

萘氧乙酸及咪唑构筑的锌(II)和铜(II)配合物的水热合成、晶体结构及荧光性质

李伟琦^{1,2} 封霞¹ 冯云龙¹ 温一航^{*,1}

(¹ 浙江师范大学物理化学研究所, 浙江省固体表面反应化学重点实验室, 金华 321004)

(² 金华广播电视大学, 金华 321022)

摘要: 通过水热的方法合成得到 2 个由萘氧乙酸及咪唑配体构筑的配合物 $\text{Zn}(\text{2-naph})_2(\text{imi})_2$ (**1**) 和 $2\text{Cu}(\text{2-naph})_2(\text{imi})_2(\text{H}_2\text{O}) \cdot \text{Cu}(\text{2-naph})_2(\text{imi})_2(\text{H}_2\text{O})$ (**2**) ($\text{2-naph} = \text{2-naphthoxyacetate}$, $\text{imi} = \text{imidazole}$), 它们的结构通过 X 射线晶体衍射、红外光谱和元素分析得到确定。在配合物 **1** 中, 锌原子与来自不同 2-萘氧乙酸配体中的 2 个羧酸氧原子和不同的咪唑分子中的 2 个氮原子形成了变形的四面体的几何构型。单个分子通过 $\text{N-H}\cdots\text{O}$ 氢键连接形成了一维链, 然后在 $\text{C-H}\cdots\pi$ 弱作用下形成了三维结构。配合物 **2** 有 2 个独立的铜中心, 它们有几乎相同的配位环境。每个铜中心都是变形的四方锥的配位构型。来自不同的 2-萘氧乙酸配体中的 2 个羧酸氧原子和不同的咪唑分子中的 2 个氮原子形成了一个相对规则的四方锥赤道平面, 配位水分子位于平面上方。配合物 **2** 的分子通过 $\text{N-H}\cdots\text{O}$ 和 $\text{O-H}\cdots\text{O}$ 氢键连接形成了二维结构。2 个配合物的热稳定和固体荧光性质在本文中也得到了研究和讨论。

关键词: 锌(II)配合物; 铜(II)配合物; 2-萘氧乙酸; 咪唑; 晶体结构; 荧光性质

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2008)06-0873-07

Hydrothermal Syntheses, Crystal Structures and Luminescence Properties of Zn(II) and Cu(II) Complexes Assembled by 2-naphthoxyacetate and Imidazole Ligands

LI Wei-Qi^{1,2} FENG Xia¹ FENG Yun-Long¹ WEN Yi-Hang^{*,1}

(¹ Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004)

(² Jinhua Radio and Television University, Jinhua, Zhejiang 321022)

Abstract: Two complexes assembled by 2-naphthoxyacetate and imidazole ligands, $\text{Zn}(\text{2-naph})_2(\text{imi})_2$ (**1**) and $2\text{Cu}(\text{2-naph})_2(\text{imi})_2(\text{H}_2\text{O}) \cdot \text{Cu}(\text{2-naph})_2(\text{imi})_2(\text{H}_2\text{O})$ (**2**) (where $\text{2-naph} = \text{2-naphthoxyacetate}$ and $\text{imi} = \text{imidazole}$) have been hydrothermally synthesized, and their structures have been determined by X-ray diffraction. In complex **1**, Zn(II) is in a distorted tetrahedron environment with two carboxylate oxygen atoms from two 2-naphthoxyacetate ligands and two nitrogen atoms from two imidazole ligands. The single molecules of complex **1** are linked by $\text{N-H}\cdots\text{O}$ hydrogen bonds to generate a one-dimensional chain, then further form a three-dimensional structure by the $\text{C-H}\cdots\pi$ weak interactions. Complex **2** has two independent Cu(II) centers with the same coordination environment. Each Cu(II) center is in a distorted tetragonal pyramid coordination geometry. Two carboxylate oxygen atoms from two 2-naphthoxyacetate ligands and two nitrogen atoms from two imidazole ligands form a relatively normal square plane of the tetragonal pyramid, and the water molecule occupies the apical position. Molecules of complex **2** are linked by $\text{N-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{O}$ hydrogen bonds to yield a two-dimensional structure. The TGA and Luminescence properties in solid state of two complexes have been further studied and discussed. CCDC: 669291, **1**; 669290, **2**.

