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Comparative study of Mössbauer spectra of iron(III) complexes of *para*-substituted tetraphenylporphyrins. Electronic effects of substituents and axial ligands

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The Mössbauer spectra of high-spin iron(III) complexes of tetra-*para*-substituted derivatives of 5,10,15,20-tetraphenylporphyrin [FeL(X)] (R = OMe, H, F or Cl; X = Cl, Br or I), have been compared with each other to clarify the electronic effects of the phenyl substituents and the axial ligands. They show a variety of patterns depending on the temperature: asymmetric broadening of the high-velocity line at higher temperatures, a symmetric doublet at a temperature T_r, and reversal in asymmetry below T_r. The temperature dependence results from the temperature-dependent spin–spin relaxation of high-spin iron(III) ion and the off-diagonal terms of the hyperfine operator, and reflects the ionic zero-field splitting. The reversal temperature, T_r, and the quadrupole splitting, ΔE_Q, show two kinds of dependence on R. This is explained by considering the σ- and π-bonding characteristics of the porphyrins under the influence of the substituents. With a given R, the values of both T_r and ΔE_Q increase in the order X = Cl < Br < I. This is interpreted as due to the predominantly ionic character of the bond between the halide and iron ions, except for R = OMe.

A number of recent studies of model haem compounds have demonstrated the importance of substituent effects in porphyrins[1–10] in connection with the diverse biological functions of haem proteins. We have recently carried out[10a] a comparative study of the visible spectra of a series of high-spin iron(III) complexes of tetra(*para*-R-substituted) derivatives of 5,10,15,20-tetraphenylporphyrin (H_2tpp), [FeL(X)] where R = OMe, H, F or Cl and X = Cl, Br or I. Analysis of the absorption bands assigned to porphyrin π, π* transitions including vibronic transitions and porphyrin-to-iron charge-transfer transitions revealed that the electron-withdrawing and -releasing ability of the phenyl substituents and the electronegativity of the axial ligands affect the energies of the iron d and porphyrin molecular orbitals, the electron–electron repulsion in the porphyrin ring and the vibrational frequencies of the porphyrin skeletal modes.

Mössbauer spectra of high-spin iron(III) complexes of porphyrins are temperature dependent.[11–14] At higher temperatures a less intense, broadened peak lies at high energy. As the temperature is lowered the pattern gradually becomes symmetric. In a further low-temperature region, however, one finds a reversal in the asymmetry of the quadrupole doublet in some cases, in the sense that now it is the lowest energy line which starts to become broader than the other. The temperature-dependent asymmetric pattern was first explained by Blume[15] on the basis of magnetic relaxation effects. Dattagupta[16] later pointed out that such a 'reversal of asymmetry' in the Mössbauer spectra as the temperature of the absorber is decreased can be accounted for by the extended stochastic theory of Clauser and Blume[17] where off-diagonal terms in the hyperfine interaction are included. The temperature at which the reversal occurs, T_r, was shown to depend only on the size of the ionic zero-field splitting, not on the strength of the dipole–dipole interaction between ionic moments nor on the hyperfine interaction constant. Thus, T_r gives information on the zero-field splitting and hence the d-orbital energies of the iron ion. To date, however, there appears to be no report on the experimental determination of T_r.

In this paper we report the Mössbauer spectra of the high-spin iron(III) complexes [FeL(X)]. It was anticipated that the electron-withdrawing and -releasing ability of the phenyl substituents and the electronegativity of the axial ligands would affect the energies of, and the electron distribution among, the d orbitals of the iron ion; consequently, T_r and the quadrupole splitting, ΔE_Q, were expected to change systematically depending upon the substituents and the axial ligands. The Mössbauer results are discussed in the context of its previous visible spectral study.[10a]

