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Article

Interchain-Solvent-Induced Chirality Change of 1D Helical Chains: From Achiral to Chiral Crystallization

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Three helical supramolecular stereoisomers of *meso*-**2**, Δ-**2**, and Δ-**3** with the formula of *cis*-[Ni(*f*-*rac*-L)][Ni(CN)$_4$] were successfully constructed based on the [Ni(*f*-*rac*-L)]$^{2+}$ and [Ni(CN)$_4$]$^{2-}$ building blocks (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). In all three supramolecular stereoisomers, *cis*-[Ni(*f*-*rac*-L)]$^{2+}$ cations are alternately bridged by [Ni(CN)$_4$]$^{2-}$ anions through two cis (in *meso*-**2** and Δ-**2**) or trans (in Δ-**3**) cyano groups to form one-dimensional (1D) helical chains of *cis*-[Ni(*f*-*rac*-L)][Ni(CN)$_4$]. In *meso*-**2**, the right/left-handed chirality of the originally formed chain is transferred oppositely to adjacent chains through the interchain hydrogen-bonding interactions of hexameric water clusters, leading to the formation of *meso*-**2** with a central symmetrical space group, $P2_1/n$, in which the 1D helical chains are packed in an alternating right- and left-handed chirality. In Δ-**2** and Δ-**3**, the right/left-handed chirality of the original chain is transferred uniformly to adjacent chains through the zipper-like interchain hydrophobic interactions, resulting in the formation of Δ-**2** and Δ-**3** with chiral space groups of $P2_12_12_1$ and $P3_121$, respectively, in which all of the 1D helical chains are arranged in the same right/left-handed chirality.

Introduction

Chirality is of fundamental importance for life and plays a key role in biological systems and pharmacy,[1] as well as in advanced materials such as nonlinear optical devices,[2] enantioselective synthesis and asymmetric catalysis,[3] and chiral magnets.[4] Recently, much interest has been focused on the construction of helical coordination polymers using chiral,[4b,f,5] or achiral[4c,d,6−9] building blocks because many important biopolymers such as DNA and peptides possess helical structures with a single right-handed chirality. In general, right- and left-handed helices are obtained in equal amounts as a meso compound when achiral or racemic building blocks are used.[6] A meso compound contains an equal amount of right- and left-handed helices in a single crystal, and each crystal is achiral and crystallizes in a central symmetrical space group. In some cases, however, spontaneous resolution occurs during the crystallization,[4c,d,7] which yields a conglomerate.[7c] A conglomerate is a mechanical and racemic mixture of chiral crystals, in which each crystal is

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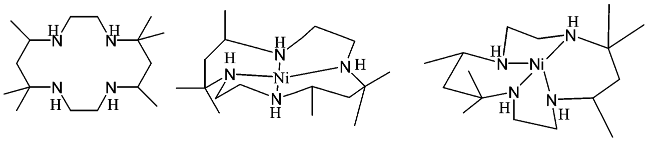
enantiopure and crystallizes in a chiral space group. Even though the discovery of spontaneous resolution by Louis Pasteur[8] happened over 100 years ago, it is still a rare phenomenon[7b] and cannot be predicted a priori because the laws of physics determining the processes are not yet fully understood.[4c] It has been found that noncovalent interactions such as hydrogen bonds may play a key role in the process of spontaneous resolution.[7c]

Supramolecular isomerism, which was defined as the existence of more than one type of network superstructure for the same molecular building block,[10] is indeed a common phenomenon in the fields of coordination polymers and crystal engineering.[11] In our previous work,[6c] two cyano-bridged supramolecular isomers, a discrete molecular square $\{cis\text{-}[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]\}_2$ (**1**) and a one-dimensional (1D) helical chain *cis*-$[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]$ (**2**) (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), were constructed (see Chart 1). In **2**, each helical chain is constructed by alternately bridging the *cis*-$[Ni(f\text{-}rac\text{-}L)]^{2+}$ cations with $[Ni(CN)_4]^{2-}$ anions through its two cis cyano groups, and the 1D chains are packed in an alternating right- and left-handed chirality to yield an achiral supramolecular isomer of *meso*-**2**. In our continuing efforts to construct new supramolecular isomers based on the $[Ni(f\text{-}rac\text{-}L)]^{2+}$ and $[Ni(CN)_4]^{2-}$ building blocks, two new chiral supramolecular stereoisomers of *cis*-$[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]$, Δ-**2** and Δ-**3** featuring 1D right-handed helical chainlike structures, were obtained. A detailed structural investigation indicates that the interchain hydrogen-bonding and hydrophobic interactions play a key role in the transfer of chirality between neighboring helical chains, leading to the 1D helical chains being packed in an achiral or homochiral manner.

Chart 1



L **[Ni(α-rac-L)]$^{2+}$** ***cis*-[Ni(*f*-*rac*-L)]$^{2+}$**

Experimental Section

Materials and General Methods. The macrocyclic ligand (L) was prepared according to the literature method[12a,b] and separated as the racemic form of *rac*-L. The nickel(II) complexes $[Ni(\alpha\text{-}rac\text{-}L)](ClO_4)_2$ and *cis*-$[Ni(f\text{-}rac\text{-}L)(CN)_2](H_2O)_2$ were prepared according to the previously reported methods.[6c,12c] $K_2Ni(CN)_4{\cdot}2H_2O$ was prepared according to the literature method.[13] Anhydrous acetonitrile and methanol were dried and distilled under N_2 by following standard procedures. All of the other chemicals are commercially available and used without further purification. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000−400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. An electrospray ionization mass spectrometry (ESI-MS) spectrum was obtained using a Shimadzu LCMS-2010A mass spectrometer. The solid-state circular dichroism (CD) spectra were recorded on a Jasco J-810 spectropolarimeter with KBr pellets.

