Contribution from the Departments of Chemistry, Hunter College, City University of New York, New York, New York 10021,
and Colorado State University, Fort Collins, Colorado 80523

Kinetics of Metal-Ion Complexation with *N*-Methyltetraphenylporphyrin. Evidence Concerning a General Mechanism of Porphyrin Metalation

MARILYN J. BAIN-ACKERMAN[1a] and DAVID K. LAVALLEE*[1b]

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The rate constants for complexation of *N*-methyltetraphenylporphyrin by Cu(II), Zn(II), Co(II), Mn(II), and Ni(II) perchlorate salts in *N*,*N*-dimethylformamide were determined at several temperatures in order to investigate general features of porphyrin metalation reactions. All reactions obey a second-order rate law, first order in porphyrin and first order in metal ion. At 25 °C, the complexation rate constants (in $M^{-1}\ s^{-1}$) are 289 ± 52 for Cu(II), 10.4 ± 0.8 for Zn(II), 0.68 ± 0.04 for Co(II), 0.010 ± 0.002 for Mn(II), and 0.0003 for Ni(II). Activation parameters for these reactions ($\Delta H^{\ddagger}$ in units of kcal/mol and $\Delta S^{\ddagger}$ in eu) are $\Delta H^{\ddagger} = 16.9 \pm 1.8$ and $\Delta S^{\ddagger} = 9.7 \pm 6.0$ for Cu(II), $\Delta H^{\ddagger} = 14.2 \pm 0.7$ and $\Delta S^{\ddagger} = -6.7 \pm 2.6$ for Zn(II), $\Delta H^{\ddagger} = 20.4 \pm 1.1$ and $\Delta S^{\ddagger} = 8.6 \pm 3.6$ for Co(II), $\Delta H^{\ddagger} = 21.6 \pm 0.5$ and $\Delta S^{\ddagger} = 4.5 \pm 1.6$ for Mn(II), and $\Delta H^{\ddagger} = 21.4 \pm 2.0$ and $\Delta S^{\ddagger} = -3.2 \pm 5.8$ for Ni(II). With the exception of the Mn(II) reaction, the order of the porphyrin metalation rate constants, Cu(II) > Zn(II) > Co(II) > Ni(II), coincides with the rates of solvent exchange of the metal ions. The Mn(II) complexation rate is slower than would be predicted from solvent-exchange rates. This anomaly has also been found for Mn(II) complexation of both tetra(*p*-sulfophenyl)porphyrin and tetrakis(4-*N*-methylpyridyl)porphyrin. The general trend supports a porphyrin metalation mechanism in which solvent dissociation from the metal ion is a rate-determining factor. The rates for complexation of *N*-methyltetraphenylporphyrin are faster than rates for planar porphyrins, indicating the importance of porphyrin deformation to the rate. The results support a dissociative interchange mechanism as a predominant path for both *N*-methyl and planar porphyrins.

Introduction

Metalloporphyrins are ubiquitous in living systems and are involved in fundamental processes including respiration, electron transport, detoxification, and photosynthesis. Generally porphyrins and related tetrapyrrole ring systems are synthesized in a metal-free form and the metal ion is subsequently inserted, often with enzyme mediation. For an understanding of the metalation mechanism and the possible role of enzymatic catalysis, thorough kinetic studies are required.

Since 1960 scores of papers dealing with metalloporphyrin formation have appeared and several reviews are available.[2-4] Despite this prodigious effort, many of the most basic features of the reaction are still conjectural. Difficulties in using existing studies to deduce porphyrin metalation mechanisms arise from the reaction conditions that have been used. Existing studies are generally incommensurable because of the use of a variety of metal salts, porphyrins, solvents, buffers, added Lewis bases capable of coordinating the metal ions, and detergents, all of which affect the metalation rate.[2-4] Two of the most significant studies which we will refer to are those of Hambright and Chock,[5] who have provided data for reactions of a series of aquated metal ions with tetrakis(4-*N*-methylpyridyl)porphyrin under carefully controlled conditions, and Longo et al.,[6] who have provided activation parameters for reactions of a series of metal chloride salts with tetraphenylporphyrin in dimethylformamide.

Herein, we report a study of the metalation of an *N*-methylporphyrin which is particularly suited to investigation of certain aspects of metalloporphyrin formation. These are (1) the effect of porphyrin deformation, (2) N–H bonding changes in the porphyrin deformation or following metal–porphyrin bond formation, and (3) the importance of ligand dissociation from the metal ion.

The *N*-methyltetraphenylporphyrin free base used in this study is readily synthesized, has been fully characterized, and is the least basic *N*-alkylporphyrin yet reported.[7] Other *N*-alkylporphyrins are very basic ($pK_a \geq 13$)[8] and are readily protonated in the presence of metal ions and even trace amounts of water. These protonated forms of porphyrins are generally unreactive in metal complexation. Many studies of porphyrin complexation have yielded ambiguous results due to competition of complexing anions with solvent molecules, making assignment of the reactive metal complex difficult.[2-4,6] Anhydrous perchlorate salts of Cu(II), Zn(II), Co(II), Mn(II), and Ni(II) have been used in this study because the perchlorate ion is poorly coordinating and the metal ions in dimethylformamide have only solvent molecules in the first coordination sphere. Dimethylformamide is sufficiently basic to absorb the low concentration of protons released from the free-base porphyrin as the complexation reaction proceeds. In addition, dimethylformamide strongly solvates metal ions and competes well against trace levels of water for coordination sites on the metal ions.

Experimental Section

Porphyrins. The *N*-methyltetraphenylporphyrin (H-*N*-CH_3TPP) was prepared and characterized by literature methods.[7] Deuterated *N*-methyltetraphenylporphyrin (D-*N*-CH_3TPP) was prepared by adding about a 900-fold excess of 38% DCl/D_2O to the H-*N*-CH_3TPP dissolved in dry CH_2Cl_2. This caused immediate formation of the diacid (D_3-*N*-CH_3TPP^{2+}) as indicated by the visible spectrum. This species was neutralized with anhydrous Na_2CO_3 while the solution was vigourously stirred under N_2. The neutralization was complete when the solution had returned to its original purple color. The excess Na_2CO_3 and NaCl formed during the neutralization were filtered and the D-*N*-CH_3TPP/CH_2Cl_2 solution was evaporated to dryness. The porphyrin was then dissolved in dimethylformamide.

