Table VIII. Exponents and Parameters for Ti and Mo

orbital	ζ_1	$-H_{ii}$/eV[a]	ζ_2[b]	C_1[b]	C_2[b]
Ti[c] 4s	1.075	8.97			
Ti 4p	0.6750	5.44			
Ti[d] 3d	4.55	10.81	1.40	0.4206	0.7839
Mo[e] 5s	1.96	8.77			
Mo 5p	1.90	5.60			
Mo[d] 4d	4.54	11.60	1.90	0.5899	0.5899

[a] 1 eV = 96.4845 kJ mol^{-1}. [b] Exponents and coefficients in the double Slater-type wave functions. [c] Reference 17. [d] Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. E. *J. Chem. Phys.* **1962**, *36*, 1057. [e] Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772.

good agreement with the values obtained by the above method.[30]

Acknowledgment. We thank Prof. Alte da Veiga (University of Coimbra) for the use of the CAD-4 diffractometer. We also thank The British Council, Gulbenkian Foundation, and Instituto Nacional de Investigação Científica, Portugal, for support.

Appendix

The extended Hückel molecular orbital calculations were made by using the ICON8 program[31] with the Wolfsberg-Helmholz modification.[32] Standard parameters were used for C, S, and H. Only 3s and 3p orbitals were considered for sulfur. The exponents and parameters for titanium and molybdenum are listed in Table VIII. The following distances (pm) and angles (degrees) were used: Ti-S, 240; Ti-Cp, 207; S-H, 150; C-C(Cp), 140; C-H, 108; Mo-S, 245; Mo-Cp, 200; Cp-M-Cp, 132.0; M-S-H, 110; S-Ti-S, 95; S-Mo-S, 85.

Registry No. W(Cp)$_2$(SC$_2$H$_5$)$_2$, 37328-24-8; W(Cp)$_2$(SC$_6$H$_5$)$_2$, 12246-20-7; Ti(Cp)$_2$(SC$_2$H$_5$)$_2$, 1291-79-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atomic coordinates (2 pages); a table of structure factors (5 pages). Ordering information is given on any current masthead page.

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(30) Dias, A. R.; Salema, M. S.; Martinho Simões, J. A.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *346*, C4.

(31) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179.

(32) Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

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Reactions of Molybdate with Dithiothreitol. Structure of [TEA]$_2$[Mo$_2$O$_5$dtt][†]

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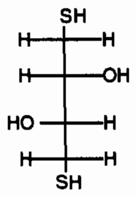
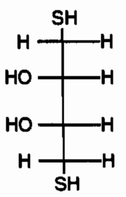
The preparation of [TEA]$_2$[Mo$_2$O$_5$(L-dithiothreitolate)] from reaction of [TEA]$_2$[MoO$_4$] and L-dithiothreitol is described. The structure of the dimer has been confirmed by X-ray crystallography. The material crystallizes in the monoclinic space group $P2_1$ with lattice parameters a = 7.402 (2) Å, b = 30.67 (2) Å, c = 18.567 (5) Å, β = 94.57 (2)°, V = 4208 (5) Å^3, and Z = 6. ^{95}Mo NMR and infrared spectral data for the dimer are given. A product having an EPR spectrum characteristic of Mo(V) is obtained when the reaction of the molybdate reagent and dithiothreitol is performed under inert-atmosphere conditions. These results are relevant to the reconstitution of molybdenum-deficient molybdenum cofactor samples using molybdate and dithiothreitol or dithioerythritol solutions.

