

Kinetics and Mechanism of Metal-Substitution Reaction of Homodinuclear Mercury(II) Porphyrin with Zinc(II) with Particular Reference to a Heterodinuclear Metalloporphyrin Intermediate

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Mercury(II) enhances the incorporation rate of zinc(II) into 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2(\text{tpps})^{4-}$). The detailed kinetics and mechanism for the metal-substitution reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) was studied at 25 °C, $I = 0.1 \text{ mol dm}^{-3}$ (NaNO_3), pH 4.5–6.5, $[\text{H}_2(\text{tpps})^{4-}] = (1-4) \times 10^{-6}$, $[\text{Hg}^{2+}] = 10^{-5} - 10^{-3}$, and $[\text{Zn}^{2+}] = 10^{-4} - 10^{-2} \text{ mol dm}^{-3}$. The reaction showed a biphasic kinetic behavior of the following steps: $\text{Hg}_2(\text{tpps})^{2-} + \text{Zn}^{2+} \rightleftharpoons \text{Hg}(\text{tpps})\text{Zn}^{2-} + \text{Hg}^{2+} \rightleftharpoons \text{Zn}(\text{tpps})^{4-} + 2\text{Hg}^{2+}$. The rate equations for the first-step and second-step reactions are expressed as $-\text{d}[\text{Hg}_2(\text{tpps})^{2-}]/\text{d}t = k_1 k_2 [\text{Zn}^{2+}] [\text{OH}^-] [\text{Hg}_2(\text{tpps})^{2-}] (k_{-1} [\text{HgOH}^+] + k_2 [\text{Zn}^{2+}])^{-1}$ and $-\text{d}[\text{Hg}(\text{tpps})\text{Zn}^{2-}]/\text{d}t = k_3 + k_4 [\text{H}^+]$, respectively. The values of the rate constants were found to be $k_1 = (1.02 \pm 0.04) \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_2/k_{-1} = (0.14 \pm 0.02)$, $k_3 = (1.09 \pm 0.02) \times 10^{-2} \text{ s}^{-1}$, and $k_4 = (3.00 \pm 0.09) \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25 °C, and the activation enthalpies and entropies were $\Delta H^\ddagger = 102 \pm 6 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 251 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_1 ; $\Delta H^\ddagger = 0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -266 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_2/k_{-1} ; $\Delta H^\ddagger = 81 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -11.9 \pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_3 ; $\Delta H^\ddagger = 100 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 157 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_4 , respectively. The formation of heterodinuclear metalloporphyrin $\text{Hg}(\text{tpps})\text{Zn}^{2-}$ was suggested by the following kinetic results. The observed rate constant for the first-step reaction decreased with increase in mercury(II) concentration, increased with the increase in concentrations of zinc(II), and leveled off at high zinc(II) concentration. The observed rate constant for the second-step reactions was characteristic of a dissociation of $\text{Hg}(\text{tpps})\text{Zn}^{2-}$: the rate constant was independent of zinc(II) and mercury(II) concentrations and of hydrogen ion concentration at high pH. A series of absorption spectra for the first- and second-step reactions supported the binding of mercury(II) and zinc(II) in the intermediate.

Introduction

A number of studies on metalloporphyrin formation have been reported over 20 years, as a result of the important role of metalloporphyrins in biological systems. The general mechanism for the metalation was first proposed by Hambright and Chock¹ and has been reviewed from time to time by Hambright,² Lavalley,^{3,4} Schneider,⁵ and Tanaka.⁶ The rate of metalloporphyrin formation is several orders of magnitude slower than that of the complex formation of open-chain ligands,⁷ and the overall mechanism is not straightforward in some cases.⁸ For example, the rate constant for the complexation of zinc(II) and 1,10-phenanthroline is about $10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in water at 25 °C,⁹ while the rate constant for the reaction of zinc(II) with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2(\text{tpps})^{4-}$) is $1.6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.¹⁰ The great difference in the reaction rates is presumably due to a less flexible porphyrin ring and a less

accessible lone-pair electron on the porphyrin for incoming metal ions.

