Stability Constants of Metalloporphyrins. A Study of the Protonation, Deprotonation, and Formation of Copper(II) and Zinc(II) Complexes of *meso*-Tetra-(*p*-sulphonatophenyl)porphyrin

Hermas R. Jiménez, Miguel Julve, José M. Moratal, and Juan Faus*

Departamento de Quimica Inorgánica de la Universidad de Valencia, C/Dr. Moliner 50, 46100-Burjassot (Valencia), Spain

Quantitative study of the protonation and deprotonation equilibria of *meso*-tetra-(*p*-sulphonatophenyl)porphyrin, H_2TPPS^{4-}, as well as the formation equilibria of the Cu^{2+} and Zn^{2+} complexes, in a Me_2SO–water (80 : 20) solution, has allowed us to determine for the first time the stability constants of two metalloporphyrins, $CuTPPS^{4-}$(log β 38.1) and $ZnTPPS^{4-}$ (log β 34.6) at 25 °C and 0.1 mol dm^{-3} ($KClO_4$ + $HClO_4$).

Although kinetics and mechanisms of the formation reactions of metalloporphyrins have been investigated exhaustively,[1] studies on the formation equilibria of these complexes are very scarce.[2] The equilibrium constant of reaction (1) has been determined in some cases, but mostly from kinetic data. No stability constant of a metalloporphyrin, *i.e.*, the equilibrium constant of reaction (2), has been determined experimentally hitherto.†

$$H_2porph + M \rightleftharpoons Mporph + 2H^+ \qquad (1)$$

$$porph^{2-} + M \rightleftharpoons Mporph \qquad (2)$$

There are two main difficulties in the thermodynamic study of the formation equilibria of metalloporphyrins: (a) reactions occurs very slowly at room temperature, and a long time is required to reach the equilibrium; and (b) it is necessary to know the acidity constants of the porphyrins, because the anion porphyrinate, P^{2-}, is the true ligand. Recently, some progress in dealing with the first point has been reported.[3] However, the second difficulty has remained unsolved to date.

As porphyrins are very weak acids, their deprotonation reactions do not generally occur in aqueous solution. Only in the case of the *meso*-tetra(methylpyridyl)porphyrin, H_2TMPyP^{4+}, has the value of the first acidity constant (pK_{a1} = 12.9 ± 0.2) been reported.[4] Clarke *et al.*[5] have studied the complete deprotonation of some porphyrins in very basic media using a mixed Me_2SO–water–toluene solvent, but they were unable to determine their acidity constants.

We report here a quantitative study of the protonation and deprotonation equilibria of H_2TPPS^{4-}, as well as the formation equilibria of the complexes $CuTPPS^{4-}$ and $ZnTPPS^{4-}$, in

Table 1. Values of the equilibrium constants determined in Me_2SO–water (80 : 20) (v : v) solution at 25 °C and 0.1 mol dm^{-3} ionic strength.

Reaction	log *K*	Background electrolyte
$TPPS^{6-} + 2H^+ \rightleftharpoons H_2TPPS^{4-}$	32.8	$KClO_4 + KOH$
$H_2TPPS^{4-} + 2H^+ \rightleftharpoons H_4TPPS^{2-}$	3.6	$KClO_4 + HClO_4$
$H_4TPPS^{2-} + Zn^{2+} \rightleftharpoons ZnTPPS^{4-} + 4H^+$	−1.8	$KClO_4 + HClO_4$
$H_4TPPS^{2-} + Cu^{2+} \rightleftharpoons CuTPPS^{4-} + 4H^+$	1.7	$KClO_4 + HClO_4$

---

† The incorrect use in some recent papers of the term 'stability constant' for the equilibrium constant of the reaction (1) should be noted.

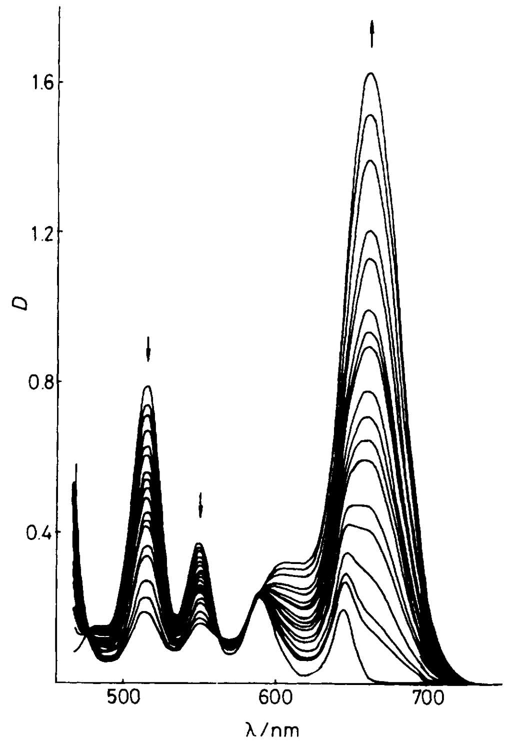

Figure 1. Changes in the spectrum of a 4 × 10^{-5} mol dm^{-3} H_2TPPS^{4-} solution in Me_2SO–water (80:20) when variable amounts of $HClO_4$ are added (path length of the cuvette 1.0 cm).

