

Mössbauer Studies on Tetra(*p*-sulphophenyl)porphyrin Iron(II) Solutions

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Abstract

Room temperature electronic spectra and frozen solution Mössbauer spectra (collected at 78 K) of TPPSFe(II) solutions are reported and discussed. Evidence for aggregation is found and discussed with reference to the known crystal structures of TPPFe(II) and TPPFe(III)(OCIO₃)·0.5(*m*-xylene). The orientation of the phenyl rings is inferred to be similar to that of known crystal structures for two of the four species found to be present in the pH range 6–14. These are the intermediate spin iron(II) and the high spin iron(II) ($\Delta = 4.15 \text{ mm s}^{-1}$) species.

Introduction

The chemistry of protoporphyrin IX–iron(II)/(III) (PPIXFe(II)/(III)) is of substantial interest for two reasons: (1) it is the prosthetic group of a large number of metalloproteins [1] and (2) to date its aqueous chemistry has not been sufficiently well documented and/or explained.

As PPIXFe(II)/(III) is so ubiquitous in nature studies of its chemistry are particularly useful for modelling the role it plays in haem proteins. We have in the past few years carried out systematic studies on the chemistry of PPIXFe(II)/(III) and related complexes [2–12].

Perhaps the main drawbacks found in studying PPIXFe in aqueous solution are: (a) PPIXFe(III) forms a μ -oxo-oligomer at all pH's above pH 7 (in the absence of competing ligands) [4], and the monomer is insoluble below pH 5.6. (b) PPIXFe(II) is insoluble below pH 7 and, in the pH range 7–14 it is present predominantly as a polymer, made up of bare PPIXFe(II) monomers, where the polymer length depends on concentration and pH [5].

These problems have been avoided by studying iron porphyrins in non aqueous solvents, however, this approach has limitations. Though investigations of porphyrin reaction kinetics, assignment of spectral parameters, and purely structural aspects of iron–porphyrin chemistry can be studied, the porphyrins

available for such studies are not those that occur naturally in nature.

The porphyrins that have been used in such studies have been based on tetra(phenyl)porphyrin iron(II)/(III), esters prepared from PPIXFe(II)/(III), or capped or picket fence porphyrins. Those based on tetra(phenyl)porphyrin iron(II)/(III) are substituted on the methine carbons, such substitution is bound to effect the electronic properties of the porphyrin and detracts from the value of such molecules as useful models for haem proteins.

However, understanding how such modified porphyrins differ from PPIX may allow greater insight into the chemistry of PPIX itself.

We have previously studied the aqueous chemistry of tetra(*p*-sulphophenyl)porphyrin iron(III) (TPPSFe(III)) [13] in order to compare its chemistry to that of PPIXFe(III). We found evidence that the monomeric [TPPSFe(III)(OH₂)]⁺ species has different electronic properties to those of [PPIXFe(III)(OH)] [4] (from the differences in the quadrupole splittings in the Mössbauer spectra of those species). These differences are likely to arise from a combination of the differences in the substituent groups on the porphyrins and the differing axial ligands.

The substituents on [TPPSFe(III)(OH₂)]⁺ are the sulphophenyl groups. Since the orientation of these groups at low pH relative to the plane of the porphyrin ring was not established. The nature of the electronic effects was unclear.

Torrens *et al.* [14] have previously discussed X-ray data indicating that: (1) the four nitrogen atoms of the porphine ring are not strictly planar, and (2) the ruffling of the porphine skeleton depends on the substituents as well as the coordinated metal ion.

These authors [14] ascribe differences in quadrupole splitting to postulated differences in the dispositions of the nitrogen atoms in the ring. They state that 'if the phenyl substituents do affect the conformations of the four nitrogens, it is still not known whether this effect is electronic or morphological in origin'. They suggest that comprehensive measurements of a few of these compounds in homogeneous frozen solution are required to settle the point definitely. Our studies [13] would add a caution to

