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Effects of Phenoxide Ligation: Synthesis and Characterization of the $[Mo_2Fe_6S_8(SEt)_3(OPh)_6]^{3-}$ Ion

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Abstract

Reaction of phenol with an alkylthiolate-ligated double cubane complex effects phenolate substitution at the terminal positions; the product can be isolated as its benzyltriethylammonium salt. The phenolate cluster possesses unaltered magnetic properties and blue shifted optical spectra, and undergoes ligand exchange reactions with electrophiles as expected for terminal phenolate substitution. Increased isotropic proton NMR shifts and large negative shifts in corresponding first and second reduction potentials are consistent with increased donation of electron density to the $[MoFe_3S_4]^{3+}$ cores for phenolate versus thiophenolate terminal ligands to iron. Similar behavior has been observed for Fe_4S_4, Fe_2S_2 and MoS_2Fe systems.

Introduction

Since 1978, a variety of heterometallic double-cubane clusters [1] possessing MFe_3S_4 (M = Mo, W) units with thiolate and halide terminal ligands have been prepared and structurally characterized. The Mo EXAFS of these clusters [2a] is similar to that of the FeMo–cofactor (FeMo–co) of nitrogenase. Analysis of the Fe EXAFS for these clusters [2b], however, reveals that they are not adequate structural models for the Fe environment in FeMo–co. Several chemical and physiochemical studies of FeMo–co [3], including iron K-edge EXAFS spectra [2b] have suggested that oxygen (or nitrogen) donor ligands are bound to the iron atoms within the FeMo–cofactor. Also FeMo–co can be extracted from the MoFe–protein without addition of thiols, which are necessary for cluster displacement of typical Fe–S centers. We have therefore prepared the first double-cubane cluster with terminal oxygen ligands to iron, $[Mo_2Fe_6S_8(SEt)_3(OPh)_6]^{3-}$, **1**. The Mo and Fe EXAFS of several double-cubane clusters including **1** have recently been reported [2c]. We report here the synthesis and characterization of the $(Et_3NCH_2Ph)_3$ salt of **1**.

Experimental

All operations were carried out under an atmosphere of pure, dry dinitrogen. Solvents and reagents were purified as previously described [4]. $(Et_3NCH_2Ph)_3[Mo_2Fe_6S_8(SEt)_9]$ was prepared by published procedures [5].

Preparation of $(Et_3NCH_2Ph)_3[Mo_2Fe_6S_8(SEt)_3(OPh)_6]$

To 3.16 g (1.65 mmol) $(Et_3NCH_2Ph)_3[Mo_2Fe_6S_8(SEt)_9]$ dissolved in 300 ml MeCN was added 14 g (150 mmol) PhOH dissolved in 76 ml MeCN. The reaction mixture was evaporated *in vacuo* at 30 °C to <50 ml. This dilution and evaporation step was repeated once, followed by addition of 200 ml THF. Slow cooling to -20 °C caused separation of the product as black plates, which were collected by filtration, washed twice with THF and vacuum dried. Recrystallization was accomplished by dissolution of the crude product in ~20 ml MeCN containing 25 mM PhOH, filtration, addition of ~150 ml THF (also 25 mM in PhOH), and slow cooling to -20 °C. Typical yields were 50–60%. *Anal.* Calcd. for $C_{81}H_{111}N_3O_6S_{11}Fe_6Mo_2$: C, 46.30; H, 5.30; N, 2.00; S, 16.80; Fe, 15.90; Mo, 9.10. Found: C, 45.39; H, 5.55; N, 1.87; S, 16.72; Fe, 16.56; Mo, 8.10. m.p. 55 °C (d).

The purity of the compound after recrystallization was estimated at 98% by proton NMR spectra. The extraordinary sensitivity of this compound to air and moisture made it extremely difficult to

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obtain satisfactory and reproducible elemental analyses; analytical results given above are typical.