***cis*-$[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]{\cdot}3H_2O$ (*meso*-2·3H_2O), *cis*-$[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]{\cdot}1.25H_2O$ (Δ-3·1.25H_2O), and *cis*-$[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]{\cdot}2H_2O$ (4·2H_2O)**. A water solution (40 mL) of $K_2Ni(CN)_4{\cdot}$

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Table 1. Crystallographic Data

compound	*meso*-**2**·$3H_2O$	Δ-**2**·MeCN	Δ-**2**	Δ-**3**·$1.25H_2O$
formula	$C_{20}H_{42}N_8Ni_2O_3$	$C_{22}H_{39}N_9Ni_2$	$C_{20}H_{36}N_8Ni_2$	$C_{20}H_{38.5}N_8Ni_2O_{1.25}$
fw	560.04	547.04	505.99	528.51
T (K)	293(2)	293(2)	173(2)	173(2)
cryst size (mm)	0.48 × 0.12 × 0.06	0.32 × 0.13 × 0.12	0.43 × 0.27 × 0.20	0.41 × 0.35 × 0.32
cryst syst	monoclinic	orthorhombic	orthorhombic	trigonal
space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P3_121$
a/Å	10.052(3)	10.026(2)	10.066(3)	16.0165(5)
b/Å	10.184(3)	15.020(4)	13.747(4)	16.0165(5)
c/Å	27.379(9)	18.179(5)	17.948(6)	18.6084(11)
β/deg	98.371(9)	90	90	90
V/Å^3	2772.7(15)	2737.6(11)	2483.6(14)	4134.0(3)
Z	4	4	4	6
D_c/g cm^{-3}	1.342	1.327	1.353	1.274
μ/mm^{-1}	1.392	1.402	1.538	1.392
F(000)	1192	1160	1072	1683
unique reflns (R_{int})	5351 (0.0631)	5341 (0.0731)	4719 (0.0505)	5414 (0.0402)
no. of param	304	305	277	289
S on F^2	1.032	1.046	1.096	1.078
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0628, 0.1296	0.0748, 0.1689	0.0636, 0.1484	0.0287, 0.0773
R1,[a] wR2[b] (all data)	0.1316, 0.1611	0.1413, 0.1990	0.0861, 0.1603	0.0290, 0.0775
absolute structure param		0.02(4)	0.03(3)	−0.007(18)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = [(F_o^2) + 2F_c^2]/3$.

$2H_2O$ (0.139 g, 0.5 mmol) was layered with an acetonitrile solution (20 mL) of [Ni(α-*rac*-L)]$(ClO_4)_2$ (0.272 g, 0.5 mmol). After about 2 weeks, thin prism-shaped purple crystals of *meso*-**2**·$3H_2O$, block-shaped crystals of **4**·$2H_2O$, and hexagonal prism-shaped violet crystals of Δ-**3**·$1.25H_2O$ formed along the wall of the tube (from bottom to top), together with small amount of crystals of *meso*-**2**·$4.5H_2O$ at the bottom of the tube. They were separated manually and dried in air. Yield: ca. 15% for *meso*-**2**·$3H_2O$, 35% for Δ-**3**·$1.25H_2O$, and 10% for **4**·$2H_2O$. Anal. Calcd for $C_{20}H_{42}N_8Ni_2O_3$ (*meso*-**2**·$3H_2O$): C, 42.90; H, 7.56; N, 20.01. Found: C, 42.89; H, 7.53; N, 20.23. Calcd for $C_{20}H_{38.5}N_8Ni_2O_{1.25}$ (Δ-**3**·$1.25H_2O$): C, 45.46; H, 7.34; N, 21.20. Found: C, 45.51; H, 7.35; N, 21.22. Calcd for $C_{20}H_{40}N_8Ni_2O_2$ (**4**·$2H_2O$): C, 44.32; H, 7.44; N, 20.68. Found: C, 44.43; H, 7.06; N, 20.67. IR (KBr): ν_{CN} 2154 (coordinated) and 2126 (uncoordinated) cm^{-1} for *meso*-**2**; 2153 (coordinated) and 2126 (uncoordinated) cm^{-1} for Δ-**3**; 2158 (coordinated) and 2122 (uncoordinated) cm^{-1} for **4**.

***cis*-[Ni(*f-rac*-L)][Ni(CN)₄]·MeCN (Δ-2·MeCN) and *cis*-[Ni(*f-rac*-L)][Ni(CN)₄] (Δ-2).** Crystalline solid of *cis*-[Ni(*f-rac*-L)$(CN)_2$]-$(H_2O)_2$ (0.043 g, 0.1 mmol) was dissolved in a mixture solution of anhydrous acetonitrile and methanol (1:1). The resulting purple solution was left in a sealed tube or evaporated slowly in a sealed desiccator over P_2O_5 at room temperature to give platelike purple crystals of Δ-**2**·$(MeCN)_n$, together with a gelatinous solid. Yield: ca. 35%. Anal. Calcd for $C_{22}H_{39}N_9Ni_2$ (Δ-**2**·CH_3CN): C, 48.31; H, 7.19; N, 23.05. Found: C, 47.63; H, 7.56; N, 22.06. IR (KBr): ν_{CN} 2162 (coordinated) and 2119 (uncoordinated) cm^{-1}; 2251 (CH_3CN) cm^{-1}. The result of ESI-MS spectral measurement indicates that the gelatinous solid is the free L ligand.

The crystals of Δ-**2** were obtained by exposing the crystals of Δ-**2**·MeCN to air for a half day.

