A Solution Study of the Protonation and Deprotonation Equilibria of 5,10,15,20-Tetra(*p*-sulphonatophenyl)porphyrin. Stability Constants of its Magnesium(II), Copper(II) and Zinc(II) Complexes

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The protonation and deprotonation equilibria of 5,10,15,20-tetra(*p*-sulphonatophenyl)porphyrin, H_2tpps^{4-}, as well as its complex formation with Mg^{2+}, Zn^{2+} and Cu^{2+} metal ions have been investigated spectrophotometrically in a dimethyl sulphoxide (dmso)–water (80:20, v/v) solution. The following equilibrium constants have been determined at 25 °C and 0.1 mol dm^{-3} ($KClO_4$ + KOH)

$$\text{(i)}\ tpps^{6-} + 2H^+ \rightleftharpoons H_2tpps^{4-}\quad \log K = 32.80 \pm 0.04$$

$$\text{(ii)}\ H_2tpps^{4-} + 2H^+ \rightleftharpoons H_4tpps^{2-}\quad \log K = 3.58 \pm 0.02$$

$$\text{(iii)}\ H_2tpps^{4-} + Mg^{2+} \rightleftharpoons [Mg(tpps)]^{4-} + 2H^+\quad \log K = -3.96 \pm 0.04$$

$$\text{(iv)}\ H_4tpps^{2-} + Zn^{2+} \rightleftharpoons [Zn(tpps)]^{4-} + 4H^+\quad \log K = -1.80 \pm 0.04$$

$$\text{(v)}\ H_4tpps^{2-} + Cu^{2+} \rightleftharpoons [Cu(tpps)]^{4-} + 4H^+\quad \log K = 1.68 \pm 0.04$$

[(i)], 0.1 mol dm^{-3} ($KClO_4$ + $HClO_4$) [(ii), (iv), (v)] and 0.1 mol dm^{-3} $KClO_4$ [(iii)], affording for the first time the stability constants of three metalloporphyrins, $[Mg(tpps)]^{4-}$ (log β = 28.8), $[Zn(tpps)]^{4-}$ (log β = 34.6) and $[Cu(tpps)]^{4-}$ (log β = 38.1). A novel and more effective procedure for the isolation of high-purity $Na_4[H_2tpps]\cdot 4H_2O$ is reported.

A lot of work has been devoted to the study of metalloporphyrins because of their relevance in biological systems[1] as well as the intrinsically interesting properties of these molecules.[2] The kinetics and mechanism of the formation reactions of metalloporphyrins have been exhaustively investigated.[3–6] However only little experimental progress pertinent to a quantitative understanding of stability phenomena has been made. The measurement of stability constants of metalloporphyrins is very difficult because of their high values, the limited solubility of the porphyrins and the interference of other equilibria. However, qualitative statements have been made.[7] These are based on empirical stability classes and on an invented quality S_i which is called the stability index. The metalloporphyrins are divided into five stability classes which indicate their resistance towards protic acids of different strength. The stability index is defined as $S_i = 100\,Z \times E_N/r_i$ where Z is the charge of the metal ion, E_N is Pauling's electronegativity and r_i the effective ionic radius (values of Shannon and Prewitt). A reasonable agreement is found between values of S_i and experimental stability orders.[7]

Studies on the formation equilibria of these complexes are very scarce. The equilibrium constant of reaction (1) has been

$$H_2por + M^{2+} \rightleftharpoons [M(por)] + 2H^+ \qquad (1)$$

determined in some cases,[8–12] but mostly from kinetic data. To our knowledge no stability constant of a metalloporphyrin [M(por)], *i.e.*, the equilibrium constant of reaction (2), has

$$por^{2-} + M^{2+} \rightleftharpoons [M(por)] \qquad (2)$$

hitherto been determined experimentally. It is clear that this situation is unsatisfactory and some efforts should be made to solve the problems associated with the experimental determination of the stability constants of metalloporphyrins.

