ligands, we find considerable variation in the frequencies of both high-frequency Raman lines (at ~1540 and ~1630 cm^{-1}, Table I). The *separation* of these lines seems to be a more accurate indication of coordination number. The resonance Raman band frequencies for the nickel corphinoid models shown in Table I demonstrate that this separation is 93 cm^{-1} in the spectrum of the four-coordinate model.[11] However, in this particular case, the separation depends somewhat on the excitation energy, for reasons that are not well understood at this time. Much smaller separations are observed for five- and six-coordinate models (80 and ~71 cm^{-1}, respectively). The 94-cm^{-1} separation of the high frequency lines in the spectrum of the F_{430} diepimer (Figure 1c) indicates that the Raman data are in agreement with nickel X-ray absorption and EXAFS results which show that the F_{430} diepimer is four-coordinate, square planar (with nickel–nitrogen distances of 1.9 Å).[6,13-15]

The simplest interpretation of the F_{430} spectrum (Figure 1b) invokes an equilibrium mixture of two species. The major species has lines at 1556 and 1629 cm^{-1}, whereas the minor species has a peak at 1534 cm^{-1} and a second unresolved feature between ~1622 and ~1632 cm^{-1} (the latter peak is evident from the asymmetry of the 1629-cm^{-1} feature). We note that the separations of these lines are 73 cm^{-1} for the major species and at least 88 cm^{-1} for the minor species. The correlation between peak separation and coordination number (vide supra) would appear to indicate that the major species is six-coordinate, whereas the minor form is four-coordinate.

Comparison of the spectra in Figure 1 (parts b and c) shows that the minor form of F_{430} is not due to contamination of the sample with diepimer: the major peak in the diepimer spectrum occurs at 1529 cm^{-1}, whereas the analogous feature occurs at 1534 cm^{-1} for the minor component in the F_{430} spectrum. One possible explanation for the spectral difference between the diepimer and the minor four-coordinate form of F_{430} is the altered configuration of the pyrrolidine ring C side chains in the diepimer relative to their "native" configuration in both F_{430} species; i.e., the equilibrium between the two species evident in Figure 1b involves changes in axial ligation but not isomerization of the macrocycle. X-ray absorption edge and EXAFS data indicate that in aqueous solution F_{430} is six-coordinate with an expanded 2.1 Å Ni-N core;[6,13,14] the X-ray results contain no evidence for the presence of a four-coordinate form. This apparent conflict may be explained by the difference in sample temperature for the X-ray and Raman experiments (10 and 298 K, respectively), with only the more stable six-coordinate form being present at the lower temperature. Consistent with this proposal is the absence of the 1534-cm^{-1} feature in preliminary low-temperature (77 K) Raman spectra of F_{430}. The nature of the axial ligands in the six-coordinate form of aqueous F_{430} is unknown at present. Further comparison to Raman spectra of model compounds and ligated derivatives of F_{430} should resolve this question. We are also pursuing an X-ray absorption study to determine the nature of the axial ligands.

These additional studies may also help to explain the anomalous nature of the methylreductase spectrum (Figure 1a). Since only F_{430} can be reconstituted into the apoenzyme to give active methylreductase,[16] one would expect the methylreductase spectrum to be more similar to that of F_{430}. Actually, the Raman spectrum of methylreductase is considerably different from that of either F_{430} or the diepimer. The frequencies of the two strong lines in the methylreductase spectrum (1575 and 1652 cm^{-1}) are much higher than the analogous features in the spectra of the isolated cofactor (Figure 1 (parts b and c)). The methylreductase peak separation (77 cm^{-1}) is between that found for the five-coordinate nickel corphinoid model complex (81 cm^{-1}) and the 71 ± 2 cm^{-1} separation observed for the six-coordinate models with a variety of axial ligands (Table I). However, more variability in the separation of the two high-frequency lines is noted for six-coordinate complexes of isolated F_{430}, and separations approaching that of the holoenzyme are observed with bis-pyridine ligation of the isolated cofactor.[17] Although no six-coordinate F_{430} complexes thus far examined reproduce the relatively high frequencies of these lines in methylreductase, it is possible that a six-coordinate cofactor with novel ligation is responsible for the anomalous holoenzyme spectrum. Since the X-ray absorption edge spectrum of methylreductase is apparently inconsistent with a 5-coordinate structure,[13,14] the latter possibility bears consideration.

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Synthesis of $[Mo_6S_8(PEt_3)_6]$ by Reductive Dimerization of a Trinuclear Molybdenum Chloro Sulfido Cluster Complex Coordinated with Triethylphosphine and Methanol: A Molecular Model for Superconducting Chevrel Phases

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The cluster core of the superconducting Chevrel phases is an octahedron of six molybdenum atoms with eight face-bridging chalcogens.[1] The preparation of the soluble molecular complexes with the cluster units found in the nonmolecular inorganic solids has been an attractive synthetic objective.[2] The relationships between the geometry of the cluster core and the cluster valence electron concentration[3] and the energy bands[4] are among the more important problems related to the Chevrel phases. The electronic states of the hypothetical molecular $Mo_6(\mu_3\text{-}S)_8$ compounds have been computed and compared with those of the solid-state Chevrel phases,[5] but the synthesis of a molecular cluster complex with this unit has not been achieved.[6,7]

We now report the first synthesis of a molecular analogue of the Chevrel phases by reductive dimerization of a trinuclear molybdenum sulfido cluster, which itself is a new class of cluster condensation.[8] The trinuclear cluster has been prepared by the

