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Mössbauer and Spectroscopic Studies on Substituted Tetraphenylporphyrinato Iron(III) Complexes in Aqueous Solutions and the Formation of the μ-oxo-bridged Species

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Abstract

Electronic and ^{57}Fe Mössbauer spectra are reported for two new water-soluble porphyrinato iron(III) complexes. Equilibrium constants for μ-oxo bishaem formation are calculated assuming two protons are released.

Comparisons are made of the data with other porphyrinato iron(III) systems and it is shown that, in the absence of well-defined fifth ligands, the mononuclear species in acidic solution probably contain two axial water ligands. The μ-oxo bishaems do not contain water or hydroxide coordinated to iron but may hold water by hydrogen-bonding to the oxygen bridge or possibly by aquation of the porphyrin ligands.

μ-Oxo bridge formation is controlled by the acid strength of the water coordinated to the iron in the mononuclear species, low pK_a values assisting oxo-bridge formation. Such low pK_a values are assisted by electron-attracting substituents on the porphyrin periphery. It is noted that this same property assists the stabilisation of iron(II) complexes. Steric inhibition of oxo-bridge formation requires large substituents, unsubstituted phenyl groups being apparently not large enough.

Introduction

There have been relatively few Mössbauer spectroscopic studies on porphyrinato iron(III) complexes in frozen aqueous solution [1, 2]. The systems that have been studied previously using Mössbauer spectroscopy are protoporphyrin IX iron(III), henceforth referred to as PPIX(Fe(III), tetrakis-(4-*N*-methylpyridyl)-porphyrinato iron(III) [3], (TMpyPFe(III)) and tetra(*p*-sulphophenyl)porphyrinato iron(III) [2] (TPPSFe(III)).

In all three cases evidence for only two species was found, at low pH a monomeric species and at high pH a μ-oxo bis(porphyrinatoiron(III)) complex. The latter species have been previously referred to as μ-oxo dimers and as μ-oxo oligomers*, neither of which is strictly accurate; we therefore refer to such species as μ-oxo bishaem complexes. We have previously shown that small changes in the ^{57}Fe Mössbauer spectra of both high and low pH complexes are induced by substitution on the periphery of the porphyrin skeleton [1, 2] indicating that the electron density at the centre of high spin iron(III) porphyrin complexes is significantly influenced even by remote substitution. This conclusion finds support from the work of Pasternak *et al.* [3] (we regret we missed this paper when writing our earlier work [2]). The quadrupole splittings (Δ) for TMpyPFe(III) [3] and TPPSFe(III) [2] are large, that for PPIXFe(III) being distinctly smaller [1]. This variation has been shown [2, 5] to depend on the nature of the fifth (axial) ligand and it is probable that the first two porphyrins have water as the fifth ligand, whereas PPIXFe(III) has OH^- in this position. It has not been possible in general to state whether the sixth coordination position on the iron was occupied or not by a water ligand in aqueous solution, and it has generally been assumed that such complexes were five-coordinate.

The Δ-values for a series of axially substituted complexes have been shown [5] to increase in the order $NCS^- \approx N_3^- < CH_3CO_2^- < Cl^- < Br^- < CF_3CO_2^- < I^-$. This is the reverse of the spectrochemical series and is quite similar (for this restricted range of ligands) to the nephelauxetic series. It is unfortunate that data for hydroxide and water complexes are not available [5] as the splittings in TPPSFe(III)-(H_2O) and TMpyPFe(III)(H_2O) are larger than the I^- complex mentioned above, suggesting the possibility of water behaving in an anomalous manner. The structure [6, 7] of $TPPFe(III)(H_2O)_2 \cdot (ClO_4) \cdot (THF)_2$ has been shown to contain a six-coordinate high spin iron(III) in the N_4 plane. This complex has Δ-values of 1.53 mm s^{-1} at 78 K and 1.69 mm s^{-1} at 298 K. As these values are close to both those found in the

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*This phrase has been accredited to J. L. Hoard by W. I. White [4].

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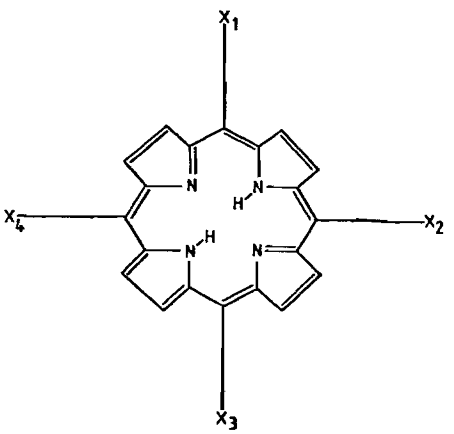


Fig. 1. The structures of $TNPSH_6$ and $(SP)_2(SMeP)_2PH_6$. For $TNPSH_6$ x_1 to x_4 = naphthysulphonic acid. For $(SP)_2(SMeP)_2PH_6$ two possible isomers (a) $x_1 = x_2$ = phenylsulphonic acid; $x_3 = x_4$ = paratolylsulphonic acid; (b) $x_1 = x_3$ = phenylsulphonic acid; $x_2 = x_4$ = paratolylsulphonic acid (positions of acid not established).

frozen solution studies [2, 3], it can be suggested that in solution the monomer meso-substituted haem species actually have two axial water ligands. This prompted us to seek other water soluble porphyrinato iron(III) complexes in order to examine the range of Δ values that could be found by varying the porphyrin and keeping the fifth ligand as a water molecule. Both the porphyrinato iron(III) complexes reported here are new complexes specially prepared for this work. The first, tetra(4-sulpho, 1-naphthyl)-porphyrinato iron(III) (TNPSFe(III)), we chose as it is similar to TPPSFe(III) in having four negative charges on the outside of the porphyrin and the 1-naphthyl moieties are inductively very similar to phenyl in their electron withdrawing properties. The second complex, bis(*p*-sulphophenyl)bis(sulpho-*p*-methylphenyl)porphyrinatoiron(III) ($(SP)_2(SMeP)_2$-PFe(III)), we designed to give negative peripheral charges (like PPIXFe(III)) and to be soluble at low pH but to have more electron density on the porphyrin. These porphyrins are shown in Fig. 1.

