



# Syntheses, three types of hydrogen-bonded assembly structures, and magnetic properties of $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{Y}\cdot\text{solvent}$ (Him = imidazole, hapen = *N,N'*-bis(2-hydroxyacetophenylidene)ethylenediamine, $\text{Y} = \text{BPh}_4^-$ , $\text{CF}_3\text{SO}_3^-$ , $\text{PF}_6^-$ , $\text{ClO}_4^-$ , and $\text{BF}_4^-$ )

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## ABSTRACT

Five iron(III) complexes of  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{Y}\cdot\text{solvent}$  with five different counter anions were synthesized, where Him = imidazole,  $\text{H}_2\text{hapen} = \text{N,N}'\text{-bis}(2\text{-hydroxyacetophenylidene})\text{ethylenediamine}$ ,  $\text{Y} = \text{BPh}_4^-$  (**1**),  $\text{CF}_3\text{SO}_3^-$  (**2**),  $\text{PF}_6^-$  (**3**),  $\text{ClO}_4^-$  (**4**), and  $\text{BF}_4^-$  (**5**), and solvent = methanol or  $\text{H}_2\text{O}$ . Each  $\text{Fe}^{\text{III}}$  ion has octahedral coordination geometry with  $\text{N}_2\text{O}_2$  donor atoms of the equatorial tetradentate ligand (hapen) and two nitrogen atoms of two imidazoles at the axial positions. The imidazole group is hydrogen-bonded to the phenoxo oxygen atom of hapen of the adjacent unit and/or to the counter anion or solvent molecule, to give three types of assembly structures involving linear dimer, cyclic dimer, and one-dimensional zigzag chain. Compound **1**, with a cyclic dimer, and **2** and **3**, with a one-dimensional chain, showed spin-equilibrium behavior between high-spin ( $S = 5/2$ ) and low-spin ( $S = 1/2$ ) states, whereas **4** and **5**, with linear dimers, are high-spin complexes. Compound **3** shows abrupt spin transition with small thermal hysteresis.

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## 1. Introduction

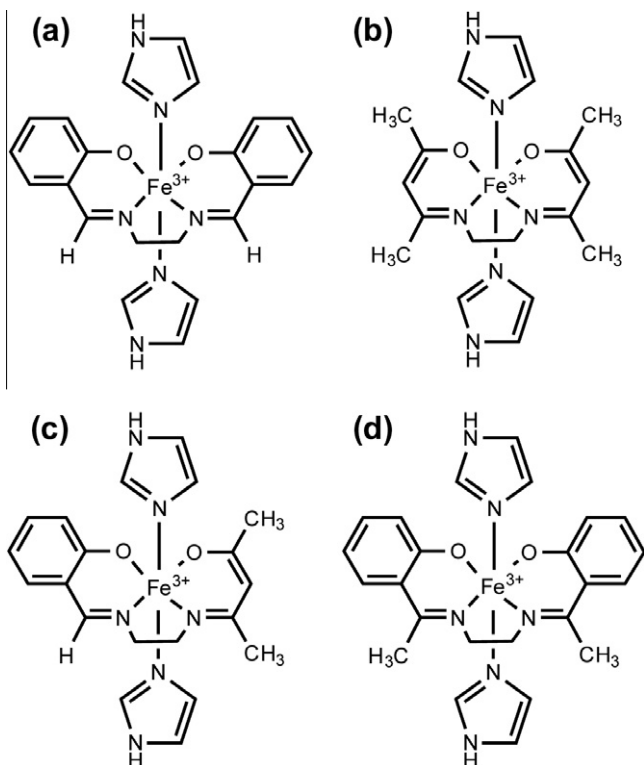
According to Tanabe–Sugano diagrams, which are based on the strong crystal-field theory of octahedral  $3d^n$  metal complexes [1], the electronic ground-state changes between low-spin (LS) and high-spin (HS) states at spin crossover (SCO) points in  $3d^n$  ( $4 \leq n \leq 7$ ) metal complexes. It is known experimentally that the SCO phenomenon, interconversion between HS and LS states, is induced by external perturbations, such as temperature, pressure, pH, and light irradiation [2]. Among the SCO complexes reported so far,  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  complexes have been the most intensively studied [2,3]. It has also been recognized for a long time that the Fe sites in some heme proteins exhibit SCO behavior [4], which plays a key role in their biological functions. From the viewpoint of developing model compound of heme proteins, a number of iron porphyrins have been synthesized and studied [5]. In 1975, in order to obtain a simple SCO model compound, Nishida synthesized a family of  $\text{Fe}^{\text{III}}$  complexes with  $\text{N}_2\text{O}_2$  Schiff-base ligands and two axial monodentate ligands, and showed that the spin states can be tuned primarily by the total ligand field strength provided by

