

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

THE EFFECTS OF PERIPHERAL SUBSTITUENTS ON THE KINETICS OF ZINC ION INCORPORATION AND ACID CATALYZED REMOVAL FROM WATER SOLUBLE SULFONATED PORPHYRINS

Timothy P. G. Sutter^a; Peter Hambright^a

^a Chemistry Department, Howard University, Washington D.C, USA

To cite this Article Sutter, Timothy P. G. and Hambright, Peter(1993) 'THE EFFECTS OF PERIPHERAL SUBSTITUENTS ON THE KINETICS OF ZINC ION INCORPORATION AND ACID CATALYZED REMOVAL FROM WATER SOLUBLE SULFONATED PORPHYRINS', *Journal of Coordination Chemistry*, 30: 3, 317 – 326

To link to this Article: DOI: 10.1080/00958979308022765

URL: <http://dx.doi.org/10.1080/00958979308022765>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE EFFECTS OF PERIPHERAL SUBSTITUENTS ON THE KINETICS OF ZINC ION INCORPORATION AND ACID CATALYZED REMOVAL FROM WATER SOLUBLE SULFONATED PORPHYRINS

TIMOTHY P.G. SUTTER and PETER HAMBRIGHT*

Chemistry Department, Howard University, Washington D.C. 20059, USA

(Received March 1, 1993; in final form May 24, 1993)

The kinetics of Zn^{2+} and $Zn(OH)^+$ incorporation into and the kinetics of the acid catalyzed removal of Zn(II) from twelve water-soluble, sulfonated derivatives of tetraphenylporphyrin with alkyl or halogen groups in the *para*, *ortho* or *di-ortho* positions were investigated. While the incorporation reactions showed little dependence on porphyrin basicity, the Zn-P (P = porphyrin derivative) acid solvolysis reactions were faster the higher the basicity of the free base (H_2 -P) compound. Equilibrium constants for the formation of cadmium porphyrins decreased with an increase in porphyrin basicity. The predeformed tetrakis(4-sulfonatophenyl)- β -octabromo-porphyrin reacted with Zn^{2+} about 10^3 times faster than porphyrins of similar basicity. These results indicate how substituents on the phenyl and beta-pyrrole rings influence the solution chemistry of water soluble porphyrins.

KEYWORDS: Zinc, water soluble, porphyrins, kinetics

INTRODUCTION

Kinetic studies aimed at elucidating the mechanisms of metal incorporation into series of related uncharged free base porphyrins in non-aqueous media are always complicated by uncertainties in the solvation sphere and nature of the metal ion reactant, the levels of protons, water or other Lewis bases present in the solvent, and intermolecular association of such porphyrins themselves.¹⁻⁷ In water, however, the various forms that many aquo ions⁸ and positive or negatively charged porphyrins can assume as a function of concentration, pH and ionic strength are fairly well understood.^{9,10} The tetrapositive porphyrins studied in aqueous solution have included tetrakis(4-N,N,N-trimethylanilinium)porphyrin (H_2 -TAP),¹¹ the 4 and 3 isomers of the tetrakis(X-quinolyl)porphyrins (H_2 -TQP(X)),¹² the 2, 3 and 4-isomers of tetrakis(N-methyl-X-pyridyl)porphyrin (H_2 -TMPyP(X)),^{13,14} and a water soluble picket fence tetra($\alpha,\alpha,\alpha,\alpha$ -*ortho*-(N-methyl-isonicotinamidophenyl)-porphyrin (H_2 -PF).¹⁵ Negatively charged species such as a number of carboxy porphyrins,^{16,17} the 2,4-disulfonated deuteroporphyrin-IX-dimethylester (H_2 -DPS₂),¹⁸ and tetrakis(4-

* Author for correspondence.

sulfonatophenyl)porphyrin (TPPS₄)¹⁹ have been examined. Kinetic comparisons also have been made between similarly charged porphyrins and chlorins.²⁰

We recently investigated²¹ the solution properties of twelve water soluble sulfonated porphyrins with alkyl or halogen groups in the *ortho* (2), *di-ortho* (2,6) or *para* (4) phenyl positions and found that their proton basicities varied over a range of 10⁵. We now report the kinetics of Zn²⁺/Zn(OH)⁺ incorporation and the kinetics of the acid catalyzed Zn²⁺ displacement reactions as well as the equilibrium constants for Cd(II)-porphyrin formation for this series of compounds. For comparison, metallation kinetics of the pre-deformed β-pyrrole substituted tetrakis(4-sulfonatophenyl)-β-octabromoporphyrin²² were examined. The results indicate how substituents on the phenyl rings influence the magnitudes and modes of porphyrin reactivity.

