Novel 2D Interpenetrated Structure and Occurrence of the Spin-crossover Phenomena of Assembled Complexes, $Fe(NCX)_2(bpp)_2$ (X = S, Se, BH_3; bpp = 1,3-Bis(4-pyridyl)propane)

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Assembled complexes, $Fe(NCX)_2(bpp)_2$ (X = S, Se, BH_3; bpp = 1,3-bis(4-pyridyl)propane), have been synthesized. $Fe(NCS)_2(bpp)_2$ had a novel 2D interpenetrated structure and showed a temperature-independent HS state, while $Fe(NCSe)_2(bpp)_2$ and $Fe(NCBH_3)_2(bpp)_2$ exhibited a slight decrease in $\chi_M T$ and a complete spin-crossover phenomenon ($T_{1/2}$ = 123 K), respectively.

Since the first discovery of spin-crossover material,[1] chemists have investigated the synthesis and nature of various kinds of spin-crossover materials. Above all, self-assembled complexes containing organic ligands and transition-metal ions with the $3d^n$ ($4 \le n \le 7$) electron configuration have great interest because of their diverse magnetic phenomena, assembled structures, potential abilities, etc.[2–6] Because occurrence of spin-crossover phenomena of assembled complexes has close relation to their assembled structures, the construction of functional assembled structures has intensive interests.[3–6] Some assembled complexes with flexible bridging-ligand 1,3-bis(4-pyridyl)propane (bpp) which has three methylenes, have been discovered to show interesting structure.[7,8]

Recently, we have synthesized assembled iron complexes $Fe(NCX)_2(bpa)_2\cdot$(guest) (X = S, Se, BH_3; bpa = 1,2-bis(4-pyridyl)ethane; guest = biphenyl, 1,4-dichlorobenzene, diphenylmethane, 2-nitrobiphenyl).[9–11] This bridging-ligand bpa has anti–*gauche* isomer; therefore, the isomerism contributes greatly to assembled structure, i.e., *anti* isomer forms 3D interpenetrated or 2D grid structure, *gauche* isomer forms 1D structure.[9,12] Moreover, we revealed that spin-crossover phenomena appeared from the tightened structure by enclathrating guest molecule.[10] In the present study, guest-free assembled iron complexes $Fe(NCX)_2(bpp)_2$ (X = S, Se, BH_3; bpp = 1,3-bis(4-pyridyl)propane) having flexible bridging-ligand bpp have been synthesized to show novel structure and spin-crossover phenomena.

$Fe(NCS)_2(bpp)_2$ (**1**) and $Fe(NCSe)_2(bpp)_2$ (**2**) were obtained by diffusion method from $FeSO_4\cdot 7H_2O$, while $Fe(NCBH_3)_2(bpp)_2$ (**3**) was obtained by the same method from $Fe(NCBH_3)_2Py_2$ (Py = pyridine).[13]

X-ray structural analysis at room temperature revealed a novel structure.[14,17] The structure of complex **1** showed a distorted octahedral geometry by coordination of the four N atoms of bpp and the two N atoms of NCS^- in the *trans* position. The Fe–N distances (2.107–2.240 Å) suggest Fe^{II} HS state at room temperature.

The projection of complex **1** to *ab* plane is shown in Figure 1a. This sheet consisted of two separate grids, and they are interpenetrated to each other. This sheet, however, is not 3D but novel 2D sheet, i.e., the two sheets are intertwined like knitwear. The intertwined sheets are piled up to form assembled structure (Figure 1b).

