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The Molecular Structure of a Diamagnetic, Doubly Oxygen-Bridged, Binuclear Complex of Molybdenum(V) Containing a Metal-Metal Bond¹

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The crystal and molecular structure of the compound $\text{BaMoO}_4(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ has been determined by a single crystal X-ray diffraction study. It is found to contain a binuclear anion, $\{[\text{MoO}(\text{C}_2\text{O}_4)\text{H}_2\text{O}]_2\text{O}_2\}^{2-}$, oxalatooxoquoquomolybdenum(V)- μ -dioxo-oxalatooxoquoquomolybdenum(V). The idealized structure consists of two octahedrally coordinated molybdenum atoms sharing an edge. The two halves are related by a (crystallographic) twofold rotation axis passing through the center of the $\text{Mo}-\text{O}-\text{Mo}$ ring. The Mo-Mo distance of only 2.541 Å. suggests that the diamagnetism of the compound is due to an Mo-Mo bond.

Studies of polynuclear, oxygen-bridged complexes of molybdenum have been reported previously from this laboratory.^{2,3} It has been shown² that the diethyl xanthate complex, $[(\text{C}_2\text{H}_5\text{OCS}_2)_2\text{MoO}]_2\text{O}$, of Mo(V) owes its diamagnetism to a pairing of electrons through a linear Mo-O-Mo bridge. In an attempt to gain structural information pertaining to spin-spin interaction between Mo(V) atoms through a double oxygen bridge (that is, in circumstances where two oxygen atoms would define the common edge of two octahedra about the Mo(V) atoms), a compound which appeared to be $\text{K}_2\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ was investigated.³ It was found from the structure analysis, however, that the compound which was actually studied was a compound of Mo(VI), *viz.*, $\text{K}_2\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$. Evidently, in the course of the long procedure used to obtain crystals, oxidation had occurred. Subsequent studies indicated that by turning to the barium analog, crystallization could be effected more easily and with less risk of oxidation.

Experimental

The compound $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ was prepared, as dark red crystals, from oxalic acid and $(\text{NH}_4)_2[\text{MoOCl}_5]$ according to the method of James and Wardlaw.⁴ The crystals were washed with cold water and then acetone and dried in a vacuum desiccator

(1) This work was supported by a grant from the National Institutes of Health.

(2) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

(3) F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

(4) R. G. James and W. Wardlaw, *J. Chem. Soc.*, 2152 (1927).

at about 25° for several days. Their composition was checked by analysis.

Anal. Calcd. for $\text{BaMo}_2\text{C}_4\text{H}_{10}\text{O}_{17}$: C, 7.29; H, 1.53. Found: C, 7.19; H, 1.63.

The density was estimated by flotation to be 2.9 ± 0.1 g. cm^{-3} .

A preliminary investigation showed that $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ crystallizes in the trigonal system, with cell dimensions $a = 10.63 \pm 0.03$ Å. and $c = 11.65 \pm 0.03$ Å. The estimated density of 2.9 ± 0.1 g. cm^{-3} indicated three molecules per unit cell (calculated density 2.89 g. cm^{-3}). Precession photographs revealed only the restriction $l = 3n$ for 00 l .

A small, equidimensional crystal (maximum dimension *ca.* 0.3 mm.) was selected for intensity measurements. Using the equi-inclination Weissenberg method and Mo $K\alpha$ radiation, levels $hk0$ through $hk11$ were recorded by the multiple film technique. This region of reciprocal space was confined to reflections with $0 < \sin \theta \leq 0.4$ and gave about 500 independent observations. The intensities were estimated visually with a calibrated wedge. Those too weak to be measured were assigned one-quarter of the minimum observable value. All the reflections were corrected for Lorentz-polarization factors, but no corrections were made for absorption, the linear absorption coefficient being 43.3 cm^{-1} .

