

Article

# Threefold Spiral Structure Constructed by 1D Chains of $[[M(NCS)_2(bpa)_2]\cdot biphenyl]_n$ (M = Fe, Co; bpa = 1,2-bis(4-pyridyl)ethane)

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**Abstract:** Assembled complexes  $[[M(NCS)_2(bpa)_2]\cdot biphenyl]_n$  (M = Fe, Co; bpa = 1,2-bis(4-pyridyl)ethane) have been synthesized because  $[Fe(NCBH_3)_2(bpa)_2\cdot biphenyl]_n$  has a novel threefold spiral structure and shows stepwise spin-crossover phenomenon. We attempted to obtain spiral structures for  $[[Fe(NCS)_2(bpa)_2]\cdot biphenyl]_n$  and  $[[Co(NCS)_2(bpa)_2]\cdot biphenyl]_n$  using a one-step diffusion method, while the reported spiral structure of  $[[Fe(NCBH_3)_2(bpa)_2]\cdot biphenyl]_n$  was obtained by diffusion method after synthesizing Fe(II)-pyridine complex. X-ray structural analysis revealed that  $[[Fe(NCS)_2(bpa)_2]\cdot biphenyl]_n$  and  $[[Co(NCS)_2(bpa)_2]\cdot biphenyl]_n$  had a chiral propeller structure of pyridines around the central metal, and they had a novel spiral structure and chiral space group  $P3_12_1$  without the presence of chiral auxiliaries. It was shown that the host 1D chain, having a chiral propeller structure of pyridines around the central metal along with its concerted interaction with an atropisomer of biphenyl, made a threefold spiral structure.

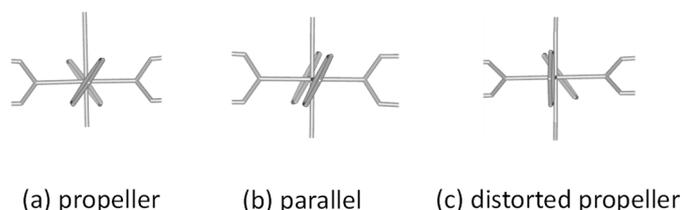
**Keywords:** spiral structure; 1,2-bis(4-pyridyl)ethane; supramolecular coordination polymer; chiral propeller structure; atropisomerism

## 1. Introduction

The first transition metal complexes with configurations  $d^4$ – $d^7$  may exist in either high-spin (HS) or low-spin (LS) state, depending on the ligand field strength. The ground state becomes a HS state in a weak field, while the ground state becomes an LS state in a strong field. The spin state changes between HS and LS states due to external perturbations, such as from changes in temperature, pressure, and light illumination in a medium field [1]. This is called spin-crossover (SCO) phenomenon. Especially in  $d^6$  Fe(II) complexes, spin appears ( $S = 2$ ) and disappears ( $S = 0$ ) depending on the SCO phenomenon, suggesting it acts as a molecular switch [2]. An interesting application is in solvatochromic spin state switching in SCO compounds [3].

The design and construction of various structures for self-assembled complexes have attracted great interest from many chemists. These self-assembled complexes may have a vacancy, and usually a solvent molecule is enclathrated in the vacancy. The bridging ligand itself is also enclathrated in rare cases [4]. It is known that the structure of self-assembled complexes changes by changing the guest molecule. Therefore, the selection of the guest molecule is an important factor in designing the assembled structure.

The SCO of assembled complexes becomes important because a variety of assembled structures are expected. The spin state is affected by guest molecules and the steepness of the transition is affected by the intermolecular interactions. There are many assembled complexes, such as Hoffman type [5–9], triazole-bridged type [10,11], tetrazole-bridged type [12], and bis(pyridyl) type [13]. Among them, we became interested in the complexes bridged by bis(pyridyl) type ligands, because these complexes easily form vacancies. We have studied SCO phenomenon for the complexes bridged by 1,2-bis(4-pyridyl)ethane [14–17], 1,3-bis(4-pyridyl)propane [18,19], 1,4-bis(4-pyridyl)benzene derivatives [20], and 1,4-bis(4-pyridyl)anthracene [21]. By changing the bridging ligand and guest molecule, the local structure is controlled to propeller, parallel type, or distorted propeller (Scheme 1). Such local structure determines whether SCO occurs or not [22,23]. This shows that the ligands can easily approach iron in the chiral propeller type local structure when the spin state becomes an LS state.



**Scheme 1.** Difference in the Fe-pyridine local structures observed in a variety of the assembled  $[\text{Fe}(\text{NCX})_2\text{L}_2]_n$  ( $\text{X} = \text{S}, \text{Se}, \text{and } \text{BH}_3$ ;  $\text{L} = \text{bridging ligand}$ ).

