

## 两个 Schiff 碱铜配合物的合成、晶体结构、光谱性质 及取代基效应

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**摘要:** 合成了 2 个含脒基 Schiff 碱 Cu(II)配合物  $[\text{Cu}(\text{L}^1)_2](\mathbf{1})$  和  $[\text{Cu}(\text{L}^2)_2](\mathbf{2})$  ( $\text{HL}^1=1-(3-((2\text{-hydroxybenzylidene)amino) phenyl) ethanone } O\text{-benzyl oxime}$ ;  $\text{HL}^2=1-(3-((2\text{-Hydroxy-naphthalen-1-ylmethylene)-amino)-phenyl)-ethanone oxime}$ ), 并通过元素分析、红外光谱、紫外光谱、荧光光谱及 X 射线单晶衍射分析进行了表征和分析。结果表明, 配合物 **1** 和 **2** 具有相似的结构, 均由 1 个中心 Cu(II)离子和 2 个双齿配体单元组成, 且 Cu(II)离子的配位数为 4, 具有平面四边形结构。配合物 **1** 和 **2** 均形成了二维层状超分子结构, 不同的是配合物 **1** 通过分子间  $\pi \cdots \pi$  堆积作用相连接, 而配合物 **2** 通过分子间 O-H $\cdots$ N 和 C-H $\cdots$  $\pi$  氢键作用而形成了超分子结构。进一步讨论了配合物 **1** 的荧光性质及两个配合物间配体的取代基效应。

**关键词:** 铜(II)配合物; 晶体结构; Schiff 碱配体; 取代基效应

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2016)02-0327-09

DOI: 10.11862/CJIC.2016.034

## Two Cu(II) Complexes with Schiff Base Ligands: Syntheses, Crystal Structures, Spectroscopic Properties, and Substituent Effect

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**Abstract:** Two new Cu(II) complexes  $[\text{Cu}(\text{L}^1)_2](\mathbf{1})$  ( $\text{HL}^1=1-(3-((2\text{-hydroxybenzylidene)amino) phenyl) ethanone } O\text{-benzyl oxime}$ ) and  $[\text{Cu}(\text{L}^2)_2](\mathbf{2})$  ( $\text{HL}^2=1-(3-((2\text{-Hydroxy-naphthalen-1-ylmethylene)-amino)-phenyl)-ethanone oxime}$ ) have been synthesized and characterized by elemental analyses, IR spectra, UV-Vis spectra, fluorescence measurement and X-ray single crystal diffraction method. X-ray crystallographic analyses have indicated that complexes **1** and **2** have the similar structure, consisting of one Cu(II) ion, two ligand units. In the complexes, the Cu(II) ion lying on an inversion centre, is four-coordinated in a *trans*- $\text{CuN}_2\text{O}_2$  square-planar geometry by two hydroxy O and two imine N atoms from two symmetry-related N,O-bidentate Schiff base ligands. The supramolecular structures of the two complexes **1** and **2** are also similar two-dimensional supramolecular structure linking by different intermolecular interaction. Complex **1** forms an infinite two-dimensional supramolecular structure by two  $\pi \cdots \pi$  interaction, while that of complex **2** by intermolecular O-H $\cdots$ N and C-H $\cdots$  $\pi$  hydrogen bond interactions. The fluorescence property of complex **1** and substituent effects of the two complexes are discussed. CCDC: 1003363, **1**; 1043506, **2**.

