Towards an Understanding of the Quadrupole Splittings Found in the Mössbauer Spectroscopic Data of a Number of Substituted Tetraphenylporphyriniron(III) Halides

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Abstract

Mononuclear and μ-oxo-dimers of a series of unsymmetrical substituted tetraphenylporphyriniron-(III) complexes have been prepared and studied using Mössbauer spectroscopy. The Mössbauer data are discussed and compared to other known data for similar high spin Fe(III) porphyrins.

A good correlation between the Hammet σ_R° (the mesomeric values) of the porphyrin substituent and the Mössbauer quadrupole splitting (Δ) has been found.

Introduction

Studies on the aqueous chemistry of protoporphyrin IX iron(II)/(III) [PPIXFe(II)/(III)] [1–6] have enabled us to make systematic investigations into the use of this important moiety as a model for a number of proteins in which it, or similar porphyrins, are the prosthetic groups [7–10]. PPIXFe-(II) (Fig. 1a) is soluble in water over the pH range 7–14 [2] and PPIXFe(III) over pH 6–14 [1]; this limitation in solubility led us to study *meso*-tetra-(*p*-sulphonato-phenyl)porphyrin iron(III) [11]. A comparison of its properties to those of PPIXFe(III) highlighted a number of differences arising from the former being substituted at the *meso*-positions, and the latter on the pyrrole rings. These differences affect the overall electronic structure of the haem and influence the iron atom at the centre of the porphyrin. They are transmitted via the π-orbitals of the porphyrin [11].

Over the last few years, a number of papers have appeared reporting the presence of, and the structures of, porphyrin π-radical cations. Such porphyrin π-radical cations have invariably been characterised by the presence of saddle shaped porphyrin rings [12–16]. To understand the nature and properties
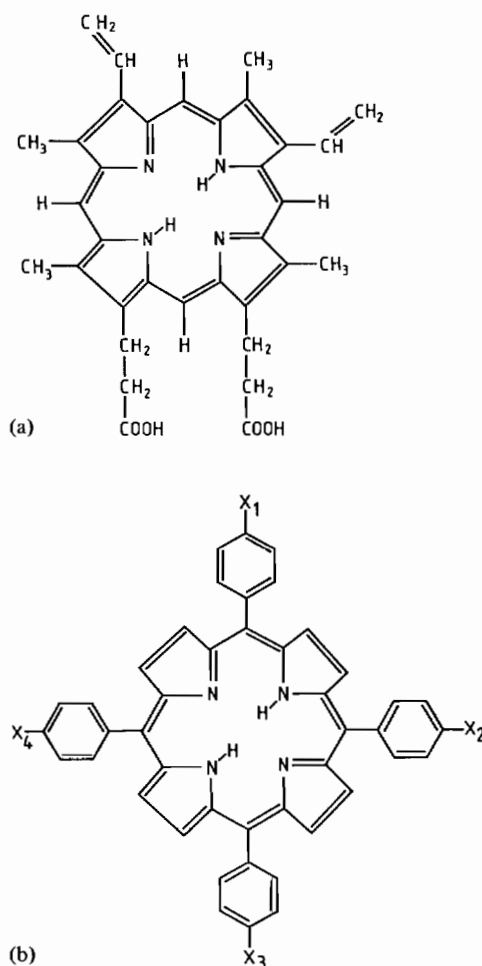

(a)

(b)

Fig. 1. (a) The structure of protoporphyrin IX. (b) The structures of the six $H_2TPP(p\text{-}CH_3)_x(p\text{-}H)_y$ isomers of this work. 1, $X_1–X_4 = CH_3$; 2, $X_1 = H$, $X_2–X_4 = CH_3$; 3, $X_1 = X_2 = CH_3$, $X_3 = X_4 = H$; 4, $X_1 = X_3 = CH_3$, $X_2 = X_4 = H$; 5, $X_1 = CH_3$, $X_2–X_4 = H$; 6, $X_1–X_4 = H$.

of such systems, it is necessary to appreciate the electronic properties of the porphyrin rings themselves.

