

Occurrence of the Spin-crossover Phenomenon of Assembled Complexes, Fe(NCX)₂(bpa)₂ (X = S, BH₃; bpa = 1,2-Bis(4-pyridyl)ethane) by Enclathrating Organic Guest Molecule

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Two assembled complexes, Fe(NCX)₂(bpa)₂ (X = S, BH₃; bpa = 1,2-bis(4-pyridyl)ethane), enclathrating biphenyl or 1,4-dichlorobenzene have been synthesized, whose skeletons are 1D chain, and are revealed to show spin-crossover phenomenon. Transition temperature changes depending on anion and guest molecules.

Spin-crossover materials have been investigated since 1931 of the first observation.¹ Some transition-metal ions with the 3dⁿ (4 ≤ n ≤ 7) electron configuration may show a spin-crossover phenomenon. In the Fe(II) spin-crossover system, spin changes between low-spin (LS; S = 0) and high-spin (HS; S = 2) states. The fundamental origin of the spin-crossover phenomenon is molecule, but the shape of the temperature dependence of the high-spin molar fraction depends strongly on the intermolecular interactions. The basic idea for the control of the transition temperature and the cooperativity in spin transition is the replacement of molecular crystals by polymers.^{2,3} Therefore, spin-crossover phenomenon in the assembled complexes becomes an important problem.^{4,5} These assembled complexes may have a vacancy and usually a solvent molecule is included in the vacancy. It is known that spin transition can be affected by the formation of solvates.⁶ In the rare case, the ligand itself is also included.⁷ There is a possibility of occurrence of the spin-crossover phenomenon of assembled complexes by enclathrating organic molecule. We have already confirmed that the third organic molecule is included to the assembled iron complexes. ⁵⁷Fe Mössbauer spectroscopy revealed that [Fe₂(NCS)₂(bpy)₄](biphenyl)₅, [Fe(NCS)₂(bpa)₂](biphenyl)₂, and [Fe(NCSe)₂(bpa)₂](biphenyl) remained in the high-spin Fe^{II} state, while the QS values changed depending on the structure.⁸ It is important to synthesize assembled coordination polymer using 1,2-bis(4-pyridyl)ethane (bpa) as bridging ligand, because the ligand has anti-gauche isomer, therefore, there is a possibility to have a variety of supramolecular isomer depending on the isomer of bpa.⁹ It is already known that the guest-free Fe(NCS)₂(bpa)₂ shows temperature-independent HS state.¹⁰ In the present study, the inclusion of organic compounds to Fe(NCX)₂(bpa)₂ was attempted and was confirmed using X-ray structural analysis and the spin change was investigated by ⁵⁷Fe Mössbauer spectroscopy and SQUID measurement.

Inclusion compounds were obtained by mixing biphenyl or 1,4-dichlorobenzene in the preparation process of the assembled iron complexes with bpa as bridging ligand.¹¹ Single crystals were obtained by diffusion method. The structures are stable

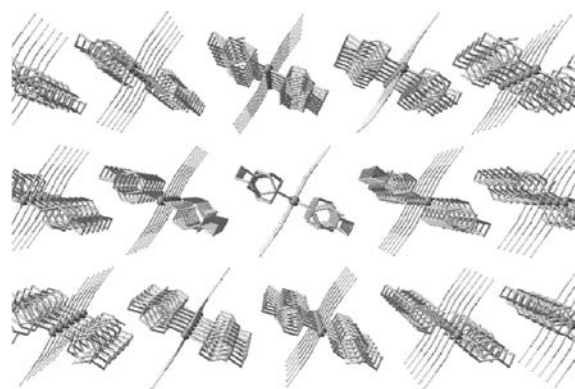


Figure 1. Packing view of **1** at room temperature. Guest molecules are omitted for clarity.