**Keywords:** Cu(II) complex; crystal structure; Schiff base ligand; substituent effect

收稿日期: 2015-09-08。收修改稿日期: 2015-11-25。

兰州交通大学青年科学基金(No.2011007)、兰州交通大学研究生教改项目(No.160012)和甘肃省科技支撑计划项目(No.1204GKCA052)资助。

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## 0 Introduction

Schiff base compounds have been playing an important part in the development of coordination chemistry because of their potential application in catalysis<sup>[1-2]</sup>, bioscience<sup>[3-4]</sup>, new materials<sup>[5]</sup>, magnetic properties<sup>[6-9]</sup> and constructing supramolecular structures<sup>[10-11]</sup>. Also, the Schiff base ligands are strong donors and therefore the oxime-containing ligands were found to efficiently stabilize high oxidation states of metal ions like Cu(II) and Ni(II). The presence of additional donor groups together with the oxime group in the ligand molecule may result in significant increase of chelating efficiency and ability to form polynuclear complexes. Herein, two new Cu(II) complexes with the Schiff base ligand, [Cu(L<sup>1</sup>)<sub>2</sub>] (**1**) (HL<sup>1</sup>=1-(3-((2-hydroxybenzylidene)amino)phenyl)ethanone *O*-benzyl oxime) and [Cu(L<sup>2</sup>)<sub>2</sub>] (**2**) (HL<sup>2</sup>=1-(3-((2-Hydroxynaphthalen-1-ylmethylene)-amino)-phenyl)-ethanone oxime) have been synthesized and characterized by elemental analyses, IR spectra, UV-Vis spectra, fluorescence measurement and X-ray single crystal diffraction. X-ray crystallographic analyses reveal that the structures of the complexes **1** and **2** are very similar. They are both mononuclear structures and all

the Cu(II) ions are four-coordinated.

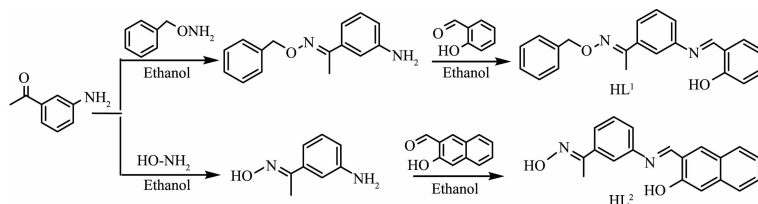
## 1 Experimental

### 1.1 Materials

3-Aminoacetophenone, *O*-benzylhydroxylamine, salicylaldehyde and 2-hydroxy naphthaldehyde were purchased from Alfa Aesar and used without further purification. The other reagents and solvent were analytical grade from Tianjin Chemical Reagent Factory.

### 1.2 Methods

C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. Elemental analysis for Cu was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. FTIR spectra were recorded on a VERTEX70 FTIR spectrophotometer, with samples prepared as KBr pellet (400~4000 cm<sup>-1</sup>). UV-Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. X-Ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.



Scheme 1 Synthetic routes of HL<sup>1</sup> and HL<sup>2</sup>

### 1.3 Syntheses of HL<sup>1</sup> and HL<sup>2</sup>

HL<sup>1</sup> (1-(3-((2-hydroxybenzylidene)amino)phenyl)ethanone *O*-benzyl oxime) and HL<sup>2</sup> (1-(3-((2-Hydroxynaphthalen-1-ylmethylene)-amino)-phenyl)-ethanone oxime) were synthesized according to the reported method (Scheme 1)<sup>[12-13]</sup>.

### 1.4 Synthesis of [Cu(L<sup>1</sup>)<sub>2</sub>] (**1**)

A solution of copper(II) acetate monohydrate (1.3 mg, 0.007 mmol) in methanol (4 mL) was added dropwise to a solution of HL<sup>1</sup> (1.7 mg, 0.005 mmol) in

dichloromethane (5 mL) at room temperature. The mixing solution turned to yellow immediately. Then it was filtered and the filtrate was allowed to stand at room temperature for about one week. Brown red block single crystals which is suitable for X-ray structural determination were obtained. Anal. Calcd. for C<sub>44</sub>H<sub>38</sub>CuN<sub>4</sub>O<sub>4</sub> (%): C, 70.43; H, 5.10; N, 7.47; Cu, 8.47. Found (%): C, 70.38; H, 5.17; N, 7.45; Cu, 8.50.

### 1.5 Synthesis of [Cu(L<sup>2</sup>)<sub>2</sub>] (**2**)

A solution of copper(II) acetate monohydrate (2.3

mg, 0.01 mmol) in methanol (3 mL) was added dropwise to a solution of HL<sup>2</sup> (1.5 mg, 0.005 mmol) in dichloromethane (5 mL) at room temperature. The color of the mixing solution turned yellow immediately, and it was allowed to stand at room temperature for three weeks. Then the solvent partially evaporated and red-brown prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calcd. for C<sub>38</sub>H<sub>30</sub>CuN<sub>4</sub>O<sub>4</sub>(%): C, 68.10; H, 4.51; N, 8.36; Cu, 9.48. Found(%): C, 67.98; H, 4.57; N, 8.29; Cu, 9.52.

