

The Crystal and Molecular Structures of Bis(η -methylcyclopentadienyl)-molybdenum(IV)di- μ -sulphido-disulphidomolybdenum(VI) and Di- μ -oxo-di- μ_3 -oxo-bis[bis(η -methylcyclopentadienyl)molybdenum(IV)dioxomolybdenum(VI)]

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(η -C₅H₄CH₃)₂Mo₂S₄ (I) is orthorhombic, *Cmcm*, with $a = 10.949$ (3), $b = 9.524$ (3), $c = 14.271$ (4) Å, $Z = 4$. [(η -C₅H₄CH₃)₂Mo₂O₄]₂ (II) is monoclinic, *C2/c*, $a = 15.380$ (5), $b = 9.049$ (3), $c = 17.717$ (5) Å, $\beta = 99.44$ (4)°, $Z = 4$. The structures were refined to $R = 0.035$ for 1018 counter reflexions (I) and $R = 0.072$ for 1671 reflexions (II). (II), with three dioxo bridges, can be described as a dimer of the binuclear group (η -C₅H₄CH₃)₂Mo₂O₄, each group being analogous to (I). An interesting feature is the planar geometry of the Mo₄O₄ unit. The structure and geometry indicate that the Mo atoms have the formal oxidation states +4 and +6.

Introduction

The role of organometallic intermediates in reactions such as dehydrosulphurization and the oxidation of olefins has received considerable attention in recent years. A first step in these reactions is thought to be the formation of organotransition metal oxides and sulphides. To further the understanding of this point, Green and coworkers prepared (η -C₅H₄CH₃)₂Mo₂S₄ and [(η -C₅H₄CH₃)₂Mo₂O₄]₂ whose crystal structures we report. This work has been the subject of a preliminary communication (Daran, Prout, Adam, Green & Sala-Pala, 1977).

Experimental

After surveys of the X-ray diffraction patterns had been made by precession techniques, the crystals were set up on a Hilger & Watts PDP8-controlled four-circle diffractometer and accurate cell dimensions and orientation matrix obtained by a least-squares procedure from the setting angles of 20 reflexions.

Crystal data

(η -C₅H₄CH₃)₂Mo₂S₄ (I), $M_r = 478$, orthorhombic, $a = 10.949$ (3), $b = 9.524$ (3), $c = 14.271$ (4) Å, $V = 1488$ Å³. $Z = 4$, $D_m = 2.10$, $D_c = 2.13$ g cm⁻³. Space group *C2cm*, *Cmc2₁* or *Cmcm*, systematic extinctions.

hkl , $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. $\mu = 21.6$ cm⁻¹, Mo $K\alpha$, $\lambda = 0.71069$ Å.

[(η -C₅H₄CH₃)₂Mo₂O₄]₂ (II), $M_r = 828$, monoclinic, $a = 15.380$ (5), $b = 9.049$ (3), $c = 17.717$ (5) Å, $\beta = 99.44$ (4)°, $V = 2432$ Å³. $Z = 4$, $D_m = 2.20$, $D_c = 2.26$ g cm⁻³. Space group *C2/c*, systematic extinctions, hkl , $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. $\mu = 20.3$ cm⁻¹, Mo $K\alpha$, $\lambda = 0.71069$ Å.

For each crystal, the intensities of every independent reflexion with $\theta < 30^\circ$ for (I) and $\theta < 25^\circ$ for (II) were measured with an $\omega/2\theta$ scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 60 steps of 0.02° . The 30 consecutive steps giving the highest total count were treated as peak, and the remaining 30 as background. Counting time at each step was 1 s. Mo $K\alpha$ radiation was used with a graphite monochromator (Bragg angle 6.05°). Reflexions with $I < 3\sigma(I)$, where σ is the standard deviation based on simple counting statistics, were not included in the subsequent calculations, which were based on the remaining 1018 and 1671 independent reflexions for (I) and (II) respectively. Reflexions for which the apparent centre was more than 0.18° from the predicted position were given an absolute weight of 0.01. An empirical absorption correction was applied in both compounds (North, Phillips & Mathews, 1968). The intensities were also corrected for Lorentz and polarization effects.

