Formation of a Chiral Host with Axially Chiral Cationic 1D Coordination Polymers Composed of Achiral Building Blocks and Inclusion of Anionic Tris-Chelate Complexes in an Unbalanced Δ/Λ Ratio

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Received June 3, 2009; E-mail: cnskor@mail.ecc.u-tokyo.ac.jp

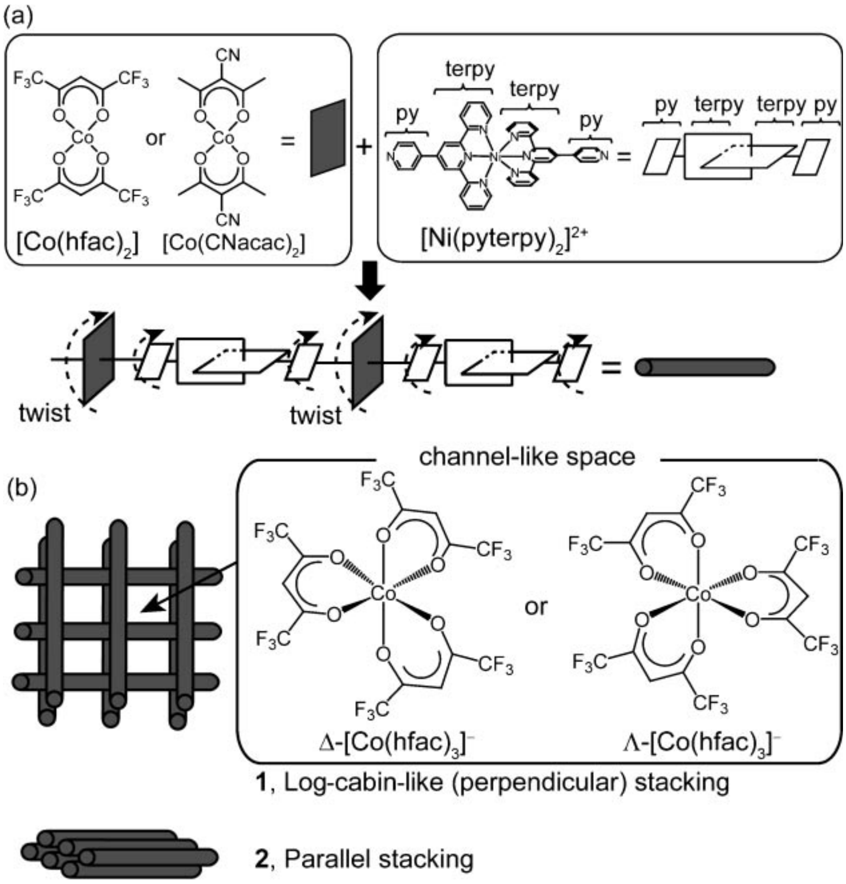
Two crystals, $[\{Co(hfac)_2\}\{Ni(pyterpy)_2\}][Co(hfac)_3]_2$ (**1**) and $[Co(CNacac)_2][Ni(pyterpy)_2]SO_4{\cdot}xG$ (**2**), composed of 1D cationic coordination polymers were prepared by self-assembly of achiral component metal complexes in solution (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato, CNacac = 3-cyanopentane-2,4-dionato, pyterpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine, G = methanol and water). **1** is chiral and spontaneously optically resolved, whereas **2** is achiral. In **1**, an alternate linkage of $[Co(hfac)_2]$ and $[Ni(pyterpy)_2]^{2+}$ forms a 1D coordination polymer and twisting of the two complexes about the principal axis of the 1D polymer makes the polymer axially chiral. The 1D polymers stack to create two-types of 1D channels, where anionic complexes $[Co(hfac)_3]^-$ are included. One channel contains only Δ-$[Co(hfac)_3]^-$, whereas the other contains an equal amount of Δ- and Λ-$[Co(hfac)_3]^-$. Therefore, the Δ/Λ ratio of $[Co(hfac)_3]^-$ is 3/1. In the case of **2**, 1D coordination polymers are formed by an alternate linkage of $[Co(CNacac)_2]$ and $[Ni(pyterpy)_2]^{2+}$. They are chiral due to twisting of one pyridine ring in $[Ni(pyterpy)_2]^{2+}$, however, there are inversion centers in **2**. These results demonstrated that axial chirality can be introduced into 1D coordination polymers by twisting the two component metal complexes alternately linked. This method is useful and prospective for preparing chiral coordination polymers from achiral building blocks.

Coordination polymers with guest inclusion ability have been intensively studied as mimics of natural and classical hosts such as clays and zeolites.[1] One of the advantages of coordination polymers is their synthetic facility. Most of them are simply prepared by self-assembly of metal ions and ligands. Further, molecular structures and intermolecular space in the crystals can be modified by changing metal ions and/or ligands. Recently, chiral coordination polymers have been actively investigated for application as chiral molecular sieves and as catalysts for asymmetric synthesis.[2] Introduction of chirality to the host structure differentiates the coordination polymers from the natural hosts.

In many cases chiral coordination polymers are prepared by using chiral ligands.[2] Although this is a reliable method to introduce chirality to the structure, the preparation of chiral ligands is a laborious task. Another approach is to form a chiral structure using chiral arrangement of achiral components.[3] Most coordination polymers are prepared in solution, and hence this approach requires spontaneous optical resolution, which produces a conglomerate, a racemic mixture of chiral crystals. Namely, to realize this approach, the following two phenomena need to occur at the same time: (1) formation of chiral units by chiral arrangement of achiral components and (2) retaining the chirality of the units in crystallization and achieving a homochiral crystal structure.[4] This approach is an interesting and challenging subject of crystal engineering. The two events however are usually difficult to control together, especially in the case of coordination polymers. This is because metal ions and ligands can have several coordination geometries and conformations, responding to the counter ions and experimental conditions.[5] Coordination polymers that are resolved spontaneously are still a minority and rational synthetic methods have not yet been established.

