Different Kinetic Behavior of Zinc(II), Cadmium(II), and Lead(II) Porphyrins in the Ligand-Substitution Reaction with Ethylenediaminetetraacetic Acid

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Kinetics and mechanism of the ligand-substitution reaction of Zn-, Cd-, and Pb(tpps)$^{4-}$ (H_2tpps^{4-}= 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin) with ethylenediaminetetraacetic acid (EDTA) have been studied at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$). The rate equation for the decrease of M(tpps)$^{4-}$ is expressed as $-d[M(tpps)^{4-}]/dt=(k_1[edta^{4-}]+k_2[Hedta^{3-}]+k_3k_4[H]^2(k_{-3}+k_4[H^+])^{-1})[M(tpps)^{4-}]$, where M=$Zn^{2+}$, Cd^{2+}, and Pb^{2+}, and $edta^{4-}$ denotes the fully deprotonated form of EDTA, respectively. The values of k_1 were found to be 0 for all of the metalloporphyrins studied, and k_2=0 mol^{-1}dm^3 s^{-1}; $k_3k_4(k_{-3})^{-1}$=8.7±0.2 mol^{-2} dm^6 s^{-1} for Zn(tpps)$^{4-}$, k_2=4.1±0.2 mol^{-1} dm^3 s^{-1}; $k_3k_4(k_{-3})^{-1}$=(8.3±0.4)×10^{12} mol^{-2} dm^6 s^{-1} for Cd(tpps)$^{4-}$ and k_2=2.0±0.1 mol^{-1} dm^3 s^{-1}; k_3(5.4±0.1)×10^7 mol^{-1} dm^3 s^{-1}; $k_3k_4(k_{-3})^{-1}$=2.0±0.1 mol^{-2} dm^6 s^{-1} for Pb(tpps)$^{4-}$, respectively. $Hedta^{3-}$ directly attacks Cd- or Pb(tpps)^4 to form its metal complex, whereas $Hedta^{3-}$ can not bind Zn(tpps)$^{4-}$. Zn(tpps)$^{4-}$ dissociates to aquazinc(II) by proton attack, then the aquazinc(II) reacts with $Hedta^{3-}$. Therefore, the ligand-substitution reaction of Zn(tpps)$^{4-}$ with EDTA is so slow that the reaction can be negligible compared with those of Cd- and Pb(tpps)$^{4-}$ in an alkaline solution. The reaction mechanism of the ligand substitution reaction and the different reactivities of the metalloporphyrins in it are discussed in detail.

Since zinc(II), cadmium(II), and lead(II) have filled d shell, they, especially zinc(II) and cadmium(II), are very similar in their chemical properties. 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] Therefore it is difficult to determine these metal ions separately. However, the chemical properties of metalloporphyrins are different considerably. Formation constant of the metalloporphyrin of 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin (H_2tpps^{4-}) with zinc(II) is about 10^9 times larger than that of cadmium(II) or lead(II),[2,3] and the acid-dissociation rate of Cd(tpps)$^{4-}$ is 10^{12} times as fast as that of Zn(tpps)$^{4-}$. These large differences have been applied to the determination of zinc(II) in a large amount of cadmium(II) or lead(II) using the acid-dissociation reaction of their metalloporphyrins or the ligand-substitution reaction with EDTA.[3-5]

It has been believed that metalloporphyrins are very stable and they are hard to be replaced with EDTA.[6-8] In addition, only a few papers concerning the formation constants of metalloporphyrins have been published.[2,9-11] Because of the slow reaction rate of metalloporphyrin formation, it will take a few months or years to reach the equilibrium at room temperature except for some metalloporphyrins of such as mercury(II), cadmium(II), and lead(II). For that reason, it is ambiguous whether thermodynamically or kinetically metalloporphyrins are not replaced with EDTA. We have succeeded in determining the formation constant of Zn(tpps)$^{4-}$ using a catalytic effect of mercury(II) on the formation rate of Zn(tpps)$^{4-}$.[2] Comparing the formation constant of Zn(tpps)$^{4-}$ with that of Zn(edta)$^{2-}$, we have noticed that the conditional formation constant of Zn(tpps)$^{4-}$ is comparable to that of Zn(edta)$^{2-}$ at a neutral pH and that Zn($tpps^{4-}$) should be replaced with EDTA thermodynamically in large excess of EDTA.