EXPERIMENTAL

Equilibrium and kinetics studies on the slower reactions were carried out on a Beckman DU 70 recording spectrophotometer, and faster kinetics were monitored using a Durrum-Gibson stopped-flow system. A Radiometer Copenhagen PHM 64 Research pH meter was used for all pH measurements. The water soluble sulfonated compounds (Table I) were prepared and purified as described previously.²¹ Zinc nitrate hydrate (99.999%) and cadmium nitrate tetrahydrate (99.999%) from Aldrich were analyzed by edta titrations, and lithium nitrate (99.99%), Aldrich was used as received.

The zinc ion incorporation kinetics were monitored at wavelengths between 413 and 419 nm, at the Soret band of the particular free-base porphyrin substrate,²¹ and the zinc-porphyrin demetallation reactions were also monitored in the Soret, at

Table I Proton equilibria, Zn²⁺/Zn(OH)⁺ incorporation and Zn-P acid solvolysis kinetics and the Cd²⁺/H₂-P equilibrium constants for a series of TPPS₄ derivatives.

Porphyrin	Basicities ^a	Zn(II) Incorporation		Acid Solvolysis	Cd ²⁺ Eq
	pK ₃ /pK ₄	Zn ²⁺ /H ₂ -P k ₁ (M ⁻¹ s ⁻¹)	Zn(OH) ⁺ /H ₂ -P k ₂ (s ⁻¹)	Zn-P/H ⁺ K ₅ k ₆ (M ⁻² s ⁻¹)	pK _{Cd}
4-OCH ₃	7.1/6.3	(8.2 ± 0.3) × 10 ^b	^c	(2.3 ± 0.1) × 10 ²	—
4-F	6.5/5.3	3.1 ± 0.2 ^b	^d	(3.6 ± 0.1) × 10	—
4-CH ₃	4.9/4.9	1.7 ± 0.1	(3.0 ± 3.) × 10	(4.0 ± 0.1) × 10	10.3
4-Cl	4.9/4.8	1.0 ± 0.1	(8.9 ± 0.5) × 10	9.1 ± 0.1	10.1
β-Br ₈	4.8/1.4	(3.0 ± 0.1) × 10 ³	(1.9 ± 0.1) × 10 ³	—	—
TPPS ₄	4.7/4.8	1.2 ± 0.1	(3.1 ± 0.3) × 10	(2.2 ± 0.1) × 10	10.3
2-OCH ₃	4.1/3.8	1.7 ± 0.2	(7.3 ± 0.7) × 10	1.6 ± 0.1	9.8
2-CH ₃	3.4/2.1	(8.0 ± 0.5) × 10 ⁻¹	(1.8 ± 0.2) × 10	5.3 ± 0.1	9.7
2-Cl	3.3/2.7	(6.1 ± 0.7) × 10 ⁻¹	(3.3 ± 0.2) × 10	(7.1 ± 0.1) × 10 ⁻¹	9.1
2-F	3.3/3.1	(6.4 ± 0.2) × 10 ⁻¹	(2.5 ± 0.1) × 10	(7.0 ± 0.1) × 10 ⁻¹	9.5
2,6-OCH ₃	3.0/2.6	(2.0 ± 0.1) × 10 ⁻¹	3.5 ± 0.2	(2.2 ± 0.1) × 10 ⁻¹	9.3
2,6-F	2.5/1.8	(3.1 ± 0.7) × 10 ⁻¹	(6.0 ± 0.3) × 10	(3.5 ± 0.1) × 10 ⁻²	8.1
2,6-Cl	1.8/1.7	(4.9 ± 0.3) × 10 ⁻³	3.5 ± 0.1	(3.0 ± 0.1) × 10 ⁻²	8.7

^a Data from ref. 21 ^b The "k₁" is [k₁ + (k₄K_H/K₃)] for these compounds. ^c The [Zn²⁺/H₃-P⁺] reaction has k₃ = (9.9 ± 0.5) M⁻¹ sec⁻¹. ^d k₃ = (1.2 ± 0.1) M⁻¹ sec⁻¹.

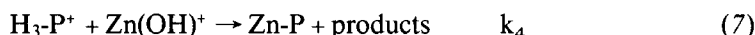
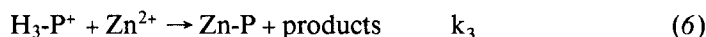
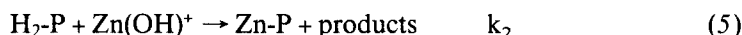
either the di-acid (431–445 nm) or the Zn-P peak (417–429 nm). The parameters for all linear relationships were obtained by the least-squares method.

The sodium salt of tetrakis(4-methoxy-3-sulfonatophenyl)porphyrin is abbreviated as 4-OCH₃ and all of the compounds (other than the 4-sulfonated H₂-TPPS₄ and β-Br₈ species) are sulfonated at one 3-phenyl position. The tetranegative charges due to the -SO₃⁻ substituents are neglected for clarity, and M(H₂O)₆²⁺ is abbreviated M²⁺ or M(H₂O)²⁺.

