

## Mössbauer Spectroscopic Studies on Tetra(sulphonaphthyl)porphine Iron(II) Solutions

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### Abstract

Mössbauer (78 K) and electronic absorption spectra (room temperature) of tetra(sulphonaphthyl)porphine iron(II) solutions are reported and discussed. Evidence for only two iron(II) electronic environments, a low spin and a high spin site is found. The nature of each iron(II) environment is deduced with reference to previous work. The influence of the steric bulk of the meso substituents is discussed in comparison to similar studies on protoporphyrin IX iron(II) solutions and tetra(*p*-sulphophenyl)iron(II) solutions. The presence of the naphthyl substituents on the methine carbons stabilises the low spin iron(II) species containing two axial water ligands.

### Introduction

The understanding of the chemistry of iron(II)/(III) porphyrins in aqueous solution is of interest to chemists and biochemists for many reasons, two of which are:

(1) Iron porphyrins, in particular protoporphyrin IX iron is the prosthetic group of a large number of metalloproteins [1], hence water soluble haems are useful in modelling its chemistry.

(2) Iron porphyrins because of their role as nature's catalysts [1] may well have industrial applications. Thus an understanding of their aqueous chemistry would be fundamental in developing and redesigning their substituent groups for such use.

Over the last five years we have studied protoporphyrin IX iron(II)/(III) (PPIXFe(II)/(III)) in aqueous solution using electronic absorption and Mössbauer spectroscopy to ascertain the species present, both in the presence and absence of additional ligands [2–11]. We extended these studies to tetra(*p*-sulphophenyl)porphine iron(II)/(III) (TPPSFe(II)/(III)) solutions and found similarities and differences to those of PPIXFe(II)/(III) [12, 13]. In aqueous frozen solutions of TPPSFe(II)

Mössbauer spectroscopic studies confirmed the presence of at least one low spin iron(II) electronic environment that was absent in the corresponding studies on the PPIXFe(II) solution system. In order to study whether such a species was wide-spread or only to be found in the TPPSFe(II) aqueous system, we prepared a tetra(sulphonaphthyl)porphine iron(II) (TNPSFe(II)) and report herein studies of its aqueous chemistry in the pH range 7–14<sup>+</sup>.

### Results and Discussion

The electronic absorption spectra of the TNPSFe(II) system in the pH range 5–14<sup>+</sup> are presented in Table I. Table II contains the frozen solution Mössbauer data.

#### Electronic Absorption Spectra

These data were recorded on solutions of low concentrations *viz.* 1 to  $7 \times 10^{-5}$  M. Typical spectra are shown in Figs. 1 to 4. At first sight evidence for up to at least three species are found in these solutions. The first exists in concentrations of  $7 \times 10^{-5}$  M or greater in the pH range 7–14 (Soret 431 nm, other bands major bands at 536 nm and 602 nm). The second is the predominant species at higher pHs in the same concentration range and is characterised by a Soret band at 444 nm and other bands at 569 nm and 608 nm. If lower concentrations are used (around  $1 \times 10^{-6}$  to  $4 \times 10^{-5}$  M), then in the same pH range (7–14) a species with a Soret at 430.8 nm and other bands at 560 nm and 603 nm exists. At the latter concentration at very high pH 14<sup>+</sup> there is evidence of a shoulder on the Soret at 444 nm. This dependence of the spectra on concentration suggests that aggregation is a factor in the understanding of the behaviour of the TNPSFe(II) aqueous system. In our studies on the corresponding TPPSFe(II) system we found aggregation to be a problem [13]. Although we did not carry out extensive studies on the aggregation present in this system, we did demonstrate its presence at pH 8.5 in the concentration range of  $2 \times 10^{-6}$  to  $7 \times 10^{-5}$  M (Fig. 5).