X-ray Crystallography. Single-crystal data of *meso*-**2**·$3H_2O$, Δ-**2**·CH_3CN, Δ-**2**, and **4**·$2H_2O$ were collected on a Bruker Smart 1000 CCD diffractometer, and those of Δ-**3**·$1.25H_2O$ were collected on a Bruker APEX CCD, with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). All empirical absorption corrections were applied by using the *SADABS* program.[14] The structures were solved using direct methods, which yielded the positions of all non-H atoms. These were refined first isotropically and then anisotropically. All of the H atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The H atoms of the water molecules were located in the difference Fourier map and refined isotropically; the O−H distances involving the water molecules were refined with a DFIX restraint of 0.86−0.91 Å. All calculations were performed using the *SHELXTL* system of computer programs.[15] The crystallographic data for *meso*-**2**·$3H_2O$, Δ-**2**·CH_3CN, Δ-**2**, and Δ-**3**·$1.25H_2O$ are summarized in Table 1. The selected bond lengths and angles (Table S2), as well as the structural details of **4**·$2H_2O$, are given in the Supporting Information.

Results and Discussion

Preparation Chemistry. In our previous report,[6c] two supramolecular isomers of **1** and *meso*-**2** were successfully synthesized. Isomer **1** could be obtained by layering a water solution of $K_2[Ni(CN)_4]$ with *an equal volume of* an acetonitrile solution of [Ni(α-*rac*-L)]$(ClO_4)_2$ (see Chart 2). Isomer *meso*-**2** could be obtained by the reaction of [Ni(α-*rac*-L)]$(ClO_4)_2$ and KCN in water/acetonitrile (1:1) or by slow conversion of a metastable compound of *cis*-[Ni(*f-rac*-L)$(CN)_2$] in methanol/acetonitrile (1:1). Interestingly, layering a water solution of $K_2[Ni(CN)_4]$ with a *half volume of* an acetonitrile solution of [Ni(α-*rac*-L)]$(ClO_4)_2$ led to the formation of four compounds, *meso*-**2**·$4.5H_2O$, *meso*-**2**·$3H_2O$, **4**·$2H_2O$, and Δ-**3**·$1.25H_2O$ (Scheme 1), along the wall of the tube (from bottom to top) in a single batch, while isomer **1** was not found in the solution. The crystallization under various MeCN/H_2O ratios has also been investigated. It was found that increasing the concentration of water (MeCN/$H_2O \leq 1{:}2$) does not affect the species of supramolecular isomers, in which the crystals of **4**·$2H_2O$ were formed near the interface of MeCN/H_2O and the crystals of *meso*-**2** (in the form of $4.5H_2O$ and $3H_2O$) and Δ-**3**·$1.25H_2O$ were

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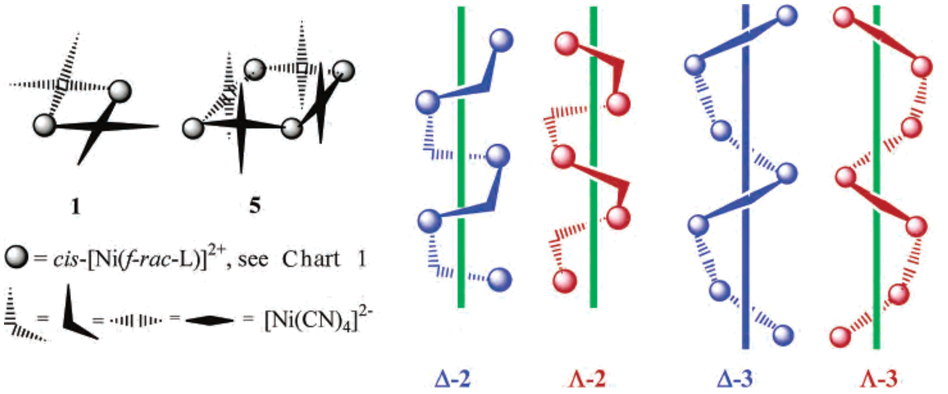
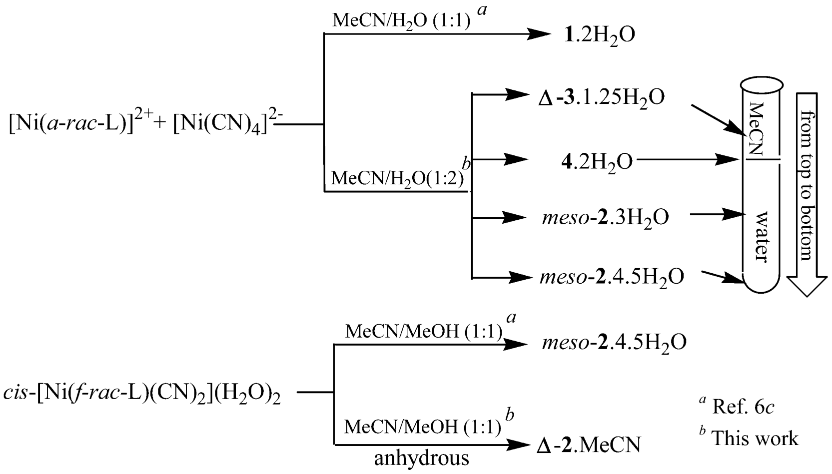
(14) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(15) Sheldrick, G. M. *SHELXS 97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Chart 2. Possible Supramolecular Isomers and Stereoisomers Based on *cis*-$[Ni(f\text{-}rac\text{-}L)]^{2+}$ and $[Ni(CN)_4]^{2-}$ Building Blocks



Scheme 1



formed below and above the interface, respectively, while still only isomer **1** was obtained if the relative ratios of $MeCN/H_2O$ are over 1:1.

