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Spin-crossover Change from Gradual to Abrupt Types for an Iron(III) Complex

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Iron(III) spin-crossover compound with acpa ligand [Fe(acpa)$_2$]ClO$_4$ (**1**) was prepared and characterized by single-crystal X-ray diffraction, Mössbauer spectra, and magnetic susceptibilities, where acpa is a tridentate ligand derived from acetylacetone and 2-aminomethylpyridine. The iron(III) compound **1** displayed a structural phase transition at 250 K, and the spin-crossover behavior for **1** changed from gradual to abrupt before and after the structural phase transition.

The design of molecules that could be utilized for information processing and information storage is a main challenge in molecular materials science. Molecules that would be suitable for such applications must exhibit bistability, which can be defined as the property of a molecular system that allows it to exist in two different electronic states over a certain range of external perturbation. A typical example of a molecular species that exhibits such a molecular bistability is spin-crossover (SCO) compounds. Since the discovery of the first SCO compound,[1] a variety of SCO compounds exhibiting bistability between the high-spin (HS) and low-spin (LS) states have been reported.[2]

Generally, the relaxation times of the HS and LS spin states for iron(III) SCO compounds are longer than those for iron(II) SCO compounds by several orders of magnitude.[3] Therefore, it is often the case that iron(II) SCO compounds show abrupt spin transition with hysteresis while iron(III) compounds tend to show gradual spin equilibrium. Previously, we found SCO iron(III) compounds exhibiting spin transition with hysteresis.[4,5] We have suggested that the introduction of strong intermolecular interactions in molecular compounds leads to larger structural change and slow spin relaxation between HS and LS states.

SCO iron(III) compounds [Fe(acpa)$_2$]X (X = PF$_6$ and BPh$_4$, where acpa is a tridentate Schiff-base ligand derived from acetylacetone and 2-aminomethylpyridine), show gradual SCO behaviors and exhibit the spin equilibrium phenomenon with fast spin relaxation time.[6–8] On the other hand, SCO iron(III) compound [Fe(acpa)$_2$]NO$_3$ shows gradual SCO behavior but exhibits slow spin relaxation.[6] Here, we synthesized new compound: [Fe(acpa)$_2$]ClO$_4$ (**1**). The single crystals were obtained, the crystal structures of the compounds were investigated, and the magnetic properties were also studied. We succeeded in observing the change of SCO behaviors from gradual to abrupt after structural phase transition for compound **1** (hereafter designated gradual SCO behavior as complex **1·g** and abrupt as **1·a**, respectively).

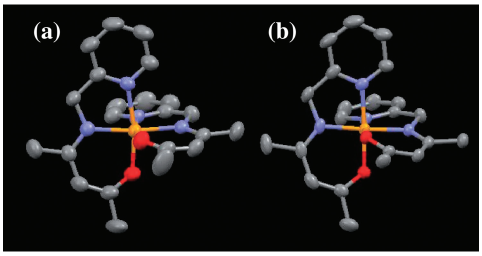

Figure 1. ORTEP view of (a) **1·g** at 298 K and (b) **1·a** at 200 K showing 50% probability displacement ellipsoids. All hydrogen atoms are omitted for clarity.

The single crystals suitable for X-ray diffraction of **1·g** were isolated by slow diffusion in methanolic solutions. The compound **1·g** crystallizes in the monoclinic $P2/n$ space group at room temperature (Figure 1a).[9] The single-crystal X-ray analysis of **1·g** revealed that the iron(III) atoms are octahedrally coordinated by four nitrogen atoms and two oxygen atoms in two acpa ligands, i.e., an N$_4$O$_2$ donor set. The Fe–O distances (1.92 Å) are shorter than the Fe–N(imine) distances (2.05 Å), and the Fe–N(imine) distances are shorter than the Fe–N(pyridine) distances (2.11 Å). The values of the bond lengths are consistent with those typical for HS iron(III) compounds. Two tridentate ligands are found to be perpendicular to one another. When the single crystal **1·g** was cooled slowly to 200 K, the crystal system was changed to the triclinic $P\bar{1}$ space group.[10] The single-crystal X-ray analysis of **1·a** also revealed (Figure 1b) that the structure of **1·a** is similar to that of **1·g** except for bond lengths. The Fe–O, Fe–N(imine), and Fe–N(pyridine) average distances are 1.89, 1.92, and 1.97 Å, respectively. The values of the bond lengths are consistent with those typical for LS iron(III) compounds.

The structural phase transition for **1** was found to be an exothermic peak at 250 K in the differential scanning calorimetry (DSC) measurement (Figure S1) on cooling, and after the transition, no peak was observed at 250 K on heating.[11] Powder XRD measurement suggested that the pattern for **1·g** at room temperature was very different from that for **1·a** at 200 K (Figure S2).[11] It is thought that a large structure phase transition occurred at 250 K.

The temperature dependence of the magnetic susceptibility for the compound **1·g** was measured in the form of the $\chi_m T$ versus T curve, where χ_m is the molar magnetic susceptibility, and T is the temperature. The compound **1·g** exhibited gradual SCO behavior in the temperature range of 5–360 K (Figure 2).

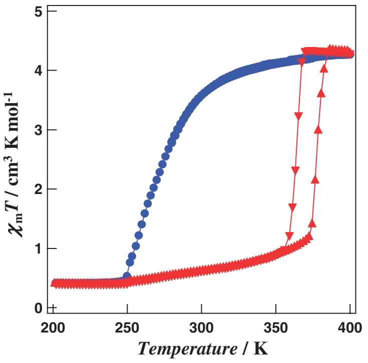

Figure 2. $\chi_m T$ versus T plots for **1·g** and **1·a**. Sample was cooled from 400 to 200 K (●), then warmed from 200 to 400 K (▲), and re-cooled from 400 to 200 K (▼) at a rate of 1 K min^{-1}.

