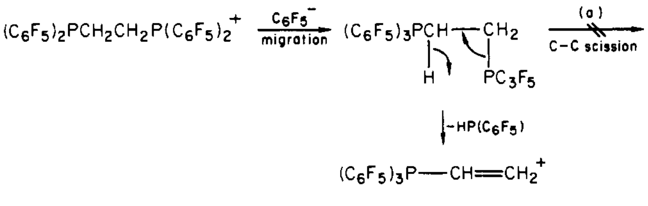
Scheme I



Similar to the formation of $(C_6H_5)_3P^+$ from dppe[12] is the formation of $(C_6F_5)_3P^+$ from pfpe. The peak at *m/e* 559 can be rationalized by C_6F_5 migration followed by loss of C_6F_5PH to give $(C_6F_5)_3P—CH{=}CH_2^+$. The C–C bond fission, which occurs at point a (Scheme I) in dppe to give $(C_6H_5)_3P{=}CH(C_6H_5)^+$, does not occur in pfpe to give the corresponding peak at *m/e* 545 for $(C_6F_5)_3P{=}CH(C_6F_5)^+$. The differences in the mass spectra of dppe and pfpe are presumably due to changes in the stability of the generated ions when F is substituted for H.

Known methods used to prepare organophosphine ligands from $RPCl_2$ precursors were expected to work in the syntheses of $R_2PCH_2CH_2PR_2$ from the $Cl_2PCH_2CH_2PCl_2$ precursors. Our recent synthesis of pfpe from $Cl_2PCH_2CH_2PCl_2$ using Grignard and metalation reactions and the recent syntheses of $R_2PCH_2CH_2PR_2$ (where R is $HOOCCH_2$–, CH_3O–, CH_3–, C_2H_5–, and cyclohexyl)[13,17,18] from $Cl_2PCH_2CH_2PCl_2$ have shown this to be the case.

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Registry No. pfpe, 76858-94-1; C_6F_5Br, 344-04-7; C_6F_5Li, 1076-44-4; $Cl_2PCH_2CH_2PCl_2$, 28240-69-9.

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Communications

Synthetic Models for the Iron-Sulfur Protein Rubredoxin: Synthesis, Structure, and Properties of a Highly Symmetric Iron(III) Tetrathiolate Anion

Sir:

Most Fe(III) and Cu(II) compounds react with thiolates to give disulfides; in the process the metal is reduced. There are several important metalloproteins in which the Fe(III)-to-cysteine and Cu(II)-to-cysteine ligation modes are stabilized with regard to autoredox reactions.[1] Herein, we report the use of a sterically hindered thiolate to prepare the first example of a stable iron(III) tetrathiolate complex containing only monodentate ligands, $(Et_4N)(Fe(SC_{10}H_{13})_4)$ (**1**).

The reaction of 4 equiv of lithium 2,3,5,6-tetramethylbenzenethiolate[2] directly with $FeCl_3$ and Et_4NBr or with $FeCl_2$ and Et_4NBr followed by controlled air oxidation gives in both cases high yields (80–90%) of **1**. Compounds **1** is thermally stable as evidenced by the fact that it is recrystallized without decomposition from hot (100 °C) DMF. The room-temperature electronic spectrum (in CH_3CN) of **1** exhibits bands at $\lambda = 295$ nm ($\epsilon = 14300$), 344 nm (6880), and 450 nm (7230).

Stable iron(III) tetrathiolate complexes are rare in spite of considerable efforts to prepare such compounds.[3] Besides the protein rubredoxin[4] the only other example is $(Fe(S_2\text{-}o\text{-}xyl)_2)^-$ (**2**), where the iron is chelated by two *o*-xylenedithiolate ligands.[5] Attempts to oxidize $(Fe(SC_6H_5)_4)^{2-}$ (**3**) to the Fe(III) derivative have not been successful.[6] A comparison of the Fe^{3+}/Fe^{2+} redox potential of **1** (–0.85 V vs. SCE), **2** (–1.0 V),[5] and **3** (–0.52 V)[7] shows the 3+ oxidation state to be more stable in **1** and **2** than it would be in the Fe(III) analogue of **3**. This result is consistent with the idea that electron-rich thiolates can stabilize highly charged metal ions. However, this effect is two-edged, since electron-rich thiolates are potential reducing reagents and could participate in the reduction of Fe(III).[8] The steric and conformational properties of the thiolate ligands are crucial in accounting for the stability of iron(III) tetrathiolate complexes.

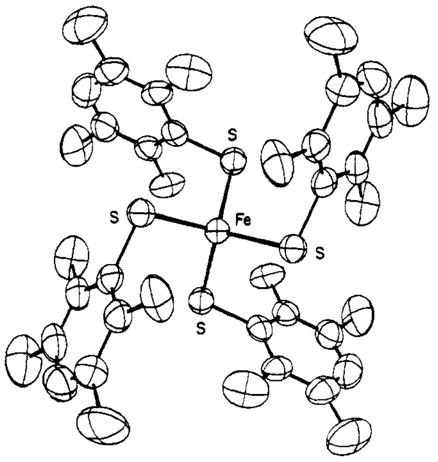

Figure 1. ORTEP diagram of $[Fe(SC_{10}H_{13})_4]^-$ viewed down the crystallographic S_4 axis. The Fe–S distance is 2.284 (2) Å.