There are two main difficulties in the thermodynamic study of the formation equilibria of metalloporphyrins: (*a*) the low rates of these reactions at room temperature; and (*b*) the lack of knowledge of the values of the acidity constants of the porphyrins. The porphyrins protonate easily in aqueous solution,[12–16] however, they are very weak acids and their deprotonation reactions do not take place in aqueous solution. Only in the case of 5,10,15,20-tetra(methylpyridyl)porphyrin, H_2tmpyp has the value of the first acidity constant ($pK_{a1} = 12.9 \pm 0.2$) been reported.[17] Clarke *et al.*[18] have studied the total deprotonation of some porphyrins in very basic media using a mixed dimethyl sulphoxide (dmso)–water–toluene solvent, but they were unable to determine the acidity constants. The only values reported of stability constants[8,19] were given on the basis of estimated values of the acidity constant.[20]

In this work we study the protonation and deprotonation equilibria of *meso*-tetra(*p*-sulphonatophenyl)porphyrin (H_2tpps^{4-}), as well as the formation equilibria of the complexes $[Mg(tpps)]^{4-}$, $[Zn(tpps)]^{4-}$ and $[Cu(tpps)]^{4-}$, in dmso–water (80:20, v/v), determining for the first time the stability constants of three metalloporphyrins. We also report a more effective procedure for the isolation of high-purity $Na_4[H_2tpps]\cdot 4H_2O$. A preliminary communication on this study has been reported elsewhere.[21]

Experimental

Synthesis of $Na_4[H_2tpps]\cdot 4H_2O$.—*meso*-Tetraphenylporphyrin (1 g) obtained by method of Adler *et al.*[22] and purified as described by Barnett *et al.*[23] was sulphonated with concentrated sulphuric acid following the procedure of Krishnamurthy.[24] To the resulting green paste 100 cm^3 of very cold water were carefully added, keeping the reaction vessel in an ice-bath, and then an aqueous sodium hydroxide solution was slowly added until the green suspension became a red solution (pH $\approx$ 6). A solution of phenanthroline hydrochloride (1.9 g, 8.1 mmol) in water (50 cm^3) was then added dropwise. The precipitate which immediately formed was left overnight. The supernatant solution was poured off and the precipitate was filtered off and exhaustively washed with water to remove any free sulphate. Finally it was dried at 80 °C for 24 h and kept over $CaCl_2$. The solid was formulated as $[Hphen]_4[H_2tpps]\cdot 2H_2O$ on the basis of elemental analysis, IR and DTA-TG data. It was a deep red powder which was insoluble in cold water and rather soluble in hot water. It was also insoluble in apolar organic solvents but soluble in dimethylformamide and dmso giving red violet solutions. To convert to the sodium salt, *ca.* 35 g of a cation-exchange resin in the Na^+ form (Lewatit S-100) were added to a suspension of $[Hphen]_4[H_2tpps]\cdot 2H_2O$ (1.5 g) in water (50 cm^3). The porphyrin dissolved nearly instantaneously giving a dark red solution which was eluted through a column of the same resin to assure complete exchange of Na^+ for $Hphen^+$. The porphyrin solution was evaporated to dryness and the solid obtained dried at 80 °C and kept over $CaCl_2$ (Found: C, 48.9; H, 3.00; N, 5.60; Na, 8.45; H_2O, 6.60. Calc. for $Na_4[H_2tpps]\cdot 4H_2O$, $C_{44}H_{34}N_4Na_4O_{16}S_4$: C, 48.3; H, 3.15; N, 5.10; Na, 8.40; H_2O, 6.60%). UV/VIS spectrum (in water at pH 7, 0.1 mol dm^{-3} $NaNO_3$): λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) 518 (13.4), 557 (7.3), 580 (5.3) and 644 (3.0).