The present study was undertaken to clarify the reaction mechanism on the replacement of Zn(tpps)$^{4-}$ with EDTA and to get the detailed information on the large differences in the reactivities of Zn-, Cd- and Pb(tpps)$^{4-}$ which have been applied to the determination of zinc(II) in the presence of a large amount of cadmium(II) or lead(II).

Experimental

Reagents. 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrine (TPPS) was synthesized and its sodium salt (Na_4H_2tpps) was purified by a previous method.[12] The purity was checked by thin-layer chromatography and ^{1}H NMR. Solutions of zinc(II), cadmium(II), and lead(II) were prepared from their nitrates, and the concentrations in these stock solutions 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 sodium nitrate. Sodium acetate (1×10^{-2} mol dm^{-3}) or sodium borate (1×10^{-2} mol dm^{-3}) containing nitric acid or sodium hydroxide was used as buffer solution. All reagents were of analytical reagent grade and 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=Zn^{2+}, Cd^{2+}, and Pb^{2+}) with EDTA was studied in a pH range 3—4.5 for Zn(tpps)$^{4-}$ and 8.0—9.3 for Cd- and Pb(tpps)$^{4-}$ at the concentrations of EDTA (1.0×10^{-3}—5.0×10^{-2} mol dm^{-3}), metal ions (Zn^{2+}, Cd^{2+}, Pb^{2+}; each at 4.0×10^{-6}—1.0×10^{-4} mol dm^{-3}) and H_2tpps^{4-} (1.0×10^{-6}—2.0×10^{-6} mol dm^{-3}). The reaction was started by mixing a

$M(tpps)^{4-}$ solution with an EDTA solution using a sample mixing device (Union Giken, MX7). The change in absorbance at Soret bands of the 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 kinetic studies for the acid-dissociation rate of Zn-, Cd-, and $Pb(tpps)^{4-}$ were carried out in a pH range of 1.2—2.0 for $Zn(tpps)^{4-}$ and that of 4.5—5.5 (acetate buffer, 10^{-2} mol dm^{-3}) for $Cd(tpps)^{4-}$ and $Pb(tpps)^{4-}$, respectively. The change in absorbance at Soret band of the metalloporphyrins was followed by a Uniongiken RA401 stopped-flow spectrophotometer at 25 °C.

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} sodium 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-$NaNO_3$), the pH meter and electrode system was calibrated in terms of $-\log[H^+]$.

Results

Ligand-Substitution Reaction of Zn-, Cd-, and $Pb(tpps)^{4-}$ with EDTA. The reaction of $M(tpps)^{4-}$ ($M=Zn^{2+}$, Cd^{2+}, and Pb^{2+}) with EDTA was studied in large excess of EDTA at pH 3—4.5 for the reaction of $Zn(tpps)^{4-}$ and at pH 8—9.3 for that of Cd- and $Pb(tpps)^{4-}$. Under the present experimental conditions, the porphyrin is in its protonated and free base forms: H_4tpps^{2-}, H_3tpps^{3-}, and H_2tpps^{4-}, since the protonation constants for $[H_3tpps^{3-}][H^+]^{-1}[H_2tpps^{4-}]^{-1}$ and for $[H_4tpps^{2-}][H^+]^{-1}[H_3tpps^{3-}]^{-1}$ are $10^{4.99}$ and $10^{4.76}$, respectively.[2] Furthermore, the chemical species of EDTA are in the forms of H_3edta^-, H_2edta^{2-}, $Hedta^{3-}$, and $edta^{4-}$. Thus the reaction of $M(tpps)^{2-}$ with EDTA is written as

$$M(tpps)^{2-} + edta' \rightleftarrows M(edta)^{2-} + tpps', \quad (1)$$

where edta' and tpps' are all chemical species of EDTA and TPPS not bound to metal ions, respectively. The equilibrium of metalloporphyrin formation is generally given by

$$M^{2+} + H_2tpps^{4-} \rightleftarrows M(tpps)^{4-} + 2H^+, \quad (2)$$

with the equilibrium constant defined by

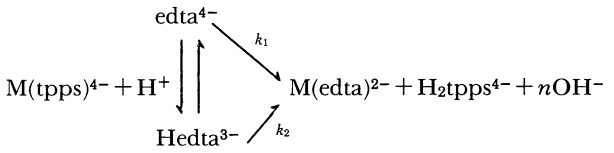
$$K_{MP} = \frac{[M(tpps)^{4-}][H^+]^2}{[M^{2+}][H_2tpps^{4-}]}, \quad (3)$$

