

两个含 2-(2-吡啶基)咪唑衍生物的铜(II) 配合物的合成、晶体结构及发光性质

范 艳¹ 瞿志荣^{*1} 金晓飞² 郭艳红² 王作祥^{*2}

(¹ 杭州师范大学有机硅实验室, 杭州 311121)

(² 东南大学化学化工学院, 南京 211189)

摘要: 通过自然挥发法, 合成了 2 个配合物 $[\text{Cu}(\text{DMPM})_2(\text{Bz})][\text{Cu}(\text{DMPM})(\text{Bz})_3] \cdot \text{H}_2\text{O}$ (**1**) 和 $[\text{Cu}(\text{PMA})\text{Cl}_2]$ (**2**) (DMPM=4,5-二甲基-2-(2-吡啶基)咪唑, PMA=[2-(2-吡啶基)咪唑-1-基]乙酸乙酯, Bz=苯甲酸根), 并对其荧光、热稳定性及电子自旋共振光谱进行了研究。结构分析结果表明化合物 **1** 属于三斜晶系, $P\bar{1}$ 空间群; 化合物 **2** 属于单斜晶系, $P2_1/c$ 空间群。化合物 **1** 通过氢键的作用形成了三维超分子框架, 化合物 **2** 通过氢键作用形成了二维层状结构。

关键词: 2-(2-吡啶基)咪唑衍生物; 合成; 晶体结构

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2015)10-2051-08

DOI: 10.11862/CJIC.2015.262

Syntheses, Crystal Structures and Luminescent Properties of Two Cu(II) Complexes with 2-(2-Pyridyl)imidazole Derivatives

FAN Yan¹ QU Zhi-Rong^{*1} JIN Xiao-Fei² GUO Yan-Hong² WANG Zuo-Xiang^{*2}

(¹Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China)

(²School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China)

Abstract: Two complexes, $[\text{Cu}(\text{DMPM})_2(\text{Bz})][\text{Cu}(\text{DMPM})(\text{Bz})_3] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{PMA})\text{Cl}_2]$ (**2**) (DMPM=4,5-dimethyl-2-(2-pyridyl)imidazole, PMA=ethyl [2-(2-pyridyl)imidazole-1-yl]acetate, Bz=benzoate anion) were synthesized and characterized by ultraviolet spectrophotometry (UV-Vis), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), electron spin resonance (ESR) and single crystal X-ray diffraction. Results show that the crystal structure of complex **1** belongs to triclinic system, space group $P\bar{1}$, and complex **2** belongs to monoclinic system, space group $P2_1/c$. Complex **1** assembles into a 3D structure by the intermolecular hydrogen bonding interactions, whereas a 2D layer structure of complex **2** is assembled by hydrogen bonds. CCDC: 1414243, **1**; 1414242, **2**.

Key words: 2-(2-pyridyl)imidazole derivatives; synthesis; crystal structure

0 Introduction

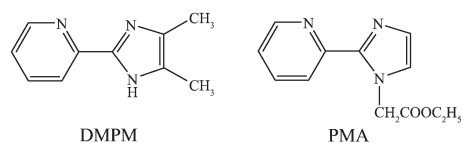
Recently, the rational design and assembly of metal-organic coordination compounds have gained

great attention because of their applications in molecular adsorption, ion exchange, fluorescence, electrical conductivity, magnetism, optical properties and heterogeneous catalysis^[1-4]. Organic ligands containing