Solvent and other Reagents.—The salt $Na_4[Mg(tpps)]$ was obtained as reported in the literature.[25] All the other reagents were analytical grade chemicals. Dimethyl sulphoxide was purified by distillation under reduced pressure (*ca.* 2 Torr, $\approx$266 Pa) and stored in a dark bottle over 4 Å molecular sieves. From this solvent the dmso–water (80:20, v:v) was obtained. All the solutions used in this work were prepared with this mixed solvent. Carbonate-free potassium hydroxide (0.1 mol dm^{-3}) and perchloric acid (0.1 mol dm^{-3}) solutions were used in the spectrophotometric studies and the potentiometric titrations. All the spectrophotometric measurements were carried out in 0.1 mol dm^{-3} ($KClO_4$ + KOH) or ($KClO_4$ + $HClO_4$) as background electrolyte; 0.1 mol dm^{-3} $KClO_4$ was used in the potentiometric titrations.

Physical Techniques.—Absorption spectra in the UV and visible regions were recorded with a Pye Unicam SP8-100 spectrophotometer using 0.1, 1.0 and 2.0 cm length cuvettes at 25.0 ± 0.1 °C. Potentiometric titrations in dmso–water (80:20) were carried out in a reaction vessel (capacity 70 cm^3) thermostatted (with water) at 25.0 ± 0.1 °C, with the titrant delivered by a Crison 738 (±0.001 cm^3) burette. Dinitrogen presaturated with the solvent was passed over the surface of the solution. The e.m.f. measurements were performed with a Radiometer PHM 84 pH-mV meter, and a 9811 Ingold combined glass electrode. The electrode was dipped in dmso–water (80:20) for 30 min before use. The Nernst equation, $E = E^{\circ\prime}_A + 0.0591 \log [H^+]$, was obeyed strictly by the electrode in this medium; $E^{\circ\prime}_A$ values as well as the pK_W of the solvent were determined using Gran's[26] method. The titration system was controlled by an Apple IIe microcomputer. Theoretical analysis of the equilibrium data has been performed using traditional graphical methods.[27,28] As in all of the studied systems there is only one equilibrium in solution, and therefore only one constant to be determined and so the use of powerful computer programs does not provide further advantages. Elemental analyses were carried out by the Service de Microanalyse of the CSIC with a Carlo Erba MOG 1106 instrument. The hydration water of the isolated compound was determined with a Setaram B-70 thermal balance recording simultaneously the TG, DTG and DTA curves. Sodium was determined with a Shimadzu AA-670/G atomic absorption spectrophotometer.

Autodissociation Constant of the Solvent.—We determined the autodissociation constant of the solvent dmso–water (80:20), K_W, by potentiometry, titrating $HClO_4$ solutions of accurately known concentration with KOH. From the acid side of the potentiometric curve the $E^{\circ\prime}_A$ value is obtained from $E = E^{\circ\prime}_A + 0.0591 \log [H^+]$, whereas $E^{\circ\prime}_B$ is obtained from the basic side through the equation $E = E^{\circ\prime}_B - 0.0591 \log [OH^-]$. The value of pK_W is given by $(E^{\circ\prime}_B - E^{\circ\prime}_A)/0.0591$ ($E^{\circ\prime}_A$ and $E^{\circ\prime}_B$ are the specific cell constants for the acidic and basic regions respectively). We obtained a value of $pK_W = 18.42 \pm 0.04$ [dmso–water (80:20 v/v), 25 °C, 0.1 mol dm^{-3} $KClO_4$].

Results and Discussion

*Synthesis of 5,10,15,20-Tetra(*p*-sulphonatophenyl)porphyrin.*—The water-soluble porphyrin H_2tpps^{4-} is obtained by sulphonation of the well known 5,10,15,20-tetraphenylporphyrin, H_2tpp, with concentrated sulphuric acid and has been isolated as the ammonium[16] and sodium[24] salts. Both of these derivatives are very soluble in water and so require evaporation to dryness of their solutions to enable their isolation. As these solutions contain very large amounts of $(NH_4)_2SO_4$ or Na_2SO_4, produced in the neutralization of the excess sulphuric acid used in the sulphonation reaction, purification requires tedious, repeated extractions of the solid residue with methanol and the purity of porphyrin obtained is uncertain.

