A Novel α-Helix-Liked Metallohelicate Series and Their Structural Adjustments for the Isomorphous Substitution

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A novel metallohelical motif is well designed and synthesized by mimicking the α-helical fold structure of protein. The 1D helical structures of $[Cd(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (**I**) and $[Zn(CH_2(COO)_2)\ (SC(NH_2)_2)_2]_n$ (**II**) are primarily induced and stabilized by the multiple long-range intrahelix hydrogen bonds. Malonate dianion acts as a bidentate ligand coordinated with metal ions to form the backbone of the helix, and thiourea molecules that bend into the helical turn are involved in the intrahelix hydrogen-bond system. The metal ion occupations in the helix of **I** and **II** can be freely substituted by simply controlling the initial ratio of those two metal ions. Single crystals of three mixed metal ion complexes of $[Cd_{0.77}Zn_{0.23}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (**III**), $[Cd_{0.50}Zn_{0.50}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (**IV**), and $[Cd_{0.21}Zn_{0.79}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (**V**) were synthesized from systems with an initial Cd/Zn mole ratio of 1:1 for **III**, 1:2 for **IV**, and 1:8 for **V**. They are isomorphous as confirmed by X-ray characterization. When the metal ion is substituted, the multiple intrahelix hydrogen interaction motifs of the coordination polymer structure are self-adjusted to sustain their 1D helical motifs.

Introduction

A key reaction in the biological and material world is the controlled link of simple building blocks, a reaction with which one can create mesoscopic structures, which for example contain cavities and display specifically desired properties. Recently, the study of self-assembly processes and properties of supramolecular system and/or molecule aggregates in natural or unnatural systems, organic or inorganic systems has attracted great interest.[1,2] Mostly, researchers focused on the topologies of the framework, the aggregation motifs, and potential applications such as their use as electrical conductors,[3] as molecular magnets,[4] in inclusion chemistry,[5] in molecular recognition,[6] and in catalysis.[7] Although some dynamic behaviors have been studied, i.e., switching properties,[8] electron transfer,[2a,9] structure conversion,[10] etc., studies of the structural adjustment of supramolecules and/or molecule aggregates, the dynamic behaviors of the weak interactions between molecules, and the isomorphous substitution of polymer structure are still a great challenge. In this paper, we report a new motif of metallohelicates $[Cd_xZn_{1-x}(tu)_2(mal)]_n$ ($x = 1-0$, tu = thiourea, mal = malonate), which shows us an exciting and rare example of a coordination polymer system which is stabilized by an intrahelix hydrogen-bond system and crystallographic 2_1 axis packing. In addition, the structural adjustment behaviors for isomorphous substitutions were observed. The flexibility and dynamic character of the hydrogen bond are the key factors in the adjustment processes.

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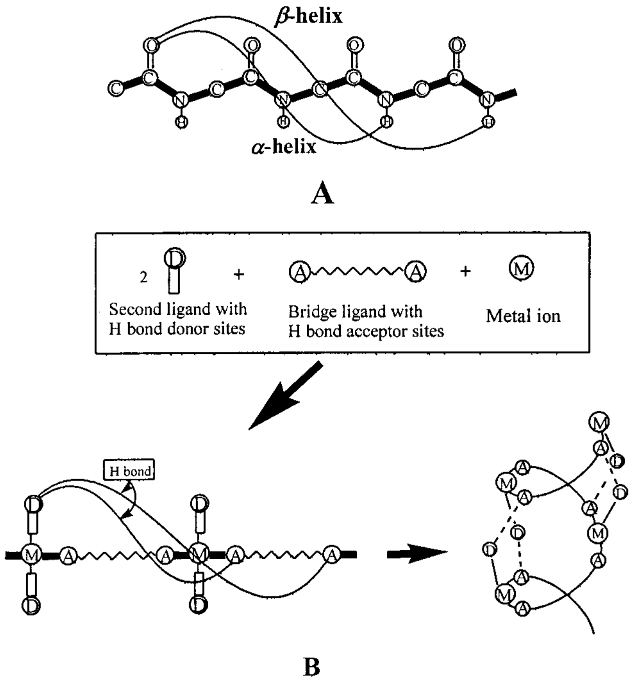
Spontaneous self-organization of helical and multiple-helical molecular structures can be found throughout Nature.[11] In the past decade, many wondrous examples of metallohelicates have been described.[12−14] The most relevant parameters of previous strategies for controlling the architecture are the molecular size, topology, stereochemistry, and shape. Three basic components were considered for construction of a complex helix: a binding site, a metal, and a ligand linking this binding site to another.[12] The helix was constructed by using the coordination preference of the metal ion as the major driving force for assembly,[13f−h,15] or by using the geometrical preference of the ligand[12b,13d,16] or necklace-like molecules.[17] It is well-known that the helical structure of protein is mostly driven and stabilized by intramolecular hydrogen-bond interactions between carbonyl groups (H-bond acceptor) and amino groups (H-bond donor) originated from the flexible polypeptide backbone. If we design a flexible coordination polymer chain bearing both hydrogen-bond acceptors and donors, what will happen? Here, we present a new strategy for construction of ideal infinite single-helical coordination polymers.[18]

Synthetic Strategy

The synthetic strategy of a series of α-helix-liked complexes is shown in Scheme 1. A 1D flexible coordination chain bearing both hydrogen-bond acceptors and donors is the primary target structure. A flexible bidentate ligand bearing hydrogen bond acceptor sites, malonate dianion, is chosen to link metal ions to form the one-dimensional backbone. Then, a second ligand, thiourea, bearing hydrogen bond donor sites is positioned into the backbone by coordinating with metal ions. Therefore, local structure recognition via intramolecular hydrogen-bond interactions primarily drives the formation of secondary structure: a single-helix polymer.