Key words: zinc(II) complex; copper(II) complex; 2-naphthoxyacetate; imidazole; crystal structure; luminescence property

收稿日期: 2007-12-10。收修改稿日期: 2008-04-01。

浙江省教育厅基金资助项目(No.20071374)。

*通讯联系人。E-mail: wyh@zjnu.cn

第一作者: 李伟琦, 女, 47 岁, 学士, 金华电大高级讲师; 研究方向: 功能配合物的分子设计。

The design of metal-organic hybrid materials has been deeply researched, due to their intriguing structural diversity and potential functions^[1]. In particular, carboxylate ligands, especially aromatic carboxylate ligands have been shown to be good building blocks in the design of metal-organic materials with desired topologies owing to their rich coordination modes. The coordination chemistry of aromatic carboxylic acids such as 2-naphthoxyacetic acid^[2], 2-naphthylacetic acid^[3], 1-naphthoxyacetic acid^[4], 1-naphthylacetic acid^[5] has captured the attention of chemists for many years due to their wide practical uses, magnetism^[6], biological activities^[7], gas adsorption^[8], photochemical properties and magnetic properties^[9]. Early reports on aromatic carboxylic acids are mostly focused on the rigid ligands^[10]. More and more attention has been focused on the flexible ligands because flexible ligands can adopt different configurations, which will lead to versatile and novel structures^[6]. 2-naphthoxyacetic acid is one of the typical flexible ligands. There are only a few reports on metal complexes of 2-naphthoxyacetic acid^[2,8]. As a sequel work of our continuing effort in synthesizing coordination polymers with 2-naphthoxyacetic acid, auxiliary ligands, such as imidazole, have been employed to observe the structure diversity. In this paper, we report the hydrothermal syntheses and characterizations of two new complexes, $\text{Zn}(\text{2-naph})_2(\text{imi})_2$ (**1**) and $2\text{Cu}(\text{2-naph})_2(\text{imi})_2(\text{H}_2\text{O}) \cdot \text{Cu}(\text{2-naph})_2(\text{imi})_2(\text{H}_2\text{O})$ (**2**), in which 2-naphthoxyacetic acid acts as monodentate ligand.

1 Experimental

1.1 Reagents and physical measurements

All starting materials and solvents for syntheses were obtained commercially and used without further purification. IR spectra were recorded on an FTIR-8700 spectrometer with KBr pellets in the range of $4\,000 \sim 400\text{ cm}^{-1}$. Elemental analysis was performed on a PE-2400(II) element analysis instrument. The crystal data collections were carried out on a Bruker SMART APEX-II CCD diffractometer. Thermogravimetric analyses were determined on a Mettler-Toledo TGA/SDTA 851^e under oxygen atmosphere. Fluorescence spectra were performed on a HITACHI F-2500

Fluorescence Spectrometer in solid state at room temperature.

1.2 Syntheses of two complexes

Complex 1: A mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.220 g, 1 mmol), imidazole (0.034 g, 0.5 mmol), NaOH (0.021 g, 0.5 mmol) and 2-naphthoxyacetic acid (0.202 g, 1 mmol) was dissolved in 17 mL of 15:2 water/ethanol. The solution was placed in a 25 mL Teflon-lined stainless-steel bomb. The bomb was heated to 433 K for 72 h. It was cooled to room temperature over 3 days. The colorless sheet crystals of **1** suitable for X-ray diffraction structure analysis were isolated from the solution. Elemental analyses: (Found (%): C, 59.75; H, 4.36; N, 9.18. $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_6\text{Zn}$ Calcd. (%): C, 59.66; H, 4.34; N, 9.28). IR (cm^{-1}): 3 431m, 3 144m, 2 950w, 2 857 w, 1 615s, 1 505s, 1 446m, 1 393s, 1 269m, 1 219m, 1 075 w, 949w, 838w, 763m, 653m, 627w, 467w.

