

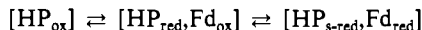
Synthesis and Study of an Analogue for the $[\text{Fe}_4\text{S}_4]^{3+}$ Center of Oxidized High-Potential Iron-Sulfur Proteins¹

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Metalloproteins containing the $[\text{Fe}_4\text{S}_4]$ cluster comprise an important class of iron-sulfur proteins.³ Extensive biochemical⁴ and inorganic⁵ model studies have established that the three $[\text{Fe}_4\text{S}_4]^{n+}$ ($n = 1, 2, 3$) oxidation levels of these proteins correspond to biologically relevant redox centers of the ferredoxins (Fd) and high-potential (HP) proteins:



Factors associated with the apparent instability of the highest core oxidation level ($n = +3$) have been discussed in the context of both the biological and the inorganic systems. Except in the HP case, reversible one-electron oxidation of the $[\text{Fe}_4\text{S}_4]^{2+}$ centers in proteins has not been observed.⁶ Furthermore, electrochemical studies of numerous model complexes of the type $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ have detected the likelihood of one-electron oxidations in only a few instances. These oxidations have been described, at best, as being near reversible and in no case has chemical or controlled potential oxidation clearly generated a stable, characterizable species containing the $[\text{Fe}_4\text{S}_4]^{3+}$ core.^{5,8-10}

Since we have shown that sterically encumbered thiolates can stabilize monomeric metal complexes in high formal oxidation states,¹¹ it was reasoned that these ligands could assist in stabilizing the $[\text{Fe}_4\text{S}_4]^{3+}$ core oxidation level. Herein, we report electrochemical and chemical studies which show the $-1/-2$ redox couple of $[\text{Fe}_4\text{S}_4(\text{S}-2,4,6-(i\text{-Pr})_3\text{C}_6\text{H}_2)_4]^{2-}$ (**1**) and $[\text{Fe}_4\text{S}_4(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4]^{2-}$ (**2**) to be reversible and report the synthesis and subsequent structural and spectroscopic characterization of a compound, $[\text{Fe}_4\text{S}_4(\text{S}-2,4,6-(i\text{-Pr})_3\text{C}_6\text{H}_2)_4](\text{Bu}_4\text{N})$ (**3**), containing the $[\text{Fe}_4\text{S}_4]^{3+}$ center.

Electrochemical studies demonstrated that compounds **1** and **2** are each capable of being oxidized and reduced by one electron in CH_2Cl_2 and in CH_3CN .¹² The reversibility of the electrode process was evaluated by normal-pulse (NP) and reverse-pulse (RP) voltammetric techniques which gave $E_{1/2}$ ¹³ (slope; $i_1(\text{cath})/i_1(\text{anod})$)¹⁴ values of the $-1/-2$ and the $-2/-3$ couples

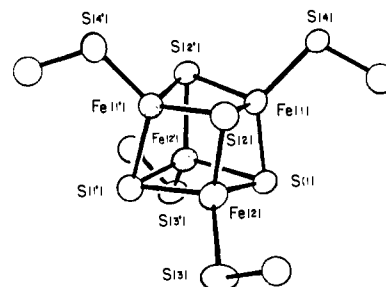


Figure 1. $[\text{Fe}_4\text{S}_4(\text{Si-C})_4]$ unit of **3**. Selected distances (Å) and angles (deg): Fe1-S2 2.280 (8), Fe1-S2' 2.279 (7), Fe1-S1 2.233 (7), Fe2-S1 2.273 (7), Fe2-S1' 2.269 (7), Fe2-S2 2.236 (7), Fe1-S4 2.203 (7), Fe2-S3 2.208 (7), Fe-S-C_{av} 104 (1), Fe-Fe(av) 2.74 (1), S₆-S₆(av) 3.55 (4).

