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The Crystal and Molecular Structures of Dioxo Mo(VI) Complexes of Tripodal, Tetradentate N,S-donor Ligands

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The crystal and molecular structures of the complexes $MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, ***I*** *and* $MoO_2((SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2)$, ***II***, *have been determined from X-ray intensity data collected by counter methods. Compound **I** crystallizes in two forms, **Ia** and **Ib**. In form **Ia** the space group is* $P2_1/n$ *with cell parameters* $a = 7.235(2)$, $b = 7.717(2)$, $c = 24.527(6)$ Å, $\beta = 119.86(2)°$, $V = 1188(1)$ Å^3, $Z = 4$. *In form **Ib** the space group is* $P2_1/c$ *with cell parameters* $a = 14.945(5)$, $b = 11.925(5)$, $c = 14.878(4)$ Å, $\beta = 114.51(2)°$, $V = 2413(3)$ Å^3, $Z = 8$. *The molecules of **I** in **Ia** and **Ib** are very similar having an octahedral structure with* cis *oxo groups,* trans *thiolates (*cis *to both oxo groups) and N and thioether sulfur atoms* trans *to oxo groups. Average distances are Mo–O = 1.70, Mo–S (thiolate) = 2.40, Mo–N = 2.40 and Mo–S (thioether) = 2.79 Å. Molecule **II** crystallizes in space group* $P2_12_12_1$ *with* $a = 7.188(1)$, $b = 22.708(8)$, $c = 7.746(2)$ Å, $V = 1246(1)$ Å^3 *and* $Z = 4$. *The coordination about Mo is octahedral with* cis *oxo groups,* trans *thiolates and N atoms* trans *to oxo. Distances in the first coordination sphere are Mo–O = 1.705(2), 1.699(2), Mo–S = 2.420(1), 2.409(1) and Mo–N = 2.372(2), 2.510(2) Å. The conformational features of the complexes are discussed. Complex **I** displays Mo–O and Mo–S distances which are very similar to those found by EXAFS in sulfite oxidase. This similarity is discussed.*

Introduction

Studies of extended X-ray absorption fine structure (EXAFS) spectroscopy on the Mo enzymes xanthine oxidase [2, 3], xanthine dehydrogenase [4], sulfite oxidase [4, 5], and nitrate reductase [6] revealed that, in the oxidized forms of these enzymes, the Mo(VI) coordination sphere contains both terminal oxo groups and sulfur donors. These results have allowed structural comparisons to be made between simple Mo complexes and the Mo sites in these enzymes. The complexes MoO_2L with $L = (SCH_2CH_2)_2NCH_2CH_2X$, $X = SCH_3$ (compound **1**), and $X = N(CH_3)_2$ (compound **2**) were prepared as part of a program using aliphatic S-, N-, and O-donor ligands in attempts to obtain structural models for Mo-containing enzymes. The Mo–S and Mo–O distances in these complexes were originally predicted based on EXAFS measurements [7]. In a preliminary communication [8] we described the results of X-ray diffraction studies of these two complexes which confirmed the EXAFS results. Detailed comparison of the EXAFS spectra from these complexes with those from the oxidized forms of xanthine oxidase and sulfite oxidase revealed that one of these compounds (**1**) displayed a startling resemblance to sulfite oxidase [8]. In this paper we report the details of the X-ray crystallographic structures of two crystal forms of compound **1** and one of **2**.

All structurally characterized dioxomolybdenum(VI) complexes have been found to have their two oxo groups *cis* to each other [9–12]. Typically, the complexes have an octahedral structure, Mo–O_t distances of 1.70 ± 0.02 Å and an O_t–Mo–O_t angle of 106 ± 3° where O_t represents a terminal oxo ligand. Recently, a second structural type has been identified for MoO_2L_2 complexes [13–15] where L is a sterically hindered bidentate amine thiolate ligand. For complexes of this type, the coordination polyhedron is best described as a skew trapezoidal bipyramid with the N and S donors forming an approximate trapezoid with the oxo groups at the skewed apices. The Mo–O_t distances are slightly lengthened while the O_t–Mo–O_t angle is opened substantially compared to the octahedral structure. The two complexes described here fit into the category of octahedral complexes. However, because of the discovery of this second structural type it is important to specify in detail the characteristics of each structural type and to examine the features which may determine the stability of one structure over the other. This paper addresses the structural

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details of **1** and **2**. Other papers [16] describe the preparation and physical and chemical properties of the complexes discussed here as well as structural aspects [14, 17] of related complexes of both structural types.

Experimental

The complexes were synthesized via the reaction of $MoO_2(acac)_2$ with the appropriate ligand in methanol [16]. Crystals of compound **1** were grown from two solvent systems which produced different crystal forms. Crystal structures of both forms have been determined. Crystals of **1a** were grown by evaporation of 4:6:3 $CH_3CN/CH_2Cl_2/C_6H_6$ whereas a 1:1 $ClCH_2CH_2Cl/C_6H_5CH_3$ solvent yielded crystals of **1b**. Crystals of compound **2** were grown from $CH_2Cl_2/ClCH_2CH_2Cl$.

Data Collection and Reduction

All X-ray diffraction experiments were performed on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator using Mo-Kα radiation. The crystals were mounted on thin glass fibers with epoxy cement. The crystallographic data are summarized in Table I. The intensity data were processed as described previously [18]. For each structure, accurate cell parameters were determined from fifteen machine-centered reflections. Three standard reflections were monitored every 60 reflections and in no case was any significant fluctuation observed. Analytical absorption corrections were applied to the complete data sets. Further details concerning the collection and processing of the data for the individual structures are given below.

$MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, **1a**

This crystal form belongs to the monoclinic crystal system with $a = 7.235(2)$, $b = 7.717(2)$, $c = 24.527(6)$ Å, and $\beta = 119.86(2)°$. The systematic absences h0l, $h + l \neq 2n$ and 0k0, $k \neq 2n$ are consistent only with the space group $P2_1/n$. There are four molecules in the unit cell, and hence, one in the asymmetric unit. All reflections of the form +h, +k, ±l with $3° < 2\theta < 60°$ were collected.

$MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, **1b**

This crystal form also belongs to the monoclinic system. The cell constants are $a = 14.945(5)$, $b = 11.925(5)$, $c = 14.878(4)$ Å and $\beta = 114.51(2)°$. The systematic absences h0l, $l \neq 2n$ and 0k0, $k \neq 2n$ indicate that the space group is $P2_1/c$. There are two independent molecules in the asymmetric unit. Again, all reflections of the form +h, +k, ±l for $3° < 2\theta < 60°$ were measured.

$MoO_2((SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2)$, **2**

This compound belongs to the orthorhombic crystal system with $a = 7.188(1)$, $b = 22.708(8)$, and $c = 7.746(2)$ Å. The space group is $P2_12_12_1$ as is uniquely determined by the systematic absences h00, $h \neq 2n$; 0k0, $k \neq 2n$; and 00l, $l \neq 2n$. Since this is an acentric space group and anomalous scattering effects due to the Mo and S atoms are significant, a full sphere of data was collected through 30° in 2θ. Only the positive octant was collected for $30° < 2\theta < 60°$. After data processing, including the ab-

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

	1a	1b	2
Formula	$C_7H_{15}MoNO_2S_3$	$C_7H_{15}MoNO_2S_3$	$C_8H_{18}MoN_2O_2S_2$
a, Å	7.235(2)	14.945(5)	7.188(1)
b, Å	7.717(2)	11.925(5)	22.708(8)
c, Å	24.527(6)	14.878(4)	7.746(2)
β, deg	119.86(2)	114.51(2)	
V, Å^3	1188(1)	2413(3)	1264(1)
Z	4	8	4
d_{calc}, g/cm^3	1.887	1.857	1.756
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
Absorption coeff, cm^{-1}	15.6	15.4	13.2
Transmission factors			
max	84.3	96.4	67.9
min	55.4	74.9	44.3
Extinction coeff, e^{-2}			4.66×10^{-6}
Number of observations	2260	3615	2186
Number of variables	127	253	137
Error in obs of unit wt.	1.13	1.30	1.20
R, %	3.9	5.3	2.3
R_w, %	4.6	5.9	3.5

sorption correction, was complete, the equivalent data reflecting the strict 222 diffraction symmetry were averaged. The asymmetric unit consists of one complete molecule.

Structure Solution and Refinement

The structures were solved using standard heavy atom methods. The Mo atoms were located using Patterson maps and the remaining non-hydrogen atoms were located from subsequent difference Fourier maps. Because of the acentric space group for compound 2 both the originally determined coordinates and those generated for the enantiomorph were refined isotropically. A small difference between the agreement factors combined with direct inspection of the Friedel pairs indicated that the second choice of coordinates was correct. These were used in subsequent refinements.

All non-hydrogen atoms were refined anisotropically using full matrix least-squares. Hydrogen atoms were calculated assuming 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 as fixed contributions in the final least-squares cycles. In addition, inspection of the observed and calculated structure factors for compound 2 showed evidence for secondary extinction so that an extinction parameter was included in this refinement. Final difference Fourier maps showed no peaks higher than 20% of the height of a carbon atom peak. The final agreement factors are shown in Table I. The positional and thermal parameters are given in Table II. Calculated hydrogen atom positions and structure factor tables are included as supplementary material.

TABLE II. Positional and Thermal Parameters[a].

