Complexes of Tetra(parasulphonatephenyl)porphyrinato Ferrate(III), FeTPPS, with 1,10 Phenanthroline and 2,2' Bipyridine Ligands

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Abstract

Iron(III) porphyrin, FeTPPS, gives high-spin 1:1 monomeric complexes with the ligands 1,10 phenanthroline, 2,9 dimethylphenanthroline and 2,2' bipyridine in aqueous solution. Absorption spectrum of the complexes is very different to the one of the monomer metalloporphyrin, but nearly identical to the visible spectrum of the μ-oxo dimer Fe_2-$(TPPS)_2O$. A spectrophotometric study of the formation equilibria yields the following values of the stability constants: Me_2phen 4.3×10^4, phen 1.1×10^4, bipy 2.0×10^2 (25 °C, 0.1 M $NaNO_3$). Analysis of the experimental data strongly suggest that the ligands are hydrogen bonded to one coordinated water molecule $(TPPS)Fe–OH_2 \rightarrow (L–L)$. Although the ligands are not directly coordinated to iron(III) they can displace both coordinated imidazoles in the complex $FeTPPS(HIm)_2$. We have isolated the phenanthroline complex as a phenanthrolinium compound $(Hphen)_3[(Fe(TPPS)H_2Ophen]$.

Introduction

Iron porphyrins have been thoroughly investigated in the last years because their relevance in the biological systems [1, 2]. Coordination chemistry of iron porphyrins has long been of interest since both, the molecular geometry and the electronic structure, are very dependent on the nature of the axial ligands [3]. So far, monodentate ligands such as imidazol, pyridine, etc., have been usually studied as axial ligands. We are interested in the behaviour of aromatic imines such as 1,10 phenanthroline and 2,2' bipyridine, which are potentially bidentate ligands. Abbot and Rafson [4] studied the interaction between imidazol and the iron(III) porphyrin Fe(DP)Cl (DP, deuteroporphyrinate IX dimethylester) in chloromethane as a solvent (eqn. (1)):

$$Fe(DP)Cl + 2HIm \rightleftharpoons Fe(DP)(HIm)_2{}^+Cl^- \qquad (1)$$
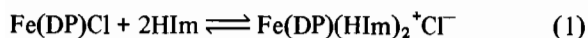
and observed that the addition of 1,10 phenanthroline, phen, to the solution favoured the formation of the bis(imidazol) complex. In absence of HIm, phen does not interact at all with the metalloporphyrin. These authors concluded [4] that phen binds the metalloporphyrin on a remote site of metal ion and implicitly suggested that a transfer charge π-complex could be formed. It is well known that a great variety of π donor or acceptor molecules form molecular complexes with porphyrins and metalloporphyrins [5]. Balch *et al.* [6] confirmed these experimental results, and from a NMR study they showed that the nature of the interaction is a hydrogen bond between phen and one axial imidazol. The lack of change, however slight, in the absorption spectrum rules out a π interaction [6].

More recently, Shelnutt [7] studied the interaction of some phenanthrolines and related species with the metalloporphyrins Cu^{II}(URO), Fe^{III}(URO) and Ni^{II}(URO), (URO, uroporphyrinate anion = 1,3,5,7 acetate, 2,4,6,8 propionate porphyrinate), in aqueous solution. Slight changes in the absorption spectra of the metalloporphyrins indicated the formation of complexes. Shelnutt concluded that the complexes were π-type and the interaction essentially occurred between the ligand porphyrin and the phenanthrolines; the metal ion played a marginal role [7].

In this paper we investigate the formation of complexes between iron(III)porphyrin FeTPPS, (TPPS, mesotetra(parasulphonatephenyl)porphyrinate) and 1,10 phenanthroline, 2,9 dimethyl 1,10 phenanthroline and 2,2' bipyridine in aqueous solution. As a comparison we have also studied the interaction with imidazol, a ligand with a well known behaviour. In addition, the isolation and characterization of the phenanthroline complex is as follows.

