

Complexation between molybdenum(VI) and oxalate: Crystal and molecular structure of [(-)Co(en)₃][MoO₃(C₂O₄)OH₂]I · 2 H₂O

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Abstract

The crystal structure of the product of the reaction between [(-)Co(en)₃]I₃ and a mixture of Na₂MoO₄ and NaHC₂O₄ in aqueous solution is reported: [(-)Co(en)₃][MoO₃(C₂O₄)OH₂]I · 2H₂O, space group *P*2₁2₁2₁, *a* = 8.131(2), *b* = 14.590(4), *c* = 17.509(4) Å; *Z* = 4. Final *R* = 0.048, *R_w* = 0.050, *w* = (*σ*²*F*)⁻¹ for 1899 reflections. The configuration of the Mo(VI) oxalate complex differs notably from that proposed previously on the basis of chemical analysis and equilibrium studies.

Introduction

Research on the formation of stable complexes between Mo(VI) and oxalic acid is not new (Perchard, 1889), and a variety of stoichiometric ratios between the molybdenum and oxalate have been proposed (Béltran *et al.*, 1981). Conclusive information as to the identity of the Mo(VI) oxalate complexes in aqueous solution is scarce as are studies of their solid state chemistry. The photochromic behavior of monomeric molybdenum (VI) oxalato complexes

$(\text{NH}_4)_2[\text{MoO}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{MoO}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$ has been investigated (Mentzen and Sautereau, 1981). Some structural parameters for these complexes were reported by the authors but no complete X-ray crystallographic determinations of the structures have been published. We are currently engaged in the potentiometric investigation of aqueous solution equilibria of a number of Mo(VI) complexes (Cruywagen and van de Water, 1986; Cruywagen *et al.*, 1986). During one such study of the complex species arising from Mo(VI) and oxalic acid (Cruywagen *et al.*, 1986), we obtained results indicating a Mo:oxalate 1:1 complex for a given set of conditions. This is in conflict with the previously proposed (Béltran *et al.*, 1981) 1:2 complex for the same conditions. Using the same method as these authors, we therefore thought it worthwhile to precipitate (using $(-)\text{Co}(\text{en})_3^{3+}$) this particular Mo(VI) oxalate complex, the crystal structure of which now follows.

Experimental

Analytical reagent grade chemicals (Merck) were used without further purification. Solutions were prepared with distilled deionized water. The compound $[(-)\text{Co}(\text{en})_3]\text{I}_3$ was prepared according to the method of Angelici (1969). To prepare the oxalato-molybdenum complex, the method outlined by Béltran *et al.* (1981) was followed. The quantities of Mo(VI) oxalate, hydrogen ions, and Co(III) were chosen to obtain in the reaction mixture a molar ratio corresponding to the stoichiometry of the complex reported by Béltran *et al.* (1981). The details of our preparation are as follows: to 10 cm³ of a solution 0.25 M in Na_2MoO_4 , 0.5 M in $\text{H}_2\text{C}_2\text{O}_4$ and 0.5 M in NaOH was added 5 cm³ of a warm solution of 0.667 M $[(-)\text{Co}(\text{en})_3]\text{I}_3$; a crystalline orange-yellow solid was immediately precipitated. This was separated by filtration and washed several times with warm water and finally with ether. Upon recrystallization from a dilute aqueous solution, well-defined orange-yellow crystals were obtained.

X-ray analysis

A single crystal was irradiated with Mo $K\alpha$ ($\lambda = 0.7107 \text{ \AA}$) on a CAD4 diffractometer. The orthorhombic cell obtained was refined using 24 reflections in the range $16 < \theta < 17^\circ$. Intensity and orientation checks were carried out periodically during the data collection. The data were corrected for Lp effects and an empirical absorption correction (North *et al.*, 1968) was applied. Further details of the data collection are given in Table 1.