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, crystal form 1a									
Mo1	0.47010(5)	0.16430(5)	0.12852(2)	2.149(8)	1.89(1)	2.94(1)	0.35(1)	1.531(6)	0.31(1)
S1	0.3927(2)	0.3585(2)	0.04275(5)	3.36(3)	2.60(5)	2.94(3)	0.21(3)	1.95(2)	0.35(3)
S2	0.4225(2)	0.0719(2)	0.21421(6)	3.99(4)	4.39(6)	3.75(4)	0.78(5)	2.36(3)	1.65(4)
S3	0.0305(2)	0.1520(2)	0.05487(5)	2.49(3)	4.19(6)	2.83(3)	−0.68(4)	1.37(2)	−0.69(4)
O1	0.4581(5)	−0.0314(4)	0.0956(2)	5.6(1)	2.1(1)	7.3(1)	0.0(1)	4.60(8)	−0.7(1)
O2	0.7290(5)	0.2246(5)	0.1715(2)	2.1(1)	4.4(2)	3.9(1)	0.2(1)	1.13(8)	0.6(1)
N1	0.3441(5)	0.4226(5)	0.1557(2)	2.7(1)	2.5(1)	2.7(1)	−0.2(1)	1.48(8)	−0.6(1)
C1	0.3732(10)	0.5773(7)	0.1268(3)	9.8(3)	2.3(2)	7.9(2)	−0.5(2)	6.6(1)	−0.4(2)
C2	0.4929(8)	0.5503(7)	0.0918(2)	4.6(2)	2.4(2)	6.5(2)	−0.8(2)	3.8(1)	−0.6(2)
C3	0.4731(10)	0.4296(8)	0.2247(2)	6.1(2)	4.7(3)	3.0(2)	−1.0(2)	2.3(1)	−1.4(2)
C4	0.4826(12)	0.2718(10)	0.2587(3)	6.3(3)	6.6(4)	2.5(2)	1.0(3)	1.0(2)	−0.2(2)
C5	0.1138(8)	0.4055(8)	0.1411(2)	3.8(2)	4.3(2)	5.0(2)	1.0(2)	2.7(1)	−0.6(2)
C6	−0.034(8)	0.3505(8)	0.0779(3)	2.7(2)	4.0(2)	5.3(2)	0.6(2)	1.7(1)	0.2(2)
C1Me	−0.0889(8)	−0.0039(8)	0.0821(3)	3.8(2)	4.5(3)	5.8(2)	−1.2(2)	2.9(1)	−1.2(2)
$MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, crystal form 1b Molecule #1									
Mo1	0.88323(5)	0.79883(5)	0.63140(4)	2.87(2)	1.78(2)	2.49(2)	−0.01(2)	1.12(2)	0.17(2)
S1	0.7653(2)	0.7506(2)	0.4667(1)	3.17(8)	4.8(1)	2.24(6)	0.36(8)	0.81(5)	0.40(7)
S2	0.9951(2)	0.7488(2)	0.7952(1)	3.91(9)	3.80(9)	2.49(7)	0.08(8)	0.69(6)	−0.41(6)
S3	0.9780(1)	0.6295(2)	0.5723(1)	3.09(7)	2.99(7)	2.48(5)	0.21(6)	1.52(4)	0.18(6)
O1	0.9585(4)	0.8881(4)	0.6049(4)	4.6(2)	3.0(2)	5.2(2)	−0.8(2)	2.6(2)	0.2(2)
O2	0.8021(4)	0.8761(4)	0.6590(4)	4.4(2)	2.8(2)	3.4(2)	0.7(2)	1.8(2)	0.2(2)
N1	0.8140(4)	0.6279(5)	0.6584(4)	2.6(2)	2.0(2)	4.2(2)	0.0(2)	2.1(2)	0.3(2)
C1	0.7108(6)	0.6143(8)	0.5830(7)	2.6(3)	5.4(4)	7.4(5)	−0.6(3)	1.9(3)	2.1(4)
C2	0.6769(7)	0.6921(14)	0.5022(7)	2.9(4)	17.(1)	3.9(4)	−2.3(6)	0.4(3)	1.7(6)
C3	0.8161(6)	0.6468(7)	0.7594(5)	6.4(3)	3.2(3)	5.3(3)	0.8(3)	4.9(2)	0.7(3)
C4	0.9185(7)	0.6659(8)	0.8377(5)	7.6(5)	4.4(4)	2.6(3)	0.9(4)	2.7(2)	0.4(3)
C5	0.8703(5)	0.5252(6)	0.6594(5)	3.2(3)	1.9(2)	3.6(2)	−0.1(2)	2.0(2)	0.0(2)
C6	0.8999(6)	0.5169(6)	0.5739(5)	3.7(3)	2.1(3)	3.9(3)	−0.2(2)	2.1(2)	−0.7(3)
C1Me	1.0931(6)	0.5854(8)	0.6666(6)	2.5(3)	4.6(4)	3.9(3)	0.8(3)	1.1(2)	0.8(3)
$MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, crystal form 1b Molecule #2									
Mo1	0.35902(5)	0.72384(5)	0.65062(4)	3.23(2)	2.03(2)	1.97(2)	0.36(2)	1.32(1)	0.26(2)

(continued overleaf)

