

Solution Studies on Tetra(*p*-carboxyphenyl)porphyrin Iron(II) Using Mössbauer Spectroscopy and Electronic Absorption Spectroscopies

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(Received June 19, 1987)

Abstract

Mössbauer (78 K) and electronic absorption spectra (298 K) of tetra(*p*-carboxyphenyl)porphyrin iron(II) solutions are reported and discussed. Evidence for only two iron(II) complexes, the first an intermediate spin and the second a high spin complex, is found in the Mössbauer spectra. Electronic absorption spectra show a low spin complex is present at very low concentrations. It is observed from these results that the carboxy groups on the phenyl rings of this porphyrin greatly influence the chemistry. From the difference in the quadrupole splitting for the intermediate spin complex compared to that found in the tetra(*p*-sulphophenyl)porphyrin iron(II) system, the substituent on the phenyl ring clearly changes the electron density on the pyrrole nitrogen atoms.

Introduction

Studies on water soluble iron(II) metalloporphyrins [1–5] have shown that the species present at a given pH depends on a number of factors. These include, (a) the nature of the porphyrin (*i.e.* whether it is substituted on the pyrrole rings or on the methine positions, and (b) the nature of the substituent groups, (both the size of the group and the electronic properties of the group being important). In addition the interplay of these factors between molecules affects stacking and aggregation commonly found in porphyrin chemistry [3–5]. The latter phenomena results in the species present in solutions often being concentration dependent [3–5].

We have previously studied the solution chemistry of protoporphyrin IX iron(II) [1–3] tetra(*p*-sulphophenyl)porphyrin iron(II) [4], and tetra(sulphonaphthyl)porphyrin iron(II) [5]. Over the pH range 7–14 these three iron(II) porphyrins show some species in common and some that are clearly dependent on their different peripheral substituents.

The understanding of the influence of the periphery groups on the solution chemistry of these

porphyrins is fundamental if (a) molecules of this type are to be developed as models for haem proteins and (b) such molecules are to have a role as catalysts in industrial processes.

The three porphyrins iron(II) systems we have so far studied all have negative charges on the periphery of the porphyrins aiding their solubility in water, but the interplay of these charges with the porphyrin cores is complicated by the other substituent moieties present. The two methine substituted porphyrins TPPS and TNPS showed species in common (at high pH) but also different species at lower pH that must reflect the differences in steric and electronic effects between the naphthyl and phenyl moieties. To gain better understanding of these interactions we have studied tetra(*p*-carboxyphenyl)porphyrin iron(II) (TCPP Fe(II)) in the pH range 5–14⁺ (where 14⁺ refers to pHs higher than 14). This porphyrin has the phenyl group in common with TPPS and is also *para* substituted with a negatively charged group, however, the carboxy group is able to be fully conjugated with the phenyl ring (this being the major difference with TPPS). We now report the results of frozen solution Mössbauer spectroscopic studies (at 78 K) together with electronic absorption spectral studies (at ambient temperature) in this work.

Results and Discussion

The electronic absorption spectra are presented in Table I and Figs. 1 and 2. The Mössbauer spectroscopic data are given in Table II.

Mössbauer Spectroscopy

All the Mössbauer spectra were poor even after long collection times. The spectra were much inferior to those we previously collected for the other porphyrin iron(II) systems under similar conditions, we cannot offer an explanation for this except that nearly all spectra showed evidence of μ -oxo-bis haem (usually referred to as μ -oxo-dimer) and thus some oxidised material was present leading to depletion of

TABLE I. Electronic Absorption Spectra of TCPPFe(II) Solutions (concentration 5.85×10^{-5} M)