收稿日期: 2015-02-25。收修改稿日期: 2015-08-04。

*通讯联系人。E-mail: quzr@hznu.edu.cn; wangzxwx@aliyun.com

multiple heterocyclic rings are very useful species in the self-assembly of metallocsupramolecular compounds^[5]. As that respect, heterocyclic compounds such as 2-(2-pyridyl)imidazole and their derivatives have been used in transition metal chemistry^[6]. The functional group of 2-(2-pyridyl)imidazolyl in 4,5-dimethyl-2-(2-pyridyl)imidazole (DMPM) and ethyl [2-(2-pyridyl)imidazole-1-yl]acetate (PMA) (see Scheme 1) can serve as a bifunctional ligand because of its potential chelating N-atoms of the pyridine and imidazole rings. It can be involved in hydrogen bonding assisted supramolecular structures and π - π stacked interactions. In addition, the O atoms of acetate may be conducive to coordinate with metal ions and useful for forming hydrogen bonds. This significant feature makes this system interesting for constructing networks. All these characteristics play important roles in the developing exploration of rational synthetic strategies leading to metal-containing extended supramolecular motifs^[7-14]. 2-(2-pyridyl)imidazole derivatives have gained much attention as chelating ligands in transition metals and rare-earth metals copper(II)^[15], zinc(II)^[16], iron(II)^[17], manganese(II)^[18], vanadium(IV)^[19], rhenium(III/IV)^[20] and ruthenium(II)^[21] as well as heterometallic Cu(II)/Re(IV) compounds^[22]. In our study, we have combined transition metal Cu(II) salts with the ligands of DMPM and PMA respectively by evaporation at room temperature to form new complexes. Imidazole derivatives with benzoic acid as auxiliary ligands lead to a 3D structure by the intermolecular hydrogen bonds. Herein, we report the syntheses and characterizations of two new metal-organic compounds based on DMPM and PMA ligands, $[\text{Cu}(\text{DMPM})_2(\text{Bz})][\text{Cu}(\text{DMPM})(\text{Bz})_3] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{PMA})\text{Cl}_2]$ (**2**), in which **1** displays a 3D structural network by the intermolecular hydrogen bonding interactions, **2** assembles into a 2D layer structure by hydrogen bonds. Furthermore, the thermal



Scheme 1

stabilities and luminescence properties of two compounds have also been investigated.

1 Experimental

1.1 Chemicals and measurement

The ligands of 4,5-dimethyl-2-(2-pyridyl)imidazole and ethyl [2-(2-pyridyl)imidazole-1-yl]acetate were synthesized as described elsewhere^[23]. Other reagents and solvents were commercially available and used without further purification. Thermogravimetric (TG) analysis were performed on a NETZSCH TG STA449F3 analyzer at a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ under nitrogen flow with a rate of $20\text{ mL} \cdot \text{min}^{-1}$. Differential scanning calorimetry (DSC) were conducted on a TA DSC-Q100 instrument at a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ under nitrogen flow and within the temperature range of $-80\sim 200\text{ }^{\circ}\text{C}$.

1.2 Preparation

1.2.1 Preparation of $[\text{Cu}(\text{DMPM})_2(\text{Bz})][\text{Cu}(\text{DMPM})(\text{Bz})_3] \cdot \text{H}_2\text{O}$ (**1**)

4,5-dimethyl-2-(2-pyridyl)imidazole (2 mmol, 0.345 g) was dissolved in 20 mL acetone, and then a solution of copper benzoate (2 mmol, 0.613 g) in 20 mL acetone was added with stirring. The mixing solution turned dark green immediately and was then filtered. Green single crystals (0.47 g) suitable for analyses were obtained by slowly evaporating of the filtrate at room temperature for about 5 days. Yield: 47.3% (based on Cu). Anal. Calcd. for $\text{Cu}_2\text{C}_{58}\text{H}_{55}\text{N}_9\text{O}_9$ (%): C, 60.62; H, 4.82; N, 10.97. Found(%): C, 60.68; H, 4.87; N, 10.89. IR (cm^{-1} , KBr): 3 325(s), 2 944(as), 2 832(as), 1 654(as), 1 449(s), 1 415(s), 1 114(s), 1 021(s), 660(ds).

1.2.2 Preparation of $[\text{Cu}(\text{PMA})\text{Cl}_2]$ (**2**)

Ethyl [2-(2-pyridyl)imidazole-1-yl]acetate (6 mmol, 1.386 g) was dissolved in 15 mL methanol, and then a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (3 mmol, 0.512 g) in 20 mL methanol was added with stirring. The mixing solution turned turquoise immediately and was then filtered. Blue single crystals (0.64 g) suitable for analyses were obtained by slowly evaporating the filtrate at room temperature for about 3 days. Yield: 58.2% (based on Cu). Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{CuN}_3\text{O}_2$ (%): C, 39.41; H, 3.58; N, 11.49. Found(%): C, 39.43; H, 3.61; N, 11.51.

