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A New Type of Single-Helix Coordination Polymer with Mixed Ligands $[M_2(phen)_2(e,a\text{-}cis\text{-}1,4\text{-}chdc)_2(H_2O)_2]_n$ (M = Co and Ni; phen = 1,10-phenanthroline; chdc = cyclohexanedicarboxylate)

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A new family of single-stranded helices coordination polymers with mixed ligands, $[M_2(phen)_2(e,a\text{-}cis\text{-}1,4\text{-}chdc)_2(H_2O)_2]_n$ (**1**, M = Co; **2**, M = Ni; chdc = cyclohexanedicarboxylic acid; phen = 1,10-phenanthroline), were prepared under hydrothermal conditions and characterized by elemental analyses, IR spectra, TG analysis, and single-crystal X-ray diffraction analysis. X-ray crystal structural analyses reveal that **1** and **2** are isomorphic and belong to the monoclinic system. $C_{40}H_{36}Co_2N_4O_{10}$, $P2_1/c$, $a = 10.0566(5)$ Å, $b = 8.8843(5)$ Å, $c = 20.2912(14)$ Å, $\beta = 100.052(3)°$, $Z = 2$ for **1**; and $C_{40}H_{36}Ni_2N_4O_{10}$, $P2_1/c$, $a = 9.8921(6)$ Å, $b = 9.0151(4)$ Å, $c = 20.1628(17)$ Å, $\beta = 100.31(2)°$, $Z = 2$ for **2**. In the structures of **1** and **2**, the 1,4-chdc ligand possesses only one kind of *e,a-cis*-conformation although there are both *cis*- and *trans*-conformations in the raw material. Two oxygen atoms of one carboxyl in 1,4-chdc ligand and another oxygen atom of contraposition carboxyl link adjacent Co or Ni atoms into an infinite 1-D zigzag chain. The most attractive structural feature of **1** and **2** is that they both exhibit an infinite chiral chainlike structure with 2_1 helices along the *b* axis. In addition, the right-handed and the left-handed chains are alternate. Meanwhile, the adjacent chains of **1** and **2** are linked via hydrogen bonds into 2-D network structures, which further form 3-D frameworks via π-π interactions of 1,10-phen.

Introduction

Over the past decade, helical structures have received much attention in coordination chemistry and materials chemistry because helicity is an essence of life and is also important in advanced materials such as optical devices, enantiomer separation, chiral synthesis, ligand exchange, and selective catalysis.[1−5] Consequently, many single-, double- and higher-order stranded helical complexes have been generated by self-assembly processes.[6−10] Most of the recent studies in this area are involved with the construction from d^{10} transition metal ions and functional ligands.[11−16] The octahedral metal (such as Co^{2+} and Ni^{2+}) complexes coordinated with chelating ligands have been considered promising owing to their inherently chiral centers.[17−18] 1,4-Cyclohexanedicarboxylic acid (chdcH2) possesses a chair-

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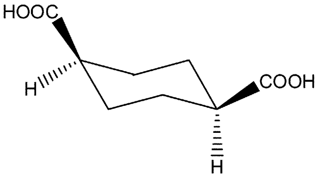
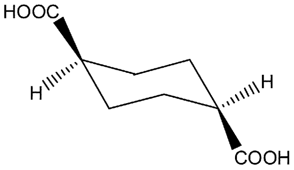
Scheme 1 Conformations of 1,4-Cyclohexanedicarboxylic Acid



cis-Cyclohexane-1,4-dicarboxylic acid



trans-Cyclohexane-1,4-dicarboxylic acid

Table 1. Crystal Data and Structure Refinement for $[Co_2(e,a\text{-}cis\text{-}1,4\text{-chdc})_2(1,10\text{-phen})_2(H_2O)_2]_n$ (**1**) and $[Ni_2(e,a\text{-}cis\text{-}1,4\text{-chdc})_2(1,10\text{-phen})_2(H_2O)_2]_n$ (**2**)

