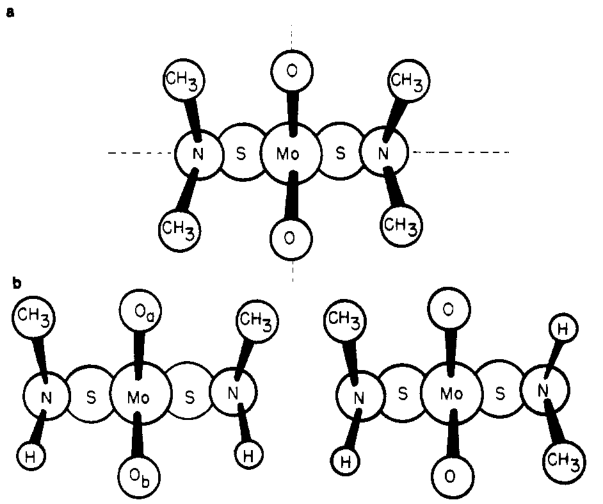

**Figure 6.** Schematic representation of skew-trapezoidal-bipyramidal structures: (a) $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$; (b) $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$.

the $^{17}O$ NMR spectrum. Upon heating, the observed coalescence (Figure 4) is attributed to averaging the environments in the two STB structure (possibly by N–Mo bond-breakage inversion about N followed by Mo–N bond re-formation). The same explanation holds for the $CH_3$ resonances. Thus, there are four types of carbon-bound $CH_3$ groups in each of the two structures, leading to a maximum of eight resonances. The same averaging process between the two STB structures would leave only two types of $CH_3$ groups, i.e., those on $C_N$ and those on $C_S$. Clearly, the static and dynamic NMR data are both consistent with the STB structure. The NMR data show that the STB structure is likely present in solution as well as in the solid state.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this work through Grants CHE 77-07026 and 79-26021.

**Registry No.** $C_6H_5CH_2NHCH_2C(CH_3)_2SH\cdot HCl$, 82626-95-7; $(CH_3)_2CHNCH_3C(CH_3)_2SH\cdot HCl$, 91229-26-4; $(CH_3)_3CNHCH_2C(CH_3)_2SH\cdot HCl$, 91229-27-5; $CH_3NHC(CH_3)_2C(CH_3)_2SH\cdot HCl$, 91229-28-6; $(CH_3)_2NCH_2C(CH_3)_2SCH_2C_6H_5$, 91229-29-7; $NH_2CH_2C(CH_3)_2SCH_2C_6H_5$, 59681-09-3; $(CH_3)_2NCH_2C(CH_3)_2SCH_2C_6H_5$ picrate, 91229-30-0; $NH_2C(CH_3)_2CH_2SCH_2C_6H_5$, 91237-78-4; $NH_2C(CH_3)_2CH_2SCH_2C_6H_5\cdot HCl$, 91237-79-5; $NH_2C(CH_3)_2CH_2SH\cdot HCl$, 4146-00-3; $CH_3NHCH_2CH_2SH$, 10061-40-2; $(CH_3)_2NCH_2C(CH_3)_2SH\cdot HCl$, 91229-31-1; $(CH_3)_2NC(CH_3)_2CH_2SCH_2C_6H_5$, 91229-32-2; $(CH_3)_2NC(CH_3)_2CH_2SCH_2C_6H_5$ picrate, 91229-33-3; $(CH_3)_2NC(CH_3)_2CH_2SH\cdot HCl$, 91229-34-4; $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5$, 91229-35-5; $CH_2{=}NC(CH_3)_2CH_2SC_6H_5$, 91229-36-6; $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5\cdot HCl$, 91229-37-7; $CH_3NHC(CH_3)_2CH_2SH\cdot HCl$, 91229-38-8; $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5$, 91229-39-9; $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5\cdot HCl$, 91229-41-3; $(CH_3)_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5\cdot HCl$, 91229-42-4; $NH_2C(CH_3)_2C(CH_3)_2SH\cdot HCl$, 79797-08-3; $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH\cdot HCl$, 91229-44-6; $MoO_2(H_2NCH_2S)_2$, 29836-54-2; $MoO_2(H_2NCH_2C(CH_3)_2S)_2$, 76757-49-8; $MoO_2(H_2NC(CH_3)_2CH_2S)_2$, 91279-42-4; $MoO_2(H_2NC(CH_3)_2C(CH_3)_2S)_2$, 79799-79-4; $MoO_2(C_6H_5CH_2NHC(CH_3)_2S)_2$, 91229-45-7; $MoO_2(C_6H_5NHCH_2C(CH_3)_2S)_2$, 91229-46-8; $MoO_2(CH_3NHCH_2CH_2S)_2$, 91229-47-9; $MoO_2(CH_3NHCH_2C(CH_3)_2S)_2$, 74005-67-7; $MoO_2((CH_3)_2NCH_2C(CH_3)_2S)_2$, 74005-68-8; $MoO_2(CH_3NHC(CH_3)_2C(CH_3)_2S)_2$, 76772-96-8; $MoO_2(acac)_2$, 17524-05-9; 2,2-dimethylthiirane, 3772-13-2; benzylamine, 100-46-9; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9; 2,2,3,3-tetrramethylthiirane, 17066-32-9; methylamine, 74-89-5; 2,2-dimethylethylene imine, 2658-24-4; benzyl mercaptan, 100-53-8; thiirane, 420-12-2; tetramethylethylene imine, 5910-14-5; 3,4,4,5,5-pentamethyl-1,3-thiazolidine, 91229-43-5.

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Department of Chemistry, Stanford University, Stanford, California 94305, and
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# Six-Coordinate Dioxomolybdenum(VI) Complexes Containing a Nonoctahedral Structure with a Short Sulfur–Sulfur Contact

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The structures of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (**1**), $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]$ (**2**), and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (**3**) have been determined by using X-ray diffraction intensity data collected by counter techniques. **1** crystallizes in space group $P2_1/c$ with $a = 10.688$ (3) Å, $b = 11.923$ (2) Å, $c = 14.032$ (3) Å, $\beta = 106.65$ (2)°, and $Z = 4$. **2** crystallizes in space group $P2_1/c$ with $a = 10.771$ Å, $b = 11.281$ (4) Å, $c = 16.021$ (3) Å, $\beta = 90.43$ (2)°, and $Z = 4$. **3** crystallizes in space group $Fdd2$ with $a = 18.441$ (b) Å, $b = 22.998$ (6)Å, $c = 8.006$ (1) Å, and $Z = 8$. The six-coordinate structures are remarkably similar with an unusual nonoctahedral geometry described as a skew trapezoidal bipyramid. An approximate $N_2S_2$ plane contains the Mo atom with equivalent oxygen atoms above and below the plane. Average distances in the first coordination sphere are Mo–O = 1.72, Mo–N = 2.30, and Mo–S = 2.42 Å. An additional unusual feature of the structures is the short S–S contact of 2.73–2.82 Å with an S–Mo–S angle of 68.8–71.0°. This is attributed to partial disulfide bond formation. The *N*-methyl substitution on the cysteamine ligand would cause severe steric hindrance were an octahedral structure adopted. The resultant skew-trapezoidal structure minimizes the steric repulsion without causing any electronically unfavorable interactions.