Perchlorate Salts. The perchlorate salts of Ni(II), Zn(II), and Ca(II) (used to maintain the ionic strength) could be dried directly by the following methods. The hexahydrate salts (G. F. Smith) were recrystallized twice from doubly distilled water. The air-dried crystals were placed in a vacuum oven at 120 °C for the Ni(II) salt, 80 °C for the Zn(II) salt, and 90–100 °C for the Ca(II) salt over $Mg(ClO_4)_2$ for 24 h to remove three waters of hydration. The final three waters were removed in a muffle oven at 140 °C for the Ni(II) salt, 120 °C for the Zn(II) salt, and 200–220 °C for the Ca(II) salt for 1 h per 0.5 g of material. The Zn(II) salt melts and remains liquid until cooled whereas the Ca(II) salt melts and sputters during the drying period. It is dry when it takes on a puffy appearance and has expanded significantly.

Solvents. The *N*,*N*-dimethylformamide was stirred over BaO for 2 h under N_2, decanted to a distillation flask, and vacuum distilled. The distillation was repeated and the distillate contained ~0.01–0.02% water, determined by a standard addition GC analysis (with a 24 × $^1/_8$ in. aluminum column packed with 80–100 mesh Porapak QS). Fisher certified DMF can be dried to the same approximate water content as that of the distilled DMF by stirring over 4-Å molecular sieves for at least 2 days. Kinetic experiments were performed in the solvent dried by each method with no apparent difference in rates of complexation.

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Solutions. The $Ni(ClO_4)_2$, $Zn(ClO_4)_2$, and $Ca(ClO_4)_2$ salts were weighed in a drybox and dissolved in appropriate volumes of DMF. The Cu(II), Co(II), and Mn(II) salts were made indirectly by mixing stoichiometric amounts of the anhydrous chloride salt solutions with an anhydrous $AgClO_4$ solution. The hydrated chloride salts were dried in an oven at 210 °C to a constant weight. $Zn(ClO_4)_2$ was prepared by this general method by using anhydrous $ZnCl_2$ prepared from a slurry of $SOCl_2$ and quinoline,[9] which was refluxed 2 h and distilled in vacuo by using a N_2 bleed. Anhydrous $AgClO_4$ was purified by dissolving in dry benzene to make a saturated solution and filtering.[10] The benzene–water azeotrope was distilled and the anhydrous $AgClO_4$ salt was precipitated with pentane and dried on a vacuum line. The MCl_2 (where M = Mn(II), Co(II), Cu(II), Zn(II)) and $AgClO_4$ were each weighed in the drybox to yield a mole ratio of 1:2 and then separately dissolved in a minimum of DMF. The two solutions were directly mixed together and the AgCl precipitate was subsequently filtered. The addition of ~5 times the volume of freshly distilled ether caused precipitation of $[M(DMF)_6](ClO_4)_2$,[11] except for the Mn(II) solution. (This final step was omitted when making the $Mn(ClO_4)_2$ solutions.) The crystals were dried in a vacuum oven, transferred to a drybox, and then dissolved in appropriate volumes of DMF. Concentrations were determined by EDTA titrations[12,13] and water content was again obtained by GC analysis. Spectra of the metal perchlorate solutions matched those of published spectra in dimethylformamide.[11,14–17]

Instruments. Spectrophotometric studies and kinetic determinations for the Ni(II), Mn(II), Co(II), and Zn(II) reactions were carried out with a Cary Model 14 recording spectrophotometer with a Haake Model FK2 constant-temperature bath attached. The Zn(II) studies were performed in magnetically stirred cells[18,19] of 1.4-cm path length. The faster reaction of the Cu(II) metal ion was followed on a Durrum-Gibson Model D-110 stopped-flow spectrometer with a Lauda-/Brinkmann circulator for temperature control.

Procedure. The metal concentration, water concentration, ionic strength, and temperature dependencies were acquired and evaluated for each metal species. All runs were done at constant wavelength under pseudo-first-order conditions with the metal concentration in at least 15-fold excess. The porphyrin concentration was generally $(1–6) \times 10^{-5}$ M and the metal concentration range was 10^{-4} to 10^{-2} M (except for the Ni(II) reaction which was run at 10^{-2} to 10^{-1} M due to the slow rate of complexation). $Ca(ClO_4)_2$ was used to maintain the ionic strength at 0.3 M. Complications caused by the presence of excess water (see Results) were avoided by carrying out all kinetic determinations with a minimum of water present.

It should be noted that a second reaction, demethylation,[20,21] which results in a nonmethylated planar product can also take place while the first reaction, $M^{2+} + H\text{-}N\text{-}CH_3TPP \rightarrow M\text{-}N\text{-}CH_3TPP^+ + H^+$, is progressing. In the case of zinc, manganese, and cobalt, no interference from the demethylation reaction was seen, even after 7 half-lives of the original complexation reaction. With Cu(II), the demethylation was observed as drift in the apparent infinite-time transmittance reading, but the calculated fit to data from 7 half-lives was of the same quality (as determined by the variance) as for the other metals. Only for the nickel complexation reaction was the first reaction (complexation) not essentially complete before the second reaction (demethylation) began.

The two steps are shown in eq 1 for the Ni(II) system. The kinetics

$$Ni(II) + H\text{-}N\text{-}CH_3TPP \rightleftharpoons Ni\text{-}N\text{-}CH_3TPP^+ + H^+ \rightarrow NiTPP + \text{products} \quad (1)$$

for demethylation have been studied previously.[21] Each reaction in eq 1 can be characterized by its own set of isosbestic points. The first step in eq 1 is characterized by five isosbestic points at 671, 595, 555, 541, and 506 nm. Gradually these points are lost and a new one develops at 542.7 nm due to the demethylation reaction. For the nickel reaction, data were collected for as long as the first set of isosbestic points was maintained, which was for 2–3 half-lives.

