case of supramolecular structure, in which a paramagnetic centre has been incorporated. Magnetic measurements show a deviation from the Curie–Weiss law below 2.5 K attributed to antiferromagnetic interactions.[48b]

Interestingly, the introduction of two bromomethyl functions in 4- and 5-positions of ethylen-1,3-dithiole-2-thione leads to a packing determined by weak interactions involving also the bromine atoms. One I_2 molecule behaves as an acceptor towards S and as donor towards the second I_2 molecule, which in turn behaves as donor towards the σ^*_{C-Br} orbital (Figure 13). Intermolecular S···Br, CH···Br and I···I contacts make up a three-dimensional network.[48c] Reaction of 5,5-dimethyl-2-selenoxoimidazoline-4-one with iodine provided the first structurally characterised compound of the type $[RR'C{=}Se \rightarrow I{-}I]$.[32] The Se–I bond is shorter (269.9 pm) and the I–I contacts are longer (296.2 pm) than in 1:1 adducts of dialkylselenides with iodine (see Chapter 8.2).

13.2.3.4.2 Cations $[(RR'C{=}Se)_2I]^+$. In the case of *N*-methylbenzothiazole-2(*3H*)-selone (mbts), one equivalent of iodine provides a molecular adduct in dichloromethane solution;[50] crystallisation, however, leads to a ionic compound of the type $[(RR'C{=}Se)_2I]^+I_3^-$.[43] This compound was the first one reported in the literature featuring a two coordinated iodine(I) complex with two donor molecules containing selenocarbonyl groups. In the solid state two molecules of mbts are linearly coordinating a central I^+ ion to give a slightly

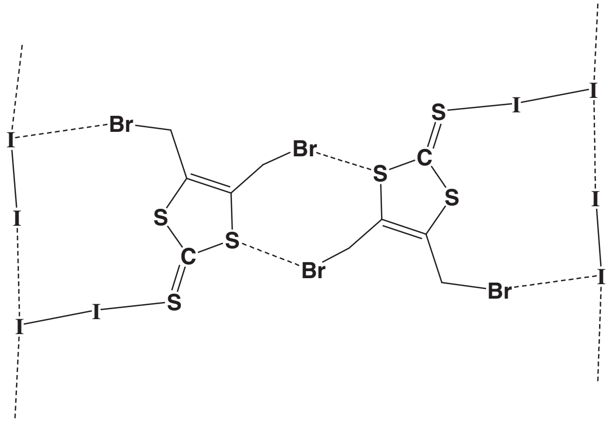


Figure 13 *4,5-Bis-(bromomethyl)ethylene-1,3-dithiole-2-thione-bis-(diiodine) complex*

asymmetric Se–I–Se arrangement [Se–I 280.0, 271.9 pm, Se–I–Se 178.0°]. The unit cell contains two of these cations centrosymmetrically related and balanced by two I_3^- ions. Related I^+ cations with sulfur ligands have been known since long.[43]

13.2.3.4.3 Bromothio- and Iodoselenocarbenium Salts. When the interaction between a selenium donor molecule and the linearly coordinated I–X (X=I, Br, Cl) acceptor is particularly strong, a remarkable fractional negative charge is induced on the terminal X atom, which can behave as donor towards another molecule of acceptor IX.[32,35,50] In the limiting case ionic $[RSe–I]^+\cdots[X–I–X]^-$ systems can be formed. This situation is well documented by the 1:2 adduct of mbts with IBr in which the first IBr molecule is so strongly bonded to the selenium atom that the Se–I distance (256.4 pm) can be formally regarded as a covalent single bond slightly perturbed by anion (donor)–cation(acceptor) interactions [Figure 14(a)] (see Chapter 3. 3). On the other hand, the elongation of the IBr molecule to the value of 312.9 pm and the strong interaction of Br- with a second IBr molecule leads to the formation of an asymmetric IBr_2^- anion [I–Br 280.3 and 264.5 pm] similar to that reported for CsIBr [I–Br 278.0 and 262.0 pm]. The mbts donor molecule also gives a 1:2 molecular adduct with I_2. The structural features of the resulting $RR'C–Se\cdots I_2\cdots I_2$ bent shaped compound do not agree with a ionic pair description as for mbts · 2IBr. In fact, in mbts · $2I_2$ the strong interaction with the selenium atom [Se–I mean value 267.4 pm] lengthens the I–I bond to 303.0 pm (mean value). The further interaction of the terminal iodine atom of the Se–I_2 system with the second I_2 molecule [$I\cdots I_2$ mean value 319.2 pm] is not strong enough to form a triiodide ion. This system can be better described as $RSe\text{-}I^+\cdots I^-\cdots I_2$, which resembles that observed in "V-shaped" pentaiodides in which an I^- ion binds two diiodine molecules $I_2\cdots I^-\cdots I_2$.

The very nucleophilic C=S function of 1,3,4,5-tetramethylimidazolium-2-dithiocarboxylate gives a molecular 1:1 C.T. complex with iodine, but with

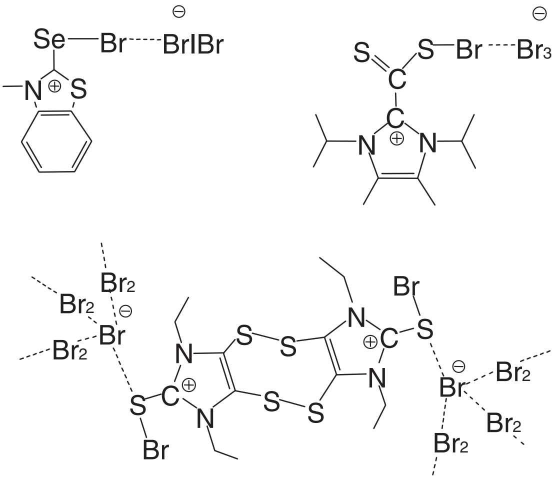


Figure 14 *Examples of Br···Br cation–anion contacts*

bromine the formation of a 1:2 product is favoured. The solid compound is an ion pair from a cation containing a remarkably short S–Br single bond (214.6 pm) and a distorted tribromide anion exhibiting a significant cation–anion Br···Br contact (321.7 pm) [Figure 14(b)].[51] The reaction of [Pd(Et_2timdt)$_2$] with an excess of Br_2 yielded few crystals of 4,5,9,10-tetrathiocino-[1,2-*b*:5,6-*b*′]-1,3,6,8-tetraethyl-2,7-di(bromothio)diimidazolium dications bearing two terminal bromothiocarbenium functions, balanced by two Br^- counterions which linearly interact with the S–Br functions ($np^2 \rightarrow \sigma^*_{S-Br}$) on the side of the sulfur atom. At the same time, each Br^- acts as donor towards three Br_2 molecules [Figure 14(c)], thus generating a tridimensional network by additional Br···Br contacts. Interestingly, the Br_2 molecules are trapped in the crystals so strongly that the compound results to be stable at air for long time without loss of Br_2. This organic donor can be rightly considered a good reservoir of bromine.[52]

13.2.3.5 *The Reactions of Phosphine Sulfides and Selenides with Iodine*

Depending on the conditions, Ph_3PS give a molecular 1:1 adduct, a V-shaped 2:3 complex in which two of the 1:1 adducts are linked by a bridging I_2 molecule,[53] or a 1:3 complex that exists as supramolecular network made up from stepped layers of polyiodide ribbons and domains of aryl groups.[54] Within this network, the ribbons may be regarded as another polymeric version of the I_5^- ion, involving iodide ions that are in donating contact with three I_2 molecules within the ribbon and with the iodine atom of the terminal Ph_3PSI^+ unit. Stepwise packing of the ribbons leads to 410–417 pm contacts between the iodine atoms of adjacent ribbons (Figure 15).[54]

Phosphine selenides are stronger soft donors than the sulfides.[55] The solid 1:1 adduct of *i*$Pr_3P{=}Se$ with I_2 is ionic (*i*$Pr_3PSe)_2I^+$ I_3^-; reaction of

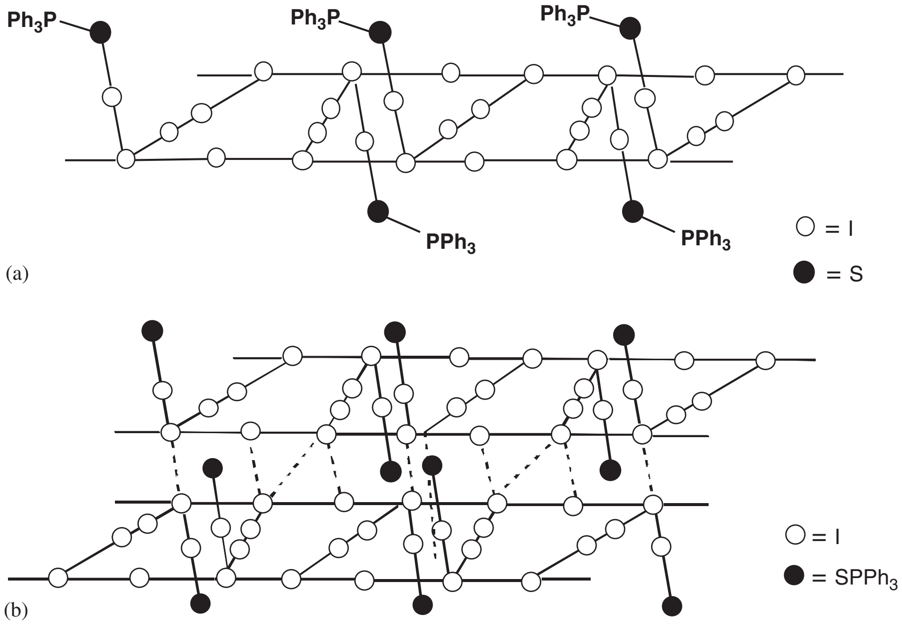


Figure 15 *(a) Ribbon structure of $Ph_3PS(I_2)_3$ and (b) stepped layers of $Ph_3PS(I_2)_3$ ribbons*

tri-t-butylphosphane selenide with one equivalent of iodine, however, leads to a solid product that contains both, a molecular 1:1 adduct *t*Bu$_3$PSe–I–I and a ionic species (*t*Bu$_3$PSe)$_2$I$^+$ I$_3^-$ [Figure 16(a)] in the same crystal.[56] Both kinds of species exhibit Se–I distances of about 276 pm that indicate bonds orders of 0.5. In other molecular adducts R$_3$PSe–I–I, more electron-releasing substituents (like dialkylamino groups) lead to stronger Se–I bonds, which correlate with decreasing bond orders within the PSe and within the I···I moieties. More electron-withdrawing substituents (like R=Ph) have the opposite effect on the P–Se–I–I moieties.[57,58] The reaction of tri-*t*-butylphosphine selenide with 1.5 equivalents of iodine leads to a solid product that contains pairs of (*t*Bu$_3$PSe)$_2$I$^+$ cations intercalated between corrugated layers of the polymeric I$_5^-$ anions. The (*t*Bu$_3$PSe)$_2$I$^+$ cation pairs are well separated from the pentaiodide layers; they exhibit, however, pairs of Se···Se contacts within the cation pairs.[56,57]

