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Dynamic recognition of metal ions by porphyrin and 18-crown-6

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Chemical properties of metalloporphyrins of zinc(II), cadmium(II) and lead(II) are significantly different in the presence of 18-crown-6 (18C6). The kinetics and mechanism of the ligand-substitution reaction of Zn-, Cd- and Pb(tpps)⁴⁻ (H₂tpps⁴⁻ = 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin) with ethylenediaminetetraacetic acid (H₄edta) has been studied to clarify the different reactivities in the presence of 18C6 at pH 8–9.5, 25°C and *I* = 0.1 mol dm⁻³ (LiNO₃). The rate equation for the decrease of M(tpps)⁴⁻ is expressed as $-d[M(tpps)']/dt = (k_1[edta^{4-}] + k_2[Hedta^{3-}]) (1 + K^{ML}[18C6])^{-1} [M(tpps)']$, where M = Zn²⁺, Cd²⁺ and Pb²⁺, respectively, and [M(tpps)'] is the total concentration of metalloporphyrin. *K*^{ML} denotes the formation constant defined by $[M(tpps)^{4-} \cdot 18C6] / [M(tpps)^{4-}] [18C6]$. The values of *k*₁ were found to be 0 for all metalloporphyrins studied, and *k*₂ = 6.4 ± 0.2 mol⁻¹ dm³ s⁻¹ and 2.9 ± 0.1 mol⁻¹ dm³ s⁻¹ for Cd(tpps)⁴⁻ and Pb(tpps)⁴⁻, respectively. The formation constants of *K*^{ML} were 10^{2.27} mol⁻¹ dm³ and 10^{1.58} mol⁻¹ dm³ for Cd(tpps)⁴⁻ and Pb(tpps)⁴⁻, respectively. The *k*₂ and *K*^{ML} values for Zn(tpps)⁴⁻ were not determined because of the very slow reaction. 18-Crown-6 forms a stable intermediate of Cd(tpps)⁴⁻ · 18C6 and suppressed the substitution reaction with EDTA. Hedta³⁻ directly attacks Pb(tpps)⁴⁻ to form Pb(edta)²⁻, but cannot bind Zn(tpps)⁴⁻. The interaction of the metalloporphyrins with 18C6 was also confirmed by ¹H-NMR and absorption spectra. The ¹NMR signal of 18C6 shifted to a higher field and the change in absorption spectra was larger for Cd(tpps)⁴⁻ than for Pb(tpps)⁴⁻.

INTRODUCTION

Chemical properties of zinc(II), cadmium(II) and lead(II) are very similar to each other. Therefore it is difficult to determine these metal ions separately. For example, the formation constants of their metal complexes with ethylenediaminetetraacetic acid (EDTA) are 10^{16.44}, 10^{16.36} and 10^{17.88}.¹ Chemical masking agents such as cyanide and EGTA (3,12-bis(carboxymethyl)-6,9-dioxo-3,12-diazadecanedioic acid) have been used to achieve selective determination of these metal ions.^{2,3} However, the chemical natures of metalloporphyrins differ considerably because of the

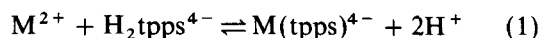
limited ring-size and the unflexibility of the porphyrin plane. The rate of metalloporphyrin formation and dissociation is several orders of magnitude slower than that of open-chain ligands. The general mechanism for porphyrins has been reviewed by the groups of Hambright,⁴ Lavallee,⁵ Schneider⁶ and Tanaka.⁷ The characteristics have been used to effect highly sensitive determinations of metal ions and anions.⁸

Herein we describe the kinetics and mechanism for dynamic recognition of zinc(II), cadmium(II) and lead(II) using the ligand-substitution reaction of the metalloporphyrins with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H₂tpps⁴⁻) by ethylenediaminetetraacetic acid (EDTA) in the presence of 18-crown-6 (18C6). Pb(tpps)⁴⁻ was rapidly replaced with EDTA and Cd(tpps)⁴⁻ was significantly suppressed by binding of 18-crown-6. On the other hand, Zn(tpps)⁴⁻ was hardly substituted by EDTA. Thus zinc(II), cadmium(II) and lead(II) are recognized sufficiently enough to determination of these metal ions separately. The detailed reaction mechanism is described from the kinetic effect of 18C6 on the ligand-substitution reaction of the metalloporphyrins with EDTA. The formation of Cd(tpps)⁴⁻ · 18C6 which is sandwiched between tpps⁶⁻ and 18C6 was also confirmed by ¹H-NMR spectroscopy and by changes in absorption spectra.