Dithiothreitol is widely used in biological studies to maintain a reducing environment for anaerobic manipulations of proteins and enzyme cofactors. For example, in the nitrate reduction assay for the molybdenum cofactor, Mo-co, maximal activity is obtained when both additional molybdenum (as MoO$_4^{2-}$) *and* dithiothreitol or dithioerythritol are added to the reconstituting mixture. This effect suggests that isolated Mo-co samples that have partially lost molybdenum can regain the needed metal if the molybdate is added in the presence of DTT or DTE. However, the simple molybdate ion may not be the effective reconstituting form of molybdenum. Aqueous MoO$_4^{2-}$/DTT solutions used during the reconstitution become yellow on standing, indicating the presence of a new species, presumably a molybdenum-dithiothreitol complex.[1] Dithiothreitol is also a required component in the aqueous reaction of MoO$_4^{2-}$, FeCl$_2$, S$_2$O$_3^{2-}$, and the sulfur-transfer enzyme rhodanese, which forms cubane clusters that model the Fe-Mo cofactor of nitrogenase.[2]

L-DTT



DTE



These reports prompted our studies of the molybdenum/dithiothreitol system through which we seek to establish the binding of the potentially polydentate dithiothreitol ligand. The arrangement of the two thiolate and two hydroxyl groups of DTT permits at least tridentate chelation at a single metal center and perhaps coordination of the fourth donor atom if distortion from octahedral geometry is allowed. We report our studies of the molybdate/dithiothreitol system, including a single-crystal X-ray structure of a dimer having a [Mo$_2$O$_5$]$^{2+}$ core bound to a single dtt tetraanion. A reduced product having an EPR spectrum characteristic of Mo(V) has also been observed.

Experimental Section

L-DTT was used as received from Sigma Biochemicals and stored in a desiccator in a freezer. Tetraethylammonium molybdate was prepared from [TEA]$_2$[SO$_4$] and BaMoO$_4$. ^{95}Mo NMR spectra were recorded on a Bruker 400-MHz instrument observing the nucleus at 25.92 MHz. Chemical shifts are referenced to 2 N sodium molybdate in D$_2$O at apparent pH 11. Infrared spectra of samples as KBr disks were recorded on a Perkin-Elmer Model 683 instrument and referenced to 906.2-cm^{-1} absorption of polystyrene. X-Band EPR spectra were examined with a Varian E-3 spectrometer.

[TEA]$_2$[Mo$_2$O$_5$dtt] was prepared by the aerobic reaction of [TEA]$_2$[MoO$_4$] and L-DTT in methanol. [TEA]$_2$[MoO$_4$], 2 mmol, was dissolved in 60 mL of methanol. A solution of 1.5 mmol of L-DTT in

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[†] Dithiothreitol and dithioerythritol are abbreviated as DTT and DTE, respectively, while dtt and dte denote the tetraanionic ligand forms.

(1) Hawkes, T. R.; Bray, R. C. *Biochem. J.* **1984**, *219*, 481.

(2) Kurtz, D. M.; Werth, M. T., personal communication.

Table I. Crystallographic Parameters for Data Collection and Structure Refinement of $[TEA]_2[Mo_2O_5dtt]$

mol formula	$Mo_2S_2O_7N_2C_{20}H_{46}$
fw	682.61
space group	monoclinic, $P2_1$ (No. 4)
a, Å	7.402 (2)
b, Å	30.67 (2)
c, Å	18.567 (5)
β, deg	94.57 (2)
V, Å^3	4208 (5)
Z	6
D(calcd), g/cm^3	1.246
μ, cm^{-1}	8.089
radiation (λ)	Mo Kα (0.71073 Å)
scan range[3d]	$3.0° < 2\theta < 45.0°$
data collcd	$\pm h,+k,+l$
scan width, deg	$0.80 + (0.35 \tan \theta)$
bkgd	25% of full peak width on each side
no. of unique data	5628
no. of data with $I > 3\sigma(I)$[3b]	3983
no. of variables	561
R[3c]	0.051
R_w	0.064
e/Å^3	0.792
largest param shift (last cycle)	0.04
esd (unit wt observn)	5.172

