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Construction of coordination polymers by different conformational flexible pyridyl-type ligands and copper (II) ions

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Abstract

The reaction of the flexible ligand 1,2-bis(4-pyridinecarboxamido)ethane (L) with copper (II) perchlorate under the same conditions lead to the formation of two coordination polymers with different network structures: $\{[Cu(L)_2(H_2O)]\cdot(ClO_4)_2\cdot(H_2O)_6\}_\infty$ (**1**), $\{[Cu(L)_2(ClO_4)]\cdot(ClO_4)\}_\infty$ (**2**). L exhibits different conformations in **1** and **2**. The copper (II) centers in **1** are bridged by two *gauche*-ligands to give a cyclic closed structure which extend to form 1-D chain, and the adjacent Cu···Cu separation is 12.73 Å. Such chains form a layer structure, which furthermore condenses into a 3-D structure through hydrogen bonds. In **2**, the copper (II) centers are bridged by *anti*-ligands to form rhombus-like grids, and the adjacent Cu···Cu separation is more than 22.00 Å. These rhombus-like grids form threefold interpenetrating nets. Water molecules or perchlorate anions fill the channels in **1** and **2**.

Keywords: 1,2-Bis(4-pyridinecarboxamido)ethane; Copper (II) complexes; X-ray structures; Hydrogen bonding; Coordination polymers; Supramolecular isomers

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1. Introduction

The synthesis and characterization of polymeric coordination networks has been an area of rapid growth in recent years for their potential applications as well as the variety of architectures and topologies [1,2]. The bipyridyl-type ligands are frequently employed as spacers for the preparation of coordination polymers. As 4,4′-bipyridine and its rigid rod like analogues have generated a large number of infinite frameworks [3], researchers are trying to utilize flexible pyridyl-type ligands such as 1,2-bis(4-pyridyl)ethane (bpe) to provide some novel polymers [4].

We choose L as ligand for it is longer and more flexible than bpe. At the same time the amido group of L is good donor and acceptor for hydrogen bonding. The CH_2 group of L plays an important role in forming conformational isomers since it can adopt either *gauche* (angular) or *anti* (linear) conformations (Scheme 1). Our previous work indicates that L adopts *anti* conformation in its free state [5].

There are few examples of different coordination polymers involving the same ligand in different conformations [6]. Herein, we focus on the preparation and crystal structure of two coordination polymers **1** and **2** self-assembled by the copper (II) and L in the same reaction condition.

2. Experimental

2.1. Materials and physical measures

Elemental analyses were determined on an Elementar GmbH VarioEL elemental analyzer. IR spectra were measured as KBr pellets on a Perkin–Elmer 983 spectrophotometer at room temperature in the range of 400–4000 cm^{-1}. All reagents were commercially available and used as received.

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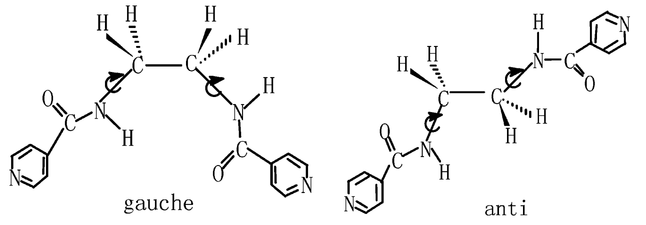

Scheme 1.

2.2. Synthesis of the complexes

An amount of 370 mg (1 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in EtOH (10 ml) was added dropwise to 50 ml of EtOH solution of L (541 mg, 2 mmol), refluxed for 1 h, then 20 ml H_2O was added. (*Caution*! Perchlorate salts are potentially explosive and should be handled carefully in small amounts.) The mixture was stirred for 24 h. The resulting solution was filtered and allowed to stand in air, by slow evaporation at room temperature for several weeks yield blue (**1**) or purple (**2**) crystals. They were filtered off, washed with a small mount of water, and dried in air. In most cases the product obtained consisted of blue crystals of **1**, and purple crystals of **2** appeared on a few occasions (the relative frequency is about 10:1). Surprisingly, the product is either **1** or **2**, and we never got a mixture of both. Yield: 55% and 35% for **1** and **2**, respectively. *Anal.* Calc. for $C_{28}H_{42}Cl_2Cu_1N_8O_{19}$ (**1**): C, 36.19; H, 4.56; N, 12.06. Found: C, 36.54; H, 4.33; N, 12.31%. *Anal.* Calc. for $C_{28}H_{28}Cl_2Cu_1N_8O_{12}$ (**2**): C, 41.88; H, 3.51; N, 13.96. Found: C, 42.09; H, 3.41; N, 13.75%.

