Table II. Comparison of Metal–Porphyrin Incorporation Rates for Various Porphyrins with Metal Ion/Water Exchange Rate Constants

porphyrin	metal ion	k_I,[a] M^{-1} s^{-1}	k^{Cu}_I/k^M_I	k_E,[b] s^{-1}	k_I/k_E, M^{-1}
TMpyP(4)[c]	Cu^{2+}	7.0×10^{-1}	1	2×10^9	4×10^{-10}
	Zn^{2+}	1.6×10^{-2}	44	3.2×10^7	5×10^{-10}
	Co^{2+}	1.1×10^{-3}	693	2×10^6	6×10^{-10}
	Ni^{2+}	2.1×10^{-6}	352000	2×10^4	1×10^{-10}
$TPPS_4$[d]	Cu^{2+}	1.6×10^2	1	2×10^9	8×10^{-8}
	Zn^{2+}	2.9×10^0	55	3.2×10^7	9×10^{-8}
	Co^{2+}	7×10^{-2}	2300	2×10^6	3×10^{-8}
	Ni^{2+}	8.6×10^{-4}	187000	2×10^4	4×10^{-8}
etio[e]	Cu^{2+}	2.1×10^{-1}	1	2×10^9	1×10^{-10}
	Cd^{2+}	1.7×10^{-2}	12	1.6×10^8	1×10^{-10}
	Zn^{2+}	5.0×10^{-3}	42	3.2×10^7	2×10^{-10}
N-methyletio[f]	Cd^{2+}	1.1×10^3		1.6×10^8	7×10^{-6}
	Zn^{2+}	5.0×10^2		3.2×10^7	2×10^{-5}

[a] At 25 °C. [b] k_E is the water-exchange rate constant; from ref 4. [c] TMpyP(4) is tetrakis(*N*-methyl-4-pyridyl)porphyrin; 25 °C, pH 3.0, $(NO_3^-) = 0.5$ M; this paper. [d] $TPPS_4$ is tetrakis(4-sulfonatophenyl)porphyrin; pH 5.4 acetate buffer, 25 °C; see ref 21. [e] etio is etioporphyrin I; DMF solvent, 25 °C; see ref 17. [f] *N*-methyletio is *N*-methyletioporphyrin I; same conditions as for etio; ref 17.

As previously demonstrated,[8,21] the metal–porphyrin incorporation rates, k^M_I, for a given metal ion parallel the corresponding water-exchange rate constant, k_E. For TMpyP(4), the rate ratios k^{Cu}_I/k^M_E are 1:44:700:350 000 for Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. Equation 12 predicts that the ratio k^M_I/k^M_E should be constant for the same porphyrin with different metals, to a first approximation, and Table II shows that this ratio varies by about a factor of 6 for TMpyP(4). The same relative consistency is also found for this ratio with metals and $TPPS_4$, etioporphyrin I, and *N*-methyletioporphyrin I (Table II).

The porphyrin formation rates should depend on electrostatic parameters in terms of K_{OS}. This might rationalize (Table II) why the tetranegative $TPPS_4$ reacts faster with metals than the tetrapositive TMpyP(4). It is noted that the ratios of the Zn^{2+}–porphyrin formation rates in water of the octa-, tetra-, and dinegatively charged uro-, copro-, and deuteroporphyrins are 10:5:1, respectively.[14] For the same porphyrin charge types, the iron(II)–porphyrin formation rates in water/pyridine media are in the ratios 420:10:1. However, with synthetic uncharged meso-substituted porphyrins[6] or modified uncharged natural porphyrin esters,[23] studied in DMF solutions, the metalation rates are fairly independent of the identity of the porphyrin, indicating a similarity in their K_{OS} and k_{NH} values. The fact that predeformed *N*-methyletioporphyrin I[17] incorporates metal ions 10^5 times faster than etioporphyrin I itself argues for larger K_D and k_{NH} for the *N*-methylporphyrin. Such N-alkylated porphyrins have in fact been shown to be more acidic toward NH dissociation than the corresponding unmethylated porphyrin.[20] In addition, small deuterium isotope effects of 2.2 ($Zn/TPPS_4$),[24] 2.4 (Zn/TAP),[11] and 1.3 ($Cu/TPPS_4$)[21] have been reported, a possible indication of NH involvement in the activated complex.