We have developed an alternative procedure, more simple and effective, to obtain this porphyrin. Addition of 1,10-phenanthrolinium cations, $Hphen^+$, to an aqueous solution of H_2tpps^{4-} results in quantitative precipitation of $[Hphen]_4[H_2tpps]\cdot 2H_2O$. This solid is dissolved instantaneously on shaking an aqueous suspension with a cation-exchange resin in the sodium form. Evaporation of this solution yields high purity $Na_4[H_2tpps]\cdot 4H_2O$. In the same way it is possible to obtain any other derivative (Li^+, K^+, NH_4^+, *etc.*). Moreover, $Hphen^+$ is easily and quantitatively recovered from the resin.

Protonation and Deprotonation Equilibria of $Na_4[H_2tpps]$.—The porphyrin $Na_4[H_2tpps]\cdot 4H_2O$ dissolves in dmso–water (80:20) to give purple solutions which display five absorption bands at 419, 515, 550, 589 and 645 nm (Table 1). These solutions are stable and the absorption values do not change with time. Beer's law is strictly obeyed in the concentration range studied 0.8×10^{-4}–2×10^{-7} mol dm^{-3}, at 25 °C and $I = 0.1$ mol dm^{-3} ($KClO_4$). We have registered the absorption spectrum of series of dmso–water solutions containing H_2tpps^{4-} (4×10^{-5} mol dm^{-3}) and variable amounts of $HClO_4$ or KOH. When adding perchloric acid the purple colour changes to green and the absorption spectrum undergoes an important modification: the Soret band is shifted to 445 nm and a new very intense band appears at 660 nm whereas the absorptions at 515 and 550 nm progressively decrease (see Fig. 1 of ref. 21).

The presence of isosbestic points in the spectra indicates the existence of only two absorbing species in the equilibrium. Owing to the high excess of acid with regard to porphyrin concentration (100–2500×), the hydrogen ion concentration of each solution is known accurately, $[H^+] = c_{HClO_4}$. The stoichiometry of the protonation reaction has been determined by applying the Asmus method,[27] revealing the formation of a 1:2 species. The protonation curve of the system, $\bar{j}$ *vs.* $-\log [H^+]$ (where $\bar{j}$ is the average number of protons bound to the porphyrin in the solution), can be determined from the experimental data (Fig. 1). The proton association constant [equation (ii) of Table 2] was obtained by the method of curve

Table 1 UV/VIS spectral characteristics of the porphyrin and its metal complexes in dmso–water (80:20) solution

	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})				
H_2tpps^{4-}	419 (491)	515 (19.5)	550 (9.5)	589 (5.9)	645 (5.1)
$tpps^{6-}$	439 (488)	586 (17.0)	629 (22.9)		
H_4tpps^{2-}	445 (398)	660 (51.4)			
$[Mg(tpps)]^{4-}$	427 (546)	564 (17.9)	604 (10.7)		
$[Zn(tpps)]^{4-}$	426 (571)	559 (22.0)	599 (11.2)		
$[Cu(tpps)]^{4-}$	418 (410)	541 (19.8)			

Table 2 Equilibrium constants determined in dmso–water (80:20, v/v) solution at 25 °C and I = 0.1 mol dm^{-3}

