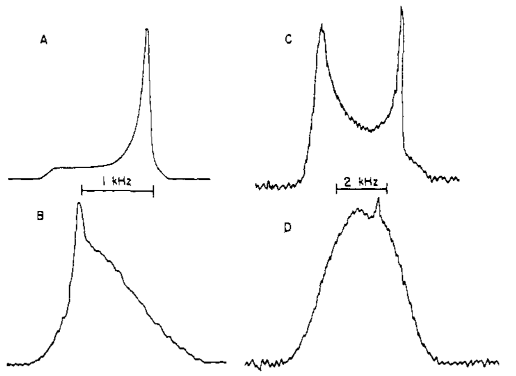

Figure 1. ^{31}P NMR Spectra of I taken at 22 °C, (A) $B_0 = 2.35$ T, proton decoupler on; (B) $B_0 = 2.35$ T, proton decoupler off; (C) $B_0 = 4.70$ T, proton decoupler on; (D) $B_0 = 4.70$ T, proton decoupler off. Removal of the orientation-dependent proton broadening[9] reveals an approximately axially symmetric line shape for (A) and line shape suggesting alignment for (C). The line shape arises from chemical shift anisotropy, and thus the two spectra (A and C) differ by a factor of 2 in frequency scale, consistent with the different spectrometer frequencies. Frequency increases from left to right.

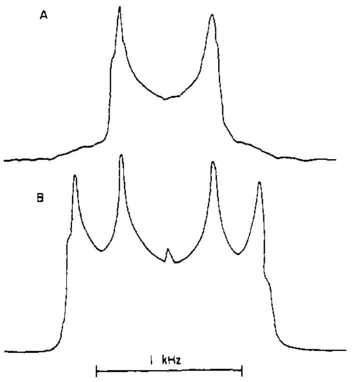

Figure 2. ^2H NMR Spectra of II taken at 22 °C. (A) $B_0 = 2.35$ T; (B) $B_0 = 4.70$ T. No proton decoupling.

to be drawn from Figure 1C is that the directors are not randomly distributed and that there is partial alignment within the sample. This apparent field-dependent alignment is consistent with the anticipated result[8] that the free energy change on alignment is proportional to B_0^2. The type line shape shown in Figure 1C has not been observed previously for ^{31}P NMR to our knowledge.

We have also observed strong evidence for spontaneous alignment in ^2H NMR spectra. Figure 2 shows spectra for a sample of composition identical with I but with specific solvent labeling as $(HOCD_2)_2$, which we designate II. These two spectra taken at different B_0 clearly show random orientation and alignment effects for the sample at $B_0 = 2.35$ and 4.70 T, respectively. The observed ^2H spectrum for $B_0 = 4.70$ T appears to be a two-dimensional spin 1 powder pattern,[7] which has been observed previously only for type I phases[7] that have been specially prepared. The preparation involves equilibration of the stationary sample in the magnetic field followed by prolonged spinning of the sample for 2 h and, finally, observation of the spectrum immediately after stopping the spinning.[7] The sample is not at equilibrium at the time of spectrum observation. In contrast, we have observed all our spectra using stationary samples that had been allowed to equilibrate in the magnetic field. Furthermore, only a few minutes were required for the equilibration.

Spontaneous alignment has been observed by us using both egg yolk and soy lecithin amphiphiles, as well as with various short-chain diol solvents. A variety of samples, ranging in age from a few months to 3 years, were used for the studies. These samples were carefully prepared under inert atmosphere. After equilibration, the lamellar structure was confirmed by polarizing microscopy, which showed typical mylein figures. Within a 2-min time frame, samples within the lecithin/ethylene glycol composition range 60:40–90:10 (w/w) have been observed to align for $B_0 = 4.70$ T. No alignment has been observed for $B_0 = 2.25$ T. The degree of alignment appears to be slightly temperature dependent.

