



## 一维螺旋链状配位聚合物 [Cu(*p*-BDOA)(2,2'-bipy)·H<sub>2</sub>O]<sub>n</sub>的合成与表征

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### Synthesis and Characterization of Coordination Polymer [Cu(*p*-BDOA)(2,2'-bipy)·H<sub>2</sub>O]<sub>n</sub> with One-dimensional Helical Chain

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**Abstract:** A new copper(II) coordination polymer, [Cu(*p*-BDOA)(2,2'-bipy)·H<sub>2</sub>O]<sub>n</sub> (*p*-BDOA<sup>2-</sup>=benzene-1,4-dioxy-acetate dianion; 2,2'-bipy=2,2'-bipyridine) has been synthesized and characterized by elemental analysis, IR, TG and single crystal X-ray diffraction. The Crystal crystallizes in orthorhombic system, the space group is *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with the unit cell parameters *a*=0.698 4(1) nm, *b*=1.559 7(3) nm, *c*=1.750 6(4) nm and *V*=1.906 8(7) nm<sup>3</sup>, *M<sub>r</sub>*=461.91, *Z*=4, *R*=0.057 5, *wR*=0.078 3. Each copper(II) atom is six-coordinated and displays a distorted square pyramidal geometry with a one-capped base by one very long semicoordinate Cu-O(carboxylate) bond. Adjacent Cu(II) ions are bridged by carboxylate groups, resulting in a one-dimensional helical chain. The adjacent Cu···Cu distance within the polymeric chain is 1.348 4 nm. Furthermore, such chains are linked through hydrogen bonds and  $\pi$ - $\pi$  stacking interactions to form supramolecular network. CCDC: 219234.

**Key words:** Copper(II) carboxylate complex; synthesis; helical structure

## 0 Introduction

In recent years many interests have been focused on the self-assembly of supramolecular architectures, especially on the coordination polymers with rigid organic aromatic carboxylic acid ligands such as terephthalate and benzene tetracarboxylate<sup>[1-3]</sup>. In contrast, the structures of the helical complexes have been

rarely reported<sup>[4,5]</sup>. The designing and constructing of the helical complexes are the most challenging and significant task owing to their potential applications as functional materials. Phenylenedioxydiacetic acids, especially *p*-BDOAH<sub>2</sub>, which has versatile binding fashions, is regarded as an excellent candidate for the construction of supramolecular architectures. Recently, we have reported the structures of some Cu(II), Zn(II),

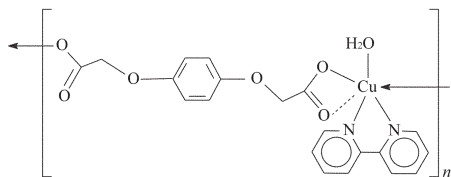
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Co(II) and Cd(II) chain polymers incorporating *m*-BDOA<sup>2-</sup> or *p*-BDOA<sup>2-</sup> groups<sup>[6-9]</sup>. In the case of the one-dimensional chain polymers, [Cu(*m*-BDOA)(2,2'-bipy)·H<sub>2</sub>O]<sub>n</sub> (**II**), the Cu(II) atom shows a square-pyramidal configuration<sup>[10]</sup>. In the present, we have used *p*-BDOAH<sub>2</sub> instead of *m*-BDOAH<sub>2</sub> in the reaction and synthesized a new coordination polymer, [Cu(*p*-BDOA)(2,2'-bipy)·H<sub>2</sub>O]<sub>n</sub> (**I**) (*p*-BDOA<sup>2-</sup>=benzene-1,4-dioxyacetate dianion; 2,2'-bipy=2,2'-bipyridine) with one-dimensional helical chain. Herein we describe the synthesis, structure and properties of the above coordination polymer.



## 1 Experimental

### 1.1 Reagent and apparatus

The *p*-BDOAH<sub>2</sub> was prepared by the method described for the synthesis of *o*-BDOAH<sub>2</sub><sup>[11]</sup>. All other chemicals were analytical reagent grade and used without further purification. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. The IR spectra were recorded in the range of 4 000~400 cm<sup>-1</sup> on a BRUKER EQUINOX 55 FTIR spectrometer using KBr pellet. Thermogravimetry (TG) analysis was measured on a PERKIN ELMER TG/DTA 6300 thermal analyzer under flowing N<sub>2</sub> atmosphere, with a heating rate of 10 °C·min<sup>-1</sup>.

### 1.2 Synthesis

The complex was prepared by the addition of the stoichiometric amount of Cu(Ac)<sub>2</sub>·H<sub>2</sub>O (4.00 g, 20 mmol) and 2,2'-bipy (3.12 g, 20 mmol) to a hot aqueous solution of *p*-BDOAH<sub>2</sub> (4.52 g, 20 mmol), the pH was adjusted to ~6 with 0.2 mol·L<sup>-1</sup> NaOH solution. The resulting solution was stirred for 30 min at room temperature and then filtered. Blue single crystals were isolated from the solution at room temperature over several days. Yield: 68 %. Anal. Calcd (%). for C<sub>20</sub>H<sub>18</sub>O<sub>7</sub>N<sub>2</sub>Cu: C, 52.00; H, 3.93; N, 6.06. Found (%): C, 51.89; H, 3.80, N, 6.01.