The coordination chemistry of hexavalent molybdenum is dominated by complexes of coordination number 6.[2,3] Of these, there are large numbers of both mononuclear and homo- and heteropolynuclear oxomolybdates and a few dinuclear complexes. Virtually all of the mononuclear complexes contain a dioxomolybdenum group and, almost without exception, possess octahedral (or distorted octahedral) coordination wherein the two oxo ligands occupy cis positions in the Mo coordination sphere.[2-4] This paper presents three complexes

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(1) (a) Exxon Research and Engineering Co. (b) Stanford University. (c) The Charles F. Kettering Research Laboratory.
(2) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(3) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.

0020-1669/84/1323-3412$01.50/0 © 1984 American Chemical Society

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

| | 1 | 2 | 3 |
|---|---|---|---|
| formula | $C_{10}H_{24}MoN_2O_2S_2$ | $C_{14}H_{32}MoN_2O_2S_2$ | $C_{12}H_{28}MoN_2O_2S_2$ |
| $a$, Å | 10.688 (3) | 10.771 (3) | 18.441 (6) |
| $b$, Å | 11.923 (2) | 11.281 (3) | 22.998 (6) |
| $c$, Å | 14.032 (3) | 16.021 (3) | 8.006 (1) |
| $\beta$, deg | 106.65 (2) | 90.43 (2) | |
| $V$, Å$^3$ | 1713 (1) | 1947 (2) | 3395 (2) |
| $Z$ | 4 | 4 | 8 |
| $d_{calcd}$, g/cm$^3$ | 1.413 | 1.435 | 1.535 |
| space group | $P2_1/c$ | $P2_1/c$ | $Fdd2$ |
| abs coeff, cm$^{-1}$ | 9.8 | 8.7 | 10.0 |
| transmssn factors | | | |
| max | 85.8 | 78.0 | 93.4 |
| min | 75.2 | 70.4 | 70.8 |
| no. of observns | 1516 | 4774 | 1377 |
| no. of variables | 160 | 196 | 88 |
| error in observn of unit wt | 1.27 | 1.26 | 1.24 |
| $R$, % | 4.9 | 2.8 | 3.1 |
| $R_w$, % | 5.4 | 4.2 | 3.9 |

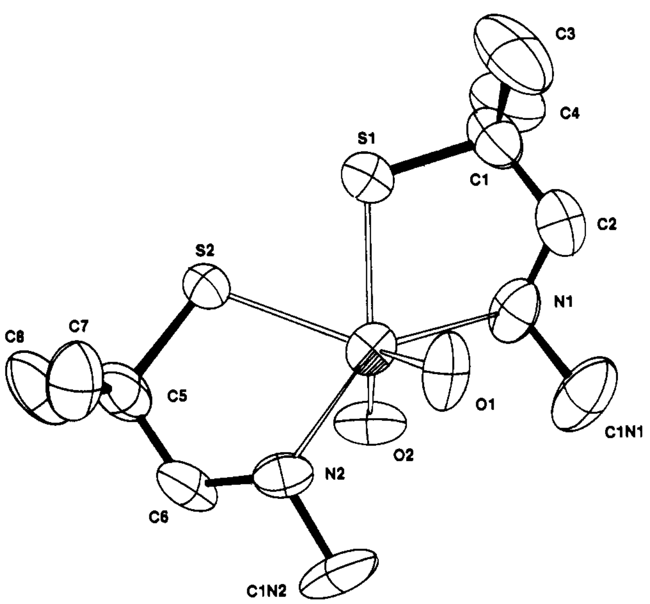
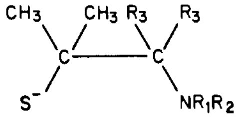


**Figure 1.** Structure of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (**1**).

that provide vivid exceptions to this structural generalization.

We have synthesized oxomolybdenum complexes[5-7] of saturated O-, N-, and S-donor ligands whose donor atom arrangement may resemble that provided to molybdenum by the metalloenzymes in which Mo serves as a catalytic component.[8] Although most of the complexes synthesized in our studies form octahedrally derived structures, unusual properties were noticed when certain bidentate substituted cysteamine ligands were used. In particular, we found that *N*-methyl substitution on the cysteamine either caused instability in the complex that precluded its isolation or, if the complexes were indeed isolated, caused spectroscopic properties that differed considerably from those of the large number of extant complexes in the class. In particular three complexes of the form $MoO_2L_2$ showed unusual $^1H$ and $^{17}O$ NMR spectra[7] as well as very low-frequency molybdenum–oxygen stretching vibrations. Complex **1** was the first to be subjected to crystallographic investigation and was found to have a highly unusual coordination geometry and a very short interligand S–S contact.[6] In view of the unusual nature of the structure and an H-bonding pattern that could have influenced that solid-state structure, the crystal structures of **2** and **3** were subsequently determined. The details of the three very similar structures are documented in this paper, and possible reasons for their occurrence are discussed. The preceding paper describes the preparations and spectroscopic studies that indicate that the new structural type is found in solution and that its presence helps explain the unusual spectroscopic properties of these complexes.



1: $R_1 = R_3 = H, R_2 = CH_3$
2: $R_3 = R_2 = CH_3, R_1 = H$
3: $R_3 = H, R_1 = R_2 = CH_3$

## Experimental Section

Crystals of **1**–**3** were grown by evaporation of the $CH_3OH$ reaction mixtures in which these complexes were prepared by reaction of the appropriate ligand and $MoO_2(acac)_2$.[7]

**Data Collection and Reduction.** All X-ray diffraction experiments were performed on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromatized Mo K$\alpha$ radiation. The crystals were mounted on thin glass fibers with epoxy cement. For each compound accurate unit cell parameters and an orientation matrix were determined from 15 machine-centered reflections. The intensity data were processed as described previously.[9] Three standard reflections