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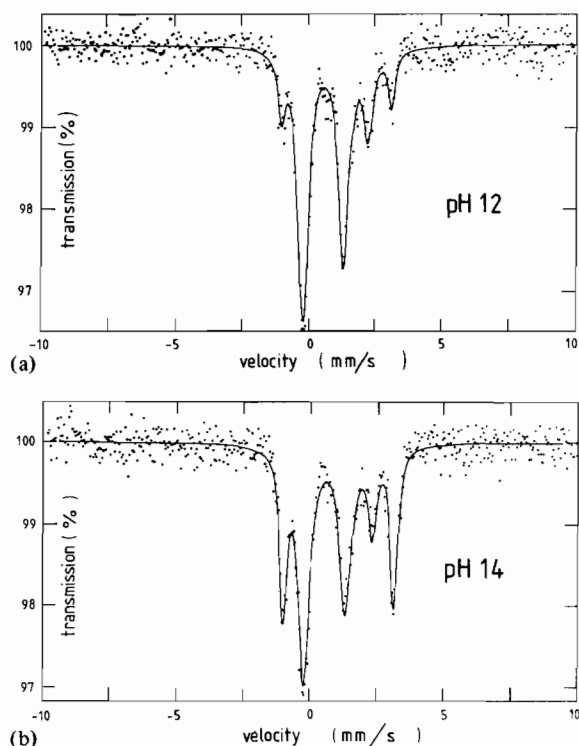


Fig. 2. Mössbauer spectra of TPPSFe(II) frozen aqueous solutions at 78 K: (a) at pH 12.0; (b) frozen at pH 14.

If we consider the expected structure of TPPSFe(II) around pH 7 we might expect the molecule to be surrounded by the four naked negative groups of the SO_3^- side groups. Such porphyrin molecules should repel each other. However, in the case of TPPSFe(III) solutions at the same pH we and others [13, 17] have demonstrated that $(\text{TPPSFe(III)})_2\text{O}$ is the species present in solution. So the negative charges are not strong enough in repulsion to stop

the formation of a μ -oxo-oligomer. Thus the repulsions are not as dominant as might be expected.

Studies have been carried out on the aggregation of both tetraphenylporphyrinsulphate (TPPS₃) and TPPS in aqueous solution at pH's around 7. Evidence for aggregation was found for TPPS₃ [18], but not for TPPS [17]. It was suggested that this is as expected for the less sulphonated systems, and that the hydrophobic phenyl group would like to get out of the water environment by associating with another porphyrin resulting in aggregation of the porphyrin species in solution [17]. However, when TPPS is made acidic to form the porphyrin diacid the behaviour though said to be complicated, has been interpreted to mean that in acidic regions the TPPS aggregates [17]. Moreover there is a more recent report that shows that TPPS dimerizes even in neutral solution [19].

We have carried out Beer's law experiments on TPPSFe(II) solutions at pH's 7.4 (Fig. 3) and ~12.7 (Fig. 4) in aqueous solutions. Plots of absorbance *versus* total concentrations of porphyrin at these pH's show considerable deviation from linearity. The curvature in the Beer's law plots we interpret as being due to aggregation of TPPSFe(II) at all the pH's studied. It should be noted that ignoring the nature of the axial ligands the TPPSFe(II) moieties will have no net charge at the centre of the haem in these solutions and TPPS^{2-} in the same pH range will have two protons at the centre.

If the axial ligands in the pH range 6–12 in these solutions were water molecules (these would be strong field ligands compared to OH^- ions), they would therefore cause the $\text{TPPSFe(II)(H}_2\text{O)}_2$ complex to be a low spin Fe(II) species (which is observed in the frozen solution Mössbauer data). Such species could encourage aggregation by the ligating water molecules hydrogen bonding to the sulphonate groups of the next $\text{TPPSFe(II)(H}_2\text{O)}_2$ molecule *viz.*

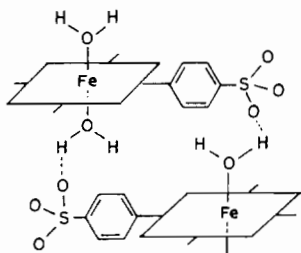
TABLE II. Electronic Spectra of TPPSFe(II) Solutions

pH	Soret		β		α		Width of Soret band ^a (nm)
	λ (nm)	ϵ (mM)	λ (nm)	ϵ (mM)	λ (nm)	ϵ (mM)	
5.0	424	59.0	555	4.46	595	3.53	a
6.0	424	51.3	555	4.10	596	3.30	18
7.0	424	44.13	555	3.90	596	3.30	c
9.0	424	34.46	556	3.70	597	3.10	c
10.2	424	34.33	557	3.90	598	3.50	20
11.2	424	27.86	557	6.30	598	5.93	27
12.0	425	24.93	566	6.10	599	5.86	36
12.4	430	21.33	564	4.16	605	4.00	36
13.0	439	26.84	567	8.67	606	6.70	30
13.0 ^{a, b}	439		568		608		c

^aFull width at half height.