For complex 2: A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g, 1 mmol), imidazole (0.034 g, 0.5 mmol), NaOH (0.022 g, 0.5 mmol) and 2-naphthoxyacetic acid (0.202 g, 1 mmol) was dissolved in 17 mL of 15:2 water/ethanol. The solution was placed in a 25 mL Teflon-lined stainless-steel bomb. The bomb was heated to 433 K for 72 h. It was cooled to room temperature over 3 days. The green block crystals of **2** suitable for X-ray diffraction structure analysis were isolated from the solution. Elemental analyses: (Found (%): C, 58.01; H, 4.58; N, 9.11. $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_7\text{Cu}$ Calcd. (%): C, 58.11; H, 4.55; N, 9.04). IR (cm^{-1}): 3 423s, 3 153vs, 3 068s, 2 967 m, 2 874w, 2 637w, 1 615s, 1 514s, 1 430m, 1 387s, 1 328 w, 1 269s, 1 219m, 1 185m, 1 074m, 956w, 915m, 838m, 763m, 661w, 458w.

1.3 Crystal structures determination

Two crystals of **1** (0.08 mm \times 0.13 mm \times 0.35 mm) and **2** (0.09 mm \times 0.29 mm \times 0.43 mm) were selected for structure analyses. Data collections were performed on a Bruker SMART APEX-II diffractometer equipped with a CCD detector (Mo $K\alpha$ radiation, $\lambda = 0.071\,073\text{ nm}$). Data intensities were corrected by Lorentz-polarization factors and empirical absorption. The structures were solved by direct methods and expanded with difference Fourier synthesis. Anisotropic displacement parameters were applied to all non-

hydrogen atoms in full-matrix least-squares refinements based on F^2 . The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by the use of

geometrical restrains. All calculations were performed with SHELXTL package^[11]. All pertinent crystallographic data for **1** and **2** are summarized in Table 1.

CCDC: 669291, **1**; 669290, **2**.

Table 1 Crystallographic data and processing parameters for **1** and **2**

Empirical formula	C ₃₀ H ₂₆ N ₄ O ₆ Zn (1)	C ₃₀ H ₂₈ N ₄ O ₇ Cu (2)
Formula weight	603.92	620.10
Crystal color and habit	Colorless, sheet	Green, block
Temperature / K	296(2)	296(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>Cc</i>
<i>a</i> / nm	1.135 66(2)	4.375 20(12)
<i>b</i> / nm	1.472 23(3)	0.581 60(10)
<i>c</i> / nm	3.383 15(6)	3.666 82(12)
β / (°)		110.955(3)
<i>V</i> / nm ³	5.65 65(18)	8.713 5(4)
<i>Z</i>	8	12
<i>D_c</i> / (g·cm ⁻³)	1.418	1.418
μ / mm ⁻¹	0.919	0.805
<i>F</i> (000)	2 496	3 852
Crystal size / mm	0.35 × 0.13 × 0.08	0.43 × 0.29 × 0.09
θ range for data collection / (°)	2.16~27.64	1.80~27.52
Limiting indices	$-13 \leq h \leq 14, -18 \leq k \leq 19, -37 \leq l \leq 43$	$-55 \leq h \leq 54, -7 \leq k \leq 7, -47 \leq l \leq 47$
Reflections collected	25 359	42 219
Reflections unique (<i>R_{int}</i>)	6 371 (0.041 5)	9 466 (0.037 7)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6 371 / 0 / 370	9 466 / 4 / 578
Goodness-of-fit on F^2	1.002	1.001
Final <i>R</i> indices [$I > 2\sigma(I)$]	<i>R</i> ₁ =0.038 0, <i>wR</i> ₂ =0.082 0	<i>R</i> ₁ =0.060 1, <i>wR</i> ₂ =0.162 2
<i>R</i> indices (all data)	<i>R</i> ₁ =0.077 5, <i>wR</i> ₂ =0.095 5	<i>R</i> ₁ =0.105 3, <i>wR</i> ₂ =0.193 6
Largest diff. peak and hole / (e·nm ⁻³)	272 and -294	1 215 and -473

