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Synthesis of the $[(\mathrm{AcO})_2\mathrm{FeS_2MS_2}]^{2-}$ (M = Mo, W) Ions and Observation of a New Bonding Mode for Complexes of $[\mathrm{MoO_2S_2}]^{2-}$

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The new complexes $[\mathrm{Et_4N}]_2[(\mathrm{AcO})_2\mathrm{FeS_2MS_2}]$ (M = Mo, W) were prepared by reaction of anhydrous ferrous acetate with $[\mathrm{Et_4N}]_2[\mathrm{MS_4}]$. The compounds were characterized by routine spectroscopic techniques and analytical procedures and may prove useful as standards for the interpretation of iron EXAFS data for nitrogenase and its cofactor. Reaction of $[\mathrm{Et_4N}]_2[\mathrm{MoO_2S_2}]$ with $\mathrm{Fe(OAc)_2}$ yields a new complex which seems to be best formulated at $[\mathrm{Et_4N}]_2[\mathrm{Fe(MoO_2S_2)_2}]$. The ir spectrum of this latter species is unusual and may indicate oligomerization via the $\mathrm{MoO_2S_2}$ moiety.

Attempts to reproduce the stoichiometric, spectroscopic and reactivity properties of the molybdenum-containing site of nitrogenase, the so-called FeMo cofactor, have resulted in the preparation of a large number of Fe–Mo–S cluster-type complexes over the past several years [1]. These cluster species have been of two types: (i) those containing $\mathrm{Fe_3MoS_4}$ cubane-type units; and (ii) those comprised of linear arrays of Fe and Mo atoms bridged by sulfide. Most of the linear-type complexes have been prepared under non-aqueous conditions by reacting $[\mathrm{MoS_4}]^{2-}$ with various iron-containing reagents, the nature of which controls, to a large degree, the identity of the final product. In some cases, a simple 1:1 or 1:2 'adduct' is formed between $\mathrm{MoS_4}^{2-}$ and the iron compound [2], *e.g.*, $[\mathrm{Cl_2FeS_2MoS_2}]^{2-}$ and $[\mathrm{Cl_2FeS_2MoS_2FeCl_2}]^{2-}$. For other iron species, partial ligand displacement occurs on reaction with $\mathrm{MoS_4}^{2-}$ as in the syntheses of $[(\mathrm{PhS})_2\mathrm{FeS_2MoS_2}]^{2-}$ [3] and $[(o\text{-xyl}-\mathrm{S_2})\mathrm{FeS_2MoS_2}]^{2-}$ [4] from $[\mathrm{Fe(SPh)_4}]^{2-}$ and $[\mathrm{Fe}(o\text{-xyl}-\mathrm{S_2})_2]^{2-}$, respectively. Finally, complete ligand substitution of the iron-containing starting material can take place, as in the preparation [5] of $[\mathrm{Fe(MoS_4)_2}]^{3-}$ from $\mathrm{Fe(dtc)_2}$ or $\mathrm{Fe(xan)_3}^-$ (dtc = dialkyldithiocarbamate, xan = alkylxanthate).

TABLE I. Spectral Data for Complexes.

Complex	Infrared[a]		Electronic[b]
1	515, 490	460	520(sh), 465(6390) 425(sh), 307(17700)
2	500	455	450(sh), 398(8090), 365(sh)
3	815, 885	455	410(4880), 480sh(2050)

[a] KBr pellets; values in $\mathrm{cm^{-1}}$. [b] MeCN solution; values in nm with molar absorptivities in parentheses.

As part of our program of preparing synthetic analogs of this nitrogenase site for use as reactivity and spectroscopic probes, we have begun to explore the reactivity of anhydrous ferrous acetate with thiomolybdates and thiotungstates under non-aqueous conditions. If 'adduct'-type complexes of this starting material could be formed, then the products should be very useful as standards for the interpretation of EXAFS data which, in preliminary reports [6], has indicated that oxygen (or nitrogen) ligands may be present on iron in the iron-molybdenum cofactor (FeMoco) of nitrogenase. Previously [7], the complex $[\mathrm{Et_4N}]_2[(\mathrm{PhO})_2\mathrm{FeS_2MoS_2}]$ was prepared and characterized, at least partially for use in the interpretation of X-ray absorption data from FeMoco. Herein, we report the synthesis of several new Fe–Mo(W)–S complexes formed from anhydrous $\mathrm{Fe(OAc)_2}$.

