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Conformation Preference of a Flexible Cyclohexanetetracarboxylate Ligand in Three New Metal-Organic Frameworks: Structures, Magnetic and Luminescent Properties

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Three novel complexes of formula $[Co_5(OH)_2(cht)_2(H_2O)_{10}]_n \cdot 2nH_2O$ (**1**) (H_4cht = cyclohexane-1,2,4,5-tetracarboxylic acid), $[Zn_2(cht)(H_2O)_3]_n \cdot nH_2O$ (**2**), and $[Cd_2(cht)(H_2O)_5]_n \cdot 2nH_2O$ (**3**) were synthesized by a hydrothermal reaction of cyclohexane-1,2,4,5-tetracarboxylic acid in the presence of sodium hydroxide with $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$, respectively. These complexes were obtained by controlling the molar ratios of starting materials and the pH values of reaction mixtures with an initial pH of 5.87 for **1**, 5.50 for **2**, and 5.57 for **3**, respectively. The single-crystal X-ray investigations reveal that the cht ligands change their conformations exclusively to the a,e,e,a form in all three complexes. Complex **1** features a two-dimensional (2D) metal-organic framework (MOF) with an axis surrounded by two zigzag structures, a rectangular channel surrounded by two a-carboxylate-metal-a-carboxlate and two e-carboxylate-metal-e-carboxylate chains, and two smaller distorted square-pyramidal channels surrounded by hydroxyl oxygen, cyclohexane, and its two a-carboxylates. Each cht ligand connects five cobalt atoms and each cobalt atom is six-coordinated with carboxylate-oxygen, hydroxyl, and water molecules. Complex **2** possesses a three-dimensional (3D) MOF structure that consists of the cht ligands and two types of cobalt; one is four-coordinated with carboxylate-oxygens and the other is six-coordinated with carboxylate-oxygens and water molecules. Each cht ligand is bonded to seven zinc atoms. Complex **3** is also a 2D MOF structure constructed by seven-coordinated cadmium atoms and the cht ligands. The e-carboxylates of two parallel cht ligands are connected to a type of cadmium atoms to form 1D chains, and these chains are further connected through a-carboxylates of the ligands and another type of cadmium atoms to give the 2D structure. Extensive hydrogen bonding interactions involving carboxylate-oxygen atoms and crystallization water molecules afford 3D supramolecular networks in complexes **1** and **2**. Magnetic susceptibility measurement of **1** confirmed a six-coordinated high-spin cobalt(II) ion and the presence of magnetic exchange coupling among the three hydroxyl-oxygen bridged cobalt ions. Fluorescent spectra of complexes **2** and **3** show strong fluorescent emissions in the blue region.

Introduction

Metal-organic framework (MOF) complexes have attracted considerable interest lately because of their potential applications in a variety of areas, including catalysis, ion exchange, sensors, shape-selective adsorption, gas storage, photochemistry, and materials with magnetic properties.[1,2] Over the past years, plenty of MOFs with variable dimensionality and different coordination styles have been designed and synthesized.[3] In particular, the structures constructed by metal and carboxylate-type ligands, such as phthalate, biphenylcarboxylate, benzenetricarboxylate, and adamantanedicarboxylate have been shown to be able to control the

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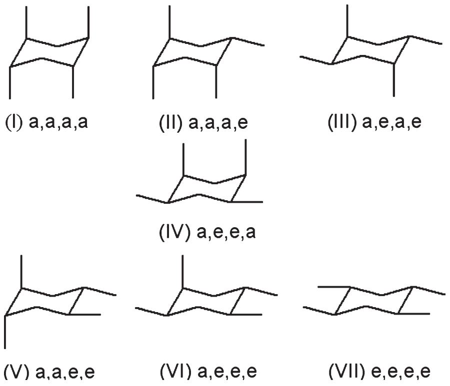
coordination styles and pore sizes.[4] Recently, the synthesis and investigation of coordination polymers with flexible multidentate ligands, which are capable of producing diversified new systems with different dimensionality and coordination styles when adding new cooperative ligands, have gradually caught the special attentions of researchers.[1a,3a,5] For instance, Ruiz-Pérez and co-workers systemically studied the structural and physical properties of malonate-bridged complexes, showing that flexible malonate is a fruitful ligand for the construction of different structures.[6] However, it is difficult to predict and control the structure of these complexes framed through the flexible ligands and metal ions because of the flexibility of its framework. Hence, the conformation control of flexible ligands in coordination networks is an important proposition to researchers. Some investigations have been focused on the conformation control and configuration conversion of flexible ligands in synthetic reactions by using 1,4-cyclohexanedicarboxylic acid (H_2chdc),[7] 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6chhc),[8] and tetrahydrofurantetercarboxylic acid (H_4thftc).[9]