Table II. Positional and Thermal Parameters with Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Mo1	0.3007 (3)	0.812	0.1855 (1)	2.53 (4)
Mo2	0.3080 (3)	0.74037 (7)	0.3108 (1)	2.74 (4)
Mo3	−0.6854 (3)	0.58882 (7)	0.6914 (1)	2.49 (4)
Mo4	−0.7161 (2)	0.66135 (7)	0.8115 (1)	2.29 (4)
Mo5	0.8089 (3)	0.96292 (7)	−0.1726 (1)	2.84 (4)
Mo6	0.8317 (3)	0.90998 (7)	−0.3201 (1)	2.87 (4)
S1	0.5779 (8)	0.8525 (2)	0.1710 (4)	3.9 (1)
S2	0.6022 (8)	0.7114 (2)	0.3591 (4)	3.6 (1)
S3	−0.3824 (9)	0.5689 (3)	0.6580 (4)	4.2 (1)
S4	−0.4441 (8)	0.6830 (2)	0.8882 (3)	3.5 (1)
S5	1.0854 (9)	0.9950 (2)	−0.1135 (3)	3.8 (1)
S6	1.0794 (8)	0.9300 (2)	−0.3934 (3)	3.9 (1)
O1	0.163 (2)	0.7739 (6)	0.2399 (8)	3.6 (4)
O2	0.218 (2)	0.8031 (4)	0.0997 (7)	3.0 (3)
O3	0.216 (2)	0.8611 (6)	0.2078 (9)	4.1 (4)
O4	0.264 (2)	0.6878 (6)	0.282 (1)	5.2 (4)
O5	0.201 (2)	0.7467 (7)	0.3869 (8)	5.0 (4)
O6	0.459 (2)	0.7965 (5)	0.3155 (8)	3.0 (3)
O7	0.490 (2)	0.7621 (6)	0.1978 (9)	4.2 (4)
O8	−0.844 (2)	0.6275 (5)	0.7382 (8)	3.2 (3)
O9	−0.786 (2)	0.5392 (5)	0.6967 (9)	3.9 (4)
O10	−0.722 (2)	0.6056 (6)	0.6043 (9)	4.1 (4)
O11	−0.795 (2)	0.6409 (6)	0.8883 (8)	3.6 (4)
O12	−0.816 (2)	0.7111 (5)	0.7986 (8)	3.5 (4)
O13	−0.527 (2)	0.6637 (5)	0.7349 (7)	2.7 (3)
O14	−0.543 (2)	0.5911 (5)	0.7929 (7)	2.6 (3)
O15	0.694 (2)	0.9235 (6)	−0.242 (1)	4.9 (4)
O16	0.813 (2)	0.8555 (6)	−0.328 (1)	5.4 (5)
O17	0.693 (2)	0.9311 (6)	−0.3910 (9)	4.2 (4)
O18	0.649 (2)	1.0011 (6)	−0.1597 (9)	4.5 (4)
O19	0.819 (3)	0.9313 (6)	−0.098 (1)	5.7 (5)
O20	1.046 (2)	0.9152 (6)	−0.2396 (8)	3.6 (3)
O21	0.920 (2)	0.9880 (6)	−0.2598 (8)	3.8 (4)
N1	−0.961 (2)	0.6718 (6)	0.0843 (9)	2.8 (3)*
N2	−0.966 (2)	0.7305 (6)	0.5855 (9)	2.6 (3)*
N3	−0.296 (2)	0.9986 (6)	0.088 (1)	3.1 (4)*
N4	−0.657 (2)	0.8378 (6)	0.8995 (9)	2.5 (3)*
N5	−0.680 (2)	0.9056 (6)	0.4039 (9)	2.9 (4)*
N6	−0.667 (2)	0.5681 (6)	0.402 (1)	3.1 (4)*
C1	0.731 (3)	0.7641 (9)	0.369 (1)	4.3 (5)*
C2	0.651 (3)	0.7920 (8)	0.307 (1)	3.5 (5)*
C3	0.665 (3)	0.7758 (9)	0.230 (1)	3.8 (5)*
C4	0.744 (4)	0.807 (1)	0.182 (1)	4.9 (6)*
C5	−0.258 (3)	0.5686 (8)	0.750 (1)	3.4 (5)*
C6	−0.355 (3)	0.6052 (8)	0.792 (1)	3.3 (5)*
C7	−0.349 (3)	0.6510 (7)	0.761 (1)	2.7 (4)*
C8	−0.278 (3)	0.6831 (8)	0.821 (1)	3.4 (5)*
C9	1.178 (4)	1.0186 (9)	−0.190 (1)	4.6 (6)*
C10	1.111 (3)	0.9909 (8)	−0.258 (1)	3.0 (4)*
C11	1.188 (3)	0.9438 (8)	−0.254 (1)	2.8 (4)*
C12	1.265 (3)	0.9340 (8)	−0.323 (1)	3.5 (5)*