Experimental

Reagents

Mesotetraphenylporphyrin, H_2TPP, was synthesized by Adler's method [8] and purified by treat-

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ment with 2,3 dichloro 5,6 dicyanobenzoquinone [9]. Mesotetraparasulphonatephenylporphyrin, H_2-TPPS, was obtained by sulphonation of H_2TPP with concentrated sulfuric acid and isolated as a sodium salt, $Na_4H_2TPPS \cdot 4H_2O$ [10]. The iron porphyrin FeTPPS was synthesized and purified by reported methods as lithium and sodium salts [11, 12]. Elemental analysis (Fe, C) agreed with the expected values. The lithium compound contains a lot of water and its hygroscopic character causes problems in handling.

Imidazol, HIm, 1,10 phenanthroline, phen, 2,9 dimethyl 1,10 phenanthroline, Me_2phen, and 2,2' bipyridine, bipy, were analytical Merck reagents. These chemicals were used as supplied except for HIm which was recrystallized from benzene. The solvents and other reagents were analytical grade chemicals.

Physical Techniques

Spectrophotometric measurements were carried out with a Pye Unicam SP 100-8 UV-Vis spectrophotometer, using 0.1 and 1.0 cm path length cells at 25.0 ± 0.1 °C. Potentiometric measurements were carried out with a Radiometer 84 pH-meter using a GK2401 glass electrode which was carefully calibrated as a hydrogen ion concentration probe. Nernst's equation $E = E^{\circ\prime} + 0.0591$ log $[H^+]$ was strictly obeyed. $E^{\circ\prime}$ values were determined before each measurement series by Gran's method. Magnetic susceptibility measurements were carried out with a Gouy balance at room temperature. They were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants, taking into account the experimental value for the TPP moiety [13]. IR spectra were recorded with a Pye Unicam Spectrophotometer Model SP 2000 on a KBr disk. The hydration water of the isolated compounds was determined with a Setaram thermal balance recording simultaneously the TG, DTG and ATD curves.

Synthesis of Phenanthrolinium Aquaphenanthroline-mesotetra(parasulphonatephenyl)porphyrinate Ferrate(III), (Hphen)₃[Fe(TPPS)H₂O phen]

A solution of 1.35 g of phen·H_2O in 100 ml of water was slowly poured into another solution of 1 g of lithium FeTPPS in 400 ml of water, the pH was previously adjusted at 4.5–5 in both solutions. The precipitate which was instantaneously formed was filtered, washed with cold water and then ethanol, and dried in the oven at 90 °C. The complex, as a black-brown powder, is obtained in quantitative yield. *Anal. Found*: C, 62.7%, Fe, 3.12%. *Calc.*: C, 62.2%; Fe, 3.14%.

Results

1. Aqueous Solutions of FeTPPS

Metalloporphyrin FeTPPS is hydrolized in aqueous solution dimerizing according to eqn. (2):

$$2FeTPPS + H_2O \xrightleftharpoons{K_D} (FeTPPS)_2O + 2H^+ \qquad (2)$$

$$K_D = [Fe_2(TPPS)_2O][H^+]^2/[FeTPPS]^2 \qquad (3)$$

Charges on both species, monomer and dimer (3- and 8- respectively) are omitted for simplicity. The equilibrium constant K_D can be determined by potentiometry using eqn. (3). From eqn. (3) and taking into account the mass balances of the system we obtained eqn. (4):

$$\tfrac{1}{2}(C_M - C_H^+[H^+] - K_w/[H^+])$$

$$= K_D[(C_H - [H^+] + K_w/[H^+])/[H^+]]^2 \qquad (4)$$

where C_M and C_H are the initial concentrations of FeTPPS and neutralizable hydrogen ions, respectively. We can write this equation as $Y = K_D \times X$. In a solution of known analytical concentrations, the experimental measurements of $[H^+]$ give the values of X and Y.

Solutions of FeTPPS ($\sim 10^{-3}$ M), with a known excess of nitric acid, were potentiometrically titrated with NaOH. The potentiometric curves display two equivalence points well differentiated. The first one corresponded to the titration of the strong acid and showed that the amount of titrated acid was notably smaller than the added one. This fact indicated that the metalloporphyrin had consumed hydrogen ions. From the calculation performed on the basis of this data, we deduced that the metalloporphyrin isolated by the literature methods [11, 12] was not the monomer but it was extensively dimerised. The second equivalence point corresponded to the titration of the iron porphyrin. In this process one proton for each Fe(III) was consumed according to eqn. (2). A straight line which intercepts the origin was obtained when plotting Y vs. X (Fig. 1). Its slope gave the equilibrium constant $K_D = 3.46 \times 10^{-8}$. The points corresponding to pH > 5.5 values have not been included in this calculus because the reaction becomes slow, leading to unreliable potential measurements.

