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Mössbauer Studies on Tetra(p-sulphophenyl)porphine Iron(III) Solutions

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The Mössbauer spectra of frozen aqueous solutions of iron(III) over the pH range 1.9 to 12 are reported. The spectra show that tetra(p-sulphophenyl)porphine iron(III) exists principally in two forms, monomeric and as μ-oxo-oligomers, depending on the pH of the solution. Above pH 4.0 only the μ-oxo-oligomer exists and at very low pHs (2.0 or less) only monomers are present. The quadrupole splitting of the monomer is the largest yet recorded for a five coordinate high spin iron(III) porphyrin.

Experimental

TPPSFe was prepared according to the method of Fleischer [12]. For Mössbauer experiments $^{57}FeCl_2$ was used to produce $TPPS^{57}Fe$. The ^{57}Fe was supplied by A.E.R.E. stable isotope division.

The TPPS Fe(III) solutions were prepared as those of ^{57}Fe.PPIX [3].

Instrumentation

Electronic and Mössbauer spectra were recorded as before [3].

Introduction

Over the past three years we have reported systematic studies of the aqueous chemistry of protoporphyrin IX ironII/III (PPIXFe) [1–9]. We have also reported studies on small soluble peptides which are breakdown products of cytochrome *c* and contain protoporphyrin *c* iron III [9–10]. Our interest has been focused on PPIXFe chemistry for two reasons:

1) it is the prosthetic group of a large number of metalloproteins [11], and

2) to date the aqueous chemistry of PPIXFe has not been sufficiently well documented and/or explained. This latter point would render it particularly useful as a model system, and obviously many differences in the physical and chemical properties of this complex in the absence of or in association with protein should further the understanding of its role in biological molecules.

Perhaps the main reasons for the lack of studies on PPIXFe in aqueous solution are,

1) PPIXFe(III) forms a μ-oxo-oligomer at all pH's above pH 7 (in the absence of competing ligands) [3] and,

2) while in the same pH range PPIXFe(II) forms predominantly a polymer made up of bare PPIXFe(II) monomers, where the polymer length depends on concentration and pH [4]. The way these problems have been overcome has been to study iron porphyrins in nonaqueous solvents, but this approach has limitations for investigations of porphyrin reaction kinetics, rather than merely a question of assignment of spectral parameters or purely structural aspects of iron–porphyrin chemistry.

We have previously reported Mössbauer spectroscopic and conductometric studies on PPIXFe(III) [4, 6] in aqueous solutions, but because of the limited solubility of PPIXFe(III) at pH's below 6.0 we have been restricted to studies above pH 6.0 for most purposes. To overcome this problem we have sought iron porphyrins which are soluble in aqueous solution at low pH. Such a porphyrin is tetra(p-sulphophenyl)porphine iron(III) (TPPSFe(III)) [12]. TPPSFe(III) has been studied in aqueous solution over the pH range 2–11 using kinetics, magnetics (Evans's method [13]), and visible absorption spectra at selected pHs [12]. Evidence for the presence of a monomer and a μ-oxo-oligomer {o-[TPPSFe(III)]$_2$} was presented.

TPPSFe differs from PPIXFe in that it has four peripheral negative charges located on the $-SO_3$ groups, whereas PPIXFe has only two negative charges on its propionic groups. To study the influence of these extra charges on the Fe electronic environment we have studied frozen solution Mössbauer spectra over the pH range 1.9 to 12 and present the results here along with parallel studies on their electronic solution spectra.

Results and Discussion

The Mössbauer data is reported in Table I and Figs. 1 and 2. Only two Mössbauer sites are found across the entire pH range. They are readily assigned

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TABLE I. Mössbauer Parameters of Frozen Aqueous Solutions of TPPSFe(III) at 80 K.

pH	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	%A
1.9	0.50(1)	1.68(1)	0.46(2)	100
3.1	0.39(1)	0.57(3)	0.18(3)	48(2)
	0.50(1)	1.69(3)	0.40(3)	52(2)
6.0	0.38(1)	0.52(2)	0.16(1)	100
12.0	0.38(1)	0.53(2)	0.16(1)	100

to a monomer (δ = 0.49 mm s^{-1}, Δ = 1.68 mm s^{-1}) and a μ-oxo-oligomer (δ = 0.38 mm s^{-1}, Δ = 0.53 mm s^{-1}). The Mössbauer parameters for the μ-oxo-oligomer are similar to those we have reported previously for μ-oxo-oligomer of PPIXFe(III) [3] and those reported by other workers for other μ-oxo species [14–16]. The μ-oxo-oligomer of TPPSFe(III) (which generates a symmetric Mössbauer spectrum) contains high-spin S = 5/2 iron(III) ions antiferromagnetically coupled through the oxygen bridge.

