of the *c* axis, which is the needle axis. Segments of two parallel chains are illustrated in Figure 2.

Supplementary Material Available: An experimental section plus tables of selected interatomic distances, selected bond angles, coordinates, coordinates for H atoms, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

New $[Fe_6S_6Cl_6(Mo(CO)_3)_2]^{n-}$ Clusters (n = 3, 4). Derivatives of either $[Fe_6S_6Cl_6]^{3-}$ or $[Fe_4S_4Cl_4]^{2-}$ with Possible Relevance to the Fe/Mo/S Center in Nitrogenase

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On the basis of analytical[1] and spectroscopic[2-4] data numerous structures have been proposed[5] for the unique Fe/Mo/S centers in nitrogenase[6] and the nitrogenase cofactor[7] (FeMoco). The design and synthesis of models for these centers must be directed by, and confined within, the constraints imposed by the available data. Our studies at present are directed toward the synthesis of analogue Fe/Mo/S clusters with Fe/Mo/S ratios of 6-7/1/6-8 and structures compatible with the Mössbauer,[2] EXAFS,[3] and ENDOR[4] characteristics of the heterometallic centers in nitrogenase and the nitrogenase cofactor.

Recently we reported on the synthesis and spectroscopic properties of the $[Fe_6S_6(OAr)_6(Mo(CO)_3)_2]^{3-}$ complex anion.[8] This cluster was obtained by the addition of two $Mo(CO)_3$ fragments to the $[Fe_6S_6(OAr)_6]^{3-}$ "prismane".[9b] We were unable to obtain single crystals for this compound for a structure determination. However, on the basis of elemental analysis and EPR, NMR, Mössbauer, and electronic spectroscopic data we proposed a heterometallic Pentlandite-type of structure for this compound with a $[Fe_6Mo_2S_6]^{3+}$ core.

In this paper, we report on the synthesis and spectroscopic properties of the structurally analogous $[Fe_6S_6Cl_6(Mo(CO)_3)_2]^{n-}$ anions (n = 3, 4) and the crystal structures of the Et_4N^+ and Ph_4P^+ salts of the $[Fe_6S_6Cl_6(Mo(CO)_3)_2]^{4-}$ tetraanion.

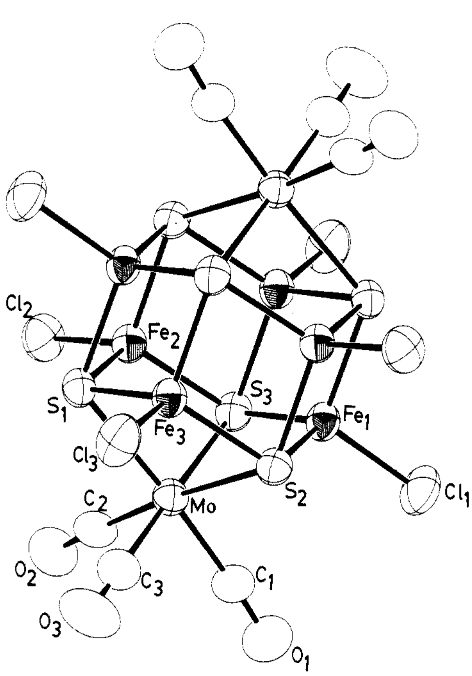

Figure 1. Structure and labeling of the anions in I and II. Thermal ellipsoids as drawn by ORTEP (Johnson, C. K., ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces.

Table I. Selected Distances[a] (Å) and Angles (deg) in the $(Ph_4P)^+$ (A) and $(Et_4N)^+$ (B) Salts of the $[Fe_6S_6Cl_6[Mo(CO)_3]_2]^{4-}$ anions and the $[Fe_6S_6Cl_6]^{n-}$ Prismanes, n = 3 (C), n = 2 (D)

	A	B	C[b]	D[c]
		Distances		
Fe–Fe[d]	3.766 (3, 11)	3.785 (3, 10)	3.790 (3, 8)	3.791 (6, 5)
Fe–Fe[e]	2.747 (3, 14)	2.761 (3, 10)	2.765 (3, 3)	2.757 (6, 5)
Fe–S[d]	2.333 (3, 3)	2.333 (3, 3)	2.284 (3, 3)	2.268 (6, 8)
Fe–S[e]	2.284 (6, 6)	2.286 (6, 5)	2.272 (6, 2)	2.254 (12, 8)
Mo–Fe	2.99 (3, 2)	3.005 (3, 11)		
Mo–S	2.608 (3, 6)	2.619 (3, 3)		
Mo–C	1.943 (3, 13)	1.958 (3, 11)		
		Angles		
Fe–S–Fe[d]	111.1 (3, 6)	111.8 (3, 5)	113.2 (3, 3)	114.5 (6, 6)
Fe–S–Fe[e]	73.0 (6, 3)	73.4 (6, 2)	74.7 (6, 1)	75.1 (12, 4)
S–Fe–S[d]	113.2 (3, 5)	113.0 (3, 4)	113.7 (3, 3)	112.0 (6, 9)
Fe–Mo–F[e]	78.1 (3, 3)	78.07 (3, 2)		
Fe–S–Mo	75.0 (6, 4)	75.2 (6, 3)		
S–Mo–S	93.9 (3, 6)	93.4 (3, 2)		

