$[Fe_4S_4(SH)_4]^{2-}$, the Simplest Synthetic Analogue for a Ferredoxin

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$(PPh_4)_2[Fe_4S_4(SH)_4]$ is obtained by the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with H_2S in organic solvents in the presence of air and $(PPh_4)Br$, and its *X*-ray crystal structure has been determined.

The structure of the ferredoxins and all their functions in the whole biosphere (including their occurrence in the most primitive anaerobic organisms) as well as the easy formation of their synthetic analogues suggest the incorporation of its prototype in very early biochemical evolution.[1] We have now succeeded in preparing $[Fe_4S_4(SH)_4]^{2-}$ (**1**) [as its PPh_4^+ salt (**1a**)], the simplest synthetic analogue for a 4Fe4S ferredoxin.

$(PPh_4)_2[Fe_4S_4(SH)_4]$

(**1a**)

Compound (**1a**) was obtained in 35% yield by the reaction of $(cp)Fe(CO)_2I$† (cp = $\eta^5\text{-}C_5H_5$) with H_2S in DMF–MeOH–Et_3N (DMF = dimethylformamide) in the presence of air and $(PPh_4)Br$ and characterized by elemental analysis, thermal analysis,‡ magnetic measurements ($\mu_{eff.}$ 2.2 μ_B at room temp.), i.r. {Nujol; ν_{as} (Fe_4S_4): 376m, ν_{as} [FeS(H)]: 342s cm^{-1}} and Mössbauer spectroscopy [δ 0.45 (0.47), ΔE_Q = 0.87 (1.27) mm/s at 77 K (4.2 K values in parentheses); relative to α-Fe at room temp.] as well as *X*-ray structure analysis.§

$(PPh_4)_2[Fe_4S_4(SH)_4]$ is isostructural with $(PPh_4)_2[Fe_4S_4Hal_4]$ (Hal = Cl or Br).[2] The $[Fe_4S_4(SH)_4]^{2-}$ cubane-type cluster anion (see Figure 1) has approximately T_d symmetry. The crystallographic symmetry is C_2. Like other $[Fe_4S_4L_4]^{n-}$ anions, $[Fe_4S_4(SH)_4]^{2-}$ also shows tetragonal distortion from the idealized symmetry ($T_d \rightarrow D_{2d}$). The Fe–Fe, Fe–S, and Fe–S(H) distances in $[Fe_4S_4(SH)_4]^{2-}$ (Figure 1) compare well with the corresponding distances in other $[Fe_4S_4L_4]^{2-}$ type clusters like $[Fe_4S_4(SPh)_4]^{2-}$.[3]

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† Compound (**1a**) can also be obtained correspondingly by using $[(cp)Fe(CO)_2]_2$.

‡ Compound (**1a**) decomposes above 90 °C producing H_2S.

§ *Crystal data:* $C_{48}H_{44}Fe_4P_2S_8$, M = 1162.73, monoclinic, space group $C2/c$, a = 15.895(5), b = 14.341(5), c = 23.465(8) Å, β = 106.28(3)°, U = 5134.2 Å^3, Z = 4, D_c = 1.50 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 15.15 cm^{-1}, $F(000)$ = 2376. Diffraction data were collected using a Syntex $P2_1$ diffractometer (ω-scan, at 21 °C). The structure was solved by conventional heavy-atom methods. Least-squares refinement [with the phenyl rings refined as regular hexagons; C–C 1.395, C–H 0.96 Å, $\angle$C–C–C = $\angle$C–C–H = 120°, U(H) = 800 pm^2] converged at an R value of 0.083 for 1989 independent reflections [$F_o > 3.92\sigma(F_o)$; $4° < 2\theta < 48°$]. Complex (**1**) occupies a twofold crystallographic axis (see Figure 1). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