Herein, we report two crystals, $[\{Co(hfac)_2\}\{Ni(pyterpy)_2\}][Co(hfac)_3]_2$ (**1**) and $[Co(CNacac)_2][Ni(pyterpy)_2]SO_4{\cdot}xG$ (**2**) of 1D coordination polymers, where hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato, CNacac = 3-cyanopentane-2,4-dionato, pyterpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine and G = methanol and water. **1** was obtained as a chiral crystal due to spontaneous resolution upon crystallization, while **2** was an achiral crystal. The 1D coordination polymers of **1** and **2** were prepared by using the following two achiral building blocks. One is bis β-diketonato Co^{II} complex, which is planar and can accept additional ligands at the axial sites keeping its planar structure.[6] $[Co^{II}(hfac)_2]$ and $[Co^{II}(CNacac)_2]$ were used in **1** and **2**, respectively. Another building block, which was

Published on the web November 10, 2009; doi:10.1246/bcsj.82.1377



Scheme 1. (a) Structure of a 1D chain coordination polymer formed by an alternate linkage of [Co(β-diketonato)$_2$] and [Ni(pyterpy)$_2$]$^{2+}$. Appropriate twisting of [Co(β-diketonato)$_2$] and the pyridine rings of [Ni(pyterpy)$_2$]$^{2+}$ bring chirality to the 1D coordination polymer. (b) Two stacking modes, a log cabin like stacking and a parallel stacking, of the 1D polymers found in **1** and **2**.

used for both crystals, is [Ni^{II}(pyterpy)$_2$]$^{2+}$. A pyterpy ligand consists of a terpyridine moiety (terpy) and a pyridine moiety (py) as shown in Scheme 1. In [Ni^{II}(pyterpy)$_2$]$^{2+}$, two terpy moieties coordinate to the Ni^{II} center and their aromatic planes are placed perpendicular to each other to form a structure with D_{2d} symmetry. The Ni^{II} complex works as a linear ligand such as 4,4′-bipyridine using two py moieties at its opposite ends.[7] An alternate linkage of these two types of building blocks form 1D coordination polymers. As shown in Scheme 1b, the resultant 1D polymers are stacked alternately perpendicular to each other in a log cabin like fashion in **1**, while they are stacked in a parallel fashion in **2**. In **1**, 1D channels are formed within the log cabin like structure of the 1D polymers. [Co(hfac)$_3$]$^-$ complexes, which are transformed from [Co(hfac)$_2$] during crystallization, occupy the space. The included complexes are stacked in the channel to form a 1D array. There are two types of arrays: an array composed of only the Δ-[Co(hfac)$_3$]$^-$ complexes (Δ–Δ array) and an array of the Δ- and Λ-[Co(hfac)$_3$]$^-$ complexes stacked alternately (Δ–Λ array). The crystal contains an equal amount of Δ–Δ and Δ–Λ arrays so that the Δ/Λ ratio of [Co(hfac)$_3$]$^-$ complexes is 3/1.

The 1D coordination polymers in **1** are axially chiral due to a twisted linkage of the building blocks, i.e., [Co(hfac)$_2$] and [Ni(pyterpy)$_2$]. Steric interactions between the chiral 1D polymers as well as those between the log cabin like host and the incorporated [Co(hfac)$_3$]$^-$ guests realized the same chirality throughout the crystal structure. The 1D coordination polymers in **2** are also chiral due to a twisted pyridine ring in a pyterpy of the Ni^{II} complex. However, the twisting is small compared to that observed in **1** and strong enough steric interactions among the 1D polymers do not occur in **2**. Moreover, small guest molecules included in **2**, methanol and water, are substantially disordered and cannot contribute to the crystal packing of **2**. As a result, the configuration of the 1D polymers in **2** is racemic.

The twisting of the building blocks in a 1D-chain type coordination polymer and the stacking manner of the 1D coordination polymers easily receive steric effects from the surroundings and hence cannot be easily controlled. In this regard, it is fortuitous that we could obtain crystal **1**, however, we believe our approach of making a chiral 1D coordination polymer from achiral building blocks is useful and prospective and the results obtained here are informative to crystal engineering. In this paper, the details of the molecular and the crystal structures of **1** and **2**, and the delicate and elaborate choice of the building blocks for the chiral 1D coordination polymer will be discussed.

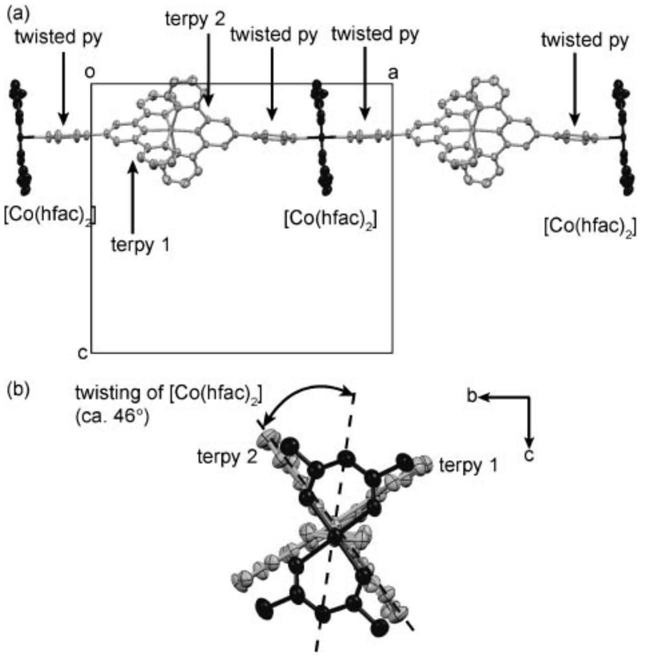


Figure 1. 1D complex in **1** formed by the alternate linkage of [Co(hfac)$_2$] and [Ni(pyterpy)$_2$]$^{2+}$ viewed (a) along the *b* axis and that (b) along the *a* axis. H and F atoms are omitted for clarity.

