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A Synthetic Iron–Sulfur Cluster with Phenoxide Terminal Ligands

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In addition to the iron–molybdenum cofactor [1], a novel molybdenum–iron–sulfur cluster of as yet unknown structure [2], the molybdenum–iron protein of nitrogenase contains additional iron–sulfur centers released as 4Fe–4S clusters upon treatment with thiols in denaturing organic solvents [3]. The only technique thus far used to examine these centers *in situ* is ^{57}Fe Mössbauer spectroscopy, which has shown that they contain iron in two distinct sites in a 1:3 ratio. Three iron atoms termed D (with a small quadrupole splitting) and one iron atom termed Fe^{2+} (with Mössbauer parameters typical of high-spin Fe^{2+} in a tetrahedral sulfur environment) comprise a diamagnetic (S = O) unit, called a 'P-cluster' [4]. This and the fact that oxidation by one electron per P-cluster yields a paramagnetic state ($S \geqslant 5/2$) has led to the conclusion that the P-clusters are a variant of normal 4Fe–4S clusters in the fully reduced ($[4Fe–4S]^{o}$) oxidation state. The most likely means of differentiating the iron atoms D from Fe^{2+} is coordination of the former by non-sulfur protein ligands, with oxygen (phenoxide or carboxylate) being most likely. Holm [5] has generated in solution and measured some physical properties of a carboxylate-substituted iron–sulfur tetramer, but to date no iron–sulfur clusters with oxygen ligands have been prepared in pure form. We report herein the preparation and some of the properties of the first such synthetic complex, $(Et_4N)_2[Fe_4S_4(OPh)_4]$ (*I*).

Reaction of 40 equivalents of anhydrous, sublimed phenol with $(Et_4N)_2[Fe_4S_4(SEt)_4]$ in acetonitrile establishes an equilibrium in which a small fraction of bound ethanethiolate is displaced by phenol [6]. Repeated removal of solvent *in vacuo* produces $(Et_4N)_2[Fe_4S_4(OPh)_4]$ (*I*), isolated as well-formed red-black plates upon recrystallization from dry acetonitrile/isopropanol. *Anal.*: Calcd. for $C_{40}H_{60}Fe_4N_2O_4S_4$: C, 48.80; H, 6.14; Fe, 22.69; N, 2.84; O, 6.50; S, 13.03. Found: C, 48.49; H, 6.26; Fe, 22.08; N, 2.87; O, 6.93; S, 13.14.

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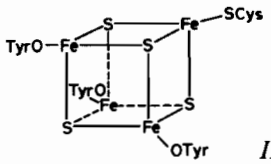
The optical spectrum of *I* in acetonitrile solution has maxima at 410 nm and 239 nm (ϵ =15,700 and 44,000 M^{-1} cm^{-1}), respectively, with shoulders at 650, 320, and 272 nm. These bands are thus blue-shifted by 38 and 21 nm, respectively, compared to similar features observed [7] for $(Et_4N)_2[Fe_4S_4(SPh)_4]$ (*II*), as expected upon replacing a sulfur donor by more electronegative oxygen. The magnetic moment per iron, μ_{Fe}, is 1.19 μ_B for *I* in the solid state at 22 °C, essentially unchanged from that reported [8] for *II* (1.09 μ_B). In zero applied field, the ^{57}Fe Mössbauer spectrum of *I* shows only a simple quadrupole doublet with δ = 0.50 and ΔE_Q = 1.21 mm/sec at 4.2 K (*vs.* metallic Fe at room temperature), compared to 0.35 and 1.10 mm/sec for *II* [9]. More interesting are ^{1}H NMR spectra and electrochemical measurements, which give unexpected results. Isotropically shifted ^{1}H NMR spectra are observed for *I* in CD_3CN solution; the observed shifts, (*o*-, *m*-, *p*-H at +2.28, –2.25, and +2.83 ppm *vs.* free PhOH at 22 °C) show a pattern typical of dominant contact interaction. At any temperature, however, the magnitude of the shifts for *I* is approximately twice that observed [10] for *II*, suggesting significantly greater delocalization of spin into the phenyl rings of the former, a result of the greater covalent character of the Fe–O bond. All isotropic shifts increase in magnitude with increasing temperature, as expected for an antiferromagnetically coupled system [10]. Electrochemical measurements (DC polarography at DME; cyclic voltammetry at platinum flag) show that *I* is reduced sequentially in reversible one-electron steps at –1.08 and –1.80 *vs.* SCE, compared to –0.98 and –1.66 V for *II*. Phenoxide ligation thus makes the $[4Fe–4S]^{2+}$ core *more* difficult to reduce (by ~100 mV) than for thiophenoxide; for comparison, substitution by chloride [11] (in the $[Fe_4S_4Cl_4]^{2-}$ ion) causes a *positive* shift in $E_{1/2}$ of about 200 mV, while carboxylate substitution (in $[Fe_4S_4(OAc)_4]^{2-}$) causes a positive shift of ~100 mV [5]. The seemingly anomalous electrochemical data may be explained by the high affinity of phenoxide ligands for *ferric* ion. Reduction of the $[4Fe–4S]^{2+}$ core will decrease the ferric character of the iron (if a delocalized description [12] is still correct in this case), and is therefore more difficult with phenoxide ligands.

