A Novel Paramagnetic Octahedral Iron Cluster: Synthesis and X-Ray Structural Characterization of [Fe₆(μ₃-S)₈(PEt₃)₆][BPh₄]₂

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Summary The reaction of H_2S with $Fe(BF_4)_2 \cdot 6H_2O$ and PEt_3 gives $[Fe_6S_8(PEt_3)_6][BPh_4]_2$, whose structure, determined by X-ray analysis, shows that in the cation the six iron atoms are in an octahedral arrangement with the sulphur atoms triply bridging each octahedral face while the six phosphine ligands are each terminally linked to a metal atom.

We report the preparation and structural characterization of the compound $[Fe_6S_8(PEt_3)_6][BPh_4]_2$ containing the first example of an octahedral iron cluster which is face-capped by sulphur atoms. This work is part of a systematic investigation of the reactions of hydrogen sulphide with 3d metal ions in the presence of tertiary phosphines which has already allowed the preparation of polynuclear species such as the trinuclear $[Ni_3S_2(PEt_3)_6][BPh_4]_2$ complex[1] and the enneanuclear confacial bioctahedral $[Ni_9S_9(PEt_3)_6][BPh_4]_2$ cluster.[2]

Acetone–ethanol deoxygenated solution of $Fe(BF_4)_2 \cdot 6H_2O$ and PEt_3 (molar ratio *ca.* 1:3) absorbed H_2S at room temperature, the solution changing colour from green to black. After several days in the air, the solution, after addition of $NaBPh_4$, deposited black crystals of $[Fe_6S_8(PEt_3)_6][BPh_4]_2$. The compound, obtained in a yield of *ca.* 20%, is air-stable and soluble in the common polar organic solvents where it behaves as a 2:1 electrolyte.

Preliminary magnetic susceptibility measurements as well as n.m.r. spectra confirm the paramagnetism of the complex. A bulk magnetic moment of 6·04 B.M. per $[Fe_6S_8(PEt_3)_6]$-$[BPh_4]_2$ unit at 291 K (χ_g + 7·50) which decreases to 5·66 B.M. at 91 K has been found. Its structure has been determined by X-ray crystallography.

Crystal data: $C_{84}H_{130}B_2Fe_6P_6S_8$, $M = 1939.0$, triclinic, space group $P\bar{1}$, $a = 11·848(6)$, $b = 14·376(8)$, $c = 15·537(9)$ Å, $\alpha = 114·93(9)$, $\beta = 90·04(8)$, $\gamma = 104·76(9)°$, $U = 2303·13$ Å³, $Z = 1$, $D_m = 1·40$, $D_c = 1·398$ g cm⁻³, μ(Mo-K_α) = 12·0 cm⁻¹.

Intensity data were collected on a Philips computer-controlled PW 1100 diffractometer using the ω–2θ scan technique and graphite-monochromated Mo-K_α radiation. The structure was solved by the heavy-atom technique. The phenyl rings of the tetraphenylborate anions were treated as rigid groups. Full-matrix least-squares refinements converged at R and R_w values of 0·082 and 0·079 for the 1721 reflections ($2\theta \leqslant 40°$) with $I \geqslant 3\sigma(I)$. An absorption correction giving transmission factors ranging from 0·986 to 0·781 was applied.†

The molecular structure of the complex consists of discrete $[Fe_6S_8(PEt_3)_6]^{2+}$ cations and BPh_4^- anions. The inner core of the cation is shown in the Figure. The
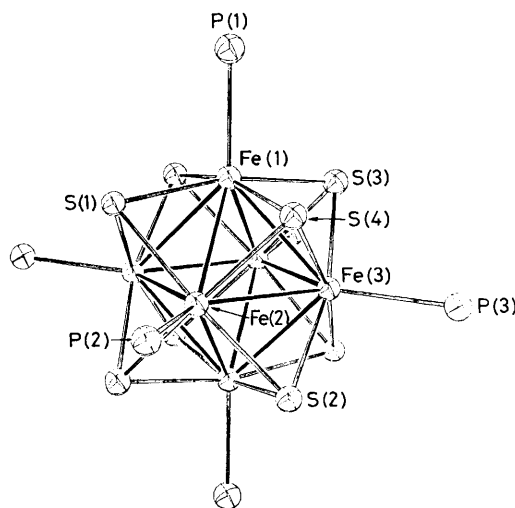

FIGURE. Inner core of $[Fe_6S_8(PEt_3)_6]^{2+}$. Selected bond distances: Fe–Fe, (1)–(2) 2·638(8); (1)–(3) 2·610(9); (1)–(2') 2·620(7); (1)–(3') 2·613(8); (2)–(3) 2·655(6); (2)–(3') 2·605(7); Fe–S, (1)–(1) 2·264(8); (1)–(3) 2·258(9); (1)–(4) 2·265(10); (1)–(2') 2·248(10); (2)–(1) 2·263(12); (2)–(2) 2·248(13); (2)–(4) 2·247(10); (2)–(3') 2·249(11); (3)–(2) 2·253(11); (3)–(3) 2·263(11); (3)–(4) 2·275(11); (3)–(1') 2·249(10); Fe–P, (1)–(1) 2·288(14); (2)–(2) 2·300(8); (3)–(3) 2·301(11).

$[Fe_6S_8(PEt_3)_6]^{2+}$ cation is built up of an octahedral cluster of iron atoms with the sulphur ligands triply bridging all the octahedral faces. The Fe_6S_8 unit may alternatively be described as a slightly distorted cube of sulphur atoms with the iron atoms in the face-centred positions. Moreover each iron atom is additionally co-ordinated by a triethylphosphine group. Therefore each metal atom is surrounded by one phosphorus and four sulphur atoms in a square-pyramidal arrangement and linked to another four iron atoms.

The $[Fe_6S_8(PEt_3)_6]^{2+}$ cation possesses crystallographic C_i–$\bar{1}$ symmetry, lying on the centre of inversion, but the inner core may be considered to possess idealized O_h symmetry. The octahedral iron framework is quite regular, the Fe–Fe distances ranging from 2·605(7) to 2·655(6) Å. The value of the average‡ Fe–Fe distance of 2·624(8) Å, which is significantly larger than the sum of the single bond radii (2·33 Å),[3] may be compared with the values reported for the octahedral cluster $[Fe_6(CO)_{16}C][Me_4N]_2$,[4] which range from 2·58(3) to 2·74(1) Å. The average value of the Fe–S bond distances [2·257(3) Å] may be compared with the value of 2·23 Å reported for the polynuclear $Fe_3S_2(CO)_9$[5] complex containing triply bridging sulphur ligands.

On the grounds of its geometry and of the relatively high formal oxidation number of the metal atoms ($+3$) the $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ complex is closely related to the class of octahedral metal atom clusters whose most representative example is $[Mo_6(\mu_3\text{-}Cl)_8Cl_6]^{2-}$. However, the Cotton and Haas MO treatment[6] which describes the M_6X_8 cluster as a saturated unit with twelve two-centre two-electron bonds (24 electrons in the M_6 skeleton) does not apply to the title complex (30 electrons in the Fe_6 skeleton). On the other hand the complex does not even fit the bonding scheme developed by Lauher for carbonyl clusters[7] which requires 86 valence electrons in the stable configuration (if each S atom is considered as contributing 4 electrons to the cluster then there are 90 electrons to be used for Fe–P bonding and in the Fe_6S_8 cluster).

Therefore a specific theoretical treatment would be necessary in order to understand the relationship between stoicheiometry, structure, and properties of the title compound as well as of the related $[Ni_9S_9(PEt_3)_6]^{2+}$ sulphide.

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