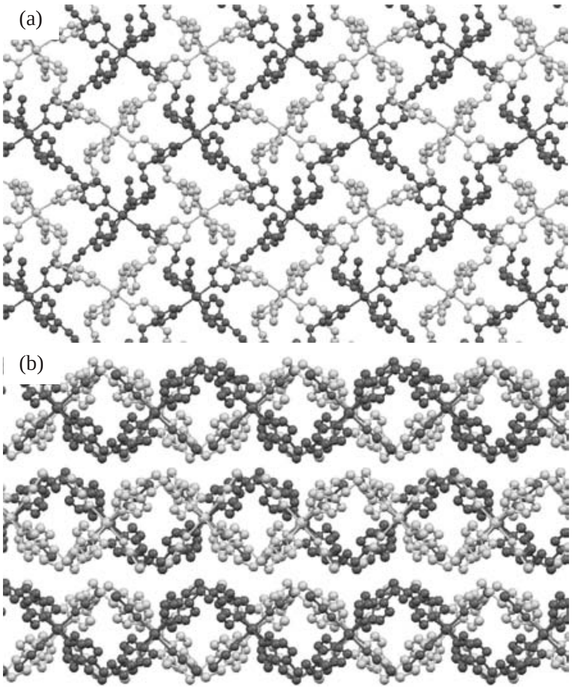

Figure 1. The projections of complex **1** to *ab* plane (a) and *a* axis (b).

Paying attention to isomerism of coordinated bpp, complex **1** had four isomers: *anti–anti*, *anti–gauche*, *gauche′–gauche*, and *gauche–gauche′* isomer, but *anti–gauche′* and *gauche–gauche* isomer can not be seen. In addition, *gauche′–gauche* and *gauche–gauche′*, *anti–gauche* and *anti–gauche′* are enantiomers to each other, respectively.

We have obtained the powder X-ray diffraction patterns of the present complexes.[17] The diffraction positions of **1** corresponded to those of simulation from the present analyzed 2D interpenetrated structure, but diffraction intensities except for (002) [$2\theta = 9.50°$] and (004) [$2\theta = 18.96°$] were much weaker. This originates from the selective orientation of 2D sheets. Complex **2** did not show the diffractions of (002) and (004) from the 2D sheets, suggesting that the assembled structure of **2** be not similar to that of **1**. The diffraction pattern of complex **3** was similar to that of **1** and shifted to lower angle direction: (002) [$2\theta = 9.14°$]; (004) [$2\theta = 18.34°$]. Therefore, this result may suggest that the assembled structure of complex **3** be similar to

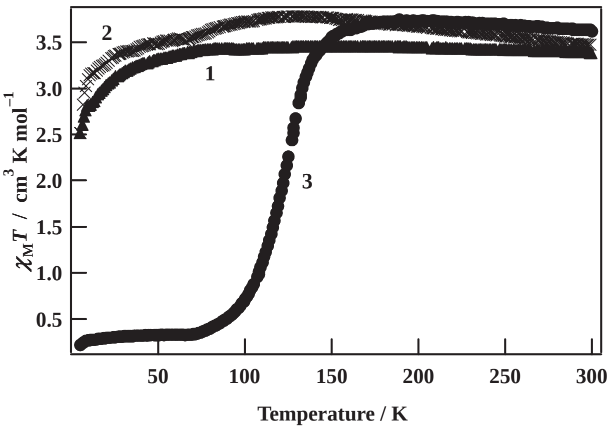

Figure 2. The magnetic susceptibilities of complexes **1**, **2**, and **3**. The scan rates are 3 K min^{-1}.

that of **1** and increases distance between layers.

The 5–300 K magnetic susceptibilities of the titled complexes were obtained on a SQUID magnetometer (Figure 2). Complex **1** did not show a spin-crossover phenomenon. $\chi_M T$ is nearly constant (ca. 3.5 cm^3 K mol^{-1}), suggesting Fe^{II}-HS state, and a decrease of the magnetic susceptibility with decreasing temperature may suggest a weak antiferromagnetic interaction between sheets and/or single-ion zero-field splitting. By changing anion from NCS to NCSe partial decrease in $\chi_M T$ was observed maybe because of thermal quenching below 64 K.[15] And then by changing to NCBH$_3$, complete change was observed, i.e., 3.7 cm^3 K mol^{-1} (Fe^{II}-HS state) at room temperature decreased to almost zero (Fe^{II}-LS state) by cooling, suggesting a spin-crossover phenomenon. This trend does not contradict the larger ligand field of NCBH$_3$ compared with NCS.[16] The change is a gradual one ($T_{1/2} = 123$ K) and the hysteresis was not observed. In relation to this phenomenon, the pale green at room temperature changed to dark red by cooling **3** with liq. N$_2$.