the equatorial and axial ligands [6]. For example (see Scheme 1),  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{salen})]\text{BPh}_4$  and  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{acacen})]\text{BPh}_4$  are HS and LS complexes, respectively, where the axial ligand was fixed as imidazole (Him), and  $\text{H}_2\text{salen}$ ,  $\text{H}_2\text{acacen}$ , and  $\text{BPh}_4^-$  denote *N,N'*-bis(salicylidene)ethylenediamine, *N,N'*-bis(acetylacetonylidene) ethylenediamine, and tetraphenylborate, respectively [6]. Within the  $[\text{Fe}^{\text{III}}(\text{Him})_2\text{L}]\text{BPh}_4$  ( $\text{L} = \text{N}_2\text{O}_2$  Schiff-base ligand) framework, salen provides a weak enough ligand field to give HS states and acacen provides a strong enough ligand field to give LS states. Later, Murray in 1987 and Real in 1998 synthesized SCO iron(III) complexes with analogous symmetrical Schiff-base ligands [7]. Matsumoto in 1984 synthesized  $[\text{Fe}(\text{Him})_2(\text{salacen})]\text{BPh}_4$  using the unsymmetrical ligand salacen ( $\text{H}_2\text{salacen} = \text{N-salicylidene-}N'\text{-acetylacetonylidene})\text{ethylenediamine}$ ) in order to provide an intermediate ligand field strength between those provided by salen and acacen, and confirmed the spin-equilibrium properties of the complex [8]. Nishida and Matsumoto also pointed out that suitable ligand field strength of the equatorial ligand  $\text{H}_2\text{L}$  can be supplied by symmetrical Schiff-base ligands such as *N,N'*-bis(benzoylacetonylidene)ethylenediamine ( $\text{H}_2\text{bzacen}$ ) and *N,N'*-bis(2-hydroxyacetophenylidene)ethylenediamine ( $\text{H}_2\text{hapen}$ ), respectively [6b,8b].

In this study, using a symmetrical ligand, i.e.,  $\text{H}_2\text{hapen}$ , five iron(III) complexes  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{Y}\cdot\text{solvent}$  with five different

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**Scheme 1.** Structures of  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{salen})]^+$  (a),  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{acacen})]^+$  (b),  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{salacen})]^+$  (c), and  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]^+$  (d).

counter anions were synthesized, where  $Y = \text{BPh}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ , and  $\text{BF}_4^-$ , and solvent = crystal solvent (see Scheme 1). As the equatorial ligand  $\text{H}_2\text{hapen}$  and the axial ligand imidazole are fixed for the five complexes, and provide a ligand field strength around the SCO point, the complex-cation of  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]^+$  with various anions may give SCO complexes. Hence, these complexes are suitable for investigating the details of the effects of the counter anion and crystal solvent on the SCO properties. These complexes gave a variety of assembly structures, constructed by hydrogen-bonding, depending on the counter anion, and some complexes showed SCO and others did not; we report their syntheses, structures, and magnetic properties.

## 2. Experimental

Caution! Perchlorate salts of metal complexes are potentially explosive. Only small quantities of material should be prepared and the samples should be handled with care.

### 2.1. General

All reagents and solvents used in this study are commercially available from Tokyo Kasei Co., Ltd., Tokyo, Japan and Wako Pure Chemical Industries, Ltd., Osaka, Japan, and were used without further purification. All of the synthetic procedures were performed in air.

### 2.2. Preparation of materials

#### 2.2.1. Preparations of tetradentate ligand $\text{H}_2\text{hapen}$ and precursor iron(III) complex $[\text{Fe}^{\text{III}}\text{Cl}(\text{hapen})]\cdot 0.5\text{CH}_3\text{OH}$

The tetradentate ligand,  $N,N'$ -bis(2-hydroxyacetophenylidene)ethylenediamine, was prepared according to the literature [9]. To a solution of 2-hydroxyacetophenone (0.1 mol, 13.63 g) in

50 mL of methanol was added a solution of ethylenediamine (0.05 mol, 3.01 g) in 50 mL of methanol, and the mixture was stirred for 1 h on a hot-plate. The resulting yellow crystalline material was collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 14.78 g (99%). Calc. for  $\text{H}_2\text{hapen}$  ( $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$ ): C, 72.95; H, 6.80; N, 9.45. Found: C, 72.93; H, 6.82; N, 9.32%. Mp = 193–196 °C. The precursor iron(III) complex  $[\text{Fe}^{\text{III}}\text{Cl}(\text{hapen})]\cdot 0.5\text{CH}_3\text{OH}$  was prepared according to the literature method [8b].