IR (cm⁻¹, KBr): 3 330(s), 2 946(as), 2 834(as), 1 652 (as), 1 449(s), 1 411(s), 1 113(s), 1 019(s), 660(ds).

1.3 X-ray crystallography

X-ray single-crystal diffraction data of complexes **1** and **2** were collected on a Bruker SMART APEX (II) -CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 296(2) K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97

program^[24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically and refined with a riding model. Detailed data collection and refinements of **1** and **2** are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. Relevant hydrogen bonding parameters of **1** are summarized in Table 4.

CCDC: 1414243, **1**; 1414242, **2**.

Table 1 Crystal data and structure refinement for complexes **1** and **2**

Complex	1	2
Empirical formula	Cu ₂ C ₅₈ H ₅₅ N ₉ O ₉	C ₁₂ H ₁₃ Cl ₂ CuN ₃ O ₂
Formula weight	1 149.19	365.70
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	1.337 7(18)	1.186 10(14)
b / nm	1.489(2)	0.734 58(9)
c / nm	1.682(4)	1.665 4(2)
α / (°)	104.28(3)	90.00
β / (°)	107.96(3)	92.329(2)
γ / (°)	108.136(19)	90.00
V / nm ³	2.803(9)	1.450 6(3)
Z	2	4
D_c / (g·cm ⁻³)	1.362	1.674
$F(000)$	1 192	740
Absorption coefficient / mm ⁻¹	0.823	1.877
θ range / (°)	1.38~25.02	2.45~27.53
h, k, l	-15~15, -15~17, -20~20	-15~15, -9~9, -21~21
Reflections collected	19 977	9 403
Independent reflections	9 730 ($R_{int}=0.074\ 5$)	3 316 ($R_{int}=0.023$)
Observed reflections	4 587	2 634
Data / restraints / parameters	9 730 / 82 / 732	3 316 / 0 / 181
Goodness-of-fit on F^2	0.953	1.076
R, wR indices ($I>2\sigma(I)$)	0.095 1, 0.252 0	0.033 7, 0.105 9
R, wR indices (all data)	0.182 1, 0.293 2	0.048 3, 0.128 3

Table 2 Selected bond lengths (nm) and angles (°) for the complex **1**

Cu1-O1	0.191 9(4)	N1-C3	0.132 2(7)	O1-C11	0.128 4(6)
Cu1-O5	0.193 3(4)	N2-C3	0.135 5(7)	O2-C11	0.121 1(7)
Cu1-N1	0.199 7(5)	N3-C8	0.134 1(7)	O2W-O2W	0.157 3(19)
Cu1-N3	0.205 1(5)	N3-C8	0.134 1(7)	O3-C18	0.124 4(6)
Cu1-O3	0.230 0(5)	N4-C39	0.135 7(7)	C1-N1	0.135 3(7)
Cu2-N7	0.193 3(6)	N5-C40	0.136 3(7)	C1-C2	0.136 9(8)
Cu2-N4	0.194 0(6)	N4-C41	0.135 5(7)	C1-C9	0.147 6(9)
Cu2-O7	0.195 4(5)	N6-C42	0.135 6(8)	C2-N2	0.133 9(7)

Continued Table 2

Cu2-N9	0.215 6(6)	N7-C49	0.123 8(10)	C2-N10	0.146 1(8)
Cu2-N6	0.220 3(6)	N8-C50	0.121 7(10)	C4-C5	0.137 4(8)
O1-Cu1-O5	92.2(2)	O5-Cu1-O3	92.54(16)	N4-Cu2-N9	93.5(2)
O1-Cu1-N1	95.7(2)	N1-Cu1-O3	90.23(17)	O7-Cu2-N9	141.6(2)
O5-Cu1-N1	171.25(18)	N3-Cu1-O3	89.79(18)	N7-Cu2-N6	94.2(2)
O1-Cu1-N3	172.35(13)	N7-Cu2-N4	170.5(2)	N4-Cu2-N6	79.1(2)
O5-Cu1-N3	91.0(2)	N7-Cu2-O7	94.5(2)	O7-Cu2-N6	124.0(2)
N1-Cu1-N3	80.7(2)	N4-Cu2-O7	94.80(18)	N9-Cu2-N6	94.41(18)
O1-Cu1-O3	97.01(18)	N7-Cu2-N9	80.3(2)		