The present apparent two-dimensional powder pattern behavior is very unusual. One additional feature is that sample probe orientations were different for the two fields (iron core magnet vs. superconducting solenoid). There may be a complex interaction involving the sample, the magnetic field, and the glass container walls. A suggestion that this is the case has been made by Forrest and Reeves,[7] but the present results put the problem in a new context. We are currently conducting further studies on this system.

Registry No. Ethylene glycol, 107-21-1.

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Synthesis, Structure, and Reactivity of $[(C_2H_5)_4N]_2[Mo_3(\mu^3\text{-}S)(\mu^2\text{-}S)_3(SCH_2CH_2S)_3]$: A Cluster with Sulfur "Vacancies" and Resonance Raman Spectral Similarity to Fe_3S_4 Proteins

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Multinuclear transition-metal–sulfur complexes (clusters) are of well-established significance in biochemistry,[2a] while extended-lattice transition-metal–sulfur solids (e.g., MoS_2) are ubiquitous in industrial hydrotreating catalysis.[2b] In both these contexts, it is important to develop rational, high-yield, general synthetic techniques for the construction and elaboration of transition-metal–sulfur clusters. Recently,[3a] a synthetic approach to complexes containing the $Mo_2S_4^{2+}$ core has been reported, via reduction of the persulfide ligands in $Mo_2(S_2)_6^{2-}$.[3b] We have now been able to extend this approach[4] to prepare complexes containing the $Mo_3S_4^{4+}$ core by starting with the cluster anion $Mo_3S(S_2)_6^{2-}$. Here, we report the synthesis and structure of $Mo_3S_4(SCH_2CH_2S)_3^{2-}$ (**1**). This anion bears an unexpected relation to the layered structure of molybdenum disulfide, while its resonance Raman spectrum resembles that of putative Fe_3S_4 clusters in proteins.

Solid $(NH_4)_2[Mo_3S(S_2)_6]$ and dry $[N(C_2H_5)_4]Br$ were added to excess (>9 equiv) $Na_2(SCH_2CH_2S)$ in acetonitrile, and the mixture was stirred at room temperature for 5 h. The deep violet, air-sensitive solution was filtered to remove insoluble oxidized mercaptide polymer, treated with 3:1 diethyl ether/isopropyl alcohol to incipient crystallization and cooled to −10 °C overnight.