The $\chi_m T$ value for **1·g** gradually decreases from 4.29 to 0.41 cm^3 K mol^{-1} at 200 K, and the small transition of the $\chi_m T$ value was observed without thermal hysteresis at 250 K. The small transition corresponds to the structural phase transition observed in DSC and powder XRD measurements (Figures S3 and S4).[11]

After structural phase transition, the $\chi_m T$ value for **1·a** slightly increased from 0.41 cm^3 K mol^{-1} at 200 K to 1.14 cm^3 K mol^{-1} at 370 K on heating. On further heating, the $\chi_m T$ value increased abruptly at $T_{1/2}\uparrow = 378$ K to 4.29 cm^3 K mol^{-1} at 400 K, showing the spin transition from LS to HS states. On cooling, $\chi_m T$ abruptly dropped at $T_{1/2}\downarrow = 365$ K, showing the spin transition from HS to LS states. This magnetic behavior shows that compound **1·a** exhibits a spin transition with thermal hysteresis ($\Delta T = 13$ K).

Mössbauer spectrum measured before structural phase transition at 298 K reveals a narrow quadrupole-split doublet (quadrupole splitting $Q.S. = 0.73$ mm s^{-1}, isomer shift $I.S. =$ 0.25 mm s^{-1}), representing the iron(III) HS state (Figure 3a). The asymmetry doublet results from bond anisotropy. When the temperature is cooled to 78 K, the spectrum shows a wide quadrupole-split doublet ($Q.S. = 2.18$ mm s^{-1}, $I.S. = 0.20$ mm s^{-1}), representing the iron(III) LS state (Figure 3b). When the temperature is raised again to 298 K, the iron(III) LS state is also observed with $\Delta Q = 2.06$ mm s^{-1}; $\delta = 0.12$ mm s^{-1}. These Mössbauer spectra are consistent with the magnetic properties described above.

Through the careful investigation of the intermolecular arrangement of the compounds **1·g** and **1·a**, it was found that the compound **1·g** does not have any strong intermolecular interactions (Figure 4a). On the other hand, the crystal packing of compound **1·a** is very tight because of the strong π–π intermolecular interaction between the acpa ligands (Figure 4b). The absence of strong intermolecular interactions in compound **1·g** can explain the gradual SCO behabior, while compound **1·a** having strong interaction exhibits abrupt spin transition with thermal hysteresis loop.

In summary, we have shown that iron(III) SCO compound [Fe(acpa)$_2$]ClO$_4$ (**1**) with a structural phase transition at 250 K displays unique magnetic properties. The iron(III) compound **1·g** before the structural phase transition exhibits gradual SCO behavior. On the other hand, compound **1·a** after structural phase transition exhibits abrupt spin transition with thermal hysteresis.

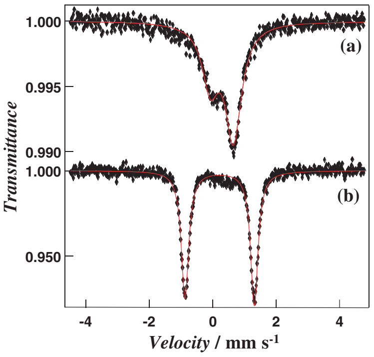

Figure 3. Mössbauer spectra for **1·g** and **1·a**. (a) Spectrum for **1·g** before structural phase transition at 298 K. (b) Spectra after structural phase transition at 78 K.

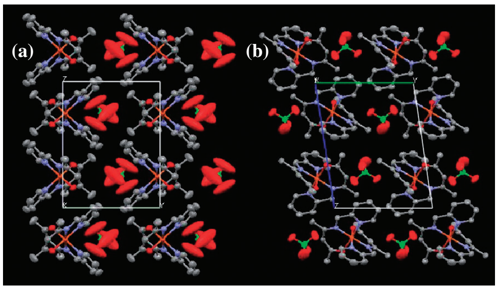

Figure 4. Crystal packing views (a) **1·g** at 298 K and (b) **1·a** at 200 K.

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9 X-ray crystallographic data for **1·g** at 293 K ($C_{11}H_{12}O_3N_2Cl_{0.5}Fe_{0.5}$): fw 265.88, violet block (0.3 × 0.2 × 0.2 mm^3), monoclinic, space group $P2/n$, $a = 10.067(5)$, $b = 9.810(5)$, $c = 13.725(5)$ Å, $\beta = 112.079(5)°$, $V = 1256.0(10)$ Å^3, $Z = 4$, $D_{\rm calcd} = 1.406$ g cm^{-3}, $R_1 =$ 0.0831 ($I > 2.0\sigma(I)$), $R_w = 0.2278$.
10 X-ray crystallographic data for **1·a** at 200 K ($C_{22}H_{24}O_6N_4Cl_1Fe_1$): fw 531.75, violet block (0.3 × 0.2 × 0.2 mm^3), monoclinic, space group $P\bar{1}$, $a = 9.306(3)$, $b = 9.870(3)$, $c = 13.252(4)$ Å, $\alpha = 81.410(5)$, $\beta = 74.705(4)$, $\gamma = 89.410(5)°$, $V = 1160.3(6)$ Å^3, $Z = 2$, $D_{\rm calcd} =$ 1.522 g cm^{-3}, $R_1 = 0.0540$ ($I > 2.0\sigma(I)$), $R_w = 0.1534$.
11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.