The above results indicate that the supramolecular isomerism and the formation of isomers **1**, *meso*-**2**, and Δ-**3** are rather dependent on their solubility. In a solution of a lower concentration of water molecules ($MeCN/H_2O \geq 1{:}1$), the supramolecular isomerism was baffled by the rapid deposition of a metastable isomer of **1** (Scheme 1) because it is slightly soluble in this solution. In a solution of a higher concentration of water molecules ($MeCN/H_2O \leq 1{:}2$), a complex isomerism process occurred, in which isomer **1** primarily formed was not isolated from the solution because of the higher solubility but slowly converted into insoluble isomers of *meso*-**2** and Δ-**3**. Therefore, the crystallization processes of *meso*-**2** and Δ-**3** are thermodynamically favored, while the self-assembly of **1** is kinetically controlled. Indeed, isomer **1** is more soluble in a $MeCN/H_2O$ (1:2) solution than in a $MeCN/H_2O$ (1:1) solution, and the previous report[6c] indicates that isomer **1** can slightly dissolve in a $MeCN/H_2O$ (1:1) solution to disintegrate the intermediate species of $[NiL(CN)(H_2O)]^+$, $[Ni(L\text{-}H)]^+$, and $\{[Ni(HL)]_2[Ni(CN)_4]\}^{4+}$, which correspond to the oligomers of *meso*-**2** and Δ-**3**. Moreover, **4**·$2H_2O$ can also slightly dissolve in a $MeCN/H_2O$ (1:1) solution to produce the intermediate species of $[Ni(L\text{-}H)]^+$, $\{[NiL](OH)(MeCN)\}^+$, $\{[NiL]_3[Ni(CN)_4]_2(OH)(MeCN)\}^+$, and $\{[Ni(HL)]_3[Ni(CN)_4]_4(H_2O)(MeCN)\}^+$ (Figure S10a in the Supporting Information), and these oligomers aggregate with $[Ni(\alpha\text{-}rac\text{-}L)]^{2+}$ and $[Ni(CN)_4]^{2-}$ in solution to form the insoluble isomers *meso*-**2** and Δ-**3**, respectively. The proposed processes for the formation of *meso*-**2** and Δ-**3**, which are confirmed by the results of ESI-MS measurements, are given in the Supporting Information.

Opposite Interchain Chirality Transfer and Achiral Crystallization in Water-Cluster-Bonded 1D Helical Chains of *meso*-2·4.5H₂O and *meso*-2·3H₂O. The structure of *meso*-**2**·$4.5H_2O$ was reported previously,[6c] and the structure of *meso*-**2**·$3H_2O$ (Figure 1a) is similar to that of *meso*-**2**·$4.5H_2O$. In *meso*-**2**·$3H_2O$, the $[Ni(CN)_4]^{2-}$ anions alternately bridge the *cis*-$[Ni(f\text{-}rac\text{-}L)]^{2+}$ cations through its two cis cyano groups to form a 1D right-handed (Δ) helical chain around the crystallographic 2_1 axis (Figure 1b). The C and N atoms of the cyano bridge in *meso*-**2**·$3H_2O$ bind to four- and six-coordinated Ni^{II}, respectively; the Ni−C distances of the bridged cyano groups [1.858(6) and 1.871(7) Å] are close to those of the terminal cyano groups [1.865(7) and 1.875(6) Å] and are shorter than the corresponding $Ni-N_{cyano}$ distances [2.084(5) and 2.092(5) Å]. The two adjacent $[Ni(CN)_4]^{2-}$ planes are perpendicular within the chain with a dihedral angle of 90.1°. It is interesting to note that the adjacent chains along the *c* axis are constructed with the opposite Λ (left-handed) chirality, leading to the formation of a meso isomer of *meso*-**2**·$3H_2O$ (Figure 2a). The Λ chirality is generated from the opposite chirality transfer through the interchain hexameric water clusters of $(H_2O)_6$ (Figures 2a and S2 in the Supporting Information). As shown

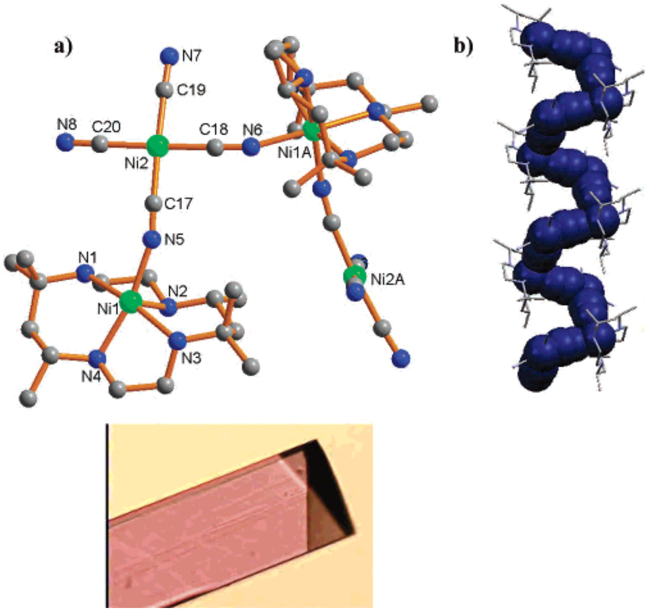


Figure 1. (a) Structural segment of *meso*-**2**·3H_2O (top) and a photograph of a single crystal of *meso*-**2**·3H_2O (bottom). (b) Side view of the 1D right-handed helical chain.