In this work, we are interested in two aspects of the formation of coordination polymers that consist of metal and flexible ligands: (1) synthetic conditions under which the polymers can be formed and the conditions that the conformation of flexible ligands can be exclusively converted to the sole form; and (2) how different kind of metals influence the conformation of ligands and the structural construction of the complexes. To help gain insights into these questions, comparative studies on the effects of different metal centers and different experimental conditions were carried out by using cyclohexane-1,2,4,5-tetracarboxylic acid as a ligand, of which the preference of coordination has never been studied. Analogous to H_2chdc and H_6chhc, cyclohexane-1,2,4,5-tetracarboxylic acid is a flexible ligand with multidentate coordination sites and possesses seven possible conformations in a mixture of cis- and trans- isomers, as shown in Scheme 1. Conformation I and II are unstable and have the tendency to convert their conformations to the most stable form, whereas conformation III−VII bear relatively similar stability considering the energy and steric influence of carboxylic groups.[10] Here we report the synthesis, structures, magnetic, and luminescent properties of three novel complexes, $[Co_5(OH)_2(cht)_2(H_2O)_{10}]_n \cdot 2nH_2O$ (**1**) (H_4cht = cyclohexane-1,2,4,5-tetracarboxylic acid), $[Zn_2(cht)(H_2O)_3]_n \cdot nH_2O$ (**2**), and $[Cd_2(cht)(H_2O)_5]_n \cdot 2nH_2O$ (**3**). In all three complexes, we successfully achieved the conformation change of all cht ligands exclusively to the a,e,e,a form by controlling the pH values of initial materials between 5 and 6 and the hydrothermal temperature at 120 °C.

Scheme 1



Experimental Section

Materials and Methods. All reagents used in the syntheses of **1**−**3** were purchased from Aldrich Chemical Co. and used without further purification. The cyclohexane-1,2,4,5-tetracarboxylic acid is a mixture of cis and trans. The X-ray powder diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA (Cu Kα radiation, $\lambda = 1.5418$ Å). The data collection was carried out with a step size 0.03 degree and counting time of 1s per step. The 2θ angular range is from 5 to 40 degrees. IR spectra were recorded on a Nicolet AVATAR 370 FTIR infrared spectrophotometer. The magnetic properties of **1** were investigated with a commercial PPMS in the temperature range of 2−300 K, and the magnetic susceptibility was measured at H = 5000 Oe. The fluorescent spectra of **2** and **3** were measured on a SPEX fluorolog-3 Tau3 system equipped with a 450 w xenon lamp and double monochromators on both excitation and emission sides.

Synthesis of the Complexes: $[Co_5(OH)_2(cht)_2(H_2O)_{10}]_n \cdot 2nH_2O$ (1). $Co(NO_3)_2 \cdot 6H_2O$ (0.2943 g), cyclohexane-1,2,4,5-tetracarboxylic acid (0.1292 g), and sodium hydroxide (0.0796 g) in a molar ratio of 2:1:4 and distilled water (8.0038 g) were mixed in a vial, and the mixture was shaken in an ultrasonic bath for 10 min. The initial pH was 5.87. The vessel was then sealed and heated at 120 °C for 48 h. The autoclave was subsequently allowed to cool to room temperature. After washing with distilled water and ethanol, plate-shaped transparent red crystals were obtained (0.0803 g, 38% yield).

$[Zn_2(cht)(H_2O)_3]_n \cdot nH_2O$ (2). $Zn(NO_3)_2 \cdot 6H_2O$ (0.2952 g), cyclohexane-1,2,4,5-tetracarboxylic acid (0.1317 g), and sodium hydroxide (0.0774 g) in a molar ratio of 2:1:4 and distilled water (7.8252 g) were mixed in a vial, and the mixture was shaken in an ultrasonic bath for 10 min. The initial pH was 5.50. The vessel was then sealed and heated at 120 °C for 68 h. The autoclave was subsequently allowed to cool to room temperature. After washing with distilled water and ethanol, plate-shaped transparent colorless crystals were obtained (0.1285 g, 56% yield).

$[Cd_2(cht)(H_2O)_5]_n \cdot 2nH_2O$ (3). $Cd(NO_3)_2 \cdot 4H_2O$ (0.3165 g), cyclohexane-1,2,4,5-tetra-carboxylic acid (0.1316 g), and sodium hydroxide (0.0978 g) in a molar ratio of 2:1:5 and distilled water (8.0897 g) were mixed in a vial, and the mixture was shaken in an ultrasonic bath for 10 min. The initial pH was 5.57.