Scheme 1. Schematic Representation of the Synthetic Strategy for Self-Assembly of the Single-Helix Motif by Intrahelix Hydrogen Bonds[a]



[a] A: Intrahelix H-bonding of backbone in the helical fold of proteins. B: Designed self-organization process of construction of helical structure which is induced by intrahelix H-bonding of complex polymer backbone.

Experimental Section

Materials and Methods. Hydrated cadmium sulfate and zinc sulfate, malonic acid, and thiourea were purchased from Aldrich Chemical Co. and used as received, without further purification. Elemental microanalysis (C, H, and N) of all products was performed on crystalline samples by the microanalytical services at the University of Science and Technology of China. The Zn:Cd ratio analysis was carried by Department of Chemistry, University of Science and Technology of China, using the ICP-AES method. Thermogravimetric (TG) analysis was performed on a WRT-3 thermal analyzer under an 80 mL/min air atmosphere. The final temperature was 800 °C with a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets using a Perkin-Elmer 1720 spectrometer. Absorptions are described as follows: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), and broad (br).

Preparation of Compounds. The synthetic methods used to obtain microcrystalline and large single-crystal samples of the compounds, including their initial characterization, are described here. All reactions and purification steps were performed under aerobic conditions.

$[Cd(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (I). Aqueous solutions of cadmium(II) sulfate hexahydrate (0.316 g, 1.00 mmol), malonic acid (0.104 g, 1.00 mmol), and thiourea (0.152 g, 2.00 mmol) were mixed together, and the pH value of the resulting solution was controlled at 5−6 by diluted NaOH and H_2SO_4. The solution was slowly evaporated at room temperature. Colorless large needlelike crystals were isolated to give 3.4 g (92%) of product in about 1 week. This compound is soluble in water, nearly insoluble in common organic solvents, and stable in air. Anal. Calcd for $C_5H_{10}N_4O_4S_2Cd$ (**I**): C, 16.36; H, 2.73; N, 15.27. Found: C, 16.45; H, 2.77; N, 15.12. FT-IR (KBr, 3500−400 cm^{-1}): 3397 (s), 3317 (s), 3115 (vs, br), 2923 (w, sh), 1663 (s, sh), 1637 (vs), 1583 (vs), 1544 (s, sh), 1506 (m), 1442 (m, sh), 1414 (s), 1390 (s), 1345 (s), 1241 (w), 1124 (m), 984 (m), 957 (w), 840 (w), 710 (s), 606 (s, br), 475 (m), 422 (w).

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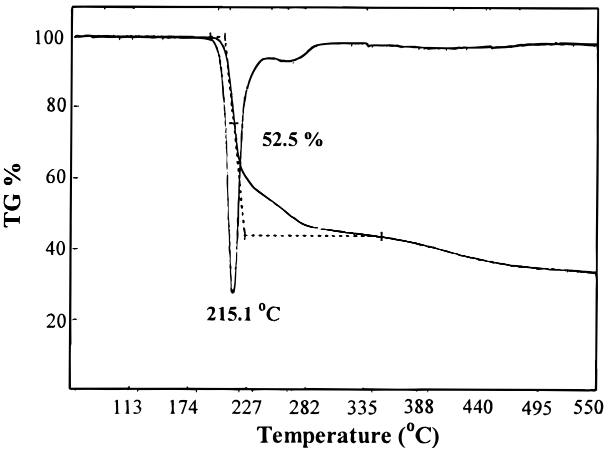

Figure 1. TG curve of **I** showing a sharp weight loss at 215.1 °C.

Thermogravimetric analysis performed under a flow of air gas on a 3.52 mg sample showed a sharp weight loss of 1.85 mg (52.5%) at 215.1 °C, indicating that the whole supramolecular 1D helical structure was destroyed at this temperature in the formation of $CdCO_3$ (calcd 52.71%). Further heating of the sample resulted in the formation of CdO at 650 °C, as indicated by the total weight loss of 2.27 mg (64.5%, calcd 64.7%). Typical TG analysis curves are shown in Figure 1.

$[Zn(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (II). Complex **II** was obtained as needlelike crystals in 90% yield by reaction of zinc(II) sulfate hexahydrate (0.269 g, 1.00 mmol) with malonic acid (0.104 g, 1.00 mmol) and thiourea (0.152 g, 2.00 mmol) similarly to **I**. Anal. Calcd for $C_5H_{10}N_4O_4S_2Zn$ (**II**): C, 18.77; H, 3.13; N, 17.52. Found: C, 18.82; H, 3.18; N, 17.70. FT-IR (KBr, 3500−400 cm^{-1}): 3477 (s), 3365 (s), 3309 (vs), 3132 (vs, br), 2923 (w, sh), 1675 (s, sh), 1625 (vs), 1619 (vs), 1594 (m, sh), 1536 (m), 1439 (m), 1411 (s), 1344 (s), 1313 (s, sh), 1246 (w), 1121 (m), 976 (m), 967 (w), 842 (w), 721 (s), 654 (m), 489 (m), 428 (w).

Thermogravimetric analysis performed under a flow of air gas on a 7.58 mg sample showed a sharp weight loss of 4.66 mg (61.5%) at 216.0 °C, indicating the formation of $ZnCO_3$ (calcd 61.77%). Further heating of the sample resulted in the formation of ZnO at 600 °C, as indicated by the total weight loss of 5.64 mg (74.4%, calcd 74.54%).