[a] Asterisk indicates on isotropically refined atom.

5 mL of methanol was added dropwise over 2 h while the reaction was stirred vigorously. The colorless molybdate solution became yellow after the first dithiol addition, and this color intensified as the remaining dithiol was added. [If the dithiol is added too rapidly, the solution adopts an orange color, indicating reduction of Mo(VI) to a Mo(V) species.] The solution of the product was taken to dryness on a rotary evaporator, causing formation of a bright yellow crystalline solid. This solid is extremely moisture sensitive and was further handled under inert-atmosphere conditions. The yellow solid was triturated with 50 mL of 30% methanol/diethyl ether (v/v) to remove excess and oxidized dithiol. The remaining yellow solid was washed with 2 × 25 mL of ether and dried, giving a 56% yield. Anal. Found: C, 34.98; H, 6.65; N, 3.99; S, 10.88; Mo, 29.33. Calcd: C, 35.19; H, 6.79; N, 4.10; S, 9.39; Mo, 28.11.

A crystal suitable for single-crystal X-ray analysis was obtained by layering diethyl ether over a methanolic solution of $[TEA]_2[Mo_2O_5dtt]$. A pale yellow rectangular parallelepiped of approximate dimensions 0.3 × 0.2 × 0.15 mm was selected, mounted on a glass fiber, and coated with epoxy. X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer at room temperature. Table I lists parameters used during data collection and refinement that proceeded by using programs available in the 1980 version of the Structure Determination Package (SDP).[3] The structure was solved by using direct methods to locate the six molybdenum atoms. Due to the large number of atoms in the asymmetric unit (99 non-hydrogen atoms), the carbon atoms of the dithiothreitol ligand and the nitrogen and carbon atoms of the tetraethylammonium cations were refined isotropically. The proper enantiomorph was chosen by using the known absolute configuration of L-dithiothreitol (R,R).[4] No absorption correction was deemed necessary for this small crystal of low μ (8.089 cm^{-1}). Very few peaks were observed in the final difference Fourier calculation that could be attributed to hydrogen atoms. No attempt was made to calculate the positions of the 138 hydrogen atoms since it was judged that this effort would not contribute significantly to the chemical understanding of this structure.

Results and Discussion

Reaction of dithiothreitol with molybdate yields two distinct products, depending on reaction conditions. The slow addition of dithiothreitol to $[TEA]_2[MoO_4]$ in methanol produces a yellow solution from which crystalline $[TEA]_2[Mo_2O_5dtt]$ is isolated. Under inert-atmosphere conditions the reaction forms an orange product that has yet to be fully characterized. This product is EPR active and is postulated to possess a Mo(V) center (see below).

