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Kinetic Studies of the Incorporation of the Zinc(II) Ion into Water-Soluble *N*-Phenyl-Substituted Porphyrins. Deformation Effect on the Metallation Rate

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Kinetics of zinc(II) ion incorporation into water-soluble *N*-phenylporphyrins (*N*-phenyl-5,10,20-tris(4-sulfonatophenyl)-15-phenylporphine: *N*-PhTPPS$_3$ and *N*-phenyl-5,10,15,20-tetrakis(4-sulfonatophenyl)porphine:*N*-PhTPPS$_4$) have been studied spectrophotometrically. The reaction proceeded through two parallel paths; one involving Zn^{2+} with a rate constant, k, and the other involving ZnOH$^+$ with a rate constant, k_{OH}. The rate constants (25 °C) and activation parameters at I=0.10 M (NaNO$_3$) were as follows (1 M=1 mol dm^{-3}): for *N*-PhTPPS$_3$ k=(2.8±0.1)×10^3 M^{-1} s^{-1}, k_{OH}=(2.1±0.1)×10^6 M^{-1} s^{-1}, $\Delta H^{\ddagger}$=54±3 kJ mol^{-1}, $\Delta H_{\mathrm{OH}}^{\ddagger}$=26±2 kJ mol^{-1}, $\Delta S^{\ddagger}$=1±10 J K^{-1} mol^{-1}, $\Delta S_{\mathrm{OH}}^{\ddagger}$=−37±8 J K^{-1} mol^{-1}; for *N*-PhTPPS$_4$ k=(5.3±0.3)×10^3 M^{-1} s^{-1}, k_{OH}=(2.0±0.2)×10^6 M^{-1} s^{-1}, $\Delta H^{\ddagger}$=62±4 kJ mol^{-1}, $\Delta H_{\mathrm{OH}}^{\ddagger}$=34±8 kJ mol^{-1}, $\Delta S^{\ddagger}$=35±14 J K^{-1} mol^{-1}, $\Delta S_{\mathrm{OH}}^{\ddagger}$=−11±28 J K^{-1} mol^{-1}. The rate of complexation for *N*-phenyl-substituted porphyrin was slower than that for the open-chain ligands, but much faster than that for the non-*N*-substituted homologues. This was due to the steric deformation of the porphyrin ring because of the presence of the bulky phenyl group. The ZnOH$^+$ species was much more reactive in comparison to the Zn^{2+} species. Such a bound-ligand effect could be partly attributed to the labilization of the coordinated water molecules by electron donation from the bound hydroxide.

Much attention has been directed to the mechanisms of the complex formation reactions of metal ions. The rate of complexation in many systems can be reasonably estimated on the basis of the Eigen mechanism.$^{1)}$ On the other hand, the rate of complexation of porphyrins is several orders of magnitude slower than that of usual open-chain ligands.$^{2)}$ Recently, extensive studies have been focused on the mechanisms of metal ion incorporation into porphyrins.$^{3-5)}$ In the case of *N*-methylporphyrin, in which a methyl group substitutes for one of the two hydrogen atoms bound to the pyrrole nitrogen atoms, displacement of the methyl group from the porphyrin plane due to its bulkiness causes tilting distortions of the pyrrole rings as shown by X-ray crystallography.$^{6)}$ The nonplanarity of an *N*-substituted porphyrin influences the rate of the metal ion incorporation reactions.$^{7)}$ The structures and abbreviations of the porphyrins cited in this paper are shown in Fig. 1. Previously, we have investigated the reaction of TPP and *N*-MeTPP with copper(II), zinc(II), and cadmium(II) in *N*,*N*-dimethylformamide (DMF) and demonstrated the difference in their reaction mechanisms.$^{3a)}$ Furthermore, the kinetics of incorporation of the first-row transition metal ions into *N*-MeTPP have been studied in DMF.$^{3b)}$ The complexation of *N*-MeTPP was slower than the corresponding solvent exchange, but still much faster than the complexation of the nonmethylated homologue (TPP). These facts indicate the deformation of the porphyrin is a rapid process occurring prior to the rate-determining step.

