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Communications

Synthesis and Structural Characterization of the Ph_4P^+ Salts of the $[MoS(MoS_4)(S_4)]^{2-}$ Anion and Its $[Mo_2S_6]^{2-}$ and $[Mo_2S_7]^{2-}$ Desulfurized Derivatives

Sir:

The importance of molybdenum–sulfur compounds in industrial catalysis[1] and in biological N_2 fixation[2] has stimulated recent interest in Mo/S chemistry. The chemistry of the binary molybdenum sulfide anions has been given particular attention,[3,4] and the complex equilibria that prevail in solutions of MoS_4^{2-}, in the presence of either sulfur or S_x^{2-} ions, have been recognized.[3] Complexes such as $[(S_4)_2MoS]^{2-}$,[3a] $[(S_2MoS(\mu\text{-}S))_2]^{2-}$,[3b,c] $[(S_4)MoS(\mu\text{-}S)]_2^{2-}$,[3a] $[(S_4)MoS(\mu\text{-}S_2)SMo(S_2)]^{2-}$,[3a,d] and $[MoS(MoS_4)_2]^{2-}$[3e] have been synthesized and structurally characterized, and various pathways that may possibly interrelate these compounds have been suggested.[3a] The interconversions among the Mo/S thio anions usually involve the addition or loss of sulfur atoms or sulfide ions and often are interpreted in terms of intramolecular electron-transfer processes.

Among the thio anions that have been proposed to coexist in equilibria or to be intermediates in the formation of the $[(S_4)_2MoS]^{2-}$,[3a] $[(S_4)MoS(\mu\text{-}S)_2SMO(S_2)]^{2-}$,[3a,d] and $[MoS(MoS_4)_2]^{2-}$[3e] complexes, are the $[Mo_2S_7]^{2-}$[3a,e] and $[MoS(MoS_4)(S_4)]^{2-}$[3a] anions. The former has been reported[5] to form in aqueous MoS_4^{2-} solutions at pH ~5 but has not been isolated in the solid state, while the latter, a possible precursor to $[Mo_2S_7]^{2-}$, is a hitherto unknown derivative of the well-known[3a,3e] $(Mo{=}S)^{2+}$ chromophore.

In this communication we report on the synthesis and structural characterization of the $[MoS(MoS_4)(S_4)]^{2-}$ anion, and the derivative $[Mo_2S_7]^{2-}$ and $[Mo_2S_6]^{2-}$ anions.

The Ph_4P^+ salt of the $[(S_4)MoS(\mu\text{-}S)_2SMo(S_2)]^{2-}$[3a,d] anion, when allowed to stand for 6 h at ambient temperature in a dimethylformamide (DMF) solution that contains a large excess (50-fold) of $NaBH_4$, affords after unexceptional workup, the microcrystalline, brown-red $(Ph_4P)_2[MoS(MoS_4)(S_4)]$ (I). Thin brown needles of this compound can be obtained from DMF/2-propanol mixtures. The infrared spectrum of I shows Mo–S vibrations at 457, 487, and 507 cm^{-1} and the electronic spectrum shows absorptions at 422 (ϵ = 6980), 350 (sh), and 298 nm (ϵ = 23 800). The structure[6] of the anion in I is shown in Figure 1. It can be described as a mixed-valence Mo^{IV}–Mo^{VI} dimer and is a "mixed-ligand" analogue of the closely related $[(S_4)_2MoS]^{2-}$

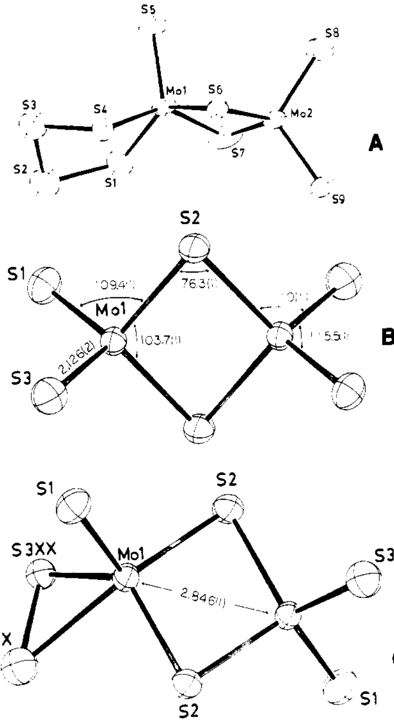

Figure 1. Structure and labeling of $[MoS(MoS_4)(S_4)]^{2-}$ (A), $[Mo_2S_6]^{2-}$ (B), and $[Mo_2S_7]^{2-}$ (C). Thermal ellipsoids as drawn by ORTEP[14] represent the 40% probability surfaces.