The method of mixing solutions for kinetic observations varied depending upon reaction rates. For cobalt, manganese, and nickel reactions, a 1-, 2-, or 5-cm cell containing necessary amounts of solvent, calcium perchlorate, and porphyrin was temperature equilibrated in the observation chamber of the spectrophotometer. The necessary amount of the metal salt solution, equilibrated in the reservoir of the accompanying temperature bath, was added into the cell with a syringe or pipet and shaken. Minor temperature variations (which affect the absorption of the porphyrin solution) lasted from 1 to 5 min, after which data collection was begun. For the somewhat faster zinc reactions, the same procedure was used except that a magnetically stirred absorption cell, immersed in a water bath within the cell compartment, was used. In this case, temperature variations are insignificant, and data collection was begun as soon as the solution was mixed—about 5 s. The copper reaction was observed by stopped-flow spectrophotometry.

Table I. Kinetic Results for the Reaction of Cu(II) with $H\text{-}N\text{-}CH_3TPP$ in Dimethylformamide[a]

$[Cu^{II}]$, M	$10^5[H\text{-}N\text{-}CH_3\text{-}TPP]$, M	T, °C	k_{obsd}, s^{-1}	$k_{obsd}/[Cu^{II}]$, $M^{-1}\ s^{-1}$
0.086	5.65	25.0	2.02×10	236
	5.65	25.0	1.92×10	224
	5.65	25.6	2.49×10	289
	4.00	25.5	1.99×10	232
	4.00	25.5	2.22×10	258
0.034	5.65	25.6	7.57	223
	5.65	25.0	8.33	245
	5.65	25.0	7.89	232
	5.65	25.0	9.08	267
	5.65	25.0	1.02×10	300
0.031	3.38	25.5	9.39	303
	3.38	25.5	9.14	295
	3.38	25.5	8.90	287
0.017	5.65	25.0	4.88	287
	5.65	25.0	6.08	358
	5.65	25.0	4.55	268
0.0062	3.38	25.5	1.69	273
	3.38	25.5	1.60	258
	3.38	25.5	1.62	261
0.0031	3.38	25.5	9.19×10^{-1}	296
	3.38	25.5	8.33×10^{-1}	269
	3.38	25.5	7.68×10^{-1}	248
	3.38	25.5	6.71×10^{-1}	216
0.00124	4.00	25.5	5.10×10^{-1}	411
	4.00	25.5	4.85×10^{-1}	391
	4.00	25.5	4.56×10^{-1}	368
	4.00	26.0	3.36×10^{-1}	271
0.0008	5.65	25.0	3.03×10^{-1}	379
	5.65	25.0	2.94×10^{-1}	367
	5.65	25.0	2.50×10^{-1}	313
	4.00	25.5	2.58×10^{-1}	323
	4.00	25.5	2.38×10^{-1}	298
				289 ± 50[b]
0.0062	4.00	13.2	7.00×10^{-1}	113
	4.00	13.2	6.48×10^{-1}	105
	4.00	40.8	9.92	1600

[a] Ionic strength 0.26–0.28 M; observation wavelength 573 nm.
[b] Overall average at 25.3 ± 0.3 °C.

Calculations. The first-order rate constants of the observed reactions, k_{obsd}, and the Eyring activation parameters were determined by using a CDC 6400 digital computer and the Los Alamos Scientific Laboratory nonlinear least-squares program,[22] with subroutines for handling kinetic data supplied by Dr. T. W. Newton.

Results

$H\text{-}N\text{-}CH_3TPP$. The data for the determination of the metal and temperature dependencies of the complexation reactions of Cu(II), Zn(II), Co(II), Mn(II), and Ni(II) with the *N*-methyltetraphenylporphyrin free base can be found in Tables I–V. In each case, there is a linear dependence of the metal ion concentration with the pseudo-first-order rate constant k_{obsd}. The rate constants at ca. 25 °C are summarized in Table VI. The rate constants are significantly different from one another so there is no ambiguity in assigning the relative order of the rates of the metal complexation with the *N*-methylporphyrin.

All reactions were found to be first order in porphyrin and in metal ion and second order overall, with the rate law

$$\text{rate} = k_{obsd}[H\text{-}N\text{-}CH_3TPP] = k[M(II)][H\text{-}N\text{-}CH_3TPP]$$

Table II. Kinetic Results for the Reaction of Zn(II) with H-*N*-CH_3TPP in Dimethylformamide[a]

$[Zn^{II}]$, M	$10^5 \times$ [H-*N*-CH_3-TPP], M	*T*, °C	k_{obsd}, s^{-1}	$k_{obsd}/[Zn^{II}]$, $M^{-1}\ s^{-1}$
0.0340	4.00	26.0	3.44×10^{-1}	10.12
	4.00	26.0	3.33×10^{-1}	9.78
	4.00	26.0	3.19×10^{-1}	9.38
	4.00	26.0	3.14×10^{-1}	9.24
0.0113	3.60	27.5	1.27×10^{-1}	11.25
0.0136	4.60	27.4	1.50×10^{-1}	11.04
0.0114[b]	4.50	28.0	1.30×10^{-1}	11.38
0.0076[b]	4.50	28.0	8.04×10^{-2}	10.58
0.0068[b]	4.50	27.7	7.40×10^{-2}	10.82
				10.4 ± 0.8[c]
0.0136	4.60	9.6	2.84×10^{-2}	2.09
0.0113	3.80	10.0	2.51×10^{-2}	2.22
0.0136	4.60	15.1	4.81×10^{-2}	3.54
0.0139	4.70	1.7	1.56×10^{-2}	1.12

[a] Ionic strength 0.28 M; observation wavelength 605 nm. [b] This stock solution was made from directly dried and weighed $Zn(ClO_4)_2$ and not prepared by the $AgClO_4$ titration procedure. [c] Overall average at 27.0 ± 1.0 °C.

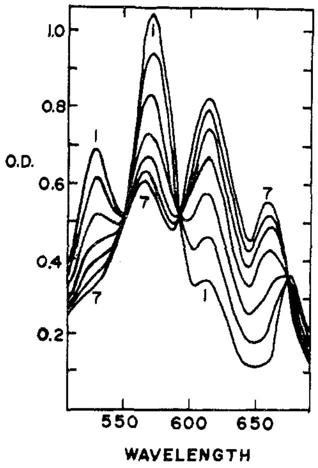


Figure 1. Optical density changes during the reaction of Mn(II) with *N*-methyltetraphenylporphyrin in dimethylformamide. Spectra were taken at approximately 10-min intervals ([Mn(II)] = 0.041 M, *T* = 25.2 °C). The initial spectrum is labeled 1 and the final spectrum is labeled 7.