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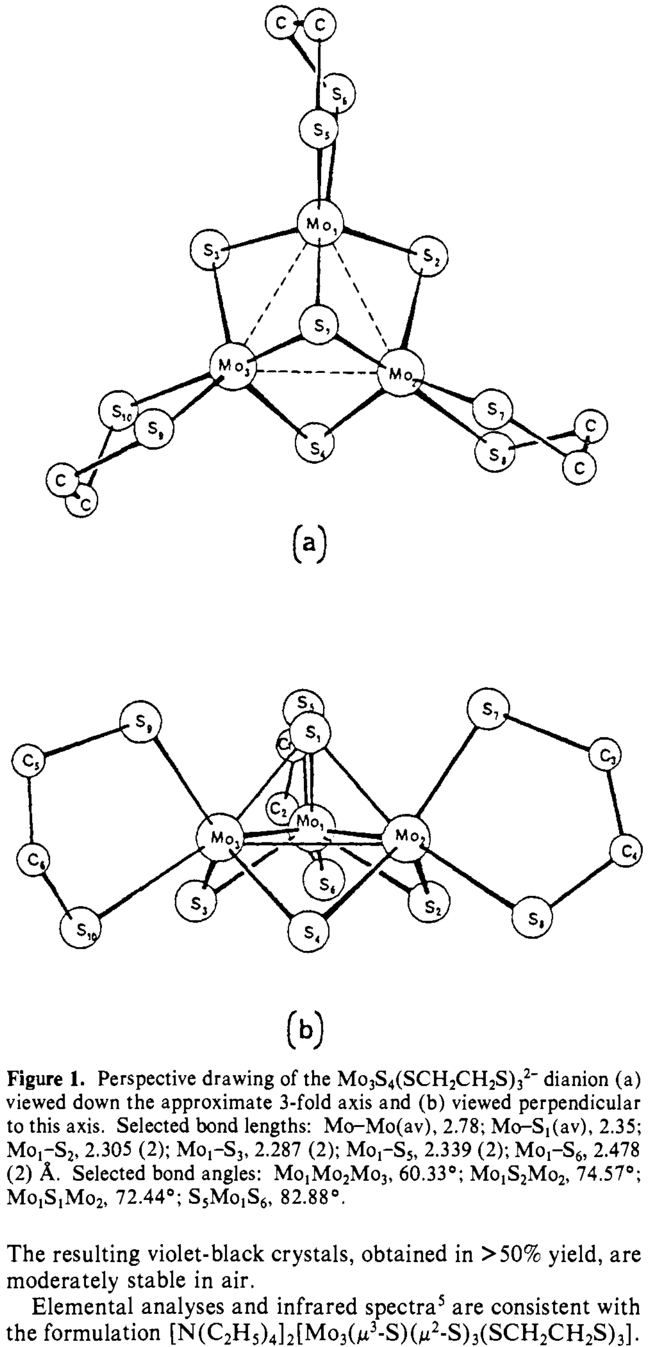
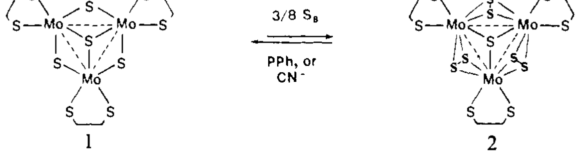


Figure 1. Perspective drawing of the $Mo_3S_4(SCH_2CH_2S)_3{}^{2-}$ dianion (a) viewed down the approximate 3-fold axis and (b) viewed perpendicular to this axis. Selected bond lengths: Mo–Mo(av), 2.78; $Mo–S_1$(av), 2.35; $Mo_1–S_2$, 2.305 (2); $Mo_1–S_3$, 2.287 (2); $Mo_1–S_5$, 2.339 (2); $Mo_1–S_6$, 2.478 (2) Å. Selected bond angles: $Mo_1Mo_2Mo_3$, 60.33°; $Mo_1S_2Mo_2$, 74.57°; $Mo_1S_1Mo_2$, 72.44°; $S_5Mo_1S_6$, 82.88°.

The resulting violet-black crystals, obtained in >50% yield, are moderately stable in air.

Elemental analyses and infrared spectra[5] are consistent with the formulation $[N(C_2H_5)_4]_2[Mo_3(\mu^3\text{-}S)(\mu^2\text{-}S)_3(SCH_2CH_2S)_3]$. A single-crystal X-ray diffraction study was carried out[6,7] on a black rectangular parallelopiped grown by vapor diffusion of isopropyl alcohol into an acetonitrile solution of **1**. The crystal contains ordered $Mo_3S_4(SCH_2CH_2S)_3{}^{2-}$ dianions as illustrated in Figure 1, along with ordered and partially disordered tetraethylammonium cations. The $Mo_3S_4{}^{2+}$ core is nearly identical with that previously found in $Mo_3S_4(CN)_9{}^{5-}$ [9] and $Mo_3S_4(\eta^5\text{-}C_5H_5)_3{}^+$,[10] with an equilateral triangle of Mo(IV) atoms bound by Mo–Mo bonds of 2.77 to 2.79 Å, a single capping μ^3-sulfido, and three bridging μ^2-sulfido ligands. The coordination sphere of each Mo ion is completed by a chelating 1,2-ethanedithiolate ligand. The arrangement of these ligands is such that six of the sulfur atoms (bridging sulfides S_2, S_3, and S_4 and thiolate sulfurs S_6, S_8, and S_{10}) form a pseudo-close-packed plane[11] with S–S distances ranging from 3.19 to 3.74 Å. The Mo atoms lie in a parallel plane (within 0.7°) in approximate trigonal sites above the bottom sulfur "layer". The remaining four sulfur atoms form another parallel plane[12] above the Mo plane. The S/Mo/S "layered" arrangement illustrated in Figure 1b is reminiscent of the "layered" structure of MoS_2. In MoS_2 the Mo ions lie in trigonal-prismatic six-coordinate sites, while the Mo ions in **1** are five-coordinated (or seven-coordinated if metal–metal bonding is included).

