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; H_2tpps^{4-}) 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, $[Hg(tpps)Co^{II}]^{2-}$, is six-coordinate octahedral with four additional water and/or acetate oxygen atoms. The Co^{II}-N and Co^{II}-O bond lengths in the intermediate are 212(2) and 221(1) pm, respectively. The product, $[Co^{II}(tpps)]^{4-}$, has a six-coordinate octahedral structure, the Co^{II}-N and Co^{II}-O bond lengths being 203(1) and 215(1) pm, respectively. The Co^{II}-N bond length in the intermediate is *ca.* 9 pm longer than that in the product. The Co^{II}-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 Co^{II}-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, $[Co^{III}(tpps)]^{3-}$, has a six-coordinate structure with two additional Co^{III}-O bonds. The Co^{III}-N and Co^{III}-O bond lengths are 189(1) and 197(2) pm, respectively, and are much shorter than those in $[Co^{II}(tpps)]^{4-}$.

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