	1	**2**
empirical formula	$C_{40}H_{36}Co_2N_4O_{10}$	$C_{40}H_{36}Ni_2N_4O_{10}$
fw	850.59	850.15
T (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	10.0566(5)	9.8921(6)
b (Å)	8.8843(5)	9.0151(4)
c (Å)	20.2912(14)	20.1628(17)
α (deg)	90.00	90.00
β (deg)	100.052(3)	100.31(2)
γ (deg)	90.00	90.00
V (Å^3)	1785.11(18)	1769.0(2)
Z	2	2
abs coeff (mm^{-1})	0.998	1.133
F(000)	876	880
cryst size (mm^3)	0.77 × 0.53 × 0.7	0.4 × 0.3 × 0.2
θ range for data collection (deg)	2.06−27.44	2.48−27.48
limiting indices	$-12 \leq h \leq 13$	$-12 \leq h \leq 12$
	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$
	$-26 \leq I \leq 26$	$-26 \leq I \leq 26$
reflns collected	7359	6747
indep reflns	4033 ($R_{int} = 0.0270$)	3810 ($R_{int} = 0.0347$)
data/restraints/params	4033/0/253	3810/0/253
GOF on F^2	1.007	1.062
final R indices [$I > 2\sigma(I)$]	R1 = 0.0373	R1 = 0.0401
	wR2 = 0.1193	wR2 = 0.0828

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths			
Co−O1	2.0472(15)	Co−OW	2.0810(15)
Co−N2	2.1108(16)	Co−N1	2.1503(16)
Co−O4#1	2.1740(14)	Co−O3#1	2.1789(15)
Co−C20#1	2.5086(19)	O1−C13	1.271(2)
O2−C13	1.235(3)	O3−C20	1.251(2)
O3−Co#2	2.1789(15)	O4−C20	1.263(2)
O4−Co#2	2.1740(14)	N1−C1	1.318(3)
N1−C5	1.351(2)	N2−C10	1.327(2)
N2−C6	1.353(2)	C1−C2	1.397(3)
C1−H1	0.9300	C20−Co#2	2.5086(19)

Bond Angles			
O1−Co−OW	92.44(6)	O1−Co−N2	91.52(6)
OW−Co−N2	107.54(6)	O1−Co−N1	168.61(7)
OW−Co−N1	87.64(6)	N2−Co−N1	77.63(6)
O1−Co−O4#1	96.93(6)	OW−Co−O4#1	91.29(6)
N2−Co−O4#1	159.03(6)	N1−Co−O4#1	94.46(6)
O1−Co−O3#1	88.68(6)	OW−Co−O3#1	151.00(5)
N2−Co−O3#1	101.39(6)	N1−Co−O3#1	96.76(6)
O4#1-Co−O3#1	59.85(5)	O1−Co−C20#1	90.16(6)
OW−Co−C20#1	121.10(6)	N2−Co−C20#1	131.21(6)
N1−Co−C20#1	99.55(6)	O4#1−Co−C20#1	30.23(6)
O3#1−Co−C20#1	29.90(6)	C13−O1−Co	127.09(14)
C20−O3−Co#2	89.80(11)	C20−O4−Co#2	89.70(11)
C10−N2−Co	127.30(14)	C6−N2−Co	114.65(12)
O3−C20−O4	119.51(17)	O3−C20−C17	121.61(17)
O4−C20−C17	118.87(16)	O3−C20−Co#2	60.29(10)
O4−C20−Co#2	60.07(10)	C17−C20−Co#2	171.50(12)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Bond Lengths			
Ni−O1	2.0472(15)	Ni−OW	2.0810(15)
Ni−N2	2.1108(16)	Ni−N1	2.1503(16)
Ni−O4#1	2.1740(14)	Ni−O3#1	2.1789(15)
Ni−C20#1	2.5086(19)	O1−C13	1.271(2)
Ni−C13	1.235(3)	O3−C20	1.251(2)
O3−Co#2	2.1789(15)	O4−C20	1.263(2)
O4−Co#2	2.1740(14)	N1−C1	1.318(3)
N1−C5	1.351(2)	N2−C10	1.327(2)
N2−C6	1.353(2)	C1−C2	1.397(3)
C1−H1	0.9300	C20−Co#2	2.5086(19)

