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Infinite Chain Structure and Steep Spin Crossover of a Fe^{III} Complex with a N_3O_2 Pentadentate Schiff-Base Ligand and 4-Aminopyridine

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A spin crossover (SC) Fe^{III} complex, $[Fe^{III}(4\text{-}NH_2py)L]BPh_4$, was synthesized and characterized, where 4-NH_2py = 4-aminopyridine, H_2L = pentadentate N_3O_2 Schiff-base ligand of the 2:1 condensation product of 3-methoxysalicylaldehyde and bis(3-aminopropyl)methylamine, and BPh_4^- = tetraphenylborate. Cryomagnetic susceptibility measurements revealed a steep spin transition between Fe^{III} low-spin ($S = 1/2$) and high-spin ($S = 5/2$) states at $T_{1/2} = 120$ K, but showed no hysteresis. Crystal-structural analyses were performed at 293 and 90 K in order to investigate the origin of the steep spin crossover, and to determine the structures of the high-spin and low-spin states. The crystal structure consisted of a one-dimensional chain constructed by hydrogen bonds between the amino group of 4-NH_2py of a molecule and the methoxy group of the adjacent molecule.

The spin crossover (SC) between the low-spin (LS) and high-spin (HS) states is observed in some octahedral $3d^n$ ($4 \le n \le 7$) metal complexes, and is induced by an external perturbation, such as temperature, pressure, or light irradiation.[1] While the SC behavior is essentially a phenomenon of a single molecule, the interaction between SC sites is an important factor to govern the SC properties, such as the steepness of the spin transition, hysteresis, and LIESST (Light-Induced Excited Spin State Trapping) effect, which are important properties for such applications as information storage, molecular switches, and visual displays.[2] From this viewpoint, the synthesis of SC compounds exhibiting interactions between spin-transition sites is of current interest. Along this line, polymeric SC compounds with the bridging ligand and mononuclear SC compounds exhibiting intermolecular interactions, such as hydrogen bonding and π–π stacking, have been extensively investigated, and have shown interesting SC behaviors.[3]

Previously, we reported a family of spin-equilibrium Fe^{III} complexes with the general chemical formula of $[Fe^{III}bL]BPh_4$, in which H_2L denotes the N_3O_2 pentadentate ligand derived from the 2:1 condensation reaction of the salicylaldehyde derivative and bis(3-aminopropyl)amine and b denotes monodentate ligands, such as pyridine and imidazole derivatives.[4] These Fe^{III} complexes assume a ligand field close to the SC point; complexes with pyridine and imidazole derivatives as the axial ligand show the SC behavior. However, the SC behavior is in general gradual, and can be described as a continuous type, because there is no intermolecular interaction. In this study, we designed a Fe^{III} complex, $[Fe^{III}(4\text{-}NH_2py)L]BPh_4$, in which 4-aminopyridine and bis(3-methoxysalicylideneiminopropyl)methylamine were used as the axial and pentadentate ligands, respectively. This complex can function as a self-complementary molecule to construct a 1D chain structure through a hydrogen bond between the amino group of a molecule and the 3-methoxy group of the adjacent molecule. We report here the steep SC behavior and the crystal structures at the HS and LS states.

Experimental

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 Perkin-Elmer FT-IR PARAGON 1000 spectrometer using KBr disks at ambient temperature. Magnetic susceptibilities were measured using a MPMS-5S SQUID (Quantum Design) in the 5–300 K temperature range under an applied magnetic field of 1 T. The calibration was done with palladium metal. Corrections for diamagnetism were applied using Pascal's constants.[5]

Materials. All chemicals and solvents were of reagent grade, and were obtained from Tokyo Kasei Co., Ltd., and Wako Pure Chemical Industries, Ltd. They were used for syntheses without further purification.

Preparation. $[Fe^{III}(4\text{-}NH_2py)L]BPh_4$: The complex was prepared in a similar way to that of a previously reported method.[4] The pentadentate ligand, H_2L, was prepared by mixing 3-methoxysalicylaldehyde (1.54 g, 10 mmol) and bis(3-aminopropyl)methylamine (0.585 g, 5 mmol) in methanol. The mixture was stirred at room temperature for 30 min, and then anhydrous iron(III) chloride (0.82 g, 5 mmol) was added. To the solution was added two equivalents of triethylamine (1.04 g, 10 mmol), and the resulting solution was warmed at 50 °C for 10 min. After standing for several hours at ambient temperature, black precipitates were filtered by suction and dried in vacuo. Yield: 2.102 g (84%).