It had been reported that  $[\text{Fe}(\text{NCS})_2(\text{bpa})_2]_n$  has a 1D chain structure and shows HS state [24]. We became interested in  $[\text{Fe}(\text{NCS})_2(\text{bpa})_2]_n$ , because the bpa has an *anti-gauche* conformation and  $\text{NCS}^-$  can be changed with other anionic ligands. We synthesized crystals by diffusion method and obtained several types crystals. We obtained 2D grid structure and 3D interpenetrated structure as well as 1D chain structure [14]. 2D grid structure and 3D interpenetrated structure enclathrated the solvent molecule. The structure changed to a 1D chain structure by desorbing the guest molecule [14]. We thought that the complexes that enclathrated larger guest molecules, such as biphenyl, have a stable structure. Therefore, we have synthesized self-assembled Fe(II) complexes  $[[\text{Fe}(\text{NCX})_2(\text{bpa})_2] \cdot (\text{guest})]_n$  ( $\text{X} = \text{S}, \text{Se}, \text{BH}_3$ ; bpa = 1,2-bis(4-pyridyl)ethane; guest = biphenyl, 1,4-dichlorobenzene, diphenylmethane, 2-nitrobiphenyl). The *anti-gauche* conformer of bpa contributed greatly to the assembled structure, i.e., *anti* conformer-formed 3D interpenetrated or 2D grid structure, and *gauche* conformer-formed 1D chain structure. Moreover, we revealed that SCO phenomena appeared by having enclathrated a guest molecule. The crystal structures and SCO phenomena are summarized in Table 1 [16].  $[[\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  usually had 1D chain structure and showed one-step spin transition [15]. In special cases, the 1D chain self-assembled sheet of  $[[\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  was stacked spirally, having a threefold axis [25], and this spiral structure showed a stepwise spin transition. Stepwise SCO phenomena play an important role in tuning the spin state precisely. Spiral structure is a key point to showing stepwise transition. Therefore, the mechanism for forming spiral structures becomes an important theme. In the present study, new series of self-assembled complexes  $[[\text{M}(\text{NCS})_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  ( $\text{M} = \text{Fe}, \text{Co}$ ) have been synthesized to obtain other novel spiral structure, and we discuss the formation mechanisms.

**Table 1.** Summary of crystal structures and their spin-crossover (SCO) phenomena for  $[[\text{Fe}(\text{NCX})_2(\text{bpa})_2]\cdot(\text{guest})]_n$ .

Anion \ Guest	NCS	NCS <sub>e</sub>	NCBH <sub>3</sub>
biphenyl	2D grid	Linear	Linear
2-nitrobiphenyl	<u>Interpenetrated</u>	<u>Interpenetrated</u>	<u>2D grid</u>
1,4-dichlorobenzene	<u>Linear</u>	<u>Linear</u>	Not included
diphenylmethane	<u>Interpenetrated</u>	<u>Interpenetrated</u>	<u>2D grid</u>

The crystals underlined showed a color change from pale yellow to deep red by cooling with Liq. N<sub>2</sub>. The color change corresponded well with the SCO phenomenon.

## 2. Materials and Methods

$[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  and  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  were obtained by diffusion method from  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  (or  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ) and  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ , respectively.  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  (or  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ) and  $\text{NaNCS}$  were dissolved to distilled water as bottom layer. Biphenyl was dissolved to a mixed solvent of water and EtOH as intermediate layer. Bpa was dissolved to EtOH as upper layer. From the vessel, block-like crystal and plate-like crystal were obtained for  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  and  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ , respectively. Anal. found (calcd)%: for  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ , C, 65.10 (65.70); H, 4.67 (4.93); N, 12.01 (12.10); S, 9.08 (9.23). Anal. found (calcd)%: for  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ , C, 65.42 (65.41); H, 4.81 (4.91); N, 12.14 (12.04); S, 8.42 (9.19).

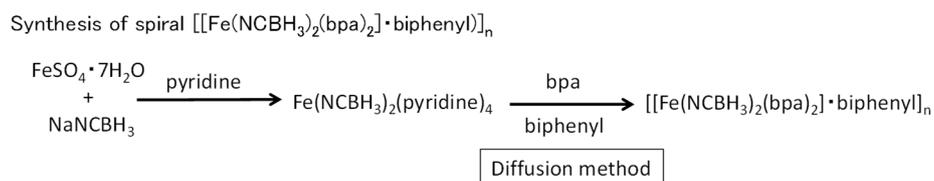
For single crystal X-ray diffraction analysis, all diffraction data were collected by using a Bruker SMART-APEX diffractometer (Bruker, Billerica, MA, USA) equipped with CCD area detector and graphite-monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ,  $\omega$ -scan mode (0.3° steps). Semi-empirical absorption corrections on Laue equivalents were applied. The samples were coated with adhesive to avoid desorption of guest molecules. The structures were solved by direct methods and refined by full-matrix least-squares against  $F^2$  of all data using SHELXL-2014/6 [26]. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (CCDC: 1892503 and 1892504).