[a] See Figure 1 for the labeling scheme. The mean values of chemically equivalent bonds are given. In parentheses the first entry represents the number of independent distances or angles averaged out, the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation: $\sigma = [\sum_{i=1}^{N}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [b] From ref 9b. [c] From ref 9c. [d] Distances or angles within the Fe_3S_3 structural units. [e] Distances or angles within the Fe_2S_2 rhombic units.

The reaction of $(CH_3CN)_3Mo(CO)_3$ with $(Et_4N)_3Fe_6S_6Cl_6$ in CH_3CN, at ca. 60 °C for 20 min, in a 2:1 molar ratio occurs readily. Upon filtering, dilution with ether, and standing, the reaction solution affords a black crystalline product. Upon recrystallization, crystals of $(Et_4N)_4[Fe_6S_6Cl_6(Mo(CO)_3)_2]$ (I) are isolated in 40% yield. The IR spectrum of I shows two CO stretching vibrations at 1896 and 1834 cm^{-1} and suggests the presence of $Mo(CO)_3$ units with C_{3v} microsymmetry. The electronic spectrum of I in CH_3CN solution shows only a shoulder at 470 nm, and no EPR signals were detected from a frozen CH_3CN solution at 9 K.

The crude product, as initially isolated in the synthesis of I, shows a weak EPR signal (g_x = 2.064) and two additional CO vibrations of minor intensity at 1921 and 1855 cm^{-1}. The paramagnetic, minor component that accounts for these spectral characteristics very likely is the $[Fe_6Mo_2Cl_6(Mo(CO)_3)_2]^{3-}$ trianion. The latter would be analogous to the paramagnetic, $S = {}^1/_2$, $[Fe_6S_6(p\text{-}CH_3C_6H_4O)_6(Mo(CO)_3)_2]^{3-}$ trianion for which the

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ν_{CO} are found[8] at 1915 and 1860 cm^{-1}.

The Ph_4P^+ salt of I also is obtained by a *remarkable*, $Mo(CO)_3$-induced rearrangement reaction. This reaction takes place upon heating (to ca. 60 °C for 20 min) a CH_3CN solution of $(CH_3CN)_3Mo(CO)_3$ and $(Ph_4P)_2(Fe_4S_4Cl_4)$[10] in a 4:3 molar ratio. After unexceptional workup, crystals of $(Ph_4P)_4[Fe_6S_6Cl_6(Mo(CO)_3)_2]$ (II), can be obtained in ~40% yield (based on $(Ph_4P)_2(Fe_3S_4Cl_4)$. The spectroscopic properties of II are identical with those of I.

Oxidation of II with 1 equiv of $(Cp)_2Fe^+$ in CH_2Cl_2 solution affords, after addition of ether, the crystalline $(Ph_4P)_3[Fe_6S_6Cl_6(Mo(CO)_3)_2]$ complex III. The IR spectrum of III contains two sharp CO vibrations (ν_{CO}, 1929, 1883 cm^{-1}) and in frozen CH_3CN solution (9 K) shows an EPR spectrum (g_x = 2.064). The EPR spectrum of III is very similar to the one observed for the $S = {}^1/_2$ $(Fe_6S_6Cl_6)^{3-}$ anion[9b] and suggests that III also is characterized by a $S = {}^1/_2$ ground state. The cyclic voltammetry traces of II and III in CH_3CN solution are identical and show reversible waves at −0.05 and −0.55 V (vs. SCE) that correspond to the 3−/4− and 4−/5− couples. The 3−/4− reduction for III occurs at nearly 350 mV more positive potential than the corresponding reduction for the $[Fe_6S_6(p\text{-}CH_3C_6H_4O)_6(Mo(CO)_3)_2]^{3-}$ trianion (−0.39 V). A similar trend was observed previously in the electrochemistry of the $[Fe_6S_6(L)_6]^{n-}$ prismanes.[9]

Single crystals of I and II were obtained by the slow diffusion of ether to CH_3CN solutions of these compounds. The crystal structures[11] of the centrosymmetric tetraanions in both I and II show virtually identical $[Fe_6Mo_2S_6]^{2+}$ cores (Figure 1). Selected structural parameters for these anions are compared (Table I) to corresponding parameters reported previously[9] for the $[Fe_6S_6]^{3+}$ and $[Fe_6S_6]^{4+}$ cores in the $[Fe_6S_6Cl_6]^{n-}$ clusters. Coordination of the $Mo(CO)_3$ units to the $[Fe_6S_6]$ central cage results in an elongation of the latter along the idealized $\bar{3}$ axis. Slight, but consistent, changes are apparent in the lengthening of the Fe–S bonds, the shortening of the Fe–Fe distances, and the concomitant closing of the Fe–S–Fe angles (Table I).