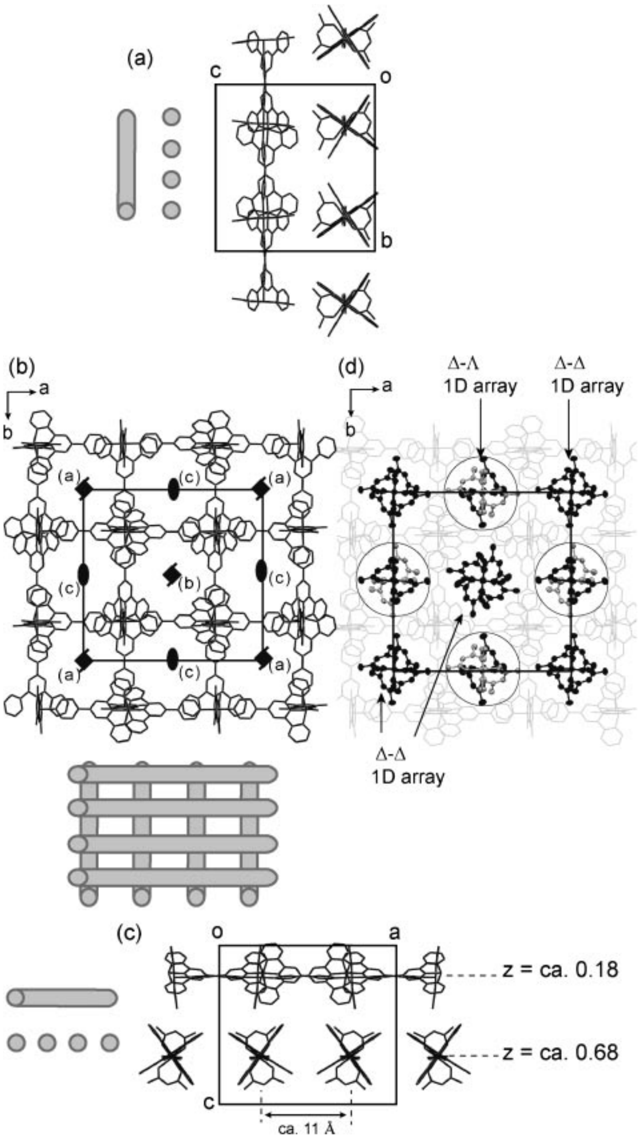


Figure 2. The 1D complexes in **1** and their schematic representations viewed along the (a) *a*, (b) *c*, and (c) *b* axes. In (b), four symmetry operations are indicated with Wyckoff letters. (d) The Δ–Δ and Δ–Λ 1D arrays of [Co(hfac)$_3$]$^-$. Δ- and Λ-[Co(hfac)$_3$]$^-$ are drawn in black and gray, respectively. H and F atoms are omitted for clarity.

Results and Discussion

Crystal Structure of [{Co(hfac)$_2$}{Ni(pyterpy)$_2$}][Co(hfac)$_3$]$_2$ (1). From a methanol solution containing [Co(hfac)$_2$] and [Ni(pyterpy)$_2$]Cl$_2$, [{Co(hfac)$_2$}{Ni(pyterpy)$_2$}][Co(hfac)$_3$]$_2$ (**1**) was prepared. After slow evaporation of the methanol solution at ambient temperature over a few weeks, **1** was obtained as red crystals. Using [Ni(pyterpy)$_2$]SO$_4$ instead of [Ni(pyterpy)$_2$]Cl$_2$, **1** was also obtained by the same procedure.

1 contains a cationic 1D continuous complex formed by the alternate linkage of [Co(hfac)$_2$] and [Ni(pyterpy)$_2$]$^{2+}$. In this linkage the orientations of [Co(hfac)$_2$] and [Ni(pyterpy)$_2$]$^{2+}$ are twisted with respect to each other as shown in Figure 1. The torsion angle between [Co(hfac)$_2$] and the terpy plane of [Ni(pyterpy)$_2$]$^{2+}$ close to [Co(hfac)$_2$] is ca. 46° (Figure 1b). This torsion breaks the S_4 axis and the two mirror planes ($\sigma_d = S_1$) of the D_{2d} symmetry of [Ni(pyterpy)$_2$]$^{2+}$ and brings chirality to the 1D complex. In addition to this torsion, twisting of two py rings of [Ni(pyterpy)$_2$]$^{2+}$ also breaks the D_{2d} symmetry (Figure 1). If we describe the chirality of the 1D complex using the torsion angle mentioned above, the 1D complex in this crystal has M helical structure. The unit cell contains four 1D complexes. The four 1D complexes are related to each other by the symmetry operations of the chiral space group $P4_2$, i.e., two independent 4_2 screw axes and two equivalent 2-fold axes parallel to the *c* axis as shown in Figure 2. All the 1D complexes in the crystal are equivalent and have the same chirality.

The 1D complexes in the crystal are stacked in a log cabin like fashion as illustrated in Scheme 1b and Figure 2b. Two 1D polymers at $z =$ ca. 0.18 in the unit cell run parallel to the *a* axis, and are related to each other by the 2-fold axis along the *c* axis so that their running directions are opposite to each other. The same situation is seen for the two 1D polymers at $z =$ ca. 0.68, although they are aligned along the *b* axis. The 1D complexes at $z =$ ca. 0.18 and 0.68 are related by the 4_2 screw axes. The long molecular axis of [Co(hfac)$_2$], which runs through the center of the molecular plane of [Co(hfac)$_2$], is almost parallel to the *c* axis as shown in Figure 1b. The terpy aromatic planes of [Ni(pyterpy)$_2$]$^{2+}$, which are twisted by the torsion angle of ca. 45° against [Co(hfac)$_2$], are arranged obliquely against the *c* axis. The Co$^{\mathrm{II}}$ and the Ni$^{\mathrm{II}}$ centers are stacked alternately along the *c* axis. This structural situation places the CF$_3$ groups of [Co(hfac)$_2$] between the orthogonally located two terpy planes of a [Ni(pyterpy)$_2$]$^{2+}$ complex as shown in Figure 3, and achieves effective contact between the

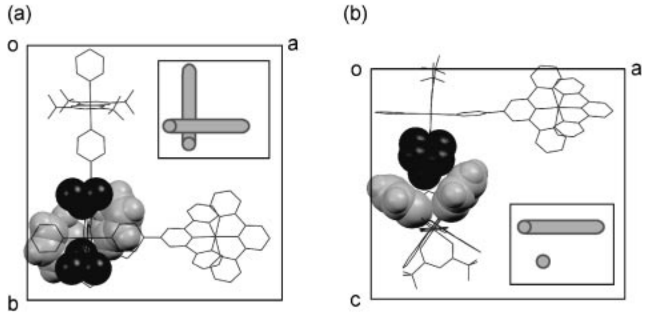


Figure 3. Two stacked 1D complexes in **1** and their schematic representations viewed along the (a) *c* and (b) *b* axes. Interacting CF_3 groups of [Co(hfac)$_2$] and terpy aromatic planes of [Ni(pyterpy)$_2$]$^{2+}$ are drawn with a black space filling model and a gray one, respectively.