and the values of K_{MP} have been found to be $10^{-0.43}$, $10^{-9.94}$, $10^{-9.97}$ for Zn-, Cd-, and $Pb(tpps)^{4-}$, respectively at 25 °C and I=0.1 mol dm^{-3}.[2,3] Moreover, the formation constants of $M(edta)^{2-}$ are respectively $10^{16.44}$, $10^{16.36}$, and $10^{17.88}$ for $M=Zn^{2+}$, Cd^{2+}, and Pb^{2+}, while the stepwise protonation constants of $edta^{4-}$ are $10^{10.17}$, $10^{6.18}$, and $10^{2.68}$.[1] Thus the equilibrium constants of Eq. 1 are calculated to be $10^{2.39}$ at pH 4 for $Zn(tpps)^{4-}$, $10^{8.13}$ at pH 8 for $Cd(tpps)^{4-}$, and $10^{8.16}$ at pH 8 for $Pb(tpps)^{4-}$, respectively. The metalloporphyrins, therefore, are completely replaced with EDTA and the reverse reaction of Eq. 1 can be neglected in large excess of EDTA compared with that of TPPS.

Thus, the pseudo-first-order kinetics was observed for the reaction of Eq. 1:

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

where k_0 denotes the conditional rate constant containing concentrations of edta', hydrogen ion, and metal ion. The k_0 values for the reactions of Cd- and $Pb(tpps)^{4-}$ increased with the edta' (Fig. 1), and this result shows that the reaction is first-order in edta'. In contrast, the k_0 values for the reaction of $Zn(tpps)^{4-}$ were independent of edta' even at its concentration of 0.05 mol dm^{-3} (Fig. 2). Figure 3 shows the dependence of rate constant on hydrogen ion concentration for the reaction of Cd- and $Pb(tpps)^{4-}$ with EDTA. The k_0 values increased with hydrogen ion concentrations and reached a plateau at pH 8, where main chemical species of EDTA is in the form of $Hedta^{3-}$. Thus the reaction mechanism to account for the kinetic data is shown in Scheme 1:



Scheme 1.

This leads to the rate equation of Eq. 5

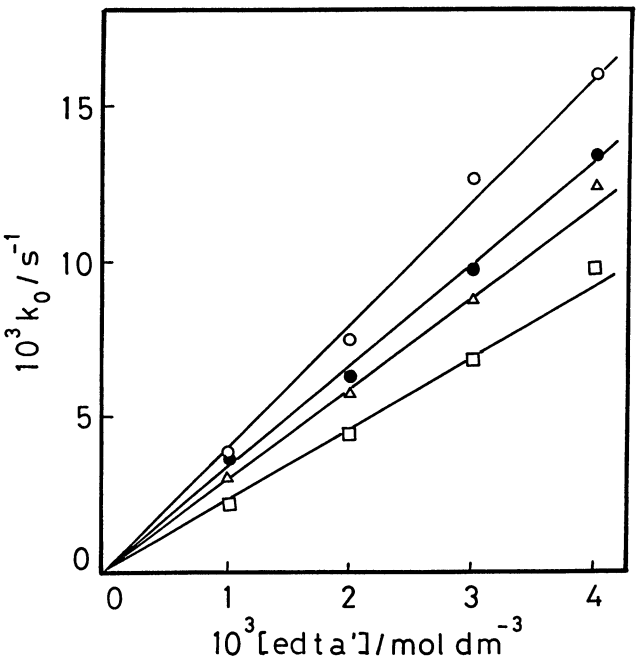


Fig. 1. Dependence of rate constants on the concentrations of edta' for the reaction of $Cd(tpps)^{4-}$ with EDTA in pH 8.01 (○), 8.48 (●), 8.69 (△), and 9.09 (□) at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$).