respectively to be -0.12 (62 mV; 0.96) and -1.20 V (61 mV; 0.87) for compound **1** and -0.05 (59 mV; 0.96) and -1.10 V (69 mV; 0.72) for compound **2** in CH_2Cl_2 .^{16,17} The reversibility of the $-1/-2$ couple was verified by controlled-potential electrolysis. Upon Coulombic oxidation, both **1** and **2** cleanly liberate 1 equiv of electrons to generate solutions of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^-$. Subsequent polarographic and cyclic voltammetric studies of these solutions show the electrolysis to be clean and quantitative. Moreover, compounds **1** and **2** can be shuttled between the $-2/-1$ states by controlled-potential electrolysis without substantial decomposition of the compound over several cycles in CH_2Cl_2 .¹⁸ The ultimate test of chemical reversibility is the synthesis and isolation of both species involved in the redox couple. The reaction of **1** with $[(\text{C}_5\text{H}_5)_2\text{Fe}]\text{BF}_4$ in CH_2Cl_2 produces **3**, which was isolated in yields of 35% after several recrystallizations from a mixture of CH_2Cl_2 and Et_2O .

The formulation of **3** was confirmed by an X-ray crystallographic study.¹⁹ The ORTEP diagram in Figure 1 shows the $[\text{Fe}_4\text{S}_4(\text{Si-C})_4]$ unit of the anion, which has crystallographic C_2 symmetry and approximate D_{2d} symmetry. The average Fe-S distance (2.26 Å) and Fe-SR distance (2.21 Å) of **3** are very similar to the corresponding distances obtained from the X-ray structure of the $[\text{Fe}_4\text{S}_4]^{3+}$ center in HP_{ox} of *Chromatium vinosum*.⁴ In comparison to the synthetic analogues containing the $[\text{Fe}_4\text{S}_4]^{2+}$ core oxidation level,^{5,20,21} the average Fe-S and Fe-SR distances in **3** are shorter by about 0.02 and 0.04 Å, respectively. Comparable metrical differences and trends have been observed for analogues containing the $n = +2$ and $+1$ core oxidation levels.^{5,21} There is no structural evidence for localized bonding in the $[\text{Fe}_4\text{S}_4]^{3+}$ core of **3**, which is formally comprised of three Fe^{3+} and one Fe^{2+} ions. Inspection of the geometry of the $[\text{Fe}_4\text{S}_4]$ core

(1) O'Sullivan, T.; Millar, M., presented in part at the 188th National Meeting of the American Chemical Society, Philadelphia, 1984, INORG #173.

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(6) Upon oxidation, many Fd_{ox} centers decay into 3-Fe clusters.⁷

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(12) Electrochemical data were obtained in 0.20 M solutions of $[(n\text{-Bu})_4\text{N}]\text{BF}_4$ using a platinum disk (Bioanalytical Systems) as the working electrode and a SCE as the reference electrode.

(13) The $E_{1/2}$ values are from the NP experiments. The difference between the $E_{1/2}$ values for the NP and RP experiments are in the range 0.00-0.02 V.

(14) In NP voltammetry, a reversible electrode process is indicated by a linear plot of E vs. $\log [(i_1 - I)/i_1]$ with a slope of $2.303RT/nF$. For a reversible redox process the NP and RP voltammetric waves are superimposable: $|i_1(\text{cath})/i_1(\text{anod})| = 1$ and the $E_{1/2}$ of the NP and RP scans are the same.¹⁵

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(16) In comparison, the E_m reported for $\text{HP}_{\text{ox}}/\text{HP}_{\text{red}}$ for *Chromatium vinosum* HP is +0.350 vs. SHE²³ (corrected to +0.11 vs. SCE).

(17) During the course of this work it was reported by Nakamura⁹ that **1** and $[\text{Fe}_4\text{S}_4(\text{S}-2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2)_4]^{2-}$ exhibit quasi-reversible and irreversible cyclic voltammetric processes, respectively, in DMF.

(18) After two complete electrolytic cycles, about 80% of the starting compounds, **1** and **2**, could be detected by electrochemical measurement and by electronic spectroscopy.

(19) $[\text{N}(n\text{-Bu})_4][\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4)_4]$ crystallizes in the monoclinic space group $C2/c$ with $a = 30.618$ (8) Å, $b = 11.909$ (4) Å, $c = 25.117$ (7) Å, $\beta = 101.94$ (2)°, $V = 8960$ (9) Å³, $Z = 4$. Due to the small size of the crystal only a limited data set was collected using Mo radiation at room temperature. The structure was solved using direct and Fourier methods. The limited data set allowed anisotropic refinement of only the iron and the sulfur atoms. The nitrogen atom in the $[\text{N}(n\text{-Bu})_4]$ cation is located on a crystallographically imposed twofold axis. Final least-squares refinement (209 variables) gave $R = 0.077$, $R_w = 0.086$ using 1036 unique reflections $I > 3\sigma(I)$ ($2\theta < 40^\circ$).