Finally, the product $K_{OS}K_Dk_Ek_{NH}$ is certainly of the right order of magnitude to account for the rates of porphyrin metalation. The inclusion of other preequilibria such as the dissociation of one additional water molecule from the metal before the simultaneous final water-proton dissociation reaction would add another k_E/k_{-E} term to the rate law. Assuming weak bonding between the porphyrin and the metal ion, we might expect that k_E/k_{-E} would have values from 10^{-1} to 1.

The inclusion of the notion of a slow N–H central-proton dissociation partially accounts for the slowness of metal–porphyrin reactions, compared to normal ligation processes. This has been suggested earlier by other workers using water-soluble metallophthalocyanine systems,[25] which apparently behave somewhat differently from porphyrins in their metalation reactions. Also, a metal ion independent term in the rate law for the formation of magnesium porphyrins was ascribed to the possible rate limiting monoanion porphyrin rearrangement.[26]

Many metalloporphyrin/metal ion exchange reactions do not involve the dissociation of the porphyrin N–H bond. For example, in the reaction

$$Cd\text{–}P + Zn^{2+} \rightarrow Zn\text{–}P + Cd^{2+} \qquad (13)$$

studied in pyridine at 25 °C, the exchange rates were about a 1000 times faster than those of the corresponding Zn^{2+}/H_2–P reactions, another possible indication of the rate limiting character of the N–H dissociation.[27] The metals found in geochemical porphyrins might involve transmetalation reactions rather than reactions with free base porphyrins themselves.

It must be noted that each porphyrin has rather specific and peculiar properties. Most synthetic[28] and natural porphyrin[29,30] derivatives dimerize and polymerize in aqueous solution, as a function of pH and ionic strength. Often porphyrins have such high pK_3 values such that the free base form is stable at pH values where most metal ions are hydrolyzed. The favorably low pK_3 of TMpyP(4) is counterbalanced by the strong dependence of its reactions on ionic strength and the ease of reduction of its free base form.[7,31] In addition, the tetrapositive H_2–TAP[11,12] behaves in many of its reactions more like the tetranegative $TPPS_4$ than the tetrapositive TMpyP(4). Such phenomena make comparisons between porphyrins difficult.

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Registry No. $Cu(H_2O)_6^{2+}$, 14946-74-8; $Zn(H_2O)_6^{2+}$, 15906-01-1; $Co(H_2O)_6^{2+}$, 15276-47-8; $Ni(H_2O)_6^{2+}$, 15365-79-4; TMpyP(4), 38673-65-3.

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An Equilibrium and Kinetic Study of Water-Soluble Cadmium Porphyrins

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The equilibrium between many metal ions and porphyrin molecules to form metalloporphyrins in aqueous solution is usually represented by the equation

$$M^{2+} + H_2P = MP + 2H^+ \quad K_e^M \qquad (1)$$

To date, only one complete mass law study of this reaction

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Table I. The Formation Constant of CdTMpyP(4) (25 °C; $\mu = 0.2$ ($NaNO_3$))

λ, nm	(Cd^{2+}), M	pH	$10^8 K_e^{Cd}$, M
575	5×10^{-4}	5.32	1.98
517	5×10^{-4}	5.32	1.95
618	5×10^{-4}	5.32	1.85
575	7.5×10^{-4}	5.49	1.97
517	7.5×10^{-4}	5.49	1.96
618	7.5×10^{-4}	5.49	1.92
575	1×10^{-3}	4.62	2.06
517	1×10^{-3}	4.62	2.23
618	1×10^{-3}	4.93	2.07
575	5×10^{-3}	5.72	2.00
517	5×10^{-3}	4.76	1.99
618	5×10^{-3}	5.18	1.92
575	7.5×10^{-3}	4.95	2.00
517	7.5×10^{-3}	4.63	2.30
618	7.5×10^{-3}	5.62	2.09
575	1×10^{-2}	6.00	1.97
575	1×10^{-2}	5.14	2.15
517	1×10^{-2}	6.00	2.02
517	1×10^{-2}	5.14	2.03
618	1×10^{-2}	5.14	1.91
618	1×10^{-2}	4.60	2.07
		av	2.0×10^{-8}

