kylation supports the zwitterion formalism for **15**, attempts to react **15** with aldehydes failed. This palladium-complexed vinyl carbene[14] also fails to give reactions typical of carbenes—a type of behavior reminiscent of some nucleophilic carbenes.[6] Nevertheless, the facility of this palladium initiated α-elimination of α-acetoxysilanes suggests a new route to metal-complexed carbenes and supports the notion that palladium complexation imparts substantial polarization to such reactive intermediates.

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Registry No. (*E*)-**4**, 86422-21-1; (*Z*)-**4**, 86422-22-2; **5**, 86422-23-3; **6**, 86422-24-4; **7**, 10472-24-9; **8**, 86422-25-5; **9**, 86422-26-6; **10**, 86422-27-7; **11**, 86422-28-8; **12**, 86422-29-9; **13**, 86422-30-2; TMSC≡CCH$_2$OH, 5272-36-6; (*E*)-TMSCH═CHCH$_2$OH, 59376-64-6; (*Z*)-TMSCH═CHCH$_2$OH, 62861-80-7; (*E*)-TMSCH═CHBr, 41309-43-7; (*E*)-TMSCH═CHCH(OH)CO$_2$C$_4$H$_9$-*n*, 86422-31-3; (*E*)-TMSCH═CHCH$_2$OTMS, 86422-32-4; (*E*)-TMSCH═CHCH(OTMS)TMS, 86422-33-5; (Ph$_3$P)$_4$Pd, 14221-01-3; D$_2$C(CO$_2$CH$_3$)$_2$, 36647-07-1; *n*-butyl glyoxalate, 6295-06-3; methyl 2-oxo-1-(3-trimethylsilyl-2-propenyl)cyclopentanecarboxylate, 86422-34-6; dimethyl malonate, 108-59-8; methyl 1-deuterio-2-oxocyclopentanecarboxylate, 86422-35-7.

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Syntheses and Structures of the $[\mathrm{Fe^{III}(SPh)_4}]^-$ and $[\mathrm{Fe^{III}(SEt)_4}]^-$ Anions. A General Route to Iron(III) Tetrathiolate Complexes

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Since the first report of the X-ray crystal structure of oxidized rubredoxin in 1969,[1] there has been a recognized need for iron(III) tetrathiolate complexes to serve as synthetic analogues for the $[\mathrm{Fe^{III}(S\text{-}cys)_4}]$ unit of this protein. Although one example of this type of complex was achieved using a bidentate ligand,[2] attempts by several groups to obtain stable $[\mathrm{Fe^{III}(SR)_4}]^-$ complexes with monodentate thiolate ligands or with other polydentate ligands have all resulted in failure.[3] This lack of success has been ascribed to the tendency of $[\mathrm{Fe^{III}(SR)_4}]^-$ complexes to oligomerize and/or to undergo autoredox reactions to Fe$^{\mathrm{II}}$ and RSSR. Our recent success using the sterically hindered thiolate ligand 2,3,5,6-tetramethylbenzenethiolate to stabilize the $[\mathrm{Fe^{III}(SR)_4}]$ coordination unit[4] has prompted us to reexamine the problem of $[\mathrm{Fe^{III}(SR)_4}]^-$ complexes with less sterically hindered ligands. We wish to report a new and general route to the synthesis of stable iron(III) tetrathiolate complexes.

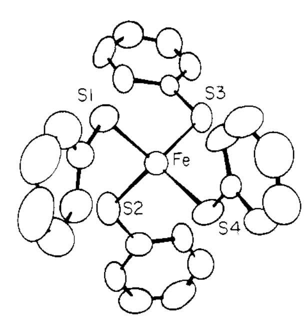

Figure 1. Anion of $[\mathrm{NEt_4}][\mathrm{Fe^{III}(SPh)_4}]$. Selected distances (Å) and bond angles (deg): Fe–S$_1$ 2.297 (3), Fe–S$_2$ 2.295 (3), Fe–S$_3$ 2.289 (3), Fe–S$_4$ 2.303 (3), Fe–S$_1$–C$_{11}$ 112.8 (4), Fe–S$_2$–C$_{21}$ 112.5 (4), Fe–S$_3$–C$_{31}$ 112.4 (5), Fe–S$_4$–C$_{41}$ 107.8 (5).

