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Syntheses, hydrogen-bonded assembly structures, and spin crossover properties of $[Fe^{III}(Him)_2(n\text{-}MeOhapen)]PF_6$ (Him = imidazole and n-MeOhapen = *N,N′*-bis(n-methoxy-2-oxyacetophenylidene) ethylenediamine); *n* = 4, 5, 6)

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ABSTRACT

Three iron(III) complexes, $[Fe^{III}(Him)_2(n\text{-}MeOhapen)]PF_6$ (**1**: *n* = 4, **2**: *n* = 5, **3**: *n* = 6), where Him = imidazole and n-MeOhapen = *N,N′*-bis(n-methoxy-2-oxyacetophenylidene)ethylenediamine, were synthesized. Each Fe^{III} ion was coordinated by N_4O_2 donor atoms of equatorial n-MeOhapen and two axial Him. The saturated FeC_2N_2 chelate ring involving the ethylenediamine moiety adopted a gauche conformation and the two phenylidene planes of $[Fe^{III}(Him)_2(n\text{-}MeOhapen)]^+$ were oriented opposite to the FeO_2N_2 coordination plane. Two adjacent $[Fe^{III}(Him)_2(4\text{-}MeOhapen)]^+$ cations in **1** were connected via PF_6^- ions by hydrogen bonds between the imidazole group and PF_6^- to give a one-dimensional chain. Two adjacent cations in **2** were connected via hydrogen bonds between the phenylidene oxygen and imidazole atoms to form a cyclic dimer structure. Two EtOH molecules were involved in a hydrogen-bonded cyclic dimer structure in **3**. Compounds **1** and **2** showed spin crossover behavior, but **3** showed incomplete spin crossover.

1. Introduction

Spin crossover (SCO) is a representative phenomenon of bistability in the electronic structure of metal complexes. SCO complexes show inter-conversion between the high-spin (HS) and low-spin (LS) states upon external physical perturbations such as temperature, pressure, and light irradiation [1]. Steepness, multi-step, and hysteresis in SCO profiles can be induced by intermolecular cooperative effects [1].

Among metal complexes that exhibit SCO, SCO Fe^{III} complexes with a d^5 electronic configuration generally exhibit a gradual spin equilibrium [2] and show no thermal hysteresis with the exception of a few complexes [3]. On the other hand, some SCO Fe^{II} complexes with a d^6 electronic configuration show steep spin transitions that exhibit thermal hysteresis [1]. Fe^{II} and Fe^{III} complexes with a tetradentate planar ligand and two monodentate axial ligands exhibit SCO [2–5], and the SCO complexes with bidentate or tridentate ligands are major groups in SCO studies [1,6]. The Fe^{II} or Fe^{III} sites in some heme proteins exhibit SCO properties [7], and iron porphyrin derivatives have been studied as model compounds [8]. As synthetic, yet simple model compounds, Nishida first reported a family of Fe^{III} complexes with N_2O_2 salen-type ligands at the equatorial plane and two monodentate ligands (monodentate ligands such as pyridine and imidazole derivatives) at the axial sites $[Fe^{III}(X)_2(salen\text{-}type)]BPh_4$ [9] and demonstrated that the ligand field of $[Fe^{III}(X)_2(salen\text{-}type)]^+$ is close to the SCO point and that some of them exhibit SCO. Subsequently, Matsumoto [10], Murray [11], and Real [12] reported SCO Fe^{III} complexes with analogous N_2O_2 Schiff-base ligands and revealed the relevant factors to determine the SCO properties. Especially, Murray [11] pointed out that the conformation of the two phenylidene planes of $[Fe^{III}(X)_2(salen\text{-}type)]^+$ with a one side opened salen-type ligand is related to “whether or not SCO occurs”. The favored conformation is not always achieved for $[Fe^{III}(X)_2(salen\text{-}type)]^+$, and even if SCO was observed, steep SCO with hysteresis was not merely observed.