TABLE II *(continued)*

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S1	0.2504(1)	0.8512(2)	0.6821(1)	3.96(8)	3.50(8)	2.81(6)	0.97(7)	1.83(5)	0.02(6)
S2	0.4672(2)	0.6749(2)	0.5749(1)	3.54(8)	4.9(1)	3.51(7)	0.82(8)	1.94(5)	−0.50(7)
S3	0.4748(2)	0.9142(2)	0.7201(1)	3.26(8)	3.37(8)	2.68(7)	0.05(8)	0.31(6)	−0.50(7)
O1	0.4270(4)	0.6780(5)	0.7665(4)	5.6(3)	4.4(2)	2.5(2)	2.3(2)	1.7(2)	1.0(2)
O2	0.2698(4)	0.6279(4)	0.5895(4)	4.4(2)	2.7(2)	5.0(2)	−1.2(2)	2.7(2)	−1.1(2)
N1	0.3081(4)	0.8475(5)	0.5109(4)	2.4(2)	2.8(2)	1.7(2)	−0.2(2)	0.6(2)	0.4(2)
C1	0.2112(6)	0.9002(8)	0.4914(6)	3.2(3)	4.6(4)	3.0(3)	0.6(3)	0.8(2)	0.9(3)
C2	0.1641(7)	0.8581(9)	0.5544(6)	3.3(3)	6.3(5)	4.6(4)	1.6(4)	1.7(3)	1.3(4)
C3	0.2972(6)	0.7706(8)	0.4269(5)	4.3(3)	4.8(4)	1.7(2)	−1.1(3)	1.0(2)	−0.6(3)
C4	0.3898(7)	0.7058(8)	0.4463(6)	5.6(4)	4.7(4)	3.2(3)	−0.2(4)	2.4(2)	−0.6(3)
C5	0.3796(6)	0.9359(7)	0.5169(6)	4.1(4)	3.4(3)	3.1(3)	−1.1(3)	1.0(2)	0.9(3)
C6	0.4154(7)	1.0019(6)	0.6128(6)	3.6(4)	2.1(3)	5.1(4)	−0.6(3)	0.3(3)	0.0(3)
C1Me	0.5956(6)	0.8985(8)	0.7215(7)	3.1(4)	4.7(4)	4.4(4)	0.1(4)	0.3(3)	−0.3(4)
$MoO_2((SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2)$, **2**									
Mo1	0.83448(3)	0.61279(1)	0.82502(3)	1.935(6)	2.487(7)	2.081(6)	0.219(6)	0.323(7)	0.155(6)
S1	0.7568(1)	0.69601(4)	0.6436(1)	3.29(3)	3.89(3)	4.04(3)	0.90(3)	−0.04(3)	1.37(3)
S2	1.0084(1)	0.52583(3)	0.9006(1)	3.35(3)	2.75(2)	4.88(4)	0.49(3)	0.17(3)	0.92(3)
O1	0.8010(4)	0.6414(1)	1.0261(3)	4.0(1)	4.9(1)	2.60(7)	0.87(9)	0.59(8)	−0.22(8)
O2	0.6384(3)	0.5757(1)	0.7684(3)	2.63(8)	4.10(9)	4.6(1)	−0.54(8)	−0.12(8)	0.08(9)
N1	0.9987(4)	0.5906(1)	0.5675(3)	2.76(9)	4.1(1)	2.36(8)	0.00(9)	0.31(9)	−0.63(8)
N2	1.1420(4)	0.6647(1)	0.8467(3)	2.49(9)	2.76(8)	3.9(1)	−0.28(7)	−0.21(9)	−0.29(8)
C1	0.9258(8)	0.6216(2)	0.4147(4)	5.9(2)	9.8(3)	2.2(1)	2.5(2)	−0.4(1)	−0.4(2)
C2	0.7405(6)	0.6515(3)	0.4485(4)	4.1(2)	10.7(3)	2.7(1)	1.1(2)	−1.0(1)	0.7(2)
C3	0.9830(6)	0.5267(2)	0.5418(5)	3.7(1)	4.3(1)	5.2(1)	−0.1(1)	0.6(1)	−2.4(1)
C4	1.0327(8)	0.4900(2)	0.6957(6)	7.6(3)	3.0(1)	7.8(2)	0.0(2)	1.4(3)	−1.4(2)
C5	1.2032(5)	0.6057(2)	0.5897(5)	2.7(1)	4.8(1)	4.0(1)	−0.3(1)	1.2(1)	−0.4(1)
C6	1.2275(5)	0.6641(2)	0.6768(4)	2.9(1)	4.3(1)	4.9(1)	−0.9(1)	0.7(1)	0.3(1)
C1Me	1.2699(5)	0.6392(2)	0.9765(4)	3.0(1)	4.3(1)	4.2(1)	0.1(1)	−1.3(1)	−0.5(1)
C2Me	1.1125(6)	0.7271(2)	0.8992(6)	3.9(1)	3.2(1)	9.8(3)	−0.1(1)	−1.1(2)	−1.5(2)

[a] The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Results and Discussion

Common Structural Features

The crystal structures consist of well separated molecules with no unusual intermolecular contacts. All of the complexes have distorted octahedral geometries as is clear from Figs. 1 and 2 which also show the atomic numbering schemes. Attention is drawn to the bond distances and bond angles found in Tables III and IV, respectively. The three independent molecules of compound **1** (one from **1a** and two from **1b**) show only small differences between corresponding bond distances and angles.

For all of the complexes, the oxo groups are *cis* to each other and *trans* to the non-thiolate donor atoms while the thiolate donors are *trans* to each other. This results in complexes with approximate C_S symmetry for the first coordination sphere. This configuration can be explained by considering the strong σ- and π-donation of the oxo ligands. Configurations which have either the oxo groups *trans* to each other or to the thiolate donors are less stable since strong *trans* donors would compete for the same set of acceptor orbitals on Mo. In the configuration which is adopted a *trans* influence from the oxo ligands is observed in the relatively long bonds to the donor atoms in the *trans* positions.

The deviations of these structures from regular octahedral geometries deserve comment. These deviations are due to repulsion between the coordinated atoms as well as to the constraints imposed by the tetradentate ligands. The substantial increase of the O1–Mo–O2 angles from 90° is attributed to repulsion between the electrons on the closely held oxo ligands. The deviation of the S1–Mo–S2 angles from 180° is attributable largely to repulsion from oxo groups and to an extent to the limited bite of the tetradentate ligands. For **1** there is significant asymmetry between the S1–Mo–S3 and S2–Mo–S3 angles (see Table IV). This can be ascribed to interactions involving the methyl group on S3 which points in the direction of S2 thereby causing

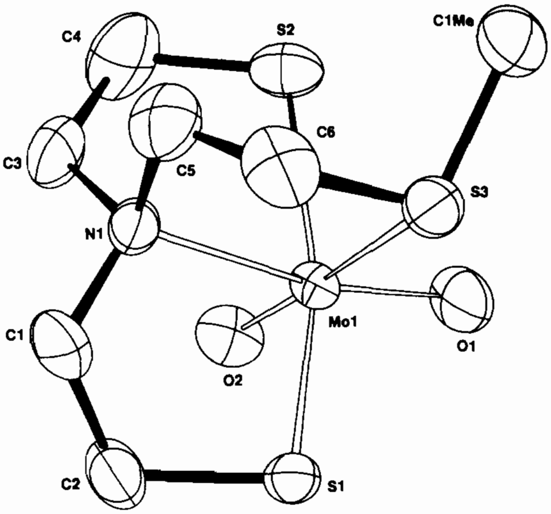

Fig. 1. ORTEP of $MoO_2[CH_3SCH_2CH_2N(CH_2CH_2S)_2]$, 1a.