The reaction of $(\mathrm{NEt_4})[\mathrm{Fe(2,6\text{-}dimethylphenolate)_4}]$[5] with excess benzenethiol in DMF at 0 °C followed by the addition of diethyl ether gives black crystals of $(\mathrm{NEt_4})[\mathrm{Fe(SPh)_4}]$ (**1**) in 60% yield.[6] Previously, this complex had been thought to be too unstable for isolation and characterization.[7,8] Its formulation and structure have been established by an X-ray diffraction study.[9] As the ORTEP view in Figure 1 indicates, the geometry of the entire $[\mathrm{Fe(SPh)_4}]^-$ anion has idealized S_4 point group symmetry. Taken alone, the $[\mathrm{FeS_4}]$ unit is distorted from T_d symmetry by a compression along the noncrystallographic S_4 axis to produce a $[\mathrm{FeS_4}]$ unit with approximate D_{2d} symmetry. If the $[\mathrm{FeS_4}]$ unit had exact D_{2d} symmetry, S$_1$–Fe–S$_4$ (114.3 (1)°) and S$_2$–Fe–S$_3$ (115.2 (1)°) would be equal and the four remaining S–Fe–S angles would be equal; rather they are 106.0 (1)° (S$_1$–Fe–S$_2$), 107.1 (1)° (S$_1$–Fe–S$_3$), 110.7 (1)° (S$_2$–Fe–S$_4$), and 103.7 (1)° (S$_3$–Fe–S$_4$). The average Fe–S distance of 2.296 (6) Å is about 0.06 Å shorter than the corresponding distance in the previously reported iron(II) complex $(\mathrm{PPh_4})_2[\mathrm{Fe(SPh)_4}]$ (**2**).[7]

For each Fe–S–Ph group, the Fe–S bond lies in the plane determined by the phenyl ring; this plane is perpendicular to and approximately bisects a triangular face of the FeS$_4$ tetrahedron. The occurrence of this basic Fe–S–Ph conformation has been previously recognized by Coucouvanis[7,10] and it has been discussed by him in detail for the structure of $(\mathrm{PPh_4})_2[\mathrm{Fe^{II}(SPh)_4}]$.[7,11] We add to this discussion by noting that if one assumes this basic conformation of the individual Fe–S–Ph groups, the overall geometry of the $[\mathrm{Fe(SPh)_4}]$ unit can have only two possible types

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(6) The electronic spectrum of **1** in DMF solution is as follows: $\lambda = 556$ nm ($\epsilon = 10\,000$), 387 nm (sh) (12 400), 342 nm (18 000). Anal. Calcd for FeS$_4$C$_{32}$H$_{40}$N: C, 61.72; H, 6.47; N, 2.25; S, 20.59. Found: C, 61.75; H, 6.46; N, 2.42; S, 21.51.

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(9) $(\mathrm{NEt_4})[\mathrm{Fe(SPh)_4}]$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.194$ (2) Å, $b = 8.892$ (2) Å, $c = 40.779$ (8) Å, $\beta = 92.69$ (1)°, $V = 3330$ (2) Å^3, and $Z = 4$. Diffraction data were collected at room temperature using an Enraf-Nonius CAD4 diffractometer. The structure was solved using direct methods and Fourier methods. The positions of the phenyl hydrogens were calculated and used in the structure factor calculations but were not refined. Final least-squares refinement with the nonhydrogen atoms of the anion anisotropic gave $R = 0.060$, $R_w = 0.075$ using 1291 unique reflections $I > 3\sigma(I)$.

(10) Coucouvanis, D.; Stremple, P.; Simhon, E. D.; Swenson, D.; Baenziger, N. C.; Draganjac, M.; Chan, L. T.; Simopoulos, A.; Papaefthymiou, V.; Kostikas, A.; Petrouleas, V. *Inorg. Chem.* **1983**, *22*, 293.

