5312 *Inorg. Chem.* **2001,** *40,* 5312−5313

Novel Coordination Polymers with Mixed Ligands and Orientated Enantiomers

Zhan Shi, Shouhua Feng,* Yan Sun, and Jia Hua

Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, P.R. China

Received February 27, 2001

Over the past several decades, a variety of zeolites and open framework inorganic solids have been synthesized for their considerable applications in selective catalysis, adsorption, and ion exchange.[1] Recently, studies in coordination polymers[2,3] as organic zeolite-like solids, built up from metals and multifunctional organic ligands, represent a rapidly expanding field.[4,5] In studies in the synthesis of microporous crystals and layered materials by racemic compounds as templates, it has been found that some inorganic frameworks or layers behave as functions for recognizing certain configurations in different channels or layers. Therefore, a motivation for the molecular recognition or separation by organic open frameworks has been raised. With this aim toward molecular recognition, we performed the design and synthesis of novel coordination polymers with both ligands such as 4,4′-bipyridine, pyrimidine, pyrazine, carboxylate, and racemic and differently conformed molecules. In our previous studies,[6] we obtained two novel coordination polymers, [Mn(maleate)(4,4′-bipy)]·0.5H_2O and [Mn(fumarate)(4,4′-bipy)(H_2O)]·0.5(4,4′-bipy), in which a structural transformation from 2D to 3D through conformation change of carboxylate ligands was observed. In this study, we report the synthesis and X-ray structural characterization of a novel coordination polymer, [Cu_2(CyDTA)(4,4′-bipy)$_2$]·12H_2O (**1**) (CyDTA = *trans*-1,2-cyclohexanediaminetetraacetate), which has a novel double-layer network, and two configurations are separated layer by layer. The synthesis and structure for another related compound synthesized in the same system, 3D [Cu_3(EDTA)(4,4′-bipy)$_{3.5}$(H_2O)$(OH)_2$]·2H_2O (**2**) (EDTA = ethylediaminetetraacetate), is also presented for comparison.

1 and **2** were prepared by diffuse reactions in an H-tube. A typical procedure for the crystal growth of **1** is as follows: A solution of 4,4′-bipy (0.50 mmol) in ethanol (5 mL) was slowly diffused into an aqueous solution (5 mL) of $Cu(NO_3)_2$ (0.50 mmol) and Na_4CyDTA (0.25 mmol) (or Na_4EDTA (0.25 mmol) in the case of **2**) at ambient temperature. Blue crystals of **1** or **2** suitable for single-crystal X-ray determination[7] were grown for 5 days in the glass pipe.

Structurally, **1** has a 2D layered structure made up of Cu^{2+} ions coordinated by 4,4′-bipy and CyDTA which is in two distinguished enantiomers (*R,R* and *S,S*). There are two different coordination environments for copper atoms, Cu(1) and Cu(2), both having distorted trigonal bipyramidal geometry. Cu(1) is coordinated to two O atoms of carboxylate of CyDTA and one N atom of 4,4′-bipy in a trigon and two N atoms of 4,4′-bipy as the apexes. In the trigonal bipyramidal environment of Cu(2), one CyDTA anion uses two N atoms to chelate to a Cu(2) ion, forming a five-membered ring. These two N atoms and another N atom of 4,4′-bipy form the trigon, and two O atoms of carboxylate occupy the axial positions. The building block of CyDTA bridges Cu(1) and Cu(2) through a hexadentate mode to form 1D chains along the *b* axis (Figure 1a). Cu(1) atoms in a chain and Cu(2) atoms in another chain are linked by 4,4′-bipy (N(1)···N(2)) and Cu(1)′ (N(3)···N(4)). Accordingly, these 1D Cu−CyDTA chains are linked by the 4,4′-bipy ligands, building up a 2D layer. These 2D layers are situated in parallel to the crystallographic *ab* plane (Figure 2).