$[Cd_{0.77}Zn_{0.23}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (III). To an aqueous solution of cadmium(II) sulfate hexahydrate (0.158 g, 0.50 mmol) and zinc(II) sulfate hexahydrate (0.135 g, 0.50 mmol) were added malonic acid (0.104 g, 1.00 mmol) and thiourea (0.152 g, 2.00 mmol). Similar to **I**, colorless large needlelike crystals were isolated to give 0.210 g (91% based on Cd) of product in about 6 days. Anal. Calcd for $C_5H_{10}N_4O_4S_2Zn_{0.23}Cd_{0.77}$ (**III**): C, 16.86; H, 2.81; N, 15.74. Found: C, 16.92; H, 2.87; N, 15.67. FT-IR (KBr, 3500−400 cm^{-1}): 3406 (s), 3317 (s), 3187 (vs, br), 2924 (w, sh), 1663 (m, sh), 1633 (vs), 1587 (vs), 1538 (m), 1505 (m), 1439 (m, sh), 1393 (s), 1343 (s), 1313 (m), 1246 (w), 1125 (m), 986 (m), 954 (w), 842 (w), 710 (s), 655 (m), 613 (m), 473 (m), 427 (w).

Thermogravimetric analysis performed under a flow of air gas on a 6.58 mg sample showed a sharp weight loss of 3.58 mg (54.4%) at 211.6 °C, indicating the formation of $Cd(Zn)CO_3$ (calcd 54.61%). Further heating of the sample resulted in the formation of CdO and ZnO at 690 °C, as indicated by the total weight loss of 4.41 mg (67.0%, calcd 67.24%).

$[Cd_{0.50}Zn_{0.50}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (IV). To an aqueous solution of cadmium(II) sulfate hexahydrate (0.105 g, 0.33 mmol) and zinc(II) sulfate hexahydrate (0.179 g, 0.67 mmol) were added malonic acid (0.104 g, 1.00 mmol) and thiourea (0.152 g, 2.00 mmol). Colorless large needlelike crystals were isolated to give 0.208 g (91% based on Cd) of product in about 5 days under the same crystallizing conditions of **I**. Anal. Calcd for $C_5H_{10}N_4O_4S_2Zn_{0.50}Cd_{0.50}$ (**IV**): C, 17.48; H, 2.91; N, 16.32. Found: C, 17.54; H, 2.95; N, 16.29. FT-IR (KBr, 3500−400 cm^{-1}): 3420 (s, sh), 3406 (s), 3317 (s), 3190 (vs, br), 2924 (w, sh), 1663 (m, sh), 1632 (vs), 1588 (s), 1538 (m), 1504 (m), 1441 (m, sh), 1397 (s), 1340 (m, sh), 1313 (m), 1252 (w), 1128 (m), 985 (m), 954 (w), 840 (w), 709 (s), 656 (m), 590 (m), 473 (m), 429 (w).

Thermogravimetric analysis performed under a flow of air gas on a 3.99 mg sample showed a sharp weight loss of 2.24 mg (56.14%) at 210.8 °C, indicating the formation of $Cd(Zn)CO_3$ (calcd 56.46%). Further heating of the sample resulted in the formation of CdO and ZnO at 610 °C, as indicated by the total weight loss of 2.76 mg (69.2%, calcd 69.29%).

$[Cd_{0.21}Zn_{0.79}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (V). To an aqueous solution of cadmium (II) sulfate hexahydrate (0.035 g, 0.11 mmol) and zinc(II) sulfate hexahydrate (0.239 g, 0.89 mmol) were added malonic acid (0.104 g, 1.00 mmol) and thiourea (0.152 g, 2.00 mmol). Colorless large needlelike crystals were isolated to give 0.161 g (93% based on Cd) of product in about 6 days under the same crystallizing conditions of **I**. Anal. Calcd for $C_5H_{10}N_4O_4S_2Zn_{0.79}Cd_{0.21}$ (**V**): C, 18.21; H, 3.03; N, 16.99. Found: C, 18.26; H, 3.07; N, 16.97. FT-IR (KBr, 3500−400 cm^{-1}): 3419 (s, sh), 3405 (s), 3318 (s), 3192 (vs, br), 2924 (w, sh), 1664 (m), 1632 (vs), 1590 (s), 1539 (m), 1504 (m), 1439 (m, sh), 1397 (s), 1348 (m, sh), 1313 (m), 1251 (w), 1130 (m), 987 (m), 954 (w), 845 (w), 711 (s), 654 (m), 585 (m), 473 (m), 427 (w).

Thermogravimetric analysis performed under a flow of air gas on a 9.58 mg sample showed a sharp weight loss of 5.17 mg (54.0%) at 213.3 °C, indicating the formation of Cd(Zn)CO3 (calcd 54.09%). Further heating of the sample resulted in the formation of CdO and ZnO at 650 °C, as indicated by the total weight loss of 6.92 mg (72.2%, calcd 72.29%).

X-ray Structure Determination. Crystals for X-ray analyses were obtained as described in the preparations. The experimental details for the structure determination are given in Table 1. The crystal structure of **I** was determined on a Siemens SMART/CCD diffractometer using graphite-monochromated Mo Kα radiation at 293 K. Cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range $2.24° < \theta < 24.93°$, measured by the computer-controlled diagonal slit method of centering. The $\omega-2\theta$ scan mode with a maximum 2θ value of 50.0° were used to collect intensity data. The data were corrected for Lorentz−polarization effects. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares calculation (SHELXL-93). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Single crystals of **II**−**V** were respectively set up on a R-AXISII diffractometer with graphite-monocromated Mo Kα radiation ($\lambda = 0.71070$). The data were collected at 173 K to a maximum 2θ value of 50°. A laser-stimulated fluorescence image plate was used as a two-dimensional area detector. The distance between the crystal and the detector was 80 mm. Thus, 43 frames were recorded at intervals of 3° and each exposure lasted for 5 min. The data were corrected for Lorentz−polarization effects. Structures were solved by direct methods using the SIR92 and refined by full-matrix least squares. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The Zn:Cd ratios in the crystals were not refined and taken as those from the bulk analyses. Selected bond lengths and angles are compiled in Table 2.