RESULTS

Formation constants of Zn-, Cd- and Pb(tpps)⁴⁻

The equilibrium of metalloporphyrin formation is generally given by



with the equilibrium constant defined by

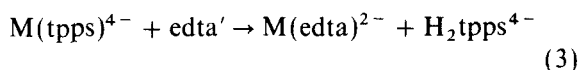
$$K_{MP} = \frac{[M(tpps)^{4-}][H^+]^2}{[M^{2+}][H_2tpps^{4-}]} \quad (2)$$

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The formation constants of Cd- and Pb(tpps)⁴⁻ were determined from the change in absorption spectra at various pH and concentrations of cadmium(II) and lead(II). The values were found to be 10^{-9.94} and 10^{-9.97} for Cd- and Pb(tpps)⁴⁻, respectively. The values of Cd- and Pb(tpps)⁴⁻ are comparable to each other, but the values are 10⁹ times smaller than the corresponding value for Zn(tpps)⁴⁻ (10^{-0.43}).¹⁰

Ligand-substitution reaction of Zn-, Cd- and Pb(tpps)⁴⁻ with EDTA

The reaction of M(tpps)⁴⁻ (M²⁺ = Zn²⁺, Cd²⁺ and Pb²⁺) with EDTA was studied in large excess of EDTA and 18C6 at pH 8–9.5. Under these experimental conditions, the porphyrin is in its free base form, H₂tpps⁴⁻, and the chemical species of EDTA are in the forms of Hedta³⁻ and edta⁴⁻. The protonation constant of EDTA is 10^{8.57} in the presence of 0.1 mol dm⁻³ LiNO₃.¹¹ Thus the reaction of M(tpps)⁴⁻ with EDTA is written as



where edta' denotes all chemical species of EDTA not bound to metal ions. The very small equilibrium constants of Cd- and Pb(tpps)⁴⁻ compared with Zn(tpps)⁴⁻ indicate that cadmium(II) and lead(II) do not incorporate well into the porphyrin core and just sit on the porphyrin plane, as shown by an X-ray study of lead(II)porphyrin.¹² The results imply the rapid replacement of Cd- and Pb(tpps)⁴⁻ with EDTA. Figure 1 shows typical kinetic runs for the ligand-substitution reaction of Zn-, Cd- and Pb(tpps)⁴⁻ with EDTA at pH 8.8. Zn(tpps)⁴⁻ is not replaced even after 2 h. Comparison of the conditional formation constants of Zn(tpps)⁴⁻ with that of Zn(edta)²⁻ predicts the complete replacement by EDTA in large excess of EDTA at pH 8.8. On the other hand, Pb(tpps)⁴⁻ was easily replaced with EDTA at a half-life time of 1 min. Furthermore, 18-crown-6 retarded the substitution reaction of Cd(tpps)⁴⁻ with EDTA and the half-life time was 10 min in the presence of 2.00 × 10⁻² mol dm⁻³ 18C6.

The reaction showed first-order kinetic behavior in large excess of EDTA and 18C6 compared with that of M(tpps)⁴⁻. The rate constants were independent of the concentrations of H₂tpps⁴⁻ ((1.00–4.00) × 10⁻⁶ mol dm⁻³). Hence the kinetic equation for the reaction is described by eq 4, where k₀ is the conditional rate constant involving concentrations of hydrogen ion, EDTA, 18C6 and metal ions.

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

The k₀ values for the reactions of Cd- and Pb(tpps)⁴⁻ increased with edta' (Fig. 2) and 18C6 suppressed the

