

## 苯并三氮唑-1-氧基乙酸、4,4'-联吡啶构筑的一维链状铜配合物的水热合成及晶体结构

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**摘要:** 水热条件下, 合成了 1 个铜(II)配位聚合物 $[\text{Cu}(\text{L})(4,4'\text{-bpy})(\text{HCOO})(\text{H}_2\text{O})]_n$  (HL=苯并三氮唑-1-氧基乙酸, 4,4'-bpy=4,4'-联吡啶), 并通过元素分析、红外光谱、热重分析、X-射线粉末衍射和 X-射线单晶衍射对其进行了表征。晶体结构表明, 配合物属三斜晶系, 空间群  $P\bar{1}$ , 晶胞参数:  $a=0.820\ 26(16)\ \text{nm}$ ,  $b=1.128\ 3(2)\ \text{nm}$ ,  $c=1.159\ 7(2)\ \text{nm}$ ,  $\alpha=76.50(3)^\circ$ ,  $\beta=70.88(3)^\circ$ ,  $\gamma=76.97(3)^\circ$ ,  $V=0.973\ 0(3)\ \text{nm}^3$ ,  $Z=2$ 。铜(II)分别与来自 2 个 4,4'-bipy 的 2 个氮原子、1 个苯并三氮唑-1-氧基乙酸的 1 个氧原子、1 个甲酸根中 1 个氧原子和 1 个水分子中的 1 个氧原子配位, 形成变形的四方锥的配位构型。由于 4,4'-bipy 的桥联作用, 配合物在空间形成了一维链状结构, 该一维链又通过分子间  $\text{O}-\text{H}\cdots\text{N}$  和分子内  $\text{O}-\text{H}\cdots\text{O}$  氢键作用形成了二维层状结构。

**关键词:** 铜(II)配合物; 苯并三氮唑-1-氧基乙酸; 4,4'-联吡啶; 晶体结构

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## Hydrothermal Synthesis and Crystal Structure of a 1D Copper(II) Coordination Polymer Based on (1-Hydroxybenzotriazole)-o1-acetic Acid and 4,4'-Bipyridine

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**Abstract:** A 1D complex  $[\text{Cu}(\text{L})(4,4'\text{-bpy})(\text{HCOO})(\text{H}_2\text{O})]_n$  (HL=(1-Hydroxybenzotriazole)-o1-acetic acid, 4,4'-bpy=4,4'-bipyridine) has been synthesized under hydrothermal conditions and structurally characterized by elemental analysis, IR spectra, thermal analyses, powder X-ray diffraction and single crystal X-ray diffraction. The title complex belongs to triclinic with space group  $P\bar{1}$ ,  $a=0.820\ 26(16)\ \text{nm}$ ,  $b=1.128\ 3(2)\ \text{nm}$ ,  $c=1.159\ 7(2)\ \text{nm}$ ,  $\alpha=76.50(3)^\circ$ ,  $\beta=70.88(3)^\circ$ ,  $\gamma=76.97(3)^\circ$ ,  $V=0.973\ 0(3)\ \text{nm}^3$ . The copper(II) ion is five-coordinated with two nitrogen atoms from two 4,4'-bpy, one oxygen atom from one HL, one oxygen atom from one formate and one water oxygen atom, forming a square-pyramidal configuration. The Cu(II) centres are bridged by Cu(II)-N coordination bond through 4,4'-bpy ligands resulting in the formation of 1D chain structure. Then the 1D chains are further packed into 2D layer structure by intermolecular  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds and intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. CCDC: 850113.