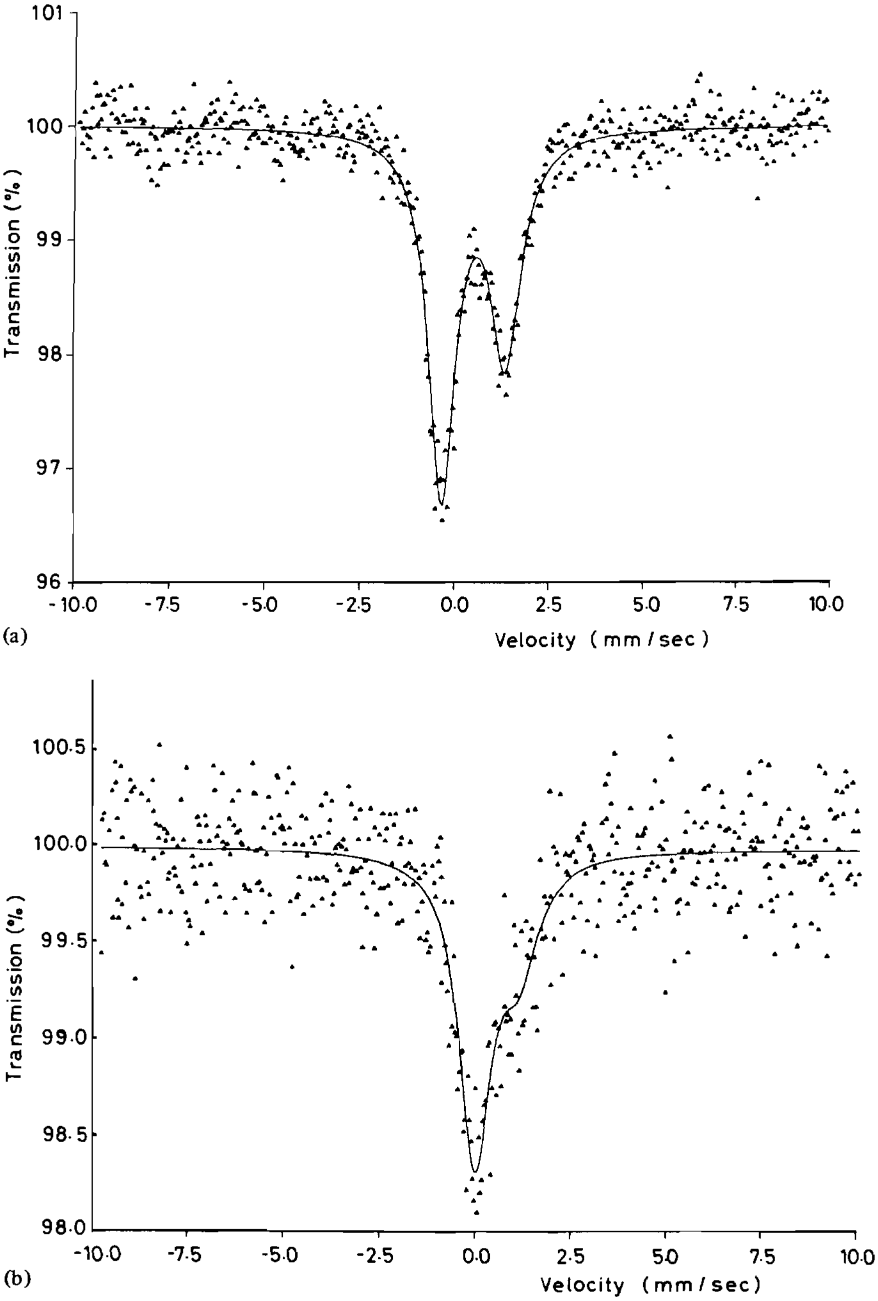

Fig. 1. Mössbauer spectra of TPPSFe(III) monomer frozen solution (pH 1.9) at (a) 80 K and (b) 140 K.

