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Synthesis, Structure, and Reactivity of Clusters Containing the $[Mo_2O_2(\mu\text{-}E)_2]^{2+}$ (E = O, S) Core and Coordinated $[Fe_2S_2(CO)_6]^{2-}$ Units

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Three compounds containing the $[Mo_2O_2(\mu\text{-}E)_2]^{2+}$ (E = O, S) cores ligated by $[Fe_2S_2(CO)_6]^{2-}$ have been prepared and structurally characterized: $(Ph_4As)_2\{Mo_2O_2(\mu\text{-}S)_2[Fe_2S_2(CO)_6]_2\}$ ($(Ph_4As)_2$**I**, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.266(12)$ Å, $b = 14.746(12)$ Å, $c = 16.643(15)$ Å, $\alpha = 101.9(2)°$, $\beta = 98.2(2)°$, $\gamma = 99.1(2)°$, $Z = 2$, $R = R_w = 0.058$, 6196 reflections with $I > 2.5\sigma(I)$), $(Ph_4P)_2\{Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)[Fe_2S_2(CO)_6]_2\}$ ($(Ph_4P)_2$**II**, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.33(1)$ Å, $b = 15.10(1)$ Å, $c = 18.00(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.6(5)°$, $Z = 2$, $R = 0.067$, $R_w = 0.047$, 3183 reflections with $I > 3\sigma(I)$), and $(Ph_4P)_2\{Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\}\cdot THF$ ($(Ph_4P)_2$**III**$\cdot$THF, triclinic, space group $P\bar{1}$ (No. 2), $a = 16.599(4)$ Å, $b = 16.963(4)$ Å, $c = 15.465(3)$ Å, $\alpha = 113.90(2)°$, $\beta = 102.06(2)°$, $\gamma = 109.29(2)°$, $Z = 2$, $R = 0.044$, $R_w = 0.066$, 5043 reflections with $I > 3\sigma(I)$). Clusters **I** and **II** contain the *cis*-bis(oxomolybdenum) core bridged by either two sulfido ligands or one sulfido and one oxo ligand, respectively. Cluster **III** contains two *cis*-$[Mo_2O_4]^{2+}$ cores connected by two methoxy bridges to give the $[Mo_4O_8(\mu\text{-}OCH_3)_2]^{2+}$ structural fragment. Clusters **I** and **III** undergo reactions with sulfide reagents to yield products that are indistinguishable from one another by IR spectroscopy, and the nature of the possible common product is discussed.

Introduction

As a result of the importance of sulfido−molybdenum compounds both biologically (in enzymes such as xanthine and sulfite oxidases, nitrite reductase,[1] and nitrogenase[1,2]) and industrially (as hydrodesulfurization catalysts[3]), numerous compounds that contain the dimeric molybdenum(V) moiety $[Mo_2O_2(\mu\text{-}E)_2]^{2+}$ (E = O or S) have been isolated and characterized. The species $[Mo_2O_2(\mu\text{-}O)_2Cl_6]^{4-}$ has been shown to be the predominant form of Mo(V) in dilute (1 M) aqueous HCl solutions,[4] and ligand metathesis reactions of this complex have produced several crystallographically characterized compounds[5] in which the structure of the $[Mo_2O_2(\mu\text{-}O)_2]^{2+}$ core is relatively ligand-independent. In many cases, one or both of the bridging oxygens can be replaced by reaction of the complex with H_2S, giving compounds that contain the $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)]^{2+}$ [6] or $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ [6a,7] cores. Bis(μ-sulfido) compounds can also be prepared by reaction of $[MoO_4]^{2-}$ with H_2S or aqueous polysulfide solutions.[8] The replacement of bridging oxo by sulfido is not reversible, an observation that indicates the greater stability of the sulfido bridge. In the compound $[Mo_2O_2S_2(C_2O_4)_2(H_2O)_2]^{2-}$, the presence of bridging sulfide has been shown to labilize other ligands coordinated to molybdenum.[8d] Direct replacement of terminal oxo by sulfido in binuclear complexes has not been reported, but compounds containing $[Mo_2OS(\mu\text{-}S)_2]^{2+}$ and $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ cores have been prepared by reactions involving $[MoS_4]^{2-}$ in aqueous or non-aqueous solvents.[9] Removal of terminal sulfide from $Mo_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2$ with Ph_3P or CN^- in the presence of trace H_2O has been reported to yield the corresponding terminal dioxo species.[9b] Coucouvanis et al. have described the synthesis of ethylenedithiolate compounds containing the $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ core by electrophilic attack of dicarbomethoxyacetylene at the disulfide bonds of $[Mo_2O_2S_n]^{2-}$ (n = 7−9).[10] In a previous study of the reaction of the dianion $[Fe_2S_2(CO)_6]^{2-}$ with high-valent Mo(V) complexes, we reported that the bis(μ-oxo) compound $\{Mo_2O_4[Fe_2S_2(CO)_6]_2\}^{2-}$ was one of the four

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products isolated.[11] Because this compound represents the first mixed-metal cluster containing the $[Mo_2O_4]^{2+}$ unit, we initiated studies to determine the effect of the $[Fe_2S_2(CO)_6]^{2-}$ ligand on the chemistry of the $[Mo_2O_4]^{2+}$ core. We report herein the structures and spectroscopic properties of several novel compounds that contain the $[Mo_2O_2E_2]^{2+}$ unit and the reactions of these products with various sulfide reagents.

Experimental Section

Solvents (acetonitrile (MeCN), tetrahydrofuran (THF), methanol (MeOH), isopropyl alcohol (*i*-PrOH)) were distilled under nitrogen from the appropriate drying reagents and were stored under dry nitrogen; *N*,*N*-dimethylformamide (DMF) was stored under nitrogen over molecular sieves. Distilled water was deionized by a Millipore Milli-Q Water System and was sparged with dry nitrogen. Molybdenum pentachloride and lithium sulfide were purchased from Aldrich, hydrogen sulfide was purchased from Matheson, and hexamethyldisilthiane was purchased from Fluka; all reagents were used as received. The compounds $Fe_2S_2(CO)_6$ and $[Fe_2S_2(CO)_6]^{2-}$ were prepared as reported previously;[12] $(Ph_4P)_4Mo_2O_4(NCS)_6$[13] and $MoOCl_3(THF)_2$[14] were prepared by published procedures. All manipulations were performed under a nitrogen atmosphere unless specified otherwise.