With two or more equivalents of iodine, phosphine selenides can furnish iodoselenophosphonium salts R$_3$PSeI$^+$I$_n^-$ that exhibit certain degrees of cation–anion I···I interactions. Reacting (Me$_2$N)$_3$PSe and (Morph)$_3$PSe (Morph=morpholino) with two equivalents of iodine provides the solid compounds (Me$_2$N)$_3$PSeI$_4$ and (Morph)$_3$PSeI$_5$[25] [Figure 16(b)]; *i*Pr$_3$PSe and *t*Bu$_2$*i*PrPSe with excess iodine provide *i*Pr$_3$PSeI$_7$ and *t*Bu$_2$*i*PrPSeI$_7$.[59] All these compounds are examples of [R$_3$PSeI]$^+$ cations with different extents of cation–anion interactions. The nucleophilicity of the iodide anion is suppressed by its coordination with increasing amounts of iodine; the decreasing nucleophilicity

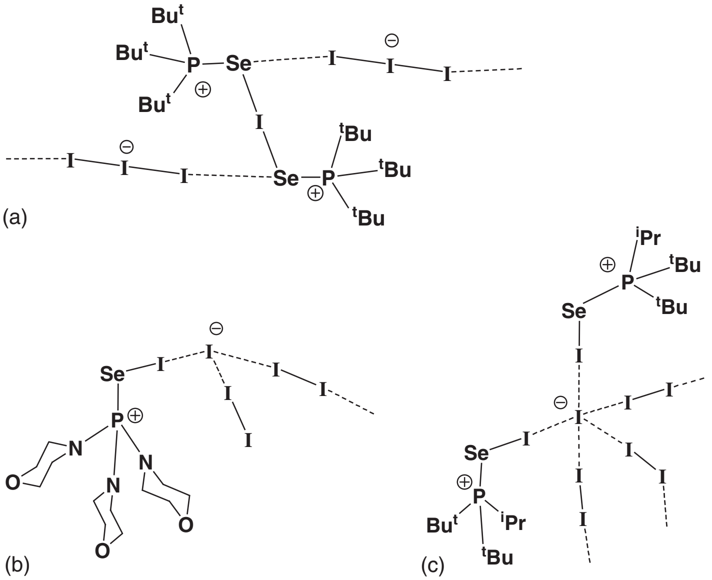


Figure 16 *(a) Cation–anion chains of* $(tBu_3PSe)_2I^+\ I_3^-$*, (b) cation–anion contacts in* $(Morph)_3PSeI^+\ I_5^-$*, and (c) cation–anion contacts in* $tBu_2iPrPSeI^+\ I_7^-$

($I^- > I^-{\cdot}I_2 > I^-{\cdot}2I_2 > \ldots$) correlates with increasing covalent Se–I bond orders, indicated by Se–I distances that are influenced by the different extents of ($n[I_x^-] \rightarrow \sigma^*[\text{Se–I}]$) overlap.

The slight steric differences between the alkyl groups of the cations lead to quite different far-orders of their polyiodide anion structures. In solid tBu$_2i$PrPSeI$_7$ [Figure 16(c)], one iodide anion bridges two of the iPr$_3$PSeI$^+$ cations and is in further contact with three I_2 molecules; the other I^- anion is in contact with five I_2 molecules.[59]

13.3 Supramolecular Aspects of Structures from Lowvalent and Divalent Chalcogen–Halogen Compounds

13.3.1 Association of Sulfenyl, Selenenyl and Tellurenyl Halides

13.3.1.1 Compounds REX (X=Cl, Br, I)

The first structure determination on a sulfenyl iodide was that of thermally labile Ph_3CSI.

In the solid state the molecules pack in a way that zigzag chains ···S–I···S–I··· (angular I···S–I, approximately linear S···I–S) are formed.[60] The kind of chain topology is similar as that of the Se–I···Se–I···Se–I chains of dureneselenenyl iodide solid (2,3,5,6-Me_4C_6HSeI). Channels of weak soft–soft interactions between the Se–I moieties of the molecules are bridged by staples of aromatic rings. These are arranged in slipped-sandwich-type pairs. The two Se–I groups of such a pair of molecules are directed to two different "soft channels" [Figure 17(a)]. These "channels" are made up from zigzag chains that consist of covalent Se–I bonds and secondary Se···I contacts (approximately linear 10-I-2).[61]

Mesityleneselenenyl iodide (2,4,6-$Me_3C_6H_2SeI$) has a very similar molecular structure, but its secondary interactions are different. Bands of soft–soft interactions are surrounded by staples of the aromatic substituents [Figure 17(b)]. The orientation of the molecules within the crystal allows each selenium atom to approach one iodine atom (383.9 pm) from a neighbouring molecule within a staple. Each iodine atoms is also in contact with two iodine atoms (384 pm) from neighbouring molecules of an adjacent staple. Including these interactions, the Se environment can be classified as (10–Se–3), whereas the iodine atoms exhibit one primary (covalent) and three secondary contacts allowing the description as (12–I–4). The longer intermolecular Se···I distance in MesSeI, compared with DurSeI, correlates with the larger coordination number of iodine (two additional secondary I···I contacts in MesSeI). In solid 2,4,6-*i*-$Pr_3C_6H_2SeI$ exists a network of weak Se···I and I···I interactions resembling the L-shaped motive of $I_2 \cdots I_2$ interactions within the sheets of solid iodine.

A compound with a supramolcecular zigzag array related to Ph_3CSI and 2,4,6-*i*-$Pr_3C_6H_2SeI$ is *p*-chlorophenylselenoacetylene (Figure 18). The very weak secondary Cl···Se bonds (370 pm) are in the range of the sum of Cl and Se *van der Waals* radii (380 pm).[62]

The solid benzenetellurenyl iodide PhTeI is associated in a different way: predominant Te···Te interactions lead to an approximately planar tetramer, the participating tellurium atoms can be classified as planar 2+2 coordinated (12–Te–4).[63]

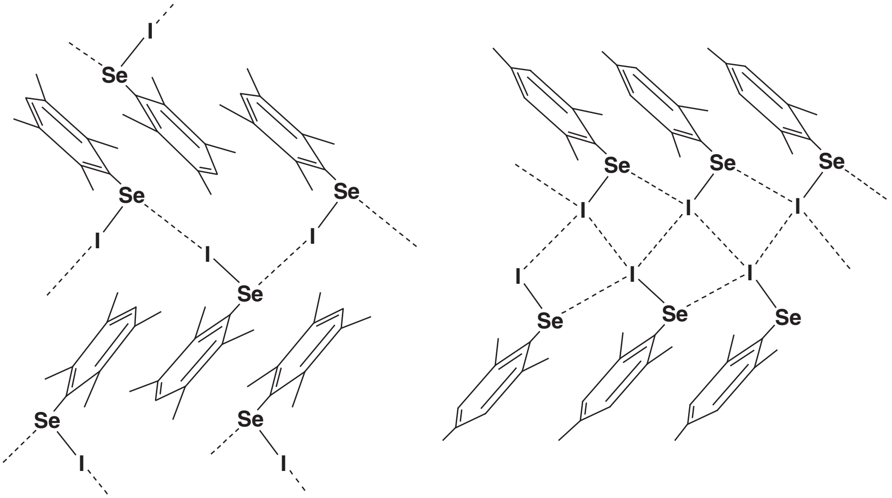


Figure 17 *Intermolecular interactions in solid (a) 2,3,5,6-$(CH_3)_4C_6HSeI$ and (b) 2,4,6-$(CH_3)_3C_6H_2SeI$*

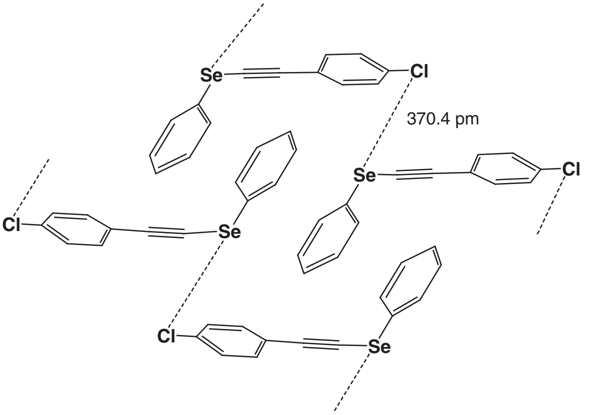


Figure 18 *Se···Cl contacts in solid p-chlorophenyl(phenylseleno)alkyne*

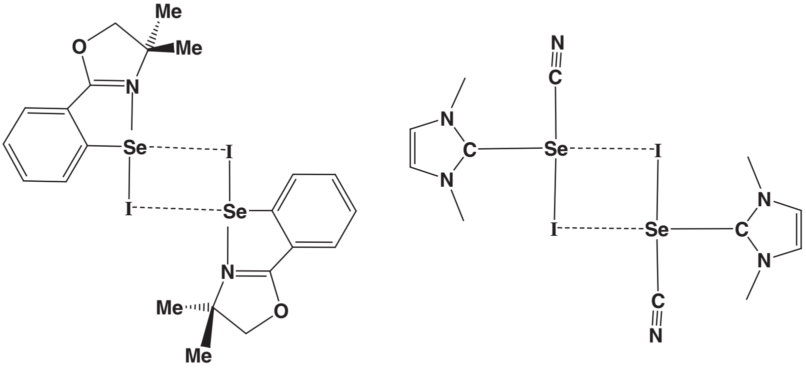


Figure 19 *Se–I···Se contacts between T-shaped selenium functions*

13.3.1.2 Association of Sulfenyl, Selenenyl and Tellurenyl Halides with Chelating Substituents

Donors can stabilise selenenyl iodides, when competing coordination of the same donor with molecular iodine is avoided.