RESULTS

Zn(II) incorporation kinetics

The kinetics of Zn(II) incorporation into the porphyrins were investigated at 25°C in 0.050 M LiNO₃ from pH 6.2 to 7.2 over a five-fold range in Zn(NO₃)₂. Such solutions contained 2.0 mM PIPES, [piperazine-N-N'-bis (2-ethanesulfonic acid), pK_a = 6.8], as the buffer, and the porphyrin concentrations were ~10⁻⁷ M. The reactions were first order in porphyrin with an observed rate constant k_{obs}, and also first order in [Zn(II)]. The reactions considered were



The dependence of k_{obs} on (H⁺) and [Zn(II)] is:

$$\{(k_{\text{obs}})Z_{\text{Zn}}Q_{\text{P}}\}/[\text{Zn}(\text{II})] = (k_1 + k_4K_h/K_3) + (k_2K_h)/(H^+) + k_3(H^+)/K_3 \quad (8)$$

In equation (8), Q_{Zn} = ((H⁺) + K_h)/(H⁺) where (1/Q_{Zn}) is the fraction of Zn(II) as Zn²⁺ and K_h = 2.92 × 10⁻⁹ at I = 0.050 M.⁸ The fraction of total porphyrin as the H₂-P is Q_P, where Q_P = (K₃K₄ + K₄(H⁺) + (H⁺)²)/K₃K₄.

The two most basic porphyrins, 4-OCH₃ and 4-F, have significant amounts of H₂-P and the monocation H₃-P⁺ present from pH 6.2 to 7.2, and both react with Zn(II). Figure 1 shows the linear relationship found between {(k_{obs})(Q_{Zn})(Q_P)/[Zn(II)]} and (H⁺) for 4-F in accord with equation (9).

$$\{(k_{\text{obs}})(Q_{\text{Zn}})(Q_{\text{P}})/[\text{Zn}(\text{II})]\} = \{k_1 + (k_4K_h/K_3)\} + (k_3(H^+)/K_3) \quad (9)$$

The other ten compounds are less basic, and only H₂-P is in appreciable concentration (Q_P ~ 1) between pH 6.2 and 7.2. Figure 1 (insert) shows a linear plot of {(k_{obs})(Q_{Zn})/[Zn(II)]} vs. (H⁺)⁻¹ for the 2-F derivative, in agreement with equation (10):

$$\{(k_{\text{obs}})(Q_{\text{Zn}})/[\text{Zn}(\text{II})]\} = k_1 + (k_2K_h)/(H^+) \quad (10)$$

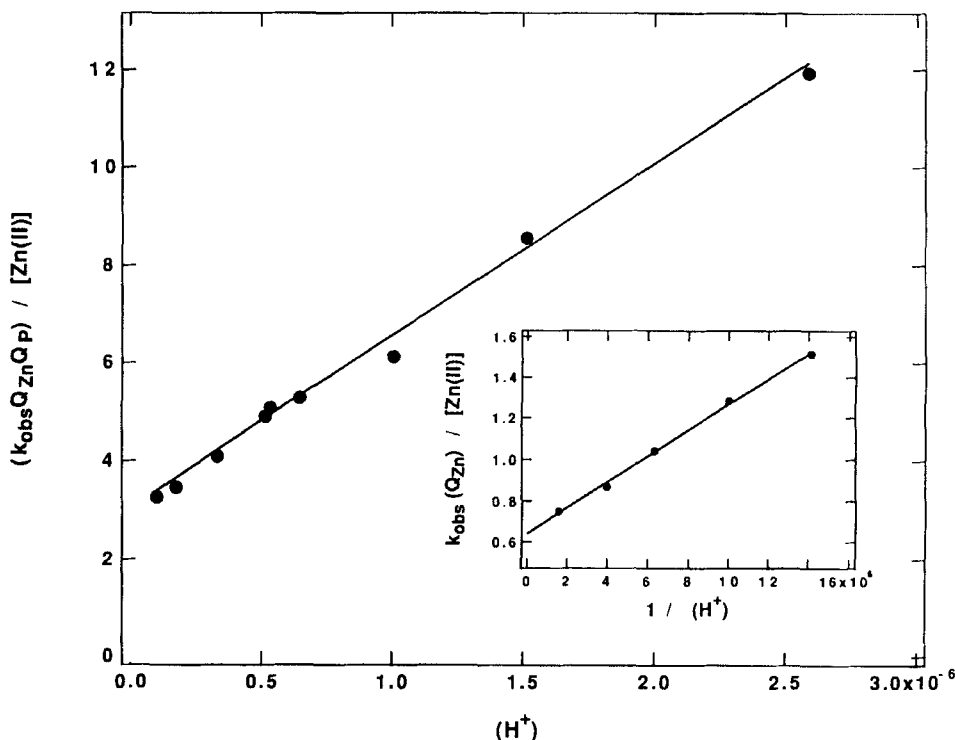
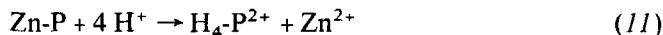


Figure 1 Graph of equation 9 for zinc incorporation into the 4-F porphyrin. (Insert). Plot of equation 10 for the reaction of Zn(II) with the 2-F compound.