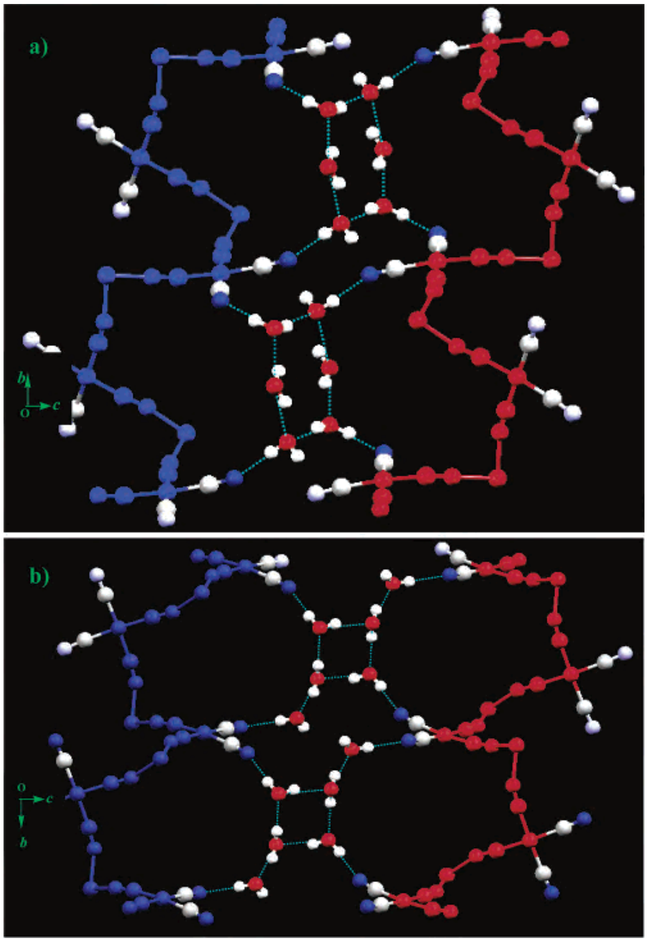


Figure 2. Interchain hexameric water clusters of $(H_2O)_6$ in (a) *meso*-**2**·3H_2O and (b) *meso*-**2**·4.5H_2O, showing the opposite chirality transfer through the hydrogen-bonding interactions between the Δ (blue) and Λ (red) helical chains.

in Figure 2a, each $(H_2O)_6$ ring forms four hydrogen bonds (see Table S2 in the Supporting Information), with two uncoordinated cyano N atoms in the Δ helical chain (blue one) on the one side and with two uncoordinated cyano N atoms in the Λ helical chain (red one) on the opposite side. Therefore, the $(H_2O)_6$ rings act like a "mirror plane" to generate an adjacent chain with opposite chirality. A similar "mirror plane" effect is also found in the previously reported structure of *meso*-**2**·4.5H_2O (Figure 2b). Accordingly, the interchain hydrogen bonding of hexameric water clusters leads to the 1D helical chains packing in a meso or an intracrystal racemic form instead of a homochiral way. Though several structures of water clusters have been reported recently,[16] most of the investigations have been focused on the structural characterization; little information related to their functions has been known except for the roles to stabilize the hydrated supramolecular structures and to fill the space of the cavities in the metal−organic frameworks. To our knowledge, the intermolecular water-cluster-induced chirality transfer has not been reported so far.

In contrast to the meso arrangement of 1D hydrogen-bonded helical chains along the *c* axis, the 1D helical chains are packed in a homochiral form along the *a* axis (Figure S3 in the Supporting Information) and the homochiral packing of the chains is induced by the zipper-like complementary interchain hydrophobic interactions (Figure S3 in the Supporting Information), allowing the chirality of the originally formed helical chain be transferred uniformly to the adjacent chains along the *a* axis.

Spontaneous Resolution and Chiral Crystallization in 1D Helical Chains of Δ-2·MeCN, Δ-2, and Δ-3·1.25H_2O with Interchain Hydrophobic Interactions. During the crystallization of Δ-**2**·MeCN and Δ-**3**·1.25H_2O, spontaneous resolution occurred and gave crystals with chiral space groups of $P2_12_12_1$ and $P3_121$ and absolute structure parameters of $+0.02(4)$ and $-0.01(1)$ for Δ-**2**·MeCN and Δ-**3**·1.25H_2O (Table 1), respectively. It should be mentioned that not all

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(16) (a) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808 and references cited therein. (b) Li, Y.; Jiang, L.; Feng, X. L.; Lu, T. B. *Cryst. Growth Des.* **2006**, *6*, 1074. (c) Liao, Y. C.; Jiang, Y. C.; Wang, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 12794. (d) Mukhopadhyay, U.; Bernal, I. *Cryst. Growth Des.* **2005**, *5*, 1687. (e) Lakshminarayanan, P. S.; Suresh, E.; Ghosh, P. *J. Am. Chem. Soc.* **2005**, *127*, 13132. (f) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2005**, *44*, 5553. (g) Ghosh, S. K.; Bharadwaj, P. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3577. (h) Ghosh, S. K.; Ribas, J.; Bharadwaj, P. K. *CrystEngComm* **2004**, *6*, 250. (i) Zhao, B.; Cheng, P.; Chen, X.; Cheng, C.; Shi, W.; Liao, D.; Yan, S.; Jiang, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3012. (j) Rodríguez-Cuamatzi, P.; Vargas-Díaz, G.; Höpfl, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3041. (k) Ma, B. Q.; Sun, H. L.; Gao, S. *Chem. Commun.* **2004**, 2220. (l) Long, L. S.; Wu, Y. R.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2004**, *43*, 3798. (m) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2003**, *42*, 8250. (n) Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533. (o) Infantes, L.; Motherwell, S. *CrystEngComm* **2002**, *4*, 454. (p) Moorthy, J. N.; Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3417. (q) Doedens, R. J.; Yohannes, E.; Khan, M. I. *Chem. Commun.* **2002**, 62. (r) Xu, J.; Radkov, E.; Ziegler, M.; Raymond, K. N. *Inorg. Chem.* **2000**, *39*, 4156. (s) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094. (t) Nauta, K.; Müller, R. E. *Science* **2000**, *287*, 293. (u) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671. (v) Cruzan, J. D.; Braly, L. B.; Liu, K.; Brown, M. G.; Loeser, J. G.; Saykally, R. J. *Science* **1996**, *271*, 59.