has been done,[1] with Zn^{2+} and tetrakis(*N*-methyl-2-pyridyl)porphyrin ($H_2TMpyP(2)$). While the results indicated that eq 1 was followed, $H_2TMpyP(2)$ is a peculiar porphyrin[2] in that only the free base H_2P form exists in acidic solutions, while most other porphyrins are mixtures of H_2P, monocations H_3P^+, and dications H_4P^{2+} (P = porphyrin) in the same pH ranges.[3] Due to the multiplicity of porphyrin types present in solution, the high K_e^M values for most metals, and the long time periods needed to reach equilibrium, K_e^M values have only been estimated for zinc porphyrins, from the ratio of the metal–porphyrin formation rate constants, k_f^M, and the acid-catalyzed dissociation rate constants, k_r^M. The conclusion, obtained from kinetic measurements made under diverse conditions, was that the most "stable" zinc porphyrins (high K_e^{Zn}) are formed from porphyrins that are the weakest Brønsted bases toward protons.[1]

We wish to report a study of the mass law derived equilibrium constants and formation rate constants of five water soluble and monomeric[4] porphyrins with Cd^{2+}. The results give further insight into the nature of metal–porphyrin interactions.

Experimental Section

The porphyrins tetrakis(*N*-methyl-4-pyridyl)porphyrin ($H_2TMpyP(4)$),[5] its 3 ($H_3TMpyP(3)$) and 2 isomers,[2] tetrakis(*N*,*N*,*N*-trimethyl-4-anilinium)porphyrin (H_2TAP),[6] and 5-phenyl-10,15,20-tris(*N*-methyl-4-pyridyl)porphyrin (H_2TMpy_3P),[7] were prepared by literature methods as the iodide or perchlorate salts. A simple method to redissolve such compounds is to warm the porphyrin salt in water in the presence of the appropriate anion-exchange resin, to form the water soluble nitrates in this case or the chlorides. The reaction studied was

$$Cd^{2+} + H_2P = CdP + 2H^+ \quad K_e^{Cd}, k_f^{Cd}, k_r^{Cd} \qquad (2)$$

All work was done at 25 °C, at an ionic strength of 0.2 ($NaNO_3$) in unbuffered solutions for the equilibrium measurements or in the presence of 2.5×10^{-2} M MES (4-morpholineethanesulfonic acid) buffer for the kinetic studies. K_e^{Cd} for $H_2TMpyP(4)$ was found to be 7% lower in the presence of the buffer.

Table II. Equilibrium and Rate Data for Cadmium Porphyrins (25 °C)

porphyrin[a]	pK_3[b]	K_e^{Cd},[c,d]	k_f^{Cd}, $M^{-1}\ s^{-1}$	k_r^{Cd}, $M^{-2}\ s^{-1}$
$H_2TMpyP(2)$	~−0.9	7.9×10^{-7}	6.9_3	8.8×10^6
$H_2TMpyP(4)$	1.4	2.0×10^{-8}	39.6	2.0×10^9
$H_2TmpyP(3)$	1.8	7.7×10^{-9}	51.7	6.7×10^9
$H_2TMpyP(4)$	2.4	6.1×10^{-9}	91.2	1.5×10^{10}
H_2TAP	3.6	1.7×10^{-10}	86.6	5.1×10^{11}

[a] The names of the porphyrins are found in the text. [b] pK_3 is for the porphyrin monocation dissociation reaction (H_3P^+/H_2P). [c] The ionic strength is 0.2 ($NaNO_3$). [d] $K_e^{Cd} = (CdP)(H^+)^2/(H_2P)\cdot(Cd^{2+})$, where $K_e^{Cd} = k_f^{Cd}/k_r^{Cd}$.

