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A Novel Synthetic Iron–Sulfur Cluster with Phenoxide Ligands

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In recent years, several Fe–S sites with unusual structures and spectroscopic properties have been identified. Examples include the P-clusters of nitrogenase [1] (presumed to be unusual 4Fe–4S clusters), the 3Fe center of inactive aconitase [2], and the Rieske iron–sulfur center from *Thermus thermophilus* [3]. One possible means by which a protein could alter the properties of Fe–S clusters is by terminal coordination of the cluster by noncysteine ligands. As a result of our continuing investigation of the effect of oxygen ligation on Fe–S clusters [4], we have prepared a series of new complexes that have the same stoichiometry as normal Fe–S tetrameric clusters (*viz.* $\{(R_4N)[Fe_2S_2(OAr)_2]\}_n$, but significantly different physical and chemical properties (**I**, R = Et, Ar = p-ClC_6H_4; **II**, R = Me, Ar = p-Tolyl; **IIa**, R = Et, Ar = p-Tolyl). These compounds were briefly alluded to earlier [4]. Based on the results presented below and on the synthesis and structural characterization of $(Et_4N)_3[Fe_6S_6Cl_6]$ (**III**) by Coucouvanis, *et al.* [5] and of $(Et_4N)_2[Fe_6S_6I_6]$ by Saak, Henkel, and Pohl [6], we propose that these new phenoxide-ligated Fe–S clusters in fact contain the $[Fe_6S_6]^{3+}$ 'prismane' unit, as shown schematically in Fig. 1. These results demonstrate that the hexameric unit can also be stabilized by phenoxide ligands and that proton NMR spectra and electrochemical measurements are useful and unambiguous means of differentiating the hexanuclear and tetranuclear clusters of the same stoichiometry.

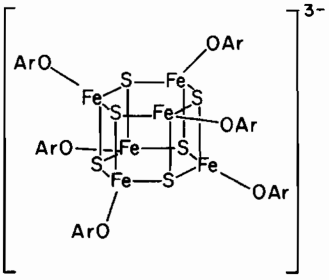

Fig. 1. Schematic drawing of proposed structure for $[Fe_6S_6(OAr)_6]^{3-}$ ion.

Reaction of 40 equivalents of anhydrous p-ClC_6H_4OH with $(Et_4N)_2[Fe_4S_4(S$-t-$Bu)_4]$ in MeCN followed by repeated evaporation of solvent *in vacuo* results in the formation of **I**, isolated as dark orange-brown crystals that were recrystallized from MeCN/i-PrOH. *Anal.* Calcd. for $C_{60}H_{84}N_3O_6S_6Cl_6Fe_6$: C, 42.80; H, 5.03; N, 2.50; S, 11.43; Cl, 12.64; Fe, 19.90. Found: C, 42.53; H, 5.02; N, 2.44; S, 12.30; Cl, 13.49; Fe, 20.80**. In an analogous manner, reaction of p-cresol with $(Et_4N)_2[Fe_4S_4(S$-t-$Bu)_4]$ produces **IIa**. Reaction of $(Me_4N)_2[Fe_4S_4Cl_4]$ with 4 equivalents of anhydrous NaO-p-Tol in MeCN, followed by filtration to remove NaCl, yields **II**, isolated as dark orange-brown crystals that were recrystallized from MeCN/i-PrOH. *Anal.* Calcd. for $C_{54}H_{78}N_3O_6S_6Fe_6$: C, 46.56; H, 5.64; N, 3.02; S, 13.81; Fe, 24.06. Found: C, 45.32; H, 5.27; N, 3.14; N, 3.14; S, 13.33; Fe, 23.30. The reaction conditions used were identical to those which produce authentic salts of $[Fe_4S_4(OAr)_4]^{2-}$ [4] and seem to represent core structure selectivity based on the size of the quaternary cation. Similar reactivity was observed by Coucouvanis [5] and co-workers where, under identical conditions, **III** was obtained rather than $[Fe_4S_4Cl_4]^{2-}$ when a smaller cation was used.

The electronic absorption spectrum of **II** in MeCN solution has maxima at 436, 282 and 242 nm. The spectrum is qualitatively similar to that of $(Bu_4N)_2[Fe_4S_4(O$-p-$Tol)_4]$ (**IV**) [4]. The major difference is a red shift of ~20 nm in the main band at 436 nm for **II** relative to **IV**. This band is tentatively assigned to terminal ligand-to-metal charge transfer. A bulk magnetic moment of 1.40 BM per Fe was obtained for **II** and suggests the presence of antiferromagnetic coupling. The ^1H NMR spectra of **I** and **II** show isotropically shifted resonances due to the aryl protons. The observed shifts (**I**, 5.32(o-H), −5.00(m-H); **II**, 5.56(o-H), −5.15(m-H), −6.10(p-CH_3) ppm *vs.* the free phenol at 22 ℃) follow the typical pattern for dominant contact interaction. The magnitude of the shifts increases with increasing temperature, as expected for an antiferromagnetically coupled system. These spectra are qualitatively similar to those obtained for the phenolate tetramer dianions [4]. At any temperature, however, the magnitude of

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**We note that obtaining reproducible and satisfactory elemental analyses of these complexes was difficult, due to their sensitivity to water and oxygen; results cited are typical. Proton NMR results indicate that the complexes are >98% pure.

