Kinetics and Mechanism of Cadmium(II) Ion Assisted Incorporation of Manganese(II) into 5,10,15,20-Tetrakis(4-sulphonatophenyl)-porphyrinate(4−)†

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The kinetics of the reaction of 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrinate(H_2tspp) with manganese(II) were studied spectrophotometrically in the presence of cadmium(II) and in the range of pH 6—8.5 at 25 °C and at an ionic strength of 0.1 mol dm^{-3} ($NaNO_3$). The incorporation of manganese(II) into H_2tspp is catalytically assisted by cadmium(II) at concentrations as low as 10^{-7} mol dm^{-3}. The rate equation for the reaction is expressed as $-d[H_2tspp]/dt = k_1[Mn^{2+}][H_2tspp] + k_2k_3[Mn^{2+}][Cd^{2+}][H_2tspp]/(k_{-2}[H^+]^2 + k_3[Mn^{2+}])$, with $k_1 = (2.50 \pm 0.32) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k_2 = (4.86 \pm 0.16) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_{-2} = (5.90 \pm 0.17) \times 10^{12}$ dm^6 mol^{-2} s^{-1}, and $k_3 = (1.98 \pm 0.10) \times 10^2$ dm^3 mol^{-1} s^{-1}. [Cd(tspp)] is formed as a reaction intermediate; it is 7 900 times as reactive as H_2tspp for the incorporation of manganese(II).

The kinetics and mechanism of metal ion incorporation into the porphyrin nucleus have been the subject of extensive study and a review article on the subject has appeared recently.[1] The apparent order in metal ion depends markedly on reaction conditions; some authors report the formation of metalloporphyrins to be second order in metal ions, while some others find first order or even fractional order. In a previous paper [2] it has been shown that, for a given pair of metal ion and porphyrin, the apparent order in metal ion differs for different metal ion concentrations. At lower metal ion concentration the metal ion weakly bound to the porphyrin nucleus just drops into the porphyrin ring, while at higher metal ion concentration another metal ion may attack the weak metal porphyrin complex from the back.

For a given metal ion, porphyrins react more slowly than usual non-cyclic ligands.[1,3,4] We found that the rate of the metal incorporation into a porphyrin to form a metalloporphyrin is assisted by mercury(II), cadmium(II), and lead(II) at a concentration as low as 10^{-7} mol dm^{-3}, and proposed kinetic methods for the determination of nanogram amounts of mercury(II) and cadmium(II).[5–7] The methods are based on the catalytic effect of mercury(II) or cadmium(II) on the complex formation reaction of manganese(II) with 5,10,15,20-tetrakis-(4-sulphonatophenyl)porphyrinate (H_2tspp), where H_2tspp denotes the free base porphyrin. In the reaction [Hg(tspp)] and [Cd(tspp)] have been proposed as reactive intermediates. Hambright and co-workers [8,9] reported that a cadmium(II)–porphyrin complex reacts more readily with some metal ions than does the free base porphyrin.

In the present paper, we describe the kinetic results on the formation of [5,10,15,20-tetrakis(4-sulphonatophenyl)-porphyrinato]manganate(III) in the presence of cadmium(II). In addition, experiments on the metal-substitution reaction of [Cd(tspp)] with manganese(II) were carried out, since [Cd-(tspp)] occurs as a reactive intermediate in the proposed mechanism.

Experimental

Reagents.—5,10,15,20-Tetrakis(4-sulphonatophenyl)porphyrinate (H_2tspp) was synthesized by the methods described in the literature.[10,11] The sodium salt of H_2tspp, [Na_4(H_2tspp)], was purified by successive reprecipitation from aqueous acetone (70% v/v) and by column chromatography. The purity of [Na_4(H_2tspp)] was checked by thin-layer chromatography and n.m.r. spectroscopy. Cadmium(II) nitrate solution was prepared by dissolving metallic cadmium (99.99%) in a small amount of nitric acid and diluting it with distilled water. Sodium nitrate, sodium borate, boric acid and hydroxylamine hydrochloride were recrystallized from distilled water. The concentrations of cadmium(II) and manganese(II) were determined by ethylenediaminetetra-acetate titration. The buffer solutions were prepared with boric acid and sodium borate (total borate concentration 4.0×10^{-3} mol dm^{-3}).

