One-dimensional Polynuclear Spin-crossover Iron(III) Complex Axially Bridged by 1,3-Bis(4-pyridyl)propane

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A one-dimensional (1D) polynuclear spin-crossover Fe^{III} complex, $[Fe^{III}(acacen)(bpyp)]_n(BPh_4)_n$, showed a gradual and complete SC over a wide temperature range of ca. 250 K between $S = 5/2$ and $S = 1/2$, where acacen = N,N'-bis(acetylacetonato)ethylenediamine, bpyp = 1,3-bis(4-pyridyl)propane, and BPh_4^- = tetraphenylborate. The single-crystal X-ray structures in the HS, LS, and midpoint between the HS and LS states were determined, and demonstrated that the SC may occur through the alternately arrayed HS- and LS-chains.

The spin crossover (SC) between the high-spin (HS) and low-spin (LS) 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 that governs the SC properties, such as the steepness of the SC, hysteresis, and light-induced excited spin state trapping (LIESST) effect. The most attractive SC complex that exhibits a steep spin transition and a wide hysteresis loop around room temperature may be the 1D polynuclear Fe^{II} complex bridged by triazole groups.[2] In this study, we focused on the 1D polynuclear Fe^{III} complex axially bridged by 1,3-bis(4-pyridyl)propane, $[Fe^{III}(acacen)(bpyp)]_n(BPh_4)_n$.[3] We now report the SC behavior, structure, and the cooperative effect of the 1D polynuclear structure on the SC behavior.

The 1D Fe^{III} complex, $[Fe^{III}(acacen)(bpyp)]_n(BPh_4)_n$, was obtained as well-grown black plate crystals by mixing $[Fe^{III}Cl(acacen)]$ and 1,3-bis(4-pyridyl)propane in a 1:1 mole ratio in methanol and then by adding a methanol solution of sodium tetraphenylborate.[4] Among the equatorial tetradentate Schiff-base ligands with N_2O_2 donor atoms like H_2salen, the ligand H_2acacen is selected so as to provide the ligand field of the SC region on the basis of the previous studies.[5] The complex showed a thermochromism in the solid state from purple at room temperature to green at liquid nitrogen temperature, suggesting an SC.

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 for the warming and cooling modes are shown in Figure 1, where χ_M is the molar magnetic susceptibility per Fe, and T is the absolute temperature. The $\chi_M T$ vs T plots showed no difference in the cooling and warming modes and revealed a gradual and reversible SC between the HS ($S = 5/2$) and LS ($S = 1/2$) states. At 350 K, the $\chi_M T$ value of 3.85 cm^3 K mol^{-1} is slightly lower than the expected value of 4.37 cm^3 K mol^{-1} for the HS Fe^{III} species ($S = 5/2$, $g = 2.00$). Upon lowering the temperature from 350 K, the $\chi_M T$ value gradually decreased and reached the plateau value of 0.58 cm^3 K mol^{-1} below 100 K, whose value is comparable with the value for the LS Fe^{III} complexes ($S = 1/2$). The complex showed a gradual and complete SC over a wide temperature range of ca. 250 K.

The present SC behavior can be compared with those of the mononuclear SC Fe^{III} complexes containing similar donor atoms.[6] In comparison with the mononuclear Fe^{III} complexes exhibiting a complete SC behavior, the present compound showed a more gradual SC behavior over a wide temperature range, probably due to the flexible 1D chain structure, in which the mononuclear Fe^{III} complexes with pyridine derivatives as the axial ligand showed a SC behavior over a wide temperature range of ca. 150 K, the typical SC for isolated SC Fe^{III} complexes.

