factors are important in determining the character (i.e., valence trapped or delocalized) of mixed-valence species is still unresolved.

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Supplementary Material Available: Tables of observed and calculated structure factors and thermal vibration parameters for both compounds (20 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Synthesis, Interconversions, and Structural Characterization of the $[(S_4)_2MoS]^{2-}$, $[(S_4)_2MoO]^{2-}$, $(Mo_2S_{10})^{2-}$, and $(Mo_2S_{12})^{2-}$ Anions

M. DRAGANJAC, E. SIMHON, L. T. CHAN, M. KANATZIDIS, N. C. BAENZIGER, and D. COUCOUVANIS*

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The MoS_4^{2-} anion reacts with elemental sulfur and "active" sulfur reagents such as organic trisulfides or ammonium sulfides to afford binary molybdenum sulfides. The successful isolation of these sulfides, which appear to be components of a complex equilibrium system, depends on the solvent system and the nature of the counterions present in solution. With $(C_2H_5)_4N^+$ as the counterion the $[(S_4)_2MoS]^{2-}$ anion, I, can be isolated from either CH_3CN or DMF solutions. The hydrolysis of I in DMF or CH_3CN affords the $[(S_4)_2MoO]^{2-}$ anion, II. In the presence of the $(C_6H_5)_4P^+$ cation the $(Mo_2S_{10})^{2-}$ (III) and $(Mo_2S_{12})^{2-}$ (IV) anions can be isolated from DMF solutions as mixed-anion $(C_6H_5)_4P^+$ salts. Both I and II crystallize in the orthorhombic space group *Ibca* with eight molecules in the unit cell. The cell dimensions are a = 15.594 (3) Å, b = 13.264 (4) Å, and c = 27.577 (5) Å for I and a = 15.470 (1) Å, b = 13.224 (2) Å, and c = 27.425 (3) Å for II. In the structure of III/IV, both anions occupy the same position in the crystal lattice, with III being the major component (72%). III/IV crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The cell dimensions are a = 22.288 (4) Å, b = 11.724 (4) Å, c = 10.512 (2) Å, α = 78.06 (4)°, β = 86.00 (3)°, and γ = 76.10 (3)°. Intensity data for all three structures were collected with a four-circle computer-controlled diffractometer by the θ–2θ scan technique. For I and II, all non-hydrogen atoms were refined with anisotropic thermal parameters. For III/IV, the S_2^{2-} ligand of $Mo_2S_{10}^{2-}$ and the S_4^{2-} ligand of $Mo_2S_{12}^{2-}$, as well as the DMF molecule of crystallization, were refined with isotropic thermal parameters. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Refinement by a full-matrix least-squares procedure, of 145 parameters on 2146 data for I, 145 parameters on 1175 data for II, and 585 parameters on 7022 data for III/IV, gave final R values of 0.025, 0.047, and 0.065, respectively. In I and II, the Mo(IV) ion is coordinated by two bidentate S_4^{2-} chelates and a terminal sulfur or oxygen atom in a distorted-square-pyramidal arrangement. The molybdenum is situated above the basal sulfur plane by 0.72 Å for I and 0.76 Å for II. The $Mo_2S_{10}^{2-}$ and $Mo_2S_{12}^{2-}$ anions have in common the $(Mo_2S_4)^{2+}$ core as well as the tetrasulfide ligand attached to Mo(1). Mo(2) is coordinated by either a persulfido group in III or a tetrasulfido unit in compound IV. The core contains two $(Mo^V{=}S)^{3+}$ units bridged asymmetrically by two sulfide ligands in the syn configuration, with a Mo—Mo distance of 2.846 (1) Å. In all three structures, an alternation of the S–S bond lengths in the S_4^{2-} chelate rings is observed, and the Mo–S_4 ring is in the "puckered" or envelope configuration. The coordinated sulfur atoms of the S_4^{2-} ligand are asymmetrically bound to the molybdenum. The MoS_4 ring conformation and the consequent effects on Mo–S bonding are attributed to intraligand sulfur electron lone-pair repulsions.

Introduction

Interest in molybdenum–sulfur coordination chemistry derives primarily from recent advances in the chemistry of molybdoenzymes[1] and from the apparent importance of molybdenum–sulfur coordination in hydrodesulfurization reactions.[2] The coordination of molybdenum by sulfur atoms in the molybdenum-containing enzymes has been demonstrated by molybdenum K-edge X-ray absorption fine structure (EXAFS) analyses. In nitrogenase, the EXAFS analyses[3] are consistent with a molybdenum surrounded by four sulfur atoms at ~2.35 Å and two or three iron atoms at ~2.7 Å. In sulfite oxidase[4] and xanthine oxidase,[5] analyses of the EXAFS data also indicate the presence of three or four sulfur atoms around the molybdenum atoms. On the basis of Mo–S bond length considerations the sulfur ligands have been characterized tentatively as either terminal sulfido groups or protein-bound cysteinyl or methioninyl sulfur atoms.

The hydrodesulfurization reaction involved in the catalytic hydrogenolysis of organosulfur compounds is an important process in the purification of petroleum products. The heterogeneous catalysts often used in this process contain "sulfided" molybdenum and cobalt salts supported on alumina. It has been proposed[6–8] that a molybdenum sulfide surface is the catalytic site for this hydrogenolysis reaction.

The basic coordination chemistry of molybdenum with sulfur ligands also has received considerable attention in recent years.[1] The intricacies of the Mo–S coordination chemistry are aptly illustrated in the chemical and crystallographic studies of the binary molybdenum thioanions. In various such Mo–S anions the sulfide (S^{2-}), persulfide (S_2^{2-}), and tetrasulfide (S_4^{2-}) ligands appear as ligands in complex anions such as [Mo$_2$-

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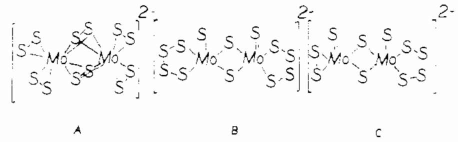

Figure 1. Binuclear thiomolybdates containing the "Mo_2S_4" cores.

$(S_2)_6]^{2-}$,[9] $[Mo_3S(S_2)_6]^{2-}$,[10] $[(S_4)_2MoS]^{2-}$,[11] $[Mo_2S_{10}]^{2-}$,[12] and $[(MoS_4)_2MoS]^{2-}$.[13]

In the very interesting $[Mo_2(S_2)_6]^{2-}$ anion only persulfide ligands are present and coordinate in both the terminal and the bridging modes[9] (Figure 1A). The $[Mo_2S_{10}]^{2-}$ anion, which is obtained by the reaction of PhS^- with $[Mo_2(S_2)_6]^{2-}$, contains three types of sulfur ligands, a bidentate S_4^{2-} chelating ligand, a chelating S_2^{2-} ligand, and bridging and terminal sulfido ligands[12] (Figure 1C). The very interesting $[(MoS_4)_2MoS]^{2-}$ complex[13] contains two MoS_4^{2-} ligands coordinated to a central $(Mo^{IV} = S)^{2+}$ unit and is obtained by the thermal degradation of MoS_4^{2-} in dimethylformamide (DMF) solution.

In a recent communication we reported[11] on the synthesis and structural characterization of the $[(S_4)_2MoS]^{2-}$ anion and the corresponding hydrolysis product $[(S_4)_2MoO]^{2-}$. The $[(S_4)_2MoS]^{2-}$ dianion, which is obtained by the reaction of MoS_4^{2-} with various sulfur reagents such as organic trisulfides, elemental sulfur, or $(NH_4)_2S_x$, apparently is a component of a complex equilibrium mixture which contains various thioanions, including $[Mo_2S_{10}]^{2-}$ and $[Mo_2S_{12}]^{2-}$.

The formation and isolation of these thioanions, from MoS_4^{2-}/RSSSR solutions, depends on the solvent employed, the ratio of reagents, and the nature of the counterions present in solution.

We report herein the synthesis, isolation, and structural characterization of the $(Et_4N)_2[(S_4)_2MoS]$, $(Et_4N)_2[(S_4)_2MoO]$, and $(Ph_4P)_2(Mo_2S_{10.56})$ complexes.[14]

In the structure of the $(Ph_4P)_2(Mo_2S_{10.56})$ complex the site of the $(Mo_2S_{10})^{2-}$ anion (Figure 1C) is partially occupied by the $(Mo_2S_{12})^{2-}$ anion (Figure 1B) such that the correct formulation of the compound is $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]$. The new $(Mo_2S_{12})^{2-}$ anion is a structural isomer of $[Mo_2(S_2)_6]^{2-}$ (Figure 1A).

Experimental Section

Synthesis. The chemicals in this research were used as purchased. Dimethylformamide (DMF) was stored over 4A Linde molecular sieves for 24 h and then distilled under reduced pressure at ~30 °C. Acetonitrile (CH_3CN) was distilled from calcium hydride (CaH_2) before use. Commercial grade methylene chloride (CH_2Cl_2) was distilled from CaH_2. Absolute ethanol and diethyl ether were used without any further purification. With the exception of dibenzyl trisulfide (BzSSSBz), all syntheses were carried out under a dinitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. Elemental analyses on samples dried under vacuum for 12 h were performed by Galbraith Analytical Laboratories, Knoxville, TN.

Physical Methods. Visible and ultraviolet spectra were obtained on Cary Model 118 and 219 spectrophotometers. A Debye-Scherrer camera with nickel-filtered copper radiation was utilized to obtain X-ray powder diffraction patterns.

Electrochemical measurements were performed with a PAR Model 173 potentiostat/galvanostat and a PAR Model 175 universal programmer. The electrochemical cell used had platinum working and auxiliary electrodes. As reference electrode a saturated calomel electrode was used. All solvents used in the electrochemical measurements were properly dried and distilled, and tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) was used as the supporting electrolyte. Normal concentrations used were ~0.001 M in electroanalyte and 0.1 M in supporting electrolyte. Purified dinitrogen was used to purge the solutions prior to the electrochemical measurements.

Preparation of Compounds. Bis(tetraethylammonium) Bis(tetrasulfido)thiomolybdate(IV), $(Et_4N)_2[(S_4)_2MoS]$ (I). Method A. An amount of $(Et_4N)_2MoS_4$, 1.0 g (2.07 mmol), was dissolved in 30 mL of CH_3CN. To this solution was added with stirring a solution of 2.8 g (10.1 mmol) of dibenzyl trisulfide,[11,15] $(C_7H_7)_2S_3$, in 30 mL of CH_3CN. After an additional 2 min of stirring the brown solution was allowed to stand at ambient temperature. Within ca. 5 min red-brown crystals started to appear on the walls of the container. After standing for $^1/_2$ h, the crystals were isolated by filtration and washed with two 10-mL portions of absolute ethanol and three 20-mL portions of diethyl ether. The weight of the product after drying was 1.20 g (90% yield).

Anal. Calcd for $C_{16}H_{40}N_2MoS_9$: C, 29.79; H, 6.26; N, 4.34; Mo, 14.87; S, 44.73. Found: C, 30.52; H, 6.40; N, 4.45; Mo, 14.61; S, 44.08. X-ray powder pattern spacings (Å): 8.2 (vs), 6.9 (s), 6.0 (w), 5.6 (w), 5.1 (w), 4.75 (m), 4.17 (s), 3.90 (w), 3.57 (w), 3.35 (w), 3.12 (w), 2.93 (w), 2.77 (w), 2.51 (w), 2.35 (w), 2.25 (w), 2.20 (w), 2.12 (w), 2.00 (w), 1.85 (w), 1.78 (w), 1.59 (w), 1.51 (w).

Method B. An amount of $(Et_4N)_2MoS_4$, 2.2 g (4.55 mmol), was dissolved in 50 mL of CH_3CN. To this solution was added with stirring solid elemental sulfur, 0.72 g (22.5 mmol). After an additional 3 min of stirring, red-brown crystals started to appear on the walls of the container. The solution was allowed to stand at ambient temperature for 10 min. The product was isolated by filtration and washed with 10 mL of carbon disulfide and 20 mL of diethyl ether. The weight of the product after drying was 2.3 g (79% yield). This material was recrystallized from a DMF/diethyl ether solvent system, yielding 2.0 g (69% yield). The X-ray powder pattern of the product was identical with the one of the product obtained by method A.

Method C. An amount of $(NH_4)_2MoS_4$, 2.0 g (7.69 mmol) was dissolved in 40 mL of H_2O. Seven mL of a fresh $(NH_4)_2S_3$ solution, prepared by dissolving elemental sulfur, 94 g (2.94 mol), in 400 mL (1.47 mol) of $(NH_4)_2S$ solution (Matheson Coleman and Bell, reagent, light, 20–24% $(NH_4)_2S$), was added with stirring. To this solution was also added with stirring a solution of Et_4NCl, 2.5 g (15.1 mmol), dissolved in 20 mL of H_2O. Brown crystals formed immediately upon standing. The solution was allowed to stand at 0 °C for ca. 3.5 h. The product was isolated by filtration and washed with three 20-mL portions of H_2O, three 20-mL portions of absolute ethanol, and two 10-mL portions of diethyl ether. The weight of the product after drying was 2.1 g (43% yield). Subsequent standing at ambient temperatures for ca. 1 week gave more material, 0.9 g (62% total yield). The X-ray powder pattern and elemental analysis of the product were identical with the one of the product obtained by method A.

