Notes

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Triply Bridged Molybdenum(V) Dimers. Crystal and Molecular Structure of μ-(2-Mercaptoethanolato-*S*,*O*)-μ-sulfido-bis[oxo(*N*,*N*-diethyldithiocarbamato)molybdenum(V)], $Mo_2O_2S(SCH_2CH_2O)(S_2CN(C_2H_5)_2)_2$

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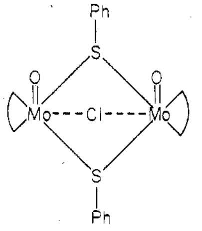
Triply bridged binuclear oxomolybdenum(V) complexes were first recognized during investigations of the reactions of di-μ-oxo-bis(oxomolybdenum(V)) compounds ($Mo_2O_4^{2+}$ complexes) with thiols.[1,2] Another triply bridged species was the unexpected result of a recrystallization from chloroform.[3] X-ray structure determinations of the products of these fortuitous syntheses of triply bridged oxomolybdenum(V) dimers have established the stereochemistries of three different bridging systems[2-4] which are shown schematically in **1**–**3**.



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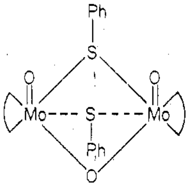

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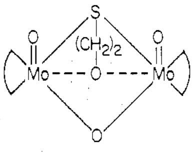

3

System **1**[3] has two equivalent SPh bridges and a bridging Cl atom trans to the terminal O atoms of each Mo atom; **2**[4] has a bridging O atom cis to the terminal O atoms of each Mo atom and two distinctly different SPh bridges; **3**[2] is similar to **2** but has a bridging OR moiety trans to the terminal O atom of each Mo atom.

Systematic extension of the chemistry of triply bridged Mo(V) complexes has recently become possible by the development of synthetic routes to other triply bridged systems.[5] Of particular interest to us are complexes with a bridging sulfido group. Herein we report the structure of $Mo_2O_2S(SCH_2CH_2O)(S_2CN(C_2H_5)_2)_2$ (**4**), the sulfido analogue of bridging system **3**, and tabulate and compare the metrical details of all four triply bridged systems.

Experimental Section

The yellow compound $Mo_2O_2S(SCH_2CH_2O)(S_2CN(C_2H_5)_2)_2$ (**4**)[5] was kindly supplied by Dr. W. E. Newton, and crystals were grown from dichloromethane by slow evaporation in air at ambient temperatures. The IR spectra of the yellow powder and the recrystallized material in KBr pellets are identical as obtained on a Perkin-Elmer Model 735 spectrophotometer. A very strong band at 940 cm^{-1} is found for the ν(Mo=O). A medium-intensity band observed at 460 cm^{-1} can be assigned[6,7] to the molybdenum–bridging sulfur stretching frequency.

Crystal Structure Determination. A crystal of the title compound which showed sharp extinction at 90° intervals under polarized light was selected for X-ray crystallography. The needle axis of the crystal (*a*) was nearly coincident with the ϕ axis of a Syntex $P2_1$ four-circle diffractometer. The measurement of unit cell parameters and the orientation matrix were based on a least-squares fit of the setting angles of 20 reflections with $2\theta = 5 \rightarrow 18°$. Peak widths at half-height of less than 0.25° for ω scans of several reflections indicated a satisfactory mosiac spread for the crystal. Axial photographs revealed C_{2h} $(2/m)$ Laue symmetry, indicating that the crystal belonged to the monoclinic crystal class. Automated data collection was carried out under the control of a NOVA 1200 computer using the Syntex $P2_1$ Fortran IV diffractometer system;[8] details are presented in Table I.

