



Synthesis and Characterization of Homo and Hetero Dinuclear and Trinuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes with 26-membered N₄S₄ Donor Macrocyclic Ligand

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Abstract

Complexes of general formula $[M_2(L)Cl_4]$, $[MZnCl_4]$ and $[M_3(L)Cl_4]$ Cl_2 where $M=Co(II), Ni(II), Cu(II)$ and $Zn(II)$ and $L=(N,N'$ -Bis [bis{(1,2-*o*-aminophenylthio)ethane}] 1-phenylbutan1,3-dilidene) were prepared from the reaction of macrocyclic ligand with the metal chloride in (1:2) and (1:3) ligand to metal molar ratio. The complexes have been characterized by elemental analysis, molar conductance measurements, spectral methods (I. R and electronic spectra), metal content and magnetic measurements. The macrocyclic ligand has two different donating atom cavities with four azomethine group and with four sulfur atoms. All the complexes show magnetic moments corresponding to a high spin configuration except for zinc complexes. On the basis of spectral and magnetic measurements a four coordinated tetrahedral geometry may be assigned to these complexes.

Keywords: Macrocyclic Schiff base, metal complexes, tetrahedral geometry.

Introduction

Considerable attention has been paid to the coordination chemistry of Schiff base ligands containing nitrogen-sulfur donors towards transition metal ions, because these complexes can present many characteristics related biological systems containing metal ions in the same coordination environment. Thus it is a challenge for chemists to design appropriate ligand frames with the purpose of synthesizing metal complexes with predetermined properties¹⁻⁵.

A hexadentate ligands, (H_2L^1) ; [1H-Pyrrole-2-yl methylene] [2-(2-([1H-Pyrrole-2-yl methylene] amino) Phenyl thio) ethyle)thiophenyl amine and [1H-Pyrrole-2-yl-methylene] [2-(4-{ [1H-Pyrrole-2-yl-methylene] amino}phenyl thio) butyl] thiophenyl amine (H_2L^2) , were prepared by condensation reaction of pyrrole-2-carboxaldehyde with [2-(2(2aminophenyl) thio) ethyl) thio) phenyl] amine and [2-(4- [(2-amino phenyl thio) butyl) thio) phenyl] amine respectively. Reaction of these ligands with nickel(II) and copper(II) acetate gave complexes of the form $[ML]$ ($L=L^1$ and L^2) and the synthesized ligands and their complexes have been characterized by a variety of physicochemical technique. The molecular structure of $[NiL^1]$, have been determined by single crystal x-ray diffraction, indicate that the structure of the complexes has a distorted octahedral coordination environment⁶.

Complexes of Cr(III) and Mn (II) of general formula $[Cr(L)X_2]$ X and $[Mn(L)X_2]$ respectively, were prepared from N_2O_2, N_2S_2 and N_4 donor macrocyclic ligands (L). The complexes have been characterized by elemental analysis, molar conductance

measurements, spectral methods (IR, mass, ¹H NMR, electronic spectra, E. P. R) and magnetic measurements. The macrocyclic ligands have three different donating atoms cavities one with two unsaturated nitrogens and the other two have saturated nitrogen, oxygen and sulfur atoms⁷.

Three new mononuclear complexes of nitrogen-sulfur donor sets, formulated as $[Fe(L)Cl_2]$ (1), $[Co(L)Cl_2]$ (2), and $[Ni(L)Cl_2]$ (3), where L=1,3-bis(2-pyridyl methylthio) propane were synthesized and isolated in their pure form. All the complexes were characterized by physicochemical and spectroscopic methods. The solid state structures of complexes (1) and (3) have been established by single crystal x-ray crystallography⁸.

A novel β-diketiminato ligand precursor, LH, containing thioether tethers was synthesized by the reaction of acetylacetone and 2-methylthioaniline. The ligand (LH) was deprotonated and used in the synthesis of two iron(II) complexes and one nickel (II) complex. All three compounds were characterized by means of single crystal x-ray diffraction and their structures are discussed⁹.