Results

The Mössbauer spectra of all the complexes show a similar temperature dependence. At higher temperatures, the less intense, broadened peak lies to higher energy. As the temperature is lowered the pattern becomes gradually symmetric. In a further low-temperature region a reversal in the asymmetry of the quadrupole doublet occurs in some cases. The spectra for R = Cl, X = Br at several temperatures are shown in Fig. 1. The data were fitted with a least-squares method using Lorenzian line shapes. The temperature, T_r, at which the reversal in the asymmetry of the quadrupole doublet occurs, was determined by plotting the linewidth ratio of the two components *versus* temperature, as shown in Fig 2. Mössbauer parameters together with the values of T_r are given in Table 1. The separate linewidths for two complexes at several temperatures are given here for examples. Values of W_1 and W_2/mm s^{-1} are: [Fe(tpp)Br] [T_r = 14(2) K)], 0.468(26) and 0.576(36) at 39.2(4) K, 0.407(26) and 0.456(29) at 19.5(2) K, 0.429(26) and 0.371(23) at 9.5(4) K, and 0.407(23) and 0.377(22) at 4.4(1) K; [Fe(tpp)I] [T_r = 29(2) K], 0.334(15) and 0.414(19) at 49.8(3) K, 0.350(14) and 0.361(14) at 34.9(9) K, 0.346(11) and 0.348(11) at 24.7(3) K, and 0.349(13) and 0.338(11) at 14.7(2) K.

Discussion

The values of ΔE_Q and δ_i in Table 1 are in the range typically observed[14] for high-spin iron(III) porphyrin derivatives. All the high-spin iron(III) porphyrin complexes so far studied are found to have nearly axial, positive electric field gradients. The ^{6}S ionic state is split by the axial crystal field into three Kramers

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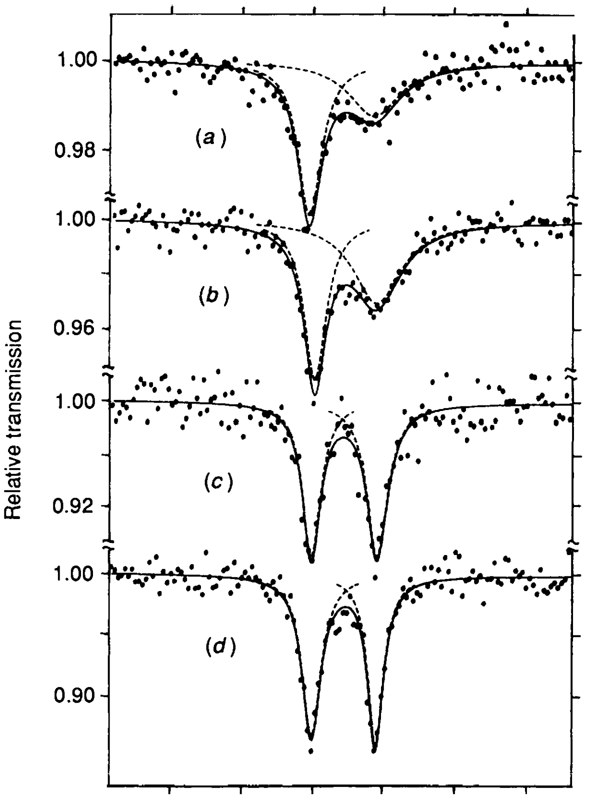


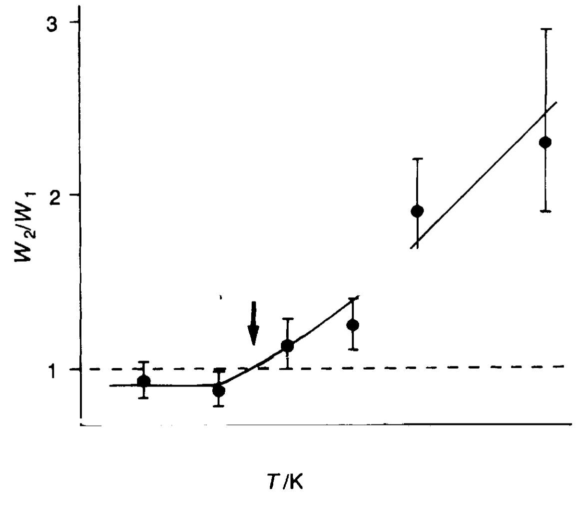


Fig. 2 Plot of the linewidth ratio of [Fe(tpp)Br] *versus* temperature; W_1 and W_2 represent the width of the low- and high-velocity lines, respectively, of a quadrupole-split Mössbauer spectrum