TABLE I. ^{57}Fe Mössbauer Parameters for High Spin Iron(III) Porphyrin Halide Compounds

Compound[a]	T (K)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ^1 (mm s^{-1})[b]	Γ^2 (mm s^{-1})[b]	$\Sigma\sigma_R^+$ c, e	$\Sigma\sigma_R^o$ d, e	Reference
1	77	0.29(4)	0.43(7)	0.28(3)	1.09(8)	−0.40	−0.40	this work
2	77	0.24(4)	0.43(4)	0.23(3)	0.95(6)	−0.30	−0.30	this work
3 + 4	77	0.28(2)	0.52(4)	0.29(2)	1.00(4)	−0.20	−0.20	this work
5	77	0.23(3)	0.41(6)	0.21(3)	1.01(7)	−0.10	−0.10	this work
6	4.2	0.41	0.46(3)			0.00	0.0	18
Fe(PClPP)Cl	4.2	0.44	0.73(5)			−0.84	−0.88	19
Fe(PFPP)Cl	4.2	0.38	0.85(5)			−1.48	−1.36	19
Fe(PMXPP)Cl	4.2	0.37	1.03(5)			−2.64	−1.72	19
Fe(TPP)Br	4.2	0.45	0.72(5)			0.0	0.0	18
Fe(PFPP)Br	4.2	0.43	1.04(5)			−1.48	−1.36	19
Fe(PMXPP)Br	4.2	0.38	1.07(5)			−2.64	−1.72	19
Fe(TPP)I	4.2	0.45	0.75(5)			0.0	0.0	18
	77	0.44(1)	0.79(1)	0.20(1)	0.26(1)	0.0	0.0	this work
Fe(PClPP)I	4.2	0.50	1.04(5)			−0.84	−0.88	18
Fe(PMXPP)I	4.2	0.49	1.33(5)			−2.64	−1.72	18
Fe(PMePP)I [f]	77	0.44(1)	0.91(2)	0.25(1)	0.39(3)	−0.40	−0.40	this work

[a]Numbers refer to compounds key in legend of Fig. 1b, but now containing Fe(III) and chloride.   [b]Γ^1, Γ^2 are half-width at half-height.   [c, e]$\Sigma\sigma_R^+$ values from ref. 20 for cases where $\sigma_R^+ = \sigma_R^+$.   [d, e]$\Sigma\sigma_R^o$ from ref. 21, IR values used.   [e]$\Sigma\sigma_R^+$ and $\Sigma\sigma_R^o$ are summed for the substituents on the four phenyl rings.   [f]Is the iodide of the iron(III) complex of compound 1.

A useful introduction and summary of some of the factors necessary to this work has appeared in a recent paper by Walker *et al.* [17] on some unsymmetrical tetraphenyl substituted porphyrins $H_2TPP(p\text{-}Cl)_x(p\text{-}NEt_2)_y$, $(x + y = 4; x = 0\text{--}4)$ and we direct the reader to it.

We report here studies on a series of six Fe(III) porphyrins (Fig. 1b), having all possible numbers of p-(methyl) and p-(H) groups $H_2TPP(p\text{-}CH_3)_x(p\text{-}H)_y$ $(x + y = 4; x = 0\text{--}4)$. We also report studies on Fe(III) complexes of the known tetra-substituted porphyrins.

The purposes of the work reported in this study were to characterise how small changes on the outside of the Fe(III) porphyrins effect the basicity of the central pyrrole nitrogens and to monitor this using Mössbauer spectroscopy. Mössbauer spectroscopy was chosen particularly in view of the apparent sensitivity of high spin iron(III) monomeric iron porphyrins to the nature of the substituents on the porphyrin ring.

Results and Discussion

The Mössbauer data for the iron porphyrins are presented in Tables I and II.

The spectra for the monomeric chlorides have isomer shifts that are typical of high spin iron(III) porphyrins. The spectra are asymmetric at 77 K for these compounds and accurate measurements of the chemical shift (δ) and the quadrupole splitting (Δ) are therefore not easy [22]. The parameters we quote are the best we could achieve, and are each based on several spectra. As it is the higher-velocity line that broadens on raising the temperature, the sign of the

TABLE II. ^{57}Fe Mössbauer Data of μ-Oxo Dimer of the Porphyrin Iron(III) Compounds at 77 K Prepared in this Work

Compound[a]	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})
1	0.404(5)	0.617(7)	0.133(6)
2	0.396(4)	0.645(5)	0.172(4)
3 + 4	0.404(2)	0.667(3)	0.190(4)
5	0.397(3)	0.641(5)	0.169(4)
6	0.415(6)	0.648(9)	0.151(7)

[a]Numbers refer to compound key in legend of Fig. 1b, but now containing Fe(III) and oxygen.

electric field gradient (EFG) is most likely to be the same throughout and the same as that found for other similar materials. It has been previously established from magnetic perturbation measurements on Fe(PP)Cl [23] and Fe(OEP)Cl [24], that $V_{zz} > 0$ in all the chlorides.