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(6) Crystal and refinement data: brown needles of $(Ph_4P)_2[MoS(MoS_4)(S_4)]$ (I) are triclinic, space group $P\bar{1}$, with a = 10.613 (3) Å, b = 12.352 (1) Å, c = 20.062 (2) Å, α = 99.96 (1)°, β = 103.81 (2)°, γ = 96.64 (2)°, and Z = 2; brown-red prisms of $(Ph_4P)_2Mo_2S_{6.62}$ (IV/V), are triclinic, space group $P\bar{1}$, with a = 9.937 (2) Å, b = 10.082 (2) Å, c = 13.112 (2) Å, α = 76.14 (1)°, β = 71.68 (1)°, γ = 70.77 (2)°, and Z = 1. Single-crystal X-ray diffraction data were collected for both compounds on a Nicolet P3F four-circle diffractometer using Mo Kα radiation and the solution of the structures was carried out by a combination of heavy-atom-Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 2583 unique reflections ($2\theta_{max}$ = 42; $I > 3\sigma$) for I; and on 1994 unique reflections ($2\theta_{max}$ = 40; $I > 3\sigma$) for IV/V. Anisotropic temperature factors were used for the non-hydrogen, nondisordered atoms, and isotropic factors were used for the positionally disordered sulfur atoms. At the current stage of refinement, with all atoms present in the asymmetric units, R = 0.051 for I and 0.029 for IV/V.

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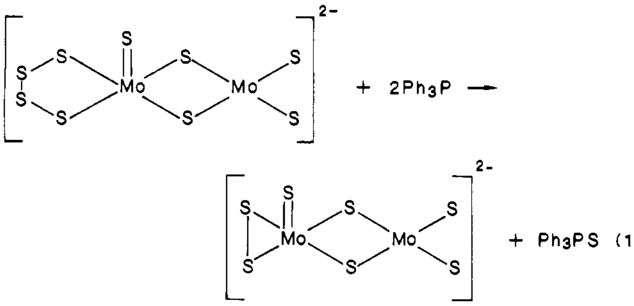
Table I. Interatomic Distances (Å) and Angles (deg) in the $[MoS(MoS_4)(S_4)]^{2-}$ (I), $[MoS(S_4)_2]^{2-}$ (II), $[MoS(MoS_4)_2]^{2-}$ (III), $[Mo_2S_6]^{2-}$ (IV), and $[Mo_2S_7]^{2-}$ (V) Anions

	I[a]	II[b]	III[c]	IV[a]	V[a]
Distances[d]					
Mo(1)–Mo(2)[d]	2.859 (1)		2.95 (2, 4)[f]	2.846 (1)	2.846 (1)
Mo(1)–S_{ax}[g]	2.105 (3)	2.128 (1)	2.086 (4)	2.141 (1)	2.141 (1)
Mo(1)–S_t[h]	2.39 (2, 2)	2.36 (2, 4)		2.126 (2)	2.356 (4)
					2.459 (5)
Mo(1)–S_b[i]	2.36 (2, 2)		2.39 (4, 2)	2.303 (1)	2.303 (1)
Mo(2)–S_b	2.25 (2, 2)		2.24 (4, 1)		
Mo(2)–S_t	2.15 (2, 1)		2.141 (4, 4)		
S(1)–S(2)	2.120 (8)	2.166 (1)			
S(3)–S(4)	2.119 (8)	2.107 (1)			
S(2)–S(3)	2.015 (11)	2.012 (1)			
S(3X)–S(3XX)					2.006 (7)[n]
Angles					
Mo–S_b–Mo				76.3 (1)[o]	76.3 (1)[o]
S–Mo(1)–S_{inter}[j]	75 (2, 5)			103.7 (1)[o]	103.7 (1)[o]
S–Mo(1)–S_{intra}[k]	89.5 (2)[l]	90.32 (3)			
	99.0 (1)[m]		94.7 (6)		
S–Mo(1)–S_{ax}	110 (2, 4)[l]				
	105.5 (2, 1)[m]		105 (4, 1.5)		