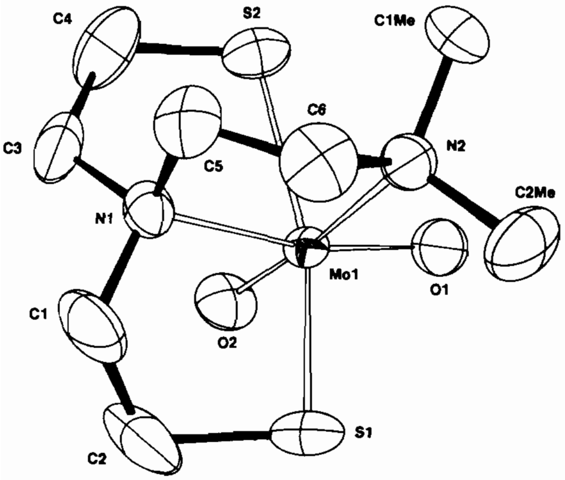

Fig. 2. ORTEP of $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$, 2.

repulsion which opens the S2–Mo–S3 angle. Finally, the slight differences in the Mo–N1 (tripod) distances and the S1–Mo–S2 angles between compound 1 and compound 2 can be attributed to the smaller bite of the variable arm in $(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$ compared to the $(SCH_2CH_2)_2NCH_2CH_2SCH_3$ ligand. We now address specific structural features of the two complexes.

TABLE III. Bond Distances for $MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, 1 and $MoO_2((SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2)$, 2 (in angströms).

	Ia	Ib		2
		molecule #1	molecule #2	
Mo1–S1	2.411(2)	2.420(2)	2.407(2)	2.420(1)
Mo1–S2	2.401(2)	2.389(2)	2.394(2)	2.409(1)
Mo1–O1	1.694(5)	1.709(6)	1.688(5)	1.705(2)
Mo1–O2	1.694(5)	1.703(6)	1.705(6)	1.699(2)
Mo1–N1	2.420(5)	2.394(6)	2.400(6)	2.372(2)
Mo1–S3	2.769(2)	2.809(2)	2.781(2)	
Mo1–N3				2.510(2)
N1–C1	1.457(9)	1.493(10)	1.493(9)	1.473(5)
N1–C3	1.472(9)	1.507(9)	1.504(8)	1.470(4)
N1–C5	1.525(9)	1.483(8)	1.477(9)	1.519(4)
C1–C2	1.508(8)	1.434(13)	1.476(11)	1.518(7)
C3–C4	1.458(9)	1.507(12)	1.505(11)	1.498(7)
C5–C6	1.439(8)	1.512(9)	1.520(10)	1.498(5)
S1–C2	1.815(5)	1.757(10)	1.801(9)	1.822(5)
S2–C4	1.813(7)	1.813(9)	1.816(8)	1.793(4)
S3–C6	1.772(6)	1.787(7)	1.804(8)	
N2–C6				1.452(4)
S3–C1Me	1.794(6)	1.790(7)	1.807(9)	
N2–C1Me				1.480(4)
N2–C2Me				1.489(4)

The Structure of 2

The difference between the Mo–N1 and Mo–N2 bond length (2.37 *vs.* 2.51 Å) is large and several explanations appear possible. There is no obvious difference in the repulsions suffered by the two nitrogen atoms due to other atoms in the Mo coordination sphere. However, the N1 atom at the apex of the tripod ligand may be subject to steric restraint due to its simultaneous presence in three chelate rings. The shortness of this Mo–N1 distance may then be attributed to the pulling in of this nitrogen by the three rings while the Mo–N2 bond with N2 at the terminus of but one ring is relatively unconstrained. Although this explanation seems logical it is not consistent with the fact that the Mo–N1 distance is longer than the nominally less constrained Mo–N distances in the near octahedral complex $MoO_2[NH_2C(CH_3)_2CH_2S]$ [17]. Thus the shorter Mo–N1 distance appears to be the normal unconstrained distance, rather than the longer Mo–N2 distance. Therefore it is the length of Mo–N2 and not the shortness of Mo–N1 which requires explanation. The length of Mo–N2 may be attributed to the two methyl groups on N2 which interact with O1 and S2 or O1 and S1, respectively. The relevant angles N2–Mo–O1, N2–Mo–S2 and N2–Mo–S1 at 83.4, 84.9, and 82.4° are sufficiently small that significant repulsion between the N-methyl groups and O1, S1, and S2 could produce the observed bond lengthening. We prefer this explanation and note that the assignment of important steric hindrance to an N,N-dimethyl grouping has been amply demonstrated in various N-methyl substituted cysteamine complexes [13, 14].

Of the three chelate rings in 2 the N,N ring has the smallest bite angle of 73.6° while the two S,N rings have 76.8 and 78.0° angles, respectively. The only other angles of less than 90° are two non-chelate

TABLE IV. Bond Angles for $MoO_2((SCH_2CH_2)_2NCH_2CH_2SCH_3)$, 1 and $MoO_2((SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2)$, 2, (in degrees).

