Equilibrium and EXAFS Studies of Mercury(II) Porphyrin in Aqueous Solution

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Formation of the 2:1 mercury(II) porphyrin complex, $Hg_2(tpps)^{2-}$ (H_2tpps^{4-}: tetrakis(4-sulfonatophenyl)porphyrin), in aqueous solution has been investigated. Equilibrium studies revealed that main chemical species is $Hg_2(tpps)^{2-}$ even in a solution of a 1:1 molar ratio of C_{tpps}/C_{Hg} and the $Hg_2(tpps)^{2-}$ complex is very stable thermodynamically. EXAFS (extended X-ray absorption fine structure) analysis of the $Hg_2(tpps)^{2-}$ complex in aqueous solution showed that the Hg–N bond length within the complex is 215(2) pm and the bond length is much shorter than the Hg–O bond length (240 pm) within the hydrated mercury(II) ion. Thus the very strong Hg–N bond is formed upon the complexation of $Hg_2(tpps)^{2-}$ and the strong bond formation supports the high stability of the $Hg_2(tpps)^{2-}$ complex. Deformation of $Hg_2(tpps)^{2-}$ is also discussed in connection with catalytic effect of mercury(II) on metalloporphyrin formation.

Large metal ions such as mercury(II), cadmium(II), and lead(II) can not incorporate well into porphyrin core, and just sit on the porphyrin plane. Barkigia et al.$^{1)}$ call the lead(II) porphyrin a "roof complex" after X-ray analysis of tetra(propylporphinato)lead(II). Lead(II) is 117 pm above the plane formed by the four nitrogen groups of the porphyrin macrocycle. These metalloporphyrins therefore are very unstable. The formation constants of lead(II) and cadmium(II) porphyrins are 10^{10} times smaller than that of zinc(II) porphyrin and the metalloporphyrins are easily replaced by EDTA and the proton of strong acids.$^{2)}$ However, mercury(II) is unique in that it forms thermodynamically very stable complex with N-donor ligands. For example, the formation constants ($\log(K/\mathrm{mol^{-1}\,dm^3})$) of the metal complexes of 1,4,7,10-tetraazacyclododecane ([12]aneN_4) are 25.5, 14.3, and 15.9 for mercury(II), cadmium(II), and lead(II), respectively.$^{3)}$ Furthermore, these metal ions accelerate the incorporation of medium-sized transition metal ions such as manganese(II) into the porphyrin core.$^{4-8)}$ The large metal ions deform the porphyrin nucleus favorably for attack by another metal ion from underneath, and mercury(II) exerts the largest catalytic effect among them.

The characteristic features of mercury(II) encourage us to study the structure of mercury(II) porphyrin in aqueous solution for elucidating the high stability and the large catalytic effect of the mercury(II) complex. Several examples of mercury(II) porphyrin complexes have been formulated from equilibrium or ^{1}H NMR studies$^{9,10)}$ and only one paper concerning X-ray structural analysis of mercury(II) porphyrin has been published for *N*-tosylamineoctaethylporphyrin in solid state.$^{11)}$ But no direct structural data of mercury(II) porphyrin has been available so far in solution. In this paper, we first characterize the high stability of the mercury(II) porphyrin complex of tetrakis(4-sulfonatophenyl)porphyrin (H_2tpps^{4-}) in aqueous solution and then apply the EXAFS method to clarify the local structure around mercury(II) ion of the porphyrin complex in relation to the high stability and the large catalytic effect of the complex.

Experimental

Sample Solution. All chemicals used were of analytical reagent grade. H_2tpps^{4-} was used without further purification.

Four test solutions were prepared for EXAFS measurements. The composition of the sample solutions is given in Table 1. Solutions A and B are aqueous mercury(II) nitrate solutions containing 0.5 and 0.1 mol dm^{-3} nitric acid, respectively. The solutions involve the solvated mercury(II) ion of the known structure in water$^{12)}$ and were used as the structure standard for an Hg–O atom pair. Two sample solutions C and D were prepared by dissolving $Hg(NO_3)_2$ and H_2tpps^{4-} in water at different C_{tpps}/C_{Hg} ratios and then adjusting to suitable hydrogen ion concentrations by sodium hydroxide: pH=3.75 and 3.78 for solutions C and D, respectively. In these solutions $Hg_2(tpps)^{2-}$ is the main sspecies as calculated from the equilibrium constants.