Internal amino[64] or imino[65–67] chelate functions can achieve this type of selenenyl iodide stabilisation. 2-(4,4-Dimethyl-2-oxazolinyl)benzeneselenenyl iodide[66] exhibits weak *inter*molecular Se···I contacts (372.5 pm) leading to a centrosymmetric dimer with longer N → Se bonds (213.3 pm) and shorter Se–I bonds (277.7 pm) [Figure 19(a)] compared to the strictly monomeric 4-ethyl-substituted isomer (Se–N 207.4).[65] The structure is related to the dimer of the T-shaped cyano derivative [Figure 19(b)].[68]

From the reaction of *bis*-(morpholinoselenocarbonyl)triselenide with iodine was produced the solid crystalline compound (*N*-morpholinocarbodiselenoato)selenium(II)iodide (Figure 20).[69] The solid compound consists of

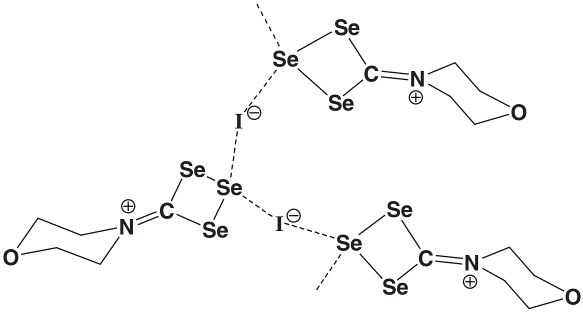


Figure 20 *Chains from (N-morpholinocarbodiselenato)selenium(II) iodide*

chains from cationic moieties $[O(C_2H_4)_2N{=}CSe_3]^+$ that are μ^2-bridged through the central selenium atom by iodide anions. The compound $[O(C_2H_4)_2N{=}CSe_3I]$ may also be described as containing triselenetane ring or as Se^{2+} cation that is chelated by a $[O(C_2H_4)_2N{=}CSe_2]^-$ (morpholinodiselenocarbamato) ligand. Within an *isolated* $[O(C_2H_4)_2N{=}CSe_3]^+$ cation, all selenium atoms would adopt 8-electron shells (8–Se–2); in that respect the heterocycle is the same as in CBr_2Se_4 (Figure 22, see below). The central selenium atom of the cyclic triselenide moiety (in β-position from the onium-like sp^2 carbon atom) in $[O(C_2H_4)_2NCSe_3I]$, however, μ_2-bridged by iodide anions, assumes a trapezoidal coordination around it and a roughly planar structure (12–Se–4). Within the chain structure, there are two crystallographically different types of cations. Those with the longer Se···I contacts (318 pm) exhibit Se–Se bond lengths of 236 and 239 pm (longer than average Se–Se distances); the other type of cations allows closer Se···I contacts (304 and 308 pm) that correlate well with increasing expansion of the adjacent Se–Se bonds (238 and 244 pm). These Se–Se bond expansions suggest site-dependent extent of the ($n[I^-] \rightarrow \sigma^*[Se–Se]$) overlap on the formation of polymeric chains of ions. Each I acts as donor towards two neighbouring cations in a bent $Se\cdots I^-\cdots Se$ sequence. A related chain-like dithiocarbamatoselenium iodide with μ2-bridging iodide ions (Se–I 312.4 and 323.2 pm) has also been reported.[70] Dithiocarbamatotellurium halides exhibit related kinds of helical polymeric structures. From the chloride to the bromide (Figure 21) and iodide, the differences between the shorter ("primary") and the longer ("intermolecular") Te–X contacts are decreasing (Te–Cl 268.6, 311.2; Te–Br 286.7, 316.9; Te–I 310.8, 327.9 pm).[71,72]

Solid 1,2,3-triselenetane-4-(*Se,Se*-dibromoselone) (CBr_2Se_4) is a three-dimensional network from planar molecules (Figure 22).[73] The carbon atom is part of a T-shaped $CSeBr_2$ group and of the triselenetane ring. As in the abovementioned $[O(C_2H_4)_2N{=}CSe_3]^+$ cation,[69] the central selenium atom ("β–Se") undergoes intermolecular interactions: these and additional secondary contacts involving both α–Se atoms and all three atoms of the linear Br–Se–Br group lead to a complicated three-dimensional network (see Ref. 72).

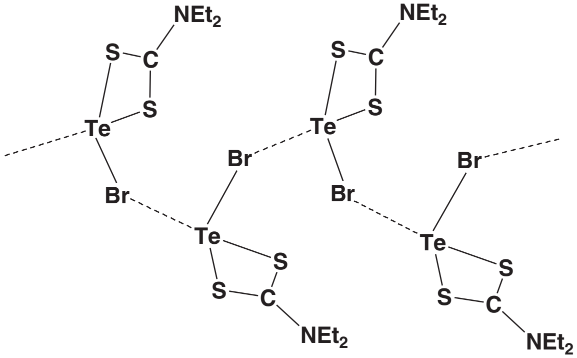


Figure 21 *Chains from a dithiocarbamatotellurium(II) bromide*

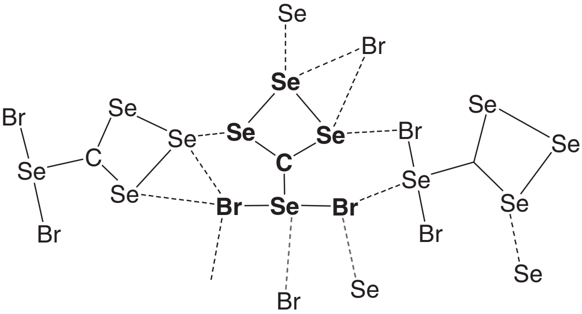


Figure 22 *Intermolecular contacts in solid CBr_2Se_4*

13.3.2 Oxidative Halogen Addition to Chalcogenocarbonyl Functions $R_2C{=}Y$ and to Phosphine Selenides $R_3P{=}Se$

13.3.2.1 Association of Molecular (10–E–3) Compounds [RR′CEX₂]

T-stacking by selenium-halogen contacts leading to (12–Se–4) arrangements is occurring in many T-shaped selenocarbonyl halogen adducts, like in the dichloromethane-solvated dimer of the *N*-methylbenzothiazol-2-selone bromine adduct [Figure 23(a)] or in the chain-like arrays of the solvent-free polymer [Figure 23(b)] or in the *N,N′*-dimethylimidazoline-2-selone bromine adduct (Figure 24).[68,74–76] Bromine adducts of imidazole-derived thiones are monomeric; the related "BrCN-adduct"[77] (compare Figure 19b) can regarded as a cyanothioimidazolium bromide with S···Br (327 pm) cation–anion interaction.

First structurally known iodine derivatives of this kind were products from the iodination of 1,3-dimethyl-4-imidazoline-2-selone,[44] of 1,2-*bis*-(3-methyl-4-imidazoline-2-selone)ethane,[44] and of 1,3-diisopropyl-4,5-dimethyl-4-imidazoline-2-selone.[42] The fragments for the three compounds

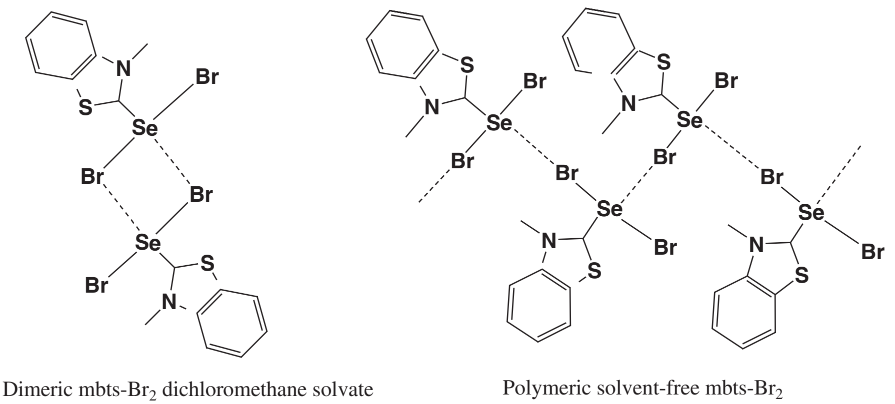


Figure 23 *T-stacking of N-methylbenzothiazol-selone dibromide*

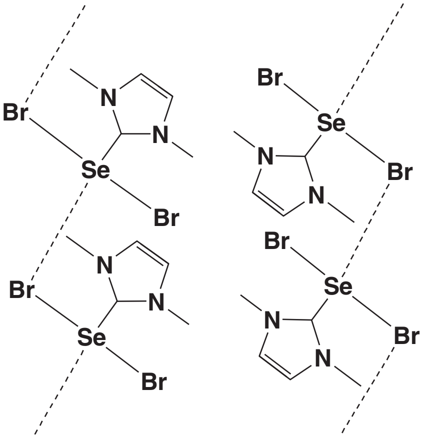


Figure 24 *T-stacking of imidazolidine-2-selone dibromide*

are asymmetric and roughly linear [I–Se–I ranging from 175.4 to 178.6 pm] and the CSeI2 moieties adopt T-shaped geometries (Se–C single bonds, Se–I bond orders close to 0.5), like those of internally chelated selenenyl iodides. From 1,3-diisopropyl-4,5-dimethyl-4-imidazoline-2-selone with a slight excess of iodine an adduct of the composition ($RR'CSeI_2.0.5\ I_2$) was obtained. In this centrosymmetric compound, an iodine molecule (I–I 276.6 pm) is inserted (I···I 345.1 pm) between two T-shaped CSeI2 functions.[45] The Se–I bonds that are participating in contacts with the inserted I_2 molecule are longer (285.1 pm) than the terminal ones (275.6).

From 1,1′-*bis*-(3-methyl-4-imidazoline-2-selone)methane with iodine bromide, a solid compound containing disordered molecules with T-shaped CSeI2 and Br–Se(C)–I functions in the same crystal was isolated; from 1,2-*bis*-(3-methyl-4-imidazoline-2-selone)ethane with iodine bromide, a solid

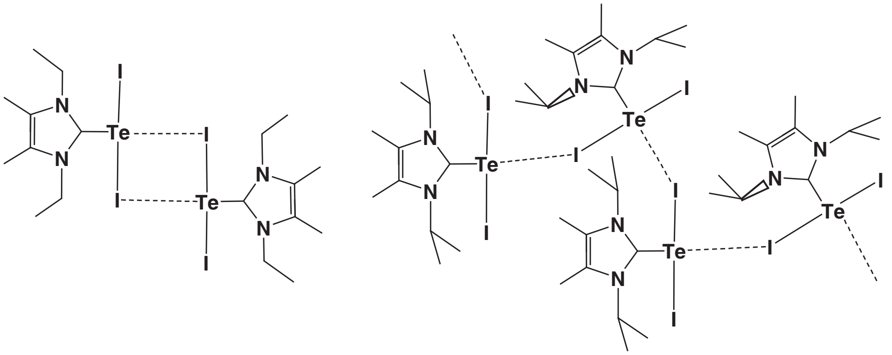


Figure 25 *Rings and chains of T-stacking of $CTeI_2$ moieties*

compound containing a molecular species with two (non-disordered) T-shaped Br–Se(C)–I functions is formed.[78] Interestingly the Se–I bond distances (260.6 and 262.9 pm) are shorter than the Se–Br ones (289.7 and 276.6 pm). Therefore the compound can be regarded as deriving from donor–acceptor interactions between Br^- anions and the Se atoms of $[Se–I]^+$ fragments.