	1a	1b		2
		molecule #1	molecule #2	
S1–Mo1–S2	151.19(7)	151.72(8)	152.49(8)	154.26(3)
S1–Mo1–O1	101.78(20)	100.79(22)	100.07(21)	101.55(9)
S1–Mo1–O2	94.38(17)	94.59(21)	94.89(21)	92.63(9)
S1–Mo1–N1	76.88(13)	77.48(18)	77.51(16)	78.01(7)
S1–Mo1–S3	76.10(6)	76.24(7)	77.19(8)	
S1–Mo1–N2				82.84(6)
S2–Mo1–O1	99.00(19)	98.15(23)	99.40(22)	99.42(9)
S2–Mo1–O2	97.66(18)	98.99(20)	96.72(21)	94.98(9)
S2–Mo1–N1	76.42(14)	77.57(18)	77.04(17)	76.83(7)
S2–Mo1–S3	86.68(6)	84.81(7)	86.37(8)	
S2–Mo1–N2				84.93(6)
O1–Mo1–O2	108.65(27)	108.73(29)	109.50(32)	107.90(12)
O1–Mo1–N1	158.24(22)	160.15(26)	157.45(28)	156.88(11)
O1–Mo1–S3	83.62(20)	84.86(21)	82.34(23)	
O1–Mo1–N2				83.38(11)
O2–Mo1–N1	93.09(22)	91.11(24)	93.06(26)	95.19(11)
O2–Mo1–S3	166.01(18)	165.04(21)	166.97(22)	
O2–Mo1–N2				168.54(10)
N1–Mo1–S3	74.93(13)	75.49(16)	75.24(15)	
N1–Mo1–N2				73.60(9)
Mo1–S1–C2	95.0(3)	96.5(4)	94.0(3)	93.7(2)
Mo1–S2–C4	100.3(3)	102.5(3)	100.8(3)	102.0(2)
Mo1–N1–C1	112.1(4)	110.5(5)	111.1(5)	113.4(2)
Mo1–N1–C3	103.7(4)	102.0(5)	103.4(5)	106.6(2)
Mo1–N1–C5	112.4(4)	114.9(5)	115.1(5)	109.8(2)
Mo1–S3–C6	99.2(3)	96.8(3)	98.2(3)	
Mo1–S3–C1Me	112.9(3)	114.3(3)	112.6(3)	
Mo1–N2–C6				107.9(2)
Mo1–N2–C1Me				114.2(2)
Mo1–N2–C2Me				109.9(2)
C1–N1–C3	111.5(6)	110.7(7)	109.5(6)	109.6(3)
C1–N1–C5	111.2(7)	108.9(7)	109.3(7)	109.1(3)
C3–N1–C5	105.5(6)	109.6(6)	108.2(6)	108.2(3)
N1–C1–C2	115.3(5)	117.1(7)	114.4(6)	112.8(3)
S1–C2–C1	109.7(4)	117.4(7)	111.4(6)	109.6(3)
N1–C3–C4	116.7(5)	112.9(6)	112.3(6)	115.1(3)
S2–C4–C3	116.0(4)	113.5(5)	116.1(5)	115.4(3)
N1–C5–C6	114.6(5)	114.1(6)	113.0(6)	111.3(3)
S3–C6–C5	115.3(4)	112.5(5)	112.5(5)	
C6–S3–C1Me	102.1(3)	100.9(4)	101.1(4)	
N2–C6–C5				111.5(3)
C6–N2–C1Me				110.4(3)
C6–N2–C2Me				108.4(3)
C1Me–N2–C2Me				105.9(3)

S–Mo–N angles of 84.9 and 82.4°, and an O1–Mo–N2 angle of 83.4°. The magnitude of these seemingly unconstrained angles of less than 90° can be viewed as a consequence of oxo–oxo repulsion (O1–Mo–O2 = 107.9°) and oxo–thiolate repulsions. Such oxo–oxo and oxo–thiolate repulsions are dominant features of the structures as discussed above and elsewhere [19, 20].

Atoms Mo, O1, O2, N1, and N2 form a least squares plane from which no atom deviates by more than 0.05 Å. S1 and S2 are roughly equidistant above and below the plane at +2.36 and –2.35 Å, respectively. Atoms C5 and C6 lie approximately 0.3 Å above and below this plane illustrating the puckered nature of the five-membered Mo–N1–C5–C6–N2 chelate ring. In this ring, called the central ring for this discussion, the puckering is such that the carbon atoms are displaced alternatively above and below the chelate plane. In contrast, the two Mo–N–C–C–S chelate rings are not close to planarity and both carbon atoms in each of these rings are bent away from the central ring. In the N1–C3–C4–S2 chelate arm the ligand arm itself is near planarity (largest deviation –0.12 for C3 and +0.15 for C4) but the Mo atom is 1.3 Å out of this plane, clearly displaced toward the oxo ligands. In the N1–C1–C2 arm the puckering is somewhat greater (C1 is 0.34 Å and C2 is –0.20 Å with respect to the best ligand plane) but again Mo is 1.3 Å out of this plane displaced toward the oxo groups. The bending back of the chelate rings is thus viewed as a consequence of the strength of the Mo–O bonds and the distortion in the coordination sphere which this causes.

The different ring conformations are a sensitive function of the location of the rings with respect to the first coordination sphere. If the central ring carbon atoms are ignored or averaged with their enantiomer then the overall structure of 2 is very close to C_S symmetry with the mirror plane reflecting the S–C–C groups of the outer rings and containing the MoO_2N_2 plane (from which no atom deviates by more than 0.05 Å). A rapid equilibration between the observed structure and its enantiomer by conformational flexing of the central chelate can explain the observed [16] NMR equivalence of the N-methyl groups and of the outer chelate rings.

The Structure of 1

Tables III and IV reveal that the differences in bond lengths and angles among the three independently determined molecules of 1 while nominally significant crystallographically are not of chemical significance. Indeed the identical conformations adopted by the three differently packed molecules in the two crystals is *prima-facie* evidence that the observed conformations are due to intramolecular and not intermolecular forces.