Results and Discussion

Synthesis. Large needlelike crystals of **I** and **II** are prepared by mixing three starting materials (cadmium sulfate or zinc sulfate, malonic acid, and thiourea) in aqueous solution at room temperature (crystallizing temperature can range from 0 to 40 °C) in the target ratio. The pH value of this system must be controlled at 5−6, otherwise, only metal−tu complexes were obtained. In this synthetic route, when the initial metal ion was a mixture of Zn(II) and Cd(II) in one system, the occupations of metal ion in the resulting structure were also a mixture. Single crystals of three mixed-metal ion complexes of **III** ($Cd_{0.77}Zn_{0.23}$), **IV** ($Cd_{0.50}Zn_{0.50}$), and **V** ($Cd_{0.21}Zn_{0.79}$) were synthesized by controlling the initial ratio of metal ions: the initial Cd:Zn mole ratio was 1:1 for **III**, 1:2 for **IV**, and 1:8 for **V**. It is seen that cadmium ion is more competitive than zinc ion in this system.

Table 1. Crystal Structure Data of Complexes **I**−**V**

	I	**II**	**III**	**IV**	**V**
formula	$C_5H_{10}N_4O_4S_2Cd$	$C_5H_{10}N_4O_4S_2Zn$	$C_5H_{10}N_4O_4S_2Zn_{0.23}Cd_{0.77}$	$C_5H_{10}N_4O_4S_2Zn_{0.50}Cd_{0.50}$	$C_5H_{10}N_4O_4S_2Zn_{0.79}Cd_{0.21}$
fw	366.69	319.67	355.86	343.17	329.54
temp (K)	293	173	173	173	173
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.6384(2)	7.503(2)	9.629(4)	9.481(2)	9.483(1)
b (Å)	8.14050(10)	8.199(7)	8.123(4)	8.076(1)	8.077(5)
c (Å)	14.8755(4)	18.36(1)	14.851(3)	14.710(8)	14.762(3)
β (deg)		90.95(3)			
V(Å^3)	1167.15(4)	1129.1(10)	1161.6(7)	1126.3(5)	1130.8(5)
Z	4	4	4	4	4
D_c g cm^{-3}	2.087	1.880	2.035	2.024	1.936
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
2θ range (deg)	5−50	5−50	5−50.1	5−50	4−50
μ (cm^{-1})	22.33	25.50	22.47	25.56	25.46
no. of reflns collcd	3767	1734	1194	1160	1145
F(000)	720	648	720	648	648
no. of reflns ($I > 3\sigma(I)$)	1989	1665	1138	1112	1073
no. of variables	146	145	146	145	146
GOF	1.050	1.73	1.91	2.57	1.87
R_{int}	0.0146	0.051	0.073	0.082	0.059
R^a	0.0154	0.051	0.073	0.082	0.059
R_w	0.0336	0.077	0.100	0.113	0.081

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o^2 \text{ to } F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **I**−**V**

	I	**II**	**III**	**IV**	**V**
	(M = Cd)	(M = Zn)	(M = $Zn_{0.23}Cd_{0.77}$)	(M = $Zn_{0.50}Cd_{0.50}$)	(M = $Zn_{0.79}Cd_{0.21}$)
M(1)−O(4)	2.258(2)	1.995(3)	2.24(1)	2.12(1)	2.061(7)
M(1)−O(2)	2.610(2)	(3.01(1))	2.65(1)	(2.73(1))	(2.89(1))
M(1)−S(2)	2.5104(7)	2.330(1)	2.478(4)	2.379(4)	2.362(3)
M(1)−S(1)	2.5282(7)	2.326(1)	2.506(4)	2.401(4)	2.347(3)
M(1)−O(1)	2.270(2)	1.989(3)	2.223(9)	2.128(9)	2.022(6)
M(1)−M(1)#1[a]	8.199	8.077	8.076	8.123	8.141
M(1)−M(1)#2[a]	6.70	6.62	6.72	6.79	6.82
O(4)−M(1)−O(2)	138.16(7)		138.3(4)		
O(4)−M(1)−S(2)	109.20(6)	111.25(8)	108.9(3)	111.5(3)	112.6(2)
O(2)−M(1)−S(2)	132.93(5)		102.0(2)		
O(4)−M(1)−S(1)	100.44(5)	106.97(8)	101.5(2)	103.4(2)	104.8(2)
O(2)−M(1)−S(1)	104.88(6)		92.4(2)		
S(2)−M(1)−S(1)	114.14(2)	107.48(4)	113.4(1)	111.8(1)	108.7(1)
O(4)−M(1)−O(1)	87.61(7)	96.8(1)	89.2(4)	89.4(4)	94.4(3)
O(2)−M(1)−O(1)	52.70(6)		51.4(3)		
S(2)−M(1)−O(1)	102.16(5)	117.72(9)	131.8(3)	128.6(3)	125.3(2)
S(1)−M(1)−O(1)	92.86(6)	115.78(8)	105.5(3)	107.6(3)	108.7(2)

[a] #1, distance between metal ions in two turns, the pitch of helix; #2, the shortest metal−metal distance.

Elemental microanalysis performed on freshly prepared samples gave the indicated formulation for the compounds. Their FT-IR spectra showed the expected absorptions of symmetric and asymmetric vibrations of malonate anion and thiourea, and the hydrogen-bonded amino groups of thiourea (3120−3195, 3300−3420 cm^{-1}).[19] The FT-IR absorptions of complexes **I** and **III**−**V** were very similar. Some differences were observed in the spectrum of complex **II**, i.e., vibration of a free NH (3477 cm^{-1}).