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shows it to be tetragonally compressed with four short Fe-S bonds [2.233 (7)-2.236 (7) Å, which approximately parallel to the idealized S_4 axis] and eight long Fe-S bonds [2.269 (7)-2.280 (8) Å, which are perpendicular to the S_4 axis]. The factors that cause the distortions in the $[\text{Fe}_4\text{S}_4]$ units of iron-sulfur proteins and their model compounds as well as the biological significance of these distortions are not well understood.^{4,20-22}

Chemical and electrochemical oxidation of orange-brown solutions **1** and **2** produce intense red-brown solutions of **3** and of $[\text{Fe}_4\text{S}_4(\text{S}-2,3,5,6-\text{Me}_4\text{C}_6\text{H}_4)_4]^{1-}$ (**4**). Upon oxidation of HP_{red} to HP_{ox} , the major band in the visible spectrum shifts to longer wavelengths,²³ which is the same trend observed on conversion of **1** into **3** and **2** into **4**.²⁴ Interestingly, the stability of **3** and **4** are very sensitive to solvent conditions; neither compound is stable in DMF or CH_3OH . Chemical, electrochemical, and electronic spectral studies indicate that **3** is more stable than **4** and that both **3** and **4** are most stable in solvents of low polarity (with the stability in DMF \ll $\text{CH}_3\text{CN} < \text{CH}_2\text{Cl}_2$). These observations are relevant to the situation in biological systems, where the unique stability of the $[\text{Fe}_4\text{S}_4]^{3+}$ core of the HP proteins has been attributed to the hydrophobic environment of the iron-sulfur center.^{4,25} Chemical and spectroscopic studies of **3** and related $[\text{Fe}_4\text{S}_4]^{3+}$ clusters are continuing.

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Registry No. **1**, 96455-57-1; **1**⁻, 96455-63-9; **2**, 96455-59-3; **2**⁻, 96455-64-0; **3**, 96455-61-7; **4**, 96455-62-8; $[(\text{C}_6\text{H}_5)_2\text{Fe}]\text{BF}_4$, 1282-37-7.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(23) Dus, K.; De Klerk, H.; Sletten, K.; Bartsch, R. G. *Biochim. Biophys. Acta* **1967**, *140*, 291.

(24) The electronic spectra of **1-4** in CH_2Cl_2 solution are as follows: for **1** $\lambda = 410$ (ϵ 24 500), 335 (19 400), 245 nm sh (52 800); for **2**, 414 (22 200), 342 (18 200), 245 nm (sh) (42 300); for **3**, 475 (28 100), 328 (13 400), 276 (sh) (23 700), 236 nm (sh) (48 000); for **4** (electrolysis solution), 458 (23 600), 331 (13 800), 274 (13 800), 240 nm (sh) (41 900).

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Dimethylsilylene: A Trisilane and a Geminal Diazide as New Photochemical Precursors. Evidence for an Absorption Maximum near 450 nm

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The yellow species ($\lambda_{\text{max}} \cong 450$ nm) produced by the irradiation of **1**³⁻⁵ or **2**⁴ in a hydrocarbon glass at 77 K (characterized by UV-vis absorption and emission) and of **1**³⁻⁵ or **3**⁶ in Ar or N_2 matrices at 10 K (characterized by UV-vis and IR) and by the flash pyrolysis⁶ of **4** or **5** with trapping in Ar or N_2 matrices (characterized by UV-vis and IR) has been identified³⁻⁶ as dimethylsilylene **6**.