### 1.3 X-ray crystallographic studies

A blue single crystal with dimensions 0.38 mm × 0.26 mm × 0.18 mm was employed for data collection

at 293 K on a RIGAKU RAXIS-RAPID diffractometer with graphite monochromatized Mo *K*α radiation (λ = 0.071 073 nm), using ω scan mode. A total of 16 530 reflections and 4 319 unique ones were collected in the range of 3.14° ≤ θ ≤ 27.48° with *R*<sub>int</sub> = 0.068, of which 3 071 observed reflections with *I* > 2σ(*I*) were used in the succeeding structural calculations. Lorentz-polarization factor and empirical absorption correction were applied to intensity data. The structure was solved by direct method and difference Fourier syntheses. The non-hydrogen atoms were refined by full-matrix least-squares techniques on *F*<sup>2</sup> with anisotropic thermal parameters. The H atoms on carbon were placed in calculated positions with C-H = 0.093 nm (aromatic) or 0.097 nm (aliphatic) and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) in the riding model approximation, and the H atoms of water molecules were located in difference Fourier synthesis maps and refined with O-H distance restraint of 0.085 (1) nm and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). All calculations were carried out by using SHELX 97 program<sup>[12]</sup>.

The crystal belongs to orthorhombic system, the space group is *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with the unit cell parameters *a* = 0.698 4(1) nm, *b* = 1.559 7(3) nm, *c* = 1.750 6(4) nm and *V* = 1.906 8(7) nm<sup>3</sup>, *M*<sub>r</sub> = 461.91, *Z* = 4, *D*<sub>c</sub> = 1.609 g·cm<sup>-3</sup>, μ = 1.193 mm<sup>-1</sup>, *F*(000) = 948, Flack parameter = 0.02(2), *R* = 0.057 5, *wR* = 0.078 3, *S* = 1.029, Δ/σ<sub>max</sub> = 0.000, (Δρ)<sub>max</sub> = 593 e·nm<sup>-3</sup> and (Δρ)<sub>min</sub> = -326 e·nm<sup>-3</sup>.

CCDC: 219234.

## 2 Results and discussions

### 2.1 IR spectra

The band of 1 728 cm<sup>-1</sup> is observed in IR spectra of the free *p*-BDOAH<sub>2</sub> and assigned to ν(C=O) absorption of carboxyl group. However, it disappears in IR spectra of the title complex. The bands of 1 636 and 1 376 cm<sup>-1</sup> are showed in IR spectra of the title complex and are related to ν<sub>asym</sub>(OCO<sup>-</sup>) and ν<sub>sym</sub>(OCO<sup>-</sup>), respectively. The absorption vibrations of ν<sub>asym</sub>(C-O-C) and ν<sub>sym</sub>(C-O-C) are observed at 1 217 and 1 078 cm<sup>-1</sup>, respectively<sup>[13]</sup>. In addition, a strong and broad band has been observed at ~3 340 cm<sup>-1</sup>, and assigned to ν(OH) absorption with the hydrogen bonds or water molecules.

### 2.2 Description of structure

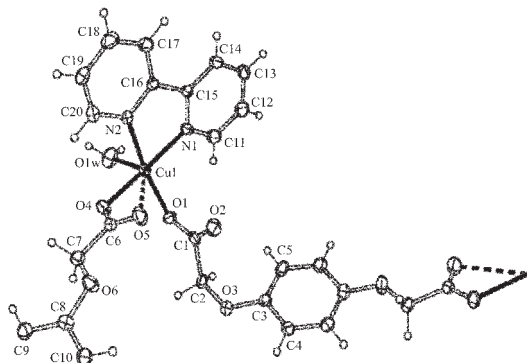
The selected bond distances and angles of the title complex are given in Table 1. The molecular structure of the title complex is illustrated in Fig.1.

**Table 1** Selected bond lengths (nm) and angles (°) for complex **I**

Cu1-O4	0.196 4(3)	O5-C6	0.122 9(5)	Cu1-O5	0.292 0(3)
Cu1-O1	0.196 6(3)	O1w···O5 <sup>i</sup>	0.284 3(5)	O1-C1	0.125 9(5)
Cu1-O1w	0.224 1(3)	Cu1-N1	0.201 2(3)	O4-C6	0.126 8(5)
C1-O2	0.123 4(5)	Cu1-N2	0.202 1(3)	O1w···O2 <sup>i</sup>	0.287 4(5)
O4-Cu1-O1	90.76(14)	O1-Cu1-N2	168.65(13)	O4-Cu1-N2	93.18(14)
O4-Cu1-N1	169.96(14)	N1-Cu1-O1w	97.56(14)	C8-O6-C7	116.8(3)
O4-Cu1-O1w	90.58(14)	N2-Cu1-O1w	98.42(13)	O1w-H1w2···O5 <sup>i</sup>	145(4)
O1-Cu1-O1w	92.17(12)	O1-Cu1-N1	94.78(13)	O1w-H1w1···O2 <sup>i</sup>	152(4)

Symmetry code: <sup>i</sup>  $x+1, y, z$ .