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TABLE I. Electronic Absorption Spectra of TNPSFe(II) Solutions

Concentration of solution used for spectra	pH	Soret				
		$\lambda_1$ (nm) ( $\epsilon$ (mM))	$\lambda_2$ (nm) ( $\epsilon$ (mM))	$\lambda_3$ (nm) ( $\epsilon$ (mM))	$\lambda_4$ (nm) ( $\epsilon$ (mM))	$\lambda_5$ (nm)
$7.0 \times 10^{-5}$ M	7.2	431.6 <sup>a</sup> (65.2)	536 (5.4)		601 (3.9)	730 <sup>b</sup> 770 <sup>b</sup>
$7.0 \times 10^{-5}$ M	8.6	431.2 <sup>a</sup> (59.1)	537 (5.4)		602 (4.0)	730 <sup>b</sup> 770 <sup>b</sup>
$7.0 \times 10^{-5}$ M	11.3	431.6 <sup>a</sup> (55.0)	535 (7.1)	564 (4.4)	603 (4.2)	730 <sup>b</sup> 770 <sup>b</sup>
$7.0 \times 10^{-5}$ M	12.1	432.4 <sup>a</sup> (50.9)	533 (5.2)	569.6 (6.1)	607 (4.8)	730 <sup>b</sup> 770 <sup>b</sup>
$7.0 \times 10^{-5}$ M	14 <sup>+c</sup>	444 <sup>a</sup> (51.8)		569.6 (6.0)	608 (4.4)	730 <sup>b</sup> 770 <sup>b</sup>
$1.0 \times 10^{-5}$ M	5.9	430 (78.0) <sup>d</sup>		557 <sup>b</sup>	601 <sup>b</sup>	735 <sup>b</sup>
$1.0 \times 10^{-5}$ M	7.2	430 (70.0) <sup>d</sup>		560 <sup>b</sup>	602 <sup>b</sup>	735 <sup>b</sup>
$1.0 \times 10^{-5}$ M	10.1	429.2 (62.0) <sup>d</sup>		560 <sup>b</sup>	602 <sup>b</sup>	735 <sup>b</sup>
$1.0 \times 10^{-5}$ M	12.1	429.2 (60.0) <sup>d</sup>		560 <sup>b</sup>	602 <sup>b</sup>	735 <sup>b</sup>
$1.0 \times 10^{-5}$ M	14 <sup>+c</sup>	430.8 <sup>e</sup> (52.1) <sup>d</sup>		569 <sup>b</sup>	603 <sup>b</sup>	735 <sup>b</sup>

<sup>a</sup>Concentration of solution used for measuring this band was  $3.8 \times 10^{-5}$  M. <sup>b</sup>Extinction coefficients were not calculated for these bands, as their accuracy would have been very low. <sup>c</sup>For pH 14<sup>+</sup> (greater than pH 14.0) large excess of NaOH was used. <sup>d</sup>The extinction coefficients have an estimated error of  $\pm 5.0$  mM. <sup>e</sup>Shoulder at 444 nm.

TABLE II. Mössbauer Parameters for the TNPSFe(II) Aqueous System, Collected from Frozen Solutions at 78 K

pH of solution before freezing	$\delta$ (mm s <sup>-1</sup> )	$\Delta$ (mm s <sup>-1</sup> )	$\Gamma^a$ (mm s <sup>-1</sup> )	Area of species (%)
10.0	0.38(1)	1.09(1)	0.23(1)	100(5)
11.6	0.43(1)	1.22(1)	0.15(1)	60(5)
	1.01(2)	3.99(2)	0.16(2)	40(5)
14 <sup>+b</sup>	0.45(1)	1.10(2)	0.18(1)	54(5)
	1.03(2)	4.06(2)	0.17(2)	45(5)

<sup>a</sup>Half-width at half-height. <sup>b</sup>pH above 14 excess NaOH used.

The electronic absorption spectrum found in the pH range 7–12 at concentrations of  $7 \times 10^{-5}$  or greater is not the same as that found in the corresponding TPPSFe(II) system, all the bands are different. However, that at lower concentrations is similar to that in the TPPSFe(II) system, although all the bands are red-shifted by around 4–6 nm. This must arise from the fact that a naphthyl ring has replaced the phenyl ring in this system.