2. Protonation Equilibria of the Ligands

Determination of the protonation constants of the ligands HIm, phen, Me_2phen and bipy was carried out in the same conditions as the study of formation of the complexes (25 °C, 0.1 M $NaNO_3$). Previously acidified solutions of the ligands were titrated with NaOH. The protonation curves were obtained from the potentiometric data and the protonation
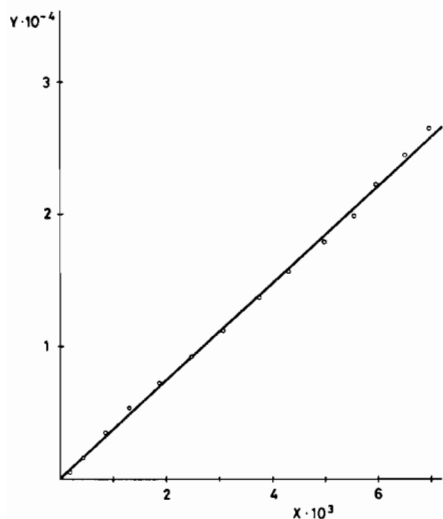
Fig. 1. Plot of $Y = \frac{1}{2}(C_M - C_H + [H^+] - K_w/[H^+])$ vs. $X = [(C_H - [H^+] + K_w/[H^+])/[H^+]]^2$ for a series of FeTPPS solutions with variable amounts of NaOH.

TABLE I. Complexes of FeTPPS.

Ligand	pK_a	Stoichiometry M:L	K
Me₂phen	5.76	1:1	4.3×10^4
phen	4.97	1:1	1.1×10^4
bipy	4.40	1:1	2.0×10^2
HIm	7.03	1:2	4.2×10^4

constants were computed using the usual graphical methods [14]. The obtained results are shown in Table I.

3. Spectrophotometric Study of Complexes Formation

We registered the visible spectrum of series of aqueous solutions of FeTPPS and each ligand, phen, Me₂phen, bipy and HIm. The ratio $x = C_L/C_M$ was modified in each series while the metalloporphyrin concentration C_M, was kept constant (*ca.* 10^{-5} M). In this study the hydrogen ion concentration was fixed at pH = 4.75 without the addition of buffers. The brown-red metalloporphyrin solution displays absorption bands at 393 (Soret), 528 and 680 nm, which are characteristic of the aqua monomer species. When adding phen the colour changes to green-yellow and the visible spectrum undergoes a drastic modification: absorptions at 528 and 680 nm progressively decrease whereas two new bands appear at 574 and 615 nm (Fig. 2). Moreover the Soret band shifts to 411 nm. Curiously, this spectrum is very similar to that displayed by the metalloporphyrin, in absence of the ligand, in basic medium, *i.e.* the absorption spectrum of the μ-oxo dimer(FeTPPS)₂O. The saturation spectrum could
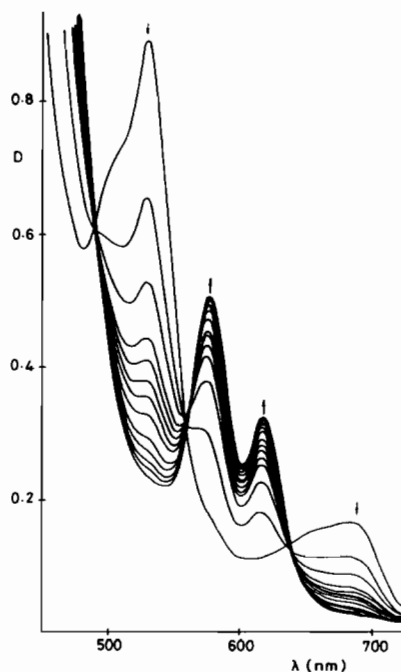

Fig. 2. Variation in the visible absorption spectrum of an aqueous solution of FeTPPS (6.45×10^{-5} M) with the addition of Me₂phen.

not be obtained because the formation of a precipitate in the solutions with $x > 15$. A slow precipitation also occurred in the solutions with lower x values by standing.

