

Note

One Dimensional Coordination Polymer Constructed by 1,2-Bis(4-pyridinecarboxamido)ethane and Copper(II)

GE, Chun-Hua^{a,b} (葛春华) ZHANG, Xiang-Dong^a (张向东) GUO, Fang^a (郭放)
 ZHANG, Li-Tian^a (张翠天) YU, Zhan^a (于湛) GUO, Wen-Sheng^a (郭文生) LIU, Qi-Tao^{a,*} (刘祁涛)

^a Institute of Chemical Science & Engineering, Liaoning University, Shenyang, Liaoning 110036, China

^b Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China

The ligand [1,2-bis(4-pyridinecarboxamido)ethane] (L) and the coordination polymer $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})] \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1) have been synthesized and characterized by IR and ^1H NMR spectra. Their molecular structures and the packing of 1 have been determined by single-crystal X-ray diffraction analysis. The Cu(II) in 1 is bridged by two ligands forming an infinite one-dimensional chain like structure and L in 1 adopts a different conformation from its free state. 1 belongs to monoclinic, space group $P2_1/n$, $a = 1.2896(3)$ nm, $b = 1.2552(8)$ nm, $c = 2.2903(19)$ nm, $\beta = 93.04(5)^\circ$, $Z = 4$, $V = 3.702(4)$ nm³. The TG and DTG experiments showed that the uncoordinated H_2O can be removed at low temperature by heating, and it does not decompose until 250 $^\circ\text{C}$.

Keywords 1,2-bis(4-pyridinecarboxamido)ethane, copper(II) complex, coordination polymer, one-dimensional chain

Introduction

In recent years, the synthesis and characterization of coordination polymers have been rapidly expanding owing to a fundamental interest in their fascinating structural diversity and potential applications as functional materials.¹⁻⁴ The synthesis of coordination polymers with 4,4'-bipyridine (4,4'-bipy) or related species as bifunctional ligand and metal ion has generated a considerable number of novel topological frameworks, such as T-shaped,⁵ ladder,⁶ brick wall,⁷ square or rectangular grid^{8,9} and other uncommon motifs.

Here we report a one dimensional chain like structure of Cu(II) coordination polymer using 1,2-bis(4-pyridinecarboxamido)ethane (L) (Fig. 1) as ligand. Choosing L as ligand was based on the consideration that there are two pyridine groups in the molecule and they could not bind the same metal center, so it can act as a bridging ligand and its flexibility would be better than that of 4,4'-bipy. On the other hand, amido group can form hydrogen bond with water or nitrate anion.

Experimental

All the reagents were of commercial reagent grade or

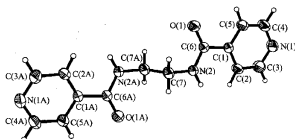


Fig. 1 View of the molecular structure of L, showing the anti-linear conformation.

better and were used without further purification.

The ^1H NMR spectra were recorded on a Varian YH300 in DMSO- d_6 . Elemental analysis was performed on an Elementar GmbH Vario EL elemental analyzer. The IR spectra were obtained with KBr pellets on a Perkin-Elmer 983 spectrophotometer. The thermal analysis was performed on a Rigaku TAS 100 Thermal Analysis Station, obtaining the TG and the DTG curves in air at a temperature-increasing rate of 10 $^\circ\text{C}/\text{min}$. XRD data collection was performed on a Y-4Q X-ray diffractometer operated at 30 kV and 20 mA with a scan speed of 0.03 ($^\circ$)/s.

Synthesis of 1,2-bis(4-pyridinecarboxamido)ethane (L)

Ethylenediamine (0.1 mol) and ethyl iso-nicotinate (0.2 mol) were mixed. The mixture was refluxed for 2 h. The crude product was recrystallized with EtOH, and the yield was about 60%. After L was dissolved in EtOH, the solution was kept at room temperature, and colorless crystals appeared soon. Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2$: C 62.21, H 5.22, N 20.73; found C 62.02, H 5.17, N 20.47.