In the TPPSFe(II) system, evidence for at least four electronically different iron(II) sites was found in the Mössbauer spectra. Of these one was a low spin iron(II) ( $S = 0$ ) site found to be the dominant site in the pH range 7.0–11.8 as verified by Mössbauer data, and the other three were respectively an intermediate spin iron(II) ( $S = 1$ ) site and two high spin iron(II) ( $S = 2$ ) sites. Evidence for only two iron species was found in the electronic absorption spectra which were carried out at much lower concentration [13]. The first of these was either due to the low spin iron(II) site or the intermediate spin iron(II) site, but most likely the former. The second site originates

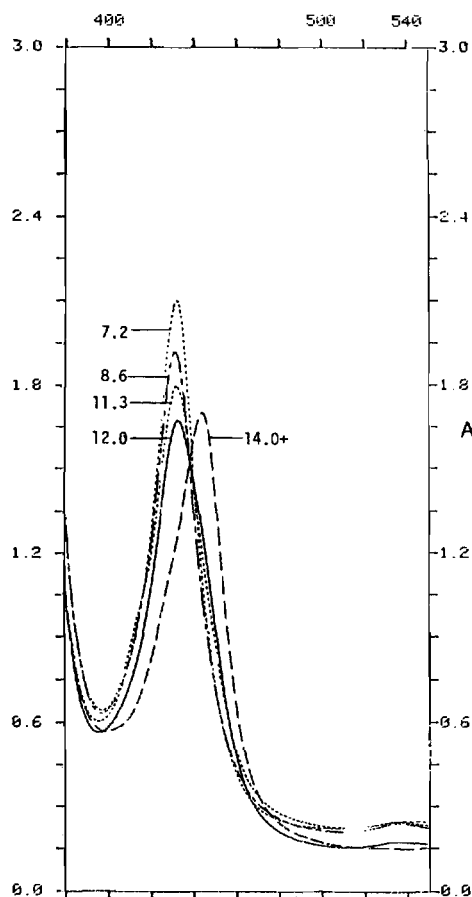


Fig. 1. Electronic absorption spectra of TNPSFe(II)  $\sim 3 \times 10^{-5}$  M in aqueous solutions at 298 K at pHs shown in the Figure in the range of 380–550 nm.

from a high spin iron(II) environment where the iron(II) atom is around 0.59 Å from the 24 atom core mean plane of the porphyrin [14] and has charac-