Equilibrium	log K	Background electrolyte
(i) $tpps^{6-} + 2H^+ \rightleftharpoons H_2tpps^{4-}$	32.80 ± 0.04	$KClO_4 + KOH$
(ii) $H_2tpps^{4-} + 2H^+ \rightleftharpoons H_4tpps^{2-}$	3.58 ± 0.02	$KClO_4 + HClO_4$
(iii) $H_2tpps^{4-} + Mg^{2+} \rightleftharpoons [Mg(tpps)]^{4-} + 2H^+$	−3.96 ± 0.04	$KClO_4$
(iv) $H_4tpps^{2-} + Zn^{2+} \rightleftharpoons [Zn(tpps)]^{4-} + 4H^+$	−1.80 ± 0.04	$KClO_4 + HClO_4$
(v) $H_4tpps^{2-} + Cu^{2+} \rightleftharpoons [Cu(tpps)]^{4-} + 4H^+$	1.68 ± 0.04	$KClO_4 + HClO_4$

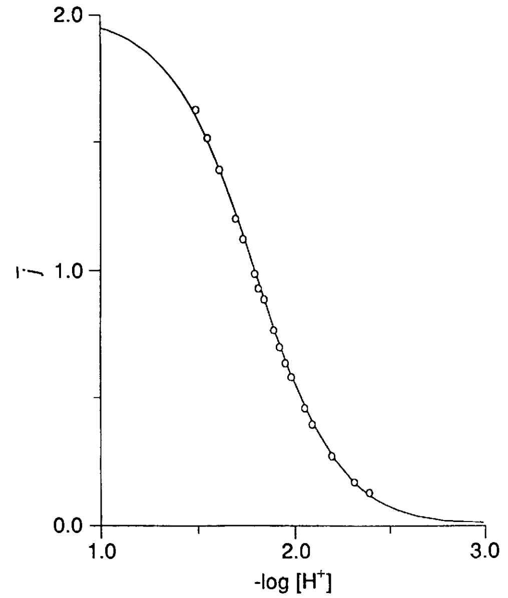

Fig. 1 Protonation curve of H_2tpps^{4-} in dmso–water (80:20). Open circles represent experimental points at λ = 660 nm. The curve is calculated using the value of the reported protonation constant

fitting.[28] Alternatively, by plotting log $\bar{j}/(2 - \bar{j})$ *vs.* log [H$^+$] a straight line of slope 2 is obtained and the value of log K is obtained from the intercept.

The porphyrin H_2tpps^{4-} is a very weak base in dmso–water (80:20) but protonates in the presence of a large excess of acid to give H_4tpps^{2-}. There is no experimental evidence of monoprotonated species. Green solutions of H_4tpps^{2-} are indefinitely stable, spectrophotometric readings remaining unaltered over a long time. This behaviour differs considerably with those previously reported in water[16] in which H_2tpps^{4-} protonates more easily but the instability of the acid solutions precludes any quantitative study of the equilibrium.

On adding potassium hydroxide the purple colour of H_2tpps^{4-} solutions changes to green and the spectrum displays absorption maxima at 439, 586 and 629 nm (see Fig. 2 of ref. 21). Again, the presence of isosbestic points indicates the existence of only two absorbing species in equilibrium. Application of the Asmus method gives the stoichiometry of the deprotonation reaction (3). As this reaction requires a very large excess of base

$$H_2tpps^{4-} + 2OH^- \rightleftharpoons tpps^{6-} + 2H_2O \qquad (3)$$

(150–1200 × the porphyrin concentration), the hydroxide ion concentration of each solution is known accurately [OH$^-$] = c_{KOH}. As we have previously determined the ionic product of the solvent (pK_W = 18.42 ± 0.04 at 25 °C and 0.1 mol dm^{-3} $KClO_4$), the hydrogen ion concentration can be easily calculated, [H$^+$] = K_W[OH$^-$]$^{-1}$. With these values and the spectrophotometric data the protonation curve of the system is determined (Fig. 2). In this case $\bar{j}$ is the average number of protons bound to the deprotonated species $tpps^{6-}$. The proton association constant of the porphyrinate anion [equation (i) of Table 2] is computed applying the usual graphic methods. Since $tpps^{6-}$ is sensitive to photochemical decomposition, absorption spectra in basic media must be recorded as soon as possible after preparation of solutions. Prolonged exposure to the light causes a change of colour to blue, then violet and finally orange.

