NMR Studies of the Electronic Structure of Low-spin Iron(III) Phosphonite Complexes: Unusual $(d_{xz},d_{yz})^4$ $(d_{xy})^1$ Configuration

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Complexation of dimethylphenylphosphonite to (5,10,15,20-tetraphenylporphyrinato)iron(III) yields a low-spin derivative $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$, showing NMR and EPR properties consistent with an iron(III) ion in the unusual ground-state configuration $(d_{xz},d_{yz})^4$ $(d_{xy})^1$.

Low-spin iron(III) porphyrins are of major interest because of the relevance of this spin state to a large number of haemoproteins, such as ferricytochromes a, b, c, d and f and the cyanomet forms of peroxidases, monooxygenases and oxygen-carrying haemoproteins. It has been accepted that most of the low-spin iron(III) haems have a $(d_{xz},d_{yz})^3$ ground state.[1] However, we recently reported that when two molecules of *tert*-butyl isocyanide are bound to iron(III) tetraphenylporphyrin $[Fe(tpp)]^+$, the NMR spectrum is indicative of a low-spin complex with an unusual $(d_{xy})^1$ ground state.[2] We now describe the preparation of a new low-spin iron(III) porphyrin bis-phosphonite compound showing also an unusual electronic structure which contrasts sharply with the electronic structure of low-spin iron(III) porphyrinato bis-phosphine analogues.[3]

Two major difficulties may be encountered in preparing iron(III) phosphonite complexes of porphyrins. First, autoreduction of the iron(III) state may occur, as previously reported with phosphine[4] and phosphite[5] ligands. Secondly, phosphonite is probably a weakly coordinating ligand for the iron(III) state due to a decrease of basicity of the ligand in comparison to phosphines, thus making iron(III) complexation difficult. Both situations have been previously encountered, although separately, with phosphine ligands[3] and with isocyanides.[2] Using perchlorate, a weak axial ligand,[6a] as an intermediate, allows us to solve this problem. Addition under argon of 8 equiv. of dimethylphenylphosphonite to $[Fe(tpp)]ClO_4$ in toluene affords the six-coordinate compound $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ **1**.† After 1 h, precipitation of a purple powder occurred and the product was collected by filtration (60% yield). For the preparation of the other iron(III) porphyrin derivatives with the phosphonite, $[Fe(omtpp)\{P(OMe)_2Ph\}_2]ClO_4$ **2** and $[Fe(tmtpp)\{P(OMe)_2Ph\}_2]ClO_4$ **3**, in which the phenyl rings of tpp are respectively fully *meta*- or *para*-methylated, the same procedure can be used with the corresponding perchlorate analogues in toluene solvent.[6b] The compound $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ exhibited an electronic spectrum with two Soret bands, one at 437 nm ($\varepsilon = 5.9 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and the second in the near-ultraviolet region (357 nm, $\varepsilon = 2.8 \times 10^4$). Spectra with a split Soret band are known as 'hyperporphyrin' spectra[7a] and have been previously reported for bis-phosphine haemin[3] and mercaptide phosphine haemin complexes.[7b,c]

The ^1H NMR spectrum of $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ is shown in Fig. 1 (273 K); isotropic shifts are listed in Table 1 (293 K). The peaks for the phenyl protons of the porphyrin ring are assigned completely by methyl substitution and in combination with proton decoupled experiments. For phosphonite axial ligands, measurement of the relative intensities and relative linewidths determines the assignment. The shifts of the phosphonite ligand remain independent of the presence of excess ligand. Hence axial ligand dissociation is not expected to be significant at ambient temperature.

However, the spectrum of $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ shows unexpected behaviour in that the pyrrole proton signal is found in a downfield position at δ 3.1 (25 °C). This contrasts with that of the pyrrole proton of $[Fe(tpp)(PMe_3)_2]ClO_4$ ($\delta = -19.6$)[3] and provides essential proof for a different electronic structure in these derivatives. Evans' magnetic measurements[8] were made for 0.03 mol dm^{-3} CD_2Cl_2 solutions of $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ employing $SiMe_4$ as reference (25 °C). The solution magnetic moment ($\mu = 1.92\ \mu_B$) is compatible with the low-spin state $S = 1/2$.

