

## 环状二核铜配合物 $[\text{Cu}(\text{nphth})(\text{phen})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ 的水热合成与晶体结构

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**摘要:** 在水热反应条件下, 合成了一个新配合物,  $[\text{Cu}(\text{nphth})(\text{phen})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$  (nphth=3-硝基邻苯二甲酸阴离子, phen=邻菲咯啉), 经元素分析、红外、热重、单晶衍射表征了配合物。该配合物为单斜晶系, 空间群  $P2_1/n$ , 结构参数:  $a=0.999\ 8(1)\ \text{nm}$ ,  $b=1.044\ 5(1)\ \text{nm}$ ,  $c=1.820\ 6(1)\ \text{nm}$ ,  $\beta=91.423(1)^\circ$ ,  $V=1.900\ 7(2)\ \text{nm}^3$ ,  $Z=2$ ,  $R=0.039\ 4$ ,  $wR=0.096\ 5$ 。结构分析表明, 配合物为分立环状二核结构, 并通过分子间氢键和  $\pi-\pi$  作用扩展为二维超分子网络结构。

**关键词:** 铜配合物; 3-硝基邻苯二甲酸; 水热合成; 晶体结构

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## Hydrothermal Synthesis and Crystal Structure of a Cyclic Binuclear Copper Complex $[\text{Cu}(\text{nphth})(\text{phen})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$

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**Abstract:** A novel complex  $[\text{Cu}(\text{nphth})(\text{phen})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$  (nphth=3-nitrophthalate, phen=1,10-phenanthroline) was synthesized by hydrothermal reaction and characterized by elemental analysis, IR, TGA and X-ray single crystal diffraction. The title complex crystallizes in monoclinic with space group  $P2_1/n$ ,  $a=0.999\ 8(1)\ \text{nm}$ ,  $b=1.044\ 5(1)\ \text{nm}$ ,  $c=1.820\ 6(1)\ \text{nm}$ ,  $\beta=91.423(1)^\circ$ ,  $V=1.900\ 7(2)\ \text{nm}^3$ ,  $Z=2$ ,  $R=0.039\ 4$ ,  $wR=0.096\ 5$ . The structure analysis shows that the complex exhibits a discrete cyclic binuclear structure. The 2D supramolecular network is constructed through hydrogen bonds and  $\pi-\pi$  interaction. CCDC: 801643.

**Key words:** copper complex; 3-nitrophthalic acid; hydrothermal synthesis; crystal structure

### 0 Introduction

Self-assemblies have attracted considerable interest in modern coordination chemistry and crystal engineering for the construction of discrete cyclic polynuclear complexes<sup>[1]</sup> and infinite polymers with potential applications<sup>[2]</sup>. Many carboxylate ligands have been shown to be good building blocks in the preparing coordination polymers with desired topologies owing to

their rich coordination modes<sup>[3]</sup>. *o*-Phthalic acid is a versatile ligand for designing new supramolecular constructions. Up to now, Numerous complexes with *o*-phthalate ligands were found to display diverse structure types<sup>[4]</sup>, but only a few 3d-series transition metal complexes with 3-nitrophthalate ligand are reported<sup>[5]</sup>. Herein, we report the hydrothermal synthesis and crystal structure of a novel cyclic discrete binuclear copper(II) complex,  $[\text{Cu}(\text{nphth})(\text{phen})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$

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(nphth=3-nitrophthalate, phen=1,10-phenanthroline), with mixed ligands of 3-nitrophthalate and phen.

## 1 Experimental

### 1.1 Reagent and apparatus

All of the chemicals were obtained from commercial sources and were used without further purification. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. The IR spectra were recorded on a Nicolet 360 FTIR spectrometer with KBr pellets in the 4 000 ~400  $\text{cm}^{-1}$  region. Thermogravimetric analysis was obtained on NETZSCH STA 449C thermogravimetric analyzer, carried out under  $\text{N}_2$  with a heating rate of at 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$ .

### 1.2 Synthesis of $[\text{Cu}(\text{nphth})(\text{phen})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$

A mixture of  $\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.061 g, 0.2 mmol), phen (0.016 g, 0.2 mmol), 3-nitrophthalic acid (0.042 g, 0.2 mmol) and distilled water (10 mL) was put into a Teflon-lined autoclave (20 mL) and then heated at 403 K for 72 h. Blue block-like crystals of the title complex in 50% yield based on Cu. Anal. Calcd. for  $\text{C}_{40}\text{H}_{30}\text{N}_6\text{O}_{16}\text{Cu}$ (%): C, 49.13; H, 3.09; N, 8.60. Found(%): C, 49.33; H, 3.19; N, 8.50.