The structure was solved using normal heavy atom methods. The I, Mo, and Co atoms were located in a Patterson map, and subsequent difference syntheses enabled the location of all other nonhydrogen atoms. The absolute structure of the crystal was inferred from the absolute configuration of the

Table 1. Crystal data, experimental details of the data collection, and final refinements of $[(-)Co(en)_3][MoO_3(C_2O_4)OH_2]I \cdot 2H_2O$

<i>Crystal data</i>		
Molecular formula	$C_8H_{30}O_{10}N_6CoMoI$	
M_r	652.14	
Space group	$P2_12_12_1$	
a (Å)	8.131(2)	
b (Å)	14.590(4)	
c (Å)	17.509(4)	
V	2077.0	
Z	4	
$F(000)$	1288	
μ (Mo $K\alpha$) (mm^{-1})	27.54	
Crystal dimensions (mm)	0.13 × 0.16 × 0.19	
Microanalysis:	Expected	Found
%C	14.73	14.8
%H	4.64	4.6
%N	12.89	12.9
%Co	9.04	8.8
%Mo	14.71	14.2
<i>Data collection</i>		
Scan mode	$\omega-2\theta$	
Scan width ($^\circ\omega$)	$0.74 + 0.35 \tan \theta$	
Aperture width (mm)	$1.12 + 1.05 \tan \theta$	
Aperture length (mm)	4	
Crystal decay (%)	1.2	
Number of unique reflections collected	2026	
θ range	1–25	
hkl range	$h: 0, 9; k: 0, 17; l: 0, 20$	
<i>Final refinement</i>		
Number of reflections observed ($I_{rel} > 2\sigma I_{rel}$)	1899	
Number of parameters	124	
$R = \Sigma \ F_o\ - F_c / \Sigma F_o $	0.048	
$R_w = \Sigma w \frac{1}{2} \ F_o\ - F_c / \Sigma w \frac{1}{2} F_o $	0.050	
w	$(\sigma^2 F)^{-1}$	

$[(-)Co(en)_3]I_3$ which is known to be a right-handed propeller (Nakatsu, 1962). In the final refinements, the I, Mo, and Co were treated anisotropically, and C, N, and O isotropically (hydrogens were not included in the final model). A weighting scheme, $(\sigma^2 F)^{-1}$, was applied. At this stage the data were examined to see if extinction effects were significant; i.e., F_{calc} lower than F_{obs} for the strong low-theta reflections. No considerable differences between F_{calc} and F_{obs} for these reflections were found and hence no correction for extinction applied. Further details of the final refinement are given in Table I and final fractional atomic coordinates and temperature factors are reported in Table 2. All computations were performed on a Sperry 1100/81 computer using SHELX-76 (Sheldrick, 1978) for structure solution and refinement, and PLUTO (Motherwell, 1974) for drawings. Complex neutral atom scattering factors were taken

Table 2. Fractional atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for nonhydrogen atoms of $[(-)\text{Co}(\text{en})_3][\text{MoO}_3(\text{C}_2\text{O}_4)\text{OH}_2]\text{I} \cdot 2\text{H}_2\text{O}$ with esd's in parentheses

Atom	x/a	y/b	z/c	U_{iso}		
I(1)	9458(1)	7158(1)	3239(1)			
Mo(1)	2889(1)	4165(1)	3963(1)			
Co(1)	5910(2)	5566(1)	1276(1)			
O(11)	2422(10)	4761(5)	2838(4)	27(2)		
O(12)	583(10)	4983(5)	1913(4)	31(2)		
O(21)	310(9)	4031(5)	3740(4)	26(2)		
O(22)	-1815(11)	4336(6)	2946(5)	37(2)		
O(31)	3418(10)	3120(6)	3570(5)	35(2)		
O(41)	4713(10)	4778(5)	3978(5)	34(2)		
O(51)	2459(10)	3903(5)	4921(5)	30(2)		
O(61)	1751(11)	5626(6)	4309(5)	38(2)		
O(1)	6015(15)	1776(8)	76(6)	71(3)		
O(2)	8080(12)	4083(6)	-473(5)	45(2)		
N(1)	4448(12)	6647(6)	1225(5)	41(2)		
N(2)	5528(12)	5618(6)	2392(5)	27(2)		
N(3)	3960(12)	4756(6)	1114(5)	26(2)		
N(4)	7200(12)	4424(6)	1352(5)	26(2)		
N(5)	7935(11)	6290(6)	1397(5)	22(2)		
N(6)	6304(11)	5676(6)	169(5)	25(2)		
C(1)	3570(14)	6747(8)	1976(6)	28(3)		
C(2)	4792(16)	6507(8)	2595(7)	31(3)		
C(3)	4553(20)	3791(10)	1068(9)	56(4)		
C(4)	6045(19)	3658(10)	1469(9)	51(4)		
C(5)	8818(15)	6364(8)	632(7)	30(3)		
C(6)	7501(15)	6427(8)	26(7)	30(3)		
Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$)						
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I	47(1)	41(1)	34(1)	-3(1)	-4(1)	6(1)
Mo	21(1)	21(1)	16(1)	3(1)	0(1)	2(1)
Co	22(1)	19(1)	13(1)	2(1)	0(1)	-1(1)