Bis(tetraethylammonium) Bis(tetrasulfido)oxomolybdate(IV), $(Et_4N)_2[(S_4)_2MoO]$ (II). An amount of $(Et_4N)_2[(S_4)_2MoS]$, 1.0 g (15.5 mmol), was dissolved in 150 mL of "wet" DMF. The brown solution was refluxed in air ca. 20 min. The resulting green solution was allowed to cool to room temperature. Addition of diethyl ether until the first crystals appeared and subsequent cooling (ca. 2 h) afforded golden green crystals. The product was isolated by filtration and washed with two 10-mL portions of absolute ethanol and three 20-mL portions of diethyl ether. The weight of the product after drying was 0.25 g (26% yield).

Anal. Calcd for $C_{16}H_{40}N_2MoS_8O$: C, 30.57; H, 6.37; N, 4.46. Found: C, 30.35; H, 6.46; N, 4.37. X-ray powder pattern spacings (Å): 8.2 (vs), 6.7 (s), 6.0 (w), 5.5 (w), 5.0 (w), 4.70 (s), 4.25 (vs), 3.92 (w), 3.72 (w), 3.57 (w), 3.35 (w), 2.92 (w), 2.77 (w), 2.66 (w),

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[14] Abbreviations used throughout this paper: Ph_4P^+ = tetraphenylphosphonium cation, $(C_6H_5)_4P^+$; Et_4N^+ = tetraethylammonium cation, $(C_2H_5)_4N^+$.

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Table I. Summary of Crystal Data, Reflection Data Collection, and Structural Refinement Parameters

	I	II	III
compd	$(Et_4N)_2[(S_4)_2MoS]$	$(Et_4N)_2[(S_4)_2MoO]$	$(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$
formula	$C_{16}H_{40}N_2MoS_9$	$C_{16}H_{40}N_2MoOS_8$	$C_{49.5}H_{43.5}P_2Mo_2S_{10.56}N_{0.5}O_{0.5}$
mol wt	645.03	628.96	1245.51
a, Å	15.594 (3)	15.470 (1)	22.288 (4)
b, Å	13.264 (4)	13.224 (2)	11.724 (4)
c, Å	27.577 (5)	27.425 (3)	10.512 (2)
α, deg	90.00 (2)	90.00 (3)	78.06 (4)
β, deg	90.00 (2)	90.00 (3)	86.00 (3)
γ, deg	90.00 (2)	90.00 (3)	76.10 (3)
V, Å^3	5704	5610	2679
Z	8	8	2
d_{calcd}, g/cm^3	1.502	1.489	1.595
d_{obsd},[a] g/cm^3	1.49 (2)	1.46 (2)	1.59 (2)
space group	*Ibca*	*Ibca*	$P\bar{1}$
cryst dimens[b]	*c*	*d*	*e*
abs coeff μ, cm^{-1}	10.89[f]	10.41[g]	10.25[h]
take-off angle, deg	3	3	3
data collected,[i] 2θ range, deg	3-50	3-40	3-50
no. of unique data	2529	1498	9201
no. of data used in refinement, $F_o^2 > 3\sigma(F_o^2)$	2146	1175	7022
no. of variables	145	145	585
error in observn of unit wt	1.076	1.805	2.617
% R	2.5	4.7	6.5
% R_w	3.8	7.0	10.6

[a] By flotation in a CCl_4/pentane mixture. [b] Perpendicular distances from crystal center, in mm. [c] $\pm(100)$, 0.073; $\pm(001)$, 0.148; (101), 0.020; $(\bar{1}01)$, 0.111; $\pm(112)$, 0.140; $\pm(11\bar{2})$; 0.189; $\pm(\bar{1}12)$, 0.176; $\pm(1\bar{1}2)$, 0.159. [d] $\pm(100)$, 0.024; $\pm(112)$, 0.143; $\pm(11\bar{2})$, 0.301; $\pm(01\bar{2})$, 0.355. [e] $(\bar{1}00)$, 0.288; $\pm(20\bar{1})$, 0.263; $\pm(201)$, 0.390; $\pm(110)$, 0.028; $(00\bar{1})$, 0.351. [f] Maximum absorption correction 1.29; minimum absorption correction 1.14. [g] Maximum absorption correction 1.39; minimum absorption correction 1.05. [h] Maximum absorption correction 1.67; minimum absorption correction 1.06. [i] Over the whole sphere of reciprocal space.

2.50 (w), 2.20 (w), 2.10 (w), 1.84 (w), 1.69 (w), 1.58 (w).

Bis(tetraphenylphosphonium) Bis(μ-thio)[persulfidosulfidomolybdate(V)sulfidotetrasulfidomolybdate(V)], $(Ph_4P)_2[Mo_2S_{10}]\cdot{}^1/_2DMF$, and Bis(tetraphenylphosphonium) Bis(μ-thio)[bis(sulfidotetrasulfidomolybdate(V))], $(Ph_4P)_2[Mo_2S_{12}]\cdot{}^1/_2DMF$ (III). An amount of $(Ph_4P)_2MoS_4$, 1 g (1.1 mmol), was dissolved in 30 mL of DMF. To this solution was added with stirring 1.25 g (6.7 mmol) of solid dibenzyl trisulfide. After an additional 5 min of stirring, 10 mL of absolute ethanol was added. Addition of diethyl ether to incipient crystallization and subsequent standing (ca. 12 h) afforded large dark red crystals. The product was isolated by filtration and washed with two 20-mL portions of absolute ethanol and three 20-mL portions of diethyl ether. The weight of the product after drying was 0.4 g (58% yield).

Anal. Calcd for $C_{49.5}H_{43.5}P_2Mo_2S_{10.56}N_{0.5}O_{0.5}$: C, 47.73; H, 3.52; P, 4.97; S, 27.16; N, 0.56. Found: C, 48.77; H, 3.60; P, 4.95; S, 27.14; N, 0.57. X-ray powder pattern spacings (Å): 10.6 (vs), 9.3 (m), 8.3 (s), 7.4 (s), 7.0 (w), 6.4 (w), 6.0 (w), 5.5 (w), 5.1 (w), 4.75 (m), 4.40 (m), 4.15 (m), 3.92 (m), 3.55 (w), 3.40 (w), 3.22 (w), 2.95 (w), 2.84 (w), 2.74 (w), 2.52 (w), 2.40 (w), 2.34 (w), 2.26 (w), 2.09 (w), 1.93 (w), 1.71 (w).

X-ray Diffraction Measurements. Collection and Reduction of Data. Details concerning crystal characteristics and X-ray diffraction methodology for $(Et_4N)_2[(S_4)_2MoS]$ (I), $(Et_4N)_2[(S_4)_2MoO]$ (II), and $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$ (III) are shown in Table I. Intensity data were obtained on a Picker-Nuclear four-circle diffractometer equipped with a scintillation counter and pulse-height analyzer and automated by a DEC-PDP8 computer. Graphite-monochromatized Mo Kα radiation ($2\theta_m = 12.50°$) was used for data collection and cell dimension measurements (Kα_1, $\lambda = 0.70926$ Å). Intensity data were collected by using a θ–2θ step scan technique.[16] The basic scan steps of 0.07° 2θ for I, 0.07° 2θ for II, and 0.10° 2θ for III were adjusted with angles to allow for α_1–α_2 separation at higher angles. Background measurements, 4 s at each end, were made at ±10 steps from the peak maximum. In all structures, 3 standard reflections were measured every 60 data measurements to monitor crystal quality. No crystal decay was observed in any of the three crystals.

The raw data were reduced to net intensities, estimated standard deviations were calculated on the basis of counting statistics, Lorentz–polarization corrections were applied, and equivalent reflections were averaged. The estimated standard deviation of the structure factor was taken as the larger of that derived from counting statistics and that derived from the scatter of multiple measurements.

The least-squares program used minimizes $\sum w(\Delta|F|)^2$. The weighting function used throughout the refinements of the structures gives zero weight to those reflections with $F^2 \leq 3\sigma(F^2)$ and $w = 1/\sigma^2(F)$ to all others ($\sigma^2(F^2) = (pF^2)^2 + \sigma^2(F^2)$ (from counting statistics)),[17] where p is 0.06 for I–III. The scattering factors of the neutral non-hydrogen atoms were taken from the tables of Doyle and Turner,[18] and real and imaginary dispersion corrections[19] were applied to all of them. The spherical hydrogen scattering factor tables of Stewart, Davidson, and Simpson[20] were used. Absorption corrections were applied by using the analytical program ABSORB,[21] which uses the analytical method of de Meulenaer and Tompa.[22]

$(Et_4N)_2[(S_4)_2MoS]$ (I) and $(Et_4N)_2[(S_4)_2MoO]$ (II). Crystals suitable for X-ray diffraction measurements were obtained in a N_2 atmosphere by the slow diffusion of diethyl ether into a solution of $(Et_4N)_2[(S_4)_2MoS]$ in DMF. Suitable crystals of $(Et_4N)_2[(S_4)_2MoO]$ were obtained in the same manner. For both I and II, a fresh crystal was mounted on a glass fiber in air, coated with acrylic spray (Krylon), and used for cell dimension measurements and data collection. The cell dimensions of I (Table I) were obtained by least-squares refinement on the 2θ values of 13 carefully centered reflections with 2θ between 38 and 50°. A total of 19 362 data were collected for a full sphere of reciprocal space to $2\theta = 50°$. The cell dimensions of II (Table I) were obtained by least-squares refinement on the 2θ values of 12 carefully centered reflections with 2θ between 29 and 43°. A total of 12 515 data were collected for a full sphere of reciprocal space to $2\theta = 40°$.

$(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$ (III). Crystals suitable for X-ray diffraction measurements were obtained in a N_2 atmosphere

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Table II. Positional and Anisotropic[a] and Isotropic[b] Thermal Parameters and Their Standard Deviations in the Compound $(Et_4N)_2[(S_4)_2MoS]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0	0.250	0.14232 (1)	2.22 (2)	2.75 (2)	2.07 (1)	0.03 (1)	0	0
S(1)	0	0.250	0.21949 (3)	3.39 (5)	5.13 (6)	2.32 (4)	0.61 (4)	0	0
N(1)	0.2311 (2)	0	0.250	2.7 (1)	2.9 (1)	2.8 (1)	0	0	−0.6 (1)
N(2)	0	0.250	0.4615 (1)	2.8 (1)	2.9 (1)	2.3 (1)	0.3 (1)	0	0
C(1)	0.2858 (2)	0.0198 (2)	0.2055 (1)	3.6 (1)	4.0 (1)	3.1 (1)	−0.7 (1)	0.80 (9)	−0.5 (1)
C(3)	0.1763 (2)	0.0922 (2)	0.2597 (1)	3.6 (1)	3.6 (1)	3.7 (1)	0.8 (1)	−0.1 (1)	0.0 (1)
C(4)	0.1123 (2)	0.0795 (3)	0.3004 (1)	4.2 (2)	5.8 (2)	4.3 (2)	2.2 (1)	0.3 (1)	−0.2 (1)
C(2)	0.3519 (2)	0.1018 (3)	0.2104 (1)	3.9 (1)	5.2 (2)	6.6 (2)	−1.4 (1)	0.9 (1)	−0.2 (2)
C(5)	0.0646 (2)	0.3006 (2)	0.49455 (9)	3.2 (1)	3.9 (1)	2.9 (1)	0.4 (1)	−0.63 (9)	−0.6 (1)
C(6)	0.1348 (2)	0.3590 (3)	0.4693 (1)	3.6 (1)	5.2 (2)	5.9 (2)	−0.8 (1)	−0.0 (1)	−1.2 (1)
C(7)	0.0444 (2)	0.1738 (2)	0.4288 (1)	3.6 (1)	4.2 (1)	3.0 (1)	−0.3 (1)	0.5 (1)	−0.9 (1)
C(8)	0.0911 (2)	0.0907 (2)	0.4547 (1)	4.0 (1)	3.7 (1)	5.1 (2)	0.5 (1)	0.6 (1)	−0.8 (1)
S(2)	0.05480 (5)	0.40109 (5)	0.11227 (3)	3.20 (3)	3.06 (3)	3.84 (3)	−0.34 (2)	−0.04 (2)	0.43 (2)
S(5)	0.12791 (4)	0.16434 (5)	0.11864 (2)	2.86 (3)	3.54 (3)	3.08 (3)	0.46 (2)	0.02 (2)	−0.43 (2)
S(4)	0.22512 (5)	0.27153 (6)	0.13120 (3)	2.47 (3)	5.14 (4)	3.57 (3)	−0.05 (3)	−0.19 (2)	−0.65 (3)
S(3)	0.18691 (5)	0.38688 (6)	0.08902 (3)	3.46 (3)	5.05 (4)	3.54 (3)	−1.18 (3)	0.46 (3)	0.27 (3)

atom	x	y	z	atom	x	y	z
H(1)	0.3822	0.1089	0.1805	H(11)	0.0518	0.0540	0.4737
H(2)	0.3909	0.0847	0.2353	H(12)	0.1342	0.1193	0.4750
H(3)	0.3246	0.164	0.2179	H(13)	0.3141	−0.0404	0.1971
H(4)	0.0807	0.1405	0.3042	H(14)	0.2478	0.0389	0.1797
H(5)	0.1421	0.0651	0.3296	H(15)	0.213	0.147	0.2677
H(6)	0.0744	0.0262	0.2928	H(16)	0.1453	0.1081	0.2310
H(7)	0.1716	0.3880	0.4929	H(17)	0.0342	0.3469	0.5148
H(8)	0.1100	0.4106	0.4501	H(18)	0.0907	0.2506	0.514
H(9)	0.1664	0.3143	0.4493	H(19)	0.0032	0.1443	0.4079
H(10)	0.1176	0.0473	0.4316	H(20)	0.0857	0.2096	0.4092

[a] The temperature factor has the form $T = -\Sigma(^1/_4 B_{ij} H_i H_j a^*_i a^*_j)$, where H is the Miller index, a^* is the reciprocal cell length, and i and j are cycled 1–3. [b] The temperature factor has the form $T = -B[((\sin\theta)/\lambda)^2]$; $B = 4.823$ Å^2.

by the slow diffusion of diethyl ether into a solution of $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$ in DMF. A fresh crystal was mounted on a glass fiber in air, coated with Krylon, and used for cell dimension measurements and data collection. The cell dimensions were obtained by least-squares refinement on the 2θ values of 13 carefully centered reflections with 2θ between 37 and 50°. A total of 18 333 data were collected for a full sphere of reciprocal space to $2\theta = 50°$.