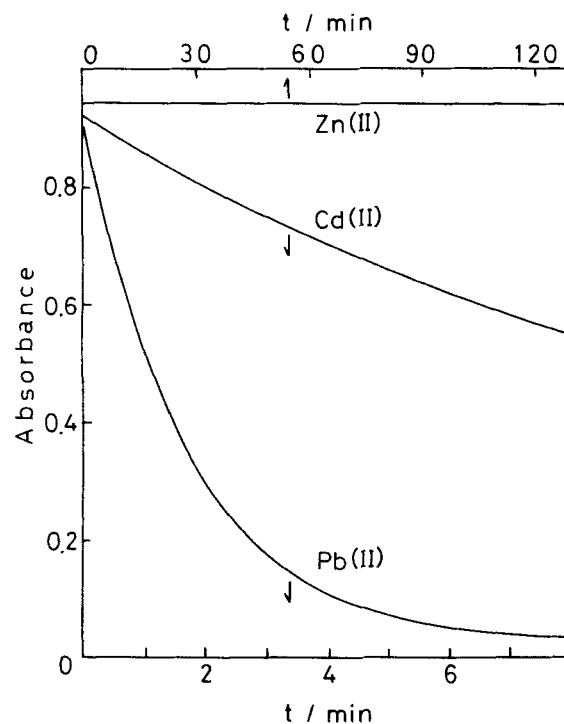


Figure 1 Ligand-substitution reaction of Zn-, Cd- and Pb(tpps)⁴⁻ with EDTA at pH 8.88 25°C. C_{EDTA}/mol dm⁻³ = 10⁻²; C_{TPPS}/mol dm⁻³ = 2.0 × 10⁻⁶ for Zn(tpps)⁴⁻ and 4.0 × 10⁻⁶ for Cd- and Pb(tpps)⁴⁻, respectively.

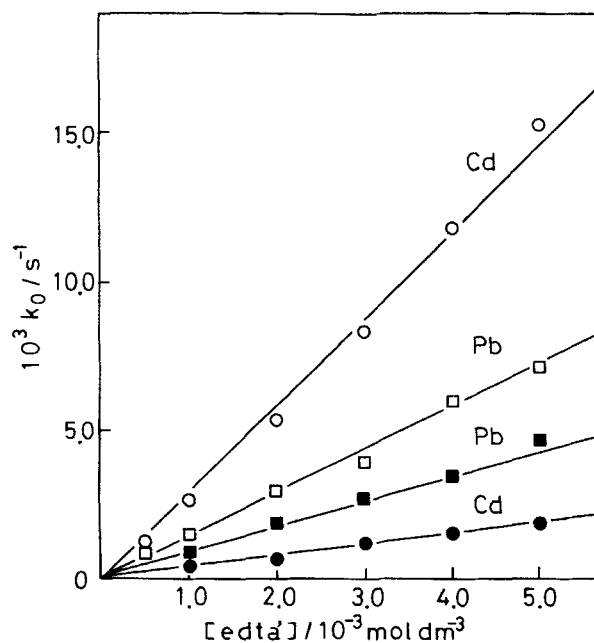


Figure 2 Dependence of the rate constants on the concentrations edta' in the absence (○, □) and the presence (●, ■) of 18C6 (1.00 × 10⁻²) for the reaction of Cd- and Pb(tpps)⁴⁻ with EDTA at pH 8.77, 25°C for I = 0.1 mol dm⁻³ (LiNO₃).

reaction rate. The results show that the reaction is of first-order in edta'. In contrast, k₀ values for the reaction of Zn(tpps)⁴⁻ were independent of edta' even at its concentration of 0.05 mol dm⁻³. Figure 3 shows

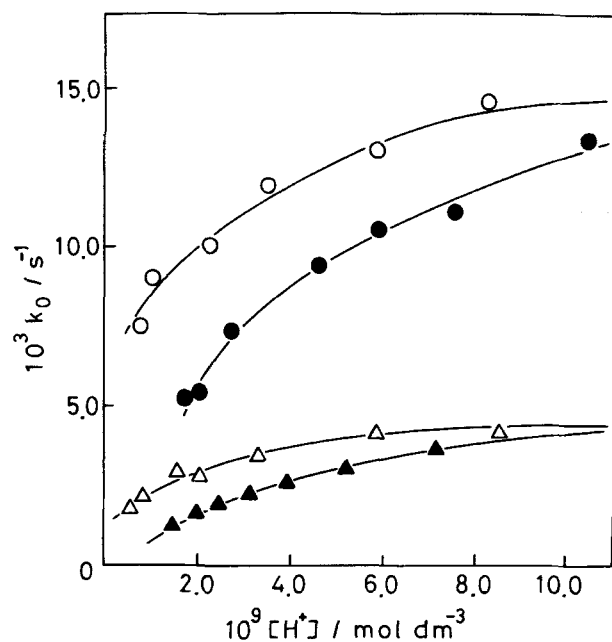
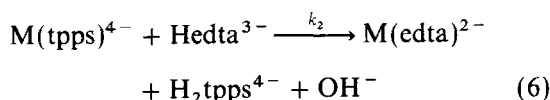
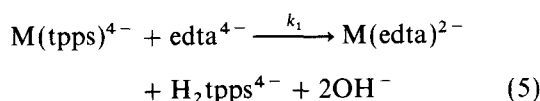