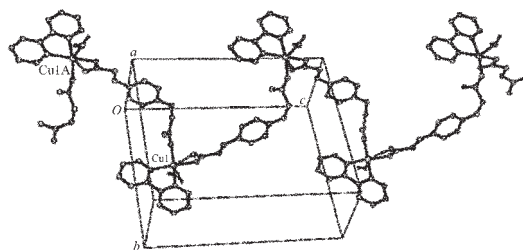
Each Cu(II) ion is six-coordinated by three carboxyl O atoms [Cu-O range, 0.196 4(3)~0.292 0(3) nm] of two *p*-BDOA<sup>2-</sup> groups, two N atoms of 2,2'-bipy ligand and one water molecule, the local coordination environment around the Cu(II) atom can be best described as a distorted square pyramidal geometry with a one-capped base by one very long semicoordinate Cu1-O5 bond of 0.292 0(3) nm<sup>[14,15]</sup>. Atoms O1, O4, N1 and N2 define the equatorial plane, and the Cu(II) atom deviates by 0.016(3) nm out of the plane. While water molecule O1w occupies the apical site, with the Cu-O1w bond distance of 0.224 1(3) nm.

Fig.1 ORTEP plot of **I** with 30% probability ellipsoid

It should be noted that the O1-C1 [0.125 9(5) nm] and O4-C6 distances [0.126 8(5) nm] are slightly longer than the O2-C1 [0.123 4(5) nm] and O5-C6 distances [0.122 9(5) nm], in accord with the monodentate coordination mode of carboxyl groups. The torsion angle [C8-O6-C7-C6] is  $-169.8(3)^\circ$ , whereas another oxyacetate group is obviously twisted out the phenyl ring plane, with the torsion angle [C3-O3-C2-C1] being  $76.0(5)^\circ$ . These demonstrate that the two oxyacetate groups have obvious different space orientation to sustain the whole crystal lattice, and suggest the remarkable conformational flexibility of *p*-BDOA<sup>2-</sup> ligand in

contrast to the rigid organic aromatic carboxylic acid ligands such as terephthalate<sup>[16]</sup>.

Each *p*-BDOA<sup>2-</sup> group serves as a bridging ligand to link two Cu(II) ions, giving rise to a one-dimensional helical chain structure (Fig.2). The adjacent Cu1···Cu1A (symmetry code: A:  $-x+1/2, -y+1, z-1/2$ ) distance within the polymeric chain is 1.348 4 nm, which is significant longer than the corresponding Cu···Cu separation of 0.877 3 nm in the reported complex(**II**)<sup>[10]</sup>. The 2,2'-bipy molecules alternately lie on two sides of the chain, and the dihedral angle of benzene ring and 2,2'-bipy ligand is  $80.8(4)^\circ$ . The chains are connected through intermolecular hydrogen bonds between the uncoordinated carboxylate O2, O5 atoms and the coordinated water molecule, with the O···O distances being 0.284 3(5) and 0.287 4(5) nm, and the O-H···O angles being  $145(4)^\circ$  and  $152(4)^\circ$ . In addition, there are weak  $\pi$ - $\pi$  stacking interactions between adjacent nitrogen heterocyclic rings of 2,2'-bipy, with the Cg···Cg (Cg is the centroid of the N-containing ring) distance of 0.390 6(3) nm. With the help of such hydrogen bonding and  $\pi$ - $\pi$  stacking interactions, the polymeric chains are assembled to form a supramolecular network.

Fig.2 One-dimensional helical chain of **I**

### 2.3 Thermal analysis

From the thermal analysis curve (TG/DTG) of the title complex, we can see that there are three weight-

loss steps (Fig.3). The first weight loss in the range of 158~213 °C, is attributed to the loss of one coordinated water molecule (found 4.09, calcd 3.90%). Then, the weight loss in the range of 213~310 °C may be related to the loss of 2,2'-bipy and phenoxy radical ( $C_6O_2H_4$ ) (found 57.45, calcd 57.21%). After gradually burning decomposition, the final residue may be  $Cu_2O$  (found 15.32, calcd 15.48%). The results show that the coordination polymer is thermally stable up to 158 °C.

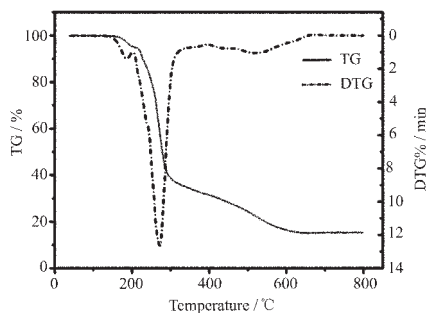


Fig.3 TG-DTG curve of complex I

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