Reduction of $[Fe^{III}(tfpp)Cl]$[tfpp = 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrinate] by Azaferrocene. The Crystal Structure of $[Fe^{II}(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$

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Azaferrocene reacts with chloro[5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato]iron(III) to give a low-spin iron(II) porphyrin, $[Fe^{II}(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$, the crystal and molecular structure of which has been determined; while air-stable in the solid state, in solution it loses co-ordinated azaferrocene and (under aerobic conditions) undergoes oxidation to Fe^{III}.

The axial ligation of amines (B) by iron-(II) and -(III) porphyrinates (Scheme 1) and the structure and electronic properties of the adducts formed continues to attract considerable interest due to the importance of histidine co-ordination in the chemistry of haemoproteins.[1]

$$[Fe^{II}(por)] \underset{-B}{\overset{+B}{\rightleftharpoons}} [Fe^{II}(por)B] \underset{-B}{\overset{+B}{\rightleftharpoons}} [Fe^{II}(por)B_2]$$

$$[Fe^{III}(por)X] \underset{-B}{\overset{+B}{\rightleftharpoons}} [Fe^{III}(por)B(X)] \underset{-B}{\overset{+B}{\rightleftharpoons}} [Fe^{III}(por)B_2]X$$

Scheme 1 por = Porphyrinate, X = halide or pseudohalide

We have recently initiated a study of the co-ordination of the organometallic redox-active base azaferrocene $[Fe(C_5H_5)(C_4H_4N)]$ to transition-metal centres[2] in the hope that the resulting bi- and tri-nuclear adducts would display interesting physical properties and chemical reactivity. Indeed, in the case of cobalt porphyrins, axial co-ordination of azaferrocene gives rise to adducts which show unusual photochemical properties. For example, the complex $[Co(tpp)\{Fe(C_5H_5)(C_4H_4N)\}(\sigma\text{-}O_2)]$ (tpp = dianion of 5,10,15,20-tetraphenylporphyrin) loses dioxygen while $[Co(tpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]BF_4$ undergoes photoreduction to [Co(tpp)] upon irradiation with visible light, whereas their counterparts containing axially co-ordinated pyridine or imidazole are photostable.[2] Consequently, it seemed interesting to study ligation of azaferrocene by iron porphyrins and the molecular structure, electronic and photochemical properties of the adducts formed. In this communication we present preliminary results of this study.

As monitored by electronic absorption spectra neither [Fe(tpp)Cl] nor [Fe(oep)Cl] (oep = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin) co-ordinate azaferrocene in $CHCl_3$ solution at porphyrin concentrations of 0.1–1.0 mmol dm^{-3}. However, spectral changes were observed upon addition of azaferrocene to chloro[5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato]iron(III) $[Fe^{III}(tfpp)Cl]$. At higher concentrations the adduct crystallized directly from the solution. For example, treatment of [Fe(tfpp)Cl] (46 mg, 0.043 mmol) in $CHCl_3$ (0.6 cm^3) with azaferrocene (41 mg, 0.219 mmol) gave purple analytically pure crystals of the adduct (21 mg) upon standing overnight at −10 °C.

Surprisingly, elemental analysis data[†] were in agreement with the co-ordination of two molecules of azaferrocene to the iron(II) porphyrin core. In order to confirm the six-co-ordination around the central iron atom a crystal structure determination was performed.[‡] The structure consists of two independent $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$ molecules with the iron atoms of the core lying on crystallographically imposed centres of symmetry. The geometries of the two molecules are very similar. The molecular structure is shown in Fig. 1. The co-ordination around the central iron atom is nearly octahedral and the average length of the axial Fe–N bonds is 2.05(2) (× 2) Å while the average Fe–N bond length in the core for the two molecules is 2.01(2) and 2.01(0) Å which is consistent with those observed for the low-spin six-co-ordinate iron(II) porphyrin complexes $[Fe^{II}(tpp)(pip)_2]$ (pip = piperidine) [2.004(4), 2.004(3) Å][4a] and $[Fe^{II}(tpp)(NH_2Pr^i)(Pr^iNO)]$ [2.000(1), 2.000(7) Å].[4b] The azaferrocene molecules in the two independent molecules have the usual sandwich structure (the angles between the cyclopentadienyl and pyrrolyl ligand planes are 3.5 and 5.5° respectively). The dihedral angles between the pyrrolyl ligand plane and the mean plane of the porphyrin core are 65 and 67°. The orientation of the azaferrocene ligand with respect to the porphyrinato core is characterized by the dihedral angles Φ between the axial ligand and the co-ordinate plane (defined by a porphyrinato nitrogen atom, the metal atom of the core and the N atom of the axial ligand), 20.0 and 19.6°, while the angles between the axis containing the three Fe atoms and that containing the central Fe perpendicular to the core are 17.4 and 17.8° for molecules 1 and 2 respectively.