Solution infrared spectra were obtained on a Mattson Cygnus FTIR spectrometer using NaCl cells of 0.1 or 0.2 mm pathlength. Electronic spectra (UV−vis) were obtained on a Cary 219 or 17D spectrometer. Negative ion mass spectra of clusters in DMF/*p*-nitrophenyloctyl ether matrices were obtained on a tandem quadrupole Fourier-transform mass spectrometer equipped with a cesium ion gun.[15]

Isolation of $(Ph_4As)_2Mo_2O_2S_2[Fe_2S_2(CO)_6]_2$, $(Ph_4As)_2$I. To a solution of 3 equiv of $[Fe_2S_2(CO)_6]^{2-}$ in THF at −78 °C was added a solution of 1 equiv of $MoOCl_3(THF)_2$ in MeCN. Upon warming of the solution to room temperature and addition of excess $(Ph_4As)Cl$ in *i*-PrOH, the previously reported compounds[11] $(Ph_4As)_2MoOFe_5S_6(CO)_{12}$ and $(Ph_4As)_2Fe_5S_4(CO)_{12}$ precipitated. Reducing the volume of the resulting orange filtrate under vacuum yielded a light orange microcrystalline precipitate of $(Ph_4As)_2$**I** (yield ca. 15%); X-ray quality crystals were obtained by slow diffusion of *i*-PrOH into an MeCN solution of the cluster. IR (MeCN), cm^{-1}: ν_{CO} 2052 (sh), 2043 (ms), 2014 (ms), 2007 (sh), 1966 (vs); $\nu_{Mo=O}$ 947 (w). Electronic spectrum (MeCN), λ (nm) (ϵ (M^{-1} cm^{-1})): 464 (3700), 330 (22 700). Mass spectrum: *m/z* 1359 ([(Ph_4As)**I**]$^-$), 976 ([**I**]$^-$).

Reaction of $[Fe_2S_2(CO)_6]^{2-}$ with $[Mo_2O_4Cl_6]^{4-}$. A deep orange solution of 1.09 g (4 mmol) of $MoCl_5$ in ca. 30 mL of MeCN was treated with H_2O just until the color changed to a bright, clear green. The solvent was removed under vacuum, the residue was dissolved in MeCN, and the IR spectrum of the solution was obtained. This procedure was repeated several times (subsequent color changes were to brown instead of bright green) until the IR spectrum showed bands only at 989 and 744 cm^{-1}. A solution of this compound in ca. 5 mL of MeCN at room temperature was added rapidly to a solution of $[Fe_2S_2(CO)_6]^{2-}$ (4 mmol) in THF at −78 °C, and the reaction mixture was warmed to room temperature. The IR spectrum revealed several ν_{CO} bands indicative of a mixture of compounds, from which two species were isolated.

A. Isolation of $(Ph_4P)_2Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\cdot THF$, $(Ph_4P)_2$III·THF. Addition of 2.3 g (6 mmol) $(Ph_4P)Cl$ in ca. 60 mL of *i*-PrOH to the mixture above followed by reduction of the solvent volume under vacuum resulted in the precipitation of a brown amorphous solid that was filtered and washed with *i*-PrOH. Attempted recrystallization of this solid by slow diffusion of MeOH:diethyl ether (Et_2O, ca. 2:1) into a THF solution of the solid resulted in precipitation of a small amount of light orange microcrystalline solid; recrystallization of this relatively insoluble solid by slow diffusion of MeOH:Et_2O (ca. 3:1) into an MeCN solution of the compound yielded a small amount of large, clear orange crystals of **III** suitable for X-ray diffraction studies. IR (MeCN), cm^{-1}: ν_{CO} 2054 (m), 2015 (vs), 1975 (ms, br), 1953 (sh); $\nu_{Mo=O}$ 974 (w), 945 (sh). Electronic spectrum (MeCN), λ (nm): 460 (sh), 325. Substitution of $(Bu_4N)Cl$ for $(Ph_4P)Cl$ in the above workup and omission of the MeOH−Et_2O recrystallization steps allowed isolation of an orange-brown amorphous solid that was readily soluble in MeCN and had IR and electronic spectra identical to those of **III** above; ^1H NMR data were consistent with formulation of this compound as $(Bu_4N)_2Mo_4O_8(\mu\text{-O-}i\text{-Pr})_2[Fe_2S_2(CO)_6]_2$, $(Bu_4N)_2$**IIIb** (maximum yield 18%). IR (MeCN), cm^{-1}: ν_{CO} 2052 (m), 2015 (vs), 1973 (s, br), 1950 (sh); $\nu_{Mo=O}$ 972 (w), 951 (sh). Electronic spectrum (MeCN), λ (nm) (ϵ (M^{-1} cm^{-1})): 460 (5140), 330 (28 800). ^1H NMR (δ, ppm) in CD_3CN: 3.03 (16 H), 1.95 (12 H), 1.58 (16 H), 1.34 (16 H), 0.94 (24 H).

B. Isolation of $(Ph_4P)_2Mo_2O_3S[Fe_2S_2(CO)_6]_2$, $(Ph_4P)_2$II. Further reduction of the volume of the filtrate from part A resulted in precipitation of a second orange microcrystalline product; X-ray quality crystals of **II** were obtained by slow diffusion of *i*-PrOH into a concentrated MeCN solution of the cluster (yield ca. 40% based on Mo). The IR and electronic spectra of this compound are virtually identical to those of **I**; the clusters could be distinguished by the 16 amu difference in their parent ions observed by mass spectrometry. IR (MeCN), cm^{-1}: ν_{CO} 2053 (sh), 2043 (ms), 2014 (ms), 2008 (sh), 1965 (vs); $\nu_{Mo=O}$ 947 (w). Electronic spectrum (MeCN), λ (nm) (ϵ (M^{-1} cm^{-1})): 465 (3700), 330 (23 000). Mass spectrum: *m/z* 1300 ([(Ph_4P)**II**]$^-$), 960 ([**II**]$^-$).

Preparation of $(Ph_4P)_2Mo_2O_4[Fe_2S_2(CO)_6]_2$, $(Ph_4P)_2$IV. A solution of 1.45 g (4 mmol) of $MoOCl_3(THF)_2$ in ca. 30 mL of MeCN was treated several times with small portions of degassed H_2O (as described above for $MoCl_5$) until the infrared spectrum of the residue in MeCN showed bands at 989 and 740 cm^{-1} only. This solution was added rapidly to a solution of $[Fe_2S_2(CO)_6]^{2-}$ (4 mmol) in THF at −78 °C, and the mixture was warmed to room temperature. The infrared spectrum of the mother liquor showed three ν_{CO} bands at 2043, 2010, and 1967 cm^{-1}, with weak shoulders at 2053 and 2015 cm^{-1}. The solvent was removed under vacuum and the residue was redissolved in ca. 40 mL of MeCN. A solution of 0.84 g (2 mmol) of $(Ph_4P)Cl$ in ca. 30 mL of *i*-PrOH was added; upon reduction of the solution volume under vacuum a dark brown amorphous solid precipitated, which was filtered and washed with *i*-PrOH. The infrared spectrum of this solid was virtually identical to that of the mother liquor; yield ca. 30%. IR (MeCN), cm^{-1}: ν_{CO} 2051 (sh), 2043 (m), 2014 (sh), 2008 (s), 1966 (vs); $\nu_{Mo=O}$ 969 (sh), 951 (mw). Electronic spectrum (MeCN), λ (nm) (ϵ (M^{-1} cm^{-1})): 460 (sh), 330 (>20 000). Mass spectra of the tetrapropylammonium salt (Table 4 and Supporting Information) indicated a mixture of the desired bis(μ-oxo) compound and the (μ-oxo)(μ-sulfido) compound **II**.