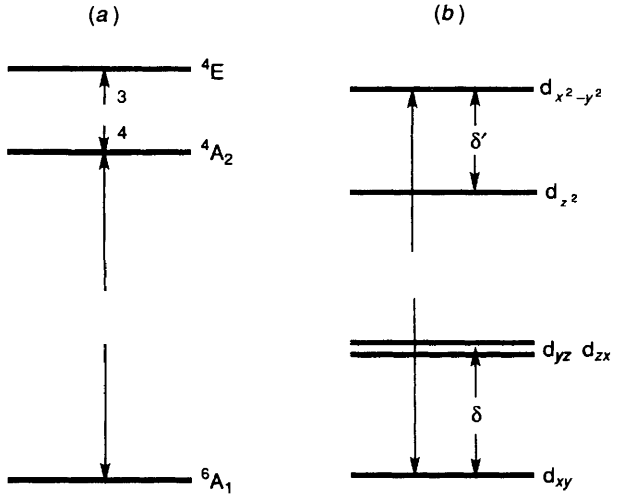
doublets with $M = \pm\frac{1}{2}$, $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$, at energies of 0, $2D$ and $6D$, respectively. The spin–spin relaxation times[15] in the $\pm\frac{5}{2}$ and $\pm\frac{3}{2}$ excited states are longer than that of the ground state. While the matrix elements of the off-diagonal terms in the hyperfine interaction are zero for the excited ionic levels, they are non-zero for the lowest doublet, $\pm\frac{1}{2}$.

At high enough temperatures the three Kramers doublets are occupied equally and the average rate of relaxation is relatively slow. The high-velocity line in the quadrupole doublet, which corresponds to the $\pm\frac{1}{2} \longrightarrow \pm\frac{3}{2}$ nuclear transition and is associated with greater magnetic hyperfine energy, is broader than the other line. At the lowest temperature only the ionic ground levels are populated. Although the relaxation rate between these two levels is rapid, the off-diagonal hyperfine terms lead to a low-temperature line broadening which is greater for the low-velocity line. Hence, a reversal in asymmetry occurs at an intermediate temperature T_r. Dattagupta's theoretical treatment[16] predicts that $2D/kT_r \approx 4$, nearly independent of the hyperfine interaction constant and the interionic spin–spin coupling. The zero-field splitting depends on the d-orbital crystal-field energies (see below).

Table 1 Mössbauer parameters for [FeL(X)]

R	X	$T_r{}^a$/K	$\Delta E_Q{}^b$/mm s^{-1}	$\delta_i{}^{b,c}$/mm s^{-1}
OMe	Cl	14(1)	1.08(2)	0.37(1)
	Br	37(5)	1.14(5)	0.40(4)
	I	24(3)	1.11(2)	0.44(1)
H	Cl	< 4	0.55(1)	0.42(1)
	Br	14(2)	0.68(1)	0.44(1)
	I	29(2)	0.76(1)	0.45(1)
F	Cl	5(1)	0.72(1)	0.42(1)
	Br	9(1)	0.73(1)	0.43(1)
	I	25(5)	0.86(3)	0.45(2)
Cl	Cl	8(1)	0.74(1)	0.42(1)
	Br	10(2)	0.90(1)	0.44(1)
	I	33(3)	1.04(1)	0.46(1)

The numbers in parentheses are the errors in the last figures. [a] Asymmetry reversal temperature. [b] Values at 4–5 K. [c] Isomer shift relative to metallic iron (α-Fe) at room temperature.



Zero-field splitting

The ground term of a high-spin iron(III) ion in a ligand field of D_4 symmetry is $^6A_1$. The spin–orbit interaction of $^6A_1$ with the low-lying $^4A_2$ and ^4E terms causes zero-field splitting of the ground term; the splitting parameter D is given by[18,19] equation (1) where ζ is the one-electron spin–orbit coupling

$$D = (\zeta^2/5)\{[1/E(^4A_2)] - [1/E(^4E)]\} \qquad (1)$$

constant, and $E(^4A_2)$ and $E(^4E)$ denote the energies of the $^4A_2$ and ^4E terms relative to the $^6A_1$ term. The energies of five-electron states are expressed[19,20] in terms of electrostatic energies and d-orbital crystal-field energies.