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In previous papers, we revealed that "hapen-type" ligands in $[Fe^{III}(X)_2(hapen\text{-}type)]^+$ (Scheme 1) can give the suitable conformation due to the steric hindrance between the methyl group on the phenylidene moiety and five-membered chelate ring [10d]. Furthermore, an imidazole group as the axial ligand X in $[Fe^{III}(X)_2(hapen\text{-}type)]^+$ can form intermolecular hydrogen-bonds to generate an assembly structure that may lead to cooperative effects and modify the SCO profile. One of these complexes, $[Fe^{III}(Him)_2(hapen)]AsF_6$, showed steep SCO with thermal hysteresis [4]. Some of SCO properties, such as steep, multi-step spin transitions, hysteresis, and light-induced excited spin-state trapping (LIESST), depend on the intermolecular hydrogen-bonds among the SCO molecules [13]. In this study, three Fe^{III} complexes $[Fe^{III}(Him)_2(n\text{-}MeOhapen)]PF_6$ (**1**: $n = 4$, **2**: $n = 5$, **3**: $n = 6$) with three isomers of the new "hapen-type" ligand (n-MeOhapen) were synthesized. In addition to the favorable conformation of the "hapen-type" ligand and intermolecular hydrogen bond by imidazole group, the methoxy group may modify the intermolecular interactions. From the above described three points; (1) the molecular conformation of the two phenylidene planes (2) intermolecular interactions by hydrogen bonds by with the imidazole moiety, and (3) modification of the assembly structure by the methoxy group, we have synthesized three Fe^{III} complexes $[Fe^{III}(Him)_2(n\text{-}MeOhapen)]PF_6$ (**1**: $n = 4$, **2**: $n = 5$, **3**: $n = 6$)(Scheme 1), and reported here the syntheses, structures, and SCO properties.

2. Experimental

2.1. General

All reagents and solvents used in the syntheses 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 H_2(n-MeOhapen) solvents and precursor iron(III) complex $[Fe^{III}Cl(n\text{-}MeOhapen)]$ solvents

2.2.1.1. H_2(4-MeOhapen). To a solution of 4-methoxy-2-hydroxyacetophenone (0.05 mol, 8.31 g) in 50 mL of ethanol, a solution of ethylenediamine (0.025 mol, 1.51 g) in 50 mL of ethanol was added, and the mixture was stirred for 30 min on a hot plate at 60 °C. The resulting yellow crystalline material was collected by suction filtration, washed with a small amount of ethanol, and dried in vacuo. Yield: 7.30 g (82%). *Anal.* Calc. for H_2(4-MeOhapen) ($C_{20}H_{24}N_2O_4$): C, 67.40; H, 6.79; N, 7.86. mp = 254 °C. Found: C, 67.09; H, 6.85; N, 7.86%. IR: $\nu_{C{=}N}$ 1583 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.38–7.36 (1H, d), 6.36 (1H, d), 6.31–6.28 (1H, q), 3.92 (2H, s), 3.79 (3H, s), 2.34 (3H, s). Here, s, d, t, and q indicate singlet, doublet, triplet, and quartet, respectively.

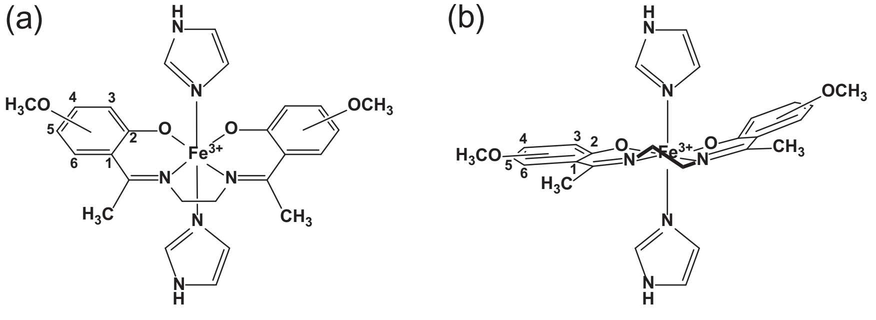
2.2.1.2. H_2(5-MeOhapen). The tetradentate Schiff-base ligand H_2(5-MeOhapen) was prepared by a similar method to that used in the preparation of H_2(4-MeOhapen), using 5-methoxy-2-hydroxyacetophenone instead of 4-methoxy-2-hydroxyacetophenone. A yellow crystalline material was obtained as the product. Yield: 6.22 g (87%). *Anal.* Calc. for H_2(5-MeOhapen) ($C_{20}H_{24}N_2O_4$): C, 67.40; H, 6.79; N, 7.86. Found: C, 67.19; H, 6.81; N, 7.77%. mp = 251 °C. IR: $\nu_{C{=}N}$ 1614 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.04 (1H, d), 6.93–6.90 (1H, q), 6.87–6.84 (1H, d) 3.97 (2H, s), 3.77 (3H, s), 2.35 (3H, s).