Mössbauer spectra at 298 and 78 K of complex **3** are shown in Figure 3. A remarkable decrease in absorption at room temperature was observed compared with the case of bpa. In such a case, a trace amount of impurities sometimes appears in the spectrum, which will explain the small absorption around 0 mm/s. The Mössbauer spectrum at 298 K was observed to show a main doublet signal with 1.06 mm/s of IS and 0.44 mm/s of QS, showing Fe^{II}-HS, while that at 78 K indicates a significant decrease in IS (0.52 mm/s) and a singlet corresponding to Fe^{II}-LS. And the small amount of Fe^{II}-HS coexists. These spectra are consistent with the magnetic susceptibility.

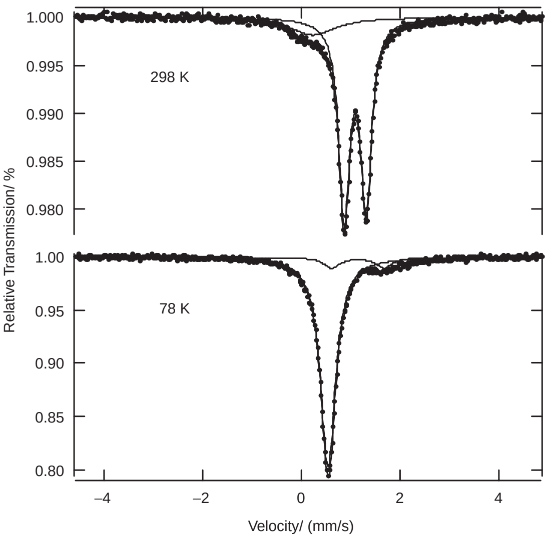

Figure 3. The Mössbauer spectra at 298 and 78 K of complex **3**.

In summary, we have synthesized assembled iron complexes Fe(NCX)$_2$(bpp)$_2$ (X = S, Se, BH$_3$) and Fe(NCS)$_2$(bpp)$_2$ has a novel 2D interpenetrated structure. Fe(NCS)$_2$(bpp)$_2$ showed a temperature-independent HS state, while Fe(NCSe)$_2$(bpp)$_2$ with different structure showed a partial transition and Fe(NCBH$_3$)$_2$(bpp)$_2$ with the same structure was observed to show a complete spin-crossover phenomenon ($T_{1/2} = 123$ K). The present bpp complexes showed spin-crossover phenomena without guest molecule, which shows a big contrast with the bpa complexes. Further studies on the synthesis of single crystal of complex **3** and spin-crossover behaviors of assembled complexes enclathrating organic guest molecule are ongoing.

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13 Anal. Calcd for C$_{28}$H$_{28}$N$_6$S$_2$Fe: C, 59.15; H, 4.96; N, 14.78; S, 11.28%. Found for **1**: C, 59.17; H, 4.94; N, 14.79; S, 11.03%. Anal. Calcd for C$_{28}$H$_{28}$N$_6$Se$_2$Fe: C, 50.77; H, 4.28; N, 12.69%. Found for **2**: C, 50.78; H, 4.30; N, 12.69%. Anal. Calcd for C$_{28}$H$_{34}$N$_6$B$_2$Fe: C, 63.20; H, 6.44; N, 15.80%. Found for **3**: C, 62.86; H, 6.42; N, 15.77%.
14 Crystal Data of **1**: C$_{28}$H$_{28}$N$_6$S$_2$Fe; Formula weight 568.55; Space group $P2_1/n$; $a = 18.7818(25)$; $b = 16.5699(22)$; $c = 20.7087(28)$ Å; $\beta = 115.5620(20)°$; $V = 5861.63(136)$ Å^3; $Z = 8$; $R/wR = 0.0602/0.1848$.
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17 Supporting Information is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/index.html.