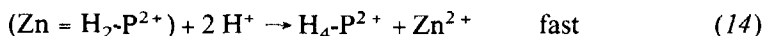
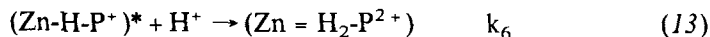
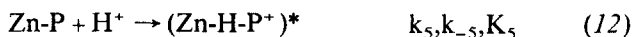
The β -octabromo derivative also followed equation (10), and the Zn(II) incorporation kinetic results for all compounds are listed in Table 1.

Acid solvolysis kinetics of Zn-porphyrins

The kinetics of protons replacing Zn^{2+} in Zn-porphyrins was studied spectrophotometrically in 0.50 M LiCl solutions with HCl at 25°C. The stoichiometry of the reactions are



The empirical rate law was first order in (Zn-P). For most of the porphyrins, the reactions were second order (Figure 2) in (H^+) . For the 2-Cl and 2,6-Cl derivatives, the kinetics were best described as between first and second order in (H^+) . A mechanism that encompasses both observations is:



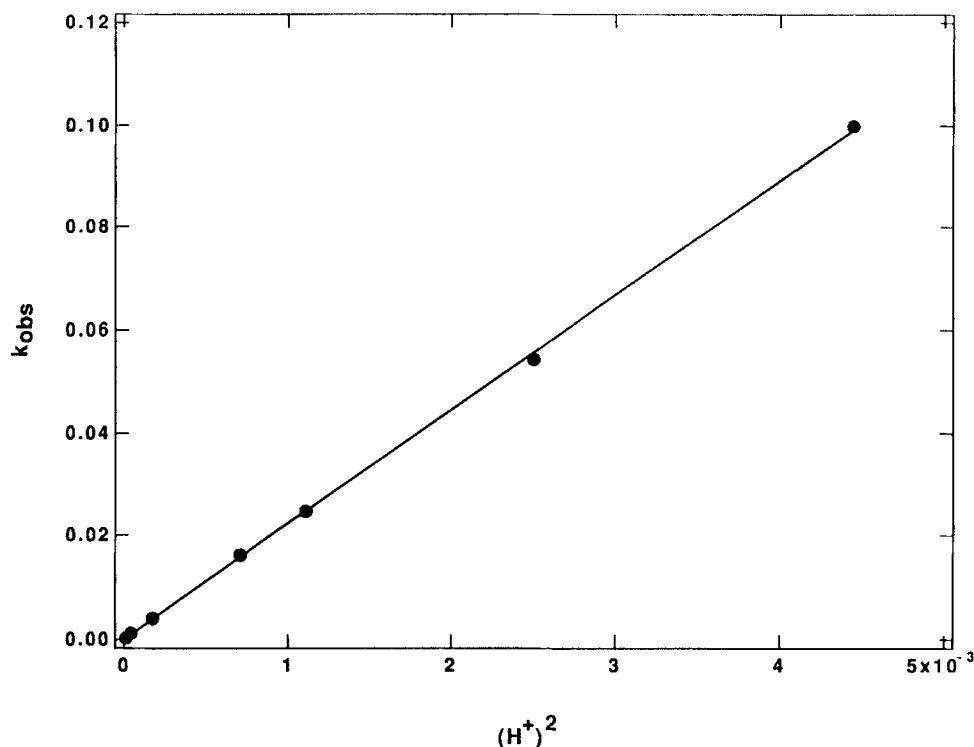


Figure 2 Graph of k_{obs} vs. $(H^+)^2$ for the acid solvolysis reaction of Zn(II)-TPPS₄.

With $(Zn-H-P^+)^*$ as a steady state intermediate, the dependence of k_{obs} on (H^+) is

$$k_{obs} = k_5(H^+)^2 / [(k_{-5}/k_6) + (H^+)] \quad (15)$$

If $(k_{-5}/k_6) \gg (H^+)$, then, as observed for the majority of the porphyrins, $k_{obs} = K_5 k_6 (H^+)^2$ and the $(K_5 k_6)$ values are compiled in Table 1. For 2-Cl, $k_5 = (3.9 \pm 0.4) \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ and $(k_{-5}/k_6) = (0.91 \pm 0.01) \text{ M}$ while for 2,6-Cl, $k_5 = (2.7 \pm 0.3) \times 10^{-2}$ and $(k_{-5}/k_6) = (0.55 \pm 0.01)$.

Formation constants for cadmium-porphyrins

Mass law based equilibrium constants (K_{Cd}) for the reaction



were measured as a function of (Cd^{2+}) and pH (~5 to 7.3) at 25°C in 0.20 M $NaNO_3$ in solutions buffered with 1.0 mM MES (4-morpholine-ethane sulfonic acid, $pK_a = 6.12$) by spectrophotometric titrations. $Cd(NO_3)_2$ of the highest purity was used to guard against Cd(II)-P catalyzed transmetallation reactions involving trace metallic impurities.²³ The K_{Cd} results are listed in Table 1.

