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Synthesis and Structural Characterization of the Et$_4$N$^+$ Salts of the New [[(S$_2$)$_2$MoO]$_2$S]$^{2-}$ and [[(S$_2$)$_2$MoO]$_2$S]$_2{}^{2-}$ Oxo–Disulfido–Molybdate(VI) Anions

Sir:

The use of "sulfided" molybdenum catalysts in the industrially important hydrodesulfurization (HDS) reaction[1] accounts in part for the recent pronounced interest in the synthesis and study of new molybdenum–sulfide complexes. Among these are included $[(S_4)_2MoS]^{2-}$,[2a] $[(S_2)MoS(\mu\text{-}S)]_2{}^{2-}$,[2b] $[(S_4)MoS(\mu\text{-}S)]_2{}^{2-}$,[2a] $[(S_4)MoS(\mu\text{-}S)_2SMo(S_2)]^{2-}$,[2a,c] $[(S_2)_2Mo(\mu\text{-}S_2)]_2{}^{2-}$,[2d] $[MoS(MoS_4)_2]^{2-}$,[2e] and $[Mo_3S_{13}]^{2-}$.[2f] With the exception of the $[MoS(MoS_4)_2]^{2-}$ and $MoS_4{}^{2-}$ anions that contain Mo(VI), all other binary Mo/S complexes contain molybdenum in oxidation states lower than +6.

By contrast the chemistry of the oxo–peroxo–molybdate(VI) anions is extensive. As a result of detailed studies, primarily by Stomberg and co-workers, the synthesis and structures of such anions as $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$,[3a] $[Mo_3O_7(O_2)_4]^{4-}\cdot 2H_2O$,[3b] $[Mo_4O_{12}(O_2)_2]^{4-}$,[3c] $[Mo_5O_{10}(O_2)_8]^{6-}\cdot 5H_2O$,[3d] $[Mo_7O_{22}(O_2)_2]^{6-}\cdot 8H_2O$,[3e] and $[Mo_{10}O_{22}(O_2)_{12}]^{8-}\cdot 16H_2O$[3f] are now well established. Common structural features are apparent in these complexes, where (a) the peroxo-bound Mo(VI) ions have an approximate pentagonal-bipyramidal structure, (b) the η^2-peroxo ligands are located in the equatorial positions, and (c) one terminal oxo ligand per molybdenum occupies one of the axial sites.

Similar *polynuclear* oxo–*disulfido*–molybdate(VI) anions have not been reported although such complexes could be molecular analogues for tertiary Mo/O/S centers that may be present in the HDS Mo/S catalysts. In this communication we report on the synthesis and structural characterization of the first examples of two such anions in $[Et_4N]_2[Mo_2(O)_2\mu\text{-}S(\eta^2\text{-}S_2)_4]$ (I) and $[Et_4N]_2[Mo_4(O)_4(\mu\text{-}S_2)(\eta^2\text{-}S_2)_8]$ (II).

The reaction of $PF_6[Fe(C_5H_5)_2]$ with $[Et_4N]_2(MoO(S_4)_2]$[2a] in a 1:1 molar ratio occurs readily in acetonitrile solution at ambient temperature, and crystalline I is obtained in 70% yield.[4] A small amount of a tetranuclear derivative of I also forms as a minor component when a slight excess of the oxidant is present. This new complex, II, can be synthesized separately and isolated in modest yields (35–40%) by the oxidative coupling of I, in dimethylformamide (DMF) at ambient temperature, with $PF_6[Fe(C_5H_5)_2]$ as the oxidizing agent.[4] The electronic spectra in dimethylformamide solution show absorption maxima at 392 (ϵ = 3840), 432 (ϵ = 4040), and 522 (ϵ = 1950) nm for I and at 338 sh (ϵ = 10450), 414 sh (ϵ = 8130), and 510 nm (ϵ = 7850) for II. The Mo=O and S—S stretching vibrations are found as strong absorptions in the infrared spectrum of I at 926 and 528 cm^{-1}, respectively. The corresponding vibrations in II are found also as strong bands at 940, 930, 911, and 534 cm^{-1}.