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Table 1. Crystallographic Collection and Refinement Parameters for **1**, **2**, and **3**

	1	**2**	**3**
formula	C20 H42 O30 Co5	C10 H16 O12 Zn2	C10 H22 O15 Cd2
M_r	1057.19	458.97	607.08
size [mm^3]	0.16 × 0.12 × 0.08	0.20 × 0.16 × 0.10	0.20 × 0.18 × 0.12
crystal system	monoclinic	monoclinic	triclinic
space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a [Å]	10.2433(2)	9.0159(6)	8.713(3)
b [Å]	6.57520(10)	8.4164(5)	9.671(3)
c [Å]	24.5222(6)	19.0635(12)	11.321(4)
α [deg]	90	90	86.07(3)
β [deg]	91.982(2)	102.9120(10)	82.97(2)
γ [deg]	90	90	64.81(2)
V [Å^3]	1650.62(6)	1409.99(15)	856.7(5)
Z	2	4	2
F(000)	1074	928	596
ρ_{calcd} [g cm^{-3}]	2.127	2.162	2.353
[mm^{-1}]	2.579	3.471	2.563
range [deg]	1.99 to 26.50	2.66 to 24.87	1.81 to 20.40
reflec. collected	8324	6619	5375
indep. reflec.	3316 (Rint = 0.0299)	2430 (Rint = 0.0246)	1662 (Rint = 0.1562)
parameters	252	217	243
$R1$ [$I > 2\sigma(I)$]	0.0337	0.0253	0.0522
$wR2$ [$I > 2\sigma(I)$]	0.0720	0.0594	0.0995
goodness of fit	1.027	1.035	0.995

The vessel was then sealed and heated at 120 °C for 65 h. The autoclave was subsequently allowed to cool to room temperature. After washing with distilled water and ethanol, plate-shaped transparent colorless crystals were obtained (0.2672 g, 88% yield).

Single-Crystal Structure Analysis. Crystallographic data and structure refinements parameters of complexes **1**−**3** are summarized in Table 1. Complexes **1**−**3** were glued to a thin glass fiber with epoxy resin and collected on a Bruker APEX II diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (Mo Kα radiation, λ = 0.7103 Å) operating at 50 kV and 30 mA at 293 K. The empirical absorption correction was based on equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. Each structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL, and final full-matrix refinements were against F^2. The SMART software was used for collecting frames of data, indexing reflections, and determining the lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling; SADABS for absorption correction; and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[11−13]

Results and Discussions

Influence of Synthetic Conditions and Metal Ions. Complexes **1**−**3** were synthesized by the hydrothermal reaction of cyclohexane-1,2,4,5-tetracarboxylic acid and sodium hydroxide with $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, or $Cd(NO_3)_2 \cdot 4H_2O$ in a molar ratio of 2:1:4. As the structures of coordination networks in MOFs have been found to be greatly influenced by the physical and chemical factors of a reaction, a slight change in the synthetic conditions may result in different reaction products.[14] Hence, a series of reactions were performed by changing the reaction conditions including pH values, reaction temperatures, solvents, and metal ions. When the pH values were controlled between 5 and 6 by changing the ratio of the initial materials and the hydrothermal temperatures were set at 120 °C, the expected products **1**−**3** were obtained. The phase purities of **1**−**3** were confirmed by comparison of their powder diffraction patterns with those calculated from single crystal analyses (Figure S1−S3, Supporting Information). FT-IR spectra showed that the characteristic absorption peaks arose from asymmetric stretching vibrations of the ligand, $\nu_{as}(COO^-)$, were shifted from 1736 cm^{-1} to 1534−1562 cm^{-1} (Figure S4, Supporting Information), indicating that all carboxyls of the ligand were deprotonated in complexes **1**−**3**. However, no solid products were formed when the reaction was conducted without sodium hydroxide or under 100 °C, and other unexpected products were obtained when using higher ratio of sodium hydroxide than the aforementioned proportion or when using *N*,*N*-dimethylformamide (DMF) and methanol as the solvent. Interestingly, when different metal ions were used at the same reaction conditions, the conformation of the ligand was transformed into the same a,e,e,a conformation, as shown in Figure 1. However, different metal ions have a great influence on the structural construction of MOFs as the ligands employed different coordination modes in different polymers as shown in Figures 2−4. These results indicate that it is crucial to regulate the pH values, reaction temperatures, and solvent systems when controlling the conformation of cht ligands in coordination polymers. Similar observations were reported on 1,4-cyclohexanedicarboxylic acid and tetrahydrofurantetercarboxylic acid, in which the pH values and reaction temperatures played an important role in the selection of conformation of the ligand.[7,9] However, it is different from the reported studies on 1,2,3,4,5,6-cyclohexanehexacarboxylic acid, in which different metal ions have an