An X-ray diffraction study of **1**[9] reveals the highly sym-

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metric structure of the anion (Figure 1). Crystal state symmetry demands that the discrete $(Fe(SR)_4)^-$ anions have the rare S_4 ($\bar{4}$) point group symmetry. The FeS_4 local symmetry is therefore rigorously D_{2d}, compressed from T_d symmetry along the S_4 axis. The two equivalent S–Fe–S angles bisected by the S_4 axis are 114.4 (1)°, while the remaining four angles are equal to 107.08 (5)°. The conformation of the arenethiolate ligands relative to each other and to the FeS_4 core is determined by the angles θ, α, and β. The Fe–S–C angle, θ = 102.4 (2)° is typical;[5,6] both the torsion angles α and β,[10] are nearly 90° and act to create a symmetric conformation, which is not crystallographically required. The conformation of molecule **1** is not distorted in spite of the steric requirements of the ortho-disubstituted ligands.

The geometry of **1** is not only aesthically pleasing but also biologically relevant. Recent refinement of the X-ray crystal structure of oxidized rubredoxin from *Clostridium pasteurianum*[11] shows that the geometry of the $Fe(SCH_2-)_4$ unit as well as the FeS_4 core closely approaches D_{2d} effective symmetry.[12] It is important to consider the position of the α-carbons in this discussion since it is the orientation of these carbons that determines the positioning of the sulfur lone pairs and in turn influences the electronic properties of the FeS_4 centers. When the nonlinearity of the Fe–S–C linkage is taken into account, D_{2d} is the highest possible symmetry for the $Fe(SCH_2-)_4$ unit of rubredoxin. In the protein, the S_4 axis bisects the angles defined as S_6–Fe–S_{39} and S_9–Fe–S_{42}.[13] In contrast to the tetragonal compression along the S_4 axis observed in **1**, the FeS_4 unit in rubredoxin is tetragonally elongated along the S_4 axis.

The electronic and ESR spectral properties of $Fe^{III}(SR)_4$ compounds are quite sensitive to structural distortions of the $Fe(SCH_2-)_4$ unit. The ESR spectrum of **1** shows a sharp resonance at $g = 4.3$ over the temperature range 6–77 K,[14] which is similar to the result reported for rubredoxin.[15] In comparison, the ESR spectrum of **2** at 6 K is more complex, exhibiting resonances at $g = 8.4$ and 5.3 as well as at $g = 4.3$, which reflects the low symmetry of the $Fe(SCH_2-)_4$ unit due to the conformational constraints of the bidentate ligands. Furthermore, the ESR spectrum of desulforedoxin from *Desulfovibrio gigas*[16] is also complex, which may indicate that the protein has a $Fe(SCH_2-)_4$ unit of low symmetry.

Work, using sterically encumbered thiolate ligands to create viable models for the metal center in metalloenzymes, is continuing.

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Registry No. 1, 82741-95-5.

Supplementary Material Available: Table of fractional coordinates and thermal parameters (1 page). Ordering information is given on any current masthead page.

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(9) **1** crystallizes as black tetrahedra in the tetragonal space group $I\bar{4}$ with $a = b = 12.366$ (2) Å, $c = 16.352$ (4) Å, $V = 2501$ (1) Å^3, and $Z = 2$. The X-ray data were collected on an Enraf-Nonius CAD4A diffractometer using molybdenum radiation. The structure was solved by using Patterson and difference Fourier methods using the computer programs of the Enraf-Nonius structure determination package. The iron atom is located at special position 2a. Final anisotropic refinement of all non-hydrogen atoms using 726 unique reflections with $I > 3\sigma(I)$ gave $R = 0.057$, $R_w = 0.076$.

(10) The torsion angle α(87°) is the dihedral angle made by the Fe–S–C plane with the S–Fe–S′ plane, where S′ is related to S by the C_2 (S_4^2) axis. The torsion angle β (90°) is measured by the angle between the Fe–S–C plane and the plane of the durenethiolate ligand.

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(13) If the FeS_4 unit had perfect D_{2d} symmetry, S_6–Fe–S_{39} (103.7°) and S_9–Fe–S_{42} (103.8°) should be equal and the four remaining S–Fe–S angles should be equal; rather, they are 112.4, 114.3, 113.8, and 109°.

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Tetragonal vs. Trigonal Coordination in Copper(II) Complexes with Tripod Ligands: Structures and Properties of $[Cu(C_{21}H_{24}N_4)Cl]PF_6$ and $[Cu(C_{18}H_{18}N_4)Cl]PF_6$

Sir:

There is a great deal of evidence supporting the notion that "Cu(I)-like" environments dominate the coordination chemistry of copper in redox-active metalloproteins. This includes the type I "blue" copper centers in copper electron-transfer proteins and multicopper oxidases[1] as well as the binuclear centers[2] in the oxygen carrier hemocyanin[3] and the monooxygenases tyrosinase and dopamine β-hydroxylase.[2,4] Evidence for coordination numbers of 4 or less,[1,2,5–7] imidazole coordination,[6–8] sulfur ligation,[7] and/or high redox potentials[1,9,10] is consistent with an environment favoring the reduced state of copper in these systems.

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