Another problem in the literature [1–3] of aqueous iron(III) porphyrin chemistry is uncertainty over the nature of the μ-oxo bishaem species; the two porphyrins studied in this work and a careful appraisement of the relevant literature [8–10] given in this paper have allowed us to throw light on this matter and also to suggest conditions necessary for the inhibition of μ-oxo bishaem formation. This has been achieved by a comparison of a number of different formation constants for μ-oxo bishaems from the literature both with each other and with our new results.

Results and Discussion

Mössbauer Spectra

The Mössbauer data for both the TNPSFe(III) and $(SP)_2(SMeP)_2PFe(III)$ solutions and solids are presented in Table I and Figs. 2 and 3. As in earlier studies, evidence for mononuclear species (high spin iron(III)) was found at low pH with characteristic Mössbauer spectra (Fig. 2). Such spectra are characterised by isomer shifts near 0.50 mm s^{-1}, by Δ-values of at least 1.65 mm s^{-1} and, most useful for assignment, an asymmetric intensity pattern in the quadrupole doublet. The asymmetry has been ex-

TABLE I. Mössbauer Parameters of Frozen Aqueous Solutions and Solids of the Porphyrins at 78 K

Compound	pH	δ (mm s^{-1})	Δ (mm s^{-1})	Γ[a] (mm s^{-1})	*A* (%)
$(SP)_2(SMeP)_2PFe(III)$	12.0	0.39(1)	0.61(1)	0.15(1)	100
$(SP)_2(SMeP)_2PFe(III)$	6.0	0.39(1)	0.60(1)	0.17(1)	100
$(SP)_2(SMeP)_2PFe(III)$	2.0	0.50(2)	2.24(2)	0.50(4)[b], 0.49(4)[b]	54(4)†, 46(4)†
Solid from high pH		0.39(1)	0.67(2)	0.17(1)	100
TNPSFe(III)	12.0	0.43(1)	0.72(1)	0.18(1)	100
TNPSFe(III)	6.1	0.42(1)	0.72(1)	0.17(1)	100
TNPSFe(III)	1.5	0.54(4)	1.65(4)	0.71(4)[b], 0.66(6)[b]	62(4)†, 38(4)†
Solid from pH 5.0 (methanol)		0.42(1)	0.72(1)	0.18(1)	100
TPPSFe(III)[c]	12.0	0.38(1)	0.53(2)	0.16(1)	100
TPPSFe(III)[c]	6.0	0.38(1)	0.52(2)	0.16(1)	100
TPPSFe(III)[c]	3.1	0.39(1)	0.57(3)	0.18(3)	48(2)
		0.50(1)	1.69(3)	0.40(3)	52(2)
TPPSFe(III)[c]	1.9	0.50(1)	1.68(1)	0.46(2)[d]	100
$(TNPFe(III))_2O$[e]		0.45	0.73	0.45[f]	

[a] Half width at half height. [b] Fitted as two single lines and areas of each line (†). [c] Data from ref. 2. [d] Fitted as two single lines and averaged. [e] Data of $(NAPPFe)_2O$ ref. 7. No errors given but ref. 5 errors are 0.04 mm s^{-1} on δ, Δ and Γ. [f] Full width at half height.

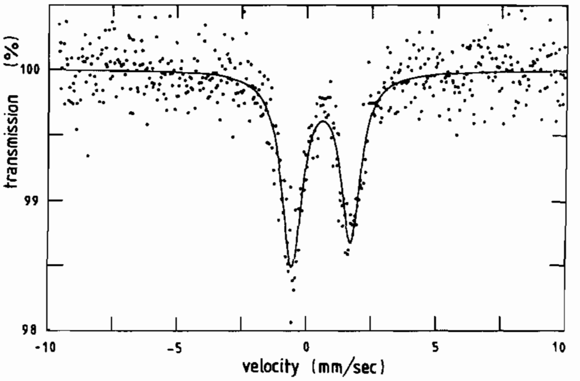


Fig. 2. ^{57}Fe Mössbauer spectrum of $(SP)_2(SMeP)_2Fe(III)$ at 78 K in frozen solution at pH = 2.0.

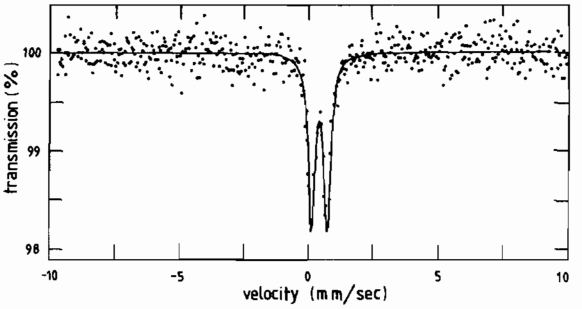


Fig. 3. ^{57}Fe Mössbauer spectrum of $(SP)_2(SMeP)_2PFe(III)$ at 78 K in frozen solution at pH = 12.0 (μ-oxo bishaem).

plained by Blume [8] in terms of a temperature-dependent spin–spin relaxation process specific for mononuclear complexes.