### 1.6 Crystal structure determination

The single crystals of complexes with approximate dimensions of 0.21×0.11×0.05 mm(**1**) and 0.18×0.14×0.09 mm(**2**) were placed on a Bruker Smart 1000 CCD area detector. The diffraction data were collected using a graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) at 298(2) K. Empirical

absorption correction was applied to the data using SADABS program<sup>[14]</sup>. The structure was solved by direct methods and refined by full-matrix leastsquares method on  $F^2$  using the SHELXTL program<sup>[15]</sup>. All nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details of the crystal parameters, data collection and refinements for complexes **1** and **2** are summarized in Table 1.

## 2 Results and discussion

### 2.1 IR spectra analyses

The FTIR spectra of HL<sup>1</sup>, HL<sup>2</sup> and their corresponding Cu (II) complexes **1** and **2** exhibit various bands in the 400~4 000 cm<sup>-1</sup> region. The most important FTIR bands for HL<sup>1</sup>, HL<sup>2</sup> and complex **1~2** are given in Table 2. The free ligand HL<sup>1</sup> and HL<sup>2</sup> exhibit characteristic C=N stretching bands at 1 617

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

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>44</sub> H <sub>38</sub> CuN <sub>4</sub> O <sub>4</sub>	C <sub>38</sub> H <sub>30</sub> CuN <sub>4</sub> O <sub>4</sub>
Formula weight	750.32	670.21
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
$a$ / nm	0.781 30(6)	2.940 0(4)
$b$ / nm	0.939 05(8)	0.584 20(7)
$c$ / nm	1.237 2(1)	1.870 0(2)
$\alpha$ / (°)	94.549(2)	90
$\beta$ / (°)	93.738(1)	102.660(2)
$\gamma$ / (°)	91.377(1)	90
$V$ / nm <sup>3</sup>	0.902 6(1)	3.159 3(4)
$Z$	1	4
$D_c$ / (g·cm <sup>3</sup> )	1.380	1.409
$\mu$ / (mm <sup>-1</sup> )	0.656	0.740
$F(000)$	391	1 388
$\theta$ range for data collection / (°)	2.61~25.02	1.41~25.10
Limiting indices	$-7 \leq h \leq 9$ ; $-9 \leq k \leq 11$ ; $-14 \leq l \leq 13$	$-35 \leq h \leq 33$ ; $-6 \leq k \leq 6$ ; $-22 \leq l \leq 22$
Reflections collected, unique	4 607, 3 119( $R_{int}$ =0.073 4)	7 968, 2 805( $R_{int}$ =0.086 0)
Completeness to $\theta$ / %	97.8( $\theta$ =25.02°)	100%( $\theta$ =25.10°)
Data, restraints, parameters	3 119, 0, 242	2 085, 0, 216
GOF on $F^2$	1.027	0.965
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.080$ 0, $wR_2=0.175$ 8	$R_1=0.057$ 0, $wR_2=0.130$ 1
$R$ indices (all data)	$R_1=0.128$ 9, $wR_2=0.196$ 5	$R_1=0.107$ 3, $wR_2=0.157$ 4
$(\Delta\rho)_{max}$ , $(\Delta\rho)_{min}$ / (e·nm <sup>-3</sup> )	521, -526	941, -876

**Table 2** Main bands in IR spectra of the ligand HL<sup>1</sup>, HL<sup>2</sup> and their Cu(II) complexes

	$\nu(\text{C}=\text{N})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Cu}-\text{O})$	$\nu(\text{C}=\text{C})$ benzene ring skeleton		
HL <sup>1</sup>	1 617	1 178	-	-	1 564	1 490	1 452
Complex <b>1</b>	1 600	1 144	540	503	1 531	1 500	1 445
HL <sup>2</sup>	1 620	1 182	-	-	1 589	1 543	1 483
Complex <b>2</b>	1 602	1 137	519	463	1 548	1 526	1 456