From an analytical point of view, porphyrins are very useful as reagents for trace-metal analysis because of their extraordinarily large molar absorption coefficients of several hundred thousand mol^{-1} dm^3 cm^{-1} at 400—500 nm (the so-called Soret band). However, a disadvantage is the fact that the metallation rate of porphyrins is abnormally slow. Several procedures have been proposed for enhancement of the rate of metalloporphyrin formation.$^{8)}$ Therefore, taking into account the deformation effect previously reported,$^{3a,b)}$ we wished to synthesize water-soluble porphyrins with bulkier substituents at the pyrrole nitrogens, clarify mechanistically the degree of the deformation effect on

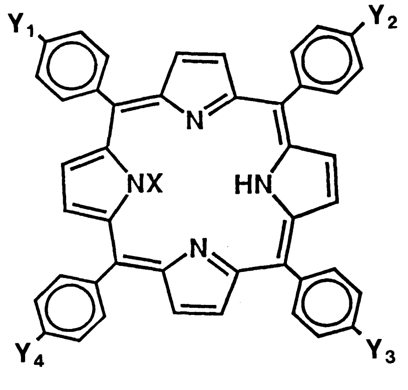

Fig. 1. Structures of porphyrins. This form of the porphyrin in which two pyrrole nitrogens are unprotonated is referred to as the free base form. TPP: X=H, Y=H; *N*-MeTPP: X=CH$_3$, Y=H; TPPS$_4$: X=H, Y=SO$_3^-$; *N*-MeTPPS$_4$: X=CH$_3$, Y=SO$_3^-$; *N*-PhTPPS$_4$: X=C$_6$H$_5$, Y=SO$_3^-$; *N*-PhTPPS$_{3(5,10,20)}$: X=C$_6$H$_5$, Y$_3$=H, Y$_1$=Y$_2$=Y$_4$=SO$_3^-$; *N*-PhTPPS$_{2(5,20)}$: X=C$_6$H$_5$, Y$_2$=Y$_3$=H, Y$_1$=Y$_4$=SO$_3^-$; *N*-PhTPPS$_{2(5,10)}$: X=C$_6$H$_5$, Y$_3$=Y$_4$=H, Y$_1$=Y$_2$=SO$_3^-$.

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the metallation rate, and use the results to shed light on the analytical aspects.

In this paper, we shall describe our studies of the kinetics and mechanisms of the reactions of water-soluble *N*-phenylporphyrins (*N*-phenyl-5,10,20-tris(4-sulfonatophenyl)-15-phenylporphine: *N*-PhTPPS$_{3(5,10,20)}$ and *N*-phenyl-5,10,15,20-tetrakis(4-sulfonatophenyl)-porphine: *N*-PhTPPS$_4$) with the zinc(II) ion in aqueous solution.

Experimental

Reagents. *N*-Phenyl-tetraphenylporphine (*N*-PhTPP) was synthesized and purified by a method previously reported.[9] Water-soluble *N*-phenylporphyrins were synthesized by the sulfonation of *N*-PhTPP. The *N*-phenyl group was not sulfonated under the present reaction conditions. All nine sulfonated species were obtained.[10] In this paper, our studies concerned *N*-PhTPPS$_4$ and *N*-PhTPPS$_{3(5,10,20)}$ (hereafter written as *N*-PhTPPS$_3$ for simplicity).

N-PhTPPS$_4$ was synthesized by heating a mixture of *N*-PhTPP (100 mg), chloroform (25 cm^3), and sulfuric acid (10 cm^3) under reflux for 48 h. After dropwise addition of 30 cm^3 of cooled water, a dark green precipitate appeared. The precipitate was extracted from the aqueous solution with chloroform as an ion pair with tetra-*n*-butylammonium ion. The solvent was evaporated under reduced pressure and the crude product was chromatographed on a silica column using chloroform–methanol (16:3) as an eluent containing 0.5% triethyl amine. The resulting dark green solution was evaporated to dryness and the residue dissolved in 0.1 M NaOH solution was desalted by a column (Bond Elut C-18, Analytichem), using methanol as an eluent. Recrystallization from methanol–diethyl ether gave dark purple crystals of the sodium salt of *N*-PhTPPS$_4$ in a 92% yield. Found: C, 46.67; H, 3.77; N, 4.34%. Calcd for $C_{50}H_{30}N_4O_{12}S_4Na_4\cdot 10H_2O$: C, 46.95; H, 3.94; N, 4.38. Sodium salt of *N*-PhTPPS$_3$ was similarly synthesized under reflux for 3 h (29% yield). Found: C, 54.40; H, 3.83; N, 5.07%. Calcd for $C_{50}H_{31}N_4O_9S_3Na_3\cdot 6H_2O$: C, 54.34; H, 3.92; N, 5.07%.

