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Models of Cytochromes b containing an Organometallic Axial Base, Azaferrocene: Synthesis and Electron Paramagnetic Resonance Study

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Azaferrocene reacted with [Fe(oep)(O_3SCF_3)] or [Fe(tpp)(O_3SCF_3)] (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate; tpp = 5,10,15,20-tetraphenylporphyrinate to afford [Fe(oep){Fe(C_5H_5)(C_4H_4N)}$_2$]O_3SCF_3 or [Fe(tpp){Fe(C_5H_5)(C_4H_4N)}$_2$]O_3SCF_3, respectively; the trinuclear complexes exhibit rhombic low-spin EPR spectra indicating the strong ligating ability of azaferrocene.

Six-co-ordinate complexes of iron(III) porphyrins with heterocyclic nitrogen bases (*e.g.* imidazoles or pyridines), [Fe(por)B_2]X, have attracted considerable attention as simple models of the microenvironment of the iron centre in cytochromes b.[1] In this communication we report that similar complexes are formed by an organometallic base, azaferrocene [Fe(C_5H_5)(C_4H_4N)];[2] these complexes exhibit rhombic low-spin EPR spectra, characteristic for strongly co-ordinating nitrogen bases such as imidazole (Him), 1-methylimidazole, 4-aminopyridine, *etc.*

We have earlier reported that azaferrocene co-ordinates to the cobalt centre in cobaloximes, cobalt-(II) and -(III) porphyrins.[3a-c] Some of the complexes formed display interesting photochemical properties. More recently, we have found that [Fe(tfpp)Cl] [H_2tfpp = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin] reacts with an excess of azaferrocene to afford [Fe(tfpp){Fe(C_5H_5)(C_4H_4N)}$_2$] (*i.e.* co-ordination is accompanied by reduction $Fe^{III} \longrightarrow Fe^{II}$ of the porphyrinic iron centre[3d]). In contrast, [Fe(oep)Cl] and [Fe(tpp)Cl] proved unreactive [H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin; H_2tpp = 5,10,15,20-tetraphenylporphyrin).

Since the rate-determining step in the formation of [Fe(por)B_2]Cl from [Fe(por)Cl] is dissociation of chloride,[4] we thought that replacement of Cl^- by the more ready leaving group triflate ($CF_3SO_3^-$) would facilitate formation of these adducts. Electronic absorption spectra show that either [Fe(oep)(O_3SCF_3)] or [Fe(tpp)(O_3SCF_3)][5] does react with azaferrocene in chloroform solution (Fig. 1). The spectra obtained in the presence of 2.2–4.4 equivalents of azaferrocene corroborate well those of bis(imidazole) adducts of iron(III) porphyrins,[6] suggesting formation of [Fe(oep){Fe(C_5H_5)(C_4H_4N)}$_2$]O_3SCF_3 **1** or [Fe(tpp){Fe(C_5H_5)(C_4H_4N)}$_2$]O_3SCF_3 **2**. The spectral changes observed at lower azaferrocene concentration may be interpreted in terms of formation of monoadducts. It has been reported that the Q band of [Fe(tpp)(SbF_6)] is shifted from 514 to 511 nm on ligation of one molecule of imidazole in toluene solution.[7] This shift is closely similar to that observed when 1.1 equivalents of azaferrocene are added to [Fe(tpp)(O_3SCF_3)] (515 to 509 nm). The complex [Fe(oep)(O_3SCF_3)] also shows a smaller blue shift of the Q band upon addition of 1.1 equivalents of azaferrocene, from 499 to 495 nm. Obviously, in quantitative analysis of these spectra one must take into account a weak absorption of azaferrocene in this region [Fig. 1(*a*)].

It is noteworthy that, up to now, examples of spectral evidence for formation of monoligated species in iron(III) porphyrin-base systems are rare, in most cases only an equilibrium between the iron(III) porphyrin and its bis(base) adduct being observed.