^bThis solution contained excess NaOH.

^cNot measured.



The Mössbauer parameters could be expected to vary with the extent of such aggregation which would be concentration dependent as seen in PPIXFe(II) solutions [16].

As the pH is raised with NaOH to around 12.0 the presence of excess Na⁺ ions may well cause ion pair formation with the sulphonate groups negating the need for hydrogen bonding to generate the

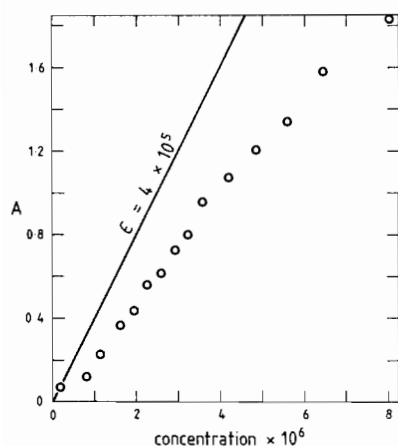


Fig. 3. Beer's law experiments for TPPSFe(II) in aqueous solution pH 7.4, with added KNO₃ (0.12 M) buffered with 0.01 M Tris as measured with a glass electrode. The line marked $\epsilon = 4 \times 10^5$ defines Beer's law behaviour for TPPSFe(II) calculated from several points on solutions around 10^{-7} M in TPPSFe(II). The circles represent experimental data.

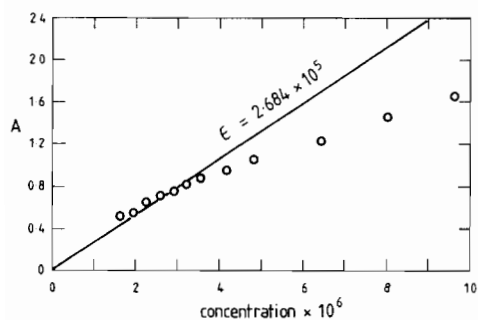


Fig. 4. Beer's law experiments for TPPSFe(II) in aqueous solution with added KCL (0.1 M) and (NaOH 0.1 M). (Prepared in the ratio 26 ml to 66 ml to form buffer pH ~ 12.7.) The line marked $\epsilon = 2.68 \times 10^5$ defines Beer's law behaviour for TPPSFe(II) calculated from several points on solutions around 2×10^{-6} M in TPPSFe(II).

stacking. This latter effect will be a natural result of ion pairing with the Na⁺ ions, the latter replacing the water molecules in the role of holding the SO₃⁻ groups of neighbouring haems together enabling overlap of haem orbitals to continue albeit modified. Replacement of the water molecules will mean that the TPPSFe(II) moieties lose their axial ligands, or the resulting different electronic overlap between the porphyrin molecules may alter the electron density at the iron(II) centres so that water molecules no longer bond to the iron atoms.

An alternative mechanism may be that at pH's near 12.0 the Na⁺ ions are better able to bind the axial water molecules ligating iron atoms and strip these from the latter allowing the porphyrin-porphyrin contacts to get closer. In addition the Na⁺ ions ion pair with the SO₃⁻ moieties, thus reducing repulsive charge effects.

The Mössbauer data indicate only intermediate spin iron(II) and high spin iron(II) species at and above pH 12.0.

We have previously suggested that the intermediate spin iron(II) species we found in PPIXFe(II) solutions contains no axial ligands [5]. At pH 12 the Soret band observed in the TPPSFe(II) (Fig. 5a) solutions is noticeably wider than at lower pH's and can be taken as evidence for the presence of more than one haem species (in agreement with the observed Mössbauer data), moreover the other visible bands become broader and more intense (Fig. 5b) (the changes in these bands we also interpret as evidence for additional haem species in solution). The presence of excess NaCl at pH's below 12 does not cause a change in the electronic or Mössbauer spectra, this we take as evidence that sodium ions ion-pairing with the sulphonate groups is not the driving force for the changes in the species at pH 12.0. This pH dependence is proved especially as a drop in pH causes a return of the original electronic spectra and Mössbauer parameters. The more likely explanation is that there is a pK_a above pH 12.0 and it is this that is tied up with the appearance of the three haem species (found in frozen solution Mössbauer spectra at this pH). The presence of a pK_a at high pH would also be indicated in the PPIXFe(II) aqueous systems [5].

