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A Synthetic Molybdenum-Iron-Sulfur Cluster with Phenoxide Terminal Ligands

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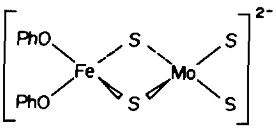
Recent studies in several laboratories have suggested that oxygen ligands such as N-methylformamide or citrate are coordinated to the FeMo-cofactor [1] of nitrogenase as isolated [2, 3], and that, for example, EDTA can bind to the cofactor with profound effects on its spectroscopic properties [4]. This is supported by comparison of preliminary Fe EXAFS (extended X-ray absorption fine structure) data [5] on the isolated FeMo-cofactor to that of the $MoFe_3S_4$ double cubane clusters [6, 8], which demonstrates the presence of low Z (non-sulfur) ligand atoms coordinated to ircn in the former. To date, efforts directed towards developing a synthetic model for the unique Mo–Fe–S cluster of FeMo-cofactor have all utilized aliphatic or aromatic thiolates [6–9] or halide [9, 10] ions as ligands. In view of this, we would like to report the synthesis and some physical properties of the first synthetic Mo–Fe–S unit with phenoxide ligands, the $[S_2MoS_2Fe(OPh)_2]^{2-}$ ion (*I*).

Reaction of two equivalents of anhydrous NaOPh with $(Et_4N)_2FeMoS_4Cl_2$ [9] in acetonitrile at room temperature results in an immediate color change from yellow–brown to red–orange and a gradual precipitation of NaCl. After filtration, the products is precipitated as red-brown crystals by the slow addition of diethyl ether. Recrystallization from acetonitrile/ether affords the product, $(Et_4N)_2FeMoS_4(OPh)_2$ (*II*) as well-formed red–black needles in 65% yield: m.p. (*in vacuo*) 87–90 °C (decomp.). *Anal.* Calcd for $C_{28}H_{50}N_2O_2FeMoS_4$: C, 46.27; H, 6.94; N, 3.86; S, 17.65. Found: C, 46.84; H, 6.70; N, 3.56; S, 16.98.

Significant features of the optical spectrum of *II* in acetonitrile include maxima at 471 nm (ϵ = 9.3 × 10^3 M^{-1} cm^{-1}), 392 nm (ϵ = 7.1 × 10^3 M^{-1} cm^{-1}), and 314 nm (ϵ = 13.9 × 10^3 M^{-1} cm^{-1}). These are blue-shifted by 18–27 nm when compared to apparently analogous features [9a] in the optical spectrum of the thiophenolate analog, $[S_2MoS_2Fe(SPh)_2]^{2-}$ (*III*) as expected upon substitution of sulfur by more electronegative oxygen donors. Magnetic susceptibility measurements on *II* show $\mu_{eff}^{(corr)}$ = 4.94 BM, consistent with an S = 2 system, and agreeing well with the value of 5.1 BM determined for salts of *III* [9a]. ^{57}Fe Mössbauer spectra of *II* diluted in a BN matrix at 4.2 K in zero applied field show only a simple quadrupole doublet with δ = 0.57 mm/sec (*vs.* Fe metal at room temperature) and ΔE_q = 1.20 mm/sec; this is consistent with an S = 2 ground state with fast electronic relaxation. Corresponding values for salts of *III* are δ = 0.47 mm/sec and ΔE_q = 1.63 mm/sec, suggesting that the iron atom in *I* has significantly greater ferrous character than in *III* (*cf.* the value of δ = 0.60 for $[S_2MoS_2FeCl_2]^{2-}$ [9a]). In contrast to the above, where the shifts expected upon replacing thiophenoxide by phenoxide are observed, electrochemical and ^{1}H NMR measurements show unexpected results. Thus, electrochemical studies on *II* in dimethylacetamide using a dropping mercury electrode show only an irreversible reduction at −1.51 V *vs.* SCE, compared to −1.34 V for salts of *III* [9a]. This is analogous to results observed for phenoxide substitution on [4Fe–4S] centers [11] and suggests, surprisingly that phenoxide ligands make the cluster *more* difficult to reduce rather than less. Proton NMR spectra of *II* in d_3-acetonitrile at 20 °C show isotropically shifted resonances at 50.7 ppm downfield of TMS and 40.5 and ~12 ppm upfield of TMS. These are assigned to the meta, para, and ortho protons, respectively, of the phenyl rings. Substitution of *p*-cresolate for phenoxide results in the appearance of an additional downfield peak at −52.4 ppm and the disappearance of the upfield resonance at 40.5 ppm. These results are analogous to those of the $[FeMoS_4(SPh)_2]^{2-}$ and $[FeMOS_4(S\text{-}p\text{-}tol)_2]^{2-}$ anions previously reported [9a], except that the isotropic shifts observed are significantly larger for *I* than for *III*. All isotropic shifts decrease in magnitude with increasing temperature, consistent with a simple S = 2 paramagnet.

Reaction of *II* with two equivalents of benzoyl chloride in acetonitrile causes a rapid color change from red–orange to yelllow–brown. The optical spectrum of the product corresponds exactly to that of $FeMoS_4Cl_2^{2-}$ [9a]. Likewise, reaction of *II* with excess thiophenol gives rise to a solution whose optical spectrum agrees with that of $FeMoS_4(SPh)_2^{2-}$ [9a]. Thus, *I* appears to possess reactivity analogous to Mo–Fe–S and Fe–S systems with thiolate ligands [9a, 10, 12].

The above data support the proposed structure



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and suggest that Mo–Fe–S clusters with phenoxide ligands should be both readily prepared and reasonably stable. As the first well-characterized example of an Mo–Fe–S complex with oxygen ligation to iron, *I* should prove especially useful in the interpretation of iron EXAFS data from the FeMo-cofactor. EXAFS studies on *II* are underway.

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