Formation Constants. Formation constants of mercury(II)-tpps were determined spectrophotometrically at $pH<3$, $I=0.1$ (H^+, $NaNO_3$) in a dark room to prevent the decomposition of mercury(II) porphyrin by sun-light or room light. Total concentration of H_2tpps^{4-} was 1.00×10^{-6} mol dm^{-3}, and aggregation of the porphyrin was negligible under the present experimental conditions because of slight absorption at 489 nm ascribed to the aggregation$^{13)}$ of H_4tpps^{2-}. Absorption spectra were measured on a Hitachi 323 spectrophotometer with a thermostated water jacket. The pH values were determined by a Radiometer Ion 85 Ion Analyzer with a

Table 1. The Composition (mol dm^{-3}) of Sample Solutions

Solution	Hg^{2+}	$tpps^{6-}$	C_{tpps}/C_{Hg}
A	0.500	0	0
B	0.100	0	0
C	0.100	0.100	1.0
D	0.0500	0.0250	0.5

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 for hydrogen ion concentration ($-\log[H^+]$).

EXAFS Measurements. EXAFS spectra were measured around the Hg L_{III}-edge in transmission mode using the BL10B station at the Photon Factory of the National Laboratory for High Energy Physics.[14] White X-rays were monochromatized by an Si(311) channel-cut crystal. The apparent absorbance μx is obtained as $\ln(I_0/I)$, where I and I_0 are X-ray intensities with and without a sample, respectively. Intensities I_0 and I were simultaneously measured by ionization chambers filled with N_2(85%)+Ar(15%) and Ar gas, respectively. Sample solutions were held in a 5 mm thick Teflon cell with polyethylene windows.

Details of the data reduction of raw EXAFS spectra have been described previously.[15,16] A curve fitting procedure in the k-space for the refinements of structure parameters was applied to the Fourier filtered $k^3 \cdot \chi(k)_{\text{obsd}}$ values to minimize $U=\sum k^6(\chi(k)_{\text{obsd}}-\chi(k)_{\text{calcd}})^2$. The model function $\chi(k)_{\text{calcd}}$ was obtained according to the single-electron and single-scattering theory.[17-20] The values of the backscattering amplitude $F(\pi, k)$ were quoted from Teo and Lee tables.[21] The total scattering phase shift $\alpha(k)$ was approximated by the function $a_0+a_1k+a_2k^2+a_3/k^3$,[22] where the coefficients a_0, a_1, a_2, and a_3 were evaluated by fitting the function to the theoretical phase shift values of Teo and Lee.[21] The threshold energy E_0 is usually treated as a parameter and evaluated from structure standards. However, the bond lengths between mercury(II) ion and ligand atoms in the standard samples examined in the present study were hardly reproducible by the refinement of the E_0 value, and thus the a_0 and a_1 values were refined instead of the usual E_0 optimization. In the fitting procedures the parameters a_0, a_1, and λ (the mean free path of a photoelectron) were determined from the standard sample of the known structure and then they were used as constants in the course of the structural analysis of unknown samples, while the interatomic distance r, the Debye–Waller factor σ, and the number of scatters n were optimized as variables.

Results

Equilibrium Study for the Formation of Mercury(II) Porphyrin. The absorption spectrum of H_2tpps^{4-} measured at pH 6.06 exhibits an absorption maximum at 413 nm ($\varepsilon=4.66\times10^5$ mol^{-1} dm^3 cm^{-1}) and another absorption maximum appears at 434 nm, in the presence of various concentrations of mercury(II), as shown in Fig. 1 (a). The molar-ratio method depicted in Fig. 1 (b) clearly demonstrates the 2:1 composition of the mercury(II) porphyrin complex and the ε_{434} value for the complex was found to be 1.70×10^5 mol^{-1} dm^3 cm^{-1}. The mercury(II) porphyrin complex is quantitatively formed at pH>6 even in lower concentrations of mercury(II) (10^{-7} mol dm^{-3}).

The equilibrium constant of the mercury(II) porphyrin complex was determined at pH<3 to avoid complexities involved due to the hydrolysis of mercury(II). At pH<3 the porphyrin is in its tetraprotonated form (H_4tpps^{2-})[23] and exhibits an absorption maximum at 434 nm ($\varepsilon=4.96\times10^5$ mol^{-1} dm^3 cm^{-1}) which is also the maximum absorption wavelength of mercury(II) porphyin complex. The absorption spectra of the porphyrin thus decreased in the presence of mercury (II) and we determined the equilibrium constants from spectral changes on the basis of the known molalr