At higher pH values the Mössbauer spectra have parameters typical of μ-oxo bishaem complexes [1, 2, 9, 10] (Fig. 3), *i.e.* isomer shifts of about 0.40 mm s^{-1} and Δ-values in the range of 0.5 to 0.8 mm s^{-1} at 80 K. The quadrupole doublets are symmetric (and sharper than the mononuclear spectra) because the strong antiferromagnetic coupling through the oxygen bridge effectively inhibits fluctuations of the electron spins [11, 12].

None of the solutions contained precipitates before freezing, but, as we have noted previously [1, 2], in the process of freezing (even rapid freezing), equilibria may shift during cooling [13]. We refer the reader to our previous discussion of what is then expected [1, 2] and also to the work of Lang *et al.* [14].

The quadrupole splittings observed in this work for the monomers present at low pH are large for a high spin porphyrinato iron(III) species and are comparable to those which we previously recorded for TPPSFe(III) [2]. As suggested previously [2, 3], at such low pH values the most likely axial ligand in these high spin iron(III) complexes is a water molecule rather than a hydroxide ion. Further evidence for this is found in the electronic spectral data for these complexes (Tables II and III).

Nature of the Fe(III) Site in the μ-Oxo Species in Aqueous Porphyrin Solutions

There has been much discussion over the exact nature of the bishaem species in water soluble porphyrin systems [1–3, 15, 16].

Three models have been proposed which differ in terms of the presence of extra axial ligands on the outside of the porphyrin planes. In model A [1, 2], there are no extra ligands and the binuclear species may be described as M–O–M where M is the porphyrinatoiron(III) unit. Model B contains two axial water molecules, *i.e.* $[H_2O–M–O–M–OH_2]$ [15] and model C [3, 16] has two axial hydroxides, *i.e.* $[HO–M–O–M–OH]^{2-}$ and low-spin iron(III). Molecules of type A have been shown to occur in the solid state by X-ray crystal structure determinations [17–20]. Fleischer *et al.* [15] suggested model B (with high spin iron(III)) on the basis of magnetic moment data previously reported by Cohen [10]. Cohen reported that μ_{eff} for $(TPPFe)_2O$ at room temperature decreased from 2.68 to 1.74 on extensive drying; he appears to have interpreted this as due to the wet starting material actually being a mixture of the mononuclear (M–OH) species (with or without water) and the μ-oxo bishaem species, which on drying yielded an increasing proportion of the binuclear unit. Fleischer *et al.* [3] on the other hand proposed that the drying process removed coordinated water from the binuclear unit thereby changing the local iron stereochemistry and causing a fall in magnetic moment, by means which were not specified.

The low spin dihydroxy species C was suggested by Pasternak *et al.* [3] and by Kolski and Plane [16], in order to explain spectrophotometric pH titrations on solutions of the mononuclear species. There is no direct evidence for such a species and in any case a dramatic change would be expected in the Mössbauer spectra if a spin change occurred. We do not consider this species to be very likely as all Mössbauer spectra reported are consistent with the binuclear compounds being strongly antiferromagnetically coupled high spin iron(III) species [12].

A most interesting variant of model A has been reported [18] in which the two porphyrins are linked through a diphenylurea unit; a water molecule is held by hydrogen bonding to the bridging oxygen atom and to two N–H groups of the urea. It is reported that the magnetic moment is a function of the water content and it may therefore be suggested that other wet μ-oxo bishaems might be able to hold water by hydrogen bonding to the bridging oxygen. Such bonding would be weaker than in the case above, but would clearly affect the magnetic

TABLE II. Visible Absorption Spectra for the Iron(III) Porphyrin Aqueous Solutions

Compound	pH	Soret band λ (nm)	β band λ (nm)	Relative peak heights	References
FePPIX[a]	6.0	365	634	52:4:–	1
FeTPPS	2.3	392	528(680)[b]	56:5:1	2, 15
FeTNPS	2.5	397	525	45:5:–	this work
$Fe(SP)_2(SMeP)_2P$	2.8	392	525(647)[b]	46:4:1	this work
Fe(TMpyP)	1.0	398	524(650)[b]	40:4:1	3
FePP(IX)[a]	12.0	387	608	29:3:–	1
FeTPPS	11.2	415	565(606)[b]	25:1.9:1	2, 15
FeTNPS	10.4	417	566	22:0.6:–	this work
$Fe(SP)_2(SMeP)_2P$	11.5	410	564(606)[b]	21:1.8:1	this work
Fe(TMpyP)	8.3	420	600(638)[b]	18:1.7:1	3

[a] This porphyrin has different peripheral substituent groups from the others and these will greatly influence the electronic spectra. [b] Some porphyrins show a distinct third band in the spectra. Because of this the relative peak heights are included and normalised so that where no third band is tabulated, its intensity, if present, is much less than 1 in relation to the relative intensity of the Soret band.