Number of spectrum	pH	Soret		$\epsilon \times 10^{-4}$ ($M^{-1} l cm^{-1}$)		$\epsilon \times 10^{-4}$ ($M^{-1} l cm^{-1}$)		λ_5 (nm)	λ_6 (nm ^a)
		λ (nm)	ϵ	λ_3 (nm)	λ_4 (nm)	ϵ	ϵ		
1	5.30	425	(4.11)	538 ^b	0.34				735
2	6.31	424	(4.81)	538 ^b	0.36	600 ^c			735
3	7.15	425	(4.50)	538 ^b	0.35	600 ^c		670 ^d	735
4	8.30	425	(4.16)	538 ^b	0.34	600 ^c		670 ^d	735
5	9.30	425	(3.75)	538 ^b	0.34	600 ^c		670 ^d	735
6	10.40	425	(3.30)	554	0.33	600 ^c		670 ^d	735
7	11.80	425	(2.11)	556	0.33	603 ^c		670 ^d	735
8	12.20	425	(1.86)	561	0.33	603	0.29	670 ^d	735
9	12.43	427	(1.77)	563	0.33	604	0.29	670 ^d	735
10	12.80	436	(1.84)	563	0.32	606	0.30	670 ^d	735
11	13.20	437	(1.91)	565	0.32	607	0.31	670 ^d	735
12	14.00 ^e	437	(1.93)	566	0.31	607	0.31	670 ^d	735

^aBand weak but grows in intensity by 0.01 A. over pH range 5.30 to 14.0⁺. ^bPresent as weak shoulder on 533 nm band ϵ not measured. ^cPresent as weak shoulder on 553 nm band ϵ not measured. ^dBand is very weak but grows in intensity over pH range 8.3 to 12.2 then stays constant to pH 14⁺. ^epH 14.00⁺ attained by adding excess NaOH.

TABLE II. ⁵⁷Fe Mössbauer Parameters of Frozen Solutions of Tetra(*p*-carboxyphenyl)porphyrin Iron(II)

pH	δ (mm s ⁻¹)	Δ (mm s ⁻¹) ^a	Γ (mm s ⁻¹) ^a	Absorption area (%)
5.50	0.61(4)	2.05(7)	0.37(6)	100(9)
6.70	0.62(4) ^b	1.99(4)	0.17(2)	41(7)
	0.35(5) ^c	0.50(5)	0.12(5)	17(10)
9.30	0.60(5) ^b	1.98(5)	0.15(4)	29(9)
	0.41(3) ^c	0.55(4)	0.15(4)	44(13)
11.2	0.64(2) ^b	2.07(3)	0.22(3)	40(5)
	0.49(4) ^c	0.55(5)	0.18(5)	23(7)
13.2	0.53(13) ^b	2.20(13)	0.18(6)	44(8)
14.0 ^{d,e}	0.63(2)	2.02(4)	0.25(3)	95(14)
μ -oxo-bis haem (solid)	0.44(2)	0.61(2)	0.17(2)	100(3)

^aHalf width at half height. ^bSpectrum fitted as two singlets hence two line widths and their respective absorption areas given. ^cEvidence for μ -oxo-bis haem species. ^dEvidence for μ -oxo bis haem not fitted. ^eSome indications of a high spin iron(II) species present $\delta \sim 1.0$ mm s⁻¹, $\Delta \sim 4.0$ mm s⁻¹.