When acetonitrile solutions of **1** are treated with 3 equiv of S (as S_8) or dibenzyltrisulfide, a red-orange crystalline product precipitates, which we formulate[13] as $[N(C_2H_5)_4]_2[Mo_3S_7(SCH_2CH_2S)_3]$ (**2**). Treatment of a solution of **2** with $^-SCH_2CH_2S^-$, PPh_3, or CN^- in CH_3CN quantitatively regenerates **1**, while treatment of either **1** or **2** with excess sulfur produces $Mo_3S_{13}{}^{2-}$. The $Mo_3S_7{}^{2+}$ core has recently been structurally characterized in $[(R_2PS_2)_3Mo_3S_7][R_2PS_2]$[14], and in $Mo_3S_7Cl_4$.[16] The interconversion of **1** and **2** therefore involves simply the interconversion between bridging sulfide and disulfide,[15] as shown in eq 1.



1 2 (1)

The concept that sulfide "vacancies" are important sites of catalytic activity has been often discussed with respect to transition-metal sulfide-based heterogeneous catalysts.[2b] The interconversion between **1** and **2** appears to be a molecular mimic for the creation and refilling of such vacancies. The process occurs in this molecular system via sulfide/polysulfide/sulfur redox *without net formal change in metal oxidation state* or *in overall charge*. The reaction occurs with preservation of the Mo_3 core and maintenance of tetravalent Mo. Similar reactivity must now be considered as possible in the solid catalysts as well. The potential relation of the transition-metal sulfide clusters of this paper and sulfide solids is clearly analogous to the relationships between organometallic clusters and metals[17] or metal oxide/hydroxide/alkoxide clusters and metal oxides.[18]

Finally, we note that this complex may be of aid in sorting out a topical bioinorganic chemistry problem. Iron–sulfur containing three-iron atom centers[19] have been detected in a number of metalloproteins and recent results are consistent with an Fe_3S_4

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(5) Anal. Calcd for $C_{22}H_{52}N_2Mo_3S_{10}$: C, 27.72; H, 5.50; N, 2.94; Mo, 30.20. Found: C, 27.45; H, 5.12; N, 3.23; Mo, 30.60. Infrared spectrum (KBr) anion peaks at 490, 475, 455, 355 cm^{-1}.

(6) The complete structure determination was carried out by Dr. C. S. Day of Crystalytics Co., Lincoln, NE 68501.

(7) Crystal data: Space group $P2_1/n$ (an alternate setting of $P2_1/c\text{-}C_{2h}^5$ (No. 14)),[8] with a = 13.694 (4) Å, b = 13.654 (4) Å, c = 20.013 (4) Å, V = 3664 (2) $Å^3$, Z = 4. The structure was solved using "direct methods" and Fourier difference techniques. R_F = 0.041 and R_{wF} = 0.047 for 4607 independent diffracted intensities ($I > 2.0\sigma(I)$) with $3° < 2\theta < 50.7°$ (Mo Kα radiation). Anisotropic thermal parameters were utilized for all non-hydrogen atoms.

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(11) Deviations from mean plance defined by S_2, S_3, and S_4 are 0.012 (2) Å for S_6, 0.135 (2) Å for S_8, and 0.045 (2) Å for S_{10}.