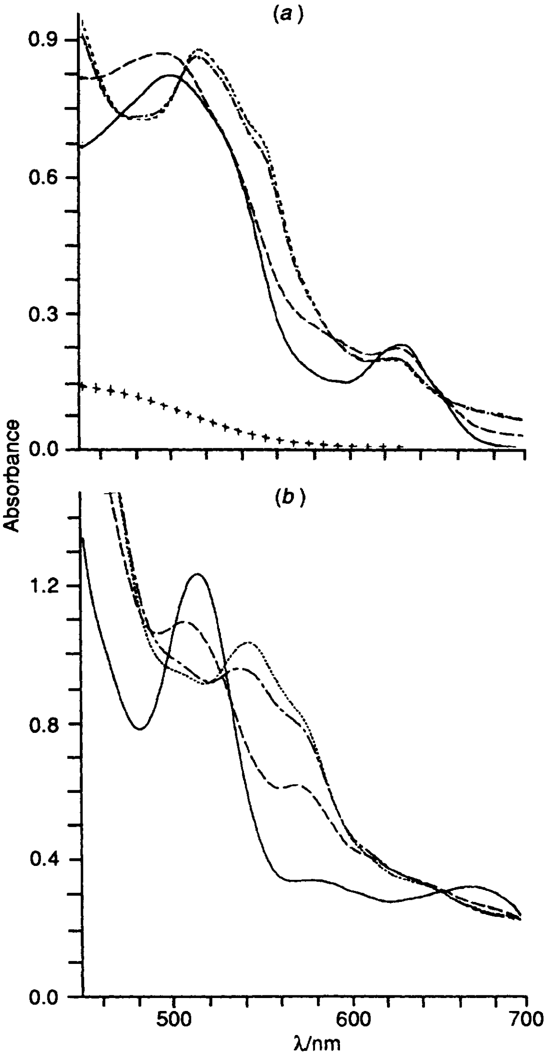

Fig. 1 Spectral changes observed when azaferrocene is added to (*a*) [Fe(oep)(O_3SCF_3)] and (*b*) [Fe(tpp)(O_3SCF_3)] in $CHCl_3$: —, before addition ($c = 10^{-3}$ mol dm^{-3}, d = 1 mm); – – –, – · – and · · · ·, after the addition of 1.1, 2.2 and 4.4 equivalents of azaferrocene, respectively; + + +, azaferrocene ($c = 8.8 \times 10^{-3}$ mol dm^{-3})

Complexes **1** and **2** crystallize from concentrated solutions of triflates, containing a five-fold excess of azaferrocene, upon

Table 1 EPR data for six-co-ordinate porphyrinatoiron(III) complexes

Complex	g_1	g_2	g_3	Δ/λ	v/Δ	Ref.
$[Fe(oep)\{Fe(C_5H_5)(C_4H_4N)\}_2]^{+\,a}$	3.24	2.05	1.31	3.97	0.33	This work
$[Fe(tpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]^{+\,a}$	3.16	2.20	1.45	3.70	0.42	This work
$[Fe(oep)(Him)_2]^+$	2.96	2.25	1.53	3.47	0.54	7
$[Fe(tpp)(Him)_2]^+$	2.87	2.29	1.56	3.24	0.63	1*e*
$[Fe(tpp)(2\text{-mim})_2]^+$	3.40	1.74^b	1.19	5.88	0.17	1*e*
Cytochrome b_5	3.03	2.23	1.43	3.23	0.52	7

[a] Frozen solution in $CHCl_3$ at 3.5 K; values obtained for polycrystalline powders did not differ more than ±0.02. [b] Calculated.

addition of heptane and concentration *in vacuo*.* They give rhombic low-spin EPR spectra in frozen chloroform solution and in the polycrystalline state, which confirm the presence of the low-spin porphyrinic iron(III) centre. The spectrum of **1** in $CHCl_3$ at 3.5 K is shown in Fig. 2. It is now well established that rhombic EPR spectra are characteristic for complexes of relatively 'unhindered' imidazoles or highly basic pyridines [$pK_a(HB^+) > 8$]. They result from the parallel orientation of the planes of both ligands. On the other hand, a perpendicular orientation is characteristic for complexes of a hindered porphyrin, $[Fe(tmp)]^+$ (H_2tmp = 5,10,15,20-tetramesitylporphyrin), or for $[Fe(oep)]^+$ and $[Fe(tpp)]^+$ with hindered imidazoles, *e.g.* 2-methylimidazole (2-mim), and pyridines of basicity $6.5 > pK_a(HB^+) > 5.0$. These complexes exhibit so-called highly anisotropic low spin or 'strong g_{max}' EPR spectra.[1a–d] Finally, the complexes with weakly basic pyridines [$pK_a(HB^+) < 3$] exhibit axial spectra.[1a] We conclude that **1** and **2** contain azaferrocene ligands oriented in parallel.

