Article

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

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Abstract: Assembled complexes \([\text{[M(NCS)}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) (M = Fe, Co; bpa = 1,2-bis(4-pyridyl)ethane) have been synthesized because \([\text{[Fe(NCBH}_3}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) has a novel threefold spiral structure and shows stepwise spin-crossover phenomenon. We attempted to obtain spiral structures for \([\text{[Fe(NCS)}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) and \([\text{[Co(NCS)}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) using a one-step diffusion method, while the reported spiral structure of \([\text{[Fe(NCBH}_3}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) was obtained by diffusion method after synthesizing Fe(II)-pyridine complex. X-ray structural analysis revealed that \([\text{[Fe(NCS)}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) and \([\text{[Co(NCS)}_2\text{(bpa)}_2]\cdot\text{biphenyl}]_n\) 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 d⁴–d⁷ 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 d⁶ 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](image)

**Scheme 1.** Difference in the Fe-pyridine local structures observed in a variety of the assembled \([\text{Fe(NCX)}_2L_2]_n \) (X = S, Se, and BH3; L = bridging ligand).

It had been reported that \([\text{Fe(NCS)}_2(bpa)_2]_n\) has a 1D chain structure and shows HS state [24]. We became interested in \([\text{Fe(NCS)}_2(bpa)_2]_n\), because the bpa has an *anti-gauche* conformation and 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 \([\text{Fe(NCX)}_2(bpa)_2\cdot\text{guest}]_n \) (X = S, Se, BH3; 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]. \([\text{Fe(NCBH}_3)_2(bpa)_2\cdot\text{biphenyl}]_n\) usually had 1D chain structure and showed one-step spin transition [15]. In special cases, the 1D chain self-assembled sheet of \([\text{Fe(NCBH}_3)_2(bpa)_2\cdot\text{biphenyl}]_n\) 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 \([\text{M(NCS)}_2(bpa)_2\cdot\text{biphenyl}]_n \) (M = Fe, Co) have been synthesized to obtain other novel spiral structure, and we discuss the formation mechanisms.
2. Materials and Methods

[[Fe(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in} and [[Co(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in} were obtained by diffusion method from FeCl\textsubscript{2}·4H\textsubscript{2}O (or FeSO\textsubscript{4}·7H\textsubscript{2}O) and CoCl\textsubscript{2}·6H\textsubscript{2}O, respectively. FeCl\textsubscript{2}·4H\textsubscript{2}O (or FeSO\textsubscript{4}·7H\textsubscript{2}O, CoCl\textsubscript{2}·6H\textsubscript{2}O) and 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 [[Fe(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in} and [[Co(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in}, respectively. Anal. found (calcd)%: for [[Fe(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in}, C, 65.10 (65.70); H, 4.67 (4.93); N, 12.01 (12.10); S, 9.08 (9.23). Anal. found (calcd)%: for [[Co(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in}, 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 Kα radiation, λ = 0.71073 Å, ω-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\textsuperscript{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 (CCDC: 1892503 and 1892504).

3. Results and Discussion

In the synthesis of spiral [[Fe(NCBH\textsubscript{3})\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in}, 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 FeCl\textsubscript{2}·4H\textsubscript{2}O was used, a large crystal having spiral structure was obtained. However, it was easily oxidized in the synthetic process. When FeSO\textsubscript{4}·7H\textsubscript{2}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 [[Fe(NCS)\textsubscript{2}(bpa)\textsubscript{2}]·biphenyl]\textsubscript{in}. 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\textsuperscript{−} in the trans position. The local structure around iron was chiral propeller type. The biphienyl molecule was enclathrated by Fe(NCS)\textsubscript{2} atom of bpa and the two N atoms of NCS\textsuperscript{−}.

![Figure 1](image)

**Table 2.** Summary of crystal structures and their spin-crossover (SCO) phenomena for [[Fe(NCX)\textsubscript{2}(bpa)\textsubscript{2}]·(guest)]\textsubscript{n}.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Guest</th>
<th>NCS</th>
<th>NCSe</th>
<th>NCBH\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>biphenyl</td>
<td>2D grid</td>
<td>Linear</td>
<td>Linear</td>
<td>2D grid</td>
</tr>
<tr>
<td>2-nitrobenzene</td>
<td>Interpenetrated</td>
<td>Linear</td>
<td>Linear</td>
<td>Not included</td>
</tr>
<tr>
<td>diphenylmethane</td>
<td>Interpenetrated</td>
<td>Linear</td>
<td>Interpenetrated</td>
<td>2D grid</td>
</tr>
</tbody>
</table>

