Spin Crossover of a Hydrogen-Bonded Dimeric Fe$^{\mathrm{III}}$ Complex with an Unequivalent Tetradentate Schiff Base Ligand and Two Imidazoles

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A spin crossover Fe$^{\mathrm{III}}$ complex, [FeHim$_2$L]BPh$_4$·2MeOH, was synthesized and studied, where Him = imidazole, H$_2$L = N$_2$O$_2$ Schiff base ligand of the 1:1:1 condensation product of acetylacetone, ethylenediamine, and *o*-hydroxyacetophenone, and BPh$_4$$^-$ = tetraphenylborate. The complex consists of a cyclic dimeric structure, {···[FeHim$_2$L]···(MeOH)···(MeOH)···}$_2$, constructed by the hydrogen bonds. Magnetic measurements revealed that a rather steep spin transition from the LS to HS Fe$^{\mathrm{III}}$ states occurs above 300 K, and the elimination of the methanol molecules changes the spin transition from steep to gradual due to destruction of the cyclic dimeric structure.

The spin crossover (SC) between the low-spin (LS) and high-spin (HS) states observed in some octahedral 3d^n ($4 \leq n \leq 7$) metal complexes is induced by an external perturbation, such as temperature, pressure, or light irradiation.[1] It is now understood that the interaction between the SC sites or the cooperative effect governs the bistability, such as the steepness, hysteresis, and LIESST (light-induced excited spin state trapping), while the SC is essentially the phenomenon of a single molecule.[2] Since the SC compounds with hysteresis and the LIESST effect can be applied to information storage, molecular switches, and visual displays, the synthesis of SC compounds exhibiting interactions between SC sites is of current interest.[3] From this viewpoint, a number of the SC compounds with various assembly structures have been reported in the latest decade.[4] It is also well known that the Fe site in some heme protein exhibits the SC behavior. From the viewpoint of a model compound for such a heme protein, Nishida et al. synthesized a series of Fe$^{\mathrm{III}}$ complexes with tetradentate N$_2$O$_2$ Schiff base ligands and two axial monodentate ligands, and showed that the spin states can be tuned by the ligand field of the equatorial tetradentate ligands and two axial ligands.[5] Nishida showed that [Fe$^{\mathrm{III}}$Him$_2$(salen)]BPh$_4$ and [Fe$^{\mathrm{III}}$Him$_2$(acacen)]BPh$_4$ are HS and LS compounds, respectively, where H$_2$salen and H$_2$acacen denote disalicylideneethylenediamine and bis(acetylacetone)ethylenediamine, respectively. On the basis of Nishida's result, Matsumoto et al. synthesized a SC Fe$^{\mathrm{III}}$ complex with unequivalent tetradentate ligand with the 1:1:1 condensation of acetylacetone, salicylaldehyde, and ethylenediamine in order to precisely tune the ligand field of the equatorial coordination environment.[6] We report here an SC complex, [Fe$^{\mathrm{III}}$Him$_2$L]BPh$_4$·2MeOH, in which two SC sites are connected by the hydrogen bonds through crystal solvent molecules; the complex shows a steep SC behavior.

The unequivalent tetradentate ligand with N$_2$O$_2$ donor atoms, H$_2$L, which is a 1:1:1 condensation product of acetylacetone, ethylenediamine, and *o*-hydroxyacetophenone, was prepared by a stepwise procedure. An Fe$^{\mathrm{III}}$ complex, [FeHim$_2$L]BPh$_4$·2MeOH, was obtained as green-black crystals from the reaction mixture of [FeClL], imidazole, and sodium tetraphenylborate with a 1:3:1 molar ratio in methanol.[6b] The green color of the complex at room temperature in the solid state changes to red color at 80 °C, suggesting a spin transition from LS to the HS Fe$^{\mathrm{III}}$ state. A chloroform solution of the complex exhibits a red color at room temperature and a green color at liquid-nitrogen temperature, suggesting a spin transition from HS to the LS Fe$^{\mathrm{III}}$ state. These observations suggest that the compound exhibits a spin crossover both in the solid and solution states and, further, that the spin state is easily changeable by the solid or solution state.