Although Na⁺ ions do not appear to be able to change the low spin iron(II) to an intermediate spin iron(II) site, nevertheless the presence of positive ions may still cause ion-pairing at pH 12.0. The change and movement in the Soret band at this pH and above is interesting, as Soret bands at 434 nm have been found in TPPS solutions [17] at acid pH (below pH 4) and attributed to the diacid (TPPSH₂²⁺) species. This movement of the Soret band has been attributed to phenyl rotation into or near to the plane of the porphyrin [17]. We do not believe that phenyl rotation is necessarily the

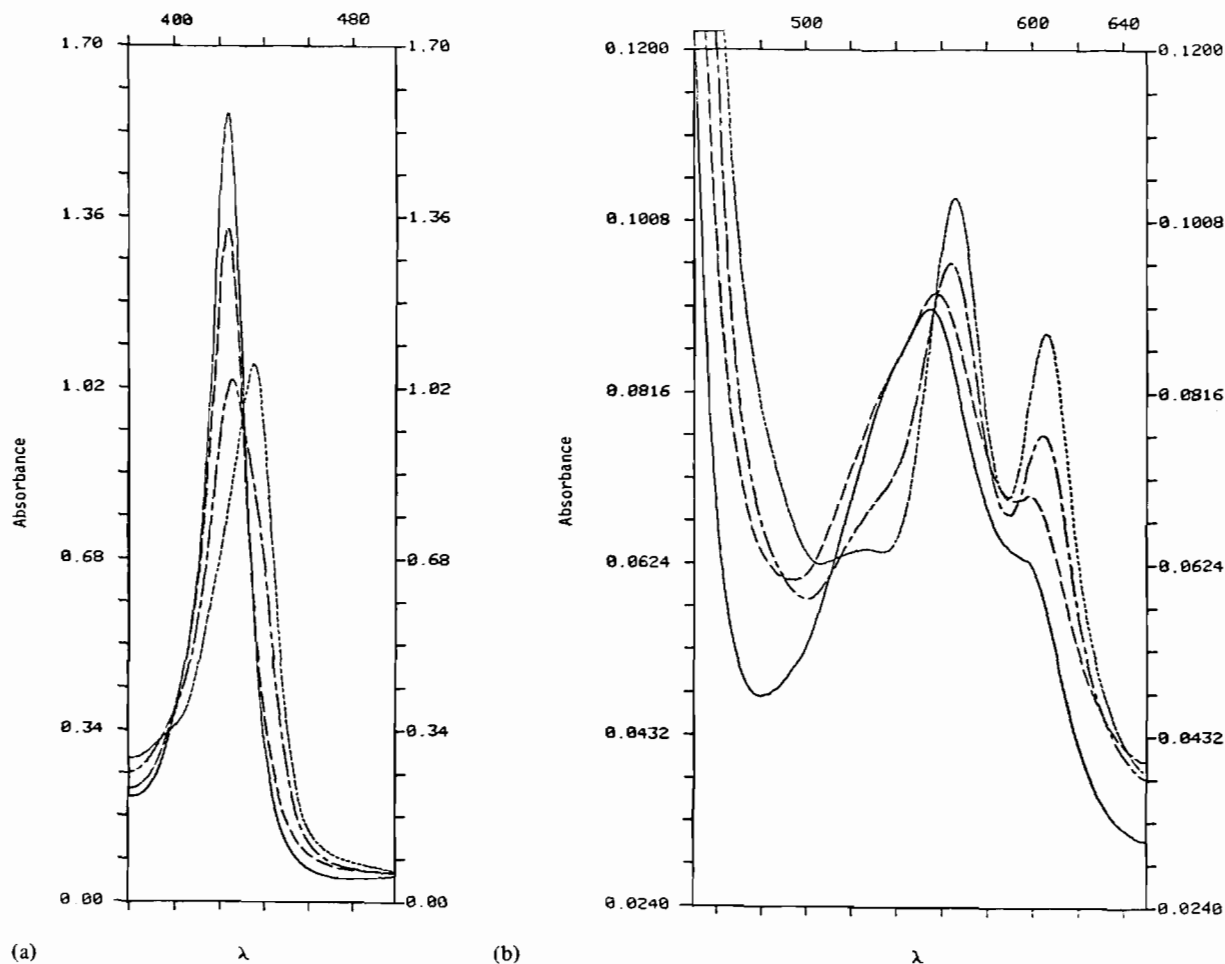


Fig. 5. Electronic absorption spectra of TPPSFe(II) 3.3×10^{-6} M in aqueous solution at 298 K at pH's: —, 6.0; ---, 10.2; - · - ·, 12.0; · · · ·, 12.8; (a) 380–500 nm; (b) 470–650 nm.