TABLE III. Equilibrium Constants for μ-Oxo Bishaem Formation

Porphyrin[a]		K_o (M^{-1})	$10^2 K_{D(JB)}$	K_D (M)	Q[b]	$pK_1^{(m)}$	Reference
TMpyP		$\sim 9 \times 10^5$	1800	3.58×10^{-4}	+4	4.7	3
ENP		1×10^5	316	1.0×10^{-4}	+6	4.5	16, 29
PPIX			450		–2		24
mfh			6.92		–2		25
dfh			3.4		–2		26
hfh			1.0		–2		27
DDS[c]			0.23		–4		30
DDS[c]		3.4×10^6	6.8	1.6×10^{-9}	–4	7.7	29
cfh			0.21		–4		28
TPPS	50 °C	10.8×10^6	108.0	108.0×10^{-9}	–4	7.0[d]	15
TPPS	25 °C	8.0×10^5	7.9	7.9×10^{-9}	–4	7.0[d]	15
TPPS	11 °C	2.0×10^5	2.0	2.0×10^{-9}	–4	7.0[d]	15
$(SP_2)_2(SMeP)_2P$	17 °C			7.0×10^{-12}	–4		this work
TNPS	17 °C			3.3×10^{-15}	–4		this work

[a] Names as in references. [b] Charge on the periphery of the porphyrin. [c] There are two sets of data for DDS. [d] From ref. 31 only at 25 °C. Measurements are at 25 °C unless otherwise stated.

properties by influencing the pathway for antiferromagnetic exchange, without changing the spin state of the iron(III).

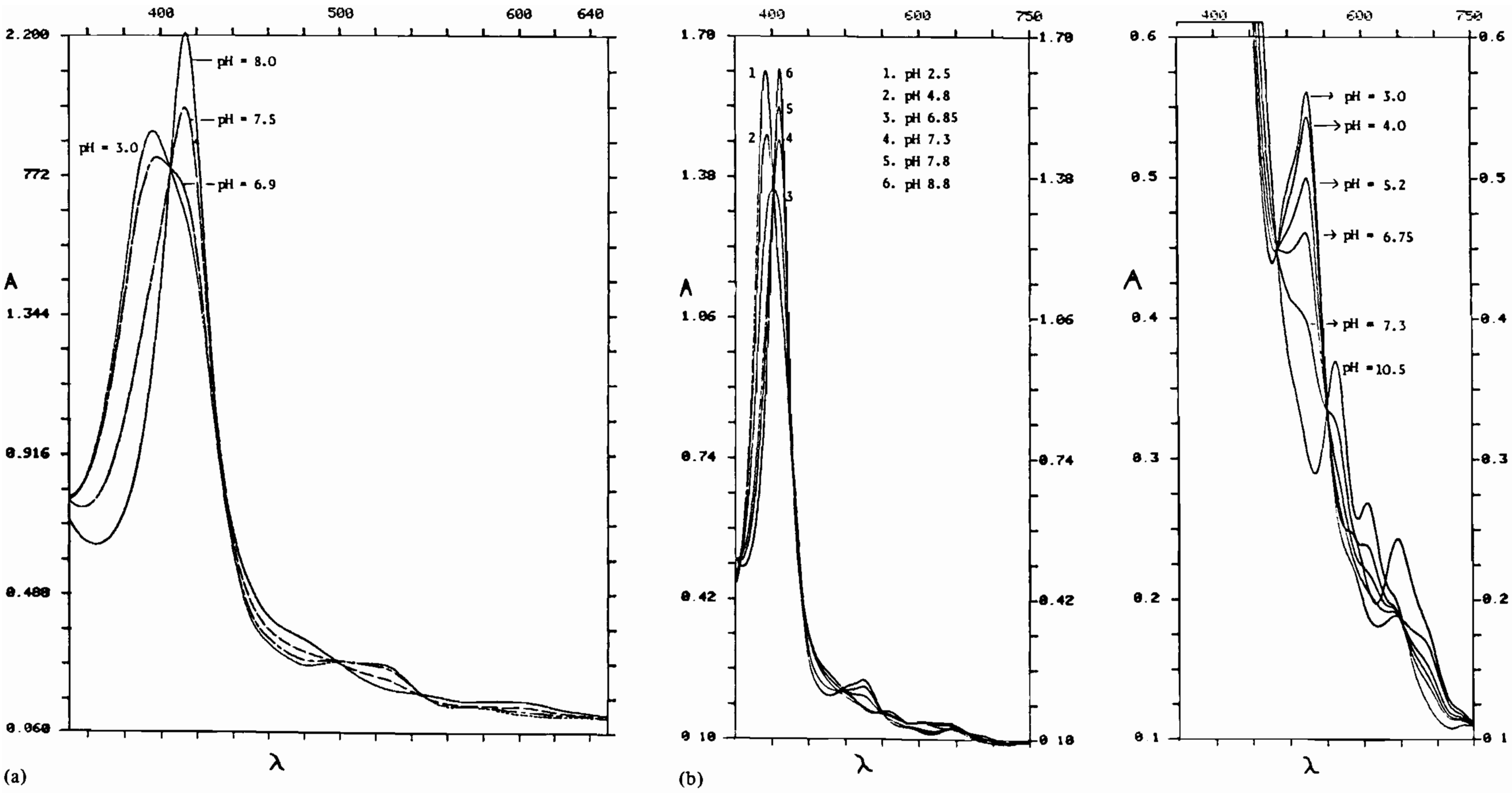
A further possibility for the position of water in μ-oxo bishaems is suggested by the structure [21] of $TPPFe(ClO_4)$ which has *m*-xylene in the lattice and by the suggested structure [22] of the aniline adduct of $(PPIXFe)_2O$. In both cases the aromatic ring lies parallel to the porphyrin ring sufficiently close for the π-electron clouds to interact. It may well be possible for water molecules to hydrate the porphyrin system in a similar way without necessarily coordinating to the iron.