Typically, small volumes of acid or base and various amounts of solid cadmium nitrate were added to 400 mL of a stirred ca. 10^{-5} to 10^{-6} M solution of the porphyrin in a water-jacketed flask. The absorption spectra as a function of pH (7.5–3.0) and Cd^{2+} (5×10^{-4} to 1×10^{-2} M) were monitored after waiting several minutes for equilibrium to be attained. For example at pH 7 with (Cd^{2+}) = 1×10^{-2} M, CdTMpyP(4) is fully formed and shows λ_{max}, nm (log ε), values of 618 (3.83), 575 (4.14), and 445 (5.23). The pattern is similar to cadmium tetraphenylporphyrin in benzene.[8] As this CdTMpyP(4) solution is titrated with acid to pH 3, isosbestic points are found at 690, 654, 485, and 433 nm, as the free base $H_2TMpyP(4)$ is formed. Further addition of acid leads to the mono- and dication porphyrins. Addition of base to pH 7 re-forms the cadmium porphyrin. The ratio (CdP)/(H_2P) or (H_2P)/(porphyrin total) can be determined from the spectral changes, and K_e^{Cd} can be calculated. Table I shows that K_e^{Cd} values for CdTMpyP(4) calculated from the major $H_2TMpyP(4)$ band (517 nm) or from the CdTMpyP(4) peaks (575 and 618 nm) are in agreement.

After obtaining K_e^{Cd} for each porphyrin, we chose conditions such that the ratio (CdP)/(H_2P) at equilibrium was greater than 10^3. The rate law for CdP formation under such conditions was found to be first order in porphyrin, first order in cadmium, and independent of pH. The specific rate constant under such conditions was considered to be k_f^{Cd}.

Results and Discussion

Table II lists the K_e^{Cd}, k_f^{Cd}, and k_r^{Cd} ($=k_f^{Cd}/K_e^{Cd}$) values for the five porphyrins studied. pK_3 for the porphyrin reaction

$$H_3P^+ = H_2P + H^+ \qquad (3)$$

is also tabulated, as a measure of relative porphyrin basicity. The cadmium porphyrin reactions come to equilibrium quickly and have rather small K_e^{Cd} values. Since the pK_a for[9] $Cd^{2+}/CdOH^+$ is ca. 10 and the pK_3 for the most basic porphyrin is 3.6, the reaction of unhydrolyzed cadmium ions with the free base porphyrin is readily accomplished. Equation 2 was found to describe the complexation of Cd^{2+} (and Zn^{2+})[1] with the porphyrins. It has been reported that hydrolyzed Hg(II) at pH 7 forms 2:1 mercury to porphyrin complexes.[10]

The directly measured M_e^M values for the cadmium porphyrins follow the same trend as the kinetically determined K_e^M constants in the zinc–porphyrin system.[1] The most stable metalloporphyrin is formed by the least basic porphyrin. The results of the two systems are internally consistent. The ratio of the K_e^M for $H_2TMpyP(2)$ and $H_2TMpyP(4)$ is 43 for the zinc porphyrins and 40 for the corresponding cadmium porphyrins.

The cadmium complex of the least basic porphyrin $H_2TMpyP(2)$, having pK_3 ca. −0.9, is 4600 times more stable than that of the most basic porphyrin, H_2TAP ($pK_3 = 3.6$). The rate constants k_f^{Cd} for the formation of the cadmium porphyrins are similar; they vary by a factor of 13 along the series. The magnitudes of the reverse rate constants, k_r^{Cd},

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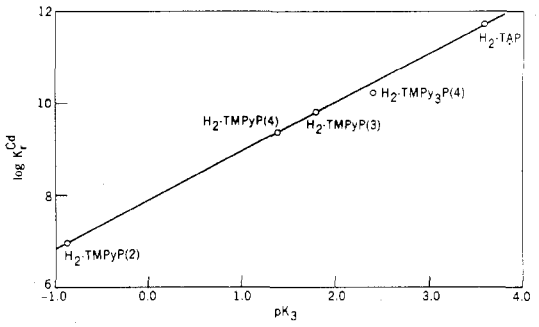

Figure 1. Plot of the log of the cadmium porphyrin dissociation rate constants, k_r^{Cd}, vs. the porphyrin protonation parameter, pK_3.

therefore primarily determine the trend in the K_e^{Cd} values. k_r^{Cd} ranges from 5×10^{11} M^{-2} s^{-1} for CdTAP to 9×10^6 M^{-2} s^{-1} for CdTMpyP(2), a factor of 58 000. The zinc porphyrins basically follow the same trend.[1]