In discussions of this structure we arbitrarily quote numbers from structure 1a. The Mo–N1, Mo–S1, and Mo–S2 distances in 1a are quite similar to the corresponding distances in 2. The great length of the Mo–S3 bond in 1 at about 2.8 Å is attributable firstly to the *trans* bond lengthening effect of the oxo group, secondly to the general weakness of thioether bonding, and thirdly to steric interference between the S-CH_3 group and S2. The long distance found for Mo–S3, has two of its three causes in common with those invoked previously for the lengthening of Mo–N2 in 2. Evidence for the repulsion between the S–CH_3 group and S2 comes from the observed difference between the S1–Mo–S3 and S2–Mo–S3 angles at 76.1° and 86.7°, respectively.

Conformations of the chelate rings in 1 are very similar to those in 2 discussed above. The central ring is of particular interest in view of the S–CH_3 group at its terminus. The bite of the N1–C5–C6–S3 chelate ring at 74.9° is not significantly different from that of the central N1–C5–C6–N2 ring in 2, this despite the greater length of Mo–S3 in 1 compared with Mo–N2 in 2. In the Mo–N1–C5–C6–S2 chelate ring the puckering is such that atoms C_5 and C_6 lie on the opposite side of the approximate Mo–N1–C5–C6–S2 plane from the S–CH_3 group. This places the S–CH_3 bond roughly parallel to the Mo–S2 bond. Flipping the conformation to the opposite puckered arrangement without breaking the Mo–S bond places the S–CH_3 much closer to the Mo–O1 bond. The greater consequent repulsion between S–CH_3 and the Mo–O1 linkage may be sufficient to disfavor this conformation.

General Discussion

The factors which decrease the stability of octahedral structures relative to the skew trapezoidal structures found in $MoO_2(CH_3NHCH_2C(CH_3)_2S)_2$, $MoO_2(CH_3NHC(CH_3)_2C(CH_3)_2S)_2$ and $MoO_2(N(CH_3)_2CH_2C(CH_3)_2S)_2$ appear to be interligand interactions involving the atoms not directly coordinated to Mo such as the methyl substituents on the donor nitrogen atoms [13, 14]. Such interactions are not found in the present complexes as the tripod ligand severely restricts the possible distorted structures. Thus the complexes form near-octahedral structures with *trans* thiolate ligands. The *trans* thiolate placement is consistent with the general rule that in a dioxo octahedral structure the next strongest donors after oxo are found in positions *cis* to oxo and therefore *trans* to each other [19]. This rule also explains the disposition of the donor atoms in such complexes as $MoO_2(tox)_2$ [21] and MoO_2Cl_2-(hmpa)$_2$ [22] (tox = thiooxine, hmpa = hexamethylphosphoramide).

The two complexes discussed here were used as test cases in the evaluation of the ability of EXAFS to determine Mo–O, and Mo–S distances in the first coordination sphere of molybdenum complexes [7, 8, 12]. Comparison of the EXAFS distances and crystallographic distances revealed that the EXAFS successfully predicted these distances to within 0.01 Å in most cases. In the case of the long thioether–molybdenum distance in 1 the two crystal structure determinations discussed here gave three independently determined distances of 2.769, 2.781, and 2.809 Å compared with the EXAFS prediction of 2.80 Å. We do not know which of the two crystalline forms of 2 was used in the EXAFS studies. If crystal form 2, with two Mo–S distances of 2.809 and 2.781 was used then the low number of atoms estimated to be at 2.80 Å from the EXAFS studies (*i.e.*, 0.5) may be attributed to effective static disorder. This disorder would appear as an increased effective Debye–Waller factor which, in the data processing protocol used in the study [7], would be manifest as a decreased number of atoms at the distance in question. Alternatively, the thioether donor is observed to have a relatively high Debye–Waller factor in all three molecules of 2. This is presumed to be a consequence of the weak binding of the thioether at 2.8 Å. This factor alone (or in combination with the static disorder) can be responsible for the low number of atoms determined at the long Mo–S distance.

Comparison with the EXAFS data for sulfite oxidase reveals that of the two complexes, 1 bears a strong resemblance to sulfite oxidase. Assuming an octahedral structure to be present in the enzyme, we are led to assign a structure such as in Fig. 3 for the Mo(VI) site in sulfite oxidase. Following the EXAFS results [5], the Mo(IV) site in sulfite oxidase, contains one less oxo group but maintains the long Mo–S bond. Assuming that the long distance represents a thioether ligand *trans* to Mo–O$_t$, we are led to the structure of Fig. 3 (X = OH_2, substrate or empty) for the Mo(IV) state of sulfite oxidase. If the structure with a single oxo group is present in the Mo(V) state then the oxo group would be expected to be along a pseudo tetragonal Mo–O$_t$ axis. This location would predict a very small value for the ^{17}O superhyperfine splitting in the Mo(V) EPR spectrum. Indeed A(^{17}O) in $MoO(SC_6H_5)_4^-$ has been found to be only 2.3 G [23]. However, Cramer and Bray and their respective coworkers [24–26] have found that in sulfite oxidase [24] and xanthine oxidase [25, 26] splittings of 10 or more gauss are present. Taken together the results on $MoO(SC_6H_5)_4^-$ and the enzymes would seem to rule against a relatively undistorted octahedral-like structure in the Mo(V) state of the enzymes. Thus, the obvious interpretation of the apparent 2.8 Å distance in the enzymes as being due to a thioether donor *trans* to an oxo group must be considered tentative. Indeed, structural studies on related complexes [13, 14] show the common occurrence of distortions from the regular octahedron. Further the long Mo–S distance is the least certain feature of the EXAFS interpretation and only slightly improves the fit of experimental and calculated spectra. It is clear that a combination of detailed crystallographic, EXAFS, EPR, and vibrational spectroscopic studies on model compounds will be required to allow for full interpretation of corresponding data that are emerging from studies on the enzyme systems [12].

