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A Nonoctahedral Dioxo Molybdenum Complex with a Coordinated Partial Disulfide Bond

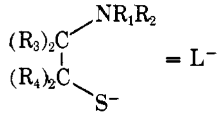
Sir:

EXAFS studies on the oxidized forms of sulfite oxidase[1] and xanthine oxidase[2] have implicated the presence of terminal oxygen atoms at an Mo–O distance of ~1.7 Å and approximately three sulfur atoms in the Mo(VI) coordination sphere. The striking similarity of the EXAFS patterns for oxidized sulfite oxidase[1] and $MoO_2[CH_3SCH_2CH_2N(CH_2CH_2S)_2]$[3,4] led to the suggestion that the Mo coordination sphere of the enzyme may contain two cis oxo groups, two mutually trans thiolates each cis to both oxo donors, and one thioether linkage trans to an oxo group as found in the crystallographic study of the complex.[4] The above and other structural discussions[5] on the Mo(VI) state in Mo oxidases have uniformly been based on the assumptions of a conventional octahedral structure and two independently acting thiolate donor atoms. In this paper we present the results of studies on the seemingly simple Mo(VI) complex $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (**1**), which reveal a distinctly nonoctahedral structure and a partial S–S bond within the "Mo(VI)" coordination sphere. Moreover, the ^{1}H NMR spectra of this and related Mo(VI) complexes demonstrate stereochemical nonrigidity which is sensitive to the nature of the ligand. Since these structural features must be considered in discussions of the Mo coordination sphere in enzymes, we also discuss in a preliminary way some of the potential biochemical implications of these findings.

Table I. Bond Distances and Angles in $MoO_2[SC(CH_3)_2CH_2NHCH_3]_2$ and Related Complexes

	1	**4**	**5**
	Bond Distances, Å		
Mo–S(1)	2.420 (3)	2.420 (1)	2.411 (3)
Mo–S(2)	2.409 (3)	2.409 (1)	2.411 (3)
Mo–O(1)	1.723 (5)	1.699 (2)	1.694 (6)
Mo–O(2)	1.711 (5)	1.705 (2)	1.712 (7)
Mo–N(1)	2.262 (9)	2.372 (2)	2.382 (9)
Mo–N(2)	2.277 (8)	2.510 (2)	2.374 (9)
S(1)–S(2)	2.764 (5)	[4.71]	[4.75]
	Bond Angles, deg		
S(1)–Mo–S(2)	69.8 (19)	154.3(3)	160.9 (1)
O(1)–Mo–O(2)	122.2 (3)	107.9 (1)	106.3 (3)
N(1)–Mo–N(2)	144.0 (3)		
S(1)–Mo–O(1)	107.7 (3)		
S(2)–Mo–O(2)	107.5 (2)		
S(1)–Mo–O(2)	118.3 (2)		
S(2)–Mo–O(1)	120.4 (2)		
S(1)–Mo–N(1)	72.9 (3)		
S(2)–Mo–N(2)	74.6 (2)		
S(1)–Mo–N(2)	142.6 (2)		
S(2)–Mo–N(1)	141.0 (2)		
O(1)–Mo–N(1)	81.8 (3)		
O(2)–Mo–N(2)	83.0 (3)		
O(1)–Mo–N(2)	80.5 (3)		
O(2)–Mo–N(1)	80.3 (3)		

Complex **1**, containing the ligand $(CH_3)NHCH_2C(CH_3)_2S^-$, was prepared as part of our program to design and synthesize new bi-, tri-, tetra- and pentadentate ligands containing N, S, and O donor atoms. The variety of ligand types is such that some arrangement of the donor atom sets is likely to be analogous to that present in Mo enzymes. In this paper we restrict our attention to complexes **1**–**3** of the bidentate ligands derived from cysteamine.



complex (MoO_2L_2)	ligand (L^-)
1	$R_1 = R_3 = H$; $R_2 = R_4 = CH_3$
2	$R_1 = R_2 = R_4 = CH_3$; $R_3 = H$
3	$R_1 = R_2 = R_4 = H$; $R_3 = CH_3$

The Mo(VI) complexes were prepared by the reaction

$$MoO_2(acac)_2 + 2LH \rightarrow MoO_2L_2 + 2\ acacH$$

where acac = acetylacetonate.