1D complexes which are perpendicularly stacked along the *c* axis. On the other hand, there is a distance of ca. 11 Å between the antiparallel 1D complexes at the same *z* position. The Co^{II} and the Ni^{II} centers stacked alternately along the *c* axis form the four corners of quadrilateral void spaces, which runs like a channel along the direction of the *c* axis. In the crystal there are four channel-like spaces along the *c* axis: two independent channels around the 4_2 screw axes, and two equivalent ones around the 2-fold axes (Figures 2b and 2d).

In addition to [Co(hfac)$_2$] which works as the building block within the 1D complex, [Co^{II}(hfac)$_3$]$^-$ was also found as an anionic guest. This [Co(hfac)$_3$]$^-$ complex was transformed from [Co(hfac)$_2$] which was added at the initial stage of the preparation. The [Co(hfac)$_3$]$^-$ complexes are stacked in the channel-like spaces to form 1D arrays of [Co(hfac)$_3$]$^-$ parallel to the *c* axis (Figure 2d). The accommodation of the [Co(hfac)$_3$]$^-$ complexes contributes to cancelling the positive electric charge of the 1D complexes. At the same time, this accommodation stabilizes the [Co(hfac)$_3$]$^-$ complexes themselves. Tris β-diketonato Co^{II} complexes are known to be unstable and labile compared with bis β-diketonato Co^{II} complexes.[8] Furthermore, in the case of [Co(hfac)$_3$]$^-$, the coordination of hfac to Co^{II} ion is considered to be weak due to the strong electron-withdrawing effect of the CF_3 groups in hfac. The accommodation of [Co(hfac)$_3$]$^-$ in the channels formed by the cationic 1D complexes in **1**, stabilizes the complex, similarly to the stabilization by crystallization with a cationic metal complex as reported.[9]

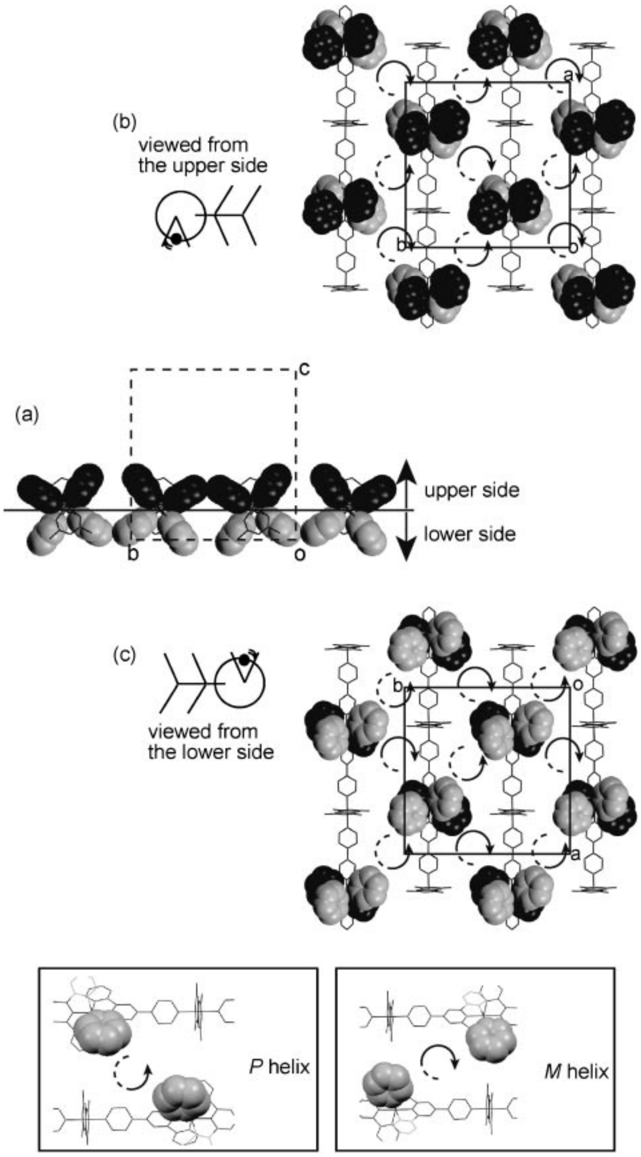


Figure 4. (a) Upper and lower side of the space between the antiparallel 1D complexes at $z =$ ca. 0.18. Aromatic planes of terpy in the upper and the lower side are drawn with a black space-filling model and a gray one, respectively. The helicity generated by the propeller-like arrangement of the aromatic plane of terpy (b) in the upper side and that (c) in the lower side.

Two channels around the 4_2 screw houses only the Δ complexes (called Δ–Δ arrays) and two equivalent channels around the 2-fold axis contain equal amount of the Δ and Λ complexes (called Δ–Λ arrays). Consequently, the ratio of Δ-[Co(hfac)$_3$]$^-$ to Λ-[Co(hfac)$_3$]$^-$ in the whole crystal is 3:1. The unbalanced Δ/Λ ratio of the [Co(hfac)$_3$]$^-$ complexes comes from delicate and complicated packing. The steric interaction between the propellers formed by the host terpy and guest hfac aromatic planes is the main factor in determining the chirality of the guest [Co(hfac)$_3$]$^-$ complexes. The terpy aromatic planes of [Ni(pyterpy)$_2$]$^{2+}$ are arranged obliquely against the direction of the *c* axis and protrude into the channel space. Due to this structural situation, the terpy aromatic planes act as a kind of propeller and give a helical character to the space between the antiparallel 1D complexes at the same *z* position. This space can be divided to two parts, the upper side and the lower side (upper and lower as seen along the *c* axis), by the plane on which the antiparallel 1D complexes are placed (Figure 4a). As shown in Figures 4b and 4c, the helicity of the upper side and the lower side is reversed.