and 1 620  $\text{cm}^{-1}$ , while that of complex **1** and complex **2** were observed in the 1 600  $\text{cm}^{-1}$  and 1 602  $\text{cm}^{-1}$ , respectively. The C=N stretching frequencies are all shifted to lower frequencies by ca. 17 and 18  $\text{cm}^{-1}$  upon complexation respectively, indicating a decrease in the C=N bond order due to the coordinated bond of the Cu(II) atom with the imino nitrogen lone pair<sup>[16]</sup>. In the 1 445~1 564  $\text{cm}^{-1}$  region, the observed bands were attributed to aromatic C=C vibrations. Upon coordination these bands shift to lower frequencies for the Cu(II) complexes<sup>[17]</sup>. The Ar-O stretching frequency appears as a strong band within the 1 178~1 144  $\text{cm}^{-1}$  as reported for similar ligands<sup>[18]</sup>. This band occurs at 1 178  $\text{cm}^{-1}$  for the ligand HL<sup>1</sup>, and at 1 144  $\text{cm}^{-1}$  for complex **1**, the band occurs at 1 182  $\text{cm}^{-1}$  for the ligand HL<sup>2</sup>, and at 1 137  $\text{cm}^{-1}$  for complex **2**. The Ar-O stretching frequency is shifted to a lower frequency, indicating that the Cu-O bond was formed between the Cu(II) ion and phenolic oxygen atom of phenolic hydroxyl group<sup>[13]</sup>. The far-infrared spectra of complexes **1** and **2** was also obtained in the region 500~100  $\text{cm}^{-1}$  in order to identify frequencies due to the Cu-O and Cu-N bonds. The FTIR spectrum of complex **1** showed  $\nu(\text{Cu}-\text{N})$  and  $\nu(\text{Cu}-\text{O})$  vibration absorption frequencies at 540  $\text{cm}^{-1}$  and 503  $\text{cm}^{-1}$  (or 519 and 463  $\text{cm}^{-1}$  for complex **2**), respectively. These assignments are consistent with the literature frequency values<sup>[19]</sup>.

## 2.2 UV-Vis absorption spectra analyses

The absorption spectra of ligand HL<sup>1</sup> and its corresponding Cu(II) complex **1** were determined in diluted  $\text{CH}_2\text{Cl}_2$  solution, and ligand HL<sup>2</sup> and its corresponding Cu(II) complex **2** were determined in diluted DMF solution as shown in Fig.1 and Fig.2.

UV-Vis spectrum of the free ligand HL<sup>1</sup> exhibits three absorption peaks at ca. 224, 262 and 347 nm

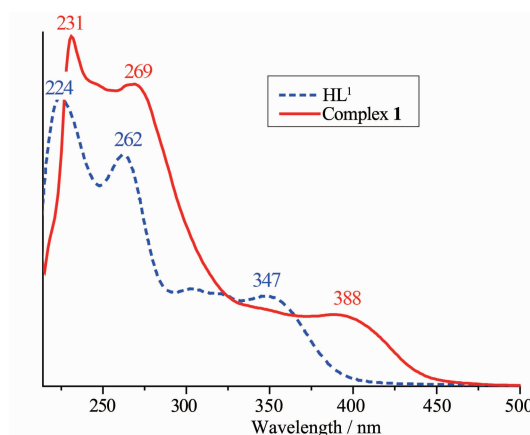


Fig.1 UV-Vis absorption spectra of HL<sup>1</sup> and the complex **1** in diluted  $\text{CH}_2\text{Cl}_2$  solution at room temperature ( $c=5\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ )

(Fig.1). The absorption peak of HL<sup>1</sup> at 224 nm assigned to the  $\pi-\pi^*$  transition of the benzene rings shifts to low energy region by ca. 7 nm in complex **1**, indicating Cu(II) ion coordinated with the O and N atoms of ligand units. The absorption peak of HL<sup>1</sup> at 262 nm attributed to the intra-ligand  $\pi-\pi^*$  transition of the C=N bonds is shifted to 269 nm in complex **1** upon complexation. The absorption peak of HL<sup>1</sup> at 347 nm is absent in complex **1**, however, a new absorption peak is observed at 388 nm assigned to an L→M charge-transfer transition which is characteristic of a transition metal complex with  $\text{N}_2\text{O}_2$  coordination sphere<sup>[20]</sup>. It can be seen that the absorption peaks of complex **2** are obviously different from those of the HL<sup>1</sup> upon complexation (Fig.2). Compared with complex **2**, an important feature of the absorption spectrum of HL<sup>2</sup> is shown that three absorption peaks are observed at 243, 382 and 437 nm, which are absent in the spectrum of complex **2**. The other feature is that the absorption peak at 267 and 320 nm in HL<sup>2</sup> is shifted to 269 and 311 nm in complex **2**, respectively, indicating that the coordination of Cu(II)