### 1.3 Crystal structure determination

A blue block-like single crystal with dimension of 0.23 mm×0.21 mm×0.20 mm for the title complex was used for X-ray diffraction analysis. Data collection was carried out at 293 K on a Rigaku RAXIS-RAPID Weissengberg IP diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda=0.071\,073\,\text{nm}$ ) in  $\omega$  scan mode. A total of 12 743 reflections and 4 100 unique ones were collected in the range of  $2.35^{\circ}\leq\theta\leq 27.00^{\circ}$  with  $R_{\text{int}}=0.030\,2$ , of which 3 135 reflections with  $I>2\sigma(I)$  were considered as observed and used in the succeeding structural calculations. The structure was solved by direct method and difference Fourier syntheses. The aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation ( $\text{C-H}=0.093\,\text{nm}$  and  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ ). The water H atoms were found in a difference Fourier map and were refined with distance restraints of  $\text{O-H}=0.085(1)\,\text{nm}$  and  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{O})$ . All calculations were carried out with SHELX 97

program<sup>[6]</sup>.

The Crystal belongs to monoclinic system, the space group is  $P2_1/n$ , with the crystal cell parameters  $a=0.999\,8(1)\,\text{nm}$ ,  $b=1.044\,5(1)\,\text{nm}$ ,  $c=1.820\,6(1)\,\text{nm}$ ,  $\beta=91.423(1)^{\circ}$ , and  $V=1.900\,7(2)\,\text{nm}^3$ ,  $M_r=977.78$ ,  $D_c=1.708\,\text{g}\cdot\text{cm}^{-3}$ ,  $\mu=1.208\,\text{mm}^{-1}$ ,  $F(000)=996$ ,  $Z=2$ ,  $R=0.039\,4$ ,  $wR=0.096\,5$ ,  $S=1.031$ ,  $\Delta/\sigma=0.000$ ,  $\Delta\rho_{\text{max}}=783\,\text{e}\cdot\text{nm}^{-3}$  and  $\Delta\rho_{\text{min}}=-441\,\text{e}\cdot\text{nm}^{-3}$ .

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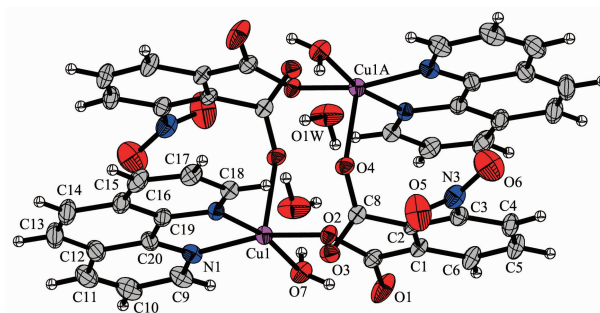
## 2 Results and discussions

### 2.1 IR spectra

The IR spectrum of the title complex reveals two strong bonds of the carboxylic groups at 1 590 and 1 379  $\text{cm}^{-1}$  for the asymmetric vibrations and symmetric vibrations, respectively. The difference between the asymmetric and symmetric stretching vibrations ( $\Delta\nu=\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-)$ ) is 211  $\text{cm}^{-1}$ , suggesting that the carboxyl group coordinates to copper(II) with monodentate mode<sup>[7]</sup>. A strong peak at 1 524  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{as}}(\text{aromatic NO}_2)$  and the other strong peak at 1 350  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{s}}(\text{aromatic NO}_2)$ . The wide peaks at about 3 451, 3 066  $\text{cm}^{-1}$  are assigned to OH vibration, suggesting the existence of the crystal and coordinated water molecules and H-bonding in the complex.