The presence of isosbestic points in the spectra of the Fig. 2 suggested there were only two absorbent species in solution and consequently only one complex FeTPPS-phen was formed. This was confirmed using the graphic method of Coleman *et al.* [15]. Phenanthroline is protonated in a 48% at the pH of the study. An increase in the acidity of the medium resulted in a decrease in the intensity of the absorption bands of the complex, which completely disappeared at pH $\leqslant$ 3. Therefore it is apparent that the active species is the phen molecule whereas the protonated form Hphen⁺ does not interact with the iron porphyrin.

The behaviour of 2,9 Me₂phen and bipy was strictly analogous to that reported above for phen, exhibiting the same modifications in the spectrum of FeTPPS. Although the formation of precipitate was not observed in the bipy system, the saturation spectrum could not be obtained because the limit of the ligand solubility is reached before. On the other hand, a red complex with maximum absorptions at 415 and 545 nm was formed by adding HIm to FeTPPS solutions.

Any of the reported spectrophotometric methods not requiring a previous knowledge of the molar extinction coefficient of the complex, ϵ, can be used
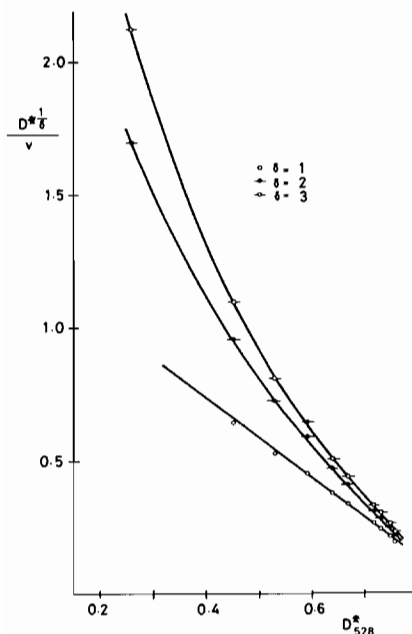
Fig. 3. Generalized Asmus plot for the system FeTPPS—phen. Absorbance values at 574 nm. A straight line is only obtained for n = 1 and δ = 1.
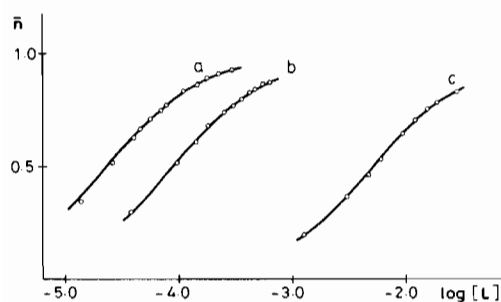

Fig. 4. Formation curves of the FeTPPS complexes of: (a) Me_2phen, (b) phen, and (c) bipy. Circles are experimental points. The solid lines are theoretical curves calculated with the computed constants.

for the determination of both stoichiometry and stability of the complexes in these systems. The application of Asmus' method [16] revealed the formation of 1:1 complexes with all the ligands excepted for imidazol which formed a 1:2 complex. Recently, a generalized version of the Asmus' method [17], which allows to differentiate mono (δ = 1) from polynuclear (δ > 1) complexes with the same stoichiometry $M_\delta L_{\delta n}$, has been reported. A straight line is only obtained for the correct δ value when plotting $D^{*1/\delta}/v^n$ vs. D^*, being D^* the excess absorbance of the solution and v the added volume of the ligand solution. In this way, we confirmed that all the studied complexes are monomer. The results obtained with the FeTPPS-phen system

are shown in Fig. 3. The intercept to the x-axis of the straight lines gives the ϵ value at the wavelength of the study, whereas the stability constant can be obtained from the slope or the ordinate in the origin [17]. The spectrophotometric data, with the ϵ values, allow the determination of the formation curves for the systems (Fig. 4) which yield the stability constants using the usual methods. The values thus obtained are in line with the ones derived from the generalized Asmus' method. Moreover, the theoretical formation curves calculated with the computer constants fitted perfectly to the experimental data $\bar{n}$, log [L]. Spectrophotometric measurements at different wavelengths lead to the same results. These are shown in Table I.