Zinc(II) nitrate (reagent grade, Wako) was purified by double recrystallization. Impurities of heavy metal ions contained in reagent grade sodium nitrate were separated by coprecipitation with iron(III) hydroxide at ca. pH 8 in the presence of active carbon. The sodium nitrate was then recrystallized twice and was used to maintain the ionic strength. Sodium acetate, 2-*N*-morpholinoethanesulfonic acid (MES), 3-*N*-morpholinopropanesulfonic acid (MOPS), and 3-(tris(hydroxymethyl)amino)-propanesulfonic acid (TAPS), used as pH buffers, were recrystallized twice from aqueous ethanol.

Measurements. The temperature of the reaction solutions was controlled to within ±0.1 °C. The ionic strength was maintained at 0.10 M with sodium nitrate. The hydrogen ion concentration was measured by a Metrohm pH meter (Model 605) with a glass electrode (Metrohm, Type EA109) and a reference electrode (Metrohm, Type EA404). A 1.000×10^{-2} M aqueous solution of nitric acid at I=0.100 M was used as a ph standard solution.[11] The glass electrode was calibrated by testing the response of the emf value to the hydrogen ion concentration during the titration of the ph standard solution by a sodium hydroxide solution at a certain temperature.

Visible absorption spectra were recorded on a Shimadzu spectrophotometer (UV-265FW). Reaction rates were followed spectrophotometrically after mixing two solutions of porphyrin and Zn^{2+} using a sample mixing device (Type MX7, Union Giken, Osaka).

Results

Determination of Protonation Constants of *N*-PhTPPS$_4$ and *N*-PhTPPS$_3$. The visible absorption spectra of *N*-PhTPPS$_4$ in the presence of acetic acid (pK_a=4.74), MES (pK_a=6.15), MOPS (pK_a=7.20), and TAPS (pK_a=8.40) as buffers were measured at I=0.100 M (NaNO$_3$) as a function of the hydrogen ion concentration which was varied by addition of a 0.100 M sodium hydroxide solution. The typical conditions are given in the figure caption.[12] The change in the spectra having clear isosbestic points at 396, 444, and 652 nm over the pH range 1—4 and at 436, 494, and 640 nm over the pH range 7 to 12 can be attributed to the following protonation reactions:

$$\mathrm{Hphps_4}^{4-} + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} \mathrm{H_2phps_4}^{3-}, \tag{1}$$

$$\mathrm{H_2phps_4}^{3-} + \mathrm{H}^+ \overset{K_2}{\rightleftharpoons} \mathrm{H_3phps_4}^{2-}, \tag{2}$$

where Hphps$_4^{4-}$ represents the free base of *N*-PhTPPS$_4$ and K_1 and K_2 are the protonation constants defined as $K_1=[\mathrm{H_2phps_4}^{3-}][\mathrm{H}^+]^{-1}[\mathrm{Hphps_4}^{4-}]^{-1}$ and $K_2=[\mathrm{H_3phps_4}^{2-}][\mathrm{H}^+]^{-1}[\mathrm{H_2phps_4}^{3-}]^{-1}$. The apparent molar absorption coefficient, ε, is expressed by Eq. 3 as a function of the hydrogen ion concentration:

$$\varepsilon=\frac{\varepsilon_1+\varepsilon_2K_1[\mathrm{H}^+]+\varepsilon_3K_1K_2[\mathrm{H}^+]^2}{1+K_1[\mathrm{H}^+]+K_1K_2[\mathrm{H}^+]^2}, \tag{3}$$

