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Effect of 18-Crown-6 on Ligand-Substitution and Acid-Dissociation Reactions of Zinc(II), Cadmium(II), and Lead(II) Porphyrins

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The ligand-substitution reaction of $M(tpps)^{4-}$ (M = Zn, Cd, Pb; H_2tpps^{4-} = 5, 10, 15, 20-tetrakis(4-sulfonatophenyl)porphyrin) with *N,N'*-1,2-ethanediylbis[*N*-(carboxymethyl)glycine] (H_4edta) and the acid-dissociation reaction of the metalloporphyrins are inhibited by the presence of 18-crown-6 (18C6). The kinetics and mechanism were studied to clarify the effect of 18C6 on the reactions at pH 8−9.5, 25 °C, and $I = 0.1$ M ($LiNO_3$). The rate suppression by 18C6 was explained by the formation of $[M(tpps)(18C6)]^{4-}$ as a precursor complex. The rate equation for the decrease of $M(tpps)^{4-}$ is expressed as $-d[M(tpps)']/dt = (k_1[Hedta^{3-}] + k_2K_{MPL}[18C6][Hedta^{3-}] + k_3[H^+]^2 + k_4K_{MPL}[18C6][H^+]^2)(1+K_{MPL}[18C6])^{-1}[M(tpps)']$, where $[M(tpps)'] = [M(tpps)^{4-}] + [M(tpps)(18C6)]$, and $K_{MPL} = [M(tpps)(18C6)^{4-}][M(tpps)^{4-}]^{-1}[18C6]^{-1}$. The values of k_1 (mol^{-1} dm^3 s^{-1}), k_3 (mol^{-2} dm^6 s^{-1}), and K_{MPL} (mol^{-1} dm^3) were found to be 0.00, 10.5 ± 0.9, and $10^{2.5\pm0.1}$ for $Zn(tpps)^{4-}$, 6.4 ± 0.2, (7.1 ± 0.3) × 10^{12}, and $10^{2.7\pm0.1}$ for $Cd(tpps)^{4-}$, and 2.9 ± 0.1, (1.85 ± 0.05) × 10^{12}, and $10^{1.8\pm0.1}$ for $Pb(tpps)^{4-}$, respectively. The k_2 and k_4 values were not able to be determined for all the metalloporphyrins because $k_1 \gg k_2$ and $k_3 \gg k_4$. The intermediate, $[M(tpps)(18C6)]^{4-}$, hinders the attack of $Hedta^{3-}$ or H^+. The intermediate is formed by the interaction of the metalloporphyrin plane with 18C6 ring, and the interaction was confirmed by ^1H NMR and absorption spectra. The ^1H NMR signal of 18C6 shifted to a higher field and the change in absorption spectra was larger for $Cd(tpps)^{4-}$ than for Zn- and $Pb(tpps)^{4-}$. The detailed reaction mechanism and the formation of the intermediates are discussed.

Introduction

The ionic radius of a metal ion is an important factor governing metalloporphyrin formation especially compared to metal complex formation of open-chain ligands.[1−3] The formation constant of the zinc(II) porphyrin of tetrakis(4-sulfonatophenyl)porphyrin (H_4tpps^{4-}) is about 10^9 times larger than those of cadmium(II) or lead(II),[4] and the acid-dissociation rate of $Zn(tpps)^{4-}$ is 10^{12} times slower than those of Cd- or $Pb(tpps)^{4-}$.[1,5−8] Furthermore, Zn^{2+} in $Zn(tpps)^{4-}$ is hardly replaced with *N,N'*-1,2-ethanediylbis[*N*-(carboxymethyl)glycine] (H_4edta) at pH 8−9.5, but Cd^{2+} or Pb^{2+} in Cd- or $Pb(tpps)^{4-}$ is easily substituted with $Hedta^{3-}$.[9] The noticeable differences in the kinetic behaviors of zinc(II), cadmium(II), and lead(II) have been applied to the determination of a small amount of zinc(II) in a large excess of cadmium(II) or lead(II).[5,6] In contrast to porphyrins, the formation constants of zinc(II) and cadmium(II) complexes with H_4edta are $10^{16.44}$ and $10^{16.36}$, respectively, and these values are comparable to each other.[10] The differences in kinetic and thermodynamic behaviors of zinc(II), cadmium(II), and lead(II) porphyrins are ascribed to their different ionic radii: Zn^{2+}(75 pm); Cd^{2+}(95 pm); Pb^{2+}(118 pm). Zinc(II) is incorporated in the porphyrin core,[11,12] but cadmium(II) and lead(II) do not fit well in the porphyrin core because of their large ionic radii.[13,14] X-ray analyses of cadmium(II) and lead(II) porphyrin complexes show displacement of cadmium(II) and lead(II) from the mean porphyrin plane by 65[13] and 117 pm,[14] respectively.