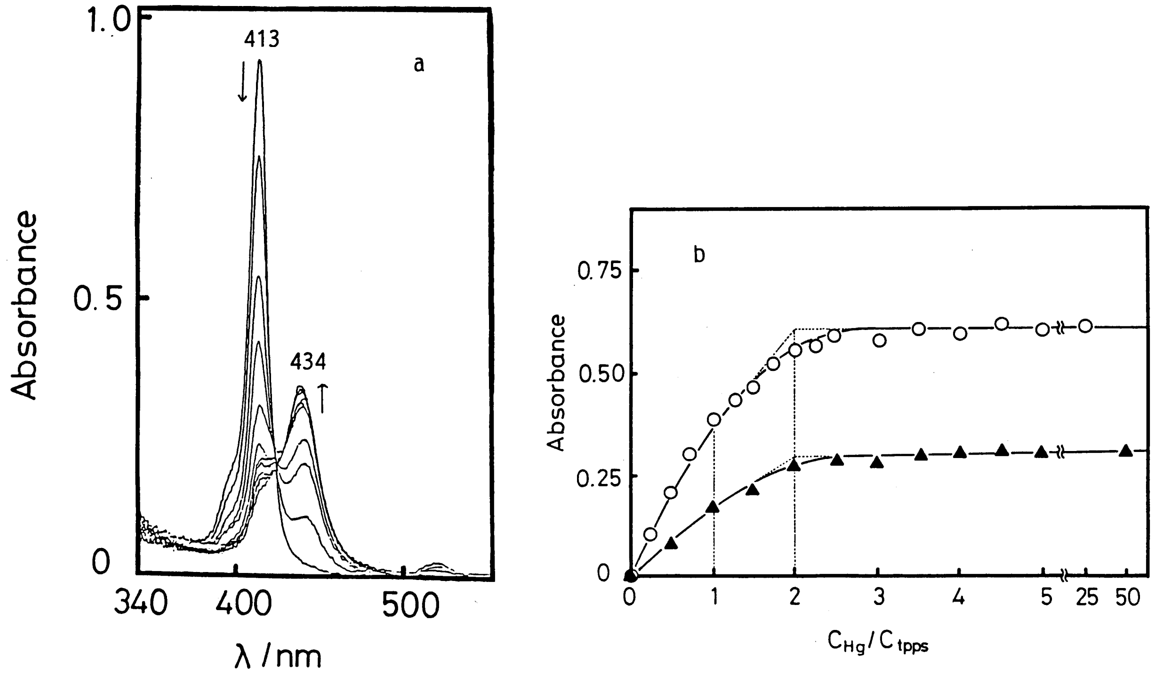

Fig. 1. Absorption spectra (a) of H_2tpps^{4-} in the presence of various concentrations of mercury(II) at pH 6.06 and $C_{tpps}=1.99\times10^{-6}$ mol dm^{-3}, and the molar-ratio method (b) at C_{tpps}/mol dm^{-3}= 1.99×10^{-6} (▲) and 3.97×10^{-6} (○).

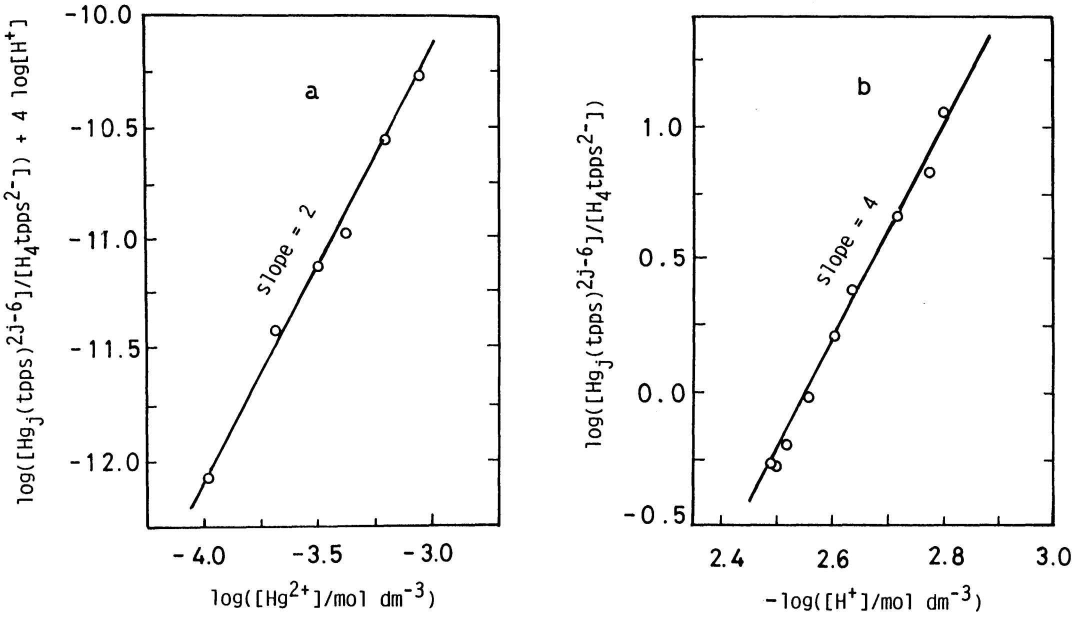

Fig. 2. Effect of concentrations of aquamercury(II) (a) and hydrogen ions (b) on the formation of $\mathrm{Hg}_j(\mathrm{tpps})^{2j-6}$ at 25 °C and I=0.1 ($\mathrm{NaNO_3}$).