The molybdenum(VI) dimer $[TEA]_2[Mo_2O_5dtt]$ is identified by elemental analysis, infrared data, and single-crystal x-ray analysis. Characteristic absorptions for the $\nu_{Mo=O}$ and asymmetric $\nu_{Mo-O-Mo}$ vibrations of the $[Mo_2O_5]^{2+}$ core are observed.[5] The terminal metal–oxo stretches appear as an intense doublet at 916 and 882 cm^{-1}, each split by 10 cm^{-1}, and the bridging mode occurs as an equally strong band at 686 cm^{-1} having a shoulder at 670 cm^{-1}. Weak absorptions at 310 and 345 cm^{-1} may be assigned to Mo–S vibrations. No strong, broad absorption in the ν_{OH} region near 3400 cm^{-1} is observed, in agreement with the tetraanionic formulation for the dtt ligand and the presence of oxo bridges rather than hydroxo bridges.

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(3) (a) Programs were utilized during structure and refinement as provided in the Enraf-Nonius structure determination package. Scattering factors are taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV. (b) $I = S(C + RB)$ and $\sigma(I) = (2S^2(C + R^2B) + (\rho I)^2)^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count time, and $\rho = 0.01$ is a correction factor. (c) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(F_o^2)]^2$ and $\sigma(F_o^2) = [\sigma^2(I) + \rho^2I^2]^{1/2}$ with ρ assigned a value of 0.01. Expressions for the residuals are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_0)^2]^{1/2}$. (d) No data were observed at values of $\theta > 45°$.

(4) Carmack, M.; Kelley, C. J. *J. Org. Chem.* **1968**, *33*, 2171.

(5) Marabella, C. P.; Enemark, J. H.; Miller, K. F.; Bruce, A. E.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 3456.

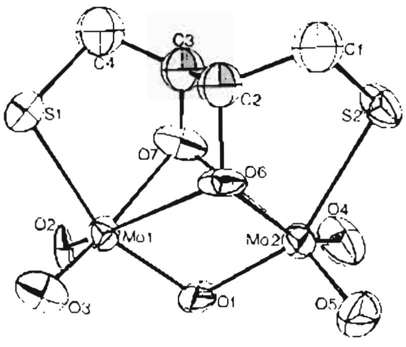

Figure 1. ORTEP drawing of one dianion, $[Mo_2O_5dtt]^{2-}$, showing the atomic labeling scheme. The thermal ellipsoids are drawn to encompass 50% of their electron density.

Table III. Mo Bond Distances for Three Independent $[Mo_2O_5dtt]^{2-}$ Dianions[a]

	Mo1/Mo2	Mo3/Mo4	Mo5/Mo6
Mo–O_b	1.889 (8)/ 1.929 (8)	1.924 (7)/ 1.903 (7)	1.912 (8)/ 1.892 (8)
Mo–O_t	1.680 (7)/ 1.72 (1)	1.703 (8)/ 1.704 (8)	1.695 (8)/ 1.685 (9)
	1.706 (9)/ 1.687 (9)	1.699 (8)/ 1.707 (8)	1.687 (8)/ 1.730 (7)
Mo–O_{dtt}	2.070 (7)/ 2.052 (7)	2.088 (7)/ 2.072 (6)	2.027 (7)/ 2.100 (7)
	2.639 (8)/ 2.666 (8)	2.673 (8)/ 2.548 (8)	2.669 (8)/ 2.70 (1)
Mo–S	2.439 (4)/ 2.456 (4)	2.453 (3)/ 2.464 (3)	2.452 (4)/ 2.448 (4)
Mo–Mo	3.193 (1)	3.171 (1)	3.200 (1)

[a] Bond distances are given in angstroms; numbers in parentheses are estimated standard deviations in the least significant digit.