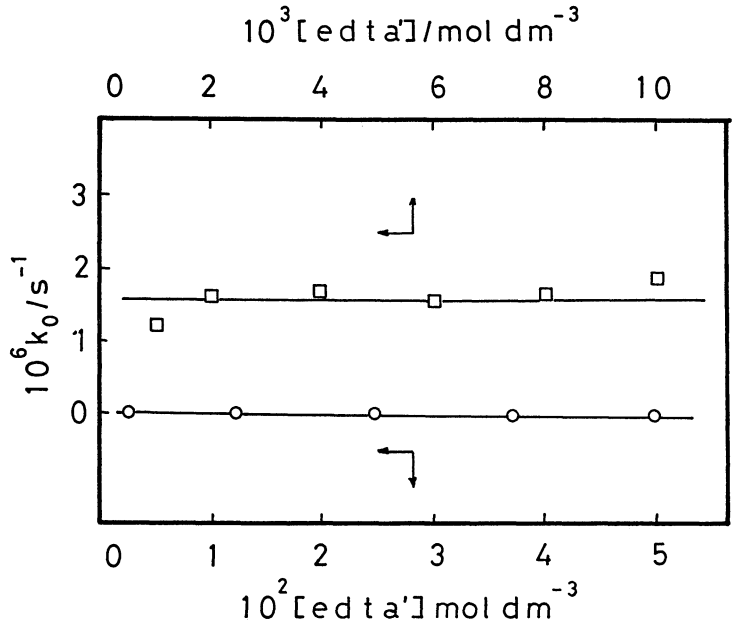


Fig. 2. Dependence of rate constants on the concentrations of edta' for the reaction of $Zn(tpps)^{4-}$ with EDTA in pH 3.30 (□) and 4.50 (○) at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$).

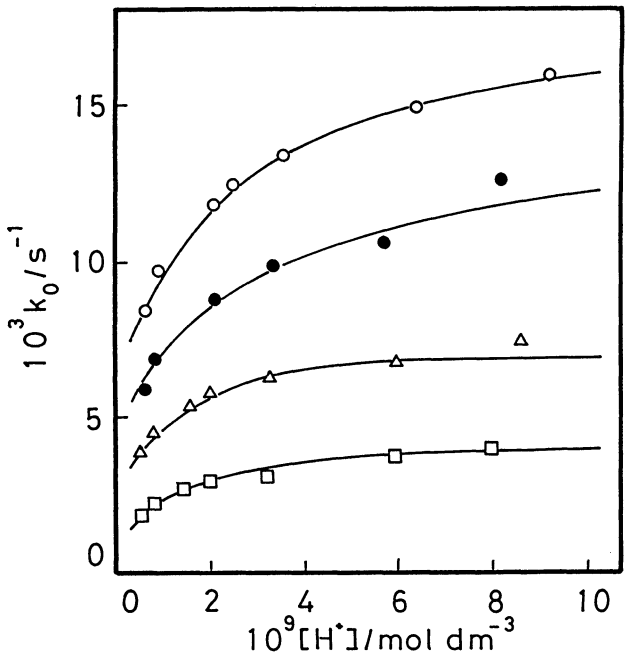


Fig. 3. Dependence of rate constants on the concentrations of hydrogen ion for the reaction of $Cd(tpps)^{4-}$ with EDTA at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$). [edta']/mol dm^{-3}=1.00×10^{-3} (□), 2.00×10^{-3} (△), 3.00×10^{-3} (●), and 4.00×10^{-3} (○).

$$k_0 = k_1[\text{edta}^{4-}] + k_2[\text{Hedta}^{3-}] \quad (5)$$

$$= \frac{(k_1 + k_2K^{H}[H^+])\,[\text{edta'}]}{1 + K^{H}[H^+]}, \quad (6)$$

where [edta']=[edta^{4-}]+[Hedta^{3-}]. Equation 6 is rearranged to

$$k_0(1 + K^{H}[H^+])\,[\text{edta'}]^{-1} = k_1 + k_2K^{H}[H^+] \quad (7)$$

where K^{H} is the protonation constant of edta^{4-}: $K^{H}=10^{10.17}$. The plots of the left-hand side of Eq. 7 against [H$^+$] give straight lines with zero intercept for Cd- and $Pb(tpps)^{4-}$ (Fig. 4). The values were found to be k_1=0 mol^{-3} dm^3 s^{-1} both for Cd- and $Pb(tpps)^{4-}$, k_2=4.1±0.2 mol^{-1} dm^3 s^{-1} for $Cd(tpps)^{4-}$ and k_2= 2.02±0.1 mol^{-1} dm^3 s^{-1} for $Pb(tpps)^{4-}$. In Fig. 5, the k_0 values are plotted against the concentrations of cadmium(II) or lead(II). The results show that the k_0 values are independent of the concentrations of these metal ions, and suggest that the metalloporphyrins do not dissociate before the attack of EDTA to Cd- or $Pb(tpps)^{4-}$.