absorption coefficients at 434 nm. The equilibrium for the formation of mercury(II) porphyrin is given by

$$j\mathrm{Hg}^{2+} + \mathrm{H_4tpps}^{2-} = \mathrm{Hg}_j(\mathrm{tpps})^{2j-6} + 4\mathrm{H}^+. \tag{1}$$

The equilibrium constant of Eq. 1, $K'=[\mathrm{Hg}_j(\mathrm{tpps})^{2j-6}]\times[\mathrm{H}^+]^4[\mathrm{Hg}^{2+}]^{-j}[\mathrm{H_4tpps}^{2-}]^{-1}$, leads to

$$\log\left(\frac{[\mathrm{Hg}_j(\mathrm{tpps})^{2j-6}]}{[\mathrm{H_4tpps}^{2-}]}\right) + 4\log[\mathrm{H}^+] = \log K' + j\log[\mathrm{Hg}^{2+}], \tag{2}$$

where j denotes the number of mercury(II) bound in $\mathrm{Hg}_j(\mathrm{tpps})^{2j-6}$. Absorbances at 434 nm were measured at various concentrations of mercury(II) (10^{-4}—10^{-3} mol dm^{-3}) and pH 2—3. A plot of the left-hand side of Eq. 2 vs. log [Hg^{2+}] (Fig. 2, a) gives a straight line with a slope of two. The result shows that two molecules of mercury(II) are bound to the porphyrin. Figure 2, b also supports the equilibrium 1. The data in Figs. 2, a and b lead to a value of $\log(K'/\mathrm{mol^2\,dm^{-6}})=-4.25\pm0.08$. Using the protonation constants[23] of $\mathrm{H_2tpps}^{4-}$ ($\log(K_1/\mathrm{mol^{-1}\,dm^3})=4.99$ for $K_1=[\mathrm{H_3tpps}^{3-}][\mathrm{H_2tpps}^{4-}]^{-1}[\mathrm{H}^+]^{-1}$ and $\log(K_2/\mathrm{mol^{-1}\,dm^3})=4.76$ for $K_2=[\mathrm{H_4tpps}^{2-}][\mathrm{H_3tpps}^{3-}]^{-1}[\mathrm{H}^+]^{-1}$), log K, defined by Eq. 3 for the present system, was found to be 5.51±0.08.

$$K=\frac{[\mathrm{Hg_2(tpps)}^{2-}][\mathrm{H}^+]^2}{[\mathrm{Hg}^{2+}]^2[\mathrm{H_2tpps}^{4-}]}. \tag{3}$$

EXAFS Analysis of Mercury(II) Porphyrin. Figures 3 and 4 depict the extracted EXAFS oscillations weighted by k^3 of sample solutions and their Fourier transforms (uncorrected for the phase shift), respectively. The first intense peaks appearing at 180 pm in the $|F(r)|$ curves of solutions A and B (Fig. 4) are due to the Hg–O bonds in the first coordination sphere within $\mathrm{Hg(H_2O)_6}^{2+}$.[12] Both $k^3\cdot\chi(k)$ and $|F(r)|$ curves are very