Structure solution and refinement

(η -C₅H₄CH₃)₂Mo₂S₄ (I): A Patterson synthesis gave Mo–Mo and Mo–S vectors consistent with *Cmcm*.

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Refinement in this centrosymmetric space group, with two Mo atoms located in the cell at positions $4-c-mm$, two S atoms at positions $8-g-m$ and two S atoms at positions $8-f-m$ gave convergence at $R = 0.16$ (full-matrix least-squares refinement with isotropic temperature factors). A Mo and S phased Fourier synthesis showed an unexpected six-membered ring. The preparative procedure involved makes it extremely unlikely that coordinated benzene is present in the structure, and the evidence from physical investigations such as infrared and NMR spectroscopy strongly indicates the presence of a coordinated methylcyclopentadienyl ligand. Indeed an attempt to refine these positions as C atoms led to an R value of 0.11 with unsatisfactory isotropic temperature factors and C—C distances. Examination of the difference electron density in the best plane of the C_6 ring showed that it was broad and diffuse (Fig. 1). Moreover there were two further peaks that appeared to belong to methyl groups either of disordered $C_3H_4CH_3$ molecules in space groups $Cmcm$ or $Cmc2_1$, to fit the map as shown in Fig. 1, or of $C_5H_4CH_3$ groups in space group $C2cm$ to which the heavy-atom phasing adds a pseudo inversion centre. Three trial

structures were set up, the first two in $Cmcm$ and $Cmc2_1$ with a disordered model, and the third in $C2cm$. All three models were refined by the full-matrix least-squares method with unit weights and anisotropic temperature factors. However, in each case, the C—C distances in the ring(s) were constrained to be 1.40 Å with an e.s.d. of 0.01 Å, by the method of Waser (1963) implemented by Rollett & Carruthers (1975) to avoid ill-conditioned normal matrices. The disordered model in $Cmc2_1$ reached convergence at 0.044, the disordered model in $Cmcm$ at 0.0431 and the ordered model in $C2cm$ at 0.0418. An F test showed ambiguity between space groups $Cmcm$ and $C2cm$, so further refinements were carried out introducing a secondary-extinction parameter (Larson, 1970) and with the weighting scheme $w = 1/\sum_{r=1}^n A_r T_r(X)$ with n coefficients, A_r , for the Chebyshev polynomial $T_r(X)$ where X was $F_o/F_o(\max.)$ (Rollett, 1965). Two cycles of refinement in each case produced an R of 0.0372 and 0.0368 in $Cmcm$ and $C2cm$ respectively; the weighted $R_w = [\sum w(F_o - F_c)^2 / \sum wF_c^2]^{1/2}$ were 0.0402 and 0.0436. Moreover examination of dimensions for the $C_3H_4CH_3$ group proved them to be unsatisfactory in

Table 1. Distances (Å) and angles (°) with e.s.d.'s in parentheses for compound (I)

Mo(1)—Mo(2)	2.970 (1)	S(1)—Mo(1)—S(1')	95.84 (7)
Mo(1)—S(1)	2.424 (1)	Mo(1)—S(1)—Mo(2)	78.87 (4)
Mo(2)—S(1)	2.247 (1)	S(1)—Mo(2)—S(1')	106.42 (6)
Mo(2)—S(2)	2.141 (1)	S(2)—Mo(2)—S(2')	111.7 (1)
Mo(1)—C(1)	2.37 (1)	S(1)—Mo(2)—S(2)	109.65 (4)
Mo(1)—C(2)	2.31 (1)	C(1)—C(2)—C(3)	109.9 (9)
Mo(1)—C(3)	2.33 (1)	C(2)—C(3)—C(4)	104.1 (7)
Mo(1)—C(4)	2.34 (1)	C(3)—C(4)—C(5)	111 (1)
Mo(1)—C(5)	2.44 (2)	C(4)—C(5)—C(1)	107 (2)
C(1)—C(2)	1.42 (1)	C(5)—C(1)—C(2)	108 (1)
C(2)—C(3)	1.40 (1)	C(4)—C(5)—C(6)	125.1 (9)
C(3)—C(4)	1.44 (2)	C(1)—C(5)—C(6)	128 (2)
C(4)—C(5)	1.40 (2)		
C(5)—C(1)	1.39 (2)		
C(5)—C(6)	1.48 (2)		