Table I. Crystallographic Details for $[Mo_2O_2S(SCH_2CH_2O)(dedtc)_2]$

color	yellow	2θ range, deg	4–50
habit	rectangular parallelepiped	scan technique	θ(cryst)–2θ(counter)
dimensions, mm	0.10 × 0.10 × 0.52	scan rate, deg/min	$2.00 \rightarrow 29.30^c$
cryst system	monoclinic	scan range, deg	$[2\theta(K\alpha_1) - 0.8] \rightarrow [2\theta(K\alpha_2) + 0.8]$
space group	$P2_1/n$		
a, Å	7.258 (2)	scan:bkgd time	1:1
b, Å	20.414 (4)		
c, Å	15.134 (5)	standards	3 every 97 reflections^d
β, deg	94.41 (2)		
V, Å^3	2235 (1)	no. of independent data	3957
temp, °C	24.0		
Z	4	no. of data with $F_o^2 > 3\sigma(F_o^2)$	2888
mol wt	628.60		
ρ(obsd), g cm^{-3}	1.843 (6)^a		
		no. of variables refined	226
ρ(calcd), g cm^{-3}	1.867		
		final R^e	0.030
cryst faces	{100}, $(0\bar{2}1)$, $(0\underline{12})$, $(02\bar{1})$, $(0\bar{1}2)$	final R_w^e	0.037
		abs coeff, cm^{-1}	16.5^f
		std dev of an observn of unit wt	1.18
radiation	Mo Kα ($\bar{\lambda}$ 0.71069 Å)^b		

[a] Density was averaged over four trials by neutral bouyancy in aqueous zinc bromide. [b] Graphite crystal monochromator. [c] Variable with more time spent on weaker reflections. [d] The maximum decrease in intensity was 1.4%, and no decay correction was required. [e] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$. [f] An empirical absorption correction was applied (see text).

Examination of the complete set of intensity data revealed the systematic absences *h*0*l* for $h + l = 2n + 1$ and 0*k*0 for $k = 2n + 1$, consistent with the nonstandard centrosymmetric space group $P2_1/n$. Data were corrected for absorption by an empirical method using a local modification of the computer program TAPER.[8] Thirteen strong reflections, distributed over the range of 2θ values used in data collection and having $274 < \chi < 296°$, were measured in 10° increments around the diffraction vector, ψ, from $\psi = 0°$ to $\psi = 350°$. The maximum empirical absorption correction factor was 1.23.

Solution and Refinement of Structure. Details concerning computer programs used can be found in a previous report.[9] Scattering factor tables for neutral nonhydrogen atoms[10] and spherically bonded hydrogen[11a] were generated from the coefficients of analytical approximations; the real and imaginary parts of the anomalous dispersion correction were included only for Mo and S.[11b] The structure was solved by direct methods which revealed the coordinates of two Mo and four S atoms. All the remaining nonhydrogen atoms were located by subsequent structure factor calculations and difference electron density maps. Hydrogen atom positions were calculated and included as fixed contributions in the final refinement using isotropic thermal parameters of 6.0 Å^2; the final *R* factors are given in Table I. Refinement was based on F_o with $\sum w(|F_o| - |F_c|)^2$ being minimized. The weights were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and a value of 0.04 was assigned to *p* in the expression for $\sigma(F^2)$.[12] Only data having $F_o^2 \geq 3\sigma(F_o^2)$ were used in refinement. A structure factor calculation for all 3957 data gave $R = 0.057$ and $R_w = 0.046$. The final electron difference map had a maximum residual of 0.52 e/Å^3, about 1.0 Å from a Mo atom. The final positional parameters for all the refined

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Table IIa. Final Atomic Parameters for $[Mo_2O_2S(SCH_2CH_2O)(dedtc)_2]^a$

Atom	x	x	z
Mo1	.15481(6)	.56763(2)	.79294(3)
Mo2	.11185(5)	.69981(2)	.80587(3)
S1	.2299(2)	.64536(7)	.67424(8)
S2	.0019(2)	.62189(6)	.90168(9)
S3	.4051(2)	.49244(7)	.75415(9)
S4	.2188(2)	.49031(6)	.91470(9)
S5	.3137(2)	.79545(7)	.78401(9)
S6	.1262(2)	.76819(6)	.94037(9)
O1	.3605(4)	.6418(2)	.8414(2)
O2	-.0219(5)	.5381(2)	.7254(3)
O3	-.0801(5)	.7216(2)	.7435(3)
N1	.4779(6)	.4015(2)	.8807(3)
N2	.3631(5)	.8690(2)	.9297(3)
C1	.5243(7)	.6511(3)	.7969(4)
C2	.4770(8)	.6553(3)	.6973(4)
C3	.3814(7)	.4525(2)	.8540(3)
C4	.2784(7)	.8193(2)	.8908(3)
C5	.6192(8)	.3713(3)	.8274(4)
C6	.8030(9)	.3991(4)	.8502(5)
C7	.4567(8)	.3705(3)	.9676(3)
C8	.3480(10)	.3085(3)	.9587(4)
C9	.5004(7)	.9075(3)	.8859(4)
C10	.6916(8)	.8792(3)	.9032(4)
C11	.3282(8)	.8897(3)	1.0203(3)
C12	.1872(9)	.9442(3)	1.0185(5)

[a] x, y, and z are in fractional coordinates. Standard deviation of the least significant digit is given in parentheses. Final thermal parameters are available as supplementary material (Table IIb).

atoms are given in Table IIa. Thermal parameters, atomic parameters for the H atoms, selected interatomic distances and angles, and tables of observed and calculated structure factors are available as supplementary material.

