Simple Synthesis of a Six-co-ordinated High-spin Iron(III) Porphyrin; *X*-Ray Structure and Magnetic Properties of Bis(ethanol)tetraphenylporphinatoiron(III) Tetrafluoroborate

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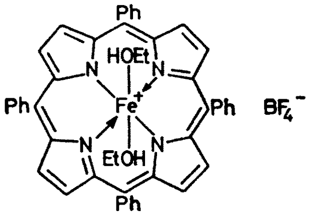
Summary Reaction of the μ-oxo-dimer of iron(III) tetraphenylporphyrin with aqueous tetrafluoroboric acid in the presence of ethanol gives bis(ethanol)tetraphenylporphinatoiron(III) tetrafluoroborate, the structure of which has been determined by *X*-ray crystallography; this complex is a rare example of a structurally characterized six-co-ordinated iron(III) porphyrin with an unambiguous $S = 5/2$ ground state.

WEAKLY co-ordinating ligands have recently been shown to bind iron(III) porphyrins, yielding isolable six-co-ordinated complexes, when strongly binding anions such as halides are absent. Thus, perchlorato(tetraphenylporphinato)iron(III), [Fe(OClO$_3$)(tpp)] reacts with various weak-field, oxygen-donor ligands such as sulphoxides, dimethylformamide, and amine or phosphine oxides in carefully dehydrated solvents to give six-co-ordinated complexes whose unusual $S = 5/2$ spin state reflects weak axial ligation.[1] We have found that the synthesis of such complexes does not necessarily require the use of inert atmosphere techniques and the preparation of a perchlorato complex as a precursor. We report here a straightforward synthetic route to bis(ethanol)tetraphenylporphinato-iron(III) tetrafluoroborate, the molecular structure of this complex, and its magnetic properties. These studies corroborate the possibility of the long unrecognized $S = 5/2$ spin state in synthetic six-co-ordinated iron(III) porphyrins.

Treatment of $[\{Fe(tpp)\}_2O]$ in chloroform–ethanol with 33% aqueous tetrafluoroboric acid, followed by evaporation to dryness of the red-brown solution and recrystallization from dichloromethane–cyclohexane afforded dark-blue crystals of $[Fe(EtOH)_2(tpp)]^+BF_4^-$ (**1**) in 85% yield.



(1)

Satisfactory elemental analyses were obtained. Uncommonly for a metallotetraphenylporphyrin, this compound is soluble in ethanol.

Crystal data: $[Fe(EtOH)_2(tpp)]^+BF_4^-$ is monoclinic, $a = 10.561(3)$, $b = 16{\cdot}826(3)$, $c = 18{\cdot}421(6)$ Å; $\beta = 142{\cdot}24(2)°$; space group $P2_1/c$; $Z = 2$; $D_c = 1.39$ g cm^{-3}; 2300 unique observed data [$\sigma(I)/I < 0{\cdot}3$, $2\theta < 60°$, Mo-K_α radiation]; $wR(F) = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2} = 0{\cdot}068$. The crystal lattice is composed of discrete $[Fe(EtOH)_2(tpp)]^+$ cations and BF_4^- anions. The space group is centrosymmetric, with the Fe and B atoms each lying on one of the two inversion centres of the asymmetric unit. Since the BF_4 tetrahedron cannot be accommodated on an inversion centre, some statistical disorder had to be introduced. Half the BF_4 tetrahedra are in one orientation, and the other half are in the orientation obtained from the former by inversion through the inversion centre; as a result, the F-atoms are statistically located in eight positions, each with an occupancy of 0·5.†

The structure and bond parameters for the co-ordination of the iron atom are in the Figure. The clearly six-co-ordinated iron(III) ion is rigorously centred in the porphyrin plane. The large radius of the central hole [average Fe–N bond distance 2·03(1) Å, compared to 1·99 Å in low-spin Fe^{III} derivatives[2]] is necessary to accommodate the high-spin iron(III) ion. The long axial Fe–O bond distance of 2·14 Å [as compared to 1·84 Å in methoxo-iron(III) mesoporphyrin-IX dimethyl ester[3]] is consistent with the weak bonding of the ethanol ligands. Large thermal motion of the latter, possibly with some degree of disorder,[4] leads to bond lengths of limited accuracy in the ethanol molecules. The structural parameters, on the whole, are close to those of the recently described $[Fe(H_2O)_2(tpp)]^+ClO_4^-$[5] and [Fe(tetramethylene sulphoxide)$_2$(tpp)]$^+ClO_4^-$.[1]