To accelerate the slow metalation, several methods have been proposed.¹¹ One interesting method is the addition of large metal ions such as mercury(II),¹² cadmium(II),^{13,14} and lead(II).¹⁵ Grant and Hambright, originally, reported that zinc(II) reacts with tetraphenylporphyrinatolead(II) ($\text{Pb}(\text{tpp})$) to form $\text{Zn}(\text{tpp})$ more rapidly in comparison with the direct reaction of zinc(II) with the free base tetraphenylporphyrin (H_2tpp).¹⁶ Afterwards, we have demonstrated the catalytic effect of mercury(II) and cadmium(II), as low as $10^{-8} \text{ mol dm}^{-3}$, on the formation of manganese(III) porphyrin complex.^{12,13} The reaction was enhanced by a factor of 7900 in the presence of cadmium(II).¹⁷ Similar catalytic effects have been observed for lead(II)¹⁵ and copper(I).¹⁸ Among these catalysts, mercury(II) exerts the largest catalytic effect.¹⁹ In these reactions, the formation of a heterodinuclear metalloporphyrin as an intermediate, in which a catalyst such as mercury(II) and an incoming metal ion like zinc(II) are bound simultaneously to the porphyrin plane on opposite sides, has been proposed.^{17,20} The structure of the intermediate was not known, but we have recently detected the intermediate from a biphasic behavior in the reaction of the

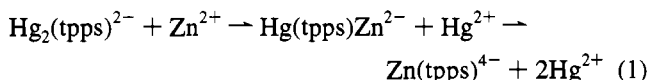
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homodinuclear mercury(II) complex of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2(\text{tpps})^{4-}$) with zinc(II) and have reported preliminary results.²¹ The present paper describes the detailed reaction mechanism for the metal-substitution reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) from the kinetic and spectral studies:



The main focus of the present work is on the formation and dissociation of the intermediate of the heterodinuclear metalloporphyrin $\text{Hg}(\text{tpps})\text{Zn}^{2-}$.

Experimental Section

Reagents. 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2(\text{tpps})^{4-}$) was synthesized by the methods described in the literature,^{22,23} and its acid form was recrystallized from ethanol/acetone solution and purified by Sephadex LH-20 gel column chromatography. Final purity was checked by ^1H NMR and thin-layer chromatography. Sodium nitrate and 2-(*N*-morpholine)ethanesulfonic acid (MES buffer) were purified by solvent extraction using phenyldiazene-carbothioic acid 2-phenylhydrazide (dithizone) and 8-quinolinol in tetrachloromethane to remove heavy metal ions like zinc(II), copper, lead(II), and iron(III) and then recrystallized. Otherwise, these impurities easily form their metalloporphyrins in the presence of mercury(II). Zinc(II) nitrate was recrystallized from distilled water. Buffer solutions were prepared with MES buffer and ultrapure sodium hydroxide (Merck Chemical Co.). All solutions were prepared using ultrapure water treated by a Milli-Q SP TOC (Nippon Millipore Ltd., Japan).

Kinetic Measurements. The kinetic studies were carried out at the pH range 4.5–6.5 (MES buffer, 10^{-2} mol dm^{-3}) under various concentrations of $\text{H}_2(\text{tpps})^{4-}$ ($(2-4) \times 10^{-6}$ mol dm^{-3}), mercury(II) (10^{-5} – 10^{-3} mol dm^{-3}), and zinc(II) (10^{-4} – 10^{-2} mol dm^{-3}) at 15, 20, 25, 30, and 35 °C with $I = 0.1$ mol dm^{-3} (NaNO_3). The reaction was started by mixing two solutions, *i.e.*, one containing $\text{H}_2(\text{tpps})^{4-}$, mercury(II) nitrate, sodium nitrate, and buffer, and the other containing zinc(II) nitrate, sodium nitrate, and buffer. The change in the absorbance was monitored as a function of time at 434 nm (λ_{max} of $\text{Hg}_2(\text{tpps})^{2-}$) and 421 nm (λ_{max} of $\text{Zn}(\text{tpps})^{4-}$). The absorption spectra of the porphyrin and the metalloporphyrins were measured in a Jasco UV-VIDEC 610 C spectrophotometer. The kinetic runs were observed by a Otsuka denshi RA415 stopped-flow apparatus with a rapid-scan system and a Jasco spectrophotometer with a recorder. The pH was varied by addition of sodium hydroxide or nitric acid to MES buffer and determined by a Radiometer 85 ion-analyzer with a combined electrode (GK 2401C). 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 ($-\log[\text{H}^+] = 2.000$; $I = 0.1$). From pH meter readings in various hydrogen ion concentrations at $I = 0.1$ mol dm^{-3} (HNO_3 – NaNO_3), the pH meter and electrode system were calibrated in terms of $-\log[\text{H}^+]$.

