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Spiral Assembly of the 1D Chain Sheet of $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$ (biphenyl) (bpa = 1,2-bis(4-pyridyl)ethane) and its Stepwise Spin-Crossover Phenomenon

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Abstract: The assembled complex, $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$, enclathrating biphenyl has been synthesized, the skeleton of which is a 1D chain. Several 1D chains gather together to form 1D chain sheet. The 1D chain sheet is stacked spirally to form novel spiral assembly. The average Fe-N distances were 2.020(2), 2.083(2), and 2.191(2) Å at 100, 175, and 298 K, respectively, reflecting spin-state change of the iron ion. The assembly showed a stepwise spin-crossover phenomenon.

Keywords: assembled complexes; spiral assembly; *anti-gauche* conformer; spin crossover

1. Introduction

Spin-crossover materials have been investigated since 1931, the time of their first observation [1]. Some transition-metal ions with the $3d^n$ ($4 \leq n \leq 7$) electron configuration may show a spin-crossover

(SCO) phenomenon. In the Fe^{II} SCO system, spin state changes between low-spin (LS; $S = 0$) and high-spin (HS; $S = 2$) states. The prerequisite for the SCO phenomenon is an intermediate field strength of the ligand in the 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 cooperativity in spin transition is the replacement of molecular crystals by polymers [2,3]. Therefore, the assembled complexes represent a special interest for the SCO phenomenon. The design and construction of various structures for assembled complexes have attracted great interest from many chemists because of their potential abilities for selective inclusion and transformation of molecules [4–13]. These assembled complexes may have 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 [14]. In the rare case, the ligand itself is also included [15]. There is a possibility of occurrence of the SCO phenomenon of assembled complexes by enclathrating organic molecules such as biphenyl. 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* conformer. Therefore, there is a possibility to have a variety of supramolecular isomer depending on the conformer of bpa. Actually, *gauche* conformer of bpa formed 1D chain structure, while *anti* conformer formed 2D grid or interpenetrated structure [16,17]. Furthermore, more variety of assembled complexes due to the *anti-gauche* conformer are obtained by using 1,3-bis(4-pyridyl)propane as a bridging ligand [18,19]. It is already known that the guest-free $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$ has a 1D chain structure and shows a temperature-independent high-spin state, while guest-introduced $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$ (biphenyl) has a 1D chain structure, in which all 1D chains are stacked along the same direction (1D assembly), and shows SCO phenomenon [20]. The spin state in 1D assembly changed completely at 220 K with hysteresis. In the present study we obtained novel spiral stacking of 1D chain sheets (spiral assembly) in $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$ (biphenyl) by changing solvent in the synthetic process. The complex also showed an interesting stepwise SCO phenomenon.

2. Experimental Section

2.1. Synthesis

Assembled complex was prepared by diffusion method under the argon atmosphere in order to prevent it from oxidation of Fe^{II} . Spiral assembly of $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$ (biphenyl) was synthesized by diffusion method using MeOH and EtOH as solvent. Bottom layer; $\text{Fe}(\text{NCBH}_3)_2\text{py}_4$ (2 mmol) and L-ascorbic acid in MeOH (20 mL). Middle layer; MeOH and EtOH (40mL). Upper layer; bpa (2 mmol) in EtOH (20 mL). Biphenyl was dissolved in all layers to almost saturation. From this solution, mixture of yellow crystals appeared. Found for spiral assembly: C, 68.95; H, 6.17; N, 12.84%. Anal. Calc. for $\text{C}_{38}\text{H}_{40}\text{B}_2\text{FeN}_6$: C, 69.34; H, 6.13; N, 12.77%.

2.2. Single Crystal X-Ray Structural Analysis

The X-ray diffraction data were collected using a Bruker analytical X-ray systems SMART-APEX diffractometer, equipped with a CCD area detector and graphite-monochromated Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, employing an ω -scan mode (0.3 step) and semiempirical absorption correction on Laue

equivalents. The structure was solved by direct method and refined by full-matrix least squares of all data, using SHELXT-97 software. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and not refined. The measurement was performed at 100, 175, and 298 K.

2.3. ^{57}Fe Mössbauer Spectra

A $^{57}\text{Co}(\text{Rh})$ source in a constant acceleration mode was used for the ^{57}Fe Mössbauer spectroscopic measurements. ^{57}Fe Mössbauer spectra were obtained by using a Wissel Mössbauer spectrometer and a proportional counter at 78 and 298 K. The isomer shift values are referred to a metallic iron foil. The Mössbauer parameters were obtained by a least-squares fitting to Lorentzian peaks.

2.4. Magnetic Measurement

Direct current (DC) magnetic susceptibility measurement was carried out using a Quantum Design MPMS-5S SQUID magnetometer at 5,000 Oe. Variable-temperature measurement was carried out in the temperature range 5–300 K. The temperature sweeping rate was 3 K min^{-1} . Measurement was performed using gel capsule perforated in order not to explode. Sample was stabilized at 300 K and was adjusted to the center before measurement.