where ε_1, ε_2, and ε_3 are the molar absorption coefficients of Hphps$_4^{4-}$, H$_2$phps$_4^{3-}$, and H$_3$phps$_4^{2-}$, respectively. Figure 2 shows the relation between ε and ph according to Eq. 3 at I=1.0 M and 25 °C. Values of $\log K_1$ and $\log K_2$ at I=1.0 M and 25 °C, and values of $\log K_1$ at I=0.100 M and 15.0, 25.0, and 35.0 °C were determined by applying a nonlinear least-squares fit to Eq. 3 (Table 1). *N*-PhTPPS$_3$, *N*-PhTPPS$_{2(5,20)}$, and *N*-PhTPPS$_{2(5,10)}$ are insoluble in acidic aqueous solution, but free bases, i.e. Hphps$_3^{3-}$ and Hphps$_2^{2-}$, in alkali solution are soluble. Monoprotonated species, i.e. H$_2$phps$_3^{2-}$ and H$_2$phps$_2^{-}$, form aggregated species that gradually precipitate. The latter precipitation is within several tens of minutes faster than the former. Thus, we measured the spectrum change as a function of the hydrogen ion concentration for *N*-PhTPPS$_3$ before the aggregation occurred. The first protonation constants have been determined at I=0.100 M (NaNO$_3$) and at 15.0, 25.0, and 35.0 °C, respectively (Fig. 3). Values for the protonation constants and corresponding thermodynamic parameters are listed in Table 1.

Kinetics of the Incorporation of the Zinc(II) Ion into *N*-PhTPPS$_3$ and *N*-PhTPPS$_4$. Rates for the complex formation of *N*-PhTPPS$_3$ and *N*-PhTPPS$_4$ with the zinc(II) ion were spectrophotometrically measured over a pH range from 5.5 to 7.5 using less than 1.5×10^{-3} M MES and MOPS as pH buffers at I=0.10 M ($NaNO_3$). In all kinetic measurements, the zinc(II) ion was used in large excess over porphyrin to guarantee pseudo first-order conditions. First-order plots were linear for at least 3 half-lives. Thus, the rate was expressed as

$$-dC_P/dt = k_{0(Zn,H)}C_P, \tag{4}$$

where $k_{0(Zn,H)}$ and C_P represent the conditional first-order rate constant and the total concentration of porphyrin uncoordinated to the zinc(II) ion, respectively. $k_{0(Zn,H)}$ at a constant pH was linearly related to the zinc(II) concentration (Fig. 4). Figure 5 shows the pH dependence of the second-order rate constant $k_{0(H)}$ for the *N*-PhTPPS₃ and *N*-PhTPPS₄ systems. Under the present experimental conditions, zinc(II) ion did not react with buffer reagents to form complexes judging from the stability constants. It was confirmed that the presence of the buffer reagents had no effect on the rates. Over the studied pH range, the porphyrin ligand existed mainly as H_2P, which was referred to as $H_2phps_4{}^{3-}$ or $H_2phps_3{}^{2-}$, and the zinc(II) ion was possibly partly hydrolyzed judging from the hydrolysis constants of Zn^{2+}.[13)] Therefore, the proportional increase in log $k_{0(H)}$ with increasing pH was attributable to the reaction of HP instead of H_2P. Moreover, the accelerated rate at the higher pH should have been caused by the contribution of the more reactive $ZnOH^+$. Thus, the reaction steps could be expressed as in Eqs. 5—7.