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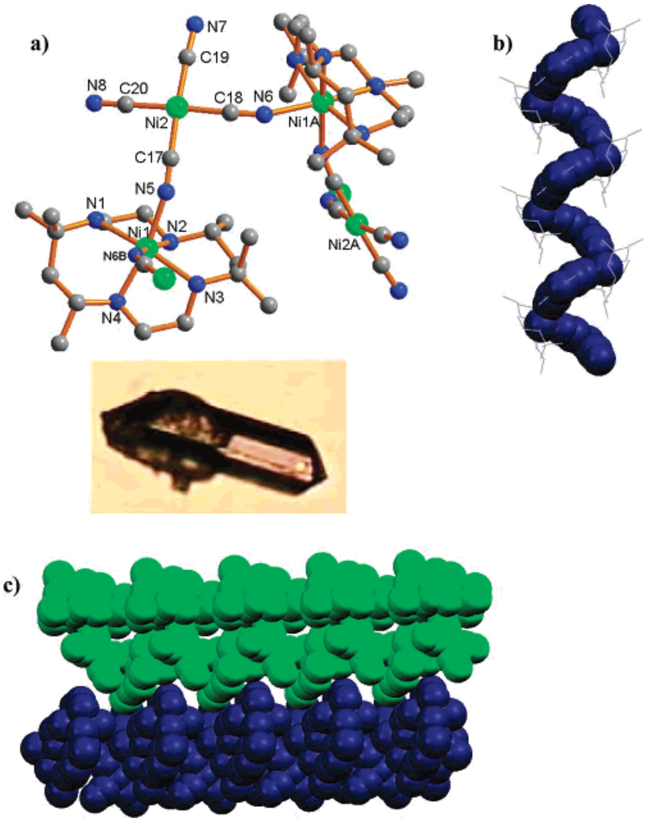

Figure 3. (a) Structural segment of Δ-**2**·MeCN, showing the coordination environments of Ni^{II} (top), and a photograph of a single crystal of Δ-**2**·MeCN (bottom). (b) Side view of the 1D helical chain with Δ chirality. (c) The space-filling mode for two adjacent chains, showing the homochirality transfer through the interchain zipper-like complementary hydrophobic interactions.

of the crystals of Δ-**3**·1.25H_2O were crystallized in homochirality in a single batch; some crystals were crystallized as racemic twinning with nonzero absolute structure parameters, while the crystallization of Δ-**2**·MeCN seems always homochiral in different batches, with near-zero absolute structure parameters. It is rather unusual that interchain solvents can affect the crystallization form of **2**·solvent: from achiral crystallizations of *meso*-**2**·4.5H_2O and *meso*-**2**·3H_2O to homochiral crystallization of Δ-**2**·MeCN.

The structure of Δ-**2**·MeCN is similar to that of *meso*-**2**·3H_2O, in which the two adjacent $[Ni(CN)_4]^{2-}$ planes are also twisted with dihedral angles of 80.5° (Figure 3a) and the $[Ni(CN)_4]^{2-}$ anions alternately bridge the *cis*-[Ni(*f*-*rac*-L)]$^{2+}$ cations through its two cis cyano groups to result in a right-handed helical chain around the 2_1 axis (Figure 3b). In Δ-**3**·1.25H_2O, however, the 1D right-handed helical chain is made up of the *cis*-[Ni(*f*-*rac*-L)]$^{2+}$ cations alternately bridged by the $[Ni(CN)_4]^{2-}$ anions through its two trans cyano groups around the crystallographic 3_1 axis (Figure 4a,b). In each helix of Δ-**3**, the three $[Ni(CN)_4]^{2-}$ planes are also twisted to avoid the repulsive interactions among the uncoordinated cyano groups (Figure 4a), with dihedral angles of 61.8°.

In Δ-**2**·MeCN, the originally formed chiral chain acts as a template to propagate its handedness uniformly to adjacent chains through the zipper-like complementary interchain hydrophobic interactions (Figure 3c), resulting in the homochiral Δ-**2**·MeCN (Figure S4 in the Supporting Information). Each chain connects with four adjacent chains through the interchain hydrophobic interactions (Figure S5 in the Supporting Information) to generate narrow channels along the *a* axis (Figures S4 and S6 in the Supporting Information), and the channels are occupied by the acetonitrile molecules.