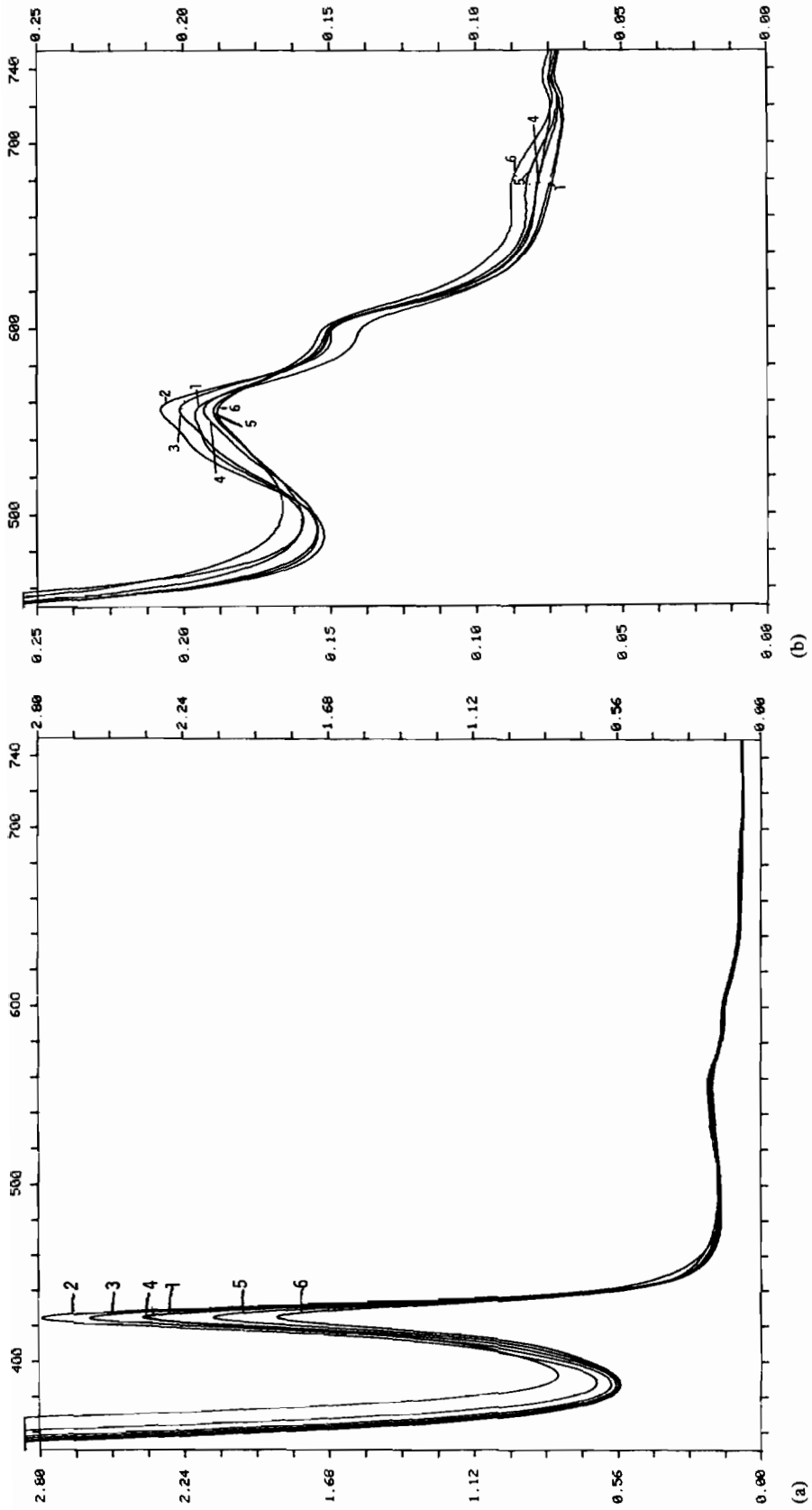


Fig. 1. Electronic absorption spectra of TCPPFe(II) 5.85×10^{-5} M in aqueous solution at 298 K covering the pH range 5.3 to 10.4. Numbers of spectra correspond to numbers given in Table I. (The pH of each is also given in Table I.)