Results

Equilibrium studies on mercury(II) porphyrin complexes have suggested the formation of some chemical species of 1:1, 2:1, and 3:2 (mercury(II)/porphyrins).^{24,25} On the basis of equilibrium and extended X-ray absorption fine structure (EXAFS)

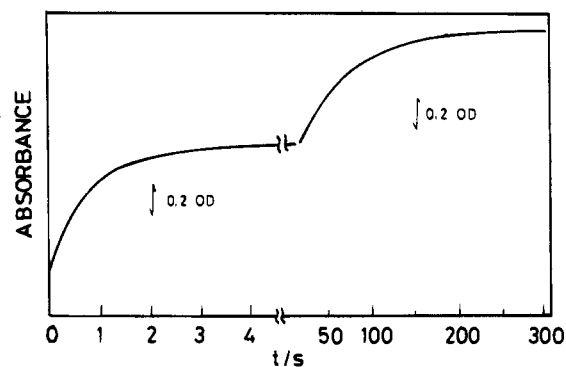


Figure 1. Typical kinetic run showing a two-step reaction (I, II) for the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) at pH 6.06, 25 °C, and $I = 0.1$ mol dm^{-3} (NaNO_3). $[\text{Hg}_2^{2+}] = 5.02 \times 10^{-4}$, $[\text{Zn}^{2+}] = 1.98 \times 10^{-3}$, $[\text{H}_2(\text{tpps})^{4-}] = 2.00 \times 10^{-6}$ mol dm^{-3} .

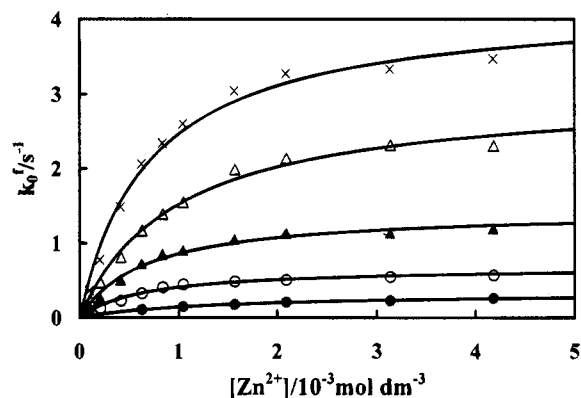


Figure 2. Dependence of the rate constant for the first-step reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) on the concentration of zinc(II) at 15 (●), 20 (○), 25 (▲), 30 (△), and 35 °C (×). $I = 0.1$ mol dm^{-3} (NaNO_3). $[\text{Hg}_2^{2+}] = 9.48 \times 10^{-5}$ mol dm^{-3} , $[\text{H}_2(\text{tpps})^{4-}] = 4.62 \times 10^{-6}$ mol dm^{-3} . The solid lines are calculated from the values of k_1 and k_2/k_{-1} at each temperature (see Table 1).

studies of the mercury(II) porphyrin complex,²⁶ we assigned the formation of the homodinuclear mercury(II) porphyrin complex, $\text{Hg}_2(\text{tpps})^{2-}$, where two mercury(II) ions are bound to one porphyrin and form the homodinuclear mercury(II) porphyrin ($\text{Hg}_2(\text{tpps})^{2-}$) with the mercury(II) ions on opposite sides of the porphyrin plane. The same has been postulated from ^1H NMR spectroscopy by Hudson and Smith.²⁷

The reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) was of pseudo-first order kinetics with respect to $\text{Hg}_2(\text{tpps})^{2-}$ in a large excess of mercury(II) and zinc(II). The metal-substitution reaction showed the biphasic kinetic behavior as shown in Figure 1. The first-step reaction was completed in a few seconds and was followed by the second-step reaction with a half-life of a few minutes. The rate constants of the first- and second-step reactions were determined separately for each reaction step by using the stopped-flow apparatus and the conventional spectrophotometer, respectively.