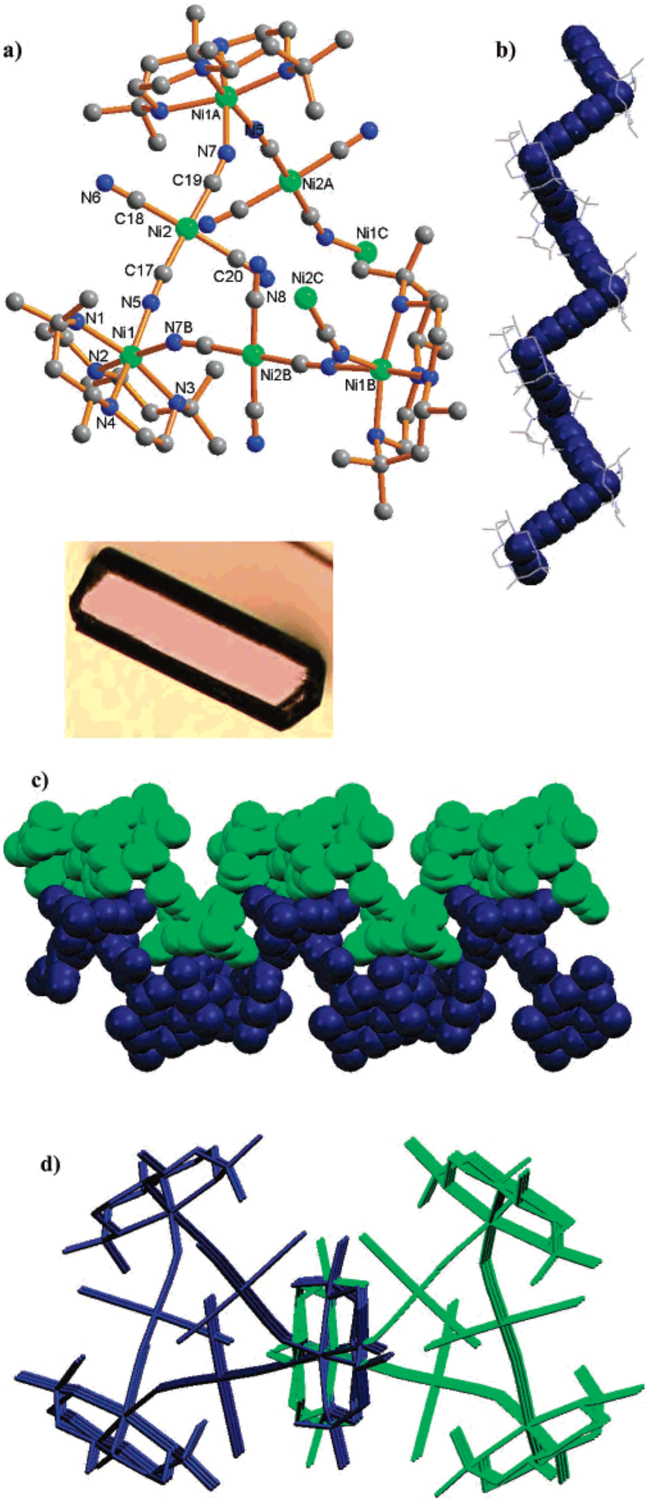

Figure 4. (a) Structural segment of Δ-**3**·1.25H_2O, showing the coordination environments of Ni^{II} (top), and a photograph of a single crystal of Δ-**3**·1.25H_2O (bottom). (b) Side view of the 1D helical chain with Δ chirality. (c) The space-filling mode for two adjacent chains. (d) View of the 1D helical chains down the polymer axis, showing that the Δ chirality of one chain (green) is transferred to the adjacent chain (blue) through the interchain zipper-like complementary hydrophobic interactions.

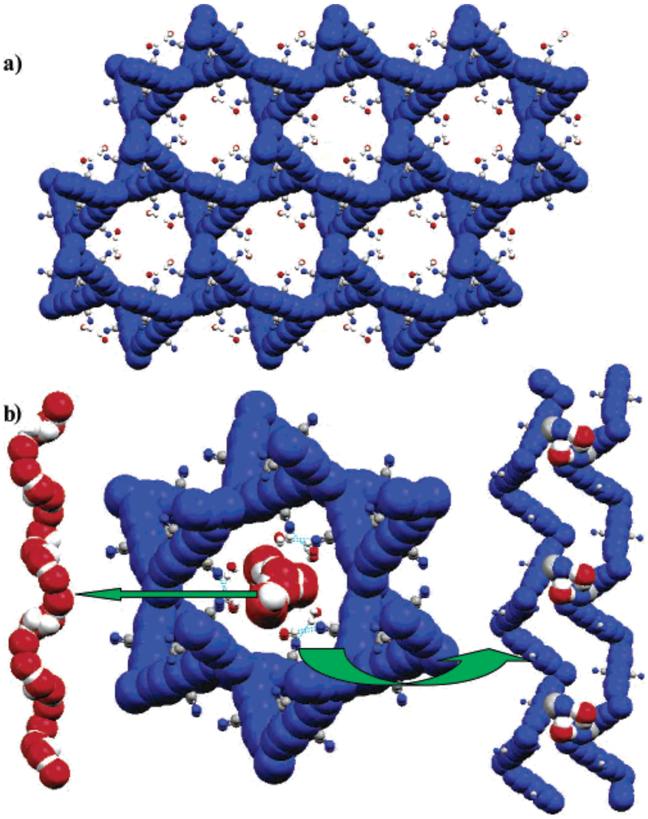

Figure 5. (a) 3D framework structure of Δ-**3**·1.25H_2O with 1D open right-handed chiral channels (the ligand and water chains are omitted for clarity). (b) View of the 1D left-handed helical water chain (left) parasitized in each 1D open chiral channel (middle) and two staplelike hydrogen-bond-linked helical chains (right).

After the loss of interchain acetonitrile solvents, Δ-**2**·MeCN converts to Δ-**2** with a reduced cell volume (Table 1). The structure of Δ-**2** is similar to that of Δ-**2**·MeCN, in which all of the helical chains show a right-handed homochirality and are packed along the *a* axis (Figure S4 in the Supporting Information), indicating that the homochiral structure is still maintained after removal of the MeCN molecules. The unit cell parameters *a* and *c* in Δ-**2** are identical with those in Δ-**2**·MeCN, while the unit cell parameter *b* is much smaller after the loss of MeCN solvents, from 15.020(4) in Δ-**2**·MeCN to 13.747(4) in Δ-**2**. Thus, the narrow channels in Δ-**2**·MeCN have almost disappeared after the loss of MeCN solvents (see Figure S6 in the Supporting Information).