4. Synthesis and Characterization of the Phenanthroline Complex

A brown precipitate instantaneously appeared when mixing aqueous solution of FeTPPS and phen at pH ~ 5 (see 'Experimental'). The compound isolated is slightly soluble in water, including precipitation at the low concentrations used in the spectrophotometric study. On the other hand it dissolves easily in basic media such as aqueous solutions of $NaHCO_3$. Elemental analysis (Fe, C) of the complex match with the formule $(Hphen)_3[Fe(TPPS)H_2O$ phen]. There are four phen molecules for each iron. Three of them should be protonated as $Hphen^+$, neutralizing the negative charge of the metalloporphyrin, since the analysis of alkali metal ions was negative. The fourth phen molecule should be coordinated to the metalloporphyrin. So, the IR spectrum of the solid, as KBr pellets, displays two bands, at 1540 and 1500 cm^{-1} which are characteristic of $Hphen^+$ and phen respectively [18]. In this wavelength the iron porphyrin has not any band. Moreover, the visible reflectance spectrum showed two absorption bands at 575 and 615 nm indicating the existence in the solid of the same complex which is formed in solution. The value of its magnetic moment μ_{eff} = 5.9 MB measured at room temperature by the Gouy method, is characteristic of a high spin Fe(III) complex (S = 5/2).

$(Hphen)_3[Fe(TPPS)(H_2O)_2]$ is obtained if the precipitation is carried out in a more acid medium, pH ~ 3 [19] instead of the above mentioned phenanthroline complex and agrees with the solution study.

5. Interaction of $[Fe(TPPS)(HIm)_2]^{3-}$ with Me_2phen in Aqueous Solution

The low spin (S = ½) exacoordinated complex $[Fe(TPPS)(HIm)_2]^{3-}$ was formed by addition of imidazol to an aqueous solution of FeTPPS. A progressive change in the absorption spectrum of this complex takes place by a further addition of Me_2phen (see Fig. 5). It is apparent that the phenanthroline removes the two imidazol molecules, which
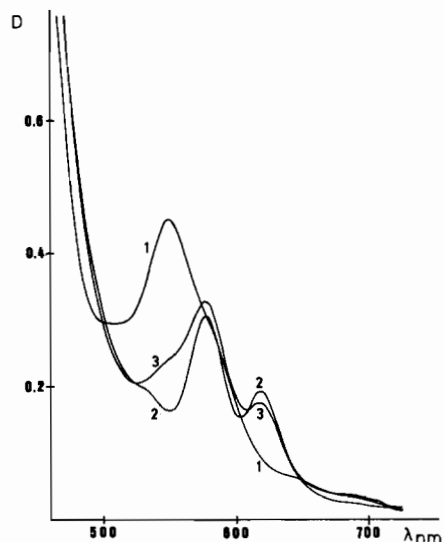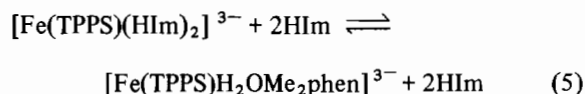
Fig. 5. Visible absorption spectra of: (1) [Fe(TPPS)-(HIm)$_2$]$^{3-}$, (2) [Fe(TPPS)H$_2$O phen]$^{3-}$, and (3) solution 1 after the addition of phen. Concentration of metalloporphyrin 4×10^{-5} M, pH = 5.

were coordinated to the iron porphyrin as axial ligands, according to the following eqn:

$$[Fe(TPPS)(HIm)_2]^{3-} + 2HIm \rightleftharpoons$$

$$[Fe(TPPS)H_2OMe_2phen]^{3-} + 2HIm \qquad (5)$$

This behaviour, which is consistent with the values of the stability constants determined above, completely differs with the one previously reported in nonaqueous solvents [4].

6. Influence of the Solvent Nature on the Formation of the Complexes

In order to investigate this influence we recorded the absorption spectra of solutions of FeTPPS and phen in methanol, MeOH, and dimethylsulphoxide, DMSO. In both solvents the visible spectra of the solution series was identical to that of the metalloporphyrin alone, even in solutions with a largely higher ligand excess than the one used in the aqueous study. Bipy and Me$_2$phen behave as phen enabling us to conclude that the formation of the complexes does not occur in these solvents. In mixed solvents MeOH–H$_2$O and DMSO–H$_2$O, a minimum water content of about 20% was required for the formation of the complexes even taking into account the presence of a large excess of the ligand.