Crystals of **1** were grown at 0 °C in CH_3OH directly from the reaction mixture. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.688$ (3), $b = 11.923$ (2), $c = 14.032$ (3) Å; $\beta = 106.65$ (2)°. The structure was solved by standard heavy-atom methods and was refined using full-matrix least squares to $R = 4.9\%$ and $R_w = 5.4\%$ as described previously[6] using 1516 reflections with $F^2_{\text{obsd}} > 3\sigma(F^2_{\text{obsd}})$. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were included as fixed contributions in the final least-squares cycles.

The structure of **1** displayed in the figure has noncrystallographic twofold symmetry with the C_2 axis bisecting the S–Mo–S, O–Mo–O, and N–Mo–N bond angles. Distances and angles are displayed in Table I along with corresponding values for $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$[4] (**4**) and MoO_2(8-mercaptoquinolinato)$_2$[7] (**5**), other complexes containing $MoO_2N_2S_2$ coordination spheres.

Inspection of Table I and Figure 1 reveals the nonoctahedral nature of the structure. There are no atoms present at sites

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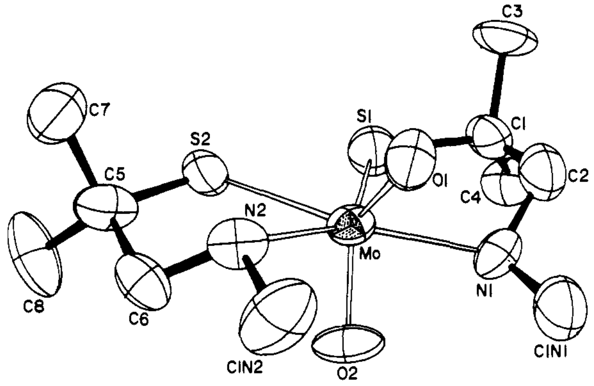


Figure 1. Molecular structure of $MoO_2[SC(CH_3)_2CH_2NH(CH_3)]_2$ (**1**).

trans to either Mo-O_t bond. The largest angle for any O-Mo-X group is only 122° and that is the angle for X = O. There are also no near-octahedral trans angles between any pair of Mo-S and Mo-N bonds. Although the structure is not close to an octahedron, it can be described as a severe distortion from an octahedral *trans*-MoO_2 complex with mutually cis N atoms and mutually cis S atoms. Opening the N-Mo-N angle in this hypothetical structure to 144° while the O-Mo-O angle closes toward this opening yields the observed structure. This structure has been aptly dubbed by Kepert[8] as a skew-trapezoidal bipyramid and previously had only been identified for complexes of Sn.[8]

The appropriateness of the skew-trapezoidal bipyramidal structural designation is enforced by examination of the plane containing the Mo and its N and S donor atoms. Deviations from the least-squares plane determined by Mo, S(1), S(2), N(1), and N(2) are −0.002, 0.210, −0.207, −0.132, and 0.131 Å for the respective atoms. The O atoms lie above and below the plane at 1.491 and 1.517 Å and the Mo-O(1)-O(2) plane is nearly perpendicular to it (dihedral angle = 87.8°). The dihedral angle between the planes determined by Mo, S(1), and N(1) and Mo, S(2), and N(2) is 13.7°, this being the largest dihedral angle for any Mo-inclusive set of three atoms within the plane. While the trapezoidal plane is only approximate, the deviations are sufficiently small to endorse the validity of the skew-trapezoidal bipyramidal designation for descriptive purposes.[9]

A further unique feature of the present structure is the S-Mo-S angle of 69.8° and the 2.76-Å separation of the sulfur atoms within the coordination sphere. This distance is far shorter than the van der Waals contact of 3.7 Å[10] and is also shorter than the nominal 3.4-Å distance expected[11] for two S atoms bound to the same metal atoms. The Mo-S bond distances at ~2.42 Å are very close to those in earlier Mo(VI) structures[4,7] as well as to those in the Mo(VI) state of sulfite oxidase.[1]

In the solid state, each molecule of MoO_2L_2 is hydrogen bonded to two other molecules to form infinite chains. It is not clear to what extent this H-bonding pattern contributes to the formation of the unusual structure. The infrared spectrum of **1** in KBr or in Nujol mull shows peaks assignable to ν(Mo-O) at 883 and 858 cm^{-1}. These values are significantly lower than ν(Mo-O) for **4** (921 and 893 cm^{-1}) and **5** (921 and 888 cm^{-1}). We are planning to analyze structurally $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (**2**), where the dimethyl-substituted nitrogen precludes the possibility of such H bonding. As **2** also has extremely low frequency ν(Mo-O) vibrations, it seems certain that the observed intermolecular H bonding is not the sole determinant of the unusual geometrical and spectroscopic properties of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$.[20]