Zinc complexes with pyrimidine-2-thionato ligands with the general formula $[Zn(Rpym)_2]$ can be easily obtained by electrochemical oxidation of zinc anode in a cell containing an acetonitrile solution of the appropriate thione (RpymSH) R=4,6-Me₂, 5Et; 4CF₃ and 4,6-CF₃, Me). When 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) were added to the cell, the corresponding adducts $[Zn(Rpym)_2L]$, L=bipy, phen. All compounds have been characterized by microanalysis, mass spectrometry, IR and ¹H and ¹³C NMR spectroscopy¹⁰.

Macrocyclic complexes of Mn(II), Co(II), Ni(II) and Cu(II) using macrocyclic ligand derived by the condensation of trimethoprim and diethyl phthalate have been prepared and characterization by electronic, IR and NMR spectral studies as well as magnetic moment and conductivity. On the basis of spectral studies, an octahedral geometry has been proposed for all the complexes¹¹.

In this paper we report the synthesis and characterization of homo and hetero dinuclear complexes as well as trinuclear complexes of Co(II), Ni(II), Cu(II) and Zn(II) with N₄S₄ donor macrocyclic ligand. An important aspect of the present work is the synthesis of a novel macrocycle Schiff base derived from the diamine containing aromatic ring with sulfur and nitrogen donating atoms and their complexes.

