Gradual Two-step Spin Crossover Behavior of Binuclear Iron(III) Complex Bridged by *trans*-1,2-Bis(4-pyridyl)ethylene

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A binuclear iron(III) complex bridged by *trans*-1,2-bis(4-pyridyl)ethylene, $[\mathrm{LFe^{III}(vibpy)Fe^{III}L}](\mathrm{BPh_4})_2$, showed a gradual two-step spin crossover behavior, where H_2L is bis(3-methoxysalicylideneaminopropyl)methylamine and $\mathrm{BPh_4}^-$ is tetraphenylborate. The single-crystal X-ray analysis at the intermediate state revealed that one of the two $\mathrm{Fe^{III}}$ ions of the binuclear complex is in the high-spin (HS) state and the other is in the low-spin (LS) state. The HS and LS sites independently form layers and these HS and LS layers alternately stack.

The spin crossover (SC) between the low-spin (LS) and high-spin (HS) states is induced by an external perturbation, such as temperature, pressure, or light irradiation.[1] While the SC behavior is essentially the phenomenon of a single molecule, the interaction between the 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.[1] The binuclear SC complex is the simplest model compound in order to investigate the synergic effect of intramolecular and intermolecular factors.[2] Though binuclear $\mathrm{Fe^{II}}$ SC compounds bridged by bipyrimidine derivatives have been extensively studied, these studies have focused on the correlation between the intramolecular magnetic interaction and the SC properties.[2] In this study, we focused on the binuclear complex exhibiting no intramolecular magnetic interaction. Because of the lack of the intramolecular magnetic interaction, the present binuclear SC complex can be a suitable compound to investigate the synergic structural effect of intramolecular and intermolecular interactions.

The binuclear $\mathrm{Fe^{III}}$ complex bridged by *trans*-1,2-bis(4-pyridyl)ethylene, $[\mathrm{LFe^{III}(vibpy)Fe^{III}L}](\mathrm{BPh_4})_2$, was obtained by mixing the precursor $\mathrm{Fe^{III}}$ complex [FeClL] and *trans*-1,2-bis(4-pyridyl)ethylene in a mole ratio of 2:1 in methanol and then by adding a methanolic solution of sodium tetraphenylborate. Recrystallization from acetonitrile and methanol gave black plate-like crystals.[3]

The magnetic susceptibilities of the crystalline sample were measured in the temperature range of 5–350 K at a 1 K min^{-1} sweeping rate under a 0.5 T applied magnetic field. The sample was quickly cooled from room temperature to 5 K, and the magnetic susceptibility was first measured in the warming mode from 5 to 350 K. Subsequently, the magnetic susceptibility was measured in the cooling mode from 350 to 5 K. The $\chi_M T$ vs T plots are shown in Figure 1, where χ_M is the molar magnetic susceptibility per 2Fe and T is the absolute temperature. There is no difference in the cooling and warming modes. The $\chi_M T$ curve revealed a gradual two-step spin transition. At 350 K, the $\chi_M T$ value of 7.70 cm^3 K mol^{-1} is slightly smaller than the expected value of 8.75 cm^3 K mol^{-1} for existing independently two HS species ($S = 5/2$, $g = 2.00$), suggesting that two $\mathrm{Fe^{III}}$ sites are mainly in the HS and HS states. Upon lowering the temperature from 350 K, the $\chi_M T$ value gradually decreases and reaches an intermediate state around 140 K, and then more gradually decreases to 2.96 cm^3 K mol^{-1} at 5 K. The $\chi_M T$ value at the intermediate state is ca. 4.7 cm^3 K mol^{-1} in the region of 140–125 K, whose value is close to the value of 4.75 cm^3 K mol^{-1} expected for the HS and LS state. Even at 5 K, the value of $\chi_M T = 2.96$ cm^3 K mol^{-1} is much larger than the value of 0.75 cm^3 K mol^{-1} expected for the LS and LS state, indicating an incomplete SC in the lower temperature region. The second SC in the lower temperature region is much more gradual than the first SC in the higher temperature region. Since the magnetic susceptibilities of the SC complex sometimes strongly depend on the crystalline states, the magnetic susceptibility measurements of this complex were carried out by using different samples with different crystalline states (ground powder and crystals without crush). The magnetic behaviors are essentially the same for each of them.