**Key words:** copper(II) complex; (1-hydroxybenzotriazole)-o1-acetic acid; 4,4'-bipyridine; crystal structure

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## 0 Introduction

Inorganic-organic hybrid polymers have attracted a great deal of attention because of their intriguing structural such as rectangular grids, brick walls, herringbones, ladders, rings, boxes, diamondoids, and honeycombs, alongside their potential applications in the areas of gas storage, catalysis, photoluminescence, nonlinear optics, molecular recognition, molecular magnetization and others<sup>[1-13]</sup>. It is possible to synthesize intriguing and useful polymeric frameworks through the appropriate choice of ligand and metal center. The heterocyclic carboxylic acids such as pyridine-, tetrazole-, imidazole-, and pyrazole-carboxylic acids containing N and O donors offer great potential for fine control over coordination architectures<sup>[14-16]</sup>. However, the synthesis of coordination polymers involving 1-hydroxybenzotriazole and carboxylate groups as bridging and terminal ligands has not been reported until now to the best of our knowledge. So, in the present paper, the new compound (1-Hydroxybenzotriazole)-*o*-1-acetic acid and popular 4,4'-bipyridine as mixed-ligand were chosen to construct a novel 1D copper (II) complex. We report here the synthesis, crystal structure and thermal stability.

## 1 Experimental

### 1.1 Materials and measurements

All reagents and solvents used for the syntheses were commercially available and were used without further purification. C, H and N contents were determined by using a PE-2400 elemental analyzer. IR spectra were recorded on a Nicolet 6700 spectrometer with KBr pellets in the 4 000~400 cm<sup>-1</sup> region.

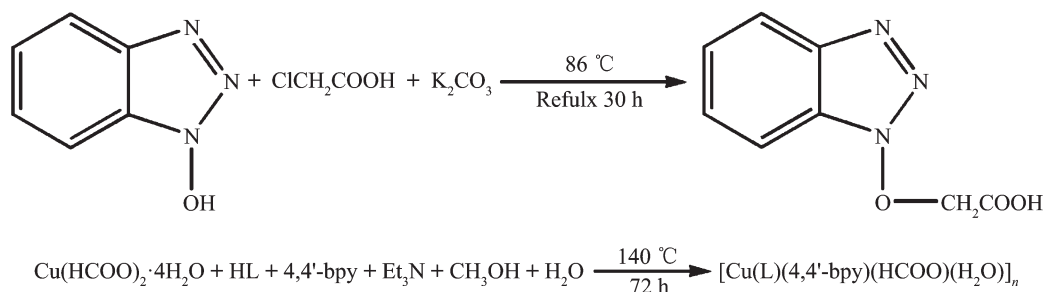
Thermogravimetric analysis (TG) data was collected on a METTLER TGA/DSC 1100 instrument under nitrogen atmosphere with a heating rate of 10 °C·min<sup>-1</sup> from 25 to 700 °C. Crystal structure determination was carried out on a Bruker Smart APEX II CCD diffractometer. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K $\alpha$  radiation (0.154 18 nm) and 2 $\theta$  ranging from 5° to 50°, in which the X-ray tube was operated at 40 kV and 30 mA.

### 1.2 Synthesis of the ligand HL

A solution of K<sub>2</sub>CO<sub>3</sub> (16.6 g, 0.12 mol) in water (50 mL) was added dropwise to a solution of chloroacetic acid (9.5 g, 0.1 mol) in water (50 mL). 1-Hydroxybenzotriazole (15.3 g, 0.1 mol) was slowly added to the resulting alkaline solution, and the mixture was refluxed at 86 °C for 24 h. The reaction mixture was then cooled to room temperature and acidified with HCl (6 mol·L<sup>-1</sup>) until the desired acid precipitated as a white solid (Scheme 1). This precipitate was collected by filtration, washed with water and recrystallised from water and methanol solution (volume ratio 4:1). Yield: 42%. Anal. Calcd. (%) for C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>: C, 49.74; H, 3.65; N, 21.75. Found (%): C, 49.65; H, 3.73; N, 21.66. IR (KBr,  $\nu$ /cm<sup>-1</sup>): 3 446, 1 740, 1 618, 1 421, 1 380 (w), 1 212, 1 103, 996, 879, 739, 687.