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(4) Examples from the recent literature include: (a) Bruce, A. E.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Spence, J. T.; Stiefel, E. I.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917. (b) Gulloth, M.; Pasini, A.; Zanderighi, G. M.; Ciani, G.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1981**, 902. (c) Brewer, G. A.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 1824. (d) Cliff, C. A.; Fallon, G. D.; Gatehouse, B. M.; Murray, K. S.; Newman, P. J. *Ibid.* **1980**, *19*, 773. (e) Berg, J. M.; Hodgson, K. O. *Ibid.* **1980**, *19*, 2180. (f) Viossat, B.; Rodier, N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2715. (g) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1977**, *16*, 2970. (h) Wieghardt, K.; Holzbach, W.; Hofer, E.; Weiss, J. *Ibid.* **1981**, *20*, 343. (i) Yamanouchi, K.; Enemark, J. H. Third International Conference on Chemistry and Uses of Molybdenum, Climax Molybdenum Co., Aug 1979. (j) Berg, J. M.; Hodgson, K. O.; Bruce, A. E.; Corbin, J. L.; Pariyadath, N.; Stiefel, E. I. *Inorg. Chim. Acta*, in press. (k) Berg, J. M.; Spira, D.; Wo, K.; McCord, B.; Co, M. S.; Belmont, J.; Barnes, C.; Kosydar, K.; Raybuck, S.; Hodgson, K. O.; Bruce, A. E.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chim. Acta*, in press.

(5) Berg, J. M.; Hodgson, K. O.; Cramer, S. P.; Corbin, J. L.; Elsberry, A.; Pariyadath, N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 2774.

(6) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.* **1980**, *102*, 3624.

(7) (a) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Heinecke, J.; Pariyadath, N.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York, 1980; p 279. (b) Corbin, J. L.; Miller, K. F.; Pariyadath, N.; Heinecke, J.; Bruce, A. E.; Wherland, S.; Stiefel, E. I. *Inorg. Chem.*, preceding paper in this issue. (c) Corbin, J. L.; Miller, K. F.; Pariyadath, N.; Wherland, S.; Bruce, A. E.; Stiefel, E. I. *Inorg. Chim. Acta*, in press.

(8) (a) Stiefel, E. I. In "Molybdenum and Molybdenum Containing Enzymes"; Coughlan, M. P., Ed.; Pergamon Press: New York, 1980; p 43. (b) Cramer, S. P.; Rajagopalan, K. V.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2772.

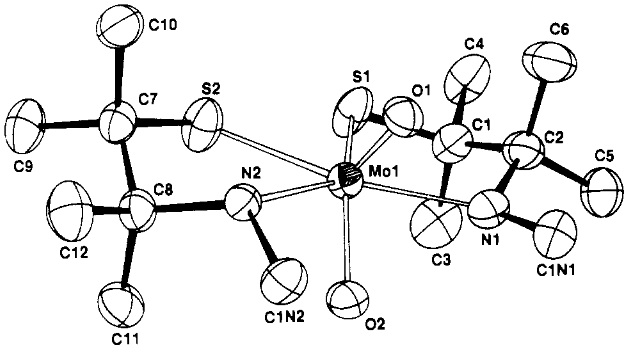

**Figure 2.** Structure of $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$ (**2**).

were measured every 60 reflections to monitor machine and crystal stability. No unusual fluctuations were observed. Analytical absorption corrections were applied to each data set. The crystallographic data are summarized in Table I. Further details concerning the data collection and processing for each structure are given below.

**$MoO_2[SC(CH_3)_2CH_2NHCH_3]_2$ (1).** This compound crystallizes in the monoclinic system with $a = 10.688$ (3) Å, $b = 11.923$ (2) Å, $c = 14.032$ (3) Å, and $\beta = 106.65$ (2)°. The systematic absences $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) are consistent only with the space group $P2_1/c$. There is one molecule in the asymmetric unit. All reflections of the form $+h,+k,+l$, and $3° < 2\theta < 50°$ were collected.

**$MoO_2[SC(CH_3)_2C(CH_3)_2NHCH_3]_2$ (2).** This compound also crystallizes in the space group $P2_1/c$ in a unit cell quite similar to that for **1**. The cell parameters are $a = 10.771$ (3) Å, $b = 11.281$ (4) Å, $c = 16.021$ (3) Å, and $\beta = 90.43$ (2)°. The same quadrant of data was collected but for $3° < 2\theta < 60°$.

**$MoO_2[SC(CH_3)_2CH_2N(CH_3)_2]_2$ (3).** This compound belongs to the orthorhombic crystal system with $a = 18.441$ (6) Å, $b = 22.998$ (6) Å, and $c = 8.006$ (1) Å. The systematic absences $hkl$, ($h + k \neq 2n$; $k + l \neq 4n$) and h0l ($h + l \neq 4n$) are consistent only with the space group $Fdd2$. There are 8 molecules in the unit cell on the basis of an observed density of 1.53 g/cm$^3$ and hence half of a molecule in the asymmetric unit. Since this is a polar space group and anomalous scattering effects are expected to be significant, all reflections of the form $+h,+k,\pm l$ were collected for $3° < 2\theta < 30°$. Reflections of the form $+h,+k,+l$ were collected for $30° < 2\theta < 50°$.

**Structure Solution and Refinement.** The structures were solved by using Patterson and Fourier techniques. For **3** the molecule lies on a twofold axis. After all non-hydrogen atoms had been located in this structure, they were refined isotropically both with the original data and with the indices inverted. A difference in the agreement factor ($R_w = 7.63\%$ vs. 7.77%) combined with inspection of the individual Friedel pairs indicated that the original data set was correct. For all three complexes, the non-hydrogen atoms were refined anisotropically by using full-matrix least squares. For **1** and **2** the N–H hydrogens were easily located from difference Fourier maps. Since these atoms participate in intermolecular hydrogen bonding (vide infra), their positions were refined with temperature factors fixed at 3.0 Å$^2$. The remaining hydrogen atoms were calculated on the assumption of tetrahedral geometries and C–H distances of 0.98 Å. The orientations of the methyl groups were determined from difference Fourier maps. These atoms were included in the final least-squares cycles as fixed contributors with temperature factors set at $B = 5.0$ Å$^2$. Final difference maps showed no peaks larger than 20% of the height of a carbon atom peak. The final agreement factors are given in Table I. The positional parameters for all refined atoms are given in Table II. Thermal parameters, calculated hydrogen atom positions, and structure factor tables are included as supplementary material.

## Results

Bond lengths and angles are displayed in Tables III and IV, respectively. The three structures reported here are quite similar, and we choose to discuss the more symmetrical structure **3** first and then move to structures **1** and **2** and note differences where they occur. A major difference is that in structure **3** the molecule has crystallographically imposed twofold symmetry, while noncrystallographic approximate twofold symmetry is present in structures **1** and **2**.

