

One-step and two-step spin crossover binuclear iron(III) complexes bridged by 4,4'-bipyridine

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ABSTRACT

Two binuclear iron(III) complexes, $[L^1Fe^{III}(bpy)Fe^{III}L^1](BPh_4)_2$ (**1**) and $[L^2Fe^{III}(bpy)Fe^{III}L^2](BPh_4)_2$ (**2**), were synthesized and characterized, where H_2L^1 and H_2L^2 denote bis(salicylicdeneaminopropyl)methylamine and bis(3-methoxysalicylideneaminopropyl)methylamine, respectively, and bpy denotes 4,4'-bipyridine and BPh_4^- denotes tetraphenylborate. Complexes **1** and **2** consist of one and two crystallographically unique Fe sites, respectively, while they have a similar binuclear complex-cation $[L^nFe^{III}(bpy)Fe^{III}L^n]^{2+}$ ($n = 1, 2$) bridged by 4,4'-bipyridine and two tetraphenylborate ions as the counter anions. The magnetic susceptibility measurements of **1** and **2** showed one-step and two-step spin crossover (SCO), respectively. The four saturated six-membered chelate rings at the aminopropyl moieties of **1** exhibit disorder throughout one-step SCO. The two chelate rings of one Fe site of **2** exhibit disorder but the other two of another Fe site do not. The different SCO behaviors of **1** and **2** were ascribed to one and two crystallographically unique Fe sites and the order/disorder at the saturated six-membered chelate rings of aminopropyl moieties.

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1. Introduction

Spin crossover (SCO) is a representative phenomenon of molecular bistability in which the high-spin (HS) and low-spin (LS) states of the molecule are inter-convertible by external physical perturbations such as temperature, pressure, magnetic field, light, ultra-short lasers, soft and hard X-ray radiation, and nuclear decay [1–4]. SCO behavior is essentially the phenomenon of a single molecule, and adjustment of the ligand field to the spin crossover point for octahedral d^4 – d^7 metal complexes can give rise to a SCO molecule [1]. However, practically useful SCO properties such as steep, multi-step and hysteresis can be obtained by the cooperative effect. Intermolecular interactions by covalent and coordination bonds, π – π stacking, and hydrogen bonds are interactions that constitute cooperative effect [5–13]. On the other hand, the SCO parameters can be reproduced by the theoretical model calculation due to elastic interaction, suggesting that the contents of cooperative effect are not so clear [1]. A number of SCO complexes exhibiting the cooperative effect have been designed and synthesized.

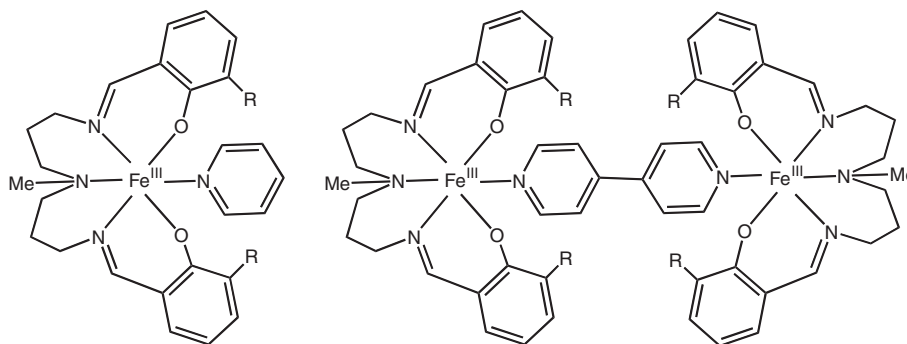
Binuclear SCO Fe^{II} complexes formed by bridging ligands have attracted attention because a binuclear SCO complex is not rele-