First-Step Reaction. The observed rate constant, k_0^f , for the first-step reaction was plotted against the concentration of zinc(II) at different temperatures in Figure 2. The rate constant increases with the increase in the concentration of zinc(II) and reaches a plateau. The rate constants decrease with the increase in the concentration of mercury(II), and the reciprocal values of k_0^f are linearly correlated to the concentrations of mercury(II) with an intercept. (Figure 3a). The plateau at the high concen-

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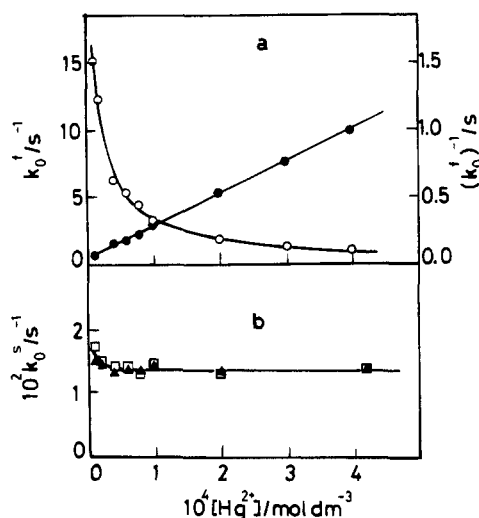
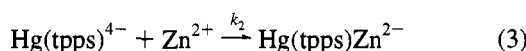
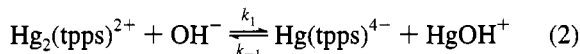


Figure 3. Effect of mercury(II) concentration on the rate constant for the first-step (a) and the second-step (b) reactions of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) at pH 5.90, 25 °C, and $I = 0.1 \text{ mol dm}^{-3}$ (NaNO_3). $[\text{Zn}^{2+}] = 1.93 \times 10^{-3}$ (○, ●), 1.00×10^{-3} (□), and 5.94×10^{-4} (▲) mol dm^{-3} .

trations of zinc(II) and the decrease in the rate constant with the increase in the concentration of mercury(II) indicate the formation of a precursor complex by the dissociation of mercury(II) before the rate-determining step. Furthermore, the rate constant increases with the increase of $-\log[\text{H}^+]$, and the plot of $\log k_0^f$ vs $-\log[\text{H}^+]$ gives a straight line with a slope of unity. The observed kinetic results suggest the following reaction mechanism for the first-step reaction:



Assuming the steady-state of $\text{Hg}(\text{tpps})^{4-}$ in the reaction mechanism, we can correlate the observed rate constant, k_0^f , with the chemical species in eqs 2 and 3 as follows.

$$k_0^f = \frac{k_1 k_2 [\text{OH}^-] [\text{Zn}^{2+}]}{k_{-1} [\text{HgOH}^+] + k_2 [\text{Zn}^{2+}]} \quad (4)$$

Using a nonlinear least-squares program on eq 4, we find the rate constants for the first-step reaction from Figures 2 and 3: $k_1 = (1.02 \pm 0.04) \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$; $k_2/k_{-1} = 0.14 \pm 0.02$, with the value of $\log K_w = 13.78^{27}$ at 25 °C. The activation enthalpies and entropies were $\Delta H^\ddagger = 102 \pm 6 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 251 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_1 ; $\Delta H^\ddagger = 0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -266 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_2/k_{-1} , respectively. The solid lines in Figures 2 and 3 are drawn by using these kinetic data.