Previously, we reported a family of mononuclear $\mathrm{Fe^{III}}$ complexes $[\mathrm{Fe^{III}bL}]\mathrm{BPh_4}$, in which H_2L is the same N_3O_2 pentadentate ligand and b is a monodentate ligand such as pyridine and imidazole derivatives.[4] The $\mathrm{Fe^{III}}$ complexes with pyridine derivatives as the axial ligand showed a gradual, but complete SC behavior, the typical SC for isolated SC complexes. In comparison with the mononuclear complex, the present binuclear compound showed more gradual and incomplete SC behaviors, in addition to the two-step SC.

The X-ray crystal structural analyses were performed at 296 and 125 K in order to investigate the structural change during the first SC spin transition.[5] The magnetic susceptibility measurements demonstrated that the two $\mathrm{Fe^{III}}$ ions are mainly in the HS and HS state at 296 K and in the HS and LS state at 125 K. At the two temperatures, the complex assumes the same space group $P2_1$, indicating that there is no phase transition during

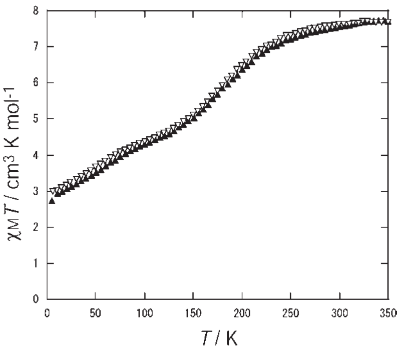

Figure 1. $\chi_M T$ vs T plots of $[\mathrm{LFe^{III}(vibpy)Fe^{III}L}](\mathrm{BPh_4})_2$ in the warming (▲) and cooling (▽) modes.

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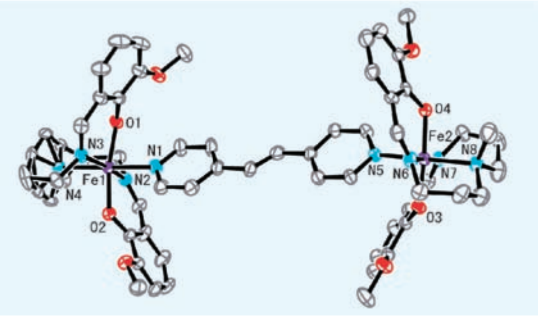

Figure 2. Binuclear structure of [LFe^{III}(vibpy)Fe^{III}L](BPh$_4$)$_2$ at 125 K with the selected atoms numbering scheme. Fe1 is in the HS state and Fe2 is in the LS state.

the spin transition. The molecular structure of the binuclear metal-complex cation at 125 K is shown in Figure 2, together with the selected atom numbering scheme.

There are two Fe ions, Fe1 and Fe2, in the crystallographically unique unit. Each Fe^{III} ion is in an octahedral coordination environment and coordinated by N$_3$O$_2$ donor atoms of the pentadentate Schiff-base ligand and one N atom of the bridging ligand. On the basis of the Fe–N and Fe–O bond distances, the spin state can be identified. At 296 K, the Fe–N and Fe–O bond distances at the Fe1 and Fe2 sites are similar to each other, the average bond distances ($\langle$Fe1–N$\rangle$ = 2.146 Å, $\langle$Fe1–O$\rangle$ = 1.916 Å; $\langle$Fe2–N$\rangle$ = 2.128 Å, $\langle$Fe2–O$\rangle$ = 1.921 Å) being consistent with the fact that the two Fe^{III} sites are in the HS states. On the other hand, at 125 K, the average bond distance at the Fe1 site ($\langle$Fe1–N$\rangle$ = 2.142 Å, $\langle$Fe1–O$\rangle$ = 1.911 Å) indicates that the Fe1 site remains in the Fe^{III} HS state, while the average bond distance of the Fe2 site ($\langle$Fe2–N$\rangle$ = 2.001 Å, $\langle$Fe2–O$\rangle$ = 1.873 Å) is of the expected value for the Fe^{III} LS state, indicating that the Fe2 site converts from HS at 296 K to LS at 125 K. As shown in Figure 2, the bis(3-aminopropyl)methylamine moiety suffered from disorder. At 300 K, this disorder is found in both the Fe1 and Fe2 sites, while at 125 K, the disorder is found only in the Fe1 site. This order–disorder might be related to the SC.