Our results show that simple iron–sulfur clusters with phenoxide ligands are stable chemical species capable of existing in several net oxidation states. The most notable effect of substituting phenoxide for thiophenoxide is a negative shift of both first and second reduction potentials, indicating that Fe_4S_4 centers coordinated to a protein *via* tyrosinate residues will have reduction potentials either comparable to or slightly more negative than normal

Fe_4S_4 clusters with cysteine ligands [13] Together with the observed change in ^{57}Fe isomer shift to higher velocity, these results are consistent with, but do not uniquely specify, a structure such as *III* for the P-clusters of nitrogenase Further experiments aimed at generating and characterizing more highly reduced clusters with phenoxide ligands are in progress



III

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References

1 V K Shah and W J Brill, *Proc Natl Acad Sci U S A, 74,* 3249 (1977)
2 J Rawlings, V K Shah, J R Chisnell, W J Brill, R Zimmerman, E Munck and W H Orme-Johnson, *J Biol Chem, 253,* 1001 (1978)
3 G B Wong, D M Kurtz, Jr, R H Holm, L E Mortenson and R G Upchurch, *J Am Chem Soc, 101,* 3078 (1979), D M Kurtz Jr, R S McMillan, B K Burgess, L E Mortenson and R H Holm, *Proc Natl Acad Sci U S A, 16,* 4986 (1949)
4 B H Huynh, M T Henzl, J A Christner, R Zimmerman, W H Orme-Johnson and E Munck, *Biochim Biophys Acta, 623,* 124 (1980), R Zimmerman, E Munck, W J Brill, V K Shah, M T Henzl, J Rawlings and W H Orme-Johnson, *ibid, 537,* 185 (1978), E Munck, H Rhodes, W K Orme-Johnson, L C Davis, W J Brill and V K Shah, *ibid, 400,* 32 (1975)
5 R W Johnson and R H Holm, *J Am Chem Soc, 100,* 5338 (1978)
6 L Que Jr, M A Bobrik, J A Ibers and R H Holm, *J Am Chem Soc, 96,* 4168 (1974)
7 B V DePamphilis, B A Averill, T Herskovitz, L Que Jr and R H Holm, *J Am Chem Soc, 96,* 4159 (1974)
8 E J Laskowski, R B Frankel, W O Gillum, G C Papaefthymiou, J Renaud, J A Ibers and R H Holm, *J Am Chem Soc, 100,* 5322 (1978)
9 R B Frankel, B A Averill and R H Holm, *J Phys (Paris), 35,* C6-107 (1974)
10 R H Holm, W D Phillips, B A Averill, J J Mayerle and T Herskovitz, *J Am Chem Soc, 96,* 2109 (1974)
11 G B Wong, M A Bobrik and R H Holm, *Inorg Chem, 17,* 578 (1978)
12 R H Holm, B A Averill, T Herskovitz, R B Frankel, H B Gray, O Siiman and F J Grunthaner, *J Am Chem soc, 96,* 2644 (1974)
13 C L Hill, J Renaud, R H Holm and L E Mortenson, *J Am Chem Soc, 99,* 2549 (1977)