3. Results and Discussion

We have already reported 1D assembly of 1D chains (1D assembly) having a guest molecule [17,20]. In the present study, we obtained new assembly of a 1D chain sheet having a guest molecule, in which the 1D chain sheet stacked spirally (see below). It is difficult to gather pure crystals of spiral assembly. A mixture of 1D assembly of 1D chains without a guest molecule, 1D assembly, and spiral assembly coexisted in the crystals from the diffusion method of $\text{Fe}(\text{NCBH}_3)_2\text{py}_4$, bpa, and biphenyl by using MeOH and EtOH as solvent. Mixture of the three crystals depended on the ratio of the diffusion rate. We controlled the diffusion rate by changing the solvent. It is thought that the diffusion rate in the MeOH and EtOH is faster than that in water and EtOH. When the diffusion rate is fast and the concentration of guest molecule is high, the spiral assembly is relatively easily obtained. On the other hand, 1D assembly was obtained by the diffusion method using water and EtOH as solvents and by using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ instead of $\text{Fe}(\text{NCBH}_3)_2\text{py}_4$. In this 1D chain assembly, all 1D chains were stacked along the same direction.

The color of the spiral assembly was yellow. The yellow color of the spiral assembly at room temperature changed to dark red by cooling the sample with liquid N_2 , suggesting SCO phenomenon. The color change in the present spiral assembly is similar to that in 1D assembly which shows SCO phenomenon.

The structure of spiral assembly was determined at 100, 175, and 298 K. The packing view at 298 K is shown in Figure 1. The selected crystal data are summarized in Table 1. The structure was a 1D chain structure with a *gauche* conformer of bpa. Disorder of the methylene in bpa was observed, which is the character in this spiral assembly, while 1D chain assembly did not show the disorder. The assembled structure of the spiral assembly is similar to this. The 1D chains gather together to form a

1D chain sheet. On this 1D chain sheet the next 1D chain sheet is stacked with an angle of 120° . Similarly, the next 1D chain sheet is also stacked with an angle of 120° . The stacking continues like this. This shows a novel spiral stacking of 1D sheet along the 3_1 screw axis. The significant change in the spiral assembly was not observed among the structures determined at three different temperatures except for Fe-N distances.

Figure 1. Packing view of spiral assembly at 298 K.