The four-fold symmetry of the porphyrinato core is lost upon complexation (the dihedral angles between the perfluorophenyl planes and porphyrinato core being 87 and 79° for molecule 1 and 82 and 78° for molecule 2). This is due to steric hindrance of the azaferrocene molecule which is tilted relative to the normal

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[†] Found: C, 53.45; H, 1.70; Fe, 11.6; N, 6.10. Calc. for $C_{62}H_{26}F_{20}Fe_3N_6$: C, 53.10; H, 1.85; Fe, 11.9; N, 6.00%. Fast atom bombardment mass spectrum (positive, 3-nitrobenzyl alcohol matrix): no parent peak (*m*/*z* 1402) but peaks at *m*/*z* 1215 (23) $\{[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}]\}$, 1028 (17.7%) {[Fe(tfpp)]} and 187 (2%) $[Fe(C_5H_5)(C_4H_4N)]$.

[‡] Crystal data. Crystals grown from dichloromethane–heptane solution. $C_{62}H_{26}F_{20}Fe_3N_6$, M = 1402.44, triclinic, space group $P\bar{1}$, a = 11.480(5), b = 14.360(6), c = 18.444(8) Å, α = 95.00(6), β = 117.21(8), γ = 98.75(6)°, U = 2687 $Å^3$, Z = 2, D_c = 1.733 g cm^{-3}, $F(000)$ = 1396, μ = 0.91 cm^{-1}. Crystal of dimensions 0.015 × 0.1 × 0.8 mm. Graphite-monochromated four-circle Philips diffractometer, λ(Mo-Kα) = 0.7107 Å, θ–2θ scan technique, range 2–35°, speed 0.120° s^{-1}, width 1.0°; 3046 measured intensities, 1969 considered as observed $[I > 1.5\sigma(I)]$. Lorentz polarization and empirical absorption corrections. Structure resolution by direct methods and refinement by full-matrix least squares using SHELX 76.[3] Owing to the rather low data: parameter ratio, refinement of fluorophenyl, cyclopentadienyl and pyrrolyl rings performed as rigid groups, with anisotropic thermal parameter refinement for only the Fe and F atoms. Hydrogen atoms introduced in calculated positions. Final weighting scheme $w = [\sigma(F)^2 + 0.0008F^2]^{-1}$. Final conventional R factor 0.084. Atomic coordinates, thermal parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

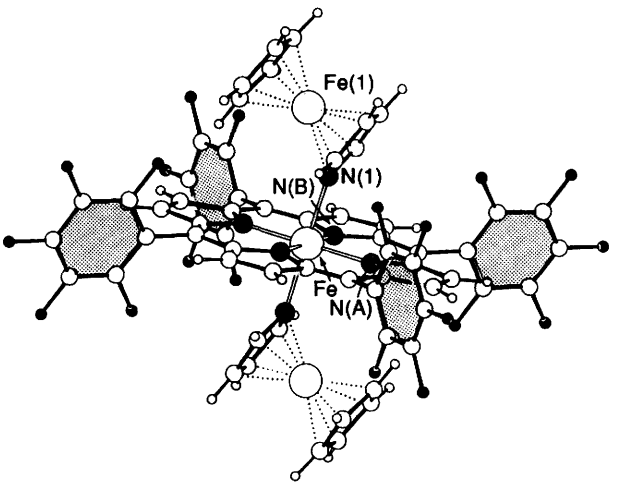

Fig. 1 A perspective view of $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$

of the porphyrinato core. It is interesting that the axial Fe–N bonds in $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$ are considerably shorter than those in [Fe(tpp)(pip)$_2$] [2.127(3) Å],[4a] and closer to those found for the adduct of [Fe(tpp)] with pyridine [2.037(1) Å].[4c] On the other hand, imidazoles co-ordinate to [Fe(tpp)] at an even shorter distance [2.004–2.014(2)].[4d] The unexpectedly tight co-ordination of azaferrocene to a metal macrocycle system (taking into consideration possible repulsion between the macrocycle and cyclopentadienyl hydrogens) has already been observed in the crystal structure of σ-azaferrocene methyl cobaloxime.[2b]

