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The Crystal Structure of the Potassium Salt of the Binuclear Mo^{III} Anion Di-μ-hydroxo-μ-acetato-μ-ethylenediaminetetraacetato-bis[molybdenum(III)], $K[Mo_2(OH)_2(C_{12}H_{15}O_{10}N_2)]$

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The complex potassium salt $K[Mo_2(OH)_2(C_{12}H_{15}O_{10}N_2)]$ crystallizes in the orthorhombic system, space group *Fdd*2, with cell dimensions $a=7{\cdot}486$, $b=25{\cdot}463$, $c=20{\cdot}133$ Å and eight molecules in the unit cell. The structure was solved by Patterson and Fourier syntheses and refined by full-matrix least-squares methods to a final *R* index of 0·06. The anion lies on a crystallographic twofold rotation axis and contains two molybdenum atoms each coordinated by six ligands in a distorted octahedral environment. The two octahedra share a common edge containing two bridging oxygen atoms. An unusual feature is the presence of two other bridging groups which complete the coordination sphere, *viz.* a hexadentate EDTA and a bidentate acetate group. The short Mo–Mo distance of 2·43 Å indicates a strong metal–metal bond.

Introduction

Molybdenum is one of the important transition metals in biological systems (see *e.g.* Spence, 1969). It is an integral part of various redox enzymes including xanthine oxidase, nitrogenase, and nitrate reductase. Its unique properties appear to be due to its ability to exist in a number of different oxidation states and to coordinate with a variety of ligands. Mo^{V} and Mo^{VI} are generally thought to be the most likely oxidation states involved but work on xanthine oxidase has implicated Mo^{III} (Palmer & Massey, 1969). Consequently a number of crystal structures of Mo^{V} and Mo^{VI} complexes with amino acids and polycarboxylic acids have been reported as possible model compounds (see *e.g.* Drew & Kay, 1971; Delbaere & Prout, 1971; Knox & Prout, 1969; Spivak & Dori, 1973; Cotton & Morehouse, 1965; Cotton, Morehouse & Wood, 1964). In view of the lack of information on suitable Mo^{III} systems we have undertaken the crystal-structure analysis of a binuclear Mo^{III} complex with the polycarboxylic amino acid ethylenediaminetetraacetic acid. Details of the preparation and characterization of this compound will be presented elsewhere (Y. Sasaki and A. G. Sykes, manuscript in preparation).

Experimental

Crystal data

$K[Mo_2(OH)_2C_{12}H_{15}O_{10}N_2]$; M. W. 612. Source: Dr A. G. Sykes, Department of Inorganic and Structural Chemistry, University of Leeds. Crystal system: orthorhombic. Space group: *Fdd*2 (No. 43). $a=7{\cdot}486$ (6), $b=25{\cdot}463$ (21), $c=20{\cdot}133$ (16) Å, $V=3838$ Å^3, $Z=8$. $D_c=2{\cdot}12$, $D_m=2{\cdot}12$ g cm^{-3}. Density measured by flotation in $CCl_4/CHBr_3$. Systematic absences: *hkl*: $h+k, k+l, l+h=2n+1$; 0*kl*: $k+l=4n+1,2,3$; *h*0*l*: $h+l=4n+1,2,3$. Radiation: graphite-monochromatized Cu $K\alpha$, $\lambda=1{\cdot}54051$ Å.

The crystals were dark green, approximately 0·5×0·5×0·3 mm, with well defined faces. Space group *Fdd*2 has 16 equivalent positions but density measurements showed only eight molecules in the unit cell. Thus two halves of the molecule arerelated by a crystallographic twofold rotation axis. Three-dimensional intensity data were collected from a single crystal using an Enraf–NoniusCAD-4 diffractometer and measured by the moving-crystal moving-counter technique in the range $3° \le \theta \le 70°$. A control reflexion was measured every 50 reflexions and varied by less than ±2% throughout. 963 independent reflexions were measured and their intensities corrected for Lorentz and polarization factors. No correction was made for absorption.