In order to characterize the iron bis-phosphonite structure, analysis of the chemical shift was made according to the method

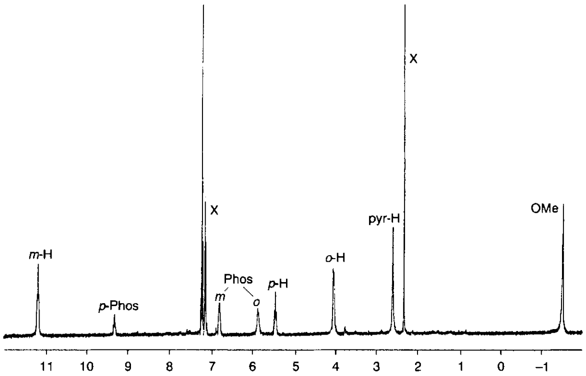

Fig. 1 Proton NMR spectrum of $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ in CD_2Cl_2 at 273 K. Assignment of the various resonances are indicated; x marks the residual solvent peaks (toluene).

Table 1 Observed shifts and separation of the isotropic shift into contact and dipolar contributions in $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$ in CD_2Cl_2 at 293 K

Proton type	$\Delta H/H$[a]	$(\Delta H/H)_{iso}$[b]	$(\Delta H/H)_{dip}$[c]	$(\Delta H/H)_{cont}$
o-H	4.50	−3.28	2.81	−6.08
m-H	10.89	3.13	1.31	1.82
	(1.99)[d]	(−0.61)	(0.82)	(−1.42)
p-H	5.73	−2.03	1.16	−3.19
	(6.09)[e]	(3.59)	(0.89)	(2.70)
pyr-H	2.56	−5.64	5.48	−11.12

[a] Chemical shifts in ppm. [b] Isotropic shift with the diamagnetic $[Fe(tpp)\{PPh(OMe)_2\}_2]$ complex as reference. [c] Based on relative geometric factors $(3\cos^2\theta - 1)/r^3$. [d] *m*-CH_3 shift in parentheses. [e] *p*-CH_3 shift in parentheses.

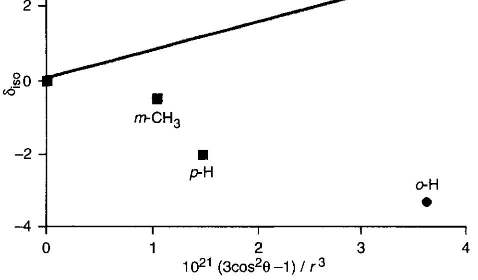

Fig. 2 Plot of isotropic shifts at 293 K *versus* the geometric factor $(3\cos^2\theta - 1)/r^3$ for aryl protons in $[Fe(tpp)\{P(OMe)_2Ph\}_2]ClO_4$

of La Mar *et al.*[9] The isotropic shifts were calculated by using [Fe(tpp){P(OMe)$_2$Ph}$_2$] **4** and related *meta-* and *para*-methyl substituted diamagnetic complexes, **5** and **6**, respectively, as references.‡ Plots of $(\Delta H/H)_{\text{iso}}$ *vs.* $(3\cos^2\theta - 1)/r^3$ for all *meso*-aryl positions for [Fe(tpp){P(OMe)$_2$Ph}$_2$]ClO$_4$ (and methyl substituents) are given in Fig. 2. The slope of the best-fit straight line yields directly the dipolar contribution to all shifts, while the magnitude of the deviation for the individual points will yield the contact contribution as previously suggested by La Mar.[9] It is clearly observed that (*i*) the fit of the isotropic shifts to the geometric factor is very poor, (*ii*) the best fit for the points yields a straight line with a weak slope with large deviations of alternating signs (Table 1). Thus the magnetic anisotropy is weak. It is interesting that the mechanism of spin-transfer appears here to give rise to a conclusion largely different to that observed from for low-spin iron(III) bis(phosphine) complexes of synthetic porphyrins.[3] In this latter case, the phenyl proton shifts of [Fe(tpp)(PMe$_3$)$_2$]ClO$_4$ were found to be essentially dipolar in origin, with a weak contact contribution in the *para* position.[3] Using the *o*-H dipolar shift, as determined above for compound **1** (Fig. 2), and the relative geometric factors,[1,9] the dipolar contribution to pyrrole-H can be obtained *via* the relation: $(\Delta H/H)^{i}\text{dip} = (\Delta H/H)^{o\text{-Hdip}}\,[(3\cos^2\theta - 1)r^{-3}]_i/[3\cos^2\theta - 1)r^{-3}]_{o\text{-H}}$. The resulting dipolar and contact contributions are also included in Table 1. The relatively small contact shift of pyrrole protons {$\Delta\delta = -11$ ppm for 1 *vs.* $\Delta\delta = -23$ ppm for [Fe(tpp)(PMe$_3$)$_2$]ClO$_4$[3]} favours the interpretation that weak spin density is placed on pyrrole carbons and accounts for the observed downfield shift.