vant just the simplest compound among the cooperative materials but it can also combine two properties such as magnetic coupling and SCO within the same molecule. In binuclear SCO complexes, three different spin-pair states: [LS–LS], [LS–HS], and [HS–HS], are possible. Some complexes exhibit a two-step SCO phenomenon: [LS–LS] \leftrightarrow [LS–HS] \leftrightarrow [HS–HS] [14–23]. Kaizaki and co-workers reported that the [LS–HS] species of their double pyrazolate-bridged two-step SCO Fe^{II} complex is a mixture of the [LS–LS] and [HS–HS] complexes [21]. Brooker and co-workers confirmed for the first time the existence of the mixed-spin state [LS–HS] from X-ray crystallographic data of the double 1,2,4-triazole-bridged complex $[Fe_2(PMAT)_2](BF_4)_2 \cdot DMF$ (PMAT = 2,3-bis(methylene-amino-methylenepyridine)-1-aminotriazole) [22]. Amore et al. structurally characterized the three spin states: [LS–LS], [LS–HS], and [HS–HS], for the first time [19], in which the complex $[Fe_2(ddpp)_2(NCS)_2] \cdot 4CH_2Cl_2$ (ddpp = 2,5-di(2',2''-dipyridylamino)pyridine) contains two crystallographically distinct Fe^{II} centers with slightly different coordination geometries and the spin transitions do not associate with the structural phase transition.

While the binuclear SCO Fe^{II} complexes have attracted much attention, less attention has been paid to binuclear SCO Fe^{III} complexes, mainly because they exhibit rarely interesting SCO such as steep SCO, hysteresis, and LIESST (Light Induced Excited Spin State Trapping). Since 1985, Matsumoto and co-workers have

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Scheme 1. Schematic drawings of $[\text{Fe}^{\text{III}}\text{pyL}^n]^+$ and $[\text{L}^n\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^n]^{2+}$; R = H for L^1 and R = OMe for L^2 .

synthesized mononuclear and binuclear SCO Fe^{III} complexes with the pentadentate Schiff-base ligands, $[\text{Fe}^{\text{III}}\text{XL}^n]\text{BPh}_4$ and $[\text{L}^n\text{Fe}^{\text{III}}(\text{brg})\text{Fe}^{\text{III}}\text{L}^n](\text{BPh}_4)_2$ (see Scheme 1), and they investigated how the spin state could be tuned for a series of Fe^{III} complexes with a d^5 electronic configuration in a pseudo O_h ligand field [24–30].

In this study, we were able to successfully prepare one-step and two-step SCO Fe^{III} complexes bridged by 4,4'-bipyridine, $[\text{L}^1\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^1](\text{BPh}_4)_2$ (**1**) and $[\text{L}^2\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^2](\text{BPh}_4)_2$ (**2**) (see Scheme 1), where H_2L^1 denotes bis(salicylideneaminopropyl)methylamine, H_2L^2 denotes bis(3-methoxysalicylideneaminopropyl)methylamine, and BPh_4^- denotes tetraphenylborate. In order to reveal the differences in the SCO properties in these two complexes, single crystal X-ray analyses at the HS, LS, and intermediate states were carried out. We report the syntheses, magnetic properties, and the X-ray structural analyses of the two binuclear Fe^{III} complexes and the influence of the disorder at the saturated six-membered chelate ring on the SCO properties.

2. Experimental

2.1. General

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

2.1.1. Preparation of $[\text{Fe}^{\text{III}}\text{CIL}^n]$ ($n = 1, 2$)

The precursor complex $[\text{Fe}^{\text{III}}\text{CIL}^1]$ was prepared according to the method previously reported [24].

The precursor complex of $[\text{Fe}^{\text{III}}\text{CIL}^2] \cdot 0.5\text{H}_2\text{O}$ was prepared in a similar way of $[\text{Fe}^{\text{III}}\text{CIL}^1]$, using H_2L^2 instead of H_2L^1 . A solution of 3-methoxysalicylaldehyde (*o*-vanillin) (1.51 g, 10 mmol) in 50 mL of methanol was added to a solution of *N,N*-bis(3-aminopropyl)methylamine (0.732 g, 5 mmol) in 20 mL of methanol. The mixture was warmed at 50 °C under stirring for 15 min and then cooled to room temperature. The ligand solution was used for the synthesis of the Fe^{III} complex, as the Schiff-base ligand can be obtained quantitatively as oily material. The yellow ligand solution of bis(3-methoxysalicylideneaminopropyl)methylamine (abbreviated as H_2L^2) thus prepared was used for the synthesis of the Fe^{III} complex without further purification. A solution of $\text{Fe}^{\text{III}}\text{Cl}_3$ (0.812 g, 5 mmol) in 10 mL of methanol at room temperature was added to the ligand solution (5 mmol). A solution of triethylamine (1.020 g, 10 mmol) in 10 mL of methanol was then added to the mixture. The resulting solution was stirred at 50 °C for 15 min, during which time black crystals precipitated. The precipitate was filtered by suction and washed with methanol and diethyl ether.