$$H_2P \overset{K_1{}^{-1}}{\rightleftharpoons} HP + H^+, \tag{5}$$

$$Zn^{2+} + HP \xrightarrow{k} ZnP + H^+, \tag{6}$$

$$ZnOH^+ + HP \xrightarrow{k_{OH}} ZnP, \tag{7}$$

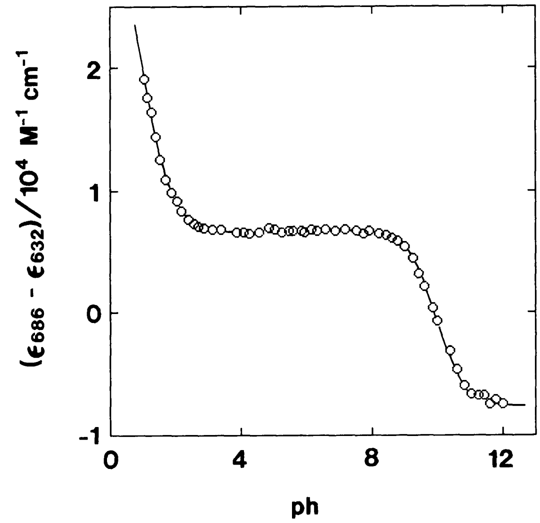

Fig. 2. Apparent molar absorption coefficient of *N*-PhTPPS₄ solution as a function of ph at T=25.0 °C and I=1.00 M. Conditions: $C_P=3.1\times10^{-6}$ M, $C_{CH_3COOH}=C_{MES}=C_{MOPS}=C_{TAPS}=C_{EDTA}=1.5\times10^{-3}$ M. ε_{686} refers to the apparent molar absorption coefficient at 686 nm. The solid curve was depicted using the protonation constants obtained.

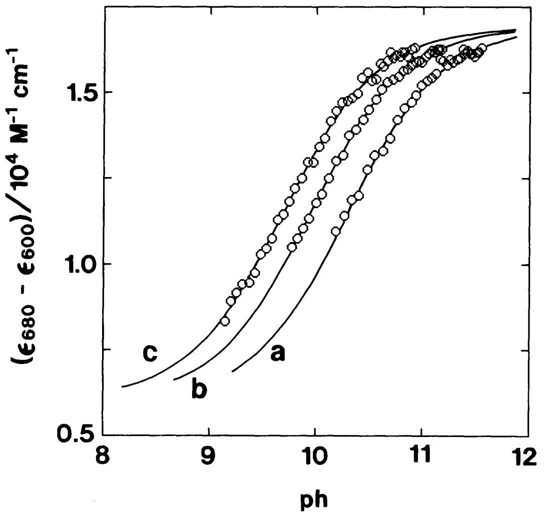

Fig. 3. Apparent molar absorption coefficient of *N*-PhTPPS₃ solution as a function of ph at I=0.100 M and T=15.0 (a), 25.0 (b), and 35.0 °C (c). $C_P=(7—8)\times10^{-6}$ M, $C_{MOPS}=C_{TAPS}=C_{EDTA}=1.5\times10^{-3}$ M. The solid curves were calculated using the protonation constants obtained.

Table 1. Values of the Protonation Constants of *N*-PhTPPS₄ and *N*-PhTPPS₃ at I=0.100 M ($NaNO_3$)

T/°C	*N*-PhTPPS₄		*N*-PhTPPS₃
	K_1/M⁻¹	K_2/M⁻¹	K_1/M⁻¹
15.0	$(1.66\pm0.04)\times10^{10}$		$(1.92\pm0.15)\times10^{10}$
25.0	$(9.52\pm0.17)\times10^{9}$		$(8.9\pm0.3)\times10^{9}$
	$(9.52\pm0.26)\times10^{9}$ a)	8.93 ± 0.60 a)	
35.0	$(3.69\pm0.07)\times10^{9}$		$(4.9\pm0.2)\times10^{9}$
ΔH/kJ mol⁻¹	−55±9		−50±3
ΔS/J K⁻¹ mol⁻¹	4±31		22±9

a) I=1.00 M ($NaNO_3$).

where HP is the free base of *N*-PhTPPS$_4$ or *N*-PhTPPS$_3$, i.e. Hphps$_4^{4-}$ or Hphps$_3^{3-}$ and for simplicity the charge is omitted. Therefore, based on the assumption of a fast hydrolysis reaction, the conditional second-order rate constant, $k_{o(H)}$, is given by Eq. 8.