All the [Co(hfac)$_3$]$^-$ complexes in **1** have a 2-fold axis running through the Co^{II} ion and a hfac chelate ring. The chirality of the [Co(hfac)$_3$]$^-$ complex does not obviously come from the flat chelate ring on a 2-fold axis but from the remaining two hfac chelate rings which are related to each other by the 2-fold axis, and form a propeller shape. We shall name the hfac on the 2-fold axis and a set of two hfac ligands

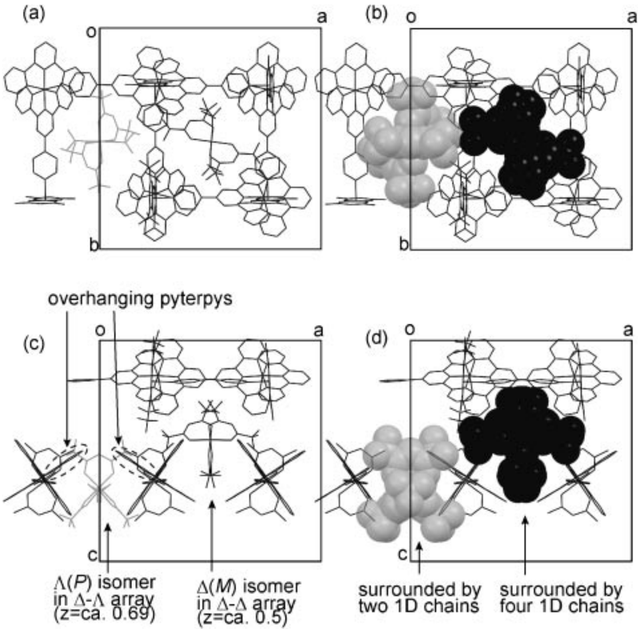


Figure 5. The relation of a Λ-$[Co(hfac)_3]^-$ in Δ–Λ array with the neighboring Δ-$[Co(hfac)_3]^-$ in Δ–Δ array viewed along the *c* axis drawn with (a) stick and (b) space-filling models and that viewed along the *b* axis drawn with (c) stick and (d) space-filling models. Δ and Λ isomers are drawn in black and gray, respectively. H atoms in all molecules and F atoms in 1D complexes were omitted for clarity.

with the propeller shape, as head-hfac and tail-hfac, respectively. Chirality of the tris-chelate $[Co(hfac)_3]^-$ complex is conveniently defined along the C_2 axis rather than the conventional definition of the Δ and Λ along the C_3 axis, as the 2-fold axis plays a crucial role in the chiral discrimination in **1**. Thus, the tail-hfac of the Δ-$[Co(hfac)_3]^-$ can be defined as M form and that of the Λ-$[Co(hfac)_3]^-$ as P form, and hence the complexes are described as Δ(*M*)-$[Co(hfac)_3]^-$ and Λ(*P*)-$[Co(hfac)_3]^-$.[10]

The channel-like spaces formed by the 1D complexes are not completely independent of each other and there are direct contacts between accommodated $[Co(hfac)_3]^-$ complexes in adjacent 1D arrays as shown in Figure 5. This steric effect places the $[Co(hfac)_3]^-$ complexes at $z =$ ca. 0 and ca. 0.5 in the two Δ–Δ arrays, whereas at $z =$ ca. 0.19 and ca. 0.69 in the two Δ–Λ arrays. Considering the two-dimensional alternate arrangement of the Δ–Δ and Δ–Λ arrays, this positioning is reasonable for reducing the steric effects. At the same time, this positioning generates a difference in the position of $[Co(hfac)_3]^-$ with respect to the 1D complexes. The $[Co(hfac)_3]^-$ complexes in the Δ–Δ arrays are located between two sets of antiparallel 1D complexes at different *z* positions and are surrounded by a total of four 1D complexes. On the other hand, having similar *z* position for the host and guest complexes, the $[Co(hfac)_3]^-$ complexes in the Δ–Λ arrays are surrounded by a set of two antiparallel 1D complexes.

In the case of the $[Co(hfac)_3]^-$ guest in the Δ–Δ array, which is surrounded by a total of four 1D complexes, its head-hfac approaches the propeller of the terpy aromatic planes of the two antiparallel 1D complexes from the lower side, and tail-hfac approaches to the other two antiparallel 1D complexes from the upper side. The chirality of the lower side is P and that of the upper side is M in the Δ–Δ array as shown in Figure 4c. The contact between the flat head-hfac and the propeller of the terpy aromatic planes does not contribute to chiral discrimination. In contrast, the interaction between tail-hfac and the propeller of the terpy aromatic planes determines the chirality of the guest. The M configuration surroundings work as a template to choose the helicity of tail-hfac, realizing the best packing (Figure S1 in Supporting Information). Thus, the $[Co(hfac)_3]^-$ guests in the Δ–Δ array have the Δ(M) configuration. This structural situation is common to the two Δ–Δ arrays, which are crystallographically independent.

On the other hand, Λ(*P*)-$[Co(hfac)_3]^-$ and Δ(*M*)-$[Co(hfac)_3]^-$ in the Δ–Λ array are interposed by two antiparallel 1D complexes. In the Δ–Λ array, the helicity of the upper side is P and that of the lower side is M as shown in Figures 4b and 4c. In the case of Λ(*P*)-$[Co(hfac)_3]^-$, the packing of its tail-hfac and the propeller of the terpy aromatic planes is excellent. The tail-hfac tightly fits the chiral space of the upper side of two antiparallel 1D complexes and has P configuration (Figure S2 in Supporting Information). Head-hfac, which has an achiral structure and is located in the lower side with M configuration, gives no effect for determining the configuration of the guest. The other guest Δ(*M*)-$[Co(hfac)_3]^-$ is considered to be a mirror image of the Λ(*P*)-$[Co(hfac)_3]^-$ which is rotated by 90° about the 2-fold axis. The orientation of Δ(*M*)-$[Co(hfac)_3]^-$ in the Δ–Λ array is reversed to that of Λ(*P*)-$[Co(hfac)_3]^-$. Therefore, tail-hfacs of Δ(*M*)-$[Co(hfac)_3]^-$ are located in the lower side with M configuration, and the guest complex has M configuration. In the Δ–Λ array, the contact of the two guests is also an important factor. The orientations of the two complexes are opposed to each other so that tail-to-tail contact exists. In this contact P tail-hfac and M tail-hfac are faced to each other with a torsion angle of 90°. In this arrangement of two propeller-shaped molecules, the engagement of the two propellers is very effective and tight. This can be confirmed in the short distance between the Co^{II} centers in tail-to-tail contact of 9.311(2) Å, while corresponding distances for head-to-head and head-to-tail contact are 10.644(2) and 9.978(1) Å, respectively (Figure S3 in Supporting Information). This close tail-to-tail contact defines their mutual configurations and stabilizes their structures.