Table IV. Selected Bond Distances (Å) for One $[Mo_2O_5dtt]^{2-}$ Dianion[a]

Mo1–Mo2	3.193 (1)	Mo2–O1	1.929 (8)
Mo1–O1	1.889 (8)	Mo2–O4	1.72 (1)
Mo1–O2	1.680 (7)	Mo2–O5	1.687 (9)
Mo1–O3	1.706 (9)	Mo2–O6	2.052 (7)
Mo1–O6	2.639 (8)	Mo2–O7	2.666 (8)
Mo1–O7	2.070 (7)	Mo2–S2	2.456 (4)
Mo1–S1	2.439 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Table V. Selected Intramolecular Bond Angles (deg) for One $[Mo_2O_5dtt]^{2-}$ Dimer[a]

Mo1–O1–Mo2	113.5 (3)	O1–Mo1–O3	101.0 (5)
Mo1–O6–Mo2	84.9 (2)	O1–Mo1–O6	67.7 (3)
Mo1–O7–Mo2	83.8 (2)	O1–Mo1–O7	83.0 (3)
S1–Mo1–O1	150.4 (2)	O2–Mo1–O3	104.9 (4)
S1–Mo1–O2	102.8 (3)	O2–Mo1–O6	160.1 (3)
S1–Mo1–O3	84.3 (3)	O2–Mo1–O7	100.5 (3)
S1–Mo1–O6	82.8 (2)	O3–Mo1–O6	94.6 (3)
S1–Mo1–O7	79.7 (2)	O3–Mo1–O7	152.5 (3)
O1–Mo1–O2	103.9 (3)	O6–Mo1–O7	61.4 (2)

[a] The atom designations in this table correspond to the atomic labeling scheme of Figure 1. Corresponding angles about Mo2 in this dimer are not significantly different.

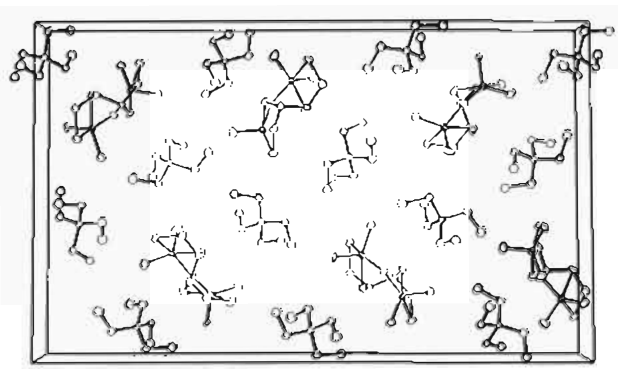

Figure 2. Packing diagram of the unit cell for $[TEA]_2Mo_2O_5dtt$, viewed down the *a* axis.

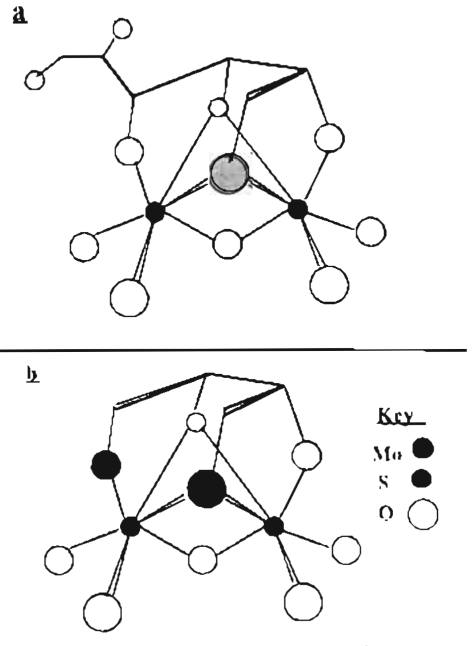

Figure 3. (a) Schematic diagram of the structure of $[Mo_2O_5(mannitolate)]$. (b) Proposed structure of $[Mo_2O_5(dtc)]^{2-}$.