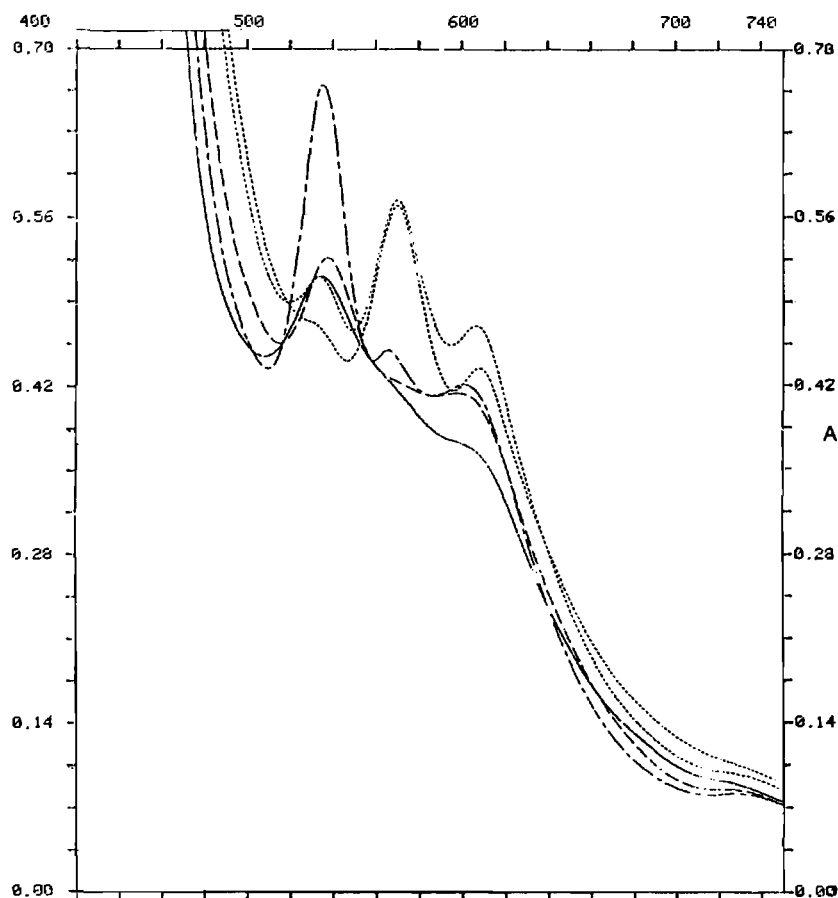


Fig. 2. Electronic absorption spectra of TNPSFe(II)  $\sim 5 \times 10^{-5}$  M in aqueous solutions at 298 K at pHs —, 5.8; ---, 7.16; - · - ·, 11.3; ·····, 12.0; - - - -, 14.0 in the range of 420–750 nm.

teristic Mössbauer data with a quadrupole splitting ( $\Delta$ ) around  $4.0 \text{ mm s}^{-1}$  and a chemical shift ( $\delta$ ) of  $1.0\text{--}1.05 \text{ mm s}^{-1}$  [5, 7, 11, 13, 14]. Such a site is found in the Mössbauer data reported in this paper of solutions frozen at high pH (discussed below) and is the explanation of the electronic absorption spectrum found at high pH in this work. (Soret 444 nm other bands 569 nm 605). We direct the reader to discussion of this type of site in ref. 13.

To return to the two species found at different concentrations in the pH range 7–12 in this work, we are unable to categorically say what these species represent. However, as discussed in the following section on the Mössbauer spectroscopic data in this pH range at much higher concentrations only one species, a low spin TNPSFe(II) complex is present. It is likely that this is the species also responsible for the electronic absorption spectra at low concentrations ( $1 \times 10^{-5}$  M) and that the changes in the spectra at concentrations around  $7 \times 10^{-5}$  M are due to aggregation, and possibly arise from intermolecular charge transfer. The absorption spectral data reflect this with the appearance of a new band at 536 nm, the modified Soret extinction coefficient (we note no

large change in position of the Soret band, Table I) and the new bands at 730 nm and 770 nm which may well be charge transfer bands. Therefore there is evidence in the electronic absorption spectra that although at first appearance two different species appear to be present in the pH range 7–12, there is in fact only one species, but it can form aggregates that are manifest by spectral changes.

#### Mössbauer Spectroscopic Data

The Mössbauer data (Table II; Figs. 6 and 7) give evidence for only two types of iron(II) environment. These are a low spin iron(II) ( $S = 0$ ) site and a high spin iron(II) ( $S = 2$ ) site. The latter site becomes more dominant at higher pHs. This site was discussed above, it has similar parameters to those we have reported in the other iron(II) systems [5, 7, 13] and is that of a five coordinate high spin iron(II) site with the iron around  $0.59 \text{ \AA}$  out of the mean porphyrin plane [14].