We believe the possibilities suggested above are preferable to model B, because coordination to the iron would bring it into the haem plane and an increase in quadrupole splitting with a concomitant reduction of antiferromagnetism would be expected.

Electronic Spectra

The electronic spectral variations with pH (Table II and Fig. 4) show evidence of only two species in agreement with the Mössbauer data. Figure 5 shows the pH dependence of the Soret band in the TNPS-Fe(III) system. Similar data for the $(SP)_2(SMeP)_2$-PFe(III) system are shown in Fig. 6. Analyses of the spectrophotometric data of Figs. 5 and 6 are given, respectively, in Figs. 7 and 8 after the method of Fleischer *et al.* [15]. The calculated K_Ds for the reaction (1):

$$2[PFe(OH_2)]^+ \overset{K_D}{\rightleftharpoons} (PFe)_2O + 2H^+ + H_2O \qquad (1)$$



(a)

(b)

Fig. 4. Electronic absorption spectra of (a) TNPSFe(III), (b) $(SP)_2(SMeP)_2PFe(III)$ at approximately 10^{-5} M.

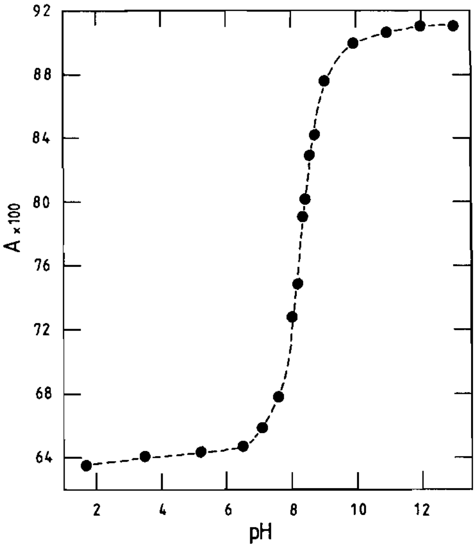


Fig. 5. Spectrophotometric titration of TNPSFe(III) at 17 °C, λ = 417 nm.

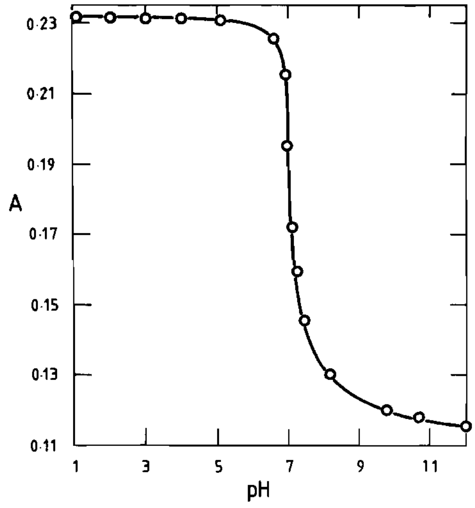


Fig. 6. Spectrophotometric titration of $(SP)_2(SMeP)_2Fe(III)$ at 17 °C, λ = 525 nm.

$$K_D = \frac{[(PFe)_2O]\,[H^+]^2}{[PFe(OH_2)]^2} = \frac{[D]\,[H^+]^2}{[M]^2}$$

(where P = porphyrin) are given along with that for the TPPSFe(III) system in Table III.

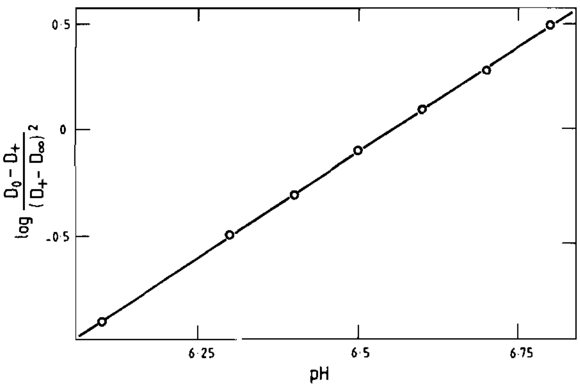


Fig. 7. Analysis of spectrophotometric data of Fig. 5.

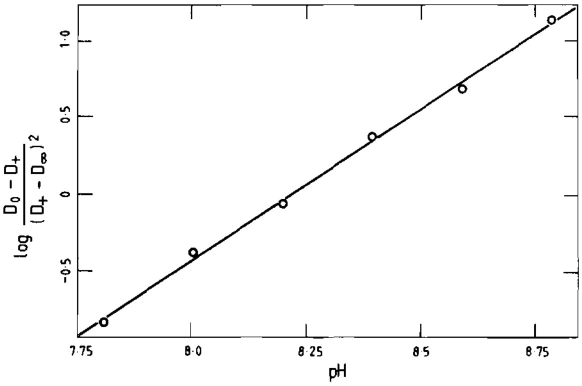


Fig. 8. Analysis of spectrophotometric data of Fig. 6.