The structure of the dianion $[Mo_2O_5dtt]^{2}$ is illustrated by an ORTEP drawing in Figure 1, and positional parameters for atoms of the three independent anionic dimers are given in Table II. Table III compares key Mo bond distances in the three anions. Tables IV and V list selected bond distances and angles, respectively, for atoms in the coordination sphere of molybdenum for one of the three independent $[Mo_2O_5dtt]^{2-}$ dimers in the asymmetric unit. The *syn*$[Mo_2O_5]^{2+}$ core is bridged and chelated by a single tetradentate L-dithiothreitolate ligand. The anion has noncrystallographic C_2 symmetry with the 2-fold axis perpendicular to the Mo–Mo axis passing through the bridging oxygen atom and the midpoint of the C2–C3 bond. Each sulfur atom of dtt is bound to one Mo atom, while both dtt oxygen atoms serve as additional unsymmetrical bridges between the two metal atoms. Each dtt oxygen atom has one long and one short Mo–O bond, which differ in length by more than 0.5 Å (average values 2.649 and 2.068 Å, respectively). The dtt sulfur atoms have bond distances to the molybdenum atoms that are typical for aliphatic thiolate ligands.[5] The terminal and bridging oxygen atoms occupy positions at normal distances from the metal atoms.

The inner coordination sphere of each Mo consists of one sulfur and five oxygen atoms in a highly distorted octahedral geometry and is similar to that in the structure of $[PPh_4]_2[Mo_2O_5(SC_6H_4O)_2]$.[6] The data listed in Table IV for one of the three independent dimers in the cell illustrate the substantial deviation from octahedral geometry of the inner coordination sphere. The most acute of these angles is defined by the two dtt oxygen atoms bound to one metal atom, O_{dtt}–Mo–O_{dtt}*, which has an average value near 60°. Other deviations from the idealized 90° angles of an octahedron are not unusual for the *syn*-$[Mo_2O_5]^{2+}$ core. For example, the average O_t–Mo–O_t and O_t–Mo–O_b bond angles of

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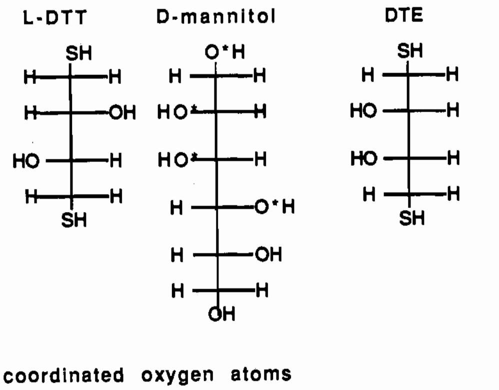
(6) Garner, C. D.; Nicholson, J. R.; Clegg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 972.

105.8 and 102.3° are similar to the angles observed for other $[Mo_2O_5]$-core dimers. Slight differences between nonbonded Mo–Mo distances in the three dimers are likely due to packing interactions in the lattice, which is illustrated in Figure 2. Bond distances and angles of the dithiothreitol ligand and the tetraethylammonium cations are unremarkable.

A related dimer having $[Mo_2O_5]^{2+}$ chelated by the D enantiomer of mannitol has been structurally characterized and is schematically shown in Figure 3a.[7] In a manner related to the binding in $[TEA]_2[Mo_2O_5dtt]$, the mannitol ligand binds the core through four consecutive hydroxylate groups. Comparison of the structures of $[Mo_2O_5dtt]^{2-}$ and $[Mo_2O_5(mannitolate)]^-$ shows that the stereochemistry of the chiral sugar ligand dictates its chelation mode to the $[Mo_2O_5]^{2+}$ moiety.



In the L-dtt complex the hydroxyl oxygen atoms in the 2- and 3-positions bridge the two molybdenum atoms, and the resultant geometrical constraints of the ligand force unequal $Mo–O_{dtt}$ bond lengths. In contrast, the configuration of the four terminal mannitol oxygen atoms that serve as ligands provides a geometry where alternate hydroxylate groups bridge the Mo–Mo group (i.e., at positions 1 and 3), which allows each oxygen atom to bridge the metal atoms in a symmetrical fashion. This chelation mode requires the $Mo–O_b–Mo$ bond angle to decrease to 107.98°. The correlation between the configurations of the chelating portion of D-mannitol to the *meso*-dithiol, dithioerythritol (DTE), suggests that where DTE is used in place of DTT in molybdate solutions, a likely product would be $[Mo_2O_5dte]^{2-}$, structurally analogous to $[Mo_2O_5(mannitolate)]^-$, as depicted schematically in Figure 3b. Models suggest that this is the only chelation mode possible for $[Mo_2O_5dte]^{2-}$ if DTE acts as a tetradentate ligand bonded to a dinuclear center.