cause of the movement in the Soret band at high pH in this system as we have also found in the PPIX-Fe(II) system that at high pH the Soret band moves from 383 nm to around 430 nm [5]. In the latter case by the addition of catechol and phenyl ligands we have shown this band to result from a five coordinate high spin Fe(II) species where the Fe(II) atom comes a long way out of the porphyrin plane [6]. This has been confirmed by a crystal structure of $[\text{Fe}(\text{TP}_{\text{Piv}}\text{P})\text{Cl}][\text{K} < 222]$, $\text{C}_6\text{H}_5\text{Cl}$ [20], in which the iron is 0.593 Å out of the porphyrin mean plane, and the Mössbauer parameters of this compound are $\delta = 1.01 \text{ mm s}^{-1}$ and $\Delta = 4.36 \text{ mm s}^{-1}$ the Soret band in this compound was at 446 nm, also the phenyl groups did not lie in the plane of the porphyrin in the solid state. It is therefore more likely that it is the high spin iron(II) environment in the haem that causes the Soret band to be at 438 nm.

The fact that the Mössbauer parameters of the intermediate spin and one of the high spin ($\Delta = 2.5 \text{ mm s}^{-1}$) iron(II) species found at high pH in this system are slightly different from those observed in

the PPIXFe(II) system (in the size of the observed Δ s) may be a result of either of two effects: (1) More extensive aggregation in this systems causes greater changes than in the PPIXFe(II) system, or (2) The nature of the substituent groups on this porphyrin modifies the electron density at the iron centre compared to PPIX.

As the two Mössbauer spectra taken at high pH were taken on more dilute solutions made up from TPPS ^{57}Fe (II) it is unlikely that the former explanation is true.

TPPFe(II) [21] in the solid has a quadruple splitting of 1.52 mm s^{-1} at 77 K and a chemical shift of 0.50 mm s^{-1} with the closest neighbouring haem distance between carbons in the pyrrole rings of about 3.5 Å. We believe this distance of 3.5 Å may indicate weak π interaction. It is worth noting that in the structure of $\text{Fe}(\text{TTP})(\text{OCIO}_3)$ a hemi-*m*-xylene solvate molecule is said to form a weak π complex at a similar distance from the porphyrin (3.34 to 3.66 Å) [22]. The Mössbauer data for solid TPPFe(II) [21] which has no axial ligands and our intermediate

TABLE III. Mössbauer Parameters of Iron(II) Porphyrin Complexes and their Crystal Structural Information (where known) Relative to this Work

Complex	Mössbauer data					Structural data (in Å) around 293 K			
	Temperature (K)	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	Spin state	Reference	Fe–Np	Fe–L	Fe(N ₄) ^a	Reference
Fe(TPP)	77	0.50	1.51	1	21	1.772(4)		0.0	21
	300	0.42	1.52	1	21				
Fe(TPP)(2-MeIm)	77	0.92	2.26	2	21 ^b	2.086(9)	2.161(5)	0.42	25
	195	0.87	1.97	2	21 ^b				
	300	0.82	1.74	2	21 ^b				
Fe(TP _{piv} P)(1-MeIm)	77	0.88	2.32	2	25 ^b	2.072(6)	2.095(6)	0.40	27
	195	0.84	2.01	2	25 ^b				
Fe(TPP)(THF) ₂	77	0.95	2.66	2	25	2.057(5)	2.351(3)	0.0 ^c	28
Fe(TP _{piv} P)(THF) ₂	77	0.93	2.64	2	25				
[Fe(TPP)(SC ₂ H ₅)] ⁻				2		2.096(4)	2.360(2)	0.52	29
[Fe(TP _{piv} P)(SC ₆ H ₄)] ⁻	77	0.82	2.37	2	20	2.076(20)	2.370(3)	0.42	20
[Fe(TP _{piv} P)Cl] ⁻	77	1.01(2)	4.36(2)	2	20	2.108(15)	2.301(2)	0.53	20

^aFe distance to plane of 4 pyrrole nitrogen atoms.

but present as a molecule of solvation.