Bond Angles			
O1−Ni−OW	92.44(6)	O1−Ni−N2	91.52(6)
OW−Ni−N2	107.54(6)	O1−Ni−N1	168.61(7)
OW−Ni−N1	87.64(6)	N2−Ni−N1	77.63(6)
O1−Ni−O4#1	96.93(6)	OW−Ni−O4#1	91.29(6)
N2−Ni−O4#1	159.03(6)	N1−Ni−O4#1	94.46(6)
O1−Ni−O3#1	88.68(6)	OW−Ni−O3#1	151.00(5)
N2−Ni−O3#1	101.39(6)	N1−Ni−O3#1	96.76(6)
O4#1-Ni−O3#1	59.85(5)	O1−Ni−C20#1	90.16(6)
OW−Ni−C20#1	121.10(6)	N2−Ni−C20#1	131.21(6)
N1−Ni−C20#1	99.55(6)	O4#1−Ni−C20#1	30.23(6)
O3#1−Ni−C20#1	29.90(6)	C13−O1−Co	127.09(14)
C20−O3−Co#2	89.80(11)	C20−O4−Co#2	89.70(11)
C10−N2−Co	127.30(14)	C6−N2−Co	114.65(12)
O3−C20−O4	119.51(17)	O3−C20−C17	121.61(17)
O4−C20−C17	118.87(16)	O3−C20−Co#2	60.29(10)
O4−C20−Co#2	60.07(10)	C17−C20−Co#2	171.50(12)

type structure with *cis*- and *trans*-conformations (Scheme 1). Thus, it can connect metal ions in different directions. Hence, chdc may be a good candidate for the construction of chiral coordination polymers. Furthermore, two N atoms from the chelate ligand 1,10-phen may occupy two coordination positions of metal ions. The rest of the coordination positions are available for other carboxylate ligands to allow the formation of a helix. To our knowledge, the hydrothermal synthesis of chiral coordination polymers constructed from different organic ligands has so far been seldom.[19,20] And the mixed ligands including carboxylate chdc and 1,10-phen have not been reported yet. We report here the preparation and crystal structure characterization of two novel helical coordination polymers $[Co_2((1,10\text{-phen})_2 e,a\text{-}cis\text{-}1,4\text{-chdc})_2(H_2O)_2]_n$ (**1**) and $[Ni_2(1,10\text{-phen})_2(e,a\text{-}cis\text{-}1,4\text{-chdc})_2(H_2O)_2]_n$ (**2**). It is worth noting that the raw material of 1,4-cyclohexanedicarboxylic acid used is a mixture of both *cis*- and *trans*-conformations, but the 1,4-chdc ligands in the title compounds possess only *e,a-cis*-conformation. Such selective coordination has rarely been observed in the process of assembly of coordination polymers and may provide possibilities for molecular recognition and separation after further exploration.