It is instructive to consider the nature of the iron electronic environments found in the three iron(II) porphyrins so far studied (in aqueous solution) before discussing the low spin site iron(II) electronic

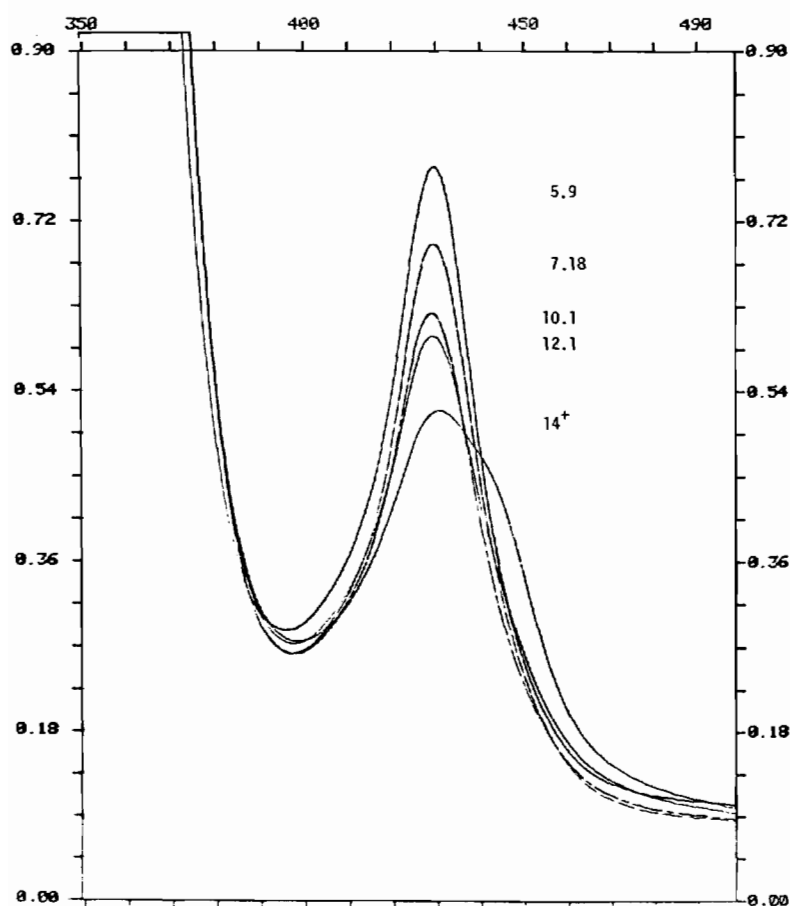


Fig. 3. Electronic absorption spectra of  $\text{TNPSFe(II)} \sim 1 \times 10^{-5} \text{ M}$  in aqueous solutions at 298 K at pHs shown in the Figure in the range of 350–500 nm.

environment in this system. To do this we have chosen to tabulate the data (Table III) explanations to the Table are found in the footnote. This Table indicates both the pH range and type of iron environment found, along with its corresponding proportion at particular pHs.

Low spin iron(II) sites (D and H) are only found in the sulphonated porphyrins. They most likely arise from two water molecules being bound to the iron atoms and the latter are thus six-coordinated and lie in the mean plane of the porphyrin N atoms. We previously suggested for site D in the  $\text{TPPSFe(II)}$  system, that although there were differences in both the Mössbauer chemical shifts and  $\Delta s$  [13], there was only one real iron(II) low spin environment. The differences in the Mössbauer data probably arose from aggregation affects [13], as we have shown [11] that aggregation can affect Mössbauer parameters. We would suggest that although there are differences in both the chemical shifts and  $\Delta s$  in the present system, again only one real iron(II) site with two axial water ligands is responsible. The extent of aggregation and/or ion pairing (the sulphonaphthyl

groups with the sodium ions) being the factors that cause the differences in chemical shift and quadrupole splitting.