Synthesis of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})] \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1)

The crystal 1 was prepared under mild condition. A so-

* E-mail: qtlm@lmu.edu.cn

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lution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.3 mmol) in EtOH (5 mL) was added dropwise to EtOH solution (20 mL) of **L** (0.6 mmol). Precipitate appeared, and the mixture was refluxed for 1 h, followed by the addition of 10 mL of H_2O . Stirring was continued for 24 h at room temperature to give a nearly clear solution, which was filtered and the filtrate was allowed to stand at room temperature. On evaporation, blue crystals were obtained after three weeks. Anal. calcd for $\text{C}_{28}\text{H}_{42}\text{CuN}_{10}\text{O}_{17}$: C 39.37, H 4.96, N 16.40; found C 39.55, H 4.93, N 16.17.

Crystal structure determination

Crystals of **L** and **1** for single-crystal X-ray diffraction with sizes $0.2 \text{ mm} \times 0.2 \text{ mm} \times 0.6 \text{ mm}$ and $0.8 \text{ mm} \times 0.6 \text{ mm} \times 0.6 \text{ mm}$ were selected, respectively. Reflection data for **L** and **1** were collected on a Bruker AXS P4 single crystal diffractometer with Mo K α radiation ($\lambda = 0.071073 \text{ nm}$) at 293(2) K. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with SHELX-97.

The crystallographic data are given in Table 1. The bond lengths and angles are listed in Table 2 and Table 3.

Result and discussion

^1H NMR spectra of **L**

δ (DMSO- d_6): 3.47 (s, 4H, $2 \times \text{CH}_2$), 7.74 (d, $J = 5.2 \text{ Hz}$, 4H, pyridine-H), 8.72 (d, $J = 5.2 \text{ Hz}$, 4H, pyridine-H), 8.89 (s, 2H, NH).

IR spectra

The IR spectra of **L** show the bands as follows (cm^{-1}): 3240 (m), 3056 (w), 2940 (w), 1666 (s), 1608 (w), 1550 (s), 1500 (m), 1450 (m), 1414 (m), 1300 (m), 1060 (m), 678 (m), in which 3240 cm^{-1} belongs to the N—H stretching vibration and 1666 cm^{-1} belongs to the C = O stretching vibration of amido group.

The IR spectra of **1** show the bands as follows (cm^{-1}):

Table 1 Crystallographic data for the investigated compound

	L	1
Formula	$\text{C}_{28}\text{H}_{42}\text{N}_{10}\text{O}_{17}$	$\text{C}_{28}\text{H}_{42}\text{CuN}_{10}\text{O}_{17}$
M_r	270.29	854.24
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 0.4270(3) \text{ nm}$ $b = 1.5070(6) \text{ nm}$ $c = 1.0259(4) \text{ nm}$ $\beta = 100.72(9)^\circ$	$a = 1.2896(3) \text{ nm}$ $b = 1.2552(8) \text{ nm}$ $c = 2.2903(19) \text{ nm}$ $\beta = 93.04(5)^\circ$
Volume (nm^3)	0.6486(6)	3.702(4)
Z	4	4
D_c (g/cm^3)	1.773	2.758
$F(000)$	356	3199
μ (mm^{-1})	0.162	1.191
Reflections collected	1173	5467
Independent reflections	1116	4174
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0571$ $wR_2 = 0.1515$	$R_1 = 0.0403$ $wR_2 = 0.1061$
R indices (all data)	$R_1 = 0.0812$ $wR_2 = 0.1708$	$R_1 = 0.0503$ $wR_2 = 0.1168$
S	1.048	1.039