Reaction of $(Ph_4P)_4Mo_2O_4(NCS)_6$ with $[Fe_2S_2(CO)_6]^{2-}$. To a solution of $[Fe_2S_2(CO)_6]^{2-}$ (2 mmol) in ca. 50 mL of THF at −78 °C was added a room-temperature solution of 1.96 g (1 mmol) of $(Ph_4P)_4Mo_2O_4(NCS)_6$ in ca. 10 mL of DMF. The dark orange solution was warmed to room temperature, during which time the color changed to greenish-brown and finally to brown. The solvent volume was reduced under vacuum to ca. 1−2 mL, and *i*-PrOH was added to precipitate 1.25 g of brown solid. The solid was identified as $(Ph_4P)_2MoOFe_5S_6(CO)_{12}$ by its infrared spectrum (yield 0.8 mmol, ca. 40% based on Mo).[11]

Reaction of $(Bu_4N)_2Mo_4O_8(\mu\text{-O-}i\text{-Pr})_2[Fe_2S_2(CO)_6]_2$ with $[Fe_2S_2(CO)_6]^{2-}$ and Isolation of $(Bu_4N)_2Mo_2OS_4[Fe_2S_2(CO)_6]$, $(Bu_4N)_2$V. To a solution of $[Fe_2S_2(CO)_6]^{2-}$ (0.16 mmol) in ca. 30 mL of THF at −78 °C was added a room temperature solution of 140 mg (0.08 mmol) of **IIIb** in ca. 5 mL of MeCN, and the resulting mixture was warmed to room temperature and stirred for ca. 3 days. Addition of excess $(Ph_4P)Cl$ in *i*-PrOH resulted in precipitation of ca. 0.13 g of a dark brown solid that was filtered and washed with *i*-PrOH; this solid was shown to be a mixture of $[Fe_5S_4(CO)_{12}]^{2-}$ and $[MoOFe_5S_6(CO)_{12}]^{2-}$

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Table 1. Summary of Crystal Data, Intensity Measurements and Structure Solution and Refinement

	$(Ph_4As)_2$**I**	$(Ph_4P)_2$**II**	$(Ph_4P)_2$**III**·THF
A. Crystal Data			
formula	$C_{60}H_{40}Fe_4Mo_2O_{15}P_2S_5$	$C_{66}H_{54}Fe_4Mo_4O_{23}P_2S_4$	$C_{60}H_{40}As_2Fe_4Mo_2O_{14}S_6$
fw	1742	1638	2012
cryst color, habit	orange prism	black prism	orange prism
cryst dimens (mm)	0.35 × 0.30 × 0.30	0.47 × 0.36 × 0.28	0.40 × 0.35 × 0.30
cryst system	triclinic	triclinic	monoclinic
a (Å)	14.266(12)	16.599(4)	15.33(1)
b (Å)	14.746(12)	16.963(4)	15.10(1)
c (Å)	16.643(15)	15.465(3)	18.00(2)
α (deg)	101.9(2)	113.90(2)	90
β (deg)	98.2(2)	102.06(2)	100.6(5)
γ (deg)	99.1(2)	109.29(2)	90
V (Å^3)	3327(20)	3448(5)	4096(16)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z	2	2	2
d_{calc} (g/cm^3)	1.739	1.58	1.690
μ(Mo Kα) (cm^{-1})	24.3	14.13	14.7
B. Intensity Measurements			
diffractometer	Siemens/Nicolet P3m	Siemens/Nicolet P3m	Siemens/Nicolet P3m
radiation	MoKα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
temperature (°C)	25	25	25
scan type	−2	−2	−2
$2\theta_{max}$ (deg)	48	45.0	50
no. of reflections	total: 9127	total: 7167	total: 6370
	unique: 8701	unique: 6707	unique: 6118
	(R_{int} = 0.022)	(R_{int} = 0.023)	(R_{int} = 0.071)
corrections	Lorentz−polarization	Lorentz−polarization	abs (trans factors: 0.81−1.00) Lorentz−polarization
C. Structure Solution and Refinement			
structure solution	SHELXS-86	direct methods (SIR88)	SHELXS-86
refinement	block-diagonal least-squares	full-matrix least-squares	block-diagonal least-squares
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
no. of observns, $I > n\sigma(I)$	6196 (n = 2.5)	5043 (n = 3.0)	2628 (n = 3.0)
no. of variables	553	553	412
refln/param	11.2	9.1	6.4
R; R_w	0.058; 0.058	0.044; 0.066	0.065; 0.0466
goodness of fit	3.5	1.50	4.2
max peak (e/Å^3) (final diff map)	−1.6	1.04	2.1

by IR spectroscopy. The mass of this solid accounted for ca. 70% of the total mass of the reactants. The solvent was removed from the light orange filtrate under vacuum; extraction with THF yielded a bright orange solution and a nearly colorless insoluble solid ($(Ph_4P)Cl$). Addition of Et_2O to the THF extract precipitated ca. 20 mg of a bright orange flocculent solid that was filtered and dried under vacuum. IR (MeCN), cm^{-1}: ν_{CO} 2047(m), 2013(s), 1968(s). Mass spectrum: *m/z* 922 ([(Bu_4N)(**V**)]$^-$), 894 ([(Bu_4N)(**V** − CO)]$^-$), 652 ([**V** − CO]$^-$).

X-ray Analyses. Crystal data and collection and refinement parameters are summarized in Table 1 for $(Ph_4As)_2\{Mo_2O_2S_2[Fe_2S_2(CO)_6]_2\}$ ($(Ph_4As)_2$**I**), $(Ph_4P)_2\{Mo_2O_3S[Fe_2S_2(CO)_6]_2\}$ ($(Ph_4P)_2$**II**), and $(Ph_4P)_2\{Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\}$·THF ($(Ph_4P)_2$**III**·THF). In all structures, the cations were crystallographically ordered with no unusual features and will not be discussed further. Tables of all positional and thermal parameters, as well as selected distances and angles, are available as Supporting Information.

$(Ph_4As)_2$I. Intensity data were collected on a Nicolet P3m diffractometer and the structure was solved using SHELXS-86.[16] The structure was refined to convergence ($(\Delta/\sigma)_{max} < 0.10$) using the block-diagonal, least squares method. All heavy atoms were refined anisotropically; no account was taken of H atoms.

$(Ph_4P)_2$III·THF. Data collection and structure solution were performed as for $(Ph_4As)_2$**I**. H atoms were included in fixed positions with $B = B_{eq} + 1.0$ for the atom of attachment.

$(Ph_4P)_2$II. Intensity data were collected on a Siemens/Nicolet P3M diffractometer and were corrected for *Lp* and absorption effects. All calculations were performed with the TEXSAN 5.0 software package on a VAXstation 3520 computer. The structure was determined by using direct methods (SIR 88). Full-matrix least-squares refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms, except the C atoms of the Ph_4P^+ cation.

Results and Discussion

Description of Structures. The structures of the new compounds $(Ph_4As)_2Mo_2O_2S_2[Fe_2S_2(CO)_6]_2$, $(Ph_4As)_2$**I**, $(Ph_4P)_2Mo_2O_3S[Fe_2S_2(CO)_6]_2$, $(Ph_4P)_2$**II**, and $(Ph_4P)_2Mo_4O_8(OMe)_2[Fe_2S_2(CO)_6]_2$·THF, $(Ph_4P)_2$**III**·THF, have been determined. A summary of the crystal data for all compounds is presented in Table 1, and selected bond distances and angles for the Mo-containing cores and within the $Fe_2S_2(CO)_6$ ligands are compared in Tables 2 and 3, respectively.