Fig. 3 is a schematic representation of the total energy of each five-electron state and orbital energies in D_4 symmetry; B and C are Racah parameters which represent electrostatic energies. A crystal field of tetragonal symmetry splits the originally five-fold degenerate d orbitals into four distinct energy levels, three singly and one doubly degenerate level. The tetragonal field parameters δ and δ' are defined as the splittings between $b_2(d_{xy})$ and $e(d_{yz}, d_{zx})$ orbitals and between $a_1(d_{z^2})$ and $b_1(d_{x^2-y^2})$ orbitals, respectively; Δ_{O_h} is a cubic field parameter which is the splitting between the t_{2g} and e_g orbitals in the limit of O_h symmetry. The requisite conditions for a larger value of D are indicated by equation (1): a lower energy of $^4A_2$ and/or a higher energy of ^4E. By inspection of Fig. 3, one can substitute orbital energies by term energies. Therefore, a larger value of D, and hence a higher temperature T_r, is obtained for larger values of Δ_{O_h} and/or δ and/or δ'.

Quadrupole splitting

While T_r reflects the crystal-field energies of the d orbitals, the quadrupole splitting ΔE_Q is determined by the electric-field gradient produced by an asymmetric distribution of electron charges about the ^{57}Fe nucleus. The asymmetry parameter is zero in D_4 symmetry, and the observed splitting is in equation (2) where $q = -V_{zz}$ and Q is the nuclear quadrupole moment

$$\Delta E_Q = eqQ/2 \qquad (2)$$

of the excited $I = \frac{3}{2}$ state of the ^{57}Fe nucleus; V_{zz} denotes the second derivative of the electrostatic potential V with respect to z.

We may separate q into two main contributions. One is the lattice contribution, q_{lat}, arising directly from charges on the five donor atoms about the iron(III) ion. The second is the valence contribution, q_{val}, resulting from an asymmetric distribution of electrons in the bonding and non-bonding orbitals. The total value of q is given[14] by expression (3) where

$$q = (1 - \gamma_\infty)q_{\mathrm{lat}} + (1 - R)q_{\mathrm{val}} \qquad (3)$$

$(1 - \gamma_\infty)$ and $(1 - R)$ are the antishielding factors accounting for induced polarization of inner electrons, and q_{lat} and q_{val} are expressed in terms of $e/4\pi\varepsilon_0$ as in equations (4) and (5). Here q_j

$$q_{\mathrm{lat}} = \sum_j q_j(3\cos^2\theta_j - 1)/r_j^3 \qquad (4)$$

$$q_{\mathrm{val}} = \sum_i p_i\langle(3\cos^2\theta_i - 1)/r_i^3\rangle \qquad (5)$$

is the charge on ion j the polar coordinates of which are θ_j and r_j, and p_i is the population of the ith valence-shell orbital, $\langle(3\cos^2\theta_i - 1)/r_i^3\rangle$ being the expected value of this population over the electronic coordinates θ_i and r_i. The summations are over all ions j and all valence-shell orbitals i.

It is often convenient[14] to use an approximation to discuss q_{val} in terms of the effective populations of the 3d and 4p orbitals, equation (6), where $N(d_i)$ and $N(p_i)$ are the effective

$$\begin{aligned} q_{\mathrm{val}} = {} & (4/7)\langle r^{-3}\rangle_{3d}\{N(d_{x^2-y^2}) - N(d_{z^2}) + N(d_{xy}) - \\ & \tfrac{1}{2}[N(d_{yz}) + N(d_{zx})]\} + (4/5)\langle r^{-3}\rangle_{4p}\{-N(p_z) + \\ & \tfrac{1}{2}[N(p_x) + N(p_y)]\} \end{aligned} \qquad (6)$$

populations of the appropriate 3d and 4p orbitals, respectively, and $\langle r^{-3}\rangle$ the expected value of $1/r^3$ taken over the appropriate 3d and 4p radial functions. Since $\langle r^{-3}\rangle_{3d} \gg \langle r^{-3}\rangle_{4p}$, it is usually considered that the major contribution to q_{val} arises from the first term in equation (6).

