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Investigations of the Coordination Chemistry of Molybdenum with Facultative Tetradentate Ligands Possessing N_2S_2 Donor Sets. 3.[1] Crystal and Molecular Structures of $[MoO_2(SCH_2CH_2NMe(CH_2)_nNMeCH_2CH_2S)]$, $n = 2$ or 3, and $[MoO_2(SC_6H_4NHCH_2CH_2NHC_6H_4S)]$ and a Comparison to the Structure of $[MoO_2(SCH_2CH_2NHCH_2CH_2SCH_2CH_2S)]$, a Complex with the NS_3 Donor Set

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The structures of four MoO_2Y complexes where Y^{2-} is a linear tetradentate ligand containing N and S donor atoms are reported. The reaction of Mo(VI) starting materials with stoichiometric amounts of the appropriate YH_2 ligand produced the MoO_2Y complexes in good yield. The relevant crystallographic parameters for the title complexes are presented in Table I and summarized herein. $[MoO_2(SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S)]$, $[MoO_2L]$, crystallized in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.169$ (2) Å, $b = 14.369$ (4) Å, and $c = 13.572$ (4) Å and $\alpha = 95.72$ (3)°, $\beta = 97.12$ (2)°, and $\gamma = 111.80$ (2)°, with $Z = 4$, to give a calculated density of 1.75 g/cm^3 (observed density of 1.74 g/cm^3). The structure was solved on the basis of 2609 reflections with $F_o \geq 6\sigma(F_o)$ and refined to final R values of 0.080 and 0.084. $[MoO_2(SCH_2CH_2N(CH_3)CH_2CH_2CH_2N(CH_3)CH_2CH_2S)]$, $[MoO_2L']$, crystallizes as yellow prisms in the monoclinic space group $C2/c$ with unit cell dimensions $a = 8.992$ (3) Å, $b = 12.468$ (3) Å, and $c = 12.204$ (2) Å and $\beta = 104.7$ (1)°. The measured density of 1.72 g/cm^3 was in good agreement with the value of 1.75 g/cm^3 calculated on the basis of 4 molecules in the unit cell. The structure has been solved and refined to R values of 0.040 and 0.067 based on 1335 reflections with $F_o \geq 6\sigma(F_o)$. $[MoO_2(SC_6H_4NHCH_2CH_2NHC_6H_4S)]$, $[MoO_2L'']$, crystallizes in the monoclinic crystal system, space group $P2_1/n$, with unit cell dimensions $a = 11.202$ (3) Å, $b = 11.468$ (4) Å, and $c = 16.033$ (3) Å with $\beta = 105.83$ (2)° and $Z = 4$ to give a calculated density of 1.58 g/cm^3 (observed density of 1.55 g/cm^3). Structure solution and refinement were based on 4325 reflections with $F_o \geq 6\sigma(R_o)$ to give final R values of 0.051 and 0.044. The complex $[MoO_2(SCH_2CH_2NHCH_2CH_2SCH_2CH_2S)]$, $[MoO_2(SNSS)]$, crystallizes in the orthorhombic space group $Pbca$, with unit cell dimensions $a = 13.787$ (2) Å, $b = 14.920$ (2) Å, and $c = 10.665$ (2) Å, with $Z = 8$ and a calculated density of 1.84 g/cm^3 (observed density of 1.85 g/cm^3). Structure refinement based on 1870 unique reflections with $F_o \geq 6.0\sigma(F_o)$ converged to R values of 0.028 and 0.023. The structural studies reveal that the molecules possess the usual *cis*-dioxo MoO_2^{2+} core and that the ligands are present as tetradentate donors coordinating through thiolate sulfur and amine nitrogen groups and, in the case of $[MoO_2(SNSS)]$, through thioether sulfur also. The structure of $[MoO_2L]$ reveals two crystallographically independent molecules in the asymmetric unit with nonequivalent Mo–S or Mo–N bond distances, in contrast to other structures with the MoO_2^{2+} core. On the other hand, $[MoO_2L']$ displays crystallographically equivalent Mo–S distances, but an unusually long Mo–N bond length of 2.486 (5) Å. Comparison of the above two structures to that of the related species $[MoO_2L'']$ suggests that minor ligand variations cause significant differences in the static structural behavior of the Mo(VI) complexes. The effects of drastic changes in the nature of the ligand donor groups are revealed in the structure of $[MoO_2(SNSS)]$, where an amine nitrogen donor has been replaced by a thioether sulfur. The most notable feature of the structure is the Mo–S(thioether) bond distance of 2.708 (1) Å. The geometries of the title complexes are compared to those previously reported for species containing the MoO_2^{2+} core.

Introduction

Molybdoenzymes other than nitrogenase have been shown to possess common molybdenum cofactor.[3,4] Spectroscopic evidence reveals that these enzymes possess similar but not identical Mo sites. Extensive electron spin resonance (EPR) studies on the Mo(V) state of xanthine oxidase[5] and early solution EPR studies on model systems led to the suggestion of sulfur as a donor atom.[6] More recently, EXAFS studies on the oxidized forms of xanthine oxidase[7] and sulfite oxidase[8] have implicated the presence of terminal oxygen atoms and sulfur atoms in the Mo(VI) coordination sphere. Model studies have provided additional insight, suggesting for example that the molybdenum coordination in sulfite oxidase may consist of two cis-oxo groups, a thioether sulfur and two thiolate sulfur donors in the usual octahedral unit.[9] However, recent model studies reveal that the molybdenum coordination geometry may be irregular as a result of steric constraints and could contain mutually cis-thiolate sulfur donors.[10]

As part of the comprehensive studies of the chemistry of molybdenum in the IV, V, and VI oxidation states with thiolate donor ligands,[9-13] we have prepared and studied the chemical behavior of $[MoO_2L]$ and $[MoO_2L']$, where L and L′ are linear tetradentate ligands with two amine donor and two thiolate sulfur donor groups. The significant differences in

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(1) For part 2 of this series see: Pickett, C.; Kumar, S.; Vella, P.; Zubieta, J. *Inorg. Chem.*, preceding paper in this issue.

(2) (a) Charles F. Kettering Research Laboratories. (b) State University of New York at Albany. (c) Utah State University.

(3) Bray, R. C. *J. Less-Common Met.* **1977**, *54*, 527.

(4) Pienkos, P. T.; Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5468.

(5) Bray, R. C.; Meriwether, L. S. *Nature (London)* **1966**, *212*, 467.

(6) Meriwether, L. S.; Marzluff, W. F.; Hodgson, W. G. *Nature (London)* **1966**, *212*, 465.

(7) Tullius, T. D.; Kurtz, D. M.; Conrodson, S. D.; Hodgson, K. O. *J. Am. Chem. Soc.* **1979**, *101*, 2776.

(8) Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1979**, *101*, 2772.

(9) 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.

(10) 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.

(11) Kim, N.; Kim, S.; Vella, P. A.; Zubieta, J. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 457.

(12) Hyde, J.; Magin, L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 204.

(13) (a) Hyde, J.; Magin, L.; Zubieta, J. In "Stereodynamics of Molecular Systems"; Sarma, R. H., Ed.; Pergamon Press: New York, 1979. (b) Spence, J. T.; Minelli, M.; Kroneck, P. *J. Am. Chem. Soc.* **1980**, *102*, 4538.

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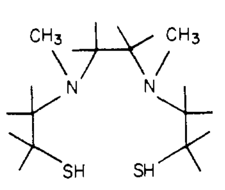
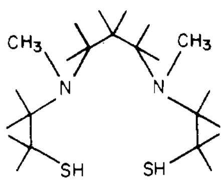
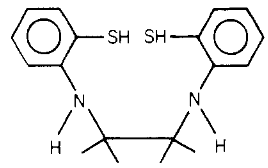


LH_2



$L'H_2$



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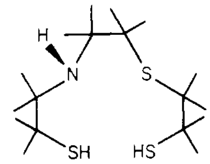

SNSS

the chemical and electrochemical characteristics of these complexes[1] suggest that minor variations in ligand geometry may cause significant differences in the structural systematics. $[MoO_2L]$ is unusual in possessing a well-behaved quasi-reversible cathodic process in the cyclic voltammetry, behavior not common to species posesssing the MoO_2^{2+} core, which are generally characterized by complex and irreversible processes in their electrochemistry.[14] Likewise, $[MoO_2L']$ upon chemical reduction rather remarkably produces $[Mo_2O_4(LH')_2]$, rather than $[Mo_2O_3L'_2]$, the species with the ubiquitous $Mo_2O_3^{4+}$ core.

$[MoO_2L'']$ has been discussed as a potential model for Mo enzymes in view of its irreversible two-electron reduction and two one-electron oxidative steps required for its regeneration. Finally, $[MoO_2(SNSS)]$ was of interest due to its possession of a thioether donor, a unit suggested to be present in Mo enzymes from EXAFS studies.

Experimental Section

$[MoO_2L]$ and $[MoO_2L']$ were prepared as discussed in part 2 of this series.[1] $[MoO_2L'']$ and $[MoO_2(SNSS)]$ were prepared from the reaction of $[MoO_2(acac)_2]$ with the appropriate ligand.[15]

Crystals of $[MoO_2L']$, $[MoO_2L]$, and $[MoO_2(SNSS)]$ of suitable quality for X-ray diffraction studies were obtained from CH_2Cl_2/methanol solutions by slow evaporation. Suitable crystals of $[MoO_2L]$ were obtained from acetonitrile/isopropyl alcohol at 4 °C.

Collection and Reduction of X-ray Data. $[MoO_2L]$. The crystal used for the structure determination was an irregularly shaped prism with the approximate orthogonal dimensions reported in Table I. A total of 25 reflections with $0° \le 2\theta \le 40°$ were carefully aligned in the counter window of a Nicolet P3 diffractometer. An autoindexing routine produced the unit cell dimensions recorded in Table I. Axial photographs and Delauney reduction of the unit cell dimensions revealed no hidden symmetry. The quality of the data crystal was checked by taking $\theta/2\theta$ scans of several strong low-angle reflections. The details of the data collection and reduction are given in Table I.