As shown in Fig. 1, the crystal structure of [FeHim$_2$L]BPh$_4$·

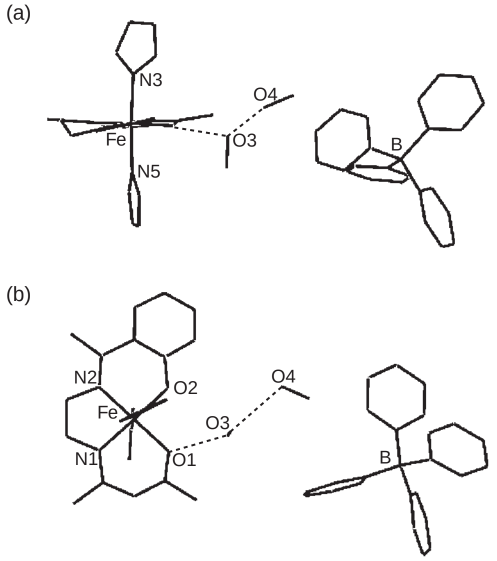

Fig. 1. X-ray structure of [FeHim$_2$L]BPh$_4$·2MeOH with the selected atom numbering scheme. (a) Side view showing the axial coordination of two imidazoles. (b) Top view showing the orientation of two imidazoles and hydrogen bonds. Selected geometric parameters: Fe–O(1) = 1.892(3), Fe–O(2) = 1.849(4), Fe–N(1) = 1.893(5), Fe–N(2) = 1.911(3), Fe–N(3) = 1.986(4), Fe–N(5) = 1.974(3) Å, O(1)–Fe–O(2) = 86.0(2), O(1)–Fe–N(1) = 94.7(2), O(2)–Fe–N(2) = 93.8(2), N(1)–Fe–N(2) = 87.6(2), N(3)–Fe–N(5) = 176.0(2)°.

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2MeOH consists of a metal complex cation, $[FeHim_2L]^+$, a tetraphenylborate ion as the counter anion, and two methanol molecules as crystal solvents. The Fe^{III} ion of the complex cation has an octahedral coordination environment with the N_2O_2 donor atoms from the equatorial unequivalent tetradentate ligand, L^{2-}, and with the N_2 donors of two imidazoles at the two axial ligands. The Fe–N and Fe–O coordination bond distances are in the range of 1.849(4)–1.986(4) Å, whose values are in the expected range for LS Fe^{III} complexes with the Schiff base type N_4O_2 environment.[7] As shown in Fig. 1(b), two imidazole rings are not coplanar and do not lie on the Fe–N and Fe–O bonds. The plane of one imidazole group is slightly tilted from the bonds of N(1)–Fe–O(2), while the plane of the other imidazole intersects the chelates of O(1)–Fe–N(1) and O(2)–Fe–N(2). The cationic metal complex of the present BPh_4 salt is similar to that of the PF_6 salt previously reported, except for the solvent molecules and the orientation of the axial imidazoles,[6a] where the PF_6 salt does not contain the crystal solvent, and two imidazole rings of the PF_6 salt lie on the Fe–N and Fe–O bonds.

The oxygen atom O(1) of the acetylacetone moiety of the complex cation is hydrogen-bonded to a methanol molecule with a distance of O(1)···O(3) = 2.764(7) Å. The oxygen atom O(3) of the methanol is further hydrogen bonded to another methanol molecule with a distance of O(3)···O(4) = 2.685(7) Å. The oxygen atom O(4) is further hydrogen-bonded to an imidazole nitrogen atom, N(6)*, of the imidazole coordinated to Fe^{III} ion with a distance of O(4)···N(6)* = 2.705(6) Å. As a result, a cyclic dimeric structure, $\{-[FeHim_2L]-(MeOH)-(MeOH)-\}_2$, consisting of two Fe^{III} sites and four methanol molecules was constructed by hydrogen bonds, as shown in Fig. 2. It should be noted that another imidazole group that does not participate in the dimeric structure assumes a short contact to a phenyl group of the BPh_4^- anion, suggesting a NH/π interaction. Such a NH/π interaction is found in the BPh_4 salt of imidazole containing the Fe(II) complex,[8] and the present NH/π interaction is easily illustrated by adapting its CIF file to the Mercury Program.

