

Structures and properties of octaethylporphinato(phenolate)iron(III) complexes with NH···O hydrogen bonds: modulation of Fe–O bond character by the hydrogen bond

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Abstract

Iron(III) porphinate complexes of phenolate that have NH···O hydrogen bonds on the coordinating oxygen, [Fe^{III}(OEP){O-2,6-(RCONH)₂C₆H₃}] (R = CF₃ (**1**), CH₃ (**3**)) and [Fe^{III}(OEP)(O-2-RCONHC₆H₄)] (R = CF₃ (**2**), CH₃ (**4**)) (OEP = 2,3,7,8,12,13,17,18-octaethyl-21*H*, 23*H*-porphinato), were synthesized and characterized as models of heme catalase. The presence of NH···O hydrogen bonds was established by their crystal structures and IR shifts of the amide NH band. The crystal structure of **1** shows an extremely elongated Fe–O bond, 1.926(3) Å, compared to 1.887(2) Å in **2** or 1.848(4) Å in [Fe^{III}(OEP)(OPh)]. The NH···O hydrogen bond decreases an electron donation from oxygen to iron, resulting in a long Fe–O bond and a positive redox potential.

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1. Introduction

Heme catalases have a high catalytic ability to disproportionate harmful hydrogen peroxide with surprisingly high acceleration [1,2]. They have a tyrosinate, which functions as an axial ligand, with double NH···O hydrogen bonds from the arginine guanidinium group [3–9].

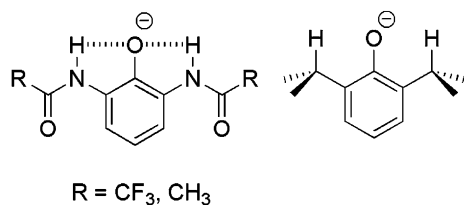
The “push–pull” concept is generally used to explain the activation of substrates in heme enzymes. The major role of axial ligands is considered to be “push”. However, we have previously established additional roles of an axial thiolate in P450 model complexes [10–12]. In these complexes, NH···S hydrogen bonds on the axial thiolate modulate the Fe–S bond character and the redox potential of iron. In the case of catalase, the roles of axial phenolate have been poorly investigated because “pull” is

considered to be predominant in catalytic activity [13]. However, the NH···O hydrogen bonds on the axial phenolate must modulate the Fe–O bond character and the redox potential of iron because of chemical similarity. Computational studies examining the axial phenolate and its hydrogen bonds have recently reported that the NH···O hydrogen bond positively shifts the oxidation potential of the axial ligand and lowers the Fe–O bond order in high-valent states, compound I and II [14,15]. In our previous report, model complexes having NH···O hydrogen bonds on the coordinating phenolate, [Fe^{III}(TPP)(O-2-CF₃CONHC₆H₄)] and [Fe^{III}(TPP){O-2,6-(CF₃CONH)₂C₆H₃}] (TPP = tetraphenylporphinato), were synthesized [11]. In that study, the positive shift of the redox potential of Fe^{III}/Fe^{II} by the NH···O hydrogen bonds to the coordinating oxygen has been established but modulation of the Fe–O bond character has not.

The present study provides an indepth discussion of the effects of NH···O hydrogen bonds, especially regard-

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Scheme 1. Phenolate ligands with hydrogen bonds and steric hindrance.

ing Fe–O bond character, by examining what role the number of hydrogen bonds plays and by making a comparison with a steric effect. Various simple 2-mono(acylamino)- and 2,6-bis(acylamino)phenolate ligands were used as models of the axial of catalase. The 2,6-di-isopropylphenolate ligand was also used as non-hydrogen bonding model with a similar bulkiness in order to approximate the steric effect of the acylamino group (Scheme 1). A series of X-ray analyses of novel model complexes with different numbers of hydrogen bonds, $[\text{Fe}^{\text{III}}(\text{OEP})\{\text{O}-2,6-(\text{CF}_3\text{CONH})_2\text{C}_6\text{H}_3\}]$, $[\text{Fe}^{\text{III}}(\text{OEP})(\text{O}-2-\text{CF}_3\text{CONHC}_6\text{H}_4)]$, $[\text{Fe}^{\text{III}}(\text{OEP})\{\text{O}-2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\}]$ and $[\text{Fe}^{\text{III}}(\text{OEP})(\text{OPh})]$ (OEP = 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphinato), have been performed. Changes in the Fe–O bond character that appear to be connected to the number of hydrogen bonds were discussed based on a comparison of the structures. Other properties associated with these complexes are also presented in this paper.

2. Experimental

2.1. Materials

All procedures were performed under Ar atmosphere by the Schlenk technique except for ligand syntheses. All organic solvents were dried over CaH_2 and distilled under Ar atmosphere before use. $[\text{Fe}^{\text{III}}(\text{OEP})_2\text{O}]$ and $[\text{Fe}^{\text{III}}(\text{OEP})(\text{OPh})]$ (**5**) were synthesized by the reported method [16]. Other reagents including 2-acetylaminophenol were purchased from Nacalai Tesque or Tokyo Chemical Industry and used without further purification.