Harris [25–27] assumed that the electric field gradient in iron(III) porphyrins mainly arises from the lattice contribution, with strong in-plane and weak axial electrostatic fields, and deduced a positive sign for V_{zz}. It has been pointed out [28] that the value that has been given to the tetragonal distortion parameter in this model is much larger than any acceptable value and probably arises through neglecting covalency effects. Extended Hückel molecular orbital calculations for ferric porphyrin chloride by Gouterman *et al.* [29] resulted in a quadrupole splitting of twice the magnitude and the wrong sign. Though the lattice contribution obtained was of the

correct sign, it was not large enough to overcome q_{val}. It therefore seems the crystal field approach is more successful in that it predicts the correct sign of V_{zz}.

Previous workers [18, 22] have reported that the small quadrupole splitting for Fe(TPP)Cl is not as expected as other tetraaryl-porphyrin derivatives have much higher values [19]. No obvious reason has yet been found to explain its magnitude. However, when it is compared to the quadrupole splittings of the other materials reported here, it is no longer out of line as many have small quadrupole splittings. The tolyl group should be a better σ-donor to the porphyrin than a simple phenyl ring. If it is assumed that the magnitude of Δ is inversely proportional to the amount of electron density on the porphyrin ring and that only inductive effects are operating, then it would be expected to be larger when electron withdrawing groups are present on the phenyl rings. The Δ values for the compounds Fe(TPP)Cl, Fe(PClPP)Cl and Fe(PFPP)Cl are then in the expected order though that for Fe(PMXPP)Cl is wrong. (We have chosen to regard PFPP as having just a *para* F on the phenyl ring and ignored the *ortho* and *meta* F atoms. This of course is not an exact approximation.)

The above argument which is based on straight inductive effects is therefore not able to explain all the known available Mössbauer data for high spin Fe(III)(por)Cl (por = tetraphenyl substituted porphyrins). In fact, poor correlations for Hammett inductive constants and the observed Δ values are found for the *para*-phenyl substituent (H, Me, F, Cl and OMe). If the $\sigma_R{}^\circ$ constants [21] (the mesometic values) are plotted against the Δ values (as in Fig. 2) then good agreement is found for all the available Fe(III)(por)Cl data. Indeed, such dependence of Δ on the porphyrin would be expected from the calculations of Harris [25–27]. We admit that little support for mesomeric effects on the phenyl substituent influencing Δ comes from known FeTPPX (X = F, Cl, Br, I) crystal structures. In all cases the bond length from the methine carbon atoms to the nearest atom

of the bonded phenyl ring is 1.500(5) Å [30–33]. This distance is shorter than a single C–C bond (1.544 Å) where the atoms are sp³, but is similar to that found in a range of biphenyl compounds where the carbons are sp² hybridised [34–37]. It has been stated [37] that for a C–C bond where both carbons are sp², the expected length is around 1.48 Å and longer values as found for biphenyls [31–33] are due to steric repulsion of the H atoms on the ring. Obviously similar steric repulsions are present in our case for the tetraphenyl porphyrin iron(III) structures [30–33], and thus could be masking mesomeric effects.

For strong overlap the distance reduces to 1.45 Å as in the porphyrin dications when the phenyl rings lie in the mean porphyrin plane [38], and the porphyrin plane itself is 'saddled' allowing the phenyl rings to adopt the coplanar arrangement and overcome the steric repulsions discussed at the end of the preceding paragraph.

In addition, the angles the phenyl ring planes make with the porphyrin mean plane in the known TPPFe-(III)X (X = halide) structures are in the range 60–80°. There is from this little evidence for mesomeric effects with such angles of twist (for 60° one might expect only around 25% of the total possible π overlap). We note in π-cation radicals [16] the angles are decreased to about 42°, presumably allowing more electron donation from the phenyl rings.