Physical Measurements

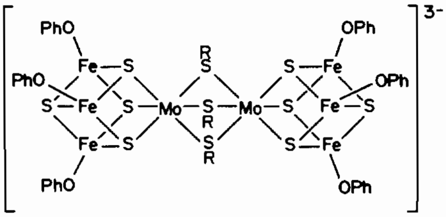
All samples were handled under anaerobic conditions. Optical spectra were obtained on a Cary 219 spectrophotometer. Proton NMR spectra were obtained on a Bruker WM-250 spectrometer. Room temperature magnetic susceptibility measurements were performed on an Alpha Faraday balance using $Hg[Co(SCN)_4]$ as calibrant. Electrochemical measurements were performed on a PAR 174A polarographic analyzer. DC polarography at a dropping mercury electrode and cyclic voltammetry at glassy carbon electrodes were performed. All solutions contained 50 mM $Et_4N(ClO_4)$ as supporting electrolyte. Potentials were measured versus the saturated calomel electrode at ~23 °C. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Results and Discussion

The phenolate double cubane complex **1** can be prepared by reaction of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ with a large excess of PhOH (reaction (1)). This reaction is completely analogous to the reaction of $[Fe_4S_4(SR)_4]^{2-}$ with excess phenol [4] and represents a ligand exchange equilibrium that is driven to completion by removal of volatile EtSH *in vacuo*. The resulting product is isolated as its tetraalkylammonium salt in 50–60% yields after recrystallization.

$$[Mo_2Fe_6S_8(SEt)_9]^{3-} + xsPhOH \longrightarrow [Mo_2Fe_6S_8(SEt)_3(OPh)_6]^{3-} + 6EtSH \qquad (1)$$

Isolation and recrystallization are difficult because of the extremely high solubility in polar organic solvents. Once prepared and isolated, however, the complex is stable in the absence of oxygen and water. A schematic view of the proposed structure is shown below:



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The electronic absorption spectra for **1** and $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ are presented in Fig. 1. Spectral data are recorded in Table I. Comparison of the spectra show the elimination of the original bands at 281 nm and 391 nm and replacement with bands at 233 nm, 270 nm, and 400 nm. Similar spectral changes are observed for the reaction of greater than six equivalents of PhSH with $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ to yield the $[Mo_2Fe_6S_8(SEt)_3(SPh)_6]^{3-}$ ion [6], which has recently been isolated as its tetraethylammonium salt and exhibits prominent shoulders at 346 nm and 418 nm. Apparently corresponding bands at 400 nm (OPh) and 418 nm (SPh) are tentatively assigned to terminal ligand-to-metal charge transfer transitions. The observed blue shift is as expected based upon substitution of a sulfur donor by the more electronegative oxygen donor and on results obtained for the phenolate Fe–S tetramer and dimer dianions.

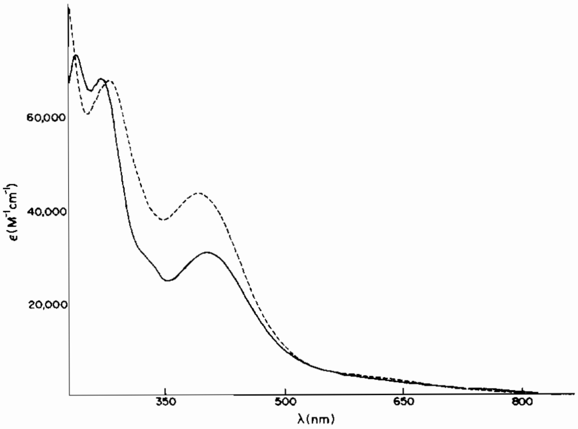

Fig. 1. Electronic spectra of $[Mo_2Fe_6S_8(SEt)_3(OPh)_6]^{3-}$ (solid line) and $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ (dashed line) in acetonitrile solution at 22 °C.

TABLE I. Electronic Spectral Features, Isotropic Shifts and Electrochemical Data for $[Mo_2Fe_6S_8(SEt)_3(OPh)_6]^{3-}$.

Electronic spectral features[a]	233(87.5), 270(74.2), 400(31.3)	
($\Delta H/H_{iso}$)[b] (ppm)	c	(o-H)
	−9.66	(m-H)
	12.55	(p-H)
	−16.36	(CH_2)[d]
DPP[e,g] (V)	$E_1 = -1.14(121)$	
	$E_2 = -1.33(120)$	
CV[f,g] (V)	$E_1 = -1.13(97)$	
	$E_2 = -1.31(108)$	

[a] Measured in MeCN at 22 °C; $\lambda_{max}(\epsilon)$, nm (M^{-1} cm^{-1} × 10^{-3}). [b] Measured in d_3-MeCN solution at 22 °C; shifts *vs.* diamagnetic reference, PhOH: −7.02. [c] Obscured. [d] Resonance due to bridging ethanethiolate. [e] $E(W_{1/2})$, V(mV). [f] $E(E_{p_c} - E_{p_a})$, V(mV). [g] In MeCN solution.