Structure determination and refinement

The Mo–Mo vectors at $2x, 2y, 0$ were readily identified on a three-dimensional Patterson map. With the molybdenum positions calculated from these a three-dimensional Fourier synthesis was computed and this revealed the coordinated nitrogen and oxygen atoms and also the potassium ion lying on the twofold axis. With these additional atoms another Fourier synthesis was performed which revealed the atoms C(1), C(2), C(3), C(4), C(5), O(5) and O(6) (see Fig. 1 for a perspective drawing of the anion showing the numbering of the atoms). The structure was refined by full-matrix least-squares methods to an *R* value of 0·10. At this stage a difference Fourier synthesis revealed two peaks lying on the twofold axis within bonding distances of each other, and one of which was within bonding distance of atoms O(2) and O(2′). The heights of these peaks indicated that they were carbon atoms. It had originally been thought that the atoms O(2) and O(2′) were the oxygen atoms of water molecules but this last difference Fourier synthesis shows that they must be the carboxylate oxygen atoms of an acetate bridging ligand (acetate was in fact used as a buffer in the preparation of the compound). With the inclusion of the two carbon atoms of this acetate group the structure refined isotropically to an R value of 0·06.*

All computations were carried out using the X-RAY 70 suite of programs (Stewart, Kundell & Baldwin, 1970). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Attempts to refine the structure further using anisotropic temperature factors resulted in one component of the thermal vibrations of several atoms going negative. This is possibly a result of the lack of correction for absorption.

Table 1. *Fractional atomic coordinates and isotropic temperature factors* ($\times 10^4$)

Estimated standard deviations are in parentheses.

	x/a	y/b	z/c	U_{iso}
Mo	3344 (2)	2092 (1)	2853	56 (3)
O(1)	634 (16)	2173 (5)	2737 (7)	140 (28)
O(2)	3338 (18)	2144 (6)	1791 (7)	154 (31)
O(3)	6127 (16)	1922 (5)	2903 (8)	157 (27)
O(4)	2747 (15)	1284 (5)	2922 (8)	144 (27)
O(5)	8343 (22)	1828 (6)	3617 (9)	286 (36)
O(6)	1417 (20)	679 (6)	3533 (8)	234 (34)
C(1)	5418 (24)	1667 (7)	4015 (10)	133 (36)
C(2)	6749 (26)	1818 (8)	3488 (11)	162 (42)
C(3)	2235 (22)	1473 (7)	4056 (9)	71 (34)
C(4)	2123 (23)	1111 (7)	3471 (9)	86 (35)
C)5)	3368 (24)	2353 (7)	4414 (10)	129 (38)
C(6)	2500	2500	747 (15)	214 (64)
C(7)	2500	2500	1478 (14)	97 (50)
N	3575 (20)	1912 (7)	3907 (9)	96 (31)
K	7500	2500	1897 (3)	142 (12)

Table 2. *Bond lengths* (Å) *and estimated standard deviations*

Mo–Mo′	2·430 (3)	C(1)–C(2)	1·51 (4)
Mo–O(1)	2·05 (2)	C(2)–O(3)	1·29 (4)
Mo–O(1′)	2·03 (2)	C(2)–O(5)	1·22 (4)
Mo–O(2)	2·14 (2)	C(3)–C(4)	1·52 (4)
Mo–O(3)	2·13 (2)	C(4)–O(4)	1·28 (4)
Mo–O(4)	2·11 (2)	C(4)–O(6)	1·23 (4)
Mo–N	2·18 (2)	C(5)–C(5′)	1·50 (5)
N—C(1)	1·53 (4)	C(6)–C(7)	1·47 (8)
N—C(3)	1·53 (4)	C(7)–O(2)	1·27 (5)
N—C(5)	1·53 (4)		