However, as the correlations with both $\sigma_R{}^\circ$, $\sigma_R{}^+$ [20] and the quadrupole splitting (Figs. 2 and 3) are apparent, then the mesomeric effect does have a part to play and even angles of around 60° must allow some mesomeric effect to operate.

We have previously found a similar relationship between Δ and $\sigma_R{}^+$ in a series of ferrocene complexes [39]. We also note that the electronic absorption maxima of the totally protonated free-base porphyrins (the dications) have been found to correlate with σ^+ as has the rates of metal incorporation into the free-base porphyrins [40].
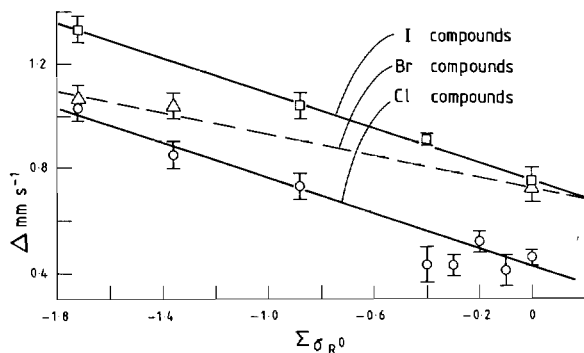

Fig. 2. Quadrupole splitting, Δ(mm s^{-1}) *vs.* Σ Hammett mesomeric constant $\Sigma\sigma_R{}^\circ$ for the Fe(III)(por)X data (por = tetraphenyl substituted porphyrins) presented in Table I.
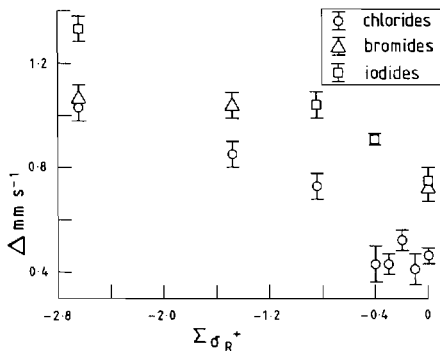

Fig. 3. Quadrupole splitting, Δ(mm s^{-1}) *vs.* Σ Hammett resonance constant $\Sigma\sigma_R{}^+$ for the Fe(III)(por)X data (por = tetraphenyl substituted porphyrins) presented in Table I.

It is worth noting that the three Fe(por)Br complexes and four Fe(por)I complexes that have had their Mössbauer data reported show similar trends with both $\sigma_R{}^\circ$ and $\sigma_R{}^+$ constants to those found for the Fe(por)Cl complexes.

The Mössbauer data for the μ-oxo dimers of the Fe(III) porphyrins presented here and those recorded previously [41–45] have isomer shifts and quadrupole splittings that exhibit only slight variation from compound to compound. In the light of the data for the monomeric chlorides, this is a little surprising as the observed data and the calculations of Harris [25–27] suggest the porphyrin ligand will have a large effect on the quadrupole splitting. To examine why for the μ-oxo dimers this is the case, a number of considerations need to be taken into account.

Firstly, all the Mössbauer data of the μ-oxo dimers are symmetric doublets at 80 K. Indeed, in all cases studied at room temperature [41, 43–45], their spectra still remain symmetric. The reason these spectra are symmetric is that the iron atoms are antiferromagnetically coupled through the oxygen bridge. The effect of the coupling is well documented in the literature [43, 44, 46, 47]. Only the appearance of the quadrupole splitting alters, not its magnitude. Such Fe–O bonds are short suggesting some double bond character [44, 48].

A number of Mössbauer data are available for Fe(PMXPP)X [19] compounds (X = Cl, Br, I, NCS, N_3, O_2CMe and O_2CCF$_3$) the order for the magnitude of the quadrupole splitting is I $> O_2$CCF$_3 >$ Br $>$ Cl $> O_2$CMe $> N_3 >$ NCS. The spread in quadrupole splitting in the series is from 1.33 to 0.63 mm s^{-1}, showing that the axial ligand influences the magnitude of Δ. Moreover, the stronger ligands NCS and N_3 cause smaller Δs. If the Δ for [Fe(PMXPP)]$_2$O [45] is added to the series, then NCS = O^{2-} and the latter is demonstrated to be a strong ligand. Also, strong ligands appear to give smaller ranges of Δ, *cf.* Cl, Br, I.