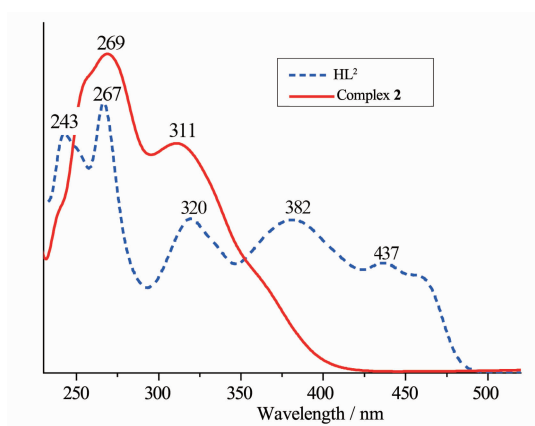
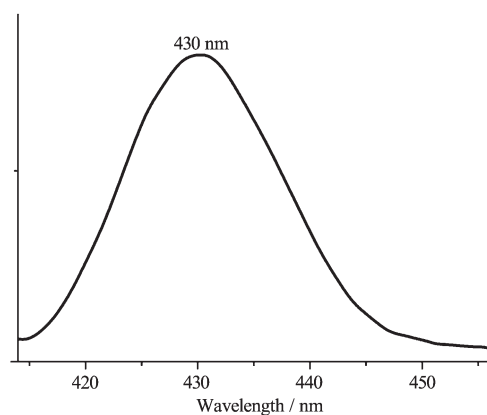


Fig.2 UV-Vis absorption spectra of HL<sup>2</sup> and the complex **2** in diluted DMF solution at room temperature ( $c=5\times 10^{-5}$  mol·L<sup>-1</sup>)

atom with HL<sup>2</sup>.

### 2.3 Fluorescence spectra

The emission spectrum of the complex **1** in



$c=5.00\times 10^{-5}$  mol·L<sup>-1</sup>,  $\lambda_{ex}=311$  nm,  $\lambda_{em}=430$  nm

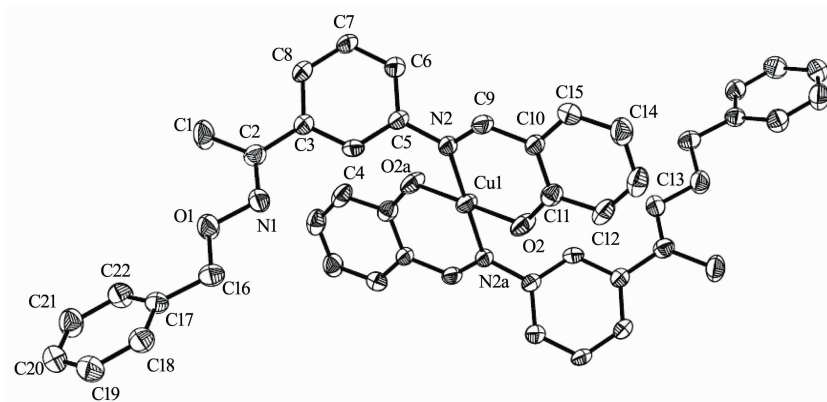
Fig.3 Emission spectrum of the complex **1** in diluted CH<sub>2</sub>Cl<sub>2</sub> at room temperature

diluted CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature is shown in Fig.3. An intense excitation peak is observed at 311 nm. The bluish violet emission for complex **1** can be observed, where the maximum emission wavelength was at 430 nm. The Stokes shift between the maximum wavelength of the fluorescence emission and the fluorescence excitation is 119 nm. This red-shift might be related to the coordination of the Cu(II) atom to the ligand and increase of the rigidity of the ligands, which can diminish the loss of energy via vibrational motions and increase the emission efficiency.