### 1.3 Synthesis of [Cu(L)(4,4'-bpy)(HCOO)(H<sub>2</sub>O)]<sub>n</sub> (1)

A mixture of Cu(HCOO)<sub>2</sub>·4H<sub>2</sub>O (1.0 mmol, 0.226 g), HL (1.0 mmol, 0.193 2 g), 4,4'-bpy (1.0 mmol, 0.156 2 g) and Et<sub>3</sub>N (1.0 mmol, 0.14 ml) in 15 mL mixed solvent of CH<sub>3</sub>OH/H<sub>2</sub>O (volume ratio 2:1). After stirring for 0.5 h, the mixture was transferred and



Scheme 1 Preparation of HL and complex 1

sealed into a 23 mL Teflon-lined stainless steel autoclave, which was heated at 140 °C for 3 d and then cooled to room temperature. Blue block crystals were produced with 45% yield based on Cu. Anal. Calcd. (%) for  $C_{19}H_{17}CuN_5O_6$ : C, 48.05; H, 3.61; N, 14.75. Found (%): C, 47.96; H, 3.72; N, 14.67. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3 373, 2 956 1 646, 1 609, 1 491, 1 408, 1 308, 1 297, 1 218, 821, 767, 613, 548.

### 1.3 Crystal structure determination

Single-crystal X-ray data of complex **1** were collected at a temperature of 295 K on a Bruker Smart APEX II CCD diffractometer equipped with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ) by using a  $\omega$ -scan mode. The structure was solved by direct method and refined by the full-matrix least-

squares fitting on  $F^2$  using SHELXS-97 program<sup>[17]</sup> and refined by the full-matrix least-squares fitting on  $F^2$  using SHELXL-97<sup>[18]</sup>. All non-hydrogen atoms were treated anisotropically. The organic hydrogen atoms were generated geometrically, fixed isotropic thermal parameters, and included in the structure factor calculations. The water hydrogen atoms were located in the difference Fourier map and refined isotropically. All calculations were performed using the SHELXL programs. The crystal data and structure refinement are summarized in Table 1. Selected bond lengths and angles are given in Table 2. The details of the hydrogen bonds are listed in Table 3.

CCDC: 850113.

Table 1 Crystal data and structure refinements of complex **1**

Empirical formula	$C_{19}H_{17}CuN_5O_6$	$\gamma / (^\circ)$	76.97(3)
Formula weight	474.92	$V / \text{nm}^3$	0.973 0(3)
Temperature / K	295(2)	$Z$	2
Size / mm	0.25×0.12×0.10	$\mu / \text{mm}^{-1}$	1.172
$\theta$ range for data collection / ( $^\circ$ )	2.42 to 25.05	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.621
Crystal system	Triclinic	$F(000)$	486
Space group	$P\bar{1}$	Reflections collected	5 079
$a / \text{nm}$	0.820 26(16)	Independent reflections ( $R_{\text{int}}$ )	3 419 (0.011 9)
$b / \text{nm}$	1.128 3(2)	Goodness of fit on $F^2$	1.064
$c / \text{nm}$	1.159 7(2)	$R_1, wR_2$ ( $I > 2\sigma(I)$ )	0.028 8, 0.075 8
$\alpha / (^\circ)$	76.50(3)	$R_1, wR_2$ (all data)	0.032 7, 0.078 2
$\beta / (^\circ)$	70.88(3)	$(\Delta\rho)_{\text{max}} (\Delta\rho)_{\text{min}} / (\text{e}\cdot\text{nm}^{-3})$	311, -309

Table 2 Selected bond lengths (nm) and angles ( $^\circ$ ) for complex **1**

Cu(1)-O(4)	0.196 78(18)	Cu(1)-O(6)	0.224 9(2)	Cu(1)-O(1)	0.199 06(17)
Cu(1)-N(4)	0.204 10(17)	Cu(1)-N(5)	0.203 90(17)	C(11)-C(11)#1	0.148 7(4)
C(17)-C(17)#2	0.148 9(4)				
O(4)-Cu(1)-O(1)	168.40(7)	N(5)-Cu(1)-N(4)	169.80(7)	O(4)-Cu(1)-N(5)	89.63(7)
O(4)-Cu(1)-O(6)	103.16(8)	O(1)-Cu(1)-N(5)	87.13(7)	O(1)-Cu(1)-O(6)	88.01(8)
O(4)-Cu(1)-N(4)	90.49(7)	N(5)-Cu(1)-O(6)	90.41(7)	O(1)-Cu(1)-N(4)	90.73(7)
N(4)-Cu(1)-O(6)	99.48(7)				

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

Table 3 Hydrogen bond lengths and angles for complex **1**

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O(6)-H(6WB) $\cdots$ O(5)	0.085	0.197	0.271 4(3)	146.5
O(6)-H(6WA) $\cdots$ N(3)#3	0.085	0.203	0.286 3(3)	165.9

Symmetry transformations used to generate equivalent atoms: #3:  $-x+1, -y, -z$ .