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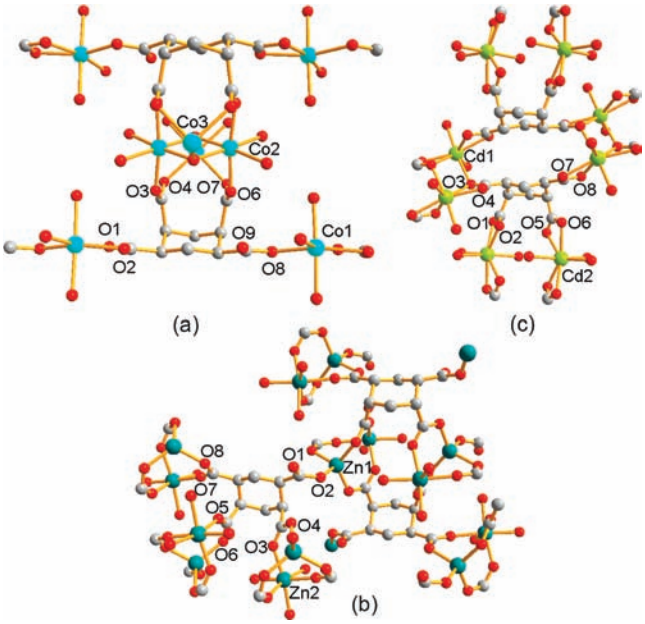

Figure 1. Coordination modes of ligands in complex **1** (a), **2** (b), and **3** (c).

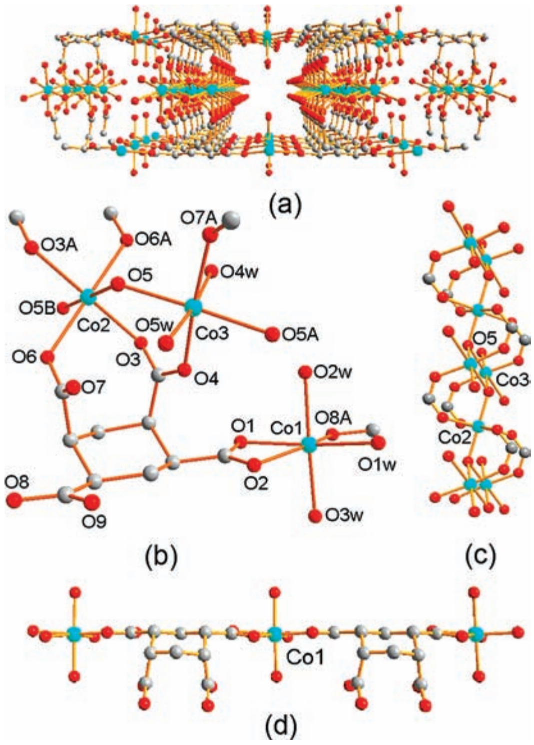

Figure 2. (a) 2D framework viewed along the *b*-axis; (b) coordination environment of metal ions; (c) the zigzag structure consisted of Co2, Co3, and cht viewed along the *a*-axis; (d) 1D chain consisting of Co1 and cht viewed along the *b*-axis in the structure of **1**.

important influence on the selection of ligands' conformation.[8]