Similar to Δ-**2**·MeCN, the Δ chirality of the originally formed 1D helical chain in Δ-**3**·1.25H_2O is also transferred uniformly to an adjacent chain through the zipper-like complementary interchain hydrophobic interactions, resulting in a second chain with the same Δ chirality, as shown in Figure 4c,d. Each Δ helical chain connects with three adjacent Δ chains through the interchain hydrophobic interactions (Figure S7 in the Supporting Information), generating a chiral supramolecular isomer of Δ-**3** with a 3D framework structure (Figure 5a) and novel 1D open right-handed helical chiral channels (Figures 5b and S8 in the Supporting Information). In each of the chiral channels, the two adjacent chains are further linked by the staplelike hydrogen bonds (Figure 5b) between the water molecules and the N atoms of uncoordinated cyano groups (O1···N6 = 2.956(7) Å, O1···N6^a = 3.184(6) Å, ∠O1−H1E···N6 = 174°, ∠O1−H1D···N6^a = 133°, a = *y*, *x*, −*z*). The most striking feature in Δ-**3**·1.25H_2O is the formation of a left-handed chiral water chain around the 3_1 axis in each of the right-handed chiral channels, as shown in Figures 5b and S8 in the Supporting Information. Though it is hard to see the hydrogen-bonding interactions between the chiral water chain and the O1 water molecules bonded to the inner wall of the chiral channel, because of the disordered arrangement of the water chain caused by high 3_1 symmetry, there is no doubt that the Λ chirality of the water chain originates from the Δ chirality of the channel.

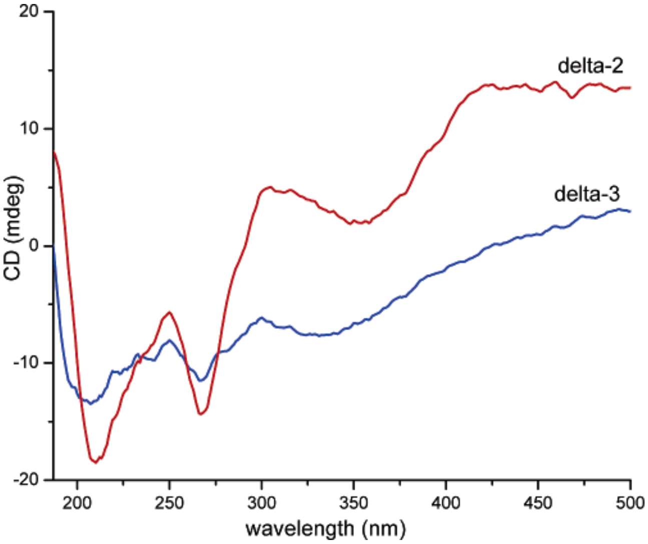

Figure 6. CD spectra for the single crystals of Δ-**2**·MeCN and Δ-**3**·1.25H_2O.

Thermogravimetric Analyses (TGA) and CD Spectra. The results of TGA indicate that *meso*-**2**·3H_2O, **4**·2H_2O, and Δ-**3**·1.25H_2O lost the water molecules around 100 °C (Figure S9 in the Supporting Information); the weight losses found (6.7% for **4**·2H_2O and 5.1% for Δ-**3**·1.25H_2O) were consistent with those calculated (6.6% for **4**·2H_2O and 4.3% for Δ-**3**·1.25H_2O). The slight difference in weight loss between found (7.6%) and calculated (9.6%) values for *meso*-**2**·3H_2O is due, in part, to the loss of water molecules at room temperature (this compound easily loses its water molecules even at room temperature; see Figure S9 in the Supporting Information). After the loss of water molecules, the three compounds are stable up to 270 °C and then decompose rapidly.

The solid-state CD measurements confirm the chiral nature of Δ-**2**·MeCN and Δ-**3**·1.25H_2O. As shown in Figure 6, a single crystal of Δ-**2**·MeCN shows three negative dichroic signals at λ_{max} = 210, 267, and 359 nm, respectively. The single crystal of Δ-**3**·1.25H_2O exhibits a CD spectrum similar to that of Δ-**2**·MeCN, with three negative dichroic signals at λ_{max} = 208, 267, and 338 nm, respectively.

Conclusions

(1) The supramolecular isomerism based on the *cis*-[Ni-(*f*-*rac*-L)]$^{2+}$ and $[Ni(CN)_4]^{2-}$ building blocks is very de-

pendent on the experimental conditions. (2) The interchain hydrogen-bonding and hydrophobic interactions can lead to chirality transfer between 1D helical chains in a different way. The interchain water clusters act like a “mirror plane” to allow the interchain chirality to propagate in an opposite manner, resulting in achiral compounds of *meso*-**2**·4.5H_2O and *meso*-**2**·3H_2O, while the interchain hydrophobic interactions propagate the interchain chirality in a uniform way, leading to the formation of chiral compounds Δ-**2**·MeCN and Δ-**3**·1.25H_2O. (3) Interchain solvents can affect the crystallizing forms of **2**·(solvent)$_n$: from achiral crystallization of *meso*-**2**·4.5H_2O and *meso*-**2**·3H_2O to chiral crystallization of Δ-**2**·MeCN.

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Supporting Information Available: X-ray crystallographic data for all compounds in CIF format, the structure of **4**·2H_2O, the proposed processes for the formation of *meso*-**2** and Δ-**3**, and structural figures for *meso*-**2**, Δ-**2**, and Δ-**3**, TGA curves, and ESI-MS spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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