It can be readily seen that as the phenyl ring becomes more substituted in the porphyrin in the order TPPS < $(SP)_2(SMeP)_2P$ < TNPS, then the equilibrium constant K_D decreases indicating less favourable bridge formation as the total phenyl substituent gets bigger. From the similarity in the spectra of TPPSFe(III), TNPSFe(III), $(SP)_2(SMeP)_2Fe(III)$ and TMpyPFe(III) at low pH to that of $TPPFe(III)(H_2O)_2 \cdot (ClO_4) \cdot (THF)_2$ [7], the suggestion is very tempting that all these methine-substituted porphyrins may have two water molecules bound to the iron at low pH. In addition we note that Fleischer *et al.* [15] measured the equilibrium for TPPS at three different temperatures and showed that reaction (1) has positive enthalpy and entropy changes. The entropy increase can be understood in terms of a greater number of molecules on the right-hand side of the equilibrium. This is possible only if the mononuclear units are doubly hydrated, *i.e.* the equilibrium is more accurately represented by eqn. (2).

$$2[PFe(H_2O)_2]^+ \overset{K_D}{\rightleftharpoons} (PFe)_2O + 2H_3O^+ + H_2O \qquad (2)$$

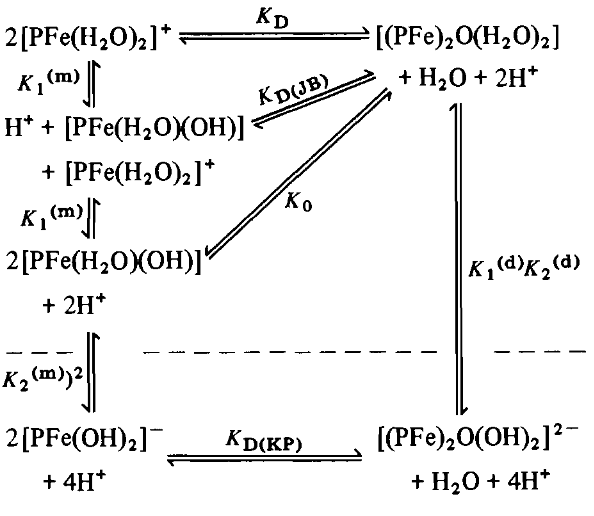
It is unfortunate that a comparison of this kind cannot be made with porphyrins substituted on the pyrrole rings, as this differing form of substitution has a large effect on the absorption spectra.

Equilibrium Constants for the Formation of μ-Oxo Bishaems

Apart from the data discussed above and that of Fleischer *et al.* [15], there have been several other studies reporting equilibrium constants for μ-oxo bishaem formation [3, 16, 23–29]. Comparison between these results is hampered by the variety of definition of the equilibrium constants. Different porphyrinato iron(III) complexes appear to release different numbers of protons on μ-oxo bishaem formation.

Fleischer's system, as in eqn. (1), was shown to release two protons. Brown, Jones and coworkers [23–28] have worked with systems that release one proton and Pasternak [3], based on Kolski and Plane's work [16, 29], assumes no protons to be released.

The resulting equilibrium constants contain $[H^+]$ to different powers and therefore have values of greatly differing orders of magnitude. We have attempted to bring these constants on to common scales as indicated in Scheme 1 with P = porphyrin.



Scheme 1.

Scheme 1 shows the cyclic relationship which ought to exist between various equilibrium constants defined in the literature, with the key that the 'dimerisation constants', K_D, $K_{D(JB)}$ and $K_{D(KP)}$, are those of Fleischer [15], Jones and Brown [23–28] and Kolski and Plane [16, 29], respectively. $K_1^{(m)}$ and $K_1^{(d)}$ refer to acid dissociation constants of monomer and μ-oxo bishaem species, respectively.

As we have already indicated, there is no direct evidence for the existence of the dihydroxy-species $[(PFe)_2O(OH)_2]^{2-}$ and we suggest that the constant $K_{D(KP)}$ used by Pasternak [3] and Kolski and Plane [16, 29] is more accurately represented by K_0 for the pH-independent equilibrium shown. Moreover, for TMPyPFe(III), the absorption spectra presented at low pH and the Mössbauer data on the solid precipitated at low pH are consistent with the formulation $[PFe(H_2O)_2]^+$ (P = Porphyrin). Dihydroxy species, mono or binuclear, are not further considered and we use only that part of the scheme above the dotted line. The data of Pasternak [3] and Kolski and Plane [16, 29] can now be transformed into the constants $K_{D(JB)}$ or K_D because the values of $K_1^{(m)}$ are available, *i.e.*

$$K_{D(JB)} = K_0 K_1^{(m)}$$

$$K_D = K_0 K_1^{(m)})^2$$

In four cases values of $pK_1^{(m)}$ are available and values of K_0, $K_{D(JB)}$ and K_D can be obtained. $K_{D(JB)}$ values only are available for several other porphyrins and, in our case, only K_D is available. These results are collected in Table III. The Table is not comprehensive as we have included only those results obtained with similar salt backgrounds. DDS appears twice as it has been studied by two separate groups [29, 30] (with different salt backgrounds). These two sets of data can be compared only on the K_D(JB) basis and the values differ by a factor of thirty.

The K_0 basis of comparison is the fundamental one as the equilibrium involves only iron-containing species and does not involve $[H^+]$. It is noticeable that the four values at 25 °C are of nearly the same order of magnitude even though in two cases there is a large positive charge on the periphery and in the others a large negative charge. This peripheral charge in itself does not appear to affect K_0 with the possible exception that there may be some effect of pyrrole-substituents, as in DDS and ENP.

Examination of the steric properties of substituents in these four porphyrins shows that DDS and ENP, with relatively small groups on the pyrrole rings, would not be expected to show steric restraint against μ-oxo bridge formation. However, TPPS and TMpyP, which have very similar bulk in their meso-substituents, might be expected to hinder μ-oxo bridge formation. That they do not appear to do so must be related to the phenyl groups (which have a dihedral angle with the haem plane in tetraphenylporphyrin) being able to avoid each other in the μ-oxo bis(haem) by rotation of the haem rings by ~45° relative to each other. Porphyrins with larger substituents than phenyl groups, however, do clearly show steric inhibition of μ-oxo bis(haem) formation [32].