The structure of **I** is shown in Figure 1. Metrical parameters for the coordinated $Fe_2S_2(CO)_6$ units are typical (Table 3), with average Fe−Fe and Fe−S bond lengths of 2.523(7) and 2.278(8) Å, respectively, and a dihedral angle between the Fe_2S planes of 80.8°(average).[11,17] The central $Mo_2O_2S_2$ core is similar to those found in other structurally characterized compounds that contain this moiety.[7a,b] The Mo1−Mo2 distance in **I** of 2.843(2) Å is the largest yet observed within this class of compounds, and the average Mo−O_t and Mo−S_b distances (and the values for angles within this core) are within the range observed for other compounds (Table 2). The geometry about each Mo atom is distorted square pyramidal, with the Mo atom displaced from the basal S_4 plane toward the terminal oxo atom; both square

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[16] Sheldrick, G. M. SHELXS-86, a Fortran program for the solution of crystal structures from diffraction data. University of Göttingen, Göttingen, BRD, 1986.

[17] (a) Lilley, G. L.; Sinn, E.; Averill, B. A. *Inorg. Chem.* **1986**, *25*, 1073. (b) Nametkin, N. S.; Tyurin, V. K.; Alexsandrov, G. G.; Kuz'min, O. V.; Nekhaev, A. I.; Andrianov, V. G.; Mavlonov, M.; Struchkow, Y. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, *6*, 1353.

Table 2. Selected Bond Distances (Å) and Angles (deg) within $Mo_2O_2E_2$ (E = O, S) Fragments for **I**, **II**, and **III**

	$(Ph_4As)_2$**I**	$(Ph_4P)_2$**II**	$(Ph_4P)_2$**III**·THF
Mo1−Mo2	2.843(2)	2.690(1)	2.592(1)
$Mo{=}O_t$(av)	1.68(1)	1.681(8)	1.68(1)
$Mo{-}E_b$(av)	2.32(1) (E = S)	1.98(2) (E = O) 2.33(1) (E = S)	1.923(9), 1.975(9)[a] 2.086(2)[b]
$E_b{-}Mo{-}Y_b$(av)	101.7(4) (E = Y = S)	96.8(2) (E = O, Y = S)	92.5 (E = Y = O)

[a] Asymmetrically bridging oxides. [b] Bridging methoxide oxygen atom.

Table 3. Selected Bond Distances (Å) and Angles (deg) within $Fe_2S_2(CO)_6$ Units of **I**, **II**, and **III**

	$(Ph_4As)_2$**I**	$(Ph_4P)_2$**II**	$(Ph_4P)_2$**III**·THF
Fe−Fe	2.523(8)[a]	2.511(3)	2.503(8)
Fe−S	2.275(8)[a]	2.283(4)	2.279(7)[a]
S−Fe−S	78.7(3)[a]	79.7(2)	80.2(3)
Fe−S−Fe	67.4(3)[a]	66.7(2)	66.7(3)
S−Mo−S[b]	71.8(3)[a]	73.1(2)	74.1(2)

[a] Average value. [b] Bite angle of chelated $Fe_2S_2(CO)_6{}^{2-}$.

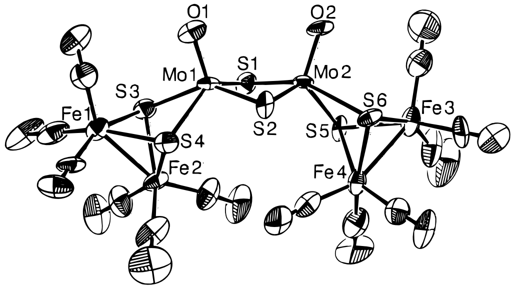

Figure 1. Structure of the $\{Mo_2O_2S_2[Fe_2S_2(CO)_6]_2\}^{2-}$ ion, **I**.

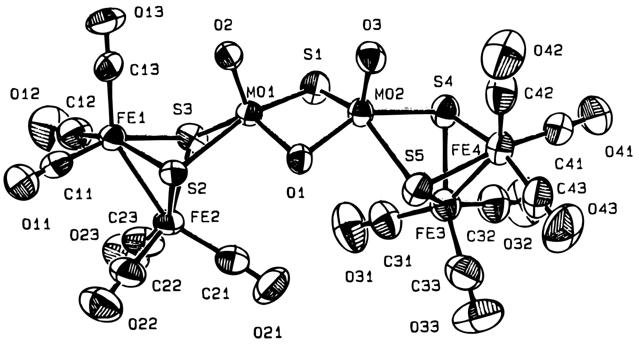

Figure 2. Structure of $\{Mo_2O_3S[Fe_2S_2(CO)_6]_2\}^{2-}$ ion, **II**.

pyramidal and trigonal bipyramidal geometries have been observed for other five-coordinate Mo centers in these complexes.[6a,7] The average $Mo{-}S_b$ distance of 2.32(1) Å is 0.14 Å shorter than the distance from the Mo to the S atoms of the $Fe_2S_2(CO)_6$ units, an observation consistent with previous reports that claim that the $Mo{-}S_b$ bond order is significantly greater than one.[8d] The two $Fe_2S_2(CO)_6$ ligands are twisted with respect to each other, apparently in order to minimize steric interactions between the terminal CO groups, and consequently the anion possesses an idealized C_2 axis perpendicular to and bisecting the Mo1−Mo2 and S1−S2 vectors. The twist of the ligands presumably results in the splitting observed in the carbonyl region of the infrared spectrum of **I** (see below). The acute bite angle of the $Fe_2S_2(CO)_6$ unit at Mo (average 71.8°) is only slightly larger than that observed in $[MoOFe_5S_6(CO)_{12}]^{2-}$.[11]

The structure of $\{Mo_2O_3S[Fe_2S_2(CO)_6]_2\}^{2-}$, **II**, is shown in Figure 2 and is similar to that of **I**. The Mo1−Mo2 distance of 2.690(1) Å is midway between the values of other Mo_2O_4- and $Mo_2O_2S_2$-containing clusters (Table 2). The average $Mo{-}O_t$ bond length of 1.681(6) Å and the average $Mo{-}O_b$ and $Mo{-}S_b$ distances (1.982(5) and 2.326(3) Å, respectively) are typical.

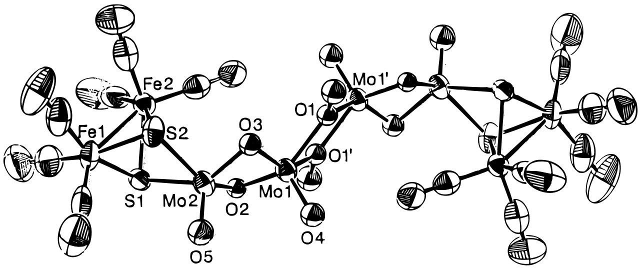

Figure 3. Structure of $\{Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\}^{2-}$ ion, **III**.

The geometry about each Mo center is again distorted square pyramidal, with the two bridging atoms and the sulfurs from one $Fe_2S_2(CO)_6$ unit occupying the basal positions and Mo1 and Mo2 displaced by 0.53 and 0.79 Å, respectively, from the basal planes. As in **I**, the $Fe_2S_2(CO)_6$ ligands have unremarkable geometries (Table 3) and are twisted with respect to one another in order to mininize steric interactions. The significantly lower value of 143° for the dihedral angle between the Mo−S1−O1 planes may also be attributed to the presence of bulky $Fe_2S_2(CO)_6$ ligands. The average S−Mo−S bite angle of the ligands is 73.1°, close to the value observed in **I**.