Analysis of the curve in the Curie plot was also made for [Fe(tpp){P(OMe)$_2$Ph}$_2$]ClO$_4$. The temperature dependences of the isotropic shifts of the protons in CD$_2$Cl$_2$ are shown in Fig. 3. The isotropic shifts vary linearly with $1/T$, but the extrapolated lines do not pass through $1/T = 0$ and the pyrrole protons show an anti-Curie behaviour. As previously reported by us[2] and by Walker and Simonis,[1,10] the pattern of isotropic shifts observed and the anti-Curie behaviour of the pyrrole protons are indicative of a $(d_{xz},d_{yz})^4\,(d_{xy})^1$ ground state.

It has been recognized that the EPR *g* values of low-spin ferriporphyrins provide valuable information about the orbital of the unpaired electron.[1] The EPR spectrum of [Fe(tpp){P(OMe)$_2$Ph}$_2$]ClO$_4$ is axial in frozen solution with $g\perp = 2.365$ and $g\| = 1.974$ at 90 K (solid state, $g\| = 1.98$ and $g\perp$ unresolved at 90 K). The relative energies of the three t_{2g} d orbitals can be calculated from the *g* values in solution, using a general theory elaborated by Taylor.[11] Thus Δ/λ is negative (-6.4) indicating that the ground state is largely $(d_{xy})^1$. It is noteworthy that the EPR *g* values reported for [Fe(tpp)(PMe$_3$)$_2$]ClO$_4$[3] are 2.687, 2.088 and 1.680 at 140 K, whereas at 8 K, only one signal is observed at $g = 3.5$.[1]

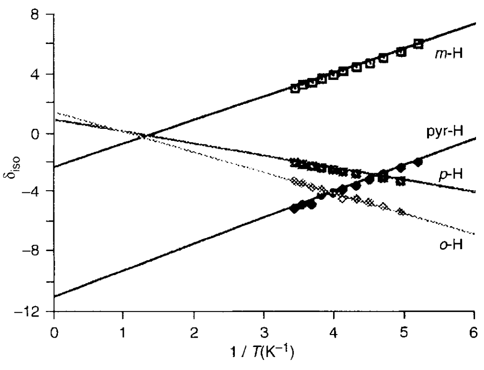

Fig. 3 Plot of isotropic shift *vs.* reciprocal temperature for [Fe(tpp){P-(OMe)$_2$Ph}$_2$]ClO$_4$ in CD$_2$Cl$_2$

The low-basicity phosphonite derivatives stabilize the unusual electronic ground state $[(d_{xy})^1]$ for low-spin Fe$^{\text{III}}$. It should be underlined that a similar situation was very recently reported with low-basicity cyanopyridine complexation to ferriporphyrins.[10] This study suggests that the $(d_{xz},d_{yz})^4\,(d_{xy})^1$ ground state is stabilized when the empty π^* orbital of the pyridine is similar to the energy of the d orbitals of the iron(III). The large π-spin delocalization to the *meso* positions, observed both with phosphonite and pyridine ligands, may occur from partial porphyrin π-cation radical character to the electronic configurations, as recently suggested.[10] In conclusion, the change in ground state of low-spin Fe$^{\text{III}}$ from the usual $(d_{xy})^2\,(d_{xy},d_{yz})^3$ to the unusual $(d_{xz},d_{yz})^4\,(d_{yz})^1$ electron configuration occurs both with trivalent phosphorus ligands and pyridine ligands and seems largely related to the basicity of the ligand.

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Footnotes

† *Selected data* for **1**: UV–VIS (CH$_2$Cl$_2$): λ/nm 357 (ε 28 dm^3 mmol^{-1} cm^{-1}), 437 (ε 59), 553 (ε 7), 605 (ε 5.3). For **2**, ^{1}H NMR: δ −1.32 (s, 12 H, OMe), 1.99 (s, 12 H, *m*-CH$_3$), 3.21 (s, 8 H, pyr), 3.7 (m, 8 H, *o*-H, por), 5.28 (t, 4 H, *p*-H, por), 5.72 (s, 4 H, *o*-H, ligand), 6.79 (s, 4 H, *m*-H, ligand), 9.12 (s, 2 H, *p*-H, ligand), 10.96 (t, 4 H, *m*-H, por). For **3**, ^{1}H NMR: δ −1.5 (s, 12 H, OMe), 3.5 (s, 8 H, pyr), 3.9 (s, 8 H, *o*-H, por), 5.7 (s, 4 H, *o*-H, ligand), 6.09 (s, 12 H, *p*-CH$_3$), 6.8 (s, 4 H, *m*-H, ligand), 9.2 (s, 2 H, *p*-H, ligand), 11.44 (m, 8 H, *m*-H, por).