## 3. Results and Discussion

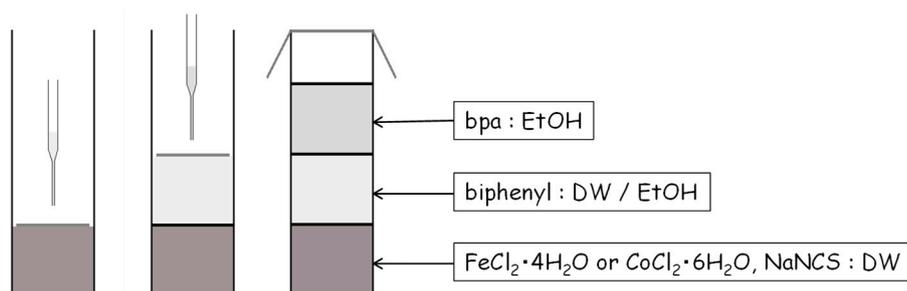
In the synthesis of spiral  $[[\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ , the pyridine complex of Fe(II) was first synthesized and then the diffusion method was used (Scheme 2). In the present study, an easier method was attempted. That is, the diffusion method was used without synthesizing a pyridine complex of Fe(II) (Scheme 2). In the synthesis of iron complex, when  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  was used, a large crystal having spiral structure was obtained. However, it was easily oxidized in the synthetic process. When  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$  was used, a small crystal having spiral structure was obtained and the oxidation was avoided. The spiral structure was not obtained by direct mixing method.

Figure 1 shows an Oak Ridge Thermal-Ellipsoid Plot Program (ORTEP) drawing of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ . The packing view is shown in Figure 2. The crystal data are shown in Table 2. The structure of the complex showed an octahedral geometry by coordination of the four N atoms of bpa and the two N atoms of NCS<sup>-</sup> in the *trans* position. The local structure around iron was chiral propeller type. The biphenyl molecule was enclathrated by  $\text{Fe}(\text{NCS})_2(\text{bpa})_2$  in the ratio of 1:1. The Fe–N<sub>Cs</sub> and Fe–N<sub>Py</sub> distances were 2.092 and 2.232 Å, respectively, suggesting a HS state. In the crystal, the biphenyl molecule showed atropisomerism. We have analyzed the present complexes in single crystal X-ray structural analysis by using the chiral space group  $P3_12_1$  (Flack parameter: 0.022). When analyzing it using  $P3_22_1$ , the Flack parameter becomes 0.9764, suggesting the space group is  $P3_12_1$ . From the result of analysis, it was found that the sign of biphenyl's dihedral angle is different between the two chiral space groups. The structure of biphenyl is shown in Figure 3. The sign of biphenyl's dihedral angle is related to the space group. The configuration of biphenyl was *R* in the

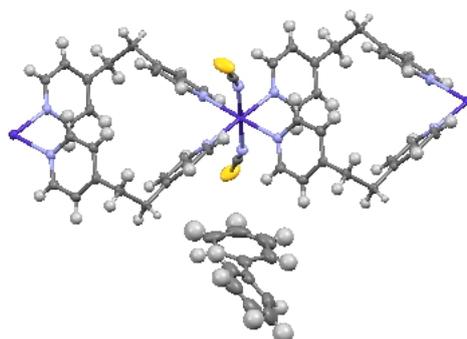
present results. This result may suggest that the chiral assembly is controlled by a chiral propeller-type local structure and biphenyl's atropisomerism.