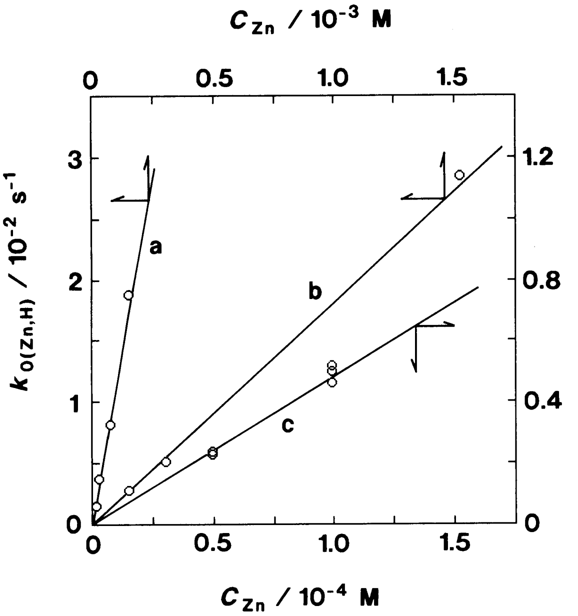

Fig. 4. Dependence of conditional first-order rate constant $k_{o(Zn,H)}$ on the zinc(II) ion concentration C_{Zn} at 25.0 °C and I=0.10 M. a: *N*-PhTPPS$_4$, ph=7.35; b: *N*-PhTPPS$_4$, ph=6.87; c: *N*-PhTPPS$_3$, ph=7.24.

$$k_{o(H)} = \frac{k + k_{OH}K_{OH}[H^+]^{-1}}{(1 + [H^+]K_1)(1 + K_{OH}[H^+]^{-1})}, \tag{8}$$

where k and k_{OH} are the second-order rate constants for reactions 6 and 7, respectively, and K_{OH} is the hydrolysis constant of Zn^{2+}: $K_{OH}=[ZnOH^+][H^+][Zn^{2+}]^{-1}$. The values of enthalpy and entropy of activation based on the Eyring equation were estimated by a nonlinear least-squares method and are summarized in Table 2. For the evaluation, we used $K_{OH}/M=3.08\times10^{-10}$ at 15 °C, 6.76×10^{-10} at 25 °C, and 1.41×10^{-9} at 35 °C.[13]

Discussion

It is known that various anionic porphyrins tend to stack spontaneously in aqueous solutions to form dimers and/or higher aggregates, the binding constants for dimerization being reported to be 10^4—10^7 M^{-1}.[14,15] The tendency to aggregate is higher with a decreasing number of sulfonate groups. We did not make a detailed study of the aggregation, but did carry out the experiments at the lowest porphyrin concentration possible and over the pH range where no aggregation occurred.

Interestingly, the log K_1 and log K_2 values for *N*-substituted porphyrins are widely separated. The difference is 9.0 for *N*-PhTPPS$_4$ and 5.8 for *N*-MeTPPS$_4$ (log K_1=8.82±0.03 and log K_2=3.04±0.20 at I=0.10 M and 25 °C)[3c] whereas it is only 0.2 for TPPS$_4$ (log K_1=4.99±0.01 and log K_2=4.76±0.02 at I=0.1 M