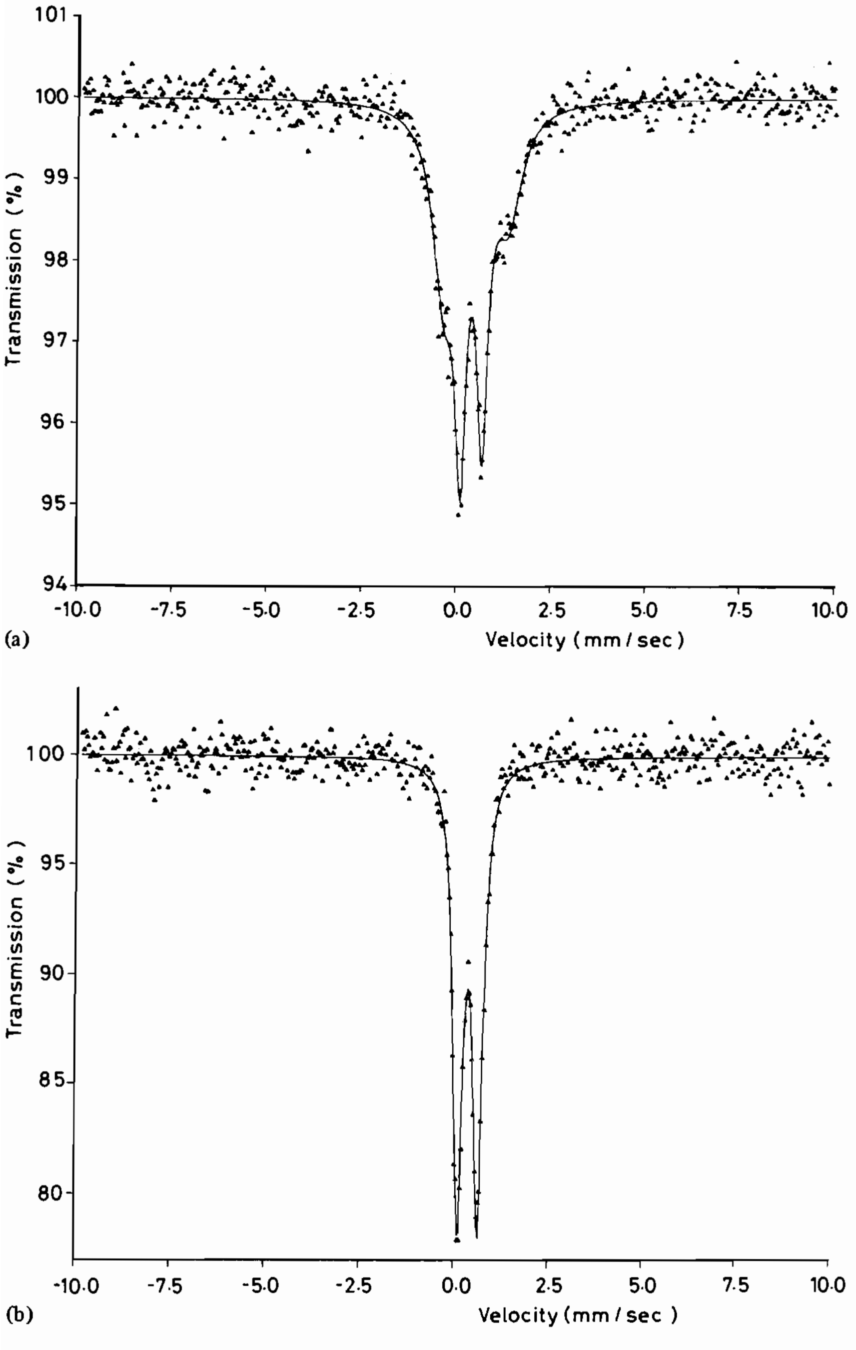

Fig. 2. Mössbauer spectra of TPPSFe(III) frozen solutions at pHs 3.1 (a) and 12 (b).

Since no fluctuations of the electron spins are possible under these conditions the Mössbauer spectrum is a symmetric doublet.

The asymmetric spectra (Fig. 1) observed for monomer of TPPSFe(III) are explained in the same way as those for haemin by Blume [17] in terms of a temperature dependent spin–spin relaxation process.

It must be noted that though all solutions contain no precipitate before freezing, on the event of freezing (even rapid freezing), equilibria may shift during cooling [18]. If this happens, then Mössbauer parameters for the frozen solution reflect the structure not of the initial room temperature solution, but of the solution at the solidification temperature. We have previously discussed that in the mechanism of rapid freezing it must be appreciated that some segregation of the Mössbauer nucleus may occur forming amorphous phase species and aggregations in such glasslike phases may be produced [3]. The results expect-

TABLE II. Visible Absorption Spectra.

Compound	Solvent	λ (nm)	Reference
FeTPPS monomer	H_2O	392 528	12
O-(FeTPPS)$_2$	H_2O	415 565	12
FeTPPS (pH 12)	H_2O	415 565	this work
FeTPPS (pH 8)	H_2O	415 565	this work
FeTPPS (pH 5.0)	H_2O	392 528	this work
FeTPPS (pH 2.0)	H_2O	392 528	this work

ed from such effects were discussed [3] and we refer the reader to this and to the work of Lang *et al.* [19].