### General Discussion

Evidence for only two major iron(II) species was found in the  $\text{TNPSFe(II)}$  system, from both the Mössbauer and the electronic absorption spectral data. This is interesting, when compared to both the  $\text{PPIXFe(II)}$  system (evidence for three iron(II) species was found) and  $\text{TPPSFe(II)}$  system (evidence for four iron(II) species was found). It is apparent that the major difference in these systems is the steric bulk of the *meso* substituents in that of the  $\text{TNPSFe(II)}$ . It is most likely that steric effects are important in permitting only two species to be present in the pH range studied, presumably by interfering with and ordering aggregation for the low spin site and not allowing an intermediate spin site to form. Moreover, the high spin iron(II) site that forms at high pH appears to be more preferred than in the  $\text{TPPSFe(II)}$  system (as

shown in Table III, 45% compared to 31% for the TPPSFe(II) system). The steric bulk of the sulphonaphthyl groups appear to be able to isolate and protect the two axial water ligands allowing them to

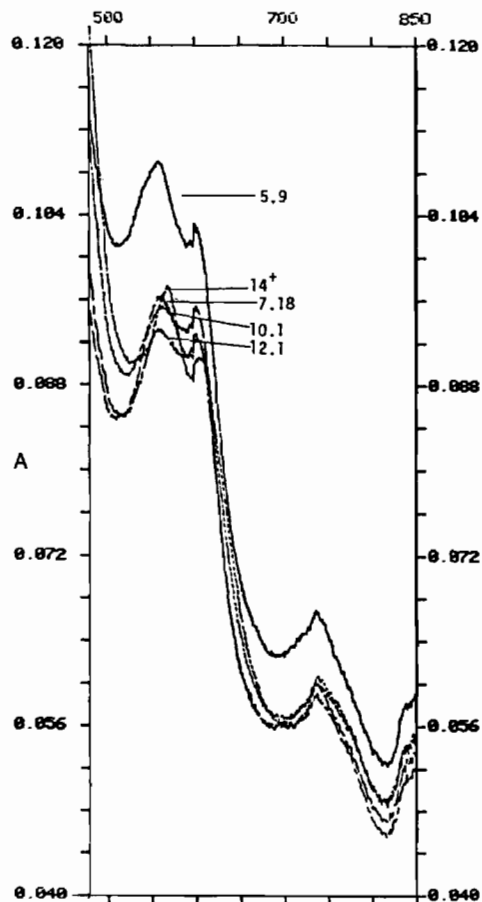


Fig. 4. Electronic absorption spectra of TNPSFe(II)  $\sim 1 \times 10^{-5}$  M in aqueous solutions at 298 K for the pHs 5.9, 7.18, 10.1, 12.1 and 14.0<sup>+</sup> (relative intensities not trusted). Figure illustrates band positions at low concentration.

persist to higher pHs in the TNPSFe(II) system than in that of the TPPSFe(II) system. This is probably the factor that deters the formation of a site similar to B or F.

It is worth mentioning that we did not separate the four possible isomers that exist in TNPSFe(II). These are depicted in line drawings, where the line represents the sulphonaphthyl group (Scheme 1). (a) has all four sulphonaphthyl groups on the same side of the haem plane; (b) has three on one side and one on the other; (c) and (d) have two on each side in *cis* and *trans* configurations, respectively. The ratios of (a), (b), (c) and (d) present in this work are not known (experimentally).

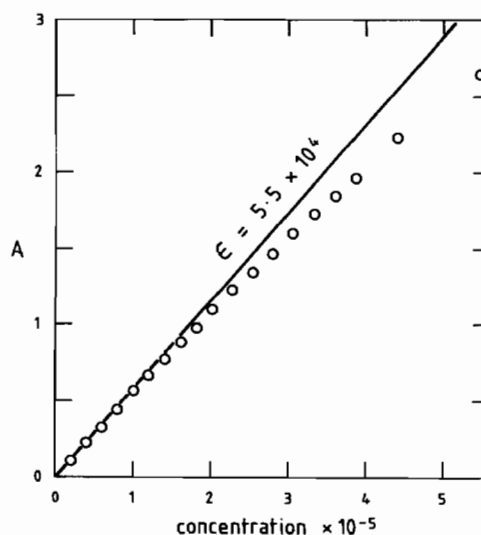


Fig. 5. Beer's Law experiments for TNPSFe(II) in aqueous solution pH 8.5 with added  $\text{NaNO}_3$  (0.1 M) buffered with 0.01 M Tris/HCl as measured with a glass electrode. The line marked  $\epsilon = 5.5 \times 10^4$  defines Beer's Law behaviour for TNPSFe(II) calculated from the first two points on the Figure. The circles represent experimental data points. The experiment was carried out at 430.8 nm.