The electronic absorption spectrum of $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$ displays the Soret band at 418 nm and the Q band at 532 nm. In aerated chloroform solution oxidation to Fe^{III} takes place [Fig. 2(*a*)] with the appearance of a new Q band at 536 nm. Two isosbestic points at 512 and 541 nm are present. The ESR spectrum at 4 K of either partially or completely oxidized solutions showed axial high-spin iron(III) features ($g_\perp = 5.9, g_\parallel = 2.0$). These data might suggest that the oxidized species is [Fe(tfpp)(OH)].[4e]

The spectral changes observed in deoxygenated solutions of $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$ [Fig. 2(*b*)] are different. The diminution of the Q band at 532 nm initially is not accompanied by the increase of the 562 nm band, confirming assignment of the latter band to Fe^{III}. The evolution of the spectra is presumably due to the dissociation of azaferrocene(L): $[Fe(tfpp)L_2] \xrightarrow{-L} [Fe(tfpp)L] \xrightarrow{-L} [Fe(tfpp)]$. Indeed, the spectra of 'bare' iron(II) porphyrins and their monobase adducts[4f,g] corroborate well these spectra.

All the above facts clearly indicate that reaction of [Fe(tfpp)Cl] with azaferrocene involves reduction of the porphyrinic iron(III) atom to Fe^{II}, while less readily reducible [Fe(tpp)Cl] and [Fe(oep)Cl] are not reduced. We have not attempted to detect the expected oxidation product, azaferrocenium cation since it is a highly unstable, putative species.[4h] The fact that ferrocene, despite its stronger reductive properties ($E_{\frac{1}{2}}^{ox}$ = 0.43 V) relative to azaferrocene (0.60 V),[4h] does not reduce [Fe(tfpp)Cl] indicates that the reduction step requires prior co-ordination of azaferrocene to the porphyrinic iron(III) centre. In this context it is of note that in contrast to [Fe(tpp)Cl] and [Fe(oep)Cl] the cobalt(III) porphyrin $[Co(tpp)(thf)_2]BF_4$ (thf = tetrahydrofuran) co-ordinates two molecules of azaferrocene without reduction at the cobalt(III) centre.[2c]

The reduction of iron(III)- to iron(II)-porphyrins by organic amines in axial position has already been observed.[4a,i] For example [Fe^{III}(tpp)Cl] reacts with piperidine to give [Fe^{II}(tpp)(pip)$_2$].[4a] For azaferrocene a more readily reducible porphyrin, tfpp, is required to make the process feasible.

In conclusion, we have found that reaction of [Fe(tfpp)Cl] with an excess of azaferrocene leads to a six-co-ordinate iron(II) porphyrin complex containing two additional iron(II) centres, situated symmetrically. It is possible that other iron(II) porphyrins with sufficiently high oxidizing properties will react in the same manner. We expect that the trinuclear complexes obtained in this way will display interesting physiochemical properties due to possible metal–metal interactions in the ground or excited states. The study of such properties is currently underway.

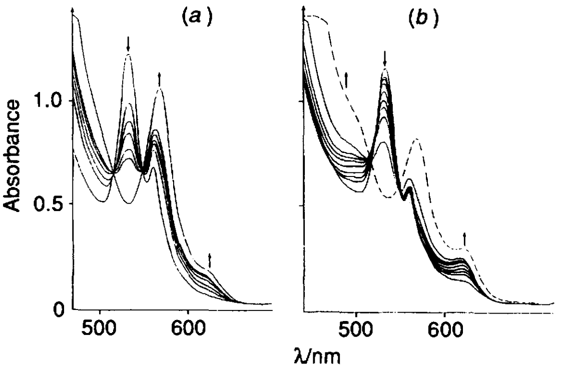

Fig. 2 The time evolution of spectra of $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$ in chloroform: (*a*) aerated solution (*c* = 0.88 mmol dm^{-3}); (*b*) deaerated solution (*c* = 0.78 mmol dm^{-3}) (pathlength = 1 mm). The first spectrum was recorded ≈15 min after dissolution, subsequent spectra every 40 min and the final spectrum after ≈17 h standing

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