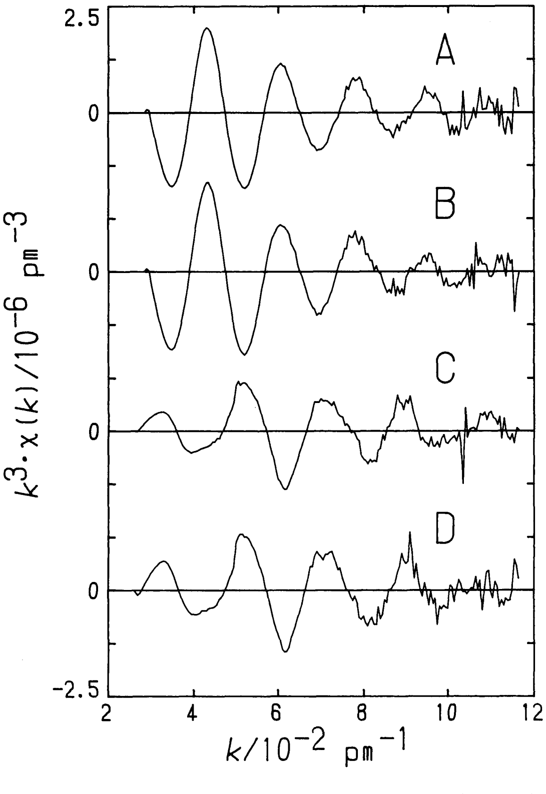

Fig. 3. The extracted EXAFS oscillations in the form of $k^3\cdot\chi(k)$ for sample solutions.

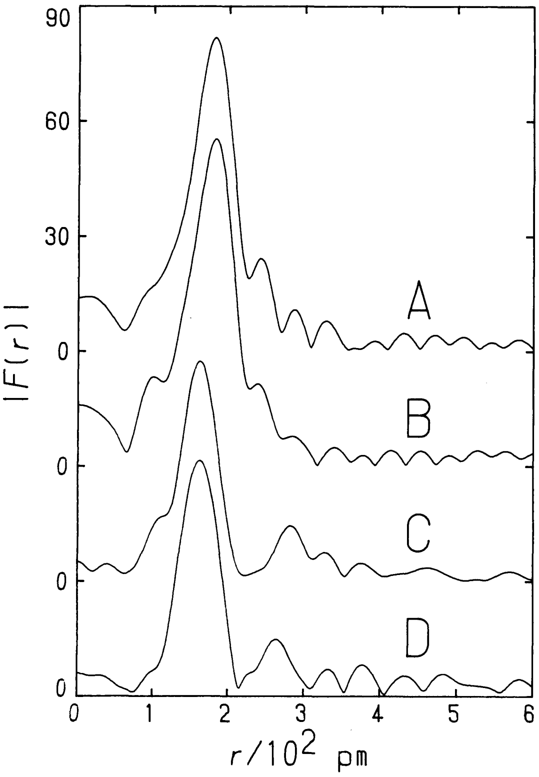

Fig. 4. The radial structure functions $|F(r)|$ for sample solutions where the phase shift is not corrected.

similar, as expected, and EXAFS spectra of reasonable quality were obtained for solutions of low concentration. The main peaks, which are due to the Hg–N (tpps) and Hg–O (H_2O) bonds, shift to significantly short r (160 pm) in the radial structure functions of solutions C and D involving mercury(II) porphyrin complexes. This may be ascribed to the short Hg–N bonds within the porphyrin complexes. Obviously, both the $k^3 \cdot \chi(k)$ and $|F(r)|$ curves of solutions C and D are virtually the same as shown in Figs. 3 and 4. The mercury(II) ions in solutions C and D are situated under very similar environments because the main chemical species is $Hg_2(tpps)^{2-}$ both in solutions C and D as clarified from the equilibrium results. Small peaks are observed around 280 pm in the $|F(r)|$ curves of solutions C and D. These peaks may consist of peaks due to the nonbonding Hg···C and Hg···Hg pairs within $Hg_2(tpps)^{2-}$. However, we were not able to separate the peak into components and no direct information on the nonbonding Hg···Hg pair was obtained in the radial structure functions, because many carbon atoms of the porphyrin around the mercury(II) were overlapped on the radial structure function of Hg···Hg.

The structure parameters of complexes in the first coordination sphere were finally determined by a curve fit in the k-space. The Fourier filtering was performed over the range $1.0 < r/10^2\ \text{pm} < 2.5$ for A and B or $1.0 < r/10^2\ \text{pm} < 2.2$ for C and D to include the main peak in the $|F(r)|$ curve (Fig. 4) and a least-squares calculation was then applied to the filtered $k^3 \cdot \chi(k)$ values over the range $4 < k/10^{-2}\ \text{pm}^{-1} < 11$ (Fig. 5). The phase function and the λ value for an Hg–O atom pair were evaluated in advance from solutions A and B containing the $Hg(H_2O)_6^{2+}$ of the known structure.[12] In the fitting procedures, the Hg–O bond length and the number of the bonds were fixed at the reported values,[12] while the

Table 2. Results of the Least-Squares Refinements for Structure Parameters of Hg^{2+}–$tpps^{6-}$ Complexes[a]