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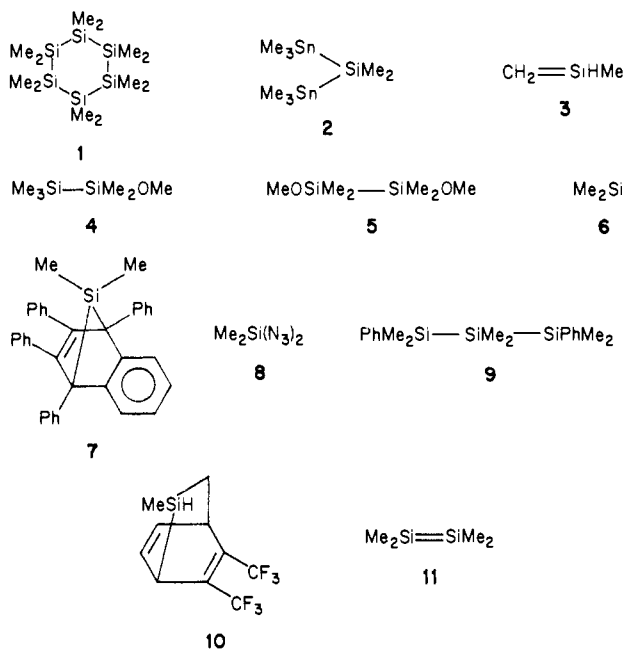
(2) University of Wisconsin.

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This assignment has been recently questioned^{7,8} since room-temperature flash photolysis of **1** and **7**, two known photochemical precursors of **6**, did not yield detectable absorption at 450 nm. Instead, flash photolysis of **1**⁸ produced a species absorbing at 350 nm in hydrocarbon solution and at 300 nm in tetrahydrofuran, whose reactivity toward Et_3SiH and MeOH was similar to that of a silylene. The authors proposed that (i) either the absorption maximum of **6** in a hydrocarbon undergoes a 100-nm hypsochromic shift from a rigid solution at 77 K to a fluid solution at 298 K (ii) or the original structure assignment³ is wrong.

We now wish to report additional evidence which favors the original assignment,³ using **8** and **9** as new precursors for **6**. We propose that (i) either the above hypsochromic shift alternative applies, although this seems unlikely for reasons discussed below, or (ii) the proposed reassignment⁸ of the 350-nm maximum to ground state **6** is wrong.

The irradiation^{9a} of matrix-isolated **8** at 10 K induced an intense yellow color. Comparison of matrix IR and UV-vis spectra with those previously obtained by irradiation of **1**³⁻⁶ or **3**⁶ showed that the yellow species originally assigned as **6** is a major product. Irradiation with visible light bleached the color as reported earlier³⁻⁶ and converted the yellow species to 2-silapropene **3** (characterized by IR and UV⁴⁻⁶). As expected,⁶ UV irradiation^{9b} of **3** caused reversion to the yellow species. Difference spectroscopy yielded the IR spectra of **3** and **6**. Photoselection with linearly polarized light confirmed the earlier polarization results.⁵ As a function of the matrix, the λ_{max} values of **6** were N_2 430, Ar 450, Kr 455, and Xe 470 nm. Although significant, these solvent shifts were not nearly as large as the 150-nm hypsochromic shift reported⁶ for CH_3SiH upon going from Ar to N_2 matrix.

UV irradiation^{9a} of **9**¹⁰ in rigid 3-methylpentane at 77 K produced a yellow glass with broad absorption bands at 326 and 450 nm. The latter had the characteristic location and broad shape obtained using other precursors for **6**. The bands disappeared upon

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(9) (a) At 254 nm (low-pressure Hg lamp). (b) At 248 nm (KrF excimer laser).

(10) Synthesized by adding a THF solution of PhMe_2SiLi (from 1.49 g of Li, 0.2 mol, and 8.27 mL of PhMe_2SiCl , 0.05 mol) dropwise to 3 mL of Me_2SiCl_2 (0.025 mol) in 20 mL of THF at 0 °C. When the red color of PhMe_2SiLi persisted, the addition was stopped and 10 mL of H_2O added. Extraction with hexane, drying over MgSO_4 , and distillation yielded 2.4 g (30%) of **9**: bp 147-150 °C (0.7 mm); $^1\text{H NMR}$ (CDCl_3) δ 0.36 (s, 6 H), 0.54 (s, 12 H), 7.36 (m, 10 H); MS (70 eV), m/z 328 (M^+ , 2.4%), 193 ($\text{M}^+ - \text{PhMe}_2\text{Si}$, 13%), 135 (PhMe_2Si , 43%), 133 (100%); exact mass for $\text{C}_{18}\text{H}_{20}\text{Si}_3$ m/e calcd 328.1491, found 328.1500.