#### 2.2.2. Preparation of iron(III) complex $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]Y\cdot\text{solvent}$ ( $Y = \text{BPh}_4^-$ (1), $\text{CF}_3\text{SO}_3^-$ (2), $\text{PF}_6^-$ (3), $\text{ClO}_4^-$ (4), and $\text{BF}_4^-$ (5), and solvent = methanol or $\text{H}_2\text{O}$ )

2.2.2.1.  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{BPh}_4\cdot 2\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$  (1). To a suspension of  $[\text{Fe}^{\text{III}}\text{Cl}(\text{hapen})]\cdot 0.5\text{CH}_3\text{OH}$  (1 mmol, 0.40 g) in 30 mL of methanol was added an excess of imidazole (10 mmol, 0.68 g), and the mixture was stirred for 10 min on a hot-plate and then filtered. To the filtrate was added a solution of  $\text{NaBPh}_4$  (1 mmol, 0.34 g) in 5 mL of methanol. The resulting solution was allowed to stand for several hours, during which time dark-purple plate-like crystals precipitated, and they were collected by suction filtration and dried in air. Yield: 0.56 g (63%). Calc. for  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{BPh}_4\cdot 2\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$  ( $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_2\text{Fe}\cdot\text{BPh}_4\cdot 2\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$ ): C, 67.65; H, 6.36; N, 9.47. Found: C, 67.59; H, 6.08; N, 9.90%.

2.2.2.2.  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{CF}_3\text{SO}_3\cdot 1.5\text{H}_2\text{O}$  (2). Compound 2 was prepared using a similar method as that used to prepare 1, using  $\text{NaCF}_3\text{SO}_3$  instead of  $\text{NaBPh}_4$ . Yield: 0.40 g (60%). Calc. for  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{CF}_3\text{SO}_3\cdot 1.5\text{H}_2\text{O}$  ( $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_2\text{Fe}\cdot\text{CF}_3\text{SO}_3\cdot 1.5\text{H}_2\text{O}$ ): C, 45.33; H, 4.41; N, 12.69. Found: C, 45.07; H, 4.39; N, 12.94%.

2.2.2.3.  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{PF}_6\cdot 2\text{H}_2\text{O}$  (3). Compound 3 was prepared using a similar method as that used to prepare 1, using  $\text{NaPF}_6$  instead of  $\text{NaBPh}_4$ . Yield: 0.44 g (66%). Calc. for  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{PF}_6\cdot 2\text{H}_2\text{O}$  ( $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_2\text{Fe}\cdot\text{PF}_6\cdot 2\text{H}_2\text{O}$ ): C, 43.19; H, 4.53; N, 12.59. Found: C, 43.13; H, 4.50; N, 13.05%.

2.2.2.4.  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{ClO}_4\cdot 0.5\text{CH}_3\text{OH}$  (4). Compound 4 was prepared using a similar method as that used to prepare 1, using  $\text{NaClO}_4$  instead of  $\text{NaBPh}_4$ . Yield: 0.35 g (58%). Calc. for  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{ClO}_4\cdot 0.5\text{CH}_3\text{OH}$  ( $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_2\text{Fe}\cdot\text{ClO}_4\cdot 0.5\text{CH}_3\text{OH}$ ): C, 48.90; H, 4.69; N, 13.96. Found: C, 48.98; H, 4.65; N, 14.32%.

2.2.2.5.  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{BF}_4\cdot 0.5\text{Him}\cdot\text{H}_2\text{O}$  (5). Compound 5 was prepared using a similar method as that used to prepare 1, using  $\text{NaBF}_4$  instead of  $\text{NaBPh}_4$ . Yield: 0.38 g (60%). Calc. for  $[\text{Fe}^{\text{III}}(\text{Him})_2(\text{hapen})]\text{BF}_4\cdot 0.5\text{Him}\cdot\text{H}_2\text{O}$  ( $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_2\text{Fe}\cdot\text{BF}_4\cdot 0.5\text{Him}\cdot\text{H}_2\text{O}$ ): C, 48.99; H, 4.84; N, 15.68. Found: C, 48.91; H, 4.80; N, 15.34%.

### 2.3. Physical measurements

Elemental analyses (C, H, and N) were carried out by Miss. Kikue Nishiyama at the Center for Instrumental Analysis of Kumamoto University. Melting points were measured by METTLER FP90 Central Processor. Magnetic susceptibilities were measured by a Quantum Design MPMS-XL5 magnetometer in the temperature range of 5–300 K at the  $2\text{ K min}^{-1}$  under an applied magnetic field of 0.5 T. The calibration was performed with palladium metal. Corrections for diamagnetism were applied using Pascal's constants [10].

### 2.4. Crystallographic data collection and structure analyses

X-ray diffraction data were collected using a Rigaku RAXIS RAPID imaging plate diffractometer using graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The temperature of the crystal was maintained at the selected value by means of a Rigaku cooling

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