To a methanol solution of $[Fe^{III}ClL]$ (0.251 g, 0.5 mmol) was added 4-aminopyridine (0.094 g, 1.0 mmol) in methanol. The mixture was warmed for 10 min and filtered. To the filtrate was

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Table 1. X-ray Crystallographic Data for [Fe^{III}(4-NH$_2$py)-L]BPh$_4$ at 293 and 90 K

	293 K	90 K
Formula	$C_{52}H_{55}BFeN_5O_4$	$C_{52}H_{55}BFeN_5O_4$
Fw	880.67	880.67
Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a/Å	18.881(4)	18.557(4)
b/Å	14.730(3)	14.527(3)
c/Å	17.753(4)	17.541(4)
β, deg	104.41(3)	103.19(3)
V/Å^3	4782.2(17)	4604.1(16)
Z	4	4
ρ_{calcd}/mg m^{-3}	1.223	1.271
μ(Mo Kα)/mm^{-1}	0.364	0.379
$R[I > 2\sigma(I)]$[a)]	0.0480	0.0475
Rw[b)]	0.1126	0.1257
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, eÅ^{-3}	0.36 and −0.37	0.84 and −0.67

a) $R = \Sigma||F_o| - |(F_c||/\Sigma|F_o|$. b) $Rw = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w(F_o{}^2|^2]^{1/2}$.

added a solution of 1 equivalent NaBPh$_4$ (0.171 g, 0.5 mmol) in methanol. The mixture was warmed for a few minutes and left standing overnight, during which time black crystals precipitated. They were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 0.190 g (43%). Anal. Calcd for [Fe^{III}(4-NH$_2$py)L]BPh$_4$: C, 70.73; H, 6.11; N, 8.20%. Found: C, 70.92; H, 6.29; N, 7.95%. IR(KBr): $\nu_{C=N}$ 1616 cm^{-1}, ν_{BPh_4} 735, 706 cm^{-1}.

X-ray Crystallography. A red block crystal of (0.63 × 0.60 × 0.10 mm^3) was mounted on an Oxford-Diffraction Xcalibur diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), and equipped with an Oxford Instruments Cryojet cooler device. The structures were solved using SHELXS-97 and refined on F^2 by full-matrix least-squares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms.[6] The carbon atoms of the trimethylene moieties were subjected to disorder at two different temperatures. Refinement was achieved with H atoms introduced in calculations using the riding model. Isotropic U_H were 1.1-times higher than those of the atom to which they were bonded. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation. X-ray crystallographic file in the CIF format is deposited at CCDC; the deposition number is 271756 and 271757. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Crystal data collection and refinement parameters are given in Table 1.

Results and Discussion

The Fe^{III} complex, [Fe^{III}(4-NH$_2$py)L]BPh$_4$, was easily obtained as well-grown black plate crystals from the reaction mixture of [Fe^{III}ClL], 4-aminopyridine, and sodium tetraphenylborate with a 1:2:1 molar ratio in methanol, where the excess of the axial monodentate ligand was added. The complex showed a thermochromism both in the solid and solution states. The complex exhibited dark-red and green colors at room temperature and liquid-nitrogen temperature in the solid state. In the methanol solution the color changed from red to green upon cooling from room temperature to liquid-nitrogen temperature. These observations suggest that the compound exhibits a spin-equilibrium both in the solid and solution states, and further that the spin state is easily changeable by the solid or solution state.

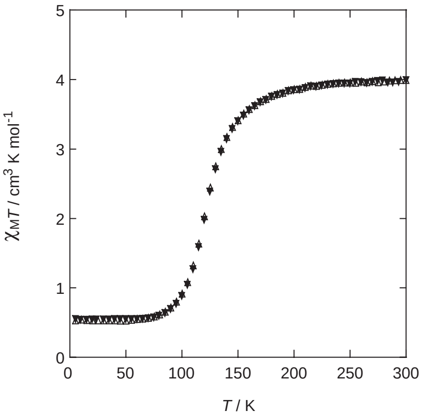

Fig. 1. The magnetic behavior of [Fe^{III}(4-NH$_2$py)L]BPh$_4$ in the form of $\chi_M T$ vs T plots. The sample was cooled from room temperature to 5 K and $\chi_M T$ was measured upon elevating the temperature from 5 to 300 K (△) in the first run. Subsequently, $\chi_M T$ was measured upon lowering the temperature from 300 K to 5 K (▼) as the second run.