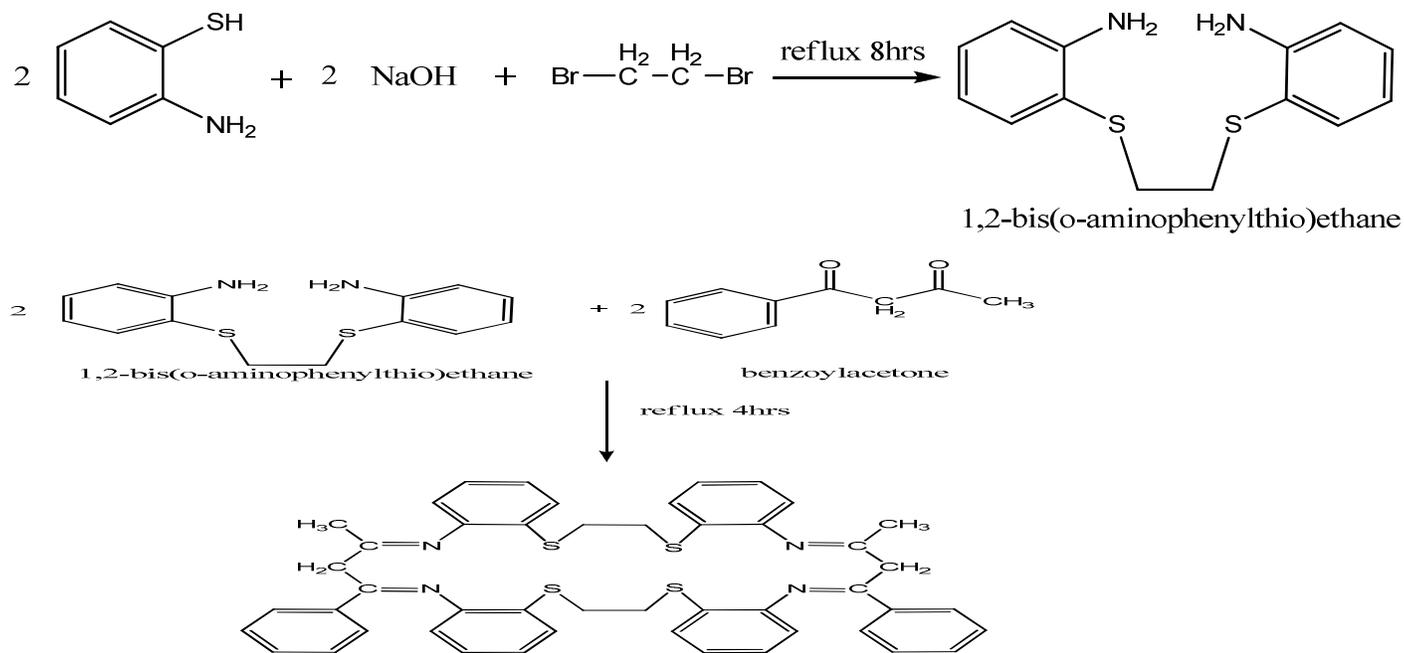
Material and Methods

All starting materials used were analar grade, were purchased from Fluka or BDH and were used as received. Analysis of ligand and complexes were carried out using CHNS elemental analyzer model 2400 Perkin Elmer. The metal content was estimated spectrophotometric using Shimadzu AA670 spectrophotometer. Melting point or decomposition temperature were determined on Buchi melting point apparatus and were uncorrected, infrared spectra were recorded on a FT. IR Brucker Tensor 27Co. Spectrophotometer in the 400-4000 cm⁻¹ range using KBr disc. Electronic spectra were obtained with Shimadzu Uv-Vis recording Uv 1600 spectrophotometer at

room temperature, these measurements were recording using a concentration of 10⁻³ M of the complexes in DMF. The magnetic measurements were carried out at 25°C on the solid state by Faraday's method using Brucker BM₆ instrument, conductivities were measured using conductivity meter model PCM3-Jenway. These measurements were obtained using DMF over the 10⁻³ solution at 25°C.

Synthesis of 1,2-bis(o-aminophenylthio)ethane: The diamine was prepared by heating equal amount of o-aminothiophenol (2.5g, 0.01mol) in absolute ethanol (10cm³) and sodium hydroxide (0.8gm, 0.01mol) in absolute ethanol (10cm³), to this solution 1,2-dibromoethane (1.9g, 0.01mol) in ethanol (5cm³) was added. The mixture was refluxed for 8h. The mixture was then cooled to room temperature. The solid mass so obtained, was filtered off washed several times with ethanol in order to remove NaBr formed, then washed with diethylether and dried under vacuum for several hours.

preparation of macrocyclic ligand (L): To an ethanolic solution (25cm³) of benzoylacetone (3.24g, 0.02mol) an ethanolic solution (25cm³) of 1,2-bis(o-aminophenylthio)ethane (5.52g, 0.02mol) was added and the resulting solution was boiled under reflux for 4h. The solution was then concentrated to half of its volume and kept overnight. The brown crystal which formed when filtered and washed with ethanol and dried under vacuum over P₄O₁₀.



L=N,N'-Bis[bis-{(1,2-o-aminophenylthio)-ethane}]1-phenylbutan-1,3-dilidene

Scheme-1
Preparation of the complexes

Preparation of $[M_2(L)Cl_4]$ complexes, $M=Co(II), Ni(II), Cu(II)$ and $Zn(II)$. These complexes were prepared according to the following method:

The metal salt (0.002 mol) in ethanol (10 ml) and the ligand (0.80g, 0.001mol) in methanol (10 ml) was added. The mixture was stirred under reflux for 2hr to ensure the completion of the reaction. The solids thus obtained was filtered off, washed with ethanol, methanol, then diethylether and dried under vacuum for several hours.

Preparation of $[MZn(L)Cl_4]$ complexes = $Co(II), Ni(II), Cu(II)$. These complexes were prepared by using the general procedure. Metal salt (0.001mol) in (10 ml) ethanol and zinc chloride (0.14g, 0.001 mol) in ethanol (10ml) were mixed with the ligand (0.80g, 0.001 mol) and the procedure continued as above.

Preparation of $[M_3(L)Cl_4] Cl_2$ complexes, $M=Co(II), Ni(II), Cu(II)$. $CoCl_2 \cdot 6H_2O$ (0.71g, 0.003 mol) in ethanol (10ml) was mixed with the ligand (0.80g, 0.001 mol) in methanol (10ml). The mixture was stirred under reflux for 2h, the solid thus

obtained was washed with ethanol, methanol and diethylether. The other complexes were prepared similarly.

Results and Discussion

The macrocyclic prepared Schiff base ligand (L) has been prepared according to Scheme 1, and characterized by elemental analysis, IR, UV-Vis spectra and conductivity measurements. The IR data is in accordance with proposed structure. Disappearance of the C=O and NH_2 stretching vibration related to the ketone and diamine functional groups respectively along with the growth of strong band in the region 1616 cm^{-1} due to C=N bands, indicate the formation of the Schiff base ligand.