As is general for porphyrins H_2tpps^{4-} is too weak a base to be deprotonated in aqueous solution but can deprotonate in dmso–water (80:20). The solvation energy of hydroxide ion in this solvent mixture is lower than in water, resulting in its ability to act as a stronger base. Moreover pK_W of dmso–water (80:20) can be determined accurately by potentiometry, allowing us to determine for the first time the acidity constants of a porphyrin.

Formation Equilibria of Metalloporphyrins.—In this section we report an equilibrium study of the interaction of H_2tpps^{4-} with Mg^{2+}, Zn^{2+} and Cu^{2+}. As the formation reaction of metalloporphyrins is very slow, evolution of absorption spectra must be carefully followed during a long time (2, 10 and 24 months for Mg^{2+}, Zn^{2+} and Cu^{2+} respectively) to be sure equilibrium is reached. We have maintained solutions thermostatted and in the dark during all times and under these conditions the stability and reliability of the spectrophotometric measurements were very good. Before definitive series of solutions were prepared we had to determine the optimum range of hydrogen ion and metal ion concentrations for each system. In the case of Mg^{2+} it is better to study demetallation of $[Mg(tpps)]^{4-}$, which was previously synthesized and purified, because the metallation reaction is slower. On the contrary, the slowness of the demetallation reaction of copper(II) and zinc(II) porphyrins led to a study of the metallation reaction in the presence of a large and variable excess of protons to control its extent.

Magnesium(II). We have recorded the absorption spectrum of a series of solutions of the magnesium porphyrin $[Mg(tpps)]^{4-}$ and $HClO_4$ in dmso–water (80:20), keeping constant the metalloporphyrin concentration ($c_{M(por)}$ = 3.9 × 10^{-5} mol dm^{-3}) and varying the c_H:$c_{M(por)}$ (1:2–7) molar ratio. The ionic

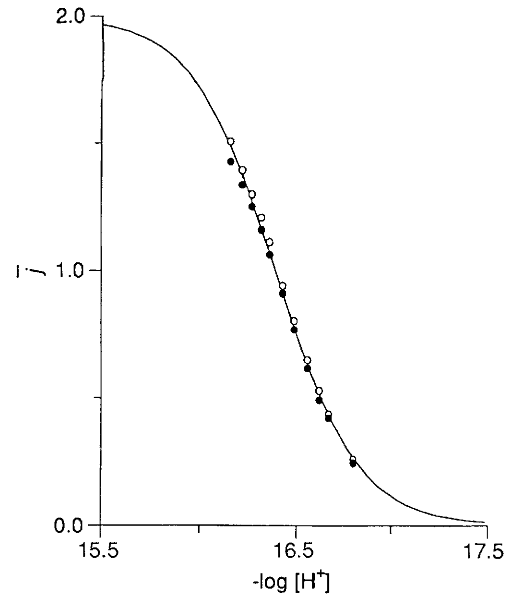

Fig. 2 Protonation curve of $tpps^{6-}$ in dmso–water (80:20). Circles represent experimental points at λ = 515 (●) and λ = 629 (○) nm. The line is calculated using the value of the reported protonation constant