Comparing the cadmium(II) and lead(II) equilibrium constants (log K(Cd) = −9.92; log K(Pb) = −9.94),[4] one may notice that their respective metalloporphyrins have comparable values in spite of the difference in their ionic radii. In this case, we have to consider another factor like solvation energy of the metal ions. The hydration free energies of Cd^{2+} and Pb^{2+} are 1802 and 1497 kJ mol^{-1}, respectively.[15] The ionic radius of Cd^{2+} is smaller than that of Pb^{2+}, but the solvation energy of Cd^{2+} is higher than Pb^{2+}. Thus the formation of a cadmium(II) porphyrin complex is compensated for by the desolvation energy of Cd^{2+} in the process of the respective metalloporphyrin. Similar chemical properties have been observed for metal complexes with crown ether, where the ionic radius of the metal ion and the cavity size of the crown ether are of prime importance.[16] Lead(II) forms a stable complex with 18-crown-6 (18C6) and the formation constant is $10^{4.27}$,[17] but zinc(II) and cadmium(II) do not form stable complexes with 18-crown-6 in

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aqueous solution, because of their small ionic radii and large hydration energies.[16,17]

We have been interested in the distinct chemical properties of the porphyrin and the crown ether complexes. If the crown ether is added to a solution containing metalloporphyrin, what type of interaction occurs between them? In this paper, we studied the interaction of the metalloporphyrins of zinc(II), cadmium(II), and lead(II) ($M(tpps)^{4-}$; M = Zn^{2+}, Cd^{2+}, Pb^{2+}) with 18-crown-6 on the ligand-substitution and the acid-dissociation reactions of the metalloporphyrins. The main purpose of this work is to elucidate how 18-crown-6 affects the reactivities of the metalloporphyrins and how these two react with each other. The reactivities and the mutual interaction were studied by kinetic, ^1H NMR, and spectrophotometric methods.

Experimental Section

Reagents. 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin (H_2tpps^{4-}) was synthesized by the methods described in the literature,[18,19] and its acidic form (H_6tpps) was purified by recrystallization from an ethanol/acetone solution and by Sephadex LH-20 gel column chromatography. Final purity was checked by ^1H NMR and thin-layer chromatography. 18-Crown-6 (Tokyo Kasei Co. Ltd., Japan) was dried, *in vacuo*, at room temperature for 3 days. Solutions of zinc(II), cadmium(II), and lead(II) were prepared from their nitrates and the concentrations of these metal ions were determined by EDTA titration using Xylenol Orange or Eriochrome Black T indicators. The ionic strength of the sample solution was held constant (0.1 mol dm^{-3}) with lithium nitrate. Lithium nitrate was a superpure reagent (Merck), free from heavy metal ions. All other reagents were of analytical reagent grade and all solutions were prepared with ultrapure water treated by a Milli-Q SP TOC (Nippon Millipore Ltd., Japan).

Kinetic Measurements. The ligand-substitution reaction of Cd- and $Pb(tpps)^{4-}$ with H_4edta was studied in the pH range 8.0–9.5 (borate buffer, 10^{-2} mol dm^{-3}) at various concentrations of H_4edta (10^{-3}–10^{-2} mol dm^{-3}), metal ions (Cd^{2+}, Pb^{2+}; each at 5×10^{-6} to 6×10^{-5} mol dm^{-3}), 18-crown-6 (1×10^{-3} to 2×10^{-2} mol dm^{-3}) and H_2tpps^{4-} (1×10^{-6} to 4×10^{-6} mol dm^{-3}), and in 0.1 mol dm^{-3} lithium nitrate. The acid dissociation rate was measured at pH 4.5–5.5 (acetate buffer, 10^{-2} mol dm^{-3}) for Cd- and $Pb(tpps)^{4-}$, at pH 1–2 (nitric acid solution) for $Zn(tpps)^{4-}$, and at various concentrations of H_2tpps^{4-}, 18-crown-6, and metal ions (Zn^{2+}, Cd^{2+}, Pb^{2+}) as described for the ligand-substitution reaction. The metalloporphyrin solutions ($(2-8) \times 10^{-6}$ mol dm^{-3}) were prepared in a 25% excess of the corresponding metal ion compared to H_2tpps^{4-}. Thus, the concentration of H_4edta bound to the free metal ions, Pb^{2+}, Cd^{2+}, or Zn^{2+}, is less than 1% to the added H_4edta (10^{-3} to 2×10^{-2} mol dm^{-3}). The Cd- and $Pb(tpps)^{4-}$ solutions were left for a day at pH 10, and in the case of $Zn(tpps)^{4-}$, the solution was heated in a water bath at pH 6. The prepared solutions were protected from light. The reaction was started by mixing a solution involving $M(tpps)^{4-}$ and 18-crown-6 with an H_4edta solution or an acid solution (HNO_3 or acetate buffer) using a sample mixing device (Otuka Denshi, MX7) or a stopped-flow apparatus. The change in the absorbance at Soret band region of metalloporphyrins (421 nm for $Zn(tpps)^{4-}$, 430 nm for $Cd(tpps)^{4-}$, and 465 nm for $Pb(tpps)^{4-}$) was monitored as a function of time on a Hitachi 323 spectrophotometer, a Unisoku stopped-flow apparatus, or an Otuka Denshi RA415 rapid-scan spectrophotometer. The pH values were determined by a Radiometer Ion 85 ion analyzer with a combined electrode (GK2401C). A 1.000×10^{-2} mol dm^{-3} nitric acid solution containing 0.09 mol dm^{-3} lithium nitrate was employed as a standard hydrogen ion concentration ($-\log[H^+] = 2.000$). From pH meter readings in various hydrogen ion concentrations at 0.1 mol dm^{-3} ionic strength (HNO_3–$LiNO_3$), the pH meter and electrode system were calibrated in terms of $-\log[H^+]$. All experiments were carried out at 25.0 ± 0.1 °C.