Table 2. Fractional atomic coordinates ($\times 10^3$) for compound (I), with e.s.d.'s in parentheses

	x	y	z
Mo(1)	0	344.1 (1)	$\frac{1}{4}$
Mo(2)	0	32.1 (1)	$\frac{1}{4}$
S(1)	164.3 (1)	173.4 (1)	$\frac{1}{4}$
S(2)	0	-94.2 (2)	$\frac{3}{4}$
C(1)	38 (1)	317 (1)	88 (1)
C(2)	116 (1)	422 (1)	126 (1)
C(3)	47 (2)	537 (1)	156 (1)
C(4)	-77 (1)	498 (1)	136 (1)
C(5)	-81 (1)	367 (1)	91 (1)
C(6)	-189 (1)	297 (1)	48 (1)
H(1)	69	218	49
H(2)	194	430	120
H(3)	69	629	187
H(4)	-148	523	152

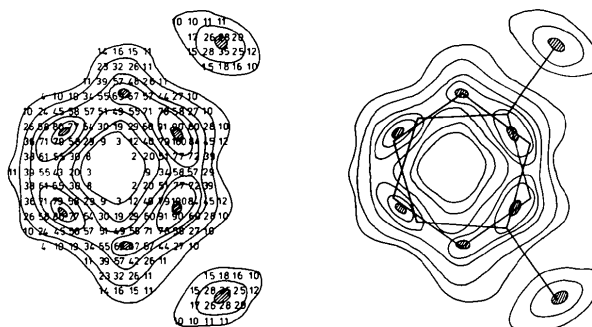


Fig. 1. The difference electron density in the best plane of the pseudo C_6 ring calculated with F_c based on contributions from only Mo and S atoms. The disordered model is shown fitted to the electron density.

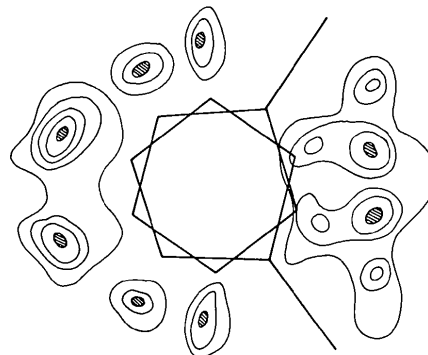


Fig. 2. Hydrogen-atom electron density shown in the slant difference synthesis calculated in the best planes of the $\eta-C_5H_5$ rings with F_c based on the disordered model for all atoms except hydrogen.

space group $C2cm$. These results led us to carry on refinement in $Cmcm$. H atoms attached to the ring were found from a difference map projected on to the best plane of this ring (Fig. 2). Positions of H atoms emphasized the disorder. A structure factor calculation with these atoms led to $R = 0.036$ and $R_w = 0.040$, but an attempt to refine atomic coordinates did not give a significantly better result. With H atoms in fixed positions found from the slant difference map, two further cycles of refinement after removal of constraints gave convergence at $R = 0.035$ and $R_w = 0.037$ with a satisfactory set of C—C distances and C—C—C angles (Table 1). The final atomic parameters are given in Table 2. All e.s.d.'s were calculated from the full variance-covariance matrix.* Three coefficients A_r were used in the Chebyshev series: 70.6, 98.4 and 33.1; the secondary-extinction parameter was 9.

