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Effect of sterically inhibited axial azaferrocene ligands on the physical properties of iron(III) porphyrins. Crystal structures of bis(azaferrocene) complexes of iron(III) and cobalt(III) porphyrinates

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The crystal structures of [Fe(oep)L_2][O_3SCF_3] and [Co(oep)L_2][ClO_4] [H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin, L = [Fe(C_5H_5)(C_4H_4N)] have been determined. The azaferrocene ligands L in both compounds are seen to be parallel. The axial M−N (azaferrocene) bonds are longer than those found in analogous imidazole and pyridine complexes. Rhombic EPR spectra for bis(azaferrocene) complexes of iron(III) porphyrins are postulated to be a result of steric interactions of the azaferrocene $H^{2,5}$ atoms splitting the degeneracy of the d_{xz} and d_{yz} orbitals. The Mössbauer spectra of these iron complexes were recorded and interpreted as evidence for σ bonding of the azaferrocene nitrogen atom to the porphyrin iron core with little or no π back bonding from the porphyrinic iron to the N atom. This is in agreement with the long bond lengths found in the structures. The rhombic EPR spectra observed are in keeping with a parallel arrangement of the ligand planes, as are the magnitudes of the Mössbauer quadrupole splittings. It is shown that the large g_z values of the complexes are not unusual and must relate to long axial bonds and to steric effects splitting the d_{xz} and d_{yz} orbitals.

There has been considerable interest in the stereochemistry and electronic properties of iron(III) and cobalt(III) porphyrins containing imidazole and pyridine ligands of the general formula [M(por)B_2]$^+$ (M = Fe^{III} or Co^{III}; por = porphyrin dianion, B = imidazole or pyridine).[1–7] In part this interest has been triggered by a need to understand the chemistry of cytochromes b.[8–15] It is now well established that the rotational orientation of the planes of the axially co-ordinated B ligands with respect to the equatorial M−N (porphyrin) bond vectors strongly influences the physicochemical properties of iron(III) porphyrin complexes such as redox potentials, spin states, NMR, EPR and ^{57}Fe Mössbauer spectra.[1,4,5,7] It has been postulated and become widely accepted that many biological functions of haem proteins may be dependent on fine tuning of the orientation of the co-ordinated imidazole ring of the histidine residue. It has been suggested that some of the physicochemical properties correlate and are diagnostic of particular types of orientation.[1,4,5,7,12,16–23] A value of 2.43 mm s^{-1} for the Mössbauer quadrupole splitting (q.s.) for the imidazolate complex [Fe(por)(Him)(Im)] was assigned to a parallel orientation of the planar axial ligands, whereas a value of 1.87 mm s^{-1} for [Fe(por)$(mim)_2$]$^+$ (mim = 2-methylimidazole) was assigned to a perpendicular orientation of the imidazole planes.[4,5] The latter Mössbauer parameters have been associated with EPR spectra described as highly anisotropic low-spin systems (HALS).[1,4,5,7,24] From extensive studies on model complexes it has been established that, for non-sterically hindered porphyrins, non-hindered imidazoles and highly basic pyridines (such as 4-aminopyridine) favour parallel orientation of their axial ligand planes. Such complexes display high q.s. values and normal rhombic EPR spectra.

In previous work we have demonstrated the ligating properties of azaferrocene [Fe(C_5H_5)(C_4H_4N)] to a variety of acceptor species including metal porphyrin complexes.[25–29] We have reported electronic absorption and EPR spectra for [Fe(oep){Fe(C_5H_5)(C_4H_4N)}$_2$][O_3SCF_3] (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin) and [Fe(tpp){Fe(C_5H_5)(C_4H_4N)}$_2$][O_3SCF_3] (H_2tpp = 5,10,15,20-tetraphenylporphyrin).[27] These complexes gave rhombic EPR spectra which allowed us to suggest that they were low spin and had a parallel orientation of the azaferrocene ligands.[27] Such an orientation was also established by X-ray studies on [Fe(tfpp){Fe(C_5H_5)(C_4H_4N)}$_2$] [H_2tfpp = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin] which is a low-spin iron(II) complex.[28]

The EPR spectra had g_z parameters of 3.24 for the oep derivative and 3.16 for the tpp derivative. These are larger than those previously reported for normal rhombic spectra ($g_z \approx 2.9$), but smaller than HALS g_z values (3.4 for tpp).[7] These larger values merited further investigation and we now report Mössbauer spectroscopic studies on [Fe(oep)L_2][O_3SCF_3] **1**, [Fe(tpp)L_2][O_3SCF_3] **2**, [Co(tpp)L_2][BF_4] **3**, [Fe(tfpp)L_2] **4** and brief crystallographic details of **1** and [Co(oep)L_2][ClO_4] **5** [L = Fe(C_5H_5)(C_4H_4N)].