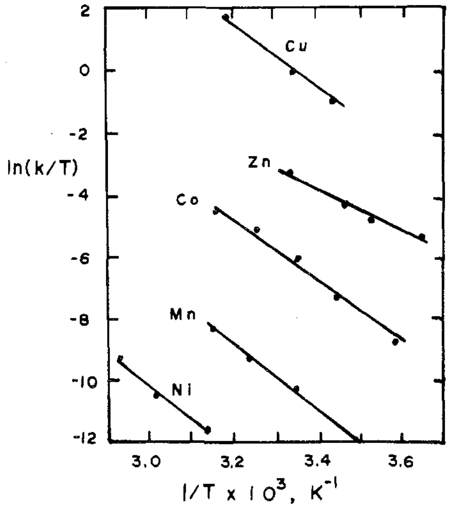


Figure 2. Temperature dependencies for complexation reactions of *N*-methyltetraphenylporphyrin dimethylformamide ($M^{-1}\ s^{-1}$). Each point is plotted as the average value of the rate constants obtained.

Table III. Kinetic Results for the Reaction of Co(II) with H-*N*-CH_3TPP in Dimethylformamide[a]

$[Co^{II}]$, M	$10^5 \times$ [H-*N*-CH_3-TPP], M	*T*, °C	k_{obsd}, s^{-1}	$k_{obsd}/[Co^{II}]$, $M^{-1}\ s^{-1}$
2.33×10^{-2}	4.00	26.0	1.52×10^{-2}	0.650
1.17×10^{-2}	4.00	26.0	7.79×10^{-3}	0.666
1.06×10^{-2}	4.00	26.0	7.18×10^{-3}	0.678
7.00×10^{-3}	4.00	26.0	4.73×10^{-3}	0.675
5.20×10^{-3}	3.20	24.2	3.71×10^{-3}	0.739
	3.20	24.2	3.58×10^{-3}	0.712
3.50×10^{-3}	4.00	26.0	2.43×10^{-3}	0.694
2.51×10^{-3}	3.20	24.2	1.70×10^{-3}	0.678
2.33×10^{-3}	4.00	26.0	1.56×10^{-3}	0.671
1.27×10^{-3}	3.20	24.2	7.32×10^{-4}	0.577
1.20×10^{-3}	4.00	26.0	8.17×10^{-4}	0.681
6.27×10^{-4}	3.20	24.2	4.52×10^{-4}	0.720
5.80×10^{-4}	4.00	26.0	3.71×10^{-4}	0.639
				0.675 ± 0.040[b]
2.33×10^{-3}	4.00	6.0	9.96×10^{-5}	0.043
	4.00	17.5	4.83×10^{-4}	0.207
	4.00	34.5	4.09×10^{-3}	1.757
2.26×10^{-3}	4.00	43.3	7.64×10^{-3}	3.382

[a] Ionic strength 0.25–0.3 M; observation wavelength 613 nm. [b] Overall average at 25.0 ± 1.0 °C.

Table IV. Kinetic Results for the Reaction of Mn(II) with H-*N*-CH_3TPP in Dimethylformamide[a]

$[Mn^{II}]$, M	$10^5 \times$ [H-*N*-CH_3-TPP], M	*T*, °C	*I*, M	k_{obsd}, s^{-1}	$k_{obsd}/[Mn^{II}]$, $M^{-1}\ s^{-1}$
0.0124	3.98	25.2	0.277	1.31×10^{-4}	1.06×10^{-2}
0.0409	4.37	25.2	0.298	4.49×10^{-4}	1.10×10^{-2}
0.0965[b]	4.00	26.2	0.288	7.61×10^{-4}	7.89×10^{-3}
					$(9.83 \pm 1.7) \times 10^{-3}$ [g]
0.0965	4.00	36.0	0.290	2.42×10^{-3}	2.50×10^{-2}
0.064	4.00	35.8	0.288	1.65×10^{-3}	2.56×10^{-2}
0.055[e]	3.78	35.7	0.291	1.67×10^{-3}	3.04×10^{-2}
0.037	3.78	35.0	0.271	9.94×10^{-4}	2.69×10^{-2}
0.037[b]	4.00	36.0	0.285	1.01×10^{-3}	2.74×10^{-2}
0.035[d]	3.78	35.8	0.281	9.79×10^{-4}	2.83×10^{-2}
0.0248[c]	3.29	35.0	0.282	7.03×10^{-4}	2.84×10^{-2}
0.0124	3.16	35.3	0.277	3.59×10^{-4}	2.89×10^{-2}
	1.97	35.0	0.277	3.74×10^{-4}	3.02×10^{-2}
0.0062	3.16	35.0	0.274	2.10×10^{-4}	3.39×10^{-2}
					$(2.85 \pm 0.26) \times 10^{-2}$ [h]
0.0965[b]	4.00	12.8	0.288	1.63×10^{-4}	1.68×10^{-3}
0.0965[f]	4.00	35.0	0.288	1.24×10^{-3}	1.29×10^{-2}
0.0124	3.29	44.8	0.277	1.11×10^{-3}	8.94×10^{-2}

[a] Observation wavelength 613 nm. [b] This solution contained a 1% excess of Cl^- relative to Mn^{2+}. [c] This determination was done by scanning from 700 to 500 nm. [d] This solution contained a 1% excess of Ag^+ relative to Mn^{2+} and 2 M 2,6-lutidine. [e] This solution contained 2.5 M 2,6-lutidine. [f] This solution contained a 1:1 mole ratio of Cl^- and Mn^{2+}. [g] Average at 25.7 ± 0.5 °C. [h] Average at 35.7 ± 0.3 °C.

The order of the rate constants is Cu(II) > Zn(II) > Co(II) > Mn(II) > Ni(II). Typical absorbance changes that occur in these reactions are illustrated by the spectra taken during the manganese reaction, shown in Figure 1.

The temperature-dependence data for the five metal ions are plotted in Figure 2 where the solid line represents a least-squares fit and the circles are the averages of experimental points at each temperature. The nickel reaction was very slow and was not studied in greater detail.