DISCUSSION

Zn(II) incorporation kinetics

This study of twelve water soluble tetrasulfonated porphyrins demonstrates how the nature and position of the substituents placed on the phenyl rings influence porphyrin reactivity. As shown previously,²¹ the *para* substituted compounds and H_2 -TPPS₄ exhibit monomer-dimer equilibria ($K_D \sim 10^4 M^{-1}$) in solution, while the *ortho* and di-*ortho* derivatives are essentially monomeric, showing no spectrophotometric or temperature-jump relaxation evidence of dimerization ($K_D < 10^2 M^{-1}$) at total porphyrin levels below $10^{-4} M$ and electrolyte concentrations $< 0.80 M$. The Zn(II) incorporation kinetics were run at $\sim 10^{-7} M$ in total porphyrin, where all of the compounds are $> 95\%$ in the monomeric form.

Figure 3 is a plot of $\log(k_1)$ vs. pK_3 , and for ten of the compounds, the linear relationship $\log(k_1) = 0.26 pK_3 - 1.13$ was found. These Zn^{2+}/H_2 -P reactions show a minimal 1.8 fold increase in rate constants with a ten-fold increase in porphyrin basicity. In related work, the kinetics of incorporation of Zn(II) into 4-substituted tetraphenylporphyrins were studied in DMF.¹ For porphyrins with non-resonating substituents, the rate constants were also relatively insensitive to porphyrin basicity.

In the present work, we find that $Zn(OH)^+$ reacts from 20–90 times faster with H_2 -P than Zn^{2+} . As noted before, this could be due to the more rapid water exchange rate and differing geometry of the hydrolyzed zinc species.^{11,13}

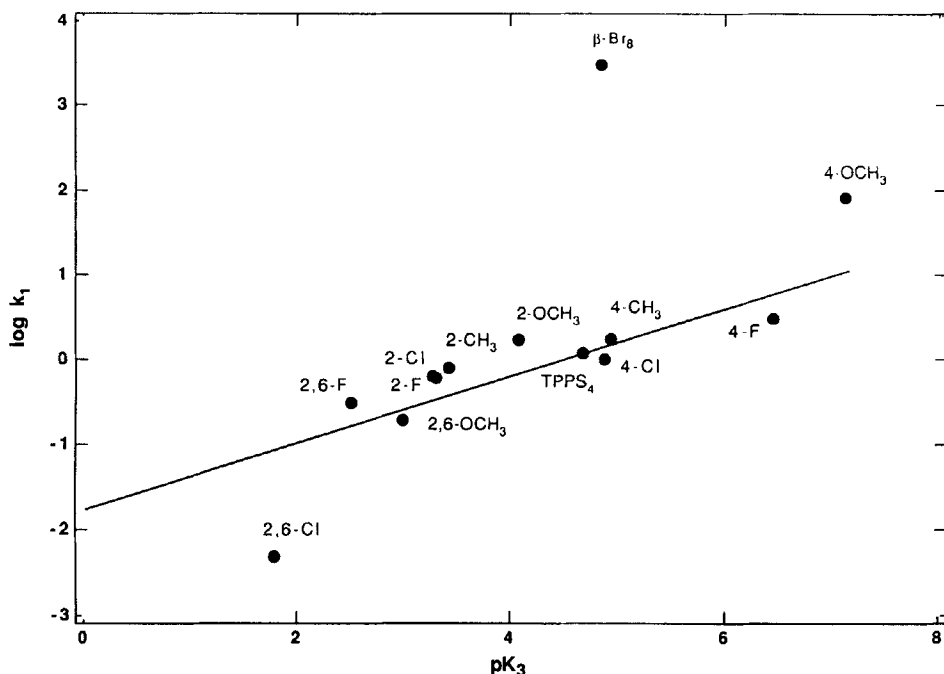


Figure 3 Plot of $\log k_1$ vs. pK_3 for Zn^{2+} incorporation into the H_2 -P forms of the water soluble porphyrins.

The β -Br₈ porphyrin is predeformed,²² due to the large bromine atoms replacing the eight β -pyrrole hydrogens, and reacts with Zn²⁺ approximately 1.5×10^3 times faster than porphyrins in this series having similar basicities. The predeformed dodecaphenyl²⁴ and octabromo-tetramesityl¹ porphyrins metallate more rapidly than their more planar counterparts in DMF. The predeformed centrally N-alkylated porphyrins are also both more basic and $\sim 10^3$ times more reactive with metal ions than their less distorted H₂-P precursors.²⁵⁻²⁷