Determination of the Structures of $(Et_4N)_2[(S_4)_2MoS]$ (I) and $(Et_4N)_2[(S_4)_2MoO]$ (II). The atomic positions of the molybdenum and the five sulfur atoms of the MoS_9^{2-} anion were obtained by direct methods using the program MULTAN[23] and confirmed by the use of a three-dimensional Patterson synthesis map. The atoms of the cation were located on subsequent Fourier syntheses following least-squares refinements of the input atomic coordinates. The refinement of all the atoms with isotropic temperature factors in the space group *Ibca* gave a conventional R value of 0.076. Further refinement of the structure with anisotropic temperature factors for all the atoms gave a conventional R value of 0.067. In the final refinement the 20 hydrogen atoms were included in the structure factor calculation at their calculated positions (0.95 Å from the carbon atoms) but were not refined. The final R value was 0.025; the weighted R (Table I) was 0.038. During the last cycle of refinement all parameter shifts were less than 10% of their esd's.

The crystallographic parameters for the $(Et_4N)_2[(S_4)_2MoS]$ complex, with an oxygen atom in place of the terminal sulfido group, were refined with use of the diffraction data for the isomorphous $(Et_4N)_2[(S_4)_2MoO]$ complex. Refinement converged to a conventional R value of 0.047. New hydrogen atom positions were calculated (0.95 Å from the carbon atoms) and used in the structure factor calculation but were not refined. The final refinement results did not change, and a conventional R value of 0.047 was again obtained. The weighted R (Table I) was 0.071, and all parameter shifts were less than 10% of the esd's.

Determination of the Structure of $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$ (III). A three-dimensional Patterson synthesis map was used to locate the positions of the two molybdenum atoms and the two bridging sulfur atoms. The atomic positions of the sulfur atoms in the tetrasulfide ligand of the $Mo_2S_{10}^{2-}$ anion and one terminal sulfur atom were obtained by direct methods using the program MULTAN.[23] The other non-hydrogen atoms were located on subsequent Fourier syntheses following least-squares refinements of the input atomic coordinates. Further refinement of the structure with anisotropic temperature factors for the non-hydrogen atoms of the cations and the $Mo_2S_{10}^{2-}$ anion at full occupancy gave a conventional R value of 0.11.

At this stage a difference Fourier synthesis map indicated the presence of a DMF molecule, with the nitrogen atom centered at the origin, and the presence of a tetrasulfide ligand surrounding the persulfido (S_2^{2-}) unit of the $Mo_2S_{10}^{2-}$ anion. The occupancy factor of the S_2^{2-} ligand was changed to 0.80, and the sulfur atoms of the "new" S_4^{2-} ligand at the same location were introduced with the appropriate atomic coordinates and a 0.20 occupancy factor. In addition the atoms of the DMF molecule were entered with the appropriate half-occupancy factors. The hydrogen atomic positions were calculated, and the hydrogen atoms were used in the structure factor calculation but were not refined. Refinement with isotropic temperature factors for the individual atoms in the S_2^{2-} ligand and the "new" S_4^{2-} ligand, and with anisotropic temperature factors for all other non-hydrogen atoms, converged to a conventional R value of 0.075.

Refinements on the anion only, as described above, but with incremental changes in the relative occupancy factors of the S_2^{2-} and S_4^{2-} ligands on Mo(2) (Figure 5) yielded the lowest conventional R value (0.065) with occupancy factors of 0.72 for the S_2^{2-} ligand and 0.28 for the S_4^{2-} ligand. At this stage the weighted R (Table I) was 0.105, and all parameter shifts were less than 10% of their esd's.

Crystallographic Results. The final atomic positional and thermal parameters with standard deviations derived as described previously are compiled in Table II for $(Et_4N)_2[(S_4)_2MoS]$, Table III for $(Et_4N)_2[(S_4)_2MoO]$, and Table IV for $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$. Intramolecular distances and angles are given in Tables V and VI. A table of selected, weighted least-squares planes has been deposited as supplementary material.

The atom-labeling scheme is shown in Figure 4 for I and II and in Figures 5–7 for III. Stereopair drawings for the crystal packing in the complexes are shown in Figures 8 and 9. Tables of the observed

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(23) Main, P.; Woolfson, M. M.; Germain, G. "MULTAN: A Computer Program for the Automatic Solution of Crystal Structures"; University of York: York, England, 1971.

Table III. Positional and Anisotropic[a] and Isotropic[b] Thermal Parameters and Their Standard Deviations in the Compound $(Et_4N)_2[(S_4)_2MoO]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0	0.250	0.14649 (3)	3.24 (6)	4.24 (6)	2.29 (6)	0.38 (3)	0	0
O(1)	0	0.250	0.2079 (3)	5.2 (4)	8.3 (5)	2.0 (3)	0.8 (3)	0	0
N(1)	0.2256 (5)	0	0.250	3.4 (3)	3.1 (4)	2.6 (4)	0	0	0.2 (3)
N(2)	0	0.250	0.4627 (3)	3.1 (4)	3.2 (4)	2.6 (4)	0.5 (3)	0	0
C(1)	0.2824 (4)	0.0197 (5)	0.2057 (3)	3.5 (3)	4.4 (4)	3.7 (3)	0.2 (3)	0.5 (3)	−0.2 (3)
C(3)	0.1714 (4)	0.0921 (5)	0.2588 (3)	3.5 (3)	4.5 (4)	3.9 (4)	0.6 (3)	0.3 (3)	−0.8 (3)
C(4)	0.1054 (5)	0.0835 (6)	0.2995 (3)	4.0 (4)	6.0 (4)	4.9 (4)	1.1 (3)	0.2 (3)	−0.5 (3)
C(2)	0.3482 (5)	0.1020 (6)	0.2110 (3)	4.4 (4)	5.9 (5)	6.7 (5)	0.0 (3)	2.5 (4)	0.9 (4)
C(5)	0.0653 (4)	0.2999 (6)	0.4957 (3)	3.4 (4)	4.8 (4)	4.9 (4)	0.4 (3)	−1.2 (3)	−1.2 (3)
C(6)	0.1348 (5)	0.3583 (7)	0.4699 (3)	4.5 (4)	6.1 (5)	6.6 (5)	−0.8 (4)	−0.4 (4)	−2.2 (4)
C(7)	0.0435 (5)	0.1736 (5)	0.4290 (2)	3.5 (3)	4.5 (4)	3.5 (3)	−0.8 (3)	0.1 (3)	−0.6 (3)
C(8)	0.0911 (5)	0.0893 (6)	0.4560 (3)	3.9 (4)	4.5 (4)	6.8 (5)	0.2 (3)	0.6 (3)	−1.1 (4)
S(2)	0.0552 (1)	0.4042 (1)	0.11615 (7)	3.9 (1)	4.0 (1)	5.1 (1)	−0.10 (8)	−0.45 (8)	0.26 (8)
S(5)	0.1288 (1)	0.1641 (1)	0.12129 (7)	3.81 (9)	4.5 (1)	3.6 (1)	0.64 (7)	−0.39 (7)	−0.29 (8)
S(4)	0.2274 (1)	0.2729 (2)	0.13260 (8)	3.0 (1)	6.3 (1)	4.2 (1)	0.14 (8)	−0.48 (8)	−0.61 (8)
S(3)	0.1867 (1)	0.3883 (2)	0.09087 (8)	4.0 (1)	6.0 (1)	4.4 (1)	−1.04 (8)	0.12 (8)	0.21 (9)

atom	x	y	z	atom	x	y	z
H(11)	0.2457	0.0370	0.1792	H(23)	0.3199	0.1637	0.2178
H(12)	0.3123	−0.0413	0.1984	H(41)	0.0745	0.1452	0.3025
H(31)	0.1413	0.1075	0.2296	H(42)	0.1342	0.0693	0.3294
H(32)	0.2093	0.1466	0.2667	H(43)	0.0662	0.0303	0.2924
H(51)	0.0921	0.2487	0.5147	H(61)	0.1730	0.3873	0.493
H(52)	0.0351	0.3452	0.5166	H(62)	0.1091	0.4106	0.4509
H(71)	0.084	0.2089	0.4092	H(63)	0.1661	0.3141	0.4490
H(72)	0.0004	0.1441	0.4089	H(81)	0.1166	0.0446	0.433
H(21)	0.3801	0.1077	0.1815	H(82)	0.0512	0.053	0.4757
H(22)	0.3864	0.0854	0.2370	H(83)	0.1348	0.1178	0.476

[a] The temperature factor has the form $T = -\Sigma(^1/_4 B_{ij}H_iH_ja^*_ia^*_j)$, where H is the Miller index, a^* is the reciprocal cell length, and i and j are cycled 1–3. [b] The temperature factor has the form $T = -B[((\sin\theta)/\lambda)^2]$; $B = 4.000$ Å^2.

values of F, their esd's, and the $|F_o| - |F_c|$ values have been deposited as supplementary material.

Results and Discussion

(1) Synthesis. The reaction of $(Et_4N)_2MoS_4$ with BzSSSBz or elemental sulfur in CH_3CN, either under a dinitrogen atmosphere or in the air, proceeds readily at ambient temperature, and $(Et_4N)_2[(S_4)_2MoS]$, complex I, is formed and can be isolated in crystalline form in excellent yields.

Attempts to exchange the Et_4N^+ cations in I with Ph_4P^+ in DMF solution were unsuccessful. Apparently, a dissociation and rearrangement of I occurs in DMF solution following the addition of Ph_4PCl. The electronic spectra of DMF solutions of I upon standing in the presence of Ph_4PCl are different than those of I either in CH_3CN solution or in DMF solution without Ph_4PCl present. From DMF solutions of I in the presence of Ph_4PCl the only product that can be isolated in crystalline form is a mixture of the $(Ph_4P)_2(Mo_2S_{10})$ and $(Ph_4P)_2(Mo_2S_{12})$ complexes. These complexes also are obtained when $(Ph_4P)_2MoS_4$ is treated with either elemental sulfur or BzSSSBz in DMF solution. When DMF solutions of $Et_4N[(S_4)_2MoS]$ are heated, in the presence of traces of water, hydrolysis takes place and the yellow-green $Et_4N[(S_4)_2MoO]$ complex can be isolated in fair yields.