The magnetic susceptibility of the polycrystalline sample was measured in the temperature range of 5–300 K at the 1 K min^{-1} sweeping mode under an applied magnetic field of 1 T. The sample was cooled to 5 K from room temperature and the magnetic susceptibility was measured while raising the temperature from 5 to 300 K in the first run. Subsequently, the magnetic susceptibility was measured while lowering the temperature from 300 to 5 K as the second run. $\chi_M T$ vs T plots for the raising (△) and lowering (▼) modes are shown in Fig. 1, demonstrating these two runs were almost identical, except for a small difference at the lowest temperature region. Both the apparent frozen-in effect and hysteresis were not observed. Upon raising the temperature from 5 to 300 K, the $\chi_M T$ value in 5–70 K was nearly constant at ca. 0.56 cm^3 K mol^{-1}, the value of which is compatible with the spin-only value, 0.375 cm^3 K mol^{-1}, of d^5 LS Fe^{III} ($S = 1/2$, $g = 2.00$). Upon further elevating the temperature from 70 K, the $\chi_M T$ value increased to approach a plateau value of 3.99 cm^3 K mol^{-1} at 200–300 K, demonstrating a spin transition from the LS to the HS Fe^{III} state at $T_{1/2} = 120$ K. The magnetic property of this complex shows a perfect spin equilibrium behavior between $S = 1/2$ and $S = 5/2$. The transition is rather steep compared with that of the continuous spin-equilibrium Fe^{III} complexes, probably due to a cooperative effect. Since a small frozen-in effect was observed in the $\chi_M T$ values at the lowest temperature region, an LIESST experiment was carried out by using the light irradiation of 600 nm. No LIESST effect was observed under the experimental condition.[3e]

In order to investigate the origin of the steep spin crossover and to determine the structures of the high-spin and low-spin states, X-ray structure analyses were performed at 293 and 90 K, where the Fe^{III} complex was in the HS and LS states at 293 and 90 K, respectively. The crystallographic data are summarized in Table 1. The crystal lattice and the dimensions of the unit-cell parameters at the two temperatures are similar to each other, and the space group $P2_1/n$ does not change with the spin transition, though the cell volume is reduced by 3.7%, associated with the HS → LS spin transition. The carbon atoms of the trimethylene moieties were subjected to disorder at both temperatures, in which the occupancy factors for the possible positions were assigned. Selected bond distances, angles, and hydrogen bond distances along with their estimated standard deviations in parentheses are given in Table 2. The crystal structure consists of the metal complex cation, $[\mathrm{Fe^{III}(4\text{-}NH_2py)L}]^+$, and a tetraphenylborate, $\mathrm{BPh_4}^-$, as the counter anion. The molecular structure of the metal complex cation, $[\mathrm{Fe^{III}(4\text{-}NH_2py)L}]^+$, is shown in Fig. 2, together with the atom numbering scheme. The $\mathrm{Fe^{III}}$ ion of the complex-cation has an octahedral coordination environment with the $\mathrm{N_3O_2}$ donor atoms from the pentadentate ligand $\mathrm{L^{2-}}$ and with an N donor of 4-aminopyridine at the axial ligand. Two salicylaldimine moieties of the pentadentate ligand is positioned at the equatorial coordination plane, and oriented at the trans position. The mean plane of 4-aminopyridine intersects the chelate ring of the salicylaldimine moiety.

Table 2. Relevant Bond Lengths (Å), Angles (deg.), and Hydrogen Bond Distance (Å) for $[\mathrm{Fe^{III}(4\text{-}NH_2py)L}]\mathrm{BPh_4}$ at 293 and 90 K

	293 K	90 K
	Bond Lengths (Å)	
Fe–O(1)	1.920(2)	1.8797(16)
Fe–O(2)	1.908(2)	1.8702(15)
Fe–N(1)	2.096(2)	1.9738(19)
Fe–N(2)	2.257(2)	2.0912(19)
Fe–N(3)	2.072(2)	1.9611(19)
Fe–N(4)	2.146(2)	1.9999(18)
	Bond Angles (deg)	
O(2)–Fe–O(1)	172.52(7)	173.37(6)
O(1)–Fe–N(1)	86.92(8)	90.19(7)
O(2)–Fe–N(1)	92.78(8)	89.87(7)
O(1)–Fe–N(2)	93.24(8)	93.11(7)
O(2)–Fe–N(2)	94.17(8)	93.52(7)
O(1)–Fe–N(3)	93.46(8)	89.48(7)
O(2)–Fe–N(3)	88.28(8)	90.94(7)
O(1)–Fe–N(4)	86.48(7)	87.07(7)
O(2)–Fe–N(4)	86.10(7)	86.30(7)
N(3)–Fe–N(1)	168.82(8)	175.85(7)
N(1)–Fe–N(2)	84.35(9)	88.02(8)
N(3)–Fe–N(2)	84.47(9)	87.87(8)
N(4)–Fe–N(2)	179.26(8)	179.51(8)
N(1)–Fe–N(4)	94.95(8)	91.53(7)
N(3)–Fe–N(4)	96.23(8)	92.59(7)
	Hydrogen Bond Distance (Å)	
N(5)···O(4)	3.009(3)	2.942(3)