**Table II.** Positional Parameters

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (1) | | | |
| Mo1 | 0.26014 (7) | 0.54022 (7) | 0.03634 (6) |
| S1 | 0.2022 (3) | 0.7286 (2) | 0.0721 (2) |
| S2 | 0.3708 (3) | 0.5885 (2) | 0.2063 (2) |
| O1 | 0.3405 (5) | 0.5492 (6) | −0.0538 (4) |
| O2 | 0.1535 (5) | 0.4338 (5) | 0.0385 (5) |
| N1 | 0.0888 (7) | 0.5938 (7) | −0.0921 (6) |
| N2 | 0.4125 (6) | 0.4036 (6) | 0.0914 (5) |
| C1 | 0.1150 (10) | 0.7927 (9) | 0.0464 (8) |
| C2 | 0.1042 (10) | 0.7088 (11) | −0.1273 (7) |
| C3 | 0.1856 (13) | 0.8959 (11) | −0.0626 (10) |
| C4 | −0.0208 (12) | 0.8283 (9) | −0.0412 (9) |
| C1N1 | 0.0586 (11) | 0.5125 (12) | −0.1741 (8) |
| C5 | 0.4690 (9) | 0.4660 (9) | 0.2643 (6) |
| C6 | 0.4269 (9) | 0.3680 (8) | 0.1948 (7) |
| C7 | 0.6126 (11) | 0.4959 (10) | 0.2811 (7) |
| C8 | 0.4422 (12) | 0.4412 (11) | 0.3601 (7) |
| C1N2 | 0.3898 (10) | 0.3047 (9) | 0.0226 (9) |
| H1N1 | 0.037 (6) | 0.602 (5) | −0.070 (4) |
| H1N2 | 0.467 (6) | 0.425 (5) | 0.084 (4) |
| $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]$ (2) | | | |
| Mo1 | 0.25228 (1) | 0.53027 (1) | 0.08830 (1) |
| S1 | 0.18614 (6) | 0.67182 (6) | 0.19253 (4) |
| S2 | 0.32284 (6) | 0.47299 (6) | 0.22609 (3) |
| O1 | 0.3625 (1) | 0.5904 (1) | 0.02299 (10) |
| O2 | 0.1404 (1) | 0.4340 (1) | 0.04999 (9) |
| N1 | 0.1193 (2) | 0.6593 (2) | 0.0187 (1) |
| N2 | 0.3834 (2) | 0.3693 (2) | 0.0683 (1) |
| C1 | 0.0650 (2) | 0.7651 (2) | 0.1439 (1) |
| C2 | 0.0969 (2) | 0.7821 (2) | 0.0518 (1) |
| C3 | −0.0615 (3) | 0.7037 (3) | 0.1571 (2) |
| C4 | 0.0637 (3) | 0.8812 (3) | 0.1942 (2) |
| C5 | −0.0118 (2) | 0.8378 (2) | 0.0031 (2) |
| C6 | 0.2139 (3) | 0.8578 (2) | 0.0396 (2) |
| C1N1 | 0.1432 (2) | 0.6534 (2) | −0.0722 (1) |
| C7 | 0.4413 (2) | 0.3570 (2) | 0.2133 (1) |
| C8 | 0.4042 (2) | 0.2807 (2) | 0.1367 (1) |
| C9 | 0.4421 (3) | 0.2873 (3) | 0.2956 (1) |
| C10 | 0.5692 (2) | 0.4150 (3) | 0.2045 (1) |
| C11 | 0.2842 (2) | 0.2108 (2) | 0.1509 (2) |
| C12 | 0.5079 (2) | 0.1940 (2) | 0.1136 (2) |
| C1N2 | 0.3594 (2) | 0.3173 (2) | −0.0150 (1) |
| H1N1 | 0.059 (2) | 0.672 (2) | 0.023 (1) |
| H1N2 | 0.443 (2) | 0.404 (2) | 0.064 (1) |
| $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (3) | | | |
| Mo1 | 0.0 (0) | 0.0 (0) | 0.0 (0) |
| S1 | 0.05672 (6) | 0.04116 (4) | −0.2470 (2) |
| O1 | −0.0594 (2) | 0.0449 (1) | 0.1041 (4) |
| N1 | 0.0817 (2) | 0.0709 (2) | 0.1024 (5) |
| C1 | 0.1437 (2) | 0.0745 (2) | −0.1816 (6) |
| C2 | 0.1509 (2) | 0.0685 (2) | 0.0087 (7) |
| C3 | 0.2057 (3) | 0.0418 (2) | −0.2640 (9) |
| C4 | 0.1462 (3) | 0.1379 (2) | −0.2472 (8) |
| C5 | 0.0500 (3) | 0.1305 (2) | 0.0970 (7) |
| C6 | 0.0969 (3) | 0.0580 (3) | 0.2795 (7) |

The complexes are all six-coordinate with two oxygen, two sulfur, and two nitrogen atoms comprising the first coordination sphere. Views of their structures are shown in Figures 1–3. The three structures are quite similar, and the different views in the three figures represent different ways of looking at the same structure rather than distinct structural types. The ranges of the M–L distances are 2.409–2.429 Å for Mo–S, 1.711–1.731 Å for Mo–O, and 2.262–2.366 Å for Mo–N in the three structures.

Our first instinct upon solving the structures was to look for the octahedral structure[10] and identify the ligands that lie

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(9) Bobrik, M. A.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1977**, *16*, 1851.

(10) Cotton, F. A. In Proceedings of the First International Conference on the Chemistry and Use of Molybdenum, Climax Molybdenum Co., 1974, p 6.

**Table III.** Bond Distances (Å) for $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (1), $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$ (2), and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (3)