The crystals underlined showed a color change from pale yellow to deep red by cooling with Liq. N\textsubscript{2}. The color change corresponded well with the SCO phenomenon.
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 \([\text{Fe} (\text{NCS})_2(bpa)_2]\cdot\text{biphenyl}]_n\)**

\[
\begin{align*}
\text{FeSO}_4 \cdot 7\text{H}_2\text{O} & \quad \text{pyridine} \quad \text{NaNCBH}_3 & \quad \rightarrow \quad \text{Fe} (\text{NCS})_2(\text{pyridine})_4 \quad \text{bpa} & \quad \rightarrow \quad \text{[[Fe} (\text{NCS})_2(bpa)_2] \cdot \text{biphenyl}]_n \\
\text{Diffusion method} & \quad \text{(Scheme 2)}
\end{align*}
\]

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

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

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

<table>
<thead>
<tr>
<th>Fe(NCS)₂(bpa)₂·biphenyl</th>
<th>RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P3₁2₁</td>
</tr>
<tr>
<td>a, b/Å</td>
<td>10.234(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>30.070(15)</td>
</tr>
<tr>
<td>α, β, γ/°</td>
<td>90, 120, 120</td>
</tr>
<tr>
<td>R factor (%)</td>
<td>0.0368</td>
</tr>
<tr>
<td>wR² factor (%)</td>
<td>0.0909</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.039</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2727(3)</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.022(26)</td>
</tr>
<tr>
<td>Flack parameter when using P₃₂₁₀</td>
<td>0.9764</td>
</tr>
</tbody>
</table>

**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.) N₂. The color change corresponded well with the SCO phenomenon. The color of the present spiral [[Fe(NCS)₂(bpa)₂·biphenyl]n was pale yellow and did not change by cooling with Liq. N₂. It was judged that the present spiral [[Fe(NCS)₂(bpa)₂·biphenyl]n does not show SCO, although we could not measure the magnetic susceptibility and ⁵⁷Fe Mössbauer spectrum because of too little quantities of crystal.

It was revealed that [[Co(NCS)₂(bpa)₂·biphenyl]n has the same structure with [[Fe(NCS)₂(bpa)₂·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 P₃₁2₁ (Flack parameter: 0.015). When analyzing it using P₃₂₁₀, the Flack parameter becomes 0.9822, suggesting the space group is P₃₁2₁.

The projection of [[Fe(NCS)₂(bpa)₂·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 M(NCS)₂(bpa)₂, which linked the two sheets. The dihedral angle in biphenyl was −35.72 and −36.55 for [[Fe(NCS)₂(bpa)₂·biphenyl]n and [[Co(NCS)₂(bpa)₂·biphenyl]n, respectively. The biphenyl molecule showed atropisomerism in the solid state.
Table 3. Crystal data of [[Co(NCS)\(_2\)(bpa)\(_2\)]·biphenyl]\(_n\).

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>173K</td>
</tr>
<tr>
<td>Space group</td>
<td>(P3_12_1)</td>
</tr>
<tr>
<td>(a,b/\AA)</td>
<td>10.1607(4)</td>
</tr>
<tr>
<td>(c/\AA)</td>
<td>30.0262(13)</td>
</tr>
<tr>
<td>(\alpha,\beta,\gamma/\degree)</td>
<td>90, 120</td>
</tr>
<tr>
<td>R1</td>
<td>0.0232</td>
</tr>
<tr>
<td>wR2</td>
<td>0.0572</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.113</td>
</tr>
<tr>
<td>Volume/(\AA^3)</td>
<td>2684.6(2)</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.015(15)</td>
</tr>
<tr>
<td>Flack parameter when using (P3_2_2_1)</td>
<td>0.9822</td>
</tr>
</tbody>
</table>

It is known that self-assembled complexes enclathrate guest molecules in order to fill their vacancies. We investigated the relationship between 1D chain \(\text{M(NCS)}_2\text{(bpa)}_2\) (\(\text{M} = \text{Fe, Co}\)) and biphenyl molecule. A Space-filling view of \([\text{Fe(NCS)}_2\text{(bpa)}_2\text{-biphenyl}]_n\) 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 \(\text{M(NCS)}_2\text{(bpa)}_2\) (\(\text{M} = \text{Fe, Co}\)) 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 \(\text{M(NCS)}_2\text{(bpa)}_2\) (\(\text{M} = \text{Fe, Co}\)) and biphenyl molecule, intermolecular interactions, such as \(\pi-\pi\) stacking and 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 \([\text{Fe(NCS)}_2\text{(bpa)}_2\text{-biphenyl}]_n\). Upper and lower 1D chain sheets and guest biphenyl are shown in (a) and middle 1D chain is shown in (b).](image-url)

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°, and we set the dihedral angle between the two phenyls in the intermolecular two biphenyls as 30°. The biphenyls are stacked with these angles, showing a threefold axis. The 1D chain of \(\text{M(NCS)}_2\text{(bpa)}_2\) (\(\text{M} = \text{Fe, Co}\)) 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° torsion angle. Therefore, the 1D chain sheet also stacks spirally with a threefold axis.
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 atropisomerism of the biphenyl. 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$_2$1$_1$ space group.

4. Conclusions

We have synthesized self-assembled complexes [[M(NCS)$_2$(bpa)$_2$]-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