Species	Model	Interaction	r/pm	σ/pm	n	U
Hg^{2+}		Hg–O	241[b,c]	10.4(2)	6[b,c]	
$Hg_2(tpps)^{2-}$ (solution C)	I	Hg–N	215(1)	7.3(1)	2[b]	0.47
		Hg–O	257(2)	15(1)	2.9(3)	
	II	Hg–N	215(1)	9.0(1)	3[b]	0.47
		Hg–O	254(2)	19(1)	10(2)	
	III	Hg–N	216(1)	10(1)	4[b]	1.12
		Hg–O	252(2)	22(2)	11(1)	
$Hg_2(tpps)^{2-}$ (solution D)	I	Hg–N	214(1)	7.0(1)	2[b]	1.65
		Hg–O	259(2)	13(1)	2.3(4)	
	II	Hg–N	215(1)	8.7(1)	3[b]	1.15
		Hg–O	256(2)	21(2)	11(1)	
	III	Hg–N	216(1)	9.4(6)	4[b]	1.58
		Hg–O	254(2)	22(2)	15(3)	

a) The values in parentheses represent standard deviation. b) The values were kept constant during the calculations. c) Ref. 12.

parameters σ, λ, a_0, and a_1 were refined as independent variables.

The interatomic distances and Debye–Waller factors of the $Hg_2(tpps)^{2-}$ comlex were refined by adopting the λ value and the phase function evaluated above. The same λ and phase shift values for the Hg–N (tpps) and Hg–O (H_2O) bonds were used because oxygen and nitrogen atoms are practically indistinguishable by the EXAFS method. The length and Debye–Waller factor of the Hg–N and Hg–O bonds and the number of Hg–O bonds were optimized in the least-squares calculations, while the number of the Hg–N bonds were kept constant on the basis of some structure models. One can expect at once that two pyrrole nitrogens bind to each mercury(II) ion on the basis of the composition of $Hg_2(tpps)^{2-}$. However, lead(II) and cadmium(II) are coordinated with four nitrogen atoms in porphyrin ligands,[1,24] while three-coordination of pyrrole nitrogens is found for mercury(II) in crystal.[11] We then examined the two-, three-, and four-coordination models (Model I, II, and III) of pyrrole nitrogens in the least-squares calculation. The results are summarized in Table 2, and the solid curves in Fig. 5 were calculated by using the parameter values of Model I since the results of Models II and III led to the abnormally large hydration number of 10—15. The solid curves are good agreement with the experimental points.

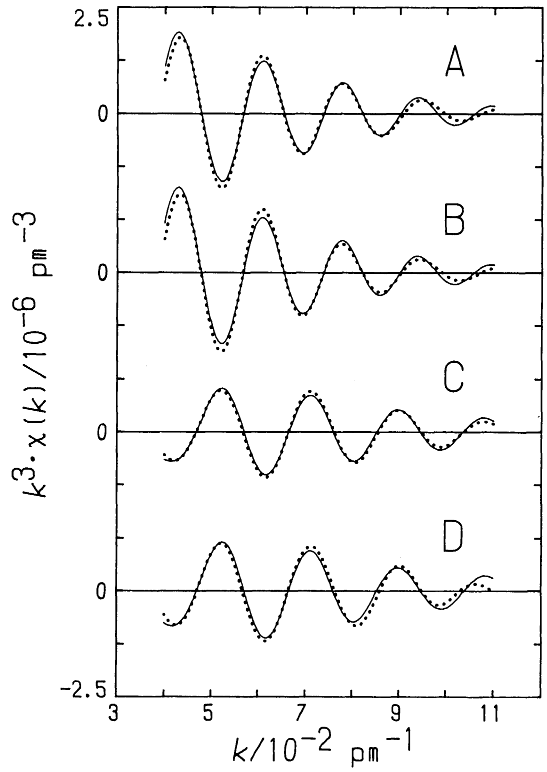

Fig. 5. The Fourier filtered $k^3 \cdot \chi(k)$ curves of the main peak shown in Fig. 4. The observed and calculated values are shown by dots and solid lines, respectively.