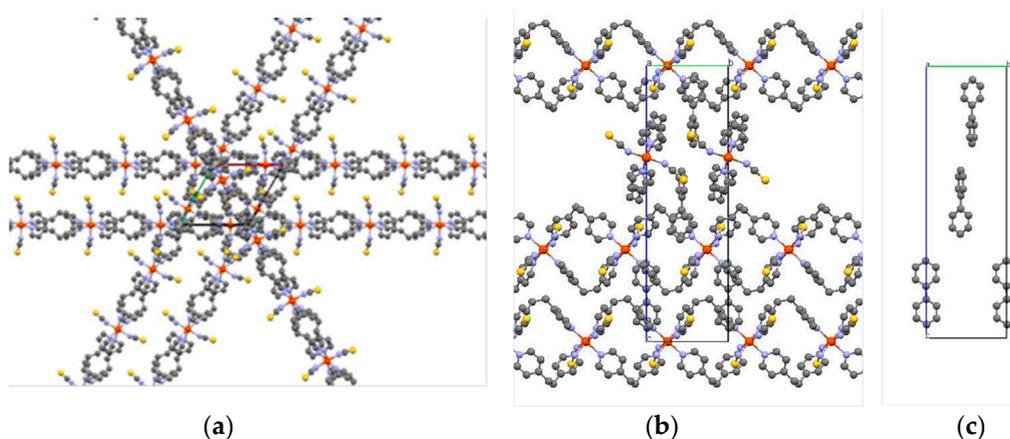
Synthesis of spiral  $[[\text{M}(\text{NCS})_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  (M = Fe, Co)



**Scheme 2.** Synthetic scheme to obtain spiral structure.



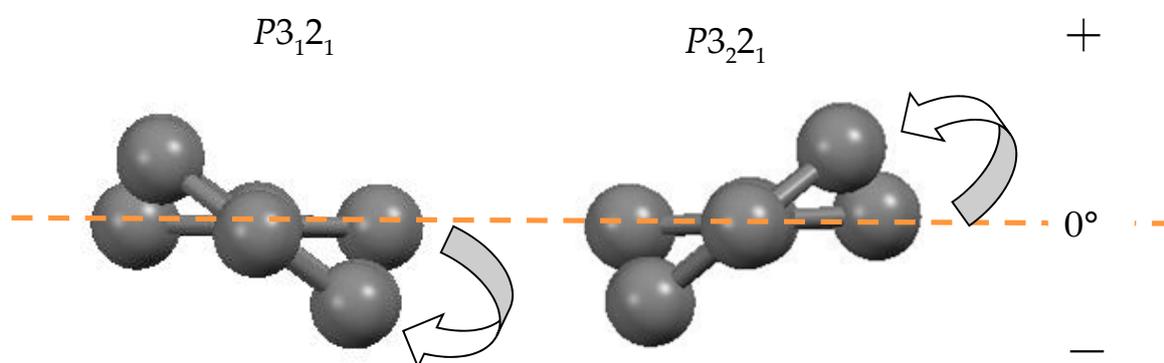
**Figure 1.** ORTEP drawing of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$ .



**Figure 2.** The projections of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  to  $ab$  plane (a),  $a$  axis (b), and the projection of biphenyl to  $a$  axis (c).

**Table 2.** Crystal data of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ .

$\text{Fe}(\text{NCS})_2(\text{bpa})_2\cdot\text{biphenyl}$	
Temperature	RT
Space group	$P3_12_1$
a,b/Å	10.234(5)
c/Å	30.070(15)
$\alpha,\beta/^\circ$	90
$\gamma/^\circ$	120
R1	0.0368
wR2	0.0909
Goodness of fit	1.039
Volume/Å <sup>3</sup>	2727(3)
Flack parameter	0.022(26)
Flack parameter when using $P3_22_1$	0.9764

**Figure 3.** Structure of biphenyl. The dashed line shows a phenyl plane in the rear.

The crystals underlined in Table 1 showed a color change from pale yellow to deep red by cooling with liquid (Liq.)  $\text{N}_2$ . The color change corresponded well with the SCO phenomenon. The color of the present spiral  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  was pale yellow and did not change by cooling with Liq.  $\text{N}_2$ . It was judged that the present spiral  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  does not show SCO, although we could not measure the magnetic susceptibility and  $^{57}\text{Fe}$  Mössbauer spectrum because of too little quantities of crystal.

It was revealed that  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  has the same structure with  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ . The crystal data are shown in Table 3. There is not much difference in structure between the Fe complex and Co complex. The local structure around cobalt was chiral propeller type. The biphenyl molecule showed an atropisomerism in this crystal. We have analyzed the present complex in single crystal X-ray structural analysis by using chiral space group  $P3_12_1$  (Flack parameter: 0.015). When analyzing it using  $P3_22_1$ , the Flack parameter becomes 0.9822, suggesting the space group is  $P3_12_1$ .