In detailed studies on the pH dependence of metal ion incorporation into water soluble porphyrins (H₂-TAP,¹¹ H₂-TMPy(4),¹³ H₂-TMPy(2),¹⁴ H₂-TQP(4,3),¹² H₂-DPS₂,⁸ N-Methyl-TPPS₄²⁶ and Uroporphyrin-1⁷) the H₃-P⁺ and H₄-P²⁺ species have been shown to be unreactive towards cations, and metallation occurred only through the free base H₂-P form. Our results on the 4-OCH₃ and 4-F derivatives clearly show that H₃-P⁺ reacts with Zn²⁺. At this stage, it is not entirely clear why H₃-P⁺ is active with the very basic fluoro and methoxy compounds, and not with the other less basic porphyrins. This unexpected result might be rationalized along the following lines. Reasonable resonance structures can be drawn in which the 4-F and 4-OCH₃-phenyl groups are in conjugation with the porphyrin *meso* carbon atoms, and such structures, which invoke electron donating resonance effects, can formally add negative charges at the central nitrogen atoms.²⁸ Such conjugation also deforms the porphyrin nucleus, tilting the negatively charged nitrogen atoms out of the porphyrin cavity towards the solvent, thus breaking up the N-H tautomerism of the two central protons around the four core nitrogens.¹⁰ This resonance and bending explains the increased proton basicity of the 4-F and 4-OCH₃ porphyrins, and might account for the observed reactivity of the H₃P⁺ forms of these compounds towards Zn²⁺. In the porphyrins mentioned above where H₃-P⁺ is non-reactive, such electron donative conjugative effects are absent. It is noted that the 4-NH₂, 4-OH, 4-N(CH₃)₂ and 4-OCH₃ phenyl porphyrins containing substituents that lead to phenyl ring conjugation with the porphyrin nucleus, are the most reactive towards porphyrin metallation in DMF.^{1,2}

Of all of the compounds in this study, the 2,6-Cl porphyrin has the lowest proton basicity, and reacts most slowly with the two forms of Zn(II). The rigidity imposed on the porphyrin nucleus by the two *ortho* chloro groups inhibits the necessary buckling which precedes metallation, and accompanies H₃-P⁺ and H₄-P²⁺ formation. In line with these notions, pulse radiolysis work indicate that the addition of two electrons to many porphyrins, such as H₂-TPPS₄, results in phlorin (*a proton added at the meso carbon atom*) formation, while reduction of the 2,6-Cl derivative produces a chlorin, where protonation is at the less hindered β -pyrrole carbons.²¹ The *ortho* chloro groups prevent deformation of the porphyrin into the sp³ hybridization necessary for protonation at the *meso* positions.

It is becoming apparent that metallation kinetics in non-aqueous solvents (DMF,¹⁻³ DMSO,⁵ DMF/H₂O²⁹ HAc⁷ and pyridine²⁰) usually give evidence of pre-equilibrium complexation between the metal and the uncharged porphyrin molecule. While such an interaction has never been noted in aqueous solution for metal ion incorporation reactions, it has been demonstrated in water for various electron transfer³⁰ and chelate demetallation processes.³¹

Zn-P acid solvolysis kinetics and Cd-P formation constants

Figure 4 shows a linear free energy relationship between log (K₅ k₆) for the acid solvolysis reactions of Zn-P and the porphyrin basicity, pK₃. The zinc complexes of

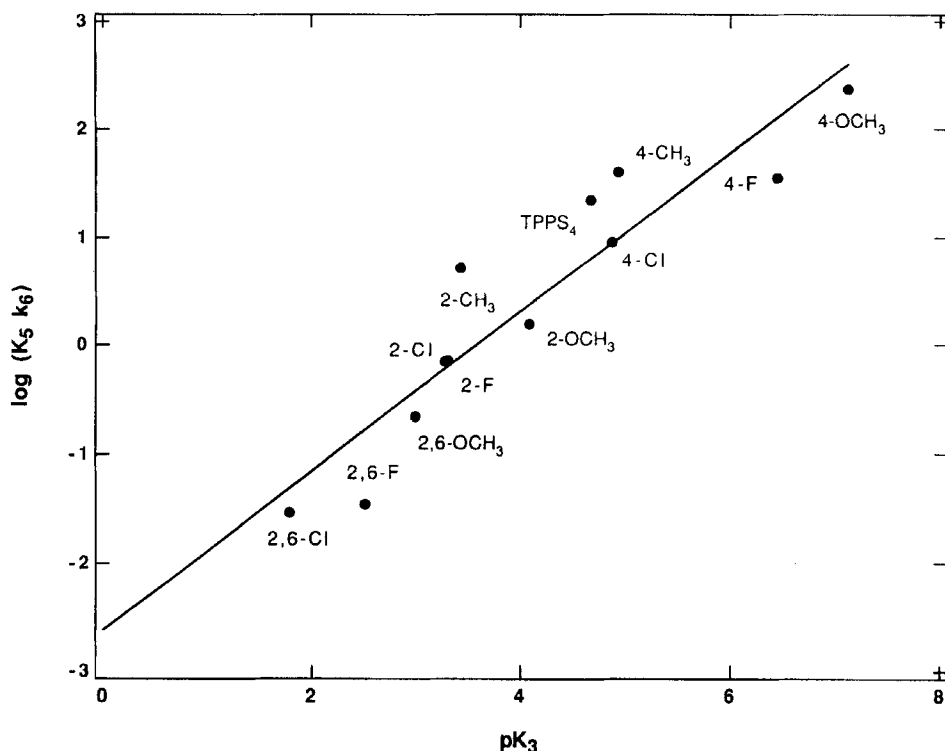


Figure 4 Graph of $\log(K_5 k_6)$ vs. pK_3 for the acid solvolysis reactions of Zn(II)-porphyrins.