Experimental

Azaferrocene and its porphyrin complexes were synthesized and purified as previously described.[27,28,30]

Synthesis of [Co(oep){Fe(C_5H_5)(C_4H_4N)}$_2$][ClO_4] 5

The complex [Co(oep)$(H_2O)_2$][ClO_4][31] (36.4 mg, 0.05 mmol) and azaferrocene (40 mg, 0.21 mmol) were dissolved in CH_2Cl_2 (1 cm^3). After 5 min of stirring at room temperature (r.t.) heptane (2 cm^3) was added and the resulting solution concentrated *in vacuo* to give purple crystals which were filtered off, washed with pentane, and dried overnight at 0.2 Torr (26.6644 Pa) at r.t. (Found: C, 60.65; H, 5.85; N, 7.90. Calc. for $C_{54}H_{62}ClCoFe_2N_6O_4$: C, 60.9; H, 5.85; N, 7.90%). Positive-ion FAB mass spectrum (*m*-nirobenzyl alcohol matrix): *m/z* 964 ([Co(oep){Fe(C_5H_5)(C_4H_4N)}$_2$]$^+$), 777 ([Co(oep){Fe(C_5H_5)(C_4H_4N)}]$^+$) and 591 {[Co(oep)]$^+$}.

Crystallography

Single crystals were obtained by crystallisation from dichloromethane–heptane: dark purple pyramidal crystals for **1**, bright purple prismatic crystals for **5**.

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Data collection. Graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å), four-circle Philips PW1100 diffractometer, 293(2) K, ω–2θ scan technique, unit-cell dimensions refined from setting angles of 25 reflections ($10 < \theta < 14°$). Three standard reflections measured every 3 h to monitor instrument and crystal stability; $\sigma(I)$ derived from counting statistics. Lorentz-polarisation effects and empirical absorption corrections applied.[32]

Structure resolution. Direct methods using SHELXS 86,[33] refinement by least-squares method using SHELXL 93[34] for compound **1** and by SHELX 76[35] for **5**.

Compound **1**. Crystal structure solved in the space group $P\bar{1}$, taking the centre of inversion at the Fe of the porphyrinate ligand. Disorder of the trifluoromethane sulfonate anion on an inversion centre could not be resolved by simple use of this space group (more than the two expected anion positions were observed). Only three peaks were clearly observed in the Fourier-difference synthesis, so the refinement was concluded in the centrosymmetric space group with the coordinates of the observed cationic complex and the three identified anion peaks, with anisotropic thermal parameters. Two of the eight ethyl chains are also disordered (occupation factors 0.67 and 0.33 respectively). Constraints were applied to chemically equivalent bonds, and H atoms were introduced at theoretical positions.

Compound **5**. Owing to the low number of data *versus* the number of parameters, only the Co, Fe and Cl atoms were refined anisotropically. Furthermore, refinement with constraints[36] was applied to chemically equivalent bonds (17 equations); H atoms were introduced in the refinement at theoretical positions (C–H 1.00 Å) and assigned an isotropic thermal parameter equivalent to 1.1 times that of the bonded atom.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/277. The list of observed and calculated structure factors is available from the authors at the Institut de Chimie des Substances Naturelles.

Mössbauer spectroscopy

The Mössbauer spectra were recorded for solids using an instrument and techniques previously described.[37]

Results and Discussion

Crystal structures for $[Fe(oep)\{Fe(C_5H_5)(C_4H_4N)\}_2][O_3SCF_3]$ 1 and $[Co(oep)\{Fe(C_5H_5)(C_4H_4N)\}_2][ClO_4]$ 5

The molecular structures of these complexes are shown in Figs. 1 (**1**) and 2 (**5**) with selected bond lengths. Crystallographic data are reported in Table 1. In both structures the X-ray analysis has revealed an identical orientation of azaferrocene ligands (they are axially linked to the central metal ion in the porphyrinato core, tilted in a parallel configuration). The geometry of these compounds may be compared with that of $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$ **4**.[28] For complex **4** the average length of the axial Fe–N bonds is 2.05(2) Å, which is similar to the distance 2.057(5) Å of **1**. This latter distance is long in comparison to those of known structures of formula $[Fe(por)L_2]^+$ where L is an imidazole type ring [range 1.965(3)–2.015(4) Å].[2,38–44] For the six-membered ring pyridine ligands[2,3,24,45] the Fe–N_{axial} range is 1.989(4)–2.031(2) Å, all but one significantly shorter than those found in compound **1**. The larger value for Fe–N_{axial} distance for **1** may be a consequence of the steric hindrance the azaferrocene suffers when binding to iron porphyrins, though it also signifies a weaker Fe–N bond than in the pyridine complexes. The Fe–N_{por} bond distances of **1** are 2.004(4) and 2.023(4) Å, in agreement with those in other low-spin Fe(oep) structures.[2,3,45] The two azaferrocene molecules related by a crystallographic centre of symmetry are obviously parallel.