## 2 Results and discussion

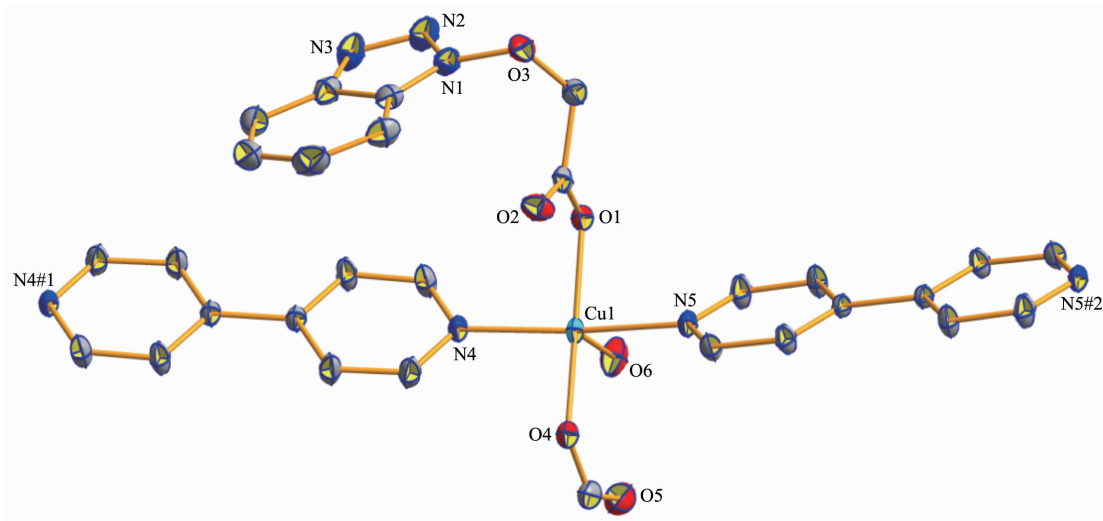
### 2.1 IR spectra

The IR spectra of complex **1** shows broad bands in the  $3\ 373\text{ cm}^{-1}$ , which may be assigned to the  $\nu(\text{O-H})$  stretching vibrations of the coordinated water molecule. The features at  $1\ 609$  and  $1\ 408\text{ cm}^{-1}$  are associated with the asymmetric ( $\text{COO}^-$ ) and symmetric ( $\text{COO}^-$ ) stretching vibrations. The value of  $\Delta[\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)]$  is  $201\text{ cm}^{-1}$ , which is larger than  $200\text{ cm}^{-1}$ , indicating that the monodentate coordination mode<sup>[19]</sup> of the carboxyl group to the metal atom. In addition, the characteristic 4,4'-bpy adsorption peaks at  $1\ 491$ ,  $821$  and  $613\text{ cm}^{-1}$ , suggesting the existence of coordinate bonds between Cu(II) and 4,4'-bpy ligand. The above analysis is consistent with the crystal determination.