the most basic free base porphyrins are solvolyzed by protons most rapidly. Since $\log(K_5 k_6) = 0.99 pK_3 - 3.5$, a unit increase in pK_3 leads to roughly a ten-fold rate enhancement. Figure 5 is a graph of $\log(K_{Cd})$ vs. pK_3 , where $\log(K_{Cd}) = -0.66 pK_3 - 7.1$. The directly determined equilibrium constant K_{Cd} is the ratio of the $[Cd^{2+} + H_2-P]$ formation and the $[Cd-P + 2(H^+)]$ acid dissociation rate constants. As noted for the zinc porphyrins, while the formation rate constants are fairly insensitive to basicity, the acid catalyzed dissociation rate constants increase with an increase in porphyrin basicity. Thus, at a given pH, the Cd-P complex of the least basic porphyrin is favored. Similar equilibrium constant/basicity trends have been found for positively charged porphyrins with Zn(II),³² Cd(II),²³ Pb(II)³³ and Hg(II).³⁴

SUMMARY

Metallation reactions of porphyrin molecules are generally viewed from a dissociative interchange framework.^{7,9,10,13} The metal and porphyrin first form an outer sphere complex,^{35,36} and the porphyrin nucleus deforms to present reactive lone pair nitrogen atoms to the incoming metal ion. The metal dissociates a solvent molecule(s) in a step independent of the nature of the porphyrin substrate. The rate

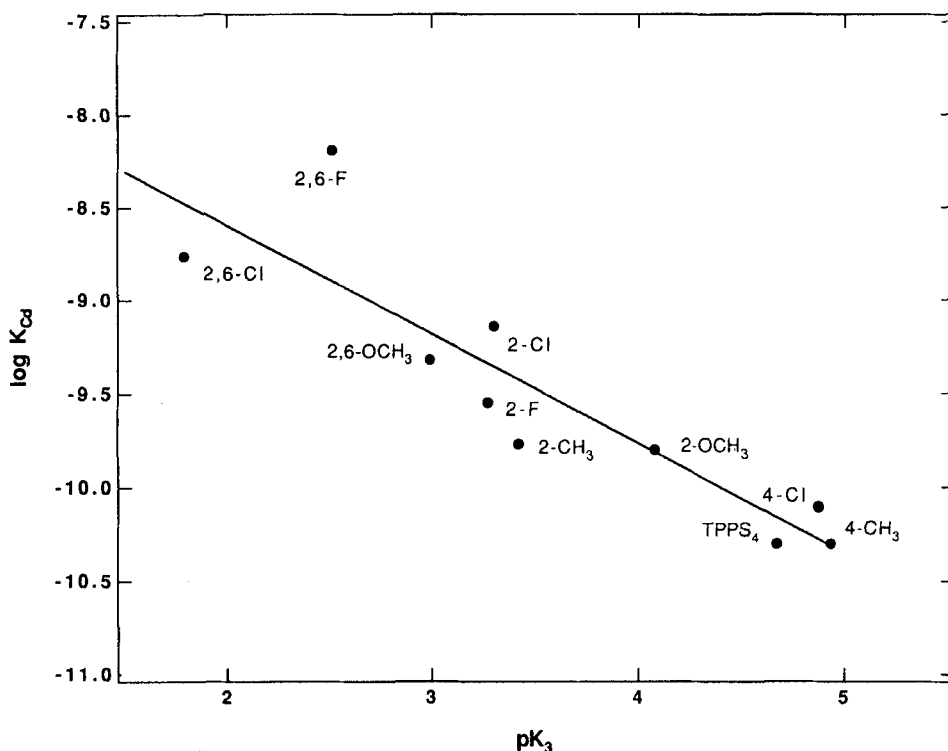


Figure 5 Graph of $\log(K_{Cd})$ vs. pK_3 for the equilibrium constants of the Cd^{2+}/H_2-P reactions.

determining reaction involves an activated complex containing the metal ion and H_2-P form of the molecule. Our present results are in accord with this scheme. The porphyrins examined have the same peripheral tetranegative charge and are expected to have similar outer sphere pre-equilibrium constants. The pre-deformed β -octabromo compound reacts with Zn^{2+} $\sim 10^5$ faster than the less deformable 2,6-Cl macrocycle, and $\sim 10^3$ times faster than porphyrins of the same basicity. Electron donating resonance interactions from the *para* fluoro and methoxy substituents leads to porphyrin core deformation, which activates their protonated H_3-P^+ species towards metal ion incorporation. The porphyrins without such features which strongly influence ring deformation react at similar rates with a given form of the metal ion, over a wide range of porphyrin basicity. The Zn-P complexes, however, where the metal is coordinated to the porphyrin, are sensitive to porphyrin basicity effects. The rate constants for the acid catalyzed solvolysis reactions are faster the more basic the porphyrin.