Description of Crystal Structures. Single-crystal X-ray structural analysis shows that complex **1** is a 2D MOF structure crystallized in the monoclinic $P2(1)/c$ space group, and the asymmetric unit consists of two and a half cobalt atoms, one deprotonated cht ligand, one hydroxyl, five coordinated water molecules, and one crystallization water molecule. Three types of central Co atoms are all six-coordinated with distorted octahedral geometry (Figure 2b). Co1 is connected to three oxygen atoms from two different e-carboxylate groups and three water molecules [Co1−O 2.065(2)−2.156(2); Co1−Ow 2.089−2.122 Å], two aqua oxygens occupy the apical site and the rest locate at the equatorial position. Co2 is bonded with two hydroxyls and four oxygen atoms from four different a-carboxylate groups [Co2−O(H) 2.061(2); Co2−O 2.129(2)−2.157(2) Å]. Co3 is coordinated by two hydroxyls, two different a-carboxylate-oxygens, and two water molecules [Co3−O(H) 2.099(2), 2.114(2); Co3−O 2.033(2), 2.047(2); Co3−Ow 2.169(2), 2.236(2)]. Selected bond lengths and bond angles for complexes **1**−**3** are listed in Tables S2−S4, Supporting Information. Interestingly, all cht ligands in compound **1** adopt a type of coordination mode which exclusively transforms their chair conformations to the a,e,e,a form (Figure 1a), and each ligand is bridged to five Co atoms through seven carboxylate-oxygens by four kinds of connection modes. As shown in Figure 2, the e-carboxylates of cht ligands are bridged to Co1 atoms to produce a 1D chain, whereas Co2 and Co3 are connected by the V-shape coordinated oxygen of hydroxyl and a-carboxylate to gain another 1D chain. Accordingly, the 2D MOF structure, which has a rectangular channel surrounded by two a-carboxylate-metal-a-carboxlate and two e-carboxylate-metal-e-carboxylate chains [the pore size defined by the cobalt−cobalt separations of adjacent cobalt atoms between two parallel chains is $11.5301(7) \times 7.1332(6)$ Å^2] (Figure 2a), two smaller distorted square-pyramidal channels [the pore size defined by the separation of two a-carboxylates and the separation between apical hydroxyl oxygen and nether cyclohexane is $3.0151(4) \times 4.1138(4)$ Å^2] (Figure 2a), and an axis surrounded by two zigzag chains (Figure 2c) along the *b*-axis, is formed by the two types of 1D chain through the linkage of a-carboxylates of cht ligands. These 2D structures are further linked to afford 3D supramolecular networks in the polymer through extensive hydrogen bonding interactions involving carboxylate-oxygen atoms and crystallization water molecules (Table S1, Supporting Information).

Complex **2** is crystallized in the monoclinic $P2(1)/n$ space group, but it possesses a 3D MOF structure with two crystallographically independent zinc atoms, one deprotonated cht ligand, three coordination water molecules, and one lattice water molecule in the structural unit. Two kinds of central Zn atoms are found; one located at the center of a tetrahedron and the other at a distorted octahedron (Figure 3d). Zn1 is bonded to four oxygen atoms from two e-carboxylate and two a-carboxylate groups [Zn1−O 1.9380(19)−1.9855(19) Å] (Figure 3b); Zn2 is connected to three oxygen atoms from two a-carboxylate and one e-carboxylate groups and three water molecules [Zn2−O 2.049(2)−2.076(2); Zn2−Ow 2.042(2)−2.135(2) Å] (Figure 3c); and each ligand is linked to seven Zn atoms through seven carboxylate-oxygens by two kinds of connection modes. Noticeably, although the cht ligands adopt a different coordination mode with metal ions in compound **2** compared to the ones in compound **1**, their chair conformations are also exclusively transformed to the a,e,e,a form (Figure 1b). Differing from the 1D chain constructed by different type