| | | | | | |
|---|---|---|---|---|---|
| | | | **1** | | |
| Mo1-S1 | 2.420 (3) | Mo1-S2 | 2.409 (3) | Mo1-O1 | 1.723 (5) |
| Mo1-O2 | 1.711 (5) | Mo1-N1 | 2.262 (9) | Mo1-N2 | 2.277 (8) |
| S1-S2 | 2.764 (5) | | | | |
| S1-C1 | 1.824 (11) | C1-C2 | 1.492 (15) | C1-C3 | 1.495 (14) |
| C1-C4 | 1.533 (15) | N1-C2 | 1.483 (14) | N1-C1N1 | 1.467 (13) |
| N1-H1N1 | 0.71 (7) | S2-C5 | 1.847 (10) | C5-C6 | 1.505 (13) |
| C5-C7 | 1.526 (14) | C5-C8 | 1.481 (12) | N2-C6 | 1.477 (12) |
| N2-C1N2 | 1.499 (12) | N2-H1N2 | 0.67 (7) | | |
| H1N1-O2′ | 2.25 (7) | H1N2-O1′ | 2.24 (7) | | |
| | | | **2** | | |
| Mo1-S1 | 2.422 (1) | Mo1-S2 | 2.417 (1) | Mo1-O1 | 1.727 (1) |
| Mo1-O2 | 1.731 (1) | Mo1-N1 | 2.321 (2) | Mo1-N2 | 2.324 (2) |
| S1-S2 | 2.734 (1) | | | | |
| S1-C1 | 1.844 (2) | C1-C2 | 1.529 (3) | C1-C3 | 1.544 (4) |
| C1-C4 | 1.538 (3) | N1-C2 | 1.504 (3) | C2-C5 | 1.537 (3) |
| C2-C6 | 1.534 (3) | N1-C1N1 | 1.482 (3) | N1-C1H1 | 0.75 (2) |
| S2-C7 | 1.841 (2) | C7-C8 | 1.550 (3) | C7-C9 | 1.534 (3) |
| C7-C10 | 1.533 (3) | N2-C8 | 1.499 (2) | C8-C11 | 1.533 (3) |
| C8-C12 | 1.531 (3) | N2-C1N2 | 1.479 (2) | N1-H1N2 | 0.75 (3) |
| H1N1-O2′ | 2.53 (2) | H1N2-O1′ | 2.52 (2) | | |
| | | | **3** | | |
| Mo1-S1 | 2.429 (1) | Mo1-O1 | 1.720 (3) | Mo1-N1 | 2.366 (3) |
| S1-S1′ | 2.821 (2) | | | | |
| S1-C1 | 1.854 (4) | C1-C2 | 1.536 (7) | C1-C3 | 1.520 (6) |
| C1-C4 | 1.550 (6) | N1-C2 | 1.481 (5) | N1-C5 | 1.491 (6) |
| N1-C6 | 1.476 (6) | | | | |

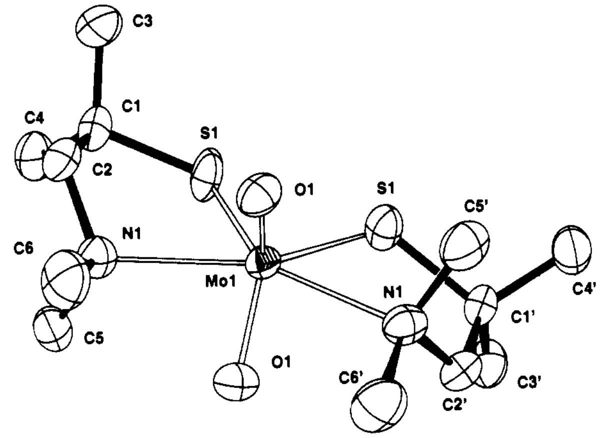

**Figure 3.** Structure of $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (3).

trans to the terminal oxo groups. This approach was doomed to failure as the closest angle to a "trans" angle about oxygen is the angle with the second oxygen at 120.8–122.2°. In related structures[4] trans angles for O–Mo–S or O–Mo–N are 155–167°. This is a clear indication of the nonoctahedral nature of the current structures. To come to an understanding of the nature of the coordination spheres, we turned to the treatment of Kepert[11] and found that the structures neatly fit into one of his categories.

We describe the structure as a skew trapezoidal bipyramid, with the oxo groups at the apices and the trapezoidal plane defined by the two S and two N atoms of the two bidentate ligands.

The appropriateness of the skew-trapezoidal-bipyramidal designation becomes apparent upon inspection of the structure. Deviations from the least-squares plane containing Mo and the donor atoms of the chelating ligands are shown in Table V. The deviations from the plane are less than 0.2 Å, and the oxo oxygen atoms are equidistant above and below the plane. This same relation holds in structures **1** and **2** where the relation between the O atoms is not required by symmetry.

Alternative descriptions of the structures are possible. Thus, in seaching for a regular structure it is possible to simply relate the observed structure to a *trans*-dioxo octahedral structure. Distortion of such a structure by opening the N–Mo–N angle and closing the O–Mo–O and (to an extent) S–Mo–S angles yields the skew trapezoidal bipyramid. The appropriateness of this description from a bonding point of view is discussed below.

The Mo–N distances display the largest range averaging 2.27 Å in **1**, 2.32 Å in **2**, and 2.37 Å in **3**. This range is well below that previously found for Mo–N distances in oxomolybdenum compounds that run from 2.38 to 2.51 Å. The low distance in the present case may be due to the fact that in all previous structures N is found trans to oxo where the trans bond lengthening influence is felt. In **1**–**3** the N is not trans to any atom (largest angle is less than 146° either to sulfur or the other nitrogen).

It is tempting to try to describe this structure in terms of a different coordination number. Thus, the structure could be viewed as an eight-coordinate dodecahedron, with the oxo ligands each occupying two coordination sites. Alternatively, the structure could be viewed as a bicapped tetrahedron with the nitrogens as capping ligands. Finally, if the two thiolate donor atoms are viewed as a single ligand (vide infra), then we have a five-coordinate structure based on a square pyramid with the two O and two N atoms in the base and the centroid of the S--S "linkage" at the apex. Although any of the above designations are descriptively valid, they each impose an artifical and we believe inappropriate coordination number on the complex. Thus, oxo groups as monoatomic ligands are not advantageously viewed as being bidentate, thereby vitiating the eight-coordinate designation. The capped tetrahedron description might be valid, if, as in previous examples, the capping nitrogens were at a relatively long Mo–N distance. However, the Mo–N distances in the **1**–**3** are on the average shorter than Mo–N distances in structures where the N clearly occupies a normal coordination position (i.e., the N atom is

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Table IV. Bond Angles (deg) for $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (1), $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$(2), and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (3)