Second-Step Reaction. The kinetic results for the second-step reaction showed a characteristic behavior. In Figure 4, the observed rate constants, k_0^s , for the second-step reaction are plotted against the concentrations of zinc(II) at different temperatures. The rate constant is independent of the concentration of zinc(II) even at a concentration less than $10^{-3} \text{ mol dm}^{-3}$, where the rate constant of the first-step reaction depends on the concentration of zinc(II). Furthermore, the observed rate constant is independent of mercury(II) at its high concentration, although the rate constant decreases with the increase of mercury(II) at its low concentration range because of dissociation of a part of $\text{Hg}_2(\text{tpps})^{2-}$ to $\text{Hg}(\text{tpps})^{4-}$ in the mercury(II) porphyrin solution before starting the reaction (Figure 3b). Furthermore, the observed rate constant is independent of the

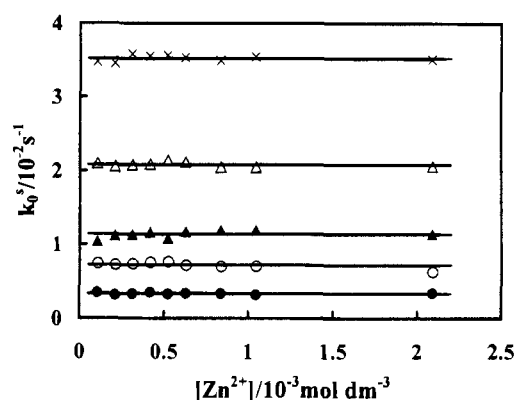


Figure 4. Dependence of the rate constant for the second-step reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) on the concentration of zinc(II) at 15 (●), 20 (○), 25 (▲), 30 (△), and 35 °C (×). $I = 0.1 \text{ mol dm}^{-3}$ (NaNO_3). $[\text{Hg}^{2+}] = 4.74 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}_2(\text{tpps})^{4-}] = 2.31 \times 10^{-6} \text{ mol dm}^{-3}$.

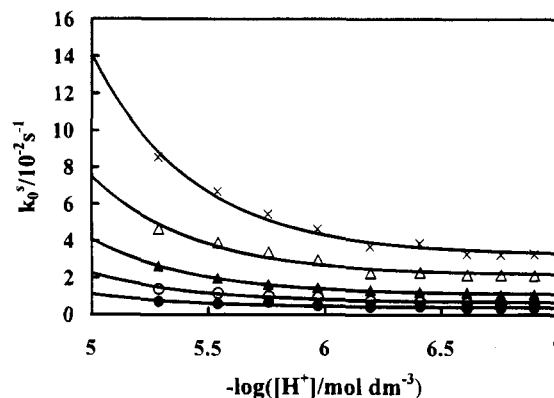
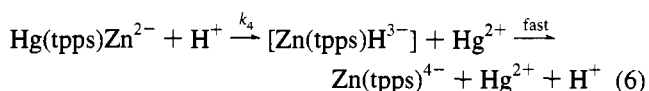


Figure 5. Dependence of the rate constant for the second-step reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) on pH at 15 (●), 20 (○), 25 (▲), 30 (△), and 35 °C (×). $I = 0.1 \text{ mol dm}^{-3}$ (NaNO_3). $[\text{Hg}^{2+}] = 9.48 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Zn}^{2+}] = 5.23 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2(\text{tpps})^{4-}] = 2.31 \times 10^{-6} \text{ mol dm}^{-3}$. The solid lines were calculated from k_3 and k_4 values at each temperature (Table 1).

hydrogen ion concentration at higher pH, and the independence becomes more clear at low temperature (Figure 5). The plot of k_0^s vs $[\text{H}^+]$ gives a straight line with an intercept. The experimental results suggest the reaction mechanism given in eqs 5 and 6 for the second step.



The rate equation for the second-step reaction, k_0^s , at high mercury(II) concentrations is given by eq 7.

$$k_0^s = k_3 + k_4 [\text{H}^+] \quad (7)$$

The rate constants were found to be $k_3 = (1.09 \pm 0.02) \times 10^{-2} \text{ s}^{-1}$ and $k_4 = (3.00 \pm 0.09) \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25 °C, and the activation enthalpies and entropies were $\Delta H^\ddagger = 81 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = (-11.9 \pm 0.5) \text{ J mol}^{-1} \text{ K}^{-1}$ for k_3 ; $\Delta H^\ddagger = 100 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 157 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ for k_4 , respectively. The solid lines in Figures 4 and 5 were calculated from these rate constants.