2.3. X-ray crystallography

Single crystals were selected and coated with epoxy glue. Data collection were collected on a Bruker Smart CCD diffractometer equipped with graphitemonochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and all calculations were performed using the SHELXL-PC program [7]. Absorption correction was semi-empirical from equivalents. The positions of H atoms were generated geometrically, and assigned isotropic thermal parameters. The structures were refined by full-matrix least-squares minimization of $\sum(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except the H atoms. Table 1 gives a structure determination summary and Tables 2 and 3 list the selected bond lengths and angles.

3. Results and discussion

3.1. IR spectroscopic study

The IR spectra of **1** and **2** exhibit the band characteristic of amido groups at 1660 cm^{-1}. For **2**, there are

Table 1
Crystallographic data for the two complexes

	Complex **1**	Complex **2**
Empirical formula	$C_{28}H_{42}Cl_2Cu_1N_8O_{19}$	$C_{28}H_{28}C_{12}Cu_1N_8O_{12}$
Formula weight	929.14	803.02
Temperature (K)	273(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pca2_1$
a (Å)	12.732(4)	16.880(5)
b (Å)	13.164(4)	9.483(3)
c (Å)	23.024(8)	22.044(7)
α (°)	90	90
β (°)	92.659(6)	90
γ (°)	90	90
V (Å^3)	3855(2)	3529(2)
Z	4	4
D_{calcd} (Mg m^{-3})	1.601	1.512
Absorption coefficient (mm^{-1})	0.795	0.841
$F(000)$	1924	1644
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$	$0.34 \times 0.24 \times 0.20$
θ Range for data collection (°)	2.35–25.03	2.41–26.40
Index ranges	$-15 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 15$, $-27 \leqslant l \leqslant 27$	$-20 \leqslant h \leqslant 20$, $-11 \leqslant k \leqslant 9$, $-21 \leqslant l \leqslant 27$
Reflections collected	15288	15309
Independent reflections (R_{int})	6658 (0.0974)	5789 (0.0876)
Completeness to θ	97.6% ($\theta = 25.03$)	97.7% ($\theta = 26.4$)
Maximum/minimum transmission	1.0000/0.9106	1.0000/0.7330
Data/restraints/parameters	6658/1/523	5789/94/478
Goodness-of-fit on F^2	1.013	0.949
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0703$, $wR_2 = 0.1375$	$R_1 = 0.0686$, $wR_2 = 0.1305$
Largest difference on peak and hole (e Å^{-3})	0.676/−0.315	0.819/−0.455

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths	
Cu(1)–O(1)	2.359(4)
Cu(1)–N(1)	2.039(4)
Cu(1)–N(5)	2.042(4)
Cu(1)–N(8)#1	2.016(5)
Cu(1)–N(4)#2	2.024(4)
Bond angles	
N(1)–Cu(1)–N(8#1)	89.8(2)
N(1)–Cu(1)–N(4#2)	91.7(2)
N(5)–Cu(1)–N(8#1)	88.9(2)
N(8#1)–Cu(1)–O(1)	90.9(2)
N(4#2)–Cu(1)–O(1)	93.1(2)

Symmetry transformations used to generate equivalent atoms: #1 $x+1, y, z$; #2 $x-1, y, z$ for complex **1**.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths	
Cu(1)–O(5)	2.368(4)
Cu(1)–N(1)	2.02(2)
Cu(1)–N(5)#1	1.97(2)
Cu(1)–N(8)	2.02(2)
Cu(1)–N(4)#2	2.12(2)
Bond angles	
N(5#1)–Cu(1)–N(8)	88.3(1)
N(5#1)–Cu(1)–N(1)	170(1)
N(5#1)–Cu(1)–N(4#2)	91.6(8)
N(8)–Cu(1)–O(5)	86.6(8)
N(1)–Cu(1)–O(5)	92.4(9)

Symmetry transformations used to generate equivalent atoms: #1 $-x+5/2, y, z+1/2$; #2 $-x+1, -y, z+1/2$ for complex **2**.

absorption bands which can be assigned to monodentate perchlorate group of C_{3v} symmetry at 1160(ν4), 1040 (ν1), 925(ν2), 660(ν3) cm^{-1} [8].