from Cromer and Mann (1968) with dispersion corrections from Cromer and Liberman (1970).

Results and discussion

The coordination around each metal ion and the atomic numbering scheme are shown in Fig. 1. A projection of the structure down a has been deposited. Selected molecular parameters are reported in Table 3. The cobalt(III) ethylenediamine cation and the molybdenum(VI) oxalate anion are discrete mono-

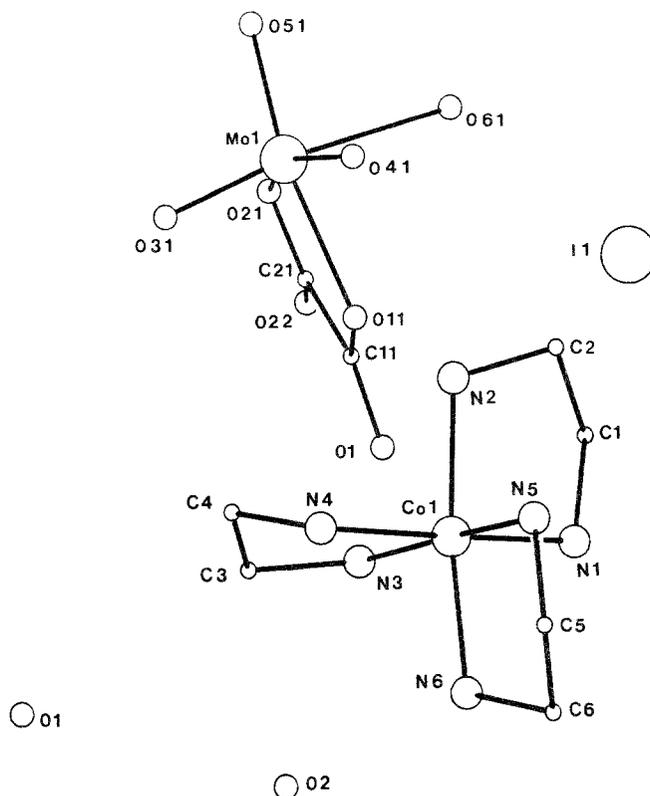


Fig. 1. Perspective view of the structure showing the coordination around each metal ion and the atomic numbering.

meric species in the ratio 1 : 1 in the structure, electrical neutrality being achieved by the cocrystallization of iodide.

The Co(III)ethylenediamine cation

Tris(ethylenediamine)cobalt(III) has been examined crystallographically in a variety of structures involving additional cations (Brouty *et al.*, 1978, 1980) and anions (Bok *et al.*, 1972; Brouty *et al.*, 1976). The $Co(en)_3^+$ cation, whether in its racemic or single enantiomeric form, has a relatively consistent set of molecular parameters in the different structures: an irregular octahedral configuration with the Co–N bond lengths in the range 1.94–2.05 Å, N–Co–N angles of the chelate rings in the range 82.5–88.5°, N–C distances 1.41–1.61 Å, C–C distances 1.48–1.55 Å. As shown in Table 3, the values obtained for $[(-)Co(en)_3]$ in this crystal structure lie within the previously reported, and therefore expected, ranges.