^1H NMR Spectroscopy. The ^1H NMR spectra were recorded on a JEOL GX-270 spectrophotometer (270 MHz) at 25 °C in D_2O solvent against sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) reference. The concentrations of 18-crown-6 and H_2tpps^{4-} were 10^{-2} mol dm^{-3}. A routine Fourier-transfer program was used to analyze the ^1H NMR spectra, where data were accumulated over 100 times.

Results

Effect of 18-Crown-6 on Ligand-Substitution Reactions of Zn-, Cd-, and $Pb(tpps)^{4-}$ with H_4edta. The reaction of the metalloporphyrins of zinc(II), cadmium(II), and lead(II) with H_4edta was studied in a large excess of 18-crown-6 at pH 8–9.5. Under the present experimental conditions, the porphyrin is in its free base form, H_2tpps^{4-}, since its protonation constants, $[H_3tpps^{3-}][H_2tpps^{4-}]^{-1}[H^+]^{-1}$ and $[H_4tpps^{2-}][H_3tpps^{3-}]^{-1}[H^+]^{-1}$, are $10^{4.99}$ and $10^{4.76}$, respectively.[4] Furthermore, H_4edta is present in the form of $Hedta^{3-}$ and $edta^{4-}$. The first protonation constant of $edta^{4-}$ is $10^{8.57}$ in the presence of 0.1 mol dm^{-3} $LiNO_3$.[10] Thus the reaction of $M(tpps)^{4-}$ with H_4edta can be written as

$$M(tpps)^{4-} + edta' \rightleftharpoons M(edta)^{2-} + H_2tpps^{4-} \qquad (1)$$

where M denotes Cd and Pb, and edta′ is a mixture of $Hedta^{3-}$ and $edta^{4-}$ not bound to the metal ions. From the formation constants of the $M(tpps)^{4-}$ with those of $M(edta)^{2-}$ ($\log K_{MP}(Cd) = -9.92$; $\log K_{MP}(Pb) = -9.94$; $\log K_{MY}(Cd) = 15.44$; $\log K_{MY}(Pb) = 16.94$)[4,10,20] the equilibrium constants of eq 1 are calculated to be $10^{8.69}$ and $10^{10.23}$ at pH 8 for cadmium and lead(II).[21] The metalloporphyrins are completely substituted with edta′ in its large excess and at pH 8–9.5, and the reverse reaction of eq 1 is neglected, where K_{MP} and K_{MY} are the formation constants of $M(tpps)^{4-}$ and $M(edta)^{2-}$, respectively and they are defined by $K_{MP} = [MP][H^+]^2[M^{2+}]^{-1}[H_2P]^{-1}$ and $K_{MY} = [M(edta)^{2-}][M^{2+}]^{-1}[edta^{4-}]^{-1}$.

Under these conditions, pseudo-first-order kinetics was observed for the reaction of eq 1

$$-d[M(tpps)^{4-}]/dt = k_0[M(tpps)^{4-}] \qquad (2)$$

where k_0 denotes the conditional rate constant containing the concentrations of 18-crown-6, edta′, hydrogen ion, and metal ion. Figure 1 shows the dependence of the rate constant on the concentration of 18C6. 18-Crown-6 slows down the reaction. The rate constant for the reaction of $Cd(tpps)^{4-}$ with edta′ is larger than that of $Pb(tpps)^{4-}$ at [18C6] = 0 mol dm^{-3}, but $Cd(tpps)^{4-}$ exchange reaction is significantly inhibited by the presence of 18-crown-6 (Figure 1). The k_0 value for the reaction of $Cd(tpps)^{4-}$ is directly proportional to the concentration of edta′ at constant pH. Figure 2 shows the dependence of the rate constant on hydrogen ion concentration for the reaction of $Cd(tpps)^{4-}$ in the presence of 1.00×10^{-2} mol dm^{-3} 18-crown-6. The k_0 value increases with the increase of hydrogen ion concentration and slows down gradually at high hydrogen ion concentrations. The hydrogen ion dependence of the rate constant can be explained by the protonation of edta′. Since the edta′ exists in the form of $Hedta^{3-}$ and $edta^{4-}$ under the present experimental conditions,[20] the rate equation can be

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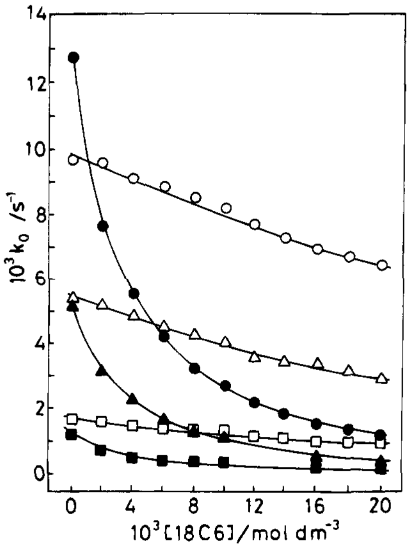


Figure 1. Effect of 18-crown-6 on the ligand-substitution reaction of Cd- (■, ▲, ●), and Pb(tpps)$^{4-}$ (□, △, ○) with H_4edta at 25 °C and I = 0.1 mol dm^{-3} ($LiNO_3$) and at pH = 8.81 and 8.62 for Cd- and Pb(tpps)$^{4-}$, respectively. 10^3[edta′]/mol dm^{-3} = 2.00 (●, ○), 6.00 (▲, △), and 10.00 (■, □).