The single-crystal X-ray structures were determined at 296 K in the HS state, at 108 K in the LS state, and at 180 K at

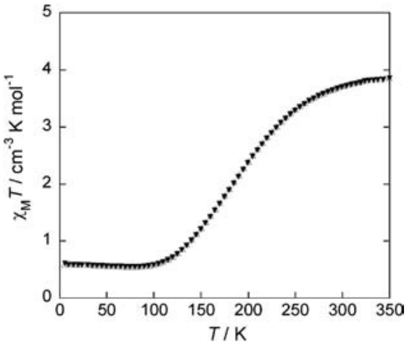

Figure 1. $\chi_M T$ vs T plots of $[Fe^{III}(acacen)(bpyp)]BPh_4$ in the warming (△) and cooling (▼) modes.

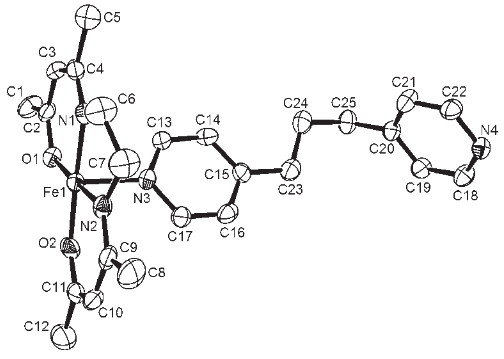

Figure 2. Molecular structure of $[Fe^{III}(acacen)(bpyp)]BPh_4$ at 180 K with the selected atoms numbering scheme. One of the two molecular units, Fe1 site, is drawn and Fe1 is coordinated by N4 of the adjacent unit.

the midpoint between the HS and LS states.[7] The temperature of 180 K was evaluated from the maximum point from the derivative of the $\chi_M T$ vs T curve. At three temperatures, the complex assumes the same space group $Pca2_1$ (No. 29), indicating no phase change during the spin transition, as expected from the gradual SC behavior. The complex consists of two molecular units as a crystallographical unique unit. The molecular structure of one of the two molecular units (Fe1 and Fe2 sites) is shown in Figure 2, together with the selected atom numbering scheme, where the same atom numbering scheme at the same positions is taken for the three temperatures. Each Fe^{III} ion is in an octahedral coordination environment with the N_4O_2 donor atoms, in which the equatorial coordination sites are occupied by the N_2O_2 donor atoms of acacen, and the two axial positions are occupied by the two pyridine N atoms of the two bridging ligands.

The cell volume is reduced by 3.9% associated with the spin transition from 296 to 108 K. On the basis of the Fe–N and Fe–O bond distances, the spin state can be identified. The axial Fe–N bond distances are more effectively affected than the equatorial distances by the spin transition. At 108 K, the axial Fe–N bond distances at the Fe1 and Fe2 sites are similar to each other, the average bond distances ($\langle \text{Fe1–N} \rangle = 2.037$ Å; $\langle \text{Fe2–N} \rangle = 2.038$ Å) being consistent with the fact that the two Fe^{III} sites are in the LS states. At 180 K, the axial Fe–N bond distances at the Fe1 and Fe2 sites are $\langle \text{Fe1–N} \rangle = 2.054$ Å and $\langle \text{Fe2–N} \rangle = 2.136$ Å, respectively, demonstrating that two Fe sites are in different spin states. At 296 K, the axial Fe–N bond distances at the Fe1 and Fe2 sites are $\langle \text{Fe1–N} \rangle = 2.178$ Å and $\langle \text{Fe2–N} \rangle = 2.225$ Å, respectively, demonstrating that the two Fe^{III} sites are almost in the HS states. These data imply that the Fe2 site converts from the LS to HS state at the lower temperature than the Fe1 site.

The SC Fe^{III} complex is axially bridged by 1,3-bis(4-pyridyl)propane to give a 1D polynuclear zigzag chain running along the *a*-axis. There is no interchain hydrogen bond and π–π stacking. At the three temperatures, the crystal contains two crystallographically independent chains, the Fe1 chain and Fe2 chain. At 108 K, the dimensions around the coordination sphere of the Fe1 chain are not different from those of the Fe2 chain. At 180 K, the dimensions of the Fe1 chain are definitely different from those of the Fe2 chain. The crystal packing diagram at 180 K is shown in Figure 3, where the LS Fe1 chain is drawn in black and the HS Fe2 chain is drawn in gray. These two chains running along the *a*-axis are alternately arrayed.