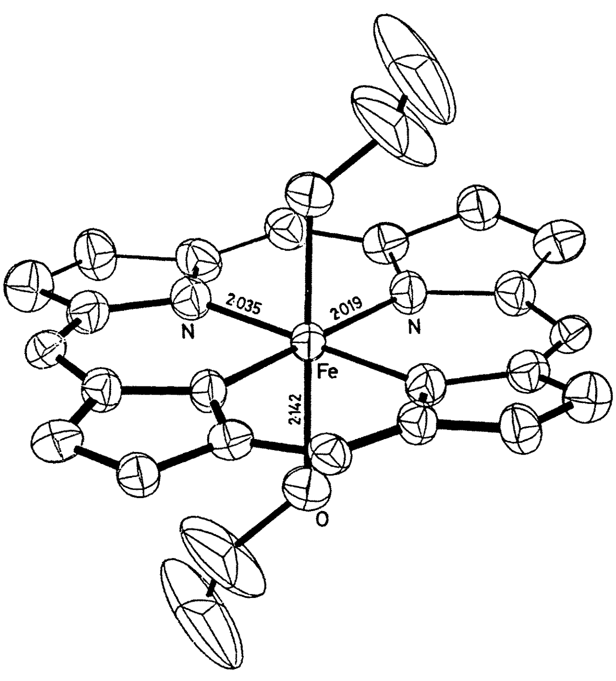


FIGURE. A perspective view of the $[Fe(EtOH)_2(tpp)]^+$ ion. Phenyl groups have been omitted. Pertinent bond distances are indicated in Å. Estimated standard deviations are 0·005 Å.

E.s.r. examination of $[Fe(EtOH)_2(tpp)]^+BF_4^-$ in frozen chloroform solution at 77 K reveals the usual features of axially symmetric high-spin iron(III) porphyrins[6] ($g_\perp$ *ca.* 6, $g_\parallel$ *ca.* 2). Consistent with these solution data, the crystalline complex shows Curie–Weiss behaviour over the range 4—100 K with an effective magnetic moment typical of a $S = 5/2$ state, $\mu_{eff.} = 5{\cdot}9$ B.M., and a Weiss constant $\theta = -3$ K. At higher temperatures, however, a transition to a lower spin multiplicity is observed, with the Curie plot being best fitted with $\mu_{eff.} = 5{\cdot}3$ B.M. and $\theta = +19$ K above *ca.* 50—100 K. The Mössbauer spectrum of polycrystalline $[Fe(EtOH)_2(tpp)]^+BF_4^-$ at 4·2 K shows two broad, asymmetric absorption lines with an isomer shift of 0·42 mm/s with respect to iron metal. The large quadrupole splitting of 1·89 mm/s may reflect deviation from octahedral symmetry due to the long axial bonds; it is slightly larger than those found in other high-spin six-co-ordinated iron(III) haem derivatives[1] and approaches the range found in low-spin six-co-ordinated hemichromes.[7] The effective magnetic field measured in the presence of a 5T external field is *ca.* 32 T. A detailed Mössbauer study at various temperatures and with various external magnetic fields is under way.

We note that a presumably analogous octaethylporphyrin (oep) complex in which two ethanol molecules may be axially ligated, $[Fe(EtOH)_2(oep)]^+ClO_4^-$, has an intermediate ($S = 3/2$) spin state at 298 K.[8] The

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

divergence between these and our results illustrates the subtle balance between the macrocycle and the axial ligands which dictates the spin state of these compounds. The ethanol solvate $[Fe(EtOH)_2(oep)]^+ClO_4^- \cdot EtOH$ has been structurally characterised, but its magnetic properties are unknown owing to crystal instability in the absence of a mother liquor.[9]

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