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The Synthesis and Structure of Deca(benzenethiolato)tetraferrate(II) Dianion, an Intermediate in the Assembly of $[Fe_4S_4(SC_6H_5)_4]^{2-}$ from Simple Reagents

KARL S. HAGEN, JEREMY M. BERG and R. H. HOLM

Department of Chemistry, Stanford University, Stanford, Calif. 94305, U.S.A.

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The synthesis of the tetranuclear clusters $[Fe_4S_4(SR)_4]^{2-}$, analogues of the 4-Fe sites of ferredoxin proteins [1], is readily accomplished by treating the reaction mixture formed from iron(III) chloride and the desired sodium thiolate in methanol with sodium hydrosulfide [2] or elemental sulfur [3]. During our investigation of the course of the reactions which lead to the assembly of clusters from these simple reagents [4], we have concentrated on the R = Ph reaction system. ^1H NMR spectral examination of the first phase of cluster assembly, consisting of a $FeCl_3$/4NaSPh reaction mixture, revealed formation of two principal products, each of which exhibited an isotropically shifted spectrum. One of these was identified as $[Fe(SPh)_4]^{2-}$ by spectral comparison with an authentic sample [5]. The other product, not previously encountered, has been independently synthesized and proven to be $[Fe_4(SPh)_{10}]^{2-}$ by an X-ray structural analysis.

Preparation of $(R_4N)_2[Fe_4(SPh)_{10}]$

All operations were performed under a dinitrogen atmosphere using degassed solvents. A solution of 5.0 g (31 mmol) of $FeCl_2 \cdot 2H_2O$ in 100 ml of methanol was added to a solution of 92 mmol of NaSPh (from 2.1 g of sodium and 9.5 ml of PhSH) in 100 ml of methanol. After several minutes 15 mmol of R_4NCl (R = Me, Et) in 100 ml of methanol was introduced, causing separation of the product in high yield. Recrystallization from acetonitrile–methanol afforded the pure product as red-brown, air-sensitive crystals. *Anal.* Calcd. for Et_4N^+ salt, $C_{76}H_{90}Fe_4N_2S_{10}$: C, 57.94; H, 5.76; Fe, 14.18; N, 1.78; S, 20.35%. Found: C, 57.84; H, 5.40; Fe, 14.23; N, 1.77; S, 20.45%.

Structural Determination

Suitable crystals of $(Me_4N)_2[Fe_4(SPh)_{10}]$ were grown from propionitrile solution. This compound crystallizes in the monoclinic space group $P2_1/n$ with a = 14.296(5) Å, b = 23.989(6) Å, c = 22.072 (4) Å, β = 96.02(2)°, V = 7528(4) Å^3, and Z = 4. The data set, collected on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromatized MoK_α radiation, consisted of 3057 reflections with $F_0^2 \geqslant 3\sigma(F_0^2)$ obtained in the range $3° < 2\theta \leqslant 40°$. The Fe_4S_{10} core structure was solved by the direct methods program MULTAN. The remaining non-hydrogen atoms were located by difference Fourier methods and were refined by full-matrix least-squares methods including anisotropic temperature factors for iron and sulfur atoms. The current R factor is 8.8%.

Structure and Properties of $[Fe_4(SPh)_{10}]^{2-}$

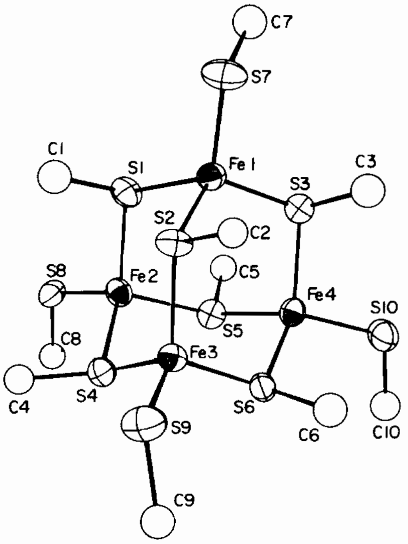

Fig. 1. Structure of the Fe_4S_{10} core of $[Fe_4(SPh)_{10}]^{2-}$, showin 50% probability ellipsoids and the atom labeling scheme. The following distances have these minimum, maximum, and mean values (Å): Fe···Fe, 3.853(4) (Fe1–Fe4), 3.970(3) (Fe1–Fe3), 3.93(5); Fe–S(bridge), 2.330(6) (Fe3–S6), 2.387(5) (Fe1–S1), 2.365(17); Fe–S(terminal, 2.269(5), (Fe3–S9), 2.305(5) (Fe2–S8), 2.287(15).