$[MoO_2L']$. A platelike crystal was used in the diffraction study. The unit cell dimensions and the space group were determined as above for $[MoO_2L]$. The $\theta/2\theta$ scans of several strong low-angle reflections had average half-widths of 0.20°. Details of the data collection and reduction appear in Table I.

$[MoO_2L'']$. The crystal used in the diffraction study was a rectangular parallelipiped with dimensions as listed in Table I. The unit cell dimensions and space group were determined by computer centering of 15 reflections with $15° \le 2\theta \le 30°$, as described above for $[MoO_2L]$. The width at half-height from ω scans of four strong low-angle reflections averaged 0.35°. The data was collected by Dr. Cynthia Day of Crystalytics Co., Box 82286, Lincoln, Neb. 68501. The details of the data collection and reduction are given in Table I.

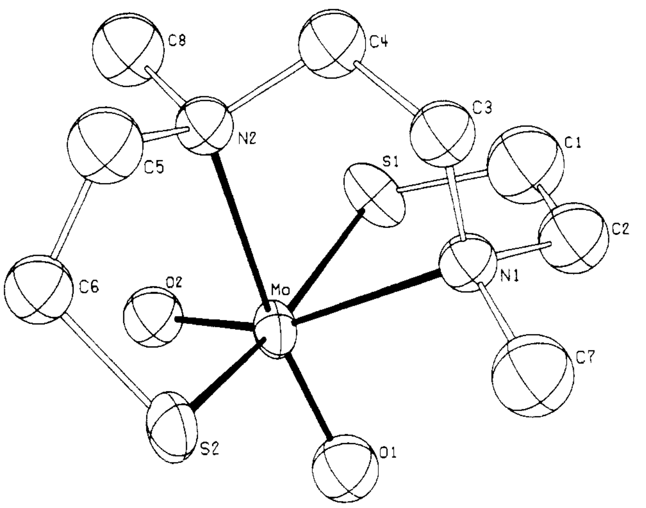

Figure 1. Structure of $[MoO_2L]$, molecule 1, showing the atom labeling scheme and 50% probability thermal ellipsoids.

$[MoO_2(SNSS)]$. The crystals used in the study was a yellow irregular block. The unit cell dimensions were determined by computer-centering of 15 reflections with $30° \le 2\theta \le 60°$. The space group was determined and checked as described above. The ω scans of several strong low-angle reflections showed average widths of 0.35°. The data was collected by Dr. Cynthia Day of Crystalytics Co. The details of data collection and reduction are presented in Table I.

Structure Solution and Refinement. $[MoO_2L]$. The structure of $[MoO_2L]$ was determined by the heavy-atom method. A Patterson map revealed the positions of the two molybdenum atoms. Subsequent difference Fourier maps revealed the positions of all nonhydrogen atoms. At this stage hydrogen atoms were introduced as fixed contributions, and all nonhydrogen atoms were refined anisotropically. Neutral-atom scattering factors for nonhydrogen atoms and corrections for anomalous dispersion effects for molybdenum and sulfur were obtained from ref 16. Scattering factors for the hydrogen atoms were those of Stewart et al.[17]

The final full-matrix leas-squares refinement converged at discrepancy values listed in Table I. The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_o|)^2$ is defined as $w = 1/\sigma_F^2$. An analysis of variance according to $|F|$ and $(\sin\theta)/\lambda$ showed satisfactory consistency, and the weighting scheme was judged satisfactory. A final difference Fourier map showed no excursions of electron density greater than 0.40 e/Å^3.

$[MoO_2L']$. The structure of $[MoO_2L']$ was solved in an analogous manner with use of Patterson and Fourier maps. Refinement converged at values of the discrepancy indices given in Table I. An analysis of variance showed no unusual trends. The largest peak on the final difference Fourier map was 0.50 e/Å^3.

$[MoO_2L'']$. The structure was solved with use of Patterson and Fourier maps as above. Details of final discrepancy indices and the number of reflections used in the analysis are given in Table I. Nonhydrogen atoms were refined anisotropically and hydrogen atoms introduced as fixed contributors with isotropic thermal parameters. On the final difference Fourier map the largest peak was 0.40 e/Å^3.

$[MoO_2(SNSS)]$. The details of the structure solution and analysis are similar to those for $[MoO_2L]$ and are given in Table I. Nonhydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and included in the refinement as invariants. There were no unusual excursions of electron density on the final difference Fourier map.

Atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the final cycle of least-squares refinement, are given in Tables II–V for $[MoO_2L]$, $[MoO_2L']$, $[MoO_2L'']$, and $[MoO_2(SNSS)]$, respectively. Tables VI–IX list interatomic distances and angles for $[MoO_2L]$, $[MoO_2L']$, $[MoO_2L'']$, and d $[MoO_2(SNSS)]$, respectively. A comparison of the nonbonded distances that determine the octahedral edges of the title compounds is provided in Table X. Tables of observed and

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(14) Dehayes, L. J.; Faulkner, J. C.; Doub, W. H.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 210.

(15) (a) Corbin, J. L.; Work, D. E. *Can. J. Chem.* **1974**, *52*, 1054. (b) Gardner, J. K.; Pariyadath, N.; Corbin, J. L.; Steifel, E. I. *Inorg. Chem.* **1978**, *17*, 897.

(16) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. Y. *J. Chem. Phys.* **1965**, *42*, 3175.

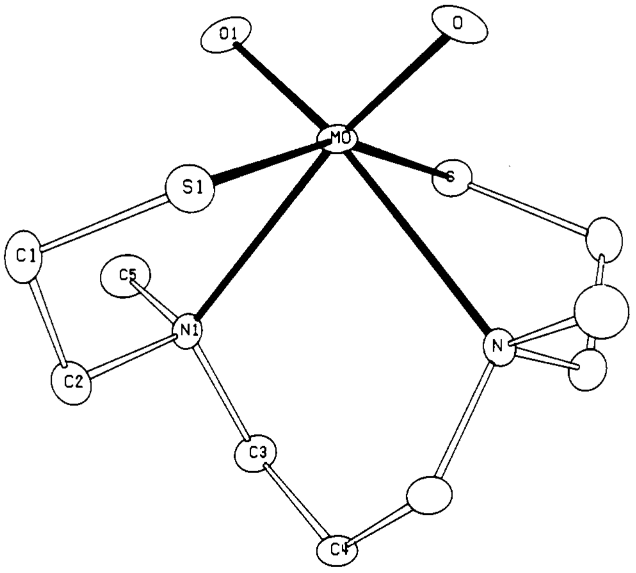

Figure 2. Structure of $[MoO_2L']$ showing the atom labeling scheme and 50% probability ellipsoids.

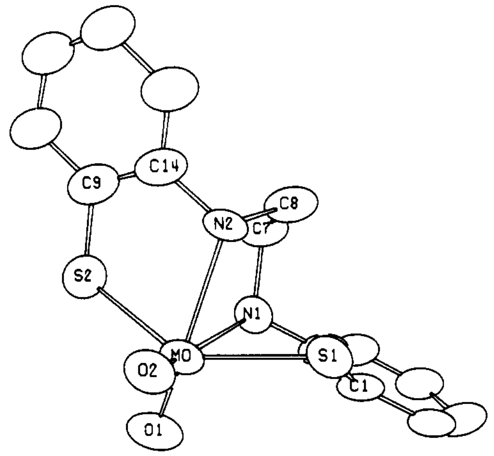

Figure 3. Structure of $[MoO_2L'']$ showing the atom labeling scheme and 50% probability ellipsoids.

calculated structure factor amplitudes and of hydrogen atom positions are provided as supplementary material. Views of the geometries of $[MoO_2L]$, $[MoO_2L']$, $[MoO_2L'']$, and $[MoO_2(SNSS)]$ along with the atom-labeling schemes are shown in Figures 1–4, respectively. Figures 5–8 illustrate the packing of the molecules in their respective unit cells.

Description of the Structures

$[MoO_2L'']$. Of the three complexes of MoO_2^{2+} with linear ligands possessing N_2S_2 donors studied in this work, $[MoO_2L'']$ exhibits unexceptional geometry and is taken as the structural prototype. The Mo–oxo distances are equivalent and fall in the range 1.69–1.72 Å, common to all structures of this type.[18-33] The O1–Mo–O2 angle of 109.9 (1)° falls slightly out of the range of 102–108°, usually observed for MoO_2^{2+} species with bidentate chelates, although angles in the range 108–110° may be more common with tetradentate groups.[9] This small increase in the O–Mo–O angle may be related to the folding of the C–N–Mo–S–C rings back toward the metal–diamine plane, a consequence of the tightly wrapped ligand chain that results from the formation of three five-membered chelated rings with the metal. As illustrated in Tables VII and XI, this produces significant deviations of the Mo valence angles from those anticipated for regular octahedral geometry. The internal chelate ring angles are thus 77.5 (1), 77.5 (1), and 74.7 (1)° for S1–Mo–N1, S2–Mo–N2, and N1–Mo–N2, respectively. The Mo–thiolate sulfur distances are equivalent and average 2.428 (2) Å, a value similar to that observed for Mo–S distances in $[MoO_2(tox)_2]$[30] and $[MoO_2(SCH_2CH_2)_2NCH_2CH_2NMe_2]$.[9] The average Mo–N distance of 2.368 (3) Å is similar to molybdenum-amine nitrogen distances trans to the multiply bonded oxo ligand.[18,37,43-49] This distance is considerably longer than the

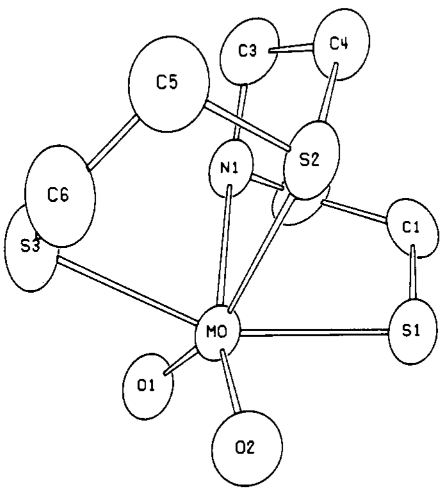

Figure 4. Structure of $[MoO_2(SNSS)]$ showing the atom labeling scheme and 50% probability ellipsoids.