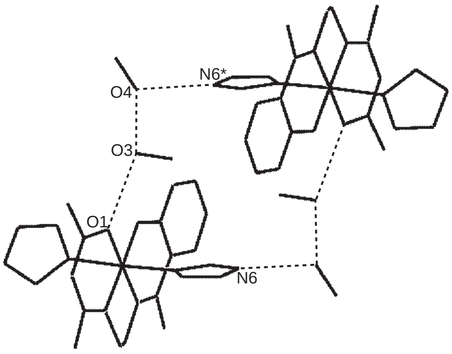

Fig. 2. A cyclic dimeric structure, $\{\cdots[FeHim_2L]\cdots(MeOH)\cdots(MeOH)\cdots\}_2$, constructed by the hydrogen bonds. The oxygen atom O(1) of the acetylacetone moiety of the complex cation is hydrogen-bonded to a methanol molecule with the distance of O(1)···O(3) = 2.764(7) Å. The oxygen atom O(3) is further hydrogen bonded to other methanol molecule with O(3)···O(4) = 2.685(7) Å. The oxygen atom O(4) is further hydrogen-bonded to an imidazole nitrogen atom coordinated to Fe^{III} ion with O(4)···N(6)* = 2.705(6) Å. The atom with * is expanded by the symmetry operation of $-x$, $-y$, $-z$, since the dimeric molecule assumes a center of symmetry.

The magnetic susceptibility of the polycrystalline sample was measured in the temperature range of 2–400 K under an applied magnetic field of 0.5 T. The sample was cooled to 2 K from room temperature, and the magnetic susceptibility was measured while raising the temperature from 2 to 400 K in the first run. Subsequently, the magnetic susceptibility was measured while lowering the temperature from 400 to 2 K as the second run. The $\chi_M T$ vs T plots for the raising (▲) and lowering (▽) modes are shown in Fig. 3. Upon raising the temperature from 2 to 400 K, the $\chi_M T$ value at 2–200 K is nearly constant at ca. 0.56 $cm^3\,K\,mol^{-1}$, whose value is compatible with d^5 LS Fe^{III} complexes ($S = 1/2$). Upon further elevating the temperature from 200 K, the $\chi_M T$ value increased to approach a plateau value of ca. 3.9 $cm^3\,K\,mol^{-1}$ at 380–400 K, demonstrating the spin transition from the LS to HS Fe^{III} state. The plateau value of 3.9 $cm^3\,K\,mol^{-1}$ is smaller than the HS ($S = 5/2$) value of 4.37 $cm^3\,K\,mol^{-1}$, which can be explained because the molecular weight decreases due to the elimination of the crystal solvent and by the spin transition may complete at a higher temperature than 400 K. The transition is rather steeper than those of the continuous spin-equilibrium Fe^{III} complexes, probably due to a cooperative effect due to the cyclic dimer structure. The TG measurement showed the weight loss corresponding to two methanol molecules until 385 K. The DSC measurement showed an endothermic broad peak around 358 K and a shoulder peak around 378 K, whose two peaks can be due to the elimination of two different methanol molecules, respectively.