This is also in accordance with the primary assumption of Harris [25–27]. Here, stronger axial ligands will better balance the strong in-plane electrostatic field and lead to smaller quadrupole splitting with smaller dependence on the nature of the porphyrin.

It is therefore to be expected that the Δ values for the μ-oxo dimers will all be similar.

Conclusions

Mössbauer spectroscopic data were found to correlate with Hammett constants where Fe(III) was incorporated into the porphyrin rings. This provides evidence that mesomeric effects are in operation when the high spin Fe(III) is out of the porphyrin plane.

It is, we believe, illuminating to examine the steric hindrances to the methine bridge substituted porphyrins. It has been pointed out in this work that all the phenyl substituted porphyrins contain long methine carbon to phenyl carbon bonds, caused by the steric repulsion of the phenyl rings with the porphyrin plane. In fact any conjugated system even a simple vinyl bonded to the methine bridge would be similarly restricted. It is interesting that no naturally occurring haem is substituted on the methine positions. Indeed, PPIXFe(II)/(III) which is ubiquitous in nature has its vinyl groups on the pyrrole rings. At the pyrrole carbon atoms the steric hindrance caused by interaction of substituent groups with the haem will be less. This will enable the vinyl groups in PPIXFe(II)/(III) to lie in the haem plane and act as an electron sink [49]. These arguments are best understood by considering the internal porphyrin angles directly opposite the substituent positions. At the methine position the angle is about 124° [16] whereas on the pyrrole ring it is about 106° [16]. Thus in the latter positions there is less steric hindrance from the ring. This can be verified by considering the porphyrin pyrrole ring to vinyl group C–C bond distance in bis(1-methylimidazole)(protoporphyrinIX)iron-(III). These have been shown to be 1.43 and 1.48 [50]. Such distances both suggest and allow good conjugation between the porphyrin ring and the vinyl groups in PPIXFe(III).

Experimental

Materials

All solvents were reagent grade and were used without further purification. All the chemicals were obtained from Aldrich and were used as received.

Preparation of New Porphyrins

The *meso*-substituted porphyrin compounds **2–4** were prepared from pyrrole and aldehydes in refluxing propionic acid according to the method of Little *et al.* [52]. Other porphyrins required some modification in the general procedure. All the porphyrins crystallised directly from the reaction mixture. Only the first and major crop of crystals was collected. The crystals were washed with methanol and hot water and dried over P$_2$O$_5$. The crystals from each preparation of the porphyrins were then dis-

TABLE III. Elemental Analysis (%) of the New Porphyrins Prepared in this Work

Compound[a]	C		H		N	
1	85.7	(85.94)[b]	5.8	(5.71)	8.45	(8.35)
2	86.0	(85.95)	5.55	(5.53)	8.40	(8.53)
3 + 4	85.9	(85.95)	5.4	(5.33)	8.55	(8.72)
5	86.05	(85.96)	5.2	(5.13)	8.7	(8.91)

[a]Numbers refer to compound key in legend of Fig. 1b.
[b]Values in parentheses are calculated.

solved in the minimum amount of chloroform and spotted on silica gel plates (according to the method of Shamim *et al.* [53]). No separating bands were found. This indicated that by collecting only the main crop of crystals the complexes are very pure.

Analyses were carried out by the Micro Analytical Laboratory, Department of Chemistry, University of Manchester, and are presented in Table III. The analyses show good agreement with the calculated values for the given formula. Crystal structures of each of these porphyrins have been solved to present R values of 0.10 (using Mo Kα radiation), but will be solved from Cu Kα data before publication [54].

Preparation of Iron Porphyrin

A refluxing solution of the porphyrin in glacial acetic acid was treated with ferrous chloride and the mixture refluxed until reaction was complete. The progress of the reaction was monitored spectrophotometrically. The reaction mixture was evaporated to dryness and then dissolved in chloroform; half of this chloroform solution was shaken with a few millimetres of concentrated hydrochloric acid to obtain the monomeric porphyrin Fe(Por)Cl. The remainder was stirred for 1 h with sodium hydroxide (50 ml, 25%) to obtain the μ-oxo dimer O(Fe(Por)$_2$. The chloroform layer was separated from the water layer, and purified by chromatography on alumina. Products were recrystallised from chloroform/heptane and dried over P$_2$O$_5$.

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