^bData for EtOH derivative (EtOH) not thought to be bonded to iron centre

^cRequired by presence of inversion centre. This complex is the only one that contains Fe(II) in six coordination.

spin TPPSFe(II) site (Table III) are therefore very similar. In solid TPPFe(II) the phenyl rings are not in the porphyrin plane [21]. From the similarity in the Mössbauer data the rings in TPPSFe(II) are likely to be at a similar angle in these frozen solutions to those in solid TPPFe(II) [20]. As the intermediate spin Fe(II) species in the dilute PPIX⁵⁷Fe(II) solutions have slightly smaller quadrupole splittings (1.41 mm s⁻¹) [5] it is reasonable to ascribe the difference to both (1) the nature of the substituent groups on the porphyrin, and (2) to less extensive aggregation. It is worth noting that in more concentrated PPIXFe(II) solutions larger quadrupole splittings are found [16].

Thus for the intermediate spin iron(II) species in this system we suggest a structure similar to that of Fe(II)TPP (in the solid crystal structure), but with Na⁺ ions balancing the –SO₃⁻ groups.

The quadrupole splitting of 4.15 mm s⁻¹ is similar to that found in the PPIXFe(II) system for the similar species which we assigned to a five coordinate species [5, 6] (as stated above) with a hydroxyl group as the axial ligand. We suggest that a hydroxyl ion is also present in this species (*viz.* [TPPSFe(II)(OH)]⁵⁻). We have previously [5] explained this large quadrupole splitting by reference to literature data including that observed for iron(II) bis(dithiocarbonates), which are five coordinate square planar in structure. These have been explained to constitute a case wherein the lattice and valence contribution to V_{zz} act in the same sense [23].

De Vries *et al.* [24] suggested a level scheme of the type $(d_{x^2-y^2})^2(d_{xz}, d_{yz})^2(d_{z^2})^1(d_{xy})^1$ for such compounds. The presence of the sixth electron in

a $d_{x^2-y^2}$ orbital brings a strong positive contribution to V_{zz} , whilst the tetragonal perturbation generated by the square-pyramidal geometry contributes positively to V_{zz} also [23]. Indeed while our work [5] was in press that of Schappacher *et al.* [20] appeared with similar Mössbauer data and a crystal structure of a five coordinate high spin Fe(II) porphyrin with the Fe(II) further removed from the mean porphyrin plane, than other Fe(II) porphyrins where the quadrupole splitting is only around 2.3 mm s⁻¹. In this work in the [TPPSFe(II)(OH)]⁵⁻ complex if we assume a similar structure to [Fe(TP_{piv}P)Cl]⁻ then the quadrupole splitting will be affected by the axial ligand and the 'domed' porphyrin nitrogen atoms. The bonding of the iron to the porphyrin nitrogen atoms is likely to have a large π electron contribution via the nitrogen atoms and also a σ electron contribution from the nitrogen atom as witnessed by the doming observed in the known structure. The doming is likely to limit the electronic conductance effects over the porphyrin molecule and the electronic effects of substituents in the porphyrin ring will be in turn limited. Also the Fe to nitrogen of the porphyrin pyrrole ring distance is long (2.1 Å) [20]. This will mean that the porphyrin contribution to the quadrupole splitting will be reduced. If the phenyl ring were in the mean porphyrin plane a greater change in the Soret λ_{max} and in the quadrupole splitting would have been expected.

The exact energy level scheme causing the larger quadrupole splitting (of 4.15 mm s⁻¹) is more likely to be $(d_{x^2-y^2})^2(d_{xz}, d_{yz})^2(d_{xy})^1(d_{z^2})^1$. It will depend on the Fe(II) being removed to about 0.52 Å [19]

from the porphyrin pyrrole nitrogen atoms. When the Fe(II) is closer to these nitrogen atoms then the order may be expected to change to $(d_{x^2-y^2})^2(d_{xz}, d_{yz})^2(d_{z^2})^1(d_{xy})^1$. It must be realised that the Fe(II) 3d orbitals will interact with ligand orbitals and cause the above discussed changes.