‡ The diamagnetic bis-phosphonite iron(II) porphyrins **4**, **5** and **6** were prepared by a method previously reported.[12] The complexes were not recrystallized and the data were obtained for solutions containing a sixfold excess of the ligand to ensure that the desired complex is the only bis-complex in solution. Selected spectroscopic data for **4**, VIS (CH$_2$Cl$_2$): λ/nm 449, 550, 588. ^{1}H NMR: δ 7.5 (m, 12 H, *m*-, *p*-H), 7.77 (m, 8 H, *o*-H), 8.2 (s, 8 H, pyr). For **5**, λ/nm 449, 551, 589. ^{1}H NMR: δ 2.6 (s, 12 H, *m*-CH$_3$), 7.6 (m, 8 H, *m*-, *p*-H), 7.91 (m, 8 H, *o*-H), 8.15 (s, 8 H, pyr). For **6**, λ/nm 450, 551, 590. ^{1}H NMR: δ 2.5 (s, 12 H, *p*-CH$_3$), 7.7–7.9 (m, 16 H, *o*-, *m*-H), 8.21 (s, 8 H, pyr). NMR spectra were recorded on a Bruker AC 300P spectrometer in CD$_2$Cl$_2$ at 300 MHz. EPR spectra were recorded on a Varian spectrometer at 90 K in CH$_2$Cl$_2$. Visible spectra were measured on a Uvikon 941 spectrometer in chloroform. Satisfactory elemental analyses were obtained for **1** and **3** but not for **2**, possibly because of partial decomposition (in this case, the solution was reduced in volume to ensure precipitation, due to the high solubility of **2** in toluene).

References

1 A. Walker and U. Simonis, in *Biological Magnetic Resonance*, 1993, ed. L. J. Berliner and J. Reuben, Plenum, New York, vol. 12, p. 132.
2 G. Simonneaux, F. Hindré and M. Le Plouzennec, *Inorg. Chem.*, 1989, **28**, 823.
3 G. Simonneaux and P. Sodano, *Inorg. Chem.*, 1988, **27**, 3956.
4 G. La Mar and J. D. Gaudio, *J. Bioinorg. Chem.*, 1977, **2**, 207.
5 T. Ohya, H. Morohoshi and M. Sato, *Inorg. Chem.*, 1984, **23**, 1303.
6 (*a*) C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kasner, W. R. Scheidt, K. Spartalian and G. Lang, *J. Am. Chem. Soc.*, 1979, **101**, 2948; (*b*) H. Goff and E. Shimomura, *J. Am. Chem. Soc.*, 1980, **102**, 31.
7 (*a*) L. K. Hanson, W. A. Eaton, S. G. Sligar, I. C. Gunsalus, M. G. Gouterman and C. R. Connell, *J. Am. Chem. Soc.*, 1976, **98**, 2672; (*b*) H. H. Ruf and P. Wende, *J. Am. Chem. Soc.*, 1977, **99**, 5499; (*c*) H. H. Ruf, P. Wende and V. Ullrich, *J. Inorg. Biochem.*, 1979, **11**, 189.
8 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
9 G. N. La Mar, T. J. Bold and J. D. Satterlee, *Biochim. Biophys. Acta*, 1977, **498**, 189; G. N. La Mar, J. Del Gaudio and J. S. Frye, *Biochim. Biophys. Acta*, 1977, **498**, 422.
10 M. K. Safo, G. P. Gupta, C. T. Watson, U. Simonis, F. A. Walker and W. R. Scheidt, *J. Am. Chem. Soc.*, 1992, **114**, 7066; M. K. Safo, F. A. Walker, A. M. Raitsimring, W. P. Walters, D. P. Dolata, P. G. Debrunner and W. R. Scheidt, *J. Am. Chem. Soc.*, 1994, **116**, 7760.
11 C. P. S. Taylor, *Biochim. Biophys. Acta*, 1977, **491**, 137.
12 P. Sodano, G. Simonneaux and L. Toupet, *J. Chem. Soc., Dalton Trans.*, 1988, 2615.