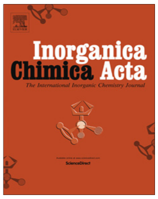
Inorganica Chimica Acta 439 (2016) 49–54

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Synthesis, hydrogen-bonded 1D structure, and abrupt spin transition between high-spin (HS) and an ordered [HS–HS–HS–LS] of a mononuclear iron(III) complex [$Fe^{III}(Him)_2$(4-MeOhapen)]CF_3SO_3 (Him = imidazole, 4-MeOhapen = *N*,*N*′-bis-(2-oxy-4-methoxyacetophenylidene)ethylenediamine)

Kyohei Miyano [a], Takahiro Nishida [a], Hiromasa Ono [a], Daisuke Hamada [a], Takeshi Fujinami [a], Naohide Matsumoto [a,*], Yukinari Sunatsuki [b]

[a] *Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan*
[b] *Department of Chemistry, Faculty of Science, Okayama University, Tsushima-naka 1-1, Okayama 700-8530, Japan*

ARTICLE INFO

Article history:
Received 19 June 2015
Received in revised form 3 September 2015
Accepted 24 September 2015
Available online 9 October 2015

Keywords:
Iron(III)
Spin crossover
Imidazole
N_2O_2 Schiff-base ligand
Hydrogen bonds
1D structure

ABSTRACT

A SCO iron(III) complex [$Fe^{III}(Him)_2$(4MeOhapen)]CF_3SO_3 was synthesized, where Him = imidazole and 4-MeOhapen = *N*,*N*′-bis(2-oxy-4-methoxyacetophenylidene)ethylenediamine. Fe^{III} ion has an octahedral coordination geometry with N_2O_2 donor atoms of the equatorial tetradentate ligand (4-MeOhapen) and two nitrogen atoms of two imidazoles (Him) at the axial positions. The adjacent cations are bridged by $CF_3SO_3^-$ ion through NH···O hydrogen bonds between Him and $CF_3SO_3^-$ to give a one-dimensional chain structure $\{[Fe^{III}(Him)_2(4MeO\text{-}hapen)]CF_3SO_3\}_{1\infty}$. The magnetic susceptibility measurements showed that complex exhibits an abrupt spin transition between a single HS phase and a symmetry-breaking [HS–HS–HS–LS] phase and another transition around 80 K. The single-crystal X-ray analyses at 296 and 150 K revealed the structures at a single HS and [HS–HS–HS–LS] states.

1. Introduction

Spin crossover (SCO) phenomenon is an inter-conversion between high-spin (HS) and low-spin (LS) states by external perturbations, such as temperature, pressure, and light irradiation [1]. Among the SCO complexes reported so far, Fe^{II} and Fe^{III} complexes have been the most intensively studied [1]. It is well known that Fe sites in some heme proteins exhibit SCO behavior [2] and as their model compounds iron porphyrin and macrocyclic complexes have been extensively studied [3]. As a simple model compound for some heme proteins, Nishida in 1975 first synthesized a family of Fe^{III} complexes [$Fe^{III}B_2L$]BPh_4 with salen-type N_2O_2 ligand L and two axial monodentate ligand B, and counter anion BPh_4^- (BPh_4^- = tetraphenylborate) [4]. Later, Matsumoto, Murray, and Real synthesized SCO Fe^{III} complexes [$Fe^{III}B'_2L'$]Y with analogous Schiff-base ligands L′, monodentate ligand B′, and various counter anion Y′ [5–7]. These studies demonstrated that (1) A favorable conformation of the planar ligand L’ can induce SCO property and especially “hapen-type” ligand gives a favorable conformation which makes a large torsion of O–Fe–O angle during the spin transition from HS to LS state due to the steric repulsion between en (ethylenediamine moiety) and methyl group of *o*-hydroxyacetophenone moieties (hapen = *N*,*N*′-bis(2-oxyacetophenylidene)-ethylenediamine) [8]. (2) Intermolecular hydrogen bond via axial imidazole group gives a positive effect to induce abrupt spin transition [9]. (3) The steric requirements from methoxy group of hapen ligand and counter anion modify the assembly structure to influence the SCO property [8,9].

A family of the complexes [$Fe^{III}(Him)_2$(hapen)]Y would give interesting SCO properties with hysteresis and multi-step. In this study, we synthesized a Fe^{III} complex [$Fe^{III}(Him)_2$(4-MeOhapen)] CF_3SO_3, where 4-MeOhapen denotes *N*,*N*′-bis(2-oxy-4-methoxyacetophenylidene)ethylenediamine). The complex has a hydrogen-bonded 1D structure bridged by $CF_3SO_3^-$ anion, and shows a spin transition between HS and ordered [HS–HS–HS–LS] phases. Such symmetry breaking-phase transition attract much attention [10]. We report here the synthesis, SCO property, and crystal structures at HS and [HS–HS–HS–LS] states (Scheme 1).

---

* Corresponding author. Tel./fax: +81 96 342 3390.
E-mail address: naohide@aster.sci.kumamoto-u.ac.jp (N. Matsumoto).

http://dx.doi.org/10.1016/j.ica.2015.09.031
0020-1693/© 2015 Elsevier B.V. All rights reserved.

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. All of the synthetic procedures were performed in air.