The apparent importance of the counterion in the isolation of different thiomolybdate anions from solution prompted us to reinvestigate the known aqueous solution chemistry of MoS_4^{2-}. Müller and co-workers have reported on the synthesis and structural characterization of the very interesting $[Mo_2(S_2)_6]^{2-}$ (Figure 1A) and $[Mo_3S(S_2)_6]^{2-}$ thioanions.[9,10] These complexes were obtained by the reaction of MoS_4^{2-} (generated in situ from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and H_2S in water under basic conditions) with aqueous $(NH_4)_2S_x$. We have reinvestigated these reactions and also have isolated as major products the ammonium salts of $[Mo_2(S_2)_6]^{2-}$ and $[Mo_3S(S_2)_6]^{2-}$ thioanions. The relative yields of these complexes depend on the amount of excess S present in the $(NH_4)_2S$ solutions. The reaction of aqueous $(NH_4)_2MoS_4$ with commercial reagent grade $(NH_4)_2S$ solution (20–24%) in a 1/8 $MoS_4^{2-}/(NH_4)_2S$ molar ratio yielded after ca. 1 h a crystalline product. Mechanical separation of the two different types of crystals from a representative sample and subsequent identification by electronic spectroscopy and comparison to "authentic" samples indicated the presence of the $[Mo_3S(S_2)_6]^{2-}$ thioanion as the major component (~90%) and the $[Mo_2(S_2)_6]^{2-}$ thioanion (Figure 1A) as a minor component (~10%). The reaction of $(NH_4)_2S_2$ or $(NH_4)_2S_3$[24] with $(NH_4)_2MoS_4$ in a 1/5 molar ratio yielded approximately equimolar mixture of the two thioanions. From this mixture, the $(NH_4)_2[Mo_2(S_2)_6]^{2-}$ complex can be separated by extraction into acetonitrile, a solvent in which $(NH_4)_2[Mo_3S(S_2)_6]$ is only sparingly soluble. The $[Mo_2(S_2)_6]^{2-}$ thioanion becomes the major product only when $(NH_4)_2S$ solutions are completely saturated with elemental sulfur prior to their reactions with aqueous $(NH_4)_2MoS_4$.

Following the addition of Ph_4PCl to CH_3CN solutions of $(NH_4)_2[Mo_2(S_2)_6]$ and upon standing, the $Mo_2S_{10}^{2-}$ and $Mo_2S_{12}^{2-}$ complex anions form and cocrystallize as Ph_4P^+ salts. A survey of the reaction of MoS_4^{2-} with "active" sulfur reagents and a consideration of the various thiomolybdate products obtained reveal a very complex system of equilibria. In such a system the individual species are interrelated either by the gain or loss of sulfur fragments or by facile molecular rearrangements. A tentative scheme that attempts to correlate the various, MoS_4^{2-}-derived, thioanions is shown in Figure 2. The formation of $(Mo_2S_7)^{2-}$ (A, Figure 2) during the acidification of aqueous solutions of MoS_4^{2-} has been proposed previously on the basis of pH and conductimetric titrations.[25] The same anion has been suggested as a bridging unit in the $[Fe(salen)]_2(Mo_2S_7)$ complex.[26] More recently the $(Mo_2S_7)^{2-}$

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[24] $(NH_4)_2S_2$ and $(NH_4)_2S_3$ were prepared in situ by the reaction of stoichiometric amounts of elemental sulfur with commercial, reagent grade, $(NH_4)_2S$ (20–24% aqueous solution).

[25] Saxena, R.; Jain, M.; Mittel, M. *Aust. J. Chem.* **1968**, *21*, 91.

[26] Mitchell, P. C. H.; Parker, D. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1821.

Table IV. Positional and Anisotropic[a] and Isotropic[b] Thermal Parameters and Their Standard Deviations in the Compound $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]\cdot{}^1/_2DMF$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(2)	0.70565 (3)	0.70287 (6)	0.07146 (6)	3.92 (3)	3.69 (3)	2.76 (3)	−0.09 (2)	−0.63 (2)	−0.77 (2)
S(6)	0.2657 (1)	0.3816 (2)	0.7376 (2)	6.2 (1)	4.5 (1)	3.71 (9)	0.18 (8)	−1.21 (8)	−0.46 (7)
S(7)	0.33418 (8)	0.0951 (2)	−0.0685 (2)	3.18 (7)	3.81 (8)	4.07 (9)	0.19 (6)	0.37 (6)	−0.25 (7)
S(8)	0.20658 (9)	0.3001 (2)	0.0531 (2)	3.89 (9)	5.7 (1)	3.99 (9)	0.20 (7)	−0.24 (7)	−2.54 (8)
S(9)	0.3981 (1)	0.3174 (3)	−0.0377 (3)	4.99 (6)					
S(10)	0.3263 (2)	0.4395 (3)	0.0311 (4)	6.01 (7)					
S(11)	0.3979 (4)	0.2616 (8)	−0.0528 (8)	4.5 (1)					
S(12)	0.4222 (5)	0.396 (1)	0.014 (1)	7.1 (2)					
S(13)	0.3464 (5)	0.533 (1)	−0.020 (1)	7.0 (2)					
S(14)	0.2811 (4)	0.4423 (7)	0.0635 (8)	4.5 (1)					
Mo(1)	0.76784 (2)	0.89289 (6)	−0.00098 (5)	2.76 (3)	4.13 (3)	2.29 (3)	0.01 (2)	−0.34 (2)	−0.64 (2)
S(1)	0.1713 (1)	0.0905 (2)	0.1985 (2)	4.5 (1)	7.3 (1)	3.66 (9)	−1.81 (9)	0.88 (7)	−1.26 (9)
S(2)	0.8202 (1)	0.0881 (3)	0.7071 (2)	6.9 (1)	8.8 (2)	3.7 (1)	−2.8 (1)	0.17 (9)	0.6 (1)
S(3)	−0.2061 (1)	0.1760 (2)	−0.1448 (3)	5.3 (1)	5.4 (1)	5.8 (1)	−1.32 (9)	−0.77 (9)	0.8 (1)
S(4)	−0.27946 (9)	0.1044 (2)	−0.0690 (2)	3.79 (9)	4.6 (1)	4.7 (1)	0.15 (7)	−0.38 (7)	0.50 (8)
S(5)	0.17890 (9)	0.1173 (2)	−0.1625 (2)	4.67 (9)	4.61 (9)	3.36 (8)	−0.03 (7)	−1.60 (7)	−1.08 (7)
P(1)	0.44386 (8)	0.2801 (2)	0.4758 (2)	3.82 (7)	3.73 (8)	3.29 (7)	−0.69 (6)	−0.16 (6)	−0.48 (6)
P(2)	0.91415 (8)	0.3958 (1)	0.3716 (2)	3.77 (7)	3.34 (7)	2.93 (7)	−0.59 (5)	−0.12 (5)	−0.49 (5)
C(1)	0.3923 (3)	0.1902 (6)	0.4506 (7)	3.5 (3)	3.1 (3)	3.9 (3)	−0.2 (2)	−0.7 (2)	−1.0 (2)
C(2)	0.3471 (4)	0.1705 (7)	0.5473 (9)	4.0 (3)	3.6 (3)	5.6 (4)	−1.2 (3)	0.5 (3)	−1.2 (3)
C(3)	0.3936 (4)	0.1475 (9)	0.3368 (9)	5.9 (5)	5.4 (4)	3.9 (4)	−1.5 (4)	−0.6 (3)	−0.7 (3)
C(4)	0.3088 (4)	0.0595 (9)	0.416 (1)	4.6 (4)	5.3 (4)	8.1 (6)	−1.5 (3)	−2.5 (4)	−0.9 (4)
C(5)	0.3055 (4)	0.1037 (9)	0.529 (1)	4.2 (4)	6.2 (5)	7.4 (6)	−1.3 (3)	−0.8 (4)	−1.5 (4)
C(6)	0.3520 (5)	0.080 (1)	0.323 (1)	7.4 (6)	7.0 (6)	6.0 (5)	−1.4 (5)	−1.0 (4)	−3.7 (5)
C(7)	0.5029 (4)	0.2786 (7)	0.3466 (8)	4.0 (3)	4.8 (4)	3.1 (3)	−0.9 (3)	−0.1 (2)	−0.5 (3)
C(8)	0.5495 (4)	0.1762 (8)	0.355 (1)	5.3 (4)	4.0 (4)	7.1 (5)	−1.1 (3)	2.3 (4)	−2.0 (4)
C(9)	0.5931 (5)	0.1686 (9)	0.252 (1)	5.8 (5)	5.8 (5)	8.7 (7)	−2.1 (4)	2.2 (5)	−3.7 (5)
C(10)	0.5921 (6)	0.264 (2)	0.153 (1)	5.9 (6)	12.8 (11)	5.3 (5)	−0.8 (6)	2.5 (4)	−2.2 (6)
C(11)	0.5490 (6)	0.371 (2)	0.154 (1)	7.5 (8)	15.2 (12)	7.1 (7)	1.7 (8)	2.9 (6)	4.7 (8)
C(12)	0.5037 (5)	0.379 (1)	0.251 (1)	5.8 (6)	11.0 (8)	5.3 (5)	0.6 (5)	1.3 (4)	0.9 (6)
C(13)	0.4824 (3)	0.2188 (6)	0.6267 (7)	3.1 (3)	3.1 (3)	3.1 (3)	−0.8 (2)	0.0 (2)	−0.5 (2)
C(14)	0.5250 (5)	0.2761 (9)	0.6604 (8)	5.9 (5)	6.6 (5)	3.3 (3)	−2.4 (4)	−1.1 (3)	−0.1 (3)
C(15)	0.5576 (4)	0.231 (1)	0.774 (1)	4.1 (4)	7.2 (6)	6.0 (5)	−2.4 (4)	−1.7 (3)	0.6 (4)
C(16)	0.5467 (4)	0.1294 (9)	0.8575 (8)	3.5 (4)	7.9 (6)	3.7 (4)	−0.7 (3)	−1.0 (3)	0.4 (4)
C(17)	0.5049 (5)	0.0719 (9)	0.8237 (9)	6.1 (5)	5.2 (5)	4.4 (4)	−1.7 (4)	−0.8 (3)	1.1 (4)
C(18)	0.4726 (4)	0.1162 (7)	0.7103 (8)	6.4 (5)	4.0 (3)	3.3 (3)	−1.2 (3)	0.2 (3)	0.2 (3)
C(19)	0.3997 (3)	0.4295 (6)	0.4794 (8)	2.7 (3)	3.5 (3)	4.7 (4)	−0.8 (2)	−0.4 (2)	−0.8 (3)
C(20)	0.3937 (4)	0.4798 (6)	0.5872 (9)	4.3 (4)	2.8 (3)	5.7 (4)	−1.3 (3)	0.6 (3)	−1.0 (3)
C(21)	0.3561 (5)	0.5923 (8)	0.588 (1)	6.1 (5)	4.4 (4)	8.3 (7)	−1.5 (4)	2.1 (5)	−2.0 (4)
C(22)	0.3266 (4)	0.6582 (8)	0.475 (1)	5.0 (4)	2.9 (4)	11.3 (9)	−0.3 (3)	−0.7 (5)	−0.2 (5)
C(23)	0.3298 (4)	0.6070 (9)	0.365 (1)	4.2 (4)	4.4 (4)	8.1 (7)	−0.4 (3)	−0.5 (4)	0.8 (4)
C(24)	0.3658 (4)	0.4912 (8)	0.3652 (9)	4.1 (4)	4.8 (4)	5.2 (4)	−0.1 (3)	−1.3 (3)	0.3 (3)
D(1)[c]	−0.0518 (4)	0.4827 (7)	0.8503 (7)	4.1 (3)	5.3 (4)	3.3 (3)	−1.1 (3)	0.6 (3)	−0.7 (3)
D(2)	0.0194 (3)	0.4478 (7)	0.2451 (8)	2.9 (3)	4.3 (4)	4.2 (3)	0.0 (2)	0.2 (2)	−1.2 (3)
D(3)	−0.0445 (3)	0.4815 (6)	0.2491 (6)	3.6 (3)	2.8 (3)	2.5 (3)	−1.1 (2)	0.2 (2)	−0.4 (2)
D(4)	0.0187 (4)	0.6190 (7)	0.0650 (8)	4.3 (4)	4.1 (3)	4.1 (4)	−1.4 (3)	1.3 (3)	−1.5 (3)
D(5)	−0.0457 (4)	0.6497 (7)	0.0735 (7)	5.4 (4)	4.1 (3)	2.9 (3)	−1.1 (3)	0.4 (3)	−0.4 (3)
D(6)	−0.0773 (3)	0.5823 (6)	0.1653 (7)	4.0 (3)	3.3 (3)	2.9 (3)	−0.8 (2)	0.0 (2)	−0.4 (2)
D(7)	−0.1337 (3)	0.3229 (6)	0.3023 (7)	3.9 (3)	2.8 (3)	3.5 (3)	−0.4 (2)	−0.1 (2)	−1.0 (2)
D(8)	−0.1556 (4)	0.3706 (8)	0.1753 (8)	5.0 (4)	5.3 (4)	3.7 (3)	0.4 (3)	−1.5 (3)	−1.5 (3)
D(9)	−0.1949 (5)	0.3109 (9)	0.126 (1)	7.0 (5)	5.1 (5)	5.7 (5)	−1.0 (4)	−2.4 (4)	−2.0 (4)
D(10)	0.7884 (4)	0.2088 (9)	0.207 (1)	4.7 (4)	5.7 (5)	10.1 (7)	−0.8 (4)	−2.0 (4)	−3.8 (5)
D(11)	0.8106 (4)	0.1666 (8)	0.327 (1)	5.4 (4)	4.2 (4)	6.7 (5)	−1.1 (3)	−0.4 (4)	−1.8 (4)
D(12)	0.8492 (4)	0.2222 (7)	0.3791 (8)	5.7 (4)	3.7 (3)	4.1 (4)	−1.9 (3)	−0.3 (3)	−1.4 (3)
D(13)	−0.0314 (3)	0.2793 (6)	0.4720 (6)	3.4 (3)	2.6 (3)	2.8 (3)	−0.8 (2)	−0.3 (2)	−0.3 (2)
D(14)	−0.0244 (4)	0.2811 (6)	0.6003 (7)	4.7 (3)	3.2 (3)	3.2 (3)	−1.1 (2)	−0.7 (2)	−0.1 (2)
D(15)	0.0194 (4)	0.1899 (7)	0.6726 (8)	5.4 (4)	4.1 (4)	4.1 (4)	−1.3 (3)	−1.9 (3)	0.4 (3)
D(16)	0.0539 (4)	0.0979 (7)	0.618 (1)	5.0 (4)	3.3 (3)	6.4 (5)	−0.8 (3)	−1.6 (3)	−0.1 (3)
D(17)	0.0482 (4)	0.0957 (7)	0.488 (1)	4.7 (4)	2.8 (3)	6.5 (5)	−0.3 (3)	0.1 (3)	−0.7 (3)
D(18)	0.0048 (3)	0.1856 (6)	0.4159 (8)	4.5 (4)	2.9 (3)	4.2 (3)	−0.1 (2)	−0.4 (3)	−0.6 (3)
D(19)	−0.1308 (3)	0.4930 (6)	0.4722 (6)	3.2 (3)	3.0 (3)	2.7 (3)	−0.5 (2)	−0.2 (2)	−0.6 (2)
D(20)	−0.1743 (4)	0.4512 (8)	0.5601 (9)	4.9 (4)	4.7 (4)	5.0 (4)	−1.9 (3)	1.5 (3)	−1.3 (3)
D(21)	−0.2071 (4)	0.5253 (9)	0.6405 (9)	4.6 (4)	5.8 (5)	5.2 (4)	−0.7 (3)	1.0 (3)	−2.1 (4)
D(22)	−0.2003 (3)	0.6390 (8)	0.6314 (8)	3.5 (3)	6.1 (5)	3.7 (4)	0.8 (3)	−0.5 (3)	−2.2 (3)
D(23)	−0.1593 (4)	0.6827 (8)	0.5402 (9)	4.9 (4)	4.8 (4)	5.0 (4)	−0.4 (3)	−0.2 (3)	−2.0 (3)
D(24)	−0.1229 (3)	0.6092 (7)	0.4616 (8)	3.8 (3)	4.0 (3)	4.2 (4)	−1.3 (3)	0.2 (3)	−1.3 (3)
F(1)[d]	−0.045 (1)	0.024 (3)	−0.036 (3)	9.1 (7)					
F(2)	0.0157 (5)	0.066 (1)	0.046 (1)	7.1 (2)					
F(3)	−0.053 (1)	0.093 (3)	0.043 (3)	7.3 (6)					
O(1)	−0.0200 (8)	0.135 (2)	0.141 (2)	7.9 (4)					
N(1)	0	0	0	1.6 (2)					