3.2. Crystal structure analysis

3.2.1. Crystal structure of complex 1

X-ray crystallography has established that **1** is made up of 1-D infinite looped chains, counterions, and water molecules. As illustrated in Fig. 1, each Cu(II) atom in the looped unit is coordinated in a distorted square pyramidal geometry by four pyridyl nitrogen atoms from four different ligands in the equatorial positions [Cu–N 2.016(5)–2.042(4) Å] and an aqua ligand occupies the remaining apical site [Cu–O 2.359(4) Å]. All L ligands in **1** adopt the *gauche*-conformation, and a pair link two Cu(II) centers to give the cyclic closed structure which extend to form a chain with an adjacent Cu···Cu separation of 12.732 Å. The N(2)–C(7)–C(8)–N(3) and N(6)–C(21)–C(22)–N(7) torsion angles are 79.1° and 60.2° which show that there is a slight conformational difference between the two independent L ligands. Adjacent chains are further connected through hydrogen bonds [N(3)···O(5) (symmetry code: $3/2+x, 1/2-y, 1/2+z$) 2.931 Å, N(3)–H(2)···O(5) 172.5°] between ligands to form a layer. These layers are further connected through other hydrogen bonds [O(1)···O(3) (symmetry code: $1/2-x, 1/2+y, 1/2-z$) 2.793 Å, O(1)–H(5)···O(3) 171.0°] between the aqua ligands and bridging L ligands to form a 3-D framework. Two type of channels are apparent when **1** is viewed along the [1 0 0] direction. Uncoordinated H_2O molecules and ClO_4^- anions are held in the channels by hydrogen bonds (Fig. 2).

3.2.2. Crystal structure of complex 2

In **2**, each Cu center also coordinates to four pyridyl nitrogen atoms of four different ligands in the equatorial positions, but an oxygen atom of the perchlorate anion occupies the remaining apical site (Fig. 3). Each Cu center is linked to four adjacent Cu centers by *anti*-L to afford an infinite rhombus-like grid with (4,4) topology (Fig. 4). The N(2C)–C(7C)–C(8C)–N(3C) and N(6)–C(21)–C(22)–N(7) torsion angles are 179.5° and 160.8°, which show the conformational difference between the two independent ligands. Since L is a flexible ligand, the rhombus-like grid is somewhat distorted. The angles in each rhombus-like unit are 78.6° (Cu(1A)–Cu(1B)–Cu(1C)), 80.0° (Cu(1A)–Cu(1)–Cu(1C)), 97.4° (Cu(1)–Cu(1A)–Cu(1B), Cu(1)–Cu(1C)–Cu(1B)). The grid is wave-like from the view of [0 0 1] direction (Fig. 5). The large void space within the rhombus-like grid of **2** (the distance between Cu atoms are 25.956 Å for Cu(1)···Cu(1B) and 22.044 Å for Cu(1A)···Cu(1C)) are effectively filled via the interpenetration of three

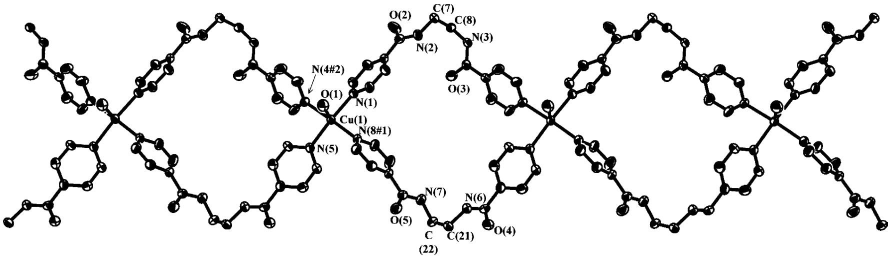

Fig. 1. ORTEP drawings of the 1-D looped polymeric chain of **1** with 50% probablity ellipsoids (H atoms and anions were omitted for clarity).