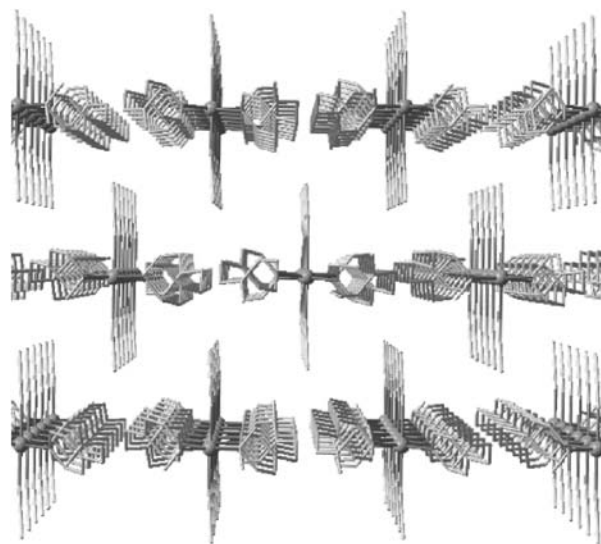


Figure 2. Packing view of **2** at room temperature. Guest molecules are omitted for clarity.

even at room temperature. This stability is characteristic of the present enclathrated complexes, because solvate assembled complexes are unstable due to desolvation. Yellow color at room temperature changed to dark red by cooling the sample with liq. N₂. X-ray structural analysis at room temperature revealed the composition of [Fe(NCS)₂(bpa)₂](1,4-dichlorobenzene)₂ (**1**) and [Fe(NCBH₃)₂(bpa)₂](biphenyl) (**2**).¹² Figures 1 and 2 show packing view of **1** and **2**, respectively. The frame of

Table 1. Mössbauer parameters

Sample	T/K	$IS^a/mm\ s^{-1}$	$QS/mm\ s^{-1}$	$\Gamma/mm\ s^{-1}$	Relative area/%
1	298	1.06	1.79	0.24	100
	78	1.16	2.38	0.28	84
		0.51	0.00	1.06	16
2	298	1.07	0.70	0.37	100
	78	0.46	0.00	0.39	100

^aRelative to iron foil.

$Fe(NCX)_2(bpa)_2$ ($X = S, BH_3$) is 1D chain type having gauche isomer of bpa. It was confirmed that the guest molecule is actually included. There is no significant change in Fe–N distances (2.107(2), 2.229(2), and 2.231(2) Å for **1**, 2.110(7), 2.117(7), 2.182(6), 2.197(6), 2.212(6), and 2.226(6) Å for **2**) compared with guest-free $Fe(NCS)_2(bpa)_2$. The distances suggest Fe^{II} HS state at room temperature.

⁵⁷Fe Mössbauer spectra of **1** and **2** showed a temperature dependence. The parameters are summarized in Table 1. Both spectra at room temperature showed about 1.1 mm s⁻¹ of isomer shift (IS) value. This reveals the Fe^{II} HS state at room temperature. The quadrupole splitting (QS) value of **2** is about half of **1**. Similar change in QS is seen in the guest-free assembled complexes.⁹ At 78 K, 16% of low-spin species superimposed to the main Fe^{II} HS species in **1**. The spectrum of **2** at 78 K shows only one singlet ($IS = 0.46\ mm\ s^{-1}$), suggesting perfect low-spin state at 78 K. The Mössbauer results suggest spin-crossover behavior.

The variable-temperature magnetic susceptibility measurements give evidence for an Fe^{II} spin-crossover behavior between HS and LS states. The magnetic behavior of $[Fe(NCX)_2(bpa)_2] \cdot guest$ is shown in Figure 3 in the form of the $\chi_M T$ versus T curves, χ_M being the molar magnetic susceptibility and T the temperature. The measurement was performed at increasing temperatures after rapid cooling. After reaching 300 K, the measurement was done at decreasing temperatures. And then increasing process was performed again, and this shows the same feature with decreasing process in **1**. At high temperatures, $\chi_M T$ is equal to about 3.70 cm³ K mol⁻¹, which lies within the expected range for a HS Fe^{II} . At low temperatures, the value is almost zero, suggesting Fe^{II} LS. **1** shows perfect transition to low-spin