The second high spin iron(II) species in the TPPS-Fe(II) system has a larger quadrupole splitting ($\Delta \sim 2.5 \text{ mm s}^{-1}$) than the corresponding site in the PPIXFe(II) system ($\Delta = 2.25 \text{ mm s}^{-1}$) though we suggest it contains the same axial ligand or ligands [5, 6]. As stated above the crystal structure of high spin iron(II) porphyrin complexes [20, 25, 27] where the observed Δ s are around 2.3 mm s^{-1} [20, 21, 26] contain iron(II) atoms that are less distant from the mean porphyrin plane (Fe(N_4)-distance, Table III) than that for [Fe(TP_{ptv}P)Cl]·[K C 222]. Such species contain the iron(II) atoms closer to the porphyrin plane and also have quadrupole splittings arising from electronic contributions from both the porphyrin and the axial ligand or ligands. Here the Fe to nitrogen of the porphyrin pyrrole distances are 2.07–2.08 Å [20, 25, 27] and must therefore alter the porphyrin contribution to the bonding at the iron(II) centre. This will be manifest in the magnitude of the observed quadrupole splitting. It is also true (Table III), that the nature of the axial ligand modifies the observed quadrupole splitting.

Conclusions

It has been demonstrated that: (1) the nature of the substituent on the porphyrin skeleton modifies the electron density at the iron(II) centre in intermediate spin iron(II) haems; (2) aggregation of haems can also affect the electronic environment of iron(II) porphyrin species in aqueous solution.

In this work we have inferred some conclusions on the orientation of the phenyl groups in two of the species found in frozen solution by comparison with data from known crystal structures. *Viz.* the intermediate spin iron(II) and the high spin iron(II) ($\Delta = 4.15 \text{ mm s}^{-1}$) species, in both cases the orientation of the phenyl groups are likely to be similar to the known structures.

We have therefore been able to demonstrate that the chemistry of substituted porphyrins can be understood in frozen solution and compared with known crystal structures by using Mössbauer spectroscopy.

Experimental

TPPSFe(III) was prepared according to the method of Fleischer [17]. For Mössbauer experiments two

different preparation procedures were used. In the first enriched ^{57}Fe was used. $^{57}\text{FeCl}_2$ was used to produce TPPS ^{57}Fe . The 90% ^{57}Fe was supplied by A.E.R.E. stable isotope division. TPPS ^{57}Fe (III) solutions were prepared as those of $^{57}\text{FePPIX}$ [4]. In the second method natural FeSO_4 (hydrated) prepared in this laboratory was used to prepare the unenriched TPPSFe(III). For the TPPSFe(II) work described in this paper the TPPSFe(III) complex was reduced in aqueous solution using a slight excess of sodium dithionite. Mössbauer data were not attempted at lower pH's due to the difficulty in handling Fe(II) porphyrins at pH's below that where sodium dithionite is a good reducing agent. The pH of the solution was adjusted as required by adding 1 M HCl for pH <12 or by adding 2 M NaOH for pH >12. For the solution of pH 14, 3 ml 1 M NaOH was used to dissolve the compound.

pH titrations were carried out using 10^{-6} M TPPSFe(II) solutions and adjusted with either 1 M HCl or 1 M NaOH (in the presence of a slight excess of sodium dithionite under N_2 atmosphere). No evidence of a pK_a in the pH range 6–11.5 was found.

The electronic spectra were recorded on solutions ranging from 10^{-7} to 10^{-5} M TPPSFe(II). At high pH the Soret band was observed to move as a function of concentration being at 434 nm in very dilute solutions (10^{-7} M) and 438–439 nm for solution of 10^{-5} M. For the electronic spectra cells of 1 ml path length containing 2.5 ml of solution were used. The cells were quartz or glass and were fitted with tap tops enabling the solutions to be kept under an N_2 atmosphere. All electronic spectra were recorded at 298 K.

Spectra recorded as a function of pH (Table II) were taken in the same cells after removal from a flask (also under N_2) containing a stock solution of 50 ml 2.2×10^{-5} M TPPSFe(II) and a slight excess of sodium dithionate. The pH of the solution was varied using 1 M NaOH or 1 M HCl.

Solutions were freshly prepared before use and were protected from direct sunlight and fluorescent light until they were inserted into the cells as in the procedure of Pasternack *et al.* [18].

Instrumentation

Electronic spectra were recorded using a Perkin-Elmer Lambda 5G Spectrophotometer. All spectra were recorded at 20 °C. Mössbauer spectra were recorded from frozen solutions at 77–78 K on a spectrometer previously described [30]. The spectrometer was calibrated with a 25 μm thick natural iron reference absorber. The isomer shifts are referred to this as zero shift. The Mössbauer spectra were computer-fitted as previously described [30].

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