The routine treatment of rhombic low-spin spectra[8] allowed us to calculate tetragonal splitting (Δ/λ) and rhombicity (v/Δ) for complexes **1** and **2**. These parameters, together with selected literature data for complexes of imidazoles, are shown in Table 1. Inspection of these data leads to the conclusion that azaferrocene behaves toward $[Fe(por)]^+$ as a strongly co-ordinating, unhindered ligand. The ligand-field parameters of **1** and **2** are similar to those of their imidazole counterparts, although some deplacement toward lower v/Δ and higher Δ/λ, characteristic for highly anisotropic low-spin systems is to be noted. The rhombic spectra, obtained for **1** and **2**, despite the relatively weak basicity of azaferrocene [$pK_a(HB^+) = 4.5$],[2a] confirm the earlier suggestion of Walker *et al.*[1e] that EPR parameters of $[Fe(por)B_2]X$ are a function of not only the axial ligand basicity but also the ligand type. In this context azaferrocene resembles organic five-membered heteroaromatic nitrogen bases such as imidazoles, pyrazoles or thiazoles.

In conclusion we have demonstrated that rhombic low-spin ESR spectra, characteristic for some cytochromes b, can be reproduced not only in the systems $[Fe(por)]^+$ with strongly co-ordinating organic nitrogen bases, but also in trinuclear complexes containing an organometallic nitrogen base, $[Fe(por)\{Fe(C_5H_5)(C_4H_4N)\}_2]^+$. We expect that complexes **1** and **2** will display interesting photo- and electro-chemical properties due to the presence of three metal centres. The study of such properties, as well as efforts to obtain crystals of **1** and **2** suitable for X-ray crystallography, will be pursued.

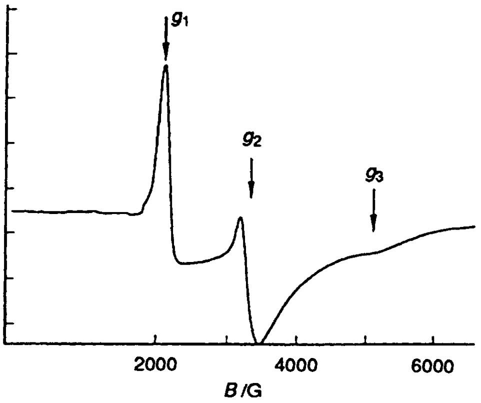

Fig. 2 The X-band EPR spectrum of complex **1** recorded in $CHCl_3$ at 3.4 K; G = 10^{-4} T

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* A solution of $[Fe(oep)(O_3SCF_3)]$ or $[Fe(tpp)(O_3SCF_3)]$ (0.06 mmol) and azaferrocene (56 mg, 0.3 mmol) in $CHCl_3$ (3 cm^3) was diluted with heptane (3 cm^3) and concentrated *in vacuo* to afford microcrystalline complexes **1** and **2** in 67 and 88% yield, respectively (Found: C, 61.60; H, 4.05; Fe, 13.75; N, 6.75. Calc. for $C_{63}H_{50}F_3Fe_3N_6O_5S$ **1**·$2H_2O$: C, 61.60; H, 3.95; Fe, 13.60; N, 6.85. Found: C, 58.65; H, 5.55; Fe, 15.10; N, 7.45. Calc. for $C_{55}H_{64}F_3Fe_3N_6O_4S$ **2**·H_2O; C, 58.45; H, 5.70; Fe, 14.85; N, 7.45%). Fast atom bombardment mass spectra (3-nitrobenzyl alcohol, positive ion): **1**, *m/z* 979(4), $[Fe(oep)L_2(H_2O)H]$ [L = $Fe(C_5H_5)(C_4H_4N)$]; 775(64), [Fe(oep)L]; 588 (100%), [Fe(oep)]; **2**, 1043(2) $[Fe(tpp)_2H]$; 855(43), [Fe(tpp)L]; 668(100%) [Fe(tpp)].