Table V. Kinetic Results for the Reaction of Ni(II) with H-N-CH_3TPP in Dimethylformamide[a]

$[Ni^{III}]$, M	I, M	T, °C	k_{obsd}, s^{-1}	$k_{obsd}/[Ni^{III}]$, M^{-1} s^{-1}
0.241[b]	0.722	45.0	5.58×10^{-4}	2.32×10^{-3}
0.161[b]	0.702	44.7	4.88×10^{-4}	3.03×10^{-3}
0.080[b]	0.719	45.8	2.47×10^{-4}	3.08×10^{-3}
0.040[b]	0.730	46.0	1.20×10^{-4}	2.99×10^{-3}
				$(2.86 \pm 0.36) \times 10^{-3}$ [d]
0.080[b]	0.720	58.4	7.70×10^{-4}	9.63×10^{-3}
0.080[c]	0.720	58.4	7.43×10^{-4}	9.28×10^{-3}
0.078[c]	0.720	69.0	2.60×10^{-3}	3.34×10^{-2}
	0.720	69.0	2.83×10^{-3}	3.63×10^{-2}
	0.720	69.0	2.11×10^{-3}	2.70×10^{-2}

[a] [H-N-CH_3TPP] = 4.00×10^{-5} M. [b] Data obtained by scanning from 700 to 500 nm. [c] Observation wavelength 570 nm. [d] Overall average at 45.4 ± 0.7 °C.

The dependence of the metal complexation rates on the presence of water was also determined (except for nickel). In the case of the cobalt reaction, no significant effect was noted. For the others, similar results were obtained in each case, namely, that the observed rates fall into two groups. For each metal, when the mole ratio of water to metal ion is 0.5 or less, the minimum rate is obtained and is independent of further decreases in this ratio. When the mole ratio is 5 or greater, the maximum rate is obtained and is independent of further increases. Between these two extremes, the rate varies constantly with increasing water to metal ratios. These results are shown in Figure 3 for the cases of zinc and manganese. The rate increase observed for copper, 1.8, is of approximately the same magnitude as that observed for the zinc reaction.

The ionic strength was varied over at least a sevenfold range. In each case, the rate increased slightly as the ionic strength was increased. The ratios of the highest and lowest second-order rate constants, obtained at the highest and lowest ionic strengths (I), are 1.2 (Co(II), I = 0.032–0.69 M) and 1.4 (Mn(II), I = 0.22–1.3 M; Cu(II), I = 0.09–0.66 M; Zn(II), I = 0.04–0.66 M).

D-N-CH_3TPP. Two sets of kinetic determinations were made. First the H-N-CH_3TPP cobalt complexation reaction was run with Co(II) = 1.05×10^{-2} M with no water added to the system. Then this reaction was repeated after adding 1.0% distilled water, resulting in a water to Co(II) mole ratio of about 50:1. The rate decreased about 10%. The same procedure was repeated with the D-N-CH_3TPP. With no water added (but 0.01% water from the solvent), the rate constant was the same as that for the metal dependence determined earlier for Co(II). The D_2O was added to give a concentration of 1.0% and the run repeated. Here (as before when the excess water was added in a water to Co(II) mole ratio of 50:1) the rate decreased about 10%, thus showing no significant change in the rate due to deuterium substitution.

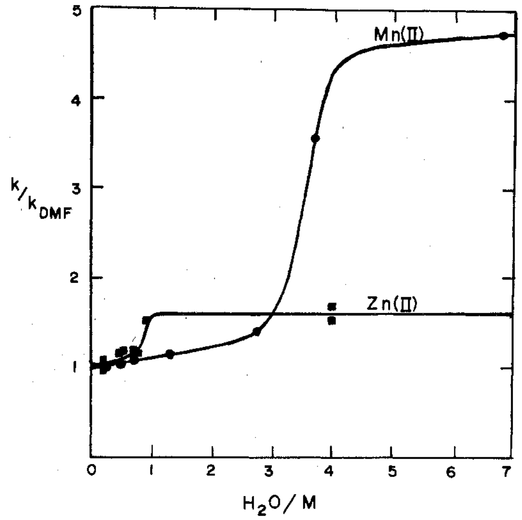


Figure 3. Dependence of rates of complexation of N-methyltetraphenylporphyrin on the concentration of water in the dimethylformamide used as solvent for the reaction. Second-order rate constants have been divided by the reaction rate at low water concentration to give the relative rates indicated in this figure. Although sigmoidal curves are shown, insufficient data were obtained to actually fit such curves to an analytical function.

The reaction with added D_2O was run as a check against possible replacement of deuterium on D-N-CH_3TPP by trace H_2O.

Discussion

The major points to be considered in a general mechanism for porphyrin complexation are[2-4] (1) outer-sphere complex formation between the porphyrin and a solvated metal ion, which is described by the equilibrium constant K_{os}, (2) rapid interconversion between planar and deformed (puckered) forms of the porphyrin free base, which is described by the equilibrium constant K_D, (3) dissociation of one or more solvent molecules (or other ligands) from the first coordination sphere of the metal ion, which is described by the rate constant k_d, (4) the existence and importance of an intermediate in which a metal atom and hydrogen atoms are bound to the nitrogens at the porphyrin coordination site (the "sitting-atop" complex), (5) the importance of N–H bond changes in the deformation step or the conversion of a sitting-atop intermediate to the product metalloporphyrin, and (6) the nature of the reactive porphyrin species as a free base or a deprotonated anion. A study of the complexation reactions of N-methyltetraphenylporphyrin provides information about several of these points which is not readily obtained by studies of planar porphyrin ligands. With respect to point 2, Hambright has previously

Table VI. Comparison of Rate Constants for Cu(II), Zn(II), Co(II), Mn(II), and Ni(II) Complexation with Tetrakis(4-N-methylpyridyl)porphyrin and N-Methyltetraphenylporphyrin