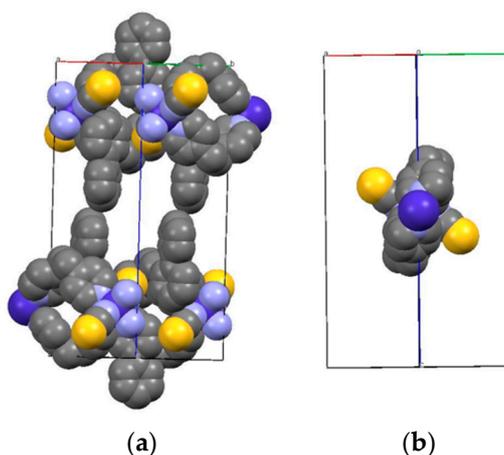
The projection of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  to  $ab$  plane is shown in Figure 2a. In this figure, divalent metal ions were bridged by bpa to form self-assembled 1D chain complex. Several 1D chains gathered together to form 1D chain sheet. The 1D chain sheet was stacked spirally to form novel spiral assembly with threefold axis. Biphenyl was stacked with threefold axis, and it was arranged between upper and lower 1D chain sheets (Figure 2b,c).

Biphenyl in the crystal is shown in Figure 3. Biphenyl molecules were stacked along a threefold spiral structure and the biphenyl was situated between the upper and lower sheet of  $\text{M}(\text{NCS})_2(\text{bpa})_2$ , which linked the two sheets. The dihedral angle in biphenyl was  $-35.72$  and  $-36.55$  for  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  and  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ , respectively. The biphenyl molecule showed atropisomerism in the solid state.

**Table 3.** Crystal data of  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ .

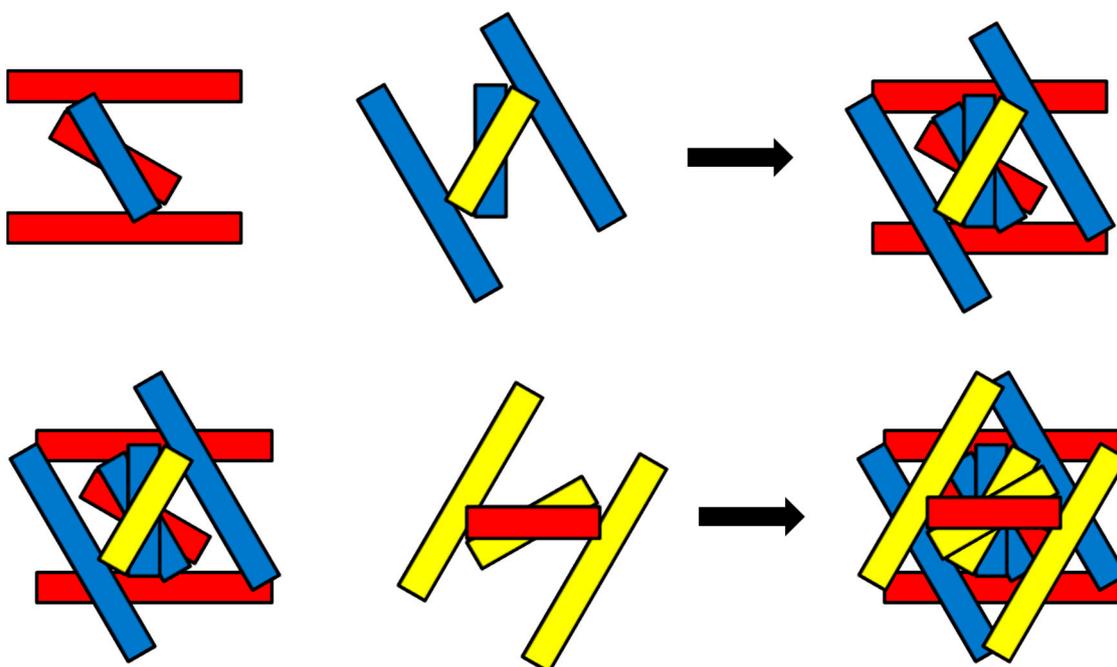
<b><math>\text{Co}(\text{NCS})_2(\text{bpa})_2\cdot\text{biphenyl}</math></b>	
Temperature	173K
Space group	$P3_12_1$
a,b/Å	10.1607(4)
c/Å	30.0262(13)
$\alpha,\beta/^\circ$	90
$\gamma/^\circ$	120
R1	0.0232
wR2	0.0572
Goodness of fit	1.113
Volume/Å <sup>3</sup>	2684.6(2)
Flack parameter	0.015(15)
Flack parameter when using $P3_22_1$	0.9822