Kinetic Measurements.—All experiments were carried out in a room thermostatted at 25 ± 0.5 °C. The ionic strength was maintained at 0.1 mol dm^{-3} with sodium nitrate.

The spectral change in the course of the reaction is characterized by the disappearance of the characteristic band of H_2tspp (Soret band at 413 nm, $\varepsilon = 5.24 \times 10^5$ dm^3 mol^{-1} cm^{-1}) and the growth of the characteristic band of [Mn^{III}-(tspp)] (Soret band at 467 nm, $\varepsilon = 1.02 \times 10^5$ dm^3 mol^{-1} cm^{-1}). Isosbestic points are observed at 388 and 426 nm. The absorbance change at 413 nm was monitored with a thermostatted 10-mm cell. The temperature of the reaction solutions was controlled at 25 ± 0.1 °C (Lauda small refrigerated thermostat, type K2RD, Lauda/Tauber). The reaction was started by mixing two solutions, *i.e.* one containing cadmium(II) nitrate, manganese(II) nitrate, hydroxylamine, borate buffer, and sodium nitrate, and the other containing [Na_4(H_2tspp], hydroxylamine, borate buffer, and sodium nitrate. The mixing of the two solutions was carried out with a sample mixing device (type MX7, Union Giken).

The pH was varied by addition of borate buffer, and determined by a Toa digital pH-meter HM-15A with a reference electrode (Metrohm EA-404) and a glass electrode (Metrohm EA 109). A 1.000×10^{-2} mol dm^{-3} nitric acid solution containing 0.090 mol dm^{-3} sodium nitrate was employed as a standard of hydrogen ion concentration ($-\log[H^+] = 2.000$). From pH-meter readings at various hydrogen ion concentrations of an ionic strength of 0.1 mol dm^{-3} (HNO_3–$NaNO_3$), the glass electrode was calibrated to read the hydrogen ion concentration.

Hydroxylamine (5×10^{-3} mol dm^{-3}) was added to the

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† The overall charges on the porphyrins and the metal-porphyrin complexes have been omitted throughout for simplicity.

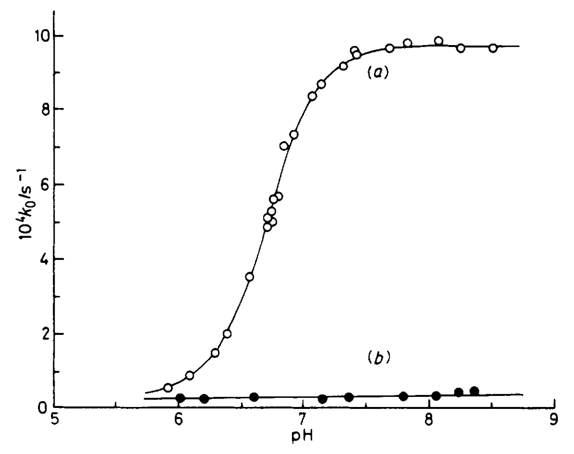

Figure 1. Effect of pH on the incorporation of manganese(II) into H_2tspp catalyzed by cadmium(II) at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). (*a*) $[Cd^{2+}] = 1.96 \times 10^{-6}$ mol dm^{-3}; (*b*) absence of cadmium. $[H_2tspp] = 2.01 \times 10^{-7}$, $[Mn^{2+}] = 1.13 \times 10^{-3}$, $[NH_2OH] = 5.10 \times 10^{-3}$ mol dm^{-3}. The solid lines are calculated with the rate constants given in the Table

reaction solution to prevent the formation of manganese(IV) oxide. The catalytic effect of cadmium(II) on the incorporation of manganese(II) into H_2tspp was found to be lower by 8% in the presence of hydroxylamine and to be independent of the concentration of hydroxylamine in the concentration range from 1×10^{-3} to 6×10^{-3} mol dm^{-3}.