The *trans*-CyDTA molecule with two chiral carbon atoms has two configurations, (*R,R*) and (*S,S*). The interesting feature for structure **1** is its selective coordination of (*R,R*) and (*S,S*) CyDTA molecules with Cu^{2+} ions. There is exclusively one type of configuration in each Cu−CyDTA chain. Additionally, two configurations are separated in the double-layer structure: one type on the top of the layer and the other on the bottom of the layer. The racemic CyDTA molecules are arranged orderly through the process of self-assembly and recognition. It was rare to observe the selective coordination of the racemic molecules in the process of assembly of coordination polymers. A similar phenomenon is encountered in a synthesis of a layered phosphate where L- and D-enantiomers in a racemic transition complex were separated layer by layer in the phosphate.[8]

---

* To whom correspondence should be addressed. Fax: (+86) 431 5671974. E-mail: shfeng@mail.jlu.edu.cn.

(1) (a) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633−2656. (b) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268−3292.

(2) For reviews: (a) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431−1434. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461−1494. (c) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638−2684. (d) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739−1753. (e) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474−484. (f) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283−288.

(3) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (b) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276−279. (c) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982−986.

(4) (a) Kasai, K.; Aoyagi, M.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2140−2141. (b) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158−5168. (c) Groeneman, R. H.; MacGillivray, L. R.; Atwood, J. L. *Inorg. Chem.* **1999**, *38*, 208−209. (d) Evans, O. R.; Lin, W. *Inorg. Chem.* **2000**, *39*, 2189−2198. (e) Tong, M. L.; Chen, H. J.; Chen, X. M. *Inorg. Chem.* **2000**, *39*, 2235−2238. (f) Dong, Y. B.; Smith, M. D.; Layland, R. C.; zur Loye, H. C. *Chem. Mater.* **2000**, *12*, 1156−1161.

(5) (a) Li, J.; Zeng, H.; Chen, J.; Wang, Q.; Wu, X. *Chem. Commun.* **1997**, 1213−1214. (b) Wang, Q.; Wu, X.; Zhang, W.; Sheng, T., Lin, P.; Li, J. *Inorg. Chem.* **1999**, *38*, 2223−2226.

(6) Shi, Z.; Zhang, L.; Gao, S.; Yang, G.; Hua, J.; Gao, L.; Feng, S. *Inorg. Chem.* **2000**, *39*, 1990−1993.

(7) Crystal data for **1**: triclinic, $P\bar{1}$; $a = 11.1593(8)$ Å, $b = 11.5796(9)$ Å, $c = 19.8628(15)$ Å, $\alpha = 90.487(2)°$, $\beta = 98.530(2)°$, $\gamma = 101.598(2)°$; $V = 2484.5(3)$ Å^3; $Z = 2$; $d_{calcd} = 1.334$ g/cm^3; μ(Mo Kα) = 0.930 mm^{-1}; λ(Mo Kα) = 0.71073 Å. R1 = 0.0588, wR2 = 0.1780, and GOF on F^2 is 1.069. Anal. Calcd for $C_{34}H_{58}N_6O_{20}Cu_2$: C, 40.92; H, 5.86; N, 8.42; Cu, 12.74. Found: C, 41.06; H, 5.65; N, 8.53; Cu, 12.61. IR (KBr pellet ν/cm^{-1}): 1605(s), 1536(s), 1489(m), 1387(s), 1220(s), 1107(m), 1072(s), 1015(m), 972(m), 925(m), 864(m), 815(s), 728(m), 644(s). Crystal data for **2**: monoclinic, $C2/c$; $a = 40.889(7)$ Å, $b = 19.545(4)$ Å, $c = 16.642(4)$ Å, $\beta = 90.717(6)°$; $V = 13299(5)$ Å^3; $Z = 8$; $d_{calcd} = 1.112$ g/cm^3; μ(Mo Kα) = 1.004 mm^{-1}; λ(Mo Kα) = 0.71073 Å. R1 = 0.0572, wR2 = 0.1189, and GOF on F^2 is 0.930. Anal. Calcd For $C_{45}H_{48}N_9O_{13}Cu_3$: C, 48.54; H, 4.34; N, 11.32; Cu, 17.12. Found: C, 48.41; H, 4.47; N, 11.42; Cu, 17.01. IR (KBr pellet ν/cm^{-1}): 1614(s), 1492(m), 1391(s), 1314(s), 1222(s), 1122(m), 1073(m), 993(m), 923(m), 886(m), 814(s), 732(s), 640(s), 481(s), 419(m).