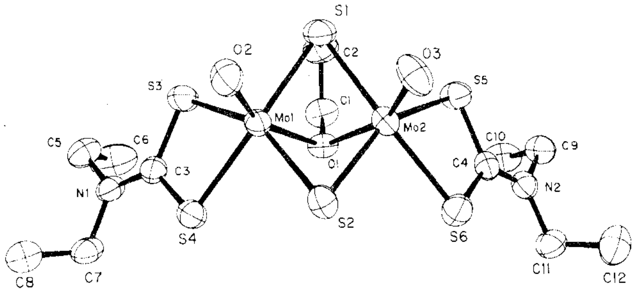


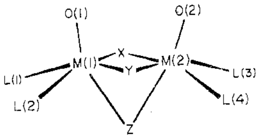
Figure 1. Perspective view of $Mo_2O_2S(SCH_2CH_2O)(dedtc)_2$. Ellipsoids enclose 50% of the probability distribution. Average distances and angles are given in Table IV.

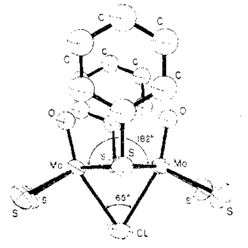
Description and Discussion of the Structure

The structure of **4** is shown in Figure 1. No symmetry is imposed on the molecule by the space group. The approximate molecular symmetry, including the ethyl groups of the dedtc ligands, is C_s (dedtc is diethyldithiocarbamate). The geometry of the dedtc ligands is very similar to that of previously reported structures.[3,4] The average interatomic distances found for the dedtc ligands in this structure are S–C = 1.731 (5) Å, C–N = 1.303 (6) Å, N–Et = 1.477 (7) Å, and C–C = 1.50 (2) Å. Other average distances and angles are summarized in Table IV.

Each Mo atom is coordinated by four sulfur and two oxygen atoms in a distorted octahedral geometry. Two coordinating

Table IV. Comparison of the Coordination Geometries of Four Triply Bridged Mo(V) Dimers[a]





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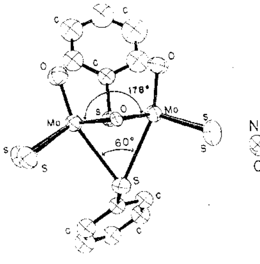

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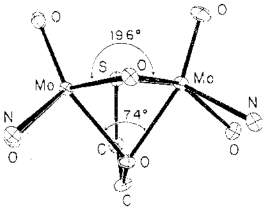

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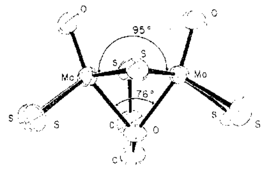