Results

The reaction of H_2tspp with manganese(II) was studied in the presence of a large excess of manganese(II) and cadmium(II) compared to H_2tspp at pH 6—8.5. Under the present experimental conditions, the product is $[Mn^{III}(tspp)]$. At the concentration of H_2tspp used (10^{-7} mol dm^{-3}), H_2tspp exists in the monomeric form.[12,13]

The first-order plot of $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ *versus* t gave a good straight line, where A_0, A_t, and A_∞ denote the absorbances of the reaction system at the reaction time 0, t, and ∞ respectively. The kinetic equation for this reaction is described by equation (1), where k_0 is the conditional rate

$$-d[H_2tspp]/dt = k_0[H_2tspp] \qquad (1)$$

constant involving concentration of hydrogen ion, cadmium(II), and manganese(II). The conditional rate constant was determined from the slope of the first-order rate plot.

In Figure 1, k_0 is plotted against pH. The rate of formation of $[Mn^{III}(tspp)]$ in the absence of cadmium(II) is independent of pH. On the other hand, the rate constant in the presence of cadmium(II) depends on pH. Cadmium(II) accelerates the formation of $[Mn^{III}(tspp)]$ at pH > 6. The conditional rate constant k_0 increases with pH, and then levels off. In Figure 2, the rate constant $k_{Cd}(= k_0 - k_{[Cd]_0})$ is plotted against the concentration of cadmium(II), where $k_{[Cd]_0}$ denotes the rate constant in the absence of cadmium(II). The plot gives a straight line with a zero intercept. The formation of $[Mn^{III}(tspp)]$ in the presence of cadmium(II) is of first order with respect to cadmium(II).

Over the range pH 6—8.5, the predominant species of H_2tspp is the free base form as judged from $K_a = [H_2tspp][H^+]/[H_3tspp^+] = 10^{-4.98}$ dm^3 mol^{-1} (ref. 14). Thus we postulate two parallel paths (Scheme 1): the direct formation of $[Mn^{II}(tspp)]$ (k_1 path) and the rapid formation of $[Cd^{II}(tspp)]$ which is subsequently substituted by Mn^{2+} (k_2 and k_3 paths). $[Mn^{II}(tspp)]$ is oxidized quickly by dissolved oxygen.

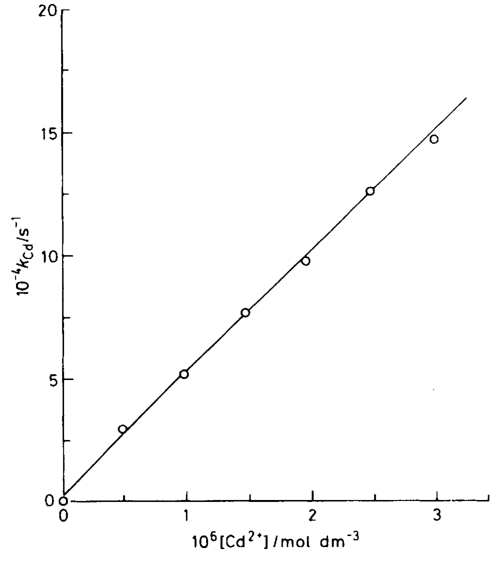

Figure 2. Catalytic effect of cadmium(II) on the incorporation of manganese(II) into H_2tspp at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). $[H_2tspp] = 2.01 \times 10^{-7}$, $[Mn^{2+}] = 1.13 \times 10^{-3}$, $[NH_2OH] = 5.10 \times 10^{-3}$ mol dm^{-3}; at pH 8.04

$$Mn^{2+} + H_2tspp \xrightarrow{k_1} [Mn^{II}(tspp)] + 2H^+$$
$$Cd^{2+} + H_2tspp \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cd^{II}(tspp)] + 2H^+$$
$$[Cd^{II}(tspp)] + Mn^{2+} \xrightarrow{k_3} [Mn^{II}(tspp)] + Cd^{2+}$$

Scheme 1.

Applying the steady-state approximation for [Cd(tspp)], we have equation (2) for k_{Cd}, which leads to equation (3). A plot of k_{Cd}^{-1} *versus* $[H^+]^2$ gives k_2 as the intercept and k_{-2}/k_3 from the slope (Figure 3). The data give $k_2 = (4.86 \pm 0.16) \times 10^2$ dm^3 mol^{-1} s^{-1} and $k_{-2}/k_3 = (2.98 \pm 0.14) \times 10^{10}$ dm^3 mol^{-1} at 25 °C and at an ionic strength of 0.1 mol dm^{-3} ($NaNO_3$).