However, HIm formed the 1:2 complex with FeTPPS in both methanol or DMSO as in water.

7. Interaction of the Free Porphyrin, H$_2$TPPS, with Phenanthroline

Adding phen to an aqueous solution of the porphyrin H$_2$TPPS does not cause any apparent colour
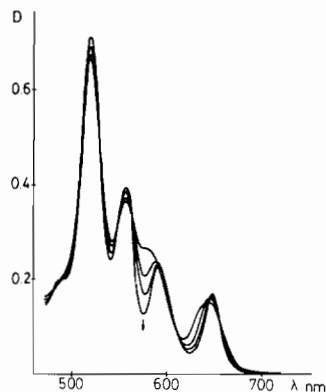

Fig. 6. Variation in the absorption spectrum of a 5×10^{-5} M aqueous solution of H$_2$TPPS^{4-} with the addition of phenanthroline (pH = 7).

change. However, the study of the visible absorption spectra showed a slight shift in the absorption bands of the porphyrin (see Fig. 6). This fact reveals an interaction between both molecules. A similar spectrophotometric study as previously discussed for the metalloporphyrin revealed the formation of a 1:1 complex with a stability constant of $K \sim 10^2$.
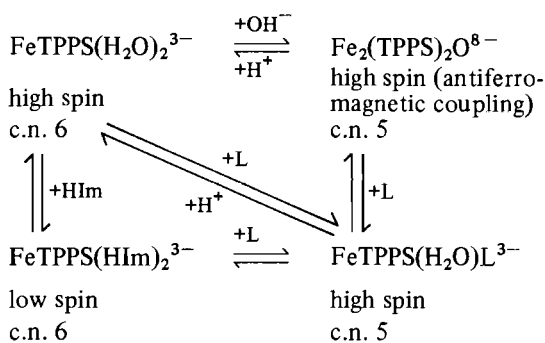
Discussion

Iron(III) porphyrin, FeTPPS, is easily hydrolized in aqueous solution according to eqn. (2). We have potentiometrically determined its equilibrium constant $K_D = 3.46 \times 10^{-8}$ (25.0 ± 0.1 °C, 0.1 M NaNO$_3$). This value is somewhat higher than the spectrophotometric result determined by Fleischer (0.79 $\times 10^{-8}$). However these values are not strictly comparable, because we used a glass electrode calibrated as a [H$^+$] probe, whereas Fleischer [12] measured the pH, calibrating the electrode with a buffer.

The isolation of this anionic metalloporphyrin as sodium or lithium salts has been reported in the literature [11, 12]. Generally it has been assumed that, in solids, the metalloporphyrin is found as the monomer species. Thus, the sodium compound has been formulated as Na$_3$FeTPPS·2H$_2$O. However, our potentiometric study of their aqueous solutions indicates that both compounds are extensively hydrolized and dimerised. We have also found that it is possible to isolate the monomeric metalloporphyrin as a pure compound, using phenanthrolinium Hphen$^+$, as a counter ion [19]. In addition this compound can be crystallized.

The monomeric species is a high spin complex according to the magnetic moment measured in acid solution. This has allowed other authors to assume that the metal ion was pentacoordinated, having a water molecule in one axial position. However, recent

progress in the stereochemistry of iron porphyrins has shown that this simple correlation between the spin state and the coordination number does not have a general validity. So, $[FeTPP(H_2O)_2]I$ is an exacoordinated high spin metalloporphyrin [3]. We believe that probably the iron(III) is also exacoordinated in the sulphonated metalloporphyrin [Fe-TPPS(H_2O)_2]^{-3}$. At present we are trying to solve the molecular structure of this metalloporphyrin as the above mentioned phenanthrolinium compound. On the other hand it is more likely that the metal ion can be pentacoordinated in the μ-oxo dimer $Fe_2(TPPS)_2O^{8-}$, taking into account the *trans* influence of the oxo ligand, contrary to Fleischer's suggestion [12].

Phen, Me$_2$phen and bipy interact with FeTPPS in aqueous solution yielding high spin 1:1 complexes (see Scheme). The complexes are only formed in water or mixed solvents with a significant water content. They are not formed in MeOH or DMSO. These results agree to the lack of interaction previously reported for some water-insoluble iron porphyrins in organic solvents [4].