Table 3. *Bond angles* (°) *and estimated standard deviations*

O(1)–Mo –O(1′)	105·5 (8)	O(3)–C(2)–O(5)	123 (3)
O(1)–Mo –O(2)	83·0 (8)	C(4)–C(3)–N	109 (2)
O(1)–Mo –O(3)	172·9 (8)	C(3)–C(4)–O(4)	117 (2)
O(1)–Mo –O(4)	84·0 (8)	C(3)–C(4)–O(6)	120 (2)
O(1)–Mo –N	102·1 (9)	O(4)–C(4)–O(6)	124 (2)
O(2)–Mo –O(1′)	80·2 (8)	N—–C(5)–C(5′)	117 (2)
O(2)–Mo –O(3)	93·6 (9)	C(6)–C(7)–O(2)	120 (4)
O(2)–Mo –O(4)	97·2 (8)	O(2)–C(7)–O(2)	121 (3)
O(2)–Mo –N	170·2 (8)	Mo—O(1)–Mo′	73·0 (8)
O(3)–Mo –O(1′)	80·0 (8)	Mo—O(2)–C(7)	123 (2)
O(3)–Mo –O(4)	90·3 (7)	Mo—O(3)–C(2)	116 (2)
O(3)–Mo –N	80·4 (9)	Mo—O(4)–C(4)	118 (2)
O(4)–Mo –O(1′)	169·7 (8)	C(1)–N—–Mo	107 (2)
O(4)–Mo –N	75·3 (9)	C(1)–N—–C(3)	105 (2)
N—–Mo –O(1′)	106·0 (9)	C(1)–N—–C(5)	107 (2)
C(2)–C(1)–N	113 (2)	C(3)–N—–Mo	107 (2)
C(1)–C(2)–O(3)	117 (2)	C(3)–N—–C(5)	110 (2)
C(1)–C(2)–O(5)	120 (3)	C(5)–N—–Mo	119 (2)

Results and discussion

The atomic coordinates and temperature factors, bond lengths, and bond angles are listed in Tables 1, 2 and 3 respectively. The anion consists of two molybdenum atoms each coordinated in a distorted octahedral environment by five oxygen atoms and a nitrogen atom. Oxygens O(1) and O(1′) are shared between the molybdenum atoms, forming a double bridge. These oxygen atoms are assumed to be protonated to give the anion unit negative charge. Atoms O(3), O(4) and N from one end of the hexadentate EDTA molecule coordinate to one of the molybdenum atoms while atoms O(3′), O(4′) and N′ coordinate to the other, forming a third bridge. The acetate group forms a fourth bridge *via* O(2) and O(2′).

The Mo–O(2), Mo–O(3) and Mo–O(4) bond lengths of 2·14, 2·13 and 2·11 Å respectively do not differ significantly between themselves or from the Mo–O(carboxyl) bonds in $[Mo_2^V(\mu\text{-}S)_2(\mu\text{-}EDTA)O_2]^{2-}$ (Spivak & Dori, 1973) and $[Mo_2^V(\mu\text{-}O)_2(\text{oxalate})_2O_2(H_2O)_2]^{2-}$ (Cotton & Morehouse, 1965). They are about 0·1 to

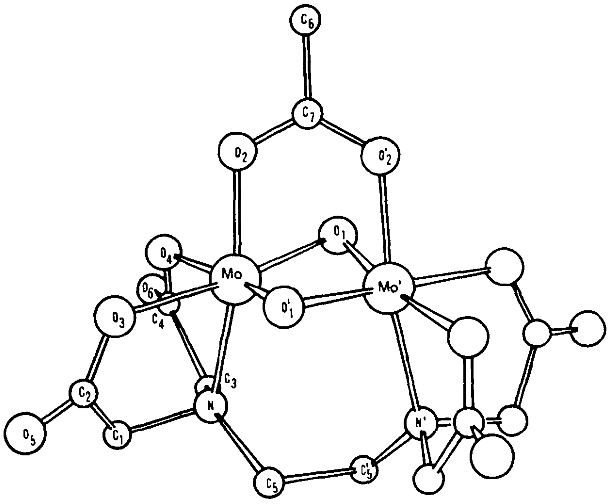

Fig. 1. Perspective view of the binuclear Mo^{III} anion. Primed and unprimed atoms are related by a twofold rotation axis bisecting and perpendicular to the line joining the molybdenum atoms and the line joining the bridging oxygen atoms.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30813 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