$[(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}_2\text{O}_4]_2$ (II): Mo and O atoms were found from an unsharpened Patterson function. A Mo phased Fourier synthesis showed all the C atoms. The refinement (full-matrix least-squares procedure with isotropic temperature factors, then anisotropic) of the trial structure in $C2/c$ gave $R = 0.075$. The refinement continued with the weighting scheme $w = \{1 + [(|F_o| - 51)/43]^2\}^{-1}$, and a Larson (1970) secondary-extinction

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33820 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates ($\times 10^3$) for compound (II), with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Mo(1)	269.4 (1)	498.6 (2)	129.0 (1)
Mo(2)	241.8 (1)	151.2 (2)	78.6 (1)
O(1)	261.2 (7)	359 (1)	33 (1)
O(2)	240.4 (8)	287 (1)	157 (1)
O(3)	148.0 (9)	49 (2)	81 (1)
O(4)	328.7 (9)	36 (2)	111 (1)
C(1)	422 (1)	444 (2)	131 (1)
C(2)	404 (1)	418 (3)	204 (1)
C(3)	375 (1)	561 (4)	232 (1)
C(4)	376 (1)	662 (3)	176 (1)
C(5)	402 (1)	597 (3)	111 (1)
C(6)	463 (1)	332 (3)	84 (2)
C(7)	113 (1)	514 (2)	129 (1)
C(8)	159 (1)	594 (3)	188 (1)
C(9)	200 (1)	709 (3)	158 (2)
C(10)	188 (1)	694 (3)	77 (2)
C(11)	133 (1)	576 (3)	60 (1)
C(12)	52 (2)	385 (3)	130 (2)
H(2)	413	327	234
H(3)	363	575	285
H(4)	361	770	180
H(5)	415	647	65
H(8)	157	576	244
H(9)	237	789	188
H(10)	221	758	44
H(11)	111	537	6

Table 4. Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses for compound (II)

Mo(1)—Mo(2)	3.276 (2)	O(1)—Mo(1)—O(2)	69.5 (4)
Mo(2)—Mo(2')	3.354 (3)	Mo(1)—O(1)—Mo(2)	103.0 (5)
Mo(1)—O(1)	2.11 (1)	Mo(1)—O(2)—Mo(2)	113.5 (6)
Mo(1)—O(2)	2.05 (1)	O(1)—Mo(2)—O(2)	73.6 (5)
Mo(2)—O(1)	2.09 (1)	Mo(2)—O(1)—Mo(2')	111.0 (5)
Mo(2)—O(1')	1.97 (1)	O(1)—Mo(2)—O(1')	69.0 (5)
Mo(2)—O(2)	1.86 (1)	O(1)—Mo(2)—O(3)	132.0 (6)
Mo(2)—O(3)	1.72 (1)	O(1)—Mo(2)—O(4)	121.4 (6)
Mo(2)—O(4)	1.72 (1)	O(3)—Mo(2)—O(4)	106.1 (7)
Mo(1)—C(1)	2.40 (2)	C(1)—C(2)—C(3)	106 (2)
Mo(1)—C(2)	2.38 (2)	C(2)—C(3)—C(4)	108 (2)
Mo(1)—C(3)	2.31 (2)	C(3)—C(4)—C(5)	109 (2)
Mo(1)—C(4)	2.26 (2)	C(4)—C(5)—C(1)	107 (2)
Mo(1)—C(5)	2.30 (2)	C(5)—C(1)—C(2)	108 (2)
Mo(1)—C(7)	2.41 (2)	C(5)—C(1)—C(6)	127 (2)
Mo(1)—C(8)	2.30 (2)	C(2)—C(1)—C(6)	124 (2)
Mo(1)—C(9)	2.28 (2)	C(7)—C(8)—C(9)	109 (2)
Mo(1)—C(10)	2.27 (2)	C(8)—C(9)—C(10)	109 (2)
Mo(1)—C(11)	2.36 (2)	C(9)—C(10)—C(11)	106 (2)
C(1)—C(2)	1.39 (3)	C(10)—C(11)—C(7)	109 (2)
C(2)—C(3)	1.48 (4)	C(11)—C(7)—C(8)	107 (2)
C(3)—C(4)	1.35 (4)	C(11)—C(7)—C(12)	123 (2)
C(4)—C(5)	1.41 (3)	C(8)—C(7)—C(12)	130 (2)
C(5)—C(1)	1.45 (3)	Mo(1)—O(1)—Mo(2')	145.8 (5)
C(1)—C(6)	1.51 (3)	O(2)—Mo(2)—O(3)	102.6 (6)
C(7)—C(8)	1.37 (3)	O(2)—Mo(2)—O(4)	104.6 (6)
C(8)—C(9)	1.37 (4)	O(1')—Mo(2)—O(3)	100.9 (5)
C(9)—C(10)	1.42 (4)	O(1')—Mo(2)—O(4)	97.0 (5)
C(10)—C(11)	1.37 (4)		
C(11)—C(7)	1.42 (3)		
C(7)—C(12)	1.50 (3)		