(11) The structural parameters described in ref 7 and applied to compound **1** are as follows: $\alpha_{\mathrm{av}} = 124$ (2)°, $\beta_{\mathrm{av}} = 117$ (2)°, $\gamma_{\mathrm{av}} = 111$ (2)°, $\delta_{\mathrm{av}} = 107$ (3)°, $\epsilon_{\mathrm{av}} = 111$ (5)°, $\epsilon_{\mathrm{av}}' = 111$ (5)°.

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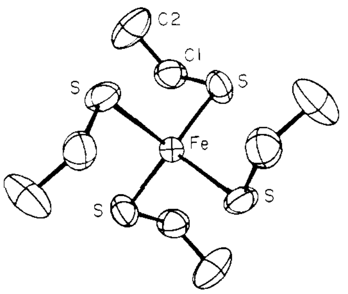

Figure 2. Anion of $[NPr_4][Fe^{III}(SEt)_4]$. The 2-fold disorder of the ethyl carbons is not shown.

of conformations, both of which have high idealized symmetry; they are the S_4 conformation observed for **1** or the D_{2d} conformation observed in **2**.[7,12] The same type of intramolecular interactions that causes the tetragonal elongation of the $[FeS_4]$ core in **2**[7] is responsible for the compression in **1**.

The $[Fe(SR)_4]^-$ unit in the recently reported $(NEt_4)[Fe^{III}(2,3,5,6\text{-tetramethylbenzenethiolate})_4]$ (**3**) also has S_4 symmetry;[4,13] however, the *o*-methyl groups prevent the phenyl rings in this complex from possessing the same conformation as in **1** and **2**. Rather, the planes of the phenyl rings in **3** are perpendicular to the Fe–S bonds. The sulfur p π lone pair orbitals are conjugated with the phenyl rings in **1** but are orthogonal to the rings in **3**. The effect of this change on the electronic properties of the iron(III) center will need to be carefully addressed by using theory and spectroscopy.

The ligand exchange reaction of alkylthiols with the iron(III) tetraphenolate complex also gives stable $[Fe^{III}(SR)_4]^-$ compounds. Stable but air-sensitive DMF solutions of $[Fe^{III}(SR)_4]^-$ (R = CH_2CH_3, CH_2Ph, CH_2CH_2Ph, and $C(CH_3)_3$), which are obtained by this reaction, display the characteristic rubredoxin-like electronic spectrum with two ligand-to-metal charge-transfer bands in the visible region.[14] $[Fe^{III}(SEt)_4][NPr_4]$ (**4**), which is isolated as black crystals in 70% yield from DMF/Et_2O, has been structurally characterized.[15,16] The $[Fe^{III}(SEt)_4]^-$ anion (Figure 2) has crystallographic S_4 symmetry. Interestingly, the FeS_4 core of $[Fe^{III}(SEt)_4]^-$ has nearly perfect T_d symmetry with the two S–Fe–S angles bisected by the S_4 axis equal to 109.43 (9)° and the four remaining angles equal to 109.49 (5)°. The Fe–S bonds are 2.272 (1) Å.

Attempts to understand the electronic structure of symmetric $[Fe(SR)_4]^{1-(2-)}$ complexes such as (**1**–**4**) are of direct biological importance since the geometry of the $[Fe(SCH_2)_4]$ unit of rubredoxin closely approximates D_{2d} symmetry.[1,4] Besides serving as models for oxidized rubredoxin, iron(III) tetrathiolates should be valuable reactants in the synthesis of iron–sulfide and iron–molybdenum–sulfide clusters.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM 32526-01) for grants made to S.K. and M.M.

Registry No. 1, 86689-74-9; **4**, 86689-79-4; $[Fe^{III}(SCH_2Ph)_4]^-$, 86689-75-0; $[Fe^{III}(SCH_2CH_2Ph)_4]^-$, 86689-76-1; $[Fe^{III}(SC(CH_3)_3)_4]^-$, 86689-77-2; $(NEt_4)[Fe(2,6\text{-dimethylphenolate})_4]$, 86689-72-7.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(12) A different ORTEP view of the anion of $[NEt_4]_2[Fe^{II}(SPh)_4]$ (Figure 8 in ref 7) would reveal its overall approximate S_4 symmetry.