The temperature dependence of K_0 for TPPS is not real in that it is calculated from Fleischer's K_D values using the same $K_1^{(m)}$ (at 25 °C) quoted by El-Awady *et al.* [31]. However, it is quite possible that the reaction is endothermic and driven by positive entropy changes originating in release of water from a hydrated mononuclear species with the formation of μ-oxo bis(haem) in an unhydrated form, e.g.

$$2[M(OH)(H_2O)] \rightleftharpoons [M{-}O{-}M] + 3H_2O$$

The $K_{D(JB)}$ and K_D values show much wider ranges. Where the $pK_1^{(m)}$ is known, this may be ascribed largely to the variations in this parameter. Perusal of the data suggests a large dependence of $pK_1^{(m)}$ on the peripheral charge of the haem, as also occurs in the pK_a values of (unmetallated) porphyrin dications [33].

The K_D values of our porphyrins are extremely low and we suggest that the p$K_1^{(m)}$ values would be near to that of TPPS because of the similar (−4) peripheral charge. The porphyrin of Zipplies *et al.* [32] has a pK of 7.25, lending support to the suggestion. If this is correct, it would yield K_0 values noticeably smaller than any which appear in Table III. We therefore believe that in these porphyrins there is a strong steric inhibition to μ-oxo bis(haem) formation, but not quite as strong as Zipplies' porphyrin. TNPS, as might be expected, shows the larger effect from our two porphyrins.

The $K_{D(JB)}$ values allow us to introduce comparison with a number of pyrrole-substituted porphyrins. With one exception (PPIX) the same broad correlation exists with peripheral charge as in the K_D values. PPIX, on this basis, behaves as though it had a positively charged periphery (*c.f.* ENP), causing charge migration from the centre [3]. The substituents on these porphyrins would not be thought of as having significantly different steric effects from each other and, again, we suggest that the major part of the variation should be ascribed to variation in p$K_1^{(m)}$. PPIX is the only compound in this series with unsaturated groups conjugated to the porphyrin ring system. These vinyl groups appear to be strongly electron-withdrawing in keeping with the Hammett σ-value. However, without a measured value for p$K_1^{(m)}$, particularly for PPIX, it is not feasible to rule out the possibility that certain substituents, like vinyl, may have special factors which enhance μ-oxo bridge formation.

It has been suggested that one of the biological functions of the vinyl groups in protoporphyrin-IX is to stabilise the iron in the +II oxidation state by means of electron withdrawal and hence support its role as an oxygen carrier. The suggestion here that the vinyl groups act as electron-withdrawing groups in the iron(III) complexes would offer confirmation of the idea. An electron-withdrawing system would be expected to stabilise a lower oxidation state as well as increasing the acidity of a system. Thus the stabilisation of iron(II) and the apparently increased tendency to form μ-oxo bis(haem), when in the iron(III) state, are symptomatic of the same electron-withdrawing property.

Experimental

Solvents were of reagent grade and were used without further purification. The aldehydes and pyrrole were purchased from Aldrich and Fluka and used as received. Chromatographic grade alumina was purchased from Aldrich. Analyses were carried out by the Microanalytical Laboratory, Department of Chemistry, University of Manchester.

Preparations

Porphines

The α, β, λ, δ-tetrasubstituted porphines were prepared from pyrrole and the appropriate aldehydes in refluxing propionic acid according to Adler *et al.* [34]. For diphenyl(di-*p*-tolyl)porphine ($Ph_2Tol_2PH_2$) a 1:1 molar mixture of benzaldehyde and *p*-tolaldehyde was used. Both porphines crystallised from the reaction as dark blue masses. The porphines were purified by chromatography on alumina columns and subsequent recrystallisation from chloroform. $TNPH_2$ has been prepared previously by this method [5, 34]. *Anal.* Calc. for $Ph_2Tol_2PH_2$ ($C_{46}H_{34}N_4$): C, 85.95; H, 5.32; N, 8.72. Found: C, 85.9; H, 5.4; N, 8.5%.

Sulphonated porphines

The porphines above were treated with concentrated sulphuric acid according to Fleischer *et al.* [15]. The naphthalene derivative was heated for 8 h and then allowed to stand for 48 h. Dark green solids were washed many times with acetone and dried. Infrared spectra indicated the presence of both water and acetone in the solids. Chromatography did not resolve isomers. *Anal.* [TNPS]. Calc. for $(C_{60}H_{40}N_4S_4O_{12})(HSO_4)_2(H_2O)_{26}(C_3H_6O)$: C, 40.75; H, 5.28; N, 3.01. Found: C, 40.4; H, 5.4; N, 3.00%. $[(SP)_2(SMeP)_2P]$. Calc. for $(C_{46}H_{36}N_4S_4O_{12})(HSO_4)_2(H_2O)_{13}(C_3H_6O)$: C, 40.55; H, 4.82; N, 3.86. Found: C, 40.9; H, 4.6; N, 3.7%. Both compounds were formulated as bisulphate salts of the fully protonated porphine dications.

Electronic Spectra

$[(SP)_2(SMeP)_2PH_2]^{4-}$ at pH 11.2 (brown–purple). λ_{max} (nm) [relative absorbance]: 414 (Soret) [86], 517 [6.0], 549 [3.5], 580 [1.5], 630 [1.0].