Why does this seemingly simple complex adopt such an unusual structure? The answer seems to lie in the unfavorable steric or electronic interactions which would be present were the standard octahedral geometry adopted. By comparison with earlier results one might have anticipated the placement of the two Mo-S linkages mutually trans and cis to the O atoms. However, this geometry would result in steric interference between the two methyl groups on adjacent N atoms (which are forced into pseudoequatorial positions of their respective chelate rings in order to avoid 1-3 interactions with the CH_3-substituted thiolate-bearing carbon). To avoid this interaction, two different octahedral structures are possible in which, respectively, either one or two S atoms lie trans to Mo-O_t. Although this placement is sterically acceptable, it may be electronically unfavorable as it places the strongly σ- and π-donating S and O_t donors in competition for the same set of p and d orbitals along the hypothesized S-Mo-O_t axis. Evidently the steric and electronic constraints conspire to produce the resultant structure in which steric hindrance is indeed minimized and there are no groups trans to the Mo-O_t linkages.

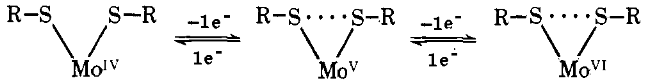
The detailed reasons for the adoption of this unusual geometry are being investigated by structural examination of other complexes in the series. We have found that a combination of NMR and IR spectroscopic studies may be suggestive of certain structural trends. The Mo-O stretching vibrations of **1** at 883 and 858 cm^{-1} are exceptionally low, probably reflecting the opening of the O-Mo-O angle, the slight lengthening and weakening of the Mo-O_t bond, and possibly the H bonding found in the solid state. The 220-MHz ^1H NMR spectrum of **1**, at 17 °C in $CDCl_3$, shows the presence of equivalent C-bound methyl groups, while the solid-state structure in the figure shows inequivalent CH_3 groups on the thiolate-bearing carbon. The NMR equivalence of the methyl groups is probably caused by a molecular rearrangement process within the Mo(VI) coordination sphere.

Results on **1** are contrasted with data on $MoO_2[NH_2C(CH_3)_2CH_2S]_2$ (**3**), which displays infrared absorptions at 907 and 872 cm^{-1}, closer to those for complexes **4** and **5**, which are known to have trans-dithiolate octahedral structures.[5,7] The NMR spectrum of **3** at 17 °C shows two resonances for the CH_3 groups and AB patterns for the CH_2 and NH_2 protons, consistent with an octahedral structure with trans thiolate and cis amine donors.

These structural and dynamic results reveal that the six-coordinate Mo(VI) sphere may be more prone to distortions than had been previously surmised. Relatively subtle changes in ligand between **1** and **3** apparently produce a dramatic structural change in both the static and dynamic properties of the Mo(VI) sphere. Clearly, small changes in steric requirements of protein or cofactor ligands might also impose unusual structural features or impart fluxionality to the Mo(VI) sphere within the enzyme. Further, the presence of a partial disulfide bond must also be considered.

The assignment of the short S-S distance in **1** to a partial disulfide bond deserves both additional justification and further comment. Sulfur-sulfur distances comparable with the 2.76-Å distance in **1** have been found in several structures where this interaction clearly plays a bonding role.[12-15] Perhaps the most vivid case is the 2.83-Å transannular S(3)-S(8) distance in S_8^{2+} which, from both structural[12] and theoretical[13] studies, has been assigned as a bonding interaction. Other examples of S-S partial bonds include S_5N_6 with S-S = 2.43 and $S_4N_4O_2(OCH_3)^-$ [15] with S-S = 2.48 Å. In various dithiolene complexes the S-S distance of 3.05 Å has been considered as a bonding interaction.[16] Thus, the 2.76-Å distance in **1** may represent the formation of a partial disulfide bond which requires concomitant transfer of charge to the Mo center. A recent structural study[11] of the Mo(V) complex $Mo_2O_4(SC_6H_5)_4^{-2}$ showed one of the two molecules in the unit cell to have an interligand S-S distance of 2.94 Å which also was considered to be indicative of S-S overlap.