Based on the coordination bond distances and coordination bond angles, the spin state could be identified. At 293 K, the Fe–N and Fe–O bond distances are distributed in the range of 1.908(2)–2.257(2) Å, whose values are in the expected range for HS $\mathrm{Fe^{III}}$ complexes with the Schiff-base type $\mathrm{N_4O_2}$ environment.[7,8] At 90 K, the Fe–N and Fe–O bond distances are distributed in the range of 1.870(2)–2.091(2) Å, whose values are in the expected range for LS $\mathrm{Fe^{III}}$ complexes with the Schiff-base type $\mathrm{N_4O_2}$ environment. Among the six coordination bonds, the bond lengths of the Fe–N(2) (central amine nitrogen) and Fe–N(4) (4-aminopyridine) are much reduced associated with the spin transition. The coordination bond angles change to a regular octahedron upon a spin transition from the HS to the LS state (see Table 2).

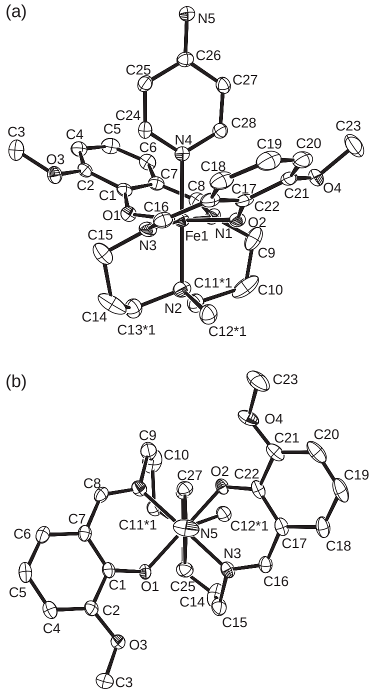

Fig. 2. X-ray molecular structure of the cation part of $[\mathrm{Fe^{III}(4\text{-}NH_2py)L}]\mathrm{BPh_4}$ with the selected atom numbering scheme. (a) Side view showing the axial coordination of 4-$\mathrm{NH_2py}$. (b) Top view showing the orientation of 4-$\mathrm{NH_2py}$ projected on the equatorial coordination plane.

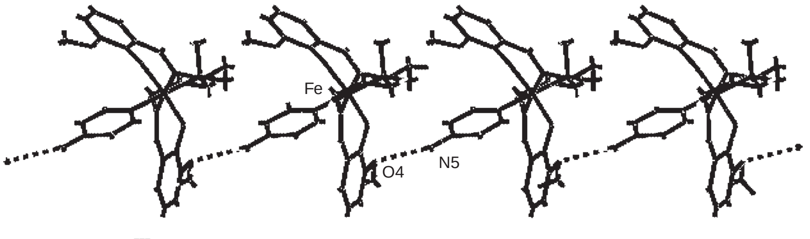

Fig. 3. Infinite chain structure of $[\mathrm{Fe^{III}(4\text{-}NH_2py)L}]\mathrm{BPh_4}$. The chain structure is constructed by hydrogen bonds between the amino group of a complex and the 3-methoxy group of the adjacent molecule; the N(5)···O(4) distance is 3.009(3) and 2.942(3) Å at 293 and 90 K, respectively.

The oxygen atom O(4) of the 3-methoxysalicylaldehyde moiety of a complex-cation is hydrogen-bonded to a nitrogen atom of 4-aminopyridine of the adjacent complex-cation with a distance of O(4)···N(5) = 3.009(3) Å at 296 K and O(4)···N(5) = 2.942(3) Å at 93 K. As a result, an infinite chain structure running along the *c*-axis is constructed by the hydrogen bonds, as shown in Fig. 3. The adjacent chains are well separated by the bulky tetraphenylborate anion, and run along different directions. Since the adjacent infinite chains are well separated by the bulky tetraphenylborate anion, it is anticipated that the steep spin crossover is due to the chain structure. The present observation gives an example that a one-dimensional structure constructed by hydrogen bonds can affect the steepness of the spin equilibrium behavior.

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