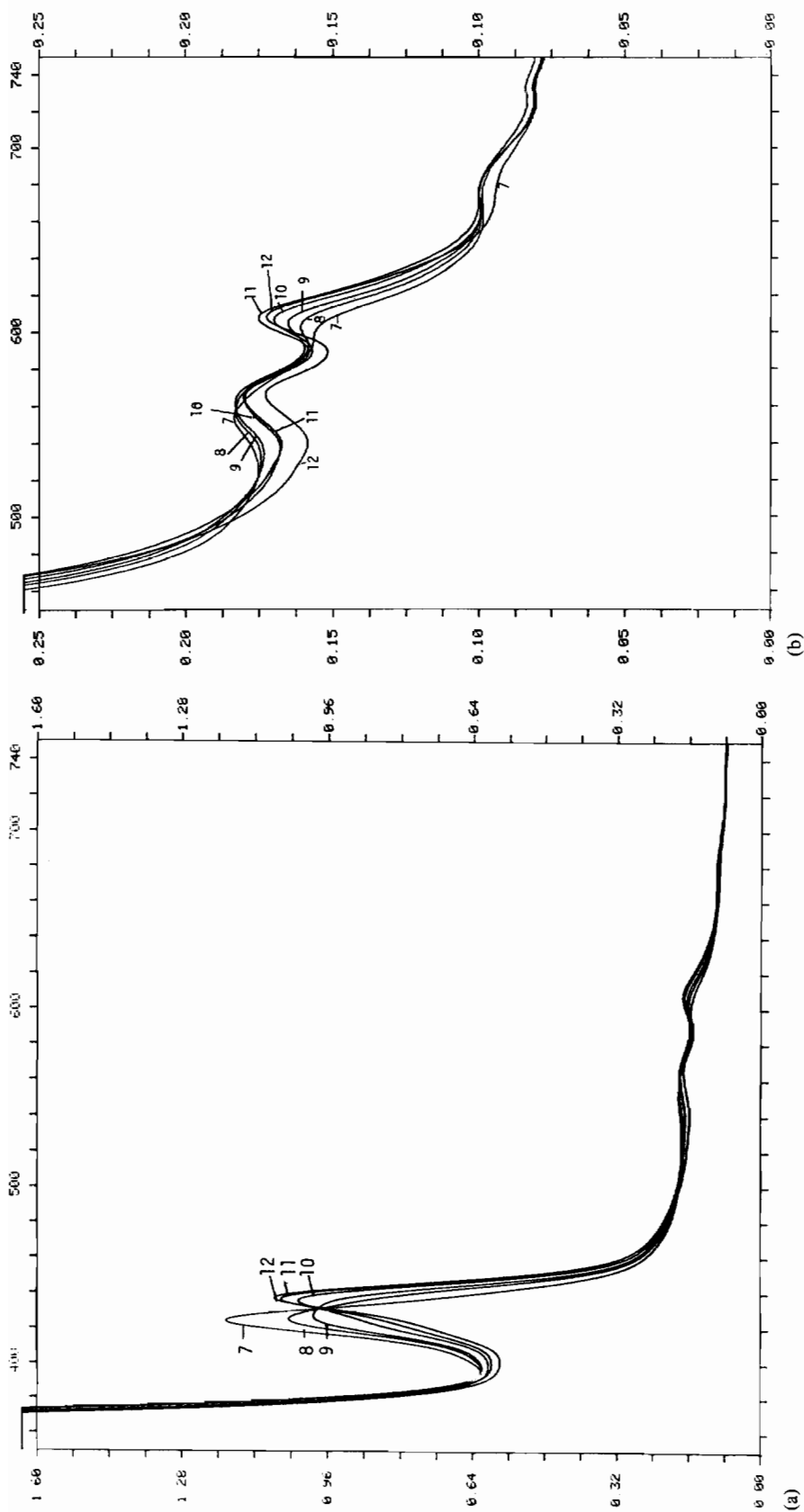


Fig. 2. Electronic absorption spectra of TCPPFc(II) 5.85×10^{-5} M in aqueous solution at 298 K covering the pH range 11.80–14*. Numbers of spectra correspond to numbers given in Table I. (The pH of each is also given in Table I.)