Melding our results with those in the literature leads to a fascinating possibility for redox processes in Mo-bis(thiolate) systems. As illustrated below, successive one-electron oxidation of Mo(IV) to (formally) Mo(V) and Mo(VI) may involve a substantial component of thiolate-disulfide oxidation. If this partial S–S bond formation occurs in Mo enzymes (and none of the existent data preclude such an occurrence), then it could explain, in part, the absence of identity between the spectroscopic, redox, and catalytic properties of Mo enzymes and their "model" systems. For example, the high g_z and low $A_z(^{95,97}Mo)$ value of the Mo(V) EPR signal in xanthine oxidase[5] may be attributable to strong delocalization of the unpaired electron into a partial S–S bond. The great range of redox potentials for different Mo enzymes (while also potentially explainable in other terms) could likewise be due to varying degrees of S–S bond formation in the different molybdenum enzymes. The presence of strategically juxtaposed sulfides in large-ring multisulfur organic heterocyclic compounds has been found to correlate with substantially lower potentials for one-electron oxidation and with increased reversibility in the electron-transfer process.[17–19] Similarly, the specific cis positioning of Mo-bound thiolates may be responsible for unusual reactivity and spectroscopic features of Mo sites in enzymes.



Regardless of the relevance of the above results to Mo enzymes, it is clear that more structural variety is possible in simple inorganic molybdenum systems than had heretofore been admitted. Recognition of this diversity may be crucial in the quest to determine the nature of the biological molybdenum sites.

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Supplementary Material Available: A list of atomic coordinates and thermal parameters for $MoO_2[SC(CH_3)_2CH_2NHCH_3]_2$ (1 page). Ordering information is given on any current masthead page.

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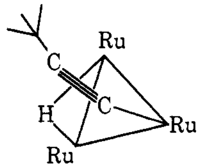
Synthesis, Structure, and Reactivity of Mercurial Derivatives of an Organoruthenium Cluster

Sir:

Hydrido organotrimetallic clusters of ruthenium are interesting model compounds for the study of transition metal cluster chemistry for several reasons. One reason is that they provide easily synthesized examples of thermally stable monohydride derivatives of the Ru_3 cluster with which to study the reactivity of the μ_2-hydrido bond. During the course of our studies on the general reactivity of $HRu_3(CO)_9(C_6H_9)$ (I)[1] we discovered that C_6H_5HgX (X = Br, I) reacts with I to give a halomercury(II) derivative $(C_6H_9)Ru_3(CO)_9HgX$ (II) and an equivalent amount of benzene:[2,3]



I

$$(C_6H_9)Ru_3(CO)_9H + C_6H_5HgX \xrightarrow[12\text{ h}]{\text{THF reflux}} (C_6H_9)Ru_3(CO)_9HgX + C_6H_6 \quad (1)$$
$$\text{II, 30–40\%,}$$

II has been fully characterized and the data are summarized in Table I for the bromo and iodo derivatives. We subsequently found that reaction of the anion of I (generated in situ[4] with HgX_2 (X = Br, I) also gives II in comparable yields:

$$HRu_3(CO)_9(C_6H_9) \xrightarrow[\text{THF-EtOH}]{\text{KOH}} Ru_3(CO)_9(C_6H_9)^-$$
$$+ K^+ + HgX_2 \xrightarrow[18\text{ h}]{25\text{ °C}} \text{II} \quad (2)$$

Thus II is a common product from two apparently different reaction pathways.

The ^{13}C NMR of a 15% ^{13}CO-enriched sample of II shows five resonances at the low temperature limit (−24 °C) in the carbonyl region (Figure 1). This suggests that the cluster has the same overall summetry as I.[5] The lowest energy exchange process averages resonances *a* and *b* at +2 °C and arises from axial-radial exchange at the unique ruthenium atom, Ru(1) ($\Delta G^{\ddagger} = 12.7 \pm 0.5$ kcal/mol).[6] At +25 °C resonances *c*, *d*, and *e* have coalesced while the resonance arising from the average of (*a* + *b*) remains relatively sharp. This second stage of the CO-scrambling process arises from localized axial-radial exchange at Ru(2) and Ru(3) ($\Delta G^{\ddagger} = 14.8 \pm 0.5$ kcal/mol).[6] At +60 °C resonances (*a* + *b*) and (*c* + *d* + *e*) coalesce to a single broad resonance. This third stage of the exchange probably arises from the onset of intermetallic CO scrambling via CO-bridging intermediates in a typical Cotton-type CO-

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