Discussion

Formation of $Hg_2(tpps)^{2-}$. The formation of a 1 : 1 mercury(II) porphyrin complex was not observed and a 2 : 1 complex ($Hg_2(tpps)^{2-}$) was the main chemical species at pH 2—3. Furthermore, $Hg(tpps)^{4-}$ would be formed in a very dilute solution containing mercury(II) lower than 10^{-8} mol dm^{-3}. Cadmium(II) and lead(II) form a 1 : 1 metal-porphyrin complex, i.e., $Cd(tpps)^{4-}$ and $Pb(tpps)^{4-}$. The equilibrium constant is defined by $K_M=[M(tpps)^{4-}][H^+]^2[M^{2+}]^{-1}[H_2tpps^{4-}]^{-1}$, where M=Cd and Pb, and the values are $10^{-9.97}$ and $10^{-9.94}$ mol dm^{-3} for cadmium(II) and lead(II), respectively.[23] Since the formation constant of $Hg(tpps)^{4-}$ was not determined, it is difficult to compare the formation constant of $Hg_2(tpps)^{2-}$ with those of $Cd(tpps)^{4-}$ and $Pb(tpps)^{4-}$ directly. But the relative stability of $Hg_2(tpps)^{2-}$ to $Cd(tpps)^{4-}$ and $Pb(tpps)^{4-}$ can be estimated from the value of $K[Hg^{2+}]/K_M$. The values are $10^{14.48}$ and $10^{14.45}$ for $Cd(tpps)^{4-}$ and $Pb(tpps)^{4-}$ at $[Hg^{2+}]=0.1$ mol dm^{-3}, where the EXAFS measurements were carried out. The mercury(II) porphyrin complex is 10^{14} times as stable as those of cadmium(II) and lead(II).

Krishnamurthy et al.[10] have studied the equilibrium between mercury(II) and the porphyrin at neutral pH, and reported the formation of mercury(II) porphyrin complex in ratio of 2 : 1 (mercury : porphyrin) and revised the ratio to 1 : 1 in low concentrations of porphyrins and to 3 : 2 in high concentrations of porphyrins. But, the hydrolysis of mercury(II) was not considered at neutral pH in their calculation of the equiibrium constants. An X-ray study of *N*-tosylamineoctaethylporphyrin of mercury(II) was explained in terms of binding of two molecules of mercury(II) to the porphyrin.[11] The present equilibrium studies strongly demonstrate the formation of $Hg_2(tpps)^{2-}$.

Structure of $Hg_2(tpps)^{2-}$. As seen in Table 2, the Hg–N and Hg–O bond lengths are 215(2) and 255(4) pm, respectively, regardless of the structure models examined. It is also obvious that the Hg–N bond length is much shorter than the Hg–O one within the hydrated ion and complexes. The Hg–N bond length almost corresponds to the sum of the covalent radii and the strong Hg–N bonds are formed upon the complexation. The fact may correspond to the high stability of the mercury(II) complex with N-donor ligands. The number of the Hg–N and Hg–O bonds was not definitely concluded from the change in error-square sum U probably due to rapid change in conformation. But, the coordination of two nitrogens to one mercury(II) seems to be reasonable because the other coordination models give the abnormal hydration number around mercury(II) (Table 2).

In the observed conformation of the fully protonated tetraphenylporphyrin (H_4tpp^{2+}),[25] the pyrrole rings are tilted alternatively up and down with respect to the porphyrin plane. The deviation of the pyrrole ring from coplanarity with the porphyrin skeleton is more than

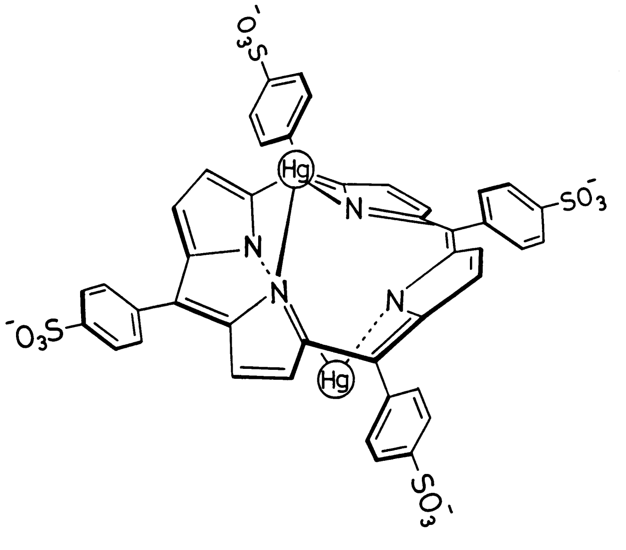

Fig. 6. A possible structure of the deformed $Hg_2(tpps)^{2-}$. Water molecules bound to mercury(II) are omitted.