Compared with S and Se, the tendency to undergo intermolecular "T–T" interactions is larger in Te compounds. Reaction of 2,3-dihydro-1,3-diethyl-4,5-dimethyl-2*H*-imidazol-2-tellurone with iodine leads to T-shaped 2,3-dihydro-1,3-diethyl-4,5-dimethyl-2*H*-imidazol-2-ylidene-diodotellurium. This compound exhibits different Te–I bond lengths: Te–I(1) 298.9 and Te–I(2) 289.7 pm [Figure 25(a)]. The longer Te–I distance involves the iodine atom that participates in intermolecular interactions (Te···I 356.4 pm) that lead to a centrosymmtric dimer.[79] When the bulkier 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene reacts with tellurium tetraiodide, the resulting solid T-shaped adduct packs as a helical polymer through Te···I contacts[80] [Figure 25(b)].

13.3.2.2 *Packing of Solid Phosphine Selenide Dibromides RR'_2PSeBr_2*

Bromination of phosphine selenides leads to molecular phosphine selenide dibromides that contain T-shaped P-$SeBr_2$ functions. Structural investigation of a series of closely related trialkylphosphine selenide dibromides RR'_2PSeBr_2 (R,R′=*i*Pr, *t*Bu) revealed remarkable differences in the packing of these T-shaped compounds.[81]

From $i\text{Pr}_3\text{PSeBr}_2$ two different crystalline phases were isolated. The intended preparation from $i\text{Pr}_3\text{PSe}$ with Br_2 led by recrystallisation of the crude product from dichloromethane/pentane (vapour diffusion method) to monoclinic crystals (phase #1). Bromination of $i\text{Pr}_3\text{PSe}$ with an excess of bromine led to a mixture of products from which a few single crystals of phase #2 were collected.

In both phases, the T-structures around Se are distorted by non-equidistant Se–Br bonds and by PSeBr angles that are larger than 90°. In the monomeric molecule $i\text{Pr}_3\text{PSeBr}_2$#1 the BrSeBr group differs from linearity by nearly 13°

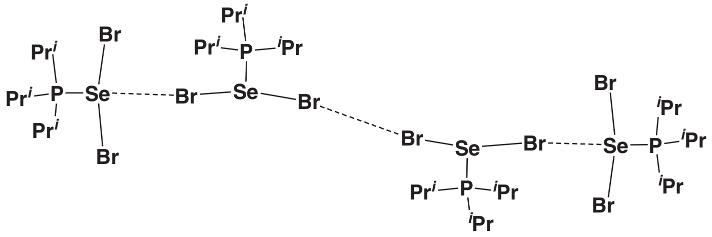


Figure 26 *T-stacking of the iPr$_3$PSeBr$_2$ (phase #2) tetramers*

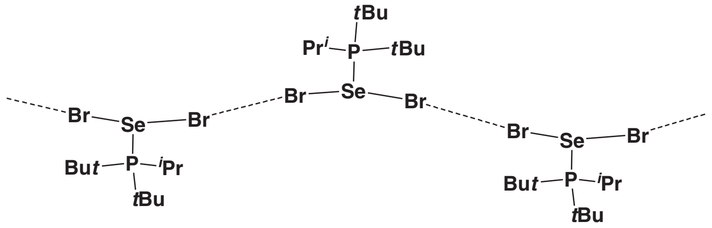


Figure 27 *Array of molecules tBu$_2$iPrPSeBr$_2$ with Br···Br contacts*

and from equidistance by about 12 pm (252.5 and 264.4 pm). One of the *i*-propyl groups adopts a conformation with a transoid H–C(1)–P–Se arrangement; this hydrogen atom is in contact with the selenium atom of an adjacent molecule. The orientation of the P–C(1) bond is about orthogonal to the BrSeBr vector; with respect to the central C atoms of one of the two other *i*-propyl groups each, the two Br atoms are in nearly identic manner in *synperiplanar* arrangements [Br(1)SePC(7) –28.5° and Br(2)SePC(4) 29.9°]. *i*Pr$_3$PSeBr$_2$#2 consists of two crystallographically different molecules that can be regarded as part of a centrosymmetric tetramer, when weak intermolecular Se···Br and Br···Br contacts are considered (Figure 26). The conformations of both *i*Pr$_3$PSe groups within #2 are very similar to those in monomeric *i*Pr$_3$PSeBr$_2$#1. With respect to their BrSeBr functions, both molecules (*terminal* and *bridging*) of #2 are less distorted (Se–Br *terminal molecule*: 257.6/260.2 pm; *bridging molecule*: 254.2/260.6 pm) than that of *i*Pr$_3$PSeBr$_2$#1. The selenium atom of the terminal molecule of #2 exhibits a contact to one of the bromine atoms [Se(1)Br(3) 346.2 pm] of the bridging molecule; the other bromine atoms of two neighboured bridging molecules exhibit a Br(4)···Br(4#) contact of 361.2 pm. In summary, the latter weak *soft* intermolecular interactions in phase #2 correlate with a decreasing distortion of the BrSeBr groups and with very slight (0.5 pm) expansion of the P–Se bonds.

In *t*Bu$_2$(*i*Pr)PSeBr$_2$ intermolecular Br···Br contacts (358.90 pm) between T-shaped moieties lead to wave-like chains (Figure 27) that are packed into layers in the crystal. The conformation of the H–C–P–Se moiety in *t*Bu$_2$(*i*Pr)P-SeBr$_2$ (involving the methyne proton from the *i*-propyl group) is synperiplanar ($\Theta = -43°$); the PSe bond is longer (230.39 pm) and the deviation of the BrSeBr

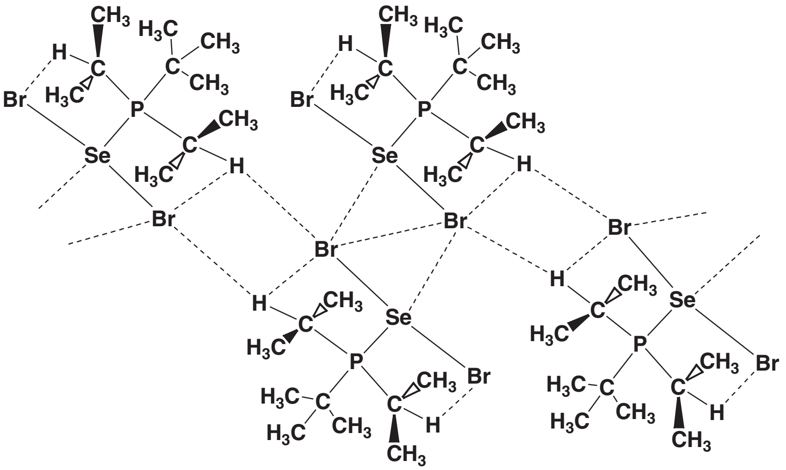


Figure 28 *Se···Br, Br···Br and H···Br contacts in solid tBuiPr$_2$PSeBr$_2$*

group from linearity (BrSeBr 159°) is larger than in any other known R$_3$PSeBr$_2$ structure.

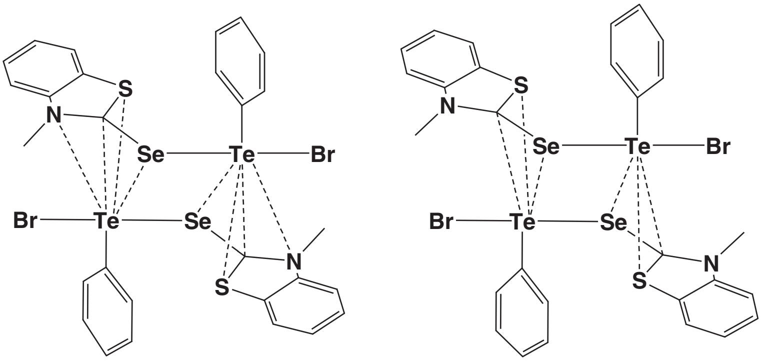
Solid *c*-Hex$_3$PSeBr$_2$ (*c*-Hex=cyclohexyl)[82] exhibits a somewhat related arrangement of wave-like chains; significant Br···Br contacts (361 pm) exist, however, only between *pairs* of one of the kind of crystallographically equivalent molecules, the other 50% of molecules do not exhibit soft–soft interactions.

Quite different is the packing of *i*Pr$_2$*t*BuPSeBr$_2$, which consists of centrosymmetric dimers due to the weak Se···Br interactions (Figure 28). Like in monomeric *i*Pr$_3$PSeBr$_2$#1, intra- and intermolecular CH···Br are also playing a significant part. Two T-shaped PSeBr$_2$ groups pack close together in a way, that the *bridging* Br atom of one molecule exhibits contacts (in the range of little less than van der Waals distances) to the Se atom (382 pm) and to the bridging Br atom (388 pm) of the neighbouring molecule. The Se–Br bond involved in these intermolecular interactions is shorter (253.6 pm) than the "terminal" Se–Br bond (264.9 pm).[81]

In summary, steric strain from *t*-butyl groups correlates with increasing deviation from linearity of the Br–Se–Br groups and with increasing P–Se distances. There is, however, no straightforward correlation of intermolecular interactions (Se···Br, Br···Br, Se···H, Br···H), steric effects and non-equidistance of Se–Br bonds in the series of related trialkylphosphane selenide dibromides.

