Structure of the Short-Lived Intermediate Formed during the Metal Substitution Reaction of the Mercury(II) Porphyrin Complex with Cobalt(II) Ion in Aqueous Solution Determined by the Stopped-Flow EXAFS Method

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The local structure around the cobalt(II) ion in the reaction intermediate formed during the metal substitution reaction of the homodinuclear mercury(II) porphyrin (5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin; H2tpps2−) complex with a cobalt(II) ion in an acetate buffer has been determined by the stopped-flow EXAFS method. The structure of the reactant and the product of the above reaction has also been determined by the same method. The coordination geometry around the cobalt(II) ion in the heterodinuclear intermediate, [Hg(tpps)CoII2−], has six-coordinate octahedral with four additional water and/or acetate oxygen atoms. The CoII-N and CoII-O bond lengths in the intermediate are 212(2) and 221(1) pm, respectively. The product, [CoII(tpps)]2+, has a six-coordinate octahedral structure, the CoII-N and CoII-O bond lengths being 203(1) and 215(1) pm, respectively. The CoII-N bond length in the intermediate is ca. 9 pm longer than that in the product. The CoII-O bond length in the intermediate is also ca. 9 pm longer than that of 212(1) pm in the reactant, the cobalt(II) acetato complex, and ca. 6 pm longer than that in the product. The longer CoII-O bond in the intermediate as compared to those in the reactant and in the product appears to be responsible for the instability of the intermediate. The oxidized product, [CoIII(tpps)]2+, has a six-coordinate structure with two additional CoIII-O bonds. The CoIII-N and CoIII-O bond lengths are 189(1) and 197(2) pm, respectively, and are much shorter than those in [CoIII(tpps)]2+.

1. Introduction

The rates of formation of metalloporphyrins are several orders of magnitude slower than those of the complex formation of open-chain ligands. The rate constants for the complexation of cobalt(II), copper(II) and zinc(II) with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H2tpps2−) are 0.08, 1.60 and 1.57×10−3 mol dm−3 s−1, respectively, in water at 25 °C [1, 2], while the rate constants for the reaction of cobalt(II), copper(II), and zinc(II) with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H2tpps2−) are 0.08, 160 and 1.6 mol−1 dm3 s−1, respectively [1, 3]. The great difference in the reaction rates is presumably due to the less flexible porphyrin ring and less available lone-pair electrons on the porphyrin for incoming metal ions.

To accelerate the slow metallation, several methods have been proposed. One interesting method is the addition of large metal ions such as mercury(II), cadmium(II), and lead(II) [1]. Among these metal ions, mercury(II) exerts the largest catalytic effect. The following reaction mechanism has been proposed for medium-sized metal(II) ions [4, 5],

\[
\begin{align*}
[Hg2(tpps)]2− & \overset{k1}{\longrightarrow} \frac{k1}{k−1} [Hg(tpps)]2+ + Hg^{2+} \quad (1) \\
[Hg(tpps)]2+ + M^{2+} & \overset{k2}{\longrightarrow} \frac{k2}{k−2} [Hg(tpps)M^{II}]2− \quad (2) \\
[CoII(tpps)]2+ & \overset{k3}{\longrightarrow} M^{III} [CoII(tpps)]2+ \quad \text{(Final product)} + Hg^{2+}
\end{align*}
\]

The rate constants at 25 °C are practically independent of the nature of the incoming metal ions [4, 5], e.g., \(k1 = 1.95 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\), \(k2/k−1 = 7.14\) and \(k3 = 1.00 \times 10^2 \text{ s}^{-1}\) for copper(II) and
$k_1 = 1.02 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_2/k_{-1} = 0.14$ and $k_3 = 1.09 \times 10^{-2} \text{ s}^{-1}$ for zinc(II). For the copper(II) system the structure of the heterodinuclear intermediate [Hg(tpps)Cu]$^{2-}$ was successfully determined by use of a stopped-flow EXAFS apparatus developed by us [6-8].