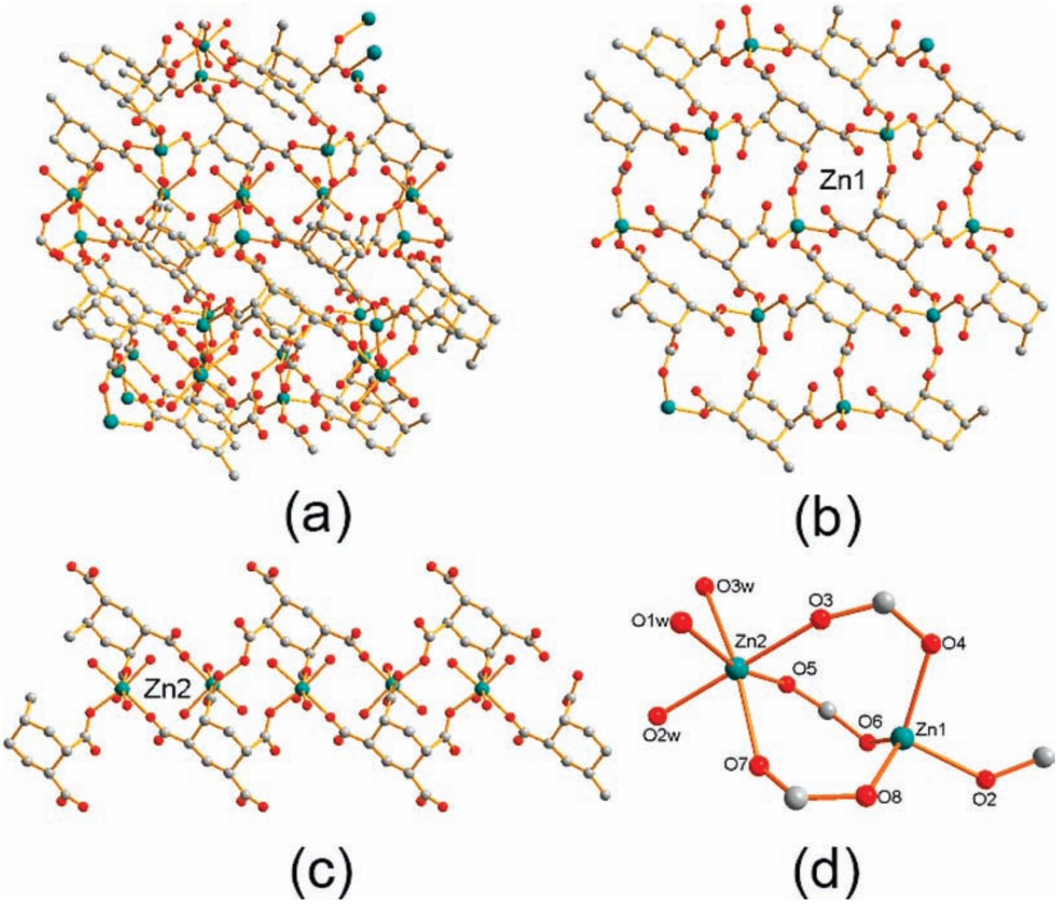

Figure 3. (a) 3D framework; (b) 3D framework consisting of Zn1 and cht; and (c) 1D zigzag chain consisting of Zn2 and cht viewed along the *b*-axis; (d) coordination environment of metal ions in the structure of **2**.

of metal atoms and relevant components in complex **1**, four vertexes of the tetrahedron with a Zn1 central atom are occupied by four oxygens from two a-bond and two e-bond carboxylates of four cht ligands along four different directions, forming a 3D structure in complex **2** (Figure 3b). However, the zigzag 1D chain is also formed by cht ligands linking with Zn2 atoms with three water molecules at the side (Figure 3c). Upon that, the more interrelated 3D MOF framework with an irregular porous structure is gained through the connection of the 1D chain and the above 3D structure by the carboxylate oxygens (Figure 3a).

Complex **3** also has a 2D MOF structure, but it is crystallized in a triclinic $P\overline{1}$ space group and the asymmetric unit consists of two cadmium atoms, one deprotonated cht ligand, five coordinated water molecules, and two crystallization water molecules. When compared to the metal atoms located at the distorted octahedron center in complex **1** and the center of tetrahedron and distorted octahedron in complex **2**, it is found that two types of central Cd atoms are located at the center of a highly distorted polyhedron with seven-coordinated geometry in complex **3** (Figure 4d). Cd1 is coordinated by five oxygen atoms from three different e-carboxylate groups and two water molecules [Cd1−O 2.365(11)−2.464(10); Cd1−Ow 2.258−2.309 Å] (Figure 4c). Cd2 is bonded to four oxygen atoms from two different a-carboxylate groups and three water molecules [Cd2−O 2.348(11)−2.424(10); Cd2−Ow 2.324−2.375 Å] (Figure 4b). Each ligand is linked to five Cd atoms through nine carboxylate-oxygens by four kinds of connection modes (Figure 1c). However, it should be pointed out that the cht ligands still adopt a kind of coordination mode that exclusively transforms their chair conformation to the a,e,e,a form in compound **3**, although their carboxylate oxygens adopt different connection modes with metal atoms in comparison with complexes **1** and **2**. Cd1 is connected by two e-carboxylate ligands to get a 1D chain similar to the one built by Co1 and e-carboxylate of the ligand in complex **1**, but the chain is further linked through the Y-shape coordinated oxygen of one carboxylate to form a 1D structure with two entrosymmetric chains. The 2D network is formed by Cd2 connecting to the a-carboxylate oxygen of the 1D structure (Figure 4a). Analogous to complex **1**, the 2D structures are further linked to give a 3D supramolecular framework in the coordination polymer by extensive hydrogen bonding interactions involving carboxylate-oxygen atoms and crystallization water molecules.

Magnetic and Fluorescent Properties. The magnetic susceptibility measurements for complex **1** were carried out with microcrystal samples in the temperature range of 2−300 K, and the results are shown in Figure 5. At room temperature, the $\chi_M T$ value is 17.06 cm^3 K mol^{-1} per three Co units, which corresponds to $\mu_{eff} = 3.89\ \mu_B$ per Co(II). This is in good agreement with a system containing a six-coordinated high-spin cobalt(II) ion [μ_{eff} (spin-only, $g = 2.0$) = 3.87 μ_B]. Upon cooling, the value