2 Results and discussion

2.1 Syntheses, IR spectra for two complexes

Complex **1** and **2** were synthesized by the hydrothermal method at 160 °C with adding sodium hydroxide for adjusting the pH value. The IR spectra of both the two complexes show absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1 400~1 615 cm⁻¹ range. The strong peaks from 3 144 to 3 431 cm⁻¹ of complex **1** are assigned to the N-H stretching vibrations of the imidazole ligand, while the strong peaks from 3 068 to 3 423 cm⁻¹ of complex **2** are ascribed to the N-H stretching vibrations of the

imidazole ligand and the O-H stretching vibrations of the coordinated water. The conspicuous carboxylate stretching at 1 615, 1 505, 1 446 and 1 393 cm⁻¹ in **1**, 1 615, 1 514, 1 430, 1 387 cm⁻¹ in **2**. **1** and **2** both present two groups of the antisymmetric $\nu_{as}(\text{COO}^-)$ and symmetric stretching frequency $\nu_s(\text{COO}^-)$. The strong and acute band appeared in the 1 219~1 269 cm⁻¹ in **1** and **2** are ascribed to the asymmetric stretching vibration of (=C-O-C). These data clearly show the formation of the complexes and hydrogen bonds.

2.2 Description of the structure of complex **1**

The structure of **1** is shown in Fig.1, and the selected bond distances and angles are listed in Table 2.

The asymmetric unit of **1** is composed of one Zn atom, two 2-naphthoxyacetate and two imidazole ligands.

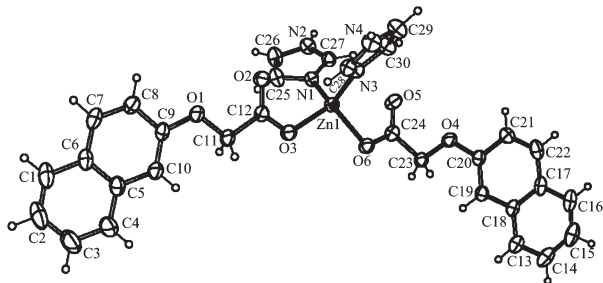


Fig.1 Molecular structure of the complex **1**

The coordination environment of the Zn atom displays a distorted ZnO_2N_2 tetrahedron coordination geometry which is formed from two carboxylate oxygen atoms of two 2-naphthoxyacetate ligands, two nitrogen atoms of two imidazole ligands. The angles around Zn center range from $99.76(7)^\circ$ to $118.60(7)^\circ$. The Zn-N1,

Zn-N3 bond lengths are 0.199 3(2) and 0.199 7(2) nm, respectively, and the Zn-O3, Zn-O6 bond lengths are 0.196 9(2) and 0.198 7(2) nm, respectively, which are comparable to those found in other Zn^{II} complexes with the same coordination environment^[12]. The C-O distances in the carboxylate groups vary from 0.122 3(3) to 0.127 6(3) nm, in which the distances between C and the coordinated O atoms vary from 0.127 4 (3) to 0.127 6(3) nm, obviously longer than that with the uncoordinated O atom 0.122 3(3), 0.123 2(3) nm. The 2-naphthoxyacetate ligand has a planar structure, in which the carboxyl group is deprotonated. Two 2-naphthoxyacetate ligands adopt monodentate modes to bond to one $\text{Zn}(\text{II})$ center. The dihedral angle between the two naphthalene ring systems is $5.843(44)^\circ$. The dihedral angle between the two imidazole ring systems is $55.516(1)^\circ$.

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

Zn(1)-O(3)	0.196 86(15)	Zn(1)-N(1)	0.199 28(18)	Zn(1)-O(6)	0.198 65(16)
Zn(1)-N(3)	0.199 73(19)				
O(3)-Zn(1)-O(6)	99.76(7)	O(3)-Zn(1)-N(3)	113.58(7)	O(3)-Zn(1)-N(1)	104.24(7)
O(6)-Zn(1)-N(3)	105.86(7)	O(6)-Zn(1)-N(1)	118.60(7)	N(1)-Zn(1)-N(3)	114.12(8)