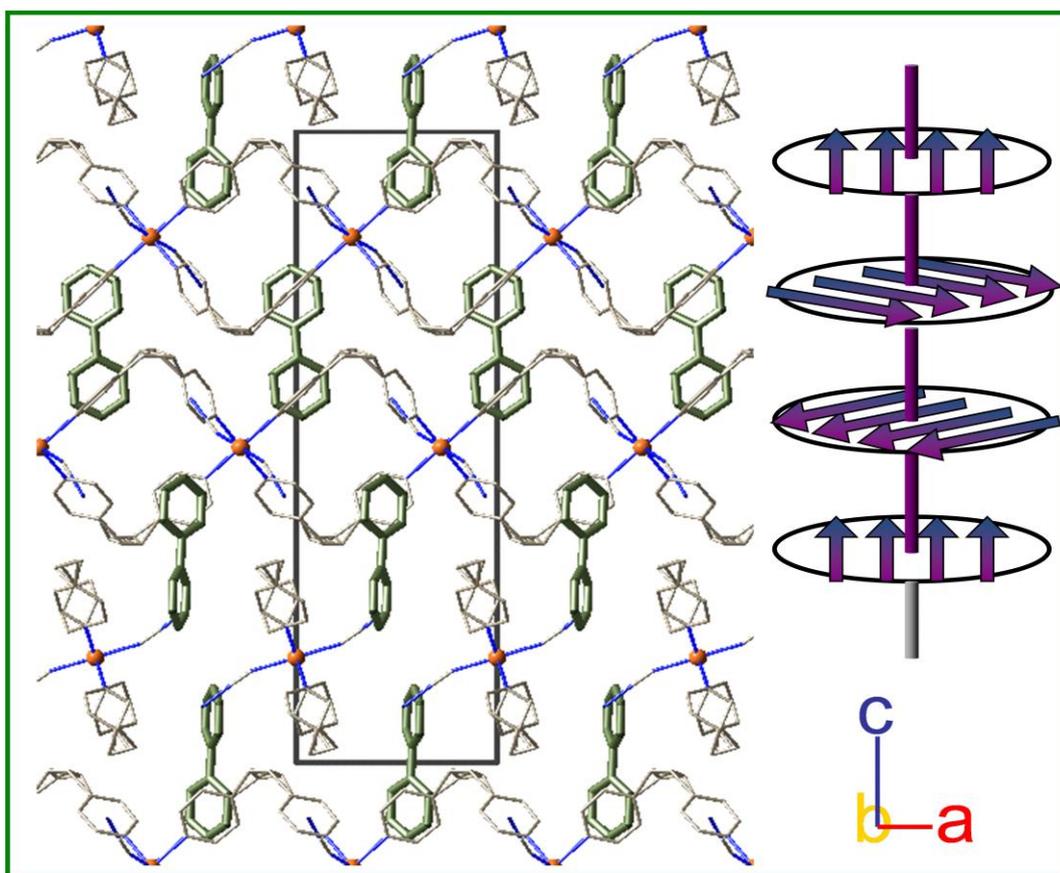


Table 1. Selected crystal data for spiral assembly.

Chemical formula	$C_{38}H_{40}B_2FeN_6$	$C_{38}H_{40}B_2FeN_6$	$C_{38}H_{40}B_2FeN_6$
Formula weight	658.23	658.23	658.23
Crystal system	trigonal	trigonal	trigonal
Space group	$P3_12_1$	$P3_12_1$	$P3_12_1$
$a, b/\text{\AA}$	10.167(5)	10.2293(3)	10.378(3)
$c/\text{\AA}$	29.245(5)	29.499(5)	29.967(12)
$\alpha, \beta/^\circ$	90	90	90
$\gamma/^\circ$	120	120	120
$V/\text{\AA}^3$	2,618.0(19)	2,673.2(7)	2,795.3(16)
T/K	100	175	298
Z	3	3	3
$D_{\text{calc}}/\text{g cm}^{-3}$	1.253	1.227	1.173
R	0.0495	0.0471	0.0569
R_w	0.1133	0.1146	0.1305
Goodness of fit	1.054	1.085	1.037

The average Fe-N distance was 2.020(2), 2.083(2), and 2.191(2) Å at 100, 175, and 298 K, respectively. The change in distance reflects the spin-state change of Fe^{II} from low-spin to high-spin state with increasing temperature, which agrees with the color change. The important point is that only one site of iron atom was observed at all temperatures. This reveals that the spin-state change intermittently occurs in all 1D sheets.

Figure 2 shows the ⁵⁷Fe Mössbauer spectra of the spiral assembly. The ⁵⁷Fe Mössbauer spectrum at 298 K was obtained to show one doublet with 1.04 mm s⁻¹ of isomer shift (IS) and 0.47 mm s⁻¹ of quadrupole splitting (QS), showing Fe^{II} high-spin state. In contrast, the spectrum at 78 K showed almost unresolved doublet with 0.49 mm s⁻¹ of IS and 0.15 mm s⁻¹ of QS, revealing Fe^{II} low-spin state. The results confirmed the SCO phenomenon of the present spiral assembly. The Mössbauer parameters are similar to those of 1D assembly. This reveals the similar coordination environment around iron atom between the two assemblies. Typically, the QS values for Fe^{II} fall within 2–3 mm s⁻¹ [6,21]. The feature of the present complex is the unresolved doublet of Fe^{II} LS state and very low QS value of Fe^{II} HS state, suggesting a good symmetry around the iron atom. The transition temperature of SCO increases when the QS value of Fe^{II} HS state becomes small among the series of the Fe(NCX)₂(bpa)₂ (guest) (X = S, Se, BH₃; bpa = 1,2-bis(4-pyridyl)ethane; guest = biphenyl, 2-nitrobiphenyl, diphenylmethane, or 1,4-dichlorobenzene) [22].

Figure 2. ⁵⁷Fe Mössbauer spectra of the spiral assembly.