FeTPPS(H_2O)_2^{3-} $\underset{+H^+}{\overset{+OH^-}{\rightleftarrows}}$ Fe_2(TPPS)_2O^{8-}

high spin   high spin (antiferromagnetic coupling)
c.n. 6   c.n. 5

FeTPPS(HIm)_2^{3-} $\rightleftarrows$ FeTPPS(H_2O)L^{3-}

low spin   high spin
c.n. 6   c.n. 5

L = Me$_2$phen, phen, bipy

Scheme 1.

The stability of the complexes follows the same trend as the ligand basicity Me$_2$phen > phen > bipy, although the bipy complex is less stable on the whole. Phen and Me$_2$phen give complexes with a surprising stability as compared with the 1:2 low spin imidazol complex. Thus, Me$_2$phen displaces the two imidazol ligands in $[FeTPPS(HIm)_2]^{3-}$ (eqn. (5)). This behaviour is contrary to that observed in nonaqueous solvents [4]. The addition of phen stabilizes the imidazol complex of iron(III) porphyrins in dichloromethane whereas it produces its dissociation in water. This fact illustrates the influence of the solvent nature on the reactivity of the metalloporphyrins.

Shelnutt [7] studied the interaction of FeURO with some phenanthrolines and related species in aqueous solution. Surprisingly, FeURO being an anionic metalloporphyrin as FeTPPS, Shelnutt's results are very different from those reported here. According to Shelnutt the addition of phen to an aqueous solution of FeURO only causes a slight shift, 3—5 nm to higher wavelengths, in the absorption maxima of the metalloporphyrin. These changes were analogous to those observed when phen was added to a solution of the free porphyrin H_2-URO. The nature of the metal ion, and even its very presence had little influence on the stability of the complex. Thus, the stability constant of the complex FeURO(phen), $K = 1.6 \times 10^3$, was only three times the stability constant of H_2URO-(phen), $K = 3.6 \times 10^2$. In addition, the position of the nitrogen atoms in the ligand and, therefore, the unshared electron pairs, has little effect on the bond energy [7].

On the other hand, our study showed that the complex FeTPPS (phen) displayed a very different visible spectrum to the monomeric metalloporphyrin. The interaction of phen with the porphyrin H_2TPPS was essentially different since it only caused a very slight perturbation on its absorption spectrum, yielding a much weaker complex. On the other hand, the unshared electron pairs of the nitrogen atoms of the ligands are very important since the protonated species do not interact at all with the metalloporphyrin.

It is not easy to understand the origin of such different behaviour. However, we must point out that the study of FeURO was carried out in very extreme conditions because 0.1 M NaOH was used as a background electrolyte. In this very basic medium it is not clear which is the metalloporphyrin species existing in solution. Generally, iron(III) porphyrins are completely hydrolized as μ-oxo dimers at much lower pH values. Shelnutt assumed that FeURO was found as a monomer species in their working conditions 'possibly as an hydroxo complex' [7]. Consequently, it is interesting to remark that adding phen to an aqueous solution of FeTPPS at pH $\sim$ 7 only produced a slight shift on the absorption bands of the metalloporphyrin. This fact is analogous to that reported by Shelnutt but in this case the metalloporphyrin is present as μ-oxo dimer. The increase in the pH aroused by the addition of phen agrees with the reaction:

$$[Fe_2(TPPS)_2O]^{8-} + 2phen \rightleftarrows$$

$$2[FeTPPS(H_2O)phen]^{3-} + 2OH^-_{aq} \qquad (6)$$
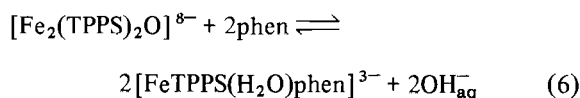
Nature of the Complexes

Phen and bipy are strong field bidentate ligands which coordinate metal ions through the nitrogen atoms. At first sight, the absorption spectra and the values of the stability constants of the complexes might suggest it is the interaction used in our systems. However, an analysis of the experimental data rules out this possibility. If the ligand was

directly bound to the metal ion, Me$_2$phen should form a weaker complex than phen because of the steric hindrance of the methyl groups in the 2,9 positions. According to our determined stability constants the former yields a stronger complex than the latter. Moreover, these complexes are high spin in spite of the strong field properties of the ligand. Finally, they are not formed in nonaqueous solvents such as methanol or dimethylsulphoxide, whereas HIm does interact with the metalloporphyrin in these solvents.