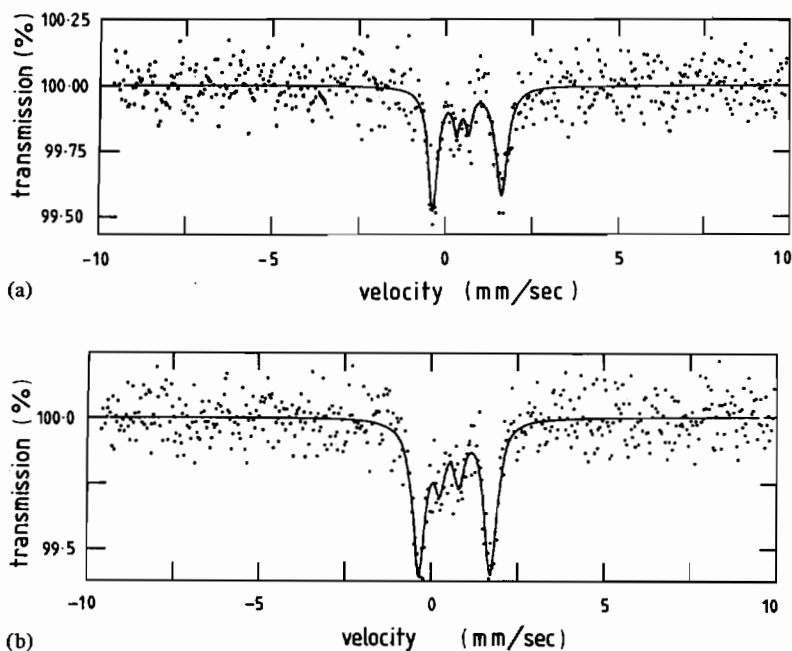


Fig. 3. Mössbauer spectra of TCPPFe(II) frozen aqueous solutions at 78 K. (a) Frozen at pH 6.7; (b) frozen at pH 11.2.

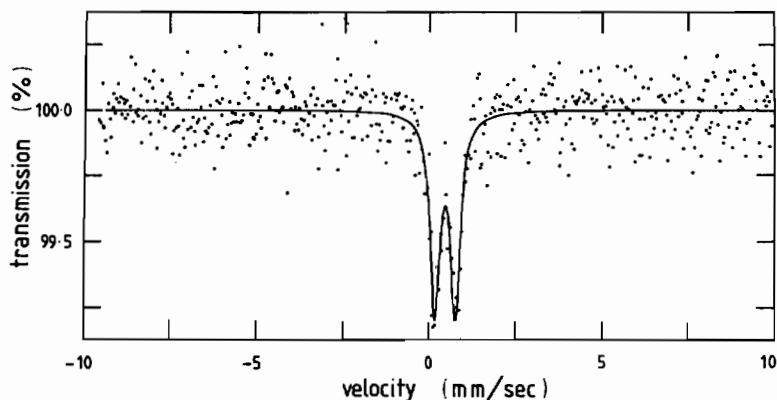


Fig. 4. Mössbauer spectra of μ -oxo-bis(TCPPFe(II)) at 78 K. (Spectrum statistics poor as only run for short time to give parameters and general features.)

the expected amount of iron(II) in the spectra. Obviously as the Mössbauer data are poor, the errors are large (Table II). Typical spectra are shown in Fig. 3a and b, and that of the Fe(III) μ -oxo-bis haem is shown in Fig. 4. One iron(II) site is found to predominate in the pH range 5.5–14.0. This has a chemical shift (δ) around 0.62 mm s^{-1} . The chemical shift is similar to those we have previously assigned as intermediate spin iron(II) environments [1–4], however the quadrupole splitting ($\sim 2.04 \text{ mm s}^{-1}$) found here is larger than those we previously reported. This must reflect the properties of the carboxy group and its interaction with the phenyl ring. At high pH there

is some indication of a high spin iron(II) site similar to those found in the other systems but much less pronounced ($\delta \sim 1.0 \text{ mm s}^{-1}$; $\Delta \sim 4.0 \text{ mm s}^{-1}$).