Figure 3 Dependence of the rate constants on the concentrations of hydrogen ion in the reaction of $\text{Pb}(\text{tpps})^{4-}$ with EDTA in the absence (\circ, \triangle) and presence (\bullet, \blacktriangle) of 18C6 (1.00×10^{-2}) at 25°C and $I = 0.1$ (LiNO_3). $10^3/C_{\text{EDTA}} = 2.00$ ($\triangle, \blacktriangle$) and 8.00 (\circ, \bullet).

the dependence of rate constant on hydrogen ion concentration for the reaction of $\text{Pb}(\text{tpps})^{4-}$ with EDTA in the absence and presence of 18C6. The k_0 values increased with hydrogen ion concentrations and reached a plateau at lower pH. Here again, 18-crown-6 slowed down the reaction. Thus the reaction mechanism to account for the kinetic data is expressed by eqs 5 and 6 in the absence 18C6.



This leads to the following rate equation:

$$k_0 = k_1[\text{edta}^{4-}] + k_2[\text{Hedta}^{3-}] \quad (7)$$

$$= \frac{(k_1 + k_2 K^{\text{H}}[\text{H}^+])[\text{edta}']}{1 + K^{\text{H}}[\text{H}^+]} \quad (8)$$

where $[\text{edta}'] = [\text{edta}^{4-}] + [\text{Hedta}^{3-}]$. Equation 8 is rearranged to

$$k_0(1 + K^{\text{H}}[\text{H}^+])[\text{edta}']^{-1} = k_1 + k_2 K^{\text{H}}[\text{H}^+] \quad (9)$$

where K^{H} is the protonation constant of edta^{4-} : $K^{\text{H}} = 10.857$. The plot of the left-hand side of eq 9 against $[\text{H}^+]$ gives straight lines with zero intercept

for Cd- and $\text{Pb}(\text{tpps})^{4-}$. The rate constants were found to be $k_1 = 0 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$ for both Cd- and $\text{Pb}(\text{tpps})^{4-}$, $k_2 = 6.4 \pm 0.2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $2.9 \pm 0.1 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for Cd- and $\text{Pb}(\text{tpps})^{4-}$, respectively. The values of k_0 were independent of concentrations of both Cd^{2+} and Pb^{2+} and suggest that the Cd- and $\text{Pb}(\text{tpps})^{4-}$ do not dissociate to their metal ions and $\text{H}_2\text{tpps}^{4-}$ before binding of EDTA to Cd- or $\text{Pb}(\text{tpps})^{4-}$. The rate constants for $\text{Zn}(\text{tpps})^{4-}$ were small but independent of concentration of EDTA.

Effect of 18C6 on the substitution reaction

As shown in Figs. 2 and 3, 18-crown-6 reduced the rate constants for the ligand-substitution reaction of Cd- and $\text{Pb}(\text{tpps})^{4-}$ with EDTA. Figure 4 shows the dependence of the rate constants on the concentrations of 18C6. $\text{Cd}(\text{tpps})^{4-}$ is easily replaced with EDTA compared with $\text{Pb}(\text{tpps})^{4-}$ in the absence of 18C6, but is dramatically suppressed by 18C6. Thus the observed rate constant is given by eq 10.

$$k_0[\text{M}(\text{tpps}')] = k_2[\text{M}(\text{tpps})^{4-}][\text{Hedta}^{3-}] + k_3[\text{M}(\text{tpps})^{4-} \cdot 18\text{C6}][\text{Hedta}^{3-}] \quad (10)$$

$$k_0[\text{M}(\text{tpps}')] = \frac{(k_2 + k_3 K^{\text{ML}}[18\text{C6}])K^{\text{H}}[\text{edta}'][\text{H}^+][\text{M}(\text{tpps}')] }{(1 + K^{\text{ML}}[18\text{C6}])(1 + K^{\text{H}}[\text{H}^+])} \quad (11)$$