10.1021/ic015518y CCC: $20.00

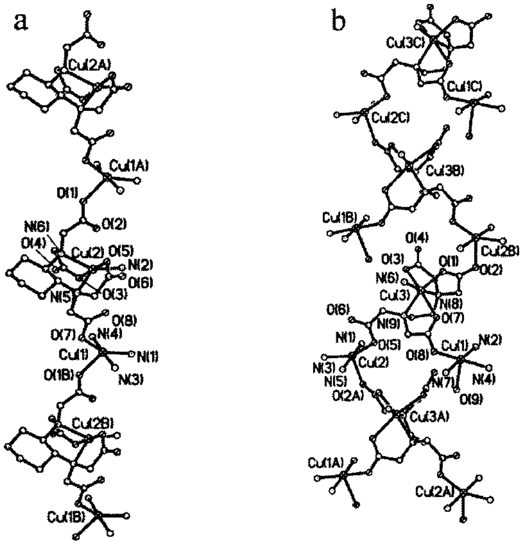

Figure 1. View of (a) Cu−CyDTA chain in **1** and (b) Cu−EDTA chain in **2**.

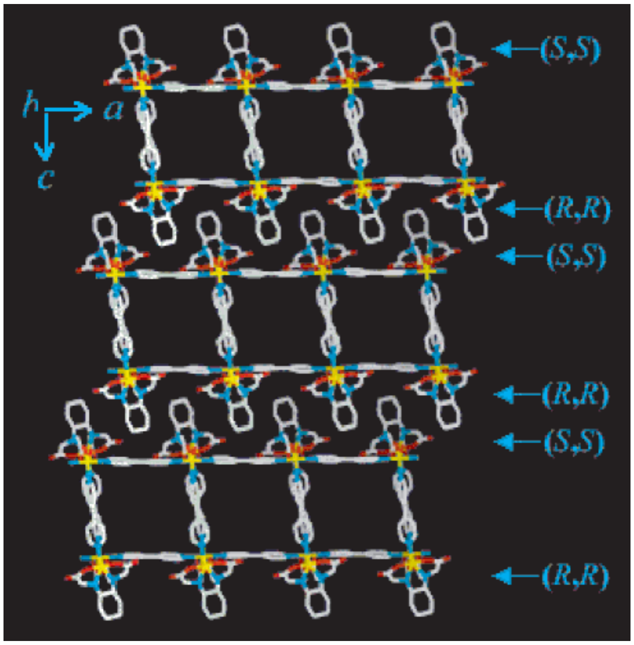

Figure 2. View of the packing structure of **1** along the *b* axis (Cu, yellow; C, white; O, red; N, blue).

In the same synthetic system, we performed a synthesis through replacing CyDTA by EDTA with no chiral carbons and obtained a novel 3D coordination polymer **2**. **2** contains mixed ligands, 4,4′-bipy and EDTA molecules. In the structure of **2**, two N atoms and four carboxyl groups of the EDTA anion coordinate to four Cu^{2+} ions with three kinds of coordination environments, forming Cu−EDTA 1D zigzag chains along the *c* axis (Figure 1b). The EDTA molecule acts as an octadentate ligand. The Cu(3) atom is in an octahedral mode with two N atoms, three O atoms from EDTA groups, and one N(6) atom from 4,4′-bipy. The Cu(2) atom bears a trigonal bipyramidal geometry. The base plane is defined by O(2A) and O(5) from a carboxyl group of EDTA and N(3) of 4,4′-bipy. The apical positions are occupied by N(1) and N(5) of two 4,4′-bipy molecules. The remaining Cu(1) atom is in a square pyramidal geometry. The equatorial plane is defined by three N donors from different 4,4′-bipy ligands and one O atom of a carboxyl group. One water molecule O(9) occupies the axial position. The 4,4′-bipy ligands link the Cu−EDTA 1D zigzag chains together to construct a 3D network structure, as shown in Figure 3.

