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## Molybdenum Enzyme Model Studies. Synthesis and Structure of the Oxo-Bridged Binuclear Complex, $\mu$ -Oxo-bis[oxo(2,2'-methyliminodiethanethiolato)molybdenum(V)], $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$

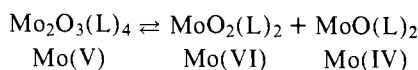
Ying-Yen P. Tsao,<sup>1a</sup> Charles J. Fritchie, Jr.,\* <sup>1a</sup> and Henri A. Levy<sup>1b</sup>

Contribution from the Percival Stern Chemical Laboratories, Tulane University, New Orleans, Louisiana 70118, and the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. Received November 21, 1977

**Abstract:** The complex  $\mu$ -oxo-bis[oxo(2,2'-methyliminodiethanethiolato)molybdenum(V)],  $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$ , has been synthesized and its crystal structure has been determined from three-dimensional x-ray diffractometer data. The crystals are monoclinic, space group  $P2_1/c$ , with four molecules in a cell having parameters  $a = 14.849$  (2),  $b = 7.956$  (2),  $c = 15.861$  (2) Å,  $\beta = 90.97$  (2)°, and  $Z = 4$ . Full-matrix least-squares refinement using 1488 observed and 54 unobserved intensities (Mo  $K\alpha$  radiation) has yielded a conventional  $R$  factor of 0.049. The asymmetric unit consists of halves of two independent molecules of  $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$  located on crystallographic centers of symmetry. Disorder of the three carbons around each nitrogen atom, representing alternate conformations of the chelate rings, has been found. The configuration of the molecule is that of two distorted trigonal bipyramids centrosymmetrically connected through the central, bridging oxygen. The terminal oxygen and two sulfur atoms of each half molecule form a trigonal plane, and the nitrogen atom is trans to the bridging oxygen atom. The average Mo–O(terminal), Mo–O(bridge), Mo–N, and Mo–S bond distances are 1.667 (8), 1.858 (1), 2.233 (10), and 2.346 (3) Å, respectively. This is the first known five-coordinate complex of the  $\text{Mo}_2\text{O}_3^{4+}$  unit with a ligand containing sulfur.

Although molybdoenzymes have been widely studied, the detailed catalytic mechanisms and three-dimensional structures around their active sites are still not well understood because of their complexity. Research on the coordination chemistry of molybdenum–sulfur complexes has been stimulated by evidence that redox reactions which are catalyzed by molybdoenzymes occur at sites where the molybdenum is coordinated by one or more sulfur atoms.<sup>2a</sup> A basic group, presumably a nitrogen atom, but possibly oxygen, is proposed to coordinate to the molybdenum in xanthine oxidase.<sup>2</sup> Recent x-ray absorption edge spectra of the molybdenum–iron component of nitrogenase and of some model compounds imply the presence of Mo(V) coordinated with at least one cysteine sulfur ligand.<sup>3,36</sup> However, the existing Mo(V) complexes containing cysteine or its ester are di- $\mu$ -oxo or di- $\mu$ -sulfido dimers<sup>4–7</sup> with short Mo–Mo distances ( $\sim 2.56$  and  $\sim 2.81$  Å, respectively) which suggest a direct metal–metal bond.<sup>8,9</sup> The existence of this direct metal–metal interaction is unlikely in enzyme systems;<sup>2a</sup> there is in fact no evidence that enzyme active sites contain more than one molybdenum atom, although all the known model complexes are binuclear.

Several  $\mu$ -oxo dimers<sup>10–13</sup> which contain the  $\text{Mo}_2\text{O}_3^{4+}$  unit have been postulated as possible models because of the following disproportionation<sup>14,15</sup> reaction:



where  $\text{L} = (\text{RO})_2\text{PS}_2^-$ , and  $\text{R}_2\text{NCS}_2^-$ . However, these ligands do not closely resemble cysteine. This led us to synthesize and study a series of Mo complexes containing aminothiols tridentate and tetradentate ligands which have an S:N mole ratio of

2 or 3. Here we first report the synthesis and structure of a five-coordinate  $\text{Mo}_2\text{O}_3\text{L}_2$  complex which contains Mo(V) in a configuration not previously observed.

### Experimental Section

**Synthesis.** 2,2'-(Methylimino)diethanethiol,  $\text{CH}_3\text{N}(\text{C}_2\text{H}_4\text{SH})_2$ , was synthesized by using the known procedure.<sup>16</sup> Under nitrogen atmosphere the following reactions were carried out: 2 mL of acetic acid was added to 0.716 g (2.96 mmol) of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  dissolved in 15 mL of water. This solution was added slowly to a solution of 0.5 mL (3.48 mmol) of  $\text{CH}_3\text{N}(\text{C}_2\text{H}_4\text{SH})_2$  in 10 mL of ethanol. Impure product in about 50% yield precipitated as a deep brown powder within a few minutes. The yellow filtrate deposited small additional amounts of analytically pure product over a few days. The solid was dissolved in a minimum amount of dimethyl sulfoxide. After 4 days of liquid diffusion of absolute ethanol into this solution, deep brown prismatic crystals were obtained. Anal. Calcd for  $\text{C}_{10}\text{H}_{22}\text{Mo}_2\text{N}_2\text{O}_3\text{S}_4$ : C, 22.31; H, 4.12; N, 5.20. Found: C, 22.35; H, 4.20; N, 5.09.

The complex is moderately air stable as the solid; it is insoluble except sparingly and with slow decomposition in dimethyl sulfoxide, dimethylformamide, and hexamethylphosphoramide. IR bands (KBr) at 945 (s) and 746  $\text{cm}^{-1}$  (m) are attributed to  $\nu_{\text{Mo}=\text{O}}$  and  $\nu_{\text{Mo}-\text{O}-\text{Mo}}$ , respectively.