The $Mo(CO)_3$ fragment resembles the analogous unit in the 1,4,7-trithiacyclononane $Mo(CO)_3$ complex.[12] The Mo–C bond (1.95 (15) Å) and the IR spectrum (ν_{CO} absorptions at 1915 and 1783 cm^{-1}) in the latter are similar to those in I and II.

As stated previously,[8] the $[Fe_6Mo_2S_6]$ core cannot be considered as a satisfactory structural analogue for the core in the Fe/Mo/S center in nitrogenase. However, derivative clusters that contain the $[Fe_6MoS_6]$ and $[Fe_7MoS_6]$ units will satisfy a number of the necessary structural and stoichiometric requirements. The suggestion that a pentlandite-type $[Fe_7MoS_6]$ unit may be an appropriate model for the Fe/Mo/S center in nitrogenase has been advanced previously.[13] Presently we attempt to synthesize such units and are exploring the organometallic and coordination chemistry of the $[Fe_6S_6L_6]^{n-}$ "ligands".

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Supplementary Material Available: Tables of structure factors and positional and thermal parameters (44 pages). Ordering information is given on any current masthead page.

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$Os_4(CO)_{14}(PMe_3)$: An Irregular, Planar Cluster Showing Remarkable Nonrigidity

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One of the intriguing problems of current inorganic chemistry is the description of the bonding in transition-metal carbonyl clusters.[1,2] The polyhedral skeletal electron pair (PSEP) theory has had considerable success in rationalizing the many geometries found for these compounds.[1] However, Evans and Mingos have pointed out that PSEP theory is often unsuccessful in accounting for the structures of clusters with $M(CO)_4$ units and have extended the theory to encompass clusters with nonconical fragments.[3] Here we describe the synthesis and structure of $Os_4(CO)_{14}(PMe_3)$ that contains one $Os(CO)_3(PMe_3)$ and two $Os(CO)_4$ units. The asymmetry present in the structure is unexpected from PSEP theory or the extension of Evans and Mingos. We believe it is best rationalized in terms of three-center–two-electron metal–metal bonds. The compound also exhibits remarkable fluxional character in solution that may be attributable to its unusual bonding.

To a solution of $(Me_3P)(OC)_4OsOs_3(CO)_{11}$[4] in CH_2Cl_2 a solution of Me_3NO in MeOH was added dropwise until the absorption in the infrared spectrum at 2085 cm^{-1} had just disappeared. The resultant solution was filtered and evaporated to dryness. The product, $Os_4(CO)_{14}(PMe_3)$ (**1**), was recrystallized from hot hexane as air-stable, dark red crystals.[5] The structure of the compound[6] (Figure 1) consists of an almost planar Os_4 skeleton (the dihedral angle between the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) is 177.10 (3)°). The periphery of the metal framework consists of two adjacent short Os–Os bonds (Os(1)–Os(2) = 2.779 (2) Å; Os(1)–Os(4) = 2.784 (2) Å) and two long Os–Os bonds (Os(2)–Os(3) = 3.013 (2) Å; Os(3)–Os(4) = 2.982 (2) Å). The short diagonal Os–Os vector is more typical of a normal Os–Os single bond (Os(1)–Os(3) = 2.935 (2) Å). (The average Os–Os bond length in $Os_3(CO)_{12}$ is 2.877 (3) Å.[7]) The structure found for **1** is unique for 62-electron tetranuclear clusters. Most clusters of this type adopt the butterfly geometry,[8] the structure most compatible with PSEP theory. We have also observed the butterfly configuration in a cluster closely related to **1**, namely, $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$.[9] On the other hand

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(6) X-ray diffraction data for $Os_4(CO)_{14}(PMe_3)$: M_r = 1230; monoclinic; space group $P2_1/a$; a = 13.525 (5) Å, b = 12.969 (6) Å, c = 14.825 (5) Å; β = 99.14 (3)°; V = 2567.54 Å^3; Z = 4, D_c = 3.185 g cm^{-3}; (an experimentally based absorption correction was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator ($\lambda(K\alpha_1)$ = 0.70930 Å); scan range = $3° \le 2\theta \le 45°$; reflections = 2424 with $I_0 \ge 2.5\sigma I_0$; R_f = 0.0385, R_W = 0.0479.

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