(12) S_1 deviates from the plane formed by S_5, S_7, and S_9 by 0.179 (2) Å toward the Mo plane. The S_5, S_7, S_9 plane is essentially coplanar with the Mo plane.

(13) Anal. Calcd for $C_{22}H_{52}N_2Mo_3S_{13}$: C, 34.21; H, 4.39; N, 2.35; Mo, 24.12. Found: C, 34.42; H, 4.38; N, 2.73, Mo, 24.00. Infrared spectrum (KBr) anion related peaks at 555, 535 (shoulder), 460, 337 cm^{-1}.

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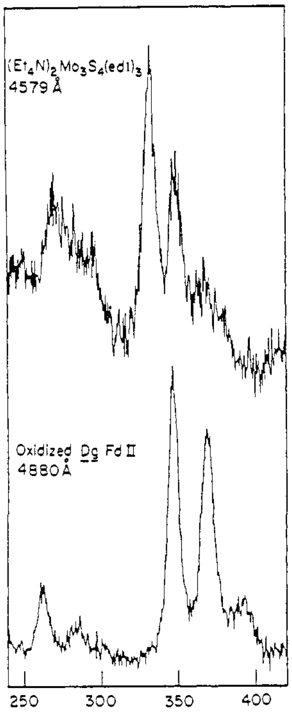

Figure 2. Resonance Raman spectra[22] of $[(C_2H_5)_4N]_2[Mo_3S_4(SCH_2CH_2S)_3]$ (solid state, 10-cm^{-1} spectral slit width) and Dg Fd II (frozen solution, 6-cm^{-1} spectral slit width) obtained via backscattering by using 4579- and 4880-Å Ar$^+$ Laser excitations, respectively (at liquid N_2 temperature). Observed frequencies: (a) $[N(C_2H_5)_4]_2[Mo_3S_4(SCH_2CH_2S)_3]$, 382, 356, 334, 287, and 270 cm^{-1}; (b) Dg Fd II, 392, 368, 347, 285, and 267 cm^{-1}.[21]

formulation for the Fe–S core.[20,21] These Fe_3S_4 centers have a distinct resonance Raman signature.[21] Although the metal atoms in the present structure are not iron atoms, the Mo_3S_4 core in the present communication is stoichiometrically and possibly structurally analogous to Fe_3S_4 cores in these proteins. The resonance Raman spectrum of $Mo_3S_4(SCH_2CH_2S)_3{}^{2-}$ and that of the 3Fe ferredoxin (Fd) from *Desulfovibrio gigas* (Dg), Fd II,[21] are shown in Figure 2. The resemblance between the spectra is striking with the shift being in the direction and of the magnitude expected for substitution of Fe by Mo. Detailed vibrational analyses of this and other inorganic model compounds are under way to provide information relevant to the analysis of the data in the protein systems.

Acknowledgment. We thank Prof. T. G. Spiro for his encouragement of the resonance Raman studies, carried out in his laboratories with support from NIH Grant GH13498-NIH. We also thank Dr. C. S. Day of Crystalytics Co. for carrying out the single-crystal diffraction study.

Registry No. 1, 88765-89-3; **2**, 88765-91-7; $(NH_4)_2[Mo_3S(S_2)_6]$, 67031-31-6; $Mo_3S_{13}{}^{2-}$, 88765-92-8; S, 7704-34-9; $^-SCH_2CH_2S^-$, 52724-23-9; PPh_3, 603-35-0; CN^-, 57-12-5; dibenzyl trisulfide, 6493-73-8.

Supplementary Material Available: Crystallography details, including tables of atomic coordinates, thermal parameters bond lengths and bond angles, structure factors, and perspective drawings of TEA$^+$ cations (38 pages). Ordering information is given on any current masthead page.