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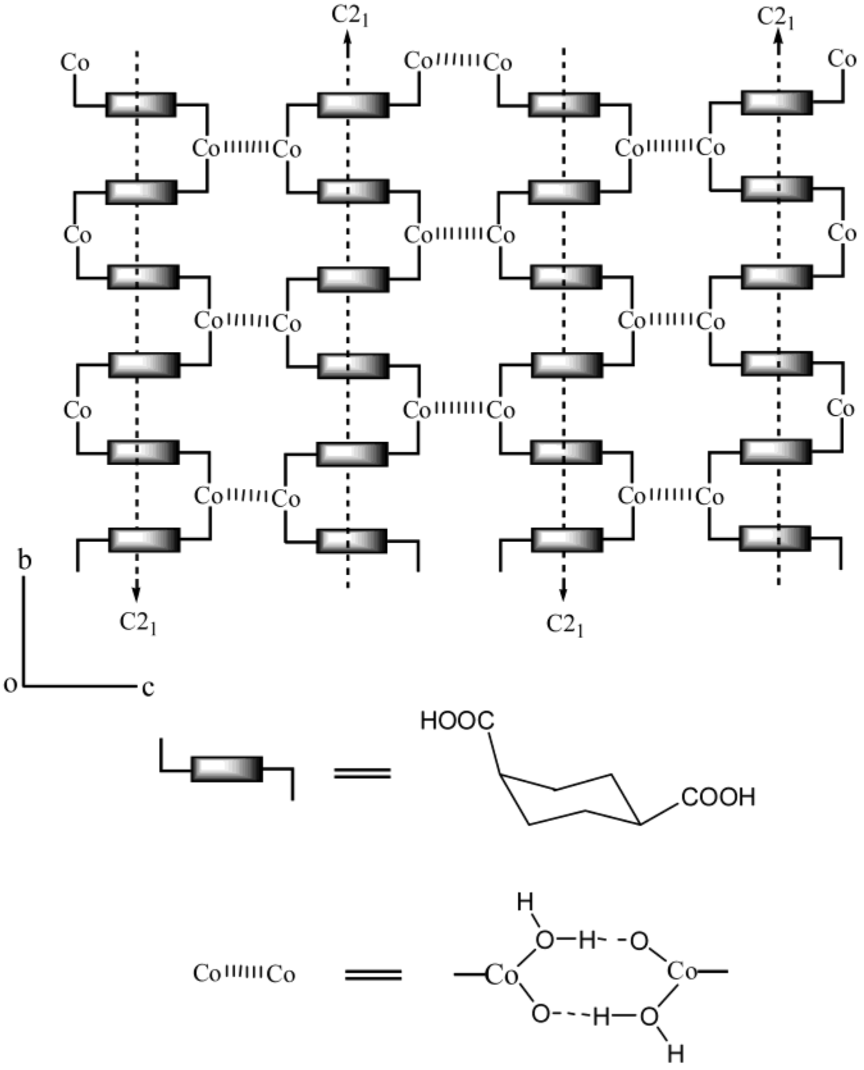
Scheme 2. Simplified Schematic Representation of the Chiral Structure of **1**



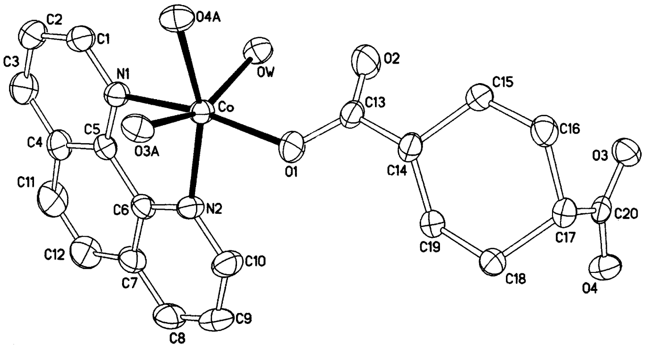


Figure 1. The coordination environment of Co in compound **1**.

Experimental Section

All reagents were purchased commercially and used without further purification. Deionized water was used for the hydrothermal synthesis. The hydrothermal reaction was performed in a 15 mL Teflon-lined stainless steel autoclave at 180 °C under autogenous pressure. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Co and Ni were determined by ICP-AES analysis. The infrared spectra of the two compounds were obtained on an Alpha Centaurt FT/IR spectrometer with pressed KBr pellets in the 4000−500 cm^{-1} region. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to obtain TGA curves in N_2 with a temperature increasing rate of 10 °C min^{-1}.

Synthesis of $[Co_2(1,10\text{-phen})_2(\textit{e,a-cis}\text{-}1,4\text{-chdc})_2(H_2O)_2]_n$ (1). A mixture of $CoCl_2{\cdot}6H_2O$ (0.1421 g, 0.6 mmol), 1,4-chdc acid (mixture of *cis* and *trans* 99%) (0.1033 g, 0.6 mmol), 1,10-phen (0.1189 g, 0.6 mmol), and H_2O (8 g, 444.4 mmol) in the mole ratio 1:1:1:741 was adjusted to pH 7 by addition of aqueous NaOH solution (6 mol·L^{-1}), and heated at 180 °C for 6 days. After the mixture was slowly cooled to room temperature, rose colored crystals of **1** were yielded. Calcd for $C_{40}H_{36}Co_2N_4O_{10}$: Co 13.87%, C 56.47%, H 4.24%, N 6.59%. Found: Co 13.6%, C 56.40%, H 4.28%, N 7.00%.