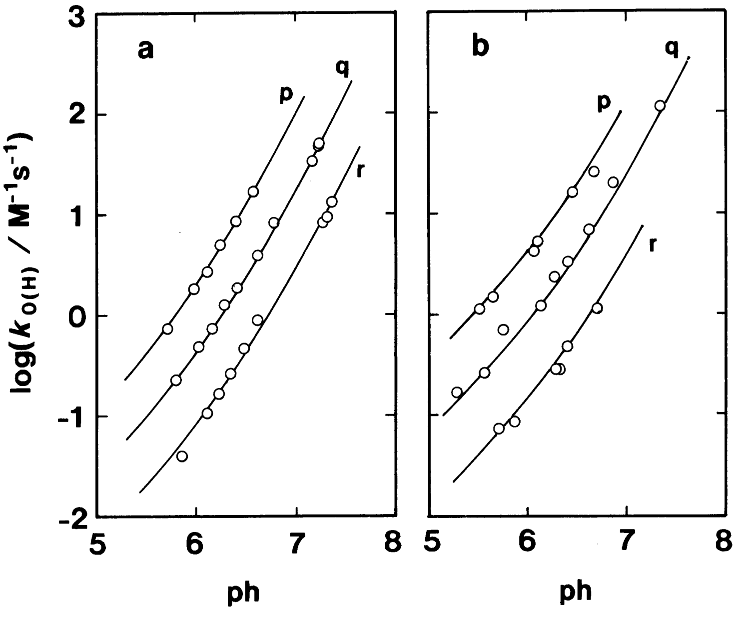

Fig. 5. Hydrogen ion concentration dependence of $k_{o(H)}$ for the metallation of *N*-PhTPPS$_3$ (a) and *N*-PhTPPS$_4$ (b). C_P=(3—9)×10^{-6} M, C_{Zn}=9×10^{-5}—5×10^{-3} M, I=0.10 M. The concentrations of the buffer reagents were less than 1.5×10^{-3} M. T=35.0 °C (p), 25.0 °C (q), 15.0 °C (r). Each point refers to the average of several determinations. The solid curves were calculated using the obtained values of enthalpy and entropy of activation.

Table 2. Rate Constants and Activation Parameters for Metalloporphyrin Formation of the Zinc(II) Ion with N-PhTPPS$_4$, N-PhTPPS$_3$, TPPS$_4$, and N-MeTPPS$_4$ in Aqueous Solution

	k	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k_{OH}	$\Delta H_{OH}^{\ddagger}$	$\Delta S_{OH}^{\ddagger}$
N-PhTPPS$_4$	$(5.3\pm0.3)\times10^3$	62 ± 4	35 ± 14	$(2.0\pm0.2)\times10^6$	34 ± 8	-11 ± 28
N-PhTPPS$_3$	$(2.8\pm0.1)\times10^3$	54 ± 3	1 ± 10	$(2.1\pm0.1)\times10^6$	26 ± 2	-37 ± 8
TPPS$_4$[a]	1.6 ± 0.1					
N-MeTPPS$_4$[b]	$(5.0\pm0.7)\times10^3$			$(4.4\pm1.8)\times10^4$		

Rate constant (25.0 °C)/$M^{-1}\,s^{-1}$; activation enthalpy/kJ mol^{-1}; activation entropy/J mol^{-1} K^{-1}. a) Ref. 5b. b) Ref. 3c.

and 25 °C).4a) Since the phenyl group is electron-withdrawing and the methyl group is electron-donating, it would be expected that the basicity of the non-N-substituted porphyrin (TPPS$_4$) is greater than that of the N-phenyl porphyrin and smaller than that of the N-methyl porphyrin. However, the $\log K_1$ value increases in the order TPPS$_4$ < N-MeTPPS$_4$ < N-PhTPPS$_4$. Since the introduction of a bulky group to one of the pyrrole nitrogen atoms distorts the porphyrin ring, the delocalized porphyrin π-system should be reduced. The effect of distortion depends largely on the bulkiness of the substituted group and it is much greater in the case of N-PhTPPS$_4$ than for N-MeTPPS$_4$. Moreover, the small difference in the $\log K_1$ value between N-PhTPPS$_4$ and N-PhTPPS$_3$ shows that the peripheral charge does not affect the porphyrin π-system.

Judging from the reported structure of ZnCl(N-PhTPP),16) the coordination geometry of the zinc(II) complexes of N-PhTPPS$_4$ and N-PhTPPS$_3$ in water is a highly distorted square pyramid, with a water molecule occupying the apical position with a long bond to the substituted nitrogen atom, and the zinc(II) ion does not lie in the central cavity of the porphyrin molecule.

The second-order rate constants, k_f, for complexation of zinc(II) ion with open-chain ligands are available: $\log(k_f/M^{-1}\,s^{-1})=6.6$ (ammonia),17) 6.0 (2,2′-bipyridine: bpy),18) 6.1 (2,2′,2″-terpyridine),18) 6.9 (acetate$^-$),19) 7.8 (glycinate$^-$),20) 6.8 (dithizone$^-$),21) and 9.60 (1,3-propylenediaminetetraacetate^{3-}).22) Coordination of ligands on the hexaaquazinc(II) ion23) is expected to follow an interchange mechanism.24) The reaction sequence is expressed in Eq. 9,