Hydrogen-bonding interactions are usually important in the synthesis of supramolecular architecture. There are intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds between N atom of the imidazole ligands and O atom of the 2-naphthoxyacetate ligands, as shown in Fig.2. The single molecules are linked by hydrogen bonds to yield a one-dimensional chain along *b* axis. The dihedral angles between two naphthalene ring systems of two adjacent Zn(II) centers on the same side of the chain are $20.370(6)^\circ$, while the dihedral angles between two naphthalene ring systems of two interphase Zn(II) centers on the same side of the chain are $0.042 (5)^\circ$, with the distance is 1.472 3 nm. Furthermore, there also exist $\text{C}-\text{H} \cdots \pi$ weak interactions between naphthalene

rings of the adjacent chains. Finally, the 1D chains are extended into a 3D supramolecular network. These supramolecular interactions together with the coordinate-covalent interactions between metal ions and organic ligands strengthen the stability of the network structure. The hydrogen-bonding distances are listed in Table 3.

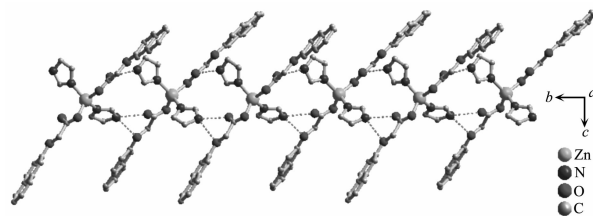


Fig.2 Hydrogen bonds in the complex **1**

Table 3 Hydrogen-bonding parameters for **1**

D-H \cdots A	<i>d</i> (D-H) / nm	<i>d</i> (H \cdots A) / nm	<i>d</i> (D \cdots A) / nm	\angle (DHA) / ($^\circ$)
N(2)-H(2B) \cdots O(2)#1	0.086	0.198	0.277 8(3)	154.8
N(4)-H(4B) \cdots O(5)#2	0.086	0.202	0.281 4(3)	153.9
N(4)-H(4B) \cdots O(4)#2	0.086	0.236	0.302 4(3)	133.9

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

2.3 Description of the structure of complex 2

The structure of complex **2** is shown in Fig.3. Selected bond lengths and bond angles are given in Table 4.

The independent unit of the complex **2** is a 2:1 copper-2-naphthoxyacetate-imidazole adduct. The two independent copper centers have the nearly same coordination environment, while their bond lengths and bond angles have a little difference, as shown in Table 4.

Each Cu atom displays a distorted CuO_3N_2 tetragonal pyramid coordination geometry which is formed from two carboxylate oxygen atoms of two 2-naphthoxyacetate ligands, two nitrogen atoms of two imidazole ligands and one coordinated water molecule. The angles around Cu center range from $87.33(11)^\circ$ to $178.68(15)^\circ$. Two carboxylate oxygen atoms and two nitrogen atoms form a relatively normal square plane of the tetragonal pyramid, with the torsion angle of $5.243(1)^\circ$, and the Cu atom is slightly deviated from the plane (-0.0073 nm), while the water molecule occupies the apical position. The Cu1-N1, Cu1-N3 bond lengths are $0.1977(3)$ and $0.1993(3)\text{ nm}$, respectively, which

are similar to those found in other Cu^{II} complexes with similar coordination environment^[13]. The Cu1-O2, Cu1-O6 bond lengths are $0.1975(3)$ and $0.1979(2)\text{ nm}$, respectively, which are similar to those found in other Cu^{II} complexes with similar coordination environment^[14]. The C-O distances in the carboxylate groups vary from $0.1214(4)$ to $0.1263(4)\text{ nm}$, in which the distances between C and the coordinated O atoms are $0.1248(4)$ and $0.1263(4)\text{ nm}$, obviously longer than that with the uncoordinated O atom ($0.1214(4)$, $0.1230(4)\text{ nm}$). The molecules of 2-naphthoxyacetate has a planar structure, in which the carboxyl group is deprotonated. Two 2-naphthoxyacetate ligands adopt monodentate modes to bond to one Cu(II) center. The dihedral angles between the two naphthalene ring systems are $71.258(9)^\circ$. The dihedral angles between the two imidazole ring systems are $83.258(2)^\circ$. The two single molecules are center symmetry and the dihedral angles between the two adjacent naphthalene ring systems of the two independent Cu centers are 2.938° , with the distance from 0.4 nm to 0.5 nm . There are extensive $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ hydrogen-bonding interactions (Table 5), and the