At higher pH ($k_{-2}[H^+]^2 \ll k_3[Mn^{2+}]$), equation (2) is reduced to equation (4). The rate constant k_{Cd} is independent

$$k_{Cd} = k_0 - k_{[Cd]_0} = \frac{k_2k_3[Mn^{2+}][Cd^{2+}]}{k_{-2}[H^+]^2 + k_3[Mn^{2+}]} \qquad (2)$$

$$k_{Cd}^{-1} = \frac{k_{-2}[H^+]^2}{k_2k_3[Mn^{2+}][Cd^{2+}]} + \frac{1}{k_2[Cd^{2+}]} \qquad (3)$$

$$k_{Cd} = k_2[Cd^{2+}] \qquad (4)$$

of both hydrogen ion and manganese(II) concentrations. The rate constants for pH 7.8—8.5 in Figure 1(*a*) are given by equation (4). The rate constants were independent of $[Mn^{2+}]$ over a concentration range from 1.13×10^{-4} to 2.27×10^{-3} mol dm^{-3} as expected from equation (4).

Rate of Oxidation of $[Mn^{II}(tspp)]$ *to* $[Mn^{III}(tspp)]$.—Reduction of $[Mn^{III}(tspp)]$ by sodium dithionite produces $[Mn^{II}(tspp)]$ which exhibits an intense Soret band with the maximum absorbance at 432 nm ($\varepsilon = 4.5 \times 10^5$ dm^3 mol^{-1} cm^{-1}), which is similar to absorption spectra reported for (5,10,15,20-tetraphenylporphyrinato)manganese(II).[15,16] The mixing of the $[Mn^{II}(tspp)]$ solution with an aqueous solution containing oxygen gives a rapid spectral change, *i.e.* absorbance at 432 nm decreases and absorbance at 467 nm increases. The half-time for the oxidation of $[Mn^{II}(tspp)]$ to $[Mn^{III}(tspp)]$ was at most 3 min. Thus the rate of the oxidation of $[Mn^{II}(tspp)]$ to

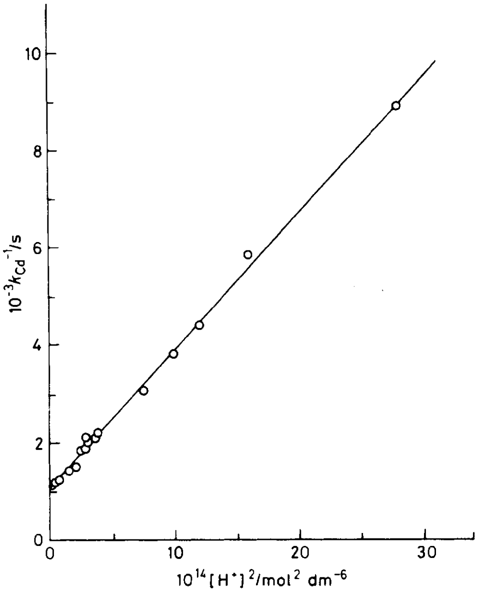

Figure 3. A plot of k_{Cd}^{-1} *versus* $[H^+]^2$ according to equation (3) for the incorporation of manganese(II) into H_2tspp catalyzed by cadmium(II) at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). [H_2tspp] = 2.01×10^{-7}, [Mn^{2+}] = 1.13×10^{-3}, [Cd^{2+}] = 1.96×10^{-6}, [NH_2OH] = 5.10×10^{-3} mol dm^{-3}

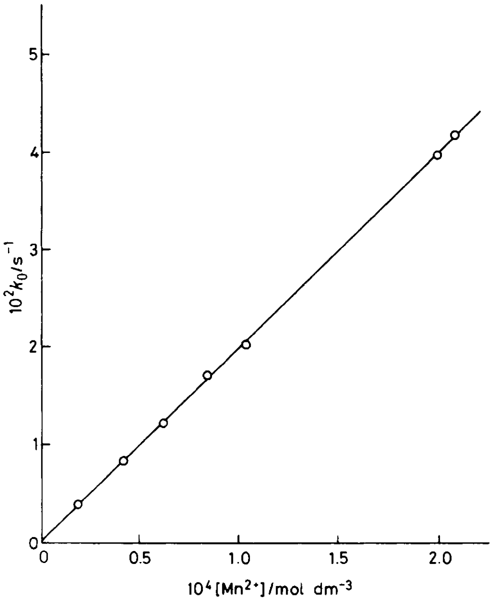

Figure 4. Plots of the pseudo-first-order rate constants *versus* manganese(II) concentrations for the metal-substitution reaction of [Cd(tspp)] with manganese(II) at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). [H_2tspp] = 1.97×10^{-7}, [Cd^{2+}] = 2.42×10^{-6}, [NH_2OH] = 5.10×10^{-3} mol dm^{-3}; at pH 7.94