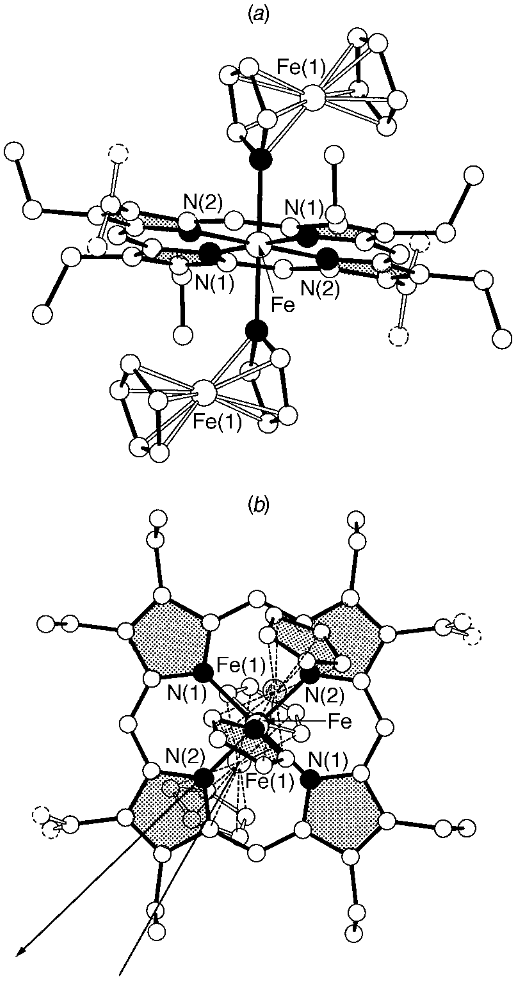

Fig. 1 (*a*) Structure of complex **1**. The Fe–N_{por} bond distances are 2.004(4) and 2.023(4) Å, the axial Fe–N bond distances 2.057(5) Å. The positions of the disordered ethyl chains are indicated by broken circles (see details of structure resolution in the text). (*b*) View showing the orientation of the two azaferrocene ligands on the porphyrin core

The dihedral angle between the pyrrolyl plane and the mean plane of the porphyrin core is 70.6(2)° presumably as a result of the steric hindrance experienced by the C_5H_5 ring and the haem plane. This compares well to angles of 65 and 67° found in the two molecules of **4**.[28] The bond lengths and angles in the azaferrocene molecules are within acceptable agreement with those in **4** and the angle between the cyclopentadienyl and pyrrolyl ligand plane is 4.3(5)° also similar to those reported (3.5 and 5.5°) for **4**.[28]

The orientation of the axial ligands with respect to the porphyrin core is usually characterised by the dihedral angle α between the axial ligand plane and the co-ordination plane [defined by a porphyrinato nitrogen atom N(1), the metal atom and the N atom of the axial ligand]. In compounds **1**, **4** and **5** the tilting of the axial ligand planes to the porphyrin plane means that reporting the angle in this way is not precise, though for **1** it is 22.9(4)°, similar to the value found in the iron(II) compound **4** (20°). One can define the orientation of the azaferrocene moiety by the angle β between the same co-ordination plane and the plane Fe–N_{axial}–Fe(1); $\beta = 72.3(3)°$. This latter description of the orientation is much more satisfying for axial ligands where tilting is encountered.

The structure of the cobalt(III) compound **5** may be com-

Table 1 Crystal data and structure refinement parameters for complexes **1** and **5**

