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Preparation and Properties of the Tetrakis[tetrathiomolybdato(VI)-μ_3-sulfidoiron] Cluster, $[Fe_4Mo_4S_{20}]^{6-}$

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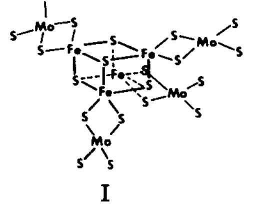
Recent spectroscopic and chemical studies [1–3] on the iron–molybdenum cofactor [4] (FeMo-co) isolated from the MoFe-protein of nitrogenase have demonstrated that it contains a novel iron–sulfur–molybdenum cluster. In particular, extended X-ray absorption fine structure (EXAFS) spectroscopy results have been interpreted as showing that the molybdenum has as nearest neighbors 4–6 sulfur atoms and either three [5] or two [6] iron atoms at ~2.7 Å, suggesting a cage [5] or extended lattice [6] structure, respectively. Inasmuch as only one such structural unit, containing an $MoFe_3S_4$ cluster, has been reported to data [5, 7], we are investigating the synthesis and chemical properties of other members of this class of compounds. A recent report [8] that acid hydrolysis of the MoFe-protein of nitrogenase produces thiomolybdate ($MoS_4^=$) makes the characterization of compounds containing Fe–S and $MoS_4^=$ units extremely pertinent. We wish to report the synthesis and some of the properties of the $[Fe_4Mo_4S_{20}]^{6-}$ cluster.

Reaction of 4 equivalents each of 2,4,6-trimethylpyridine hydrochloride and $(Me_4N)_2MoS_4$ with 1 equivalent of $(Me_4N)_2[Fe_4S_4(S\text{-t-Bu})_4]$ [9] in acetonitrile/N-methylformamide solution results in the formation of $(Me_4N)_6[Fe_4Mo_4S_{20}]$ (*I*), obtained as black microcrystals, mp. >300 °C. *Anal.* Calc. for $C_{24}H_{72}F_4Mo_4N_6S_{20}$: C, 17.02; H, 4.30; Fe, 13.19; Mo, 22.66; N, 4.96; S, 37.87. Found: C, 16.94; H, 4.46; Fe, 12.90; Mo, 22.32; N, 4.81; S, 37.65 (Spang Microanalytical Laboratories, Eagle Harbor, Michigan, U.S.A.). The reaction is most readily formulated as an exchange of $MoS_4^=$ for $t\text{-BuS}^-$ on the intact $Fe_4S_4^{2+}$ core. We propose the structure shown schematically (*I*), in which each Fe of an Fe_4S_4 cluster is coordinated by a bidentate thiomolybdate ligand, based on the following. Far-infrared spectra (Nujol mulls) show a splitting of the 472 cm^{-1} band of free $MoS_4^=$ into three bands (492, 471, 435 cm^{-1}). The optical spectrum (Fig. 1) shows a shift of the lowest energy band of free $MoS_4^=$ (467 nm) to longer wavelength (580 nm, $\epsilon = 1.40 \times 10^4$). Both of these effects are typical of compounds containing bidentate tetrathiometallate ions coordinated to first-row transition metals [10] and suggest strongly that FeS_2Mo units are present. Preliminary Mössbauer spectra at 4.2 K and in zero field give the following parameters (mm/sec): isomer shift (*vs.* metallic Fe), 0.44; quadrupole splitting, 1.08; linewidth, 0.45. The first two parameters are similar in magnitude to those observed for tetranuclear Fe–S clusters with simple thiolate ligands [11]. This is somewhat surprising, since the quadrupole splitting is normally quite sensitive to the local symmetry and should be affected by a change from four- to five-coordinate iron. The observed linewidths are a factor of two larger than normal. Examination of the sample in high applied fields (*ca.* 50 kG) shows the system to be much more complex than the simple clusters, with at least two distinct iron environments; further studies are necessary and will be reported elsewhere.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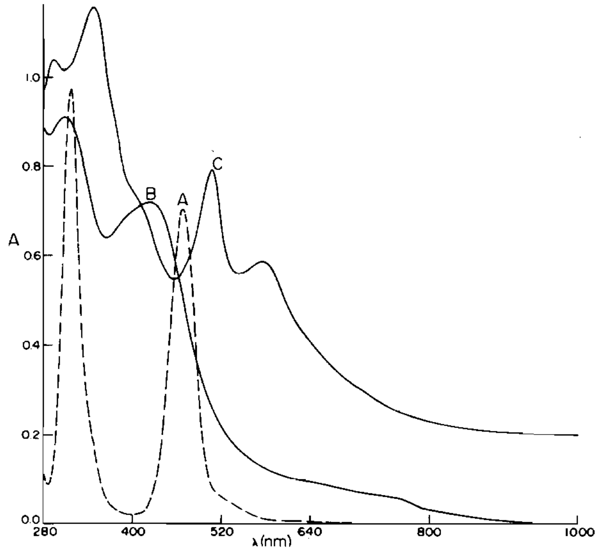

Fig. 1. Optical spectra of (A) $(Me_4N)_2MoS_4$, 1.1 m*M*; (B) $(Ph_4As)_2[Fe_4S_4(s\text{-t-Bu})_4]$, 4.1 m*M*; (C) $(Me_4N)_6[Fe_4Mo_4S_{20}]$, 2.7 m*M*. Optical pathlengths: 0.1 mm (B, C), 0.5 mm (A). Note that spectrum C is offset by +0.2 A.

The parent iron–sulfur tetramers are characterized by two kinds of reactivity [12]: electron transfer [13] and ligand exchange [14] reactions. Polarographic measurements on *I* in N,N-dimethylacetamide

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(0.05 *M* Et_4NClO_4 supporting electrolyte, dropping mercury electrode) show only an irreversible reduction at –0.97 V (*vs.* SCE), before an irreversible multi-electron reduction at ~–1.6 V. The irreversible nature of the first, presumably one electron, reduction may well be due to adsorption of the sulfur-rich cluster on the mercury electrode; the second is apparently due to reductive decomposition. Examination of the reactivity of *I* with thiols indicates that the FeS_2MoS_2 unit is kinetically rather inert. Thus, treatment of *I* with 8 equivalents of $PhSH/Et_3N$ in MeCN gives no apparent reaction; in contrast, simple alkylthiolates are rapidly and quantitatively displaced from the Fe_4S_4 center by thiophenol under these conditions [14]. At very high concentrations of thiophenol, optical spectra show that a slow reaction occurs to give a new species in which the FeS_2Mo unit is apparently retained, but in which attack of thiolate at Mo has occurred. The structure of this new cluster is being investigated.

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