The rate constants at 25 °C for all reaction paths and the activation enthalpies and entropies are summarized in Table 1.

Table 1. Rate Constants and Activation Parameters of the Reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with Zinc(II)^a

rate constants (298.2 K)		$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ mol^{-1}\ K^{-1}$
$k_1/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$	$(1.02 \pm 0.04) \times 10^8$	102 ± 6	251 ± 12
k_2/k_{-1}	0.14 ± 0.02	0	-266 ± 16
k_3/s^{-1}	$(1.09 \pm 0.02) \times 10^{-2}$	81 ± 2	-11.9 ± 0.5
$k_4/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$	$(3.00 \pm 0.09) \times 10^3$	100 ± 3	157 ± 5

^a $I = 0.1\ \text{mol}\ \text{dm}^{-3}$ (NaNO_3), MES buffer = $1.00 \times 10^{-2}\ \text{mol}\ \text{dm}^{-3}$.

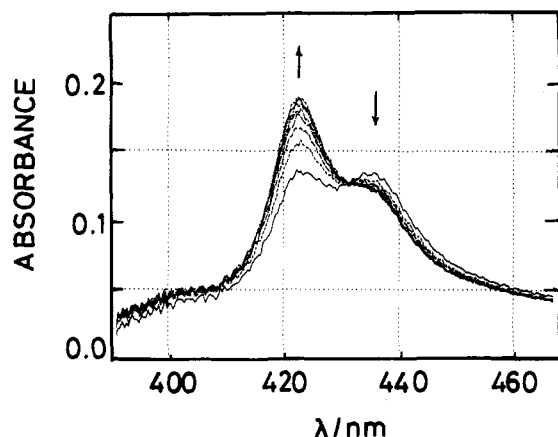


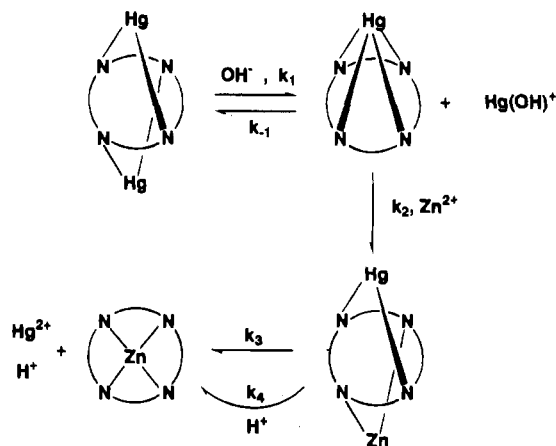
Figure 6. Change in absorption spectra during the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) observed at 200 ms intervals for the first-step reaction at pH 5.96, 25 °C, and $I = 0.1\ \text{mol}\ \text{dm}^{-3}$ (NaNO_3). $[\text{Hg}_2^{2+}] = 5.05 \times 10^{-5}$, $[\text{Zn}^{2+}] = 2.09 \times 10^{-3}$, $[\text{H}_2(\text{tpps})^{4-}] = 4.04 \times 10^{-6}\ \text{mol}\ \text{dm}^{-3}$.

Rapid-Scan Spectrophotometry. A series of absorption spectra during the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) was measured. Typical spectral change is given in Figure 6 for the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II). For the first-step reaction, the change in absorbance at 434 (the Soret band of $\text{Hg}_2(\text{tpps})^{2-}$) was smaller than that of the second-step reaction, and an increase in the absorbance was observed at 421 nm (the Soret band of $\text{Zn}(\text{tpps})^{4-}$). This indicates the binding of both mercury(II) and zinc(II) in the reaction intermediate. For the second-step reaction, a large spectral change was observed at 421 and 434 nm, because of the complete release of mercury(II) and the incorporation of zinc(II). The isosbestic point of the second-step reaction shifted a little to 429 nm from 431 nm of the first-step reaction. Similar behavior was also found at the Q-band of $\text{Zn}(\text{tpps})^{4-}$ (551 nm) and $\text{Hg}_2(\text{tpps})^{2-}$ (564 nm). The spectral change supports the formation of the heterodinuclear intermediate, $\text{Hg}(\text{tpps})\text{Zn}^{2-}$, in the first-step reaction.