Synthesis of $[Ni_2(\textit{e,a-cis}\text{-}1,4\text{-chdc})_2(1,10\text{-phen})_2(H_2O)_2]_n$ (2). The synthesis was similar to that described above except using $NiCl_2{\cdot}6H_2O$ (0.1421 g, 0.6 mmol) instead of $CoCl_2{\cdot}6H_2O$, and green crystals of **2** were yielded. Calcd for $C_{40}H_{36}Ni_2N_4O_{10}$: Ni 13.87%, C 56.47%, H 4.24%, N 6.59%. Found: Ni 13.6%, C 56.40%, H 4.28%, N 7.00%.

X-ray Crystallography. Structure measurements of **1** and **2** were performed at 293 K on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K, and the ω scan mode in the ranges $2.06° < \theta < 27.44°$ and $2.48° < \theta < 27.48°$, respectively. Cell parameters were obtained by the global refinement of the positions of all collected reflections. An empirical absorption

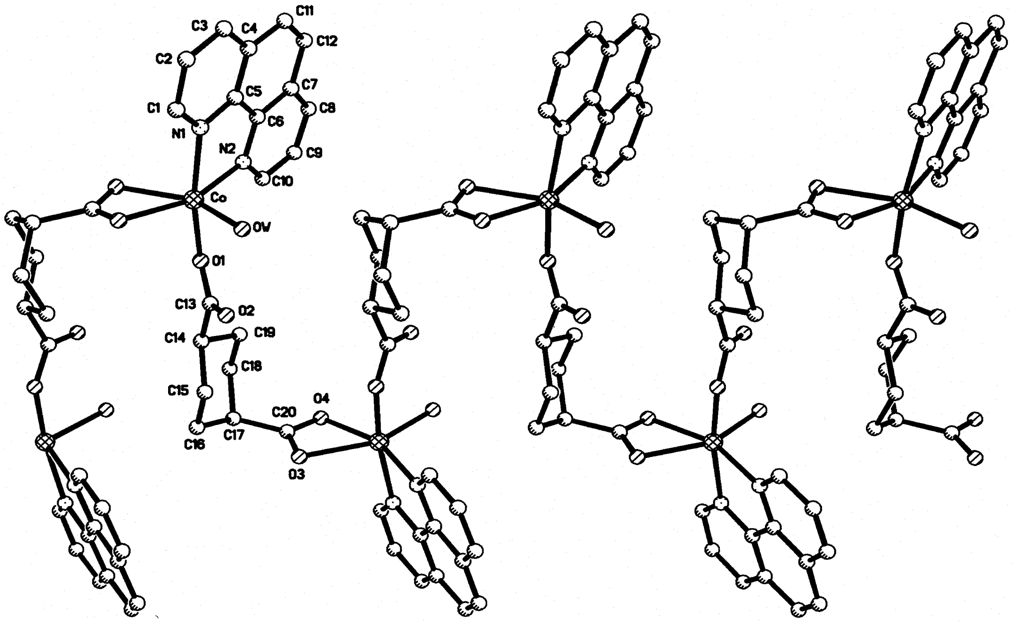


Figure 2. The 1-D zigzag chain structure of **1**.

correction was applied. The two structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL-97 program. All of the nonhydrogen atoms were refined anisotropically. Crystallographic details for the structures of **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are given in Tables 2 and 3.

The CIF files of **1** and **2** have been deposited at the Cambridge Crystallographic Data Center and allocated the following deposition numbers: CCDC 207778 for **1** and CCDC 210811 for **2**.

Results and Discussion

Structures of 1 and 2. The X-ray crystal structure analyses of **1** and **2** revealed that the two complexes are isomorphic (Table 1). Therefore, we will restrict our description to the cobalt compound and only mention pertinent points for the nickel compound where appropriate.