The quadrupole splitting of 1.68 mm s^{-1} for monomer TPPSFe(III) at low pH is much larger than is expected for a high spin iron(III) porphyrin [15, 16, 20, 21] though the isomer shift is typical [15, 16]. Although the isomer shift for this species was characteristic of high spin iron(III) porphyrins we collected a spectrum at a higher temperature to verify the iron spin state. The data at 140 K (Fig. 1) clearly show the presence of a broad asymmetric spectrum typical for high spin iron(III) porphyrins [17]. The Mössbauer data for the TPPFe(III)X (X = I, Br, Cl, NCS) have quadrupole splitting data in the range 0.46–0.75 mm s^{-1}. The quadrupole splitting for PPIXFeOH is 1.06 mm s^{-1} [3]. However the quadrupole splitting of 1.68 mm s^{-1} recorded for the low pH TPPSFe(III) species is by far the greatest so far recorded for a high spin iron(III) porphyrin (larger than 1.33 mm s^{-1} of [PMxPPFeI] [15]) and must reflect the nature of the fifth ligand. This axial ligand is more likely to be a water molecule rather than a hydroxyl ion as this TPPSFe(III) species is only found at pH 3.1 and below. It is to be noted that though our electronic spectral data (Table II) on the pH dependence of the TPPSFe(III) species agree with those of Fleischer [12], the concentration of the solutions used for the Mössbauer studies was much higher. Thus the pH dependence of the species present *i.e.* monomer and olimer are different. The crossover point from monomer to μ-oxo oligomer being much lower (around pH 4.0) in the more concentrated solution. The TPPSFe(III) monomer is likely to have a water as the axial ligand below pH 4.0 as the pK_a of a water molecule bonded to TPPS-Fe(III) would be expected to be higher than 4.0 In the dilute solutions used for the electronic spectra it is probable that a species of the form TPPSFe(III) OH does exist around pH 6 but we were unable to record Mössbauer spectra for such dilute solutions. Other workers [15, 20, 21] have established that for halide derivatives the order of increasing quadrupole splitting values is [TPPFeCl] < [PClPPFeCl] < [PFPPFeCl] < [PMXPPFeCl]. This dependence of the quadrupole splitting on the phenyl substituent was unexpected [15] as the phenyl rings were considered to be perpendicular to the porphyrin ring. Thus any electronic effects of these substituents must be transmitted to the porphine π system by the bond between the phenyl group and the methine carbon. However Fleischer [12] points out that it is known "that the phenyl groups, which in the free base and metalloporphyrins are near to being perpendicular to the porphyrin ring rotate toward the porphyrin plane in the diacid species", [24]. He postulated that this behaviour might account for some of the observations he had made in acidic solutions of TPPS [12].

The large quadrupole splitting reported here for the acidic TPPSFe(III) species clearly demonstrates that the substituent on the phenyl group is important and does effect the quadrupole splitting. As the orientation of these groups has not been clearly established at low pH, the nature of the electronic effect is unclear.

Torrens *et al.* [15] have discussed X-ray data [22, 23] indicating that the four nitrogen atoms of the porphine ring are not strictly planar, and the magnitude of the porphine skeleton ruffling depends upon the substituents as well as the coordinated metal ion. These authors 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 compound in homogeneous frozen solution are required to settle the point definitely.

Our studies would add a caution to the above in that the nature of the orientation of the phenyl rings as well as the axial ligand must be clearly established in solution before such questions can be answered.

The other sources of difference that can effect the quadrupole splitting are

1) the distance of the iron from the mean porporphyrin plane (such differences have been established in chlorohemin [25] and TPPFeCl [26] where the distances are 0.475 and 0.383 Å respectively) and

2) the nature of the fifth ligand in the iron(III) porphyrins has also been shown to be very sensitive for the size of the quadrupole splitting [15]. The quadrupole splitting for such complexes has been shown to increase in the order $NCS^- \sim N_3^- < CH_3CO_2^- < Cl^- < Br^- < CF_3CO_2^- < I^-$. Interestingly this is the reverse of the spectrochemical series

and is in fact similar to the order found for the nephelauxetic effect. It should be noted however that if in the case of the monomer TPPSFe(III) species stable at acid pH the axial ligand is a H_2O molecule then this would be completely out of place in the nephelauxetic effect. That is because the quadrupole splitting is greater than that of a porphyrin iron(III)I but in the nephelauxetic series it would be expected to be less than caused by NCS as the axial ligand. We feel this is additional evidence for a phenyl substituent effect on the four nitrogen atoms of the TPPS ring.

We note from the assymmetry of the TPPSFe(III)OH_2 Mössbauer spectrum that the sign of the efg is positive as is found for most other monomeric high spin iron(III) porphyrins [11].

Conclusions

The pH behaviour of these concentrated TPPSFe(III) species is different from that for the PPIXFe(III) system which we reported previously [3]. These differences are significant and emphasise the different chemical properties of the Fe(III) atoms generated by these porphyrins. These differences are a useful illustration why modelling haemoproteins with porphyrins other than PPIXFe is dangerous. Porphyrins with different substituents cause changes of electron density at the iron atom centre and thus modify the redox properties as well as solvation properties.

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