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(18) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.
(19) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(20) Ricard, L.; Estienne, J.; Karagiannidis, P.; Toledano, P.; Fischer, J.; Mitschler, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277.
(21) Kamer, B.; Penavic, M.; Prout, C. K. *Cryst. Struct. Commun.* **1971**, *2*, 41.
(22) Fenn, R. H. *J. Chem. Soc. A* **1969**, 1764.
(23) Craven, B. M.; Ramey, K. C.; Wise, W. B. *Inorg. Chem.* **1971**, *10*, 2626.
(24) Atovmyan, L. O.; Sokolovia, Yu A. *J. Struct. Chem.* (*Engl. Transl.*) **1971**, *12*, 780.
(25) Florian, L. R.; Corey, E. R. *Inorg. Chem.* **1968**, *7*, 722.
(26) Grandjean, D.; Weiss, R. *Bull. Soc. Chim. Fr.* **1969**, 3049.
(27) Sergienko, V. S.; Porai-Koshits, M. A.; Khodashova, R. S. *Zh. Strukt. Khim.* **1973**, *13*, 461.
(28) Kopwillen, A. *Acta Chem. Scand.* **1972**, *26*, 2941.
(29) Kojic-Prodic, B.; Ruzic-Toros, Z.; Grdenic, D.; Golic, L. *Acta Crystallogr., Sect. B* **1974**, *B30*, 300.
(30) Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979**, *18*, 1926.
(31) Cliff, C. A.; Fallon, G. D.; Gatehouse, B. M.; Murray, K. S.; Newman, P. J. *Inorg. Chem.* **1980**, *19*, 773.
(32) Berg. J. M.; Hodgson, K. O. *Inorg. Chem.* **1980**, *19*, 2180.
(33) Stiefel, E. I.; Miller, K. F.; Alice, A. E.; Pariyadath, N.; Heinecke, J.; Corbin, J. L. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York, 1980; p 279.
(34) Zahrobsky, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 3313.
(35) Yamanouchi, K.; Enemark, J. H. *Chem. Uses Molybdenum, Proc. Int. Conf., 3rd* **1979**.
(36) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1.
(37) Spivack, B.; Dori, Z. *J. Chem. Soc., Daltron Trans.* **1973**, 1173.
(38) Dahlstrom, P. L.; Hyde, J. R.; Vella, P. A.; Zubieta, J. *Inorg. Chem.* following paper in this issue.
(39) Dahlstrom, P. L.; Dilworth, J. R.; Schulman, P.; Zubieta, J. *Inorg. Chem.*, second following paper in this issue.
(40) Hu, W.-j.; Lippard, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 2366.
(41) Baltusis, L. M.; Karlin, K. D.; Rabinowitz, H. N.; Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2627.
(42) Hawkins, C. J. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971.
(43) Knox, J. R.; Prout, C. K. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1857.
(44) Delbaere, L. T. J.; Prout, C. K. *J. Chem. Soc. D* **1971**, 162.
(45) Drew, M. G. B.; Kay, A. *J. Chem. Soc. A* **1971**, 1846.
(46) Drew, M. G. B.; Kay, A. *J. Chem. Soc. A* **1971**, 1851.
(47) Spivack, B.; Dori, Z. *J. Chem. Soc., Dalton Trans.* **1975**, 1077.

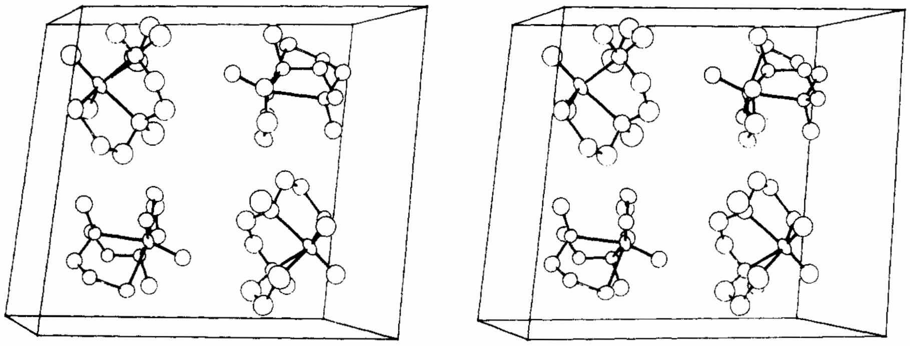

Figure 5. Stereodrawing of the unit cell contents of [MoO_2L].

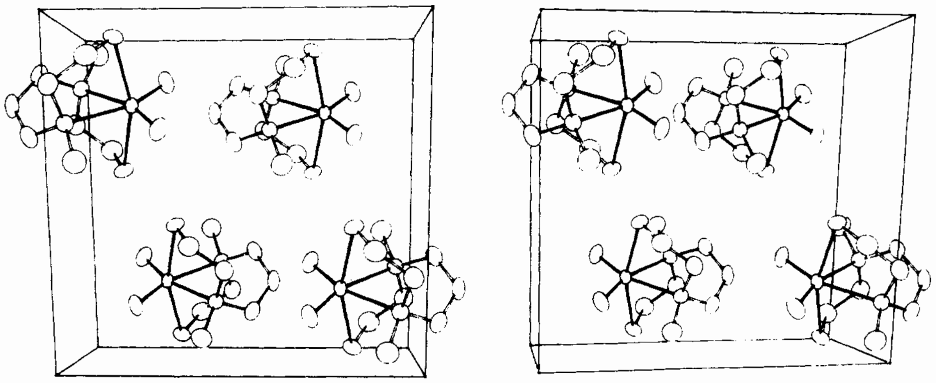

Figure 6. Stereodrawing of the unit cell contents of [MoO_2L'].

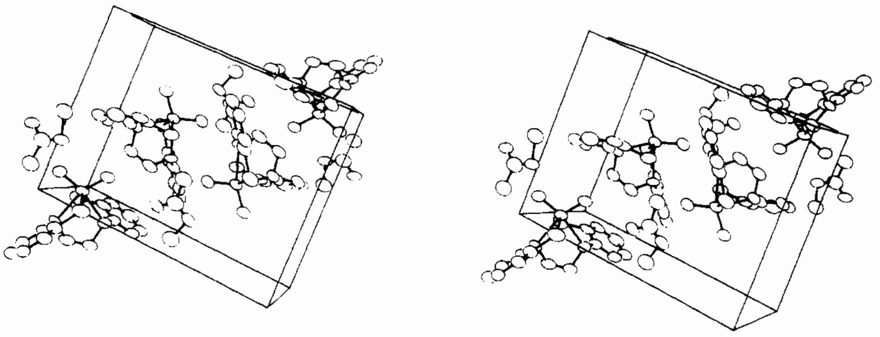

Figure 7. Stereodrawing of the unit cell contents of [MoO_2L''].

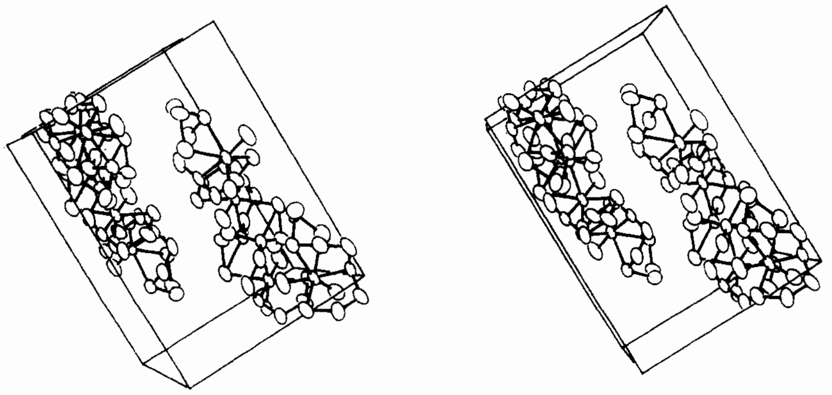

Figure 8. Stereodrawing of the unit cell contents of [MoO_2(SNSS)].

distance of 2.298 (8) Å found for Mo–N1 in [$Mo_2O_3L_2$],[38] where the nitrogen is trans to a bridging group, and is also longer than values in the range of 2.20 Å for an Mo–N distance unaffected by trans-influencing ligands.[18]

The ligand geometry in [MoO_2L''] is unexceptional. The N1C1C2C3C4C5C6S1 plane is nearly perpendicular to the N2C9C10C11C12C13C14S2 plane as a result of the ligand folding pattern, which requires that the thiolate groups be trans to each other and cis to the oxo groups. The folding pattern of the ligand planes is unexceptional as shown in Table XII. The ligand is folded toward the terminal oxygens along the S···N vectors, making dihedral angles of 22.5 and 21.4° with the coordination planes.

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(48) Spivack, B.; Dori, Z. *J. Chem. Soc., Dalton Trans.* **1973**, 1173.
(49) Brown, D. H.; Jeffreys, J. A. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1173.