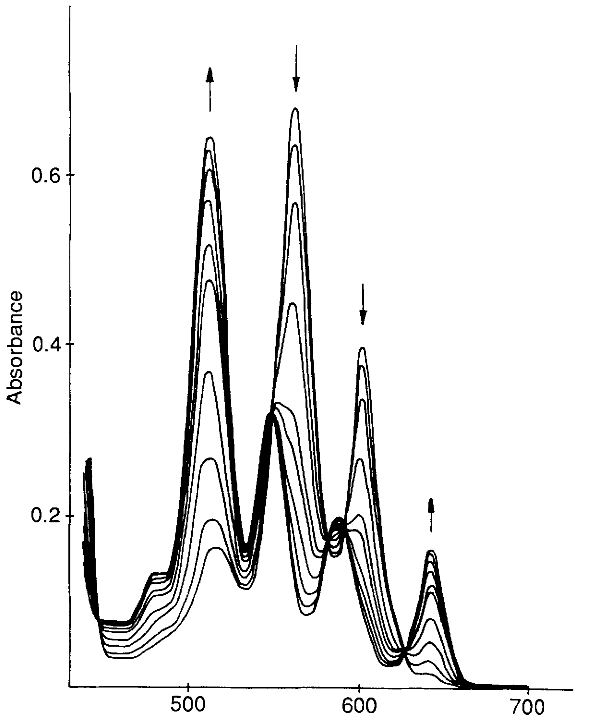

Fig. 3 Visible absorption spectra of a series of solutions of $[Mg(tpps)]^{4-}$ (3.9×10^{-5} mol dm^{-3}) in dmso–water (80:20) with variable amounts of $HClO_4$ (path length of cuvette 1.0 cm)

strength of solutions was maintained constant with $KClO_4$ (0.1 mol dm^{-3}). Addition of acid produces a change in the absorption spectrum of $[Mg(tpps)]^{4-}$, the absorbances at 427, 564 and 604 nm decreasing progressively whereas the bands of H_2tpps^{4-} appear at 419, 515, 550, 589 and 645 nm (see Fig. 3) (Soret band is not shown). The hydrogen ion concentration of each solution was measured by potentiometry.

We applied a linear extrapolation[28] method to measure the equilibrium. A plot of log ($[H_2tpps^{4-}]/[Mg(tpps)^{4-}]$) *vs.* log

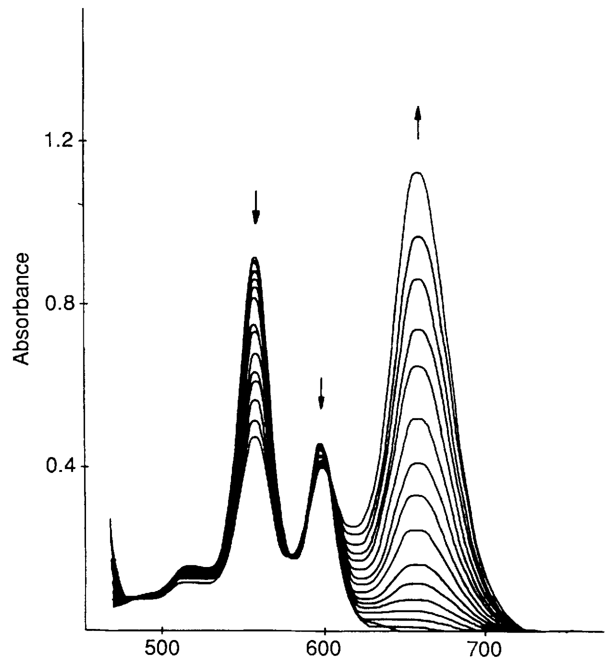

Fig. 4 Visible absorption spectra of a series of solutions of H_2tpps^{4-} (4×10^{-5} mol dm^{-3}), and Zn^{2+} ($c_M/c_{por} = 49.6$) in dmso–water (80:20) with variable amounts of $HClO_4$ (pathlength of cuvette 1.0 cm)

($[H^+]^2/[Mg^{2+}]$) gave a straight line (correlation coefficient 0.999) with slope 1 and whose abscissa at the origin gave log *K* [equation (iii) of Table 2].