Determination of Structure

Since the only observed systematic absence was 00 l , $l \neq 3n$, the space group was limited to $P3_121$ or $P3_112$ (or their enantiomorphs). The measured $|F|^2$ values were used to compute a three-dimensional Patterson synthesis. This calculation and all the following electron density summations were carried out using the Fourier program⁵ MIFR-2. A twofold

(5) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "I.B.M. 709/7090 Fourier Program," 1962.

axis located in the xy plane at $z = 1/3$ identified the space group as $P3_121$. The coordinates of the barium atoms, on threefold special positions (3a), were immediately evident from the Harker peaks \bar{x} , $x, 1/3$; $2x$, $x, 1/3$; and \bar{x} , $-2x, -2/3$. Positions for the molybdenum atoms were deduced from the double-weight peaks at $z = 1/3$ and the coordinates chosen were those which correctly predicted all the barium-molybdenum vectors. The Mo-Mo distance in each dimeric unit was estimated at 2.64 Å, with the dimeric anions then being on the other (3b) threefold special position. A three-dimensional Fourier synthesis phased on the two heavy atoms yielded positions for four of the oxygen atoms coordinated to the molybdenum. One of these atoms was located approximately 1.9 Å from each of the dimeric metal atoms. Its coordinates could be transformed across the Mo-Mo axis to complete the double oxygen bridge. In view of the large series termination errors arising from the barium and molybdenum atoms, subsequent electron density syntheses were calculated as three-dimensional difference Fouriers. A difference map of this kind revealed the remaining three oxygen atoms and the two carbon atoms of the oxalate group. At this point, it was possible to distinguish the coordinated water from the terminal oxygen, the latter being considerably closer to the molybdenum atom.

Least-squares refinement was then commenced, using the full-matrix least-squares program of Prewitt.⁶ The positional parameters and eventually the isotropic thermal parameters were allowed to vary. Twelve separate scale factors were assigned to each of the equi-inclination levels recorded. The electron density synthesis calculated after this cycle led to the placement of an uncoordinated water molecule in a general position. Since the multiplicity of the general position is six, the remaining water molecule was required to lie in one of the two types of threefold special positions. Successive least-squares refinement followed by three-dimensional difference summations showed that the oxygen atom was located at a 3b position.

Refinement was continued, permitting variation of all the parameters except the fixed coordinates of the atoms on special positions. The residual (defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$) reached a value of 10.8%, at which point the variations were less than their corresponding standard deviations. An additional cycle of refinement was carried out using Cruickshank's weighting scheme.⁷ This cycle produced a final residual of 10.2%.

The final positional and thermal parameters are listed in Table I. Their standard deviations are obtained from the usual least-squares formula $\sigma^2(j) = a_{jj}(\sum w\Delta^2)/(m - n)$, where a_{jj} is the appropriate element of the matrix inverse to the normal equation

TABLE I

Atom	x/a	y/a	z/c	$B, \text{Å}^2$
Ba	0.1185 (4)	0.0	$1/3$	1.27 (9)
Mo	0.9452 (4)	0.5029 (4)	0.0666 (4)	1.29 (9)
O ₁	0.087 (3)	0.380 (3)	0.296 (3)	1.6 (6)
O ₂	0.058 (4)	0.717 (4)	0.291 (3)	1.7 (6)
O ₃	0.277 (4)	0.669 (4)	0.339 (3)	3.1 (7)
O ₄	0.136 (3)	0.567 (3)	0.117 (3)	1.2 (6)
O ₅	0.972 (4)	0.483 (4)	0.436 (3)	1.6 (6)
O ₆	0.306 (3)	0.915 (3)	0.438 (3)	1.5 (6)
O ₇	0.044 (3)	0.201 (3)	0.430 (3)	1.1 (5)
C ₁	0.049 (5)	0.312 (5)	0.396 (4)	1.1 (8)
C ₂	0.038 (5)	0.404 (5)	0.865 (4)	1.2 (8)
O ₈	0.885 (4)	0.648 (4)	0.586 (4)	4.0 (10)
O ₉	0.0	0.097 (5)	$1/6$	2.5 (12)

^a Numbers in parentheses represent standard deviations which occur in the last decimal place of the preceding number.

matrix. Table II contains the absolute values of the observed and calculated structure factors. Atomic scattering factors used were as follows: for barium and for molybdenum, those tabulated by Thomas and Umeda,⁸ corrected for the real part of anomalous dispersion⁹; for carbon and oxygen, those tabulated by Hoerni and Ibers.¹⁰

Discussion

General Structure.—The main structural feature in $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ is the occurrence of the binuclear complex anion with a double oxygen bridge as depicted in Figures 1 and 2. There is a rigorous (*i.e.*, crystallographic) twofold rotation axis which is a perpendicular bisector of both the Mo-Mo line and the line between the bridging oxygen atoms. The details will be discussed presently. The structure is essentially of the type postulated on the basis of indirect considerations by Garside and French¹¹ and by Mitchell.¹² The Mo-Mo distance of only 2.541 Å suggests that the low magnetic moment, corresponding to about 0.4 B.M. per Mo atom, is explainable on the basis of direct Mo-Mo interaction. This point will be discussed more fully below.