Reaction of $\mathrm{Fe(OAc)_2}$ (0.34 g; 1.95 mmol) with $[\mathrm{Et_4N}]_2[\mathrm{MoS_4}]$ (0.96 g; 1.98 mmol) in MeCN (40 ml) for 30 min at ambient temperature gave a dark brown solution. Addition of $\mathrm{Et_2O}$ (50 ml) to the reaction mixture caused the separation of the product which was isolated by filtration, washed with $\mathrm{Et_2O}$, and dried *in vacuo*. Cooling of the combined filtrate and washes at −20 °C for 18 hrs resulted in the formation of additional, more-crystalline product. The total yield of $[\mathrm{Et_4N}]_2[(\mathrm{AcO})_2\mathrm{FeS_2MoS_2}]$ (*1*) was 1.0 g (76%). *Anal.* Calcd for $\mathrm{C_{20}H_{46}N_2O_4FeMoS_4}$: C, 36.47; H, 6.99; N, 4.25. Found: C, 36.53; H, 7.44; N, 4.32. A similar reaction sequence employing $[\mathrm{Et_4N}]_2[\mathrm{WS_4}]$ instead of $[\mathrm{Et_4N}]_2[\mathrm{Mo_4}]$ gave $[\mathrm{Et_4N}]_2[(\mathrm{AcO})_2\mathrm{FeS_2WS_2}]$ (*2*) in 54% yield. *Anal.* Calcd for $\mathrm{C_{20}H_{46}N_2O_4FeWS_4}$: C, 32.17; H, 6.16; N, 3.75. Found: C, 31.77; H, 6.34; N, 3.78.

The routine spectral characterization of *1* and *2* is summarized in Table I where UV/vis and infrared data are presented. The complete UV–visible spectra of the complexes are shown in Fig. 1 as an aid to future identification. The infrared spectra of *1* and

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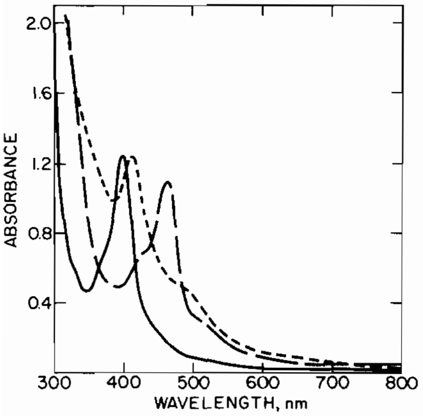

Fig. 1. Electronic spectra of *1* (– – –), *2* (———), and *3* (------) in MeCN.

2 are consistent with their formulation, containing bands due to the terminal M=S groups and the FeS_2M bridge at the appropriate positions as well as absorptions due to coordinated acetate and $[Et_4N]^+$. As pointed out previously [4], the presence of two terminal M=S bands for *1* and only one for its tungsten analog *2* is typical of these systems. The major peaks in the UV/vis spectra of the complexes are virtually unshifted from the free MS_4^{2-} charge transfer band positions. The many shoulders observed, along with the lowering of the molar absorptivity from that of the free thiometallates, however, does indicate significant perturbation of the MS_4^{2-} energy manifolds. In this light, it is interesting to note that for the complexes $[X_2FeS_2MS_2]^{2-}$, the perturbation of the electronic spectrum from that of MS_4^{2-} to lower energy proceeds in the following order as a function of X_2: $(SCH_2)_2C_6H_4 > (SPh)_2 > Cl_2 > (OAc)_2$. This order would seem to reflect a stronger interaction between the MoS_4^{2-} and the FeX_2 units when X is a softer sulfur donor ligand than when it is a harder O or Cl donor ligand.

The acetate ligands on iron in *1* can be substituted by reaction with excess PhSH (eqn. 1) as evidenced by visible spectral changes which showed the quantitative formation of the known thiophenolate product [3]. Similar reactivity was observed [7] for $[(PhO)_2FeS_2MoS_2]^{2-}$. This behavior may prove to be a useful synthetic route to other $[X_2FeS_2MoS_2]^{2-}$ species.

$$[(AcO)_2FeS_2MoS_2]^{2-} + 2PhSH \longrightarrow [(PhS)_2FeS_2MoS_2]^{2-} + HOAc \qquad (1)$$