The ^{95}Mo NMR spectrum of the $[TEA]_2[Mo_2O_5dtt]$ in DMSO exhibits a broad singlet (line width at half-height 500 Hz) at −2.5 ppm. A similar value (−3.7 ppm) was observed for the dimer $[Mo_2O_5(xanthopterinate)_2]^{2-}$, whose structure also consists of a triply bridged $[Mo_2O_5]^{2+}$ core.[8,9] It appears that the characteristic chemical shift is near zero ppm for the equivalent molybdenum(VI) atoms in a *syn*-$[Mo_2O_5]^{2+}$ core, where the metals have five oxygen atoms in the inner coordination sphere. This complements data reported by Piggott et al. in which a series of complexes having a linear $[Mo_2O_5]^{2+}$ core show chemical shifts near 120 ppm.[10]

Executing the reaction of $[TEA]_2[MoO_4]$ and DTT in methanol under anaerobic conditions causes formation of a bright red-orange solid that precipitates from the reaction solution. This material has one strong, broad $\nu_{Mo=O}$ near 935 cm^{-1}, two medium-strong bands possibly due to $\nu_{Mo—O—Mo}$ at 660 and 605 cm^{-1}, and two medium-intensity absorptions at 350 and 372 cm^{-1} for $\nu_{Mo—S}$. Acetonitrile solutions give room-temperature EPR spectra having a single signal characteristic of a Mo(V) center at $g = 1.997$ and $A_{av}(^{95}Mo,^{97}Mo) = 40$ G. A Mo(V) signal observed by EPR spectroscopy for DMSO solutions containing $MoO_2(acac)_2$, dithiothreitol, and borohydride was attributed to a monomeric Mo(V)–oxo complex in a recent report.[11] Difficulty in purifying the orange material described above by recrystallization has prevented an accurate formulation to be made. In addition to the possibility of a monomeric $Mo(V)O(dtt)^{n-}$, this unknown may be a mixed Mo(VI)–Mo(V) dimer.[12] Further study is clearly required.

The investigation reported in this paper shows that dithiothreitol, like the sugar mannitol, may employ four consecutive heteroatoms on the carbon chain to chelate a $[Mo_2O_5]^{2+}$ group. This chelation may precede formation of a Mo(V) center in anaerobic reactions of dithiothreitol and molybdate. Such reactions possibly represent the preliminary steps in the incorporation of added molybdenum into molybdenum-deficient Mo-co solutions and into Fe–Mo cubane clusters.

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Registry No. $[TEA]_2[Mo_2O_5dtt]$, 114445-92-0; Mo-co, 73508-07-3.

Supplementary Material Available: Complete tabulations of the positional parameters of all atoms in the asymmetric unit, thermal parameters, and bond distances and angles (18 pages); observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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(9) The dimolybdate ion, $[Mo_2O_7]^{2-}$, also has a single chemical shift at −7.0 ppm. To prove that the resonances observed for both the dimers $[Mo_2O_5dtt]^{2-}$ and $[Mo_2O_5(xanthopterinate)_2]^{2-}$ were not due to trace polymolybdates from sample decomposition, the sample was recovered from the NMR sample solutions and inspected by infrared spectroscopy. No additional $\nu_{Mo=O}$ absorptions due to new polymolybdates were observed.

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(12) A mixed-valence dimer having a $[Mo^VMo^{VI}O_5]$ core has been reported by: Herrmann, W.; Wieghardt, K. *Polyhedron* **1986**, *5*, 513.