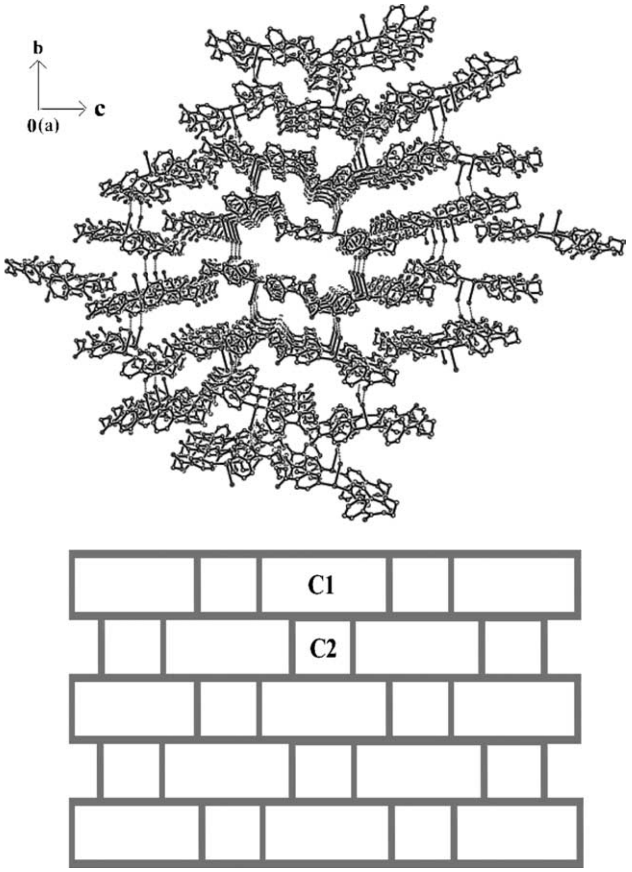

Fig. 2. Top: viewed along the [1 0 0] direction of the stacking of the chains with channels and hydrogen bonds indicated by the dashed lines, water molecules and anions were omitted for clarity; bottom: schematic view of the two type of channels.

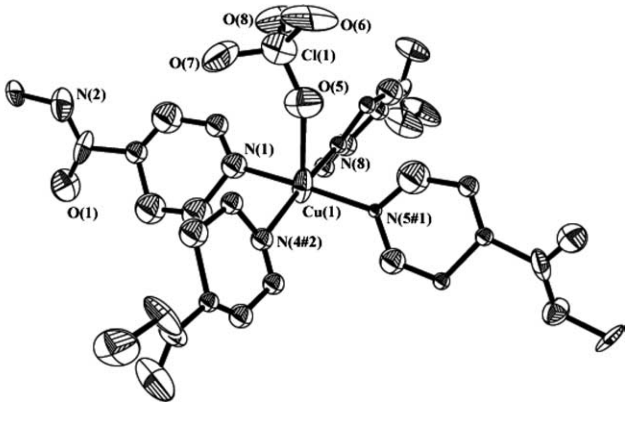

Fig. 3. Coordination environment of the metal atom in **2**.

independent grids (Fig. 6). In the threefold interpenetrated layer, every grid connects to others by hydrogen bonds between the amido groups. Adjacent layers are further connected by hydrogen bonds. Even after threefold interpenetration of three identical 2-D grids, 1-D channels still remain and are filled with perchlorates.

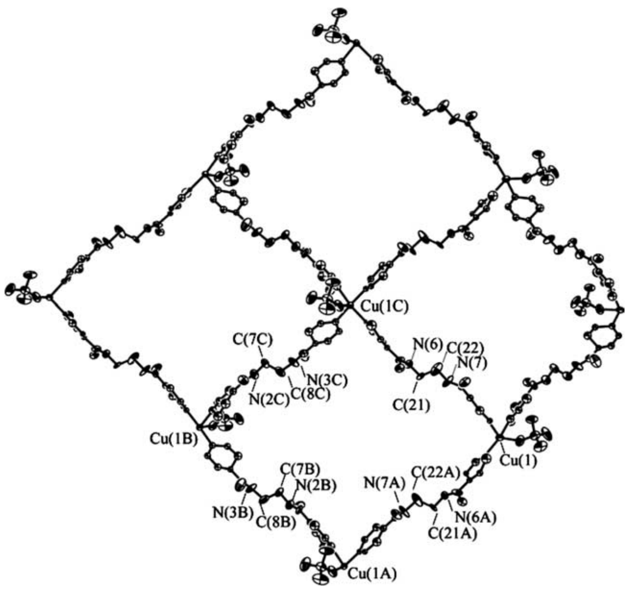

Fig. 4. A view of the rhombus-like grid of **2**.

Fig. 5. Side view of the wave-like layer of **2** viewed from the [0 0 1] direction; the uncoordinated anions were omitted for clarity.