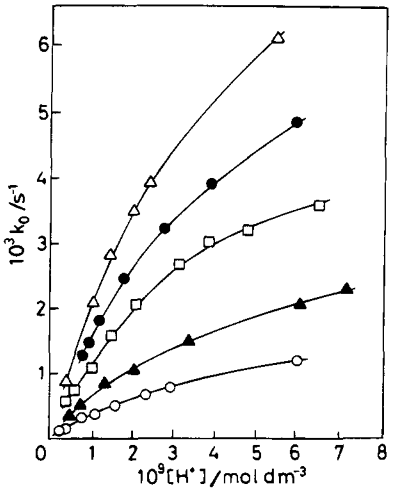


Figure 2. Dependence of the rate constant on the concentration of hydrogen ion for the reaction of Cd(tpps)$^{4-}$ with H_4edta in the presence of 18-crown-6 (1.00 × 10^{-2} mol dm^{-3}) at 25 °C and I = 0.1 mol dm^{-3} ($LiNO_3$). 10^3[edta′]/mol dm^{-3} = 2.00 (○), 4.00 (▲), 6.00 (□), 8.00 (●), and 10.0 (△).

written as

$$k_0 = k_{1(18C6)}[\text{edta}^{4-}] + k_{2(18C6)}[\text{Hedta}^{3-}] \qquad (3)$$

$$k_0 = \frac{(k_{1(18C6)} + k_{2(18C6)}K^{H}[H^+])[\text{edta}']}{1 + K^{H}[H^+]} \qquad (4)$$

where $k_{1(18C6)}$ and $k_{2(18C6)}$ are conditional rate constants involving the concentrations of 18C6, and K^H is the protonation constant of edta^{4-}: $K^H = 10^{8.57}$ in 0.1 mol dm^{-3} $LiNO_3$.[20] Equation 4 can be rearranged to give

$$k_0(1 + K^{H}[H^+])[\text{edta}']^{-1} = k_{1(18C6)} + k_{2(18C6)}K^{H}[H^+] \qquad (5)$$

The plot of the left-hand side of eq 5 against [H$^+$] gives a straight line with zero intercepts for both Cd- and Pb(tpps)$^{4-}$. The zero intercept indicates that $k_{1(18C6)} \ll k_{2(18C6)}K^H[H^+]$: the reactive chemical species of edta′ is Hedta^{3-}. The results are the same as those observed in the absence of 18-crown-6.[9] The k_0 values were determined at different concentrations of cadmium(II) and lead(II) and the k_0 value was independent of the concentrations of the metal ions. The results suggest that it is negligible for cadmium(II) or lead(II) to dissociate from Cd(tpps)$^{4-}$ or Pb(tpps)$^{4-}$ by the reaction of Hedta^{3-} with the free meal ions.

As shown in Figure 1, 18-crown-6 reduces the rate for the ligand-substitution reaction of Cd- or Pb(tpps)$^{4-}$ with edta′. If we assume the formation of a precursor complex like [M(tpps)(18C6)]$^{4-}$ which is formed through the interaction of the 18-crown-6 with the metalloporphyrin, the observed rate constant in the presence of 18-crown-6 can be given as

$$k_0[\text{M(tpps)}'] = k_1[\text{M(tpps)}^{4-}][\text{Hedta}^{3-}] + k_2[\text{M(tpps)(18C6)}^{4-}][\text{Hedta}^{3-}] \qquad (6)$$

$$k_0[\text{M(tpps)}'] = \frac{(k_1 + k_2K_{\text{MPL}}[\text{18C6}])K^{H}[H^+][\text{edta}'][\text{M(tpps)}']}{(1 + K_{\text{MPL}}[\text{18C6}])(1 + K^{H}[H^+])} \qquad (7)$$

where

$$[\text{M(tpps)}'] = [\text{M(tpps)}^{4-}] + [\text{M(tpps)(18C6)}^{4-}] \qquad (8)$$

$$[\text{M(tpps)}'] = [\text{M(tpps)}^{4-}](1 + K_{\text{MPL}}[\text{18C6}]) \qquad (9)$$

and

$$K_{\text{MPL}} = [\text{M(tpps)(18C6)}^{4-}][\text{M(tpps)}^{4-}]^{-1}[\text{18C6}]^{-1} \qquad (10)$$

Since the rate constant decreases with the increase of the 18-crown-6 concentration, it is supposed that $k_1 \gg k_2K_{\text{MPL}}[\text{18C6}]$, and we obtain the following simplified expression:

$$k_0 = \frac{k_1K^{H}[H^+][\text{edta}']}{(1 + K_{\text{MPL}}[\text{18C6}])(1 + K^{H}[H^+])} \qquad (11)$$

Equation 10 is also rearranged to give

$$k_0^{-1}K^{H}[H^+][\text{edta}'](1 + K^{H}[H^+])^{-1} = k_1^{-1} + K_{\text{MPL}}k_1^{-1}[\text{18C6}] \qquad (12)$$

