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Synthesis and characterization.
Synthesis and Characterization of \([\text{Et}_4\text{N}]_3[\text{Fe}(\text{MoS}_4)_2]\). A New Fe-Mo-S Complex

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Studies using extended X-ray absorption fine structure (EXAFS) [1, 2] and Mössbauer [3, 4], spectroscopy have implicated the presence of an iron-molybdenum-sulfur moiety in the iron-molybdenum cofactor (FeMo-co) of the enzyme nitrogenase [3, 5, 6]. The results have prompted the synthesis of a number of inorganic complexes of this nature [7–11]. Herein, we report the synthesis and characterization of a new Fe-Mo-S compound, \([\text{Et}_4\text{N}]_3[\text{Fe}(\text{MoS}_4)_2]\), along with some of the physicochemical properties of the new species.

Reaction of two equivalents of \([\text{Et}_4\text{N}]_3\text{MoS}_4\) with one equivalent of the Fe(II) dithiocarbamate complex \(\text{Fe}[\text{S}_2\text{CN(CH}_2)_2\text{SH}]_2\) [12] in \(\text{CH}_2\text{Cl}_2\) results in the precipitation of a dark solid which, after washing with \(\text{H}_2\text{O}\) and recrystallization from \(\text{MeCN}\text{Et}_2\text{O}\), is obtained as purplish microcrystals. Elemental analytical data (Caled. for \(\text{C}_{24}\text{H}_{60}\text{N}_3\text{FeMo}_2\text{S}_2\): C, 32.2; H, 6.71; N, 4.70; Fe, 6.26; Mo, 21.5; S, 28.6%. Found: C, 32.0; H, 6.78; N, 4.59; Fe, 6.22; Mo, 20.8; S, 29.0%) indicates that the compound should be formulated as \([\text{Et}_4\text{N}]_3[\text{Fe}(\text{MoS}_4)_2]\) (1). The fact that the isolated anion is trinegative indicates that reduction of molybdenum has occurred, possibly via formation of thiuramdisulfide from the dithiocarbamate ligands displaced from iron. A previous attempt to prepare the dinegative analog of \([\text{Et}_4\text{N}]_2\text{Fe}((\text{MoS}_4)_2)\) [13] by reaction of \((\text{NH}_4)_2\text{MoS}_4\) with \(\text{Fe}_2\text{(SO}_4)_7\text{H}_2\text{O}\) apparently yielded an impure species [13]. Although we have thus far been unable to obtain crystals of 1 suitable for X-ray analysis, the structure shown schematically in Fig. 1 would seem to be a reasonable proposal for that of the new complex.

\[
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{Fe} \\
\text{S} \\
\text{S} \\
\end{array}
\]

Fig. 1. Schematic structural representation of \(1\).

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The physicochemical properties of 1 are consistent with the above formulation. The IR spectrum of the complex contains three bands [497(s), 486(s), 441(m) cm\(^{-1}\)] in the region characteristic of bidentate tetrahalomolybdate ions \([\text{MoS}_4^2\text{S}_2]^\text{2−}\) [14] and this pattern is very similar to that exhibited by a recently reported compound postulated to contain the \([\text{Fe}_2\text{S}_4\text{MoS}_4\text{S}_2]^\text{6−}\) group [11]. The electronic spectrum of 1 is shown in Fig. 2 with peak positions and molar absorptivities given in the figure legend. The presence of the sharp peaks and their shift to lower energy (from those of free \(\text{MoS}_4^2\)) are again characteristic of complexes containing bidentate \(\text{MoS}_4^2\) groups [14]. The cyclic voltammogram of
Fig. 4. EPR spectrum of a frozen solution of I (-5 x 10^{-4} M) in MeCN at 14 K.

I in MeCN (Fig. 3) shows a couple at very negative potential as well as an oxidation wave at -0.075 V whose irreversibility appears consistent with the reported [13] difficulty in obtaining pure [Fe-(MoS₄)₃]²⁺ salts.

A solution of I in MeCN is EPR-silent at ambient temperature but, at 14 K, exhibits the spectrum shown in Fig. 4. The spectrum is somewhat similar to that of FeMo-co which has g values at 4.6, 3.3, and 2.0 characteristic of an S = 3/2 ground state [3, 6]. However, the significance, if any, of this gross similarity is unclear. Thus, it should be noted that reduction of [Fe₆Mo₉S₉(SPh)₉]³⁻ (a very different type of complex which contains two Fe₃MoS₃ cubane-like clusters bridged by three thiolate groups) with sodium acenaphthylenide also yields a species whose EPR spectrum (g = 5.1, 4.3, 2.0) is similar to that of FeMo-co [15]. Our results do show that a fairly simple Fe–Mo–S complex could be responsible for an EPR signal of this type.

Further studies to detail the spectroscopic properties, the structure and the reactivity of I are currently in progress.

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