With cobalt(II), the [Co$^{II}$(tpps)]$^{4-}$ complex is formed as the product but the complex is further oxidized by dissolved oxygen to [Co$^{III}$(tpps)]$^{3-}$.

$$\text{Co}^{2+} + \text{H}_2\text{tpps}^{4-} \xrightarrow{\text{very slow}} \text{Co}^{II}(\text{tpps})^{4-} + 2\text{H}^+ \quad (3)$$

The much slower rate of the metallation as compared to that of the oxidation precludes the determination of the structural parameters of the [Co$^{III}$(tpps)]$^{3-}$ complex by the usual solution X-ray and EXAFS methods. Since the presence of a small amount of mercury(II) as catalyst enhances the formation rate of the [Co$^{II}$(tpps)]$^{4-}$ complex, we can employ the stopped-flow EXAFS method to determine the structure of the intermediate, [Hg(tpps)Co$^{II}$]$^{2-}$, but also [Co$^{II}$(tpps)]$^{3-}$.

$$[\text{Hg(tpps)}]^{4-} + \text{Co}^{2+} \xrightarrow{k_2} [\text{Co}^{II}(\text{tpps})]^{4-}$$

$$\xrightarrow{\text{O}_2, \text{slow}} [\text{Co}^{III}(\text{tpps})]^{3-} \quad (4)$$

It is reasonable to assume that the short-lived heterodinuclear intermediate [Hg(tpps)Co$^{II}$]$^{2-}$ formed at mixing a solution containing the mercury(II) porphyrin complex with an aqueous solution of cobalt(II). In the presence of a small amount of mercury(II), the formation of the [Co$^{II}$(tpps)]$^{4-}$ complex reaches 100% within 300 s, and in the absence of an oxidant the cobalt(II) complex is present for at least 1500 s [9]. However, the lifetime of the complex in air is too short to determine the structure of the complex by the usual procedure. The stopped-flow EXAFS method is a useful tool for such a structural determination. The structure of the finally oxidized product, stable [Co$^{III}$(tpps)]$^{3-}$, can also be determined by using this method.

Knowledge on the structure of reaction intermediates is very important to elucidate reaction mechanisms. However, structural information of reaction intermediates in the literature is very limited in spite of a huge accumulation of kinetic and mechanistic data. In this report we describe the local structure around the cobalt(II) ion in the short-lived reaction intermediate formed during the metal substitution reaction of the homodinuclear mercury(II) porphyrin complex with cobalt(II) ion in an acetate buffer determined by the stopped-flow EXAFS method and the structure determination of the reactant, cobalt(II) acetato complex, of the product, [Co$^{II}$(tpps)]$^{4-}$, and of the finally oxidized [Co$^{III}$(tpps)]$^{3-}$ complex.

### 2. Experimental

#### 2.1. Reagents

All chemicals of reagent grade were used without further purification. For the structure determination of the cobalt(II) complex, solutions A, B, C and D listed in Table I were prepared.

An aqueous solution of cobalt(III) porphyrin was prepared by mixing cobalt(II) acetate and H$_4$ttpps which had been neutralized with a stoichiometric amount of NaOH in water, and then, by heating the resultant solution on a water bath for several hours to oxidize cobalt(II) to cobalt(III) by dissolved oxygen. The concentration of the cobalt(III) ion in the solution was 0.1 mol dm$^{-3}$.

Aqueous solutions (0.1 mol dm$^{-3}$) of cobalt(II) perchlorate and hexaamminecobalt(III) chloride were prepared as structure standards for the EXAFS analysis.