A plot of the left-hand side of eq 12 against [18C6] gives a straight line with an intercept (Figure 3). The intercept and the slope of the straight line give the values of k_1 and K_{MPL}, which were found to be k_1 = 6.4 ± 0.2 mol^{-1} dm^3 s^{-1} and $K_{\text{MPL}} = 10^{2.8\pm0.1}$ mol^{-1} dm^3 for Cd(tpps)$^{4-}$ and k_1 = 2.9 ± 0.1 mol^{-1} dm^3 s^{-1} and $K_{\text{MPL}} = 10^{1.6\pm0.1}$ mol^{-1} dm^3 for Pb(tpps)$^{4-}$. 18-Crown-6 more strongly interacts with Cd(tpps)$^{4-}$ than Pb(tpps)$^{4-}$. The straight line also confirms the assumption that $k_1 \gg k_2K_{\text{MPL}}[\text{18C6}]$. Finally, the reaction mechanism to account for the kinetic data for the ligand-substitution reaction of M(tpps)$^{4-}$ with edta′ is

$$\text{M(tpps)}^{4-} + \text{18C6} \xrightleftharpoons{K_{\text{MPL}}} [\text{M(tpps)(18C6)}]^{4-} \qquad (13)$$

$$\text{M(tpps)}^{4-} + \text{Hedta}^{3-} \xrightarrow{k_1} \text{M(edta)}^{2-} + H_2\text{tpps}^{4-} + OH^- \qquad (14)$$

and the rate equation is rewritten as

$$k_0 = k_1[\text{Hedta}^{3-}](1 + K_{\text{MPL}}[\text{18C6}])^{-1} \qquad (15)$$

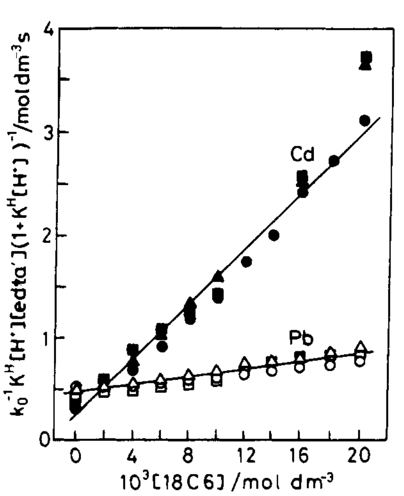


Figure 3. Plot of $k_0^{-1}K^H[H^+][edta'](1 + K^H[H^+])^{-1}$ vs [18C6] for the reaction of Cd- (■, ▲, ●) and $Pb(tpps)^{4-}$ (□, △, ○) with H_4edta at 25 °C and I = 0.1 mol dm^{-3} ($LiNO_3$). 10^3[edta′]/mol dm^{-3} = 2.00 (■, □), 6.00 (▲, △), and 10.0 (●, ○).

Effect of 18-Crown-6 on Acid-Dissociation of Zn-, Cd-, and Pb(tpps)$^{4-}$. As described above, 18-crown-6 inhibits the ligand substitution reaction of Cd- and $Pb(tpps)^{4-}$ with edta′. In order to know the effect of 18-crown-6 on another reaction system, we studied the acid-dissociation reaction of the metalloporphyrins of zinc(II), cadmium(II), and lead(II). This reaction is, in particular, suitable for knowing the effect of 18-crown-6 on $Zn(tpps)^{4-}$, as we were not able to get clear information on $Zn(tpps)^{4-}$ from its ligand-substitution with H_4-edta due to the very slow reaction. 18-Crown-6 suppressed the acid-dissociation reaction of Zn-, Cd-, and $Pb(tpps)^{4-}$ like the ligand-substitution reaction of $M(tpps)^{4-}$ with edta′. The hindering effect of 18-crown-6 decreases in the following order: $Cd(tpps)^{4-}$ > $Zn(tpps)^{4-}$ > $Pb(tpps)^{4-}$. A plot of k_0 against $[H^+]^2$ gives a straight line for all the three metalloporphyrins in the presence of 18-crown-6. The hydrogen ion dependence on the demetalation of the metalloporphyrins is the same as that observed in the absence of 18-crown-6. This suggests that 18-crown-6 inhibits the demetalation reaction by acid and that the rate-determining-step of the reaction is proton attack. Thus, we can assume the formation of the same precursor complex, $[M(tpps)(18C6)]^{4-}$, as proposed in the ligands-substitution reaction. The acid-dissociation rate of $M(tpps)^{4-}$ in the presence of 18-crown-6 is given by the following equation:

$$-d[M(tpps)']/dt = k_3[M(tpps)^{4-}][H^+]^2 + k_4[M(tpps)(18C6)^{4-}][H^+]^2 \quad (16)$$

Since 18-crown-6 retards the acid-dissociation reaction, $k_3 \gg k_4$. Thus, we have the following reduced equation:

$$k_0 = \frac{k_3[H^+]^2}{(1 + K_{MPL}[18C6])} \quad (17)$$

This equation can be rearranged to

$$\frac{[H^+]^2}{k_0} = \frac{1}{k_3} + \frac{K_{MPL}[18C6]}{k_3} \quad (18)$$

A plot of the left-hand side of eq 18 against [18C6] gives a straight line with an intercept (Figure 4). The slope and the intercept give the rate constant, k_3, and the equilibrium constant, K_{MPL}. The values of k_3/mol^{-2} dm^6 s^{-1} are 10.5 ± 0.9, (7.1 ± 0.3) × 10^{12}, and (1.85 ± 0.05) × 10^{12}, and the values of K_{MPL} are $10^{2.5\pm0.1}$, $10^{2.7\pm0.1}$, and $10^{1.8\pm0.1}$ for Zn-, Cd-, and $Pb(tpps)^{4-}$, respectively. The values of k_3 are in good agreement with the previous work[9] and the K_{MPL} values are also consistent with the values determined from the ligand-substitution reactions.