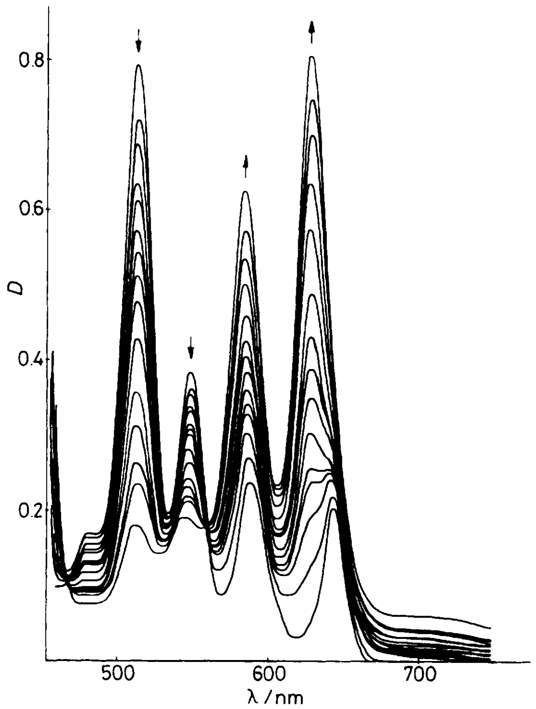

Figure 2. Changes in the spectrum of a 4 × 10^{-5} mol dm^{-3} H_2TPPS^{4-} solution in Me_2SO–water (80:20) when variable amounts of KOH are added (path length of the cuvete 1.0 cm).

Me_2SO–water (80:20, v:v), determining for the first time the stability constants of two metalloporphyrins.

The porphyrin $Na_4H_2TPPS \cdot 4H_2O$ has been synthesized by a modification of the previously reported method.[6] Our procedure involves the precipitation of the porphyrin as the phenanthrolinium derivative $(Hphen)_4H_2TPPS \cdot 2H_2O$, instead of attempting the isolation and purification of the very soluble sodium porphyrin from a concentrated aqueous solution of Na_2SO_4. High-purity sodium porphyrin is obtained by treating an aqueous suspension of the phenanthrolinium compound with a cation-exchange resin.

The changes produced in the visible absorption spectrum of an H_2TPPS^{4-} solution in Me_2SO–water (80:20) when adding variable amounts of $HClO_4$ and KOH respectively, are shown in Figures 1 and 2. The purple solution becomes green in both cases. Because of the high excess of acid with regard to porphyrin concentration (100—2500 times), the hydrogen ion concentration of each solution is known accurately, $[H^+] = [HClO_4]$. In the basic solutions and for the same reason $[OH^-] = [KOH]$. Potentiometric determination of K_w in this mixed solvent ($pK_w = 18.42 \pm 0.02$ at 25 °C and 0.1 mol dm^{-3} $KClO_4$) allows us to obtain the hydrogen ion concentration, too, $[H^+] = K_w[OH^-]^{-1}$. The stoicheiometry and the equilibrium constants of the protonation and deprotonation reactions have been determined by applying the Asmus[7] and the linear extrapolation[8] methods. Only one species is formed in each case: H_4TPPS^{2-} and $TPPS^{6-}$, respectively. The values of the equilibrium constants are shown in Table 1. H_2TPPS^{4-} is a very weak base, being very readily protonated in water solution,[3] and an extremely weak acid in Me_2SO–water (80:20). As far as we know this is the first reported experimental value of the acidity constant of a porphyrin. Curiously our value is very similar to that predicted for *meso*-porphyrin in detergent solutions many years ago (p*K* *ca.* 32).[9]

Moreover, we have studied spectrophotometrically the interaction between H_4TPPS^{2-} and the metal ions Cu^{2+} and Zn^{2+}. The metallation reactions take place very slowly, much more slowly than in aqueous solution, but we have followed them carefully for some months to be sure the equilibrium was reached. The equilibrium constants are shown in Table 1. The stability constants of both metalloporphyrins are easily inferred from these data, log β 38.1 and 34.6 for $CuTPPS^{4-}$ and $ZnTPPS^{4-}$, respectively.

We thank the Comisión Asesora de Investigación Científica y Técnica de la Presidencia del Gobierno (Spain) for financial support of this work (Proyecto nº 1688/82). One of us (H. R. J.) thanks the Consellería de Cultura, Educació i Ciència de la Generalitat Valenciana for a grant.

Received, 24th November 1986; Com. 1677

References

1 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1980, vol. V, p. 459 and refs. therein.
2 P. Hambright, *Inorg. Chem.*, 1977, **16**, 2987 and refs. therein.
3 M. Tabata and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1985, 42.
4 P. Hambright and E. B. Fleisher, *Inorg. Chem.*, 1970, **9**, 1757.
5 J. A. Clarke, P. J. Dawson, R. Grigg, and C. H. Rochester, *J. Chem. Soc., Perkin Trans. 2*, 1973, 414.
6 E. B. Fleisher, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93**, 3162.
7 E. Asmus, *Fresenius' Z. Anal. Chem*;. 1960, **178**, 104.
8 F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, New York, 1961, p. 274.
9 W. McEwen, *J. Am. Chem. Soc.*, 1936, **58**, 1124.