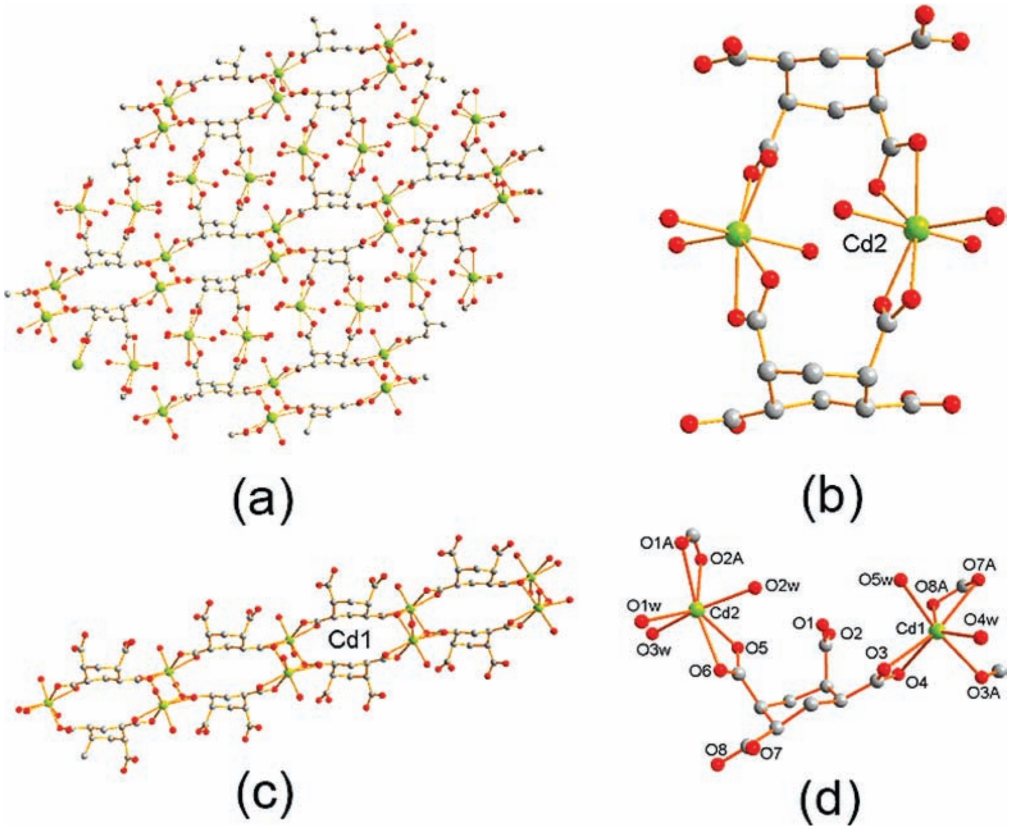

Figure 4. (a) 2D framework; (b) the structure consisting of Cd2 and cht; and (c) 1D chain consisting of Cd1 and H_4cht viewed along the 111-axis (d) coordination environment of metal ions in the structure of **3**.

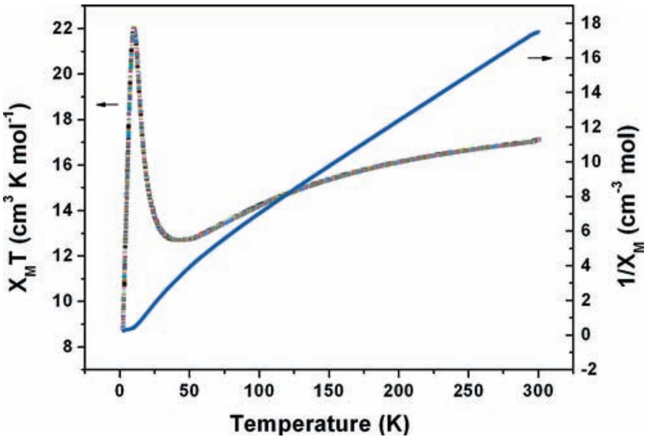

Figure 5. Plot of $\chi_M T$ and $1/\chi_M$ vs T for complex **1** in the temperature range of 2−300 K.

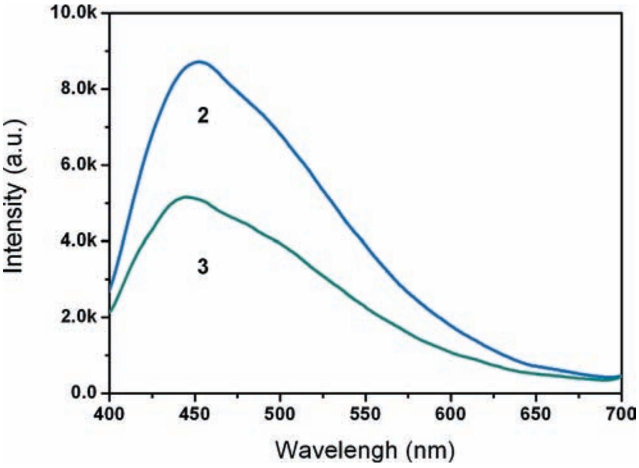

Figure 6. Solid-state emission spectra of complex **2** and **3** at the room temperature.