Although we expect $q_{\mathrm{val}} \gg q_{\mathrm{lat}}$, owing to the r^{-3} dependence, q_{val} is formally zero in high-spin iron(III) complexes because there is formally one electron in each of the five d orbitals; q_{lat} usually makes the dominant contribution to the total q. However, high-spin iron(III) porphyrin complexes have non-zero q_{val} arising from an imbalance in the effective populations of the five d orbitals. The positive signs of q observed for all the high-spin iron(III) porphyrin complexes so far studied indicate that the covalent bonding to the planar porphyrin is stronger than that to the axial ligands. In sum, we must take into consideration both q_{lat} and q_{val} in order to interpret the effects of the phenyl substituents and axial ligands on ΔE_Q.

Effects of the axial ligands

Table 1 shows that both T_r and ΔE_Q increase with the atomic number of the halide axial ligand. We can judge from this result which of the two types of bonding, ionic or covalent, is the major contribution to the bond between the central iron and the axial ligand. The ligand covalency is known to increase in the order $Cl^- < Br^- < I^-$ (nephelauxetic series[21]). If the bond were predominantly covalent, the expected results would be contrary to those in Table 1 both in respect of T_r and ΔE_Q. Increased covalency of the axial ligand would elevate the iron d_{z^2} orbital and increase the effective population of this orbital. As the energy of the $d_{x^2-y^2}$ orbital is not affected by the axial ligand to the first approximation, the value of δ' would decrease (Fig. 3). This would make the value of T_r smaller, in contrast to the experimental result. The increased $N(d_{z^2})$ would result in a smaller q_{val} [equation (6)] and ΔE_Q, which is also contrary to observation. Thus, the possibility that the bond between the central iron and the axial ligand is predominantly covalent is dismissed by both the T_r and ΔE_Q.

On the other hand, the results are explained by the assumption that the bond is predominantly ionic. A point-charge model in the framework of a crystal-field treatment is appropriate in such a case. We consider an iron ion at the origin of the x, y and z coordinate axes, replacing the axial ligand with an effective point charge $-ae$ (axial) placed at Z along the z axis, and replacing the four in-plane porphyrin nitrogen donors with effective charges $-he$ (horizontal) placed at $\pm R$ along the x and y axes. Then expression (7) is derived for the crystal-field

$$\delta + (3/4)\delta' = (5/12)[(2h/R^5) - (a/Z^5)]\langle r^4\rangle \qquad (7)$$

parameters[22] in units $e^2/4\pi\varepsilon_0$, where $\langle r^n\rangle$ is the expected value of r^n taken over an iron 3d orbital. Although the out-of-plane displacement of the iron atom is not taken into consideration for simplicity, the subsequent conclusions are valid qualitatively.

The electronegativity of the halogen atom, and hence the absolute value a of the negative charge of the axial halide ion, decreases in the order Cl > Br > I. This means that the value of a, not the extent of decrease in the value, is smallest for I. Equation (7) together with Fig. 3 indicate that a smaller value of a gives a larger value of the energy difference between the ^4E and $^4A_2$ terms, and hence a larger value of T_r. Thus, the expected order of T_r agrees with the experimental result. The ΔE_Q data are also explained by the same model. An axial ligand with effective point charge $-ae$ corresponds in equation (4) to $q_j = -a$ and $\theta_j = 0$. A smaller value of a gives a larger value of q_{lat}, and leads to a larger value of ΔE_Q through equations (3) and (2). The expected order of ΔE_Q is Cl < Br < I, which is again in agreement with experiment.