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Studies[a]

	$[MoO_2L]$	$[MoO_2L']$	$[MoO_2L'']\cdot DMF$	$[MoO_2(SNSS)]$
(A) Crystal Parameters at 21 °C[b]				
a, Å	7.169 (2)	8.992 (3)	11.202 (3)	13.787 (2)
b, Å	14.369 (4)	12.468 (3)	11.468 (4)	14.920 (2)
c, Å	13.572 (4)	12.204 (2)	16.033 (3)	10.665 (2)
α, deg	95.72 (3)	90.0	90.0	90.0
β, deg	97.12 (2)	104.7 (1)	105.83 (2)	90.0
γ, deg	111.80 (2)	90.0	90.0	90.0
V, Å^3	1272	1323.1 (6)	1982 (1)	2193.7 (5)
$F(000)$	680	712	1084	1288
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
absences	none	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	$h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$; $0kl$, $k = 2n + 1$
space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$Pbca$
Z	4	4	4	8
ρ(calcd), g/cm^3	1.75	1.75	1.58	1.84
ρ(obsd),[c] g/cm^3	1.74 (2)	1.72 (2)	1.55 (2)	1.85 (2)
mol wt	334.31	348.3	471.4	304.2
(B) Measurement of Intensity Data				
cryst dimens, mm	0.18 × 0.14 × 0.20	0.25 × 0.58 × 0.43	0.38 × 0.69 × 0.69	0.30 × 0.25 × 0.35
instrument	Nicolet R3/m	Nonius CAD4	Nicolet R3/m	Nicolet R3/m
radiation	Mo K$\bar{\alpha}$, graphite monochromatized ($\bar{\lambda}$, 0.710 73 Å)	Mo K$\bar{\alpha}$, graphite monochromatized (λ, 0.710 73 Å)	Mo K$\bar{\alpha}$, graphite monochromatized (λ, 0.710 73 Å)	Mo K$\bar{\alpha}$, graphite monochromatized (λ, 0.710 73 Å)
scan technique	θ–2θ	θ–2θ	ω	ω
scan range, deg	1.0	1.0	1.0	1.0
scan rate, deg/min	8.0–29.3	4.0	2.0–4.0	3.0–4.0
max 2θ, deg	45	55	60.4	55
bkgd measts	stationary cryst, stationary counter, 10-s counts at each end of 2θ scan range	stationary cryst, stationary counter, 10-s counts at each end of 2θ scan range	stationary cryst, stationary counter, 15-s counts at each end of ω scan range	stationary cryst, stationary counter, 15-s counts at each end of ω scan range
stds[d]	3 reflctns every 100 data reflctns	3 reflctns every 100 data reflctns	6 reflctns every 300 data reflctns	6 reflctns every 300 data reflctns
no. of reflctns collected	3800	1335	5885	2520
(C) Treatment of Intensity Data				
reductn to F_o^2 and $\sigma(F_o^2)$	corr for bkgd, attenuators, and Lorentz–polarization in the usual manner[g]			
μ, cm^{-1}	13.07	12.6	8.75	16.9
transmission coeff; T_{max}, T_{min}	0.92, 0.86	0.88, 0.76	0.85, 0.69	0.90, 0.84
obsd unique data, $F_o \geqslant 6\sigma(F_o)$	2349	1335	4325	1870
R_1[e]	0.067	0.040	0.051	0.028
R_2[f]	0.065	0.067	0.044	0.023

[a] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words with use of versions of the Nicolet SHELXTL interactive crystallographic software package as locally modified. [b] From a least-squares fitting of the setting angles of 15 reflections. [c] Flotation. [d] In all cases showed only random, statistical fluctuations. [e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [f] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2}$. [g] The intensity data for $[MoO_2L']$ and $[MoO_2L'']\cdot DMF$ were corrected for absorption, with use of programs supplied in the Enraf-Nonius package and ψ scans of five reflections at $\chi = 90°$, respectively.

In the solid state, each molecule of $[MoO_2L'']$ is hydrogen bound to a centrosymmetrically related neighbor, as suggested by the N2–O2 distance of 2.98 Å and the (N2)H···O2 distance of 2.00 Å. In addition, the dimethylformamide molecule of crystallization is hydrogen-bonded to a neighboring $[MoO_2L'']$ molecule through the interaction of O3 with H(N1), with O3···N1 and O3···H(N1) distances of 2.88 and 1.93 Å, respectively. This pattern of hydrogen bonding between pairs of $[MoO_2L'']$ molecules and between $[MoO_2L']$ and a molecule of crystallization is distinct from the H-bonding pattern previously observed for $[MoO_2(SCMe_2CH_2CH_2NHMe)_2]$[10] and $[MoO_2(MeHNCMe_2CMe_2S)_2]$, where infinite chains are formed.

$[MoO_2L]$. The overall geometry of $[MoO_2L]$ is similar to that observed for $[MoO_2L'']$. Closer inspection of the bond lengths and valence angles, however, reveals that the geometry of $[MoO_2L]$ is highly irregular. In addition to the distortions common to complexes of the MoO_2^{2+} core with multidentate ligands, the two crystallographically independent molecules of $[MoO_2L]$ characterized in this study display small but significant differences in bond lengths and valence angles that are chemically equivalent and appear undistorted in other structures with linear tetradentate ligands. Thus, molecule 1 exhibits a statistically significant difference in the Mo–S bond lengths (Table VI) and a more pronounced difference in the O1–Mo–S1 and O2–Mo–S2 angles, which are expected to be equivalent. The corresponding angles in $[MoO_2L']$ are crystallographically identical while those in $[MoO_2L'']$ are statistically equivalent. More pronounced bond length distortions are observed in molecule 2 where the Mo–N bond lengths differ by 7σ and the Mo–O distances by 8σ. The valence angles O3–Mo–S3 and O4–Mo–S4 are nonequivalent, and likewise the O3–Mo–S4 and O4–Mo–S3 pair. These small geometric distortions may reflect the relatively greater flexibility of two methylene carbon bridges between S and N donor groups in L as compared to the geometrically constrained phenyl carbon bridges in L″. On the other hand, it should be noted that suitable single crystals of $[MoO_2L]$ were of relatively poor quality, hence the rather large errors in the final esd's for bond lengths and angles. We feel, therefore, that some caution must be exercised in interpreting these relatively small distortions in bond lengths and valence angles about the molybdenum in $[MoO_2L]$.

A common structural feature of both $[MoO_2L]$ and $[MoO_2L'']$ is the steric strain associated with the intrachelate valence angles, as listed in Table XI. The unusual electro-

Table II. Atomic Positional and Thermal $(\times 10^2)$ Parameters for $[MoO_2(SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.27429 (9)	0.61761 (8)	0.25885 (9)	2.82 (6)	3.46 (7)	6.07 (8)	1.23 (6)	1.05 (6)	1.68 (5)
S1	0.1295 (4)	0.5950 (3)	0.4109 (2)	5.0 (2)	8.8 (3)	6.3 (2)	4.0 (2)	1.5 (2)	2.1 (2)
S2	0.3541 (4)	0.6760 (2)	0.1031 (2)	4.6 (2)	5.7 (2)	5.2 (2)	1.0 (2)	2.4 (2)	1.0 (2)
O1	0.226 (1)	0.4981 (7)	0.2047 (7)	5.7 (6)	5.2 (6)	9.9 (8)	1.0 (6)	3.2 (6)	2.4 (5)
O2	0.508 (1)	0.6661 (7)	0.3303 (7)	1.5 (5)	8.6 (8)	7.4 (6)	3.0 (6)	1.0 (5)	3.1 (5)
N1	0.074 (1)	0.5906 (7)	0.1992 (8)	1.1 (5)	5.0 (7)	5.0 (7)	−0.5 (6)	0.5 (5)	−0.2 (5)
N2	0.264 (2)	0.7840 (7)	0.2806 (7)	5.5 (7)	3.0 (6)	4.5 (7)	−0.6 (5)	0.3 (6)	1.1 (6)
C1	−0.136 (2)	0.548 (1)	0.365 (1)	10.4 (16)	13.6 (17)	5.0 (11)	3.2 (12)	4.6 (11)	−3.7 (13)
C2	−0.206 (2)	0.522 (1)	0.264 (1)	3.2 (9)	7.6 (1)	10.8 (13)	4.6 (11)	1.6 (9)	0.3 (8)
C3	−0.094 (2)	0.6898 (9)	0.2015 (9)	4.4 (8)	4.4 (8)	7.2 (10)	1.0 (7)	1.9 (7)	2.3 (7)
C4	0.043 (2)	0.769 (1)	0.282 (1)	7.9 (11)	4.9 (9)	9.3 (12)	1.5 (8)	5.0 (9)	4.3 (8)
C5	0.338 (2)	0.844 (1)	0.197 (1)	8.4 (12)	4.0 (8)	9.3 (12)	3.8 (8)	2.5 (9)	1.5 (8)
C6	0.472 (2)	0.8079 (9)	0.148 (1)	3.7 (8)	5.7 (9)	7.4 (10)	1.7 (8)	3.1 (8)	1.8 (7)
C7	−0.150 (2)	0.537 (1)	0.098 (1)	3.7 (9)	9.4 (14)	8.9 (13)	−2.1 (11)	0.9 (9)	0.7 (9)
C8	0.386 (2)	0.846 (1)	0.377 (1)	9.5 (12)	4.9 (9)	8.2 (12)	0.8 (8)	3.6 (10)	1.9 (9)
Mo2	−0.19903 (12)	−0.10558 (9)	0.75787 (10)	5.52 (9)	5.79 (9)	6.87 (9)	2.65 (7)	2.23 (7)	3.71 (7)
S3	0.0779 (6)	−0.0123 (3)	0.6745 (3)	8.3 (3)	5.6 (3)	8.6 (3)	1.6 (2)	2.2 (3)	1.8 (2)
S4	−0.4045 (6)	−0.2293 (4)	0.8490 (3)	5.8 (3)	5.1 (5)	3.2 (4)	1.1 (4)	5.0 (3)	5.1 (3)
O3	−0.407 (2)	−0.103 (1)	0.6876 (9)	9.7 (9)	10.7 (11)	11.3 (10)	4.6 (8)	−0.2 (8)	6.6 (9)
O4	−0.098 (2)	0.0032 (8)	0.8495 (8)	12.9 (13)	8.1 (8)	7.2 (8)	−1.3 (6)	1.0 (8)	9.3 (9)
N3	−0.180 (2)	−0.2334 (4)	0.6404 (9)	8.9 (10)	5.7 (8)	5.8 (9)	1.9 (7)	1.1 (8)	1.6 (8)
N4	0.040 (2)	−0.1688 (9)	0.8421 (8)	5.8 (8)	6.7 (8)	5.7 (8)	1.0 (6)	0.6 (6)	3.1 (7)
C9	0.060 (2)	−0.101 (1)	0.567 (1)	8.7 (13)	10.0 (13)	6.3 (11)	0.6 (10)	4.2 (10)	1.0 (11)
C10	−0.127 (3)	−0.192 (1)	0.546 (1)	13.6 (18)	10.5 (14)	6.2 (11)	−1.0 (11)	3.0 (12)	2.9 (14)
C11	−0.050 (3)	−0.279 (1)	0.679 (1)	10.9 (25)	9.4 (15)	7.9 (14)	−0.3 (12)	5.6 (12)	9.6 (14)
C12	0.100 (3)	−0.223 (1)	0.765 (1)	14.5 (18)	13.3 (16)	13.1 (16)	−7.2 (11)	−5.2 (14)	12.6 (16)
C13	−0.043 (3)	−0.232 (2)	0.911 (1)	5.0 (12)	13.9 (20)	16.2 (21)	11.6 (20)	3.4 (13)	2.5 (15)
C14	−0.224 (3)	−0.240 (1)	0.941 (1)	12.8 (17)	18.8 (23)	11.3 (15)	11.3 (16)	8.2 (12)	13.3 (17)
C15	−0.415 (3)	−0.310 (1)	0.612 (2)	15.9 (20)	8.3 (18)	18.9 (20)	6.0 (16)	2.1 (12)	2.5 (13)
C16	0.228 (2)	−0.083 (1)	0.901 (1)	6.5 (12)	7.6 (12)	10.8 (14)	0.2 (11)	−5.6 (11)	−0.8 (10)