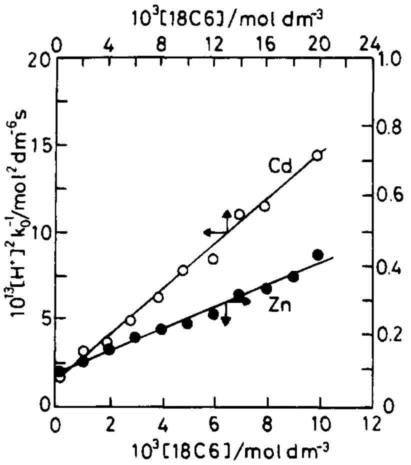


Figure 4. Plot of $[H^+]^2k_0^{-1}$ vs [18C6] for the acid-dissociation of Zn- (●) and $Cd(tpps)^{4-}$ (○) at 25 °C and I = 0.1 mol dm^{-3} ($LiNO_3$). The pH values are 5.55–5.61 and 1.51–1.53 for $Cd(tpps)^{4-}$ and $Zn(tpps)^{4-}$, respectively.

Table 1. Kinetic and Equilibrium Parameters for the Reaction of Zn-, Cd-, and $Pb(tpps)^{4-}$ with $Hedta^{3-}$ or H^+ at 25 °C and I = 0.1 M ($LiNO_3$)

	Zn(II)	Cd(II)	Pb(II)
k_1/mol^{-1} dm^3 s^{-1}	0.00	6.4 ± 0.2	2.9 ± 0.1
k_3/mol^{-2} dm^6 s^{-1}	10.5 ± 0.9	(7.1 ± 0.3) × 10^{12}	(1.85 ± 0.05) × 10^{12}
K_{MPL}/mol^{-1} dm^3		$10^{2.8\pm0.1}$ [a]	$10^{1.6\pm0.1}$ [a]
	$10^{2.5\pm0.1}$ [b]	$10^{2.7\pm0.1}$ [b]	$10^{1.8\pm0.1}$ [b]

[a] The equilibrium constants were determined by the ligand-substitution reactions of $M(tpps)^{4-}$ (M = Zn, Cd, and Pb) in the presence of 18-crown-6. [b] Equilibrium constants determined by the acid-dissociation reactions of $M(tpps)^{4-}$.

Combining the rate equations both for the ligand-substitution $M(tpps)^{4-}$ with $Hedta^{3-}$ (eq 6) and the acid-dissociation reaction (eq 16) and in the presence of 18-crown-6, we have eq 19 for the rate of the decrease of M(tpps)′ as

$$-d[M(tpps)']/dt = (k_1[Hedta^{3-}] + k_2K_{MPL}[18C6] \times [Hedta^{3-}] + k_3[H^+]^2 + k_4K_{MPL}[18C6][H^+]^2) \times (1 + K_{MPL}[18C6])^{-1}[M(tpps)'] \quad (19)$$

In Table 1, the kinetic and equilibrium constants are summarized for the ligand-substitution and the acid-dissociation reactions of Zn-, Cd-, and $Pb(tpps)^{4-}$, where the k_2 and k_4 values are not shown as they were not able to be determined due to $k_1 \gg k_2$ and $k_3 \gg k_4$ for all the $M(tpps)^{4-}$.

^{1}H NMR of $[M(tpps)(18C6)]^{4-}$. In the above kinetic studies, we assumed the formation of $[M(tpps)(18C6)]^{4-}$ as a precursor complex. ^{1}H NMR spectroscopy was used to confirm the formation of $[M(tpps)(18C6)]^{4-}$. The ^{1}H NMR spectra of 10^{-2} mol dm^{-3} 18C6, Zn(18C6), Cd(18C6), and Pb(18C6) show singlet signals at δ = 3.69, 3.69, 3.69, and 3.85 ppm, respectively. The chemical shift of the methylene proton of 18-crown-6 shifted to higher field by addition of H_2tpps^{4-} or $M(tpps)^{4-}$ as follows: 3.45 for H_2tpps^{4-}, 3.36 for $Pb(tpps)^{4-}$, 3.14 for $Zn(tpps)^{4-}$, and 2.81 for $Cd(tpps)^{4-}$ in D_2O. Typical ^{1}H NMR spectra are shown in Figure 5. The ^{1}H NMR signal of the methylene proton of 18-crown-6 shifts to higher field due to the ring-current effect of the porphyrin. $[Cd(tpps)(18C6)]^{4-}$