**Collection and Reduction of the X-Ray Data.** On the basis of Weissenberg photographs, the crystals were assigned to the monoclinic system. The observed systematic absences are  $h0l$  for  $l = 2n + 1$  and  $0k0$  for  $k = 2n + 1$ , which suggest that the space group is  $P2_1/c$ . A specimen with dimensions of  $0.12 \times 0.21 \times 0.09$  mm along  $a$ ,  $b$ , and  $c$ , respectively, was mounted in a glass capillary with the  $b$  axis approximately along the  $\phi$  axis of the goniometer. A computer-controlled Picker x-ray diffractometer equipped with a scintillation-counter detector was used with filtered, Mo  $K\alpha$  radiation to obtain intensity data and for measurement of angles for precise determination of the unit-cell dimensions. The cell parameters obtained by the least-squares

method<sup>17</sup> are  $a = 14.849$  (2),  $b = 7.956$  (2),  $c = 15.861$  (2) Å, and  $\beta = 90.97$  (2)° ( $\lambda_{\text{MoK}\alpha} = 0.71069$  Å,  $T = 24 \pm 2$  °C). A density of  $1.909$  g/cm<sup>3</sup> is calculated for four formula units in the cell; a value of  $1.90$  (1) g/cm<sup>3</sup> was measured by flotation in 1,3-dibromopropane/carbon tetrachloride solution.

Intensities of 2291 nonequivalent reflections up to  $2\theta = 43.8^\circ$  were recorded by a  $\theta$ - $2\theta$  scan technique, with the background counted at the ends of the  $2\theta$  scan. The takeoff angle was  $1.2^\circ$ . Two reference reflections, which were measured after every 29 reflections, showed no variance other than that predicted by counting statistics. Reflections are defined as observed by the criterion  $I \geq 2\sigma_I$  where  $I$  is the net intensity and  $\sigma_I$  is the standard deviation.  $\sigma_I$  was calculated by  $\sigma_I = [C + J^2(B_1 + B_2) + p^2I^2]^{1/2}$  where  $C$ ,  $B_1$ , and  $B_2$  are the total peak and two background counts,  $J$  is the ratio of scan time to background time, and  $p$  is a factor which incorporates instrumental instability and possibly other errors. The value chosen for  $p$  was 0.02. The values of  $I$  and  $\sigma_I$  were converted to corresponding values of  $|F_c|$  and  $\sigma_F$  by application of transmission, Lorentz, and polarization factors.

The absorption coefficient of this compound for Mo K radiation is  $17.46$  cm<sup>-1</sup>, and for the crystal chosen the transmission factors calculated by using program ORABS by Busing and Levy<sup>18</sup> ranged from 0.814 to 0.860. Reflections for which  $I \leq 2\sigma_I$  were considered unobserved and were assigned a threshold intensity of  $2\sigma_I$ ; 1488 reflections were classified as observed and 803 as unobserved using this criterion. The unobserved reflections were included in calculations only when  $|F_c|$  exceeded the threshold value.

**Solution and Refinement of the Structure.** The positions of the two independent molybdenum atoms were determined from a three-dimensional Patterson map, which gave vectors consistent with two independent oxo-bridged binuclear molecules. The remaining nonhydrogen atoms were found in subsequent Fourier and difference Fourier maps. At a late stage of refinement, the carbon atoms attached to nitrogen were found to be disordered in a manner consistent with two alternate conformations of the chelating ligand. The structure was refined by the method of least squares<sup>19</sup> in which the function minimized was  $w(|F_o| - s|F_c|)^2$ , where  $w$  is the weighting factor given by  $1/\sigma^2(F_o)$  and  $s$  is a scale factor. In calculation of  $F_c$ , the atomic scattering factors for Mo, S, O, N, and C were taken from Cromer and Waber<sup>20</sup> and those of H from Stewart, Davidson, and Simpson.<sup>21</sup> Anomalous dispersion effects were included in the calculations, values of  $\Delta f'$  and  $\Delta f''$  for all of the nonhydrogen atoms being taken from Cromer and Liberman.<sup>22</sup>

In the final disordered model, the populational parameters  $p$  of the carbon atoms attached to nitrogen, and of their associated hydrogen atoms, were constrained to correspond to two alternate conformations per molecule as follows:

$$p(\text{C5a}) = 1 - p(\text{C5b}) = p(\text{C6a}) \\ = 1 - p(\text{C6b}) = p(\text{C7a}) = 1 - p(\text{C7b}) \\ p(\text{C8a}) = 1 - p(\text{C8b}) = p(\text{C9a}) \\ = 1 - p(\text{C9b}) = p(\text{C10a}) = 1 - p(\text{C10b})$$

Three more cycles of full-matrix least-squares<sup>23</sup> refinement resulted in convergence with final values of the discrepancy indexes<sup>37</sup>  $R$  and  $R_w$  being 0.049 and 0.040, respectively. The final calculation included 54 unobserved reflections. In these final anisotropic calculations 60 atoms were included, but the 12 disordered carbons were still refined isotropically because of limited reflection data from the small crystal. Ideally located H atoms except those of methyl groups were included in  $F_c$  calculations but not refined. In addition, the temperature factor for all 32 H atoms was fixed at  $5.5$  Å<sup>2</sup>. A final Fourier difference synthesis was essentially featureless, with no peak higher than  $0.7$  e/Å<sup>3</sup> and most of the high peaks in the vicinity of Mo atoms. Final atomic positional, populational, and thermal parameters are given in Tables I and II.