correction with parameter 17 gave convergence at $R = 0.072$ and $R_w = 0.082$. Difference maps in the planes of the C_5 rings indicated H-atom sites but when these were included in the refinement there was no improvement in R .

The final atomic parameters are in Table 3. Table 4 gives the interatomic distances and angles with e.s.d.'s calculated from the full variance-covariance matrix.

All calculations were carried out on the OUCI ICL1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1975). The scattering factors and corrections for the real part of the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962).

Discussion

$(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}_2\text{S}_4$ exists in the solid state as a discrete dimer. The two parts are linked by two bridging S atoms such that Mo and S atoms form a planar four-membered ring (Figs. 3 and 4), with Mo—Mo = 2.970 Å. This distance is longer than has been suggested for a Mo—Mo single bond: 2.541 Å in $\text{Ba}[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ (Cotton & Morehouse, 1965), but falls within the range 2.1–3.2 Å for

Mo—Mo bonds (Lawton & Mason, 1965; Churchill & Bird, 1968) and therefore indicates a slight interaction between the two atoms. This interaction is also shown by the angles within the planar ring, since that at S is reduced from the normal 109 to 78.87°, whilst that at Mo(1), 95.84°, is larger than would be expected from a d^2 electron configuration (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974), and that at Mo(2) is 106.42°.

In the bridge the Mo(1)—S(1) and Mo(2)—S(1) distances, 2.424 (1) and 2.247 (1) Å respectively, are significantly different. The first is similar to values observed for Mo—S lengths in different bis(cyclopentadienyl) complexes of the type $(\eta\text{-C}_5\text{H}_5)_2\text{MoL}_2$, e.g. 2.464 (5) in $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\mu\text{-SBu})_2\text{FeCl}_2$ (Cameron & Prout, 1972), 2.46 (1) in $\text{H}[(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{cysteine})]\text{-PF}_6$ (Prout, Allison, Delbaere & Gore, 1972), and 2.438 (6) Å in $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_2\text{H}_4\text{NH}_2)$ (Knox & Prout, 1969). Mo(2)—S(1), 2.247 Å, is shorter than the usual Mo—S single bond (Blake, Cotton & Wood, 1964). This shortness suggests that there must be considerable multiple-bond character, related to $d\pi\text{-}p\pi$ bonding. An Mo—S length of 1.937 (6) Å was found in

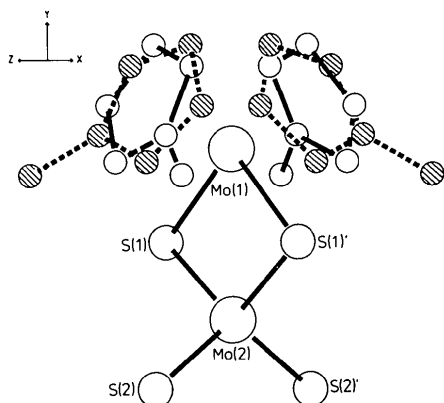


Fig. 3. The $(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}_2\text{S}_4$ molecule seen projected down a direction perpendicular to c .