### 2.2 Crystal structure

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



Symmetry code A: 1-x, 1-y, 1-z

Fig.1 Cyclic binuclear structure of the title complex with 30% probability ellipsoid

The Cu1 atom in title complex adopts a square-pyramidal  $\text{N}_2\text{O}_3$  environment, with the basal plane defined by atoms N1 and N2 from phen, atom O2 from

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

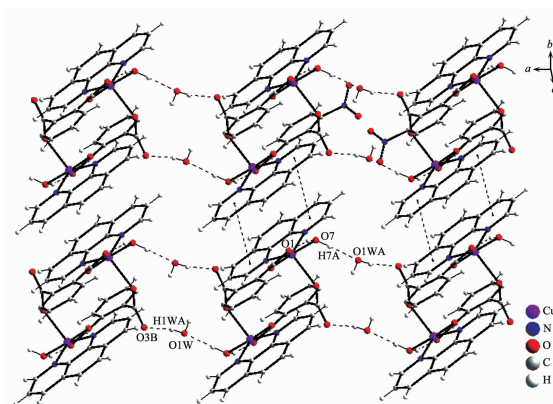
Cu(1)-O(7)	0.196 2(2)	Cu(1)-O(2)	0.199 6(2)	Cu(1)-N(2)	0.199 4(2)
Cu(1)-N(1)	0.203 2(3)	Cu(1)-O(4)A	0.223 0(2)		
O(7)-Cu(1)-O(4)A	90.26(9)	N(1)-Cu(1)-O(4)A	97.48(9)	N(2)-Cu(1)-N(1)	81.54(10)
O(2)-Cu(1)-N(1)	162.86(9)	O(7)-Cu(1)-N(2)	167.72(11)	O(7)-Cu(1)-N(1)	89.73(10)
O(7)-Cu(1)-O(2)	93.88(8)	N(2)-Cu(1)-O(4)A	99.38(8)	N(2)-Cu(1)-O(2)	92.07(8)
O(2)-Cu(1)-O(4)A	99.25(8)				

Symmetry code: A: 1-x, 1-y, 1-z.

one 3-nitrophthalate ligand, and O7 from a H<sub>2</sub>O, O4A atom from the other 3-nitrophthalate ligand occupies the apical position with a Cu1-O4A distance of 0.223 0(1) nm. Two Cu(II) centers are linked by carboxylate groups from two phth<sup>2-</sup> bridges, showing a good centro-symmetry in the whole molecule. Thus, a discrete cyclic binuclear structure is constructed by two Cu(II) atoms, two phen and two phth bridges, the core of the binuclear structure being an fourteen-membered ring with Cu...Cu distance of 0.522 7(1) nm.

The title complex has rich hydrogen bonds formed by the crystal and coordinated water molecules and uncoordinated oxygen atoms of carboxylate groups. Detailed data are given in Table 2. Then adjacent binuclear structure units are connected together by the hydrogen bonds to 1D chain along the *a* axis. There are  $\pi$ - $\pi$  interactions between the aromatic rings of phen of

the neighboring chain with a centroid-centroid distance between neighbouring aromatic rings of 0.359 5(1) nm, generating an extended two-dimensional architecture (Fig.2).

Symmetry code: A: 1-x, 1-y, 1-z; B: -x, 1-y, 1-z; Hydrogen bonds and  $\pi$ - $\pi$  interactions are shown as dashed lines**Fig.2** Extended 2D structure in the title complex**Table 2** Hydrogen bond geometry for the complex

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	$\angle$ (DHA) / (°)
O(7)-H(7a)...O(1W)A	0.085(1)	0.180(1)	0.264 1(4)	173(3)
O(1W)-H(1Wa)...O(3)B	0.085(1)	0.183(1)	0.267 9(3)	170(3)
O(7)-H(7b)...O(1)	0.085(1)	0.174(2)	0.254 7(3)	159(3)

Symmetry code: A: 1-x, 1-y, 1-z; B: -x, 1-y, 1-z.

### 2.3 Thermogravimetric analysis

The thermogravimetric analysis of the title complex was performed under N<sub>2</sub> atmosphere. The weight loss of 7.40% (calcd. 7.36%) between 110 and 156 °C corresponds to the loss of the crystal and coordinated water molecules. The main framework began to collapse at above 156 °C.

In summary, a novel discrete cyclic binuclear complex [Cu(nphth)(phen)(H<sub>2</sub>O)]<sub>2</sub>·2H<sub>2</sub>O bridged by two 3-nitrophthalate was synthesized. A two-dimensional

supramolecular network is constructed through hydrogen bonds and  $\pi$ - $\pi$  interactions.

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