Alternate explanations of the apparent disorder were considered. Intensity data and highly unequal (roughly  $2/3$  and  $1/3$ ) populational factors seemed to rule out space groups other than  $P2_1/c$ . However, the nearly equal major site occupancies (0.65 and 0.63, each  $\pm 0.02$ ) of molecules I and II indicated possible microtwinning of two polymorphs. Seven reflections were found which gave significantly different values of  $|F_c|$  for twinned and disordered models. Depending on adjustment of the populational factors, either a twinned or a disordered model could be made to show better agreement. However,

Table I. Fractional Coordinates and Anisotropic Thermal Parameters<sup>a</sup>

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mo(1)	0.074 66 (7)	0.128 38 (13)	0.069 90 (6)	0.002 71 (6)	0.010 00 (21)	0.002 34 (5)	-0.000 31 (10)	-0.000 03 (4)	-0.000 57 (10)
Mo(2)	0.533 42 (7)	0.332 53 (15)	0.075 70 (7)	0.004 07 (7)	0.013 67 (25)	0.003 12 (6)	0.003 03 (11)	-0.000 58 (5)	0.000 47 (11)
S(1)	0.1360 (2)	0.2505 (5)	0.0509 (2)	0.005 82 (23)	0.019 39 (82)	0.002 90 (16)	0.000 08 (35)	0.001 08 (15)	0.000 44 (31)
S(2)	-0.0540 (2)	0.2301 (5)	0.1365 (2)	0.003 27 (18)	0.018 25 (80)	0.004 76 (19)	-0.000 01 (30)	0.000 98 (15)	-0.001 32 (32)
S(3)	0.6056 (3)	0.2045 (5)	-0.0381 (2)	0.007 98 (26)	0.022 12 (95)	0.002 97 (17)	0.004 43 (40)	-0.000 08 (17)	-0.001 15 (33)
S(4)	0.6075 (3)	0.5546 (5)	0.1592 (2)	0.007 30 (27)	0.015 31 (82)	0.004 72 (21)	0.000 61 (37)	0.000 16 (19)	-0.000 24 (34)
O(1)	0	0	0	0.0053 (8)	0.0131 (25)	0.0044 (7)	-0.0019 (11)	0.0008 (5)	-0.0030 (11)
O(2)	$1/2$	$1/2$	0	0.0119 (11)	0.0249 (35)	0.0043 (7)	0.0088 (16)	-0.0033 (7)	-0.0042 (13)
O(3)	0.1377 (5)	-0.0098 (10)	0.1239 (5)	0.0045 (5)	0.0173 (20)	0.0047 (5)	0.0015 (8)	-0.0006 (4)	0.0003 (8)
O(4)	0.4367 (5)	0.2551 (12)	0.1099 (5)	0.0038 (5)	0.0301 (24)	0.0071 (6)	0.0015 (9)	-0.0001 (4)	-0.0005 (10)
N(1)	0.1366 (6)	0.3553 (13)	0.1305 (6)	0.0034 (6)	0.0188 (24)	0.0027 (5)	-0.0009 (11)	0.0007 (4)	0.0000 (10)
N(2)	0.6204 (6)	0.1551 (13)	0.1492 (6)	0.0032 (6)	0.0142 (23)	0.0038 (5)	-0.0009 (10)	-0.0004 (4)	0.0000 (10)
C(1)	0.1942 (10)	0.4316 (19)	-0.0072 (10)	0.0107 (12)	0.0229 (37)	0.0057 (9)	-0.0090 (17)	0.0007 (8)	0.0021 (15)
C(2)	-0.0116 (9)	0.4154 (19)	0.1883 (9)	0.0071 (10)	0.0308 (42)	0.0070 (9)	0.0054 (16)	0.0008 (8)	-0.0070 (16)
C(3)	0.6778 (9)	0.0573 (18)	0.0157 (10)	0.0069 (10)	0.0218 (36)	0.0095 (11)	0.0082 (15)	-0.0008 (8)	-0.0033 (17)
C(4)	0.6768 (9)	0.4072 (20)	0.2293 (8)	0.0081 (10)	0.0290 (43)	0.0047 (8)	-0.0003 (17)	-0.0031 (7)	-0.0012 (15)

<sup>a</sup> The form of the thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

**Table II.** Fractional Coordinates<sup>a</sup> and Isotropic Thermal Parameters

Atom <sup>b</sup>	x	y	z	B <sup>c</sup>
C(5a) <sup>a</sup>	0.2178 (15)	0.4122 (29)	0.0861 (14)	6.0 (7)
C(5b) <sup>b</sup>	0.1404 (27)	0.4956 (51)	0.0701 (26)	4.9 (11)
C(6a) <sup>a</sup>	0.0682 (14)	0.4928 (26)	0.1412 (13)	4.5 (6)
C(6b) <sup>b</sup>	0.0982 (33)	0.3944 (65)	0.2071 (33)	8.0 (15)
C(7a) <sup>a</sup>	0.1718 (14)	0.3098 (27)	0.2218 (13)	5.0 (6)
C(7b) <sup>b</sup>	0.2268 (25)	0.3085 (50)	0.1686 (24)	5.0 (11)
C(8a) <sup>c</sup>	0.7036 (12)	0.1240 (25)	0.1035 (11)	3.0 (5)
C(8b) <sup>d</sup>	0.6284 (37)	-0.0041 (75)	0.1038 (37)	11.1 (18)
C(9a) <sup>c</sup>	0.6389 (14)	0.2367 (28)	0.2365 (13)	4.0 (6)
C(9b) <sup>d</sup>	0.6961 (35)	0.2394 (67)	0.1841 (33)	8.6 (15)
C(10a) <sup>c</sup>	0.5746 (15)	-0.0143 (29)	0.1674 (15)	4.7 (6)
C(10b) <sup>d</sup>	0.5723 (27)	0.0629 (60)	0.2096 (29)	6.6 (12)
H(1a) <sup>a</sup>	0.1567	0.5275	-0.0137	
H(1b) <sup>a</sup>	0.2485	0.4480	-0.0368	
H(2a) <sup>b</sup>	0.1977	0.5179	-0.0481	
H(2b) <sup>b</sup>	0.2534	0.4005	0.0109	
H(3a) <sup>a</sup>	0.2372	0.5166	0.1087	
H(3b) <sup>a</sup>	0.2644	0.3310	0.0931	
H(4a) <sup>b</sup>	0.0811	0.5259	0.0523	
H(4b) <sup>b</sup>	0.1697	0.5889	0.0948	
H(5a) <sup>a</sup>	0.0484	0.5332	0.0878	
H(5b) <sup>a</sup>	0.0932	0.5821	0.1734	
H(6a) <sup>b</sup>	0.1242	0.4964	0.2272	
H(6b) <sup>b</sup>	0.1107	0.3067	0.2457	
H(7a) <sup>a</sup>	0.0075	0.3866	0.2437	
H(7b) <sup>a</sup>	-0.0587	0.4961	0.1906	
H(8a) <sup>b</sup>	-0.0414	0.4302	0.2402	
H(8b) <sup>b</sup>	-0.0224	0.5104	0.1531	
H(9a) <sup>c</sup>	0.7313	0.0425	-0.0158	
H(9b) <sup>c</sup>	0.6478	-0.0469	0.0209	
H(10a) <sup>d</sup>	0.7342	0.1098	0.0287	
H(10b) <sup>d</sup>	0.6878	-0.0373	-0.0193	
H(11a) <sup>c</sup>	0.7363	0.2250	0.0984	
H(11b) <sup>c</sup>	0.7386	0.0424	0.1326	
H(12a) <sup>d</sup>	0.6665	-0.0795	0.1344	
H(12b) <sup>d</sup>	0.5724	-0.0521	0.0925	
H(13a) <sup>c</sup>	0.6814	0.1685	0.2662	
H(13b) <sup>c</sup>	0.5847	0.2424	0.2659	
H(14a) <sup>d</sup>	0.7362	0.2625	0.1368	
H(14b) <sup>d</sup>	0.7270	0.1648	0.2209	
H(15a) <sup>c</sup>	0.6788	0.4570	0.2834	
H(15b) <sup>c</sup>	0.7359	0.4003	0.2075	
H(16a) <sup>d</sup>	0.6453	0.3841	0.2796	
H(16b) <sup>d</sup>	0.7313	0.4638	0.2424	

