A New Iron–Sulphide Cluster containing the 'Prismane' $[Fe_6(\mu\text{-}S)_6]^{3+}$ Core. Synthesis, Structure, and Properties of $[Et_4N]_3[Fe_6S_6Cl_6]$

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The synthesis and structural (crystallographic and spectroscopic) characterization of the new Fe–S–Cl cluster $[Fe_6S_6Cl_6]^{3-}$ is described.

Studies in the synthetic and structural chemistry of iron–sulphide complexes have made available a number of interesting clusters which show a wide variety in stoicheiometry and structure. Among these compounds are included the thoroughly studied[1] and biologically relevant $[Fe_4S_4(SR)_4]^{2-,3-}$ and $[Fe_2S_2(SR)_4]^{2-,3-}$ clusters which contain the $[Fe_4(\mu\text{-}S)_4]^{2+,1+}$ and $[Fe_2(\mu\text{-}S)_2]^{2+,1+}$ cores, respectively. More recently, equally interesting clusters of less direct biological relevance have been reported and include the $[Fe_6S_9(SR)_2]^{4-}$,[2] $[Fe_3S_4(SR)_4]^{3-}$,[3] and $[Fe_6(S)_8(PEt_3)_6]^{2+}$ [4] ions. In these complex ions the structures of the $[Fe_6(\mu\text{-}S)_6(\mu_3\text{-}S)_2(\mu_4\text{-}S)]^{2-}$, $[Fe_3(\mu\text{-}S)_4]^{+}$, and $[Fe_6(\mu_3\text{–}S)_8]^{2+}$ cores, respectively, have been established by *X*-ray crystallographic studies.

A continued interest in the search for new polynuclear metal–sulphide core units at present is reinforced by evidence that such units occur in certain metalloproteins. Among these, the spectroscopically identified[5] 3Fe sites in certain non-heme iron proteins and the crystallographically established[6] cyclic $[Fe_3(\mu\text{–}S)_3]$ core in *Azotobacter vinelandii* ferredoxin (Fd) I are not represented by any of the known synthetic, active site analogue, complexes. Similarly analogue complexes are not available for the Fe–S sites in certain metalloproteins with unconventional properties such as the Fd III and Mo–Fe–S proteins from *Desulfovibrio africanus*[7,8] and the Fe–S sites in certain hydrogenases.[9] Herein we report on the synthesis and structural characterization of the new $[Fe_6S_6Cl_6]^{3-}$ cluster which contains the hitherto unknown $[Fe_6(\mu\text{-}S)_6]^{3+}$ 'prismane' core.

$[Ph_4P]_2[Fe_4S_4Cl_4]$
(1)

In a previous communication we have reported[10] on the convenient synthesis of $[Ph_4P]_2[Fe_4S_4Cl_4]$, (**1**), from a reaction between $[Ph_4P]_2[Fe_4(SPh)_6Cl_4]$ and dibenzyl trisulphide in MeCN solution. A recent modification of this procedure allows for the high yield synthesis of (**1**) using readily available reagents. In the latest synthetic approach, (**1**) is obtained in high yields by the reaction in MeCN of elemental sulphur, anhydrous $FeCl_2$, KSPh, and Ph_4PCl in a 5:4:6:2 molar ratio. Under *identical* synthetic conditions but with the replacement of Ph_4PCl by $Et_4NCl{\cdot}H_2O$ the reaction follows a different

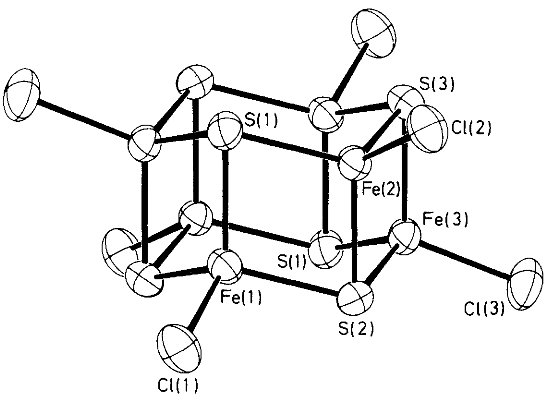

Figure 1. Structure of the $[Fe_6S_6Cl_6]^{3-}$ anion in (**2**). Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-4794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965) represent the 50% probability surfaces.

Table 1. Interatomic distances[a] (Å) and angles (°) in the $[Fe_6S_6Cl_6]^{3-}$ anion.

Distances[b]		Angles[b]	
Fe–Fe (3)[c,d]	3.790(15)	S–Fe–S (3)[c]	113.7(6)
Fe–Fe (3)[e,f]	2.765(6)	S–Fe–S (6)[e]	105.2(2)
Fe–S (3)[c,g]	2.284(6)	Fe–S–Fe (3)[c]	113.2(6)
Fe–S (6)[e,h]	2.272(5)	Fe–S–Fe (6)[e]	74.8(2)
Fe–Cl (3)	2.224(2)	Fe–Fe–Fe (3)[c]	60.0(4)
S–S (3)[c]	3.801(16)	Fe–Fe–Fe (3)[e]	86.5(5)
S–S (3)[e]	3.618(9)		