#### 2.2. EXAFS measurements

EXAFS spectra were measured around the cobalt K edge on a laboratory EXAFS spectrometer of the energy dispersive type combined with a stopped-flow apparatus [6,7]. A rotating anode X-ray generator (RU-300,
Table II. Conditions for stopped-flow EXAFS measurements.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Gate time [s]</th>
<th>Accumulation times</th>
<th>Total time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co}^{II}(\text{CH}_2\text{COO})<em>2])</em>{2-p}^+</td>
<td>30</td>
<td>100</td>
<td>3000</td>
</tr>
<tr>
<td>([\text{Hg}(\text{tpps})\text{Co}^{II}]^{2-})</td>
<td>10</td>
<td>266</td>
<td>2660</td>
</tr>
<tr>
<td>([\text{Co}^{II}(\text{tpps})]^{4-})</td>
<td>30</td>
<td>90</td>
<td>2700</td>
</tr>
<tr>
<td>([\text{Co}^{III}(\text{H}_2\text{O})_6\text{Co}^{III}]^{2+})</td>
<td>30</td>
<td>80</td>
<td>2400</td>
</tr>
<tr>
<td>([\text{Co}^{III}(\text{tpps})]^{3-})</td>
<td>30</td>
<td>111</td>
<td>3330</td>
</tr>
<tr>
<td>([\text{Co}^{III}(\text{NH}_3)_6\text{Co}^{III}]^{2+})</td>
<td>30</td>
<td>100</td>
<td>3000</td>
</tr>
</tbody>
</table>

Rigaku) was operated at the voltage of 12 kV and the current of 160 mA, and Mo target was used as an X-ray source. A stopped-flow cell was located near the X-ray generator. The windows of the cell were made of pyrolytically prepared boron nitride (thickness :150 μm). White X-rays passing through the stopped-flow cell were reflected by a flat LiF(200) crystal and were detected by a position-sensitive self-scanning photodiode array (S3904-1024Q, Hamamatsu Photonics). The apparent absorbance was obtained as \(\ln(I_0/I)\), where \(I_0\) and \(I\) are X-ray intensities transmitted through the stopped-flow cell filled with water and a sample solution, respectively.

First, aqueous solutions containing cobalt(II) perchlorate, hexaamminecobalt(III) chloride and cobalt(III)-tpps were measured by mixing the same solutions in the stopped-flow unit in order to check the reproducibility of the measurements including the mixing process. The results obtained were compared with those obtained by the usual EXAFS and solution X-ray diffraction methods.

The EXAFS pattern \(\chi(k)\) was then extracted and normalized as

\[
\chi(k) = \left\{ \mu(k) - \mu_0(k) \right\}/\mu_0(k),
\]

where \(k\) is the photoelectron wave vector and given as \(2\pi(2m(E-E_0))^{1/2}/\hbar\). The parameter \(E\) represents the energy of the incident X-rays. The threshold energy of a \(K\)-shell electron, \(E_0\), was selected as the position of the inflection point of the edge jump in each sample. Other notations are of usual meaning. The \(\chi(k)\) values weighted by \(k^3\) were converted to the radial structure function \(F(r)\) as

\[
F(r) = \sqrt{\frac{1}{2\pi}} \int_{k_{\min}}^{k_{\max}} k^3 \chi(k) W(k) \exp(-2ikr) dk,
\]

where \(W(k)\) is the window function of the Hanning type [10].

The structure parameters were optimized in the \(k\)-space by comparing the observed EXAFS spectrum with the model function \(\chi(k)_{\text{calc}}\) given by the single-electron and single-scattering theory [11 - 14] as

\[
\chi(k)_{\text{calc}} = \sum \frac{n_j}{k r_j^2} \exp(-2\sigma_j^2 k^2 - 2r_j/\lambda) \cdot F_j(\pi, k) \sin(2kr_j + \alpha_j(k)),
\]

where \(F_j(\pi, k)\) is the backscattering amplitude from each of \(n_j\) scatterers \(j\) at distance \(r_j\) from the X-ray absorbing atom. \(\sigma_j\) is the Debye-Waller factor and \(\lambda\) is the mean
free path of the photoelectron. $\alpha_j(k)$ is the total scattering phase shift experienced by the photoelectron. The values of $F_j(\pi, k)$ and $\alpha_j(k)$ in eq. (7) were quoted from the literature [15, 16]. By comparing the Fourier filtered $k^3 \chi(k)$ curve with the model function to minimize the error-square sum $\sum k^6(\chi(k)_{obs} - \chi(k)_{calc})^2$, the parameters $E_0$ and $\lambda$ were evaluated from EXAFS spectra of standard samples. The parameters were then used as constants in the course of the subsequent structure analysis of unknown samples, while the $r$, $\sigma$ and $n$ values were optimized as variables.