13.3.3 Complexes of Chalcogen Donors with Organotellurium Electrophiles

Arenetellurenyl halides are dihalogen-like electrophiles: nucleophiles coordinate with tellurium and generate in many cases linear Y–Te–X arrangements (Y=O, S, Se, Te nucleophile donor atom, X=Cl, Br, I). Examples with Se- or Te-containing ligands are not so numerous.[9,83]



mbts-Te(Ph)Br, molecule **A** **mbts-Te(Ph)Br,** molecule **B**

Figure 29 *T–T interactions through intermolecular contacts*

The solid complex of *N*-methylbenzothiazol–2(3H)-selenone (mbts) with Te(Ph)Br contains two symmetry-independent molecules, both of which pack in a way that weak dimers through "T–T" contacts are formed (Figure 29). In molecule A the distance between the Te atom and the neighbouring conjugated π-system is 365.6 pm, and the Te atom is positioned over the central carbon atom of selenoamide function (Te···Se 413.8; Te···S 396.1; Te···N 393.4 pm). In molecule B, the distance from Te to the π-system is 370.5 pm, and the Te atom is "shifted" away from the central carbon atom towards the endocyclic sulfur atom (Te···Se 422.7; Te···S 390.6; Te···N 450.2 pm). Related "T–T" contacts are a general kind of packing for Se and Te-centred T-structures.

There are a number of examples known from weak-halogen bridges between T-shaped Y–Te–X complexes, like tuTe(Ph)Cl [Figure 30(a)]; related weak cation–anion interaction occurs in the 2:1 complex $[tu_2Te(Ph)]^+$ Cl^- [Figure 30(b)]. The weak contact is generally the one *trans* to the Te–C bond ("trans effect" of the strong Te–C bond).[84,85]

Tris(morpholino)phosphine selenide and tris(dimethylamino)phosphine selenide are among the strongest coordinating ligands towards PhTeCl and PhTeBr.[86–88] In these complexes, loose "T—T" association is apparently precluded by bulky ligands. Related tellurenyl iodide complexes $R_nR'_{3-n}PSeTe(Ar)I$ (R, R′=*i*Pr, *t*Bu; Ar=4-methylphenyl or 2,4,6-trimethylphenyl) are also monomeric;[89] with excess of the tellurenyl halide abstraction of the iodide anion from the primary product occurs and aryltelluroselenophosphonium aryldiiodotellurate(II) salts are formed.[89] The salt, shown in Figure 31(a), exhibits a unique kind of Te···Te interaction (318 pm) between two-coordinated (8–Te–2) and T-shaped (10–Te–3) atoms. With consideration of this Te–Te bond, the tellurium atom from the cation becomes T-shaped and the one from the anion becomes four-coordinated (non-planar 10–Te–4).

Thermal decomposition of a 1:2 product with loss of a mesityl (2,4,6-trimethylphenyl) substituent furnished the crystalline compound $(iPr_3PSeTeI)_2TeI_6$ in which two of the unusual cations $iPr_3PSeTeI^+$ are stabilised

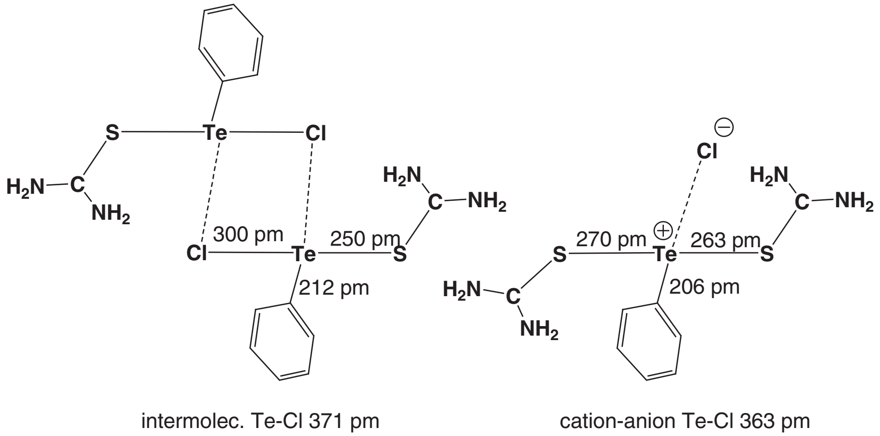


Figure 30 *Thiourea 1:1 and 2:1 complexes of benzenetellurenyl cloride*

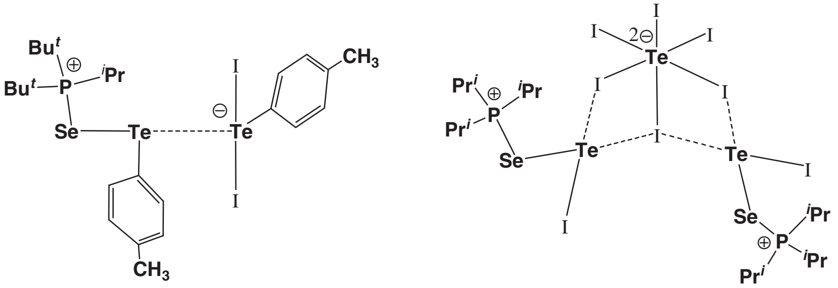


Figure 31 *Cation–anion interactions in (telluroseleno)phosphonium salts*

through iodine-bridging soft–soft interactions with a distorted TeI_6^{2-} anion [Figure 31(b)].[89]

In solid $dppeSe_2[Te(I)Mes]_2$, the bidentate phosphine selenide ligand $Ph_2P(=Se)CH_2CH_2P(=Se)Ph_2$ ($dppeSe_2$) is bridging two T-shaped SeTe(Mes)I moieties (Figure 32) to give centrosymmetric binuclear complexes.[90] The molecules are packed in a way that allows side-on intermolecular soft–soft interactions in pairs of approximately linear Se–Te–I units, thus linking the molecules to chain-like supramolecular arrays. The "T-T" Te···I distances (399 pm) are in the order of the sum of van der Waals radii.

13.3.4 Intermolecular Interactions in Tellurium(II) Halide Complexes with S or Se Donors

Tellurium dihalide complexes L_2TeX_2 (L=ligand) tend to give planar 4-coordinated structures.[2,3,9] From bidentate phosphine selenides $dppmSe_2$ [$Ph_2P(=Se)CH_2P(=Se)Ph_2$] and $dppeSe_2$ two different kinds of 1:1 complexes

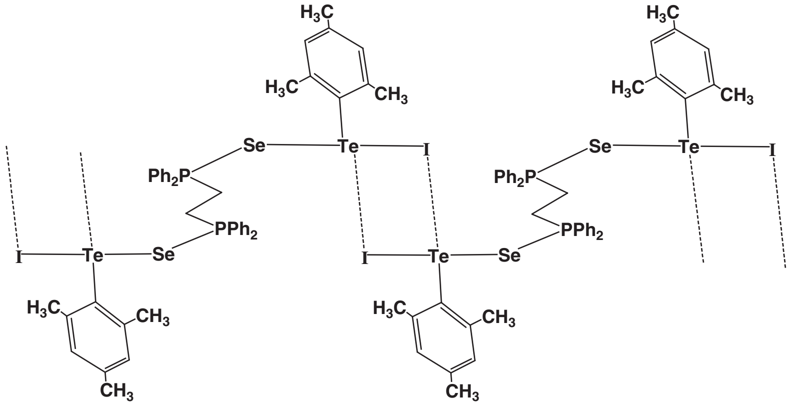
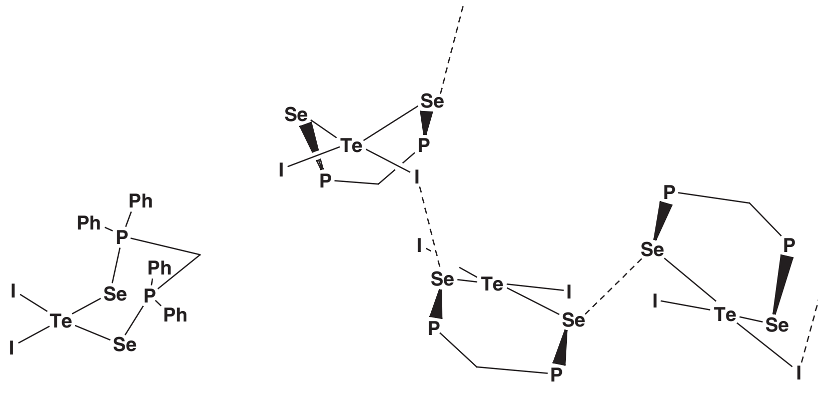


Figure 32 *T-stacking in dppeSe$_2$(MesTeI)$_2$*



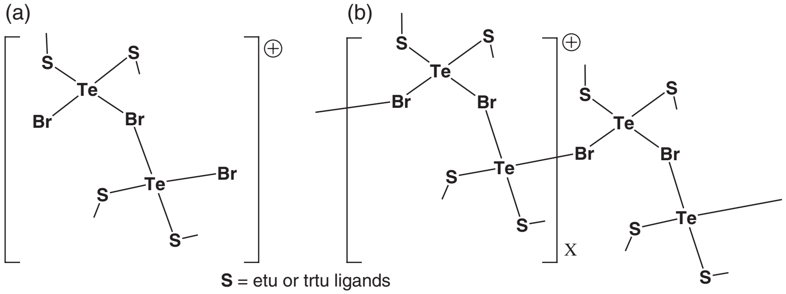
Se(1)···Se(1#) 345 pm, Se(2)···I (2#) 415 pm

(a) (b)

Figure 33 *Molecular structure of (a) dppmSe$_2$TeI$_2$ and (b) weak intermolcular Se···I and Se···Se contacts*

with tellurium diiodide were isolated: dppmSe$_2$TeI$_2$ is a molecular six-membered chelate complex (12–Te–4) [Figure 33(a)] that exhibits intermolecular Se···I and Se···Se contacts [Figure 33(b)], whereas dppeSe$_2$TeI$_2$ crystallises as helical coordination polymer containing bridging dppmSe$_2$ ligands between *trans*-TeI$_2$ moieties.[90]

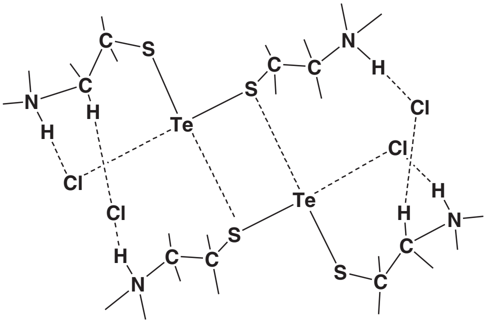
In compounds Te$_7$(etu)$_{12}$Br$_{16}$ [etu=ethylenebis(thiourea)] [Figure 34(a)] and Te$_3$(trtu)$_4$Br$_8$ [trtu=trimethylenebis(thiourea)] [Figure 34(b)] bromide ions are abstracted by a stronger Lewis acid (TeBr$_4$) and the coordinative needs of Te (preferring the 12-Te-4 configuration) in the cations [Te$_2$(etu)Br$_3$]$^+$ and coordination-polymeric [Te(trtu)$_2$Br]$^+{}_x$ are met by halide bridging.[91]



A cation $[Te_2(etu)_4Br_3]^+$ fromTe$_7$(etu)$_{12}$Br$_{16}$

The cation chain $\{[Te(trtu)_2Br]^+\}_x$ fromTe$_3$(trtu)$_4$Br$_8$

Figure 34 *Topology of (a) the cation* $[Te_2(etu)Br_3]^+$ *and (b) the cationic chain* $[Te(trtu)_2Br]^+{}_x$



$\{Te(SCH_2CH_2NH_3^+)_{2,}\ 2\ Cl^-\}$

Figure 35 *Interactions in solid bis-(ß-ammonioethylthio)tellurium(II) dichloride*

In the salt $[Te(etu)_4]^{2+}$ $[TeCl_6]^{2-}$, cations and anions are packed in stacks to endless arrays in way that the two opposite chlorine atom from octahedral $TeCl_6{}^{-2}$ exhibit contacts (378 pm) with tellurium atoms of the cations.[92] Related cases of very unsymmetric halide that bridges between tellurium atoms are abovementioned $[(C_6H_5CH_2)(C_2H_5)_3N]_4[TeI_4][TeI_6]$[7] and in triorganyltelluronium iodotellurate salts (see Te^{IV} compounds).