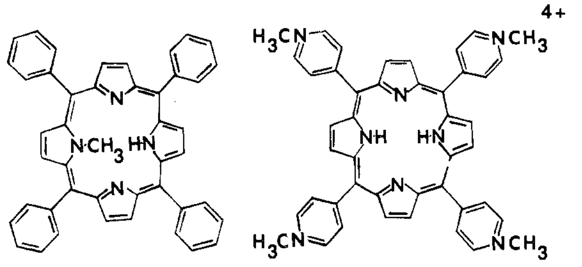
	tetrakis(4-N-methylpyridyl)porphyrin in H_2O[a]				N-methyltetraphenylporphyrin in DMF			
ion	k(20 °C), M^{-1} s^{-1}	normalized rate constant	k_d,[b] s^{-1} (H_2O)	$10^9 k/k_d$, M^{-1}	k(25 °C), M^{-1} s^{-1}	normalized rate constant	k_d,[b] s^{-1} (DMF)	$10^6 k/k_d$, M^{-1}
Cu(II)	2.3 ± 0.3	46000	2.5×10^9	0.86	289 ± 50	9.6×10^5	2.5×10^8 [c]	1.15
Zn(II)	$(50 \pm 3) \times 10^{-3}$	1000	3.2×10^7	1.58	10.4 ± 0.8	3.5×10^4	3×10^6 [c]	3.3
Co(II)	$(22 \pm 2) \times 10^{-4}$	43	2.5×10^6	0.86	0.68 ± 0.04	2.3×10^3	2.5×10^5	2.70
Mn(II)	$(25 \pm 2) \times 10^{-4}$	50	3.2×10^7	0.08[d]	0.010 ± 0.002	33	4.0×10^6	0.0027
Ni(II)	5×10^{-5}	1	2.8×10^4	1.78	0.0003[e]	1	4.0×10^3	0.075

[a] Reference 5. [b] Reference 27a. [c] Comparisons of relative rates of H_2O, methanol, acetronitrile, and dimethylformamide[27] show that the order of exchange rates for Cu(II), Zn(II), Mn(II), Co(II), and Ni(II) remains the same but the rates differ for each solvent. The water exchange rates are the fastest of the four solvents, being about 2 orders of magnitude faster than the CH_3OH rates and 10 times faster than the DMF rates. The k_d values for DMF exchange from Cu(II) and Zn(II) have been estimated as one-tenth those of the H_2O exchange rates. [d] Reaction product was the Mn(III) porphyrin. [e] Extrapolated value from temperature-dependence data.

pointed out that the *N*-methylporphyrin ligand is deformed in the manner which has been proposed as an important step in the metalation mechanism;[5] the lone pairs of the porphyrin nitrogen atoms are oriented away from the plane of the nitrogen atoms because the van der Waals radius of the methyl group does not allow the free base to be planar. Structures of *N*-methylporphyrin complexes demonstrate the nonplanar nature of the ligand.[23] Concerning points 1 and 3, similar effects of solvent dissociation from the metal atom should apply to reactions of both *N*-methyl and planar porphyrin ligands and the outer-sphere complexation constants should also be similar. (There is a statistical disadvantage for complexation with the *N*-methylporphyrin since the metal atom may only complex on one side of the porphyrin, however.) Points 4 and 5 are addressed by studies of *N*-methylporphyrin complexes since they serve as models for the sitting-atop complex. Parallel kinetic patterns for the *N*-methylporphyrin and planar porphyrins would support formation of a sitting-atop complex as the rate-determining step in porphyrin metalation and make it likely that the conversion of the sitting-atop intermediate to the product metalloporphyrin would be relatively rapid. The role of N–H bonding changes in deformation or the conversion of the sitting-atop complex can also be probed with the *N*-methylporphyrin. If the kinetic isotope effect due to substitution of deuterium for hydrogen (measured to be 2.2 for the reaction of Zn(II) with tetra(*p*-sulfophenyl)porphyrin in D_2O[24] and 1.4 for the reaction of Cu(II) with the same porphyrin in 95% D_2O[25]) is a result of the porphyrin deformation, no kinetic isotope effect should be seen in *N*-methylporphyrin complexation reactions. Finally, the rapid complexation rates of *N*-methylporphyrins can be used to establish the free-base porphyrin as the reactive species under the conditions used in this study (point 6).

The kinetic data for the reaction of *N*-methyltetraphenylporphyrin with dimethylformamide complexes of divalent metal ions of the first transition series (Tables I–V) are all consistent with a second-order rate law, first order in metal ion and first order in H-*N*-CH_3TPP. Under pseudo-first-order conditions with metal ion in excess, the disappearance of H-*N*-CH_3TPP and appearance of the corresponding metal complex are first order for over 95% of the reaction. If the protons released by the complexation affect the reaction, the rate of complexation would decrease more rapidly than predicted from first-order behavior as the reaction progresses. Since such behavior was not found in dimethylformamide, buffering was not required. The small variation of rate with increasing ionic strength is consistent with a reaction sequence involving one neutral reactant (the *N*-methyltetraphenylporphyrin free base rather than an anionic form).

One of the parameters which has been scrutinized in deducing porphyrin mechanisms is the rate of the ligand exchange of each metal ion in a series.[5] In order to investigate the importance of this process on the overall reaction rate, it is necessary to be certain of the composition of the reactive metal species. In addition to using the weakly coordinating perchlorate anion, we investigated the dependence of the reaction rate on water concentration. When the ratio of water to metal ion is low ($[H_2O]/[M^{2+}] < 0.5$), the amount of water causes no significant difference in the complexation rate and we assume that the rate is representative of the reaction of a metal ion with only dimethylformamide in the coordination sphere. As the water content is increased, the rate eventually reaches a constant value. Since water exchange rates are generally somewhat different from dimethylformamide exchange rates,[27] this result indicates the effect of replacement of dimethylformamide by water in the coordination sphere of the metal ion. All kinetic data used in the mechanistic analysis were obtained with a water to metal ion ratio less than 0.5.



HNCH₃TPP TMPyP

Figure 4. Structures of *N*-methyltetraphenylporphyrin and tetrakis(4-*N*-methylpyridyl)porphyrin cation. The latter is alkylated at the periphery of the ligand but not at the central coordination site.