Description of the Structure of $[Cd(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (I). X-ray analysis reveals that complex **I** possesses a one-dimensional single-helical structure, which is consistent with the result derived from elemental analysis. The fundamental building unit of the crystal structure is shown in Figure 2. It is composed of one Cd(II) center that is coordinated by two tu molecules (S1 and S2), one malonate anion (O4) and chelated by another one malonate anion (O1 and O2). The progression of the structure in the crystal employs this unit and its linkage motif using the remaining carboxylate oxygen atoms (O1B, O2B, and O4A) on two malonate anion units. In this way, each malonate unit acts as a tridentate unit to link two cadmium atoms and yield a half turn unit of the helical structure. The shortest metal−metal distance in **I** was 6.82 Å. Extension of the structure in one dimension gives a 1D helical Cd−malonate network as shown in Figure 3. The helix has a straight line helical axis, a pitch of 8.14 Å, and an average radius of 2.20 Å. The inner channel running parallel to the helical axis is in fact constructed even though its effective void size is quite small and of no practical use (about 1.5 Å in diameter). It shows us a possible method for designing a functional molecular channel. Two tu molecules are bent into the helical turn and involved in the intrahelix hydrogen bond system. Similar to the helical fold in protein, the hydrogen bonds span two adjacent turns and are nearly parallel to the helical axis. All carboxyl and amino groups in the backbone are allowed to be involved in the hydrogen-bond interactions. Four N−H···O intrahelix hydrogen bond large ring motifs spanning two helical turns and strongly reinforcing the helical structure can be described in

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[19] (a) Zhang Y.; Nishiura, M.; Li, J.; Deng, W.; Imamoto, T. *Inorg. Chem.* **1999**, *38*, 825. (b) Bott, R. C.; Bowmaker, G. A.; Davis, C. A.; Hope, G. A.; Jones, B. E. *Inorg. Chem.* **1998**, *37*, 651.

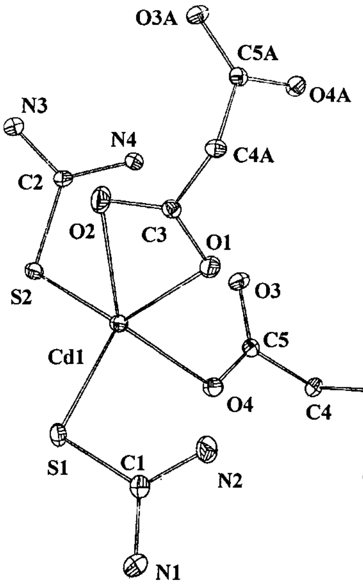
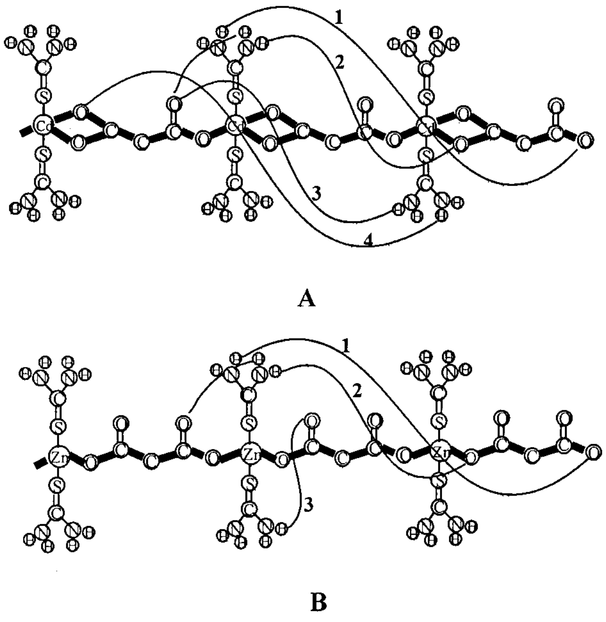


Figure 2. Fundamental structure unit of **I**.

Scheme 2. Schematic Representation of the Intrahelix Hydrogen Bond Motifs in **I** and **II**[a]



[a] A: Four intrahelix H-bond rings of the backbone in **I**; **1**, 16-atom H-bond ring $R_1^1(16)$; **2**, 14-atom H-bond ring $R_2^2(14)$; **3**, 14-atom H-bond ring $R_1^1(14)$; **4**, 16-atom H-bond ring $R_1^1(16)$. B: Three intrahelix H-bond rings in complex **II**; **1**, 16-atom H-bond ring $R_1^1(16)$; **2**, 14-atom H-bond ring $R_2^2(14)$; **3**, 8-atom H-bond ring $R_1^1(8)$.

Etter's graph set notation as $R_1^1(16)$, $R_1^1(14)$, $R_1^1(16)$, and $R_2^2(14)$,[20] Scheme 2. On the other hand, the helical axis takes a crystallographic 2_1 axis. The efficient packing motif of the 2_1 axis in crystallography is also one factor for assembling and stabilizing the helical conformation. The parameters of hydrogen bonds observed in all structures (**I**−**V**) are presented in Table 3. This helical conformation sustained via intrahelix hydrogen bonds was synthesized from aqueous solution in nearly quantitative yield. An effect of solvent competition is not observed.[21] Here, compound **I** apparently shows spontaneous resolution of enantiomers, due to the weak interhelix hydrogen bond interactions and also the packing of helixes, Figure 4.[14a,22]