<sup>a</sup> Positions for hydrogen atoms are ideally calculated. <sup>b</sup> Populational parameters  $a = 0.65$  (2),  $b = 0.35$  (2),  $c = 0.63$  (2),  $d = 0.37$  (2). <sup>c</sup> Isotropic thermal parameter for hydrogen atoms is fixed at 5.5.

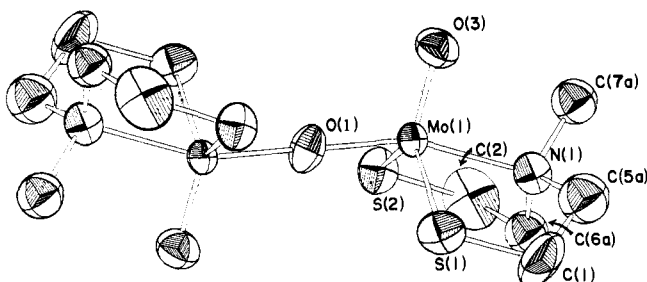
**Table III.** Bond Distances (Å) and Bond Angles (deg)

Molecule I		Molecule II	
Mo(1)-S(1)	2.347 (3)	Mo(2)-S(3)	2.347 (4)
Mo(1)-S(2)	2.343 (3)	Mo(2)-S(4)	2.345 (4)
Mo(1)-O(1)	1.860 (1)	Mo(2)-O(2)	1.856 (1)
Mo(1)-O(3)	1.671 (8)	Mo(2)-O(4)	1.662 (8)
Mo(1)-N(1)	2.236 (10)	Mo(2)-N(2)	2.229 (10)
S(1)-C(1)	1.812 (15)	S(3)-C(3)	1.794 (15)
S(2)-C(2)	1.796 (15)	S(4)-C(4)	1.811 (15)
N(1)-C(5a)	1.48 (3)	N(2)-C(8a)	1.46 (2)
N(1)-C(5b)	1.47 (4)	N(2)-C(8b)	1.46 (6)
N(1)-C(6a)	1.50 (2)	N(2)-C(9a)	1.55 (2)
N(1)-C(6b)	1.39 (5)	N(2)-C(9b)	1.41 (5)
N(1)-C(7a)	1.57 (2)	N(2)-C(10a)	1.54 (3)
N(1)-C(7b)	1.51 (4)	N(2)-C(10b)	1.41 (5)
C(1)-C(5a)	1.52 (3)	C(3)-C(8a)	1.53 (2)
C(1)-C(5b)	1.56 (4)	C(3)-C(8b)	1.66 (6)
C(2)-C(6a)	1.54 (2)	C(4)-C(9a)	1.47 (3)
C(2)-C(6b)	1.66 (5)	C(4)-C(9b)	1.54 (6)
S(1)-Mo(1)-S(2)	123.8 (1)	S(3)-Mo(2)-S(4)	121.1 (1)
S(1)-Mo(1)-O(1)	88.6 (1)	S(3)-Mo(2)-O(2)	86.3 (1)
S(2)-Mo(1)-O(1)	88.6 (1)	S(4)-Mo(2)-O(2)	89.5 (1)
S(1)-Mo(1)-O(3)	118.0 (3)	S(3)-Mo(2)-O(4)	119.9 (3)
S(2)-Mo(1)-O(3)	116.7 (3)	S(4)-Mo(2)-O(4)	118.0 (3)
S(1)-Mo(1)-N(1)	81.6 (3)	S(3)-Mo(2)-N(2)	81.9 (3)
S(2)-Mo(1)-N(1)	82.0 (3)	S(4)-Mo(2)-N(2)	82.9 (3)
O(1)-Mo(1)-O(3)	105.5 (3)	O(2)-Mo(2)-O(4)	104.7 (3)
O(1)-Mo(1)-N(1)	159.4 (2)	O(2)-Mo(2)-N(2)	160.0 (2)
O(3)-Mo(1)-N(1)	95.0 (4)	O(4)-Mo(2)-N(2)	95.2 (4)
C(1)-S(1)-Mo(1)	101.9 (5)	C(3)-S(3)-Mo(2)	101.2 (5)
C(2)-S(2)-Mo(1)	102.0 (5)	C(4)-S(4)-Mo(2)	102.7 (5)
C(5a)-N(1)-C(6a)	112.9 (14)	C(8a)-N(2)-C(9a)	112.0 (13)
C(5a)-N(1)-C(7a)	104.4 (13)	C(8a)-N(2)-C(10a)	108.9 (13)
C(5a)-N(1)-Mo(1)	112.1 (10)	C(8a)-N(2)-Mo(2)	109.5 (9)
C(6a)-N(1)-C(7a)	106.1 (12)	C(9a)-N(2)-C(10a)	105.8 (12)
C(6a)-N(1)-Mo(1)	111.2 (9)	C(9a)-N(2)-Mo(2)	107.2 (10)
C(7a)-N(1)-Mo(1)	109.7 (9)	C(10a)-N(2)-Mo(2)	113.5 (10)
C(5b)-N(1)-C(6b)	114.8 (26)	C(8b)-N(2)-C(9b)	122.2 (31)
C(5b)-N(1)-C(7b)	113.9 (22)	C(8b)-N(2)-C(10b)	86.0 (28)
C(5b)-N(1)-Mo(1)	110.7 (16)	C(8b)-N(2)-Mo(2)	110.0 (23)
C(6b)-N(1)-C(7b)	94.6 (27)	C(9b)-N(2)-C(10b)	112.9 (28)
C(6b)-N(1)-Mo(1)	112.7 (22)	C(9b)-N(2)-Mo(2)	110.8 (22)
C(7b)-N(1)-Mo(1)	109.3 (16)	C(10b)-N(2)-Mo(2)	112.9 (20)
S(1)-C(1)-C(5a)	113.1 (12)	S(3)-C(3)-C(8a)	110.1 (11)
S(2)-C(2)-C(6a)	111.9 (11)	S(4)-C(4)-C(9a)	110.5 (11)
C(1)-C(5a)-N(1)	108.5 (16)	C(3)-C(8a)-N(2)	108.0 (14)
C(2)-C(6a)-N(1)	106.9 (14)	C(4)-C(9a)-N(2)	112.2 (14)
S(1)-C(1)-C(5b)	108.3 (17)	S(3)-C(3)-C(8b)	108.8 (21)
S(2)-C(2)-C(6b)	109.6 (20)	S(4)-C(4)-C(9b)	107.9 (21)
C(1)-C(5b)-N(1)	106.8 (25)	C(3)-C(8b)-N(2)	101.5 (33)
C(2)-C(6b)-N(1)	106.4 (32)	C(4)-C(9b)-N(2)	116.0 (35)