The crystal structure contains discrete anions and cations; dimensions of cations and phenyl rings are unexceptional. The Fe_4S_{10} core structure is depicted in Fig. 1. It consists, approximately, of a tetrahedron of iron atoms (mean Fe···Fe distance, 3.93(5) Å) surrounded by an octahedron of sulfur atoms, which function as bridges between two iron atoms. The core assumes an adamantane-like stereochemistry, but the idealized T_d symmetry of such an arrangement is not achieved. Irregular distortions from cubic symmetry are found, as shown by the Fe–S (bridge) bond distances summarized in Fig. 1 and by bond angle variations. Thus at Fe1, for example, the angles S1–Fe–S2, S1–Fe S3, and S2–Fe–S3 are 98.5(2)°, 107.7(2)° and 117.4(2)°, respectively, at the current stage of refinement. Spatial orientation of phenyl groups is also irregular. Distorted tetrahedral coordination at each iron site is completed by one terminal thiolate ligand. In their mean values Fe–S (bridge) bonds are longer than Fe–S (terminal) bonds by 0.08 Å. $[Fe_4(SPh)_{10}]^{2-}$ is then structurally formulated as $[(\mu\text{-}SPh)_6Fe_4(SPh)_4]^{2-}$. As such it could be considered as an oligomerization product of mononuclear tetrahedral $[Fe(SPh)_4]^{2-}$ [5]. Indeed, the two species are in equilibrium in protic solvents.

Among transition metal complexes with monodentate ligands, the adamantane-like structure of $[Fe_4(SPh)_{10}]^{2-}$ is precedented only by $[Cu_4(SPh)_6]^{2-}$ [6] and $[Co_4(SPh)_{10}]^{2-}$ [7]. The Me_4N^+ salts of the two $[M_4(SPh)_{10}]^{2-}$ complexes are not isomorphous but their core stereochemistries, apart from differences in distortions from cubic symmetry, are quite similar.

In acetonitrile solution at ambient temperature $[Fe_4(SPh)_{10}]^{2-}$ maintains its structural integrity, as seen from its ^1H NMR spectrum. Chemical shifts (100 MHz) at higher (+) and lower (–) fields *vs.* TMS suggest the presence of contact interactions: bridge *o*-H (+9.0), *m*-H (–16.2), *p*-H (+12.0); terminal *o*-H (+3.2), *m*-H (–16.2), *p*-H (+9.0 ppm). At higher temperatures the spectrum collapses to one set of phenyl resonances, indicating fluxional behavior. In the context of cluster synthesis, $[Fe_4(SPh)_{10}]^{2-}$ reacts smoothly with 4 equiv. of elemental sulfur at room temperature according to the reaction,

$$[Fe_4(SPh)_{10}]^{2-} + 4S \rightarrow [Fe_4S_4(SPh)_4]^{2-} + 3PhSSPh,$$

to afford $[Fe_4S_4(SPh)_4]^{2-}$ in $> 80\%$ yield upon isolation as a R_4N^+ salt. The role of $[Fe_4(SPh)_{10}]^{2-}$ in cluster assembly in protic media, as well as other of its reactivity features and its full structural details, will be described subsequently.

Acknowledgments

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References

1 R. H. Holm and J. A. Ibers, *Iron-Sulfur Proteins, 3,* 205 (1977).
2 B. A. Averill, T. Herskovitz, R. H. Holm and J. A. Ibers, *J. Am. Chem. Soc., 95,* 3523 (1973).
3 G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.,* 1093 (1979).
4 J. G. Reynolds, K. S. Hagen and R. H. Holm, research in progress.
5 D. Coucouvanis, D. Swenson, N. C. Baenziger, D. G. Holah, A. Kostikas, A. Simopoulos and V. Petrouleas, *J. Am. Chem. Soc., 98,* 5721 (1976).
6 I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta, 19,* L41 (1976).
7 I. G. Dance, *J. Am. Chem. Soc., 101,* 6264 (1979). It is mentioned here that certain Zn(II) complexes, including $[Zn_4(SPh)_{10}]^{2-}$, possess adamantane-like core structures.