$[Zn(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (II). The X-ray crystal structure of the fundamental building unit of **II** is shown in Figure 5, which is consistent with the result derived from elemental analysis. The coordination geometry around Zn(II) ion is a tetrahedron in which the Zn(II) ion is coordinated by two sulfur atoms (S1 and S2) originating from two tu molecules and by two carboxylate oxygen atoms (O1 and O4A) of two different malonate anions. Progression of the structure in the crystal employs this unit and its linkage motif using the remaining carboxylate oxygen atoms (O4 and O1A) on two malonate anion units. In this way, each malonate unit acts as a bidentate (O1, O4) unit, linking two zinc atoms to yield a half turn unit of the helical structure. The shortest metal−metal distance in **II** was 6.70 Å. Extension of the structure in one dimension gives a 1D helical Zn−malonate network as shown in Figure 3. X-ray analysis reveals that there are a pair of right-handed and left-handed single helixes in **II**. The helix has a straight line helical axis (2_1 axis), a pitch of 8.199 Å, and an average radius of 1.70 Å. One of the two tu molecules was bent into the helical turn and involved in the intrahelix hydrogen bond system, Table 3. Another tu molecule was extended out of the helix turn. This structure motif is different from that of **I** due to the small ion radius of the Zn(II) ion and consistent with the observed FT-IR absorptions. Two N−H···O intrahelix hydrogen bond large ring motifs spanning two helical turns can be described in Etter's graph set notation as $R_1^1(16)$ and $R_2^2(14)$ and play a great role in stabilizing the helical structure, Scheme 2. Here, the helical axis is also a crystallographic 2_1 axis, corresponding to the efficient way of packing molecules.

$[Cd_xZn_{1-x}(CH_2(COO)_2)(SC(NH_2)_2)_2]_n$ (x = 0.77 for III, 0.50 for IV, 0.21 for V). X-ray analyses reveal that complexes **III**, **IV**, and **V** are structure analogues to **I**. The helical structures of **III**, **IV**, and **V** fill the gap of structural characters between **I** and **II**, and self-assembled under the same process, Figure 3. The coordination geometry and the fundamental building unit of **III** (five-coordinated) are similar to those of **I**, and those of **IV** and **V** (tetrahedral geometry) are similar to those of **II**, which are consistent with the result derived from elemental analysis, Figure 6. Also, the progression rule of the structure and linkage motif of the fundamental unit of **III** is similar to that of **I**, and that of **IV** and **V** is the same as that of **II**. By extension of their structures in one dimension, complexes **III**, **IV**, and **V** form similar 1D infinite single-helical structures in which metal positions are statistically occupied by Cd(II) and Zn(II) in different ratios as shown in their formulas. The M−O and M−S distances of helical structures **III** (2.231, 2.492 Å), **IV** (2.124, 2.390 Å), and **V** (2.041, 2.354 Å) are consistent with their metal ion ratios, Table 4. The shortest metal−metal distances in **III**, **IV** and **V** are 6.79, 6.72, and 6.62 Å, respectively. The helixes of **III**, **IV**, and **V** have a straight line helical axis, a pitch of 8.123 Å for **III**, 8.076 Å for **IV**, and 8.077 Å for **V**, and an average radius of 2.18 Å for **III**, 2.17 Å for **IV**, and 2.12 Å for **V**, respectively. Just as in compounds **I** and **II**, all helix axes in **III**, **IV**, and **V** are crystallographic 2_1 axes. In the helical structures of **III**, **IV**, and **V**, both two tu molecules are bent into the helical turn and involved in the intrahelix hydrogen bond system, Table 3. Their intrahelix hydrogen bond motifs are similar to that of **I** and consistent with the observed FT-IR absorptions. Four N−H···O intrahelix hydrogen bond large ring

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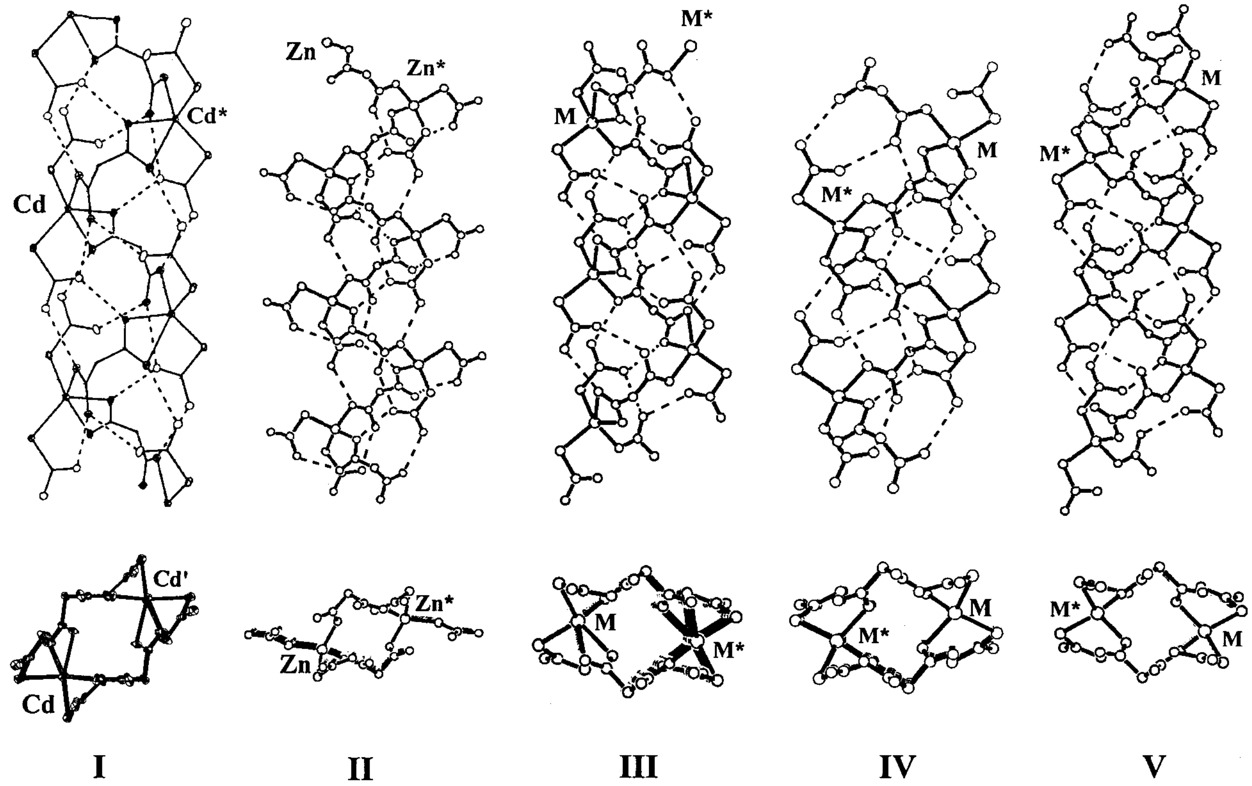