The data which we have obtained for the reactions of dimethylformamide complexes of Cu(II), Zn(II), Co(II), Mn(II), and Ni(II) with *N*-methyltetraphenylporphyrin are accommodated within the following mechanistic scheme:

$$\text{H-}N\text{-CH}_3\text{TPP} + \text{M(DMF)}_6{}^{2+} \overset{K_{os}}{\rightleftharpoons} \text{H-}N\text{-CH}_3\text{TPP}\cdots\text{M(DMF)}_6{}^{2+} \quad (2)$$

$$\text{H-}N\text{-CH}_3\text{TPP}\cdots\text{M(DMF)}_6{}^{2+} \underset{k'_{d,-1}}{\overset{k'_{d,1}}{\rightleftharpoons}} \text{H-}N\text{-CH}_3\text{TPP–M(DMF)}_5{}^{2+} + \text{DMF} \quad (3)$$

$$\text{H-}N\text{-CH}_3\text{TPP–M(DMF)}_5{}^{2+} \underset{k'_{d,-2}}{\overset{k'_{d,2}}{\rightleftharpoons}} \text{H-}N\text{-CH}_3\text{TPP=M(DMF)}_4{}^{2+} + \text{DMF} \quad (4)$$

$$\text{H-}N\text{-CH}_3\text{TPP=M(DMF)}_4{}^{2+} \xrightarrow{\text{fast}} N\text{-CH}_3\text{TPP–M(DMF)}^+ + \text{H}^+ + 3\text{DMF} \quad (5)$$

The outer sphere equilibrium constant K_{os} has been defined and values have been estimated by Fuoss[29] and Eigen.[30] This equilibrium step is currently postulated for all ligand-substitution reactions.[26–30] It is not the rate-determining step in this case because the rate constants vary considerably for the metal ions studied, all of which are divalent and of nearly the same size, leading to similar estimates of K_{os}.[29] We postulate solvent dissociation from the metal ion as the rate-determining step on the basis of a comparison of the observed overall complexation rate constant (k) with the solvent dissociation rate constants (k_d). It should be noted that the rate constant specified in eq 3, $k'_{d,1}$, is smaller than the simple solvent dissociation rate constant (k_d) because this step also involves bond formation between the metal atom and the porphyrin molecule. If solvent dissociation is important in determining the overall rate, these two rate constants should correlate.[5] As shown in Table VI, the range of values for k/k_d is much smaller than the range of k values. This correlation was pointed out previously by Hambright and Chock for complexation reactions of tetrakis(4-*N*-methylpyridyl)porphyrin[5] (Figure 4), and the complexation reaction of tetra(*p*-sulfophenyl)porphyrin also shows this correlation.[25] In all three cases the Mn(II) complexation is anomalously slow. The Mn(II) ion is the largest of those studied and the step designated by $k'_{d,-1}$ may be more important in that case. If Mn(II) is omitted, the comparison of the k/k_d and k ranges for *N*-methyltetraphenylporphyrin is 44 compared with 9.6×10^5 and for tetrakis(*N*-methylpyridyl)porphyrin it is 6 vs. 4.6×10^4.

When rate ratios for these N-methylated and planar porphyrins are compared, the *N*-methylporphyrin rates are seen to be significantly faster (by $\simeq 10^3$ for Cu(II), Zn(II), and Co(II) and by $\simeq 40$ for Ni(II); note that differences in solvent-exchange rates have been accounted for in arriving at these values). Previously, Hambright found a rate increase of 10^5 for Zn(II) and Cd(II) complexation of *N*-methyletio-

Table VII. Comparison of the Activation Parameters for the Reaction of the Metal Ions Cu(II), Zn(II), Co(II), Mn(II), and Ni(II) with *N*-Methyltetraphenylporphyrin and Planar Tetraphenylporphyrin in Dimethylformamide

	N-methyltetraphenylporphyrin[a]			tetraphenylporphyrin[b]		
ion	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Cu(II)	14.0 ± 3.6	16.9 ± 1.8	9.7 ± 6.0	20.4	16.3	−9.8
Zn(II)	16.2 ± 1.5	14.2 ± 0.7	−6.7 ± 2.6	21.6	15.3	−18.3
Co(II)	17.8 ± 2.2	20.4 ± 1.1	8.6 ± 3.6	23.1	24.9	5.2
Mn(II)	20.3 ± 0.9	21.6 ± 0.5	4.5 ± 1.6			
Ni(II)	22.4 ± 3.6	21.4 ± 2.0	−3.2 ± 5.8	23.2	23.4	0.6

[a] These determinations were done with metal perchlorate salts. [b] These determinations were done with metal chloride salts.[6]

porphyrin III compared with the complexation of planar etioporphyrin III.[31] These results indicate the importance of porphyrin deformation to the overall complexation rate. It appears that the effect is greatest when the metal ions undergo rapid ligand dissociation. The deformation depends upon the flexibility of the porphyrin molecule. Such flexibility is well documented in crystallographic structure determinations which show that the porphyrin free base can be either planar or ruffled in the solid state.[32,33] Porphyrins are readily protonated and the dicationic species must be severely puckered to accommodate the additional protons.[34] Pasternack et al.[35] measured a relaxation phenomenon attributed to the deformation equilibrium of tetrakis(4-*N*-methylpyridyl)porphyrin in water at 25 °C and determined rate constants of 4.6×10^7 s^{-1} for deformation and 1.2×10^9 s^{-1} for the return to a planar conformation. A rate constant of this magnitude would make deformation competitive in the case of metal ions with relatively rapid solvent dissociation rates (Table VI). In the case of Ni(II), the deformation of a planar porphyrin can be considered as a rapid preequilibrium step. The magnitude of the deformation equilibrium constant that can be estimated from a comparison of the complexation rates for Ni(II) (~0.025) is in reasonable agreement with that determined by Pasternack for tetrakis(4-*N*-methylpyridyl)porphyrin (0.038).

