The Reaction of Fe(III) with Sterically Hindered Thiolate Ligands

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The reaction of thiols with Fe(III) was first reported in 1879 [1]. In that report and in many subsequent studies, intensely colored solutions containing Fe(III) thiolates were observed to bleach to give solutions of Fe(II) and RSSR [1–5]. We have found that the steric capacity of the thiolate ligand has a marked effect on this autoredox reaction.

The reaction of $FeCl_3$ in methanol with excess benzenethiolate gives a transient red-violet colored solution which rapidly decays to Fe(II) thiolate complexes [6, 7]. We have recently reported that a nearly quantitative yield of $[NEt_4][Fe(SC_{10}H_{13})_4]$ (*I*) can be isolated from the analogous reaction with the more sterically hindered 2,3,5,6-tetramethylbenzenethiolate ligand [8]. If the precipitating cation is not initially present in the reaction mixture but is added after several minutes, only reduced yields of *I* are isolated. The reduction in yield parallels the bleaching of the red color of the solution. The reaction of the five equivalents of lithium 2,4,6-triisopropylbenzene thiolate with $FeCl_3$ in methanol gives intensely red solution containing the $[Fe(III)(SC_{15}H_{23})_4]^-$ anion. The electronic spectrum of this complex showed no decrease in absorbance after 24 hours. Addition of PPh_4Br to this solution gives crystalline $[PPh_4][Fe(SC_{15}H_{23})_4]$ (*II*) in 90% yield. The electronic spectrum of *II* in CH_3CN is as follows: $\lambda = 470$ nm (ϵ = 12,500), 347nm (8,870), 288nm (sh) (11,300).

The formulation of *II* was confirmed and its structure determined by means of an X-ray crystal structure. Compound *II* crystallizes in the triclinic space group $P\bar{1}$, with $a = 14.709(2)$ Å, $b = 20.928(5)$ Å, $c = 13.901(2)$ Å, $\alpha = 90.97(3)°$, $\beta = 105.43(3)°$, $\gamma = 78.13(3)°$, $V = 4033(2)$ Å^3, $Z = 2$. Diffraction data were collected at room temperature using an Enraf-Nonius CAD4 diffractometer using molybdenum radiation. The structure was solved using Patterson and Fourier methods. Final least squares refinement with all non-hydrogen atoms anisotropic gave $R = 0.059$, $R_w = 0.079$ using 5315 unique reflections with $I > 3\sigma(I)$.

The structure of the anion which is shown in Fig. 1 demonstrates that four of the sterically hindered 2,4,6-triisopropylbenzenethiolate ligands can coordinate to the iron(III) center. Neither the $[Fe(SR)_4]^-$ anion nor the $[FeS_4]$ core possess any overall symmetry. The $[FeS_4]$ core also is distorted from tetrahedral symmetry in no systematic fashion; the S–Fe–S angles vary from 98 to 114°. The large deviations from the normal tetrahedral angles of 109.5° result from steric interactions among the ligands. The Fe–S–C angles average 112(2)° which is 10 degrees larger than the corresponding angles in *I*. These steric interactions have no observed effect on the Fe–S bond distances (2.27(2) Å) which are normal [8–10].

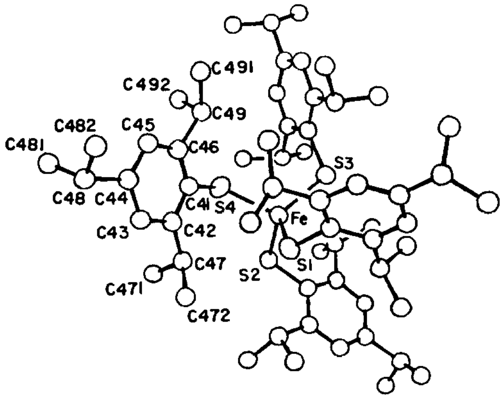

Fig. 1. ORTEP diagram of the anion of $[Ph_4P][Fe(SC_{15}H_{23})_4]$; selected distances (Å) and angles (deg): Fe–S1 2.263(3), Fe–S2 2.263(3), Fe–S3 2.310(3), Fe–S4 2.252(3), S1–Fe–S2 106.9(1), S1–Fe–S3 114.2(1), S1–Fe–S4 112.4(1), S2–Fe–S3 112.5(1), S2–Fe–S4 97.8(1), S3–Fe–S4 111.7(1).

An attractive explanation for the stability of iron(III) complexes of sterically hindered ligands follows the mechanistic suggestion of McAuley [2]. Based on kinetic evidence, he proposed that the autoredox reaction proceeds through a non-radical process involving a dimeric intermediate with two Fe(III) ions bridged by two thiolates. Since we have found in related studies that these ortho-disubstituted benzenethiolate ligands have a significantly reduced tendency to bridge metal centers compared to benzenethiolate [11, 12], it would follow that by limiting dimer formation, the sterically encumbered thiolate ligands could inhibit the autoredox reaction. From our work [9] and that of others, there are a number of factors beside the steric capacity of the thiolate ligands which effect the rate of the autoredox reaction; these include the solvent, the reducing power

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of the thiolate ligand, and the redox potentials of the iron(III) reagent, intermediates and the product. Synthetic studies are underway in our laboratories to use sterically hindered thiolate ligands to control autoredox reactions involving other metal ions.

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