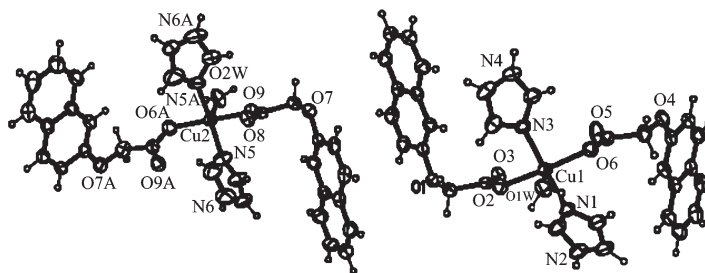


Fig.3 Structure of the complex **2**

Table 4 Selected bond lengths (nm) and bond angles ($^\circ$) of **2**

Cu(1)-O(2)	0.197 5(3)	Cu(2)-O(8)#1	0.194 9(3)	Cu(1)-N(1)	0.197 7(3)
Cu(2)-O(8)	0.194 9(3)	Cu(1)-O(6)	0.197 9(2)	Cu(2)-N(5)#1	0.197 0(3)
Cu(1)-N(3)	0.199 3(3)	Cu(2)-N(5)	0.197 0(3)	Cu(1)-O(1W)	0.223 3(3)
Cu(2)-O(2W)	0.225 3(4)				
O(2)-Cu(1)-N(1)	92.55(12)	O(8)#1-Cu(2)-O(8)	178.68(15)	O(2)-Cu(1)-O(6)	175.54(10)
O(8)#1-Cu(2)-N(5)#1	88.96(14)	N(1)-Cu(1)-O(6)	89.16(12)	O(8)-Cu(2)-N(5)#1	90.94(14)
O(2)-Cu(1)-N(3)	87.33(11)	O(8)#1-Cu(2)-N(5)	90.94(14)	N(1)-Cu(1)-N(3)	174.16(12)
O(8)-Cu(2)-N(5)	88.96(14)	O(6)-Cu(1)-N(3)	90.55(11)	N(5)#1-Cu(2)-N(5)	171.25(19)
O(2)-Cu(1)-O(1W)	93.35(9)	O(8)#1-Cu(2)-O(2W)	90.66(7)	N(1)-Cu(1)-O(1W)	95.43(11)
O(8)-Cu(2)-O(2W)	90.66(7)	O(6)-Cu(1)-O(1W)	90.59(9)	N(5)#1-Cu(2)-O(2W)	94.37(9)
N(3)-Cu(1)-O(1W)	90.40(11)	N(5)-Cu(2)-O(2W)	94.37(9)		

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

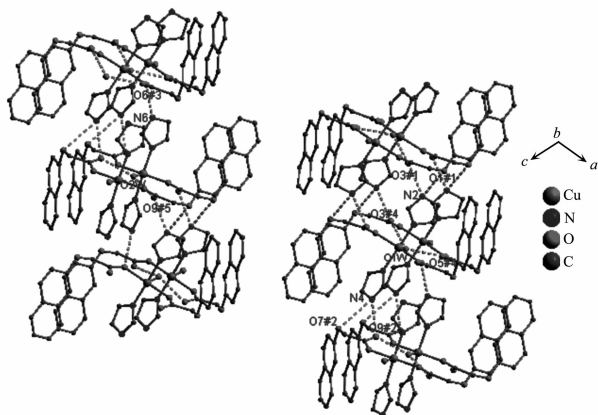
Table 5 Hydrogen-bonding parameters for **2**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
N(2)-H(2B)...O(3)#1	0.086	0.208	0.287 7(4)	153.7
N(2)-H(2B)...O(1)#1	0.086	0.260	0.318 0(4)	125.5
N(4)-H(4B)...O(9)#2	0.086	0.200	0.283 6(4)	162.9
N(4)-H(4B)...O(7)#2	0.086	0.261	0.318 9(4)	125.5
N(6)-H(6B)...O(6)#3	0.086	0.219	0.298 7(5)	154.8
O(1W)-H(1WA)...O(3)#4	0.086 2(18)	0.191(2)	0.275 6(3)	167(4)
O(1W)-H(1WB)...O(5)#4	0.086 5(18)	0.186 5(18)	0.272 1(4)	170(3)
O(2W)-H(2W)...O(9)#5	0.082 3(19)	0.198(2)	0.279 7(3)	171(5)