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for **L**

N(1)—C(4)	0.1331(4)	N(1)—C(3)	0.1337(4)	O(1)—C(6)	0.1225(3)
N(2)—C(6)	0.1335(3)	N(2)—C(7)	0.1453(3)	C(1)—C(2)	0.1377(4)
C(1)—C(5)	0.1378(4)	C(1)—C(6)	0.1509(3)	C(5)—C(4)	0.1378(4)
C(2)—C(3)	0.1379(4)				
C(4)—N(1)—C(3)	116.4(2)	C(6)—N(2)—C(7)	121.3(2)	C(2)—C(1)—C(5)	117.8(2)
C(2)—C(1)—C(6)	124.6(2)	C(5)—C(1)—C(6)	117.6(2)	O(1)—C(6)—N(2)	122.6(2)
O(1)—C(6)—C(1)	120.6(2)	N(2)—C(6)—C(1)	116.7(2)	C(4)—C(5)—C(1)	119.0(3)
C(1)—C(2)—C(3)	119.3(3)	N(1)—C(4)—C(5)	124.0(3)	N(1)—C(3)—C(2)	123.5(3)

Table 3 Selected bond lengths (nm) and angles ($^{\circ}$) for **1**

Cu(1)—N(1)	0.1942(3)	N(1B)—Cu(1)—N(1)	177.11(11)	C(6)—N(2)—C(7)	122.7(4)
Cu(1)—N(1A)	0.2136(3)	N(1B)—Cu(1)—N(1A)	87.97(13)	C(6A)—N(2A)—C(7A)	124.2(3)
Cu(1)—N(1B)	0.1922(3)	N(1)—Cu(1)—N(1A)	93.10(13)	C(6B)—N(2B)—C(7B)	117.5(3)
Cu(1)—N(1C)	0.2158(4)	N(1B)—Cu(1)—N(1C)	91.09(13)	C(6C)—N(2C)—C(7C)	123.8(3)
Cu(1)—O(1W)	0.2348(3)	N(1)—Cu(1)—N(1C)	87.64(13)		
		N(1A)—Cu(1)—N(1C)	175.80(11)		
		N(1)—Cu(1)—O(1W)	94.41(12)		

3420 (m), 3242 (m), 3056 (w), 2940 (w), 1664 (s), 1640 (s), 1550 (s), 1500 (m), 1384 (s), 1300 (m), 1068 (m), 1060 (m), 680 (m). The 3420 cm^{-1} band is attributed to water molecules in the complex. The absorptions shift from 1608 cm^{-1} for the free ligand to 1640 cm^{-1} for the complex suggesting that N atom from pyridyl ring coordinated to Cu. O atom from amido group does not coordinate to Cu.

Crystal structure

The molecular structure of ligand is shown in Fig. 1. As a derivative of ethane, it has an *anti*-linear conformation. The dihedral angle between N(2)—C(7)—C(7A) plane and C(7)—C(7A)—N(2A) plane in **1** is 180.0 $^{\circ}$ (see Table 2). The structure and partial structural parameters of **1** are shown in Figs. 2–4 and Table 3 respectively. The Cu(II) atoms in **1** exist in a distorted square pyramidal coordination environment. The coordination to the Cu(II) center is provided by four pyridyl nitrogen atoms from four ligands in the equatorial positions. N(1), N(1A), N(1B), N(1C) and Cu(1) are nearly coplanar. At the same time the four pyridyl groups are not coplanar, dihedral angles between the plane formed by N(1), N(1A), N(1B), N(1C) and four pyridyl planes involving N(1), N(1A), N(1B), N(1C) are 57.3 $^{\circ}$, 44.0 $^{\circ}$, 59.5 $^{\circ}$ and 45.1 $^{\circ}$, respectively (Fig. 2). The four N—Cu bonds do not have the same bond lengths [Cu—N 0.1922(3)—0.2158(4) nm] (Table 3). A water molecule occupies the remaining apical site [Cu(1)—O(1W) 0.2348(3) nm], and other waters and nitrate anions reside in the holes of the framework shown in Fig. 3 and were fixed by hydrogen bonds. It is interesting to notice that all ligands in **1** adopt *gauche* rather than *anti* conformation so that every two *gauche* **L** can

link two Cu(II) centers to give cyclic closed structure which looks like continuous macrocycle [the adjacent Cu(1) ... Cu(1A) separation is 1.2895 nm] to form one dimensional chain-like coordination polymer (Fig. 3). In **1**, all ligands can be divided into two motifs so that each side of the chain was same. The dihedral angle between N(2)—C(7)—C(7AB) plane and C(7)—C(7AB)—N(2AB) plane is 69.5 $^{\circ}$, that