The reaction of the prepared Schiff base ligand with $Co(II), Ni(II), Cu(II)$ and $Zn(II)$ in (1:2) or (1:3) ratio in ethanol gives $[M_2(L)Cl_4], [MZn(L)Cl_4]$ and $[M_3(L)Cl_4] Cl_2$ complexes. The elemental analysis are consistent with the proposed molecular formula that show the ratio ligand / metal are (1:2) or (1:3) (table 1). The molar conductivity of $10^{-3}M$ solution of the complexes (No. 1-7) indicates that they are non-electrolyte in DMF, while the complexes (No. 8-10) are (1:2) electrolyte¹². That is consistent with the stoichiometry of the complexes on the basis of analytical data.

Table 1
Elemental analysis, molar conductivities and magnetic data of the complexes

Compound	Colour	m. p (°C)	Yield %	Found (calculated) (%)						μ_{eff} (B. M.)	$\Lambda_m^{in DMF}$ $\Omega^{-1}cm^2mol^{-1}$
				C	H	N	S	M	Cl		
Ligand	Dark brown	150-152	82	71.60 (71.64)	5.41 (5.47)	6.91 (6.96)	15.89 (15.92)	-----	-----	-----	-----
$[Co_2(L)Cl_4]$	Green-maroon	136-138	80	54.10 (54.14)	4.10 (4.13)	5.20 (5.26)	11.97 (12.03)	10.38 (11.07)	12.92 (13.34)	4.11	21
$[Ni_2(L)Cl_4]$	Green	134-136	78	54.09 (54.16)	4.09 (4.13)	5.21 (5.26)	12.00 (12.03)	10.69 (11.03)	13.06 (13.35)	3.23	31
$[Cu_2(L)Cl_4]$	Black	124-126	81	53.61 (53.68)	4.08 (4.10)	5.19 (5.21)	11.89 (11.92)	11.60 (11.83)	12.78 (13.23)	1.85	31
$[Zn_2(L)Cl_4]$	Redish-brown	118-120	77	53.40 (53.49)	4.03 (4.08)	5.13 (5.20)	11.80 (11.88)	11.73 (12.14)	13.49 (13.18)	Dia*	6
$[CoZn(L)Cl_4]$	Dark green	122-124	68	53.73 (53.81)	4.09 (4.11)	5.21 (5.23)	11.89 (11.95)	11.33 (11.61)	12.90 (13.26)	4.39	15
$[NiZn(L)Cl_4]$	Grey	128-130	70	53.80 (53.82)	4.09 (4.11)	5.20 (5.23)	11.91 (11.96)	11.80 (11.59)	12.81 (13.27)	3.31	55
$[CuZn(L)Cl_4]$	Black	108-110	65	53.51 (53.58)	4.01 (4.09)	5.15 (5.20)	11.87 (11.90)	11.65 (11.99)	13.01 (13.21)	1.95	34
$[Co_3(L)Cl_4] Cl_2$	Dark green	102-104	75	48.20 (48.24)	3.60 (3.68)	4.61 (4.69)	10.65 (10.72)	14.36 (14.80)	17.39 (17.84)	3.50	131
$[Ni_3(L)Cl_4] Cl_2$	Grey	110-112	72	48.20 (48.27)	3.62 (3.68)	4.60 (4.69)	10.69 (10.72)	15.11 (14.75)	17.54 (17.85)	2.65	167
$[Cu_3(L)Cl_4] Cl_2$	Black	116-118	78	47.30 (47.70)	3.61 (3.64)	4.60 (4.63)	10.53 (10.60)	15.87 (16.26)	17.26 (17.63)	1.58	150