The same model in the framework of crystal-field theory has been successfully applied[10a] to interpret the visible spectral data for this series of complexes. A brief outline is reproduced here. The porphyrin $a_{1u}(\pi)$, $a_{2u}(\pi) \longrightarrow$ iron $e(d_{yz}, d_{zx})$ charge-transfer bands shift to lower energy in the order Cl < Br < I. The present model predicts depression of the d_{yz} and d_{zx} levels in this order, thereby leading to the red shift. When the expression for the tetragonal splitting parameter δ is partially differentiated by a, we obtain equation (8). We note that

$$\partial\delta/\partial a = [(3\langle r^2\rangle/Z^2) = (5/3)(\langle r^4\rangle/Z^4)]/7Z \qquad (8)$$

$\langle r^n\rangle/Z^n < 1$ and decreases with increasing n. Hence, the first term in equation (8) is greater than the second, *i.e.* $\partial\delta/\partial a > 0$. Since the energy of the d_{xy} orbital is not affected by the axial ligand to the first approximation, a less electronegative axial ligand causes a larger stabilization of the d_{yz} and d_{zx} orbitals. Stabilization of the orbital to which an electron is promoted in the $a_{1u}(\pi)$, $a_{2u}(\pi) \longrightarrow e(d_{yz}, d_{zx})$ charge-transfer transitions explains the observed red shift in the order Cl < Br < I.

Despite the decrease in the parameter δ [equation (8)] with decreasing electronegativity of the axial ligand, the sum $\delta + (3/4)\delta'$ increases [equation (7)]. It follows that δ' increases to overcome the decrease in δ. Thus, the energies of both the a_1 (d_{z^2}) and $e(d_{yz}, d_{zx})$ levels are lowered with decreasing electronegativity, or a, of the axial ligand. We can readily understand this conclusion intuitively by considering the electron distribution of these orbitals.

Effects of the phenyl substituents

The influence of the phenyl substituents on T_r and ΔE_Q is interpreted as due to electronic effects. Steric effects are considered to be of little significance in a series of complexes with not very bulky substituents at the phenyl *para* positions. The Hammett substituent constants σ_p are commonly used as the measure of the electron-withdrawing ability of substituents. The values of σ_p are -0.28, 0, 0.06 and 0.22 for OMe, H, F and Cl, respectively:[23] OMe is electron releasing and F and Cl are electron withdrawing relative to H. It seems most likely that OMe shifts the porphyrin molecular orbitals to higher energies through both inductive and resonance effects, and F and Cl shift them to lower energies. Such electronic effects are transmitted to an iron ion through the σ and π bonds between the iron and the porphyrin.

Table 1 indicates that the values of both T_r and ΔE_Q are larger for the complexes with R = OMe than those for R = H. The result is attributed to the increased σ donation to the iron from the porphyrin with R = OMe. This shifts the iron $d_{x^2-y^2}$ orbital to higher energy, and gives larger values of Δ_{O_h} and δ' (Fig. 3), since the energies of the other iron d orbitals are not affected by the porphyrin σ donation to a first approximation. As can be seen from equation (1) and Fig. 3, larger values of Δ_{O_h} and δ' result in a larger value of D, and hence a higher temperature T_r. In addition, the larger σ donation increases the effective population $N(d_{x^2-y^2})$, and leads to a larger value of ΔE_Q through equations (6), (3) and (2). Evidence in support of the increased σ donation in the case of R = OMe is provided by the smaller values of δ_i for the complexes with R = OMe than those for R = H. The δ_i values suggest substantial σ donation from the R = OMe ligand into the iron 4s orbital and increased s-electron density at the ^{57}Fe nucleus.

The values of both T_r and ΔE_Q for [FeL(I)] (R = OMe) deviate from those expected from their dependence on X: they should be larger than those for X = Br, if the bond between the iron and X were purely ionic. The deviation is probably caused by the increased σ donation. Stronger porphyrin-to-iron donation depresses the effective positive charge on the iron, and hence weakens the ionic bond to an axial ligand. Accordingly, the fraction of covalency in the bond increases. On the other hand, iodide has the largest covalency of the three halide ions studied here (see above). Thus, the fraction of covalency in the bond between the iron and the iodide ions when R = OMe is believed to be considerably high. The high covalency of the axial ligand elevates the iron d_{z^2} orbital and increases the effective population of this orbital; the decreased value of δ' makes the value of T_r smaller, and the increased $N(d_{z^2})$ results in a smaller q_{val} [equation (6)] and ΔE_Q.