	$[Fe(oep)\{Fe(C_5H_5)(C_4H_4N)\}_2][O_3SCF_3]$	$[Co(oep)\{Fe(C_5H_5)(C_4H_4N)\}_2][ClO_4]$
Empirical formula	$C_{55}H_{62}F_3Fe_3N_6O_3S$	$C_{54}H_{62}ClCoFe_2N_6O_4$
M	1115.77	1069.24
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.616(5)	12.987(5)
b/Å	11.193(5)	33.065(13)
c/Å	12.882(6)	12.215(5)
α/°	95.28(4)	
β/°	110.49(5)	110.21(5)
γ/°	109.40(5)	
U/Å^3	1314.3(11)	4922(7)
Z	1	4
D_c/g cm^{-3}	1.41	1.36
μ/mm^{-1}	0.92	1.02
F(000)	583	2240
Crystal size/mm	0.15 × 0.35 × 0.40	0.05 × 0.10 × 0.15
θ/°	2–28	2–25
hkl Ranges	−14 to 12, −14 to 14, 0–16	−15 to 14, −38 to 39, 0–12
Collected reflections	5668	5465
Observed reflections $[I > 2\sigma(I)]$	4605	1026
Least-squares refinement	Full matrix on F^2	Blocked matrix on F
Data, parameters	5659, 323	1026, 328
Goodness of fit	0.763	1.10
Final R $[I > 2\sigma(I)]$	0.094	0.056
(all data)	0.111	
Weighted R	0.284	0.057
Weighting scheme, w	$[\sigma^2(F_o^2) + (0.3P)^2 + 2.8P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	$[\sigma^2(F_o) + 0.05F_o^2]^{-1}$
Largest difference peaks/e Å^{-3}	1.9, −0.7	0.8, −0.5

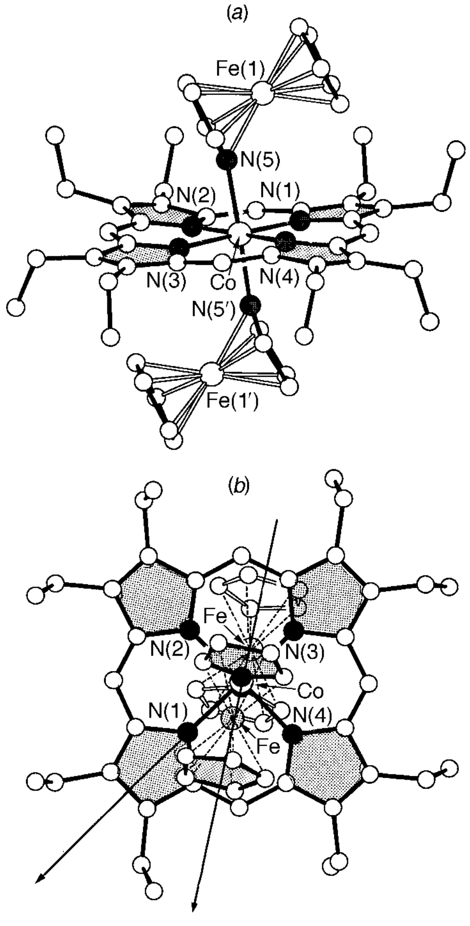

Fig. 2 (*a*) Structure of complex **5**. The Co–N_{por} bond distances range from 1.96(2) to 2.00(2) Å, the axial Co–N bond lengths 1.94(2) and 2.01(2) Å. (*b*) View of the structure showing the orientation of the two azaferrocene ligands on the porphyrin core

pared with those of the low-spin iron(III) structures from the point of view of the charge on the central metal but also to the iron(II) structures[28,42] from the point of view of the $3d^6$ electron count on the central metal. The precision of this structure is not sufficient (the crystal was too small) to facilitate discussion on the bond lengths and angles. The two azaferrocene ligands which are not related by symmetry elements (in contrast to compounds **1** and **4**) are in parallel configuration. The dihedral angles α between the axial ligands planes and co-ordinate plane N_{axial}–Co–$N(4)_{por}$ vary from 38(1) to 39(1)°. The rotational orientation of the azaferrocene moieties, which may be defined by the angle β between the co-ordinate plane Co, N_{axial}, $N(4)_{por}$ and the plane (Co, N_{axial}, Fe), is 56(1)°. The dihedral angles between the pyrrolyl ligand planes and the mean plane of the porphyrin core are 66(1) and 67(1)° again similar to those in structures **1** and **4**.[28] So once again the steric interaction between the C_5H_5 ring and the porphyrin plane is manifest. The bond lengths and angles are in acceptable agreement with those found in **1** and **4** and also those reported previously in alkyl(η^1-azaferrocene)cobaloximes.[26,28]

Mössbauer spectroscopy

The data from the Mössbauer spectra of compounds **1**–**5** and those of azaferrocene and other relevant literature data appear in Table 2. Compound **4** shows a change of 0.09 mm s^{-1} in the q.s. of co-ordinated azaferrocene compared to azaferrocene itself suggesting a small reduction in the electron density of the donation from the e_1 orbital on the ring to the iron centre. This change in q.s. is small compared to changes we have previously found for substituted ferrocenes compared to ferrocene itself,[46–48] however, protonation of azaferrocene only causes a change of 0.15 mm s^{-1}.[25] Thus the first question is does the q.s. of azaferrocene tell us anything about the bonding properties to the Fe^{II} in the porphyrin centre? In principle the bonding of the azaferrocene to Fe(tfpp) could be caused in three ways: (*a*) due to the nitrogen lone-pair σ bonding to the Fe of the porphyrin ring (donation of its electrons) and causing a slight polarisation of the ring e_1 electrons toward the now electron-deficient N atom; (*b*) by a combination of (*a*) and pyrrolyl ring π bonding to the iron porphyrin (by π donation to the metal); (*c*) by a combination of (*a*) and pyrrolyl ring