2.2. Preparation of materials

2.2.1. Preparations of H_2(4-MeOhapen) and precursor iron(III) complex [Fe^{III}Cl(4-MeOhapen)]·H_2O

The ligand, *N,N′*-bis(4-methoxy-2-hydroxyacetophenylidene) ethylenediamine, abbreviated as H_2(4-MeOhapen), was prepared according to the general synthetic procedure of salen-type Schiff-base ligand [8]. To a solution of 4-methoxy-2-hydroxyacetophenone (0.1 mol, 16.62 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 30 min on a hot-plate and cooled to room temperature. Yellow crystals precipitated were collected by suction filtration, washed with a small amount of methanol and diethyl ether, and dried in vacuo. Precursor iron(III) complex [Fe^{III}Cl(4-MeOhapen)]·H_2O was prepared by the reaction of H_2(4-MeOhapen) (17.8 g, 0.05 mol), $FeCl_3$ (8.1 g, 0.05 mol), and trimethylamine (10.1 g, 0.1 mmol) with 1:1:2 in methanol according to the method applied for [Fe^{III}Clsalen] [5b]. Black precipitates were collected by suction filtration and washed with diethyl ether. Yield: 20.3 g (92%).

2.2.2. Preparation of iron(III) complex [$Fe^{III}(Him)_2$(4-MeOhapen)] CF_3SO_3

To a suspension of [Fe^{III}Cl(4-MeOhapen)]·H_2O (1 mmol, 0.44 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 $NaCF_3SO_3$ (1 mmol, 0.17 g) in 5 mL of methanol. The resulting solution was allowed to stand for a few days, during which time black plate-like crystals precipitated, and they were collected by suction filtration, washed with small amount of diethyl ether, and dried in air. Black plate crystals were obtained. Yield: 0.172 g (25%). *Anal.* Calc. for [$Fe^{III}(Him)_2$(4-MeOhapen)]CF_3SO_3 ($C_{26}H_{30}N_6O_4FeCF_3SO_3$): C, 46.63; H, 4.35; N, 12.08. Found: C, 46.83; H, 4.34; N, 12.09%.

2.3. Physical measurements

Elemental analyses (C, H, and N) were carried out at the Center for Instrumental Analysis of Kumamoto University. Thermogravimetric analysis (TGA) was measured on a TG/DTA6200 (Seiko Instrument Inc.). The sample of ca. 2 mg was heated from room temperature to 120 °C in the heating mode at 2 °C min^{-1}, kept at 120 °C for 60 min and then cooled from 120 °C 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 [11].

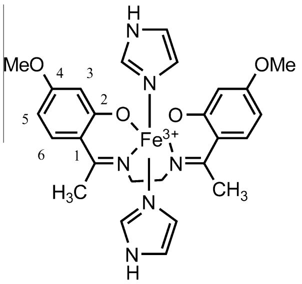
2.4. Crystallographic data collection and structure analyses

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 were collected at 296, and 150 K. After the data collection at 296 K, the crystal was cooled from 296 to 200 K with the cooling rate of 3 K min^{-1}, and then the crystal was cooled slowly from 200 to 150 K at the rate of 0.1 K min^{-1}. The crystal was kept at 150 K for one day, and the data collection was started. The X-ray diffraction data collected after quick cooling showed a poor quality to determine the crystal structure. The data were corrected for Lorentz, polarization and absorption effects. 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 riding model. All calculations were performed using the CrystalStructure crystallographic software package [12].

3. Results and discussion

3.1. Synthesis and characterization of iron(III) complex [$Fe^{III}(Him)_2$ (4-MeOhapen)]CF_3SO_3

The Fe^{III} complex [$Fe^{III}(Him)_2$(4-MeOhapen)]CF_3SO_3 was prepared according to the synthetic procedure applied for the synthesis of [$Fe^{III}(Him)_2$(4-MeOhapen)]PF_6 [8b]. The precursor Fe^{III} complex [Fe^{III}Cl(4-MeOhapen)]·H_2O was obtained by mixing the ligand H_2(4-MeOhapen), iron(III) chloride anhydrate, and triethylamine in a 1:1:2 M ratio in methanol. The Fe^{III} complex [$Fe^{III}(Him)_2$ (4-MeOhapen)]CF_3SO_3 was obtained as well grown black plate-like crystals by mixing [Fe^{III}Cl(4-MeOhapen)]·H_2O, imidazole, and $NaCF_3SO_3$ in a 1:10:1 M ratio in methanol. The C, H, and N elemental analyses agreed with the formula [$Fe^{III}(Him)_2$ (4-MeOhapen)]CF_3SO_3. The thermogravimetric analysis (TGA) detected no crystal solvent. Thermochromic behaviors in the solution and solid states are shown in Fig. 1. The ethanol solution of the compound showed a visible thermochromism from orange red at room temperature to dark green–blue at liquid nitrogen temperature. Red and green–blue colors are typical colors for HS and LS states with this type of Fe^{III} complexes, respectively. In the solid state, brown color of the ground sample at room temperature changed to a black brown at liquid-nitrogen temperature, suggesting an incomplete SCO in the solid state.



Scheme 1. Structure of [$Fe^{III}(Him)_2$(4-MeOhapen)]$^+$.

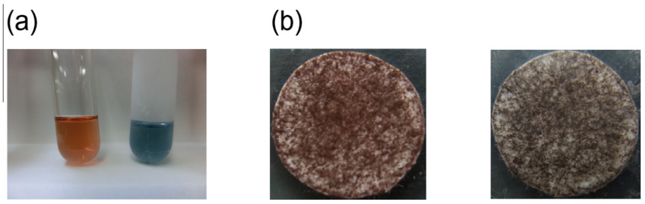


Fig. 1. (a) Thermochromism of [$Fe^{III}(Him)_2$(4-MeOhapen)]CF_3SO_3 at room (left) and liquid nitrogen (right) temperatures in the diluted ethanol solutions. (b) Thermochromism of the ground sample at room (left) and liquid nitrogen (right) temperatures in the solid state.