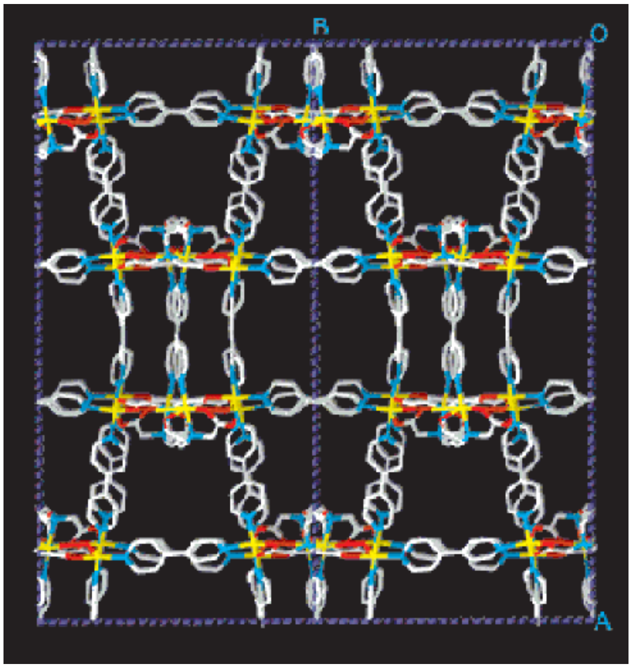

Figure 3. View of the packing structure of **2** along the *c* axis (Cu, yellow; C, white; O, red; N, blue).

A comparison between two structures of **1** and **2** is made for understanding the function of selective coordination of the two enantiomers in **1**. On one hand, two $-N(CH_2COO^-)_2$ groups of CyDTA are located at the *trans*-1,2-positions while those of EDTA can rotate freely, which defined the low dimension for **1** and high dimension for **2**. On the other hand, two kinds of Cu^{2+} ions (unlike three kinds of Cu^{2+} ions in **2**) in different chains on the layers of **1** are structurally coordinated by either the (*S*,*S*)- or (*R*,*R*)-configured enantiomer of CyDTA.

We have been focusing on the formation of helical structures for both inorganic solids and inorganic−organic hybrid compounds[9] and molecular recognition and separation by selective coordination. Obviously, molecular recognition is the first step for a full separation for a racemic compound. Current investigation provides the possibility to reach the aim for racemic separation through selective coordination of one kind of enantiomer and leaving the other in solution.

Acknowledgment. This work was supported by the National Natural Science Foundation of China.

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

IC015518Y

---

(8) (a) Yuan, H. M.; Chen, J.; Shi, Z.; Chen, W.; Wang, Y.; Zhang, P.; Yu, J.; Xu, R. *J. Chem. Soc., Dalton Trans.* **2000**, 1981−1984. (b) Gray, M. J.; Jasper, J. D.; Wilkinson, A. P.; Hanson, J. C. *Chem. Mater.* **1997**, *9*, 976−980. (c) Morgan, K.; Gainsford, G.; Milestone, N. *Chem. Commun.* **1995**, 425−426.

(9) (a) Shi, Z.; Feng, S.; Gao, S.; Zhang, L.; Yang, G.; Hua, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2325−2327. (b) Shi, Z.; Feng, S.; Zhang, L.; Yang, G.; Hua, J. *Chem. Mater.* **2000**, *12*, 2930−2935. (c) Shi, Z.; Zhang, L.; Zhu, G.; Yang, G.; Hua, J.; Ding, H.; Feng, S. *Chem. Mater.* **1999**, *11*, 3565−3570.