Zinc(II) *and copper*(II). For zinc(II) we recorded the absorption spectrum of two series of solutions of the porphyrin, H_2tpps^{4-}, zinc(II) nitrate and $HClO_4$ in dmso–water (80:20), keeping constant the concentrations of porphyrin (c_{por}) and metal ion ($c_{por} = 4 \times 10^{-5}$ mol dm^{-3}, $c_M/c_{por} = 49.6$ or 99.1) and varying the $c_H:c_{por}$ molar ratio. The ionic strength of solutions was maintained constant with 0.1 mol dm^{-3} ($KClO_4 + HClO_4$). The absorption spectrum of zinc porphyrin $[Zn(tpps)]^{4-}$ changes after addition of acid, the absorbances at 426, 559 and 599 nm decrease progressively whereas the bands of protonated porphyrin H_4tpps^{2-} appear at 445 and 660 nm (see Fig. 4) (Soret band not shown). As the excess of acid is 500–2200 ×, the hydrogen ion concentration of each solution is known $[H^+] = c_{HClO_4}$. Under these conditions all free porphyrin is in the protonated form. We have applied the linear extrapolation method to the experimental data. A plot of $[H^+]^4/[Zn^{2+}]$ *vs.* $[H_4tpps^{2-}]/[Zn(tpps)^{4-}]$ gave a straight line (correlation coefficient 0.999) whose slope is *K* [equation (iv) of Table 2]. Spectrophotometric measurements performed on solutions containing different excesses of metal ion led to the same results.

We have carried out an analogous study with Cu^{II}, which exhibits similar behaviour. However, the stoichiometric ratio, $c_M/c_{por} = 1$ is more convenient in this case. The value of the equilibrium constant is given in Table 2 [equation (v)].

Stability Constants of Metalloporphyrins.—The porphyrin H_2tpps^{4-}, or its protonated form, interacts with Mg^{2+}, Cu^{2+} and Zn^{2+} in dmso–water (80:20) to form the corresponding metalloporphyrins. Although metallation reactions are very slow, even slower than in aqueous solution, we have succeeded through a careful study in determining their equilibrium constants (Table 2). By adequate combination of equations (iii)–(v) with (i) and (ii), the stability constants of metalloporphyrins can be easily calculated [equations (vi)–(viii)].

The values of the stability constants (Table 3) clearly show that these metalloporphyrins are very stable complexes. So, it is interesting to compare the stability constant of $[Cu(tpps)]^{4-}$

Table 3 Stability constants of metalloporphyrins determined in dmso–water (80:20, v/v) solution at 25 °C and I = 0.1 mol dm^{-3}

Equilibrium	log β
(vi) $tpps^{6-} + Mg^{2+} \rightleftharpoons [Mg(tpps)]^{4-}$	28.8
(vii) $tpps^{6-} + Zn^{2+} \rightleftharpoons [Zn(tpps)]^{4-}$	34.6
(viii) $tpps^{6-} + Cu^{2+} \rightleftharpoons [Cu(tpps)]^{4-}$	38.1

(log β = 38.1) with that of [Cu(salen)] (log β = 27.16) recently determined in the same medium[29] where H_2salen is the well known tetradentate Schiff base *N,N′*-ethylenebis(salicylideneimine). Apparently both the nature of the donor atoms and the cyclic character of the ligand contribute to the greater stability of the metalloporphyrin.

The trend in the values of the stability constants $Mg^{2+} < Zn^{2+} < Cu^{2+}$ is as expected (Irving–Williams order) and agrees with the classification of these metalloporphyrins in different stability orders (IV, III and II respectively).[7]

Conclusion

The use of dmso–water (80:20) as solvent allows the determination of the acidity constants of porphyrins and hence the stability constants of metalloporphyrins. However the sluggishness of metallation (or demetallation) reactions remains a problem. It is necessary to find effective catalysts for these reactions before the experimental method reported here can be extended to other metal ions such as Ni^{2+} or Fe^{3+}. It has been reported[30] that Hg^{2+} increases the formation rate of $[Zn(tpps)]^{4-}$ in aqueous solution, but more work in this area is needed.

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