atom	x	y	z	atom	x	y	z
H(12)	0.3442	0.1995	0.625	H(56)	−0.1069	0.6047	0.0983
H(13)	0.2753	0.0881	0.5976	H(62)	−0.1995	0.3783	0.1699
H(14)	0.2797	0.0129	0.405	H(63)	−0.2375	0.3125	0.1175
H(15)	0.3546	0.0493	0.2456	H(64)	0.8322	0.2035	0.1999

Table IV (*Continued*)

atom	x	y	z	atom	x	y	z
H(16)	0.4246	0.162	0.2693	H(65)	0.8548	0.159	0.3363
H(22)	0.5493	0.1106	0.427	H(66)	0.8923	0.2179	0.3875
H(23)	0.6241	0.0969	0.2494	H(72)	−0.049	0.3436	0.6373
H(24)	0.6234	0.2510	0.084	H(73)	0.0251	0.1904	0.7602
H(25)	0.5516	0.4452	0.0908	H(74)	0.0834	0.0343	0.6694
H(26)	0.4733	0.455	0.2543	H(75)	0.0729	0.0330	0.449
H(32)	0.5328	0.3477	0.6044	H(76)	−0.0016	0.1833	0.3279
H(33)	0.5882	0.2683	0.7930	H(82)	−0.1805	0.3718	0.5637
H(34)	0.5683	0.1033	0.9375	H(83)	−0.2362	0.4970	0.701
H(35)	0.4972	0.002	0.8795	H(84)	−0.2223	0.6895	0.6867
H(36)	0.4424	0.0757	0.6876	H(85)	−0.1551	0.7638	0.5331
H(42)	0.4152	0.4353	0.6649	H(86)	−0.0954	0.6373	0.3987
H(43)	0.3512	0.6258	0.6645	H(91)	−0.0662	−0.0151	−0.1002
H(44)	0.3027	0.7382	0.4732	H(92)	−0.078	0.1073	−0.0576
H(45)	0.3087	0.6509	0.2875	H(93)	−0.0855	−0.0061	0.0427
H(46)	0.3689	0.4561	0.2902	H(94)	0.0964	−0.0123	−0.0123
H(52)	0.0534	0.3858	0.226	H(95)	0.0686	0.0101	0.1223
H(53)	−0.0546	0.4728	0.9425	H(96)	0.0597	0.1147	0.0025
H(54)	0.0381	0.6487	−0.0137	H(97)	−0.0902	0.0834	0.0809
H(55)	−0.0520	0.6940	−0.0142				

[a] The temperature factor has the form $T = -\Sigma(^1/_4 B_{ij}H_iH_ja^*_ia^*_j)$, where H is the Miller index, a^* is the reciprocal cell length, and i and j are cycled 1–3. [b] The temperature factor has the form $T = -B[((\sin\theta)/\lambda)^2]$; $B = 6.000$ for all hydrogen atoms shown. [c] D denotes phenyl carbon atoms attached to P_2. [d] F denotes carbon atoms of the DMF molecule.

Table V. Selected Interatomic Distances (Å) and Angles (Deg) in the $[(S_4)_2MoS]^{2-}$ and $[(S_4)_2MoO]^{2-}$ Anions

	$[(S_4)_2MoS]^{2-}$	$[(S_4)_2MoO]^{2-}$
	Distances	
Mo-S(1),O(1)	2.128 (1)	1.685 (7)
Mo-S(5)	2.331 (1)	2.363 (2)
Mo-S(2)	2.387 (1)	2.395 (2)
Mo-S(4)	3.735 (1)	3.743 (2)
Mo-S(3)	3.535 (1)	3.551 (2)
S(4)-S(5)	2.166 (1)	2.159 (3)
S(3)-S(4)	2.012 (1)	2.008 (3)
S(2)-S(3)	2.107 (1)	2.120 (3)
S(2)-S(5)	3.345 (1)	3.376 (3)
S(2')-S(5)	2.984 (1)	2.990 (3)
	Angles	
S(2)-Mo-S(5)	90.32 (3)	90.40 (8)
S(2')-Mo-S(5)	78.45 (3)	77.86 (7)
S(1),O(1)-Mo-S(5)	110.83 (3)	110.62 (17)
S(1),O(1)-Mo-S(2)	105.88 (3)	106.77 (17)
Mo-S(5)-S(4)	112.28 (3)	111.69 (7)
Mo-S(2)-S(3)	103.59 (3)	103.57 (7)
S(3)-S(4)-S(5)	100.17 (4)	100.76 (11)
S(2)-S(3)-S(4)	101.83 (5)	101.91 (12)

intermediate has been suggested to precede the formation of the $[(MoS_4)_2MoS]^{2-}$ complex (B, Figure 2) from MoS_4^{2-} in DMF solution. In a tentative proposed mechanism,[13b] internal electron transfer within the $(Mo_2S_7)^{2-}$ will yield the $[Mo^{VI}S_4Mo^{IV}S(S_2)]^{2-}$ anion, in which displacement of S_2^{2-} by MoS_4^{2-} will give the $[(MoS_4)_2MoS]^{2-}$ complex (B, Figure 2). Alternatively, this complex and the $[(S_2)MoS(S_2)]^{2-}$ anion could be obtained also by the disproportionation of the $[Mo^{VI}S_4Mo^{IV}S(S_2)]^{2-}$ anion.

In reactions where either "active" sulfur (S_x^0, $x = 2$) or polysulfide anions (S_x^{2-}, $x = 4$) are available, the $[(MoS_4)MoS(S_2)]^{2-}$ intermediate could undergo either addition of S_2^0 or displacement of S_2^{2-} by S_4^{2-} to yield the $[(MoS_4)MoS(S_4)]^{2-}$ complex, which could exist in a disproportionation equilibrium with the $[(MoS_4)_2MoS]^{2-}$ and $[(S_4)_2MoS]^{2-}$ complexes.

In a series of sulfur transfer equilibria, and with the possible involvement of solvent ligation, either the $[(S_4)_2MoS]^{2-}$ anion or the (as yet unknown) MoS_5^{2-} anion could give the $[Mo_2S_{12}]^{2-}$ anion or the (as yet unknown) MoS_5^{2-} anion could give the $[Mo_2S_{12}]^{2-}$, $[Mo_2S_{10}]^{2-}$, and $(Mo_2S_8)^{2-}$ thioanions (D–F, Figure 2). The first two of these anions can be isolated and are reported in this paper while the last, $(Mo_2S_8)^{2-}$, would

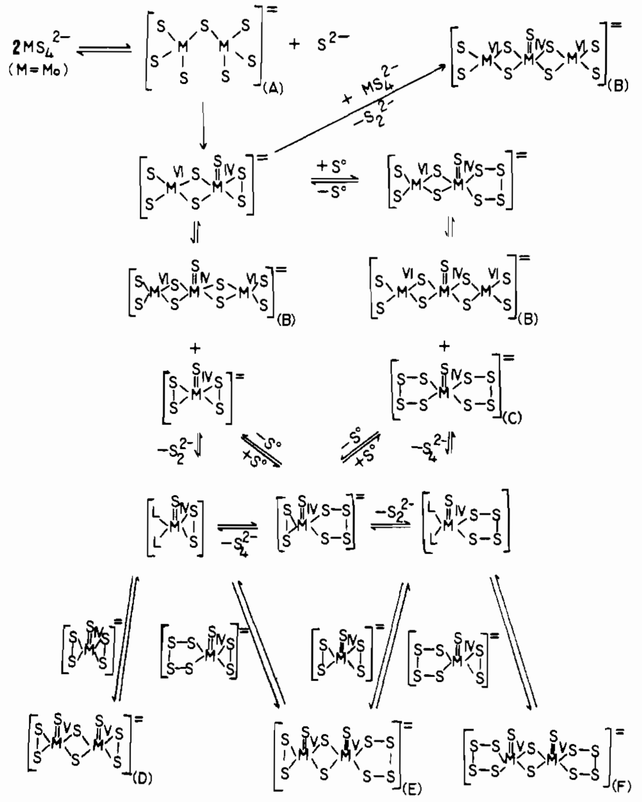

Figure 2. Tentative scheme for the generation and interconversions of the thiomolybdate anions.

be structurally analogous to the corresponding oxo complex,[27] $(Mo_2S_6O_2)^{2-}$.

At present the $[(S_2)MoS(S_2)]^{2-}$ and $[(S_2)MoS(S_4)]^{2-}$ anions have not been isolated or detected, and their introduction in the general scheme (Figure 2) is only speculative. However, their possible existence is justified on the basis of the demonstrated ability of the S_2^{2-} and S_4^{2-} anions to serve as ligands for either the $(Mo{=}S)^{2+}$ or $(Mo{=}S)^{3+}$ units. A consideration of the synthetic aspects of thiomolybdate chemistry shows that

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(27) (a) Clegg, W.; Mohan, N.; Müller, A.; Neumann, A.; Rittner, W.; Sheldrick, G. M. *Inorg. Chem.* **1980**, *19*, 2066. (b) Clegg, W.; Sheldrick, G. M.; Garner, C. D.; Christou, G. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2784.