Coordination of Molybdenum.—Each molybdenum atom lies at the center of a distorted octahedron of oxygen atoms, consisting of two bridging oxygen atoms (O_b), one terminal oxygen atom (O_t), one oxygen atom of a water molecule, and two oxygen atoms of an oxalate ion. The Mo-O distances are given in Table III, and the O-Mo-O bond angles in Table IV. The various deviations of bond distances and bond angles from the values and equivalences expected for a regular octahedron seem to be explicable in a straightforward manner, and they are generally, though not entirely, in accord with similar deviations in the compounds

(8) L. F. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 239 (1957).

(9) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(10) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(11) C. M. French and J. H. Garside, *J. Chem. Soc.*, 2006 (1962).

(12) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **26**, 1967 (1964). Mitchell did not suggest exactly the right structure, due, at least in part, to the fact that he took account of an indication from preliminary X-ray data for the potassium compound that the structure had to be centrosymmetric. This has subsequently been shown to be incorrect, because of an accidental and unfortunate misidentification of a compound. See ref. 3 for discussion.

(6) C. J. Prewitt, "A Full Matrix Least-Squares Refinement Program for the I.B.M. 709/7090 Computer," 1962.

(7) D. W. J. Cruickshank, D. E. Pilling, *et al.*, in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Eds., Pergamon Press, New York, N. Y., 1961.

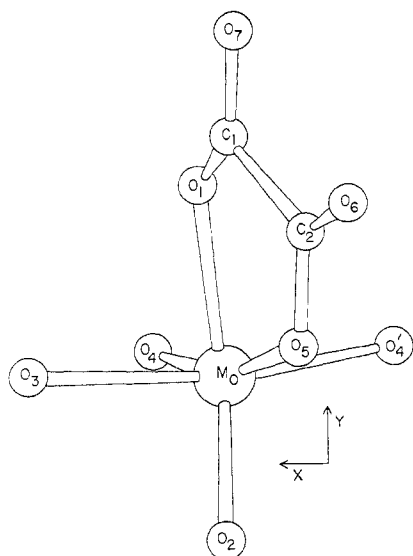


Figure 1.—The actual structure of one-half of the anion.

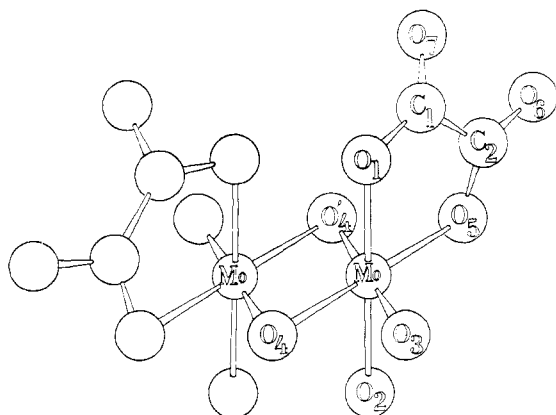


Figure 2.—An idealized sketch of the entire dimeric anion indicating the numbering of the atoms.

TABLE III
MOLYBDENUM-OXYGEN BOND LENGTHS

Bond	Length, Å.	Std. dev.
Mo-O ₁ (oxalate)	2.11	0.03
Mo-O ₃ (oxalate)	2.14	0.04
Mo-O ₃ (H ₂ O)	2.22	0.04
Mo-O ₄ (bridge)	1.93	0.03
Mo-O ₄ '(bridge)	1.88	0.03
Mo-O ₂ (terminal)	1.70	0.03

TABLE IV
BOND ANGLES ABOUT MOLYBDENUM AND AT
BRIDGE OXYGEN ATOMS

Bond pair	Angle, deg. ^a	Bond pair	Angle, deg. ^a
Mo-O ₄ -Mo'	83.5 (1.2)	O ₃ -Mo-O ₃	88.7 (1.4)
O ₄ -Mo-O ₃	160.6 (1.3)	O ₂ -Mo-O ₃	85.4 (1.5)
O ₁ -Mo-O ₂	159.0 (1.5)	O ₂ -Mo-O ₃	90.9 (1.5)
O ₃ -Mo-O ₄ '	169.0 (1.5)	O ₁ -Mo-O ₄	85.7 (1.4)
O ₂ -Mo-O ₄	108.2 (1.5)	O ₃ -Mo-O ₄	89.2 (1.4)
O ₂ -Mo-O ₄ '	104.1 (1.5)	O ₄ '-Mo-O ₃	85.6 (1.3)
O ₄ -Mo-O ₄ '	92.9 (1.8)	O ₁ -Mo-O ₃	78.9 (1.4)
O ₁ -Mo-O ₃	75.0 (1.3)	O ₁ -Mo-O ₄ '	90.5 (1.3)