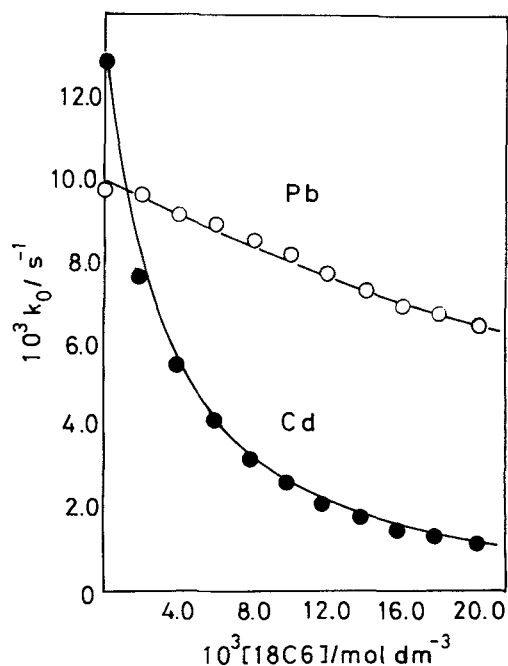


Figure 4 Dependence of the rate constants on the concentrations of 18C6 on the ligand-substitution reaction of Cd- (\bullet) and $\text{Pb}(\text{tpps})^{4-}$ (\circ) with EDTA ($1.00 \times 10^{-2} \text{ mol dm}^{-3}$) at 25°C and $I = 0.1$ (LiNO_3). The values of pH are 8.81 and 8.62 for Cd- and $\text{Pb}(\text{tpps})^{4-}$, respectively.

where

$$\begin{aligned} [M(\text{tpps})'] &= [M(\text{tpps})^{4-}] + [M(\text{tpps})^{4-} \cdot 18\text{C6}] \\ &= [M(\text{tpps})^{4-}](1 + K^{\text{ML}}[18\text{C6}]) \end{aligned}$$

$$K^{\text{ML}} = [M(\text{tpps})^{4-} \cdot 18\text{C6}][M(\text{tpps})^{4-}]^{-1}[18\text{C6}]^{-1}$$

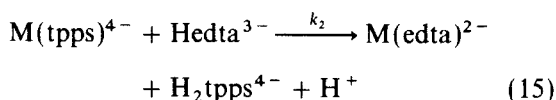
Since the rate constants decrease with 18C6, it is supposed that $k_2 \gg k_3$, resulting in the following simplified expression:

$$k_0 = \frac{k_2 K^{\text{H}}[\text{edta}'][\text{H}^+]}{(1 + K^{\text{ML}}[18\text{C6}])(1 + K^{\text{H}}[\text{H}^+])} \quad (12)$$

Thus eq 12 rearranges to

$$\begin{aligned} K^{\text{H}}k_0^{-1}[\text{edta}'][\text{H}^+](1 + K^{\text{H}}[\text{H}^+])^{-1} \\ = k_2^{-1} + K^{\text{ML}}k_2^{-1}[18\text{C6}] \end{aligned} \quad (13)$$

The plots of the left-hand side of eq 13 against $[18\text{C6}]$ give straight lines. The results for $\text{Cd}(\text{tpps})^{4-}$ are shown in Fig. 5. The slopes give the values of $K^{\text{ML}} = 10^{2.77} \text{ mol dm}^{-3}$ and $10^{1.58}$ for $\text{Cd}(\text{tpps})^{4-}$ and $\text{Pb}(\text{tpps})^{4-}$, respectively. 18-Crown-6 is more strongly bound to $\text{Cd}(\text{tpps})^{4-}$ than $\text{Pb}(\text{tpps})^{4-}$. The straight line also confirms $k_2 \gg k_3$. Finally, the effect of 18C6 on the reaction $M(\text{tpps})^{4-}$ with EDTA is expressed as



In Table 1, the kinetic and the equilibrium parameters are summarized for the ligand-substitution reaction of Zn-, Cd- and $\text{Pb}(\text{tpps})^{4-}$, where the values of k_1 are not shown as they were 0 for all $M(\text{tpps})^{4-}$.

$^1\text{H-NMR}$ of $M(\text{tpps})^{4-} \cdot 18\text{C6}$

The above kinetic studies suggest the formation of $M(\text{tpps})^{4-} \cdot 18\text{C6}$ as an intermediate and the strong interaction of $\text{Cd}(\text{tpps})^{4-}$ with 18C6 compared with that of $\text{Pb}(\text{tpps})^{4-}$. $^1\text{H-NMR}$ spectroscopy was used to confirm the intermediate in D_2O . The chemical shift (3.69 ppm) of the methylene proton of 18C6 shifted to higher field (2.81 ppm) for $\text{Cd}(\text{tpps})^{4-}$, and shifted to 3.36 ppm for $\text{Pb}(\text{tpps})^{4-}$, where chemical shifts are given against a standard of sodium 3(trimethylsilyl)-1-propanesulfonate (DSS). Chemical shifts to higher fields were also observed for $\text{H}_2\text{tpps}^{4-}$ (3.45 ppm) and $\text{Zn}(\text{tpps})^{4-}$ (3.14 ppm). Typical $^1\text{H-NMR}$ spectra are shown in Fig. 6.

Absorption spectra of $M(\text{tpps})^{4-} \cdot 18\text{C6}$

Absorption spectra of $M(\text{tpps})^{4-}$ were measured at various concentrations of 18C6 in the Soret region.