Table 2 Iron-57 Mössbauer data (mm s^{-1}) for compounds **1**–**5** and azaferrocene[a]

	Porphyrinic site			Azaferrocene site		
Complex	δ	Δ	Γ	δ	Δ	Γ
1	0.30(6)	2.24(6)	0.29(2) (0.55)(6)	0.52(1)	2.45(1)	0.12(1)
2	0.27(2)	1.92(4)	0.58(4)	0.54(1)	2.42(1)	0.14(4)
3				0.55(1)	2.47(1)	0.12(2)
4	0.44(1)	1.25(2)	0.13(1)	0.53(1)	2.42(1)	0.11(1)
5				0.56(1)	2.42(1)	0.11(1)
Azaferrocene[b]				0.54(1)	2.51(1)	0.14(1)

[a] δ = Isomer shift, Δ = quadrupole splitting, Γ = half-width at half-height. [b] Taken from ref. 25.

π bonding to the iron porphyrin (by metal to ring back bonding).

The reduction in the q.s. of the azaferrocene on bonding to Fe(tfpp) provides evidence for which of the above mechanisms is correct. Consider how the q.s. arises in azaferrocene: q.s. $\propto 2p_2 - p_1$, where p_2 and p_1 are the electron populations of the azaferrocene e_2 and e_1 orbitals.[46] The e_2 orbitals have twice the effect of the e_1 orbitals on the q.s.[47,48] Thus removal of electron density from the e_1 orbitals [due to bonding to Fe(tfpp)] would increase the q.s. of the azaferrocene if there was no concomitant back bonding from the iron in the azaferrocene to the pyrrolyl ring *via* the e_2 orbitals. A decrease in q.s. as in this case is consistent with greater back bonding from the iron in the azaferrocene to the pyrrolyl ring showing that electron density has been removed from the pyrrolyl ring on bonding to Fe(tfpp). The q.s. decrease signifies that the e_1 orbital is more electron deficient after the azaferrocene binds to the Fe(tfpp). Thus this bonding removes electron density from the ring e_1 orbitals. The question is how? Mechanism (*c*) would involve increase in electron population of the ring e_1 orbitals and thus less need for e_2 back bonding and hence an increase in the q.s. and so can be ruled out as a possibility.

However, both mechanisms (*a*) and (*b*) would fit the reduction seen in the q.s. of azaferrocene on bonding to Fe(tfpp). To gain further insight into which is correct we now turn to the Mössbauer data for the iron in the Fe(tfpp) site. The isomer shift and q.s. values for the iron(II) in the porphyrin plane are typical of low-spin iron(II) porphyrins. For such compounds where the axial ligand is imidazole the q.s. is found to be between 0.9 and 1.0 mm s^{-1}.[49–51] For pyridine ligands higher q.s. values are observed between 1.11 and 1.20 mm s^{-1} at 77 K; the value of 1.25(2) mm s^{-1} for compound **4** is larger than the end of the latter range suggesting bonding similar to but weaker than that of pyridines.[49,51–56] Indeed for [Fe(tpp)(py)$_2$] (py = pyridine) the q.s. is 1.15 mm s^{-1}.[56] This suggests that in complex **4** the axial Fe–N bonds are purely σ with little or no π back bonding. The axial Fe–N bond distances support this interpretation.[28] Thus mechanism (*b*) can be eliminated and (*a*) is verified. It should be noted that in compound **4** the iron t_{2g} orbitals on the iron in the porphyrin are filled and thus further donation to them from the e_1 orbitals is impossible again eliminating mechanism (*b*).

Compound **1** (Table 2) is a low-spin iron(III) complex and the Mössbauer parameters for the iron(III) site are typical of a parallel configuration of the axial ligands (Table 2 also shows comparable compounds). Indeed this is found in the structure (see above). This is not surprising in view of our earlier report[28] of the EPR spectrum which is rhombic, however it has a large g_z value which we will discuss in the next section more fully. The q.s. of the co-ordinated azaferrocene in compound **1** is only 0.06(1) mm s^{-1} less than that of azaferrocene itself. Again a long axial bond in this structure suggests little back bonding (if any). Yet the dihedral angles of the ligand pyrrolyl planes with the plane defined by one N_{por}, the central iron and the azaferrocene N was 23°, which although not ideal is close to values found by other workers where back bonding was said to occur.[2,3,7] We note that in compound **4** similar angles were found[28] and as shown (see above) little evidence of back bonding is apparent.