### 2.4 Structural Description of the complexes **1** and **2**

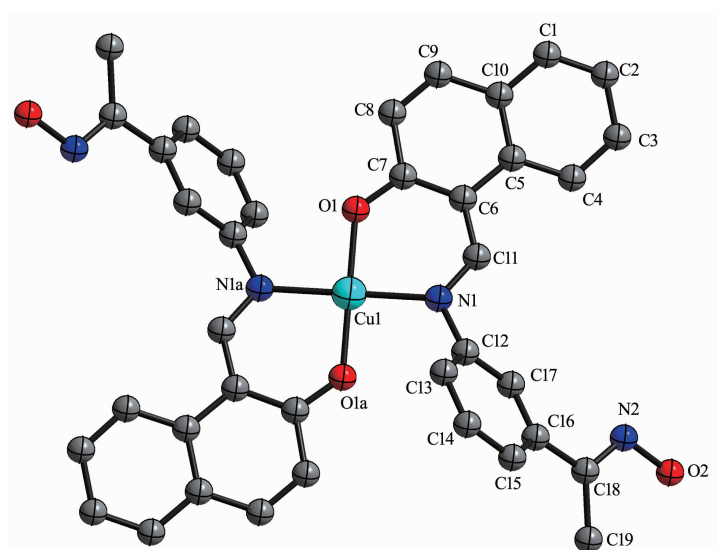
The single crystal structures of complexes **1** and **2** were confirmed by X-ray crystallography (Fig.4 and 5). The selected bond lengths and angles of complexes **1** and **2** are listed in Table 3. The complex **1** crystallizes in the triclinic system and  $P\bar{1}$  space group, whereas the complex **2** crystallizes in the monoclinic system and  $C2/c$  space group. Both of the complexes can be described as centrosymmetric mononuclear Cu(II) complexes. The Cu(II) ion lying on the inversion centre, is four-coordinated in a *trans*-CuN<sub>2</sub>O<sub>2</sub> square-planar geometry, with two phenolic O and two imino N atoms from two N,O-bidentate oxime-type ligands (HL<sup>1</sup> and HL<sup>2</sup>).

As shown in Fig.6, complex **1** is stabilized by the  $\pi_{\text{centroid}}(\text{C10-C15})-\pi_{\text{centroid}}(\text{C10-C15})$  stacking interactions of benzene rings linking the neighboring molecules into a 1D infinite chain parallel to the *a* axis (Table 4). In addition, this adjacent chains along *a* axis are further



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

Fig.4 Molecular structure of complex **1** showing 30% probability displacement ellipsoids



Symmetry code: a:  $-x, 1-y, 2-z$

Fig.5 Molecular structure of complex **2** showing 30% probability displacement ellipsoids

Table 3 Selected bond lengths(nm) and bond angles( $^{\circ}$ ) for complexes **1** and **2**

<b>1</b>					
Cu1-O2a	0.188 8(4)	Cu1-O2	0.188 8(4)	Cu1-N2a	0.200 0(4)
Cu1-N2	0.200 0(4)				
O2a-Cu1-O2	180.00(1)	O2-Cu1-N2a	88.35(2)	N2a-Cu1-N2	180.00(2)
C5-N2-Cu1	121.8(4)	O2a-Cu1-N2a	91.65(2)	O2a-Cu1-N2	88.35(2)
C9-N2-Cu1	121.5(3)	C11-O2-Cu1	127.0(4)		
<b>2</b>					
Cu1-O1b	0.188 5(3)	Cu1-O1	0.188 5(3)	Cu1-N1b	0.201 4(3)
Cu1-N1	0.201 4(3)				
O1-Cu1-O1b	180.00(9)	O1-Cu1-N1b	89.61(1)	N1b-Cu1-N1	179.99(2)
C12-N2-Cu1	120.7(3)	O1b-Cu1-N1b	90.39(1)	O1b-Cu1-N1	89.61(1)
C11-N2-Cu1	123.1(3)	C7-O1-Cu1	130.5(3)		