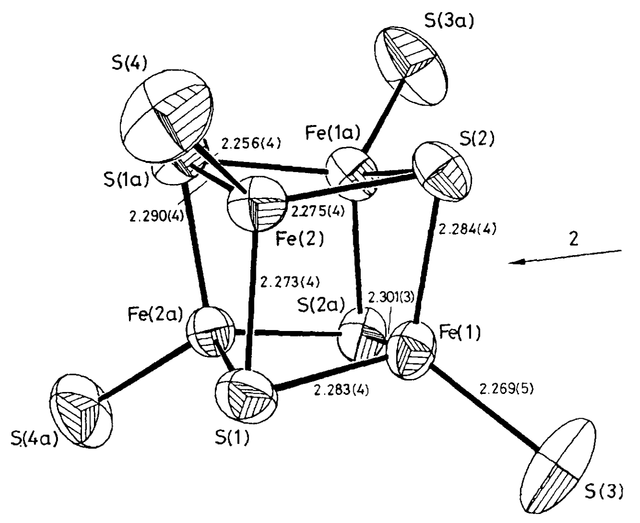

Figure 1. Structure of the $[Fe_4S_4(SH)_4]^{2-}$ anion in crystals of $(PPh_4)_2[Fe_4S_4(SH)_4]$. Bond lengths (Å): Fe(1)–Fe(2) 2.770(3), Fe(1)–Fe(1a) 2.762(4), Fe(1)–Fe(2a) 2.769(3), Fe(2)–Fe(2a) 2.738(3), S(1)–S(2) 3.563(6), S(1)–S(1a) 3.610(6), S(1)–S(2a) 3.593(6), S(2)–S(2a) 3.623(6). Bond angles (°): S(1)–Fe(1)–S(2) 102.6(1), S(1)–Fe(1)–S(2a) 103.2(1), S(1)–Fe(1)–S(3) 116.6(2), S(2)–Fe(1)–S(2a) 104.4(1), S(2)–Fe(1)–S(3) 114.1(2), S(3)–Fe(1)–S(2a) 114.3(2), S(1)–Fe(2)–S(2) 103.2(2), S(1)–Fe(2)–S(1a) 104.6(1), S(1)–Fe(2)–S(4) 112.1(2), S(2)–Fe(2)–S(1a) 103.8(1), S(2)–Fe(2)–S(4) 118.4(1), S(4)–Fe(2)–S(1a) 113.4(2), Fe(1)–S(1)–Fe(2) 74.9(1), Fe(1)–S(1)–Fe(2a) 74.5(1), Fe(2)–S(1)–Fe(2a) 73.7(1), Fe(1)–S(2)–Fe(1a) 74.1(1), Fe(1)–S(2)–Fe(2) 74.8(1), Fe(1a)–S(2)–Fe(2) 74.5(1). {The arrow indicates the twofold crystallographic axis, which runs through the $[Fe_4S_4(SH)_4]^{2-}$ anion.}

The isolation of (**1**) is particularly important as it represents the most simple synthetic analogue for the 4Fe4S ferredoxins and more sophisticated M.O. calculations are possible for it than, *e.g.*, for the thiolato clusters. (These types of calculations have already been performed and are in accord with, *e.g.* experimental Mössbauer data.[4])

It should be pointed out that the formation of (**1**) proceeds under *aerobic* conditions which is unusual (see ref. 5) from an Fe^{II} species. The reaction takes place with O_2 as primary electron acceptor though, *e.g.*, polysulphido species might be involved in the reaction pathway. A comparable very simple aerobic (self-assembly) reaction of $FeSO_4{\cdot}7H_2O$ with H_2S in organic solvents in the presence of oxygen and $(PPh_4)Br$, whereby $(PPh_4)_2[Fe_4S_4Br_4]$ is formed, also takes place.[6]

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References

1 H. Follmann, 'Chemie und Biochemie der Evolution,' Quelle und Meyer, Heidelberg, 1981; R. V. Eck and M. O. Dayhoff, *Science*, 1966, **152**, 363; D. O. Hall, R. Cammack, and K. K. Rao, *Nature (London)*, 1971, **233**, 136; D. O. Hall, R. Cammack, and K. K. Rao, *Origins Life*, 1974, **5**, 363; W. E. Newton, 'Sulfide and other Sulfur Containing Ligands in Metalloproteins and Enzymes,' in 'Sulfur—its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology,' eds. A. Müller and B. Krebs, Elsevier, Amsterdam, 1984.

2 A. Müller, N. H. Schladerbeck, E. Krickemeyer, H. Bögge, K. Schmitz, E. Bill, and A. X. Trautwein, to be published; A. Müller, N. H. Schladerbeck, H. Bögge, *Chimia*, 1985, **39**, 24.

3 J. M. Berg and R. H. Holm, 'Structures and Reactions of Iron–Sulfur Protein Clusters and Their Synthetic Analogs,' in 'Iron–Sulfur Proteins,' ed. T. G. Spiro, Wiley, New York, 1982.

4 R. Bläs, E. Bill, S. Lauer, A. X. Trautwein, H. Winkler, M. Grodzicki, A. Kostikas, 'Molecular Orbital Theory and Mössbauer Spectroscopy: Electronic Structure Studies of Bioinorganic Iron Sulfur Clusters,' in 'Frontiers in Bioinorganic Chemistry,' ed. A. V. Xavier, VCH Verlagsgesellschaft, Weinheim, 1986; A. X. Trautwein, A. Müller, unpublished results; A. Aizman and D. A. Case, *J. Am. Chem. Soc.*, 1982, **104**, 3269, and references cited therein.

5 G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1979, 1093; K. S. Hagen, J. G. Reynolds, and R. H. Holm, *J. Am. Chem. Soc.*, 1981, **103**, 4054.

6 A. Müller and N. H. Schladerbeck, *Chimia*, 1985, **39**, 23.