2.2.1.3. H_2(6-MeOhapen)·0.25EtOH. The tetradentate Schiff-base ligand H_2(6-MeOhapen)·0.25EtOH was prepared by a similar method to that used in the preparation of H_2(4-MeOhapen), using 6-methoxy-2-hydroxyacetophenone instead of 4-methoxy-2-hydroxyacetophenone. A yellow crystalline material was obtained. Yield: 6.16 g (67%). *Anal.* Calc. for H_2(6-MeOhapen)·0.25EtOH ($C_{20}H_{24}N_2O_4 \cdot 0.25EtOH$): C, 66.91; H, 6.99; N, 7.61. Found: C, 66.67; H, 6.91; N, 7.72%. mp = 197 °C. IR: $\nu_{C{=}N}$ 1600 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.17–7.13 (1H, t), 6.54–6.52 (1H, q), 6.28–6.26 (1H, q), 3.91 (2H, s), 3.81 (3H, s), 2.47 (3H, s).

*2.2.1.4. [FeCl(4-MeOhapen)]·H_2O **1**′.* The precursor iron(III) complex $[Fe^{III}Cl(4\text{-}MeOhapen)] \cdot H_2O$ was prepared according to the method applied for $[Fe^{III}Cl(salen)]$. To a solution of H_2(4-MeOhapen) (0.01 mol, 3.56 g) in 150 mL of methanol, anhydrous $Fe^{III}Cl_3$ (0.01 mol, 1.62 g) was added, and the mixture was stirred for 30 min on hot-plate at 65 °C. To the hot solution, a solution of triethylamine (0.02 mol, 2.02 g) in 10 mL of methanol was added dropwise. The resulting black crystals were collected by suction filtration, washed with a small amount of diethylether, and dried in vacuo. Yield: 4.18 g (93%). *Anal.* Calc. for [FeCl(4-MeOhapen)]·H_2O ($C_{20}H_{24}N_2O_4FeCl \cdot H_2O$): C, 51.80; H, 5.22; N, 6.04. Found: C, 51.97; H, 4.96; N, 6.03%. IR: $\nu_{C{=}N}$ 1599 cm^{-1}.

*2.2.1.5. [FeCl(5-MeOhapen)]·0.5MeOH **2**′.* Precursor complex **2**′ was obtained as a black crystalline material by a similar method to that used in the preparation of **1**′, using H_2(5-MeOhapen) instead of H_2(4-MeOhapen). The product was obtained as black crystals. Yield: 3.84 g (86%). Found: C, 53.13; H, 5.08; N, 6.24%. Calcd. for [FeCl(5-MeOhapen)]·0.5MeOH ($C_{20}H_{24}N_2O_4FeCl \cdot 0.5MeOH$): C, 53.33; H, 5.24; N, 6.07%. IR: $\nu_{C{=}N}$ 1614 cm^{-1}.

*2.2.1.6. [FeCl(6-MeOhapen)]·0.25EtOH **3**′.* The precursor complex **3**′ was obtained as a black crystalline material by a similar method to that used in the preparation of **1**′, using H_2(6-MeOhapen) and ethanol instead of H_2(4-MeOhapen) and methanol. The product



Scheme 1. (a) $[Fe^{III}(Him)_2(n\text{-}MeOhapen)]^+$ (**1**: $n = 4$, **2**: $n = 5$, **3**: $n = 6$). (b) Favorable conformation of two phenylidene planes for SCO.