It is known that self-assembled complexes enclathrate guest molecules in order to fill their vacancies. We investigated the relationship between 1D chain  $\text{M}(\text{NCS})_2(\text{bpa})_2$  ( $\text{M} = \text{Fe}, \text{Co}$ ) and biphenyl molecule. A Space-filling view of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$  is shown in Figure 4. Figure 4a shows upper and lower 1D chain sheets and guest biphenyl. Figure 4b shows middle 1D chain. The size of 1D chain of  $\text{M}(\text{NCS})_2(\text{bpa})_2$  ( $\text{M} = \text{Fe}, \text{Co}$ ) and the chiral propeller type local structure around metal center fit in the space made by upper and lower biphenyl molecules. In spite of the good fit between 1D chain of  $\text{M}(\text{NCS})_2(\text{bpa})_2$  ( $\text{M} = \text{Fe}, \text{Co}$ ) and biphenyl molecule, intermolecular interactions, such as  $\pi$ - $\pi$  stacking and  $\text{CH}/\pi$  interaction, were not observed in space-filling view and short-contact analysis. These results may suggest that biphenyl enclathrated by the host framework causes the biphenyl's dihedral angle to be fixed by a weak interaction. Therefore, the crystal shows a chirality, reflecting the chiral propeller type local structure around the metal center and biphenyl's atropisomerism.



**Figure 4.** Space-filling view of  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2]\cdot\text{biphenyl}]_n$ . Upper and lower 1D chain sheets and guest biphenyl are shown in (a) and middle 1D chain is shown in (b).

The schematic packing mechanism is shown in Figure 5. Threefold spiral structure is explained as shown below. For simplicity, we set the dihedral angle between the two phenyls in the biphenyl molecule at  $30^\circ$ , and we set the dihedral angle between the two phenyls in the intermolecular two biphenyls as  $30^\circ$ . The biphenyls are stacked with these angles, showing a threefold axis. The 1D chain of  $\text{M}(\text{NCS})_2(\text{bpa})_2$  ( $\text{M} = \text{Fe}, \text{Co}$ ) grows along the space that is formed by the phenyls of the top and bottom of the biphenyls. It can easily be seen that the upper and lower sheets have a  $60^\circ$  torsion angle. Therefore, the 1D chain sheet also stacks spirally with a threefold axis.



**Figure 5.** Schematic view of packing of spiral  $[[M(NCS)_2(bpa)_2] \cdot biphenyl]_n$  ( $M = Fe, Co$ ). The long stick shows  $M(NCS)_2(bpa)_2$  ( $M = Fe, Co$ ) chain, while the short stick shows biphenyl. Elements with the same color have the same height.

In general, many enclathrated complexes are formed to fit the vacancies constructed by host structure with a guest molecule. In the present spiral complexes, both 1D chains having chiral propeller type structure of pyridines around the central metal and atropisomer of biphenyl constructed a spiral structure. That is, the chiral propeller type local structure determines the chiral structure and atropisomer of the biphenyl determines the “threefold” spiral structure. Moreover, it is expected that the 1D chain of  $M(NCS)_2(bpa)_2$  ( $M = Fe, Co$ ), having opposite direction of chiral propeller structure around the central metal and atropisomer of biphenyl, constructs a spiral structure having  $P3_22_1$  space group.

#### 4. Conclusions

We have synthesized self-assembled complexes  $[[M(NCS)_2(bpa)_2] \cdot biphenyl]_n$  ( $M = Fe, Co$ ;  $bpa = 1,2$ -bis(4-pyridyl)ethane), which have a novel spiral structure, by one-step diffusion method. The present spiral complexes showed a chirality related with chiral propeller structure of pyridines around the central metal and biphenyl’s atropisomerism. From the point of view of space-filling, 1D chain and biphenyl molecule formed a crystal, leading to the threefold spiral structure. Such structure conducts stepwise SCO if the anionic ligand is changed from  $NCS^-$  to  $NCBH_3^-$ , as reported by the present author et al. [25]. Although the propeller structure of pyridines around the iron atom is a key point to showing SCO, the slight difference in ligand field between  $NCS^-$  to  $NCBH_3^-$  also affects the SCO phenomenon.

**Author Contributions:** S.T. was involved in all stages of the work, including conducting experiments and analyzing the data; H.D. was involved in the X-ray structural analysis; S.N. acted as the supervisor and helped with the data analysis and work planning; and S.T. and S.N. wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Gütllich, P.; Bill, E.; Trautwein, A.X. *Mössbauer Spectroscopy and Transition Metal Chemistry*; Springer-Verlag: Berlin/Heidelberg, Germany, 2011; pp. 391–476, ISBN 978-3-540-88427-9.