Table III. Final Atomic Positional and Thermal $(\times 10^2)$ Parameters for $[MoO_2(SCH_2CH_2N(CH_3)CH_2CH_2CH_2N(CH_3)CH_2CH_2S)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.00000	0.22925 (4)	0.25000	5.36 (4)	2.20 (3)	3.24 (4)		1.89 (3)	
S	0.0776 (2)	0.1963 (1)	0.0782 (1)	7.13 (9)	5.87 (9)	3.73 (6)	0.51 (7)	2.86 (7)	1.03 (6)
N	0.1838 (5)	0.0778 (4)	0.3043 (4)	3.36 (20)	4.27 (23)	3.72 (19)	−0.29 (16)	0.88 (17)	0.17 (1)
O	0.1476 (8)	0.3098 (4)	0.3184 (5)	9.48 (39)	4.13 (22)	6.91 (29)	−2.71 (26)	2.56 (28)	−1.42 (2)
C1	0.2663 (8)	0.1460 (7)	0.1384 (6)	5.1 (3)	7.4 (4)	6.3 (4)	−0.3 (3)	3.3 (3)	−0.1 (3)
C2	0.2590 (8)	0.0508 (6)	0.2096 (7)	4.9 (3)	5.6 (3)	6.8 (3)	0.7 (3)	1.8 (3)	−0.1 (3)
C3	0.1221 (8)	−0.0238 (6)	0.3349 (6)	5.2 (3)	4.3 (3)	6.7 (4)	0.4 (3)	−0.1 (3)	1.4 (3)
C4	0.0000	−0.0816 (6)	0.2500	5.6 (5)	2.9 (3)	7.8 (6)		2.4 (4)	
C5	0.3028 (9)	0.1130 (7)	0.4041 (8)	6.1 (4)	6.9 (5)	7.7 (5)	−0.2 (4)	−2.3 (4)	−0.8 (4)

Table IV. Final Atomic Positional and Thermal $(\times 10^2)$ Parameters for $[MoO_2(SC_6H_4NHCH_2CH_2NHC_6H_4S)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.04417 (5)	0.08926 (4)	0.16709 (3)	5.28 (3)	2.26 (2)	2.91 (2)	0.13 (2)	1.05 (2)	0.35 (3)
S1	0.23412 (14)	0.07463 (11)	0.12237 (8)	6.03 (10)	3.48 (7)	3.75 (7)	0.14 (6)	1.76 (7)	−0.64 (7)
S2	−0.12178 (14)	0.02149 (12)	0.22548 (9)	5.63 (10)	4.3 (8)	4.51 (8)	−0.29 (6)	2.18 (7)	0.73 (8)
O1	−0.0321 (3)	0.1357 (3)	0.0648 (2)	6.1 (3)	3.5 (2)	3.5 (2)	0.4 (1)	0.8 (2)	0.5 (2)
O2	0.0716 (4)	0.2049 (3)	0.2369 (2)	9.0 (3)	2.9 (2)	3.6 (2)	−0.4 (2)	1.5 (2)	0.3 (2)
N1	0.1729 (4)	−0.0234 (3)	0.2790 (2)	4.6 (3)	2.5 (2)	2.9 (2)	−0.0 (2)	0.9 (2)	0.3 (2)
N2	0.0162 (4)	−0.1067 (3)	0.1169 (2)	5.2 (3)	2.3 (2)	2.7 (2)	−0.4 (2)	1.1 (2)	−0.2 (2)
C1	0.3433 (5)	0.0341 (4)	0.2191 (3)	4.6 (3)	2.7 (3)	4.6 (3)	−1.2 (2)	1.6 (3)	−0.5 (2)
C2	0.4686 (5)	0.0443 (4)	0.2278 (4)	6.4 (4)	4.3 (3)	6.5 (4)	−1.8 (3)	2.9 (4)	−0.8 (3)
C3	0.5555 (5)	0.0152 (5)	0.3049 (4)	4.6 (4)	5.8 (4)	7.2 (4)	−2.6 (3)	1.2 (4)	−0.2 (3)
C4	0.5154 (6)	−0.0262 (5)	0.3746 (4)	6.1 (5)	5.1 (4)	6.0 (4)	−1.8 (3)	−0.5 (4)	0.7 (4)
C5	0.3897 (5)	−0.0384 (4)	0.3658 (3)	5.8 (4)	3.9 (3)	4.1 (3)	−0.4 (3)	0.5 (3)	0.6 (3)
C6	0.3034 (5)	−0.0092 (4)	0.2883 (3)	4.7 (3)	2.2 (2)	3.9 (3)	−0.7 (2)	0.7 (3)	0.1 (2)
C7	0.1360 (5)	−0.1508 (4)	0.2664 (3)	4.4 (3)	2.9 (3)	4.4 (3)	1.0 (2)	0.9 (2)	0.4 (3)
C8	0.1195 (5)	−0.1811 (4)	0.1719 (3)	4.2 (3)	2.1 (2)	5.8 (3)	−0.4 (2)	1.3 (3)	−0.0 (2)
C9	−0.1763 (5)	−0.1039 (4)	0.1626 (3)	4.4 (3)	4.0 (3)	4.2 (3)	0.6 (2)	1.1 (3)	0.5 (3)
C10	−0.2871 (5)	−0.1554 (5)	0.1633 (4)	4.8 (4)	6.2 (4)	7.1 (4)	0.5 (3)	2.0 (3)	0.4 (3)
C11	−0.3297 (6)	−0.2516 (5)	0.1108 (4)	4.5 (4)	7.0 (5)	7.8 (5)	1.6 (4)	0.3 (3)	−1.5 (4)
C12	−0.2624 (6)	−0.2975 (5)	0.0591 (4)	6.5 (5)	4.8 (4)	6.0 (4)	0.2 (3)	−0.2 (3)	−1.6 (3)
C13	−0.1495 (5)	−0.2489 (4)	0.0593 (3)	5.9 (4)	3.6 (3)	4.5 (3)	−0.0 (3)	0.5 (3)	−0.6 (3)
C14	−0.1059 (5)	−0.1535 (4)	0.1122 (3)	4.6 (3)	2.8 (3)	3.5 (3)	0.8 (2)	0.7 (2)	−0.2 (2)
O3	−0.3432 (5)	0.4425 (4)	−0.0543 (3)	10.22 (6)	7.9 (4)	6.6 (3)	0.3 (3)	3.1 (3)	−5.4 (4)
N3	−0.3429 (7)	0.3256 (9)	−0.0500 (5)	7.3 (6)	13.0 (10)	13.6 (7)	0.8 (8)	0.9 (5)	−3.8 (7)
C15	−0.3571 (5)	0.2731 (5)	0.0181 (3)	5.3 (4)	4.7 (3)	3.3 (3)	0.7 (2)	1.5 (3)	−0.6 (3)
C16	−0.3644 (8)	0.1483 (6)	0.0125 (5)	15.5 (9)	14.6 (8)	11.5 (7)	2.7 (6)	3.5 (7)	5.6 (7)
C17	−0.3643 (9)	0.3170 (8)	0.0913 (5)	20.6 (11)	16.8 (9)	11.5 (8)	−5.3 (7)	7.2 (8)	−5.5 (9)

Table V. Final Atomic Positional and Thermal ($\times 10^2$) Parameters for $[MoO_2(SCH_2CH_2NHCH_2CH_2SCH_2CH_2S)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.00364 (3)	0.40856 (2)	0.28371 (3)	1.69 (1)	2.99 (2)	2.34 (2)	−0.11 (2)	0.07 (2)	0.11 (2)
S1	0.12268 (8)	0.46682 (8)	0.13844 (11)	3.41 (6)	4.16 (7)	2.72 (6)	0.54 (6)	0.72 (5)	−0.33 (6)
S2	0.11335 (8)	0.26077 (7)	0.24388 (11)	3.33 (6)	3.32 (6)	3.13 (6)	−0.63 (6)	0.45 (5)	0.16 (5)
S3	−0.05580 (9)	0.30954 (8)	0.44554 (12)	4.22 (7)	3.71 (7)	3.70 (7)	0.10 (6)	1.75 (6)	−0.35 (6)
N1	0.1405 (2)	0.4302 (2)	0.4128 (3)	2.01 (17)	3.63 (22)	1.92 (17)	−0.57 (16)	0.01 (15)	−0.11 (16)
O1	−0.0467 (2)	0.5005 (2)	0.3562 (3)	2.70 (15)	3.30 (17)	3.66 (18)	−0.44 (16)	0.81 (15)	0.76 (14)
O2	−0.0690 (2)	0.3780 (2)	0.1600 (3)	2.65 (16)	6.00 (23)	3.50 (18)	−0.40 (18)	−0.67 (15)	−0.46 (16)
C1	0.2188 (3)	0.5100 (3)	0.2365 (4)	3.1 (2)	3.7 (3)	5.5 (3)	0.9 (3)	0.2 (3)	
C2	0.1898 (3)	0.5135 (3)	0.3737 (4)	3.4 (3)	4.3 (3)	4.3 (3)	−0.5 (3)	−0.8 (2)	−1.0 (2)
C3	0.2043 (3)	0.3534 (3)	0.4372 (4)	2.5 (2)	4.4 (3)	3.1 (3)	0.2 (2)	−0.3 (2)	0.1 (2)
C4	0.2234 (3)	0.2958 (3)	0.3223 (4)	2.3 (2)	3.8 (3)	4.4 (3)	−0.1 (2)	0.1 (2)	0.8 (2)
C5	0.0647 (3)	0.1777 (3)	0.3522 (5)	5.0 (3)	2.5 (3)	5.3 (3)	0.1 (3)	0.6 (3)	−0.3 (2)
C6	−0.0420 (3)	0.1994 (3)	0.3780 (4)	4.9 (3)	3.7 (3)	4.6 (3)	0.3 (3)	1.3 (3)	−1.7 (2)