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	1	2^b	3	4
M(1)–M(2), Å	2.822 (2)	2.677 (5)	2.628 (1)	2.725 (1)
M–X, Å	2.455 (4)	2.491 (7)	2.484 (2)	2.489 (3)
M–Y, Å	2.460 (8)	2.045 (31)	1.937 (12)	2.334 (1)
M–Z, Å	2.613 (12)	2.688 (11)	2.190 (17)	2.202 (14)
M–O, Å	1.656 (6)	1.673 (5)	1.693 (6)	1.686 (7)
M–L, Å	2.426 (5)	2.462 (19)	2.030 (4) (M–O) 2.205 (10) (M–N)	2.467 (21)
M–plane LLXY, Å	0.396 (6)	0.392 (40)	0.392 (6)	0.389 (3)
σ(plane LLXY), Å	0.032 (6)	0.040 (30)	0.060 (8)	0.016 (16)
O–M–X, deg	95.7 (10)	93.0 (26)	90.2 (2)	89.4 (2)
O–M–Y, deg	95.6 (13)	102.5 (12)	103.6 (4)	102.7 (2)
O–M–Z, deg	158.2 (2)	160.6 (19)	158.9 (3)	155.5 (4)
O–M–L, deg	104.6 (6)	102.8 (27)	105.9 (8)	104.1 (38)
X–M–Y, deg	109.9 (1)	106.6 (9)	104.5 (2)	110.39 (5)
X–M–Z, deg	73.1 (3)	70.8 (2)	70.4 (2)	68.0 (1)
Y–M–Z, deg	71.9 (1)	73.6 (3)	74.6 (4)	77.9 (2)
M–X–M, deg	70.17 (7)	64.99 (5)	63.86 (6)	66.37 (4)
M–Y–M, deg	69.99 (7)	81.8 (16)	85.5 (2)	71.43 (4)
M–Z–M, deg	65.35 (7)	59.73 (9)	73.85 (2)	76.48 (9)
X–M–L_{cis}, deg	85.1 (6)	93.3 (11)	91.2 (4)	90.6 (5)
Y–M–L_{cis}, deg	86.6 (10)	82.3 (2)	80.6 (2)	81.8 (6)
Z–M–L, deg	92.9 (12)	92.2 (21)	89.1 (50)	93.1 (36)
X–M–L_{trans}, deg	152.8 (14)	157.6 (27)	161.1 (5)	156.6 (1)
Y–M–L_{trans}, deg	153.4 (19)	148.8 (10)	147.1 (5)	148.8 (2)
L–M–L, deg	72.2 (1)	71.2 (3)	76.2 (7)	71.19 (9)
[X–M1–Y]–[X–M2–Y], deg	182.3 (1)	178.0 (3)	195.9 (9)	195.4 (1)
ref	3	4	2	this work

[a] Average values are presented with root-mean-square deviations (in parentheses) given in units of the last significant figures. The chemical formulas for **1–3** are the following: 7, $[Mo_2O_2Cl(S_2CNEt_2)_2]^+$; **2,** $Mo_2O_3(SPh)_2(S_2CNEt_2)_2$; **3,** $Mo_2O_3(SCH_2CH_2O)(OC_9H_6N)_2$. [b] Values averaged for both molecules in the asymmetric unit.

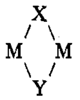
sulfur atoms from a dedtc chelate, the sulfido ligand, and the mercapto group of 2-mercaptoethanolate form a plane of sulfur atoms around each metal. Each coordination sphere is completed by the oxygen of the 2-mercaptoethanolate group which is trans to the oxo ligands of both metal centers.

Compound **4** is the first example of a triply bridged binuclear structure in which the two Mo atoms are bridged by S, SR, and OR moieties. Table IV compares all four known molybdenum dimers involving triple bridges. Complex **1** is a cation while **2**, **3**, and **4** are all neutral species. Each dimer contains two six-coordinate Mo(V) centers which share a common face. In each case the metal is displaced about 0.39 Å from a square plane of ligand atoms toward the apical, or terminal, oxygen ligand (see M–plane LLXY, Table IV). The deviations of these atoms from their respective plane σ(plane LLXY) is small for all four structures. The terminal oxo ligands are in the syn conformation[13] for all the compounds and the Mo=O bond distance shows a slight increase as the trans ligand varies from chloride to thiolate to ethanolate.

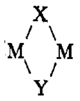
The long M–Z bonds trans to the short, strong Mo=O bonds in compounds **1**–**4** are characteristic[14] of six-coordinate molybdenum in mononuclear and binuclear complexes containing the oxo ligand. The distances from molybdenum to the bridging thiophenolate ligands in compounds **1** and **2** are in good agreement for the M–X and M–Y values, but the M–Z distance is about 0.2 Å longer in **2** where SPh is trans to oxo. Compounds **3** and **4** show the same effect. The M–Y value of 1.94 Å in **3** is representative of molybdenum–bridging oxygen distances,[14,15] but the Mo–O distances to 2-mercaptoethanolate in **3** and **4** are about 2.20 Å.

The differences in the Mo···Mo distances among the four complexes can be related to the relative sizes of the X, Y, and Z bridging atoms. All four compounds have X = SR but varying Y and Z bridges. The longest Mo···Mo distance (2.822 Å) occurs in **1** where X = Y = SR and Z = Cl. The shortest Mo···Mo distance (2.628 Å) occurs in **3** in which Y and Z are oxygen atoms. Compounds **2** and **4** show that the bridging system Y = O, Z = SR gives a shorter Mo···Mo distance than Y = S, Z = OR.