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

#3: $x-1/2, y+3/2, z$; #4: $x, y-1, z$; #5: $x, y+1, z$.

molecules are linked by hydrogen bonds to yield a two-dimensional network structure, respectively, as depicted in Fig.4.

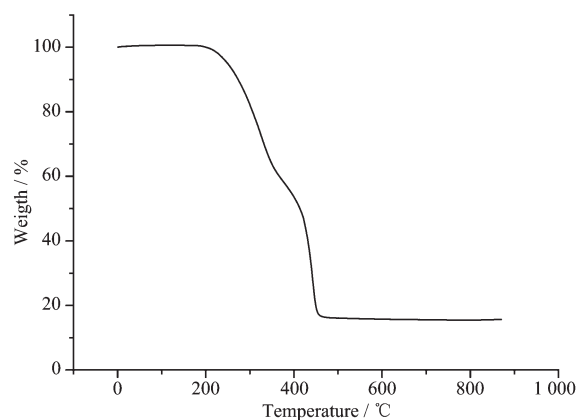
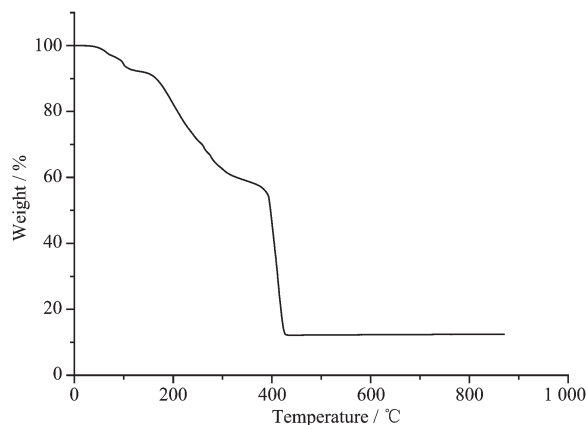
Fig.4 Hydrogen bonds in complex **2**

2.4 Thermal properties

Combined TGA-DSC analysis was carried out in the interest of studying the thermal behaviors of the open framework polymer materials. The sample of the complex **1** was heated to 800 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$ under O_2 atmosphere. As shown in Fig.5, the TGA diagram reveals the distinct weight loss regions from 187 to 472 $^\circ\text{C}$, which indicate that the complex **1** can exist stably below 187 $^\circ\text{C}$ and decomposed slowly when the temperature is over 187 $^\circ\text{C}$. From this picture we can see there is no clear weight loss of water molecule in the TGA curve. The loss weight of 86.13% (calcd 89.51%) may be ascribed to the loss of 2-naphthoxyacetate and imidazole ligands and the remaining products may be ZnO (obsd 13.31%, calcd 13.47%).

The complex **2** is air stable at room temperature. However, decomposition occurred at elevated temper-

ature. As shown in Fig.6, the thermal analysis curve indicates that the weight loss attributed to the release of the water is observed below 80 $^\circ\text{C}$ (obsd 3.1%, calcd 2.9%). The second weight loss occurs in the range 95~427 $^\circ\text{C}$, which is attributed to the elimination of the 2-naphthoxyacetate and imidazole ligands (obsd 84.13%, calcd 84.27%). The residue may be copper oxide (obsd 12.77%, calcd 12.83%).