0·2 Å shorter than similar Mo–O bonds in $[\mathrm{Mo}^{\mathrm{V}}_{2}(\mu\text{-}\mathrm{S})_2\mathrm{O}_2(\mathrm{histidine})_2]^{2-}$ (Spivak & Dori, 1973), and $[\mathrm{Mo}^{\mathrm{V}}_{2}(\mu\text{-}\mathrm{O})_2\mathrm{O}_2(\mathrm{cysteine})_2]^{2-}$ (Knox & Prout, 1969), but the increased length of the latter may be due to the *trans* effect of a double-bonded terminal oxygen atom, although this effect does not appear to occur in the Mo^{V} oxalate complex noted above. The Mo–O(1) and Mo–O(1′) bond distances of 2·05 and 2·03 Å respectively would seem to be at least 0·1 Å longer than the corresponding values found in other dioxo bridged compounds [see *e.g.* the tabulated comparisons in Spivak & Dori (1973)].

The Mo–N bond length of 2·18 Å is much shorter than the value of 2·45 Å found in $[\mathrm{Mo}^{\mathrm{V}}_{2}(\mu\text{-}\mathrm{S})_2(\mu\text{-}\mathrm{EDTA})\mathrm{O}_2]^{2-}$. Spivak & Dori had suggested that the lengthening of the Mo–N bond in the latter compound arose from a combination of steric and *trans* effects. In view of the similar stereochemistry of this compound and the one presently under investigation, and the absence of a double-bonded terminal oxygen atom in the latter, it would appear that the *trans* effect is the most important contributor.

The Mo–Mo′ distance of 2·430 Å is the shortest yet observed in dioxo or dihydroxo bridged compounds and indicates a strong metal–metal bond. Pauling (1960) estimated the single-bond length as 2·64 Å. Comparable distances are 2·569 Å in $[\mathrm{Mo}^{\mathrm{V}}_{2}(\mu\text{-}\mathrm{O})_2\mathrm{O}_2(\mathrm{cysteine})_2]^{2-}$ (Knox & Prout, 1969), 2·541 Å in $[\mathrm{Mo}^{\mathrm{V}}_{2}(\mu\text{-}\mathrm{O})_2\mathrm{O}_2(\mathrm{oxalate})_2(\mathrm{H_2O})_2]^{2-}$ (Cotton & Morehouse, 1965) and 2·552 Å in $[\mathrm{Mo}^{\mathrm{V}}_{2}(\mu\text{-}\mathrm{O})_2\mathrm{O}_2(\mathrm{histidine})_2]^{2-}$ (Delbaere & Prout, 1971). The Mo–Mo distances in sulphur-bridged compounds are generally much longer at around 2·8 Å.

The geometry of the coordination around the molybdenum atoms is illustrated by the three orthogonal views in Fig. 2. The deviations from 90° of the X–Mo–X angles range from −15 to +16°. The largest distortions are shown by the N–Mo–O(1) and N–Mo–O(1′) angles and these are caused by the nitrogen atoms being held apart by the ethylene bridge. Although these distortions will also tend to decrease the N–Mo–O(4) and N–Mo–O(3) angles below 90°, the latter are constrained well below this value anyway by the necessity for ring closure. While the ethylene bridge holds the Mo–N bond about 13° away from the *z*-axis direction (Mo′–Mo–N = 102·8°) the acetate bridge draws in the Mo–O(2) and Mo–O(2′) bonds about 3° towards the twofold rotation axis [Mo′–Mo–O(2) = 86·9°]. The strong metal–metal bond has compressed the Mo–O(1)–Mo′ angle down to 73° and at the same time opened up the O(1)–Mo–O(1′) angle to 105°.