As shown in Figure 1, each Co^{II} atom is coordinated with two nitrogen atoms from the 1,10-phen ligand (Co−N = 2.1108(16) and 2.1503(16) Å, N(1)−Co-N(2) = 77.63(6)°), three oxygen atoms from two *e,a-cis*-1,4-chdc ligands (Co−O(1) = 2.0472(15) Å, Co−O(4)#1 = 2.1740(14) Å, Co−O(3)#1 = 2.1789(15) Å, O(1)−Co−O (3)#1 = 88.68(6)°, O(1)−Co−O(4)#1 = 96.93(6)°, O(4)#1−Co−O(3)#1 = 59.85(5)°), and one aqua ligand (Co−OW = 2.0810(15) Å, O(1)−Co−OW = 92.44(6)°). So the cobalt atoms exhibit a distorted octahedral geometry.

The most interesting feature of **1** and **2** is that the 1,4-chdc ligand possesses only one kind of *e,a-cis*-conformation. There exist two different coordination modes of the two carboxyls in the 1,4-chdc ligand. One is monodentate, and the other is bidentate. And two adjacent Co and Ni ions are bridged by two oxygen atoms of a carboxyl from one 1,4-chdc ligand and an oxygen atom from a carboxyl of another 1,4-chdc ligand to afford the repeating dinuclear units and to form an infinite zigzag 1-D chain (Figure 2).

The most attractive structural feature of the two compounds is that they both possess an infinite chiral chainlike structure with 2_1 helices along the *b* axis (Scheme 2). In addition, the right- and left-handed chains are alternating, so the two compounds are mesomeride (Figure 3). Meanwhile, an intrachain hydrogen bonding interaction is found between O4 and OW with a distance of approximately 2.762 Å for **1** (2.704 Å for **2**), by which the right- and left-handed chains are connected into a 2-D network with rectangle

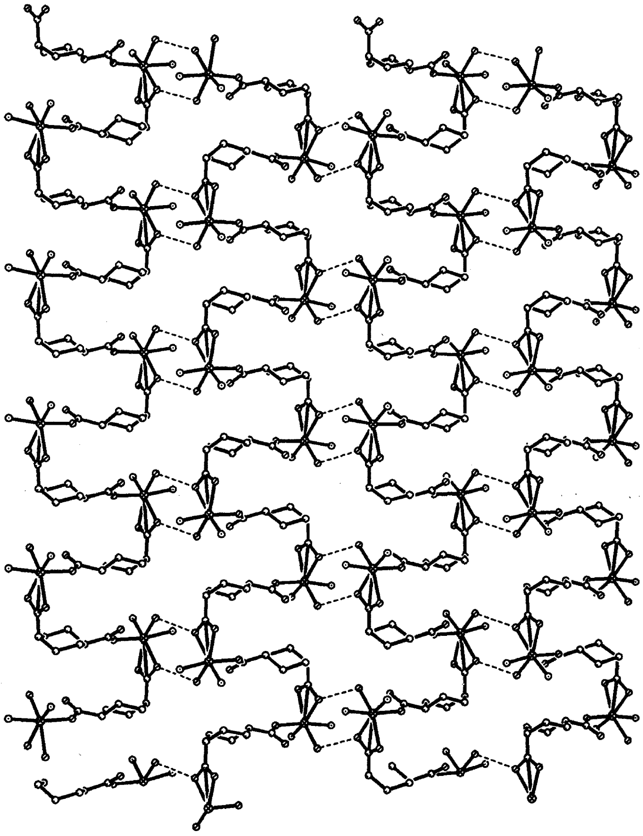


Figure 3. The view of alternation of right- and left-handed helices of **1** along the *b* axis. In the 2D structure of **1**, the carbon atoms of 1,10-phen and hydrogen atoms are omitted for clarity.