$Te(SCH_2CH_2NH_3)_2Cl_2$, a solid tellurium(II) thiolate with remote cationic functions (side chain alkylammonium chloride) pack in a way that both, Te···S contacts (as in other tellurium(II) thiolates) and Te···Cl$^-$ contacts contribute to the coordination sphere expansion of Te from (8-Te-2) to trapeziodal TeS_3Cl (12-Te-4) (Te-S 2 x 239, Te···S 348, Te···Cl 350 pm) (Figure 35).[93] The "intermolecular" Cl$^-$ bridge between $NH_3{}^+$ and Te is supposed to enable the gauche–gauche conformation of the C-S-Te-S-C chain. N-H···Cl and C-H···Cl contacts contribute to a three-dimensional network between the cations and the Cl$^-$ ions.[93] $[Te(dchtu)_3Cl]Cl$ is another case of the rare $Te^{II}S_3Cl$ coordination modes.[94]

13.4 Supramolecular Aspects of Structures from Tetravalent Chalcogen–Halogen Compounds

As mentioned above (Section 2.1), inorganic and organic halides of Te^{IV} are generally exhibiting halide-bridged supramolecular structures.[1–3,6,7] Both Te···X and X···X contacts are occurring, depending on the substitution patterns of compounds $R_{4-n}TeX_n$ ($n = 3, 2, 1$).

13.4.1 Cation-Anion Interactions Involving Selenonium and Telluronium Salts

Most compounds R_3EX can be described as essentially ionic, exhibiting structures that exhibit directed n(halide) → σ*(E–C) contacts between pyramidal R_3E^+ cations and X^- anions.[3]

In crystalline Me_3SeI, the "classic" compound with Se···I cation–anion interaction, there are pairs of pyramidal Me_3Se^+ cations and iodide anions. The Se···I distance (378 pm) is shorter than the sum of Se and I van der Waals distances (415 pm) and than the S···I distance in the sulfur analogue (389 pm). The Se–I contact and one of the Se–C bonds are almost collinear, *i.e.* the coordination environment of Se can be regarded as ψ-trigonal-bipyramidal.[95] Compared with Me_3SeI, Ph_3SeI exhibits a slightly shorter Se···I contact (372.2 pm).[96]

R_3Te^+ cations tend to give higher aggregates with pentacoordinated monocapped octahedral tellurium (14–Te–6).[97–100] In Me_3Te^+ Cl^-, H_2O, tellurium undergoes two Te···Cl contacts approximately *trans* to Te–C, and one further long O···Te contact (308.9 pm), hydrogen bridging from H_2O to Cl leads to infinite chains. Solid Ph_3TeCl $^1/_2CHCl_3$ is a stair-like tetramer with two central (14–Te–6) and two outside (12–Te–5) Te atoms; two central Cl^- ions interact with three Te atoms, the two outside Cl^- ions interact with two Te atoms (the solvent is only weakly held in the lattice). The unsolvated compound is based on dimeric units.[98] The solid fluorinated telluronium salt $(C_6F_5)_3TeCl$ [Figure 36(a)] is an unsymmetrically chloride-bridged chain polymer.[100]

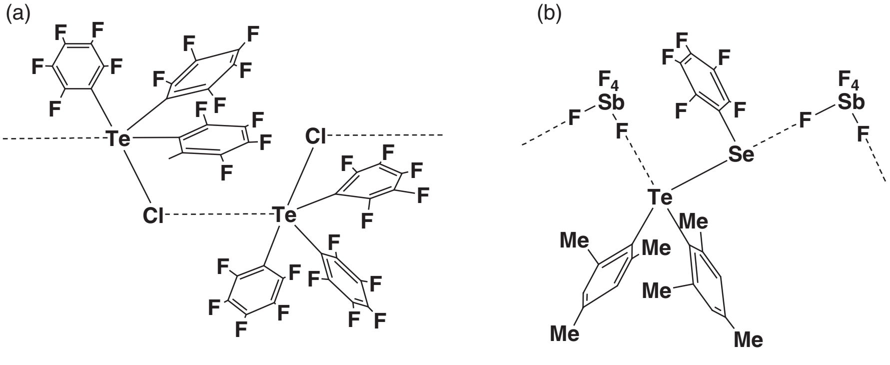


Figure 36 *Anion bridging in (a) solid tris(pentafluorophenyl)telluronium chloride and (b) dimesityl(pentafluorophenylseleno)telluronium hexafluoroantimonate*

Even weakly coordinating anions ($MeTeI_4^-$ in ß-Me_2TeI_2; Me_3Te^+ $MeTeI_4^-$),[101] give directed anion–cation contacts, leading to dimers, oligomers and extended chains. In Me_3Te^+ $MeTeI_4^-$, the cation tellurium atom exhibits three strong Te–C bonds (201, 208, and 213 pm) and three Te···I secondary contacts (Te···I 384, 397, 400 pm), the anion tellurium atom participates in one (apical) TeC bond (215 pm), four (basal) TeI bonds (284, 289, 295, 298 pm) and one secondary contact (Te···I 388 pm); two of the latter lead to centrosymmetric dimers of the cations.[101]

In telluronium ions with α-heteroatoms, like Mes_2TeBr^+ SbF_6^-,[102] $Mes_2TeTeMes^+$ SbF_6^- or $Mes_2TeSeC_6F_5^+$ SbF_6^- [Figure 36 (b)][102] both, the tricoordinated tellurium atom and the α-heteroatom exhibit electrophilic behaviour towards the hexafluoroantimonate couteranion, leading to rings or chains from ion pairs.

Solid $Te_2(OMe)_7Cl$, *formally* an adduct of the two telluranes $Te(OMe)_3Cl$ and $Te(OMe)_4$, exhibits two Te–O(Me)–Te bridges: a very short nearly symmetric one (Te–O 226.8, 225.3), and another very unsymmetric (Te–O 191.0, 307.8) (Figure 37).[103] The symmetrically bridging oxygen atom is the apical position of the ψ-tbp sawhorse structure-like $Te(OMe)_4$ unit from Te(2), and in a basal position of the ψ-octahedral square pyramid around Te(1). Further weak Te···O interactions lead to chains of the $Te(OMe)_4.Te(OMe)_3Cl$ moieties. Linear Te(1)–Cl····Te(2)# contacts are linking these chains with each other. Calculations on the gas phase structure of the model compound $[Te(OH)_4.Te(OH)_3Cl]$ suggest that in the solid the Te(1)–Cl bond is expanded (about 8%) due to its involvement into the supramolecular bonding network. In CD_2Cl_2 solution at room temperature, rapid alkoxy group scrambling is indicated by ^1H- and^{125} Te-NMR.

13.4.2 Some new Supramolecular Aspects of Diorganylselenium and -tellurium Dihalide Structures

Compounds R_2EX_2 are in many case dimers or coordination polymers;[3,6,99,105] the particular structures are influenced by electronic, steric and π-stacking effects of the ligands at Se or Te. In the series of compounds Me_2SeX_2, the

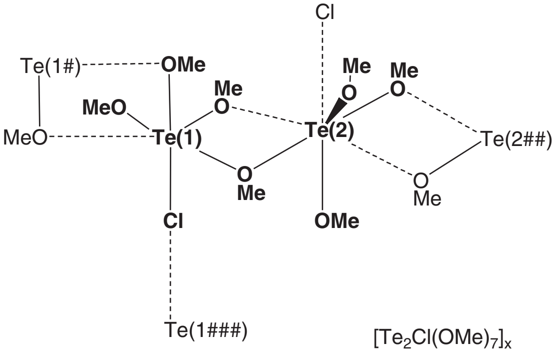


Figure 37 *Ditellurium moiety in $Te_2(OMe)_7Cl$*

dichloride exhibits long range Se···Cl contacts between discrete ψ-tbp 10-Se-4 units (341–361 pm) lead to Se in distorted octahedral environment (14-Se-6), the dibromide is made up from discrete ψ-tbp 10-Se-4 units and intermolecular Se···Br contacts 360 and 363 pm, whereas the diiodide is a coordination compound of Me_2Se with linear Se-I-I units (Se–I 276.8, I–I 291.6 pm) and intermolecular Se···I contacts 391 pm.

Recently, studies on *para*-substituted diaryltellurium dihalides (p-$Me_2NC_6H_4$)(p-YC_6H_4)TeX_2, and on partially fluorinated compounds $R^F{}_2TeX_2$, allowed to recognise the interplay and the competition of π-stacking, Te···X [Figure 38(a)] or X···X contacts [Figure 38(b)].[106,107]

It had been recognised since long that (p-$Me_2NC_6H_4$)$_2TeCl_2$ shows an exceptionally bright yellow colour[108] standing out from compounds (p-YC_6H_4)$_2TeCl_2$ (Y=H, Me, MeO). McCullough *et al.*[109] observed that the appearance of dark red or violet compounds R_2TeI_2 exhibiting metallic lustre correlates well with intermolecular I···I interactions of the solid compounds.