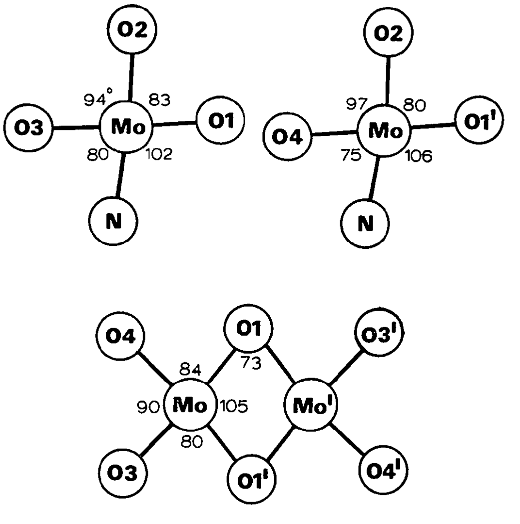

Fig. 2. Schematic views along the *x*, *y* and *z* axes illustrating the distortions of the molybdenum coordination.

The bond angles and lengths found in the EDTA part of the complex are not significantly different from those found in the crystal structure of EDTA alone (Cotrait, 1972). Although the difference in bond length between the coordinated and uncoordinated carboxyl groups is only one or two standard deviations, the latter are *always* longer than the former (see Table 2) so that this could be a meaningful difference. The identity of the acetate group is confirmed by C(6)–C(7) and C(7)–O(2) bond lengths of 1·47 and 1·27 Å respectively and an O(2)–C(7)–O(2′) angle of 121°.

Table 4. *Displacements from the plane of best fit through atoms* O(1), O(1′), O(3) *and* O(4)

Equation of plane: $-0{\cdot}0632x+0{\cdot}1134y+0{\cdot}9915z=6{\cdot}0665$.

Atom	Displacement
O(1)	−0·006 Å
O(1′)	0·006
O(3)	−0·007
O(4)	0·007

The atoms O(1), O(1′), O(3) and O(4) are coplanar within experimental error and the distances of these atoms from the least-squares plane of best fit are shown in Table 4. The molybdenum atom is displaced 0·05 Å out of this plane towards O(2). The dihedral angle between the planes through O(1), O(1′), O(3), O(4) and O(1), O(1′), O(3′), O(4′) is 166°, and the angle between the planes defined by Mo, O(1), O(1′) and Mo′, O(1), O(1′) is 158°. Dahl, Frisch & Gust (1973) have suggested that in dimeric bridged $\mathrm{M}_2(\mu\text{-}\mathrm{B})_2$ complexes there is a critical value of the M–B–M angle below which bending of the $\mathrm{M_2B_2}$ rhombus about the B···B line must occur to reduce bonding electron-pair repulsion on the bridging atoms. In sulphur-bridged compounds this angle is about 76° but in oxygen-bridged complexes a planar rhombus has not been found even with oxygen angles as high as 83°. In the present case the non-planarity of the $\mathrm{M_2O_2}$ rhombus means that the Mo–Mo′ vector intersects the crystallographic twofold axis 0·23 Å away from the intersection with the O(1)–O(1′) vector.