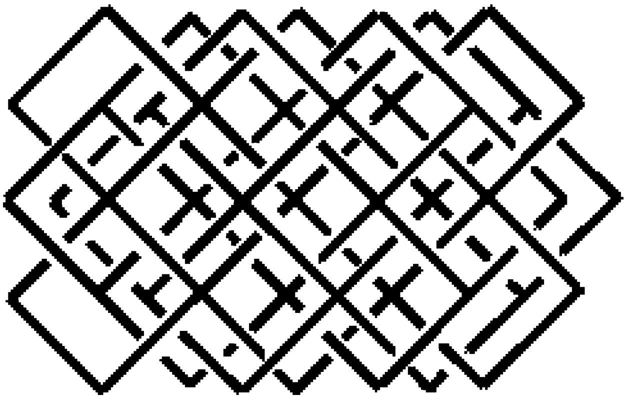

Fig. 6. A schematic showing the interpenetration of three independent rhombus-like grids.

In summary, two different copper (II) coordination architectures utilizing the same kind of flexible pyridinyl-type ligand containing amido groups have been prepared and structurally characterized. This work reveals that the conformation of a flexible ligand plays a key role in the formation of different coordination polymeric motifs.

4. Supplementary material

Crystallographic data (X-ray data in *.cif files) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205602 for compound **1** and CCDC No. 205603 for compound **2**. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] (a) O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511;
(b) O. Kahn, Acc. Chem. Res. 33 (2000) 647;
(c) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (1998) 474.
[2] (a) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
(b) K.T. Holman, A.M. Pivovar, J.A. Swift, M.D. Ward, Acc. Chem. Res. 34 (2001) 107;
(c) M.J. Zaworotko, Chem. Commun. (2001) 1;
(d) S.R. Batten, R. Robson, Angew. Chem., Int. Ed. Engl. 37 (1998) 1460;
(e) M. Fujita, Chem. Soc. Rev. 27 (1998) 417;
(f) C.J. Jones, Chem. Soc. Rev. 27 (1998) 289.
[3] (a) J. Zhang, M.M. Matsushita, X.X. Kong, J. Abe, T. Iyoda, J. Am. Chem. Soc. 123 (2001) 12105;
(b) Y.L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin, K.-S. Jeong, J. Am. Chem. Soc. 123 (2001) 1258;
(c) K. Biradha, M. Fujita, Chem. Commun. (2001) 15;
(d) K. Biradha, Y. Hongo, M. Fujita, Angew. Chem., Int. Ed. Engl. 39 (2000) 3843;
(e) K. Biradha, M. Fujita, J. Chem. Soc., Dalton Trans. (2000) 3805;
(f) H. Gadbjartson, K. Biradha, K.M. Poirier, M.J. Zaworotko, J. Am. Chem. Soc. 121 (1999) 2599;
(g) A.J. Blake, N.R. Champness, A. Khlobystov, D.A. Lemenovskii, W.-S. Li, M. Schröder, Chem. Commun. (1997) 2027.
[4] (a) M.-L. Tong, Y.-M. Wu, J. Ru, X.-M. Chen, H.-C. Chang, S. Kitagawa, Inorg. Chem. 41 (2002) 4846;
(b) M.J. Plater, M.R. St, J. Foreman, T. Gelbrich, M.B. Hursthouse, Inorg. Chim. Acta 318 (2001) 171;
(c) M.J. Plater, B.M. Silva, J.M.S. Skakle, R.A. Howie, A. Riffat, T. Gelbrich, M.B. Hursthouse, Inorg. Chim. Acta 325 (2001) 141;
(d) M.L. Hernández, M.K. Urtiaga, M.G. Barandika, R. Cortés, L. Lezama, N. Pinta, M.I. Arriortua, T.J. Rojo, J. Chem. Soc., Dalton Trans. (2001) 3010;
(e) M.J. Plater, M.R. St, J. Foreman, R.A. Howie, J.M.S. Skakle, Inorg. Chim. Acta 318 (2000) 175;
(f) L. Carlucci, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato, Angew. Chem., Int. Ed. Engl. 39 (2000) 1506;
(g) M. Fujita, Y.J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, J. Am. Chem. Soc. 117 (1995) 7287;
(h) M. Fujita, Y.J. Kwon, M. Miyazawa, K.J. Ogura, J. Chem. Soc., Chem. Commun. (1994) 1977.
[5] C.-H. Ge, X.-D. Zhang, F. Guo, L.-T. Zhang, Z. Yu, W.-S. Guo, Q.-T. Liu, Chin. J. Chem. 21 (2003) 581.
[6] T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko, Angew. Chem., Int. Ed. Engl. 36 (1997) 972.
[7] G.M. Sheldrick, SHELXL-97: Program for X-ray Crystal Structure Solution and Refinement, Göttingen University, Germany, 1997.
[8] J.-C.G. Bünzli, J.-R. Yersin, C. Mabillard, Inorg. Chem. 21 (1982) 1471.