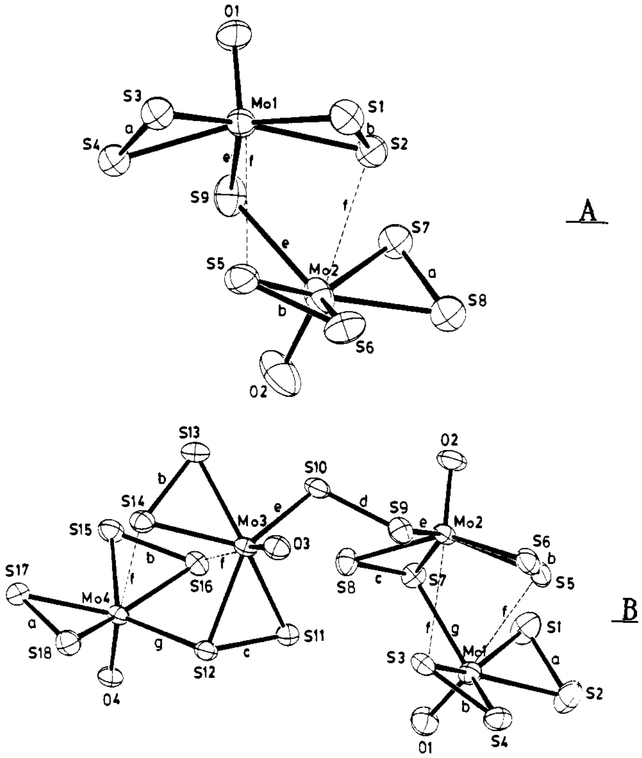

Figure 1. Structure and labeling of [[(S$_2$)$_2$MoO]$_2$S]$^{2-}$ (A) and [[(S$_2$)$_2$MoO]$_2$S]$_2{}^{2-}$ (B). Thermal ellipsoids as drawn by ORTEP[7] represent the 40% probability surfaces. The interatomic distances identified by letters in both structures are chemically similar, and their values are given in Table I.

Crystals of I and II suitable for X-ray diffraction measurements were obtained respectively by the slow diffusion of tetrahydrofuran into a dimethylformamide (DMF) solution of I and by the slow diffusion of 2-propanol into a DMF solution of II.

Crystal Data: red-brown prisms of $(Et_4N)_2Mo_2O_2S_9$ (I) are monoclinic, space group $P2_1/c$, with a = 16.734 (2) Å, b = 10.407 (2) Å, c = 17.457 (3) Å, β = 97.06 (1)°, and Z = 4; dark brown

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(4) Satisfactory elemental analysis has been obtained for this compound.

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Table I. Interatomic Distances[a] (Å) and Angles (deg) in the $[[(S_2)_2MoO]_2S]^{2-}$ and $[[(S_2)_2MoO]_2S]_2^{2-}$ Anions of I and II

	I	II
	Distances	
Mo(1)–Mo(2)	3.606 (1)	3.606 (1)
Mo(3)–Mo(4)		3.562 (1)
Mo–S(a)[b]	2.371 (19, 4)	2.387 (3, 4)
Mo–S(b)[b,c]	2.377 (3, 2)	2.374 (5, 4)
	2.409 (6, 2)	2.380 (5, 4)
Mo–S(c)[b,c]		2.387 (11, 2)
		2.458 (8, 2)
Mo–S(e)[b]	2.503 (20, 2)	2.418 (3, 2)
Mo–S(f)[b,d]	2.856 (3, 2)	2.919 (9, 4)
Mo–S(g)[b]		2.536 (9, 2)
Mo–O	1.676 (6, 2)	1.680 (6, 4)
S–S(d)[e]		2.083 (4)
	Angles	
S_{eq}–Mo–O	102.1 (7, 10)	103.2 (6, 20)
S_{ax}–Mo–S_{eq}	78.1 (1.8, 10)	76.9 (1.0, 20)
S_{ax}–Mo–O	171.2 (3, 2)	171.4 (5, 4)

[a] See Figure 1 for the labeling scheme. The mean values of chemically equivalent bonds are reported. The first number in parentheses represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation $\sigma = [\sum_{i=1}^{N}(X_i - \bar{X})^2/N(N-1)]^{1/2}$; If only two values are averaged out, the first number represents the scatter from the average. The second number represents the independent distances or angles averaged out. [b] The letter in parentheses corresponds with the letters in Figure 1 in identifying the different types of S_2^{2-} bonding. [c] The longer Mo–S distance is associated with the sulfur atom that also interacts with another molybdenum atom in a η^1 fashion. [d] Intramolecular Mo–S interactions that populate the second axial coordination site. [e] The other (η^2) S_2^{2-} units in both structures show normal S–S distances that range from 2.028 (3) to 2.066 (4) Å.