2. Kahn, O.; Kröber, J.; Jay, C. Spin transition molecular materials for displays and data recording. *Adv. Mater.* **1992**, *4*, 718–728. [[CrossRef](#)]
3. Gentili, D.; Demitri, N.; Schäfer, B.; Liscio, F.; Bergenti, I.; Ruani, G.; Ruben, M.; Cavallini, M. Multi-modal sensing in spin crossover compounds. *J. Mater. Chem. C* **2015**, *3*, 7836–7844. [[CrossRef](#)]
4. Nakashima, S.; Yamamoto, Y.; Asada, Y.; Koga, N.; Okuda, T. New assembled Fe-*trans*-1,2-Bis(4-pyridyl)ethylene-NCS(NCSe) complexes—Hydrogen bonded and  $\pi$ - $\pi$  interacted structure and grid structure enclathrating ligand. *Inorg. Chim. Acta* **2005**, *358*, 257–264. [[CrossRef](#)]
5. Kitazawa, T.; Gomi, Y.; Takahashi, M.; Takeda, M.; Enomoto, M.; Miyazaki, A.; Enoki, T. Spin-crossover behaviour of the coordination polymer  $\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5\text{N})_2\text{Ni}^{\text{II}}(\text{CN})_4$ . *J. Mater. Chem.* **1996**, *6*, 119–121. [[CrossRef](#)]
6. Niel, V.; Martinez-Agudo, J.M.; Muñoz, M.C.; Gaspar, A.B.; Real, J.A. Cooperative Spin Crossover Behavior in Cyanide-Bridged Fe(II)–M(II) Bimetallic 3D Hofmann-like Networks (M = Ni, Pd, and Pt). *Inorg. Chem.* **2001**, *40*, 3838–3839. [[CrossRef](#)]
7. Muñoz, M.C.; Gaspar, A.B.; Galet, A.; Real, J.A. Spin-Crossover Behavior in Cyanide-Bridged Iron(II)–Silver(I) Bimetallic 2D Hofmann-like Metal-Organic Frameworks. *Inorg. Chem.* **2007**, *46*, 8182–8192. [[CrossRef](#)]
8. Agustí, G.; Muñoz, M.C.; Gaspar, A.B.; Real, J.A. Spin-Crossover Behavior in Cyanide-bridged Iron(II)–Gold(I) Bimetallic 2D Hofmann-like Metal-Organic Frameworks. *Inorg. Chem.* **2008**, *47*, 2552–2561. [[CrossRef](#)]
9. Rodriguez-Velamazan, J.A.; Carbonera, C.; Castro, M.; Palacios, E.; Kitazawa, T.; Letard, J.-F.; Burriel, R. Two-step thermal spin transition and LIESST relaxation of the polymeric spin-crossover compounds  $\text{Fe}(\text{X-py})_2[\text{Ag}(\text{CN})_2]_2$  (X = H, 3-Methyl, 4-Methyl, 3,4-Dimethyl, 3-Cl). *Chem. Eur. J.* **2010**, *16*, 8785–8796. [[CrossRef](#)]
10. Dirtu, M.M.; Naik, A.D.; Rotaru, A.; Spinu, L.; Poelman, D.; Garcia, Y.  $\text{Fe}^{\text{II}}$  Spin Transition Materials Including an Amino–Ester 1,2,4-Triazole Derivative, Operating at, below, and above Room Temperature. *Inorg. Chem.* **2016**, *55*, 4278–4295. [[CrossRef](#)]
11. Roubeau, O. Triazole-Based One-Dimensional Spin-Crossover Coordination Polymers. *Chem. Eur. J.* **2012**, *18*, 15230–15244. [[CrossRef](#)]
12. Quesada, M.; Koojiman, H.; Gomez, P.; Costa, J.S.; Koningsbruggen, P.J.; Weinberger, P.; Reissner, M.; Spek, A.L.; Haasnoot, J.G.; Reedjik, J.  $[\text{Fe}(\mu\text{-btzmp})_2(\text{btzmp})_2](\text{ClO}_4)_2$ : A doubly-bridged 1D spin-transition bistetrazole-based polymer showing thermal hysteresis behavior. *Dalton. Trans.* **2007**, 5434–5440. [[CrossRef](#)] [[PubMed](#)]
13. Moliner, N.; Muñoz, M.C.; Létard, S.; Salmon, L.; Tuchgues, J.P.; Boussksou, A.; Real, J.A. Mass Effect on the Equienergetic High-Spin/Low-Spin States of Spin-Crossover in 4,4'-Bipyridine-Bridged Iron(II) Polymeric Compounds: Synthesis, Structure, and Magnetic, Mössbauer, and Theoretical Studies. *Inorg. Chem.* **2002**, *41*, 6997–7005. [[CrossRef](#)] [[PubMed](#)]
14. Morita, T.; Asada, Y.; Okuda, T.; Nakashima, S. Isomerism of assembled iron complex bridged by 1,2-di(4-pyrisyl)ethane and its solid-to-solid transformation accompanied by a change of electronic state. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 738–744. [[CrossRef](#)]
15. Morita, T.; Nakashima, S.; Yamada, K.; Inoue, K. Occurrence of the spin-crossover phenomenon of assembled complexes,  $\text{Fe}(\text{NCX})_2(\text{bpa})_2$  (X = S,  $\text{BH}_3$ ; bpa = 1,2-bis(4-pyridyl)ethane) by enclathrating organic guest molecule. *Chem. Lett.* **2006**, *35*, 1042–1043. [[CrossRef](#)]
16. Nakashima, S.; Morita, T.; Inoue, K. Spin-crossover phenomenon of the assembled iron complexes with 1,2-bis(4-pyridyl)ethane as bridging ligand studied by Mössbauer spectroscopy. *Hyperfine Interact.* **2009**, *188*, 107–111. [[CrossRef](#)]
17. Dote, H.; Kaneko, M.; Inoue, K.; Nakashima, S. Synthesis of Anion-Mixed Crystals of the Assembled Complexes Bridged by 1,2-Bis(4-pyridyl)ethane and Ligand Field of  $\text{Fe}(\text{NCS})(\text{NCBH}_3)$  Unit. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 71–81. [[CrossRef](#)]
18. Atsuchi, M.; Higashikawa, H.; Yoshida, Y.; Nakashima, S.; Inoue, K. Novel 2D Interpenetrated Structure and Occurrence of the Spin-crossover Phenomena of Assembled Complexes,  $\text{Fe}(\text{NCX})_2(\text{bpp})_2$  (X = S, Se,  $\text{BH}_3$ ; bpp = 1,3-Bis(4-pyridyl)propane. *Chem. Lett.* **2006**, *36*, 1064–1065. [[CrossRef](#)]
19. Atsuchi, M.; Inoue, K.; Nakashima, S. Reversible structural change of host framework triggered by desorption and adsorption of guest benzene molecules in  $\text{Fe}(\text{NCS})_2(\text{bpp})_2 \cdot 2(\text{benzene})$  (bpp = 1,3-bis(4-pyridyl)propane). *Inorg. Chim. Acta* **2011**, *370*, 82–88. [[CrossRef](#)]