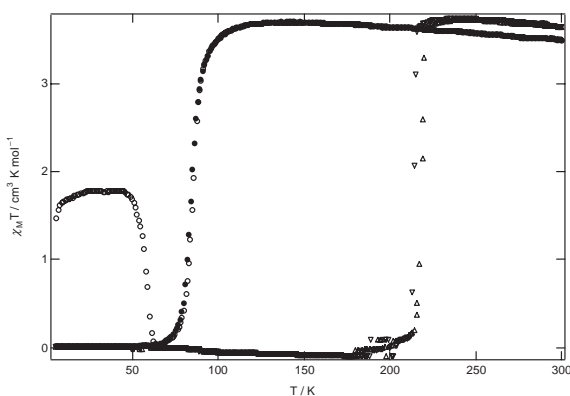


Figure 3. Magnetic susceptibility of **1** (circle) and **2** (triangle). Open circles and triangles denote the heating process after rapid cooling, while solid circles and inverted triangles denote the cooling process. The scan rates are 3 K m⁻¹.

state by gradual cooling, while about 50% of HS species survive by rapid cooling. The metastable HS state becomes LS state by increasing to ca. 60 K and then spin-crossover phenomenon occurs with increasing temperature. The transition temperatures are 84 and 216 K for **1** and **2**, respectively. The difference in the transition temperature may reflect the difference in the ligand field strength between the NCS and NCBH₃ ligands for each complex.¹³ The transition-temperature regions from HS to LS state are relatively narrow for both complexes. The transition does not show any hysteresis in **1**, while **2** reveals abrupt transition and hysteresis loop with a width of about 5 K. Usually, the spin-crossover behaviors for the complexes having NCBH₃ are more gradual than those for the complexes having NCS group.¹³ But the present case, **2** shows sharp and abrupt transition with hysteresis, which reveals a cooperativity. Usually cooperativity occurs from the intermolecular interaction. In the case of **2**, we observed heat anomaly at spin-transition temperature using DSC, showing phase transition. As the 1D chain structure is not different between them and the large interaction of chain with guest molecule is not observed, it is useful to compare the stacking of the 1D chain between **1** and **2** (Figures 1 and 2). In the case of **1**, the 1D chain is inclined and the sheets of inclined chains are stacked. On the other hand, in the case of **2**, the 1D chain is not inclined and the sheets of chains are stacked. The difference may explain the hysteresis.

In conclusion, we have synthesized two assembled complexes enclathrating guest molecule. These complexes showed spin-crossover phenomenon by including guest molecule. It is thought that the interaction of iron d orbital with the orbital of ligand will change slightly as pressure effect by the inclusion of organic molecule. This may be the reason why the inclusion complexes revealed spin-crossover phenomena. The transition temperature is also controlled by changing guest molecule and anion.

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- Anal. Calcd for C₃₈H₃₂Cl₄FeN₆S₂: C, 54.69; H, 3.87; N, 10.07; S, 7.69%. Found for **1**: C, 54.49; H, 4.06; N, 10.30; S, 7.54%. Calcd for C₃₈H₄₀B₂FeN₆: C, 69.34; H, 6.13; N, 12.77%. Found for **2**: C, 69.11; H, 6.18; N, 12.79%.
- Crystal Data: C₃₈H₃₂Cl₄FeN₆S₂; Formula weight, 834.47; Space group, C2/c; $a = 20.468(4)$; $b = 9.8853(19)$; $c = 20.399(4)$ Å; $\beta = 101.634(4)^\circ$; $V = 4042.7(13)$ Å³; $Z = 4$; $D_{\text{calcd}} = 1.371\ g\ cm^{-3}$; $R/wR = 0.0365/0.0973$. C₃₈H₄₀B₂FeN₆; Formula weight, 658.23; Space group, P $\bar{1}$; $a = 10.587(2)$; $b = 20.026(4)$; $c = 20.227(4)$ Å; $\alpha = 60.323(3)$; $\beta = 89.990(4)$; $\gamma = 90.004(4)^\circ$; $V = 3276.1(13)$ Å³; $Z = 4$; $D_{\text{calcd}} = 1.173\ g\ cm^{-3}$; $R/wR = 0.0733/0.3049$.
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