3. Results and Discussion

Figures 1 and 2 depict the extracted Co $K$-edge EXAFS spectra in the form of $k^3 \chi(k)$ and their Fourier transforms, respectively. The first peaks in the $|F(r)|$ curves in Fig. 2 are due to the Co-N and/or Co-O bonds in the first coordination sphere of the cobalt(II) and cobalt(III) ions. The main peaks in the $|F(r)|$ curves of the cobalt(III) complexes appear around 145 pm, while those of the cobalt(II) complexes are located at an $r$-value larger than 150 pm. This is due to the smaller size of the cobalt(III) ion than that of the cobalt(II) ion. The peak position of $[\text{Co(tpps)}]^{4-}$ is 153 pm, which is significantly smaller than the 174 pm of $[\text{Hg(tpps)}\text{Co}^{II}]^{2-}$ and the 166 pm of $[\text{Co}^{II}(\text{H}_2\text{O})_6]^{2+}$. This fact indicates that the structure of the $[\text{Co}^{II}(\text{tpps})]^{4-}$ complex is very different from those of the other cobalt(II) complexes.

The $r$, $\sigma$ and $n$ values of the metal complexes in the first coordination sphere were finally optimized by a least-squares calculation applied to the Fourier filtered $k^3 \chi(k)$ values in the $k$-space ($4.5 \times 10^{-2} < k/\text{pm}^{-1} < 9.5 \times 10^{-2}$). The inverse Fourier transformation of the $F(r)$ values was performed over the $r$ range to include the main peak in the radial structure functions in each sample. The phase-shift correction was made by using the standard samples of aqueous solutions involving the $[\text{Co}^{II}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}^{III}(\text{NH}_3)_6]^{3+}$ ions. The $\text{Co}^{II}$-$\text{O}$ and $\text{Co}^{III}$-$\text{N}$ bond lengths finally obtained were 210(1) and 194(1) pm, respectively. The $\text{Co}^{II}$-$\text{O}$ bond length agrees well with that determined by the solution X-ray diffraction [17] and the $\text{Co}^{III}$-$\text{N}$ distance with those found in crystalline $[\text{Co}^{III}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}^{III}(\text{NH}_3)_6]\text{I}_3$ [18, 19]. The structure parameters for the acetato and porphyrin complexes were optimized as independent variables except for the number of the Co-N bonds. The cobalt(II) and cobalt(III) ions are expected to fully interact with the four nitrogen atoms of the porphyrin in $[\text{Co}^{II}(\text{tpps})]^{3-}$ and $[\text{Co}^{III}(\text{tpps})]^{3-}$. Thus, the number of $\text{Co}^{II}$-$\text{N}$ and...
Table III. Structure parameters for the cobalt(II) and cobalt(III) complexes in water.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Interaction</th>
<th>$r$ [pm]</th>
<th>$\sigma$ [pm]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co$^{II}$(\text{CH}_3\text{COO})]$^{2-}$</td>
<td>Co$^{II}$-O</td>
<td>212 (1)</td>
<td>8.4 (0.1)</td>
<td>6.4 (0.1)</td>
</tr>
<tr>
<td>[Hg(tpps)Co$^{II}$]$^{2-}$</td>
<td>Co$^{II}$-N</td>
<td>212 (2)</td>
<td>1.3 (0.2)</td>
<td>2$^b$</td>
</tr>
<tr>
<td></td>
<td>Co$^{II}$-O</td>
<td>221 (2)</td>
<td>1.3 (0.2)</td>
<td>3.6 (0.3)</td>
</tr>
<tr>
<td>[Co$^{II}$(tpps)$]^4-$</td>
<td>Co$^{II}$-N</td>
<td>203 (1)</td>
<td>2.7 (0.4)</td>
<td>4$^b$</td>
</tr>
<tr>
<td></td>
<td>Co$^{II}$-O</td>
<td>215 (1)</td>
<td>2.7 (0.4)</td>
<td>2.3 (0.1)</td>
</tr>
<tr>
<td>[Co$^{II}$(\text{H}_2\text{O})]$^{2+}$</td>
<td>Co$^{II}$-O</td>
<td>210 (1)</td>
<td>6.9 (0.3)</td>
<td>6$^b$</td>
</tr>
<tr>
<td>[Co$^{II}$(tpps)$]^3-$</td>
<td>Co$^{III}$-N</td>
<td>189 (1)</td>
<td>1.0 (5.7)</td>
<td>4$^b$</td>
</tr>
<tr>
<td></td>
<td>Co$^{III}$-O</td>
<td>197 (2)</td>
<td>1.0 (5.7)</td>
<td>1.8 (0.1)</td>
</tr>
<tr>
<td>[Co$^{III}$(NH$_3$)$_6$]$^{3+}$</td>
<td>Co$^{III}$-N</td>
<td>194 (1)</td>
<td>5.6 (0.2)</td>
<td>6$^b$</td>
</tr>
</tbody>
</table>