[a] See Figure 1 for the labelling scheme. The mean values of chemically equivalent bonds are reported. The standard deviations in parentheses are the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation $\sigma = [\Sigma_{i=1}^{N} (X_i - \bar{X}^2)/(N-1)]^{1/2}$. [b]The values in parentheses represent the number of independent distances or angles averaged out. [c] Distances or angles within the Fe_3S_3 structural unit. [d] Range: 3.778(1)—3.806(1) Å. [e] Distances or angles outside the Fe_3S_3 hexagonal unit. [f] Range: 2.760(1)—2.771(1) Å. [g] Range: 2.278(2)—2.290(3) Å. [h] Range: 2.263(2)—2.278(2) Å.

course and the black crystalline material† isolated, (**2**), is not the Et_4N^+ analogue of (**1**). By comparison with (**1**), which in MeCN solution displays a characteristic electronic spectrum with absorptions at 680 and 506 nm, (**2**) has a featureless electronic spectrum in the visible region and shows an intense absorption at 270 nm. Cyclic voltammetry of (**2**) in MeCN solution shows a quasireversible reduction wave, on a platinum bead, with a cathodic peak at −0.82 V (*vs.* saturated Calomel electrode). Under the same conditions (**1**) undergoes reversible reduction at −0.76 V.

Crystal data: black single crystals of (**2**) are monoclinic, space group $C2/c$, $a = 20.092(5)$, $b = 17.937(6)$, $c = 13.790(4)$ Å, $\beta = 91.33(2)°$; $Z = 4$. Single crystal, *X*-ray diffraction data were collected on a Nicolet P3F four circle diffractometer using Mo-K_α radiation. The solution of the structure by a combination of heavy atom Patterson, direct methods, and Fourier techniques and refinement by full-matrix least-squares methods was based on 2604 unique reflections. Anisotropic temperature factors for the atoms in the anion and one of the cations‡ were used and at the current stage of refinement with all atoms present in the asymmetric unit $R = 0.049$.§

The anion in (**2**) is situated on a crystallographic centre of symmetry at 3/4, 1/4, 0 and the $[Fe_6(\mu\text{-}S)_6]^{3+}$ core can be described as a hexagonal prism with alternating Fe and S atoms at the 12 apices. The six terminal Cl^- ligands are co-ordinated one to each of the iron atoms and complete the tetrahedral co-ordination environment in the six FeS_3Cl subunits. The structure of the anion in (**2**) is shown in Figure 1. There exist two different types of Fe–Fe distances and Fe–S–Fe angles in the $[Fe_6S_6]^{3+}$ core (Table 1). Of these, the mean Fe–Fe distances and Fe–S–Fe angles within the Fe_3S_3 hexagonal bases of the prism at 3.780(1) Å and 113.2(5)° are unusually large. The Fe–Fe distances and Fe–S–Fe angles associated with the rhombic Fe_2S_2 sides of the prism have mean values of 2.765(6) Å and 74.7(2)° which are conventional and quite similar to corresponding values in the known $[Fe_2S_2]^{2+}$ or $[Fe_4S_4]^{2+}$ cores.[1] The mean value of all independent Fe–S bonds [2.276(8) Å] in (**2**) is similar to the corresponding value[11] in the homologous (**1**) at 2.283(5) Å.

The Fe_3S_3 hexagonal units in (**2**), which have not been observed previously in analogue complexes, are qualitatively similar to the Fe_3S_3 site in Fd I from *A. vinelandii.*[6] For the latter, which exists in a 'twist-boat' conformation, Fe–Fe distances of 4.1, 4.2, and 4.4 Å and Fe–S–Fe angles of 113, 126, and 131° have been reported.[6c] The Mössbauer spectrum of (**2**) in the crystalline state (at 125 K *vs.* Fe) shows one quadrupole doublet with isomer shift (δ_{Fe}) and quadrupole splitting (ΔE_q) values of 0.494(1) mm/sec and 1.095(1) mm/sec, respectively. In frozen MeCN solution at the same temperature $\delta_{Fe} = 0.496(1)$ mm/sec and $\Delta E_q = 1.048$ mm/sec. The δ_{Fe} values are very similar to those found for (**1**) under comparable conditions and underscore the electronic similarities of the Fe atoms in (**1**) and (**2**). The e.s.r. spectrum at 6.6 K shows an asymmetric signal for which the highest *g* value is 2.029 and which undergoes extensive broadening above 10 K. The integrated area of this signal measured from 6.6—19 K shows Curie behaviour and is consistent with an effective $S = 1/2$ system.

Upon heating in MeCN solution, (**2**) is quantitatively transformed into (**1**) according to equation (1). Furthermore

$$2[Fe_6S_6Cl_6]^{3-} \rightarrow 3[Fe_4S_4Cl_4]^{2-} \qquad (1)$$

the reaction of (**2**) (at ambient temperatures) with an excess of KSPh in MeCN results in the formation of the $[Fe_4S_4(SPh)_4]^{2-}$ [12] cluster. The role of the counterion (Et_4N^+) in the stabilization of $[Fe_6S_6Cl_6]^{3-}$ (an apparently metastable homologue of $[Fe_4S_4Cl_4]^{2-}$) is not clear. However the successful isolation of (**2**) suggests that similar 'non-conventional' metastable Fe–S clusters may be stabilized in certain protein environments. The Fe_3S_3 core in *A. vinelandii* Fd I appears to be such a Fe–S cluster.

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† Satisfactory elemental analysis has been obtained for this material which is isolated as an MeCN monosolvate.

‡ The other cation and the MeCN molecule of solvation are located on the two fold axes at 0, *y*, 1/4 and 1/2, *y*, 1/4, respectively and show positional disorders.

§ The atomic co-ordinates for this work are available on request from the Director of the Chemical Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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