Upon lowering the temperature from 400 K, the $\chi_M T$ value decreases rather gradually to a value that is considerably larger than the initial value. The gradual spin-transition behavior can be mainly ascribed to destruction of the cyclic structure due to

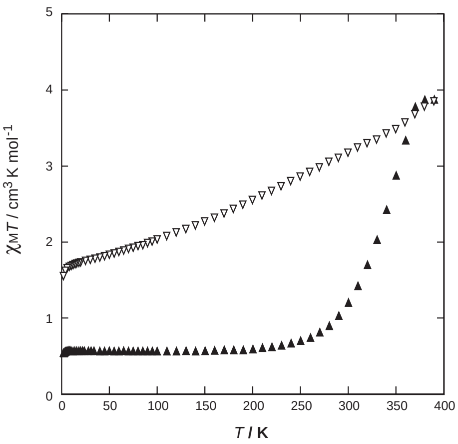

Fig. 3. The magnetic behavior of $[FeHim_2L]BPh_4\cdot 2MeOH$ in the form of the $\chi_M T$ vs T plots. The sample was cooled from room temperature to 2 K and the $\chi_M T$ was measured upon elevating the sample temperature from 2 to 400 K (▲) in the first run. Subsequently, the $\chi_M T$ was measured upon lowering the sample temperature from 400 K to 2 K (▽) as the second run.

solvent elimination. It should be noted that the $\chi_M T$ value decreased to the initial value when the sample was warmed to 350 K, and then cooled back from 350 K to 2 K, though the process was more gradual.

As demonstrated by an X-ray analysis, two SC Fe^{III} sites are connected through the hydrogen bonds to give a cyclic dimer structure, $\{\cdots[\mathrm{FeHim_2L}]\cdots(\mathrm{MeOH})\cdots(\mathrm{MeOH})\cdots\}_2$, consisting of two complex cations and four methanol molecules. The elimination of the methanol molecules would destroy the hydrogen-bonded cyclic structure and affect the spin crossover behavior. The present observation gives an example that even the short-range hydrogen bonds within two SC sites significantly affect the SC behavior.

Experimental

Preparation. [FeHim$_2$L]BPh$_4$·2MeOH: The starting compound, [FeClL], and [FeHim$_2$L]BPh$_4$·2MeOH were prepared according to a method previously reported.[6] To a suspension of [FeClL] in 15 mL of methanol (0.351 g, 1.0 mmol) was added a solution of imidazole (0.212 g, 3.1 mmol) in 10 mL of methanol. The mixture was added to a solution of NaBPh$_4$ (0.346 g, 1.0 mmol) in 15 mL of methanol. The solution was allowed to stand for two hours, during which time the precipitated green powders were collected by suction filtration, washed with a small volume of methanol, and dried in vacuo. The crude product was recrystallized from a mixture of dichloromethane and methanol. Yield: 0.667 g (86%). Found: C, 67.75; H, 6.57; N, 9.88%. Calcd for [FeHim$_2$L]BPh$_4$·2MeOH: C, 67.72; H, 6.53; N, 10.08%. IR(KBr): $\nu_{\mathrm{C=N}}$ 1596, 1580 cm^{-1}, $\nu_{\mathrm{BPh_4}}$ 733, 706 cm^{-1}.

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 2–400 K temperature range under an applied magnetic field of 0.5 T. The calibration was done with palladium metal. Corrections for diamagnetism were applied using Pascal's constants.[9]

X-ray Crystallography. X-ray diffraction data were collected using a Rigaku Rapid diffractometer at 296 K. The data were corrected for Lorentz, polarization and absorption effects. The structure was 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.[10]

X-ray crystallographic data for [FeHim$_2$L]BPh$_4$·2MeOH at 296 K: formula = $\mathrm{FeC_{47}H_{54}BN_6O_4}$, fw = 833.64, triclinic, space group = $P\bar{1}$ (No. 2), $a = 12.397(6)$, $b = 15.541(6)$, $c = 12.102(4)$ Å, $\alpha = 110.20(1)$, $\beta = 98.41(1)$, $\gamma = 85.37(2)°$, $V = 2163(1)$ Å^3, $Z = 2$, $D_{\mathrm{cal}} = 1.280$ g cm^{-3}, $\mu(\mathrm{Mo\,K\alpha}) = 3.99$ cm^{-1}, $\lambda = 0.71069$ Å, $R = 0.074$, GOF = 1.004. Crystallographic data in the CIF format have been deposited under the deposition number 271484 of CCDC. 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).

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