References

1. L.R. Robinson and P. Hambright, *Inorg. Chim. Acta*, **185**, 17 (1991).
2. F. Longo, E. Brown, D. Quimby, A. Adler and M. Meot-Ner, *Ann. NY. Acad. Sci.*, **206**, 420 (1973).

3. S. Funahashi, Y. Yamaguchi and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **57**, 204 (1984).
4. D. Lavallee and G. Onady, *Inorg. Chem.*, **20**, 907 (1980).
5. R.F. Pasternack, C.G. Vogel, C.A. Skowronek, R.K. Harris and J.C. Miller, *Inorg. Chem.*, **20**, 3763 (1981).
6. R. Freitag, and D. Whitten, *J. Phys. Chem.*, **87**, 3918 (1983).
7. M. Tanaka, *Pure Appl. Chem.*, **55**, 151 (1983).
8. C.F. Bases and R.E. Mesmer, "The Hydrolysis of Cations", 4th Edition Wiley — Interscience, New York, 1976.
9. D. Lavallee, *Coord. Chem. Rev.*, **61**, 55 (1985).
10. P. Hambright, "Porphyrins and Metalloporphyrins", Smith, K.M., Ed.; Elsevier, Amsterdam, 1975, Chap 6.
11. A.N. Thompson and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **41**, 1251–1255 (1979).
12. A. Adeyemo, A. Shamim, P. Hambright and R.F.X. Williams, *Indian J. Chem.*, **21A**, 763 (1982).
13. P. Hambright and P.B. Chock, *J. Am. Chem. Soc.*, **96**, 3123 (1974).
14. J.B. Reid and P. Hambright, *Inorg. Chem.*, **16**, 968 (1977).
15. A. Valiotti, A. Adeyemo, R.F.X. Williams, L. Ricks, J. North and P. Hambright, *J. Inorg. Nucl. Chem.*, **185**, 2653 (1981).
16. J. Turay and P. Hambright, *J. Inorg. Nucl. Chem.*, **41**, 1385 (1975).
17. A. Shamim and P. Hambright, *Inorg. Chem.*, **22**, 694 (1983).
18. J. Weaver and P. Hambright, *Inorg. Chem.*, **8**, 167 (1969).
19. S. Cheung, F. Dixon, E. Fleischer, D. Jeter and M. Krishnamurthy, *Bioinorg. Chem.*, **2**, 281 (1973).
20. T.P.G. Sutter and P. Hambright, *Inorg. Chem.*, **31**, 5089 (1992).
21. T.P.G. Sutter, R. Rahimi, P. Hambright, J. Bommer, M. Kumar and P. Neta, *J. Chem. Soc., Faraday Trans.*, **89**, 495 (1993).
22. P. Bhyrappa and V. Krishnan, *Inorg. Chem.*, **30**, 239 (1991).
23. A. Shamim and P. Hambright, *Inorg. Chem.*, **19**, 564 (1980).
24. J. Takeda, T. Ohya and M. Sato, *Inorg. Chem.*, **31**, 2877 (1992).
25. B. Shah, B. Shears and P. Hambright, *Inorg. Chem.*, **10**, 1828 (1971).
26. S. Funahashi, Y. Ito, H. Kakito, M. Inamo, Y. Hamada and M. Tanaka, *Mikrochim. Acta*, **4**, 33 (1986).
27. D.K. Lavallee, "The Chemistry and Biochemistry of N-Substituted Porphyrins", VCH Publishers, New York, 1987.
28. L.R. Milgrom, C.C. Jones and A. Harriman, *J. Chem. Soc., Perkin Trans. II.*, 71 (1988).
29. D.A. Buckingham, C.R. Clark and W.S. Webley, *J. Chem. Soc., Chem. Commun.*, 192 (1981).
30. R. Langley, P. Hambright and R.F.X. Williams, *Inorg. Chem.*, **24**, 3716 (1985).
31. S. Haye and P. Hambright, *J. Coord. Chem.*, **22**, 315 (1991).
32. P. Hambright, *Inorg. Chem.*, **16**, 2987 (1977).
33. S. Haye and P. Hambright, *Inorg. Chem.*, **23**, 4777 (1984).
34. L.R. Robinson and P. Hambright, *Inorg. Chem.*, **31**, 652 (1992).
35. W. Schneider, *Struct. Bond.* (Berlin), **23**, 123 (1975).
36. J. Nwaeme and P. Hambright, *Inorg. Chem.*, **23**, 1990 (1984).