For the complexes with electron-withdrawing substituents F and Cl the values of ΔE_Q are larger than those for those with R = H, whereas the values of T_r remain essentially unaltered. This result is not simply explained. A tpp ligand with an electron-withdrawing substituent at each *para* position is weaker both as a σ and π donor to the central iron than is unsubstituted tpp. The increase in ΔE_Q is probably attributed to decreases in $N(d_{yz})$ and $N(d_{zx})$, arising from the weaker porphyrin-to-iron π donation. However, the differences in iron–porphyrin π bonding must make δ and hence T_r smaller in the complexes with electron-withdrawing substituents, and some other mechanism is needed to account for the unchanged T_r.

It is known[14,24–26] that porphyrins act as 'electron sinks' or 'electron buffers', that is they are able to modify both their σ- and π-bonding characteristics towards iron in such a way that they maintain the effective number of electrons around the iron nearly constant. The virtually substituent-independent values of T_r make it seem likely that a decrease in porphyrin-to-iron π donation is accompanied by an increase in porphyrin-to-iron σ donation. This makes both Δ_{O_h} and δ' larger, and so a slight increase in the σ donation is sufficient to keep T_r practically constant. An increase in the σ donation makes $N(d_{x^2-y^2})$ larger, which further increases ΔE_Q in addition to the direct effect of the decrease in π donation.

It is probably the case that the porphyrin with R = OMe also acts as an 'electron sink': an increase in porphyrin-to-iron σ donation discussed is believed to be accompanied by a decrease in porphyrin-to-iron π donation. This second-order effect makes $N(d_{yz})$, $N(d_{zx})$ and δ smaller. The first-order effect of the increase in $N(d_{x^2-y^2})$ on ΔE_Q is amplified by the decrease in $N(d_{yz})$ and $N(d_{zx})$: the second-order effect leads to a larger ΔE_Q. The smaller δ as a result of the second-order effect counteracts the first-order effect of increased Δ_{O_h} and δ' on T_r: the values of T_r are diminished as compared to those in the absence of the second-order effect. The conclusions inferred here for R = OMe are consistent with the results in Table 1.

Conclusions

In order to investigate the effects of axial ligands and phenyl substituents on the electronic properties of iron porphyrin complexes, the values of the temperature T_r at which asymmetry reversal occurs and the quadrupole splitting ΔE_Q of the Mössbauer spectra have been determined for a series of high-spin iron(III) complexes [FeL(X)]. Both T_r and ΔE_Q were found to increase with the atomic number of the halide axial ligand. This indicates that the bond between the central iron and the axial ligand is predominantly ionic, and is explained on the basis of a point-charge model in the framework of a crystal-field treatment. The values of T_r and ΔE_Q show two kinds of dependence on R. Derivatives with the electron-releasing methoxy group have larger values of T_r and ΔE_Q than those for R = H. The result is attributed to increased σ donation to the iron for the porphyrin with R = OMe, probably accompanied by a decrease in π donation. On the other hand, complexes with electron-withdrawing substituents R have larger values of ΔE_Q but essentially unaltered values of T_r as compared to those for R = H. The result is explained by considering the 'electron-sink' capability of porphyrin macrocycles, whereby they are able to modify both their σ- and π-bonding characteristics towards iron in such a way that the effective number of electrons around the iron is maintained nearly constant. Such behaviour may well be responsible in part for the diverse functions in which metalloporphyrins participate in biological systems.

Experimental

The complexes [FeL(X)] were prepared as described previously.[10a] Powder samples were used for the Mössbauer measurements. A Toyo Research FGX-100S Mössbauer spectrometer was operated in conventional constant-acceleration mode with a source of 1.85 GBq ^{57}Co/Rh (Amersham). Isomer shifts, δ_i, are given relative to metallic iron (α-Fe) at room temperature. An Air Products LT-3-110 refrigerator was used to maintain the samples at temperatures in the liquid-helium region.