Discussion

Large metal ions like mercury(II) significantly accelerate the rate of metalloporphyrin formation. But why these metal ions enhance the reaction has not been clarified yet. Hambright *et al.* proposed that the activated complex has the form $[\text{M}-\text{P}-\text{M}^*]$, with incoming (M) and leaving (M^*) metal ions on the opposite sides of the porphyrin plane (P) (trans-metalation),^{16,20} but they also suggested cis-metalation for the reaction of Cd-*N*-methylporphyrin with Cu(II).²⁸ We have repeatedly suggested the formation of a heterodinuclear metalloporphyrin complex as an intermediate in the catalytic effect of large metal ions like mercury(II), cadmium(II), lead(II), and copper(I) on the formation of manganese(III) porphyrin.^{12,13,15,17,18}

The large metal ions cannot fit well into the porphyrin core and are displaced over the porphyrin plane. For example,

Scheme 1. Reaction Mechanism for the Reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with Zinc(II) Involving the Formation of the Heterodinuclear Intermediate ($\text{Hg}(\text{tpps})\text{Zn}^{2-}$)

mercury(II), lead(II), and cadmium(II) are situated apart from the mean porphyrin plane by 205–128,²⁹ 117,³⁰ and 40 pm,³¹ respectively. The coordination of these large metal ions deforms the porphyrin plane favorably for the incorporation of medium-sized metal ions: the lone-pair electron on the pyrrole nitrogen of the porphyrin is available to the incoming metal ions. The deformation of the porphyrin plane is the most important factor governing the reaction mechanism of metalloporphyrin formation. This is, in fact, supported by the recent studies on metalation reactions of nonplanar porphyrins using dodecaphenylporphyrin,³² octabromotetramesitylporphyrin,³³ octabromotetraphenylporphyrin,³⁴ and *N*-substituted porphyrins.³⁵

The reaction path for the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II) is shown in Scheme 1. According to the extended X-ray absorption fine structure (EXAFS) study on $\text{Hg}_2(\text{tpps})^{2-}$, each mercury(II) in $\text{Hg}_2(\text{tpps})^{2-}$ is bound to the two nitrogen atoms and two mercury(II) ions are displaced over and under the porphyrin plane.^{26,36} The pyrrole rings are twisted alternatively up and down, like a saddle porphyrin skeleton³⁷ and deviated more than 30° from the mean porphyrin plane. Hydroxide assists dissociation of mercury(II) prior to attack by zinc(II), and the formed $\text{Hg}(\text{tpps})^{4-}$ reacts with zinc(II) to form the heterodinuclear metalloporphyrin, $\text{Hg}(\text{tpps})\text{Zn}^{2-}$, as an intermediate. The final step is the dissociation of mercury(II) from the intermediate. Since hydrogen ion cannot attack directly the heterodinuclear intermediate, the k_4 path implies formation of a protonated species that facilitates insertion of zinc(II): $\text{Zn}(\text{tpps})\text{Hg}^{2-} + \text{H}^+ \rightarrow \text{Zn}(\text{tpps})\text{H}^{3-} + \text{Hg}^{2+}$. Similar first-order dependence of hydrogen ion was also observed for the acid-dissociation reaction of zinc(II) or cadmium(II) with their *N-p*-nitrobenzylporphyrin complex.³⁸ The *N*-substituent is placed over the porphyrin plane and blocks the attack of the proton as the mercury(II) of the $\text{Hg}(\text{tpps})\text{Zn}^{2-}$ does, and the pyrrole nitrogens are occupied by zinc(II) or cadmium(II). The acid-

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demetalation reaction of mercury(II) from the intermediate may take place in a mechanism similar to the acid-demetalation of the N-substituted porphyrin.