Electronic Absorption Spectra

The electronic absorption spectra were obtained on solutions of concentration $5.85 \times 10^{-5} \text{ M}$. These are very much weaker than those used for the Mössbauer spectra. Evidence for only two distinct species are found. The first in the pH range 5.3 to 12.2 has a Soret band at 425 nm and another band at 555 nm with shoulders 538 nm and 600 nm, respec-

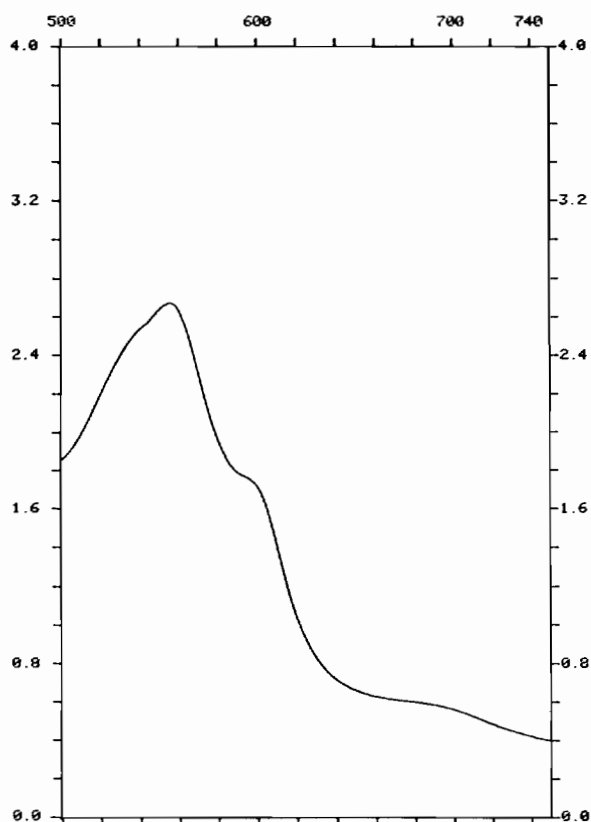


Fig. 5. Electronic absorption spectrum of TCPPFe(II) 1.16×10^{-3} M in aqueous solution at 298 K at pH 7.0.

tively. There are also two very weak bands (possibly charge transfer) that occur at 670 nm and 735 nm.

The second species dominates above pH 12.8. Its Soret band is at 437 nm and there are two lesser bands at 565 nm and 607 nm. The two very weak bands found at lower pH are still apparent and more intense. The three main bands are similar to those found in the TPPSFe(II) and TNPSFe(II) systems and are typical of high spin iron(II) when it is around 0.6 Å out of the porphyrin plane. This site is that which is usually associated with Mössbauer data characterized by δ s of 1.00 mm s^{-1} and Δ s around 4.00 mm s^{-1} . The fact that only a slight indication of this site was found in the Mössbauer data in this system, we suggest is connected with the other species that dominates the Mössbauer data over the entire pH range studied.

The dominant site we assign as an intermediate spin iron(II) species. Previous studies on the other systems have led us to the conclusion that the intermediate spin iron(II) sites are found only when extensive aggregation occurs. In this system at the concentrations for the Mössbauer spectra this species persists across the entire pH range. We conclude that the presence of the carboxy groups encourages this species and aids in the aggregation.

The electronic absorption spectra found in the pH range 5–12.2 are similar to those found in the TPPSFe(II) system and cannot be directly linked to the intermediate spin site found in the Mössbauer spectra, but may be due to the low spin iron(II) site that is able to form at low concentrations. Such a low spin site was found in the TPPSFe(II) [4] system (in the pH range 7–11.8) and in the TNPSFe(II) [5] system (pH range 7–12). In order to obtain evidence for such a site we studied the electronic absorption spectrum in the range 500 to 750 nm (Fig. 5) of a solution of 1.16×10^{-3} M and found the spectrum was very similar to those of lower concentration and also similar to that of Fig. 5b ref. 4, of TPPSFe(II) at pHs 6 and 10.2. Thus electronic absorption spectral evidence for an intermediate spin iron(II) site was not found.