[a] This work. The cited values for II and III are in reference to the labeling scheme used for the thioanions reported in this paper (Figure 1). [b] Reference 3a. [c] Reference 3d. [d] When two numbers are given in parentheses, the first entry represents the number of independent distances or angles averaged out and the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation $\sigma = [\sum_{i=1}^{n}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [e] The distances and angles in II and III have been chosen in analogous reference to chemically equivalent distances and angles in I. [f] The major component of a positionally disordered anion is used. [g] S_{ax} represents the axially located sulfur atoms (S(5) in Figure 1). [h] S_t refers to nonbridging, equatorially located S atoms. [i] S_b represents bridging sulfur atoms. [j] Interligand angles. [k] Intraligand angles. [l] With the S_4^{2-} ligand. [m] With the MoS_4^{2-} "ligand". [n] For the η^2-S_2^{2-} ligand. [o] Angles within the Mo_2S_2 rhombic unit.

(II),[3a] and $[(MoS_4)_2MoS]^{2-}$ (III)[3e] anions. A comparison of related structural details is shown in Table I. In view of the apparent similarities in the three anions and detailed previous[3a,e] discussions of the structures of II and III, a discussion of the structure of I will be deferred to a later detailed report.

The reaction of I with triphenylphosphine, in a 1:2 molar ratio, was considered a rational route for the synthesis of the $[Mo_2S_7]^{2-}$ anion. This reaction (eq 1) was attempted in DMF solution and



(1)

afforded after prolonged heating (80–90 °C; 22 h) and nonexceptional workup, a brown-black microcrystalline product. The electronic spectrum (556, 482 (sh), 452, 358 (sh), 290 nm) and the infrared spectrum in the area usually associated with Mo–S vibrations (503 (m), 476 (m), 457 cm^{-1} (w)) suggested that the compound contained a new thio anion; furthermore, the analysis[7] was consistent with the stoichiometry $(Ph_4P)_2(Mo_2S_7)\cdot$DMF.

The crystal structure of this compound has been determined[6] and shows that a center of symmetry in the unit cell (0, 0, $^1/_2$) is occupied by the new $[Mo_2S_6]^{2-}$ (IV) and $[Mo_2S_7]^{2-}$ (V) anions (Figure 1b,c). The relative occupancy factors for IV and V were refined to final values of 0.37 and 0.63 respectively.[8] The noncentrosymmetric V (Figure 1c) occupies the site in two "equal-weight" orientations that are diametrically related by the center of symmetry.[9] In the structure of IV, two edge-sharing Mo^VS_4 tetrahedra form a dimer with a Mo(V)–Mo(V) distance of 2.846 (1) Å (Figure 1b). The Mo–S_t bonds at 2.141 (1) and 2.126 (2) Å are considerably shorter than the Mo–S bond in the MoS_4^{2-} anion,[10] (2.177 (6) Å) but longer than the Mo–S_t bonds in the *syn*-$[Mo_2S_8]^{2-}$ anion[3c] (2.108 (1) and 2.128 (1) Å). They are similar to the Mo–S_t bonds in the $[S_2MoS_2FeL]^{2-}$ (L = $(SPh)_2$, S_5^{2-}) dimers[11] (range: 2.135 (6)–2.161 (6) Å). In the latter, intramolecular Fe(II)–Mo(VI) charge transfer results in partial reduction of the Mo(VI) center. The Mo–S_b bridging bond in the rhombic Mo_2S_2 unit in IV at 2.303 (1) Å is similar to the Mo(V)–S_b bond in the $[Mo_2S_{10/12}]^{2-}$ anions[3a,d] (2.32 (2) Å) and the *syn*-$[Mo_2S_8]^{2-}$ anion[3c] (2.306 (1) Å).