*=Diamagnetic

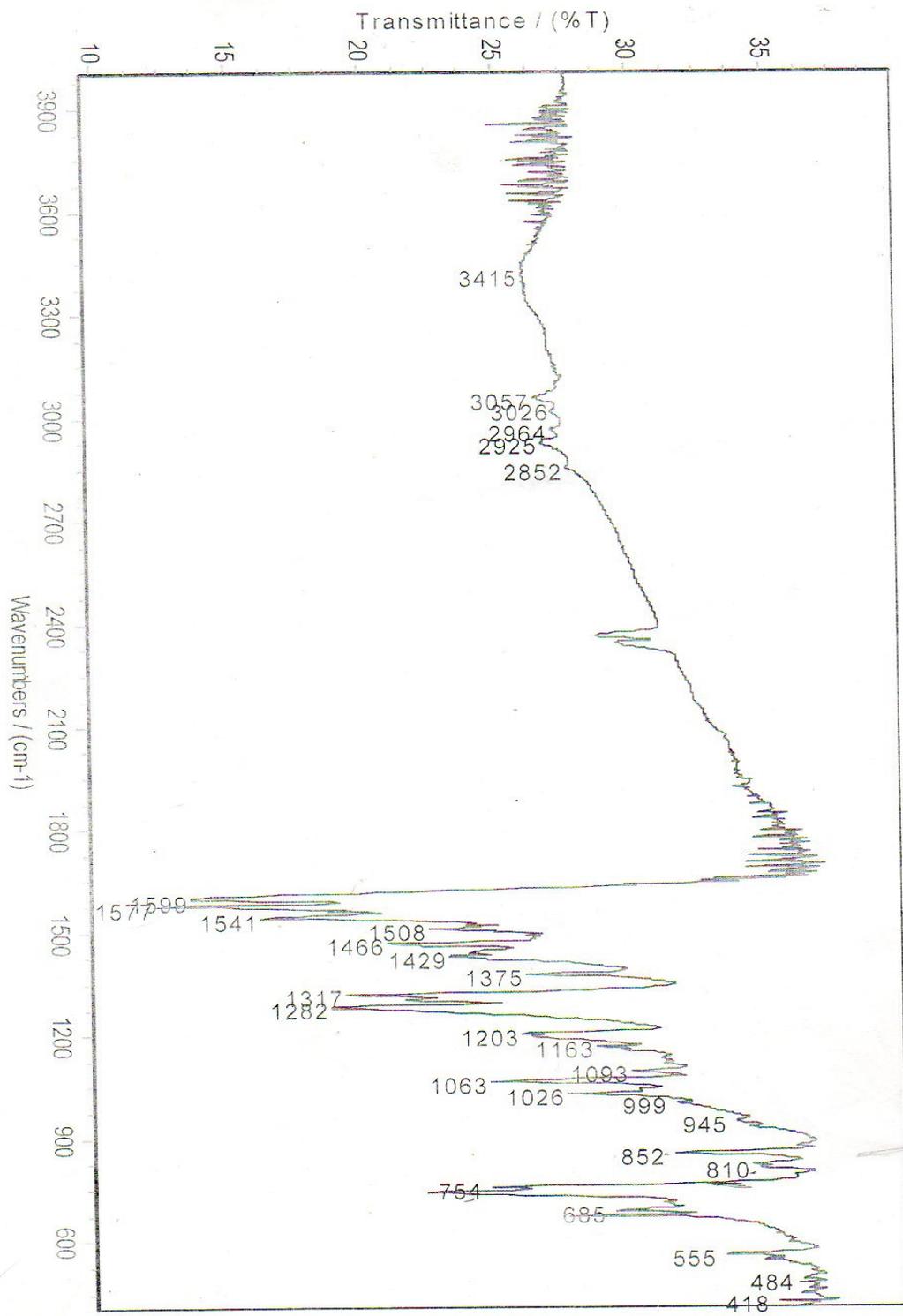


Figure-1
I. R spectra for the complex [Co₂(L)Cl₄]