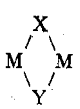
The



moiety is almost flat in compounds **1** and **2** where Z is Cl or SPh. In **3** and **4** where Z is the O atom of 2-mercaptoethanolate the dihedral angles between the two MXY planes of the four-membered



rings are ~195°. The dihedral angles of the



rings of **1**–**4** contrast with those for syn di-μ-bridged structures[13-16] which are usually ~150°. For **3** and **4** the S–C–C–O chelate ring has torsional angles of 1.9 (7) and 1.0 (6)°, respectively.

The bridging system of **1** with X = Y = SR shows effective C_{2v}-mm symmetry. However, **2**–**4** with X = SR and Y = O or S show a consistent pattern of distortions in the angles about Mo. All three have O–M–Y > O–M–X and Y–M–Z > X–M–Z. It is surprising that their Y–M–L_{cis} angles are all ~82° and in each case 10° *less* than the X–M–L_{cis} angles. No detailed bonding descriptions have appeared for triply bridged binuclear Mo(V) complexes, but the above pattern of angles for compounds **2**–**4** is consistent with a substantial π-bonding interaction in the μ-oxo and μ-sulfido M–Y–M bridges. Such a bonding interaction would concentrate electron density above and below the M–Y–M plane and make nonbonded repulsions of Y with O and Z more important than those with L_{cis} in determining the angles about Mo.

Triply bridged Mo(V) dimers are a new and intriguing addition to the rich and complicated stereochemistry of molybdenum compounds.[18] The chemical and physical properties of triply bridged complexes have not yet been extensively investigated, but **3** has been shown to exhibit complex electrochemical reactions in dimethyl sulfoxide solution.[17]

Acknowledgment. We thank Dr. W. E. Newton for a sample of the compound. We thank Professor F. A. Schultz for a preprint of ref 6. We gratefully acknowledge support of this research by the National Institutes of Health (Grant ES-00966) and a generous allocation of computer time by the University of Arizona Computer Center. We are especially grateful for technical assistance by Mr. R. Hoskins, a participant in the CATALYST program sponsored by the American Chemical Society. We thank the National Science Foundation for funds for the diffractometer (Grant CHE-76-05481).

Registry No. 4, 67774-30-5.

Supplementary Material Available: Table IIb, anisotropic thermal parameters for **4**; Table III, interatomic distances and angles; Table V, a listing of fractional coordinates for the 24 calculated hydrogen positions for **4**; Tables VI, VII, and VIII, listings of final positional and thermal parameters for both molecules of compound **2**, $[Mo_2O_3(SC_6H_5)_2(dedtc)_2]$, not available in ref 4; Table IX, listings of structure factor amplitudes ×10 for $[Mo_2O_2S(SCH_2CH_2O)(dedtc)_2]$ (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) W. E. Newton, J. L. Corbin, and J. W. McDonald, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. INOR 35.

(2) J. I. Gelder, J. H. Enemark, G. Wolterman, D. A. Boston, and G. P. Haight, *J. Am. Chem. Soc.*, **97**, 1616 (1975).

(3) G. Bunzey, J. H. Enemark, J. I. Gelder, K. Yamanouchi, and W. E. Newton, *J. Less-Common Met.*, **54**, 101 (1977).

(4) K. Yamanouchi, J. H. Enemark, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **99**, 3529 (1977).

(5) W. E. Newton, G. J.-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, **98**, 5387 (1976).

(6) V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, **16**, 2538 (1977).

(7) W. E. Newton and J. W. McDonald, *J. Less-Common Met.*, **54**, 51 (1977).

(8) "Syntex *P*2$_1$ Fortran Operations Manual", Syntex Analytical Instruments, Cupertino, Calif., 1975.

(9) J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, **14**, 624 (1975).

(10) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(11) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99–101; (b) pp 149–150.

(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(13) G. Bunzey, J. H. Enemark, J. K. Howie, and D. T. Sawyer, *J. Am. Chem. Soc.*, **99**, 4168 (1977).

(14) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).

(15) B. Spivack and Z. Dori, *Coord. Chem. Rev.*, **17**, 19 (1975).

(16) J. I. Gelder and J. H. Enemark, *Inorg. Chem.*, **15**, 1839 (1976).

(17) J. K. Howie and D. T. Sawyer, *Inorg. Chem.*, **15**, 1892 (1976).

(18) Recent synthetic approaches to the molybdenum site in nitrogenase have also resulted in triply bridged binuclear molybdenum species: T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **100**, 4630 (1978); G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, submitted for publication (we thank C. D. Garner for a preprint).