it is considered unlikely that two polymorphs would have such similar unit cells; therefore the disordered model is accepted as final.

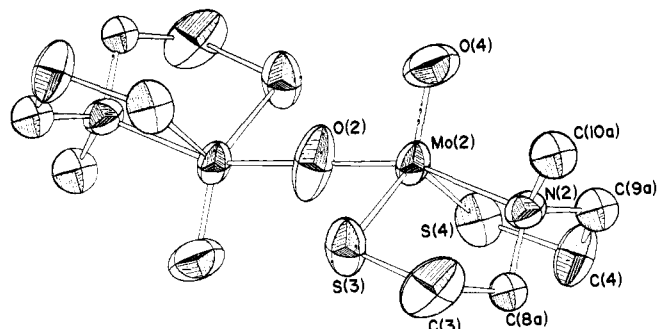
### Results

**Description of the Structure.** The structure contains two crystallographically independent  $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$  molecules. Molecules I and II are centered at (0, 0, 0) and  $(\frac{1}{2}, 0, 0)$ , respectively.



**Figure 1.** Perspective view of conformation A of molecule I; thermal ellipsoids are drawn at the 50% probability level.

The configuration of each molecule is that of two distorted trigonal bipyramids sharing a common vertex occupied by the bridging oxygen atom, with the nitrogen atoms occupying the opposite vertices; the terminal oxygen and the two sulfur atoms occupy the trigonal planes. The Mo atoms



**Figure 2.** Perspective view of conformation A of molecule II; thermal ellipsoids are drawn at the 50% probability level.