| | | | |
|---|---|---|---|
| | 1 | | |
| S1-Mo1-S2 | 69.82 (9) | S1-Mo1-O1 | 107.74 (25) |
| S1-Mo1-O2 | 118.25 (20) | S1-Mo1-N1 | 72.94 (26) |
| S1-Mo1-N2 | 142.60 (23) | S2-Mo1-O1 | 120.36 (21) |
| S2-Mo1-O2 | 107.46 (23) | S2-Mo1-N1 | 141.00 (24) |
| S2-Mo1-N2 | 74.60 (23) | O1-Mo1-O2 | 122.24 (31) |
| O1-Mo1-N1 | 81.80 (28) | O1-Mo1-N2 | 80.54 (29) |
| O2-Mo1-N1 | 80.34 (34) | O2-Mo1-N2 | 83.02 (26) |
| N1-Mo1-N2 | 144.03 (34) | | |
| Mo1-S1-C1 | 107.1 (5) | Mo1-S2-C5 | 107.7 (3) |
| Mo1-N1-C2 | 112.6 (6) | Mo1-N1-C1N1 | 112.6 (7) |
| Mo1-N1-H1N1 | 104 (7) | Mo1-N2-C6 | 113.7 (5) |
| Mo1-N2-C1N2 | 112.1 (6) | Mo1-N2-H1N2 | 104 (7) |
| S1-C1-C2 | 108.7 (8) | S1-C1-C3 | 109.6 (8) |
| S1-C1-C4 | 108.5 (9) | C2-C1-C3 | 111.6 (12) |
| C2-C1-C4 | 110.7 (9) | C3-C1-C4 | 107.8 (10) |
| C1-C2-N1 | 111.0 (9) | C2-N1-C1N1 | 111.7 (10) |
| C2-N1-H1N1 | 114 (7) | C1N1-N1-H1N1 | 114 (7) |
| S2-C5-C6 | 107.6 (7) | S2-C5-C7 | 107.6 (7) |
| S2-C5-C8 | 108.9 (7) | C6-C5-C7 | 112.5 (8) |
| C6-C5-C8 | 109.5 (10) | C7-C5-C8 | 110.7 (9) |
| C5-C6-N2 | 110.0 (7) | C6-N2-C1N2 | 111.1 (8) |
| C6-N2-H1N2 | 115 (7) | C1N2-N2-H1N2 | 101 (7) |
| N1-H1N1-O2′ | 157 (9) | N2-H1N2-O1′ | 165 (9) |
| | 2 | | |
| S1-Mo1-S2 | 68.81 (2) | S1-Mo1-O1 | 111.45 (5) |
| S1-Mo1-O2 | 116.78 (5) | S1-Mo1-N1 | 74.60 (4) |
| S1-Mo1-N2 | 142.43 (4) | S2-Mo1-O1 | 116.46 (5) |
| S2-Mo1-O2 | 111.67 (5) | S2-Mo1-N1 | 142.66 (4) |
| S2-Mo1-N2 | 74.34 (4) | O1-Mo1-O2 | 120.76 (7) |
| O1-Mo1-N1 | 83.50 (6) | O1-Mo1-N2 | 78.59 (6) |
| O2-Mo1-N1 | 78.33 (6) | O2-Mo1-N2 | 83.29 (6) |
| N1-Mo1-N2 | 142.82 (5) | | |
| Mo1-S1-C1 | 107.2 (1) | Mo1-S2-C7 | 107.6 (1) |
| Mo1-N1-C2 | 120.6 (1) | Mo1-N1-C1N1 | 109.5 (1) |
| Mo1-N1-H1N1 | 100 (2) | Mo1-N2-C8 | 120.5 (1) |
| Mo1-N2-C1N2 | 109.4 (1) | Mo1-N2-H1N1 | 98 (2) |
| S1-C1-C2 | 108.4 (1) | S1-C1-C3 | 108.0 (2) |
| S1-C1-C4 | 105.9 (2) | C2-C1-C3 | 113.1 (2) |
| C2-C1-C4 | 113.7 (2) | C3-C1-C4 | 107.4 (2) |
| C1-C2-N1 | 105.2 (2) | C1-C2-C5 | 111.4 (2) |
| C1-C2-C6 | 112.5 (2) | N1-C2-C5 | 108.7 (2) |
| N1-C2-C6 | 112.5 (2) | C5-C2-C6 | 109.5 (2) |
| C2-N1-C1N1 | 114.7 (2) | C2-N1-H1N1 | 106 (2) |
| C1N1-N1-H1N1 | 103 (2) | S2-C7-C8 | 108.0 (1) |
| S2-C7-C9 | 105.6 (1) | S2-C7-C10 | 109.3 (2) |
| C8-C7-C9 | 113.3 (2) | C8-C7-C10 | 113.0 (2) |
| C9-C7-C10 | 107.4 (2) | C7-C8-N2 | 104.2 (2) |
| C7-C8-C11 | 112.4 (2) | C7-C8-C12 | 111.2 (2) |
| N2-C8-C11 | 109.3 (2) | N2-C8-C12 | 110.8 (2) |
| C11-C8-C12 | 109.0 (2) | C8-N2-C1N2 | 114.8 (2) |
| C8-N2-H1N2 | 107 (2) | C1N2-N2-H1N2 | 105 (2) |
| N1-H1N1-O2′ | 145 (2) | N2-H1N2-O1′ | 165 (9) |
| | 3 | | |
| S1-Mo1-S1′ | 71.00 (5) | S1-Mo1-O1 | 115.79 (11) |
| S1-Mo1-O1′ | 110.75 (11) | S1-Mo1-N1 | 74.90 (9) |
| S1-Mo1-N1′ | 145.55 (9) | O1-Mo1-O1′ | 122.00 (22) |
| O1-Mo1-N1 | 79.87 (13) | O1-Mo1-N1′ | 80.79 (13) |
| N1-Mo1-N1′ | 139.46 (17) | | |
| Mo1-S1-C1 | 107.7 (2) | Mo1-N1-C2 | 110.3 (2) |
| Mo1-N1-C5 | 111.9 (2) | Mo1-N1-C6 | 108.4 (3) |
| S1-C1-C2 | 108.5 (3) | S1-C1-C3 | 108.9 (3) |
| S1-C1-C4 | 108.6 (3) | C2-C1-C3 | 108.8 (4) |
| C2-C1-C4 | 114.8 (4) | C3-C1-C4 | 107.2 (4) |
| C1-C2-N1 | 115.1 (3) | C2-N1-C5 | 111.0 (3) |
| C2-N1-C6 | 108.3 (4) | C5-N1-C6 | 106.7 (4) |

Table V. Deviations from the $MoN_2S_2$ Least-Squares Plane in 3

| atom | dist from plane,[a] Å | atom | dist from plane,[a] Å |
|---|---|---|---|
| Mo | 0.000 (0) | N1′ | −0.159 (4) |
| S1 | −0.025 (1) | O1 | 1.501 (3) |
| N1 | 0.159 (4) | O1′ | −1.501 (3) |
| S1′ | 0.025 (1) | | |

[a] Estimated standard deviations given in parentheses.

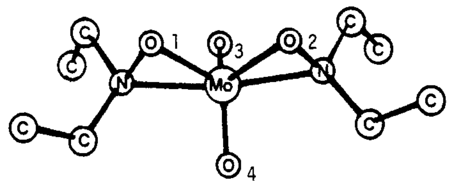

**Figure 4.** Structure of $MoO_2(NR_2O)_2$ as reported in ref 14.

not a capping ligand). Finally, the designation of the S- -S grouping as a single ligand occupying one coordination position is questionable. Thus, even for $S_2^{2-}$ where no doubt exists as to the presence of an S–S bond, it is often appropriate to consider $S_2^{2-}$ as a bidentate ligand. Therefore, in the present case, where the S- -S interaction is weak, if at all present, it seems inappropriate to designate the two thiolate ligands found at the normal 2.4-Å distance from the Mo as constituting a single ligand. Our predilection, largely supported by the reasonable values for Mo–O, Mo–N, and Mo–S bond lengths, is to consider this structure as six-coordinate, and as such, its best description is in terms of the skew trapezoidal bipyramid.