Table VI. Selected Bond Lengths (Å) and Angles (Deg) for $[MoO_2L]$

Molecule 1

Mo1-S1	2.420 (4)	N1-C2	1.53 (2)
Mo1-S2	2.408 (4)	N1-C3	1.48 (2)
Mo1-O1	1.693 (9)	N1-C7	1.44 (2)
Mo1-O2	1.684 (7)	C3-C4	1.45 (2)
Mo1-N1	2.401 (9)	N2-C4	1.52 (2)
Mo1-N2	2.411 (11)	N2-C5	1.53 (2)
S1-C1	1.77 (2)	N2-C8	1.47 (2)
S2-C6	1.769 (12)	C5-C6	1.44 (2)
C1-C2	1.36 (2)		
S1-Mo1-S2	160.6 (2)	Mo1-N1-C3	109.5 (6)
S1-Mo1-O1	104.2 (4)	Mo1-N-C7	113.5 (9)
S1-Mo1-O2	88.8 (3)	C2-N1-C3	113.3 (11)
S1-Mo1-N1	78.2 (3)	C2-N1-C7	105.3 (9)
S1-Mo1-N2	86.1 (3)	C3-N1-C7	107.6 (11)
S2-Mo1-O1	88.9 (4)	Mo1-N2-C4	106.9 (7)
S2-Mo1-O2	100.5 (3)	Mo1-N2-C5	113.0 (8)
S2-Mo1-N1	88.0 (3)	Mo1-N2-C8	111.9 (9)
S2-Mo1-N2	77.1 (3)	C4-N2-C5	109.4 (11)
O1-Mo1-O2	109.1 (5)	C5-N2-C8	107.6 (11)
O1-Mo1-N1	89.1 (4)	C5-N2-C8	107.9 (9)
O1-Mo1-N2	158.8 (4)	S1-C1-N1	119.8 (14)
O2-Mo1-N1	159.9 (4)	C1-C2-N1	115.4 (11)
O2-Mo1-N2	89.3 (4)	N1-C3-C4	115.0 (12)
N1-Mo1-N2	74.8 (3)	C3-C4-N2	111.0 (12)
Mo1-S1-C1	102.8 (6)	N2-C5-C6	111.5 (13)
Mo1-S2-C6	98.8 (5)	C5-C6-S2	111.5 (8)
Mo1-N1-C2	107.6 (8)		

Molecule 2

Mo2-S3	2.429 (5)	N3-C10	1.50 (2)
Mo2-S4	2.410 (5)	N3-C11	1.42 (3)
Mo2-O3	1.677 (9)	N3-C15	1.58 (2)
Mo2-O4	1.750 (10)	C11-C12	1.42 (2)
Mo2-N3	2.363 (9)	N4-C12	1.44 (2)
Mo2-N4	2.435 (12)	N4-C13	1.40 (2)
S3-C9	1.80 (2)	N4-C16	1.51 (2)
S4-C14	1.76 (2)	C12-C14	1.42 (3)
C9-C10	1.45 (2)		
S3-Mo2-S4	161.2 (2)	Mo2-N3-C11	113.5 (9)
S3-Mo2-O3	103.6 (4)	Mo2-N3-C15	101.4 (11)
S3-Mo2-O4	84.4 (4)	C10-N3-C11	112.7 (11)
S3-Mo2-N3	76.8 (3)	C10-N3-C15	105.7 (12)
S3-Mo2-N4	86.1 (3)	C11-N3-C15	113.1 (13)
S4-Mo2-O3	91.8 (4)	Mo2-N4-C12	107.5 (9)
S4-Mo2-O4	101.3 (3)	Mo2-N4-C13	113.1 (10)
S4-Mo2-N3	91.9 (3)	Mo2-N4-C16	111.2 (10)
S4-Mo2-N4	76.2 (3)	C12-N4-C13	110.2 (11)
O3-Mo2-O4	107.8 (7)	C12-N4-C16	108.7 (13)
O3-Mo2-N3	92.9 (5)	C13-N4-C16	106.3 (12)
O3-Mo2-N4	161.0 (5)	S3-C9-C10	114.7 (13)
O4-Mo2-N3	154.9 (5)	C9-C10-N3	111.3 (12)
O4-Mo2-N4	89.3 (5)	N3-C11-C12	116.7 (16)
N3-Mo2-N4	73.1 (4)	C11-C12-N4	117.5 (18)
Mo2-S3-C9	104.3 (5)	N4-C13-C14	119.9 (20)
Mo2-S4-C14	103.2 (7)	C13-C14-S4	115.2 (14)
Mo2-N3-C10	109.6 (9)		

Table VII. Selected Bond Lengths (Å) and Angles (Deg) for $[MoO_2L']$

Mo-S	2.408 (2)	C1-C2	1.49 (1)
Mo-N	2.486 (5)	N-C2	1.52 (1)
Mo-O	1.704 (6)	N-C3	1.469 (9)
S-C1	1.783 (7)	N-C5	1.469 (9)
S-Mo-S′	160.34 (7)	S-C1-C2	110.1 (5)
S-Mo-N	77.4 (1)	C1-C2-N	111.3 (6)
S-Mo-N′	87.6 (1)	C2-N-C3	105.9 (5)
S-Mo-O	99.5 (2)	C2-N-C5	109.0 (5)
S-Mo-O′	92.0 (2)	C3-N-C5	106.8 (5)
S′-Mo-N	87.6 (1)	C2-N-Mo	111.1 (3)
N-Mo-N′	81.1 (1)	C3-N-Mo	117.0 (4)
N-Mo-O	86.3 (2)	C5-N-Mo	106.8 (4)
O-Mo-O′	107.8 (3)	N-C3-C4	119.9 (5)
Mo-S-C1	99.0 (3)	C3-C4-C3′	122.1 (6)

Table VIII. Selected Intramolecular Bond Lengths (Å) and Angles (Deg) for $[MoO_2(SC_6H_4NHCH_2CH_2NHC_6H_4S)]$

Mo1-S1	2.429 (2)	N1-C7	1.516 (5)
Mo1-S2	2.426 (2)	C7-C8	1.515 (7)
Mo1-O1	1.715 (3)	N2-C8	1.512 (5)
Mo1-O2	1.708 (3)	N2-C14	1.452 (7)
Mo1-N1	2.357 (3)	C9-C10	1.377 (8)
Mo1-N2	2.379 (3)	C10-C11	1.391 (8)
S1-C1	1.756 (5)	C11-C12	1.368 (9)
S2-C9	1.767 (5)	C12-C13	1.382 (9)
C1-C2	1.377 (8)	C13-C14	1.389 (7)
C2-C3	1.390 (7)	O3-C15	1.34 (11)
C3-C4	1.396 (9)	N3-C15	1.293 (11)
C4-C5	1.384 (9)	N3-C16	1.435 (9)
C5-C6	1.392 (6)	N3-C17	1.399 (10)
N1-C6	1.438 (7)		
S1-Mo-S2	156.5 (1)	C5-C6-N1	120.3 (5)
S1-Mo-O1	89.3 (1)	C1-C6-N1	119.7 (4)
S1-Mo-O2	103.4 (1)	C6-N1-Mo	114.2 (3)
S1-Mo-N1	77.5 (1)	C6-N1-C7	110.8 (4)
S1-Mo-N2	83.1 (1)	C7-N1-Mo	109.8 (2)
S2-Mo-O1	103.6 (1)	N1-C7-C8	108.0 (4)
S2-Mo-O2	90.9 (1)	C7-C8-N2	108.6 (4)
S2-Mo-N1	84.5 (1)	C8-N2-Mo	109.0 (2)
S2-Mo-N2	77.5 (1)	C14-N2-Mo	113.7 (3)
O1-Mo-O2	109.9 (1)	C8-N2-C14	112.4 (3)
O1-Mo-N1	160.1 (2)	N2-C14-C13	119.4 (5)
O1-Mo-N2	89.1 (1)	N2-C14-C9	119.5 (4)
O2-Mo-N1	87.9 (1)	C14-C13-C12	119.2 (6)
O2-Mo-N2	159.8 (1)	C13-C12-C11	119.9 (5)
N1-Mo-N2	74.7 (1)	C12-C11-C10	121.1 (6)
Mo-S1-C1	102.3 (2)	C11-C10-C9	119.8 (6)
S1-C1-C2	120.8 (4)	C10-C9-C14	118.9 (5)
S1-C1-C6	120.0 (4)	C10-C9-S2	121.1 (5)
C2-C1-C6	119.3 (4)	C14-C9-S2	120.1 (4)
C1-C2-C3	121.1 (6)	O3-C15-N3	120.6 (8)
C2-C3-C4	119.5 (6)	C15-N3-C16	115.5 (7)
C3-C4-C5	119.6 (5)	C15-N3-C17	120.3 (7)
C4-C5-C6	120.5 (5)	C16-N3-C17	115.2 (6)
C5-C6-C1	120.0 (5)		

chemical properties of these complexes may be related to this inherent strain and to the ability of L to expand valence angles in accomodating other molybdenum oxidation states and geometries. Thus, the S1–Mo–N1 angle may expand to 80.8° in the Mo(V) species $[Mo_2O_3L_2]$[38] and the central N1–Mo–N2