The room temperature magnetic susceptibility of the Et_3NCH_2Ph salt of **1** has been measured by the Faraday method. A corrected effective magnetic moment, μ_{eff}, of 5.74 BM was obtained for the cluster, suggesting the presence of intramolecular antiferromagnetic coupling. This result is virtually identical to that measured for $(Et_3NCH_2Ph)_3[Mo_2Fe_6S_8(SEt)_9]$ [7] (5.73 BN) and $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ [8] (5.70 BM) and corresponds to a spin-only value of $S = 5/2$ at room temperature. These results suggest that the magnetic properties of the double cubane clusters, as with the Fe–S tetramers and dimers, are not sensitive to the nature of the terminal ligand.

Proton magnetic resonance spectra of the Et_3NCH_2Ph salt of **1** have been measured as a function of temperature in acetonitrile solution. Isotropically shifted resonances due to the meta and para protons of the phenol group and to bridging ethanethiolate groups are observed; the *ortho* protons are presumably too broad for detection. Representative 250 MHz spectra are shown in Fig. 2, while spectral data are collected in Table I.

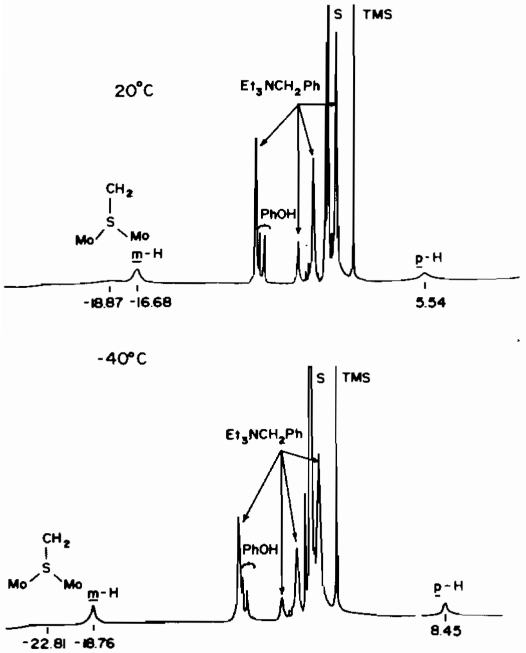

Fig. 2. Proton NMR (250 MHz) spectra of $(Et_3NCH_2Ph)_3[Mo_2Fe_6S_8(SEt)_3(OPh)_6]$ in acetonitrile-d^3 solution at 20 and −40 °C. Assignments are indicated; S indicates residual protons of solvent. Chemical shifts are *vs.* internal tetramethylsilane (TMS).

Assignments were made based on the features demonstrated in the spectra of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ [7, 8] and $[Mo_2Fe_6S_8(SEt)_3(SPh)_6]^{3-}$ [6] and are shown in Fig. 2. The data suggest that, for reasons already described [7, 8] contact interactions are responsible for the isotropic shifts of the phenyl protons and that there is an appreciable dipolar contribution to the shifts of the bridging ethanethiolate groups of **1**.

Comparison of the magnitudes of the isotropic shifts of the phenyl protons of **1** (Table I) with those of the thiophenolate analog (−6.6 ppm (*m*-H), +10.9 ppm (*p*-H)) [7, 8] shows that the general trend of substantially larger shifts for phenolate *versus* thiophenolate analogs established for the phenolate Fe–S clusters [4, 9] is followed for the double cubanes. These results once again suggest that phenolate is capable of donating more electron density to the metal center than thiophenolate, and are consistent with the electrochemical results discussed below.

The temperature dependence of the observed isotropic shifts for the phenolate protons shows that the magnitudes of the shifts increase with decreasing temperature. This behavior parallels that obtained for the terminal thiophenolates of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ [8], and is also consistent with the temperature dependence of the magnetic susceptibility of several double cubane complexes [7, 10] of the same type.