$^a$ Standard deviations of curve fits are given in parentheses; $^b$ the values were kept constant during the calculations.

The cobalt(II) ion in an acetate buffer shows an $n$ value of practically six. According to the stability constants of the cobalt(II) acetato complexes [21], the cobalt(II) ions are expected to be present as a mixture of [Co(H$_2$O)$_6$]$^{2+}$ and [Co(CH$_3$COO)]$^+$.

However, because of the high concentration of acetate ions in the present solution, the cobalt(II) ions may form some higher cobalt(II) acetato complexes. Thus, the structure of [Co(CH$_3$COO)$_2$]$^{2-}$ is octahedral.

The number of the Co$^{II}$-O (water and/or acetate) bonds in the [Hg(tpps)Co$^{II}$]$^{2-}$ intermediate was found to be practically 4 and that of the Co$^{II}$-N bonds is 2, i.e., the cobalt(II) ion in the intermediate is situated in an octahedral environment. The Co$^{II}$-N and Co$^{II}$-O bond lengths are 212(2) and 221(2) pm, respectively. The Co$^{II}$-N bond length is slightly shorter than that within the octahedrally solvated cobalt(II) ion in nitrogen-donor solvents, e.g., 214 pm in 3-methylpyridine, 216 pm in 4-methylpyridine [22] and 217 pm in 1,3-propanediamine and in $n$-propylamine [23].

The cobalt(II) ion in the [Co$^{II}$(tpps)$]^4-$ complex exhibits coordination number 6, i.e., there exist four Co$^{II}$-N and two Co$^{II}$-O (water and/or acetate) bonds with bond lengths of 203(1) and 215(1) pm, respectively. Three structures of cobalt(II) complexes with 5,10,15,20-tetraphenylporphyrin, its derivatives and 2,3,7,8,12,13,17,18-octaethylporphyrin, i.e., four-coordinate square-planar, five-coordinate square-pyramidal and six-coordinate octahedral structures, have been known, and the cobalt(II) ions have a $d^7$ low-spin electronic configuration in all of these complexes [24–31]. The average Co$^{II}$-N bond lengths are 192–195 pm in four-coordinate cobalt(II) porphyrin complexes [24,25] and are shorter than the average Co$^{II}$-N bond lengths of 196–200 pm in five- [26–29] and six-coordinate complexes [30,31]. The Co$^{II}$-N bond length in the six-coordinate [Co$^{II}$(tpps)$]^4-$ complex in aqueous solution is 203 pm and the value lies in a reasonable range.