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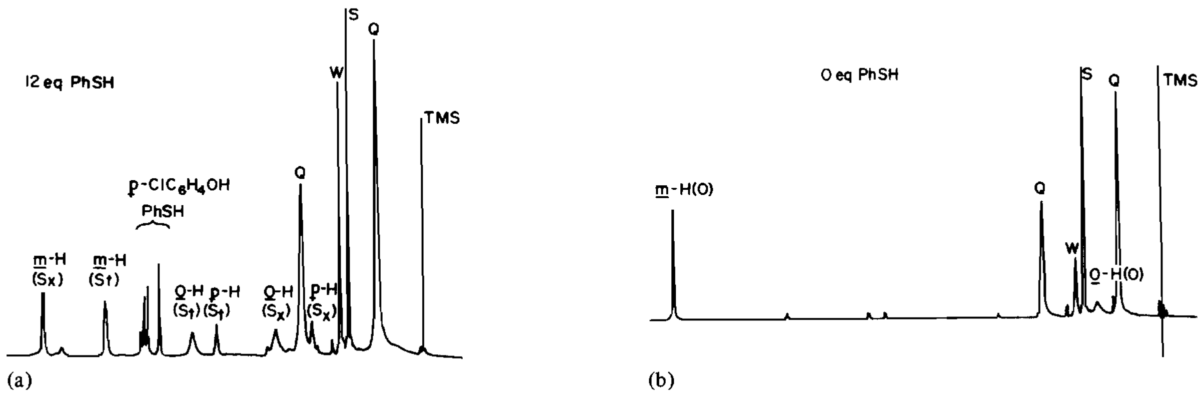

Fig. 2. Proton NMR spectra of $(Et_4N)_3$ $[Fe_6S_6(OC_6H_4\text{-}p\text{-}Cl)_6]$ in MeCN treated with indicated amounts of PhSH. Peaks are labelled as follows: TMS, tetramethylsilane; Q, cation; S, solvent; W, residual water; *m*- or *o*-H(0), *meta*- or *ortho*-protons of coordinated $p\text{-}ClC_6H_4O^-$; S_t, peaks due to coordinated thiophenoxide in $[(Fe_4S_4(SPh)_4]^{2-}$; S_x, peaks due to thiophenoxide coordinated to unidentified Fe–S center, presumably $[Fe_6S_6(SPh)_6]^{3-}$.

the shifts for **II** is approximately twice that observed for **IV**, suggesting a greater degree of spin delocalization in the former. The zero field ^{57}Fe Mössbauer spectrum of polycrystalline **II** at 4.2 K shows a single quadrupole doublet with δ = 0.54 mm/s and ΔE_Q = 1.12 mm/s (*vs.* Fe metal at room temperature). Application of a small (600 G) magnetic field results in essentially no change in the spectrum, suggesting a diamagnetic ground state. In addition, δ and ΔE_Q are not significantly different from those obtained for **IV** under the same conditions [4]. These results demonstrate the similarity of the electronic environment of the Fe atoms in **II** and **IV**. This behavior is paralleled in the ^{57}Fe Mössbauer results [5] of **III** and $[Fe_4S_4Cl_4]^{2-}$. Electrochemical measurements on **I** and **II** (DC polarography at DME and cyclic voltammetry at glassy carbon) show three reductions (**I**, E_1 = −1.12 V, E_2 = −1.73 V, E_3 = −2.04 V; **II**, E_1 = −1.19 V, E_2 = −1.73 V, E_3 = −1.99 V, differential pulse polarographic peak potentials *vs.* SCE) in contrast to **IV**, which shows only two reductions (E_1 = −1.20 V, E_2 = −1.85 V) over the same potential range (0 to −2.5 V). Examination of the data indicates that the first reduction of **I** and **II** is quasireversible, while the second and third reductions are irreversible. Electrochemical measurements [5] on **III** also show a quasireversible reduction in the same range as the first reduction of $[Fe_4S_4Cl_4]^{2-}$.

In an effort to obtain more detailed information on the nature of **I** and **II**, a ligand exchange reaction was performed and monitored by proton NMR spectra. Solutions containing **I** and PhSH in various ratios were examined. Selected spectra are presented in Fig. 2. As with the phenolate tetramers, addition of PhSH results in release of free $p\text{-}ClC_6H_4OH$, shown by the appearance of appropriate peaks at ~−7 ppm, and a decrease in intensity of the isotropically shifted resonances of coordinated $O\text{-}p\text{-}C_6H_4Cl$ ligands.

At −9 eq. PhSH, resonances due to $[Fe_4S_4(SPh_4)]^{2-}$ begin to appear. At 12 eq. PhSH, two isotropically shifted resonances in approximately a 1:1 ratio are apparent. One set clearly corresponds to $[Fe_4S_4(SPh)_4]^{2-}$ [7], and the other set corresponds to no presently known Fe–S cluster. At the same time, resonances due to free PhSH appear for the first time, indicating that the titration is complete. Presumably **I** was converted to $[Fe_6S_6(SPh)_6]^{3-}$ with partial decomposition to $[Fe_4S_4(SPh)_4]^{2-}$. Additional equivalents of PhSH result in further reaction to produce substantial quantities of thiophenolate tetramer. These results are in agreement with the observation [5] that **III** is converted to $[Fe_4S_4(SPh)_4]^{2-}$ on addition of excess KSPh.

The results presented here for **I** and **II** are consistent with the proposed structure shown in Fig. 1. In addition, they represent evidence that oxygen terminal ligands available to a protein in the tyrosinate moiety can stabilize unusual or 'metastable' Fe–S cluster core structural types. An oxygen donor ligand has been tentatively identified as a ligand to the $[Fe_3S_3]$ center of *Azotobacter vinelandii* ferredoxin I [8]. Together with the results of Coucouvanis [5] and Pohl [6], these results also suggest the possibility of obtaining novel synthetic Mo–Fe–S clusters related to the FeMo-cofactor of nitrogenase [9] via the use of terminal ligands that are more electronegative than thiolate sulfur.

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