^a Standard deviations in parentheses.

previously^{2,3,13} investigated. The twelve bond angles which would all be 90° in a regular octahedron lie in the range 75.0 to 108.2°. The angle of 75.0° is subtended by the two oxalate oxygen atoms, and its smallness may be attributed to the constraint imposed by the chelate ring. It is comparable to the angle found in the similar Mo(VI) complex.³ The angles between the short Mo-O bonds, *i.e.*, those involving O₂, O₄, and O₄', are the largest (108.2, 104.1, 92.9°); as in previous cases,^{3,13} this is to be expected because of the greater O···O repulsions between oxygen atoms with short bonds to the metal atom.^{13a} Of the remaining eight O-Mo-O bond angles, four differ insignificantly ($\Delta/\sigma < 3$) from 90°, while the other four are significantly different in the statistical sense, but not in a chemically significant sense which we can perceive.

The Mo-O distances range from 1.70 to 2.22 Å. The Mo-O_t distance of 1.70 Å. has been considered in relation to other such Mo-O distances and shown¹⁴ to indicate a bond order of around 2.4. The Mo-OH₂ distance of 2.22 Å. appears to be shorter than that found in the Mo(VI) oxalate complex³ (2.33 Å.), but the difference is probably not significant. The distances to the oxalate oxygen atoms are about equal to the mean (2.14 Å.) of the corresponding distances in the Mo(VI) complex.³ In this case, no significant difference is found between the lengths of Mo-O(oxalate) bonds *trans* to Mo-O_t and Mo-O_b. The Mo-O_b lengths do not differ significantly ($\Delta/\Sigma\sigma = 0.8$); the mean Mo-O_b, 1.91 Å., is indicative of significant π bonding. From the correlations of Cotton and Wing,¹⁴ the Mo-O_b bond orders would be estimated as about 1.3.

The Mo-Mo Interaction.—Garside and French¹¹ have shown that the molar susceptibility of BaMo₂O₄·(C₂O₄)₂·5H₂O, after correction for diamagnetism, is 92×10^{-6} e.g.s. unit both at 300 and at 90°K. Thus, as they suggested, a dimeric anion with an electron coupling energy in excess of kT at 300° is indicated. The structural results confirm this and indicate the nature of the coupling process in detail.

In the absence of detailed structural information, two mechanisms would merit consideration: (1) superexchange coupling through the bridging oxygen atoms,¹⁵ and (2) a direct metal-metal interaction. The Mo-Mo distance of only 2.541 Å. indicates that direct interaction is the dominant process and that the interaction is of such strength as to be considered a metal-metal bond. There is no established relationship between bond orders and internuclear distances specifically for such compounds as the one in question. However, in the [Mo₂Cl₈]⁴⁺ group, the distance of about 2.6 Å. is considered to correspond to a single bond.¹⁶ For the heavier transition metals in their

(13) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).(13a) NOTE ADDED IN PROOF.—*Cf.* the discussions by J. Donohue, *ibid.*, **4**, 921 (1965), and F. A. Cotton, S. M. Morehouse, and J. S. Wood, *ibid.*, **4**, 922 (1965).(14) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 867 (1965).(15) See, for example, W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.*, **86**, 3888 (1964).(16) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

common oxidation states, covalent radii of about 1.32 Å. have been estimated by Pauling,^{17a} who also proposes a single-bond metallic radius^{17b} of 1.29 Å. for Mo. These numbers appear to support the idea that the Mo-Mo interaction can be described as a two-electron covalent bond. If the coordinate axes are chosen in the conventional way (*i.e.*, along the bond axes) for the two octahedra, the orbitals which overlap to form this bond would be the d_{xy} orbitals.

