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Synthesis, structure, and spin equilibrium properties of $[Fe^{III}X_2L]BPh_4{\cdot}solvents$ (X = 1-methylimidazole and imidazole; L = *N*, *N*′-bis(3-ethoxycarbonylsalicylidene)ethylenediamine)

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ABSTRACT

Two iron(III) complexes $[Fe^{III}X_2L]BPh_4{\cdot}solvents$ (X = 1-Meim (**1**), Him (**2**)) were synthesized and the crystal structures were determined, where H_2L = *N*, *N*′-bis(3-ethoxycarbonylsalicylidene)ethylenediamine, 1-Meim = 1-methylimidazole, Him = imidazole, BPh_4^- = tetraphenylborate. Fe^{III} ion has an octahedral coordination environment by N_2O_2 donor atoms of equatorial L^{2-} and N_2 donor atoms of axial imidazoles. Complex **1** is described as isolated molecule, while complex **2** has a hydrogen-bonded cyclic dimer structure constructed by hydrogen-bond between imidazole group and ethoxycarbonyl oxygen via ethanol. Complex **1** is in a high-spin (S = 5/2) state over the whole temperature region 5–300 K, while complex **2** showed a gradual complete spin equilibrium between high and low-spin states at $T_{1/2}$ = 192 K.

1. Introduction

Spin-crossover (SCO) is a phenomenon that high-spin (HS) and low-spin (LS) states of metal complexes with d^4–d^7 electronic configurations are inter-convertible by temperature, pressure, and light irradiation [1]. SCO properties observed in the solid state, such as steepness, multi-step, and hysteresis, depend on the cooperative effect associated with intermolecular interaction among the SCO sites. From the view point of thermal hysteresis, one of the most successful SCO complexes is Fe^{II} complex $[Fe^{II}(Him)_2(L^W)]$ (see Scheme 1(c)) and Him = imidazole) reported by Weber et al. which showed a 70 K wide thermal hysteresis around room temperature [2]. The SCO Fe^{II} complex has a 2D network structure constructed by two kinds of hydrogen bonds of (1) intermolecular H bond between the first imidazole and coordinated oxygen atom and (2) intermolecular H-bond between the second imidazole and ethoxycarbonyl group. Although SCO Fe^{III} complex generally exhibits gradual spin equilibrium without thermal hysteresis [3] except for a few complexes [4], SCO property with hysteresis may be realized in Fe^{III} complex when a similar ligand of Weber's complex was properly selected.

From the view point, we have selected a planar ligand L (see Scheme 1(d)) consisting of (1) salen-type N_2O_2 coordination sites and (2) 3-ethoxycarbonyl group at the benzene ring. In this study, two iron(III) complexes $[Fe^{III}(1\text{-}Meim)_2L]BPh_4{\cdot}0.5H_2O$ (**1**) and $[Fe^{III}(Him)_2L]BPh_4{\cdot}EtOH$ (**2**), were synthesized by the use of two axial ligands of 1-methylimidazole (1-Meim) and imidazole (Him). We report here the synthesis, structure, and magnetic properties.

2. Experimental

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.

2.2. Preparation of materials

2.2.1. Preparation of (3-formyl-4-hydroxy)benzoic acid

(3-Formyl-4-hydroxy)benzoic acid was prepared according to the literature [5]. Pale yellow powder material. Yield: 36%. ^1H NMR (CD_3OD) δ/ppm: 10.11 (1H, s, *H*–C═O), 8.40 (1H, d, Ar–*H*), 8.15 (1H, dd, Ar–*H*), 7.02 (1H, d, Ar–*H*).

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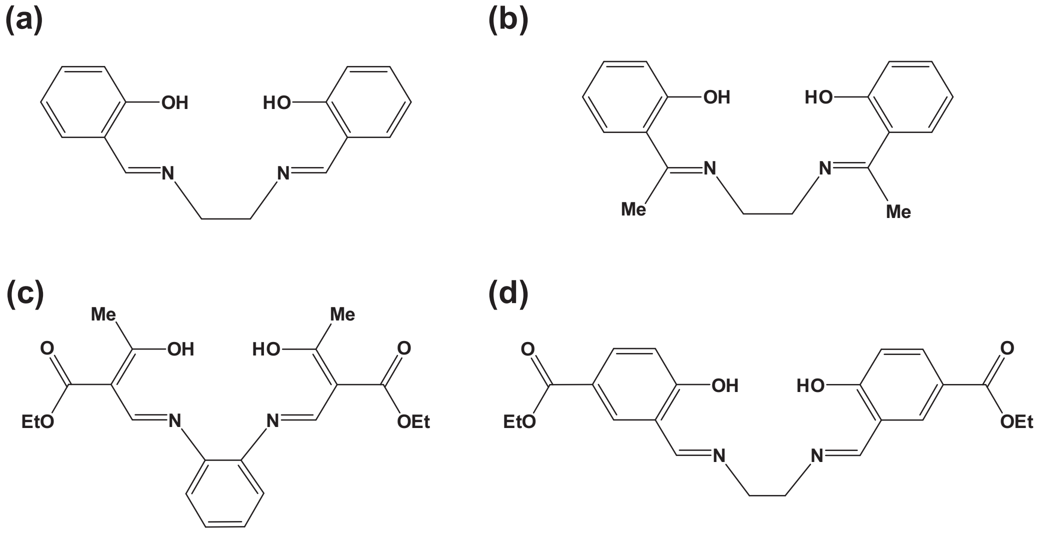

Scheme 1. Structures of N_2O_2 Schiff-base ligands (a) H_2salen, (b) H_2hapen, (c) Weber's ligand H_2L^W, and (d) H_2L.