Table VI. Selected Interatomic Distances (Å) and Angles (Deg) in the $(Mo_2S_{10})^{2-}$ and $(Mo_2S_{12})^{2-}$ Anions (Figure 3) in the $[(C_6H_5)_4P]_2(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}$ "Salt"

Distances	value from this work	corresponding value[a] from ref
Common $(S_4)Mo_2S_4$ Fragment		
Mo(1)-Mo(2)	2.846 (1)	2.837 (1)
Mo(1)-S(1)	2.399 (2)	2.403 (3)
Mo(1)-S(4)	2.427 (2)	2.409 (2)
Mo(1)-S(7)	2.319 (2)	2.332 (2)
Mo(1)-S(8)	2.365 (2)	2.351 (2)
Mo(1)-S(5)	2.123 (2)	2.112 (2)
Mo(2)-S(7)	2.316 (2)	2.303 (2)
Mo(2)-S(8)	2.274 (2)	2.289 (2)
Mo(2)-S(6)	2.114 (2)	2.108 (2)
S(1)-S(2)	2.093 (4)	2.115 (5), 2.096 (16)[b]
S(2)-S(3)	2.018 (4)	1.970 (6), 1.936 (19)
S(3)-S(4)	2.053 (3)	2.019 (5), 2.167 (14)
S(1)-S(4)	3.372 (3)	
Mo(1)-S(2)	3.727 (3)	
Mo(1)-S(3)	3.517 (3)	
S(7)-S(8)	3.603 (3)	
S_2^{2-} and the $(Mo_2S_{10})^{2-}$ Component		
Mo(2)-S(9)	2.439 (3)	2.395 (3)
Mo(2)-S(10)	2.425 (4)	2.394 (3)
S(9)-S(10)	2.074 (5)	2.071 (3)
S(7)-S(9)	3.336 (4)	
S(8)-S(10)	3.421 (4)	
S_4^{2-} and the $(Mo_2S_{12})^{2-}$ Component		
Mo(2)-S(11)	2.260 (8)	
Mo(2)-S(14)	2.387 (8)	
S(9)-S(11)	0.706 (8)	
S(10)-S(14)	1.037 (8)	
S(11)-S(12)	2.049 (15)	
S(12)-S(13)	2.025 (16)	
S(13)-S(14)	2.053 (13)	
S(11)-S(14)	3.278 (12)	
Mo(2)-S(12)	3.557 (12)	
Mo(2)-S(13)	3.398 (12)	
S(1)-S(8)	2.863 (3)	
S(4)-S(7)	2.962 (3)	
S(7)-S(11)	2.712 (9)	
S(8)-S(14)	2.642 (8)	

Angles	value from this work	corresponding value[a] from ref
Common $(S_4)Mo_2S_4$ Fragment		
Mo(1)-S(7)-Mo(2)	75.75 (5)	75.5 (1)
Mo(1)-S(8)-Mo(2)	75.64 (6)	75.4 (1)
S(7)-Mo(1)-S(8)	100.53 (10)	100.7 (1)
S(7)-Mo(2)-S(8)	103.42 (10)	103.4 (1)
S(1)-Mo(1)-S(4)	87.17 (9)	85.1 (1)
S(5)-Mo(1)-S(4)	104.90 (12)	106.5 (1)
S(5)-Mo(1)-S(1)	111.32 (11)	109.5 (1)
S(5)-Mo(1)-S(7)	108.17 (10)	107.5 (1)
S(5)-Mo(1)-S(8)	106.48 (10)	107.6 (1)
S(6)-Mo(2)-S(7)	108.28 (11)	108.3 (1)
S(6)-Mo(2)-S(8)	106.29 (11)	106.4 (1)
S(1)-Mo(1)-S(8)	73.88 (9)	74.4 (1)
S(4)-Mo(1)-S(7)	77.20 (7)	78.2 (1)
Mo(1)-S(4)-S(3)	103.14 (9)	105.0 (1), 100.3 (5)[b]
S(4)-S(3)-S(2)	100.21 (17)	97.1 (3), 109.7 (8)
S(3)-S(2)-S(1)	101.83 (14)	102.1 (2), 81.5 (9)
S(2)-S(1)-Mo(1)	111.95 (10)	110.5 (2), 104.0 (4)
S_2^{2-} and the $(Mo_2S_{10})^{2-}$ Component		
S(6)-Mo(2)-S(9)	110.49 (13)	111.6 (1)
S(6)-Mo(2)-S(10)	109.05 (13)	110.5 (1)
S(9)-Mo(2)-S(10)	50.47 (12)	51.2 (1)
Mo(2)-S(9)-S(10)	64.41 (14)	64.4 (1)
Mo(2)-S(10)-S(9)	65.12 (14)	64.4 (1)
S(10)-Mo(2)-S(8)	93.37 (11)	90.9 (1)
S(9)-Mo(2)-S(7)	89.08 (11)	89.4 (1)
S_4^{2-} and the $(Mo_2S_{12})^{2-}$ Component		
S(6)-Mo(2)-S(11)	111.9 (2)	
S(6)-Mo(2)-S(14)	110.2 (2)	
S(7)-Mo(2)-S(11)	72.7 (3)	
S(8)-Mo(2)-S(14)	69.0 (2)	
S(11)-Mo(2)-S(14)	89.7 (4)	
Mo(2)-S(11)-S(12)	111.7 (2)	
S(11)-S(12)-S(13)	103.4 (6)	
S(12)-S(13)-S(14)	98.4 (6)	
Mo(2)-S(14)-S(13)	99.6 (4)	

[a] Values from ref 12, major component. [b] Values from ref 12, minor component.

the nature of the counterions present in solution (and lattice dynamics) are very important in the isolation of specific complexes from equilibrium mixtures. It appears that the serendipitous choice of counterion may well be very important for the isolation of such proposed species as the $[(S_2)MoS(S_2)]^{2-}$, $[S_2MoS(S_4)]^{2-}$, and $[(MoS_4)MoS(S_4)]^{2-}$ anions.

Spectroscopic and Electrochemical Properties. The electronic spectra of the Mo/S thioanions reported herein are shown in Figure 3. The spectrum of I in DMF solution is dominated by a strong absorption at 316 nm (ϵ = 15 750) and shoulders at 470, 405, and 340 nm. The spectrum of II in the same solvent shows shoulders at 555 and 475 nm and a strong absorption at 316 nm (ϵ = 6620). The intense high-energy transition in I and II very likely is an internal ligand transition associated with the S_4^{2-} ligands. The transitions occurring at larger wavelengths tentatively can be assigned to $S_4^{2-} \rightarrow$ Mo charge-transfer absorptions. The bathochromic shift of these transitions in II is not unexpected considering the greater electron-withdrawing effect of the terminal oxygen in II in comparison to that of the terminal S in I.

The spectrum of the $[Mo_2S_{10}]^{2-}/[Mo_2S_{12}]^{2-}$, 0.72/0.28, mixture in DMF solution shows absorptions (shoulders) at 570, 438, 316, and 290 nm.

The infrared spectrum of the Et_4N^+ salt of I shows the Mo=S vibration at 525 cm^{-1}. In the infrared spectrum of the Et_4N^+ salt of II no such vibration is observed, where instead

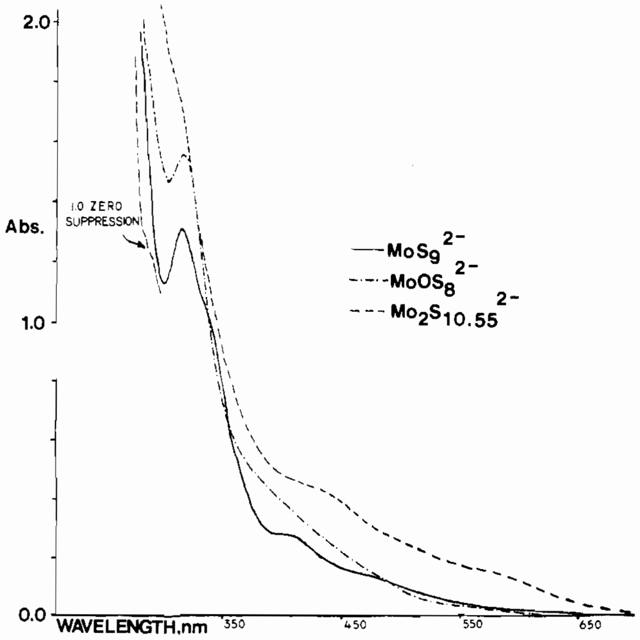

Figure 3. Electronic spectra of the $(MoS_9)^{2-}$, $(MoOS_8)^{2-}$, and $(Mo_2S_{10.55})^{2-}$ anions in DMF solution. Solution concentrations are 8.5 × 10^{-4}, 23 × 10^{-4}, and 10.3 × 10^{-4} M, respectively.

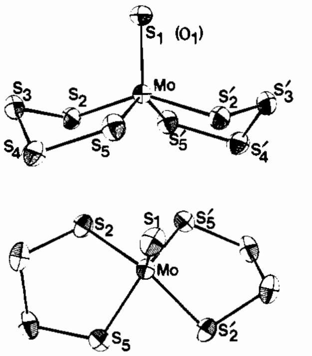

Figure 4. Two views of the $[\mathrm{(S_4)_2MoS}]^{2-}$ and $[\mathrm{(S_4)_2MoO}]^{2-}$ anions. Thermal ellipsoids are drawn by ORTEP (Johnson, C. K. *Oak Ridge Natl. Lab.* [*Rep.*] *ORNL* (*U.S.*) **1965**, ORNL-3794) and represent the 50% probability surfaces.

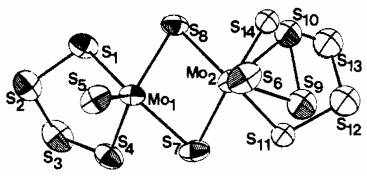

Figure 5. Anion site contents in the structure of $\mathrm{(Ph_4P)_2(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}}$.

the Mo=O vibration is observed as a strong absorption band at 930 cm^{-1}. The frequency of the Mo=O vibration in the $[\mathrm{MoO(SAr)_4}]^-$ complexes (Ar = phenyl, *p*-tolyl) also is observed[28] at 930–940 cm^{-1}. The infrared spectrum of the $\mathrm{Ph_4P^+}$ mixed salt of the $\mathrm{(Mo_2S_{10})^{2-}/(Mo_2S_{12})^{2-}}$ anions is obscured by $\mathrm{Ph_4P^+}$ vibrations in the region where the Mo=S vibration is expected to be found.

Electrochemical measurements of the complexes I, II, and III in either $\mathrm{CH_2Cl_2}$ or DMF solutions show only irreversible redox behavior over the -1.5 to $+1.3$ V range (vs. SCE).

(2) Structures. (a) $\mathrm{(Et_4N)_2[(S_4)_2MoS]}$ (I) and $\mathrm{(Et_4N)_2[(S_4)_2MoO]}$ (II). The two compounds are X-ray isomorphous and isostructural. The $[\mathrm{(S_4)_2MoS}]^{2-}$ and $[\mathrm{(S_4)_2MoO}]^{2-}$ anions (Figure 4) are located on the crystallographic twofold axes (at 0, $^1/_4$, *z*) of the *Ibca* space group. The $\mathrm{(Mo^{IV}{=}S)^{2+}}$ and $\mathrm{(Mo^{IV}{=}O)^{2+}}$ units are situated along the twofold axes and are coordinated by the two symmetry-related $\mathrm{S_4^{2-}}$ bidentate chelates.

In the distorted-square-pyramidal $\mathrm{Mo^{IV}S_5}$ and $\mathrm{Mo^{IV}OS_4}$ units the Mo atoms are displaced from the basal planes of the square pyramids toward S(1) and O by 0.725 (1) and 0.760 (1) Å, respectively. A similar type of displacement of the Mo atoms also is observed in the distorted-square-pyramidal $\mathrm{Mo^{IV}OS_4}$ units of the $\mathrm{MoO[(}i\mathrm{\text{-}C_3H_7)_2NCS_2]_2}$[29] and $\mathrm{MoO(S_2CS\text{-}}i\mathrm{\text{-}C_3H_7)_2}$[30] complexes at 0.83 and 0.86 Å, respectively.

The Mo=S(1) distance in I, at 2.128 (1) Å, is near the upper end of the range for doubly bonded Mo–S distances[31] (1.937–2.129 Å). The Mo=O distance in II at 1.685 (7) Å is quite similar to the mean value of the two independent $\mathrm{Mo^V{=}O}$ distances in the two $\mathrm{MoOS_4}$ units of the $[\mathrm{Mo_2O_2S_2(S_2)_2}]^{2-}$ complex, 1.683 (6) Å.[27] The $\mathrm{Mo^{IV}{=}O}$ distances in the $\mathrm{MoO[(}n\mathrm{\text{-}C_3H_7)_2NCS_2]_2}$[29] and $\mathrm{MoO(S_2CS\text{-}}i\mathrm{\text{-}C_3H_7)_2}$[30] complexes, 1.695 and 1.66 Å, respectively, also are similar and within 2σ from the Mo=O distance in II.

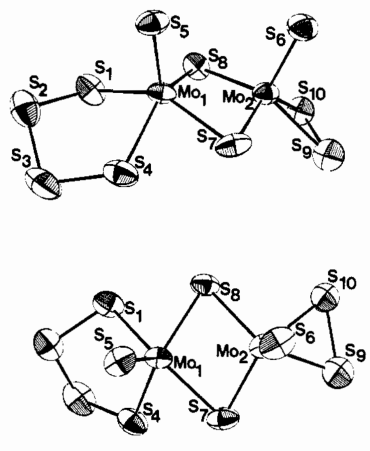

Figure 6. Two views of the $\mathrm{(Mo_2S_{10})^{2-}}$ major component in the structure of $\mathrm{(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]}$.