It is of interest to compare the $\text{Mo}^{\text{V}}-\text{Mo}^{\text{V}}$ interaction in the oxalato complex with the $\text{Mo}^{\text{IV}}-\text{Mo}^{\text{IV}}$ interaction occurring in MoO_2 . This substance has a deformed rutile structure,¹⁸ in which there are infinite chains of MoO_6 octahedra sharing opposite edges along the chain direction. The Mo-Mo distances across these shared edges are alternately long (3.10 Å.) and short (2.50 Å.). Magnetic studies¹⁹ indicate that the substance is diamagnetic or very nearly so. Since the short distances are little different from the Mo-Mo distances in the oxalato complex, one might conclude that there is only a single strong Mo-Mo bond, which means that the coupling of the remaining electron spins (one for each Mo) must occur either by a superexchange mechanism through the bridging oxygen atoms or by a longer range, weaker $\text{Mo}\cdots\text{Mo}$ interaction. A reinvestigation of the magnetic properties of MoO_2 , especially at higher temperatures, might provide some data bearing on this question.

Finally, it may be noted that the four atoms of the bridge system deviate from coplanarity by a significant amount. The $\text{O}_4\cdots\text{O}_4'$ line intersects the crystallographic twofold axis 0.32 ± 0.03 Å. from where the $\text{Mo}\cdots\text{Mo}'$ line intersects it. Due to the various irregularities in the octahedron about Mo, it is not possible to regard this as a consequence of some simple deviation from regularity in joining the octahedra. It may, perhaps, be regarded as a means of shortening the Mo-Mo distance without unduly lengthening the Mo-O_b bonds or unduly expanding the O_b-Mo-O_b bond angles.

The Coordinated Oxalate Ions.—The dimensions of the coordinated oxalate ions are in accord with reasonable expectations and previous observations.^{8,20} They

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960: (a) Table 7-15, 249; (b) Table 7-18, p. 256.

(18) A. Magnéli and G. Andersson, *Acta Chem. Scand.*, **9**, 1378 (1955).

(19) B. T. Tjabbes, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **35**, 693 (1932).

(20) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

TABLE V

DIMENSIONS OF THE OXALATE GROUP^{a,b}

Bond lengths, Å.		Bond angles, deg	
C ₁ -O ₁	1.32 (0.06)	O ₁ -C ₁ -O ₇	132 (5)
C ₁ -O ₇	1.23 (0.06)	O ₅ -C ₂ -O ₈	126 (5)
C ₂ -O ₅	1.26 (0.06)	O ₇ -C ₁ -C ₂	116 (4)
C ₂ -O ₈	1.24 (0.06)	O ₁ -C ₁ -C ₂	110 (4)
C ₁ -C ₂	1.55 (0.07)	O ₅ -C ₂ -C ₁	116 (4)
		O ₈ -C ₂ -C ₁	117 (4)

^a Standard deviations in parentheses. ^b The deviations of individual atoms from the mean (least-squares) plane: C₁, 0.08; C₂, -0.07; O₁, -0.05; O₅, 0.05; O₈, -0.03; O₇, 0.02.

are collected in Table IV. The only notable difference from the dimensions found in the Mo(VI) complex lies in the fact that there is no significant difference in the average values of the C-O(coor) and C-O(uncoor), although the uncertainties are such that a difference of as much as 0.1 Å. could exist. A difference of about this magnitude appeared to exist in the similar Mo(VI) compound.

Coordination of the Barium Ion.—The barium ions are extensively coordinated by oxygen atoms, of which there are ten lying within the range 2.78 to 2.86 Å. These data are collected in Table VI. These ten oxy-

TABLE VI

BARIUM-OXYGEN PACKING DISTANCES (Å.)^a

O ₂	2.79 ± 0.03	O ₇ '	2.86 ± 0.03
O ₂ '	2.79 ± 0.03	O ₇ ''	2.86 ± 0.03
O ₈	2.85 ± 0.03	O ₇ '''	2.85 ± 0.03
O ₈ '	2.85 ± 0.03	O ₉	2.78 ± 0.03
O ₇	2.85 ± 0.03	O ₉ '	2.78 ± 0.03

^a Based on last cycle of refinement using unweighted data.

gen atoms are rather evenly distributed about the barium ion, but not in any recognizable regular or semi-regular polyhedron, so far as we can see.

Water Molecules.—Of the fifteen water molecules in the unit cell of $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$, six are coordinated to the molybdenum atoms only (O₃'s), three more are coordinated to barium ions (O₉'s), and six (O₈'s) are bound only by hydrogen bonds to other oxygen atoms. It would be interesting to know if a thermogravimetric study would show steps corresponding to these three sets. For the potassium compound, $\text{K}_2\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$, such a study¹² shows a plateau at $\text{K}_2\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, corresponding to the $[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ anion.

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