Table 3 Selected bond lengths (nm) and angles (°) for the complex 2

Cu1-N1	0.198 1(2)	Cu1-N3	0.203 8(2)	Cu1-Cl2	0.223 71(8)
Cu1-Cl3	0.224 11(7)	N1-C3	0.132 5(3)	N1-C2	0.137 6(4)
N2-C3	0.135 5(3)	N2-C9	0.146 2(3)	N3-C8	0.133 7(4)
N3-C4	0.135 2(3)				
N1-Cu1-N3	80.04(9)	N1-Cu1-C12	94.59(7)	N3-Cu1-C12	165.88(7)
N1-Cu1-Cl3	151.24(8)	N3-Cu1-Cl3	94.41(6)	C12-Cu1-Cl3	96.39(3)

Table 4 Hydrogen bond lengths (nm) and angles (°) for the complex 1

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O1W-H1WA...O4 ⁱ	0.097 3(16)	0.248 3(14)	0.307 5(12)	119.0(9)
O1W-H1WB...O4 ⁱ	0.096 4(14)	0.249 2(17)	0.307 5(12)	118.8(13)
O2W-H2WA...O1W	0.085 5(19)	0.183 0(16)	0.219 3(14)	103.5(13)
O2W-H2WB...O1W	0.085 3(15)	0.183 3(16)	0.219 3(14)	103.3(13)
N2-H2...O4 ⁱⁱ	0.085 95	0.191 34	0.272 9(9)	157.89
N5-H5A...O6 ⁱⁱⁱ	0.085 98	0.190 24	0.271 6(9)	157.29
N8-H8A...O8 ^{iv}	0.085 92	0.219 85	0.303 0(11)	162.72

Symmetry codes: ⁱ 1+x, 1+y, z; ⁱⁱ -x, -y, 2-z; ⁱⁱⁱ 1+x, y, -1+z; ^{iv} 2-x, 1-y, 1-z

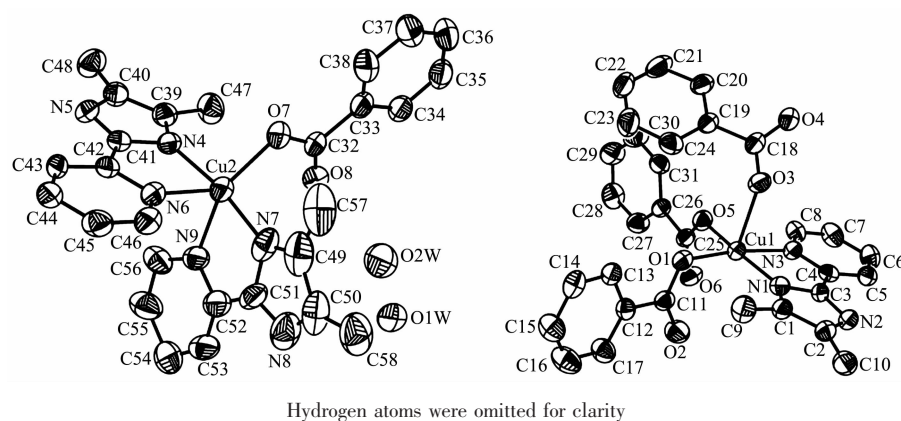
2 Results and discussion

2.1 Structural description of complex 1

The crystal structure of complex **1** belongs to triclinic system, space group $P\bar{1}$. Single-crystal X-ray diffraction analysis of complex **1** reveals that each asymmetric unit consists of two central Cu(II) ions, three DMPM ligands, four benzoate anions and two halves molecule of solvent water (Fig.1). Cu1 and Cu2 are five coordinated but under different coordination environment in the structure of complex **1**. The Cu1(II) atom lies on a two-fold axis and is coordinated by two N atoms and three O atoms to give a distorted tetragonal pyramid geometry. The Cu1-O distances fall