Figure 3. 1D helical structures and their top views of complexes **I**−**V**.

Table 3. Hydrogen-Bond Parameters: Lengths D−A (Å) and Angles ∠D−H···A (deg) for **I**−**V**[a]

	I	**II**	**III**	**IV**	**V**
N1−H1···O1$^{\#1}$	2.834, 156.7 (N4−O1)	2.842, 148.8 (N1−O2)	2.83, 142.7	2.84, 164.7	2.919, 159.5
N1−H2···O3$^{\#2}$	2.927, 159.1 (N4−O3)	2.924, 153.3 (N4−O1)	2.94, 150.9	2.87, 153.6	2.904, 147.0
N2−H3···O4$^{\#3}$	2.919, 172.2 (N3−O4)	2.924, 162.8 (N3−O4)	2.90, 164.2	2.90, 170.8	2.935, 175.6
N3−H6···O3$^{\#4}$	2.863, 150.8 (N1−O2)	2.853, 166.1 (N4−O3)	2.93, 120.1	2.95, 134.1	2.811, 145.3
N4−H8···O2$^{\#5}$	2.947, 139.9 (N2−O3)		2.89, 128.4	2.85, 137.7	2.979, 131.4
average	2.898, 155.7	2.887, 157.7	2.89, 141.3	2.882, 152.2	2.910, 151.8

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z + 2$ for **I**; $x, y + 1, z$ for **II**; $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z$ for **III**, **IV**, and **V**; #2, x, y, z for **I**; $x, y - 1, z$ for **II**; $-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z$ for **III**, **IV**, and **V**; #3, $-x, y - 1, z$ for **I**; $x, y - 1, z$ for **II**; $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z$ for **III**, **IV**, and **V**; #4, $x, y + 1, z$ for **I**; $x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$ for **II**; $x, y - 1, z$ for **III**, **IV**, and **V**; #5, $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + 2$ for **I**; $x, y - 1, z$ for **III**, **IV**, and **V**.

motifs can be described in Etter's graph set notation as $R_1^1(16)$, $R_1^1(14)$, $R_1^1(16)$, and $R_2^2(14)$. It is those hydrogen bonds spanning two helical turns that strongly reinforce their helical structures. Similarly to **I**, compounds of **III**, **IV**, and **V** also show spontaneous resolution of enantiomers due to the weak interhelix hydrogen bond interactions and also the packing of helixes.[14a,22]

Structure Adjustment for Isomorphous Substitution. Helical structure motifs in **I** and **II** have apparent differences, although both of the helical motifs are driven and sustained by long-range (spanning two turns) intrahelix hydrogen bonds, Scheme 2. Generally, this is due to the metal ion radius of Zn(II) and Cd(II). In complex **I**, both two tu molecules bent into the helical turn and were involved in the hydrogen-bond system. But in **II**, as to fitting the small ion size of Zn(II), one tu molecule was pushed out of the helical turn and only one tu group was involved in the long-range intrahelix hydrogen bond system. That resulted in a more tightly bound helical structure and smaller inner channel void size (from 1.5 to 0.5 Å). It is remarkable that metal ion occupations of Cd in **I** or Zn in **II** can be freely substituted by each other; even the ion radii of Cd(II) (0.97 Å) and Zn(II) (0.74 Å) are in different periods and have a great effect on their helical structures. In the compound series from **I**, **III**, **IV**, **V**, to **II**, metal ion Cd(II) was gradually substituted by Zn(II), and the helical structure was also adjusted to adapt to this substitute process and sustain the isomorphic structure, Tables 3 and 4, Figure 3. Average M−O and M−S distances of compounds from **I**, **III**, **IV**, **V**, to **II** are gradually decreased that are consistent with the decreasing of the average metal ion radius.[23] M−O2 (chelating carboxylate oxygen atom) distances of this compound series are apparently increased corresponding to the more tightly bound helical structure when the radius of the metal ion is decreased. The bond angles of O1−M−O4, C1−C2−C3 (malonate backbone), and C−O−M also show clearly the adjustment behaviors of this helix series, Table 4. The structure changes for the isomorphous substitution in this series are driven by the formation of a strong multi-hydrogen-bond set. In other words, the target of the structural adjustment is to form a high-quality long-range hydrogen-bond system. In fact, it is seen that, when the metal ion is substituted

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(23) (a) Chung, K. H.; Hong, E.; Do, Y.; Moon, C. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2333; *J. Chem. Soc., Dalton Trans.* **1996**, 3363. (b) Pajunen, A.; Pajunen, S.; Kivikoski, J.; Valkonen, J. *Acta Crystallogr.* **1996**, *C52*, 2689. (c) Burrows, A. D.; Menzer, S.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 4237 and references therein.