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Configuration Chirality of Metal–Metal Multiple Bonds: Preparation and Circular Dichroism Spectrum of Tetrachlorobis-[(*S*,*S*)-2,3-(diphenylphosphino)butane]dimolybdenum (Mo_2Cl_4(*S*,*S*-dppb)$_2$)

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Chiral compounds containing a metal–metal multiple bond present an exciting new area of study. Complexes have been reported in which an $Mo\overset{4}{-}Mo$ unit is bridged by (*S*)-leucinate,[1] (*S*)-isoleucinate,[2] or (*R*)-mandelate[3] ions. In all cases the bridging groups are planar, the ligating atoms are practically eclipsed,[3] and the chirality is due effectively to the asymmetric carbon atoms, which are at some distance from the Mo_2O_8 core. Preliminary circular dichroism (CD) spectra have been recorded for the mandelate complex, and as expected the optical activity is rather weak as the dimolybdenum chromophore is not intrinsically chiral. Qualitative CD spectra have been published[4] for solutions of $Mo_2(CH_3COO)_4$ in which one or more of the acetate groups have been replaced by chiral carboxylate ions. The structures of the species present are not known but again the chirality can arise only from the vicinal effect of an asymmetric carbon atom at some distance from the chromophore.

We reasoned that the most informative complexes to investigate would be ones that are configurationally chiral[5] due to two sets of MX_4 or MX_2Y_2 units being twisted with respect to each other about the metal–metal bond. For such complexes it is possible to derive a direct relationship between the absolute configuration and the CD of the $\delta \rightarrow \delta^*$ transition. We accordingly present the first report of the preparation and CD spectrum of a configurationally chiral metal–metal bonded complex, Mo_2Cl_4(*S*,*S*-dppb)$_2$, where *S*,*S*-dppb represents the $Ph_2PCH(CH_3)CH(CH_3)PPh_2$ ligand, (*S*,*S*)-2,3-(diphenylphosphino)butane.

Mo_2Cl_4(*S*,*S*-dppb)$_2$ has been prepared in two different ways: (1) by refluxing $K_4Mo_2Cl_8$ with 2 equiv of *S*,*S*-dppb in methanol for 2 h, (2) by reaction of $Mo_2(O_2CCF_3)_4$ with Me_3SiCl and *S*,*S*-dppb in THF. The green solid is soluble in a variety of organic solvents including THF, MeOH, EtOH, CH_3CN, CH_2Cl_2, and benzene, and solutions appear to be stable for periods of weeks. The compound gave a satisfactory elementary analysis. Its identity was conclusively confirmed and the molecular structure revealed by two independent x-ray crystal structure determinations.[6]

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(5) This sort of system is clearly of the type that is said to contain an *inherently dissymmetric* chromophore, whereas those mentioned above are likely to be examples of a *symmetric chromophore in a chiral molecular environment*. Somewhat different theroretical approaches have been developed for these two classes. See, for example, Mason (Mason, S. F. "Molecular Optical Activity and the Chiral Discriminations", Cambridge University Press: New York, 1982), for details and literature references.

(6) Compound **1** (Mo_2Cl_4(*S*,*S*-dppb)$_2$·THF) forms crystals in space group $P2_12_12_1$ with a = 14.57 (1) Å, b = 36.69 (1) Å, c = 11.84 (1) Å. Compound **2** (Mo_2Cl_4(*S*,*S*-dppb)$_2$·4CH_3CN) also crystallizes in space group $P2_12_12_1$ with a = 13.535 Å, b = 21.044 Å, c = 23.214 Å, and Z = 4 in each case. The dimensions of the Mo_2Cl_4(*S*,*S*-dppb)$_2$ molecule in the two cases were virtually identical: D(Mo–Mo) = 2.150 (3) Å and 2.143 (2) Å for **1** and **2**, respectively, while the P–Mo–Mo–P torsion angles were −24.3°, −25.2° in **1** and −23.2°, −22.6° in **2**. The structure of **2** was obtained in collaboration with K. W. Muir and Lj. Manojlovic-Muir.