The reaction of $Fe(OAc)_2$ with the dithiomolybdate ion $MoO_2S_2^{2-}$ proceeds differently and yields an interesting but as yet not completely characterized product. A mixture of solid $[Et_4N]_2[MoO_2S_2]$ (1.35 g; 2.99 mmol) and $Fe(OAc)_2$ (0.51 g; 2.93 mmol was dissolved in MeCN (35 ml) and stirred for 2 hr at ambient temperature. After filtration, Et_2O (40 ml) was added to the reaction mixture causing the precipitation of the product (*3*) (0.50 g) which was isolated by filtration, washed with Et_2O and dried *in vacuo*. Cooling of the combined filtrate and washes at –20 °C for 2 weeks produced more *3* which was isolated similarly. The total yield was 1.0 g. Recrystallization of the product from DMF/THF gave an analytical sample *4*, which was shown by ir spectroscopy to contain DMF of crystallization ($\nu_{C=O}$ = 1690 cm^{-1}). Elemental analysis indicates that *4* is best formulated as $[Et_4N]_2[Fe(MoO_2S_2)_2]\cdot 1/3DMF$. *Anal.* Calcd. for $C_{17}H_{42.33}N_{2.33}FeMo_2O_{2.33}S_4$: C, 28.17; H, 5.84; N, 4.50. Found: C, 28.54; H, 5.98; N, 4.22. We have, however, had difficulty in obtaining consistent iron and molybdenum analyses on this product. A product *5*, which was very similar spectrally to 3 and 4 was produced by reaction of $Fe(S_2CNR_2)_2$ with $[Et_4N]_2[MoO_2S_2]$ in CH_2Cl_2. The analytical data for this solid were also consistent with $[Et_4N]_2[Fe(MoO_2S_2)_2]$ but obviously without DMF of crystallization. *Anal.* Calcd for $C_{16}H_{40}N_2FeMo_2O_4S_4$: C, 27.43; H, 5.11; N, 4.00. Found: C, 27.56; H, 5.91; N, 3.82.

The ir spectral data for *5* are given in Table I and in Fig. 2 where the entire spectrum is shown. The lack of bands in the 1600–1700 cm^{-1} spectral region [8] clearly indicates that no coordinated dithiocarbamate is present in *5*. The broad, strong bands in the 800–900 cm^{-1} region of the spectrum are its most characteristic feature and are atypical for complexes where the $[MoO_2S_2]^{2-}$ ion behaves as a simple bidentate sulfur donor ligand. For example, the ir spectrum of the well-characterized [9] $[Et_4N]_2[Co(MoO_2S_2)_2]$ is also given in Fig. 2 for comparison and it can be seen that its terminal Mo=O vibrations are

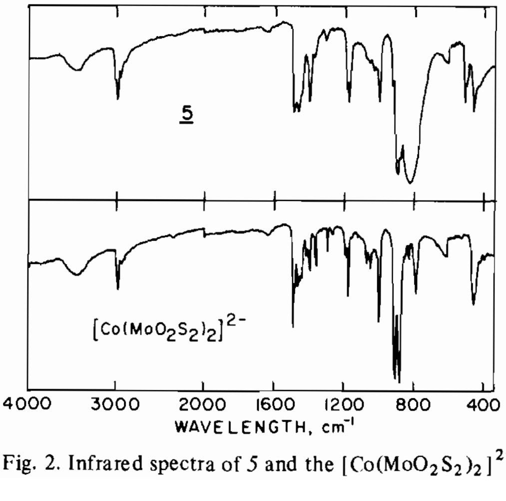

Fig. 2. Infrared spectra of *5* and the $[Co(MoO_2S_2)_2]^{2-}$ ion.

sharp and appear at higher energy than those of *3–5*. Previously [10], we have observed similar spectral properties ion oxomolybdenum species and the behavior has been attributed to the formation of oligomers via interaction of the terminal oxo group of one monomer with the molybdenum of another. It is possible a similar bonding pattern is responsible for the unusual ir spectral properties of *3–5*. However, because of the aforementioned difficulty with Fe and Mo analyses and the lack of suitable crystals for X-ray analysis, much uncertainty exists as to the exact nature of this species. We are reporting our preliminary results on *3–5* here because its spectral properties are indicative of a new mode of interaction of the $[MoO_2S_2]^{2-}$ ion with other metals. Attempts are continuing to overcome the above problems and fully characterize these products.

Thus, $Fe(OAc)_2$ has been shown to be a versatile starting material for the synthesis of Fe–Mo(W)–S species, producing both 'adduct-type' species, containing an intact $Fe(OAc)_2$ unit, and species where the acetate ligands have been completely displaced. The use of $Fe(OAc)_2$ as a reagent in pure Fe–S systems is currently being explored, as is the reactivity of the $[(AcO)_2FeS_2MS_2]^{2-}$ ions. Finally, attempts are continuing to produce crystals of these complexes which are suitable for X-ray structural determination.

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8 The initially isolated solid indeed exhibited broad bands in this spectral region but we feel certain these bands are due to either unreacted $Fe(OAc)_2$ or $[Et_4N]OAc$. These broad bands disappear on recrystallization from DMF/THF and are replaced by a single sharp band at 1690 cm^{-1} which we attributed to DMF of crystallization but which could have been due to acetate. This latter possibility is excluded by the fact that the product from reaction of $Fe(dtc)_2$ with $[Et_4N]_2[MoO_2S_2]$ is identical spectrally to the product from $Fe(OAc)_2$ except that the 1690 cm^{-1} band is missing.

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