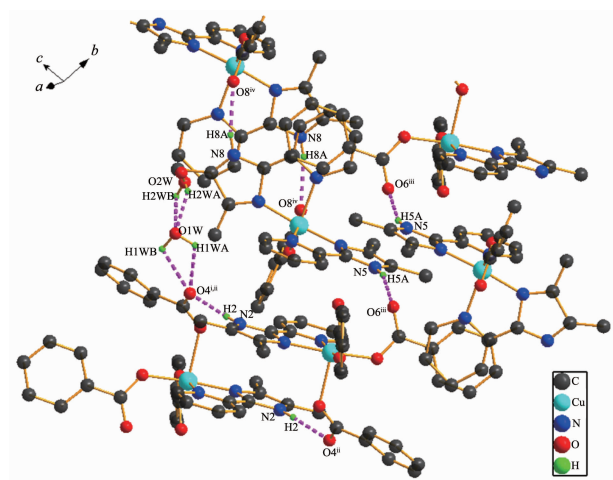
in a range from 0.191 9(4) to 0.230 0(5) nm, the Cu1-N distances are 0.199 7(5) and 0.205 1(5) nm. O1, O5, N1 and N3 are atoms in the equatorial plane distributed around the center Cu1(II), with the O3 atom at the axial position to form a distorted tetragonal pyramid geometry. The Cu2(II) center adopts a distorted trigonal bipyramid geometry by the coordination of four N atoms from two individual DMPM ligands and one O atom from benzoate anion. The Cu2-N bond lengths range from 0.193 3(6) to 0.220 3(6) nm, Cu2-O7 bond length is 0.195 4(5) nm (Table 2).

The imidazole and pyridine groups are nearly coplanar with the dihedral angle between them is

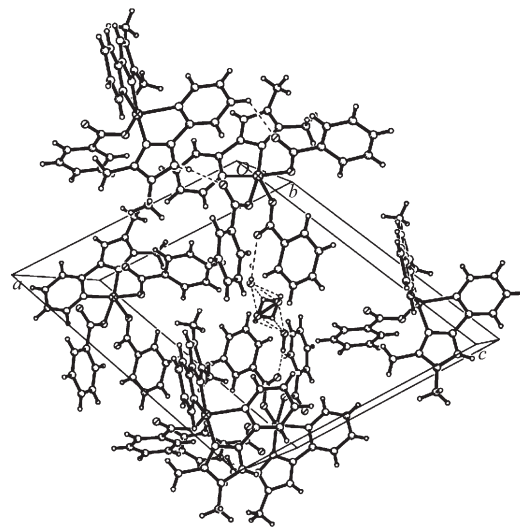
Fig.1 Crystal structure of complex **1** with 30% thermal ellipsoids

2.4°. The angle between the two DMPM planes in molecule is 88.5(5)°. Neighboring molecules are linked by classical N–H···O and O–H···O hydrogen bonds and weak C–H···O hydrogen bonds into a three-dimensional supramolecular network (Fig.3). There are strong hydrogen bonds existing between the O atoms of the solvent water molecules, intermolecular hydrogen bonds of N2–H2···O4ⁱⁱ, N5–H5A···O6ⁱⁱⁱ and N8–H8A···O8^{iv} (Symmetry code: ⁱⁱ $-x, -y, 2-z$; ⁱⁱⁱ $1+x, y, -1+z$; ^{iv} $2-x, 1-y, 1-z$). The distances and the angles of the hydrogen bonds are listed in Table 4. The C–H··· π interactions are responsible for the stabilization of structural elements. The interactions between two kinds of aromatic C–H donors and aromatic-acceptors are described. Analysis of the crystal structures reveals aromatic C–H··· π hydrogen bonds existing

between benzene and pyridine rings, including interactions of C27–H27···Cg9 (Cg9 is the centroid of the pyridine ring N6, C42, C43, C44, C45, C46 with symmetry operation $1-x, 1-y, 1-z$ of 0.300 nm) and C58–H58A···Cg10 (Cg10 is the centroid of the pyridine ring N9, C52, C53, C54, C55, C56 with symmetry operation $2-x, 1-y, 1-z$ of 0.269 nm), as shown in Fig.2. In addition, an intermolecular face-to-face interaction between the neighboring imidazole ring and pyridine ring is observed with the centroid-to-centroid distance of 0.359 5(9) nm (Fig.3).