Shelnutt [7] also excluded direct coordination to the metal ion, concluding that phenanthrolines and metalloporphyrins interacted through the aromatic electron clouds forming π complexes where the phenanthroline is the acceptor. However, our experimental data cannot be understood on the basis of a simple π donor–acceptor interaction. The prime difficulty consists of the major change produced on the absorption spectrum of the metalloporphyrin. Usually a π interaction only causes slight changes in the spectrum, such as is observed when phen was added to an aqueous solution of the free porphyrin H$_2$TPPS^{4-}. This is very different to that which occurs on the metalloporphyrin [Fe(TPPS)(H$_2$O)$_2$]$^{3-}$. This difficulty may be overcome if we assume that phen displaces one water molecule coordinated to the iron(III), changing the coordination number of the metal ion (see Fig. 7). A similar phenomenon has been suggested to explain the spectral changes when phen was added to an aqueous solution of the vanadyl porphyrin VO(URO) [20].

The lack of complex formation in more acidic media (pH $\leqslant$ 3), where the ligands are completely protonated, is more difficult to explain. If the interaction between the metalloporphyrin and phen was only carried out through the π electron clouds of both molecules it should not be affected by the ligand protonation. In any case, the complex should be stronger because of the electrostatic atraction between the cation Hphen$^+$ and the anionic metalloporphyrin. Recent studies of the aqueous solutions of phen [21] showed the existence of a π interaction between the phen molecules which are 'self-packed'. Even with the low association constant (K = 24)
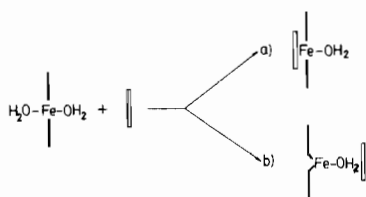
a nearly saturated solution contained about 30% of dimers and smaller amounts of more associated species. When these solutions were acidified the phen molecules became protonated but the 'self-packing' among the Hphen$^+$ cations remained, although it was weaker (K = 12) because of the electrostatic repulsion between them.

Thus our results cannot be accepted on the basis of a simple π interaction. Apparently, the binding is provided by the lone electron pairs of the N atoms although they do not directly interact with the metal ion. There could be an intercalated species between phen and FeTPPS. In fact, we think that phen is hydrogen bonded to a H$_2$O ligand coordinated to Fe(III), Fe–OH$_2$·····phen (see Fig. 7).

Although such an interaction is not usual, neither is unknown. As indicated above an analogous interaction is evident between phen and the complex Fe(TPP)(HIm)$_2^+$. In this case the intercalated species is an axial imidazol ligand. On the other hand, the molecular structure of the complex [Mn(232-N$_5$)(H$_2$O)$_2$(phen)](ClO$_4$)$_2$ (232-N$_5$ is a planar unsaturated pentadentate ligand) showed that phen was hydrogen-bonded to the axial H$_2$O ligands of Mn(II) [22]. More recently, other systems with this kind of bonding have been reported [23]. In these two compounds, any change on the absorption spectrum did not arise by the binding of phen. Therefore we have to assume that the formation of the complex in our systems modifies the coordination number of Fe(III), losing one of the axial H$_2$O ligands (Fig. 7) similarly to the dimerization of the metalloporphyrin. Thus, it is significative that the μ-oxo metalloporphyrin dimer and the phen monomeric complex display are nearly identical on the visible absorption spectra.

By building a molecular model of the complex we have observed that the hydrogen bond formation implied that the molecular planes of both molecules, FeTPPS and phen, remained nearly parallel. Thus making possible an additional π interaction which should strengthen the stability of the complex.

We were able to isolate the phen complex as a phenanthrolinium compound (Hphen)$_3$[FeTPPS-(H$_2$O)phen], but up to the present we have not obtained suitable single crystals to define the molecular structure.

Fig. 7. Two possible structures for the complex [Fe(TPPS)-H$_2$O phen]$^{3-}$: (a) π bond between phen and porphyrin, (b) hydrogen bond between phen and one coordinated H$_2$O. Our experimental data strongly suggest that (b) is the correct one.

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