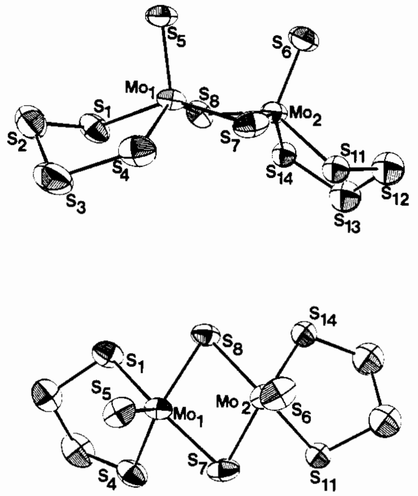

Figure 7. Two views of the $\mathrm{(Mo_2S_{12})^{2-}}$ minor component in the structure of $\mathrm{(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]}$.

(b) $\mathrm{(Ph_4P)_2(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}}$. Both of the $\mathrm{(Mo_2S_{10})^{2-}}$ and $\mathrm{(Mo_2S_{12})^{2-}}$ anions occupy the same site in the lattice of the $\mathrm{Ph_4P^+}$ mixed-anion salt with site occupancies of 0.72 and 0.28, respectively. The $\mathrm{(Mo_2S_{10})^{2-}}$ and $\mathrm{(Mo_2S_{12})^{2-}}$ anions share a common $\mathrm{(S_4)Mo(1)S_2Mo(2)}$ unit and differ only in the type of the bidentate terminal ligand ($\mathrm{S_2^{2-}}$ vs. $\mathrm{S_4^{2-}}$) on Mo(2). The $\mathrm{(Mo_2S_4)^{2+}}$ central core in $\mathrm{(Mo_2S_{10})^{2-}}$ and $\mathrm{(Mo_2S_{12})^{2-}}$ anions (Figures 6 and 7) contains two $\mathrm{(Mo^V{=}S)^{3+}}$ units bridged by two sulfide ($\mathrm{S^{2-}}$) ligands. The square-pyramidal $\mathrm{MoS_5}$ units in the two anions are linked by edge sharing in the syn configuration. In these units the Mo atoms are situated above the basal plane, and toward the axial sulfur atoms, at distances that vary from 0.68 to 0.73 Å.

The overall configuration of the $\mathrm{Mo_2S_4(S,S)_2}$ framework in the $\mathrm{(Mo_2S_{10})^{2-}}$ and $\mathrm{(Mo_2S_{12})^{2-}}$ anions is similar to that found in other complexes with the same basic structure such as *syn*-$[\mathrm{Mo_2S_4(S_2C_2H_4)_2}]^{2-}$ [32] and $[\mathrm{Mo_2S_4(S_2CNEt_2)_2}]$.[31] A comparison of these last two complexes and $\mathrm{(Mo_2S_{10})^{2-}}$ has been presented previously and shows considerable similarities in the Mo coordination spheres and the $\mathrm{(Mo_2S_4)^{2+}}$ bridge units.

A comparison between the structural parameters in $\mathrm{(Mo_2S_{10})^{2-}}$, as determined in this study, and the parameters reported previously[12] is shown in Table VI. A general agreement is apparent. In the previous structure determination, a disorder of the two central S atoms of the $\mathrm{S_4^{2-}}$ ligand was encountered. In the structure reported herein no such disorder is observed and as a result a somewhat better precision

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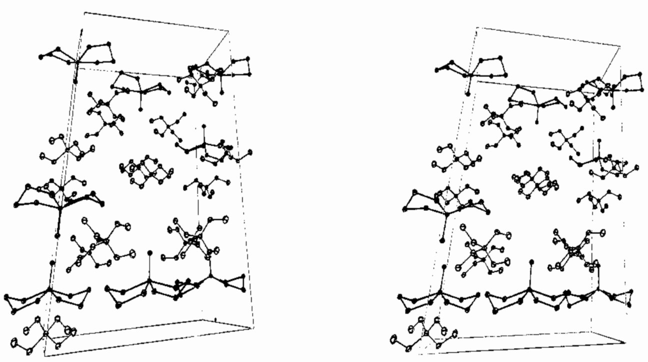

Figure 8. Unit cell contents of $(Et_4N)_2[(S_4)_2MoS(O)]$.

is available for the molecular parameters of the coordinated S_4^{2-} ligand. By contrast, the parameters associated with the S_2^{2-} ligand are less precise in the present structure. The lower precision can be traced to the fractional occupancy of the S_2^{2-} ligand and its close proximity to the sulfur atoms of the S_4^{2-} ligand of the $(Mo_2S_{12})^{2-}$ minor component (Figure 5).

The slight asymmetry in the bridging region, originally detected and reported[12] by Clegg et al., also is apparent in the present structure. The mean values of the Mo(1)–S_b and Mo(2)–S_b bonds, in the present structure, at 2.34 (3) and 2.29 (3) Å, respectively, compare very well with the corresponding values of 2.34 (1) and 2.30 (1) Å reported previously. The rather large standard deviations from these mean values make it difficult either to ascribe a particular significance to or to attempt to interpret the results in terms of electronic effects.

An examination of the individual MoS_5 pyramids in the $Mo_2S_4(S,S)_2$ cores of the $Mo_2S_{10}^{2-}$ and $Mo_2S_{12}^{2-}$ anions shows certain rather short interligand S–S contacts. The S–S distances between adjacent bridging and S_4^{2-} sulfur atoms in $(Mo_2S_{10})^{2-}$ are 2.863 (3) and 2.962 (3) Å with a mean value of 2.91 (5) Å. These short contacts can be attributed to the large bite of the S_4^{2-} chelating ligand of 3.372 (3) Å. As pointed out previously,[12] the magnitude of these interligand S–S contacts, in the $Mo_2S_4(S,S)_2$ complexes, increases as the bite of the terminal ligand decreases. The possibility of interligand S–S bonding interactions at ~2.9 Å cannot be ruled out in the structure of $(Mo_2S_{10})^{2-}$; however, they don't appear to be the cause of the short S–S interligand contacts.

The S–S distances in the S_5 square pyramids of the MoS_5 units can be separated into two major groups: (a) the axial distances between the S(5) and S(6) atoms and the basal S atoms and (b) the distances between adjacent S atoms in the basal plane. The mean values for the first group of S–S distances in $(Mo_2S_{10})^{2-}$ are 3.64 (6) and 3.64 (9) Å, respectively, for the $Mo(1)S_5$ and $Mo(2)S_5$ pyramids. The corresponding values in $(Mo_2S_{12})^{2-}$ are 3.64 (6) and 3.61 (6) Å. For the second group of S–S distances (basal plane distances) the mean values in the $Mo(1)S_5$ and $Mo(2)S_5$ pyramids in $(Mo_2S_{10})^{2-}$ are 3.2 (3) and 3.1 (6) Å. The corresponding distances in $(Mo_2S_{12})^{2-}$ are 3.2 (3) and 3.1 (4) Å. These values are quite similar to the values found in the structures of the *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$[32] and $[Mo_2S_4(S_2CNEt_2)_2]$[31] complexes. Thus for the former complex the mean values for the axial and basal distances are 3.61 and 3.17 Å, respectively, while for the latter these values are 3.61 and 3.18 Å. The similarities in the axial edge distances (~3.6 Å) in the MoS_5 pyramids very likely arise from an optimization of the S–S contacts between the axial and basal sulfur atoms to a value near the van der Waals distance for two sulfur atoms (~3.7 Å).[33] The optimum positioning of the sulfur atoms and restrictions imposed by the Mo^V–S axial and basal bond lengths are a major cause for the displacement of the Mo atoms from the basal planes of the MoS_5 pyramids.

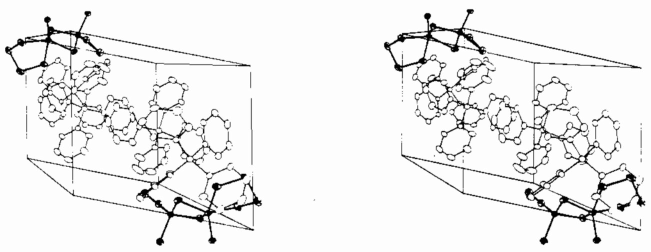

Figure 9. Unit cell contents of $(Ph_4P)_2[(Mo_2S_{10})]$. The $(Mo_2S_{12})^{2-}$ minor component at the anion site has been omitted for clarity.

The packing in the $(Ph_4P)_2(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}$ lattice is dominated by the Ph_4P^+ cations (Figure 9) and the major component anion, $(Mo_2S_{10})^{2-}$. Unusually close intermolecular contacts are observed (Table VII) primarily between the sulfur atoms of the minor component anion $(Mo_2S_{12})^{2-}$ and phenyl hydrogen atoms of the cations. The anisotropic thermal motions of the carbon atoms on the second phenyl ring of P(1) (Figure 9) suggest that the very close contacts between H(25) and S(12) and H(25) and S(13) are probably avoided by a small twist of the phenyl ring away from the S(11)S(12)S(13)S(14) ligand when the $(Mo_2S_{12})^{2-}$ anion occupies the site.

(c) The S_2^{2-} and S_4^{2-} Ligands. A number of Mo–S complexes have been structurally characterized and shown to contain the $Mo(S_2)$ unit. A survey of these complexes and a discussion of the bonding therein have been presented.[34] A common feature in these complexes is the side-on binding of the disulfide ligand, which appears to occupy two coordination sites on the Mo atom. The S–S bond length in various $Mo(S_2)$ complexes is found over a narrow range, from 2.03 Å in $[Mo(O)(S_2)_2(COSCO_2)]^{2-}$[36] to 2.074 (5) Å in the structure of $(Mo_2S_{10})^{2-}$ reported herein. A comparison of these values to the S–S distance in S_2^0 (1.887 Å in the gas phase)[37] and S_2^{2-} (2.13 Å in solid Na_2S_2)[41] supports the persulfido formulation (S_2^{2-}) for the S_2 ligand in the $Mo(S_2)$ complexes.

The $\overline{\text{Mo–S}}$ and the persulfide S–S distance in the $(Mo_2S_{10})^{2-}$ anion at 2.432 (7) and 2.074 (5) Å, respectively, are within 3σ from the corresponding distances in the $[Mo_2O_2S_2(S_2)_2]^{2-}$ complex (2.394 (11), 2.066 (4) Å)[35] and within the range (2.01–2.09 Å) reported for various other metal–persulfido complexes.[34]

The symmetry of binding of the $(S_2)^{2-}$ ligands to the Mo atoms seems to vary slightly for different $Mo(S_2)$ complexes. In $(Me_4N)_2[Mo_2O_2S_2(S_2)_2]$[27a] the Mo–$S_2$ bond lengths of 2.424 (5), 2.432 (5), 2.384 (6), and 2.390 (5) Å show an asymmetry in binding. This asymmetry is not as pronounced in the structure of the Et_4N^+ salt of the same anion[27b] (Mo–S_2 bond lengths: 2.409 (1), 2.394 (1), 2.390 (1), 2.381 (1) Å). A slight asymmetry in S_2^{2-} binding also is apparent in the structure of the $[Mo_2(S_2)_6]^{2-}$ anion[10] (2.463 (4)–2.507 (4), 2.382 (4)–2.454 (4) Å). In $(Ph_4As)_2(Mo_2S_{10})$[12] no asymmetry in binding of the $(S_2)^{2-}$ ligand is present while in $(Ph_4P)_2$-

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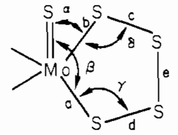
Table VII. Nonbonded Contacts (Å) Shorter Than 2.8 Å in $(Ph_4P)_2(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}$

H(24)–S(13)	2.711	H(63)–S(13)	2.770
H(25)–S(12)	2.141	H(83)–S(14)	2.770
H(25)–S(13)	2.397	H(54)–S(5)	2.779
H(56)–S(8)	2.698		

Table VIII. Selected Structural Parameters in the $Mo(5)S_4$ Units



	$[(S_4)_2MoS]^{2-}$	$[(S_4)_2MoO]^{2-}$	$(Mo_2S_{10})^{2-}$
a, Å	2.387 (1)	2.395 (2)	2.427 (2)
b, Å	2.331 (1)	2.363 (2)	2.399 (2)
c, Å	2.166 (1)	2.159 (3)	2.093 (4)
d, Å	2.107 (1)	2.120 (3)	2.053 (3)
e, Å	2.012 (1)	2.008 (3)	2.018 (4)
α, deg	110.83 (3)	110.6 (2)	111.3 (1)
β, deg	105.88 (3)	106.8 (2)	104.9 (1)
γ, deg	103.59 (3)	103.57 (7)	103.14 (9)
δ, deg	112.28 (3)	111.69 (7)	111.95 (10)

(Mo_2S_{10}) some asymmetry is apparent (Table VI).