The structure of $\{Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\}^{2-}$, **III**, is shown in Figure 3. The centrosymmetric anion is comprised of two *cis*-Mo_2O_4 moieties bridged by two methoxide ligands and chelated at the terminal Mo atoms by one $Fe_2S_2(CO)_6$ unit per Mo. The $Mo_4O_8(\mu\text{-}OR)_2$ core has been observed only once previously, namely in the centrosymmetric compound $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$, **VI**;[18] in this compound two $MoO(O\text{-}i\text{-}Pr)_5$ units replace the $Fe_2S_2(CO)_6$ ligands present in **III**. There is no significant difference in the average $Mo{-}O_t$ distance between the two compounds (1.68(1) and 1.672(2) Å for **III** and **VI**, respectively), and the Mo1−Mo2 distance of 2.592(1) Å in **III** is only marginally longer than that found in **VI**. The Mo1−O1′ (alkyl) and Mo1−Mo1′ distances are slightly longer than those found in **VI**. The Mo1−(*μ*-O)−Mo2 units in both **III** and **VI** are asymmetric, with average Mo1−(*μ*-O) distances (1.923(9) and 1.924(2) Å for **III** and **VI**, respectively) significantly shorter than the average Mo2−(*μ*-O) distances (1.975(9) and 1.939(2) Å, respectively). The difference is more pronounced for **III**, in which the markedly longer Mo2−(*μ*-O) distance is presumably due to the more electron-rich $[Fe_2S_2(CO)_6]^{2-}$ ligand (as compared to $MoO(O\text{-}i\text{-}Pr)_3(\mu\text{-}O\text{-}i\text{-}Pr)_2$) and may indicate a lower effective nuclear charge on Mo2 with respect to Mo1. The chelated $Fe_2S_2(CO)_6$ moieties are again typical, with Fe−Fe and Fe−S average distances of 2.503(8) and 2.279(7) Å, respectively, an Fe_2S dihedral angle of 79.2°, and an S−Mo−S bite angle of 74.1° (Table 3).

Mass Spectroscopy of Clusters. Negative-ion mass spectroscopy has been used in our laboratory to detect a wide variety of anionic Fe−S and Mo−Fe−S carbonyl clusters.[19] Samples generally display a parent [(cation)(cluster)]$^-$ peak and a peak due to the one-electron-oxidized cluster ([cluster]$^-$); consecutive

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(18) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(19) Barber, D. E. Ph.D. Dissertation, University of Virginia, 1991.

Table 4. Negative-Ion Mass Spectra of Clusters

compound	[(cation)(cluster)]$^-$ (mass, amu)	[cluster]$^-$ (mass, amu)	major ions, *m/z* (% abundance)
$(Ph_4As)_2Mo_2O_2S_2[Fe_2S_2(CO)_6]_2$ (**I**)	1359	976	1360 (30), 1332 (40), 976 (20), 948 (15), 921 (30), 893 (10), 864 (25), 836 (20), 807 (20), 779 (25), 669 (60), 655 (95), 639 (100)
$(Ph_4P)_2Mo_2O_3S[Fe_2S_2(CO)_6]_2$ (**II**)	1300	960	1300 (25), 1272 (40), 1244 (10), 1216 (15), 1188 (15), 1160 (10), 1132 (5), 960 (10), 933 (20), 905 (15), 877 (25), 849 (35), 821 (20), 792 (30), 764 (20), 681 (20), 655 (100), 639 (95), 623 (90), 567 (30)
[a]$(Pr_4N)_2Mo_2O_4[Fe_2S_2(CO)_6]_2$ (**IV**)	1130	944	*1146 (12)*, 1130 (25), *1118 (15)*, 1102 (40), 963 (25), 935 (35), 776 (25), 655 (40), 639 (100), 623 (95), 607 (50), 553 (40)
$(Ph_4As)_2Mo_4O_8(OMe)_2[Fe_2S_2(CO)_6]_2$ (**III**)	1602	1262	655,[b] 639, 623, 607, 551
$(Bu_4N)_2Mo_4O_8(O\text{-}i\text{-}Pr)_2[Fe_2S_2(CO)_6]_2$ (**IIIb**)	1560	1318	926,[b] 911, 783, 758, 655, 639, 623, 607
$(Bu_4N)_2Mo_2OS_4[Fe_2S_2(CO)_6]$ (**V**)	922	680	922 (20), 894 (20), 652 (35), 640 (60), 624 (100)

[a] Numbers in italics represent peaks due to impurity of compound **II**. [b] Relative abundance not reported due to poor spectral quality.

loss of CO ligands from both the ion pair and the oxidized cluster is observed. Rearrangements to other clusters are not observed, particularly in the high mass region ($m/z > 400$) where parent ion peaks are found. Table 4 lists mass spectral data for $(Ph_4As)_2$**I**, $(Ph_4P)_2$**II**, and $(Ph_4P)_2$**III** (mass spectra of the clusters have been deposited as Supporting Information). The purity of the samples was confirmed by the lack of extraneous peaks in their mass spectra. For the compounds of interest in this paper, mass spectroscopy provides a better indication of sample purity and homogeneity than elemental analysis, since elemental analysis would be unable to distinguish (for example) between a pure sample containing only mono-sulfide-bridged **II** and a mixture containing equal amounts of bis(μ-sulfido) **I** and bis(μ-oxo) **IV**. Such a mixture would be easily identified by the observation of different parent ion peaks in the mass spectrum; indeed, a sample of compound **II** was first identified during our studies by observation of its parent ion 16 amu lower than expected for a sample of the bis(μ-sulfido) complex **I** (see below).

Preparation of Compounds. The orange compound $(Ph_4As)_2\{Mo_2O_2S_2[Fe_2S_2(CO)_6]_2\}$, $(Ph_4As)_2$**I**, was isolated as a microcrystalline byproduct from the reaction of $MoOCl_3(THF)_2$ with the dianion $[Fe_2S_2(CO)_6]^{2-}$, a reaction that forms $[MoOFe_5S_6(CO)_{12}]^{2-}$ as the major product.[11] Fractional recrystallization from an MeCN−*i*-PrOH solvent mixture allowed the separation of **I** as the most soluble component; X-ray quality crystals were grown by slow diffusion of *i*-PrOH into a concentrated MeCN solution of the cluster. The structure of **I** (Figure 1) is comprised of the well-known $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ core[1b,7a,b] chelated by two $[Fe_2S_2(CO)_6]^{2-}$ units. The infrared spectrum of **I** (see Figure 4a) displays a splitting of the two higher-energy ν_{CO} bands,[20] indicating an inequivalence in the carbonyl ligands that presumably results from steric crowding of the two $Fe_2S_2(CO)_6$ moieties coordinated to the bent $Mo_2O_2S_2$ core; a single band at 946 cm^{-1} can be assigned to the terminal Mo═O stretch.[1b] The electronic spectrum of **I** (Figure 1S(a), Supporting Information) reveals a barely resolved maximum at 470 nm and intense absorptions below 350 nm; the high intensity results from superposition of intense absorptions expected for both the $Mo_2O_2S_2$ core[1b,8a] and the coordinated $Fe_2S_2(CO)_6$ units.[11,12]