In compound **3** the azaferrocene only shows a slight change in q.s., 0.04(1) mm s^{-1} from the parent, and so again this may be explained by azaferrocene being a weak σ donor.

The Mössbauer parameters for the low-spin iron(III) site in compound **2** are close to others that have been interpreted as belonging to a site in which the axial ligands are nearly perpendicular.[2,4] We fitted the Mössbauer spectrum using a simple doublet for this site rather than two singlets. The fact that the spectrum seems to suggest a perpendicular arrangement of the axial ligands is worthy of note; first the three known structures (compounds **1**, **2** and **5**) all show parallel configurations, and secondly the EPR data recorded at 3.5 K were rhombic with $g_z = 3.24$, which is consistent with a parallel configuration (but again high). We will return to this below.

The azaferrocene q.s. value for both compounds **2** and **4** is 0.09 mm s^{-1} smaller than that of azaferrocene itself. This value is in keeping with no back bonding from the iron(III), especially as there is no change on the azaferrocenyl iron when the oxidation state of the porphyrin iron changes.

As both compounds **3** and **4** contain a 3d^6 electron configuration at the porphyrinic metal centre then these two centres might have been expected to be good π donors to azaferrocene. No Mössbauer evidence was found in favour of this suggestion, and the fact that the planes of the pyrrolyl rings were found to make an angle of around 70° to the porphyrin plane would also discourage π back bonding. Further reinforcement of this argument comes from the q.s. for compound **5**; here again a lowering of 0.09(1) mm s^{-1} relative to azaferrocene is observed, again a 3d^6 electron configuration is present and a similar structural pattern occurs and thus no evidence for back bonding is found in the Mössbauer data.

Compounds **1** and **2** contain 3d^5 electronic configurations and have a hole in the t_{2g} orbitals into which pyrrolyl π electrons could donate; again no evidence is found for this in the Mössbauer parameters or in the structure of **1**.

Electron paramagnetic resonance

The EPR spectra of complexes **1** and **2** have been previously reported.[27] The data appear in Table 3 along with relevant literature data.[57–62] The spectra of **1** and **2** are of rhombic type but with relatively high g_z values approaching those found in HALS spectra.

Previously rhombic type spectra of iron porphyrins have only been found for strongly co-ordinating unhindered imidazoles and highly basic pyridines. It is therefore somewhat surprising that compounds **1** and **2** manifest such spectra, although the crystal structure of **1** shows that the pyrrolyl planes are parallel. The Mössbauer spectrum of **1** is also in keeping with such an axial arrangement of the ligands, whereas that of **2** does not fit such an arrangement very well. To explain these observations it

Table 3 The EPR data of bis-ligated imidazole, azaferrocene and pyridine porphyrinatoiron(III) complexes in solution at 77 K