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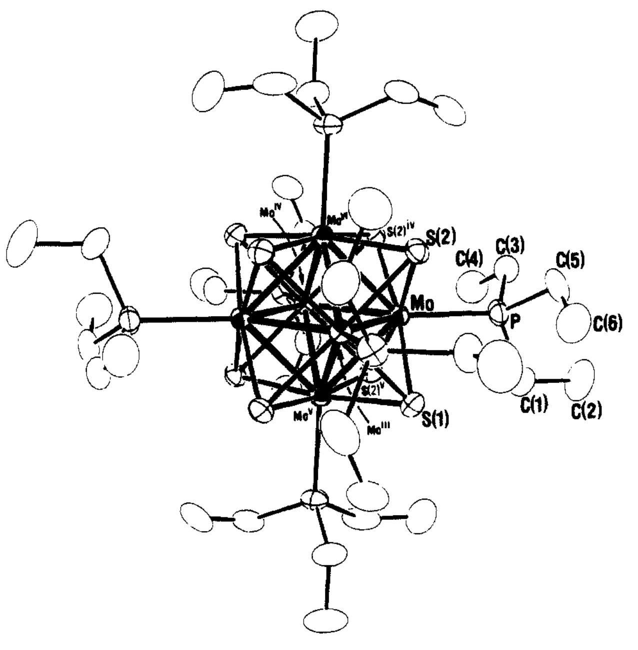

Figure 1. Structure with 50% probability ellipsoids and an atom-labeling scheme of $[Mo_6S_8(PEt_3)_6]$.

reaction of triethylphosphine on $Mo_3S_7Cl_4$.[9]

Thus the treatment of $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$ (1.00 g, 0.94 mmol) with magnesium metal (0.06 g, 2.4 mmol) in THF (10.0 mL) at room temperature under argon for 24 h formed $[Mo_6S_8(PEt_3)_6]$ in 30% yield as a dark purple crystalline compound.[10] The complex was recrystallized from tetrahydrofuran, and the structure was determined by X-ray crystallography.[11] An ORTEP drawing of the molecule is illustrated in Figure 1. The result shows that the cluster has a regular octahedral core of six molybdenum atoms with eight face-bridging sulfur atoms and six triethylphosphines coordinated to each molybdenum. The Mo–Mo distances (2.664 and 2.662 Å, prependicular to and along the C_3 axis, respectively) are almost identical and shorter than those of the solid-state Mo_6S_8 (2.698 and 2.862 Å).[12]

The complex has 20 cluster valence electrons, and the formal oxidation state of the molybdenum atoms can be described as $Mo_2^{II}Mo_4^{III}$. However, it may be better to regard them as having an average oxidation state of 16/6 because of the equivalence of the Mo–Mo bond distances and the sharp peaks in the ^1H and ^{31}P NMR spectra suggesting the absence of unpaired electrons. In the Chevrel phase compounds, the relationship between the cluster valence electrons and the Mo–Mo bond distances has been established,[13] and the 20 e compounds exhibit the largest elongation along the C_3 axis of the trigonal antiprism. Although our cluster is a 20 e complex, the Mo–Mo bond distances are close to those of the solid-state Chevrel compounds with 24 cluster electrons.[14] It seems unlikely that the complex is more reduced and possesses either a hydrogen, carbon, or magnesium cation, because careful elemental analyses and ^1H and ^{13}C NMR spectra as well as the X-ray structure determination have not revealed the presence of an extra cation. The fact that the present complex displays a regular octahedral structure with relatively short Mo–Mo distances may be explained by the electron flow from basic triethylphosphines, lack of the intercluster interaction, or by the packing disorder due to the symmetrical nature of the cluster molecule.

The cyclic voltammetry and coulometry on a dichloromethane solution indicated reversible one-electron reduction and oxidation waves at −1.03 and +0.24 V, respectively.[15] The electronic spectrum of a benzene solution showed the bands at 289 nm (ϵ 31 000), 491 nm (ϵ 8100), 991 nm (ϵ 1200), and 1200 nm (ϵ 870). The analyses of these measurements together with the calculation of the energy levels for the present compound and for the more reduced clusters $[M_xMo_6X_8(PR_3)_6]$ which we are now trying to prepare will shed light on the above problem.

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Supplementary Material Available: Detailed crystal data and listings of atomic coordinates, thermal parameters, and bond distances and angles (6 pages); listings of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead pages.

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$[(CH_3)_5C_5]_2Th(CH_3)_2$ Surface Chemistry and Catalysis. Direct NMR Spectroscopic Observation of Surface Alkylation and Ethylene Insertion/Polymerization on $MgCl_2$

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It is well-established that adsorption on inorganic surfaces can dramatically alter the reactivity of organometallic molecules;[1] however, the structural chemistry of the resulting adsorbates is frequently ill-defined. From CPMAS NMR studies of $Cp'_2Th(CH_3)_2$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$) on dehydroxylated γ-alumina (DA), we inferred the transfer of methyl groups to DA surface Lewis acid sites and the formation of less saturated "$Cp'_2Th(CH_3)^+$" species with cationic character.[2] Although model studies in solution support much of this chemical/spectroscopic hypothesis,[3-5] the small percentage ($\lesssim$4%) of $Cp'_2Th(CH_3)_2$/DA sites highly

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