References

1 M. F. Isaac, Q. Lin, U. Simonis, D. L. Siffian, D. L. Wilson and F. A. Walker, *Inorg. Chem.*, 1993, **32**, 4030.

2 H. N. Fonda, J. V. Gilbert, R. A. Cormier, J. R. Sprague, K. Kamioka and J. S. Connolly, *J. Phys. Chem.*, 1993, **97**, 7024.

3 P. G. Gassman, A. Ghosh and J. Almlöf, *J. Am. Chem. Soc.*, 1992, **114**, 9990.

4 Y. Naruta, F. Tani and K. Maruyama, *Tetrahedron Lett.*, 1992, **33**, 1069.

5 T. G. Traylor, K. W. Hill, W.-P. Fann, S. Tsuchiya and B. E. Dunlap, *J. Am. Chem. Soc.*, 1992, **114**, 1308; T. G. Traylor, Y. S. Byun, P. S. Traylor, P. Battioni and D. Mansuy, *J. Am. Chem. Soc.*, 1991, **113**, 7821; T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, 1991, **26**, 1338.

6 T. Yoshimura, H. Toi, S. Inaba and H. Ogoshi, *Inorg. Chem.*, 1991, **30**, 4315.

7 G. Wu, W. Gan and H. Leung, *J. Chem. Soc., Faraday Trans.*, 1991, 2933.

8 T. Akasaka, M. Haranaka and W. Ando, *J. Am. Chem. Soc.*, 1991, **113**, 9898.

9 H. J. Callot, A. Giraudeau and M. Gross, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1321.

10 (*a*) T. Ohya and M. Sato, (*a*) *Abstr. 7th Symposium on Roles of Metals in Biological Reactions, Biology and Medicine*, Hamamatsu, 1995, 1-02; (*b*) *Nucl. Instrum. Methods*, 1993, **B76**, 313; (*c*) *J. Pharmacobio-Dyn.*, 1991, **14**, s-124.

11 R. G. Shulman and G. K. Wertheim, *Rev. Mod. Phys.*, 1964, **36**, 459.

12 C. Maricondi, D. K. Straub and L. M. Epstein, *J. Am. Chem. Soc.*, 1972, **94**, 4157; M. A. Torrens, D. K. Straub and L. M. Epstein, *J. Am. Chem. Soc.*, 1972, **94**, 4160, 4162.

13 G. W. Wang, J. L. Groves, A. J. Becker, L. M. Chirovsky, W. P. Lee, T. E. Tsai and C. S. Wu, *Hyperfine Interact.*, 1978, **4**, 910.

14 J. R. Sams and T. B. Tsin, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1979, vol. 4, pp. 425–478.

15 M. Blume, *Phys. Rev. Lett.*, 1967, **18**, 305; 1965, **14**, 96.

16 S. Dattagupta, *Phys. Rev. B*, 1975, **12**, 3584.

17 M. J. Clauser and M. Blume, *Phys. Rev. B*, 1971, **3**, 583.

18 M. Weissbluth, *Struct. Bonding (Berlin)*, 1967, **2**, 1.

19 A. S. Rispin, M. Sato and H. Kon, *Theor. Chim. Acta*, 1978, **50**, 95.

20 G. Harris, *J. Chem. Phys.*, 1968, **48**, 2191.

21 C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon, Oxford, 1962.

22 S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets of Transition-metal Ions in Crystals*, Academic Press, New York, 1970.

23 M. Charton, *Prog. Phys. Org. Chem.*, 1981, **13**, 119.

24 B. R. James, J. R. Sams and T. B. Tsin, *J. Chem. Soc., Chem. Commun.*, 1978, 746.

25 T. Ohya, H. Morohoshi and M. Sato, *Inorg. Chem.*, 1984, **23**, 1303.

26 H. Kashiwagi and S. Obara, *Int. J. Quantum. Chem.*, 1981, **20**, 843.

Received 24th July 1995; *Paper* 5/04896F