Acid-Dissociation of Zn-, Cd-, and $Pb(tpps)^{4-}$. Protolytic demetallation of Zn-, Cd, and $Pb(tpps)^{4-}$ was studied in acidic medium. Cd- and $Pb(tpps)^{4-}$ easily dissociate in a dilute acid solution of pH 4—6 and $Zn(tpps)^{4-}$ dissociates at lower pH than 2. The observed first-order rate constants were plotted against [H$^+$]^2. The plots for Zn- and $Cd(tpps)^{4-}$ were straight lines, while those for $Pb(tpps)^{4-}$ were proportion to[H$^+$]^2 at the low concentration of hydrogen ion but suppressed at the high concentrations of hydrogen ion. This indicates that the rate for the second-proton attack to $Pb(Htpps)^{3-}$ which is formed in the first-protonation of $Pb(tpps)^{4-}$ as shown in Scheme 2 becomes comparable to that for the dissociation $Pb(Htpps)^{3-}$.

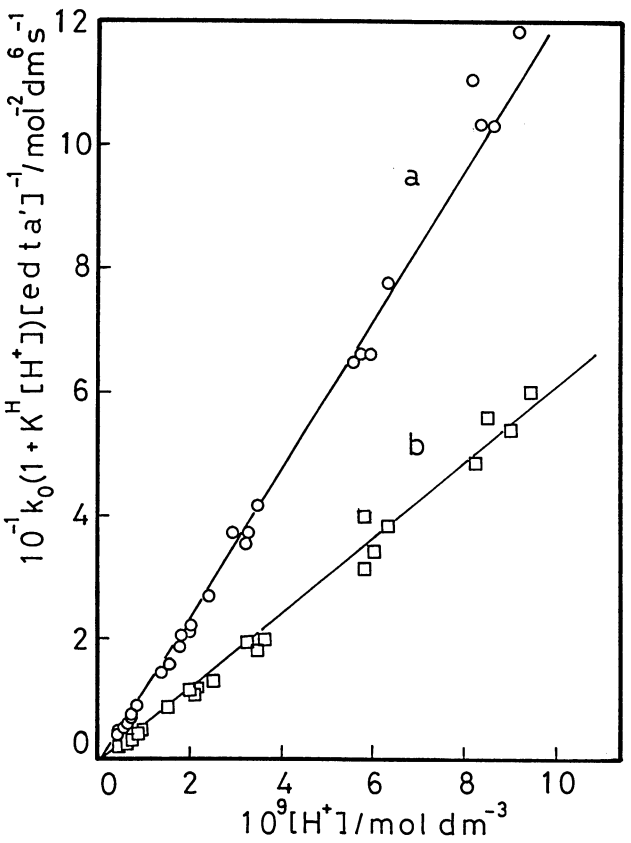


Fig. 4. Plots of 10^{-1} k_0 $(1+K^H[H^+])/[edta']$ vs. $[H^+]$ for the reaction of $Cd(tpps)^{4-}$ (a) and $Pb(tpps)^{4-}$ (b) with EDTA at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$).

$$M(tpps)^{4-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} M(Htpps)^{3-} \quad (8)$$

$$M(Htpps)^{3-} + H^+ \xrightarrow{k_4} M^{2+} + H_2tpps^{4-} \quad (9)$$

$$H_2tpps^{4-} + 2H^+ \xrightarrow{fast} H_4tpps^{2-} \quad (10)$$

Scheme 2.

Applying the steady-state approximation for $M(Htpps)^{3-}$, we have Eq. 11

$$k_0 = \frac{k_3k_4[H^+]^2}{k_{-3}+k_4[H^+]}. \quad (11)$$

The equation agrees with the observed kinetic results. That is, $k_{-3} \gg k_4[H^+]$ for Zn- and $Cd(tpps)^{4-}$, and $k_{-3} \approx k_4[H^+]$ for $Pb(tpps)^{4-}$ at the high concentration of hydrogen ion. Equation 11 is rearranged to

$$[H^+]^2k_0^{-1} = k_{-3}(k_3k_4)^{-1} + k_3^{-1}[H^+]. \quad (12)$$

The plots of $[H^+]^2k_0^{-1}$ vs. $[H^+]$ are shown in Fig. 6. For Cd- and $Zn(tpps)^{4-}$, only $k_3k_4(k_{-3})^{-1}$ was found, while for $Pb(tpps)^{4-}$ both k_3 and $k_3k_4(k_{-3})^{-1}$ were determined.