Crystal Structure of $[Co(CNacac)_2][Ni(pyterpy)_2]SO_4\cdot xG$ (2). Red crystals of $[Co(CNacac)_2][Ni(pyterpy)_2]SO_4\cdot x$G (**2**) were obtained after leaving a methanol solution containing $[Co(CNacac)_2]$ and $[Ni(pyterpy)_2]SO_4$ for a few days at ambient temperature. Elemental analysis and TG measurement indicated the inclusion of methanol and water molecules as guests.

As shown in Figure 6a, **2** contains a 1D chain type coordination polymer formed by an alternate linkage of $[Co(CNacac)_2]$ and $[Ni(pyterpy)_2]^{2+}$. The axis through the Co^{II} and the Ni^{II} ions is on a 2-fold axis of the crystal so that the symmetry of the 1D chain complex is exactly C_2, from which a chiral structure is expected. However, the chirality of the 1D chain complex does not come from the twisting of the Co^{II} and

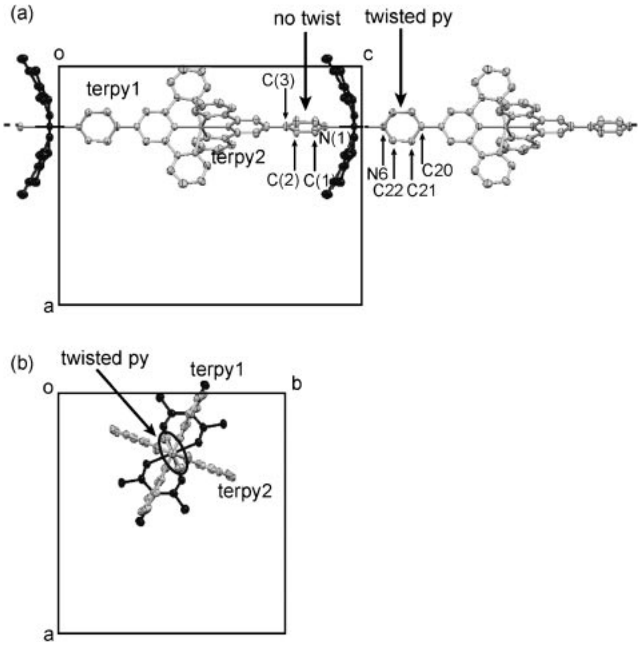


Figure 6. A 1D chain complex in **2** formed by the alternate linkage of $[Co(CNacac)_2]$ and $[Ni(pyterpy)_2]^{2+}$ viewed along the (a) *b* and (b) *c* axes. $[Co(CNacac)_2]$ and $[Ni(pyterpy)_2]^{2+}$ are drawn in black and gray, respectively.

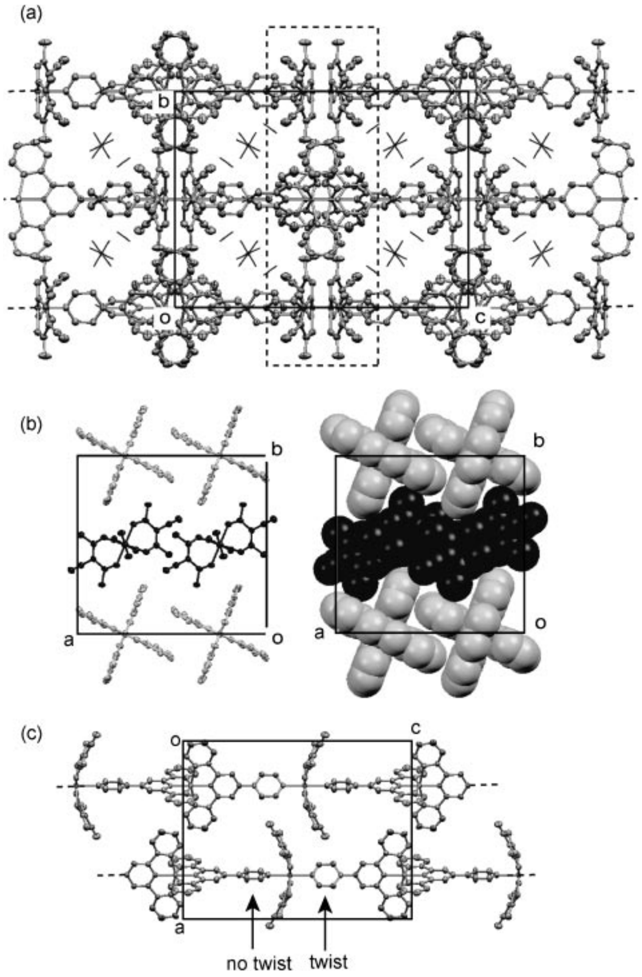


Figure 7. (a) Crystal structure of **2** viewed along the *a* axis, in which sulfate ions and guest molecules are drawn with a stick model. (b) Sectional views of the region between $z = -0.15$ and $z = 0.15$ drawn with a ball-and-stick and a space-filling models. (c) A view of 1D complexes at $b = 0$ along the *b* axis.

the Ni^{II} complexes. As shown in Figure 6b, the direction of $[Co(CNacac)_2]$ agrees with that of a terpy aromatic ring of $[Ni(pyterpy)_2]^{2+}$. As a result, the S_4 axis of $[Ni(pyterpy)_2]^{2+}$ is broken but the two mirror planes (σ_v) remain. The chirality of the 1D complex comes from the twist of the pyridine ring labeled with C(20), C(21), C(22), and N(6). Its torsion angle between the nearest terpy plane is ca. 52° (Figure 6b). This torsion lowers the symmetry of the 1D complex to C_2. Another pyridine ring labeled with C(1), C(2), C(3), and N(1), which is located at the opposite side of the Ni^{II} center, is not twisted because of steric effects coming from a curved structure of $[Co(CNacac)_2]$ as mentioned below. This pyridine is not involved in the appearance of the chirality. Each 1D complex in **2** is chiral. However, all 1D complexes are related to each other by inversion centers coming from the space group of *Pnna* so that their chirality is cancelled in the whole of the crystal.