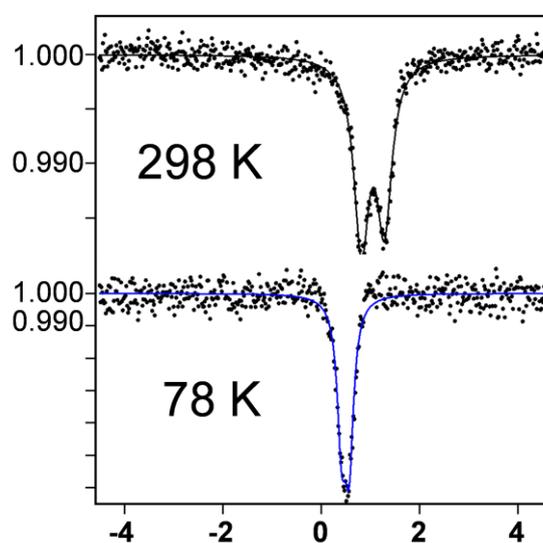
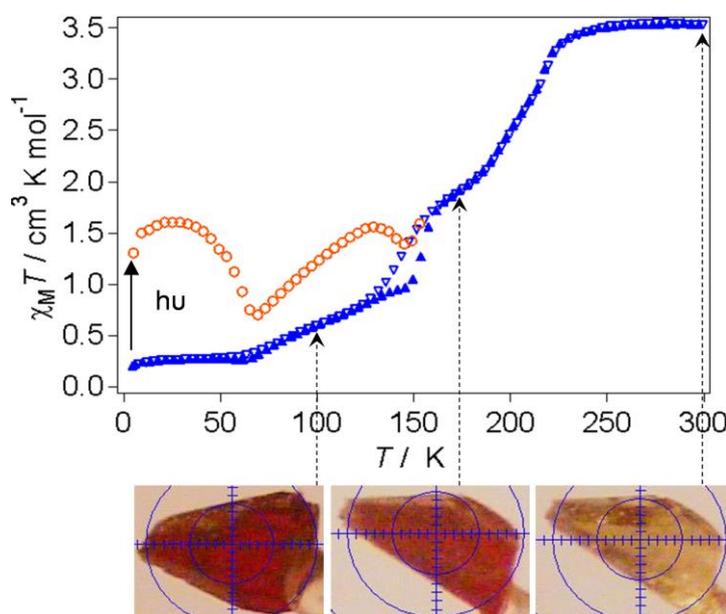


Figure 3 shows the magnetic behavior of the spiral assembly. It can be seen that magnetic susceptibility changes stepwise. The change at 220 K is observed in 1D chain assembly. 1D assembly shows complete SCO phenomenon at 216 K. The separation of the spiral assembly from 1D assembly was very difficult. The ratio of the transition at 220 K to the total change of magnetic susceptibility alters by changing the sample. This might suggest that the slight change at 220 K is due to the impurity of the 1D assembly having biphenyl. The magnetic susceptibility presents a two-step spin conversion with a plateau at around 175 K. At this temperature approximately 50% of irons have changed their spin state. The low-temperature step is more abrupt than high-temperature step and presents a thermal hysteresis. The hysteresis is probably kinetic in origin and could be associated with the order-disorder

transition in the methylene group of the bpa ligand [23]. There are no significant changes among the three points in the results of X-ray structure except for Fe-N distance. The stepwise change in magnetic susceptibility reveals the stepwise spin-crossover phenomenon. At low temperatures, all the iron atoms are in Fe^{II} low-spin state. By increasing the temperature, Fe^{II} low-spin state changes to Fe^{II} high-spin state step by step. It is understood from the results of X-ray structure that the spin-state change intermittently occurs in all 1D sheets. It is well established that the two-step spin crossover can be observed in two cases: (a) coexistence of two crystallographically distinct metal sites at all temperatures [24–27]; (b) appearance of two crystallographically independent metal sites as a result of a crystallographic phase transition [23,28,29]. Recently, a two-step SCO was observed for several systems involving crystallographically unique metal center whatever the temperature. The occurrence of two-step spin crossover has been attributed to random disorder of the HS/LS species at the intermediate state in [30], to the special cross-linked arrangement of the 1D chains in [31], and to the interchain interactions in [32]. By comparing the present results in spiral assembly with those in 1D assembly, it is thought that the spiral assembly having a 3₁ screw axis causes the stepwise spin-crossover phenomenon.

Figure 3. Magnetic susceptibility of the spiral assembly. Solid triangles show the results with increasing temperature, open triangles show the results with decreasing temperature, and open circles show the results after illumination of light.



The present complex showed light induced excited spin state trapping (LIESST). We exposed the light (550 nm) to the sample at 5 K. About half irons reached to the metastable high-spin state. After stopping the exposure, temperature was increased. The magnetic susceptibility decreased to the minimum value at 68 K by the thermal relaxation. But the value is somewhat larger than that observed in thermal change. The value increased with increasing temperature from 68 to 130 K, in which the slope is larger than that of the thermal change, and then decreased to the minimum value around 150 K, suggesting other metastable state. The value increased again and then approached the thermal change. This means that the metastable state reached a stable state around this temperature. The metastable

state shows a more drastic change compared with the change in stable state, maybe because of the looseness of the crystal packing. This can tentatively be suggested to be due to the special spiral assembly.

4. Conclusions

We have already reported 1D chain, 2D grid, and interpenetrated assembled complexes depending on the *anti-gauche* conformer of bpa in $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2$ (guest). In the present study, we added a new assembly of a 1D chain having *gauche* conformer of bpa. The difference between the 1D assembly of the 1D chain structure and the spiral assembly of the 1D chain sheet is only the stacking. The coordination environment around the iron ion and the 1D chain structure itself are the same between the two assemblies except for the disorder of the methylene in bpa. Therefore, it can be concluded that the stepwise spin-crossover phenomenon is due to the novel spiral assembly of the 1D chain sheet.

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