At this point the work of Brault and Rougee [6, 7] is pertinent. They have shown that tetraphenylporphyrin iron(II) (TPPF(II)) in benzene solution exists as a four co-ordinate species even in the presence of water molecules (which would be potential axial ligands) [6]. Thus our conclusions that four co-ordinate porphyrin iron(II) species occur in PPIXFe(II) [1–3] and TPPSFe(II) [4] aqueous solutions agree with their work. The electronic absorption spectrum we find in the concentration ranges studied in this work is very similar to that reported for TPPFe(II) in DMF [6, 7] (see Fig. 2, ref. 7). In their work [6, 7], Brault and Rougee state DMF to be a co-ordinating solvent [6], and that the TPPFe(II) species present is five co-ordinate [7]. The fact that we have found this type of spectrum present in solutions, which at higher concentrations contain low spin iron(II) (evidence from Mössbauer data), suggests that in our case such spectra represent six-coordinate species [4, 5]. The electronic absorption evidence for TPPFe(II) in DMF being five co-ordinate rather than six is scant [6, 7]. (Susceptibility data [7] are used to confirm five coordination, but this is in much more concentrated solutions.)

The electronic absorption spectrum of TPPFe(II) in benzene (where it is four coordination) shows a single peak around 535 nm (see Fig. 2, ref. 7). We note that a shoulder is found in the pH range 6–10.2 (Fig. 5, ref. 4) and also in the pH range 7–11 in the TNPSFe(II) solution [5]. This may be coincidence, but could be evidence for an intermediate spin species. We note that deuteroporphyrin dimethyl ester iron(II) in benzene shows two bands centred around 545 nm (Fig. 1, ref. 7) and is said to be four co-ordinate [7]. For PPIXFe(II) we recorded two similar bands centred around 560 nm in the pH range where we found intermediate spin iron(II) present [1–3]. It therefore appears that the electronic absorbance spectra of four co-ordinate porphyrins differ depending on whether they are substituted on the pyrrole or methine carbon atoms.

Conclusions

It appears that the presence of the carboxy groups on the phenyl rings has a dramatic effect on the iron(II) chemistry of this porphyrin in aqueous solution. The quadrupole splitting found for the intermediate spin site was much larger than that found for TPPFe(II) and TPPSFe(II) and shows a greater electronic imbalance in the iron(II) 3d orbitals [4]. This must arise because of a very different electron density on the pyrrole nitrogen atoms in this porphyrin compared to TPPS, and this in turn must reflect the difference in the electron density on the porphyrin periphery caused by the carboxy groups on the phenyl ring.

Experimental

TCPP was synthesized and purified by a method described in the literature [8]. O(TCPPFe(III))₂ was prepared according to the method of Fleischer *et al.* [9], and complexes of this nature have been prepared by others [10]. For the TCPPFe(II) work described in this paper the O(TCPPFe(III))₂ complex was reduced in aqueous solution using a slight excess of sodium dithionite. The solutions used for Mössbauer experiments contained between 100–200 mg of TCPPFe(II) in 2–3 ml of aqueous solution. The solutions were only studied above pH 5.0 because of solubility problems below this pH. The pH of the solution was adjusted as required by adding 1 M HCl for pH < 12 or by adding 2 M NaOH for pHs > 12. For the solution of pH 14, 3 ml of 1 M NaOH was used to dissolve the compound. The solutions were transferred to nylon cells and frozen in liquid nitrogen.

The electronic absorption spectra were recorded as a function of pH (Table II) in 1 cm² cells at 298 K. Solutions were freshly prepared and kept in the dark

until they were inserted into the spectrometer. The preparation method of the solutions has been described [4], the concentrations are given in Figs. 1, 2 and 5. The cuvettes were sealed under a nitrogen atmosphere.

Instrumentation

Electronic spectra were recorded using a Perkin-Elmer Lambda 5G Spectrophotometer. All spectra were recorded at 298 K. Mössbauer spectra were recorded from frozen solutions at 77–78 K on a spectrometer described previously [11]. The spectrometer was calibrated with 25 μm thick natural iron reference absorber. The isomer shifts are referred to this as zero shift. The Mössbauer spectra were computer-fitted (details previously described [11]).

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