Symmetry code: ⁱ $1+x, 1+y, z$; ⁱⁱ $-x, -y, 2-z$; ⁱⁱⁱ $1+x, y, -1+z$; ^{iv} $2-x, 1-y, 1-z$

Fig.2 Intrachain hydrogen bonds formed in **1**

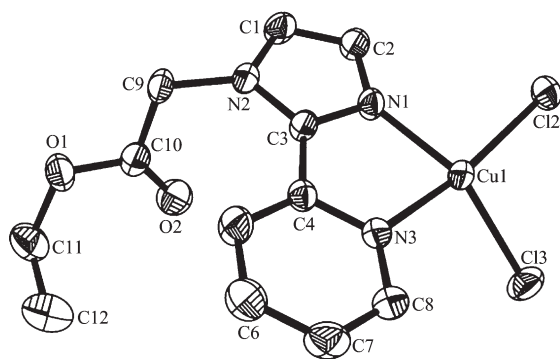
Dashed lines indicate hydrogen bonds

Fig.3 A view of the packing of the organic groups

2.2 Structural description of complex **2**

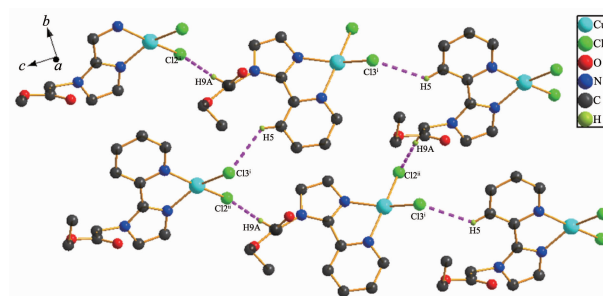
The crystal structure of complex **2** is shown in Fig.4. The four-coordination of Cu(II) atom can be best described as a slightly distorted polyhedron formed by two chelating nitrogen atoms from the imidazole ring

and pyridine ring of one ligand, two chlorine anions from CuCl_2 . The main distortion of the ideal quadrilateral plane geometry is due to the short bite angle of the bidentate ligand PMA. The imidazole ring and pyridine ring are nearly coplanar, making a dihedral angle of 7.9° . The bond distances of Cu1-N1, Cu1-Cl2 and Cu1-N3 in the quadrilateral plane are 0.197 6(2) nm, 0.223 56(9) nm and 0.203 3(2) nm, respectively. The bond angles of N1-Cu1-N3, N1-Cu1-Cl2 and N1-Cu1-Cl3 are $95.9(3)^\circ$, $95.3(2)^\circ$ and $95.1(3)^\circ$, respectively. All these observations implied that the geometry around the Cu(II) in **2** should be an elongated distorted polyhedron. Furthermore, the units are linked into a 2D layer structure by C-H \cdots Cl hydrogen-bonding interactions between the neighboring ligands (Fig.5), including interactions of C5-H5 \cdots Cl3ⁱ with the distance of 0.274 74 nm and C9-H9A \cdots Cl2ⁱⁱ with the distance of 0.266 95 nm (Symmetry code: ⁱ $x, 3/2-y, 1/2+z$; ⁱⁱ $x, 5/2-y, 1/2+z$). In addition, weak C-H \cdots O interactions are also observed for the stabilization of structural elements.