All the 1D chain complexes are aligned along the *c* axis in a parallel fashion as shown in Scheme 1b and they are in van der Waals contact with each other. Between two 1D complexes adjacent to the *a* axis, the overlap of terpy planes of the Ni components is significant. Two terpy planes adjacent to the *a* axis overlap each other and this contact pattern is successively repeated along the *a* axis to form a plane-like 1D chain complex assembly extending over the *ac* plane. This contact scheme is illustrated in Figure 7b which is a sectional view of the region between $z = -0.15$ and $z = 0.15$. The plane-like assemblies are stacked along the *b* axis to form a layered structure. These plane-like assemblies are related by a diagonal glide plane so that the contact between two 1D complexes adjacent along the *b* axis takes place between $[Co(CNacac)_2]$ and terpy planes of the Ni component. As illustrated in Figure 7b $[Co(CNacac)_2]$ complexes are sandwiched between two plane-like assemblies. Due to this firm fitting the planar $[Co(CNacac)_2]$ complex is largely curved as shown in Figures 6a and 7c. This curved structure hinders the pyridine ring labeled with C(1), C(2), C(3), and N(1) from twisting against the terpy part.

In addition to the 1D coordination polymers, a sulfate ion and six methanol molecules were found between the 1D complexes in our structure refinement (Figure 7a). However, their displacement factors are large and distorted. These findings suggest that their packing is loose and they are in a dynamic disordered state rather than a static one. Besides the molecules found in the refinement, the existence of approximately six water molecules was suggested from TG measurements (Figure S4 in Supporting Information) and elemental analysis. However, their positions were not clearly determined in the X-ray analysis. In the TG measurement, slow weight loss was observed even at room temperature. This instability comes from the ineffective packing and interaction between the 1D chain complexes and the trapped molecules.

The formation of the 1D chain structure by the alternate linkage of the two types of metal complexes was also confirmed in another case where [Co(pyterpy)$_2$]SO$_4$ was used instead of [Ni(pyterpy)$_2$]SO$_4$. From a methanol solution containing both [Co(CNacac)$_2$] and [Co(pyterpy)$_2$]SO$_4$, black crystals of [Co(CNacac)$_2$][Co(pyterpy)$_2$]SO$_4$•xG (**2**-Co) were obtained. Single-crystal X-ray diffraction revealed **2** and **2**-Co to be isomorphous (Figure S5 in Supporting Information). The loose packing of the trapped species was similarly observed. Besides six methanol molecules found in the refinement process, elemental analysis and TG measurement also suggested the inclusion of six water molecules.

Conclusion

Our approach to synthesize a chiral coordination polymer using achiral components appears simple and easy. However, we have made several tricks. In general, prediction of the resultant structure of the coordination polymer formed from self-assembly of metal ions and ligands is difficult. This is because metal ions and ligands can have several coordination geometries and conformations, respectively. To realize a chiral arrangement of achiral components in a coordination polymer is more difficult. We consider however that it is not so difficult to control the formation of 1D coordination polymers if we use planar metal complexes and linear ligands. Planar complexes, in which the equatorial sites are blocked with ligands but the axial sites are free, accept additional ligands at the axial sites keeping their planar structure. Namely, planar complexes work as a metal ion with a linear coordination form. Linear ligands with two coordinating sites at their opposite sides make a bridge between planar complexes to form a 1D continuous structure. This coordinating scheme leaves little room for the formation of other structures. Moreover, introducing chirality to such type of 1D coordination polymer is possible. If appropriate twisting about the principal axis of the 1D coordination polymer is generated between the two building blocks, the 1D coordination polymer has a chance to be chiral. For appearance of this type of chirality, appropriate choice of building blocks is required considering the molecular symmetry. A planar complex is expected to have a mirror plane perpendicular to the molecular principal axis of the resultant 1D coordination polymer. Therefore, the choice of a linear ligand that does not have such a mirror plane is important.

In this study, we used bis β-diketonato Co^{II} complexes, [Co(hfac)$_2$] and [Co(CNacac)$_2$], as a planar complex and [Ni(pyterpy)$_2$]$^{2+}$ as a linear ligand. In the Ni^{II} complex, two terpy aromatic planes, which cross perpendicularly, generate D_{2d} symmetry. If the Co^{II} planar complex is twisted and its orientation does not agree with those of the terpy planes, the D_{2d} symmetry is lowered to C_2 symmetry and the 1D structure becomes chiral. Moreover, the pyridine rings of the Ni^{II} complex also have the possibility that they lower the D_{2d} symmetry by twisting. The former and the latter twisting scheme were observed in **1** and **2**, respectively. The results obtained in the X-ray structural analysis confirmed that our approach works at the stage where a piece of chiral 1D coordination polymer is formed.

As difficult problems, the control of the twisting of the building blocks in a 1D coordination polymer and that of the stacking mode of 1D coordination polymers still remain. In **2**, to afford twisting to the planar β-diketonato Co^{II} complex we introduced a CN group to acac (acetylacetonato) moiety with the intent that the bulky protruding CN group brings appropriate twisting to the planar complex. The result obtained, the suppression of the steric effects of the CN group by the curved structure of the planar complex, was beyond our expectation. The counter anions and included solvent molecules did not function as an effective packing material due to their structural disorder and **2** was an achiral crystal. On the other hand, in **1**, the chirality of the 1D complex was preserved in a crystal. Although this is also a result of total crystal packing, the following two factors are considered to work there. One is the good packing observed in the log cabin like stack of the 1D complexes as mentioned above. Another factor is the [Co(hfac)$_3$]$^-$ guests as a packing material. The [Co(hfac)$_3$]$^-$ guests have their own chirality and engage with the host of the 1D complexes. This engagement contributes effectively to the preservation of the chirality in the crystal. Examples a chiral guest that works as a template to induce host molecules to form a chiral assembly are known.[11] In our case, the [Co(hfac)$_3$]$^-$ complexes are labile and it is difficult to consider that they works as a rigid template, however, they undoubtedly functioned as a good packing material. As a way for dealing with the problem of crystal packing, examination of packing materials including rigid and labile species may be a possible approach.

