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Preparation and Properties of the Bis(phenylmercapto)iron(III)-di-μ-sulfidoiron(II)-di-μ-sulfidodisulfidomolybdate(VI) Ion, $[(PhS)_2FeS_2FeS_2MoS_2]^{3-}$

R. H. TIECKELMANN and B. A. AVERILL*

Department of Chemistry, Michigan State University, East Lansing, Mich. 48824, U.S.A.

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In the last two years, extended X-ray absorption fine structure (EXAFS) results [1, 2] have confirmed that the iron–molybdenum cofactor (FeMo-co) of nitrogenase [3] contains a novel iron–sulfur–molybdenum cluster with unusual spectroscopic properties [4, 5]. The EXAFS results have been interpreted as indicating that the molybdenum has 4–6 sulfur atoms and either three [6] or two [7] iron atoms as nearest neighbors. Only two types of related structural units are known from synthetic work to date. One consists of two $MoFe_3S_4$ cubane cages joined at the molybdenum atoms via three mercaptides [8–11], one sulfide and two mercaptides [6, 8] or an $Fe(SR)_6$ bridge [12]. The second contains the FeS_2Mo unit, with two bridging sulfides; examples are the $[X_2FeS_2MoS_2]^{2-}$ ions (X = PhS [13, 14], Cl [14]) and apparently the $[Fe_4Mo_4S_{20}]^{6-}$ cluster [15]. These last two may be viewed as arising from coordination of tetrathiomolybdate to the monomeric and tetrameric members of the by now well-known series of synthetic analogs of the iron–sulfur protein prosthetic groups. Such complexes are of particular interest in view of the fact that acid hydrolysis of the MoFe-protein of nitrogenase produces thiomolybdates [16]. We wish to report herein the preparation and some properties of a complex containing thiomolybdate coordinated to the dimeric Fe–S center, namely the $[(PhS)_2FeS_2FeS_2MoS_2]^{3-}$ cluster.

Prolonged reaction of $(Et_4N)_2[Fe_2S_2(SPh)_4]$ [17] with one equivalent of $(Et_4N)_2MoS_4$ in acetonitrile at room temperature results in the disappearance of the characteristic optical spectrum of MoS_4^{2-} and formation of a new complex with an optical spectrum characteristic of coordinated thiomolybdate (Fig. 1). Reduction of solvent volume of recrystallization affords $(Et_4N)_3[(PhS)_2FeS_2FeS_2MoS_2]$, *I*, as purple-black microcrystals, mp 190–1(d). *Anal:* Calcd for $C_{36}H_{70}Fe_2MoN_3S_8$: C, 42.85; H, 7.00; Fe, 11.07; Mo, 9.51; N, 4.16; S, 25.42. Found: C, 42.97; H, 7.24; Fe, 11.23, Mo, 8.97, N, 4.21; S, 25.45 (Galbraith Laboratories, Inc., Knoxville, Tenn., U.S.A.).

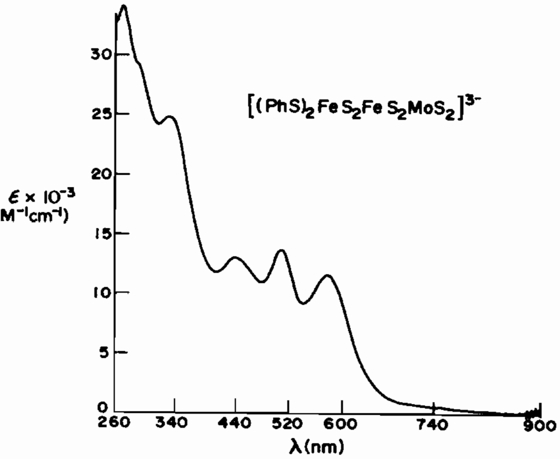
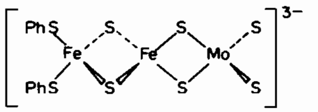


Fig. 1. Optical spectrum of $(Et_4N)_3[(PhS)_2FeS_2FeS_2MoS_2]$ in acetonitrile.



The reaction cannot be viewed as a simple displacement of two phenyl mercaptide ligands by a bidentate thiomolybdate, but involves reduction of the [2Fe-2S] core as well (presumably by liberated phenylmercaptide) to yield a *tri-anion*. The proposed structure for *I*, shown below, is based on elemental analysis and the following data. The optical spectrum of *I* shows the splitting and shift of the 467 nm band of $MoS_4^{=}$ to longer wavelengths (578 nm, $\epsilon = 1.19 \times 10^4$; 510 nm, $\epsilon = 1.40 \times 10^4$), as expected for coordination of tetrathiomolybdate to Fe–S centers [13–15] and divalent first-row transition metal ions in general [18]. Mössbauer spectra of the solid at 4.2 K in small (<1 kG) applied magnetic fields show only two quadrupole doublets of equal intensity rather than a magnetic spectrum, indicative of rapid electronic relaxation. Relevant parameters are (mm/sec):

	Isomer Shift (*vs.* Metallic Fe)	Quadrupole Splitting
A	0.42	1.41
B	0.30	0.68

The parameters for doublet A, especially the isomer shift, are very similar to those obtained for $[(PhS)_2FeS_2MoS_2]^{2-}$ [13, 14], while those for doublet B are characteristic of high-spin Fe^{3+} in tetrahedral sulfur environments, such as oxidized rubredoxin [19]. The overall charge of 3- on the anion suggests a paramagnetic ground state. This is confirmed by

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*Author to whom correspondence should be addressed.

magnetic susceptibility measurements, which give a value of ~1.7 BM per formula unit at room temperature, and by EPR spectra of *I* in frozen solutions, which show an intense, narrow isotropic signal at g = 2.005 at 4.2 K. Together with the Mössbauer data, these suggest an antiferromagnetic coupling of high-spin Fe^{3+} ($S = 5/2$) with the $Fe^{2+}S_2Mo^{6+}S_2$ unit ($S = 2$) to give a net $S = 1/2$ ground state. Proton NMR spectra (d^3-acetonitrile, 25 °C) show isotropically shifted resonances at 49.1 ppm downfield of TMS and at 46.5 and ~30 ppm upfield of TMS, tentatively assigned to the *m*-, *p*-, and *o*-H's of the phenyl rings, respectively. The magnitude of the isotropic shifts *decreases* with increasing temperature over the range 25–75 C, consistent with $2J \gg kT$ and thus little population of $S > 1/2$ excited states. Preliminary electrochemical experiments show only an irreversible oxidation at ~ +0.05V and an irreversible reduction at −1.1 V *vs.* SCE.

Taken together, the data presented above provide strong evidence for the structure proposed (*I*). This new complex may be viewed as either arising from insertion of an Fe^{3+} and two S^{2-} into the known $[(PhS)_2FeS_2MoS_2]^{2-}$ or as the first example of a synthetic analog of a *reduced* 2Fe-2S ferredoxin, here stabilized by an MoS_4^{2-} ligand. In either case, it is of interest as an example of an Mo–Fe–S cluster containing iron in two distinct sites, with only one near the molybdenum; as such, it should prove valuable in interpreting spectroscopic results on FeMo-co, which also contains at least two distinct iron sites [5]. Mössbauer, EXAFS and crystallographic studies are in progress.

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