$$[Zn(OH_2)_6]^{2+} + L\text{-}L^{n-} \overset{K_{OS}}{\rightleftharpoons} [Zn(OH_2)_6{}^{2+}, L\text{-}L]^{(2-n)+} \xrightarrow{k^*} [(H_2O)_5Zn\text{-}L\text{-}L]^{(2-n)+} \xrightarrow{\text{fast}} \left[(H_2O)_4Zn\begin{smallmatrix}L\\ L\end{smallmatrix}\right]^{(2-n)+}, \tag{9}$$

where K_{OS} is the equilibrium constant for the outer-sphere association and k^* is the first-order rate constant for the interchange of a coordinated water molecule with an incoming ligand, L-L^{n-} (here a bidentate). The initial diffusion-controlled approach of the incoming ligand in the vicinity of the aqua ion to form an outer-sphere complex is followed by the inner-sphere complex formation. Mostly, the ring-closure process in the case of an open-chain polydentate ligand is not rate-limiting. If a dissociative interchange (I_d) takes place, the rate constant, k^*, may be comparable to the rate of the exchange of water on the zinc(II) ion. Recently, Ducommun et al. have claimed a dissociative interchange mechanism for complexation of the zinc(II) ion with bpy on the basis of the positive activation volume (7.1 cm^3 mol^{-1}).25)

As is apparent from the figures in Table 2, the second-order rate constants for metallation of N-substituted porphyrins are much larger than those for non-N-substituted homologues such as TPPS$_4$, but much smaller than those for the open-chain ligands described earlier. We have previously investigated the kinetics of incorporation of metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}) into N-MeTPP in DMF, and demonstrated that the rate of metallation of N-MeTPP is parallel to the rate of solvent exchange at the relevant solvated metal ion.3b) These findings indicate that the rate-determining step is the interchange process between a coordinated DMF molecule and the donor atom of the porphyrin, and that the deformation of the porphyrin is a rapid process occurring prior to the rate-determining step. This is the case for the present systems.

If we accept the rapid deformation equilibrium of the porphyrin nucleus prior to the rate-determining step for the interchange between the donor atom of the porphyrin and the coordinated water molecule, we have

$$k = K_{OS}K_D k^*, \tag{10}$$

where K_D refers to the deformation equilibrium constant.3b,6,26) A lone electron pair on the donor nitrogen atoms of the porphyrin should be directed away from the porphine ring for accepting the zinc(II) ion. Since, in the case of N-phenylporphyrins, partial deformation has already been established due to the steric bulkiness of the substituted phenyl group, the K_D value for the N-phenyl-substituted porphyrin should be much larger than that for the non-N-substituted planar porphyrin.

The fact that the $ZnOH^+$ species is much more reactive in comparison to the Zn^{2+} species in both N-PhTPPS$_3$ and N-PhTPPS$_4$ systems is strongly reflected in the activation enthalpy. Such a rate enhancement should be attributed to the labilization of the coordinated water molecules by electron donation from the bound hydroxide, as already reported for the complexation of the monohydroxoiron(III) ion.[27] Existence of such a bound ligand effect implies that the substitution of hydrated water molecules on the zinc(II) ion plays an important role in the rate-determining step. However, the degree of the bound ligand effect would be much larger than that predicted by the relation previously proposed.[28] The fact that the entropy term $\Delta S_{\mathrm{OH}}^{\neq}$ is considerably smaller than $\Delta S^{\neq}$ may indicate the entropy change contribution in the deformation equilibrium (K_{D}). The deformation process would involve a specific interaction such as hydrogen-bonding between the monohydroxozinc(II) ion and the pyrrole proton.

From an analytical point of view, several points can be summarized. The tendency to aggregation for *N*-PhTPPS$_n$ in water becomes high with a decreasing number (n) of sulfonate groups. The basicity of the free base (HP), i.e. the protonation constant K_1, is only slightly affected by the degree of sulfonation, whereas it is affected by the bulkiness of the substituents at the pyrrole nitrogens: the deformation effect. The larger the degree of deformation, the faster the metallation rate (k) for the free base and the larger the K_1 value.

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