The formation of **I** was initially postulated to have occurred via replacement of bridging oxo atoms in $\{Mo_2O_4[Fe_2S_2(CO)_6]_2\}^{2-}$, **IV**, by sulfide present in the reaction mixture. The existence of cluster **IV** has been previously suggested,[11] and replacement of oxo by sulfido bridges is well-known.[6−8] Therefore, the synthesis and characterization of **IV** were undertaken in order to examine this proposal. The synthetic method was based upon studies of the aqueous chemistry of Mo^{V} that have shown that the $[Mo_2O_4]^{2+}$ dimeric species is the primary form of molybdenum in dilute acidic solution (pH ca. 0−6).[4a,b,21] The $[Mo_2O_4]^{2+}$ species was prepared by reaction of an MeCN solution of $MoCl_5$ with water, followed by removal of the solvent under vacuum; this process was repeated until the infrared spectrum of the residue displayed peaks at 989 and 744 cm^{-1} characteristic of terminal and bridging Mo−O stretches, respectively.[1b] Reaction of this product with 2 equiv of $[Fe_2S_2(CO)_6]^{2-}$ generally yielded a mixture of compounds as determined by IR spectroscopy. Two of the compounds in this mixture have been separated and their identities determined by X-ray diffraction studies.

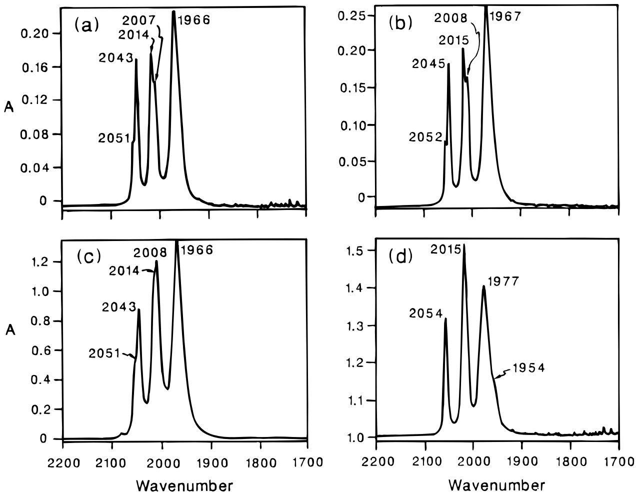

Figure 4. Infrared spectra (ν_{CO} region, MeCN solution) of (a) $\{Mo_2O_2S_2[Fe_2S_2(CO)_6]_2\}^{2-}$ (**I**), (b) $\{Mo_2O_3S[Fe_2S_2(CO)_6]_2\}^{2-}$ (**II**), (c) mixture of **II** and $\{Mo_2O_4[Fe_2S_2(CO)_6]_2\}^{2-}$ (**IV**), and (d) $\{Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\}^{2-}$ (**III**).

Addition of $(Ph_4P)Cl$ in isopropyl alcohol to the above reaction mixture resulted in precipitation of an orange solid which, upon recrystallization from MeCN/MeOH, yielded $(Ph_4P)_2\{Mo_4O_8(\mu\text{-}OCH_3)_2[Fe_2S_2(CO)_6]_2\}$ ($(Ph_4P)_2$**III**). The structure of the anion (Figure 3) consists of two $[Mo_2O_4]^{2+}$ units connected by two methoxy bridges and chelated by two $[Fe_2S_2(CO)_6]^{2-}$ ligands. The infrared spectrum of **III** (Figure 4d) shows ν_{CO} bands at higher energy than those of **I**; in addition, no significant splitting is observed in the spectrum of **III**, presumably because the steric congestion between the terminal $Fe_2S_2(CO)_6$ units is relieved. The electronic spectrum

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[20] The IR spectrum of the symmetrically coordinated $Fe_2S_2(CO)_6$ unit typically displays three distinct ν_{CO} bands separated from each other by ca. 20−40 cm^{-1}.[11,12,17a]

[21] Haight, G. P., Jr. *J. Inorg. Nucl. Chem.* **1962**, *24*, 663.

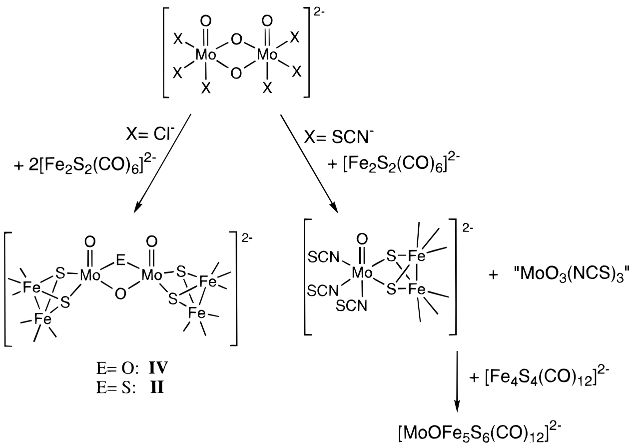
of **III** (Figure 1S(d)) displays a shoulder at ca. 460 nm and intense absorptions similar to those of **I** below 400 nm. Addition of $(Bu_4N)Cl$ instead of $(Ph_4P)Cl$ during workup and omission of the MeOH recrystallization yield a more soluble compound with IR and electronic spectra identical to those of **III**; the ^1H NMR spectrum of this compound displays broadened resonances due to Bu_4N^+ and an additional resonance at 1.95 ppm (vs CD_3CN solvent) that integrates to six protons per Bu_4N^+. These data are consistent with formulation of this compound as $(Bu_4N)_2\{Mo_4O_8(\mu\text{-O-}i\text{-Pr})_2[Fe_2S_2(CO)_6]_2\}$, $(Bu_4N)_2$**IIIb**. The maximum yield of **IIIb** obtained from the reaction mixture is ca. 18% (based on total Mo). The fact that cluster **IIIb** with bridging isopropoxide ligands yields the methoxide-bridged cluster **III** upon recrystallization indicates that the isopropoxide ligands are relatively labile.

The second compound isolated from the reaction of the presumed $[Mo_2O_4]^{2+}$ species with $[Fe_2S_2(CO)_6]^{2-}$ was obtained in crystalline form as its Ph_4P^+ salt. Its infrared and electronic spectra (see Figures 4b and 1S(b), respectively) are nearly indistinguishable from those of the bis(μ-sulfido) cluster **I**; however, the negative ion mass spectrum of this sample showed a parent ion 16 mass units lower than that of cluster **I**. This compound was formulated therefore as $(Ph_4P)_2Mo_2O_3S[Fe_2S_2(CO)_6]_2$, $(Ph_4P)_2$**II**, and the structural determination confirmed this formulation. The structure of **II** (Figure 2) is analogous to that of **I** except that the Mo atoms in **II** are bridged by one O^{2-} and one S^{2-}. The similarity between **II** and **I** in their structural and electronic properties is not unexpected, since such similarity has been observed in other compounds for which both the $[Mo_2O_3S]^{2+}$ and the $[Mo_2O_2S_2]^{2-}$ cores are known.[6a,8a] Cluster **II** can be isolated in ca. 40% yield (based on total Mo), which indicates that replacement of bridging oxo by sulfido is a facile process. No other compounds could be isolated in pure form from these reaction mixtures.