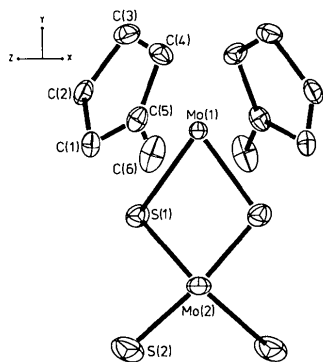


Fig. 4. Thermal ellipsoids of the $(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}_2\text{S}_4$ molecule seen projected down a direction perpendicular to c .

$\text{Mo}_2\text{S}_4[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_2$ (Spivack, Dori & Steifel, 1975) and a bond order of 2 was suggested. Therefore, in our case, a bond order of 1.5 can be assumed.

The coordination around Mo(2) is almost a perfect tetrahedron with angles at Mo of 106.42 (6), 111.7 (1) and 109.65 (4)°. The Mo(2)—S(2) distance, 2.141 Å, again suggests multiple-bond character with a bond order of nearly 1.5. Therefore, Mo(2) can be formally regarded as Mo^{VI} . Such an environment is unusual for a Mo atom with this oxidation state in organometallic systems.

The Mo(1) coordination is similar to that found in the bent bis(η -cyclopentadienyl) MX_2 (Prout *et al.*, 1974). In the ring the average bond length is 1.41 Å and within one e.s.d. of that found by these authors; the average bond angle is 108°. The Mo—C distances lie in the range 2.27–2.38 Å. The length of the normal to the C_5 ring at the Mo atom is 2.027 Å and the angle between the normals is 128.2°. The line of intersection of the S—Mo(1)—S plane and the ring-normals plane bisects this angle. The torsion angle of these planes is 90°.

The unit cell of (II) contains four molecules with the structure shown in Fig. 5. This system with three dioxo bridges can be best described as a dimer of the binuclear group $(\text{C}_5\text{H}_4\text{CH}_3)_2\text{Mo}_2\text{O}_4$, which is analogous to (I). A crystallographic inversion centre relates the two parts of the molecule and is located in bridge (2) (Fig. 5). Therefore this bridge is planar with a Mo—Mo distance of 3.353 Å, and two significantly different Mo—O lengths, 2.09 (1) for Mo(2)—O(1) and 1.97 (1) Å for Mo(2)—O(1)'. The *trans* relation of the first one to the multiple Mo—O terminal bonds could explain the lengthening. The two independent angles, 69.0 (5)° at Mo(2) and 111.0 (5)° at O(1), suggest a mutual repulsion between metal atoms and tend to confirm that the Mo—Mo contact of 3.357 Å cannot be considered as a bond.

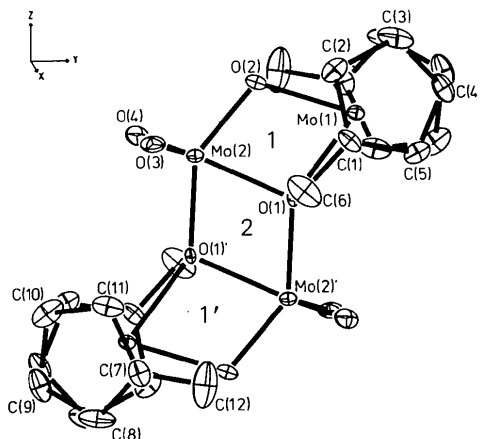


Fig. 5. The $[(\eta\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Mo}_2\text{O}_4]_2$ molecule in projection on to the best plane defined by the Mo_2O_4 unit. The labelled atoms C(7)—C(11) are related to those in Table 3 by an inversion centre.