Fig.5 TGA diagram of compound **1**Fig.6 TGA diagram of compound **2**

2.5 Luminescence properties

Measurement of the solid state luminescence spectra of the complexes **1** and **2** reveals a stronger blue emission maximum at approximately 390 nm, while a weaker blue-fluorescent emission band is observed at 381 nm, upon excitation at 339 nm (Fig.7). These emission are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Zn^{2+} ions are difficult to oxidize or to reduce due to its d^{10} configuration which can probably be assigned to the intraligand (π - π^*) fluorescent emission^[15]. Comparably, free 2-naphthoxyacetate and imidazole in the solid state displays the emission band centered at about 363 and 382 nm, respectively, when excited at 339 nm. The emission band of complex **2** is similar to the imidazole ligand. The luminescence emission of **2** might therefore probably be assigned to the intraligand (π - π^*) emission of imidazole ligand. It is clear that the red-shift of emission occurs in complex **1**, which is probably due to the differences of ligands and coordination environment around central metal ions, because photoluminescence behavior is closely associated with the local environment around metal ions^[16].

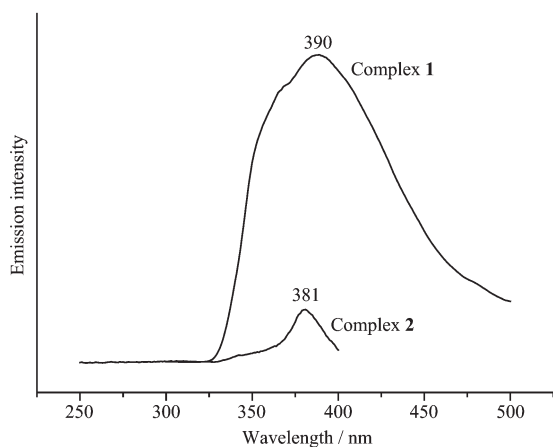


Fig.7 Fluorescence emission spectrum of **1** and **2** in the solid state at room temperature

3 Conclusions

In summary, two new complexes with different su-

pramolecular architectures have been successfully synthesized from the 2-naphthoxyacetic acid and imidazole ligands. These non-covalent interactions, such as hydrogen-bonding and $\text{C-H}\cdots\pi$ weak interactions, play very important role in the constructions of supramolecular architectures. Two complexes both display blue fluorescent emission in the solid state.

References:

- [1] Harrison R G, Fox O D, Meng M O, et al. *Inorg. Chem.*, **2002**, **41**:838~843
- [2] Ma C L, Han Y F, Zhang R F. *J. Organomet. Chem.*, **2004**, **689**: 1675~1683
- [3] Koman M, Melnik M, Moncol J, et al. *Inorg. Chem. Commun.*, **2000**, **3**:489~492
- [4] WANG Yong(王 勇), YIN Han-Dong(尹汉东), XUE Sheng-Cai(薛绳才), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2006**, **22**:656~660
- [5] Chen L F, Zhang J, Song L J, et al. *Acta Cryst.*, **2004**, **E60**: m1032~1034
- [6] Picraux L B, Weldon B T, McCusker J K. *Inorg. Chem.*, **2003**, **42**:273~282
- [7] Zhang A P, Yang P, Wang Y K. *Chem. Res. and Appl.*, **1997**, **9** (1):57~59
- [8] Zheng S L, Tong M L, Fu R W, et al. *Inorg. Chem.*, **2001**, **40**: 3562~3569
- [9] Nakai M, Funabiki T, Ohtsuki C, et al. *Inorg. Chem.*, **2006**, **45**: 3048~3056
- [10] Hu T L, Li J R, Liu C S, et al. *Inorg. Chem.*, **2006**, **45**:162~173
- [11] Sheldrick G M. *SHELXTL, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.
- [12] Gao S, Liu J W, Huo L H, et al. *Acta Cryst.*, **2004**, **E60**:m1329~m1330
- [13] Huang X C, Zhang J P, Chen X M. *Cryst. Growth Des.*, **2006**, **6**:1194~1198
- [14] Psomas G, Dendrinou-Samara C, Philippakopoulos P, et al. *Inorg. Chim. Acta*, **1998**, **272**:24~32
- [15] Wen L L, Dang D B, Duan C Y, et al. *Inorg. Chem.*, **2005**, **44**: 7161~7170
- [16] Fu Z Y, Wu X T, Dai J C, et al. *Eur. J. Inorg. Chem.*, **2002**: 2730~2735