33.0°. The same deviation as H_4tpp^{2+} may also apply to fully protonated H_4tpps^{2-} due to the similarity in their porphyrin skeleton. Moreover, $Hg_2(tpps)^{2-}$ shows the deformation of pyrrole rings as well as H_4tpps^{2-} because both species give the absorption maximum at 434 nm in UV spectra. Thus, the most plausible structure is that two mercury(II) ions bind to two pyrrole nitrogens from both upper and lower sides of the mean porphyrin plane and that two or three water molecules coordinate to each mercury(II) ion (see Table 2, Model I). The structure of the mercury(II) porphyrin is given in Fig. 6. The nonbonding Hg···Hg length may be ca. 310 pm based on the above deformation of porphyrin with the aid of the Hg–N bond length of 215 pm. The Hg···Hg interaction was not clearly observed in the second peak of the $|F(r)|$ curve (see Fig. 4) due to the overlapping of the Hg···C interaction on Hg···Hg interaction. In the bis[chloromercury(II)] complex of *N*-tosylamineocta-ethylporphyrin one mercury(II) is out of plane by 205 pm and the other mercury(II) is 128 pm from the porphyrin plane in opposite directions.[11]

Conclusion

The present EXAFS study, for the first time, shows the shortened bond length between mercury(II) and pyrrole nitrogens and supports the large stability constant of the mercury(II) porphyrin complex. Furthermore, the structure of mercury(II) porphyrin complex is proposed as two mercuries bound to the porphyrin with the deformed pyrrole rings in opposite directions with respect to the porphyrin plane. The deformed structure causes the catalytic effect on the incorporation of other metal ions. Recently, Barkigia et al., have reported that porphyrin skeletons are flexible and this distortion of the macromolecules can be imposed by steric interactions.[26] The structural variations provide another reaction mechanism for a wide range of chemical and physical properties of porphyrins. Thus the binding of mercury(II) to porphyrin offers a way to accelerate the rate of the metalloporphyrin formation by the deformation of the porphyrin skeleton.

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References

1) K. M. Barkigia, J. Fajer, A. D. Adler, and G. J. B. Williams, *Inorg. Chem.*, **19**, 2057 (1980).

2) M. Tabata and K. Suenaga, *Bull. Chem. Soc. Jpn.*, **64**, 469 (1991).

3) A. E. Martell and R. M. Smith, "Critical Stability Constants," Plenum Press, New York(1982), Vol. 5, p. 183.

4) M. Tabata and M. Tanaka, *J. Chem. Soc., Dalton Trans.*, **1983**, 1955.

5) M. Tabata and M. Tanaka, *Anal. Lett., Part A*, **13**, 427 (1980).

6) M. Tabata and M. Tanaka, *Mikrochim. Acta*, **1982 I**, 149.

7) M. Tabata, *Analyst*, **112**, 141 (1987).

8) M. Tabata and M. Tanaka, *Trends Anal. Chem.*, **10**, 128 (1991).

9) M. F. Hudson and K. M. Smith, *J. Chem. Soc., Chem. Commun.*, **1973**, 515; *Tetrahedron Lett.*, **1974**, 2223; *Tetrahedron*, **31**, 3077 (1975).

10) A. O. Adeyemo and M. Krishnamurthy, *Inorg. Chem.*, **16**, 3355 (1977); *Inorg. Chim. Acta*, **83**, L41 (1984).

11) H. J. Callot, B. Chevrier, and R. Weiss, *J. Am. Chem. Soc.*, **101**, 7729 (1979).

12) G. Johansson, *Acta Chem. Scand.*, **25**, 2787 (1971).

13) R. F. Pastenack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Venturo, and L. dec. Hinds, *J. Am. Chem. Soc.*, **94**, 4511 (1972).

14) M. Nomura, KEK Report 85-7, National Laboratory for High Energy Physics, Tsukuba, Japan, 1985.

15) K. Ozutsumi and T. Kawashima, *Inorg. Chim. Acta*, **180**, 231 (1991).

16) K. Ozutsumi, Y. Miyata, and T. Kawashima, *J. Inorg. Biochem.*, **44**, 97 (1991).

17) D. E. Sayers, E. A. Stern, and F. W. Lytle, *Phys. Rev. Lett.*, **27**, 1204 (1971).

18) E. A. Stern, *Phys. Rev. B*, **10**, 3027 (1974).

19) E. A. Stern, D. E. Sayers, and F. W. Lytle, *Phys. Rev. B*, **11**, 4836 (1975).

20) B. Lengeler and P. Eisenberger, *Phys. Rev. B*, **21**, 4507 (1980).

21) B.-K. Teo and P. A. Lee, *J. Am. Chem. Soc.*, **101**, 2815 (1979).

22) P. A. Lee, B.-K. Teo, and A. L. Simons, *J. Am. Chem. Soc.*, **99**, 3856 (1977).

23) M. Tabata and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1985**, 42.

24) P. F. Rodesiler, E. A. H. Griffith, N. G. Charles, and E. L. Amma, *Inorg. Chem.*, **24**, 4595 (1985).

25) E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1970).

26) K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner, and K. M. Smith, *J. Am. Chem. Soc.*, **112**, 8851 (1990).