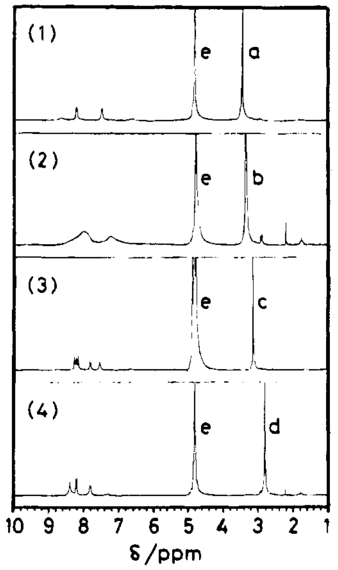


Figure 5. ^{1}H-NMR spectra of 18C6 (1) 1:1 $H_2tpps^{4-}/18C6$, (2) 1:1 $Pb(tpps)^{4-}/18C6$ (3) 1:1 $Zn(tpps)^{4-}/18C6$, and (4) $Cd(tpps)^{4-}/18C6$ in D_2O at 25 °C. The values of chemical shifts of 18-crown-6 in the corresponding system are 3.45 (a), 3.36 (b), 3.14 (c), and 2.82 ppm (d). Signal e shows the chemical shift of HOD. The concentrations of 18C6 and/or $M(tpps)^{4-}$ are 10^{-2} mol dm^{-3}. Chemical shifts are given as a standard of 3-(trimethylsilyl)-1-propanesulfonate (DSS).

showed the largest upfield shift compared to other metalloporphyrins and the upfield shifts decreased in the order of $Cd(tpps)^{4-} > Zn(tpps)^{4-} > Pb(tpps)^{4-} > H_2tpps^{4-}$. The order of the change in chemical shift of ^{1}H NMR is in agreement with the order of the formation constants of $[M(tpps)(18C6)]^{4-}$. The ^{1}H NMR experiments on the $M(tpps)^{4-}/18C6$ system directly indicate the interaction between the 18C6 ring and the porphyrin plane. The large changes in chemical shifts for $Cd(tpps)^{4-}$ show the strong interaction for the 18C6 ring with the porphyrin. In contrast, the small changes in chemical shifts for $Pb(tpps)^{4-}$ show that $Pb(tpps)^{4-}$ interacts very weakly with the 18C6.

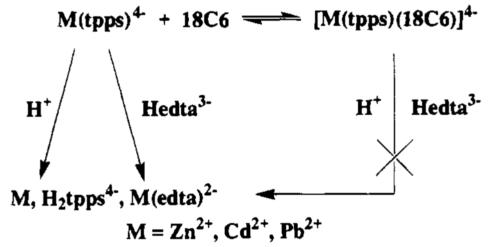
Absorption Spectra of $[M(tpps)(18C6)]^{4-}$. Absorption spectra of $M(tpps)^{4-}$ were measured at various concentrations of 18C6 (10^{-3}–10^{-2} mol dm^{-3}) and (2–4) × 10^{-6} mol dm^{-3} H_2tpps^{4-} in the Soret band region. The largest spectral change was observed for $Cd(tpps)^{4-}$ by addition of 18C6 and decreased in the order Cd- > Zn- > $Pb(tpps)^{4-}$. Hence, $Cd(tpps)^{4-}$ strongly interacts with 18C6 as expected from the kinetic and the ^{1}H NMR studies. The formation constant of $[Zn(tpps)(18C6)]^{4-}$ was found to be $10^{2.5\pm0.2}$, but the formation constants of $[Cd(tpps)(18C6)]^{4-}$ and $[Pb(tpps)(18C6)]^{4-}$ were not determined because of a trace amount of zinc(II) (*ca.* 10^{-8} mol dm^{-3} level) involved in the sample solution as an impurity.[2]

Discussion

The interesting results of the present study are that 18-crown-6 interferes with the metal-substitution of $M(tpps)^{4-}$ (M = Zn, Cd, Pb) with H_4edta or acid-dissociation reaction of $M(tpps)^{4-}$ through the interaction of $M(tpps)^{4-}$ with 18C6. The features are discussed below.

Reaction of $M(tpps)^{4-}$ with H_4edta. The kinetic differences between zinc(II), cadmium(II), and lead(II) can be ascribed to their ionic radii: 75 pm for Zn^{2+}, 95 pm for Cd^{2+}, and 118 pm for Pb^{2+}. Large metal ions such as cadmium(II) and lead(II) do not incorporate well into the porphyrin core and just sit on the porphyrin plane. Barkigia *et al.* have described the lead(II) porphyrin as a "roof complex" after the X-ray analysis of (tetrapropylporphyrinato)lead(II).[14] The roof metalloporphyrin, therefore, can be bonded with a segment (the two carboxylates and the one nitrilo group) of $Hedta^{3-}$ at pH 8–9.5 and is easily replaced with $Hedta^{3-}$.[9] On the other hand, zinc(II) incorporates well into the porphyrin core to form stable $Zn(tpps)^{4-}$. Thus, $Hedta^{3-}$ cannot pull away zinc(II) from $Zn(tpps)^{4-}$ by the coordination of $Hedta^{3-}$.[9]

Scheme 1. Reaction Pathway for the Reaction of $M(tpps)^{4-}$ with $Hedta^{3-}$ or H^+ in the Presence of 18-Crown-6