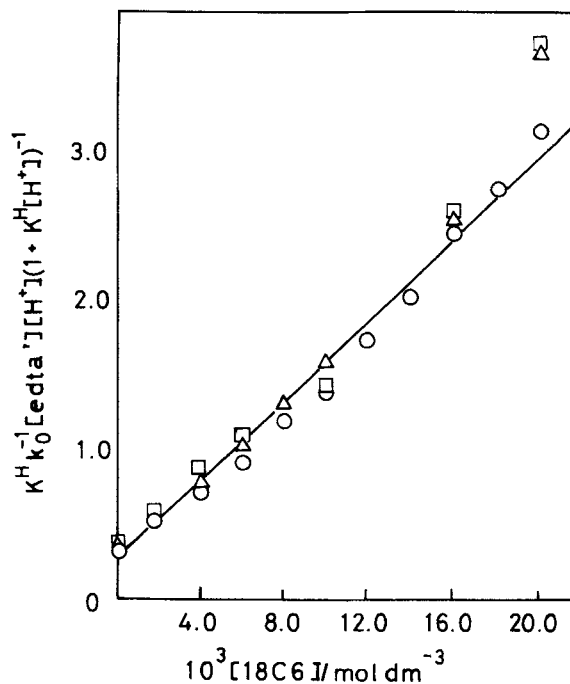


Figure 5 Plots of $K^{\text{H}}k_0^{-1}[\text{edta}'][\text{H}^+](1 + K^{\text{H}}[\text{H}^+])^{-1}$ vs. $[18\text{C6}]$ in the reaction of Cd- and $\text{Pb}(\text{tpps})^{4-}$ at 25°C and $I = 0.1 \text{ mol dm}^{-3}$ (LiNO_3). $10^3[\text{edta}']/\text{mol dm}^{-3} = 2.00$ (\square), 6.00 (\triangle) and 1.0 (\circ).

Table 1 Kinetic and equilibrium parameters for the reaction of Zn-, Cd- and $\text{Pb}(\text{tpps})^{4-}$ with EDTA at 25°C and $I = 0.1$ (LiNO_3)

	Zn(II)	Cd(II)	Pb(II)
$\frac{K^{\text{MP}}}{\text{mol}^{-1} \text{ dm}^3}$	$10^{-0.43}$	$10^{-9.94}$	$10^{-9.97}$
$\frac{k_2}{\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$	0.00	6.4 ± 0.2	2.9 ± 0.1
$\frac{K^{\text{ML}^a}}{\text{mol}^{-1} \text{ dm}^3}$	—	$10^{2.27}$	$10^{1.58}$
$\frac{K^{\text{M18C6}}}{\text{mol}^{-1} \text{ dm}^3}$	—	—	$10^{4.27}$
$r/\text{\AA}$	0.89	1.09	1.32

^a K^{MP18C6} denotes the formation constant of metal-18C6 complex.¹³

Figure 7 shows the change in difference absorption spectra of metalloporphyrin in the presence of 18C6 with respect to the reference $M(\text{tpps})^{4-}$ in the absence of 18C6. $\text{Cd}(\text{tpps})^{4-}$ gave a larger spectral change than did $\text{Pb}(\text{tpps})^{4-}$. Hence, $\text{Cd}(\text{tpps})^{4-}$ interacts with 18C6 strongly.

DISCUSSION

We can see the following aspects from the kinetic, $^1\text{H-NMR}$ and spectral studies. (1) $\text{Zn}(\text{tpps})^{4-}$ is hard to replace with EDTA, whereas Cd- and $\text{Pb}(\text{tpps})^{4-}$

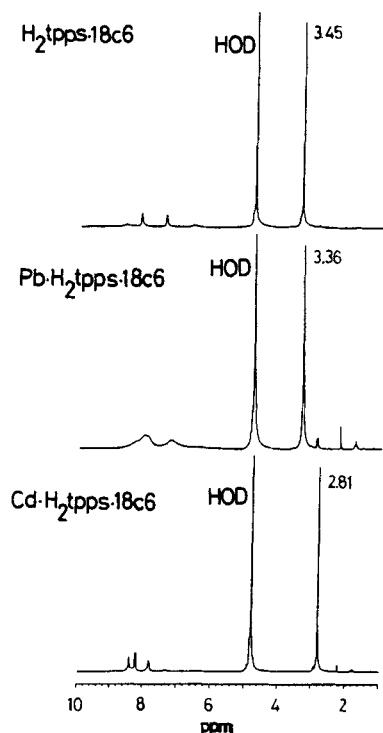


Figure 6 $^1\text{H-NMR}$ spectra of a 1:1 molar ratio of $\text{H}_2\text{tpps}^{4-}$ to 18C6 and that of $\text{M}(\text{tpps})^{4-}$ to 18C6 ($\text{M} = \text{Zn}^{2+}$, Cd^{2+} and Pb^{2+}) in D_2O . Chemical shifts are given as a standard of DSS.