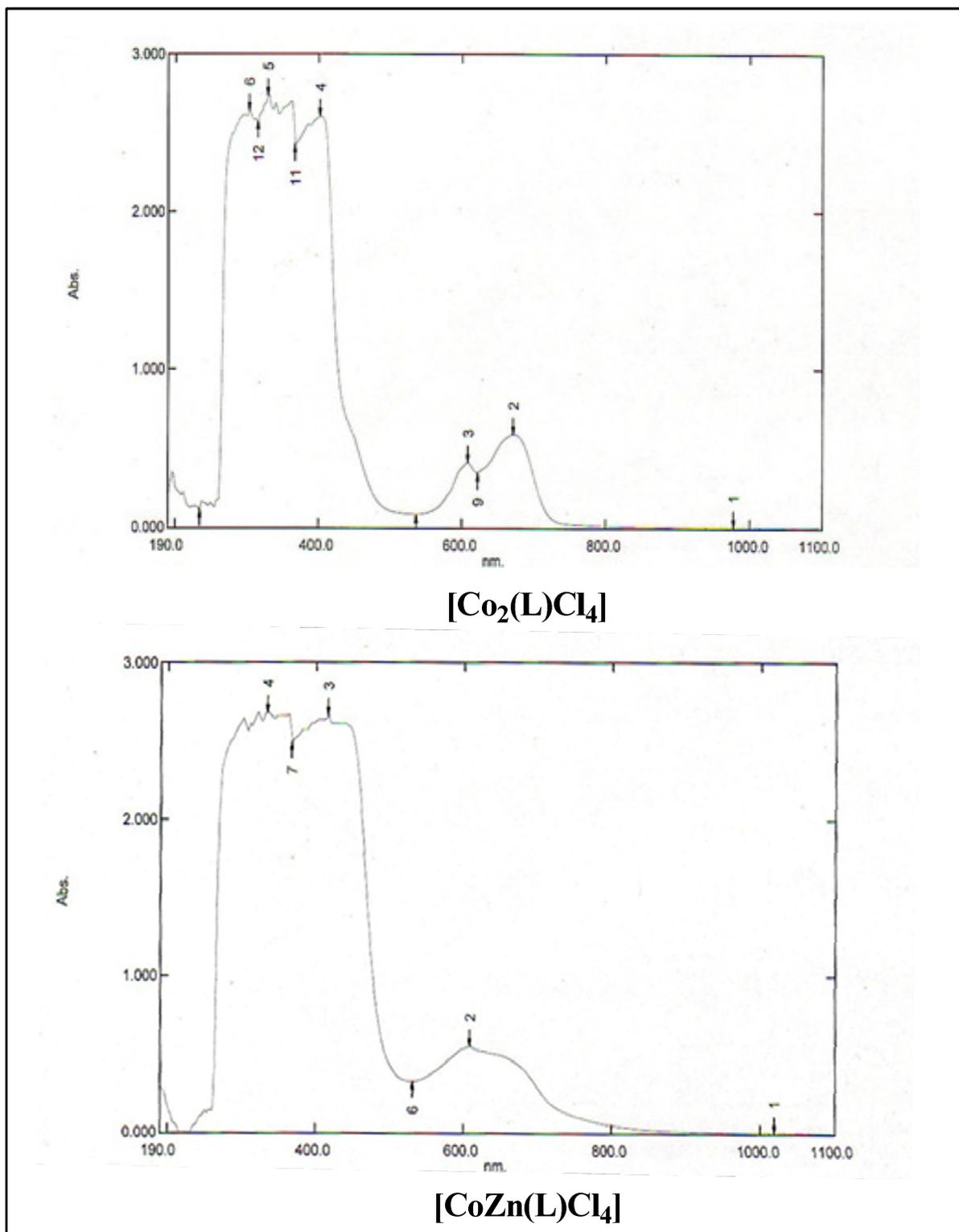


Figure-2
Electronic spectra for complexes $[Co_2(L)Cl_4]$ and $[CoZn(L)Cl_4]$

Table- 2
IR and electronic spectra data of the ligand and their metal complexes

No.	Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	Uv-Vis absorption bands cm^{-1}
	Ligand	1616(s)	852(m)	-----	24630,32679
1	[Co ₂ (L)Cl ₄]	1599(s)	852(m)	418(m)	14880,16447,24875,30303
2	[Ni ₂ (L)Cl ₄]	1601(s)	852(m)	430(m)	13123,14619,31250
3	[Cu ₂ (L)Cl ₄]	1601(s)	852(m)	424(m)	11337,32894
4	[Zn ₂ (L)Cl ₄]	1603(s)	852(m)	469(m)	29585
5	[CoZn(L)Cl ₄]	1599(s)	852(m)	453(m)	16447,24038,29940
6	[NiZn(L)Cl ₄]	1601(s)	852(m)	444(m)	15873,31447
7	[CuZn(L)Cl ₄]	1601(s)	852(m)	469(m)	14706,32895
8	[Co ₃ (L)Cl ₄]Cl ₂	1601(s)	820(m)	444(m)	14925,16447,33333
9	[Ni ₃ (L)Cl ₄]Cl ₂	1637(s)	833(m)	430(m)	13123,14409,30675
10	[Cu ₃ (L)Cl ₄]Cl ₂	1630(s)	823(m)	474(m)	14286,34014