### 2.2 Structure description

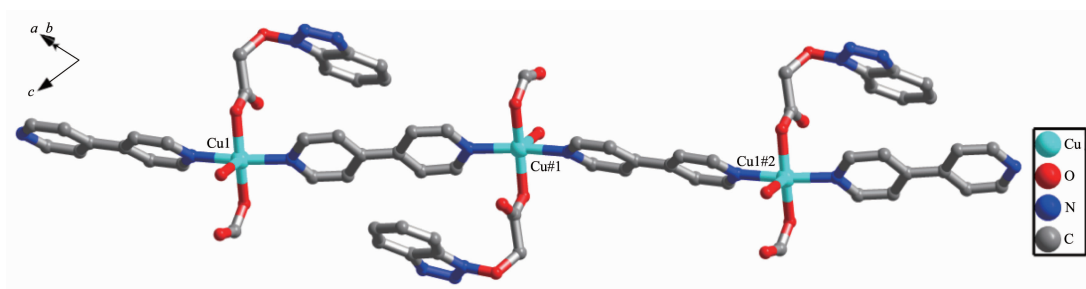
X-ray structural analysis revealed that the complex crystallizes in a triclinic system with space group  $P\bar{1}$ . The asymmetric unit has one Cu(II) atom, two halves of 4,4'-bpy ligands, one L ligand, one  $\text{HCOO}^-$  anion and one water molecule. The Cu(II) atom is five-coordinated by one oxygen atom from one water molecule, one oxygen atom from  $\text{HCOO}^-$  ligand, one oxygen atom from L ligand and two nitrogen atoms from two 4,4'-bpy ligands. The bond lengths of Cu-O and Cu-N are  $0.196\ 78(18) \sim 0.224\ 9(2)\text{ nm}$  and

$0.203\ 90(17) \sim 0.204\ 10(17)\text{ nm}$ , which are normal bond distances. The coordination sphere around Cu(II) atom is a distorted  $\{\text{CuN}_2\text{O}_3\}$  tetragonal pyramid environment (Fig.1). The equatorial plane is formed by N(4), N(5), O(1) and O(4), and the axial position is occupied by O6. Here, the sum of the angles subtended at the Cu(II) atom in the equatorial plane is  $357.98^\circ$  (close to  $360^\circ$ ), so that the atoms N(4), N(5), O(1), O(4) and Cu(1) are almost in the same plane. The deviation of Cu1 from equatorial tetragonal plane is  $0.015\ 05\text{ nm}$ . Furthermore, the bond angles O(6)-Cu(1)-N(4), O(6)-Cu(1)-N(5), O(6)-Cu(1)-O(1) and O(6)-Cu(1)-O(4) are  $99.48(7)^\circ$ ,  $90.41(7)^\circ$ ,  $88.01(8)^\circ$  and  $103.16(8)^\circ$ , which deviate from  $90^\circ$ . The above analysis illustrate the Cu(II) atom is in a distorted tetragonal pyramid environment. The 4,4'-bpy ligands link the Cu(II) atoms to form a 1D infinite chain with the  $\text{Cu}\cdots\text{Cu}$  separation  $1.117\ 94(25)\text{ nm}$  and  $1.119\ 62(24)\text{ nm}$ , stacked with the sequence  $\cdots\text{ABCABC}\cdots$  of the bridging 4,4'-bpy ligands (Fig.2). This 1D infinite chain is further extended into an intriguing 2D framework structure through strong intermolecular hydrogen bonds  $\text{O}(6)-\text{H}(6\text{WA})\cdots\text{N}(3)\#3$  ( $\#3: -x+1, -y, -z$ ) as illustrated in Fig.3. Furthermore, there also exist intramolecular hydrogen bonding interactions  $\text{O}(6)-\text{H}(6\text{WB})\cdots\text{O}(5)$  between the coordination water molecules and the oxygen atoms of  $\text{HCOO}^-$  ions,



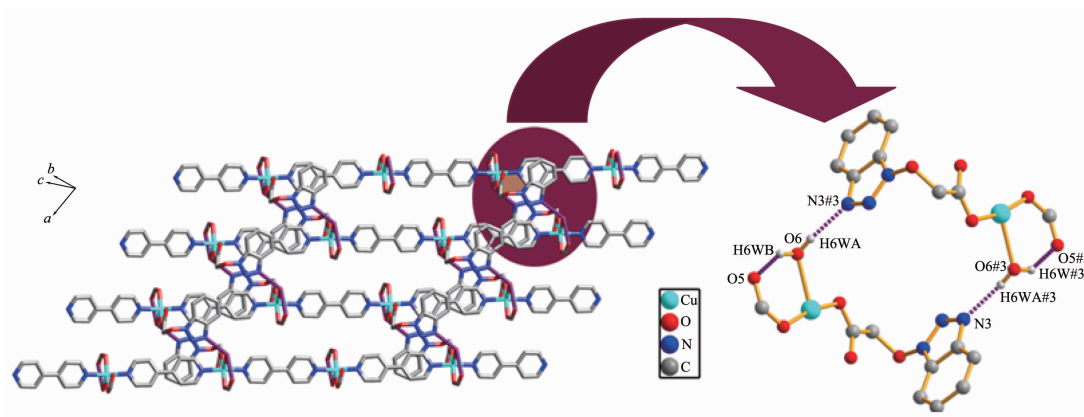
Symmetry code: #1:  $-x, -y, -z$ ; #2:  $-x+1, -y+1, -z+1$ ; Hydrogen atoms are omitted for clarity