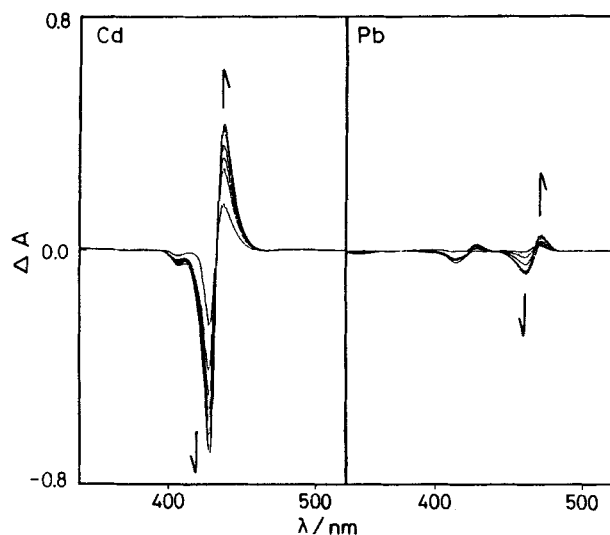


Figure 7 Change in difference absorption spectra of Cd- and $\text{Pb}(\text{tpps})^{4-}$ in the various concentrations of 18C6 (2.00×10^{-3} – $2.00 \times 10^{-2} \text{ mol dm}^{-3}$) at pH 9.11, 25°C and $I = 0.1 \text{ mol dm}^{-3}$ (LiNO_3). $C_{\text{TPPS}} = 5 \times 10^{-6} \text{ mol dm}^{-3}$. Difference absorption-spectra were measured with respect to the reference of $\text{M}(\text{tpps})^{4-}$.

are easily substituted with EDTA. (2) The formation constant of $\text{Zn}(\text{tpps})^{4-}$ is about 10^9 times as large as those of Cd- and $\text{Pb}(\text{tpps})^{4-}$. (3) 18-Crown-6 slows the substitution reaction of Cd- and $\text{Pb}(\text{tpps})^{4-}$ with EDTA. (4) $\text{Cd}(\text{tpps})^{4-}$ is significantly suppressed by 18C6. (5) Large changes in $^1\text{H-NMR}$ spectra and

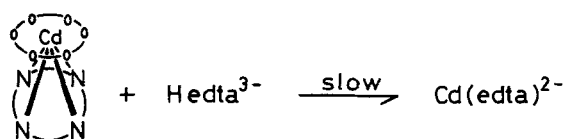
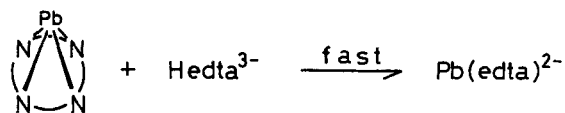
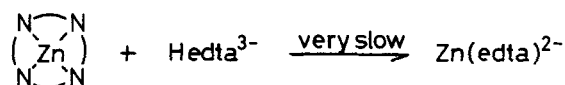
absorption spectra were observed for $\text{Cd}(\text{tpps})^{4-}$ in the presence of 18C6. These differences are discussed below.

Reaction with EDTA

The kinetic difference between zinc(II), cadmium(II) and lead(II) can be ascribed to their ionic radii: 0.89 \AA for Zn^{2+} , 1.09 \AA for Cd^{2+} and 1.32 \AA for Pb^{2+} . Large metal ions such as cadmium(II) and lead(II) cannot incorporate well into the porphyrin core and just sit on the porphyrin plane. Barkigia *et al.* have called lead(II)porphyrin a 'roof complex' following the X-ray analysis of tetrapropylporphyrinato lead(II).¹² The roof metalloporphyrin, therefore, can be bound with a segment of Hedta^{3-} : two carboxylato and nitrito groups, and then is easily replaced with Hedta^{3-} . On the other hand, zinc(II) incorporates well into the porphyrin core to form stable $\text{Zn}(\text{tpps})^{4-}$. Thus, Hedta^{3-} cannot pull zinc(II) away from $\text{Zn}(\text{tpps})^{4-}$ by coordination of Hedta^{3-} .