Complex	Solvent	g_z	g_y	g_x	Ref.
Imidazole derivatives					
$[KL^2][Fe(tpp)(4\text{-mim})_2]$	CH_2Cl_2	2.60	2.24	1.82	57
$[FeL^1(1\text{-mim})_2(OH)]$	Water–ethanol (1 : 1)	2.74	2.27	1.72	11
$[FeL^1(Him)(Im)]$	Me_2SO + OH	2.76	2.28	1.68	58, 59
$[Fe(tpp)(4\text{-Hmim})_2]I$	CH_2Cl_2	2.847	2.288	1.590	60
$[Fe(tpp)(bim)_2]I$	CH_2Cl_2	2.860	2.306	1.561	60
$[Fe(tmp)(1\text{-mim})_2]ClO_4$	CH_2Cl_2	2.886	2.325	1.571	2
$[Fe(tpp)(1\text{-mim})_2]I$	CH_2Cl_2	2.886	2.294	1.549	60
$[Fe(tpp)(1\text{-mim})_2]ClO_4$	CH_2Cl_2	2.890	2.291	1.554	61
$[FeL^1(1\text{-mim})_2]^+$	Me_2SO	2.97	2.27	1.51	16
$[FeL^1(Him)_2]^+$	Me_2SO	3.02	2.24	1.51	59
$[Fe(tpp)(dmim)_2]I$	CH_2Cl_2	3.40			60
$[Fe(tpp)(2\text{-Hmim})_2]I$	CH_2Cl_2	3.40			60
$[Fe(tpp)(2\text{-Hmim})_2]Cl$	$HCONMe_2$	3.41			15
$[Fe(tpp)(Hdmbim)_2]I$	CH_2Cl_2	3.43			60
$[FeL^1(2\text{-Hmim})_2]^+$	$HCONMe_2$	3.48	2.36	1.05	62
Azaferrocene derivatives					
$[Fe(tpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]^+$	$CHCl_3$	3.16	2.20	1.45	27
$[Fe(oep)\{Fe(C_5H_5)(C_4H_4N)\}_2]^+$	$CHCl_3$	3.24	2.05	1.31	27
Pyridine derivatives					
$[Fe(tpp)(dmadmpy)_2]I$	CH_2Cl_2	2.785	2.281	1.675	60
$[Fe(tpp)(dmapy)_2]I$	CH_2Cl_2	2.786	2.284	1.657	60
$[Fe(oep)(dmpapy)_2]ClO_4$	CH_2Cl_2	2.828	2.278	1.642	2
$[Fe(tpp)(apy)_2]I$	CH_2Cl_2	2.830	2.289	1.603	60
$[Fe(tpp)(dapy)_2]I$	CH_2Cl_2	2.864	2.280	1.597	60
$[Fe(tpp)(dmampy)_2]I$	CH_2Cl_2	2.865	2.286	1.591	60
$[Fe(tdcpp)(apy)_2]ClO_4$	CH_2Cl_2	3.24			2
$[Fe(tmp)(dmapy)_2]ClO_4$	CH_2Cl_2	3.33			2
$[Fe(tpp)(dmpy)_2]ClO_4$	CH_2Cl_2	3.40			60
$[Fe(tdcpp)(dmapy)_2]ClO_4$	CH_2Cl_2	3.54			2

L^2 = 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; 4-mim = 4-methylimidazolate; 1-mim = 1-methylimidazole; Him = imidazole; bim = 1-benzylimidazole; H_2tmp = 5,10,15,20-tetramesitylporphyrin; dmim = 1,2-dimethylimidazole; 2Hmim = 2-methylimidazole; Hdmbim = 5,6-dimethylbenzylimidazole; dmadmpy = 4-dimethylamino-3,5-dimethylpyridine; dmapy = 4-dimethylaminopyridine; apy = 4-aminopyridine; dapy = 3,4-diaminopyridine; dmampy = 4-dimethylamino-3-methylpyridine; H_2tdcpp = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin; dmpy = 3,4-dimethylpyridine.

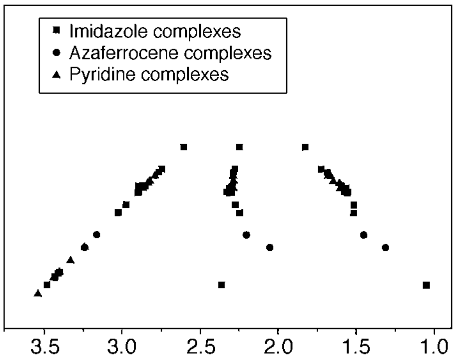

Fig. 3 A Symons diagram showing the range of g values for various low-spin iron(III) porphyrin complexes based on literature data for solid-state imidazole pyridines and our results for the azaferrocene derivatives given in Table 3. The g_1 values were placed on a 45° line for display purposes only; the vertical axis has no specific significance

is interesting to plot the known EPR spectra in such a way that the g_z values for the series are linear (Fig. 3).[57–62] Such a plot is known as a Symons plot.[63] When this is done it can be appreciated how close to the HALS positions compounds **1** and **2** are. To consider the orbital arrangements for HALS and rhombic splittings three possible cases must be considered.

The first (*a*) is when $V \gg \lambda$ and $D \gg \lambda$ (V is the rhombic distortion parameter, D is the tetragonal distortion parameter and λ is the spin–orbit coupling constant) the ground state is an orbital singlet (^2B) and the unpaired electron is localised in d_{yz} (see Fig. 2, ref. 4). This then generates an unequal distribution of charge density in the x and y directions and gives rise to a large crystal field. This is the situation that arises when the two axial ligands are parallel and interact in some way with the iron d_{yz} orbital making it the highest-energy orbital (as shown by analysis of EPR data).[62,64] Scheidt and co-workers[1,65,66] have shown that such a parallel arrangement of axial ligand planes is thermodynamically the more stable form. Such compounds display rhombic EPR spectra.[2,11,16,59–61]