The $[Mo_2S_6]^{2-}$ anion can be obtained in pure form from the reaction of the $[(S_4)MoS(\mu\text{-}S)_2SMo(S_2)]^{2-}$[3a,d] complex with a 6-fold excess of Ph_3P in DMF solution.[12] The $[Mo_2S_6]^{2-}$ anion (diamagnetic at ambient temperature) is characterized by a spin-coupled magnetic ground state that is due to strong intermetallic interactions commonly observed with bis(μ-sulfido)molybdenum(V) dimeric compounds. It reacts, in DMF, with 1 equiv of dibenzyl trisulfide (BzSSSBz) to give pure[13] $[Mo_2S_7]^{2-}$ (Figure 1c) and with 2 equiv of BzSSSBz to give the known[3b,3c] *syn*-$[Mo_2S_8]^{2-}$ anion. The sequential addition of sulfur atoms to

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(7) Anal. Calcd for $(Ph_4P)_2Mo_2S_7\cdot$DMF ($Mo_2S_7P_2C_{51}H_{47}ON$): Mo, 16.45; S, 19.19; P, 5.31; C, 52.44; H, 4.03. Found: Mo, 16.12; S, 18.76; P, 5.55; C, 52.59; H, 4.00.

(8) The crystallographic results indicate that the correct formulation of the product is $(Ph_4P)_2Mo_2S_{6.62}$. For this formulation the calculated analysis is as follows: Mo, 16.63; S, 18.34; P, 5.37; C, 52.99; H, 4.07.

(9) An alternative structural model compatible with both the $Mo_2S_{6.63}$ stoichiometry and the crystallographic results could be one that places $[Mo_2S_6]^{2-}$ and *anti*-$[(S_2)MoS(\mu\text{-}S)]_2^{2-}$ at the same site with occupation factors of 0.685 and 0.315, respectively. At this time we cannot rule this model out.

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(12) The $[Ph_4P]_2[Mo_2S_6]$ obtained by this method has a unit cell virtually identical with that of IV/V and a slightly lower density. The center of symmetry is *singly* occupied by $[Mo_2S_6]^{2-}$, and following refinement based on a new data set, the new structural parameters for the anion are very similar to those obtained previously. The electronic spectrum of pure $[Mo_2S_6]^{2-}$ shows maxima at 290, 310, 362 (sh), 454, and 482 nm (sh), and in the FT infrared spectrum the Mo–S vibrations appear at 452 (w), 475 (m), and 503 cm^{-1} (m).

(13) The electronic spectrum of $[Mo_2S_7]^{2-}$ shows absorption at 296 (sh), 360 (sh), 422 (sh), 450, and 560 nm and the Mo–S vibrations in the FT infrared spectrum appear at 454 (w), 480 (m), and 504 cm^{-1} (m).

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$[Mo_2S_6]^{2-}$ appears to be a convenient route for the synthesis of most known thio anions and may be useful in the synthesis of related, hitherto unknown Mo/S complexes.

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Supplementary Material Available: Listings of positional and thermal parameters for $(Ph_4P)_2[MoS(MoS_4)(S_4)]$ and $(Ph_4P)_2[Mo_2S_6/Mo_2S_7]$ (8 pages); listings of structure factors for both compounds (18 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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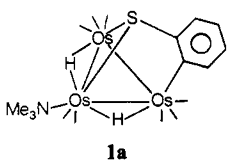
High-Nuclearity Clusters Containing Carbene Ligands. Synthesis, Structural Analyses, and Isomerization of Disulfidohexaosmium Carbonyl Cluster Compounds Containing Secondary (Dimethylamino)carbene Ligands

Sir:

The synthesis in 1964 of the first transition-metal complex to contain a heteronuclear carbene ligand proved to be the beginning of an extensive and exciting new area of transition-metal chemistry.[1,2] Curiously, however, to date there have been very few reports of transition-metal cluster compounds that contain heteronuclear carbene ligands and no examples of complexes where the metal nuclearity is higher than 3.[3-9] We have recently discovered that trimethylamine can serve as a precursor to the formation of secondary (dimethylamino)carbene ligands in triosmium clusters. We have now found that pyrolysis of the trimethylamine complex $Os_3(CO)_8(NMe_3)(\mu_3\text{-}SC_6H_4)(\mu\text{-}H)_2$ (**1**) yields the first examples of hexanuclear cluster compounds that contain heteronuclear carbene ligands.