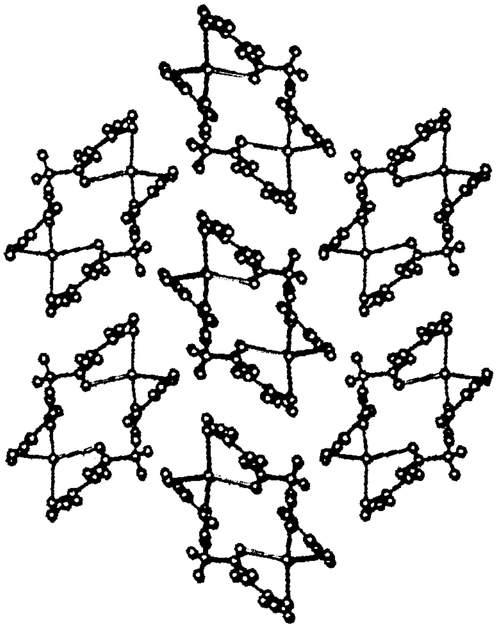

Figure 4. A portion of the crystal lattice for **I** (view of *ac* plane). Each metallohelix is positioned at the center of hexagon composed of six surrounding metallohelixes.

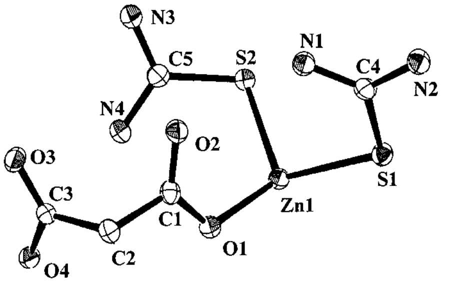

Figure 5. Fundamental structure unit of **II**.

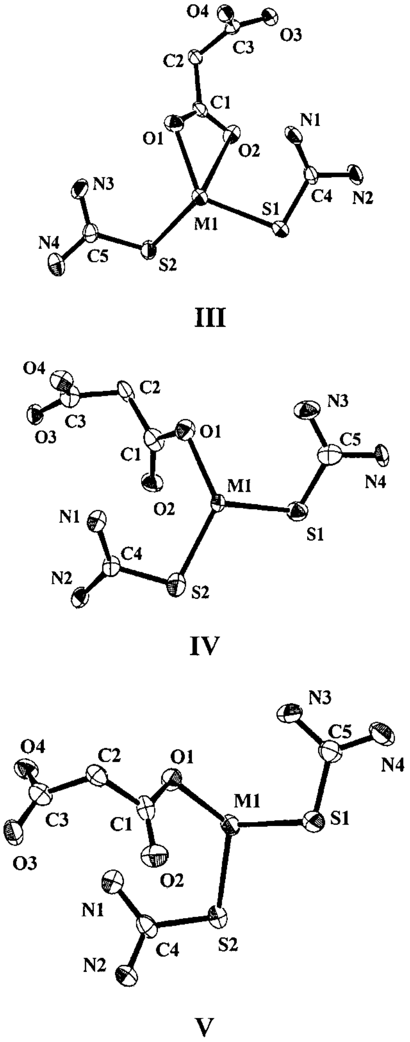

Figure 6. Fundamental structure units of **III**−**V**.

Table 4. Structural Adjustment Behaviors (besides Hydrogen-Bond Motif) Observed in **I**−**V**

	I	III	IV	V	II
M−O (Å) (av)	2.264	2.231	2.124	2.041	1.992
M−S (Å) (av)	2.519	2.492	2.390	2.354	2.328
S1−M−S2 (deg)	114.4	113.4	111.8	108.7	107.5
O1−M−O4 (deg)[a]	87.6	89.2	89.4	94.4	96.8
C1−C2−C3 (deg)[b]	110.0	110.3	108.3	108.6	108.3
C−O−M (av) (deg)[c]	108.1	110.9	111.8	114.3	118.1

[a] O1 and O4 are the coordinated carboxylate oxygen atoms originating from two different malonate anions. [b] C1, C2, and C3 are the backbone of malonate dianion. [c] Here, C−O is from coordinated carboxylate group.

and the structural characters are changed, high-quality intrahelix hydrogen bonds are always observed and take effect on the structures from **I** to **V**, Table 3, corresponding to the flexibility and dynamic property of hydrogen bonds.

Properties. The coordination polymer helixes of **I**−**V** are almost insoluble in common organic solvents but soluble in water. The thermal behaviors of compounds from **I** to **V** are very similar, Figure 1. TGA of the crystalline samples showed no chemical decomposition up to about 210 °C, indicating that the 1D infinite helical structures were quite stable for the reason of multiple long-range hydrogen-bond interactions. The whole coordination polymer helical structures were destroyed at temperatures ranging from 200 to 300 °C in the formation of carboxylates. Further heating of the samples resulted in the formation of oxides at temperatures above 600 °C.

Conclusion

Molecular design for construction of a single-stranded helix bearing a small inner channel is successfully achieved by mimicking helical fold structures in protein. Pre-positioning of the suitable hydrogen bond acceptor and donor sites in a polymer backbone is the key step in assembly of this hydrogen-bonded helix. The flexibility of the bridge and second ligands, the metal size, and coordination geometry are also important components that should be considered. The well-designed coordination polymer helix system is mainly induced and sustained via intrahelix hydrogen bonds. The metal ion occupation in the helix motif can be freely substituted by the other one. As a result, structures are self-adjusted to sustain their isomorphous conformation of 1D coordination polymer helix.

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Supporting Information Available: X-ray crystallographic files of complexes **I**−**V**, in CIF format. This materials is available free of charge via the Internet at http://pubs.acs.org.

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