Table 3. Selected molecular parameters of $[(-)\text{Co}(\text{en})_3][\text{MoO}_3(\text{C}_2\text{O}_4)\text{OH}_2] \cdot 2\text{H}_2\text{O}$

Bond lengths (Å)			
Mo(1)–O(11)	2.186(8)	Co(1)–N(1)	1.976(9)
Mo(1)–O(21)	2.142(8)	Co(1)–N(2)	1.980(9)
Mo(1)–O(31)	1.727(8)	Co(1)–N(3)	1.998(9)
Mo(1)–O(41)	1.732(8)	Co(1)–N(4)	1.974(9)
Mo(1)–O(51)	1.756(8)	Co(1)–N(5)	1.967(9)
Mo(1)–O(61)	2.402(8)	Co(1)–N(6)	1.971(9)
O(11)–C(11)	1.284(13)	N(1)–C(1)	1.503(14)
O(21)–C(21)	1.292(13)	N(2)–C(2)	1.473(14)
C(11)–O(12)	1.239(13)	N(3)–C(3)	1.490(17)
C(21)–O(22)	1.237(15)	N(4)–C(4)	1.474(16)
C(11)–C(21)	1.539(15)	N(5)–C(5)	1.524(14)
		N(6)–C(6)	1.487(14)
		C(1)–C(2)	1.511(16)
		C(3)–C(4)	1.415(21)
		C(5)–C(6)	1.510(16)
Angles (deg)			
O(21)–Mo(1)–O(11)	72.6(3)	N(1)–Co(1)–N(2)	85.4(4)
O(31)–Mo(1)–O(11)	92.0(3)	N(1)–Co(1)–N(3)	89.3(4)
O(31)–Mo(1)–O(21)	95.2(3)	N(1)–Co(1)–N(4)	175.0(4)
O(41)–Mo(1)–O(11)	87.6(3)	N(1)–Co(1)–N(5)	94.6(4)
O(41)–Mo(1)–O(21)	152.6(3)	N(1)–Co(1)–N(6)	89.4(4)
O(41)–Mo(1)–O(31)	104.4(4)	N(2)–Co(1)–N(3)	92.2(4)
O(51)–Mo(1)–O(11)	155.9(3)	N(2)–Co(1)–N(4)	92.8(4)
O(51)–Mo(1)–O(21)	87.7(3)	N(2)–Co(1)–N(5)	90.3(4)
O(51)–Mo(1)–O(31)	103.8(4)	N(2)–Co(1)–N(6)	173.2(4)
O(51)–Mo(1)–O(41)	105.6(4)	N(3)–Co(1)–N(4)	86.1(4)
O(61)–Mo(1)–O(11)	78.9(3)	N(3)–Co(1)–N(5)	175.5(4)
O(61)–Mo(1)–O(21)	75.5(3)	N(3)–Co(1)–N(6)	92.2(4)
O(61)–Mo(1)–O(31)	168.5(4)	N(4)–Co(1)–N(5)	90.1(4)
O(61)–Mo(1)–O(41)	82.4(3)	N(4)–Co(1)–N(6)	92.8(4)
O(61)–Mo(1)–O(51)	82.8(3)	N(5)–Co(1)–N(6)	85.8(4)
C(11)–O(11)–Mo(1)	118.8(7)	Co(1)–N(1)–C(1)	108.9(6)
C(21)–O(21)–Mo(1)	121.5(7)	Co(1)–N(2)–C(2)	109.6(7)
C(21)–C(11)–O(11)	114.5(9)	Co(1)–N(3)–C(3)	108.0(8)
C(11)–C(21)–O(21)	112.2(10)	Co(1)–N(4)–C(4)	108.1(8)
C(21)–C(11)–O(12)	121.3(10)	Co(1)–N(5)–C(5)	109.7(6)
C(11)–C(21)–O(22)	121.0(10)	Co(1)–N(6)–C(6)	109.4(7)
O(11)–C(11)–O(12)	124.1(10)		
O(21)–C(21)–O(22)	126.8(11)	N(1)–C(1)–C(2)	107.0(9)
		N(2)–C(2)–C(1)	107.4(9)
		N(3)–C(3)–C(4)	112.3(13)
		N(4)–C(4)–C(3)	111.9(12)
		N(5)–C(5)–C(6)	106.7(9)
		N(6)–C(6)–C(5)	107.5(9)
Nonbonded distances (Å)			
O(1) ^a ⋯ O(61)	2.697(15)		
O(1) ^b ⋯ O(2)	2.783(15)		
O(2) ^c ⋯ O(41)	2.628(15)		