[Mn^{III}(tspp)] is much faster than that of the incorporation reaction of manganese(II) into H_2tspp.

Metal-substitution Reaction of [Cd^{II}(tspp)] *with Manganese*(II).—The kinetics of the incorporation reaction of manganese(II) into H_2tspp in the presence of cadmium(II) indicates that [Cd(tspp)] is an intermediate (see Scheme 1). Therefore we studied the reaction of manganese(II) with [Cd(tspp)]. The reaction was followed spectrophotometrically at 428 nm {$\lambda_{max.}$ of [Cd(tspp)]}.

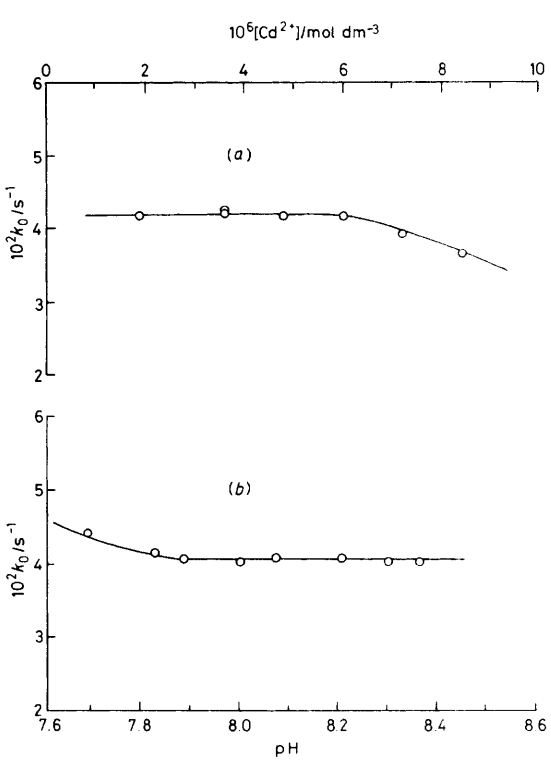

Figure 5. Effect of (*a*) cadmium(II) concentrations (at pH 7.88) and (*b*) pH ([Cd^{2+}] = 4.81×10^{-6} mol dm^{-3}) on the metal-substitution reaction of [Cd(tspp)] with manganese(II) at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$). [H_2tspp] = 1.91×10^{-7}, [Mn^{2+}] = 2.07×10^{-4}, [NH_2OH] = 5.10×10^{-3} mol dm^{-3}

The rate of reaction is first order with respect to [Cd(tspp)] in the presence of a large excess of manganese(II). The kinetic equation for the reaction is described by (5). The

$$-d[Cd(tspp)]/dt = k_0[Cd(tspp)] \qquad (5)$$

plot of k_0 *versus* [Mn^{2+}] (Figure 4) shows that the reaction is first order in the concentration of manganese(II). In Figure 5, k_0 is plotted against $-\log[H^+]$ and [Cd^{2+}]. Over the range of pH 7.9—8.4, the reaction is independent of pH. At pH <7.8, [Cd(tspp)] is demetallated by acid (reaction path k_{-2} in Scheme 1). Thus the rate of reaction of [Cd(tspp)] increases with increasing pH. The solid line in Figure 5(*b*) is calculated from rate constants k_{-2} and k_3 in the Table. Over a concentration range of cadmium(II) from 2×10^{-6} to 6×10^{-6} mol dm^{-3}, the metal-substitution reaction of [Cd(tspp)] with manganese(II) is independent of the concentration of cadmium(II).[17,*]