An examination of the S–Mo–S angles in $[Mo_2(S_2)_6]^{2-}$, $(Mo_2S_{10})^{2-}$, and $[Mo_2O_2S_2(S_2)_2]^{2-}$ shows that the coordination geometries around the Mo atoms in these molecules could be described as being tetrahedral, with the midpoints of the S_2^{2-} ligands and sulfur atoms occupying the vertices of the tetrahedra. Such a description is consistent with a bonding scheme where the in-plane π_h molecular orbital of the coordinated S_2^{2-} anion is involved in strong σ bonding with the Mo atom. The slight asymmetries in the $Mo–S_2$ bonding can be explained if the point of maximum overlap with the Mo atom is located near the midpoint of the S_2^{2-} ligand. Packing forces within a given lattice could tilt the S_2^{2-} ligand without affecting seriously the position of the midpoint and the $Mo–S_2$ bonding.

The tetrasulfide ligands in $[(S_4)_2MoS]^{2-}$, $[(S_4)_2MoO]^{2-}$, and $(Mo_2S_{10})^{2-}$ show an interesting alternation in the lengths of the S–S bonds (Table VIII). Thus the two terminal S–S bonds (bonds c and d, Table VIII) are significantly longer than the $\overline{\text{S–S}}$ bond in orthorhombic sulfur[39] (2.037 (5) Å). The central S–S bonds (e, Table VIII) are significantly shorter than any of the above values. This alternation in the S–S bond lengths is not observed for the S_4^{2-} dianion in the structure[40] of $BaS_4 \cdot H_2O$ ($\overline{\text{S–S}}$ = 2.069 (2) Å); however, it is observed for the S_4^{2-} ligands in the structures of the $(C_5H_5)_2MoS_4$[41] and $(C_5H_5)_2WS_4$[42] complexes.

The alternation in the S–S bonds of coordinated S_4^{2-} has been rationalized[41] in terms of significant $Mo(d_\pi)–S(d_\pi)$ interactions. The data presented in Table VIII seem to support the presence of such interactions in the three Mo thioanions reported herein. In each of the three complexes the S_4^{2-} ligand is asymmetrically bound with two unequal Mo–S bond lengths. The S atoms of the shorter Mo–S bonds (b, Table VIII) always are found in the longer S–S bond of the S_4^{2-} ligand (c, Table VIII). The asymmetry in Mo–S binding is demonstrated further in the systematic variations of the $S–Mo–S_t$ angles (α and β, Table VIII). Thus, the angle that contains the S atom closer to the Mo atom (α) always is larger than the angle that contains the S further from the Mo atom (β).

Asymmetry in the binding of the S_4^{2-} ligand is not found in the structures of the $(C_5H_5)_2MoS_4$ and $(C_5H_5)_2WS_4$ complexes, which show Mo–S and W–S bonds of 2.455, 2.451 and 2.413, 2.413 Å, respectively. In these complexes the conformation of the tetrasulfido group is such that the central sulfur atoms lie at approximately equal distances from and on opposite sites of the plane that contains the Mo and two coordinated S atoms. For $(\eta^5-C_5H_5)_2MoS_4$ these distances are 0.53 and 0.65 Å. A different conformation is found with the S_4^{2-} chelates in $[(S_4)_2MoS]^{2-}$, $[(S_4)_2MoO]^{2-}$, and $[Mo_2S_{10}]^{2-}$. The central sulfur atoms in the S_4^{2-} ligands of these complexes lie above the plane that contains the Mo and two coordinated S atoms and toward the apex of the MoS_5 pyramids. In $[(S_4)_2MoS]^{2-}$ (Figure 4), S(3) and S(4) lie 0.22 and 1.20 Å above the S_2MoS_5 plane. The corresponding distances for the $[(S_4)_2MoO]^{2-}$ complex are 0.19 and 1.18 Å. In the $(Mo_2S_{10})^{2-}$ complex (Figure 6) the distances of S(2) and S(3) from the S(1)Mo(1)S(4) plane are 0.37 and 1.32 Å. In the $(Mo_2S_{12})^{2-}$ minor component (Figure 7) the distances of S(12) and S(13) from the S(11)Mo(2)S(14) plane are 0.45 and 1.39 Å, respectively.

The two different conformations observed for the $(S_4)M$ rings in the $(Cp)_2M(S_4)$ complexes and the Mo–S complexes reported herein are analogous to the "half-chair" and "puckered" (envelope) conformations possible with the cyclopentane ring.

In the $(Cp)_2M(S_4)$ complexes, where the metal atom is tetrahedrally coordinated by two Cp^- ligands and two S atoms, the "half-chair" conformation is found for the $M(S_4)$ ring. In these complexes the orientation of the lone pairs on the Mo-bound sulfur atoms, relative to the Cp^- rings, is such that interligand interactions are not likely to be significant.

In the $[(S_4)_2MoS(O)]^{2-}$, $(Mo_2S_{10})^{2-}$, and $(Mo_2S_{12})^{2-}$ complexes the "puckered" conformation for the $M(S_4)$ rings and the obligatory orientation of the lone pairs on the Mo-bound sulfur atoms result in a structure where interligand S–S interactions within the MoS_5 pyramidal units are minimized.

An examination of a molecular model shows that in the MoS_5 pyramidal units the "half-chair" conformation brings the lone pairs of the Mo-bound sulfur atoms in a position where one might expect closer interligand lone-pair contacts.

The positions of the lone pairs on the sulfur donor atoms for the hypothetical "half-chair" and the observed "envelope" conformations of the $(S_4)Mo$ ring in I were calculated with the assumption of tetrahedral sulfur atoms and lone-pair lengths of 1 Å. The mean values of the four S(2) lone pairs–S(5′) lone pairs interligand distances were 3.22 and 3.55 Å for the "half-chair" and "envelope" conformations, respectively, in a model where the unequal Mo–S bond lengths were maintained at their crystallographically determined values. In a model where all of the Mo–S bonds were made equal to the mean value (2.359 Å) of the experimentally determined values, the lone-pair contacts were calculated at 3.49 Å for both conformations. It appears therefore that both the asymmetry in binding and the conformation of the S_4^{2-} ligands in I, II, $(Mo_2S_{10})^{2-}$, and $(Mo_2S_{12})^{2-}$ reflect the structural adjustments necessary for a configuration with minimum electron-pair repulsions. The puckered conformation of the S_4^{2-} ligand also is observed in the structure of $(Ph_4As)_2(Mo_2S_{10})$,[12] where no significant difference in the Mo–S bond lengths was observed. The conformational disorder (two possible "puckered" rings in the same site) may well have caused the superposition of "long" and "short" Mo–S bonds which in the structure appear "averaged out" and nearly equal.

As noted previously the close interligand contact in Mo–S complexes containing the S_4^{2-} ligands can best be considered as a steric consequence of the large bite of the S_4^{2-} ligand rather than as a result of interligand bonding interactions.

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Registry No. I, 76581-48-1; II, 76581-46-9; III, 82336-38-7; IV, 82311-91-9; $(Et_4N)_2MoS_4$, 14348-09-5; BzSSSBz, 6493-73-8; S, 7704-34-9; $(NH_4)_2MoS_4$, 15060-55-6; $(NH_4)_2S_3$, 12259-92-6; $(Ph_4P)_2MoS_4$, 14348-10-8.

Supplementary Material Available: Listings of structure factors for $(Et_4N)_2[(S_4)_2MoS]$, $(Et_4N)_2[(S_4)_2MoO]$, and $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]$ and a table of selected, weighted least-squares planes (53 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University College, Belfield, Dublin 4, Ireland, and the School of Chemistry, Macquarie University, North Ryde, New South Wales 2113, Australia

Reaction of $[Fe_3(CO)_{12}]$ with Dicyclohexylcarbodiimide. Formation and Structure of $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$

JOHN DOHERTY, A. R. MANNING,*[1a] and F. S. STEPHENS[1b]

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The reaction of the carbodiimide $C_6H_{11}NCNC_6H_{11}$ (C_6H_{11} = cyclohexyl) with $[Fe_2(CO)_9]$ in boiling hexane gives the same products as it does with $[Fe(CO)_5]$, i.e., $[Fe(CO)_4(CNC_6H_{11})]$ (I) and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II), but with $[Fe_3(CO)_{12}]$ in boiling heptane it also gives the previously unknown derivative $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$ (III). The molecular structure of III has been determined by a single-crystal X-ray diffraction study. This shows that the $Fe_2(CO)_6$ fragment has the familiar "saw horse" structure with each of the two N atoms of the coordinated carbodiimide molecule bridging its two iron atoms and the carbodiimide carbon atom acting as an axial carbene ligand to a distorted trigonal-bipyramidal $Fe(CO)_4$ moiety. The structure was solved by the heavy-atom method and refined by least squares to R = 0.074 for 1559 nonzero unique photographic reflections. Crystals of the compound are monoclinic, space group $P2_1/n$, with a = 10.876 (4) Å, b = 16.609 (7) Å, c = 14.982 (5) Å, and β = 90.7 (1)° for Z = 4. The IR spectrum of III is consistent with the presence of two isomers in solution arising from restricted rotation of the $Fe(CO)_4$ moiety about the Fe–C(carbene) bond. The X-ray structure determination shows that this behavior is probably due to steric interactions between the $Fe(CO)_4$ carbonyl ligands and the cyclohexyl groups. Although *i*-PrNCN-*i*-Pr reacts similarly with $[Fe_3(CO)_{12}]$ to give products analogous to I, II, and III, with the last again exhibiting rotational isomerism, *p*-MeC_6H_4NCN-*p*-MeC_6H_4 forms counterparts of I and II but not III.

Introduction

The thermal reaction of $[Fe(CO)_5]$ with an organocarbodiimide, RNCNR, has been shown to give two products, $[Fe(CO)_4(CNR)]$ and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(RN)_2CNR\}]$.[2,3] Three different mechanisms have been proposed for this interesting reaction.[2-4] They involve the following reactive intermediates: (a) a carbene complex, $[Fe_2(CO)_6\{\mu,\mu'\text{-}(RN)_2C\}]$,[2] (b) a metal–nitrene complex,[3] or (c) an intermediate containing a cyclic $Fe(C_2N_4R_4)$moiety[4] similar to those proposed, and sometimes observed, for the metal-promoted rearrangement reactions of other heterocumulenes such as RNCS, CS_2, or CO_2 (e.g., the references in ref 4).

In a continuation of previous work on the reaction of iron carbonyls with organocumulenes,[5] we have studied the reactions of dicyclohexylcarbodiimide, $C_6H_{11}NCNC_6H_{11}$ (C_6H_{11} = cyclohexyl), with the polynuclear carbonyls $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$. We had hoped to be able to isolate mononuclear $[Fe(CO)_2(L)_2(\eta^2\text{-}RNCNR)]$ derivatives when the reaction was carried out in the presence of other ligands (cf. the analogous reaction with CS_2[5]). Unfortunately we have not, as yet, been successful, but we have shown that, whereas the reaction of $[Fe_2(CO)_9]$ with $C_6H_{11}NCNC_6H_{11}$ gave the same products as does $[Fe(CO)_5]$, $[Fe_3(CO)_{12}]$ also gave $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$. The structure of this complex has been determined by an X-ray diffraction study and is closely related to that of the reactive intermediate proposed by Farona et al.[2] in (a) above.

Experimental Section

$[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ were prepared as described elsewhere.[6] Other chemicals were purchased. The organocarbodiimides were used as received.

All reactions were carried out under an atmosphere of nitrogen with solvents that had been dried over calcium hydride and distilled prior to use.

A mixture of $[Fe_2(CO)_9]$ (1.5 g), $C_6H_{11}NCNC_6H_{11}$ (0.85 g), and PPh_3 (0.72 g) in tetrahydrofuran (50 mL) was stirred. When all of the $[Fe_2(CO)_9]$ had dissolved, the IR spectrum of the reaction mixture was measured. It showed that only $[Fe(CO)_4(PPh_3)]$, $[Fe(CO)_3(PPh_3)_2]$, and unchanged $C_6H_{11}NCNC_6H_{11}$ were present. These were separated (chromatography with alumina and C_6H_6) and identified unambiguously.

A mixture of $[Fe_2(CO)_9]$ (2 g) and $C_6H_{11}NCNC_6H_{11}$ (1.13 g) in hexane (50 mL) was heated to reflux. When all of the $[Fe_2(CO)_9]$ had dissolved, the solvent was removed from the mixture at reduced pressure. The residue was dissolved in benzene and chromatographed on alumina. Two compounds could be isolated, $[Fe(CO)_4(CNC_6H_{11})]$ (I) and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II). They were identified by IR spectroscopy and by analyses. Reaction yields were low and variable; that of II averaged 5%.

A solution of $[Fe_3(CO)_{12}]$ (5 g) and $C_6H_{11}NCNC_6H_{11}$ (2 g) in heptane (60 mL) was heated to reflux until the green color disappeared. The brown reaction mixture was filtered and the solvent removed at reduced pressure. The residue was redissolved in hexane and chromatographed on alumina. In order of elution, the products were $[Fe(CO)_4(CNC_6H_{11})]$ (I), $[Fe(CO)_3(CNC_6H_{11})_2]$ (a trace amount), yellow $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II), and a red material.

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[1] (a) University College. (b) Macquarie University.

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