Hydrogen atoms were omitted for clarity

Fig.4 Crystal structure of complex **2** with 30% thermal ellipsoids



Symmetry code: ⁱ $x, 3/2-y, 1/2+z$; ⁱⁱ $x, 5/2-y, 1/2+z$

Fig.5 Hydrogen-bonding between the mono-molecules of complex **2**

2.3 UV-Vis spectra and fluorescent spectra analysis

The UV-Vis spectra of the complexes **1** and **2** in methanol solutions with the concentration of $10^{-5} \text{ mol} \cdot \text{L}^{-1}$ at room temperature are shown in Fig.6. Complex **1** shows an intense absorption band at 324 nm and a weak one at 290 nm, and complex **2** shows intense absorption band at 304 nm and weak band at 264 nm. The former is owing to the $\pi-\pi^*$ transition of the coordination between the ligand and the metal ions. The emission spectra of **1** and **2** were measured in methanol solution with the concentration of $10^{-5} \text{ mol} \cdot \text{L}^{-1}$ at room temperature, as depicted in Fig.7. The complex **1** displays a weak photoluminescence with an emission maximum at 417 nm when the exciting radiation was set at 324 nm, and a strong fluorescence emission peak of complex **2** is found at 353 nm when the exciting radiation was set at 304 nm. The observed strong photoluminescence of **2** indicates that the compound can be an excellent candidate for potential application as a photoactive material.

2.4 Thermal analyses

2.4.1 TG and DSC analysis of complex **1**

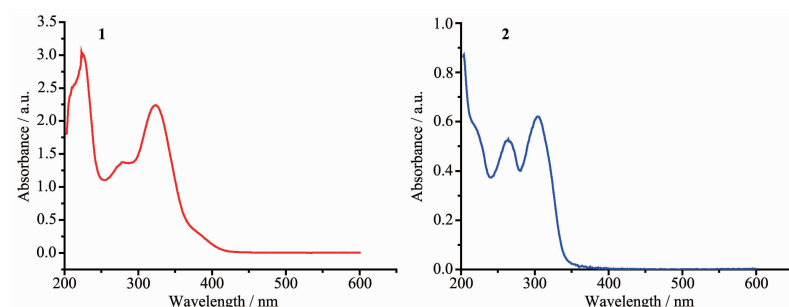
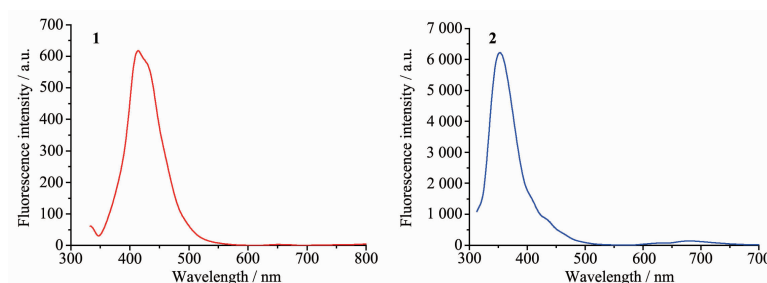


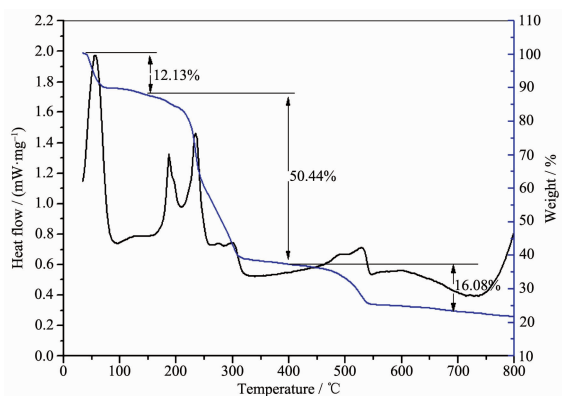
Fig.6 UV-Vis absorption spectra of complexes **1** and **2**

Fig.7 Fluorescent emission spectra of complexes **1** and **2** at room temperature