From the above results, the rate of the metal-substitution reaction of [Cd(tspp)] with manganese(II) is expressed by equation (6). Under conditions where $k_3[Mn^{2+}] \gg k_{-2}[H^+]^2$, equation (6) simplifies to equation (7). The horizontal

$$-d[Cd(tspp)]/dt = (k_3[Mn^{2+}] + k_{-2}[H^+]^2)[Cd(tspp)] \qquad (6)$$

$$-d[Cd(tspp)]/dt = k_3[Mn^{2+}][Cd(tspp)] \qquad (7)$$

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[*] At a cadmium(II) concentration greater than 6×10^{-6} mol dm^{-3}, [Cd_2(tspp)] (maximum absorbance at 421 nm) is formed during the metal-substitution reaction. Similar dimetallic metalloporphyrins have been reported for mercury(II).[17]

Table. Rate constants for the incorporation of manganese(II) into H_2tspp catalyzed by cadmium(II) at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$)

Reaction path *	Rate constant
k_1	$(2.50 \pm 0.32) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}
k_2	$(4.86 \pm 0.16) \times 10^{2}$ dm^3 mol^{-1} s^{-1}
k_{-2}	$(5.90 \pm 0.17) \times 10^{12}$ dm^6 mol^{-2} s^{-1}
k_3	$(1.98 \pm 0.10) \times 10^{2}$ dm^3 mol^{-1} s^{-1}

* See Scheme 1.

line in Figure 5 is given by equation (7) with $k_3 = (1.98 \pm 0.10) \times 10^2$ dm^3 mol^{-1} s^{-1}.

The rate constants for the reaction paths in Scheme 1 are summarized in the Table.

Discussion

The incorporation of manganese(II) into H_2tspp is catalyzed by cadmium(II). The catalytic effect of cadmium(II) can be explained by the reaction proceeding through [Cd(tspp)] as shown in Scheme 1. [Cd(tspp)] is 7 900 times as reactive as H_2tspp for the incorporation of manganese(II). Cadmium(II) liberated after the incorporation of manganese(II) reacts relatively rapidly with the free base porphyrin and acts as a catalyst.

In previous papers,[5-7] we have found that large metal ions such as mercury(II), cadmium(II), and lead(II) accelerate the incorporation reactions of manganese(II), cobalt(II), copper(II), and nickel(II) into H_2tspp. Shamin and Hambright[9] reported that a cadmium(II)-porphyrin complex reacts 90—2 000 times faster than the free base porphyrin for metal ion.[9] Because of their large ionic radii, mercury(II), cadmium(II), and lead(II) cannot fit well into the plane of the porphyrin. The co-ordination of cadmium(II) will give a highly expanded or distorted porphyrinato core as observed in [In(tpp)Cl] or [Sn(tpp)Cl_2] (where tpp = 5,10,15,20-tetraphenylporphyrinate).[18,19] It is likely that cadmium(II) facilitates the attack of the porphyrin nucleus by manganese(II) from the back. It is well known that the metal incorporation into *N*-alkylporphyrins is faster than that into the non-*N*-alkylated analogues, and it has been explained by the distortion of the porphyrin by *N*-alkylation.[20-22] The deformation of the porphyrin by co-ordination of large metal ions such as mercury(II), cadmium(II), and lead(II) seems to exert a similar effect.

From the present kinetic study on the catalytic effect of cadmium(II), the formation rate constant of [Cd(tspp)] was determined as $k = (4.86 \pm 0.16) \times 10^2$ dm^3 mol^{-1} s^{-1} at 25 °C and ionic strength of 0.1 mol dm^{-3} ($NaNO_3$). A comparable value was also obtained from an independent experiment on the reaction of cadmium(II) with H_2tspp by a stopped-flow method: $k = (5.10 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1} under the same condition. Shamin and Hambright[23] have determined the rate constants of formation of complexes of cadmium(II) with some water-soluble porphyrins (see Figure 6): 5,10,15,20-tetrakis(*N*-methyl-4-pyridinio)porphyrin (H_2L^1), its *N*-methyl-3-pyridinio and *N*-methyl-2-pyridinio isomers (H_2L^2 and H_2L^3 respectively), 5,10,15,20-tetrakis-(4-trimethylammoniophenyl)porphyrin (H_2L^4), and 5,10,15-tris(*N*-methyl-4-pyridinio)-20-phenylporphyrin (H_2L^5).[23]