crystals of $(Et_4N)_2Mo_4O_4S_{18}$ (II) are triclinic, space group $P\bar{1}$, with a = 11.726 (3) Å, b = 12.851 (3) Å, c = 16.183 (4) Å, α = 79.21 (2)°, β = 82.68 (2)°, γ = 79.65 (2)°, and Z = 2. Single-crystal X-ray diffraction data were collected on a Nicolet P3F four-cycle diffractometer using Mo Kα radiation, and the solution of the structures was carried out by a combination of heavy-atom Patterson, direct-methods, and Fourier techniques. The refinement of the two structures by full-matrix least-squares methods was based on 3065 unique reflections ($2\theta_{max}$ = 40°; $I > 3\sigma(I)$) for I and on 5094 unique reflections ($2\theta_{max}$ = 45°; $I > 3\sigma(I)$) for II. Anisotropic temperature factors were used for the appropriate[5] non-hydrogen atoms in both structures, and with all atoms present in each of the asymmetric units, R = 0.061 and 0.041 for I and II, respectively. Following the successful refinement of both structures, the calculated structure factors were used to calculate the expected X-ray powder pattern of these compounds. The calculated powder patterns were found in good agreement with the patterns obtained experimentally from the bulk samples.

Both I and II are structurally related, and the two anions (Figure 1) contain pseudo-seven-coordinate Mo(VI) ions. In I two η^2-S_2^{2-} ligands and the bridging sulfido ligand define the equatorial plane of a pentagonal bipyramid around each of the molybdenum atoms. On each molybdenum a terminal oxo ligand occupies one axial site and an intramolecularly weakly interacting sulfur occupies the other. The two pentagonal bipyramids share the sulfido ligand as a common equatorial site. The two Mo(VI) ions are elevated from the respective pentagonal planes toward the terminal oxo groups by 0.47 and 0.54 Å.

The structure of the anion in II is best described as the result of oxidative coupling between two $[Mo_2(O)_2\mu\text{-}S(\eta^2\text{-}S_2)_4]^{2-}$ anions. This coupling occurs between the two sulfido ligands that subsequently form a μ-disulfido ligand. The latter serves as a bridge for the two "central" $Mo(O)(S_2)_2$ subunits in II. The other two, "terminal", $Mo(O)(S_2)_2$ subunits are attached to the central ones by a new type of η^2,η^1-S_2^{2-} bridging ligand (Figure 1B). Selected structural parameters for the anions in I and II are shown in Table I. The coordination geometries of the Mo(VI) ions in both I and II are remarkably similar and resemble closely the geometries found for the molybdenum ions in the oxo–peroxo–molybdate(VI) anions.[3]

Neither of the anions in I or II has an exact structural analogue among the oxo–peroxo–molybdate(VI) anions. However, the structure of I is almost idential with that of the isoelectronic oxo–peroxo–vanadate(V) anion $[V_2(O)_3(O_2)_4]^{4-}$[6] and very similar to that of the $[Mo_2O_3(O_2)_4(H_2O)]^{2-}$ anion.[3a] In the latter, one of the axial sites (across from the oxo groups) for each of the pentagonal bipyramids is occupied by a H_2O molecule.

The reactivities of I and II presently are under study in our laboratory.

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Registry No. I, 105597-76-0; II, 105618-24-4; $[Et_4N]_2[MoO(S_4)_2]$, 76581-46-9; $PF_6[Fe(C_5H_5)_2]$, 11077-24-0.

Supplementary Material Available: Listings of positional and thermal parameters for $(Et_4N)_2[[(S_2)_2MoO]_2S]$ and $(Et_4N)[[(S_2)_2MoO]_2S]_2$ (6 pages); listings of structure factors for these two compounds (33 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48109

D. Coucouvanis*
A. Hadjikyriacou

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(5) The site of the bridging ligand in the anion of I is occupied primarily (86%) by S^{2-} and also by a minor component of S_2^{2-} (14%). The S^{2-} component was refined with anisotropic temperature factors while the minor S_2^{2-} component was refined isotropically. Four of the Et_4N^+ cations in the unit cell are located on general positions. The other four are located on the following centers of symmetry: 0, 0, 0; 0, $^1/_2$, $^1/_2$; $^1/_2$, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$. These cations consequently are disordered.

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