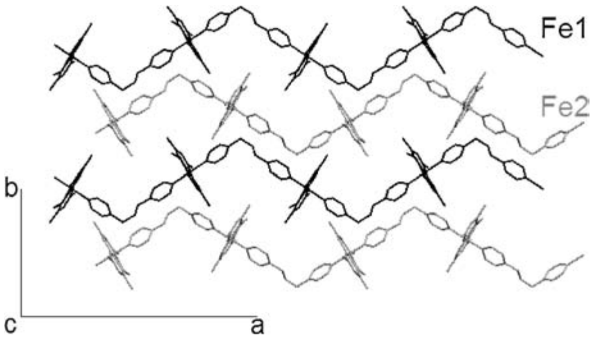

Figure 3. One-dimensional zigzag chains running along the *a*-axis in the crystal at 180 K (the midpoint of the HS and LS states). The hydrogen atoms and BPh_4^- are omitted for clarity. A 1D chain (black color, the LS species) and the adjacent 1D chain (gray color, the HS species) are alternately arrayed.

The gradual SC behavior over a wide temperature range of ca. 250 K can be ascribed to the 1D zigzag chain axially bridged by a flexible ligand and the two Fe sites exhibiting SC at the different temperature regions, suggesting that the present chain structure may produce a negative effect for the purpose of gaining a steep SC and hysteresis. Another noteworthy result is that the SC may occur through the alternately arrayed HS and LS zigzag chains. The present results would give relevant information to the molecular design of functional polynuclear SC material.

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References and Notes

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4 To a solution of $[Fe^{III}Cl(acacen)]$ (157 mg, 0.5 mmol) in 30 mL of methanol was added a solution of 1,3-bis(4-pyridyl)propane (100 mg, 0.5 mmol). The mixture was warmed and stirred for 10 min and then filtered. The filtrate was added to a solution of sodium tetraphenylborate (171 mg, 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 $[Fe^{III}(acacen)(bpyp)]BPh_4$, $C_{49}H_{52}N_4O_2FeB$: C, 73.97; H, 6.59; N, 7.04%. Found: C, 73.54; H, 6.72; N, 7.10%. IR(KBr): $\nu_{C=N}$(imine), 1610, 1507 cm^{-1}; $\nu_{B-C}(BPh_4^-)$ 730, 709 cm^{-1}.

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7 The X-ray diffraction data were collected using a Rigaku R-Axis Rapid diffractometer at 296, 180, and 108 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 $[Fe^{III}(acacen)(bpyp)]BPh_4$ at 296 K: formula = $C_{49}H_{52}N_4O_2FeB$, fw = 795.63, orthorhombic, space group $Pca2_1$ (No. 29), $a = 25.132(2)$, $b = 13.925(4)$, $c = 24.136(3)$ Å, $V = 8466(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.251$ g cm^{-3}, μ(Mo Kα) = 4.01 cm^{-1}, $R = 0.067$, $R_w = 0.150$. X-ray crystallographic data at 180 K: orthorhombic, space group $Pca2_1$ (No. 29), $a = 24.839(7)$, $b = 13.914(3)$, $c = 23.883(5)$ Å, $V = 8254(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.280$ g cm^{-3}, μ(Mo Kα) = 4.10 cm^{-1}, $R = 0.072$, $R_w = 0.204$. X-ray crystallographic data at 108 K: orthorhombic, space group $Pca2_1$ (No. 29), $a = 24.708(3)$, $b = 13.893(24)$, $c = 23.704(3)$ Å, $V = 8136(1)$ Å^3, $Z = 8$, $D_{calcd} = 1.299$ g cm^{-3}, μ(Mo Kα) = 4.16 cm^{-1}, $R = 0.071$, $R_w = 0.211$. Crystallographic data in CIF format has been deposited at the deposition numbers 600523, 600524, and 600525 of CCDC.

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