Compound **1** was obtained as a mixture of two slowly interconverting isomers, **1a** (21% yield) and **1b** (10% yield), from the reaction of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ with an excess of Me_3NO in refluxing CH_2Cl_2 for 3 h.[10] When 26 mg of **1a** was refluxed in heptane solvent for 20 min, it was transformed into a mixture of three new hexaosmium clusters that are all isomers with the



1a

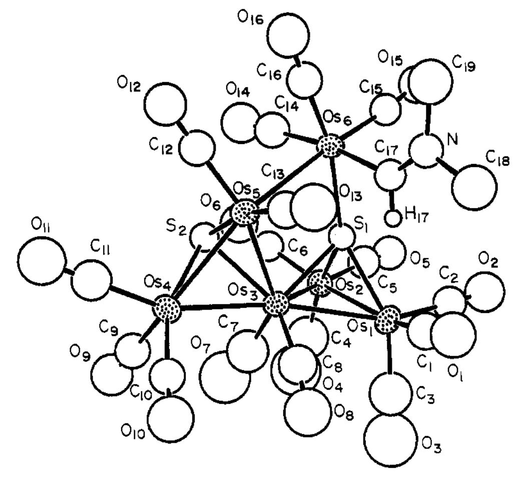


Figure 1. ORTEP diagram of $Os_6(CO)_{16}[C(H)NMe_2](\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2a**) showing 50% probability thermal ellipsoids.

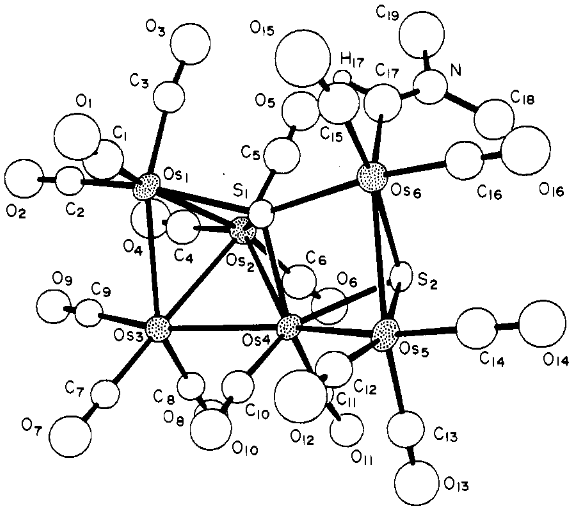
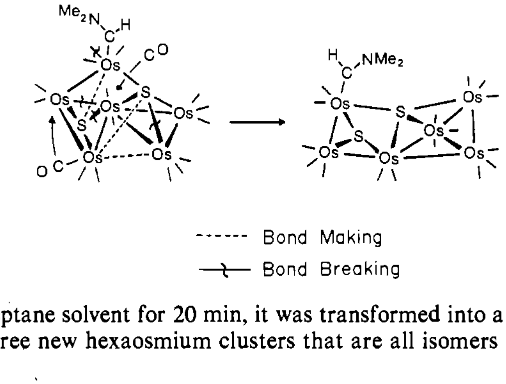


Figure 2. ORTEP diagram of $Os_6(CO)_{16}[C(H)NMe_2](\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2b**) showing 50% probability thermal ellipsoids.

Scheme I



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(10) Compounds **1a** and **1b** are yellow products that were isolated by TLC on silica gel plates by using a 20% CH_2Cl_2/80% hexane solvent mixture. IR (ν(CO), in hexane, cm^{-1}): for **1a**, 2086 m, 2048 s, 2036 s, 2005 s, 1995 m, 1972 m; for **1b**, 2085 m, 2049 s, 2035 s, 2007 s, 1990 m, 1970 m. ^1H NMR (δ, in $CDCl_3$): for **1a**, 7.51–6.22 (m, 4 H), 3.35 (s, 9 H), −13.51 (s, 1 H), −21.46 (s, 1 H); for **1b**, 7.40–6.30 (m, 4 H), 3.13 (s, 9 H), −13.03 (s, 1 H), −22.00 (s, 1 H). Compounds **1a** and **1b** isomerize to a 4/1 **1a**/**1b** equilibrium in a $CHCl_3$ solution. This takes a period of several days at 25 °C. Compound **1a** was also characterized by a single-crystal X-ray diffraction analysis. Compound **1a** contains a triply bridging orthometalated benzenethiolato ligand on the face of a triosmium cluster. A trimethylamine ligand is coordinated to one of the sulfur-bridged metal atoms. Additional details will be provided in the full report on this work. Satisfactory elemental analyses (C, H, N) have been obtained: Anal. Calcd (found) for **1a**: C, 21.17 (21.29); H, 1.56 (1.38); N, 1.45 (1.43). Calcd (found) for **1b**: C, 21.17 (21.43); H, 1.56 (1.46); N, 1.45 (1.43).