20. Yoshinami, K.; Kaneko, M.; Yasuhara, H.; Nakashima, S. Effect of methyl substituent on the spin state of iron(II) assembled complex using 1,4-bis(4-pyridyl)benzene. *Radioisotopes* **2017**, *66*, 625–632. [[CrossRef](#)]
21. Iwai, S.; Yoshinami, K.; Nakashima, S. Structure and Spin State of Iron(II) Assembled Complexes using 9,10-Bis(4-pyridyl)anthracene as Bridging Ligand. *Inorganics* **2017**, *5*, 61. [[CrossRef](#)]
22. Kaneko, M.; Tokinobu, S.; Nakashima, N. Density Functional Study on Spin-crossover Phenomena of Assembled Complexes,  $[\text{Fe}(\text{NCX})_2(\text{bpa})_2]_n$  ( $X = \text{S}, \text{Se}, \text{BH}_3$ ;  $\text{bpa} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}$ ). *Chem. Lett.* **2013**, *42*, 1432–1434. [[CrossRef](#)]
23. Kaneko, M.; Nakashima, S. Computational Study on Thermal Spin-Crossover Behavior for Coordination Polymers Possessing  $\text{trans-Fe}(\text{NCS})_2(\text{pyridine})_4$  Unit. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1164–1170. [[CrossRef](#)]
24. Hernández, M.L.; Barandika, M.G.; Urriaga, M.K.; Cortés, R.; Lezama, L.; Arriortuac, M.L.; Rojo, T. Structural analysis and magnetic properties of the 1-D compounds  $[\text{M}(\text{NCS})_2\text{bpa}_2]$  [ $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$  and  $\text{bpa} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}$ ]. *J. Chem. Soc. Dalton Trans.* **1999**, 1401–1406. [[CrossRef](#)]
25. Nakashima, S.; Morita, T.; Inoue, K.; Hayami, S. Spiral assembly of the 1D chain sheet of  $\text{Fe}(\text{NCBH}_3)_2(\text{bpa})_2 \cdot (\text{biphenyl})$  ( $\text{bpa} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}$ ) and its stepwise spin-crossover phenomenon. *Polymers* **2011**, *4*, 880–888. [[CrossRef](#)]
26. The SHELX Homepage. Available online: <http://shelx.uni-ac.gwdg.de/> (accessed on 14 February 2019).



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