Symmetry codes: a:  $1-x, 1-y, 1-z$  for **1**; b:  $-x, -y+1, -z+2$  for **2**

Table 4 Putative  $\pi$ - $\pi$  stacking interactions for complex **1**

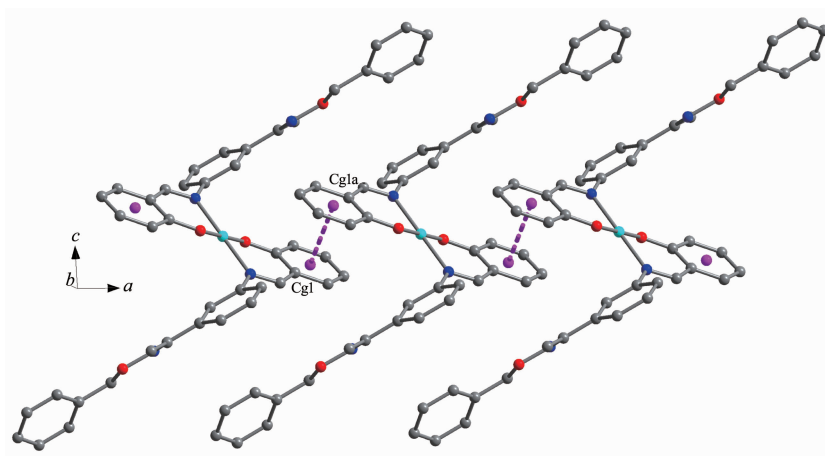
Ring(I)	Ring(J)	$d(\text{Cg-Cg}) / \text{nm}$	$d(\text{Cg(I)-perp}) / \text{nm}$	$d(\text{Cg(J)-perp}) / \text{nm}$	Slippage / nm
Cg1*	Cg1	0.406 6(4)	0.353 8(3)	0.353 7(3)	0.200 5
Cg2*	Cg2	0.387 2(4)	0.357 3(3)	0.357 3(3)	0.149 2

\*Cg1 and Cg2 are the centroids of benzene ring C10-C15 and C17-C22 of complex **1**, respectively

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

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^{\circ})$	Symmetry code
O2-H2A $\cdots$ N2	0.082 0	0.208	0.278 9 (6)	145	$1/2-x, 3/2-y, 2-z$
C17-H17 $\cdots$ Cg3*	0.093 0	0.295	0.379 8(4)	153	$x, 1+y, z$

\*Cg3 is the centroid of benzene ring C1-C5-C10 of complex **2**



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

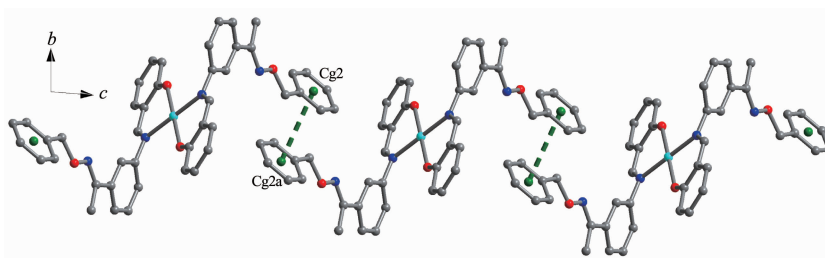
Fig.6 View of the 1D single chain motif within complex **1** along the  $a$  axis

held together by the other intermolecular  $\pi_{\text{centroid(C17-C22)}} - \pi_{\text{centroid(C17-C22)}}$  stacking interactions (Fig.7) to form 2D supramolecular structure parallel to the  $ac$  planes (Fig.8). Whereas in complex **2**, as illustrated in Fig.9, each oxime nitrogen atom N2 of the two ligand molecules is hydrogen-bonded to the -O2H2A group of the oxime group from the other neighboring molecule, which resulted in the formation of a classical six-member ring and a 1D infinite chain synchronously.

Furthermore, this linkage is further stabilized by four C17-H17 $\cdots\pi$ (Cg3) interactions to form the 2D infinite supramolecular planar (Fig.10 and Table 5).

## 2.5 Substituent effects

The overall structures of the two complexes are found to be identical except that the oxime portion and aromatic ring differs in the ligands. The bond lengths of complex **1** are different from those of complex **2** due to the different substituent group in



Symmetry code:  $a: 3-x, 1-y, 2-z$

Fig.7 View of the 1D single chain motif within complex **1** along the  $c$  axis

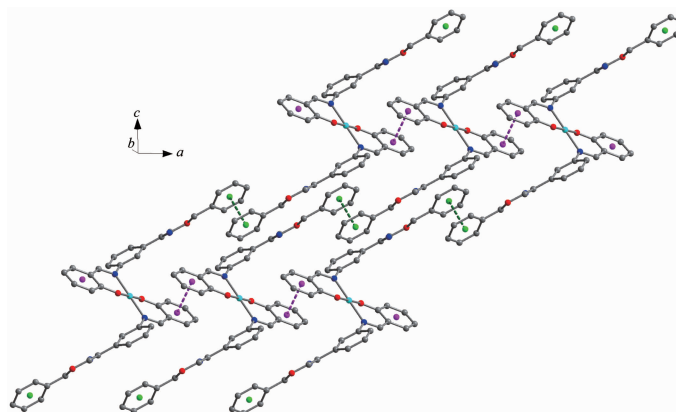
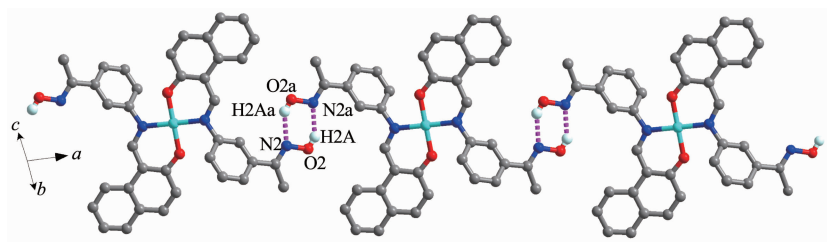