Beckmann *et al.* detected that solid compounds (p-$Me_2NC_6H_4$)$_2TeX_2$ (X=Cl, Br, I) do not exhibit pairswise intermolecular interactions *via* Te–X···Te bridging (as in Ph_2TeX_2, Figure 38(a)),[2,3] but the molecules pack in a way that halogen contacts occur in linear X-Te–X···X–Te–X··· arrays [Figure 38(b)]. The iodine derivative shows metallic lustre, and the exceptional yellow colour of the chlorine derivative can now be explained by extended chains with Cl···Cl contacts (Figure 39). Extended chains with X···X contacts were not observed in mixed substituted compounds $ArAr'TeCl_2$ (Figure 38(c): Ar=p-$EtOC_6H_4$-, Ar′= p-$Me_2NC_6H_4$-; Figure 38(d): Ar=C_6H_5, Ar′= p-$Me_2NC_6H_4$-). In the first

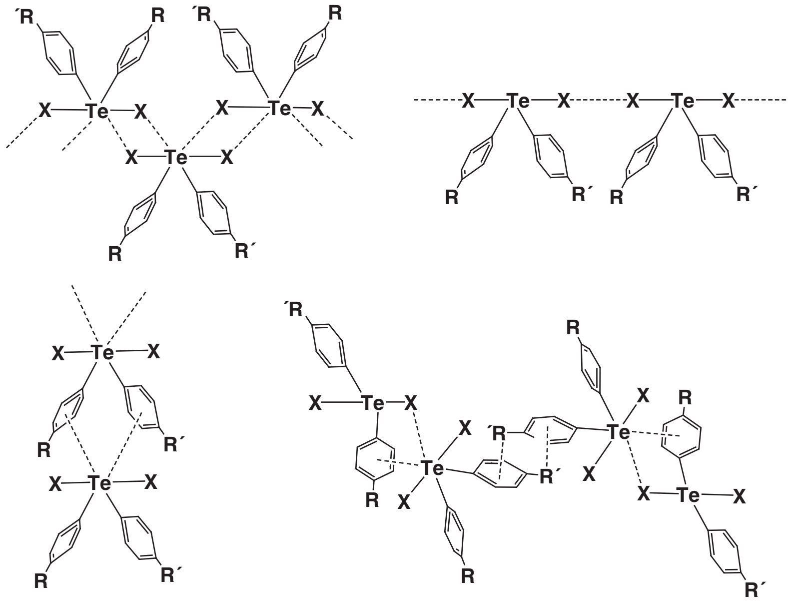


Figure 38 *Four types of packing of compounds Ar_2TeX_2*

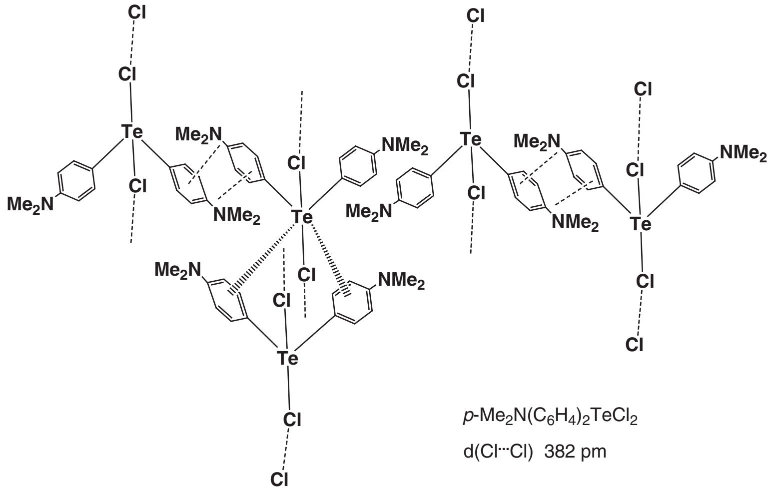


Figure 39 *The packing of bright yellow* $(4\text{-}Me_2NC_6H_4)_2TeCl_2$

compound the monomeric molecules undergo intermolecular Te$\cdots\pi$(aryl) contacts [Figure 38(c)]; in the second compound a Te–X$\cdots$Te bridge and a Te-Ph(π) Te contact are connecting two molecules. Inter-dimer slipped sandwich-like pairs of aminoaryls lead altogether to centrosymmetric moieties from four molecules [Figure 38(d)].

The lack of secondary Te$\cdots$Cl interactions can be correlated with the presence of two aryl substituents with π-donating NMe_2 groups. In an opposite way, electron-withdrawing fluorine atoms enhance the Lewis acidity of compounds $(R_F)_2TeX_2$, leading to fluorine-bridged chains (with X=F) and related chain structures with X=Cl or Br.[107]

Using the octafluorotolyl substituents, chains of doubly fluoride-bridged dimers are formed. Fluorine atoms in *ortho*-position of the aryl substituents contribute to tellurium coordination through intramolecular F$\cdots$Te contacts in the range of 320–330 pm.[107]

The role of intramolecular $n \rightarrow \sigma^*$ donor-acceptor interactions in compounds $TeCl_2(OR)_2$ and $TeCl_3OR$ (R=alkyl with ß-donor atom) has been elucidated experimentally and with help from *ab initio* calculations.[110] Solid $(MeOCH_2CH_2O)_2TeCl_2$ exhibits a network of intramolecular O$\cdots$Te and intermolecular O$\cdots$Te (267.4 pm) and Cl$\cdots$Te (357.7 pm) contacts involving heptacoordinated tellurium.

13.4.3 The Role of Cations for Aryltetrahalogenotellurate(IV) Structures

A number of compounds from the types $RTeX_3$, $RTeX_4^-$, $RTeX_5^{2-}$ and related species were studied in classic papers on *secondary bonds* from N.W. Alcock *et al.*,[1] J.D. McCullough *et al.*[6] and S. Husebye *et al.*;[11,111] fundamental structures of tetravalent organotellurium compounds are well-covered in books and reviews.[2,3,7,9] Substituent effects influencing the interplay of X···X, Te···X and π stacking are a current field of research. In this context, Schulz Lang *et al.* have recently been studying the role of cations for inter-anion attractive interactions in tetrahalogeno(phenyl)tellurate(IV) salts with the help of a number of structure determinations.[112–115] From previous structure determinations it was known that anions $PhTeX_4^-$ contain square pyramidal structures with the phenyl group in apical position and that secondary Te···X bonding is observed to form halogen atom bridged dimeric structures,[101,116] except when the bulky n-Bu_4N^+ cation is present.[117]

From methanol solutions, the cesium salts $Cs[PhTeCl_4].CH_3OH$ and $Cs[PhTeBr_4]$ were isolated.[112] In the former compound (Figure 40), there are pairs of weak Te···Cl between the $PhTeCl_4$ anions; three terminal ones and one bridging chlorine atom from each $(PhTeCl_4^-)_2$ group are in a chelating way coordinating a pair of Cs^+ cations that is bridged by two oxygen atoms from methanol molecules. Eight Cs–Cl contacts per cesium also involve two chlorine bridges in addition to the methanol bridges.

In $Cs[PhTeBr_4]$, whose lattice does not contain solvent molecules, "chelating" bromine atoms of four single $PhTeBr_4^-$ anions surround each Cs^+ ion, achieving a quasi-pentagonal prism (seriously distorted dodecahedral, CN 8 at Cs). The pentagonal prisms are linked through faces and edges alternatively (Br–Cs–Br links).[112] Using 2-bromopydridinium cations, typical pairs $(PhTeCl_4^-)_2$ are formed; bifurcated hydrogen bonds exist between an acidic hydrogen atom of the cation and two Cl atoms (*cis* to each other), a terminal and a bridging one [Figure 41(a)].[113] With pyridinium cations, the anions adopt a trimeric structure with two halogen atoms of each monomer forming secondary bonds to an

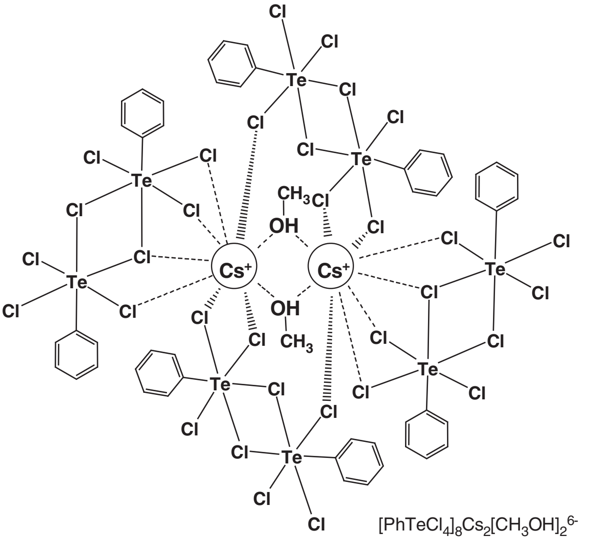
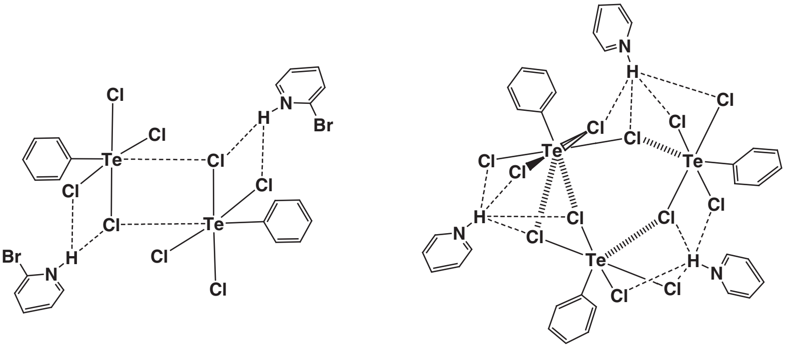
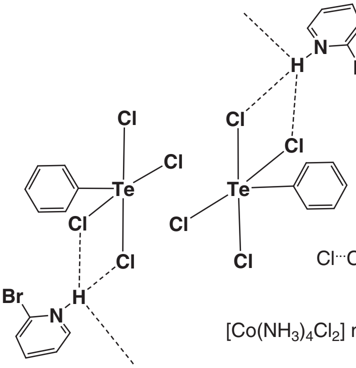