Aside from H_2TMpyP(2) which shows atypical behavior,[2] it is becoming clear that metal–porphyrin formation rates for similarly charged porphyrins are relatively independent or increase slightly with an increase in porphyrin basicity. This is found for the cadmium porphyrins in this study and for both the Cu^{2+}/meso-substituted tetraphenylporphyrins[11] and the Zn^{2+}/3,8-disubstituted deuteroporphyrin ester[12] metalation reactions. The metalloporphyrin acid-catalyzed dissociation reactions usually depend on porphyrin basicity. A linear relationship was noted between log k_r^{Zn} and pK_3 for the H^+/3,8-disubstituted deuteroporphyrin ester zinc complex reactions in methanol.[13] Figure 1 shows that a similar relationship of the form

$$\log k_r^{Dd} = 1.05pK_3 + 7.85 \quad (4)$$

holds for these meso-substituted CdP reactions in aqueous solution. log K_e^{Cd} is also linearly related to pK_3 in the same fashion.

For H_2TMpyP(4),[1] the ratio k_f^{Cd}/k_f^{Zn} is 10^3, while the dissociation rate ratio k_r^{Cd}/k_r^{Zn} is 10^{11}. The zinc porphyrins are thus 10^8 times more stable than their corresponding cadmium porphyrin counterparts. The greater lability of aquo Cd^{2+} as compared to Zn^{2+} partially explains the formation rate differences. The smaller charge/radius ratio of Cd^{2+} as opposed to that of Zn^{2+} and the fact that cadmium probably lies further out of the mean porphyrin plane than does zinc both suggest weaker metal to porphyrin bonding in cadmium porphyrins. This in turn might favor a higher (than with zinc) equilibrium concentration of porphyrins where the cadmium ion is bonded to three (rather than four) central porphyrin nitrogen atoms, producing intermediates having vacant coordination positions for proton attack. The higher equilibrium concentration of such reactive entities in cadmium–porphyrin systems would lead to faster acid-solvolysis rates.

The kinetics of the electrophilic substitution of Zn^{2+} for Cd^{2+} in cadmium porphyrins has been studied,[14] and as with the H^+/CdP reactions, the Zn^{2+}/CdP rates depend strongly on porphyrin basicity. At ambient temperatures, cadmium coordinated to the more basic porphyrin is displaced faster by Zn^{2+}. Such displacement rates parallel[15,16] the relative porphyrin basicity parameter, $E_{1/2}^r(1)$, the reduction potential of the free base porphyrin forming the radical anion $H_2P^{-\cdot}$.

A number of studies are appearing on the uses of water-soluble porphyrins for the analytical determination of low concentrations of metal ions.[17,18] Our present results indicate what porphyrin factors lead to maximal complexation in aqueous solutions.

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Synthesis and Characterization of a Hydroxycarbonyl Complex of Platinum: *trans*-[PtCl(COOH)(PEt_3)$_2$]

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(Hydroxycarbonyl)metal complexes, [L_nM–COOH], have been postulated as intermediates in the oxidation of (free or coordinated) CO by metal ions,[1-3] in the isotopic oxygen exchange of metal carbonyls with H_2O,[4,5] in the homogeneous catalysis of the water-gas shift reaction,[6] and in reactions (exemplified by eq 1) of metal carbonyls with water to form the corresponding hydrides.[7,8] Notwithstanding the widespread roles attributed to such species as transient intermediates in a variety of important reactions, only a few hydroxycarbonyl complexes have actually been isolated and even partially characterized.[9-12] We now wish to report the synthesis, isolation, and direct characterization of the (hydroxycarbonyl)platinum complex, *trans*-[PtCl(COOH)(PEt_3)$_2$] (**2**). We also present evidence for the previously postulated role of **2** as an intermediate in the reaction of *trans*-[PtCl(CO)(PEt_3)$_2$]$^+$ (**1**) with water (eq 1).[8] In addition we describe the first characterization of a hydroxycarbonyl complex, *trans*-[PtCl(^{13}COOH)(PEt_3)$_2$], by ^{13}C NMR.

$$\underset{\mathbf{1}}{trans\text{-}[PtCl(CO)(PEt_3)_2]^+} \xrightarrow[-H^+]{H_2O} \underset{\mathbf{2}}{trans\text{-}[PtCl(COOH)(PEt_3)_2]} \xrightarrow{-CO_2} trans\text{-}[PtHCl(PEt_3)_2] \quad (1)$$

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