Table IV. Dihedral Angles<sup>a</sup> (deg) of Interest

Molecule I		Molecule II	
S(1)-C(1)-C(5a)-N(1)	-49	S(4)-C(4)-C(9a)-N(2)	52
S(2)-C(2)-C(6a)-N(1)	-54	S(3)-C(3)-C(8a)-N(2)	57
C(1)-C(5a)-N(1)-C(6a)	-75	C(4)-C(9a)-N(2)-C(8a)	66
C(1)-C(5a)-N(1)-C(7a)	171	C(4)-C(9a)-N(2)-C(10a)	-176
C(1)-C(5a)-N(1)-Mo(1)	52	C(4)-C(9a)-N(2)-Mo(2)	-54
C(2)-C(6a)-N(1)-C(5a)	-180	C(3)-C(8a)-N(2)-C(9a)	-175
C(2)-C(6a)-N(1)-C(7a)	-66	C(3)-C(8a)-N(2)-C(10a)	68
C(2)-C(6a)-N(1)-Mo(1)	53	C(3)-C(8a)-N(2)-Mo(2)	-57
S(1)-C(1)-C(5b)-N(1)	59	S(4)-C(4)-C(9b)-N(2)	-50
S(2)-C(2)-C(6b)-N(1)	54	S(3)-C(3)-C(8b)-N(2)	-61
C(1)-C(5b)-N(1)-C(6b)	174	C(4)-C(9b)-N(2)-C(8b)	179
C(1)-C(5b)-N(1)-C(7b)	67	C(4)-C(9b)-N(2)-C(10b)	-81
C(1)-C(5b)-N(1)-Mo(1)	-57	C(4)-C(9b)-N(2)-Mo(2)	47
C(2)-C(6b)-N(1)-C(5b)	72	C(3)-C(8b)-N(2)-C(9b)	-71
C(2)-C(6b)-N(1)-C(7b)	-169	C(3)-C(8b)-N(2)-C(10b)	175
C(2)-C(6b)-N(1)-Mo(1)	-56	C(3)-C(8b)-N(2)-Mo(2)	62
C(5a)-N(1)-Mo(1)-S(1)	-30	C(9a)-N(2)-Mo(2)-S(4)	29
C(5a)-N(1)-Mo(1)-S(2)	-156	C(9a)-N(2)-Mo(2)-S(3)	152
C(5a)-N(1)-Mo(1)-O(3)	87	C(9a)-N(2)-Mo(2)-O(4)	-89
C(6a)-N(1)-Mo(1)-S(1)	97	C(8a)-N(2)-Mo(2)-S(4)	-93
C(6a)-N(1)-Mo(1)-S(2)	-29	C(8a)-N(2)-Mo(2)-S(3)	30
C(6a)-N(1)-Mo(1)-O(3)	-145	C(8a)-N(2)-Mo(2)-O(4)	150
C(7a)-N(1)-Mo(1)-S(1)	-146	C(10a)-N(2)-Mo(2)-S(4)	145
C(7a)-N(1)-Mo(1)-S(2)	88	C(10a)-N(2)-Mo(2)-S(3)	-92
C(7a)-N(1)-Mo(1)-O(3)	-28	C(10a)-N(2)-Mo(2)-O(4)	28
C(5b)-N(1)-Mo(1)-S(1)	29	C(9b)-N(2)-Mo(2)-S(4)	-21
C(5b)-N(1)-Mo(1)-S(2)	-97	C(9b)-N(2)-Mo(2)-S(3)	102
C(5b)-N(1)-Mo(1)-O(3)	146	C(9b)-N(2)-Mo(2)-O(4)	-139
C(6b)-N(1)-Mo(1)-S(1)	159	C(8b)-N(2)-Mo(2)-S(4)	-159
C(6b)-N(1)-Mo(1)-S(2)	33	C(8b)-N(2)-Mo(2)-S(3)	-36
C(6b)-N(1)-Mo(1)-O(3)	-84	C(8b)-N(2)-Mo(2)-O(4)	83
C(7b)-N(1)-Mo(1)-S(1)	-98	C(10b)-N(2)-Mo(2)-S(4)	106
C(7b)-N(1)-Mo(1)-S(2)	136	C(10b)-N(2)-Mo(2)-S(3)	-131
C(7b)-N(1)-Mo(1)-O(3)	20	C(10b)-N(2)-Mo(2)-O(4)	-11

<sup>a</sup> Values taken as positive when bond between first two atoms rotates clockwise to eclipse bond between third and fourth atoms.

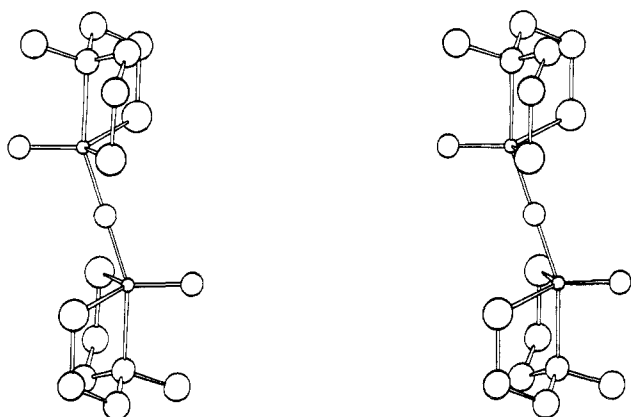


Figure 3. Stereoview of conformation A of molecule I.

lie 0.16 and 0.12 Å out of the S-S-O<sub>t</sub> planes toward the bridging oxo atoms in molecules I and II, respectively.

Bond distances and bond angles are listed in Table III. The dihedral angles associated with the ligands are listed in Table IV. Figures 1 and 2 show molecules I and II, respectively, in the more highly populated conformation A. A stereoview of conformation A, molecule I, is shown in Figure 3, and a view of the packing is given in Figure 4.

Figure 5 illustrates the approximate mirror relationship of conformations A and B, as viewed along the N-Mo bond of molecule I. The five-member chelate rings are in envelope conformation, with N-Mo-S-C nearly planar and the carbon attached to nitrogen bending either upward or downward to

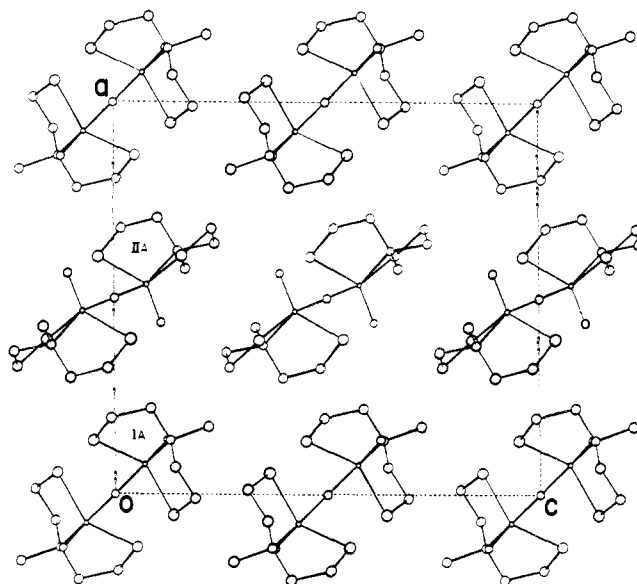


Figure 4. [010] projection of packing. Only conformation A is shown.

form the two observed disorder sites. Dihedral angles listed in Table IV illustrate approximate staggering about C-C and N-C bonds. In examining these angles one should realize that, in principle, all corresponding atoms of conformers A and B, even those represented by a single electron density peak, actually occupy different mean sites. This effect is particularly pronounced in the carbon atoms attached to sulfur, where the

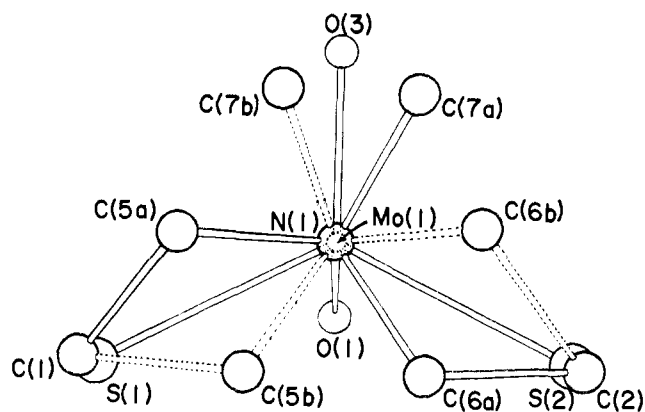


Figure 5. One-half of molecule I, showing both conformers. Conformation B is dashed.