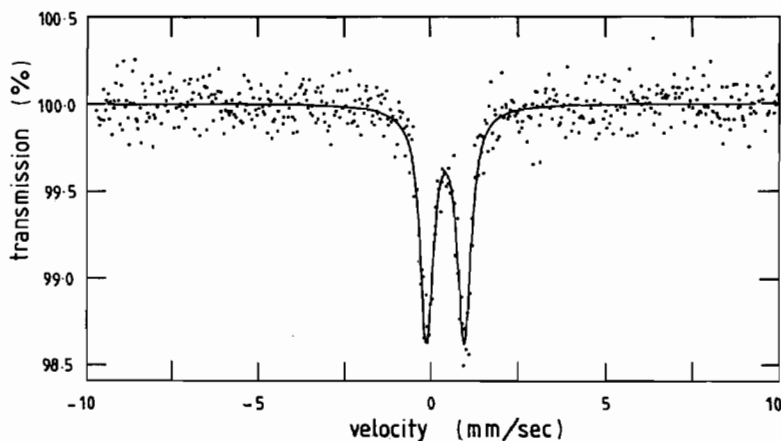


Fig. 6. Mössbauer spectrum of frozen solution of TNPSFe(II) at 77 K (frozen at pH 10.0).

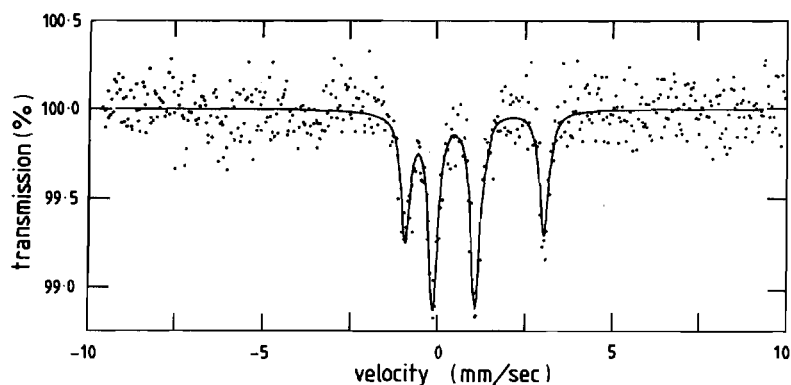


Fig. 7. Mössbauer spectrum of frozen solution of TNPSFe(II) at 77 K (frozen at pH 11.6).

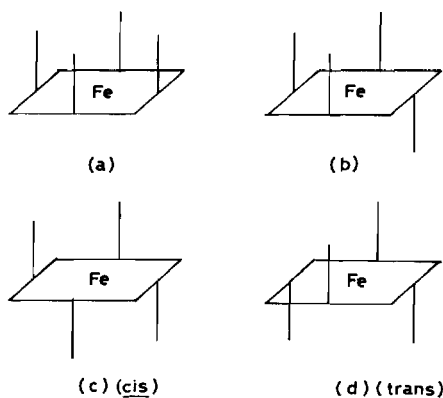
TABLE III. pH Dependence of Iron(II) Species in Water Soluble Porphyrin Systems<sup>a</sup>

pH	PPIXFe(II)	TPPSFe(II)	TNPSFe(II)
5			not studied
6	insoluble		
7			
8			
9	100		
10	72	100	
11	A	D	
12	67	67	100
13			
14	59		
14 <sup>+</sup> b	43		

Site	PPIXFe(II)	TPPSFe(II)	TNPSFe(II)
A	100		
B	28		
C	11		
D		100	
E	67	67	
F	22	22	
G	11	11	
H			60
I			40
14 <sup>+</sup> b	43	52	54
14 <sup>+</sup> b	15	17	45
14 <sup>+</sup> b	28	31	