The electrochemical behavior of **1** has been examined by differential pulse polarography and cyclic voltammetry. The complex exhibits two well-defined, quasireversible one-electron reductions, corresponding to sequential formation of the 4− and 5− ions. A typical cyclic voltammogram and differential pulse polarogram are shown in Fig. 3. Electrochemical data are provided in Table I.

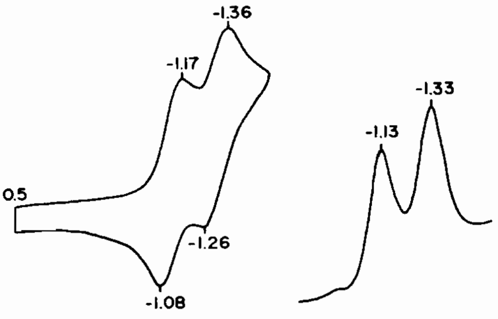

Fig. 3. Cyclic voltammogram and differential pulse polarogram for $(Et_3NCH_2Ph)_3[Mo_2Fe_6S_8(SEt)_3(OPh)_6]$ in acetonitrile solution. CV scan rate, 100 mV/sec.

Examination of the cyclic voltammetric results suggests that, while reduction of the complex is not strictly electrochemically reversible (shown by $|E_{p_c} - E_{p_a}| > 59$ mV), it does approximate chemical reversibility, as shown by the value of $i_{p_c}/i_{p_a} \sim 1$. Peak half-widths obtained by DPP measurements are in reasonable agreement with values obtained for the quasireversible one-electron reductions of the phenolate [4] and thiophenolate [11] tetramers under similar conditions.

Comparison of the corresponding reduction potentials for $[Mo_2Fe_6S_8(SEt)_3X_6]^{3-}$, where X = SPh ($E_1 = -1.01$ V, $E_2 = -1.19$ V) [6], OPh (Table I), Cl ($E_1 = -0.83$ V, $E_2 = -1.01$ V)) [6] shows the same order of decreasing ease of reduction, Cl < SPh < OPh, established for the Fe–S tetramer [4] and dimer [9] series. The shift of approximately −120 mV for each of the two reductions upon substitution of phenolate for thiophenolate represents further evidence of the ability of phenolates to donate more electron density to the metal sulfur center than thiophenolates, therefore rendering them more difficult to reduce. Similar results have also been obtained for the $[MoFeS_4X_2]^{2-}$ system, where X = SAr [12], OAr [13].

The phenolate cluster **1** is extraordinarily sensitive to water, acidic solvent impurities, and strongly donating solvents, as are the phenolate Fe–S clusters. It also undergoes reactions with electrophiles. Reaction with benzoyl chloride smoothly converts the phenolate complex to the corresponding chloro cluster [6, 14] in quantitative yield as shown by optical spectra (reaction (2)).

$$\mathbf{1} + 6PhCOCl \longrightarrow [Mo_2Fe_6S_8(SEt)_3Cl_6]^{3-} + 6PhCO_2Ph \qquad (2)$$

Reaction with thiophenol quantitatively converts the phenolate complex to the thiophenolate analog [6] (reaction 3).

$$\mathbf{1} + 6PhSH \longrightarrow [Mo_2Fe_6S_8(SEt)_3(SPh)_6]^{3-} + 6PhOH \qquad (3)$$

As expected, only the terminal phenolates and not the bridging ethanethiolates are reactive under the conditions examined. The observed ligand exchange reactivity is expected based on the evident lability of phenolate ligands and the analogous reactivity of the phenolate Fe–S clusters [4, 9].

Results obtained for **1** are entirely consistent with the proposed structure. The data indicate that phenoxide is a more labile ligand than ethanethiolate. In addition, electrochemical results indicate that **1** exhibits reduction potentials in the same range as $[Mo_2Fe_6S_8(SEt)_9]^{3-}$. These results suggest that substitution of a cysteinyl thiolate ligand by a tyrosyl phenolate ligand to iron in FeMo–co should provide a more labile coordination site without significantly changing cluster reduction potentials. To date, the double cubane, **1**, and the binuclear cluster $[MoFeS_4(OPh)_2]^{2-}$ [13] are the only examples of synthetic MoFeS clusters possessing phenolate oxygen ligation to iron. Preliminary data on the only other oxygen-ligated MoFeS cluster known, $[MoFeS_4(OAc)_2]^{2-}$, suggest that carboxylates behave as typical electronegative ligands [15].

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