Table V. Shortest Nonbonded Contacts<sup>a</sup>

Atom...atom of equivalent position	Contact distance, Å	Conformation of contact atoms
S(4)...H(1b) (1 - x, 1 - y, -z)	2.80	II...IA
H(3)...H(13a) (1 - x, 0.5 + y, 0.5 - z)	2.39	IA...IIA
H(6a)...S(2) (-x, 0.5 + y, 0.5 - z)	2.95	IB...I
H(8b)...O(3) (-x, 0.5 + y, 0.5 - z)	2.53	IB...I
H(14a)...H(2a) (1 - x, 1 - y, -z)	2.28	IIB...IB
H(16a)...S(3) (x, 0.5 - y, 0.5 + z)	2.93	IIB...II
H(11a)...H(2a) (1 - x, 1 - y, -z)	2.19	IIA...IB

<sup>a</sup> Less than van der Waals contacts calculated by using the following van der Waals radii:<sup>24</sup> H, 1.20; C, 1.70; N, 1.50; O, 1.40; and S, 1.85 Å. For the purpose of van der Waals calculations, hydrogen atoms were moved to a distance of 1.07 Å from the attached atom.

large anisotropy is in part interpreted as describing two sites which are perceptibly different, yet unresolved. This systematic error, which affects principally atoms C(1)-C(4), is not included in calculations of standard deviations.

The generally larger thermal parameters and positional standard deviations of molecule II in both conformations can similarly be interpreted as representing either greater thermal motion, or more relative displacement of unresolved atoms, in

comparison with molecule I. The shortest van der Waals contacts are listed in Table V.

## Discussion

There are seven previously known crystal structures containing the Mo<sub>2</sub>O<sub>3</sub><sup>4+</sup> unit.<sup>11-13,25-27</sup> In all of them, molybdenum has octahedral rather than trigonal bipyramidal coordination. Some of these complexes are syn, others are anti with respect to the two terminal oxygen atoms.

We summarize below the ranges of pertinent distances and angles within the Mo<sub>2</sub>O<sub>3</sub><sup>4+</sup> group in these complexes and compare these with values observed in molecules I and II.

Parameter	Previously obsd range	Molecule I	Molecule II
Mo-O <sub>b</sub>	1.86-1.87 Å	1.860 (1) Å	1.856 (1) Å
Mo-O <sub>t</sub>	1.65-1.68 Å	1.671 (8) Å	1.662 (8) Å
O <sub>b</sub> -Mo-O <sub>t</sub>	102-105°	105.5 (3)°	104.1 (3)°

Comparing these figures, we conclude that the Mo<sub>2</sub>O<sub>3</sub><sup>4+</sup> unit is essentially invariant to the changes in coordination number involved. Although the four Mo-S bond lengths are essentially identical, the S-Mo-S and S-Mo-O<sub>(b or t)</sub> angles of molecules I and II are not equal within their combined standard deviation. The differences are sufficiently small, however, to be attributed to the difference in packing in the unit cell. Comparisons of pertinent structural features of Mo<sub>2</sub>O<sub>3</sub>[NCH<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>S)<sub>2</sub>]<sub>2</sub> with those of other oxomolybdenum(V) complexes which have ligands containing thiol, nitrogen, or both are listed in Table VI. All of the bond lengths and angles in the present complex are found to be typical except the Mo-S and S-C bond lengths and the S-Mo-O<sub>t</sub> bond angle. The average S-C bond length in Mo<sub>2</sub>O<sub>3</sub>[NCH<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>S)<sub>2</sub>]<sub>2</sub> (1.803 (15) Å) is shorter than those in the remaining complexes (which, however, are less accurately determined). The present measurement, nevertheless, agrees fairly well with accurately measured S-C distances in L-cysteine,<sup>32</sup> 1.811 (3) Å; H[π-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(L-cysteine)Mo<sup>IV</sup>]Cl,<sup>33</sup> 1.816 (8) Å; and L-cysteine-2HCl,<sup>34</sup> 1.810 (7) Å.

The average Mo-S distance in the present complex (2.346 Å) is much shorter than that in the six-coordinate Mo-cysteine complexes (2.49 and 2.50 Å); it is significantly shorter, but closer to the average Mo-S distances in the five-coordinate cysteine ester complexes containing di-μ-O or di-μ-S bridges (2.385, 2.38 Å), and in two recently studied isomers of the di-μ-sulfido-bis(sulfido-1,2-dimercaptoethanolatomolybdate(V)) dianion<sup>35</sup> (2.387 to 2.414 Å). The latter complexes are also five coordinate, but tetragonal pyramidal rather than

Table VI. Relevant Structural Parameters (Mean Values) for Oxomolybdenum(V) Complexes Which Have Ligands Containing Thiol, Nitrogen, or Both

Complex <sup>a</sup>	Mo-O <sub>t</sub> , Å	Mo-S, Å	Mo-N, Å	S-C, Å	S-Mo-O, deg	S-Mo-N, deg	O <sub>t</sub> -Mo-N, deg	Mo-S-C, deg	Mo-N-C, deg	Ref
I	1.667 (8)	2.346 (3)	2.23 (1)	1.803 (15)	118.2 (3)	82.1 (3)	95.1 (4)	102.0 (5)	111.1 (1)	This work
II	1.71 (2)	2.490 (6)	2.23 (3)	1.87 (2)	94.4 (6)	80.3 (4)	93.2 (7)			4
III	1.66 (2)	2.385 (8)	2.22 (2)	1.85 (3)	109.8 (6)	81.0 (7)	96.6 (9)	101 (1)	116 (2)	5
IV	1.71 (3)	2.38 (1)	2.24 (3)	1.86 (5)	114 (1)	79 (1)	97 (1)	103 (1)	112 (2)	6
V	1.62 (3)	2.50 (1)	2.27 (3)	1.82 (5)	97 (3)	80 (3)	95 (3)	102		7
VI	1.693 (5)	2.484 (2)	2.205 (6)							28
VII	1.683 (6)		2.448 (8) <sup>f</sup>				161.6 (6) <sup>f</sup>		105.5 (6)	29
VIII	1.71		2.23							30
IX	1.676 (6)		2.265 (8) <sup>g</sup> 2.241 (8) <sup>h</sup>				90.4 (3)		111.0 (6) <sup>g</sup>	31