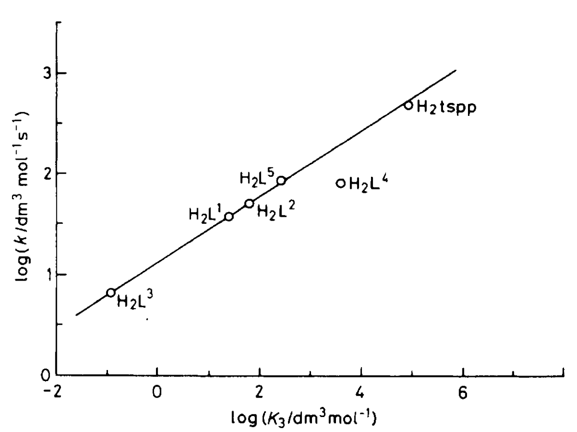


Figure 6. Relationship between the formation rate constants of cadmium(II)-porphyrin complexes (log *k*) and the basicity of the porphyrin (log K_3) (see Discussion section for definitions of porphyrins)

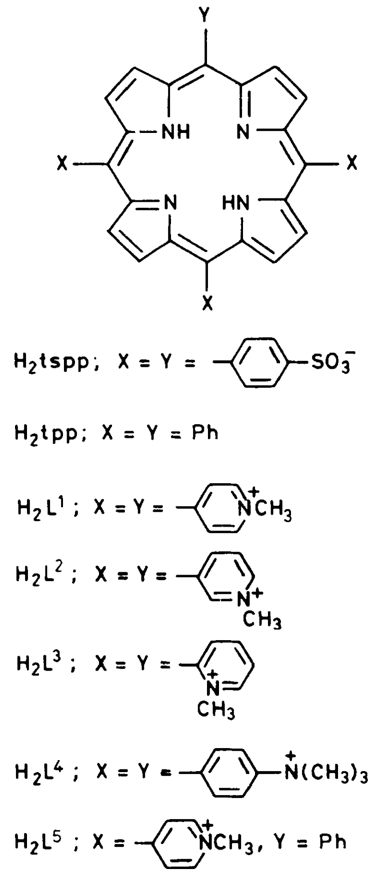
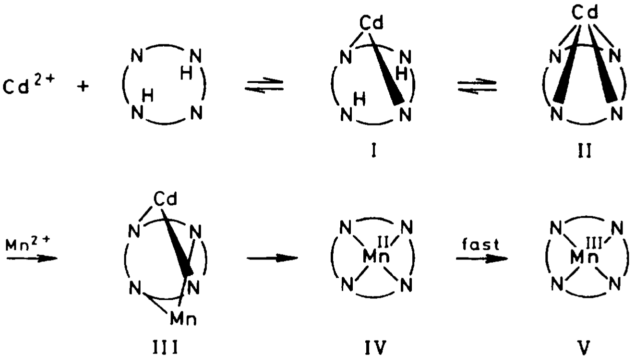


Figure 6 shows a relationship between the complex formation rate constant of cadmium(II) (log *k*) and the basicity of the porphyrin (log K_3), where K_3 is the protonation constant of the porphyrin (H_2L), *i.e.* $K_3 = [H_3L^+]/[H_2L][H^+]$. The rate of metal ion incorporation into porphyrins increases with the basicity of the porphyrin, but it does not correlate with charge: in these porphyrins the formal charge is -4 for H_2tspp, $+3$ for H_2L^5, and $+4$ for the others. The rate constant of the cadmium(II) complex of the most basic porphyrin (H_2tspp) is 86 times as high as that for the least basic porphyrin (H_2L^3). Similar relationships were observed for copper(II)[24,25] and zinc(II)[26] porphyrins. The increase in the rate constant with increasing basicity of porphyrin suggests the formation of a species in which the metal ion is weakly bound to nitrogen in porphyrin as an important process in the incorporation of metal ion into porphyrin.

From the above results, we suggest a mechanism for the cadmium ion assisted formation of [Mn^{III}(tspp)] is as shown in Scheme 2. Compound II is a proposed intermediate [Cd(tspp)]. At pH > 7.8, the formation of [Cd(tspp)] (step I ⟶ II) is the rate-determining step [see equation (3)]. At pH < 7, Cd^{2+} and [Cd(tspp)] are in a rapid equilibrium and step III ⟶ IV is the rate-determining step. The rate of the oxidation of [Mn^{II}(tspp)] to [Mn^{III}(tspp)] by dissolved oxygen (step IV ⟶ V) is relatively fast.