The rate of the ligand-substitution reaction of Pb- or $Cd(tpps)^{4-}$ with $Hedta^{3-}$ was suppressed in the presence of 18C6 and $Cd(tpps)^{4-}$ was more affected by 18C6 than $Pb(tpps)^{4-}$. In general, 18-crown-6 forms stable complex with Pb^{2+}, where the formation constant is $10^{4.27}$ in aqueous solution.[17] $Cd(18C6)^{2+}$ has not been found yet in aqueous solution and known only in methanol.[17] The present kinetic effect of 18C6 indicates the stable complex formation of $[Cd(tpps)(18C6)]^{4-}$ than $[Pb(tpps)(18C6)]^{4-}$. From the ligand-substitution reaction, the formation constants of Cd- and $[Pb(tpps)(18C6)]^{4-}$ were found to be $10^{2.8}$ and $10^{1.6}$, respectively. The ^{1}H NMR signal of the methylene proton of 18C6 in the presence of $Cd(tpps)^{4-}$ shifts to higher field due to the ring-current effect of the porphyrin. The absorption spectrum of $Cd(tpps)^{4-}$ is also drastically changed by the presence of 18-crown-6. These kinetic, ^{1}H NMR, and spectral studies clearly suggest the strong interaction of $Cd(tpps)^{4-}$ with 18-crown-6.

Acid-Dissociation of Zn-, Cd-, and $Pb(tpps)^{4-}$. Since we were not able to get kinetic information on $Zn(tpps)^{4-}$ in the presence of 18-crown-6 from the ligand-substitution reaction studies, the acid-dissociation reaction of these metalloporphyrins in the presence of 18C6 was investigated. The 18-crown-6 suppressed the acid-dissociation reactions in a similar manner as observed for the ligand-substitution reactions. The kinetic effect of 18C6 is of the following order: Cd- > Zn- > $Pb(tpps)^{4-}$. The formation constants of the corresponding $[M(tpps)(18C6)]$ are $10^{2.7}$, $10^{2.5}$, and $10^{1.8}$, respectively. The inhibition of 18-crown-6 for the reaction of H^+ with $M(tpps)^{4-}$ suggests the same reaction mechanism being operative as that for the reaction of $Hedta^{3-}$. That is, the rate-determining step is a bond breaking between the metal ion and the pyrrole nitrogen in $M(tpps)^{4-}$.

Reaction Mechanism. The proposed reaction mechanism is summarized in Scheme 1. 18-Crown-6 coordinates to $M(tpps)^{4-}$ to form $[M(tpps)(18C6)]^{4-}$, which is stabilized by the hydrophobic interaction between the porphyrin plane and the 18C6 ring. The intermediate prevents the attack of $Hedta^{3-}$ or H^+. Thus, the reaction of $M(tpps)^{4-}$ with $Hedta^{3-}$ or H^+ is suppressed by the presence of 18-crown-6. $Pb(tpps)^{4-}$ interacts weakly with 18C6 and is easily replaced with $Hedta^{3-}$ or H^+ to form $Pb(edta)^{2-}$ or Pb^{2+}.

We have previously reported that the interaction of H_2tpps^{4-} with 18C6 is enhanced by the presence of alkali or alkali earth metal ions and that the extensive hydration in metal ion in M(18C6) makes the interaction difficult between the porphyrin and M(18C6).[22] In comparing Zn- and $Cd(tpps)^{4-}$, $Zn(tpps)^{4-}$

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[22] Tabata, M.; Yamada, I. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3235.

seems to be hyrated much strongly than Cd(tpps)$^{4-}$ as expected from hydration of water molecule in a solid state of Zn(tpp)[23] and higher solvation of pyridine (py) to Zn(tpp) than to Cd(tpp) (H_2tpp = 5,10,15,20-tetraphenylporphyrin) in benzene. The formation constants (log *K*) of M(tpp)py are 3.68 and 3.58 for Zn- and Cd(tpp) in benzene, respectively.[24,25] The hydration or solvation energy of lead(II) porphyrin has not been available. The following characteristic of Pb(tpps)$^{4-}$ may result in the weak interaction of Pb(tpps)$^{4-}$ with 18C6. The lead(II) in Pb(tpps)$^{4-}$ is located above the porphyrin plane by 117 pm[14] and exposed to aqueous solvent. Thus it is expected that the lead(II) in Pb(tpps)$^{4-}$ would be extensively hydrated than Zn- and Cd(tpps)$^{4-}$. The hydration of the metal in [M(tpps)]$^{4-}$ seriously affects the formation constant of [M(tpps)(18C6)]$^{4-}$ and the following order was observed: Cd- > Zn- > Pb(tpps)$^{4-}$.

In summary, the differences in reactivity of Zn-, Cd-, and Pb(tpps)$^{4-}$ in the presence of 18C6 for the ligand-substitution and the acid-dissociation reactions can be explained by the formation of [M(tpps)(18C6)]$^{4-}$ as a precursor complex. The intermediate was also confirmed by ^{1}H NMR and absorption spectra. The intermediate protects the M(tpps)$^{4-}$ against the attack of Hedta^{3-} or H$^+$. The formation constant of the intermediate decreases in the order of Cd(tpps)$^{4-}$ > Zn(tpps)$^{4-}$ > Pb(tpps)$^{4-}$. The strong interaction of 18C6 with Cd(tpps)$^{4-}$ implies the possibilities of the analysis of cadmium in an excess of zinc(II) and/or lead(II). This work is in progress in our laboratory.

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