<sup>a</sup> (I) Mo<sub>2</sub>O<sub>3</sub>[NCH<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>S)<sub>2</sub>]<sub>2</sub>,<sup>c</sup> (II) Na<sub>2</sub>[Mo<sub>2</sub>O<sub>4</sub>(L-cysteine)]·5H<sub>2</sub>O,<sup>b</sup> (III) Mo<sub>2</sub>O<sub>4</sub>(L-cysteine ethyl ester)<sub>2</sub>,<sup>d</sup> (IV) Mo<sub>2</sub>S<sub>2</sub>O<sub>2</sub>(L-cysteine methyl ester)<sub>2</sub>,<sup>d</sup> (V) Na<sub>2</sub>[Mo<sub>2</sub>S<sub>2</sub>O<sub>2</sub>(L-cysteine)]·2H<sub>2</sub>O,<sup>b</sup> (VI) Mo<sub>2</sub>O<sub>3</sub>(SC<sub>2</sub>H<sub>4</sub>O)(oxine)<sub>2</sub>,<sup>b,e</sup> (VII) Cs<sub>2</sub>[Mo<sub>2</sub>S<sub>2</sub>O<sub>2</sub>EDTA]·2H<sub>2</sub>O,<sup>b</sup> (VIII) Mo<sub>2</sub>O<sub>4</sub>(L-histidine)<sub>2</sub>·3H<sub>2</sub>O,<sup>b</sup> (IX) Mo<sub>2</sub>S<sub>2</sub>O<sub>2</sub>(L-histidine)<sub>2</sub>·1.5H<sub>2</sub>O.<sup>b</sup> <sup>b</sup> Octahedral geometry. <sup>c</sup> Five-coordinate trigonal bipyramidal geometry with linear Mo-O<sub>b</sub>-Mo bonding. <sup>d</sup> Five-coordinate trigonal bipyramidal geometry with direct Mo-Mo interaction (two bridging atoms). <sup>e</sup> The two Mo atoms are bridged by one oxo ligand and by the sulfur and oxygen atoms of the 2-mercaptoethanol. <sup>f</sup> N trans to O<sub>t</sub>; this is different from the rest of the listed octahedral complexes, where N is cis to O<sub>t</sub>. <sup>g</sup> α-Amino nitrogen. <sup>h</sup> Ring nitrogen.

trigonal bipyramidal. The contraction of average Mo-S distance from six- to five-coordinate complexes is not unexpected, even though the former contain weakly bound carboxylate groups as the sixth ligand.

The number of five-coordinate complexes of Mo(V) with cysteinato and thiolato ligands establishes this as a reasonable coordination mode of Mo(V) in enzymes, whether the active site complex is mono- or binuclear. Such a geometry provides ready access to the sixth coordination site by a potential substrate, without a prior ligand dissociation step.

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**Supplementary Material Available:** A listing of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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# Photochemical Substitution Reactions of $Mn_2(CO)_{10}$ <sup>1</sup>

Dennis R. Kidd and Theodore L. Brown\*

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received November 4, 1977

**Abstract:**  $Mn_2(CO)_{10}$  undergoes photosubstitution by tributylphosphine,  $PBu_3$ , or triethyl phosphite,  $P(OEt)_3$ , in heptane, with 350-nm radiation, to yield mainly disubstituted dimer as initial product. In the absence of added CO, the quantum yields for disappearance of  $Mn_2(CO)_{10}$ ,  $\Phi_d$ , in both cases are on the order of 0.9. For  $[Mn_2(CO)_{10}] = 4 \times 10^{-4}$  M, and ligand concentrations in the range  $2-20 \times 10^{-3}$  M,  $\Phi_d$  is independent of the nature and concentration of ligand. Addition of  $10^{-2}$  M purified CO results in a lowered quantum yield, 0.6-0.7. The results can be accounted for most satisfactorily by assuming that  $Mn(CO)_5$  radicals undergo facile dissociative loss of CO. Substituted dimers,  $Mn_2(CO)_8L_2$ ,  $L = PBu_3$  or  $P(OEt)_3$ , undergo photosubstitution by CO to yield  $Mn_2(CO)_9L$  and  $Mn_2(CO)_{10}$ , with quantum yield for disappearance of starting carbonyl of about 0.2.  $Mn_2(CO)_8L_2$  compounds also undergo photosubstitution by  $L'$  to yield a complex array of products.

## Introduction

The chemical and physical properties of organometallic radicals, especially those derived from transition elements, are not as well understood as those of organic radicals. However, in recent years the importance of radical pathways in many organometallic reactions has become more widely appreciated.<sup>2-6</sup> There has thus been a considerable interest in the production and study of transition element organometallic radicals.<sup>7-12</sup>

We are concerned in the work reported here with the substitution characteristics of transition metal carbonyl radicals, of the form  $M(CO)_n$  or  $M(CO)_mL_n$ . These are formed under conditions suitable for study of their chemical characteristics mainly by thermal or photochemical homolysis of metal-metal bonds.

Formation of metal carbonyl radicals has been invoked to account for the kinetics and product distributions observed in the thermal substitution reactions of several metal carbonyl dimer species, including  $[Ru(CO)_4Si(CH_3)_3]_2$ ,<sup>13</sup>  $Mn(CO)_{10}$ .<sup>14</sup>