<sup>a</sup>A and E are intermediate spin iron(II) sites. The proportion of site A is also dependent on haem concentration [5, 7, 11]. B and F are high spin iron(II) sites where the iron is only around 0.48 Å out of the mean porphyrin plane [5, 7, 11, 13, 14]. The proportion of site B is dependent on concentration [11]. C, G and I are high spin iron(II) sites where the iron(II) is around 0.59 Å out of the mean porphyrin plane [5, 7, 11, 13, 14]. D and H are low spin iron(II) sites [3]. The numbers signify the proportion of each site present (calculated from Mössbauer data, areas under peaks) around the pH indicated, and for each porphyrin system all the numbers quoted are for solutions of similar concentrations. <sup>b</sup>14<sup>+</sup>: these solutions contained excess NaOH.



Scheme 1.

It might be expected that isomer (a) would aggregate better than (b) and that both of these would aggregate more than (c) and (d). The former two isomers could well be responsible for the formation of the high spin iron(II) site at high pH, as (c) and (d) would afford more protection for both water ligands in the low spin iron(II) sites. Moreover, isomer (a) would be expected to be present to the least extent, whereas on a statistical ground (c) and (d) would be expected to predominate, this would be well reflected in the proportion of low spin iron(II) present at high pH (~55–60%). We note that the presence of these different isomers may have contributed to the concentration dependence of the electronic absorbance spectra in the pH range 7–12.

## Conclusions

The nature of the meso-substituent influences (a) the type of iron(II) site found in solution and (b) the extent to which it forms and (c) the pH range over which it forms.

The nature of the substituent on the porphyrin periphery affects the position of the Soret band in the high spin iron(II) sites (Table III, sites C, G and I). The Soret bands for these high spin iron(II) sites are progressively red-shifted for PPIX 430 nm, TPPS 439 nm and TNPS 444 nm. This is most likely a direct result of the withdrawal of electron density from the porphyrin by the substituent groups, and the order reflects their overall ability to do this.

## Experimental

Tetra(sulphonaphthyl)porphine iron(II) was prepared by reducing  $\mu$ -oxo bis(tetra(sulphonaphthyl)porphine iron(III)), O(TNPSFe(III))<sub>2</sub>, in solution with sodium dithionite. O(TNPSFe(III))<sub>2</sub> was prepared as previously described [15].

For Mössbauer spectroscopic data FeSO<sub>4</sub> (hydrated) prepared in this laboratory was used to prepare the O(TNPSFe(III))<sub>2</sub>. 200 mg of O(TNPSFe(III))<sub>2</sub> was dissolved in 2.5 ml water. The O(TNPSFe(III))<sub>2</sub> was reduced in aqueous solution using a slight excess of sodium dithionite at high pH. The pH desired for each experiment was adjusted using either 1 M HCl for pH < 12 or by adding 2 M NaOH for pH > 12. The solutions were transferred to cells and frozen in liquid nitrogen for the experiments.

The electronic absorption spectra were recorded on solutions that had been freshly prepared in a three-necked flask. One neck allowed N<sub>2</sub> in and out, another, the samples to be removed, the third was used for a pH electrode. 50 ml of TNPSFe(III), solutions of appropriate concentration were used. The concentrations are given in Table I and Figs. 1–5. The solutions were reduced using a slight excess of sodium dithionite using a magnetic stirrer. The desired pH was adjusted as for the Mössbauer spectroscopic experiments. The spectra were obtained using 1 cm path length cells containing 2.5 ml of solution. The quartz cells are sealed under an N<sub>2</sub> atmosphere. All electronic absorption spectra were taken at 298 K.

## 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 [16]. This was calibrated with a 25  $\mu$ M thick natural iron reference absorber. The isomer shifts are referred to this as zero shift. The Mössbauer spectra were computer-fitted (details described elsewhere [16]).

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