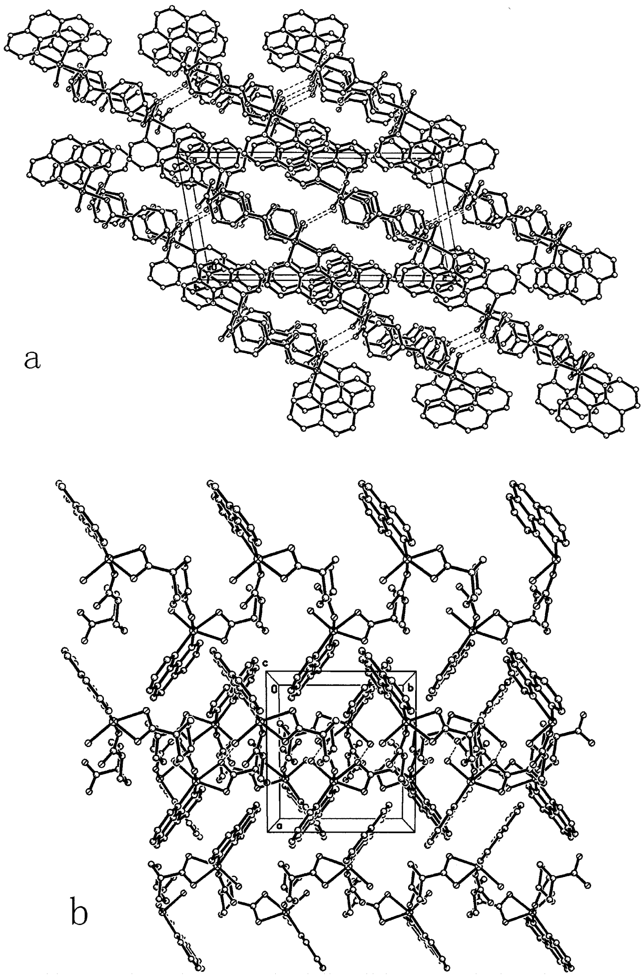


Figure 4. The 3-D networks of **1** along the b axis (a) and **2** along the c axis (b).

channels (4.44 × 17.11 Å^2), as shown in Figure 3. In the packing arrangement of **1** (Figure 4), the adjacent 2D layers form a 3-D framework via $\pi-\pi$ interactions of 1,10-phen. The interplanar distance is about 3.46 Å.

Infrared Spectrum Studies. The infrared spectra of the two compounds are shown in Figure 5, and the band wavenumbers are given in the Experimental Section. The spectra are characterized by a broad band at 3341 cm^{-1} due to the vibrational modes of water. A couple of weak bands at 2925 cm^{-1} identify the C−H modes of the cyclohexane rings. The vibration modes that involve the metal atoms are found in the low energy region, and there is a consistent difference of a few wavenumbers between those of cobalt and nickel. In the middle of the spectra are a series of strong bands at 1693.55 and 1677.51 cm^{-1}, due to the 1,4-cyclohexanedicarboxylic acid stretching. Bands at 1426.37, 1554.76, 1515.22, 1550.72, and 1645.25 cm^{-1} are the characteristic ones of 1,10-phen.

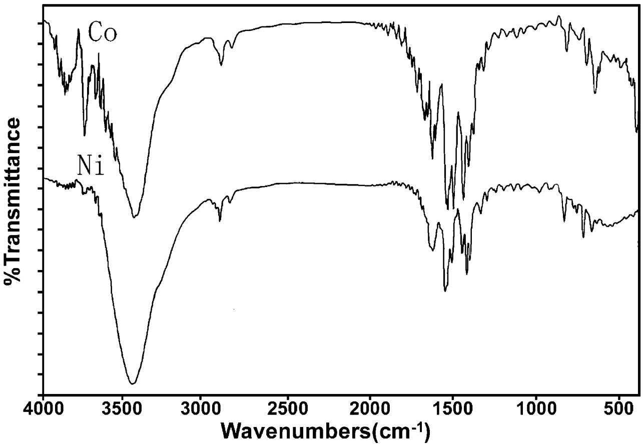


Figure 5. Infrared spectra of **1** and **2**.

TG Analysis. The thermogravimetric analysis (TGA) curve recorded at 20−750 °C reveals that there are two-stage weight losses for compound **1**. The first stage occurred between 179.29 and 196.38 °C and was attributed to the loss of the two aqua ligands per formula. The observed weight loss (4.685%) is in agreement with the calculated value (4.24%). The second stage occurred from 332.25 to 378.08 °C, and the product began to lose 1,4-chdc and 1,10-phen ligands. The observed weight loss (76.52%) is in agreement with the calculated value (77.6%). Then the compound began to decompose.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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