s=strong, m=medium

The I. R spectra of the ligand showed a characteristic band due to $\nu(\text{C}=\text{N})$ appeared at 1616 cm^{-1} , the $\nu(\text{C}-\text{S})$ at 852 cm^{-1} , $\nu(\text{C}-\text{H})$ at 2933 cm^{-1} for aliphatic and 3064 cm^{-1} for CH aromatic respectively. In the complexes (Table 2) the $\nu(\text{C}=\text{N})$ stretching frequency shifted to lower frequency by (13-17) cm^{-1} in complexes (1-8), suggesting that this group takes part in coordination. The coordination of nitrogen to metal atom would be expected to reduce the electron density on the azomethine link and thus cause a shift in the $\nu(\text{C}=\text{N})$ band^{13,14}. While in complexes (9 and 10) the $\nu(\text{C}=\text{N})$ stretching frequency shifted to higher frequency by (14-21) cm^{-1} . The shifting to the higher frequency indicated this group was affected by complexation¹⁵.

The $\nu(\text{C}-\text{S})$ band observed at the same position for complexes (1-7) indicating that this band was not shared in coordination, while for complexes (8-10) this band was shifted to lower frequency by (19-32) cm^{-1} which indicated it was shared in coordination with the metal ions, further support for the above coordination provided by the appearance of new bands at $418-474 \text{ cm}^{-1}$ which tentatively attributed to $\nu(\text{M}-\text{N})$ ^{16,17}.

In order to obtain some information about the coordination properties of the metal ions, the electronic spectra has been recorded as 10^{-3} M solution in DMF and the results were listed in table 2.

The band observed at 24630 and 32679 cm^{-1} due to the ligand which may assigned to ($n \rightarrow \pi^*$) or ($\pi \rightarrow \pi^*$) transition respectively. The spectrum of Cobalt (II) complexes (1,5 and 8) show bands at $14880-14925$ and 16447 cm^{-1} , these bands are assigned to ${}^4\text{A}_2\text{F} \rightarrow {}^4\text{T}_1(\text{p})$ (ν_3) transition and charge transfer, which consistent with proposed tetrahedral symmetry for these complexes¹⁸ as shown in figure 1 and figure 2.

The electronic spectra for Ni (II) complexes (2,6,9), the observed band at $13123-15873 \text{ cm}^{-1}$ are due to ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})(\nu_3)$ transition in tetrahedral symmetry¹⁹. In case of Cu (II) complexes (3,7,10) a bands ($11337-14706 \text{ cm}^{-1}$

were assigned to ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ transition in tetrahedral environment. The electronic spectra of Zn (II) complexes do not show any d-d bands.

The magnetic measurements give an idea about the electronic state of the metal ion in the complex. The experimental magnetic moment for each complex listed in table 1. The magnetic moments for Co(II) complexes (1,5,8) are (4.11, 4.39, 3.24) B.M. respectively, while for Ni(II) complexes (2,6,9) are (3.23, 3.31, 2.65) B. M., for Cu(II) complexes (3,7,10) are (1.85, 1.99, 1.58) B.M., while Zn(II) complexes are diamagnetic.

Conclusion

The preparation of homo and hetero dinuclear and trinuclear complexes with new macrocyclic ligand N,N'-Bis [bis{(1,2-o-aminophenylthio)ethane}] 1-phenylbutan-1,3-dilidene (N₄S₄) was strongly supported by analytical data. The formation of imine group was apparent from infrared spectra. The effective magnetic moment and electronic spectral data supported tetrahedral environment in the metal ions. The macrocyclic ligand used in this study, coordinate to the metal ions intradentate or octa fashion as shown in figure 3.

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complexes with Schiff base 4,4'(1,4-phenylene bis (azan-1-yl-1-ylidene)) bis (methan-1-yl-1,1-ylidene)-1,2-diol
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