(13) S_4 symmetry is common for many R_4M compounds: Karipides, A.; Iroff, L. D.; Mislow, K. *Inorg. Chem.* **1979**, *18*, 907.

(14) The electronic spectra of DMF solutions of the $[Fe^{III}(SR)_4]^-$ complexes are as follows: for R = CH_2Ph, λ = 498 nm (ϵ = 6000), 357 nm (11 000); R = CH_2CH_2Ph, 500 nm (6400), 362 nm (11 500); R = $C(CH_3)_3$, 505 nm (4800), 358 nm (9000). These spectra as well as those of **1** and **4** maintain greater than 90% of their intensities after standing at room temperature for 24 h under a nitrogen atmosphere.

(15) The electronic spectrum of **4** in DMF is as follows: λ = 496 nm (ϵ = 5900), 356 nm (10 000), 284 nm (4400). Anal. Calcd for $FeS_4C_{20}H_{48}N$: C, 49.36; H, 9.94; N, 2.88; S, 26.35. Found: C, 49.58; H, 9.63; N, 2.83; S, 26.69.

(16) $[Fe^{III}(SEt)_4][NPr_4]$ crystallizes in the tetragonal space group $I\bar{4}$ with $a = b = 10.598$ (2) Å, $c = 12.588$ (2) Å, $V = 1413.8$ (8) Å^3, $Z = 2$. The Fe is located at special position 2d and the nitrogen at position 2a. A crystallographic model with a 2-fold disorder of the methylene carbons of the cation and a 2-fold disorder of the ethyl groups of the anion was successfully refined. Final least-squares refinement gave $R = 0.053$ and $R_w = 0.070$ for 595 unique data with $I > 3\sigma(I)$. The analogous gallium compound $[Ga^{III}(SEt)_4][NPr_4]$ is isomorphous and isostructural with **4**.

Application of Proton NMR Spectral Editing Techniques for Selective Observation of N-H Protons in an Actinomycin D Complex with a Tetranucleotide Duplex

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The complexity of many biological molecules can make proton NMR spectral assignment a challenging task. This task would be facilitated by any technique allowing selective observation of a certain type of resonance. Such a technique is potentially furnished by editing methods that permit exclusive observation of protons directly bonded to a spin-$^1/_2$ nucleus.[1] If this nucleus can be introduced into a molecule selectively, the scope of the method is considerably increased. The assignment of N–H protons is of particular importance considering their role in the stabilization of protein and nucleic acid secondary structure. Two factors can complicate such assignments; analog to digital conversion limitations accompanying the necessity of working in H_2O, and possible overlap with other signals, especially in the aromatic region. The ready availability of many antibiotics biosynthetically enriched in ^{15}N provides the possibility of using editing techniques for spectral simplification in complexes of these antibiotics with suitable receptors.

Uniformly enriched actinomycin D[2] may be prepared from *Streptomyces parvulus* grown on a medium containing $Na^{15}NO_3$ as the sole nitrogen source. The complex formed between the drug and the duplex of the self-complementary tetranucleoside triphosphate d(A-G-C-T) is in slow exchange on the ^1H NMR time scale below 30 °C.[3] NMR spectra were acquired on a Bruker WH-400 modified to pulse protons and ^{15}N simultaneously and observe protons. Editing out of proton resonances other than those directly bonded to ^{15}N was achieved using the multinuclear pulse sequence

$$\begin{gathered}\pi/2[^1\text{H},x] - 1/(2J) - \pi[^1\text{H},x] - 1/(2J) - \text{acquire} \\ \pi[^{15}\text{N},1,0]\end{gathered} \tag{1}$$

where J is the one-bond proton–^{15}N coupling constant (ca. 90 Hz), and ...1,0... signifies that the π-pulse on nitrogen is applied only on alternate scans. If these alternate scans are subtracted, signals result exclusively from ^{15}N–H protons (Figure 1); $\pi/2[^1H] = 35$ μs and $\pi[^{15}N] = 50$ μs. Experimental considerations vital to the success of the sequence are discussed elsewhere,[4] and its application

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