Combining the rate equations both for the ligand-substitution reaction of $M(tpps)^{4-}$ with EDTA (Eq. 5) and the acid-dissociation reaction of $M(tpps)^{4-}$ (Eq. 11), we have Eq. 13 for the the rate of the decrease of $M(tpps)^{4-}$

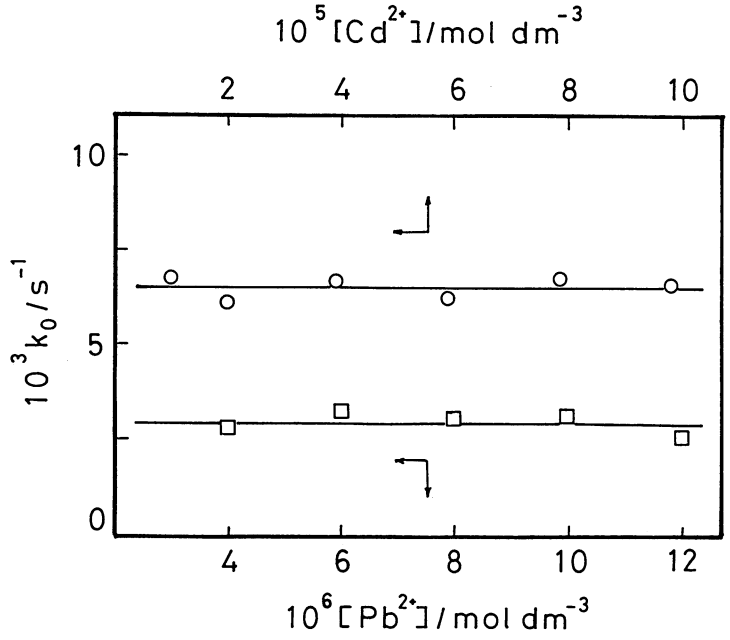


Fig. 5. Dependence of rate constants on the concentrations of cadmium(II) (○) and lead(II) (□) for the reaction of Cd- and $Pb(tpps)^{4-}$ with EDTA at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$). Concentrations of edta' (mol dm^{-3}) and pH are 2.00×10^{-3} and 8.26 for $Cd(tpps)^{4-}$, and 4.00×10^{-3} and 8.69 for $Pb(tpps)^{4-}$, respectively.

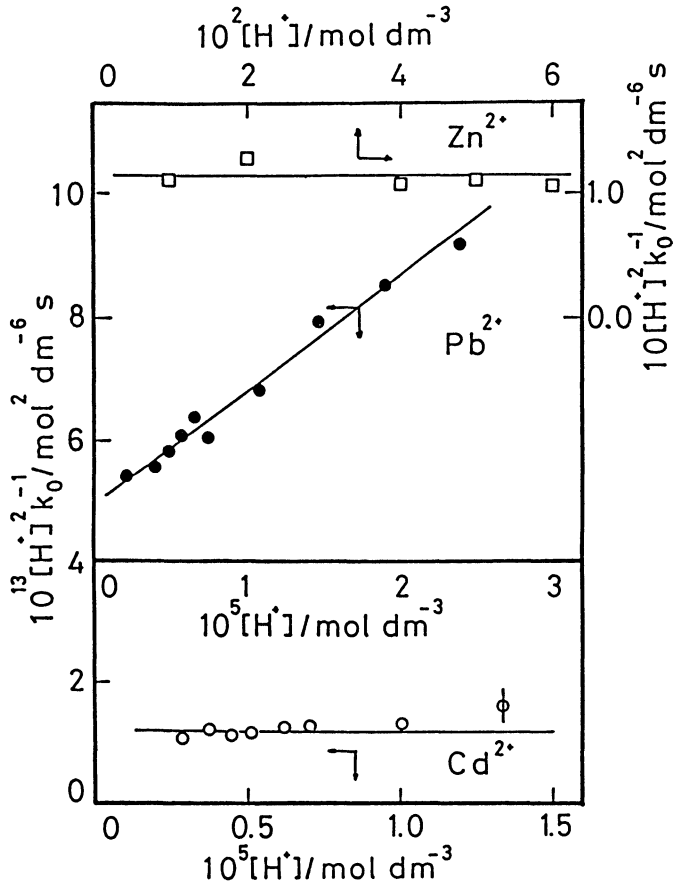


Fig. 6. Plots of $[H^+]^2(k_0)^{-1}$/mol^2 dm^{-6} s vs. $[H^+]$ for the acid-dissociation of Zn(tpps)$^{4-}$ (□), Pb(tpps)$^{4-}$ (●), and Cd(tpps)$^{4-}$ (○) at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$).