Table IX. Selected Intramolecular Bond Lengths (Å) and Angles (Deg) for $[MoO_2(SCH_2CH_2NHCH_2CH_2SCH_2CH_2S)]$

Mo-S1	2.418 (1)	C2-N1	1.477 (6)
Mo-S2	2.708 (1)	N1-C3	1.468 (5)
Mo-S3	2.415 (1)	C3-C4	1.519 (6)
Mo-O1	1.721 (3)	C4-S2	1.810 (4)
Mo-O2	1.718 (3)	S2-C5	1.822 (5)
Mo-N1	2.358 (3)	C5-C6	1.532 (6)
S1-C1	1.806 (4)	C6-S3	1.805 (5)
C1-C2	1.518 (6)		
S1-Mo-S2	79.2 (1)	S2-Mo-S3	78.7 (1)
S1-Mo-S3	155.2 (1)	S2-Mo-O1	160.9 (1)
S1-Mo-O1	106.0 (1)	S2-Mo-O2	89.4 (1)
S1-Mo-O2	89.9 (1)	S2-Mo-N1	75.9 (1)
S1-Mo-N1	77.4 (1)		
S3-Mo-O1	91.7 (1)	C2-N1-Mo	108.6 (2)
S3-Mo-O2	100.9 (1)	C3-N1-Mo	108.4 (2)
S3-Mo-N1	86.4 (1)	N1-C3-C4	113.7 (3)
O1-Mo-O2	108.8 (1)	C3-C4-S2	113.0 (3)
O1-Mo-N1	87.2 (1)	C4-S2-C5	102.2 (2)
O2-Mo-N1	162.0 (1)	C4-S2-Mo	99.2 (1)
Mo-S1-C1	104.8 (2)	C5-S2-Mo	104.4 (1)
S1-C1-C2	112.2 (3)	S2-C5-C6	108.9 (3)
C1-C2-N1	111.4 (4)	C5-C6-S3	111.4 (3)
C2-N1-C3	115.5 (3)	C6-S3-Mo	103.7 (2)

angle to 79.6° in $Mo(N_2C_6H_4OCH_3)_2L$.[39]

The ligand geometry of $[MoO_2L]$ is unexceptional for complexes of this type.[38–41] Atoms C1 and C2 are on opposite sides of the N1–Mo–S1 plane, and atoms C5 and C6 are on opposite sides of the N2–Mo–S2 plane in molecule 1, producing a symmetric skew conformation for the two C–N–Mo–S–C rings.[42] The two methyl groups are on opposite sides of the diamine chelate rings. Molecule 2 exhibits an identical conformation.

$[MoO_2L']$. The structure of $[MoO_2L']$ has a crystallographic twofold axis bisecting the O···P′ vector and passing through the molybdenum and C4 of the trimethylene bridge between the amine nitrogen donors. The overall structural effect of introducing an additional methylene group to the central chelate ring is thus to produce a more regular geometry and concomitantly a less severely strained chelate configuration. The effect of the additional methylene group is most apparent in the N–Mo–N′ angle of 81.1 (1)° in $[MoO_2L']$ as compared to angles of 75.9 (3) and 76.6 (3)° in $[MoO_2L]$.

The Mo–O and Mo–S distances and the general pattern of valence angles in $[MoO_2L']$ are unexceptional and follow trends discussed above in the general consideration of structures of this type (see Table X).

An unusual feature of the structure is the exceptionally long Mo–N bond length of 2.486 (5) Å. Comparison to other Mo–N bond lengths trans to the strongly bound oxo group lead us to anticipate a bond length in the range 2.35–2.42 Å.[18,19] The only other exception to this trend is the Mo–N2 bond distance of 2.510 (2) Å in $[MoO_2(SCH_2CH_2)_2NCH_2CH_2NMe_2]$,[9] where the steric influence of the two bulky methyl substituents associated with N2 produce the dominant effect in bond lengthening. This suggests a significantly weakened Mo–N interaction for $[MoO_2L']$, which may account for the preferential reduction of $[MoO_2L']$ to $[Mo_2O_4(L'H)_2]$ rather than reduction to the more common $[Mo_2O_3L'_2]$.[38] The stability of the 14-membered ring in $[Mo_2O_4(L'H)_2]$ is associated with the formation of the H–N–C–C–C–N ring in the stable chair conformation.[41] The long Mo–N bond length in $[MoO_2L']$ may allow facile protonation at an amine nitrogen and consequent ligand rearrangement to adopt the preferred chair conformation, thus favoring formation of the unusual dimer $[Mo_2O_4(L'H)_2]$.

The ligand geometry of $[MoO_2L']$ is unexceptional for complexes of L′. Atoms C1 and C2 are on opposite sides of the N–Mo–S plane to produce a C2–N–Mo–S–C1 chelate ring with a symmetric skew configuration. The geometric constraints of the twofold axis passing through the Mo and C4 atoms require that the C4–C3–N–Mo–N′–C3′ six-membered ring adopt a skew conformation rather than the symmetric chair conformation adopted by the diamine ring in $(FeL')_2$[40] and $[FeL'(NO)]$.[41] The two methyl groups C5 and C5′ are on opposite sides of the N–Mo–N′ plane.

A further consequence of the additional methylene bridge between the diamine donors is to open the N···N′ ligand bite distance to 3.23 Å, a significant and anticipated increase from values in the 2.90-Å range for $[MoO_2L]$ and $[MoO_2L'']$, as illustrated in Table IX.

$[MoO_2(SNSS)]$. The structure of $[MoO_2(SNSS)]$ was determined in order to systematize the effects of thioether substitution into the central five-membered chelate ring of tetradentate ligands with MoO_2^{2+}. The overall geometric consequence is to remove the symmetry of the complex.

The bond lengths and angular parameters are unexceptional as shown in Tables IX and XI. As anticipated, the thioether sulfur occupies a position trans to a terminal oxygen, with

Table X. Intramolecular Contacts Defining the Octahedral Edges

	$[MoO_2L]$				
	1	2	$[MoO_2L']^a$	$[MoO_2L'']$	$[MoO_2(tox)_2]^b$
O1···O2	2.734	2.775	2.749	2.802	2.726
O1···S1	3.257	3.253	3.171	3.278	3.294
O1···S2	2.918	2.964	2.998	2.989	2.899
O1···N1	2.902	2.957	2.992	2.860	2.908
O2···S1	2.900	2.887	2.998	2.956	2.907
O2···S2	3.181	3.215	3.171	2.989	3.224
O2···N2	2.925	2.984	2.992	2.911	2.844
S1···N1 (bite)	3.039	2.982	3.061	2.997	2.975
S1···N2	3.292	3.336	3.338	3.190	3.327
S2···N1	3.329	3.437	3.388	3.217	3.398
S2···N2 (bite)	3.000	2.981	3.061	3.009	2.944
N1···N2 (bite)	2.913	2.902	3.233	2.874	3.095

	$[MoO_2(SNSS)]$		$[MoO_2(SNSS)]$		$[MoO_2(SNSS)]$		$[MoO_2(SNSS)]$
O1-O2	2.796	O1-N1	2.851	O2-S3	3.217	S2-S3 (bite)	3.255
O1-S1	3.332	O2-S1	2.966	S1-N1 (bite)	2.987	S2-N1 (bite)	3.127
O1-S3	3.007	O2-S2	3.191	S1-S2	3.276	S3-N1	3.269

[a] For purposes of comparison ligands have been numbered as for $[MoO_2L]$ and $[MoO_2L']$; thus, O, N, S, O′, N′, and S′ are labeled as O1, N1, S1, O2, N2, and S2 to follow the same convention. [b] Ligands have been relabeled to conform to the convention established for $[MoO_2L]$.

Table XI. Comparison of Relevant Bond Lengths and Angles for MoO_2^{2+} Core Complexes with Amine Nitrogen and Thiolate Sulfur Donors

(a) Complexes of the Types $[MoO_2(SNNS)]$ and $[MoO_2(SN)_2]$

	$[MoO_2L]$						
	1	2	$[MoO_2L']$	$[MoO_2L'']$	MoO_2-$[(SCH_2CH_2)_2$-NCH_2CH_2-$NMe_2]$	$[MoO_2(tox)_2]$	MoO_2-$SCMe_2$-CH_2CH_2-$NHMe]_2$
Mo-O1	1.693 (9)	1.677 (9)	1.704 (6)	1.708 (3)	1.699 (2)	1.694 (6)	1.723 (5)
Mo-O2	1.684 (7)	1.750 (10)	*a*	1.715 (3)	1.705 (2)	1.712 (7)	1.711 (5)
Mo-N1	2.401 (9)	2.363 (9)	2.486 (5)	2.357 (3)	2.372 (2)	2.382 (9)	2.262 (9)
Mo-N2	2.411 (11)	2.435 (12)	*a*	2.379 (3)	2.510 (2)	2.374 (9)	2.277 (8)
Mo-S1	2.420 (4)	2.429 (5)	2.408 (2)	2.429 (2)	2.420 (1)	2.411 (3)	2.420 (3)
Mo-S2	2.408 (4)	2.410 (5)	*a*	2.426 (2)	2.409 (1)	2.411 (3)	2.409 (3)
O1-Mo-O2	109.1 (5)	107.8 (7)	107.8 (1)	109.9 (1)	107.9 (1)	106.3 (3)	122.2 (3)
S1-Mo-N1	78.2 (3)	76.8 (3)	77.4 (1)	77.5 (1)	*b*	76.7 (3)	72.9 (3)
S2-Mo-N2	77.2 (3)	76.2 (3)	*a*	77.5 (1)	*b*	75.9 (3)	74.6 (2)
N1-Mo-N2	74.8 (3)	73.1 (4)	81.1 (1)	74.7 (1)	*b*	81.2 (3)	144.0 (3)
S1-Mo-S2	160.6 (2)	161.2 (2)	160.34 (7)	156.5 (1)	154.3 (3)	160.9 (1)	69.8 (19)

(b) Complexes of the Type $[MoO_2(SNSS)]$

	MoO_2-$[SCH_3CH_2$-$NHCH_2$-CH_2SCH_2-$CH_2S]$	MoO_2-$(SCH_2CH_2)_2$-NCH_2CH_2-$SCH_3]$		MoO_2-$[SCH_2CH_2$-$NHCH_2$-CH_2SCH_2-$CH_2S]$	MoO_2-$[(SCH_2$-$CH_2)_2$-NCH_2CH_2-$SCH_3]$
Mo-O1	1.721 (3)	1.695	O1-Mo-O2	108.8 (1)	*b*
Mo-O2	1.718 (3)	1.694	S1-Mo-N1	77.4 (1)	*b*
Mo-N1	2.358 (3)	2.418	S2-Mo-N1	75.9 (1)	*b*
Mo-S1	2.418 (1)	2.411	S3-Mo-S2	78.7 (1)	*b*
Mo-S2	2.708 (1)	2.769	S1-Mo-S3	155.2 (1)	*b*
Mo-S3	2.415 (1)	2.400			

[a] Value crystallographically identical with the previous entry in the table. [b] Not reported.