Table 5. *Least-squares best planes defined by atomic positions, and distances (Å) of atoms from these planes (X, Y and Z are fractional coordinates)*

Plane 1: atoms Mo(1), Mo(2), O(1) and O(2)

$$\text{Equation of plane: } 14.713X - 1.401Y + 1.533Z = 3.424$$

Mo(1)	0.039	O(1)	-0.037
Mo(2)	0.042	O(2)	-0.045

Plane 2: atoms Mo(1), Mo(2), O(1), O(2), Mo(1'), Mo(2'), O(1') and O(2')

$$\text{Equation of plane: } 14.85X - 1.449Y + 0.782Z = 3.35$$

Mo(1)	0.083	O(1)	0.03
Mo(2)	0.029	O(2)	-0.07

Plane 3: atoms Mo(1), Mo(2) and Mo(2')

$$\text{Equation of plane: } 15.024X - 1.215Y + 0.073Z = 3.46$$

Mo(1)	-0.01	Mo(2')	-0.011
Mo(2)	-0.006	O(1)	0.026

Bridge (1) (and 1') is also planar (Table 5). Although the Mo—Mo distance is shorter than in bridge (2), the very acute O—Mo—O angles, 69.5 (4) and 73.6 (5)°, and the obtuse bridging angles, Mo—O—Mo 113.5 (6) and 103.0 (5)°, are inconsistent with metal—metal bonding (Dahl, de Gil & Feltham, 1969). Within experimental error, Mo(1)—O(1) 2.11 (1) and Mo(1)—O(2) 2.05 (1) Å are identical, and are in good agreement with 2.10 (2) Å for Mo—O bonds in $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{glycine, or sarcosine})\text{Cl}$ (Prout, Allison, Delbaere & Gore, 1972) and 2.07 (1) and 2.09 (1) Å in $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-}\eta\text{-C}_5\text{H}_4\text{-}\eta\text{-C}_5\text{H}_4)(\mu\text{-H})(\mu\text{-OH})]2\text{PF}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ (Prout & Couldwell, 1977). The O(2)—Mo(1)—O(1) angle, 69.5°, is rather less than those previously observed for a d^2 electron configuration which lie in the range 72–83° (Prout *et al.*, 1974). The same value of 69° has been found in bridge (2). The remaining angle at Mo(2), 73.6 (5)°, is comparable to those found by Beaver & Drew (1973) in $\text{Mo}_4\text{O}_6(\text{OC}_3\text{H}_7)_6\text{Cl}_4$, 75.1 (4) and 72.5 (5)°.

Mo(2) has a trigonal-bipyramidal geometry. Although the Mo(2)—O(1) distance, 2.09 Å, to the bridging O atom in the equatorial plane is longer than that to the two bridging O atoms at the apices, 1.86 and 1.98 Å, they all suggest that the bonding is multiple in character. The equatorial plane also contains two terminal O atoms (*O_t*) with Mo—O length of 1.72 (1) Å and O—Mo—O angle of 106.1°. Spivack & Dori (1975) indicate that with Mo in the oxidation state +6, the most reasonable values for the Mo—*O_t* distance and the *O_t*—Mo—*O_t* angle are 1.69 ± 0.01 Å and $105 \pm 1^\circ$, respectively. Therefore the structure and geometry strongly suggest, as in (I), that Mo(2) has the formal oxidation state +6.

The geometry around Mo(1) is as commonly found in bent bis(η -cyclopentadienyl) systems (Prout *et al.*, 1974). The rings are roughly staggered. The average C—C length and C—C—C angle are 1.41 Å and 108°

respectively. The normals to the mean planes of the rings are both 1.99 Å and are inclined at an angle of 128.6°. The line of intersection of the O—Mo—O plane and the ring-normals plane roughly bisects this angle, making angles of 64.8 and 63.8°.

O(1) [and O(1')] bridges three Mo atoms and is shared between bridge (2) and (1) (and 1'). These three dioxo bridges, namely Mo_4O_4 , almost make up a planar system; the maximum deviation of an atom from the plane being 0.083 Å. Therefore the Mo_3O unit is also planar, with a maximum deviation of 0.026 Å. The occurrence of planar geometry in a three-coordinated O atom is rare, and is attributed to interaction of the O atom lone pair with suitable π orbitals (Hessel & Romers, 1969). Such interaction is certainly promoted by the high positive charge on Mo(2).