Anal. Calc. for $[\text{Fe}^{\text{III}}\text{CIL}^2] \cdot 0.5\text{H}_2\text{O} = \text{C}_{23}\text{H}_{29}\text{O}_4\text{N}_3\text{FeCl} \cdot 0.5\text{H}_2\text{O}$: C, 53.97; H, 5.90; N, 8.21. Found: C, 53.73; H, 5.87; N, 8.30%. IR(KBr): $\nu_{\text{C}=\text{N}}(\text{imine})$ 1615 cm^{-1} .

2.1.2. Preparation of $[\text{L}^n\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^n](\text{BPh}_4)_2$ ($n = 1, 2$)

The binuclear complex $[\text{L}^1\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^1](\text{BPh}_4)_2$ (**1**) was prepared according to the method previously reported [25]. *Anal.* Calc. for $[\text{L}^1\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^1](\text{BPh}_4)_2 = \text{C}_{100}\text{H}_{98}\text{O}_4\text{N}_8\text{Fe}_2\text{B}_2$: C, 74.64; H, 6.14; N, 6.96. Found: C, 74.41; H, 6.12; N, 7.02%. IR(KBr): $\nu_{\text{C}=\text{N}}(\text{imine})$ 1611 cm^{-1} , $\nu_{\text{B}-\text{C}}(\text{BPh}_4^-)$ 733, 707 cm^{-1} .

The complex $[\text{L}^2\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^2](\text{BPh}_4)_2$ (**2**) was prepared in a similar way of **1**, using $[\text{Fe}^{\text{III}}\text{CIL}^2] \cdot 0.5\text{H}_2\text{O}$, instead of $[\text{Fe}^{\text{III}}\text{CIL}^1]$. A solution of 4,4'-bipyridine (0.039 g, 0.25 mmol) in 20 mL of methanol at room temperature was added to the suspension of $[\text{Fe}^{\text{III}}\text{CIL}^2] \cdot 0.5\text{H}_2\text{O}$ (0.255 g, 0.5 mmol) in 50 mL of methanol. The mixture was stirred for 10 min at 50 °C and filtered. A solution of NaBPh_4 (0.171 g, 0.5 mmol) in 10 mL of methanol was then added to the filtrate. The resulting solution was stirred at room temperature for 5 min and then filtered. The filtrate was left to stand overnight, during which time black crystals were obtained. They were collected by suction filtration and dried. *Anal.* Calc. for $[\text{L}^2\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^2](\text{BPh}_4)_2 = \text{C}_{104}\text{H}_{106}\text{O}_8\text{N}_8\text{Fe}_2\text{B}_2$: C, 72.23; H, 6.18; N, 6.48. Found: C, 71.91; H, 6.41; N, 6.52%. IR(KBr): $\nu_{\text{C}=\text{N}}(\text{imine})$ 1611 cm^{-1} , $\nu_{\text{B}-\text{C}}(\text{BPh}_4^-)$ 732, 705 cm^{-1} .

2.2. Physical measurements

Elemental C, H, and N analyses were carried out by Miss Kikue Nishiyama at the Center for Instrumental Analysis of Kumamoto University. Infrared spectra were recorded on a Nicolet Avatar 370 DTGS (Thermo Electron Corporation) spectrometer using KBr disks at ambient temperature. Magnetic susceptibilities were measured by a Quantum Design MPMS XL5 SQUID magnetometer in the temperature range of 5–350 K for **1** and at 5–300 K for **2** at 1 K min^{-1} under an applied magnetic field of 0.5 T. Palladium metal was used for the calibration. Corrections for diamagnetism were made using Pascal's constants [31]. Mössbauer spectra were recorded using a Wissel 1200 spectrometer and a proportional counter. The radioactive source was provided by $^{57}\text{Co}(\text{Rh})$, moving in a constant acceleration mode. Hyperfine parameters were obtained by a least-squares fitting of the Lorentzian peaks. Isomer shifts were reported relative to iron foil at 293 K. The sample temperature was controlled by means of a Heli-tran liquid transfer refrigerator (Air Products and Chemicals, Inc.) to an accuracy of ± 1 K.

2.3. Crystallographic data collection and structure analyses

The X-ray diffraction data were collected by 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

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