2.2.2. Preparation of (3-formyl-4-hydroxy)ethyl benzoate

(3-Formyl-4-hydroxy)ethyl benzoate was prepared according to the literature [6]. White powder material. Yield: 71%. ^{1}H NMR (CD_3OD) δ/ppm: 11.41 (1H, s, Ar–O*H*), 9.96 (1H, s, *H*–C=O), 8.32 (1H, d, Ar–*H*), 8.19 (1H, dd, Ar–*H*), 7.03 (1H, d, Ar–*H*), 4.40 (2H, t, CH_2) , 1.39 (3H, q, CH_3).

2.2.3. Preparation of N, N′-bis(3-ethoxycarbonylsalicylidene)ethylenediamine abbreviated as H_2L

A solution of (3-formyl-4-hydroxy)ethyl benzoate (3.881 g, 20 mmol) in 60 mL of ethanol and a solution of ethylenediamine (0.601 g, 10 mmol) in 10 mL of ethanol were mixed and the mixture was stirred at 60 °C for 1 h and then cooled to room temperature. The resulting yellow crystalline material was collected by suction filtration, washed with a small amount of ethanol, and dried in vacuo. Yield: 3.810 g (92%). *Anal.* Calc. for $H_2L = C_{22}H_{24}N_2O_6$: C, 63.67; H, 5.86; N, 6.67. Found: C, 64.07; H, 5.87; N, 6.79%.

2.2.4. Preparation of precursor iron(III) complex $[Fe^{III}ClL]\cdot 1.5CH_3CN\cdot 4H_2O$

To a solution of H_2L (2.062 g, 5 mmol) in 100 mL of methanol was added an iron(III) chloride anhydrate (0.811 g, 5 mmol), and the mixture was stirred at 60 °C for 30 min and then cooled to room temperature. The black crystalline material precipitated was collected by suction filtration, washed with a small amount of diethyl ether, and dried in vacuo. Recrystallized was performed from acetonitrile. Yield: 1.651 g (66%). *Anal.* Calc. for $[Fe^{III}ClL]\cdot 1.5CH_3CN\cdot 4H_2O$ ($C_{22}H_{22}N_2O_6FeCl\cdot 1.5CH_3CN\cdot 4H_2O$): C, 47.26; H, 5.43; N, 7.72. Found: C, 47.03; H, 5.04; N, 7.86%. Thermogravimetric analysis (TGA) of the dried sample. 21.3% weight loss corresponding to $1.5CH_3CN + 4H_2O$ (the calculated value is 21.0%) was observed in the heating mode from 23 to 140 °C.

2.2.5. Preparation of iron(III) complex $[Fe^{III}(1\text{-Meim})_2L]BPh_4\cdot 0.5H_2O$ (**1**)

To a suspension of $[Fe^{III}ClL]\cdot 1.5CH_3CN\cdot 4H_2O$ (0.25 mmol, 0.159 g) in 10 mL of ethanol was added 1-methylimidazole (2.5 mmol, 0.205 g), and the mixture was stirred for 30 min on a hot-plate at 65 °C and then filtered. To the filtrate was added a solution of sodium tetraphenylborate (0.25 mmol, 0.086 g) in 3 mL of methanol. The resulting solution was allowed to stand for several hours. Black plate crystals precipitated were collected by suction filtration and dried in air. Yield: 0.188 g (78%). *Anal.* Calc. for $[Fe^{III}(1\text{-Meim})_2L]BPh_4\cdot 0.5H_2O$ ($C_{54}H_{54}BFeN_6O_6\cdot 0.5H_2O$): C, 67.65; H, 5.78; N, 8.77. Found: C, 67.64; H, 5.79; N, 8.77%. TGA: 0.9% weight loss corresponding to $0.5H_2O$ (0.94%) was observed in the heating mode from 23 to 140 °C.

2.2.6. Preparation of iron(III) complex $[Fe^{III}(Him)_2L]BPh_4\cdot EtOH$ (**2**)

Complex **2** was prepared using a similar method of **1**, using imidazole instead of 1-methylimidazole. Black plate crystals. Yield: 0.223 g (91%). *Anal.* Calc. for $[Fe^{III}(Him)_2L]BPh_4\cdot EtOH$ ($C_{52}H_{50}BFeN_6O_6\cdot EtOH$): C, 67.02; H, 5.83; N, 8.68. Found: C, 66.40; H, 5.88; N, 8.60%. TGA: 4.8% weight loss corresponding to one EtOH (4.75%) was observed in the heating mode from 23 to 140 °C.

2.3. Physical measurements

Elemental analyses (C, H, and N) were carried out at the Center for Instrumental Analysis of Kumamoto University. ^{1}H NMR spectra were recorded on a JEOL ECX 500 FT-NMR spectrometer in $(CD_3)_2CO$ at 500 MHz. Thermogravimetric analyses (TGA) were performed on a TG/DTA6200 (Seiko Instrument Inc.). The samples of ca. 5 mg were heated from room temperature to 140 °C at the heating rate of 10 °C min^{-1}, kept the temperature at 140 °C for 180 min, and then cooled to room temperature. Magnetic susceptibilities were measured by a Quantum Design MPMS-XL5 magnetometer in the temperature range of 5–300 K at the 2 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 [7].

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 Mo Kα radiation ($\lambda = 0.71073$ Å). The temperature of the crystal was maintained at the selected value by means of a Rigaku cooling device within an accuracy of ±2 K. The X-ray diffraction data at 296 K was collected, and then the diffraction data at 100 K was collected. The structures were solved by a direct method, and expanded using the Fourier technique. Hydrogen atoms were fixed at the calculated positions and refined using a