2.2. Synthesis of axial ligands

2.2.1. 2,6-Diaminophenol dihydrochloride

2,6-Dinitrophenol (1.5 g, 8.2 mmol) was suspended in concentrated hydrochloric acid (36 ml). Then, tin powder (3.0 g) was added slowly to the mixture with stirring at room temperature. After this solution turned yellow, it was slowly cooled to 4 °C. The obtained white needles were collected and recrystallized from hot water/concentrated hydrochloric acid. Yield: 1.5 g (91%) ^1H NMR (DMSO- d_6); δ ppm 9.02 (OH, NH₃), 7.11 (*m*-H), 6.89 (*p*-H).

2.2.2. 2,6-Bis(acetylamino)phenol

To an aqueous solution (10 ml) of 2,6-diaminophenol dihydrochloride (1.8 g, 9.1 mmol), acetic anhydride (3 ml, 32 mmol) and sodium acetate trihydrate (3.5 g, 26 mmol) were added and heated. After cooling down to room temperature, there appeared white needles. Yield: 1.2 g (70%); m.p. 178–179 °C. *Anal.* Calc. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$: C, 57.68; H, 5.81; N, 13.45. Found: C, 57.64; H, 5.77; N, 13.41%. ^1H NMR (DMSO- d_6); δ ppm 9.99 (OH), 9.70 (NH), 7.40 (*m*-H), 6.82 (*p*-H), 2.18 (CH₃).

2.2.3. 2,6-Bis(trifluoroacetylamino)phenol

To a CH_2Cl_2 solution (20 ml) of 2,6-diaminophenol dihydrochloride (0.5 g, 2.5 mmol), including triethylamine (1.6 ml, 11 mmol), trifluoroacetic anhydride (0.90 ml, 5.6 mmol) was slowly added at 0 °C. After the solution was stirred for 60 min, 10 ml of water was added and then CH_2Cl_2 was removed under reduced pressure. The residue was dissolved in ethyl acetate (100 ml) and the organic layer was washed with 100 ml of water twice. After drying over anhydrous Na_2SO_4 , the solution was concentrated. The obtained residue was recrystallized from diethyl ether/*n*-hexane. Yield: 340 mg (42%); m.p. 136–138 °C. *Anal.* Calc. for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_3\text{F}_6$: C, 37.99; H, 1.91; N, 8.86. Found: C, 37.84; H, 1.83; N, 9.47%. ^1H NMR (DMSO- d_6); δ ppm 10.70 (NH), 9.81 (OH), 7.37 (*m*-H), 6.96 (*p*-H).

2.2.4. 2-Trifluoroacetylaminophenol

2-Trifluoroacetylaminophenol was synthesized from 2-aminophenol in a similar method to 2,6-bis(trifluoroacetylamino)phenol. ^1H NMR (DMSO- d_6); δ ppm 10.51 (NH), 9.93 (OH), 7.38 (3-H), 7.20 (5-H), 6.99 (6-H), 6.89 (4-H).

2.3. Synthesis of $[\text{Fe}^{\text{III}}(\text{OEP})\{\text{O}-2,6-(\text{CF}_3\text{CONH})_2\text{C}_6\text{H}_3\}]$ (**1**), $[\text{Fe}^{\text{III}}(\text{OEP})(\text{O}-2-\text{CF}_3\text{CONHC}_6\text{H}_4)]$ (**2**), $[\text{Fe}^{\text{III}}(\text{OEP})\{\text{O}-2,6-(\text{CH}_3\text{CONH})_2\text{C}_6\text{H}_3\}]$ (**3**), $[\text{Fe}^{\text{III}}(\text{OEP})(\text{O}-2-\text{CH}_3\text{CONHC}_6\text{H}_4)]$ (**4**), and $[\text{Fe}^{\text{III}}(\text{OEP})\{\text{O}-2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\}]$ (**6**)

$[\text{Fe}^{\text{III}}(\text{OEP})_2\text{O}]$ was mixed with corresponding phenol (1 equiv. for **1–4** and 5 equiv. for **6**) in CH_2Cl_2 at room temperature. After being stirred for 1 h, the solution was concentrated to dryness. **1** was recrystallized from toluene/*n*-hexane, **2** was from dichloromethane/diethyl ether, **3** and **4** were from toluene, and **6** was from toluene/acetonitrile. **1–4** were dark purple crystals and **6** was black.

2.3.1. $[\text{Fe}^{\text{III}}(\text{OEP})\{\text{O}-2,6-(\text{CF}_3\text{CONH})_2\text{C}_6\text{H}_3\}]$ (**1**)

Anal. Calc. for $\text{C}_{46}\text{H}_{49}\text{N}_6\text{O}_3\text{FeF}_6$: C, 61.13; H, 5.46; N, 9.30. Found: C, 60.18; H, 5.30; N, 9.14%. UV/Vis (CH_2Cl_2 , r.t.); λ_{max} ($\epsilon \times 10^{-4} \text{ cm}^{-1} \text{ M}^{-1}$) 625 (6.8), 527

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