Fig.1 View of the coordination environment of Cu(II) atom with thermal ellipsoids drawn at the 30% probability level for the complex **1**



Symmetry code: #1:  $-x, -y, -z$ ; #2:  $-x+1, -y+1, -z+1$ ; Hydrogen atoms are omitted for clarity

Fig.2 View of 1D infinite chain of the complex **1**



Symmetry code: #3:  $-x+1, -y, -z$ ; Some hydrogen atoms are omitted for clarity

Fig.3 View of 2D framework of the complex **1** constructed by O-H...N and O-H...O hydrogen bonding

which further stabilize the crystal structure.

### 2.3 Thermal analysis

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of complex **1**. The samples were heated up in flowing  $N_2$  with a heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The TG curve is depicted in Fig. 4, which shows two weight loss steps. The first weight loss of 3.41% (Calcd. 3.79%) between 52 and  $128\text{ }^{\circ}\text{C}$  corresponds to the release of coordinated water molecules in the complex. The further decomposition

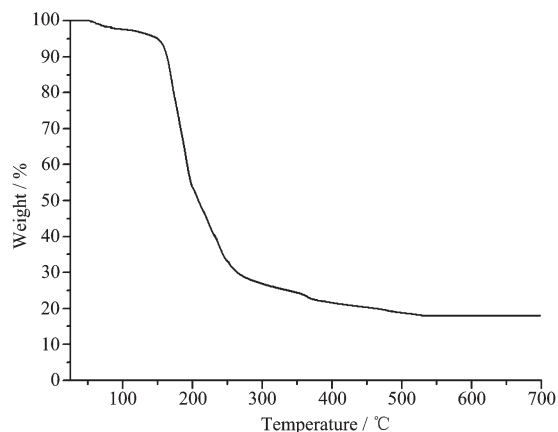


Fig.4 Thermal analysis curve of the complex **1**

occurred in the range of  $128\sim 525\text{ }^{\circ}\text{C}$ , which may be attributed to the elimination of  $\text{HCOO}^-$  anion, 4,4'-bpy and L. The remaining products may be CuO (Obsd. 17.22%, Calcd. 16.75%)

### 2.4 Powder X-ray diffraction analysis

In order to check the phase purity of the title complex, the powder X-ray diffraction (PXRD) pattern was recorded at room temperature. As shown in Fig.5, the peak positions of simulated and experimental

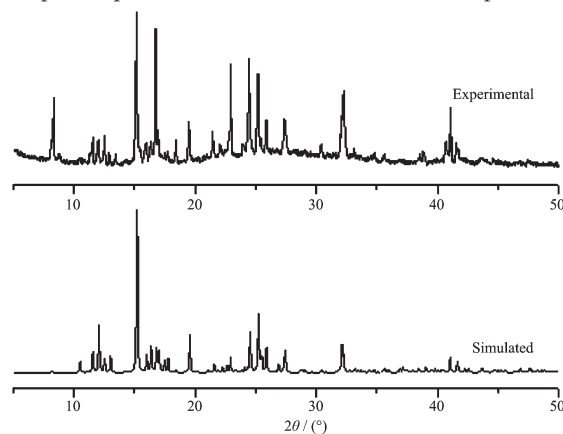


Fig.5 Experimental and Simulated powder X-ray diffraction patterns of the complex **1**

pattern are in good agreement with each other, indicating the phase purity of the product. The differences in intensity may be due to the preferred orientation of the powder samples.

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