The data for complexation reactions of *N*-methyltetraphenylporphyrin allow comment to be made on the role of the much discussed sitting-atop intermediate.[36–52] Fluorescence spectrometry distinguishes out-of-plane complexes in which there is metal–nitrogen bonding, analogous to that postulated for sitting-atop complexes, from ion pairs that produce similar visible absorption spectra.[3,46–48] Investigations of possible sitting-atop species formed from the first-row transition-metal ions have thus far resulted in the conclusion that only ion pairs are actually isolated. It is likely, however, that the sitting-atop structure is an intermediate, though not long-lived, in porphyrin metalation. Rates for solvent dissociation from the metal ion have been shown to correlate with complexation rates but it is also possible that the conversion of a sitting-atop intermediate to the planar product could show the same trend. Two observations argue against the sitting-atop to planar product step being rate determining. Studies have been carried out of the conversion of *N*-methyltetraphenylporphyrin complexes to planar tetraphenylporphyrin complexes.[20,21] In this reaction the methyl group is transferred to a nucleophile in analogy to the transfer of a proton from a sitting-atop intermediate to a nucleophile (often the solvent).[49–52] The conversion rates correlate with the stability of the planar porphyrin product, making the Ni(II) reaction one of the fastest rather than the slowest. The relative rates of these reactions are Cu(II) > Ni(II) >> Zn(II) >> Mn(II) which is much different from the relative overall rates of porphyrin metalation. A second and more direct observation concerns the kinetic isotope effect for replacement of free-base hydrogen atoms by deuterium. Kinetic isotope effects of about 2 have been attributed to the difference in N–H bonding between the planar ground-state conformation of the porphyrin free base and a deformed higher energy conformation.[24,25] We find no kinetic isotope effect in complexation of Co(II) to D-*N*-$\mathrm{CH_3}$TPP vs. H-*N*-$\mathrm{CH_3}$TPP. This result rules out N–H bond breaking as a rate-determining feature of the metal-bonding step in the mechanism of the *N*-methylporphyrin and, by inference, in the mechanism of metalation of nonmethylated porphyrins.

The relatively slow complexation rates of porphyrins compared with those of nonmacrocyclic multidentate ligands has been discussed in terms of a predissociation of hydrogen atoms from the porphyrin free base to form a more reactive monoanion.[3] Attempts to test this feature of the mechanism by the pH dependence of complexation lead to ambiguous results because an increase in pH also leads to deprotonated metal complexes that are more reactive. Free-base porphyrins are not very acidic, with estimated values for the pK_a of about 16.[2] The relatively rapid rates of reaction found in this study for Cu(II) complexation to H-*N*-$\mathrm{CH_3}$TPP (~300 M^{-1} s^{-1} at 25 °C) and by Hambright[31] for Zn(II) and Cd(II) complexation with *N*-methyletioporphyrin III (500 and 1100 M^{-1} s^{-1} at 25 °C) in the absence of added base preclude anionic porphyrin species as the predominant precursors.

The activation parameters for complexation of H-*N*-$\mathrm{CH_3}$TPP are summarized in Table VII along with those found by Longo et al.[6] for reactions of planar tetraphenylporphyrin ($\mathrm{H_2}$TPP). Both series of reactions were run in dimethylformamide but the $\mathrm{H_2}$TPP reactions involved metal chloride salts which form a variety of species of different charge in nonaqueous solvents. The variety of species present in such solutions[11,16] leads to some difficulty in establishing the identity of the reactive metal species. Nonetheless, those data are the best available since few studies report activation parameters and that study is the most extensive compilation for a series of metal ions reacting with the same porphyrin. In the case of the $\mathrm{H_2}$TPP reactions, the free energy of activation varies by only 15% from Cu(II) to Ni(II), with significant compensation of enthalpy changes by entropy changes. For the H-*N*-$\mathrm{CH_3}$TPP reactions, there is a larger variation in the free energy of activation, 60% from Cu(II) to Ni(II), with no evidence for a compensation effect. The order of increasing free energies of activation is the same for both series. Detailed evaluation of activation parameters for these reactions will require further studies under comparable conditions.

In summary, the mechanism for metalation of *N*-methyltetraphenylporphyrin deduced from reaction kinetics is similar to a mechanism proposed by Hambright and Chock[5] for metalation of planar porphyrins. The mechanism involves solvent dissociation from the metal ion as an important rate-determining factor. The more rapid rates of complexation for *N*-methylporphyrins demonstrate the importance of porphyrin deformation in determining rates of complexation for planar porphyrins. Formation of a sitting-atop intermediate during the metalation process is likely but its conversion to the product metalloporphyrin is generally not rate determining. The N–H bond breaking during the metalation reaction is of minor importance in determining complexation rates. The aspects of this reaction which appear to be likely candidates for catalysis are the acceleration of ligand dissociation from the metal ion and deformation of the porphyrin. The former would appear to be easier to accomplish.

It should be noted that these conclusions relate to reactions of 2+ metal ions of the first transition series under mildly acidic (Hambright and Chock's study[5]) or neutral conditions (this work and Longo's study[6]). Other mechanisms may pertain under strongly basic conditions or with more highly charged metal ions and almost certainly pertain to metalation reactions involving oxidative addition.[53-56]

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Registry No. H-*N*-CH$_3$TPP, 51552-53-5; Cu(II), 15158-11-9; Zn(II), 23713-49-7; Co(II), 22541-53-3; Mn(II), 16397-91-4; Ni(II), 14701-22-5.

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Contribution from the Department of Chemistry,
Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Axial Labilization by Macrocyclic Ligands. 1. Kinetics of Replacement of Axial Acetonitrile by Imidazole and *N*-Methylimidazole in Iron(II) Complexes of 2,3,9,10-Tetramethyl- and 2,3,9,10-Tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraenes

DOROTHY E. HAMILTON, THOMAS J. LEWIS, and NICHOLAS K. KILDAHL*

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The results of a study of the kinetics of substitution of axial acetonitrile by imidazole and *N*-methylimidazole in two complexes of the type FeL(An)$_2$$^{2+}$, where L represents a 14-membered, tetraaza macrocyclic ligand, in acetonitrile and acetone solvents are presented. The axial substitution kinetics are consistent with a dissociative (D) mechanism, with dissociation of the first acetonitrile molecule as the rate-determining step. The dissociative rate constant changes substantially when peripheral substituents on the macrocycle, L, are changed from methyl to phenyl groups, the difference stemming primarily from a higher activation enthalpy in the latter case. The difference in activation parameters is discussed in terms of the structures of the macrocycles. The results are compared with those from similar studies.

Introduction

Transition-metal complexes containing macrocyclic ligands have been studied in recent years as models for biological molecules which contain porphyrin-bound metal ions. One particular area of interest in these model studies has been the labilization of metal–axial donor bonds by macrocyclic ligands