Experimental

Materials and Physical Measurements. CNacacH (3-cyanopentane-2,4-dione), pyterpy (4′-(4-pyridyl)-2,2′:6′,2″-terpyridine), [Co(CNacac)$_2$], and [Co(hfac)$_2$] were synthesized according to reported procedures.[12–14] [Ni(pyterpy)$_2$]X•nH$_2$O (X = Cl$_2$, SO$_4$, and (NO$_3$)$_2$) and [Co(pyterpy)$_2$]SO$_4$•nH$_2$O were synthesized based on a reported method[7] by refluxing pyterpy and corresponding metal salts. TG measurement was conducted for **2** and **2**-Co using a TA Instruments TGA-2950 thermobalance under N$_2$ flow. The crystal structures of **1**, **2**, and **2**-Co were determined by single-crystal X-ray diffraction. The crystal of **2** and **2**-Co was coated with epoxy resin in order to prevent spontaneous liberation of the neutral guests. The diffraction data measurements for all samples were carried out using a Rigaku R-AXIS RAPID imaging plate diffractometer at 153 K. The structures were solved by the direct method using the program SHELXS-97[15] or SIR-92.[16] The refinement and all further calculations were performed using the program SHELXL-97.[15] All non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. H atoms were generated geometrically. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-721201, -721202, and -721203 for **1**, **2**, and **2**-Co, respectively. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

[{Co(hfac)$_2$}{Ni(pyterpy)$_2$}][Co(hfac)$_3$]$_2$ (1). A methanol solution of [Co(hfac)$_2$] (15 mmol L^{-1}, 4 mL) and that of [Ni(pyterpy)$_2$]Cl$_2$•nH$_2$O (16 mmol L^{-1}, 4 mL) were mixed. After slow evaporation of the solvent over a week at room temperature, wine red crystals were obtained (28 mg, 17% yield). Found: C, 38.08; H, 1.73; N, 4.697%. Calcd for $C_{80}H_{36}N_8O_{16}F_{48}Co_3Ni$: C, 38.24; H, 1.44; N, 4.46%.

Crystal data: $C_{80}H_{36}N_8O_{16}F_{48}Co_3Ni$, FW: 2512.67, tetragonal, space group $P4_2$ (No. 77), $a = 22.064(2)$ Å, $c = 19.956(2)$ Å, $U = 9714(1)$ Å^3, $Z = 4$, $T = 153$ K, 215151 reflections measured, 11460 unique ($R_{\text{int}} = 0.047$) which were all used in the refinement. The final $wR2$ and GOF (on F^2) were 0.132 and 1.110, respectively, for 1418 parameters. The Flack parameter was refined to be 0.083(12), indicating the discussion on the chirality is reliable.

[Co(CNacac)$_2$][Ni(pyterpy)$_2$](SO$_4$)·*x*(Guest) (2). A methanol solution of [Co(CNacac)$_2$] (15 mmol L^{-1}, 6 mL) and that of [Ni(pyterpy)$_2$](SO$_4$)·nH$_2$O (8.5 mmol L^{-1}, 10 mL) were mixed. After the mixed solution was left for a few days, red crystals were obtained (84 mg, 67% yield). The TG curve, which is shown in Figure S4 in Supporting Information, suggested the inclusion of six methanol molecules and six water molecules as guests. However, the crystal was unstable due to spontaneous liberation of the guest molecules. Elemental analysis did not give results with an accuracy of within ±0.4%.

Crystal data: $C_{52}H_{40}N_{10}O_8SCoNi \cdot 6CH_3OH \cdot 6H_2O$, FW: 1383.01, orthorhombic, space group *Pnna* (No. 52), $a = 17.5001(3)$ Å, $b = 16.5072(2)$ Å, $c = 22.3439(3)$ Å, $U = 6454.7(2)$ Å^3, $Z = 4$, $T = 153$ K, 106127 reflections measured, 11713 unique ($R_{\text{int}} = 0.078$) which were all used in the refinement. The final $wR2$ and GOF (on F^2) were 0.3062 and 0.808, respectively, for 388 parameters. Structural disorder was observed for the methanol molecules and even for the sulfate ion. The water molecules were not included in the refinement because their positions were unable to be determined clearly.

[Co(CNacac)$_2$][Co(pyterpy)$_2$](SO$_4$)·*x*(Guest) (2-Co). A methanol solution of [Co(CNacac)$_2$] (17 mmol L^{-1}, 15 mL) and that of [Co(pyterpy)$_2$](SO$_4$) (8.8 mmol L^{-1}, 30 mL) were mixed. After the mixed solution was left for a few days, black crystals were obtained (149 mg, 42% yield). Although the TG curve, which is shown in Figure S4, suggested the inclusion of six methanol molecules and six water molecules as guests, the crystal was unstable due to spontaneous liberation of the guest molecules and elemental analysis did not give results with an accuracy of within ±0.4%.

Crystal data: $C_{52}H_{40}N_{10}O_8SCo_2 \cdot 6CH_3OH \cdot 6H_2O$, FW: 1383.25, orthorhombic, space group *Pnna* (No. 52), $a = 17.5454(1)$ Å, $b = 16.4751(2)$ Å, $c = 22.1790(3)$ Å, $U = 6411.1(1)$ Å^3, $Z = 4$, $T = 153$ K, 118564 reflections measured, 11662 unique ($R_{\text{int}} = 0.067$) which were all used in the refinement. The final $wR2$ and GOF (on F^2) were 0.2899 and 0.884, respectively, for 392 parameters. Structural disorder was observed for the methanol molecules and the sulfate ion. The water molecules were not included in the refinement because their positions were unable to be determined clearly.

This work is supported by Grant-in-Aid for the Japan Society for the Promotion of Science (JSPS) Fellows, No. 1811462.

Supporting Information

Diagrams of crystal structure for **1** (Figures S1, S2, and S3) and that for **2**-Co (Figure S5), and TG curves for **2** and **2**-Co (Figure S4), are deposited in Supporting Information. This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

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