Figure 40 *Cation–anion and anion–anion interactions in* $Cs[PhTeCl_4]CH_3OH$



$\{[2\text{-Br-}C_5NH_5][PhTeCl_4]\}_2$ $\{[C_5NH_6][PhTeCl_4]\}_3$

Figure 41 *$PhTeCl_4^-$ oligomers*

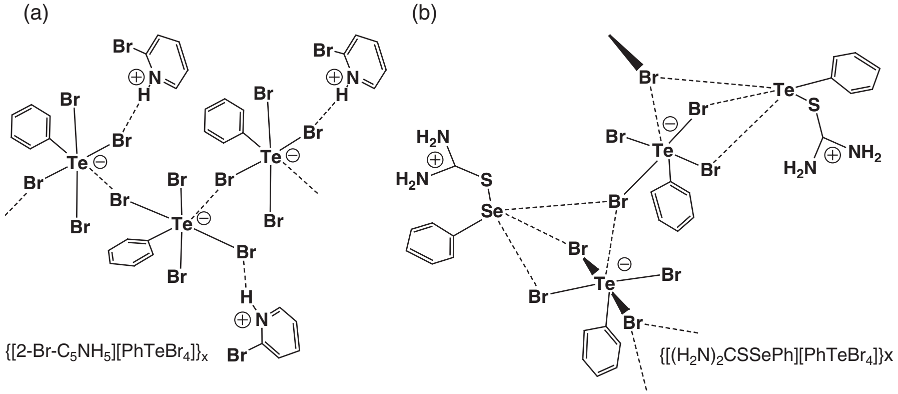


Cl···Cl 389 - 398 pm; Te···Te 381 - 386 pm

$[Co(NH_3)_4Cl_2]$ not shown $\{[2\text{-Br-}C_5NH_5][[Co(NH_3)_4Cl_2]PhTeCl_4]\}_2$

Figure 42 *A "pseudo-dimer" of $PhTeCl_4^-$ ions*

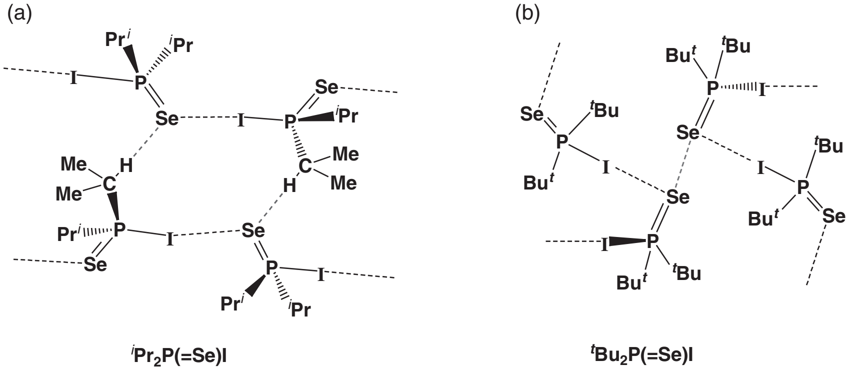
adjacent tellurium atom. A four-centred hydrogen bond exists between the pyridinium proton and two pairs of chlorine atoms [Figure 41(b)]. With two kinds of cations, the $[Co(NH_3)_4Cl_2]^+$ and the 2-bromopyridium cation, only the latter participates with H-bridging contacts to the $(PhTeCl_4^-)_2$ anion moiety (Figure 42).[113] $PhTeBr_4^-$ and $PhTeI_4^-$ aggregate as chain polymers, when 2-bromopyridium is used as the cation.[114] In the iodide case, the iodine atom *trans* to that participating in the hydrogen bridging contact to the cation is *terminal*; in the bromide structure two terminal Br atoms are *trans* to each other and from the other pair of *trans* Br atoms, one is part of the Te–Br···Te bridge whereas the second one undergoes H-bonding with the 2-bromopyridiumum cation [Figure 43(a)]. In a related salt with the thiourea-derived diamino(phenylselenothio)carbenium cation,[115] the Se atom in ß-position from the carbenium centre (compare Figure 31) undergoes acceptor–donor interactions with two neighboured Br atoms from one $PhTeBr_4^-$ anion (Se···Br 371 and 393 pm), and with one weakly bridging Br atom (Te···Br 357 pm; Te-Br 277 pm) from the next $PhTeBr_4^-$ anion (Se···Br 368 pm).[115]



$\{[2\text{-Br-}C_5NH_5][PhTeBr_4]\}_x$

$\{[(H_2N)_2CSSePh][PhTeBr_4]\}x$

Figure 43 *N–H···Br contacts to (a) $PhTeBr_4^-$ chains and (b) Se···Br contacts to $PhTeBr_4^-$ chains*



$^iPr_2P(=Se)I$

$^tBu_2P(=Se)I$

Figure 44 *PSe···I links and CH···Se crosslinks in (a) $iPr_2P(Se)I$ and (b) PSe···I links and Se···Se crosslinks in $tBu_2P(Se)I$*

13.5 Base Pair-Like Chalcogen–Halogen Arrays

13.5.1 Intermolecular Donor–Acceptor Interactions in Solid Iodophosphine Selenides

Iodine atoms adjacent to $\sigma^4\lambda^5$-phosphonium centres like R_3PI^+ behave as soft electrophiles,[59] phosphine selenide $R_3P{=}Se$ functions act as soft nucleophiles.[57] The combination of these two kinds of functional groups leads to novel kinds of *base pairing* building blocks for supramolecular chemistry, when soft donor and acceptor functions are expressed in one type of molecule. The simplest combination of a $\sigma^4\lambda^5$-P-I acceptor function with a P=Se donor function within one molecule is expressed in iodophosphine selenides $R_nP(=Se)I_{3-n}$.[57]

Solid iodophosphine selenide $[(i\text{-}C_3H_7)_2P(=Se)I]$ consists of chains of molecules held together by secondary Se···I interactions [Figure 44(a)]. Directed weak Se···H–C contacts are interlinking these chains.[118] $[(t\text{-}C_4H_9)_2P(=Se)I]$

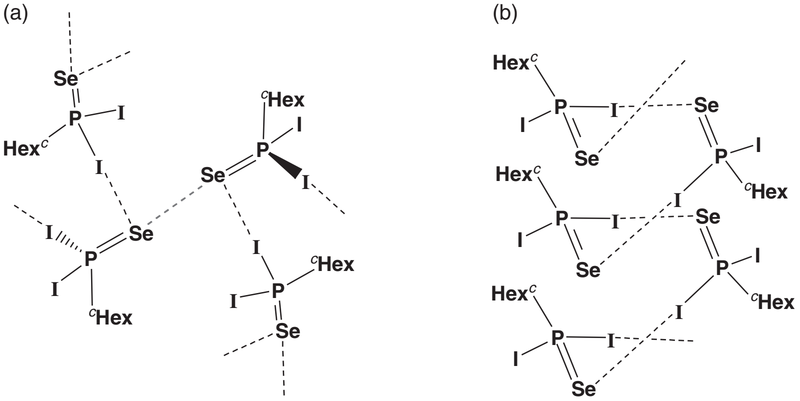


Figure 45 *PSe···I links and Se···Se crosslinks in (a) [cHexP(Se)I]$_2$ and (b) "staircase" stacks in cHex$_2$P(Se)I*

crystallises with two independent molecules. The compound can be described as a helical chain-like polymer when intermolecular P–Se···I–P contacts are taken into consideration. Bond angles and distances within the two molecules are very similar; the most significant deviation between molecules I and II is the slightly larger P–Se distance in molecule II (P1–Se1 210.4(2) pm, P2–Se2 212.1(2) pm), which is involved in weak inter-chain Se···Se contacts [Se2···Se2′ 359.4(2) pm] [Figure 44(b)].[57]

The secondary Se···I contacts (Se1-I2′ 369 and Se2-I1 384.4 pm) are only slightly shorter than the sum of the van der Waals radii of Se and I. However, the "L-shaped" geometry of the P=Se···I–P bridges, with the iodine atoms being approximately linearly coordinated, is consistent with the expectations for typical Se (donor)→I (acceptor) interactions [∠ P1-I1-Se2 158.62(4), ∠P2-I2-Se1′ 167.68(4)].

The related diiodophosphine selenide *c*-HexP(=Se)I$_2$ [Figure 45(a)] contains a P=Se donor function; however from the two electrophilic iodine atoms attached to phosphorus atom, only one is participating to soft–soft interactions. L-shaped P–Se···I–P donor-acceptor interactions (Se···I 347.6 pm) form one motif of the supramolecular structure of *c*-HexP(=Se)I$_2$ and P–Se···Se–P contacts (361.2 pm) the other [Figure 45(a)]. Staircase-like helices are formed by interconnection of two stacks of molecules through L-shaped P–Se···I–P bridges [Figure 45(b)]; layers are built up by connection of these helices through Se···Se contacts. The "non-participating" terminal P–I groups approach in a herringbone pattern, creating domains of iodine atoms from adjacent layers.

Coordination of [(*t*-C$_4$H$_9$)$_2$P(=Se)I] with molecular iodine furnishes a 1:1 adduct that crystallises as cyclic dimer in the solid state (Figure 46).[57] From each I$_2$ molecule within the structure, one atom acts as acceptor towards selenium, and the other one becomes *very weak* donor towards the iodine atom bonded to phosphorus. This compound fulfills the requirements of a "*soft-soft base pair*". As in the structure of the parent donor molecule [(*t*-C$_4$H$_9$)$_2$P(=Se)I],

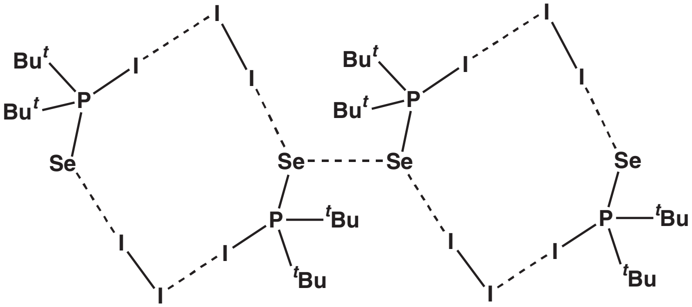


Figure 46 *P-Se-I-I and I-I···I links in dimers [tBu$_2$P(Se-I-I)I]$_2$, and inter-dimer Se···Se contacts*

selenium atoms of the dimer are involved in long secondary Se···Se contacts leading to chains from dimers.

13.6 Conclusion

The enhanced tendency of the heavier chalcogens (S < < Se < Te) and halogens (Cl < < Br < I) to expansion of their coordination spheres, either by donor–acceptor interactions with Lewis acids or bases, or by intermolecular association, allowed to characterise crystallographically in recent years a considerable amount of supramolecular structures.

In many cases, the interactions are directed in accordance with the VSEPR rules, confirming the concept of *n*(donor) → σ*(acceptor) overlap. The above collection of structural data reveals that in most cases particular supramolecular networks were "observed", not "designed".

The improved understanding of the interplay of different types of intermolecular interactions should, however, allow in future also "supramolecular architecture" with heavier chalcogen–halogen interactions.

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