Table 1. Kinetic Parameters for the Reaction of Zn-, Cd-, and Pb(tpps)$^{4-}$ with EDTA and the Acid-Dissociation Reaction of the Metalloporphyrins at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$)

	Zn(II)	Cd(II)	Pb(II)
k_2 / mol^{-1} dm^3 s^{-1}	0.00	4.1±0.2	2.0±0.1
k_3 / mol^{-1} dm^3 s^{-1}	—	—	(5.4±0.3)×10^7
$k_3k_4(k_{-3})^{-1}$ / mol^{-2} dm^6 s^{-1}	8.7±0.2	(8.3±0.4)×10^{12}	(2.0±0.1)×10^{12}
K_{MP} / mol dm^{-3}	10$^{-0.43}$	10$^{-9.94}$	10$^{-9.97}$

$$-d[M(tpps)^{4-}]/dt = (k_1[edta^{4-}] + k_2[Hedta^{3-}] + k_3k_4[H^+]^2 \times (k_{-3} + k_4[H^+])^{-1})\,[M(tpps)^{4-}]. \quad (13)$$

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

Discussion

We can see the followings from Table 1. 1. Zn(tpps)$^{4-}$ is hard to be replaced with EDTA, whereas Cd- and Pb(tpps)$^{4-}$ are easily substituted with EDTA. 2. Acid-dissociation rate of Cd- and Pb(tpps)$^{4-}$ is 10^{12} times faster than that of Zn(tpps)$^{4-}$. 3. The formation constant of Zn(tpps)$^{4-}$ is about 10^9 times as large as those of Cd- and Pb(tpps)$^{4-}$. These large differences are discussed below.

Reaction with EDTA. The rate of the ligand-substitution reaction of Cd- or Pb(tpps)$^{4-}$ with EDTA increased linearly along with the concentrations of edta', while that of Zn(tpps)$^{4-}$ was independent of edta'. The kinetic difference between zinc(II) and cadmium(II) or lead(II) can be ascribed to their ionic radii: 109 pm for Cd^{2+}; 132 pm for Pb^{2+}; 89 pm for Zn^{2+}. Large metal ions such as cadmium(II) and lead(II) can not incorporate well into porphyrin core and just sit on the porphyrin plane. Barkigia et al. called lead(II) porphyrin a "roof complex" after X-ray

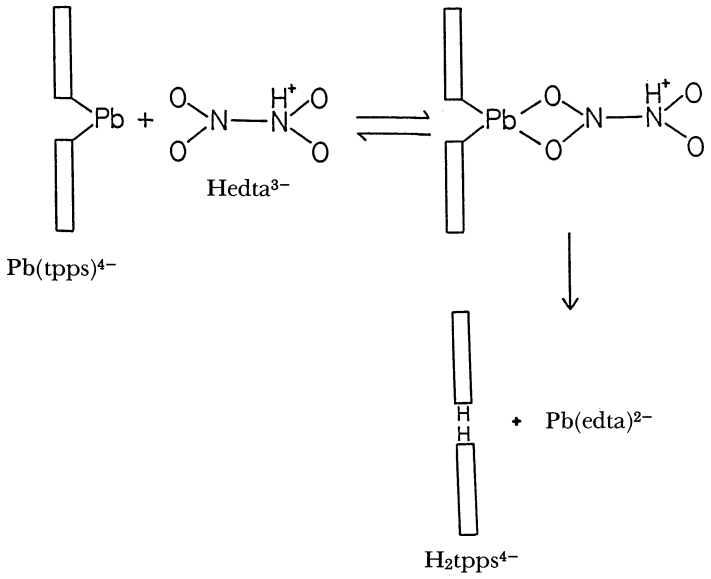


Fig. 7. Reaction mechanism for the reaction of $Pb(tpps)^{4-}$ with EDTA. ▭ H-H ▭ denotes H_2tpps^{4-}.

analysis of tetrapropylporphyrinato lead(II).[13] The roof metalloporphyrin, therefore, can be bound with a segment of $Hedta^{3-}$: two carboxylato and nitrilo groups, and then is easily replaced with $Hedta^{3-}$ (see Fig. 7). On the other hand, zinc(II) incorporates well into porphyrin core to form stable $Zn(tpps)^{4-}$.[14-16] Thus, $Hedta^{3-}$ can not pull zinc(II) away from $Zn(tpps)^{4-}$ by means of an axial ligation of $Hedta^{3-}$.