In general 18-crown-6 forms the stable complex $\text{Pb}(\text{18C6})^{2+}$,¹³ but the present kinetic effect of 18C6 indicates the formation of stable complex of $\text{Cd}(\text{tpps})^{4-} \cdot \text{18C6}$. The $^1\text{H-NMR}$ signal of the methylene proton of 18C6 in $\text{Cd}(\text{tpps})^{4-} \cdot \text{18C6}$ shifts to higher field due to the ring-current effect of the porphyrin. Since the formation constant of $\text{Pb}(\text{18C6})^{2+}$ complex is large ($10^{4.27}$).¹³ Some quantity of $\text{Pb}(\text{tpps})^{4-}$ is replaced with 18C6 instead of the formation of $\text{Pb}(\text{tpps})^{4-} \cdot \text{18C6}$. The binding of 18C6 to $\text{Cd}(\text{tpps})^{4-}$ retarded the substitution rate. $\text{Cd}(\text{tpps})^{4-}$ is stabilized by coordination of 18C6, which inhibits binding of EDTA to Cd^{2+} .

The proposed reaction mechanism is summarized in Scheme 1. Hedta^{3-} cannot bind $\text{Zn}(\text{tpps})^{4-}$, but directly attacks $\text{Pb}(\text{tpps})^{4-}$ to form rapidly $\text{Pb}(\text{edta})^{2-}$. 18-Crown-6 coordinates to $\text{Cd}(\text{tpps})^{4-}$ to form $\text{Cd}(\text{tpps})^{4-} \cdot \text{18C6}$ which is stabilized by the



Scheme 1

interaction of the porphyrin plane (hydrophobic interaction). The intermediate blocks the attack of EDTA.

CONCLUSION

Present paper clearly shows the different reactivity of Zn-, Cd- and Pb(tpps)⁴⁻ in the presence of 18C6. Because of its large ionic radius, Pb(tpps)⁴⁻ is easily replaced with EDTA, and Cd(tpps)⁴⁻ forms Cd(tpps)⁴⁻·18C6 which retards the substitution reaction rate. The formation of Cd(tpps)⁴⁻·18C6 was confirmed by ¹H-NMR and absorption spectra. Since zinc(II) incorporates well the porphyrin core, Zn(tpps)⁴⁻ is hardly replaced with EDTA. The differences in the kinetic behavior of Zn, Cd and Pb strongly support analytical methods for the determination of zinc(II) in a large excess of cadmium(II) and lead(II) using the ligand-substitution reaction with EDTA or the acid-dissociation rate of these metalloporphyrins.¹⁴⁻¹⁶ The strong interaction of 18C6 with Cd(tpps)⁴⁻ implies an analysis of cadmium in a excess of zinc(II) and lead(II), which will be reported elsewhere.

EXPERIMENTAL

Reagents

5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin (H₂-tpps⁴⁻) was synthesized and its sodium salt (Na₄H₂-tpps) was purified by a previous method.⁸ 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 as indicators. The ionic strength of the sample solutions was held constant (0.1 mol dm⁻³) with lithium nitrate. Lithium nitrate was a super-pure reagent (Merck) being free from heavy metal ions and all other reagents were of analytical reagent grade. All solutions were prepared in water deionized and then distilled from alkaline permanganate. The solutions of the metalloporphyrins were prepared just before the kinetic measurements in volumetric flasks covered with aluminum foil to shield from light. The formation of the metalloporphyrins was confirmed spectrophotometrically.

Measurement

The ligand-substitution reaction of M(tpps)⁴⁻ (M = Zn²⁺, Cd²⁺ and Pb²⁺) with EDTA was studied in a

pH range of 8.0–9.5 (borate buffer, 10⁻² mol dm⁻³) at the various concentrations of EDTA (1.0 × 10⁻³–5.0 × 10⁻² mol dm⁻³), metal ions (Zn²⁺, Cd²⁺ and Pb²⁺; each at 4 × 10⁻⁶–5 × 10⁻⁵ mol dm⁻³), 18-crown-6-ether (1 × 10⁻³–2 × 10⁻² and H₂tpps⁴⁻ (1.0 × 10⁻⁶–4.0 × 10⁻³ mol dm⁻³). The reaction was started by mixing a solution involving M(tpps)⁴⁻ and 18C6 with an EDTA solution using a sample mixing device (Ohtuka Denshi, MX7). The change in absorbance at Soret bands 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. 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 (HNO₃–LiNO₃), the pH meter and electrode system was calibrated in terms of –log[H⁺].

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