In one preparation, $MoOCl_3(THF)_2$ was substituted for $MoCl_5$ and the treatment with H_2O was repeated as before until the IR spectrum of the residue was identical to that obtained previously. After reaction of this compound with 2 equiv of $[Fe_2S_2(CO)_6]^{2-}$, however, the infrared spectrum of the mother liquor showed three major ν_{CO} bands (usually indicative of a single $Fe_2S_2(CO)_6$-containing product[20]), a terminal Mo═O band at 950 cm^{-1}, and a broad band at ca. 750 cm^{-1} indicative of an Mo—O—Mo bridge. A brown solid was obtained by addition of $(Ph_4P)Cl$ in *i*-PrOH, and the ν_{CO} region of its infrared spectrum (Figure 4c) was virtually identical to that of the mother liquor. The general pattern of the ν_{CO} bands was similar to that observed for clusters **I** and **II**: the two higher-energy bands were split, although the splitting was not as well resolved as for **I** and **II**, and the lowest-energy band was the most intense. However, the electronic spectrum of this solid (Figure 1S(c)) was more similar to that of the tetranuclear cluster **III**, displaying a shoulder at ca. 460 nm and the typical intense absorptions below 400 nm. The Pr_4N^+ salt of this compound a showed weak parent ion and fragment ions in the negative ion mass spectrum consistent with the presence of both the desired $[Mo_2O_4]^{2+}$ species **IV** and the monosulfido-bridged analog **II** (see Table 4 and Supporting Information). We were unable to isolate a pure sample of **IV** from this mixture.

Other Attempted Syntheses of $\{[Mo_2O_4[Fe_2S_2(CO)_6]_2\}^{2-}$. Alternate syntheses utilizing starting materials known to contain the $[Mo_2O_4]^{2+}$ core were attempted in order to obtain pure samples of **IV**. Reaction of $[Mo_2O_4(NCS)_6]^{4-}$ [13] with 2 equiv of $[Fe_2S_2(CO)_6]^{2-}$ gave $[MoOFe_5S_6(CO)_{12}]^{2-}$ (identified by its IR spectrum[11]) as the major product. An estimated 75−80% of the available $[Fe_2S_2(CO)_6]^{2-}$ was consumed in formation of the product; no other pure compounds were isolated from this reaction. This observation leads us to propose that different pathways must be followed in the reactions of $[Fe_2S_2(CO)_6]^{2-}$ with either $[Mo_2O_4(NCS)_6]^{4-}$ or $[Mo_2O_4Cl_6]^{4-}$, pathways that presumably are determined by the stronger coordination of SCN^- versus Cl^- to the $[Mo_2O_4]^{2+}$ core; a plausible scheme is shown in Scheme 1. In the case of $[Mo_2O_4Cl_6]^{4-}$, substitution of Cl^- by $[Fe_2S_2(CO)_6]^{2-}$ is expected to be facile at low temperature (as proposed for reactions of other metal halides with $[Fe_2S_2(CO)_6]^{2-}$ [22]) and results in formation of the desired product **IV** (as well as the sulfido-bridged product **II** due to replacement of bridging oxo ligands). However, substitution is less facile in the case of $[Mo_2O_4(NCS)_6]^{4-}$ due to the more strongly coordinated thiocyanate ligands, and therefore cleavage of the dioxo bridge to yield monomeric species is more likely than when X = Cl^-. Cleavage of dinuclear $[Mo_2O_4]^{2+}$ compounds by bidentate thiolate ligands has been reported.[1b] The monomeric MoS_2Fe_2 fragment then could react with $[Fe_4S_4(CO)_{12}]^{2-}$ (formed as the reaction warms[23]) by an intramolecular oxidative addition as described elsewhere.[24]

Scheme 1



The reaction of 2 equiv of $[Fe_2S_2(CO)_6]^{2-}$ with the tetrameric cluster **IIIb** was also performed in an attempt to prepare cluster **IV**. After the initial reaction mixture was warmed to room temperature, the infrared spectrum revealed a mixture of compounds, one of which appeared to be $[Fe_4S_4(CO)_{12}]^{2-}$.[23] Over several days, the spectrum changed to that of what appeared to be a mixture of at least three compounds. The two major products were separated by precipitation as their Ph_4P^+ salts and were identified by their infrared spectra as $[MoOFe_5S_6(CO)_{12}]^{2-}$ [11] and $[Fe_5S_4(CO)_{12}]^{2-}$.[11,24] A small amount (ca. 20 mg) of a light orange solid was isolated from this reaction filtrate by precipitation with THF−Et_2O. The infrared spectrum of this solid (Figure 5) maintains the three peaks characteristic of coordinated $Fe_2S_2(CO)_6$ units. The negative ion mass spectrum of this solid (Table 4 and Supporting Information) shows a weak parent ion pair at 922 amu and peaks corresponding to consecutive CO loss from this species and from the oxidized cluster. The mass spectroscopic data are most readily explained by formulation of the unknown compound as $(Bu_4N)_2\{Mo_2OS_4[Fe_2S_2(CO)_6]\}$, $(Bu_4N)_2$**V**; we discuss a possible structure for this cluster below.

Reactions of Clusters with Sulfide Reagents. Clusters **I** and **III** undergo reactions with sulfide reagents to yield products

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(22) Eldredge, P. A.; Bose, K. S.; Barber, D. E.; Bryan, R. F.; Sinn, E.; Rheingold, A.; Averill, B. A. *Inorg. Chem.* **1991**, *30*, 2365.

(23) Bose, K. S.; Sinn, E.; Averill, B. A. *Organometallics* **1984**, *3*, 1126.

(24) Barber, D. E.; Bryan, R. F.; Sabat, M.; Sinn, E.; Averill, B. A. *Organometallics* **1995**, *14*, 3229.

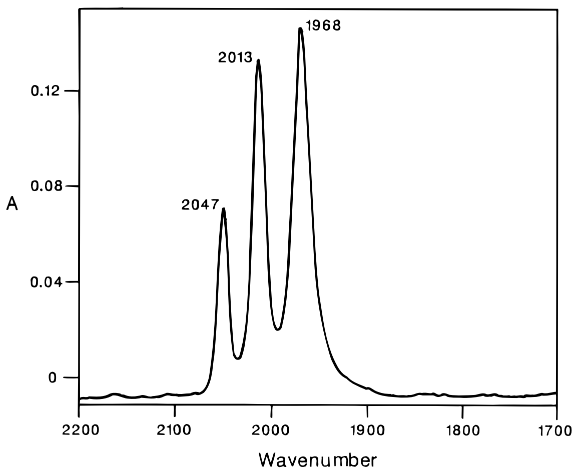
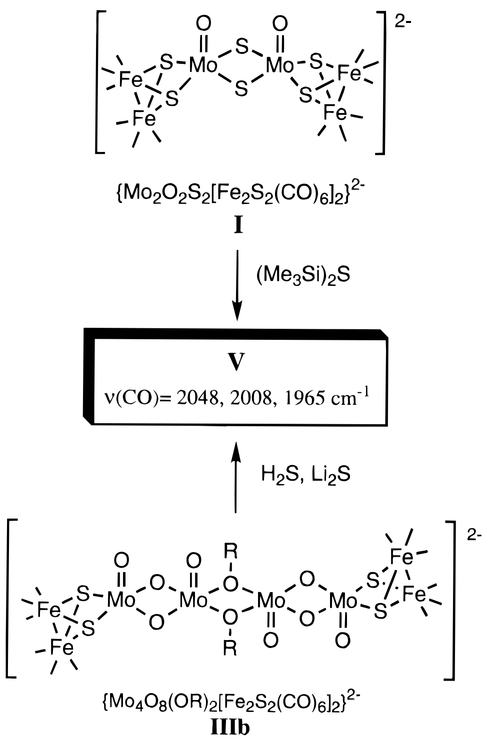


Figure 5. Infrared spectrum (ν_{CO} region, MeCN solution) of cluster **V**.

