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Synthesis and Characterization of $[Et_4N]_3[Fe(MoS_4)_2]$. 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 enzyne 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, $[Et_4N]_3[Fe(MoS_4)_2]$, along with some of the physicochemical properties of the new species.

Reaction of two equivalents of $[Et_4N]_2MoS_4$ with one equivalent of the Fe(II) dithiocarbamate complex $Fe[S_2CN(CH_2)_5]_2$ [12] in CH_2Cl_2 results in the precipitation of a dark solid which, after washing with H_2O and recrystallization from $MeCN/Et_2O$, is obtained as purplish microcrystals. Elemental analytical data (Calcd. for $C_{24}H_{60}N_3FeMo_2S_8$: 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 $[Et_4N]_3[Fe(MOS_4)_2]$ (*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 $[Fe(MOS_4)_2]^{3-}$ by reaction of $(NH_4)_2MoS_4$ with $Fe(So_4)\cdot 7H_2O$ 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.

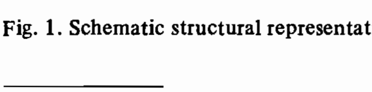


Fig. 1. Schematic structural representation of *1*.

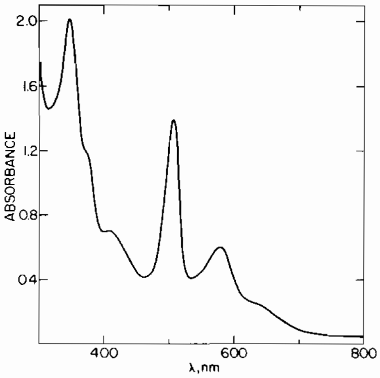


Fig. 2. Electronic spectrum of *1* in MeCN. Peak and shoulder positions in nm with molar absorptivities in parentheses are as follows: 630sh(3000), 577(7750), 507(18970), 409(9150), 372(16070), 347(26920).

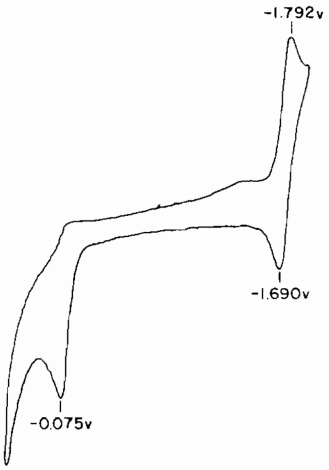
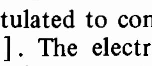


Fig. 3. Cyclic voltammogram of a $\sim 10^3$ *M* solution of *1* in MeCN containing 0.1 *M* $[Bu_4N]BF_4$ *vs.* SCE. The scan rate was 0.48 V/sec.

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 tetrathiomolybdate ions  [14] and this pattern is very similar to that exhibited by a recently reported compound postulated to contain the $[Fe_4S_4(MoS_4)_4]^{6-}$ 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 MoS_4^{2-}) are again characteristic of complexes containing bidentate MoS_4^{2-} groups [14]. The cyclic voltammogram of

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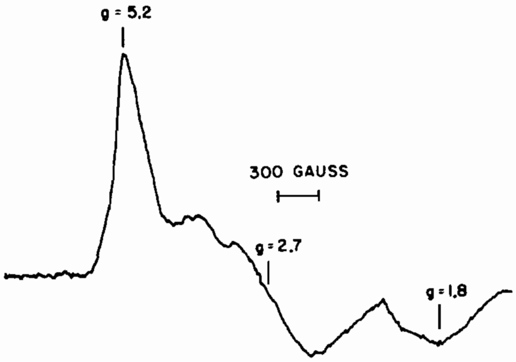

Fig. 4. EPR spectrum of a frozen solution of *1* (~5 × 10^{-4} *M*) in MeCN at 14 K.

1 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 $[Fe(MoS_4)_2]^{2-}$ salts.

A solution of *1* 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 $[Fe_6Mo_2S_8(SPh)_9]^{3-}$ (a very different type of complex which contains two Fe_3MoS_4 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 *1* are currently in progress.

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