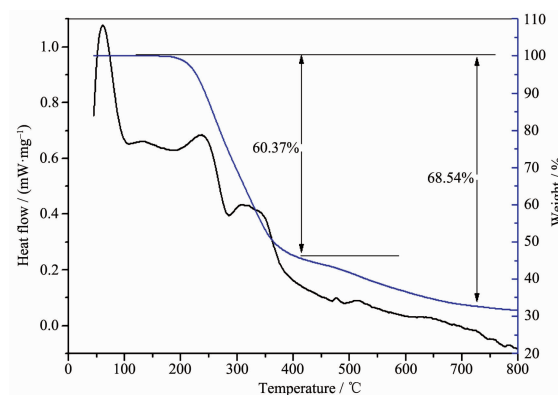
The thermal stability of complex **1** has been analyzed by thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) (Fig.8). As TGA curves show, the weight loss of 12.13% (Calcd. 12.44%) from room temperature to 160 °C, corresponds to the escape of one solvent water molecule and one benzoate anion. With the increase of temperature, the second weight loss of 50.44% (Calcd. 48.01%) from 160 °C to 400 °C results from the decomposition of the excess of benzoate anions and one DMPM ligand. With the temperatures continue to rise, decomposition of complex **1** become slow, the total weight loss at 790 °C is 78.65%.

2.4.2 TG and DSC analysis of complex **2**

The thermal stability of complex **2** has been analyzed by thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) (Fig.9). As TGA curves show, Complex **2** did not show obvious weight losses before the decomposition of the framework at about 200 °C indicating no solvent molecules and being in agreement with the result of the crystal structure. With the increase of temperature, the sharp continual weight decrease from 200 °C to 400 °C

Fig.8 TG and DSC curves of complex **1**

corresponds to the release of PMA ligand with the weight loss of 60.37% (Calcd. 63.17%). The total weight loss at 790 °C is 68.54%.

Fig.9 TG and DSC curves of complex **2**

2.5 ESR of complexes **1** and **2**

The complex containing unpaired electrons in general is paramagnetic. The movement of electron spin can produce spin magnetic moment. When we put the spin magnetic moment in a magnetic field its energy level split (Zeeman Effect), because the spin magnetic moment in the magnetic field has two kinds of sports orientation. The division of the energy level difference is:

$$\Delta E = g\beta H \quad (1)$$

(g : Lande factor, β : Bohr magneton, H : Magnetic field)

If we add an electromagnetic radiation field near the magnetic field, and its frequency type satisfies the equation:

$$h\nu = g\beta H \quad (2)$$

(h : Planck constant, ν : Frequency)

The system can absorb energy, making the low level of the spin transit to high level, and the electron paramagnetic resonance happened.

The ESR spectrum of complexes **1** and **2** consist

of one intense and asymmetric line with $g=2.101\ 7$ and $g=2.126\ 5$ (Fig.10); the asymmetric nature could result from the superposition of more than one resonance

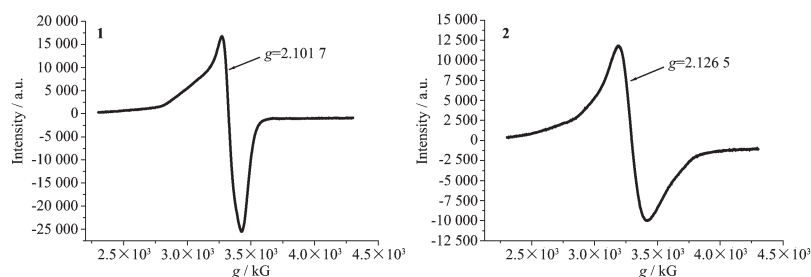


Fig.10 ESR spectrum of complexes **1** and **2**

3 Conclusions

Two Cu (II) complexes based on 2-(2-pyridyl) imidazole derivatives have been synthesized and characterized in detail by X-ray crystal structure analyses. For the title complexes, the 1D hydrogen-bonded chains of complex **1** are assembled into 3D network by intermolecular hydrogen bonding and π - π stacking interactions. The ethyl [2-(2-pyridyl) imidazole-1-yl]acetate ligand adopts a bidentate chelating mode to link metal ions into mononuclear units, and complex **2** are assembled into a 2D layer structure by intermolecular hydrogen-bonding interactions. The Fluorescent Spectra of **1** and **2** in methanol solutions exhibit emission peaks with wavelengths of 417 and 353 nm respectively. Complex **2** shows remarkable thermal stabilities. ESR spectra show that $g_1=2.101\ 7$, $g_2=2.126\ 5$. Not only fluorescence properties, but also thermal analyses suggest the potential application of **1** and **2** as a photoactive material.

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