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The Crystal Structure of Tris(oxamide oxime)cobalt(III) Trichloride, $\text{Co}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_3\text{Cl}_3$

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Monoclinic, $P2_1/c$, $a = 13.429$ (2), $b = 15.831$ (2), $c = 9.455$ (3) Å, $\beta = 115.63$ (2)°. There are four discrete formula units in the unit cell, forming a racemate. The Co^{III} atoms are octahedrally coordinated by the bidentate ligand. The structure was solved by Patterson and Fourier methods and refined by a least-squares procedure to $R = 0.037$ for 4990 independent reflections.

Introduction

The compound under investigation has been synthesized by dissolving bis(oxamide oximate)cobalt(II)–oxamide oxime, $\text{Co}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)_2 \cdot \text{C}_2\text{H}_6\text{N}_4\text{O}_2$ (I) (Bekaroglu, Sarisaban, Koray & Kiegler, 1977), in water and recrystallizing the brown precipitate which appeared after 2 h from hydrochloric acid (Sarisaban, 1976). The possibly chelating ligand oxamide oxime ('diaminoglyoxime') recently received new interest when the X-ray structure determinations of (I) and bis(oxamide oximate)nickel(II)–water–dimethylformamide, $\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)_2 \cdot \text{H}_2\text{O} \cdot \text{C}_3\text{H}_7\text{O}$ (II) (Endres, 1978), were reported. In the Co complex mentioned above the Co atom has a pseudooctahedral environment, being coordinated by four oxime N atoms of two chelating $\text{C}_2\text{H}_5\text{N}_4\text{O}_2^-$ groups (OAOH) and one amino N of two adjacent complex molecules each. By this mechanism a chain polymer is formed. In contrast to the Co^{II} complex, there are no interactions between the Ni central atom and amino N atoms of adjacent molecules, there being discrete square-planar $\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)_2$ units with DMF acting solely as a 'space filler'. We now report the X-ray structure determination of tris(oxamide oxime)cobalt(III) trichloride, $\text{Co}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_3\text{Cl}_3$ (III), in which the oxamide oxime ligands are bonded in

a different way from that which has been reported for the Ni and Co complexes discussed above and also from that known for diacetyldioxime complexes.

Rotating-crystal and Weissenberg photographs ($\text{Cu } K\alpha$ radiation) showed the crystal to be monoclinic and provided rough lattice constants. Exact lattice parameters could be calculated by the least-squares method (Berdiesinski & Nuber, 1966) from diffractometrically determined exact θ values of 75 selected reflections. Intensity measurements were performed on a computer-controlled single-crystal diffractometer (AED-Siemens, $\text{Mo } K\alpha$, θ – 2θ scans, five-value method) up to $2\theta = 69.98^\circ$. Reflections with an intensity less than 2.58 times the standard deviation were not considered. A total of 4990 observed independent intensities remained for calculations. They

Table 1. *Crystal data*

$\text{Co}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_3\text{Cl}_3$	$Z = 4$
Space group $P2_1/c$	$V = 1812.30 \text{ \AA}^3$
$\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$	$D_o = 1.87 \text{ g cm}^{-3}$
$a = 13.429$ (2) Å	$D_c = 1.881$
$b = 15.831$ (2)	$F(000) = 1060.00$
$c = 9.455$ (3)	FW 516.56
$\beta = 115.63$ (2)°	$\mu(\text{Mo } K\alpha) = 7.84 \text{ cm}^{-1}$
Systematic absences $\left. \begin{array}{l} 0k0: k = 2n + 1 \\ h0l: l = 2n + 1 \end{array} \right\}$	$69.977 \geq 2\theta \geq 4.235^\circ$
Crystal size: $0.4 \times 0.2 \times 0.2 \text{ mm}$	Independent reflections: 4990

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