^aSymmetry element: $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.^bSymmetry element: $x + \frac{1}{2}, -y + \frac{1}{2}, -z$.^cSymmetry element: $-x + 1\frac{1}{2}, -y + 1, z + \frac{1}{2}$.

The molybdenum oxo-oxalate anion

A small number of x-ray structures of oxalate with molybdenum in oxidation states IV, V, and VI have been determined (Bino *et al.*, 1978; Cotton and Morehouse, 1965; Atarmyan and Bokii, 1963; Cotton *et al.*, 1964; Stomberg, 1970). The structure reported here is novel and is an important addition to this group.

The Mo(VI) is in an irregular octahedral environment: three short Mo–O distances in the range 1.727(8)–1.756(8) Å allow the assignment of double bonds (Cotton and Wing, 1965) between Mo(1) and O(31), O(41), and O(51); in addition, these three oxo groups are facially oriented with respect to each other, describing O–Mo–O angles in the range 103.8(4)–105.6(4)°. These O–Mo–O bond angles are the largest in the anion; this is expected in terms of the greater O ··· O repulsions between oxygen atoms with short bonds to the metal atom. The long Mo(1)–O(61) bond length, 2.402(8) Å, is typical of that of coordinated water (Cotton *et al.*, 1964). The two oxalate oxygen atoms O(11) and O(21) are at distances 2.186(8) and 2.142(8) Å from the coordinated metal ion, and subtend an angle of 72.6(3)° at the molybdenum; its smallness may be attributed to the constraint imposed by the chelate ring. It is comparable to the related angle in a similar dimeric Mo(VI) complex (Cotton *et al.*, 1964).

In contrast to the *cis*-dioxomolybdenum(VI) core which occurs in many complexes, the *cis*-trioxo unit MoO₃ has not proved to be common. In fact, only a few complexes having a MoO₃ unit are known and in these complexes molybdenum(VI) is coordinated with tridentate ligands such as diethylenetriamine (Cotton and Elder, 1964), 1,4,7-triazacyclononane (Herrmann and Wieghardt, 1986), and nitrolotriacetate which behaves in a tridentate manner via coordination with the nitrogen and two of the three carboxylate groups (Butcher and Penfold, 1976).

The structure of the molybdenum(VI) oxalato complex is the first to be characterized in which the MoO₃ core is obtained with a bidentate ligand, the 6-coordination sphere being completed with a water molecule.

The dimensions of the MoO₃ unit in the oxalate complex are similar to those found in the diethylenetriamine complex for which average Mo–O distances of 1.74 Å and average O–Mo–O bond angles of 106° have been reported (Cotton and Elder, 1964). The increase in Mo–O bond distance from about 1.68 (for MoO₂) to 1.74 Å (for MoO₃) has been explained in terms of weaker *dπ* bonding in the latter moiety where each of the three *dπ* orbitals (*d_{xy}*, *d_{yz}*, and *d_{xz}*) has to be shared by two oxygens. In the *cis* dioxo complexes each oxygen has the exclusive use of one *dπ* orbital while sharing only the third *dπ* orbital.

The structure reported here differs fundamentally from that previously proposed by Béltran *et al.* (1981). Conclusions from TGA and IR measurements

based on an anion structure containing two monodentate oxalate ligands (Béltan-Porter *et al.*, 1984) will therefore have to be reconsidered.

Packing in the crystal

The non-bonded O ··· O distances less than 2.8 Å involving the waters of crystallization O(1), O(2), and the oxygens on the molybdenum O(41) and O(61) imply the existence of an intermolecular hydrogen bonding network. There are no other interesting short intermolecular atomic contacts.

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