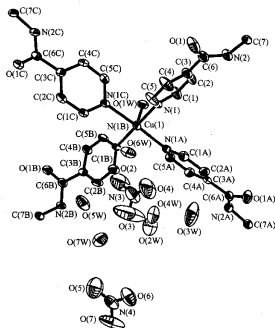


Fig. 2 Drawing of the environment of Cu(II) (hydrogens are omitted for clarity).

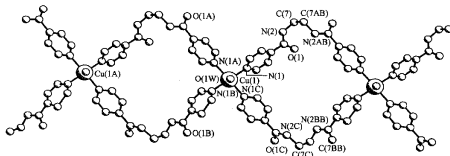


Fig. 3 View of the one-dimensional chain-like structure of **1** (nitrate anions and water molecules except the coordinated one are omitted for clarity).

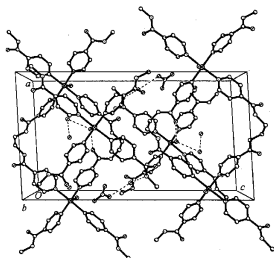


Fig. 4 Packing diagram of **1** (the dashed lines represent hydrogen bonds).

between N(2C)-C(7C)-C(7BB) plane and C(7C)-C(7BB)-N(2BB) plane is 60.2° , respectively. Different rotational ways put O atoms of —CONH— groups to various positions so that O(1A), O(1B), O(1C) point outside the cycle and O(1) points inside the cycle which is interesting in the point of view of chiral structure. Chirality arises from the different conformational isomers which are contained in the asymmetric unit

1,2-Bis(4-pyridyl)ethane (bpe), as an analogue of **L**, has rarely been observed to adopt all-*gauche* conformation in coordination polymers.¹⁰ Most of reported structures contain two *gauche*-bpe units that link ion centers to give a cyclic closed structure which is linked to the next one by an *anti*-bpe unit to form linear chains. The reason why **L** can adopt all-*gauche* conformation in **1** is the formation of hydrogen bond networks (Fig. 4). O and N atoms of —CONH— groups connect water molecules or nitrate anions by inter- or intra-molecular hydrogen bonds [N(2A)⋯O(3W) 0.2775 nm, N(2B)⋯O(7W) 0.2987 nm, N(2C)⋯O(5W) (symmetry code: $1 + x, y, z$) 0.2777 nm, O(2)⋯O(5W) 0.2685 nm, *etc.*]. Hydrogen bonds act as "string" to draw **L** torsional to coordinate with Cu center, and their formation

counteract the energy changes caused by staggered conformation of **L** and make the final structure stable. The formation of hydrogen bond may not only fix O atoms of amino groups in asymmetric position but also prevent interpenetration of chains. Adjacent chains are further connected through hydrogen bonds [O(1W)⋯O(1) (symmetry code: $5/2 - x, y - 1/2, 1/2 - z$) 0.2767 nm] between the bridging ligand and coordinated water molecule of neighboring chains. π - π stackings between these ligands were not found. The structural key to the formation of the infinite framework is the hydrogen-bonded arrangement.

Thermoanalysis and XRD analysis

The TG-DTG of **1** showed that in the range of 68.2°C to 87.9°C six water molecules were lost (observed 12.65%, calculated 12.64%), and it does not decompose until 250.3°C . XRD spectra indicated that the framework of the one-dimensional coordination polymer was stable after the uncoordinated water molecules were removed.

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