Table XII. Dihedral Angles (Deg) for $[MoO_2L'']$

plane 1	plane 2	angle
ligand 1[a]	ligand 2[b]	109.1
ligand 1	Mo, N1, S1	22.5
ligand 2	Mo, N2, S2	21.4
Mo, N1, S1	Mo, N2, S2	74.6

[a] Ligand 1 = N1-C1C2C3C4C5C6-S1. [b] Ligand 2 = N2-C9C10C11C12C13C14-S2.

S2-Mo-O1 of 160.9 (1)°, and exhibits a Mo-S bond length of 2.708 (1) Å, a value in the range of 2.68-2.80 Å observed for Mo-S trans to oxo groups in the dithioacid complexes of the type $[MoO_2(LL)_2]$ and $[Mo_2O_3(LL)_4]$. This distance is significantly shorter than the 2.769-Å Mo-thioether sulfur distance in $[MoO_2(SCH_2CH_2)_2NCH_2CH_2SCH_3]$.[9] In the present case the thioether occupies an internal position in the chelate ring system and lies at the intersection of two five-membered rings.

In contrast in $[MoO_2(SCH_2CH_2)_2NCH_2CH_2SCH_3)]$, the thioether ligand is at the terminus of the ring systems. It may be that this lack of constraint allows the longer distance to occur.

The ligand bite distances, S2⋯S3 and S2⋯N1, are expanded to 3.255 and 3.127 Å, as a result of introducing the bulky thioether donor into the central chelate ring. Comparison of structural parameters of $[MoO_2(SNSS)]$ with those reported for the complex with a tripodal ligand with a similar NS_3 donor set[9] in Table XI reveals that the geometry is unexceptional for this type of complex.

An analysis of the ligand geometry reveals that the five-membered chelate ringe C1-S1-Mo-N1-C2 has atoms C1 and C2 on opposite sides of the N1-Mo-S1 plane in an asymmetric skew configuration. Atoms C5 and C6 of the C5-S2-Mo-S3-C6 ring are on opposite sides of the S2-Mo-S3 plane but with equal displacements producing a symmetric skew conformation. Since C3 is nearly in the N1-Mo-S2 plane while C4 is considerably displaced to the other side (0.4 Å), the C3-N1-Mo-S2-C4 chelate ring is best described as an asymmetric envelope.[42]

The structure reveals that each molecule of $[MoO_2(SNSS)]$ is hydrogen bonded to one neighbor wth O1⋯N1 at 2.97 Å and O1⋯H(N1) at 2.06 Å. This pattern of hydrogen bonding is distinct from that previously observed for $[MoO_2(SCMe_2CH_2NHMe)_2]$[10] where infinite chains are formed and from $[MoO_2L'']$ where a molecule of crystallization also participates in the hydrogen-bonding pattern.

Results and Discussion

General Trends. The structures containing the MoO_2^{2+} core with ligands possessing the N_2S_2 donor set, $[MoO_2L]$, $[MoO_2L']$, and $[MoO_2L']$, are distinctly similar in overall geometry and in the conformation of the multidentate liand. As shown in Figures 1-3 all are monomeric molecules displaying approximate twofold symmetry (noncrystallographic with the exception of $[MoO_2L']$) with the C_2 axis bisecting the O-Mo-O, N-Mo-N, and S-Mo-S valence angles. The coordination geometry about the molybdenum atom is severely distrted from idealized octahedral geometry, coordinating in all cases to the amine nitrogen and thiolate sulfur donors of the tetradentate ligand and to two unidentate oxo groups. The oxo groups, in common with all complexes possessing the MoO_2^{2+} core structurally characterized to date,[9,10,18-33] occupy cis positions. The thiolate donors from the tetradentate ligands are trans to each other, and the amine nitrogen atoms are trans to the terminal oxo groups.

Replacement of an amine donor by a thioether sulfur in $[MoO_2(SNSS)]$ removes the C_2 symmetry discussed above as one amine nitrogen is replaced by a thioether sulfur. Except for this difference, the overall configuration of donor groups about the central molybdenum atom is as above: the oxo groups are cis to each other and the thiolate sulfur donors are trans to each other, placing the nitrogen and thioether group in positions trans to the terminal oxo groups.

The invariant cis configuration of the oxo groups in complexes possessing the MoO_2^{2+} core has been rationalized on the basis of the multiple-bond character of the Mo–O_t interaction, which requires a cis orientation for most effective overlap with the metal π orbitals.[19] The favored trans configuration of the thiolate sulfur donors may also be rationalized on the basis of simple steric arguments, with use of a stereochemical model based on nonbonded intramolecular van der Waals interactions defined in terms of steric angles.[34] Alternatively, an electronic interpretation also places the S donors along an axis not coincident with either Mo–O_t, and they are thus trans to each other. The only exceptions to the trans thiolate arrangement are $[MoO_2(MeNHCH_2CMe_2S)_2]$,[10] $[MoO_2(Me_2NCH_2CMe_2S)_2]$, and $[MoO_2(MeHNCMe_2CMe_2S)_2]$;[50] a trans arrangement would lead to steric interference between *N*-methyl and *C*-methyl substituents of the same or different ligands, consequently providing a unique example of cis-thiolate geometry.

In all four complexes presented in this study, the molybdenum atom is displaced from the "center" of each irregular octahedron toward the terminal oxo group. These displacements fall in the range of 0.25–0.35 Å from the respective OSNS planes. This is a common effect in complexes with the MO_2^{2+} core, and a more detailed discussion may be found in a recent paper.[30]

A general feature of all the structures is the pattern of angular distortions of the coordination polyhedra in complexes with the MoO_2^{2+} core with tetradentate ligands. For example, in $[MoO_2L'']$ the O2–Mo–S1 angle is 89.3 (1)° while the O2–Mo–S2 angle is 103.6 (1)°, a significant difference. Likewise, the O1–Mo–S1 and O1–Mo–S2 angles are 103.4 (1) and 90.9 (1)°, respectively. Also, the O1–Mo–N1 and O2–Mo–N2 angles of 87.9 (1) and 89.1 (1)° are unusually small when compared to those of compounds containing only unidentate ligands where angles involving terminal oxo groups and equatorial atoms are greater than 90°.

As pointed out previously by Yamanouchi and Enemark,[35] these angular distortions are related to nonbonded repulsions. Thus, in $[MoO_2L'']$, the O1···S2 distance of 2.99 Å is considerably shorter than the O1···S1 distance of 3.28 Å and is also shorter than the calculated van der Waals distance of 3.25 Å. As illustrated in Table X, the pattern is consistent throughout the series of complexes with N_2S_2 donors and similar to that observed for $[MoO_2(tox)_2]$.[30] It has been noted that short nonbonded contacts occur when the Mo–oxo group and the chelate ring are coplanar, whereas longer nonbonded contacts, comparable to the sum of the van der Waals radii, occur for the Mo–O_t group perpendicular to the Mo–chelate plane. The irregular geometries of complexes possessing the MoO_2^{2+} core have been rationalized on the basis of the repulsions between the π-electron density in the short Mo–O_t bond and the electrons in the sp^2-type orbitals and π system of the ligand.[30] Alternatively, the sense of the distortions can be predicted by calculating the ligand–ligand repulsive energy with the assumption of a point charge or sphere model.[36]

Conclusions. In gross geometric features, the title compounds conform to the structural trends observed for other complexes possessing the MoO_2^{2+} core, recently analyzed by several authors. The complex $[MoO_2L'']$ is prototypical for complexes of MoO_2^{2+} with linear tetradentate ligands possessing N_2S_2 donor sets. The geometry of $[MoO_2L]$ is much more irregular than that observed for either $[MoO_2L']$ or $[MoO_2L'']$ in the series or for that previously reported for $[MoO_2(tox)_2]$.[30] Certainly, ligand constraints are important in determining chelate geometry in $[MoO_2L]$ and may provide a rationale for the unusual chemical and electrochemical properties of this species.

The structure of $[MoO_2L']$ is characterized by unusually long Mo–N distances, which may be reflected in the unusual chemical reduction of $[MoO_2L']$ to the 14-membered chelate complex $[Mo_2O_4(L'H)_2]$. The solution chemistry of $[MoO_2L']$ may also reflect the accessibility of the amine nitrogen to protic attack.[1]

The effect of thioether sulfur substitution for nitrogen in the central chelate $[MoO_2(SNSS)]$ lowers the overall symmetry of the structure. The thioether sulfur occupies a position trans to a terminal oxo group, leaving the thiolate sulfur groups mutually trans and cis to the oxo groups. The preferential thiolate configuration is maintained throughout the series of this study and appears to be disrupted only by the introduction of severe steric constraints.

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Registry No. MoO_2L, 80287-02-1; MoO_2L', 80287-01-0; MoO_2L'', 80287-03-2; $MoO_2(SNSS)$, 80228-84-8.

Supplementary Material Available: Listings of observed and calculated structure factors and calculated hydrogen atom positions (64 pages). Ordering information is given on any current masthead page.

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(50) Stiefel et al., manuscript in preparation.