The Co$^{II}$-N bond length within the [Hg(tpps)Co$^{II}$]$^{2-}$ intermediate is much longer than that within the [Co$^{II}$(tpps)$]^4-$ product. The electronic configuration of the cobalt(II) ion in the [Hg(tpps)Co$^{II}$]$^{2-}$ intermediate is expected to be high-spin, while the cobalt(II) ion in the [Co$^{II}$(tpps)$]^4-$ complex is in a low-spin state. The different Co$^{II}$-N bond length mainly results from the different spin states of the...
cobalt(II) ions in the two complexes, because a low-spin cobalt(II) ion generally has a smaller ionic radius than a high-spin one [32]. The Co$^{ll}$-O (water and/or acetate) bond length in the intermediate is much longer than those in the reactant (cobalt(II) acetato complex) and the product ([Co$^{ll}$(tpps)]$^{4-}$). The longer Co$^{ll}$-O bond in the intermediate as compared to that in the reactant and in the product is probably responsible for the instability of the intermediate.

An $n$ value of nearly two was obtained for the Co$^{ll}$-O bonds within [Co$^{ll}$](tpps)$^{3-}$, and the cobalt(III) ion is coordinated with four nitrogen atoms of porphyrin and two additional oxygen atoms. Thus, the structure of the complex is six-coordinate octahedral. The Co$^{ll}$-N bond length is 189(1) pm and the Co$^{ll}$-O distance is 197(1) pm. These values are much smaller than those in the [Co$^{ll}$](tpps)$^{3-}$ complex. In the crystalline state, cobalt(III) complexes with 5,10,15,20-tetraphenylporphyrin and its derivatives have a six-coordinate octahedral structure with two pyridine, imidazole, or piperidine molecules. The average Co$^{ll}$-N bond lengths in the crystallographic data are in the range of 195 - 198 pm [33 - 36], and the values are larger than those in the octahedral [Co$^{ll}$](tpps)$^{3-}$ in aqueous solution. On the other hand, an EXAFS analysis for the octahedral cobalt(III) porphyrins in chloroform has revealed an average Co$^{ll}$-N bond length of 191 - 195 pm [25], which is to be compared with the value obtained for octahedral [Co$^{ll}$](tpps)$^{3-}$ in the present study. The hole size of the porphyrin ring depends on the planarity of the ring. A ruffled ring structure often results in a shorter metal-nitrogen bond length as compared to a planar structure [24]. Thus, the short Co$^{ll}$-N bond length in solution indicates a ruffled ring structure of porphyrins.

4. Conclusions

The structure of the cobalt complexes determined in the present study is shown in Fig. 4. The cobalt(II) ions are present as a mixture of acetato complexes in an acetate buffer. Upon mixing cobalt(II) ions with an equivalent solution containing mercury(II) and porphyrin, in which the homodinuclear mercury(II) porphyrin complex exists and each mercury(II) ion forms a three-coordinate structure by combining with an acetate ion [20], the hetero-

![Fig. 4. Scheme of the metal substitution and oxidation reactions of Co(II) ions with mercury(II) porphyrin complex. 4-Sulfonatophenyl groups are omitted.](image)
that of 215 pm in the product. The present EXAFS study directly shows the longer Co\textsuperscript{II}-O bond in the short-lived unstable intermediate as compared to both the reactant and the product. Finally, the [Co\textsuperscript{II}(tpps)]\textsuperscript{4-} complex is oxidized by dissolved oxygen to give [Co\textsuperscript{III}(tpps)]\textsuperscript{3-}. The [Co\textsuperscript{III}(tpps)]\textsuperscript{3-} complex has an octahedral structure and the Co\textsuperscript{III}-N and Co\textsuperscript{III}-O bond lengths are 189 and 197 pm, respectively.

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