The crystal packing diagram at 125 K is shown in Figure 3, where the Fe1 moiety in the HS state is drawn in red and the Fe2 moiety in the LS state is drawn in blue. There is no intermolecular hydrogen bond and π–π stacking. The Fe1 site in the HS state (red) and the Fe2 site in the LS state (blue) are bridged by vibpy. As shown in Figure 3, the HS species (red) form a layer and the LS species (blue) form another layer. The red HS layer and the blue LS layer alternately stack.

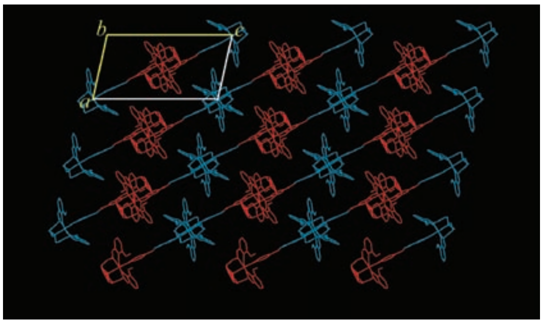

Figure 3. Packing diagram of the HS and LS sites of [LFe^{III}(vibpy)Fe^{III}L](BPh$_4$)$_2$ at 125 K. The hydrogen atoms and BPh$_4{}^-$ are omitted.

In summary, a binuclear Fe^{III} complex shows a gradual two-step spin transition that should be related to the alternately arrayed HS and LS layers. The SC behavior of this series of binuclear complexes is detailed by the magnetic, structural, and theoretical studies in order to determine the details of the SC behavior.

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3 The pentadentate ligand H$_2$L was prepared by the 2:1 condensation reaction of 3-methoxysalicylaldehyde and bis(3-aminopropyl)methylamine in methanol and the ligand solution was used for the synthesis of the precursor iron(III) complex without the isolation of the ligand. The precursor Fe^{III} complex, [Fe^{III}ClL], was prepared according to the method reported previously.[4] To a solution of [Fe^{III}ClL] (0.5 mmol) in 30 mL of methanol was added a solution of *trans*-1,2-bis(4-pyridyl)ethylene (0.25 mmol). The mixture was warmed and stirred for 10 min and then filtered. The filtrate was added to a solution of sodium tetraphenylborate (0.5 mmol) in 10 mL of methanol. The resulting solution was kept to stand for overnight, during which time black plate crystals precipitated. They were collected by suction filtration, washed with methanol and dried. Anal. Calcd for [LFe^{III}(vibpy)Fe^{III}L](BPh$_4$)$_2$, $C_{106}H_{108}N_8O_8Fe_2B_2$: C, 72.53; H, 6.20; N, 6.38%. Found: C, 71.98; H, 6.17; N, 6.48%. IR(KBr): $\nu_{C=N}$(imine), 1614, 1599 cm^{-1}; ν_{B-C}(BPh$_4{}^-$) 735, 706 cm^{-1}.

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5 The X-ray diffraction data were collected using a Rigaku R-Axis Rapid diffractometer at 296 and 125 K. Hydrogen atoms were fixed at the calculated positions and refined using a riding model. All calculations were performed using the CrystalStructure software package. X-ray crystallographic data for [LFe^{III}(vibpy)Fe^{III}L](BPh$_4$)$_2$ at 296 K: formula = $C_{106}H_{108}N_8O_8Fe_2B_2$, fw 1755.38, monoclinic, space group $P2_1$ (No. 4), $a = 22.016(5)$, $b = 19.547(4)$, $c = 11.375(2)$ Å, $\beta = 102.811(8)^\circ$, $V = 4773(1)$ Å^3, $T = 300$ K, $Z = 2$, $D_{calcd} = 1.221$ g cm^{-1}, μ(Mo Kα) = 3.640 cm^{-1}, 46844 reflections measured, 46832 unique ($R_{int} = 0.058$), $R = 0.086$, $R_w = 0.248$. X-ray crystallographic data at 125 K: formula $C_{106}H_{108}N_8O_8Fe_2B_2$, fw 1755.38, monoclinic, space group $P2_1$ (No. 4), $a = 21.703(5)$, $b = 19.428(4)$, $c = 11.202(2)$ Å, $\beta = 102.842(8)^\circ$, $V = 4605(1)$ Å^3, $T = 125$ K, $Z = 2$, $D_{calcd} = 1.266$ g cm^{-1}, μ(Mo Kα) = 3.773 cm^{-1}, 43602 reflections measured, 19422 unique ($R_{int} = 0.052$), $R = 0.057$, $R_w = 0.073$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-281482 and 281483. 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; or deposit@ccdc.cam.ac.uk).

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