Robinson and Hambright have studied the metal-substitution reaction of tetrakis(1-methylpyridinium-4-yl)porphyrinatodimercury(II) ($\text{Hg}_2(\text{tmpyp})^{6+}$) with zinc(II) and copper(II) and proposed the formation of heterodinuclear mercury porphyrins like $\text{Hg}(\text{tmpyp})\text{Zn}^{6+}$ or $\text{Hg}(\text{tmpyp})\text{Cu}^{6+}$ as intermediates.²⁰ However, they have not succeeded in detecting the intermediate as the two-step reaction under the conditions where $\text{Hg}_2(\text{tmpyp})^{6+}$ and $\text{H}_4\text{tmpyp}^{6+}$ coexist in the sample solution. Their rate constants linearly increased with zinc(II) or copper(II), implying negligible concentrations of the intermediates under the conditions.

Activation parameters give useful information on the reaction mechanism. The large activation enthalpies of k_1 , k_3 , and k_4 , 80–102 kJ mol⁻¹, suggest the dissociation of mercury(II) from the pyrrole nitrogens. Furthermore, the large positive entropy of k_1 supports the dissociative mechanism. The k_2/k_{-1} was independent of temperature and led to a negative entropy. That is, the activation enthalpy of k_2 (binding of zinc(II)) is comparable to that of k_{-1} (binding of mercury(II)), and the activation entropy of k_2 is smaller than that of k_{-1} . Considering the large positive enthalpy and the small negative entropy of k_3 , the reaction path k_3 is an interchange dissociative mechanism (I_d). These findings are consistent with the proposed reaction mechanism shown in Scheme 1.

The present kinetic study provides evidence for the formation of the heterodinuclear metalloporphyrin as an intermediate from the following results for the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II): (1) the two-step reaction; (2) the concentration dependence of zinc(II), mercury(II), and hydrogen ions for both first- and second-step reactions; (3) activation parameters; and (4) rapid-scan spectrophotometry.

The structure of the $\text{Hg}_2(\text{tpps})^{2-}$ in solution determined by EXAFS methods^{26,36} is a deformed structure which favors the binding of zinc(II) from underneath (see Scheme 1). Very recently, Ohtaki et al.³⁹ have directly determined, by using a stopped-flow EXAFS, the structure of a heterodinuclear metalloporphyrin complex, $\text{Hg}(\text{tpps})\text{Cu}^{2-}$, formed in the metal-

substitution reaction of mercury(II) porphyrin with copper(II). Copper(II) is bound to $\text{Hg}(\text{tpps})^{4-}$ from underneath and is displaced by 40 pm from the mean porphyrin plane.⁴⁰

Conclusion

The present kinetic study on metalloporphyrin formation demonstrates the formation of the heterodinuclear metalloporphyrin complex as a short-lived intermediate for the reaction of $\text{Hg}_2(\text{tpps})^{2-}$ with zinc(II). Important features of the catalytic effect of large metal ions like mercury(II) on the incorporation of other medium-sized metal ions like zinc(II) are the deformation of the porphyrin ring by coordination of the large metal ions. The deformed structure makes it easy to form intermediates of heterodinuclear metalloporphyrins. This is an important reason why large metal ions accelerate the formation of metalloporphyrin complexes.

Previously, we reported that some reducing agents such as hydroxylamine and metal copper accelerate the formation of copper(II) porphyrin of 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin ($\text{H}_2(\text{tmpyp})^{4+}$) by a factor of 10^4 .¹⁸ The ionic radius of Cu^+ (96 pm) is significantly larger than Cu^{2+} (72 pm). Copper(I) sits on the top of the porphyrin plane. The mechanism is similar to the effect of the large metal ions like mercury(II), and the intermediate is a mixed-valence metalloporphyrin complex, $[\text{Cu}^{\text{II}}(\text{tmpyp})\text{Cu}^{\text{I}}]^{5+}$, like $\text{Hg}(\text{tpps})\text{Zn}^{2-}$, as found in this work. The formation of the heterodinuclear metalloporphyrin seems to be a general mechanism for the metalloporphyrin formation catalyzed by large metal ions. Furthermore, our results imply a possibility of the synthesis of various heterodinuclear metalloporphyrins, and some experiments on this relation are in progress in our laboratory.

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