Scheme 2

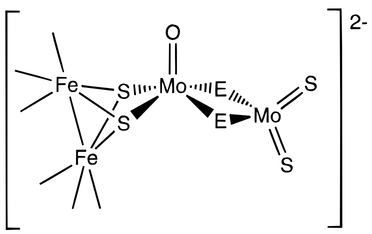


that are indistinguishable from one another by IR spectroscopy. The reactions are summarized in Scheme 2 and described in more detail below.

Cluster **I** ($\{Mo_2O_2S_2[Fe_2S_2(CO)_6]_2\}^{2-}$) reacted with excess $(Me_3Si)_2S$ in MeCN at 40 °C to produce what appears to be a single product. Over the course of ca. 5 days, bands at 2035 and 1919 cm^{-1} appeared and were slowly replaced by new bands at 2048, 2008, and 1965 cm^{-1} before a significant amount of insoluble black precipitate was observed. The ν_{CO} bands did not show the splitting observed when the $[Mo_2O_2E_2]^{2+}$ core is ligated by two $Fe_2S_2(CO)_6$ units; therefore the product contains either identical $Fe_2S_2(CO)_6$ ligands that are not interacting sterically or only one $Fe_2S_2(CO)_6$ ligand. The terminal Mo=O stretch remained visible. No reaction was observed at room temperature with either H_2S or Li_2S.

In contrast to the slow reaction of **I**, the room-temperature reactions of $\{Mo_4O_8(O\text{-}i\text{-}Pr)_2[Fe_2S_2(CO)_6]_2\}^{2-}$ (**IIIb**) with H_2S(g) in MeCN and with excess Li_2S in an MeCN–MeOH mixture were quite rapid. Overnight reaction with H_2S (and immediate reaction with Li_2S) yielded the spectrum of a nearly pure carbonyl compound with ν_{CO} bands identical to those of the reaction product of **I** + $(Me_3Si)_2S$ (see Figure 3S(b)). No precipitation of solid was noted in these reactions. The rapid reaction may indicate facile replacement of bridge oxides and/or alkoxides by sulfides, which is possible due to the more open structure of cluster **IIIb**.

The IR spectrum of the common product shown in Scheme 2 is nearly identical to that of cluster **V**, the minor product of the reaction of **IIIb** with $[Fe_2S_2(CO)_6]^{2-}$ (see above). The mass spectroscopic data are most consistent with formulation of **V** as $\{Mo_2OS_4[Fe_2S_2(CO)_6]\}^{2-}$, and the similarity of this cluster to the common product in Scheme 2 has led us to speculate about a possible structure for the cluster. The appearance of the ν_{CO} bands indicates the presence of an intact $Fe_2S_2(CO)_6$ ligand, and the IR spectrum also displayed bands indicative of an Mo=O unit. The remaining Mo and four S atoms in **V** are most easily incorporated as a thiomolybdate unit, yielding the hypothetical structure for **V** shown. The MoO(μ-S)$_2$MoS$_2$ fragment has been observed previously in the clusters $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_8O]^{2-}$, and Holm et al. have suggested that the oxidation states of the Mo atoms are +4 for the square pyramidal Mo and +6 for the tetrahedral thiomolybdate-type Mo.[25] These oxidation states are consistent with our formulation of **V** as a dianion.



V
(E= S, O)

Assuming that the common product of Scheme 2 has a structure similar to **V** provides a convenient explanation for the reactions of **I** and **IIIb** with sulfide reagents. Cluster **I** reacts with $(Me_3Si)_2S$ slowly to yield a product with a single $Fe_2S_2(CO)_6$ unit; oxidative decarbonylation of **I** and loss of the iron as iron sulfide would readily yield a cluster with a structure similar to **V**. The decomposition observed in these reactions may be explained by the fact that *all* $Fe_2S_2(CO)_6$ units are susceptible to attack by $(Me_3Si)_2S$, resulting in the slow destruction of **I** and of the product **V**. In the reaction of **IIIb** with sulfide, rapid replacement of bridging oxide and alkoxide by sulfide could result in cleavage of the tetranuclear starting material to yield **V**. We note that, when **IIIb** is the reactant, E in the structure shown may be either O or S depending upon the lability of the bridging oxo groups; our results are inconclusive in this regard, and the IR spectral properties (ν_{CO} and $\nu_{Mo=O}$) would not be expected to change significantly. In the absence of a crystal structure for the common product, structure **V** provides a reasonable explanation for the experimental observations.

Conclusions

Clusters **I**, **II**, and **III** represent the first structurally characterized Mo-Fe-S clusters to contain the $[Mo_2O_2E_2]^{2+}$ (E = O, S) core. The formation of **I** and **II** by reaction of $[Mo_2O_4Cl_6]^{4-}$ with $[Fe_2S_2(CO)_6]^{2-}$ illustrates the high formation tendency of

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[25] Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2827.

the μ-sulfido bridge and underscores the difficulty of preparation of the oxo-bridged analog **IV**, which has been observed only in impure form. The isolation of **III** in significant yield from these reactions may indicate that stable tetranuclear and perhaps higher oligomers of Mo^V are present in weakly acidic aqueous solutions. Such higher oligomers may have escaped detection thus far due to the marked similarity between their electronic spectra and those of the dinuclear species, since electronic spectroscopy has been the primary method used to examine equilibria in solution.[4,20] The reactions of **III** and $[Mo_2O_4(NCS)_6]^{4-}$ with $[Fe_2S_2(CO)_6]^{2-}$ demonstrate that, in the presence of strongly coordinated ligands, the dioxo bridge is cleaved to yield species mononuclear in Mo. Finally, clusters **I** and **IIIb** react with sulfide reagents to produce a similar product, tentatively formulated as $\{Mo_2OS_4[Fe_2S_2(CO)_6]\}^{2-}$, **V**. Cluster **V** forms during reaction of **I** with $(Me_3Si)_2S$, presumably by oxidative decarbonylation of the $Fe_2S_2(CO)_6$ units, while **IIIb** reacts more readily with sulfide because of the cluster's more open structure.

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Supporting Information Available: Tables of anisotropic thermal parameters and bond distances and angles for $(Ph_4As)_2$**I**, $(Ph_4P)_2$**II**, and $(Ph_4P)_2$**III**·THF, a table of coordinates of introduced H atoms for $(Ph_4P)_2$**III**·THF, figures showing electronic spectra of compounds **I**−**IV** (Figure 1S) and infrared spectra of reaction mixtures (Figures 2S), and figures showing mass spectra of samples of compounds **I**−**V** (19 pages). Ordering information is given on any current masthead page.

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