The second case (*b*) is when $V < \lambda$ and $D \gg \lambda$ the unpaired electron is delocalised over the d_{xz} and d_{yz} orbital giving rise to an orbital-doublet (^2E) ground state for the complex. This situation is brought about by an effective electronic axial symmetry; the crystal field is obviously smaller than that of case (*a*). This case arises when one of the axial ligands interacts with the iron d_{xy} orbital and the other with the iron d_{xz} orbital. For greatest interaction the ligands should be orientated perpendicular to each other. An example of this is in the structure and EPR spectrum of $[Fe(tpp)(py)_2]^+$ where two pyridine molecules adopt a perpendicular geometry and the d_{xz} and d_{yz} orbitals are nearly degenerate.[24] Thus this situation gives rise to highly anisotropic low-spin (HALS) spectra.[2,15,60]

The third case (*c*) arises when $V < \lambda$ and $D < \lambda$ and the energy states are close together. Electrostatic interactions or spin–orbit coupling may mix the ^2E and ^2B states or an interaction may arise where there is only a slight preference to split the energies of the d_{xz} and d_{yz} orbitals.

It is noted that very small q.s. values for low-spin iron(III) porphyrin complexes have been observed, for example 0.53 mm s^{-1} at 80 K in $Na[FeL^1(CN)_2]$ (H_2L^1 = protoporphyrin IX = 3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropanoic acid)[67] and in $[Fe(tpp)(cpy)_2]ClO_4$ (cpy = 4-cyanopyridine);[68] in these compounds the ground state has been explained as either '$^2B_{2g}$' or as a mixed '$^2B_2$ and ^2E_g' state.[68]

As there should be little or no π–π interactions between the porphyrin iron and the pyrrolyl ring of the azaferrocene ligand (as seen from the Mössbauer data discussed above), we had therefore expected near degeneracy in the d_{xy} and d_{yz} orbitals thus giving g_z values of ≈3.5 or higher, despite the fact that in compound **1** the pyrrolyl rings are parallel. Thus we would have expected a HALS spectrum. Significantly the α angle of 22.9(4) is not large and by comparison to the work of Quinn *et al.*[44] we would not expect a large g_z value (smaller or equal to 2.9 which is contrary to what we observe). This relatively large g_z value is therefore more surprising. The long porphyrin iron to axial pyrrolyl nitrogen bond length of 2.06(1) Å (which suggests little or no π bonding) must be a factor in generating the large g_z value. The steric interaction of the H atoms on the pyrrolyl rings with the d_{xz} or d_{yz} orbitals will be the main reason for splitting their degeneracy to produce a rhombic-type spectrum. Clearly here we demonstrate that a π interaction is not needed to produce this splitting, a steric effect is sufficient.

Such a long axial bond was also found in $[Fe(tfpp)\{Fe(C_5H_5)(C_4H_4N)\}_2]$[28] and a similar α angle for the eclipsed pyrrolyl rings [in the iron(II) compound no ligand π donation could occur as the metal t_{2g} orbitals are filled]. The long axial bonds therefore are the result of weak binding and the steric interactions of the H atoms with the d_{xz} or d_{yz} orbital containing the single electron, and also to the steric interaction of the other end of the azaferrocene molecule with the porphyrin π electrons trying to attain a minimum-energy position. Thus our finding is that the axial bond strength will affect the magnitude of g_z. The fact that for compound **1** the q.s. is 2.24(6) mm s^{-1} yet the pyrrolyl rings are totally parallel means that for long axial bonds of this type this q.s. is a maximum, 0.16 mm s^{-1} lower than that found for imidazole ligands.[4] Thus a similar lower value for a perpendicular arrangement where the d_{xz} and d_{yz} orbitals are degenerate might also be expected. This means that the q.s. for compound **2** may in fact also represent a parallel arrangement with the q.s. value for perpendicular being below 1.8 mm s^{-1}. Indeed for **2** the g_z is 3.16, which though still higher than 2.9 is lower than that for **1** as is the q.s.

Conclusion

We have found for compounds **1** and **2** that rhombic spectra with unusually large g_1 values can arise from cases where the axial ligands are parallel, but are sterically hindered. In these cases π bonding from the metal to the ligand is non-existent or very weak. Under such circumstances the Mössbauer q.s. values are consistent with a parallel arrangement of the azaferrocene pyrrolyl planes.

Recently Nakamura *et al.*[69] have reported sterically hindered porphyrin complexes which although manifesting perpendicular arrangements of the ligands gave g_z values that are more typical of rhombic spectra. It thus appears from this work and that of Nakamura *et al.*[69] that what is important is not the absolute value of g_z but the overall shape of the EPR spectrum. Thus there is a region of overlap in g_z between values of 3.0 and 3.3 where both rhombic and HALS spectra can occur depending on the nature of the axial ligands and/or steric effects on the porphyrin. We note that these azaferrocene-ligated iron(III) porphyrins give EPR spectra quite different to those we reported for aliphatic ligands.[70]

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