Scheme 2.

It should be noted that the rate constants for the formation of cadmium(II) porphyrins {[Cd(tspp)] and [Cd(L^1)]} are greater than expected from a correlation between the rate constant of metalloporphyrin formation and the rate of loss of a water molecule from the aquated metal ion (*i.e.* log k *versus* log $k_{M}^{-H_2O}$).[27,28] This may suggest that the formation of the cadmium(II) porphyrin complex differs in some respect from the formation of metalloporphyrin with the bivalent first-row transition metal ions from Mn^{2+} to Zn^{2+}.

There are few reported values of constants for equilibria involving metalloporphyrins [17a] due to their extreme thermodynamic stability. From values of k_2 and k_{-2} in the Table, it is possible to calculate the constant for the equilibrium (8) as

$$\mathrm{Cd^{2+} + H_2tspp \overset{K_2}{\rightleftharpoons} [Cd^{II}(tspp)] + 2H^+} \qquad (8)$$

$K_2 = k_2k_{-2}^{-1} = 8.24 \times 10^{-11}$ mol dm^{-3}.

Acknowledgements

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References

1 F. R. Longo, E. M. Brown, W. G. Rau, and A. D. Adler, ' The Porphyrins,' Academic Press, New York, 1978, vol. 5, part C, pp. 459—481 and refs. therein.
2 S. Funahashi, K. Saito, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2695.
3 D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, ' Coordination Chemistry,' American Chemical Society, Washington, D.C., 1978, vol. 2, ch. 1.
4 J. P. Hunt, *Coord. Chem. Rev.*, 1971, **7**, 1.
5 M. Tabata and M. Tanaka, *Inorg. Chim. Acta Lett.*, 1980, **40**, X71.
6 M. Tabata and M. Tanaka, *Anal. Lett.*, 1980, **13**, 427.
7 M. Tabata and M. Tanaka, *Mikrochim. Acta*, 1982, **2**, 149.
8 J. Reid and P. Hambright, *Inorg. Chim. Acta*, 1979, **33**, L135.
9 A. Shamin and P. Hambright, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1645.
10 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
11 E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93**, 3162.
12 M. Krishnamurthy, J. R. Sutter, and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 1975, 13.
13 J. Turay, P. Hambright, and N. Datta-Gupta, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1687.
14 J. Ito, T. Yotsuyanagi, and K. Aomura, *Anal. Chim. Acta*, 1975, **74**, 53.
15 B. M. Hoffman, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, 1976, **98**, 5473.
16 I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, 1979, **101**, 6456.
17 (*a*) A. Adeyemo and M. Krishnamurthy, *Inorg. Chem.*, 1977, **16**, 3355; (*b*) M. F. Hudson and K. M. Smith, *J. Chem. Soc., Chem. Commun.*, 1973, 515; H. J. Callot, B. Chevrier, and R. Weiss, *J. Am. Chem. Soc.*, 1979, **101**, 7729.
18 R. G. Ball, K. M. Lee, A. G. Marshall, and J. Trotter, *Inorg. Chem.*, 1980, **19**, 1463.
19 D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, 1972, **94**, 6689.
20 B. Shar, B. Shears, and P. Hambright, *Inorg. Chem.*, 1971, **10**, 1828.
21 M. J. Bain-Ackerman and D. K. Lavallee, *Inorg. Chem.*, 1979, **18**, 3358.
22 S. Funahashi, Y. Yamaguchi, K. Ishihara, and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1982, 976.
23 A. Shamim and P. Hambright, *Inorg. Chem.*, 1980, **19**, 564.
24 M. Meot-Ner and A. D. Adler, *J. Am. Chem. Soc.*, 1972, **94**, 4763.
25 J. B. Reid and P. Hambright, *Inorg. Chem.*, 1977, **16**, 968.
26 P. Hambright, *Inorg. Chem.*, 1977, **16**, 2987.
27 P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, 1974, **96**, 3123.
28 J. Turay and P. Hambright, *Inorg. Chem.*, 1980, **19**, 562.

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