There are a few other $MoO_2^{2+}$ structures with which these $MoO_2L_2$ complexes can be compared. Mentzen et al.[12] report the structure of $MoO_2$(TTP) (where TTP is 5,10,15,20-tetra-*p*-tolylporphyrinate). Here, the *cis*-$MoO_2^{2+}$ core is found with an O–Mo–O angle of 95.1°, and the donor atom sphere is described as a distorted trigonal prism. The large deviations of the porphyrin ligand from planarity illustrate the contortions that can be tolerated in order to accommodate *cis*-dioxo groups in the Mo coordination sphere. The $MoO_2$(TTP) structure is very different from the one found here. In $MoO_2$(TTP) both O atoms lie on the opposite side of the Mo from the $N_4$ donor set of the porphyrin. In **1**–**3** the oxo ligands are on opposite sides of the plane determined by $MoN_2S_2$.

Wieghardt et al.[13] and Saussine et al.[14] recently reported complexes of the form $MoO_2L_2$ where L is an O-deprotonated hydroxylamine ligand. If the hydroxylamino ligand is considered as a bidentate ligand, then the structure found is related to a skew trapezoidal bipyramid, with N and O substituting for the N and S donors of the cystamine ligands in the present study. However, as shown in Figure 4, the two N donor atoms are on opposite sides of the Mo from the oxo donors and the N–Mo–N angle of 166° opens in the opposite direction from $O_3$–Mo–$O_4$ and contains the $O_1$–Mo–$O_2$ angle. Further, the $O_1$–Mo–$O_2$ angle at 85° in $MoO_2(CH_3NHO)_2$ is significantly greater than that found for the S–Mo–S angle in **1**–**3**. The deprotonated hydroxylamine (–H) complexes[13,14] are perhaps best considered as similar to peroxo complexes where a case can be made that the peroxo ligand occupies a single donor position. In that case these hydroxylamine (–H) complexes have pseudotetrahedral coordination and structural parameters close to those of the peroxo complexes.[2]

Another feature of structures **1** and **2** is an H-bonding interaction between one Mo–O on each Mo and the N–H group of a neighboring complex. Figure 5 illustrates this interaction, which causes the molecules to be grouped in H-bonded chains. While the H bonding may affect the detailed structure and Mo–O stretching vibrations of **1** and **2**, the fact that the structure of **3** has no H bonding and is ex-

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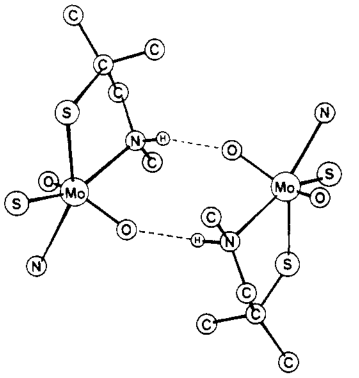

**Figure 5.** Hydrogen-bonding pattern in $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$.

tremely similar to that of **1** and **2** indicates that the unusual structure found is not a consequence of the intermolecular H-bonding pattern.

## Discussion

For the complexes in this paper the structure that would be expected by analogy with all previous[2–5] work is one in which the oxo groups are cis, the thiolate donors are trans, and the amino groups are trans to oxo and thus cis to each other. When the amino groups are methyl substituted as in the present compounds, there is steric hindrance between the methyl groups on the cis nitrogens in this structure. Thus, the normal octahedral structure is expected to be destabilized. The alternative octahedral structures would involve flipping of one or both ligands such that either one or two thiolate donors would be placed trans to oxo. These octahedral structures are not obviously impeded from forming by any steric encumbrance. Nevertheless, they are not the observed structures. It seems likely that placement of oxo and thiolate on the same axis constitutes an unstable arrangement. The resultant nonoctahedral structure avoids placing the thiolate group trans to oxo.

The structural results presented herein reveal that the formally Mo(VI) coordination sphere is prone to distortion. While this lack of firm preference for octahedral structures is perhaps not surprising for a nominally $4d^0$ Mo system, it does emphasize that small changes in ligands can greatly influence the detailed nature of the Mo coordination sphere. However, the Mo–S distance averaging 2.41 Å in the skew-trapezoidal-bipyramidal structures is essentially the same as that found in the octahedral structures. It is also very similar to the Mo–S distance of 2.40 Å predicted by EXAFS for the Mo(VI) state of sulfite oxidase.[8a] Steric requirements of a protein or cofactor ligand could impose unusual structural features on the Mo(VI) coordination sphere within the enzyme. However, the distortion need not change the Mo–S distance. A structural assignment based on an octahedral sphere is thus not required by the EXAFS results.

A remarkable feature of the present structure is the close approach of the two sulfur donors on the short edge of the trapezoid. The S–Mo–S angles lie between 68.8 and 71° and are thus considerably smaller than the nominal 90° angle expected for the octahedral structure. There is no obvious steric reason for the small angle and the short S- -S distance that that angle requires. Thus, the sulfur atoms are well separated from the O donors; O–Mo–S is >107°. Further, twisting of the N,S ligands with respect to each other to destroy the trapezoidal plane could increase the S–S distance while not forcing any new unacceptable contacts. As this distortion does not occur, we are drawn to consider the possibility that the interaction between the sulfurs may in fact be attractive.

The intramolecular interligand S–S distances vary from 2.73 Å in **2** to 2.82 Å in **3**. This distance is substantially smaller than the 3.7-Å van der Waals contact distance given by Pauling[15] and shorter also than the 3.45-Å distance quoted by van der Helm et al.[16] Distances of comparable magnitude in the literature have been assigned to weak sulfur–sulfur bonding.[17–30] For example, the S- -S distance in $S_8^{2+}$ is 2.83 Å and on the basis of theoretical[18] and experimental[17] criteria has been assigned as a partial disulfide bond. Other examples of S–S contacts of between 2.4 and 3.1 Å have been assigned as S–S interactions.[19,20] Further, many workers have attributed unusual spectroscopic and redox features to weak S–S interactions.[30–34]

The consequences of partial disulfide bond formation can best be assessed by considering a hypothetical situation where complete disulfide formation has occurred. A two-electron oxidation of the dithiolate within the Mo coordination sphere requires the concomitant reduction of Mo(VI) to Mo(IV). In the Mo(IV) state the orientation of the two oxo groups should be trans as it is in other $d^2$ systems, e.g., Mo(IV) or Re(V). Thus, the opening of the O–Mo–O angle toward 180° can be explained as due to partial charge transfer to the Mo center. The slight lengthening of the Mo–O bond and the lowering of $\nu$(Mo–O) can be viewed as a consequence of the charge transfer.