Dependence of rate constant on pH for the reaction with EDTA indicates that $Hedta^{3-}$ is more reactive than $edta^{4-}$. Similar results were also observed for the reaction of $Gd^{III}(tpps)^{4-}$ with EDTA.[17] A proton-transfer pathway might contribute to the dissociation of metalloporphyrin as in the case of the ligand-substitution reaction of metal-peptide complexes.[18-20] First, the carboxylato and the nitrilo groups of $Hedta^{3-}$ coordinate to lead(II) or cadmium(II), then the proton bound to the other nitrilo nitrogen of $Hedta^{3-}$ transfers to the pyrrole nitrogen of the porphyrin. Binding of the proton to the pyrrole nitrogen makes the demetallation of Cd- or $Pb(tpps)^{4-}$ easier (vide infra).

Proton-Assisted Demetallation. The metalloporphyrins of Cd-, Pb-, and $Zn(tpps)^{4-}$ were demetallated in acidic solution. The rate for the acid dissociation of $Cd(tpps)^{4-}$, is only four times as fast as that for $Pb(tpps)^{4-}$, while the dissociation rate for $Zn(tpps)^{4-}$ is about 10^{12} times slower than those for $Cd(tpps)^{4-}$ and $Pb(tpps)^{4-}$. The large kinetic difference also results from the ionic radii as described before. In the case of the demetallation of $Pb(tpps)^{4-}$, the present kinetic data clearly indicate that hydrogen ion attacks the

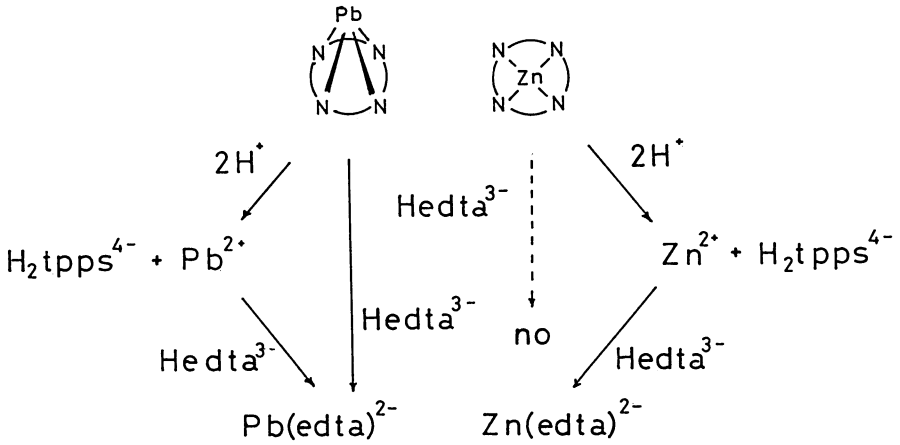


Fig. 8. Summary of the reaction pathways for the reaction of Pb- and $Zn(tpps)^{4-}$ with EDTA. $Cd(tpps)^{4-}$ goes through the same reaction pathway as $Pb(tpps)^{4-}$.

porphyrin core step by step to bind the pyrrole nitrogens. The first step is the formation of $Pb(Htpps)^{3-}$ through the protonation, and the second step is the dissociation of the metalloporphyrin after the formation of the diprotonated metalloporphyrin: $Pb(H_2tpps)^{2-}$.

Proposed reaction mechanism is shown in Fig. 8. $Hedta^{3-}$ directly attacks Pb- or $Cd(tpps)^{4-}$ to form its metal complex. On the other hand, $Hedta^{3-}$ can not bind $Zn(tpps)^{4-}$. Therefore, $Zn(tpps)^{4-}$ dissociates to aquazinc(II) and the free-base porphyrin after the proton attack, then the aquazinc(II) reacts with $Hedta^{3-}$ to form $Zn(edta)^{2-}$. Pb- and $Cd(tpps)^{4-}$ also dissociate to their aqua ions in an acidic medium. The rate-determining step for Pb- and $Cd(tpps)^{4-}$ is the $Hedta^{3-}$ attack at pH 8—9.3, which shifts to the proton attack at pH 4—6.

Present paper clearly shows the different behavior of Zn-, Cd-, and $Pb(tpps)^{4-}$ in their reaction mechanism and rate constants. $Zn(tpps)^{4-}$ is replaced with EDTA although the reaction is very slow compared with Cd- and $Pd(tpps)^{4-}$, and the rate-determining step for $Zn(tpps)^{4-}$ is the proton attack. The differences in the kinetic behavior of Zn-, Cd-, and $Pb(tpps)^{4-}$ also strongly support the experimental results in the previous analytical methods for the determination of zinc(II) in large excess of cadmium(II) and lead(II) using the ligand substitution reaction with EDTA or the acid-dissociation rate of these metalloporphyrins.

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