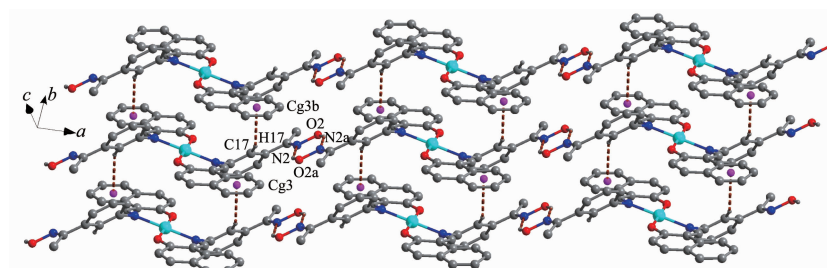
Fig.8 Part of 2D supramolecular structure of the complex **1** showing the formation the two  $\pi\cdots\pi$  stacking interaction





Hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity; Symmetry code: a:  $1/2-x, 3/2-y, 2-z$

Fig.9 View of a 1D single chain motif containing hydrogen bonds for complex **2**



Symmetry code: a:  $1/2-x, 3/2-y, 2-z$ ; b:  $x, 1+y, z$

Fig.10 Part of 2D supramolecular structure of the complex **2** showing the formation of C17-H17...Cg3 and O2-H2A...N2 hydrogen bond

the bidentate ligands. In both bases, two imino nitrogen and two phenolic oxygen atoms form the square base with the Cu-N bonds being slightly longer than the corresponding Cu-O bonds. The elongation of the Cu-N bonds probably due to the weaker coordination ability of the nitrogen atom than that of phenolic oxygen atom. Similar elongation has been observed in Cu(II) complexes with Schiff base ligands<sup>[21-22]</sup>. However, the coordination bond Cu-N (0.200 0 nm) of complex **1** is shorter than the Cu-N (0.201 4 nm) of complex **2**, but Cu-O (0.188 8 nm) of complex **1** is almost equal to the Cu-O (0.188 5 nm) of complex **2**. Meanwhile, the angle of N2-Cu1-O2 (88.35°) in complex **1** is smaller with the angle of N1-Cu1-O1 (89.61°) in complex **2**. In addition, the supramolecular structures of the two complexes **1** and **2** are also similar two-dimensional supramolecular structure linking by different intermolecular interaction, in which complex **1** is stabilized by two  $\pi \cdots \pi$  interaction, while that of complex **2** by intermolecular O-H...N and C-H... $\pi$  hydrogen bond interactions. The substituent effects also give rise to the variations in IR and UV-Vis spectra in complexes **1** and **2**.

### 3 Conclusions

According to the data and discussion above, two Schiff base mononuclear Cu(II) complexes **1** and **2** have been synthesized and characterized structurally. The Cu(II) complexes are tetra-coordinated by two nitrogen atoms and two oxygen atoms of two deprotonated L<sup>-</sup> units defining the N<sub>2</sub>O<sub>2</sub> basal plane. The coordination environment around Cu(II) atom is best regarded as the square-planar geometry. Complexes **1** and **2** also formed a 2D -layer supramolecular structure by different intermolecular interaction,  $\pi \cdots \pi$  interaction and O-H...N, C-H... $\pi$  hydrogen bond interactions, respectively. Consequently, the intermolecular non-classical hydrogen-bonding plays a very important role in the construction of supramolecular networks structure. Furthermore, the substituted groups on the ligands could play a small impact on the coordination geometries and supramolecular structure of complexes **1** and **2**.

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