of $\chi_M T$ decreased smoothly to a minimum (12.74 cm^3 K mol^{-1}) at 38 K, indicating the presence of antiferromagnetic coupling among the three hydroxyl-oxygen bridged cobalt ions. After the $\chi_M T$ value reached the minimum, it rapidly increased up to 21.86 cm^3 K mol^{-1} at 9 K, which is characteristic of ferromagnetic behavior. The sharp decrease of $\chi_M T$ below 9 K resulted from the saturation of the χ_M value and/or a zero-field splitting effect. The magnetic susceptibility obeys the Curie−Weiss law down to 90 K with a Curie constant $C = 18.71$ cm^3 K mol^{-1} and a Weiss constant $\theta = -6.92$ K. It is known that the sign of the exchange depends on the M−O−M angles.[15] When the M−O−M angles are close to 90°, it favors ferromagnetic interactions; whereas the antiferromagnetic interactions are expected for large M−O−M angles. Considering the 1D zigzag chain structure (Figure 2c), where Co2 and the two Co3′s are close [$d_{\text{Co2−Co2}}$ = 3.1102(6) Å, $d_{\text{Co2−Co3}}$ = 3.6456(5) Å, 3.6281(5) Å], it is reasonable to postulate that the antiferromagnetic interactions come from Co2 and Co3 [Co2−O−Co3 =

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[15] (a) Guillou, N.; Pastre, S.; Livage, C.; Férey, G. *Chem. Commun.* **2002**, 2358–2359. (b) Konar, S.; Mukherjee, P. S.; Zangrando, E.; Lloret, F.; Chaudhuri, N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1561–1563. (c) Tong, M. L.; Wang, J.; Hu, S. *J. Solid State Chem.* **2005**, *178*, 1518–1525.

121.18(10)°, 121.11(10)°], while the ferromagnetic couplings are from Co3 and Co3 [Co3−O−Co3 = 94.92(9)°].

Photoluminescent properties of complexes **2** and **3** were investigated in the solid state at room temperature. Upon the irradiation of ultraviolet light at 370 nm, complexes **2** and **3** show strong fluorescent emissions with a maximum at 453 and 445 nm, respectively (Figure 6). Since Zn^{2+} and Cd^{2+} ions are difficult to oxidize or to reduce owing to their d^{10} configurations, the emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature. According to the close emission energy, they are tentatively attributed to the intraligand transition of cht that is modified by metal coordination. The emissions in the blue region suggest that both complexes may potentially be useful for blue-fluorescent materials.

Conclusions

In summary, we have researched the conformation selection of flexible ligand H_4cht in coordination polymers by changing the reaction conditions including pH values, reaction temperatures, solvents, and metal ions. Three novel complexes were obtained only when we controlled the pH values of initial materials between 5 and 6 and the hydrothermal temperature at 120 °C. In these complexes, the cht ligands exclusively changed their chair-shaped conformation to the a,e,e,a form. Interestingly, while using different metal ions at similar reaction conditions, the ligands exhibited different coordination modes in MOF polymers; however, their conformations were converted to the same a,e,e,a form. These results suggest that the pH values, reaction temperatures, and solvent systems have a crucial effect on regulating the conformation of ligands in coordination polymers and that the preferred conformation of cht is the a,e,e,a form under our experimental conditions. Moreover, different metal ions have a great influence in the structural construction of MOFs. Magnetic susceptibility measurements for complex **1** confirmed a six-coordinated high-spin cobalt(II) ion and the presence of antiferromagnetic coupling among the Co2 and the two Co3 ions from room temperature to 38 K. From 38 K to 9 K, ferromagnetic behavior was observed, which is attributed to Co3/Co3 interactions. The magnetic susceptibility obeys the Curie−Weiss law down to 90 K with a Curie constant $C = 18.71$ cm^3 K mol^{-1} and a Weiss constant $\theta = -6.92$ K. Photoluminescent properties of complexes **2** and **3** show strong fluorescent emissions (at 453 nm for **2** and 445 nm for **3**) in the blue region, which have been attributed to the intraligand transition of cht that is modified by metal coordination.

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Supporting Information Available: Three X-ray crystallographic file in CIF format for the structure determinations, the geometrical parameters of hydrogen bonds, the selected bond lengths (Å) and bond angles (deg), the infrared spectra, and the X-ray powder diffraction diagrams for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.