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References

COTRAIT, M. (1972). *Acta Cryst.* B**28**, 781–785.
COTTON, F. A. & MOREHOUSE, S. M. (1965). *Inorg. Chem.* **4**, 1377–1381.
COTTON, F. A., MOREHOUSE, S. M. & WOOD, J. S. (1964). *Inorg. Chem.* **3**, 1603–1608.
DAHL, F., FRISCH, P. D. & GUST, G. R. (1973). *Chemistry and Uses of Molybdenum.* Proceedings of a conference at the Univ. of Reading, September 1973, p. 134.
DELBAERE, L. T. J. & PROUT, C. K. (1971). *J. Chem. Soc.* (*D*), p. 162.
DREW, M. G. B. & KAY, A. (1971). *J. Chem. Soc.* (*A*), pp. 1846–1850.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
KNOX, J. R. & PROUT, C. K. (1969). *Acta Cryst.* B**25**, 1857–1866.
PALMER, G. & MASSEY, V. (1969). *J. Biol. Chem.* **244**, 2614–2620.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
SPENCE, J. T. (1969). *Coord. Chem. Rev.* **4**, 475–498.
SPIVAK, B. & DORI, Z. (1973). *J. Chem. Soc. Dalton*, pp. 1173–1177.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY 70 System of Crystallographic Programs, Univ. of Maryland.

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Contribution à l'Etude de la Dynamique dans les Cristaux Moléculaires: Structures Cristallines du Difluoro-1,5 Naphtalène et du Difluoro-1,8 Naphtalène

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The crystal structures at 25°C of two difluoronaphthalene compounds have been resolved by X-ray diffraction. 1,5-Difluoronaphthalene crystallizes in the monoclinic system, space group $P2_1/c$, with $a=7{\cdot}593$ (3), $b=3{\cdot}912$ (3), $c=14{\cdot}005$ (5) Å, $\beta=115{\cdot}41$ (10)°, $Z=2$, $D_c=1{\cdot}46$, $D_m=1{\cdot}43$ g cm^{-3}. 1,8-Difluoronaphthalene also crystallizes in the monoclinic system, space group $P2_1/c$, with $a=11{\cdot}288$ (4), $b=5{\cdot}654$ (3), $c=13{\cdot}988$ (5) Å, $\beta=122{\cdot}75$ (10)°, $Z=4$, $D_c=1{\cdot}50$, $D_m=1{\cdot}45$ g cm^{-3}. Existence of molecular motions observed in the solid state by n.m.r. methods can be interpreted for the first compound by a probable slow-frequency reorientation of the whole molecule (motion I) around its binary axis of symmetry and for the second compound by a strong librational motion of fluorine atoms perpendicular to the molecular plane.

Introduction

L'étude du désordre moléculaire en phase solide, menée ces dernières années sur la série des dérivés naphtaléniques monosubstitués en position β, tant par diffraction des rayons X (Chezeau, 1971; Chanh & Haget, 1972; Chanh, Haget, Leroy & Hannoteaux, 1973; Chanh, Dufourcq, Haget & Lemanceau, 1973), par résonance magnétique nucléaire (Cazeaux, 1972) que par spectroscopie infrarouge (Loyzance, Pineau & Lascombe, 1974) a permis de mettre en évidence des structures cristallines affectées de désordre d'orientation moléculaire, stables à températures élevées, avant leur point de fusion. Ce phénomène paraît *a priori* étonnant, compte tenu de la taille et de l'anisotropie de la molécule elle-même. Nous avons voulu étendre l'étude de cette dynamique moléculaire aux composés d'encombrement stérique plus important, tout en conservant le squelette naphtalénique. Nous avons choisi les dérivés difluorés en position 1,5 et en 1,8, composés pour lesquels une étude relativement récente par r.m.n. de Lauer, Stehlik & Hausser (1972) des temps de relaxation nucléaire T_1 et $T_{1\varrho}$ a permis de déceler l'existence de plusieurs types de mouvements moléculaires dans le domaine de température supérieur à 180K. Selon ces auteurs, ces mouvements étaient probablement du type de réorientations moléculaires de faible fréquence, s'effectuant autour des axes binaires du cycle naphtalène (Fig. 1). Pour étayer cette hypothèse, la connaissance, et surtout la comparaison des structures cristallines de ces composés devraient fournir l'argument décisif.

En effet:

– dans le cas du difluoro-1,5 naphtalène, toutes réorientations autres que celles autour de l'axe A_1, perpendiculaire au plan de la molécule feraient apparaître