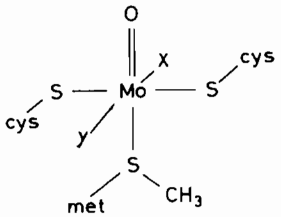

Fig. 3. Possible structure for Mo site in sulfite oxidase based on EXAFS. For Mo(VI), x = O, for Mo(IV) x is substrate, product, water, hydroxide or vacant. y may represent the substrate binding site in the Mo(VI) form.

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References

1 (a) Address correspondence to this author at Stanford University.
(b) Address correspondence to this author at Exxon Research and Engineering Co.
2 T. D. Tullius, D. M. Kurtz, S. D. Conradson and K. O. Hodgson, *J. Am. Chem. Soc., 101*, 2776 (1979).
3 J. Bordas, R. C. Bray, C. D. Garner, S. Gutteridge and S. S. Hasnain, *Biochem. J., 191*, 499 (1980).
4 S. P. Cramer, R. Wahl and K. V. Rajagopalan, *J. Am. Chem. Soc., 103*, 7721 (1981).
5 S. P. Cramer, H. B. Gray and K. V. Rajagopalan, *J. Am. Chem. Soc., 101*, 2772 (1979).
6 S. P. Cramer, M. W. W. Adams and L. E. Mortenson, submitted for publication.
7 S. P. Cramer, K. O. Hodgson, E. I. Stiefel and W. E. Newton, *J. Am. Chem. Soc., 100*, 2748 (1978).
8 J. M. Berg, K. O. Hodgson, S. P. Cramer, J. L. Corbin, A. Elsberry, N. Pariyadath and E. I. Stiefel, *J. Am. Chem. Soc., 101*, 2774 (1979).
9 F. A. Cotton, in *Proceedings of the First International Conference on the Chemistry and Use of Molybdenum, Climax, Molybdenum*, 1974, p. 6.
10 B. Spivack and Z. Dori, *Coord. Chem. Rev., 17*, 99 (1975).
11 E. I. Stiefel, *Progr. Inorg. Chem., 22*, 1 (1977).
12 E. I. Stiefel, in M. P. Coughlan, (Ed.), 'Molybdenum and Molybdenum Containing Enzymes', Pergamon Press, New York, 1980, p. 43.
13 E. I. Stiefel, K. F. Miller, A. E. Bruce, J. L. Corbin, J. M. Berg and K. O. Hodgson, *J. Am. Chem. Soc., 102*, 3624 (1980).
14 J. M. Berg, D. J. Spira, K. O. Hodgson, A. E. Bruce, K. F. Miller, J. L. Corbin and E. I. Stiefel, *Inorg. Chem.* in press.
15 J. L. Corbin, K. F. Miller, N. Pariyadath J. Heinecke, A. E. Bruce, S. Wherland and E. I. Stiefel, *Inorg. Chem.*, in press. See also E. I. Stiefel, K. F. Miller, A. E. Bruce, J. Heinecke, N. Pariyadath, J. L. Corbin, J. M. Berg and K.

O. Hodgson, in W. E. Newton and S. Otsuka, (Eds.), 'Molybdenum Chemistry of Biological Significance', Plenum Press, New York, 1980, p. 279.

16 J. L. Corbin, K. F. Miller, K. Pariyadath, S. Wherland, A. E. Bruce and E. I. Stiefel, *Inorg. Chim. Acta, 90,* 41 (1984).

17 J. M. Berg, D. Spira, K. Wo, B. McCord, B. Lye, M. S. Co, J. Belmont, C. Barnes, K. Kosydar, S. Raybuck, K. O. Hodgson, A. E. Bruce, J. L. Corbin and E. I. Stiefel, *Inorg. Chim. Acta, 90,* 35 (1984).

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

19 K. Yamanouchi and J. H. Enemark, *Proc. Third Int. Conf. on Chem. and Uses of Molybdenum, Climax, Molybdenum* (1979).

20 A. E. Bruce, J. L. Corbin, P. L. Dahlstrom, J. R. Hyde, M. Minelli, E. I. Stiefel, J. Spence and J. Zubieta, *Inorg. Chem., 21,* 917 (1981).

21 K. Yamanouchi, J. T. Huneke and J. H. Enemark, in W. E. Newton and S. Otsuka, (Eds.), 'Molybdenum Chemistry of Biological Significance', Plenum Press, New York, 1980, p. 309.

22 B. Viossat, P. Khodadad and N. Rodier, *Acta Cryst., B33,* 3793 (1977).

23 K. F. Miller and E. I. Stiefel, unpublished observations, G. R. Hanson, A. A. Brunette, A. C. McDonell, K. S. Murray and A. G. Wedd, *J. Am. Chem. Soc., 103,* 1954 (1981).

24 S. P. Cramer, J. L. Johnson, K. V. Rajagopalan and T. N. Sorrell, *Biochem. Biophys. Res. Commun., 91,* 434 (1979).

25 S. Gutteridge and R. C. Bray, *Biochem. J., 189,* 615 (1980).

26 S. Gutteridge, M. T. Lamy and R. C. Bray, *Biochem. J., 191,* 285 (1980).