Our results illustrate a fascinating possibility for redox processes in bis(thiolato)molybdenum systems. Thus, successive one-electron oxidations of Mo(IV) to (formally) Mo(V) and Mo(VI) may involve a component of dithiolate to disulfide oxidation. If this partial S–S bond formation occurs in molybdoenzymes (extant data does not preclude such an occurrence), it could explain, in part, the absence of identity between the spectroscopic, redox, and catalytic properties of molybdoenzymes and their "model" systems. For example, the high $g_z$ and low $A_z$ ($^{95,97}$Mo) value of the Mo(V) EPR signal in xanthine oxidase may be attributable to strong delocalization of the unpaired electron into the S–S partial bond. Further, the great variability in redox potential for different molybdoenzymes (while also potentially explainable in other terms) could be due to different degrees of S–S bond formation. Recently, Musker[31] and others have shown that the presence of strategically juxtaposed sulfides in large-ring multisulfur organic heterocyclic compounds is found to correlate with substantially lower potentials for one-electron oxidation and with increased reversibility in the electron-

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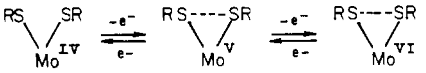
transfer process. It is possible that the cis positioning of molybdenum-bound thiolates brings these reactivity changes to molybdenum sites in enzymes, such that a triatomic unit may be responsible for some of the unique spectroscopic and reactivity parameters of these sites.



The static distortions of the Mo(VI) coordination sphere observed in these studies have potential impact on structural and mechanistic considerations for the molybdenum sites in enzymes. Heretofore, all suggestions for the structure of the molybdenum site have been based on octahedral geometries. However, the results of our studies clearly show that relatively small, but sterically demanding, changes in the ligands can lead to severe distortions in the molybdenum coordination sphere. Certainly, a set of donor ligands from a protein or cofactor could be equally demanding and, in attempting to model the molybdenum site, we must take account of this deformability in our choice or design of ligand systems.

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**Registry No.** **1**, 74005-67-7; **2**, 76772-96-8; **3**, 74005-68-8.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, calculated hydrogen atom positions, and observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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# Reduction of Perchlorate Ion by (*N*-(Hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III)

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In acidic, aqueous chloride media (LiCl, 2 M) at 25 °C, reduction of perchlorate ion by (*N*-(hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III) (Ti(Hedta)) follows the rate law rate = $(k[\mathrm{ClO_4^-}][\mathrm{H^+}]^2 + k')[\mathrm{Ti(Hedta)}]$, where $k = 2 \times 10^{-3}\ \mathrm{M^{-3}\ s^{-1}}$ and $k' = 2 \times 10^{-8}\ \mathrm{s^{-1}}$. The acid dependence is consistent with an inner-sphere mechanism with rate-determining distortion of protonated perchlorate. Such distortion leads to increased interaction between an electron-donor orbital centered on titanium and an electron-acceptor orbital centered on chlorine.

In acidic aqueous solutions, $\mathrm{Cr^{2+}}$ shows no reaction with perchlorate ion, but $\mathrm{Ti^{3+}}$ (thermodynamically a weaker reductant) does react at a measurable rate.[1] Two explanations have been proposed for this anomaly. Kallen and Earley[2] concluded that the rate-determining factor is interaction of polarizable d orbitals of the metal ion with a chlorine-centered orbital. Taube[3] proposed an alternative rationalization, that the relative stability of the –yl product is dominant. ($\mathrm{TiO^{2+}}$, titanyl ion, is well-known, but there is no corresponding chromium species.) We now report results of experiments designed to distinguish between these two plausible explanations.

The stoichiometry of the reaction between (*N*-(hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III)[4] (hereafter, Ti(Hedta)) and $\mathrm{ClO_4^-}$ was determined spectrophotometrically to be

$$8\mathrm{Ti^{3+}} + \mathrm{ClO_4^-} + 8\mathrm{H^+} \rightarrow 8\mathrm{Ti(IV)} + 4\mathrm{H_2O} + \mathrm{Cl^-}$$

Kinetics were studied at 25 °C by measuring the decrease in absorbance at 550 nm, due to Ti(Hedta). Procedures were generally as previously described.[4] Preequilibrated Ti(Hedta) was injected to start the reaction. Kinetic runs followed first-order kinetics for at least 2 half-times (perchlorate was in large excess). In some experiments, there was a small initial increase in absorbance during times up to 50 min. This effect was not present if mixing was complete. There was a slow increase in absorbance at long times, assignable to polymerization of Ti(IV). Rate constants were calculated by linear least squares. Kinetic data are shown in Table I.

Increasing [Hedta] to values higher than the stoichiometric amount does not affect the rate of the reaction at constant acidity. Change of medium from hydrochloric acid to trifluoromethanesulfonic acid (hereafter, HTFMS) has small effect, but the reaction is definitely slower in less concentrated salt media. At constant acidity, the observed first-order rate constant increases linearly as $\mathrm{ClO_4^-}$ concentration increases. At constant [Ti(Hedta)] and $[\mathrm{ClO_4^-}]$, rate increases as $[\mathrm{H^+}]$ increases, but acid catalysis is not linear. The data at high acidity are best fitted by second-order dependence on $[\mathrm{H^+}]$. At low acidity and/or low perchlorate concentration, the observed rate is somewhat higher than that to be expected on the basis of a one-term rate law. This is taken into account here by a second, constant term. Ti(Hedta) is somewhat more stable than $\mathrm{Ti^{3+}}$, insofar as air oxidation is concerned, but some loss of Ti(III) occurred over the (several days!) course of these reactions. Any perchlorate reduction through acid-independent and linearly acid-dependent terms are also included in this small correction. Our data are adequately fitted by the rate law

$$\text{rate} = (k[\mathrm{ClO_4^-}][\mathrm{H^+}]^2 + k')[\mathrm{Ti(Hedta)}]$$

where $k = 2 \times 10^{-3}\ \mathrm{M^{-3}\ s^{-1}}$ and $k' = 2 \times 10^{-8}\ \mathrm{s^{-1}}$ at 25 °C in 2 M lithium chloride medium.

In the case of the reduction of perchlorate ion by $\mathrm{Ru^{2+}}$, there is convincing evidence that the overall rate of the redox reaction

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