$[(SP_2)(SMeP)_2PH_8]^{2+}$ at pH 2.1 (green). λ_{max} (nm) [relative absorbance]: 436 (Soret) [37.2], 599 [1.0], 650 [4.1].

A pK_a of ~4.8 is found for the reaction (in 0.1 M $NaNO_3$)

$$[(SP)_2(SMeP)_2PH_4]^{2-} \rightleftharpoons [(SP)_2(SMeP)_2PH_2]^{4-} + 2H^+,$$

where it is assumed that two protons are released from the tetra-protonated porphyrin centre.

$[TNPSH_2]^{4-}$ at pH 10.3 (brown–purple). λ_{max} (nm) [relative absorbance]: 419 (Soret) [58.2], 516 [4.0], 550 [2.2], 578 [1.7], 633 [1.0].

$[TNPSH_8]^{2+}$ at pH 2.9 (green). λ_{max} (nm) [relative absorbance]: 445 (Soret) [47.6], 583 [5.0], 636 [7.0].

The Soret bands of this porphine are broad. Broad signals are also found in the ^1H NMR spectrum and it is thought that this porphine may be structurally different in the protonated form from $[TPPH_4]^{2+}$ in that the 1-naphthyl groups are unable to lie in the mean porphine plane as do the phenyl groups in $[TPPH_4]^{2+}$.

A pH titration carried out rapidly (at ionic strength 0.1) gave a value of ~3.8 for the pK_a of the reaction: $[TNPSH_4]^{2-} \rightleftharpoons [TNPSH_2]^{4-} + 2H^+$.

Iron(III) Complexes

The complexes were prepared by Fleischer's [15] method using the neutral porphine and a fourfold amount of iron(II) sulphate. The yellow–brown solutions were heated at 90 °C in air for about one hour until the spectrum showed the disappearance of the free base porphine. After cooling, the pH was adjusted to about 3 and the excess iron(III) removed on an acidic cation exchange column. The eluted solutions were immediately neutralised to prevent hydrolysis. Unsuccessful attempts were made to remove sodium sulphate by precipitating the haem by addition of acetone. Recrystallisation was carried out six times by dissolving in methanol and subsequently adding acetone. *Anal.*: $[(SP)_2(SMeP)_2PFe)]$. Calc. for $C_{52}H_{60}N_4S_5O_{30}FeNa_5$: C, 40.25; H, 3.87; N, 3.61; Fe, 3.60. Found: C, 39.8; H, 3.6; N, 3.6; Fe, 3.6%. The compound was formulated as $Na_3((SP)_2(SMeP)_2PFe)(Na_2SO_4)(H_2O)_{13}(C_3H_6O)_2$. [TNPSFe]. Samples contained variable amounts of Na_2SO_4 and analytical figures are not given. The compound was characterised by its UV and Mössbauer spectra.

Spectrophotometric Titrations

Spectrophotometric titrations of the two iron porphyrins reported in this work were carried out at 17 °C using TNPSFe(III) (1×10^{-5} M) and $(SP)_2$-$SMeP)_2PFe(III)$ (1.6×10^{-5} M) with NaOH (in 0.1 M $NaNO_3$ to hold the ionic strength constant). For the TNPSFe(III) solutions isosbestic points were found at 406 ± 1 nm, 498 ± 1 nm and 546 ± 1 nm. For the $(SP)_2(SMeP)_2PFe(III)$ system isosbestic points exist at 403 ± 1 nm, 486 ± 1 nm and 552 ± 1 nm.

The method used to calculate the monomer–dimer equilibrium constant is that of Fleischer *et al.* [15]. For the TNPSFe(III) system the wavelengths used were 417 and 525 nm, the data reported being those taken for 417 nm (although those at 525 nm were in close agreement). The value of A at 17 °C and 417 nm is 1.12×10^{-4} [$\log A = -3.95$]. The computer fitted plot gave a straight line with a slope of 1.99(5) giving good agreement to the formulation of eqn. (1) (see text). Figures 5 and 7 show the results of these computations.

For the $(Sp)_2(SMeP)_2PFe(III)$ system, two wavelengths were also used, at 392 nm and 525 nm, the calculations were again in close agreement, those of the latter wavelength being reported here. The value of A at 17 °C and 525 nm was 1.17×10^{-4} [$\log A = -3.93$]. A slope of 2.02(1) was found in the computer fit again in good agreement with eqn. (1). Figures 6 and 8 show these results.

Mössbauer Spectroscopy

The Mössbauer spectra were recorded on both solids and frozen solutions. The solutions used were prepared containing 200 mg of haem in 2 ml of solutions and the pH was adjusted using 0.1 M HCl or 0.1 M NaOH. The solutions were transferred to 0.13 cm diameter home-made cells, quench frozen in liquid nitrogen and placed in a cryostat. The solids from high pH were prepared by removing the solvent by rotary evaporation. That from pH 5 in methanol was prepared by precipitation on acetone addition. Both solids from their Mössbauer parameters were obviously μ-oxo-bishaems. All spectra were computer fitted by a simple non-linear least-squares fitting program; all isomer shifts are referred to natural iron.

Instrumentation

Electronic spectra were recorded spectrophotometers using either a Beckman DU7 or a Perkin-Elmer Lambda 5G. The Mössbauer spectrometer has been previously described [35]. The pH measurements were carried out using a Philips PW9409 digital pH meter and a glass electrode.

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