

含肟基的 Schiff 碱 Cu(II)和 Ni(II)配合物的合成、超分子结构和光谱性质

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摘要: 合成了 2 个含肟基 Schiff 碱的 Cu(II)和 Ni(II)配合物 $[\text{Cu}(\text{L}^1)_2] \cdot (1,4\text{-dioxane})$ (**1**)和 $[\text{Ni}(\text{L}^2)_2]$ (**2**),并通过元素分析、红外光谱、紫外可见光谱、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** 均包含 1 个中心金属离子和 2 个双齿配体单元,且金属离子的配位数均为 4,均具有轻微扭曲的平面四边形几何构型。不同的是配合物 **1** 通过分子间氢键以及 $\pi \cdots \pi$ 堆积作用相连接形成了三维超分子结构,而配合物 **2** 仅通过分子间的 $\pi \cdots \pi$ 堆积作用形成了一条一维超分子链。

关键词: Schiff 碱配体; Cu(II)和 Ni(II)配合物; 超分子结构; 荧光性质

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Syntheses, Supramolecular Structures and Spectroscopic Properties of Cu(II) and Ni(II) Complexes with Schiff Base Containing Oxime Group

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Abstract: Two Cu(II) and Ni(II) complexes, $[\text{Cu}(\text{L}^1)_2] \cdot (1,4\text{-dioxane})$ (**1**) ($\text{HL}^1 = 8\text{-}(((4\text{-}(1\text{-}((\text{benzyloxy})\text{imino})\text{ethyl})\text{phenyl})\text{imino})\text{methyl})\text{-}7\text{-hydroxy}\text{-}4\text{-methyl}\text{-}2H\text{-chromen}\text{-}2\text{-one})$) and $[\text{Ni}(\text{L}^2)_2]$ (**2**) ($\text{HL}^2 = 1\text{-}(4\text{-}(((2\text{-hydroxynaphthalen}\text{-}1\text{-yl})\text{methylene})\text{amino})\text{phenyl})\text{ethanone } O\text{-benzyloxime})$), have been synthesized and characterized by elemental analyses, IR spectra, UV-Vis spectra, fluorescence spectra and X-ray single crystal diffraction method. X-ray crystallographic analysis shows that the Cu(II) and Ni(II) ions are all four-coordinated in a *trans*- N_2O_2 slightly distorted square-planar geometry by two hydroxy O and two imine N atoms from two N,O-bidentate Schiff base ligands. Moreover, complex **1** links some other molecules into an infinite 3D supramolecular structure by intermolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions, while complex **2** forms 1D infinite chain via intermolecular $\pi \cdots \pi$ stacking interactions. Furthermore, the fluorescence property of HL^1 , HL^2 and their metal complexes **1** and **2** are discussed. CCDC: 1542901, **1**; 1857932, **2**.

Keywords: Schiff base ligand; Cu(II) and Ni(II) complexes; supramolecular structure; fluorescence property

0 Introduction

Much attention has been focused on oxime-based ligands in recent years due to their high stability and playing an important role in the development of coordination chemistry [1-5]. The design of new Schiff-base

compounds has received long-lasting research interest because of not only their appealing structural and topological novelty [6-10] but also their potential wide application in the fields of biochemistry [11-16], catalysis [17-20] and optical [21-33], magnetic materials [34-40] and constructing supramolecular structures [41-52]. Schiff-base

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compounds and its derivatives are very important as versatile ligands, properties of interest in materials science. Also, the Schiff base ligands with N- and O-group are strong donors and therefore the oxime-containing ligands were found to efficiently stabilize high oxidation states of metal ions and prepare complexes with different structures and functionalities like Cu(II) and Ni(II) complexes^[53-58]. So, as an extension of our work^[9-10,55,59], two new Cu(II) and Ni(II) complexes, [Cu(L¹)₂] · (1,4-dioxane) (**1**) (HL¹ = 8-(((4-(1-((benzyloxy)imino)ethyl)phenyl)imino)methyl)-7-hydroxy-4-methyl-2H-chromen-2-one) and [Ni(L²)₂] (**2**) (HL² = 1-(4-(((2-hydroxynaphthalen-1-yl)methylene)amino)phenyl)ethanone *O*-benzyloxime), have been synthesized and characterized. Complexes **1** and **2** are both mononuclear structures and the central metal Cu(II) and Ni(II) ions are all four-coordinated with the slightly distorted square-planar geometry. In addition, the fluorescence property of HL¹, HL² and their metal complexes **1** and **2** are discussed.

1 Experimental

1.1 Materials

7-Hydroxy-4-methyl-chromen-2-one, hexamethylenetetramine, 4-aminoacetophenone, *O*-benzylhydroxy-

lamine, 2-hydroxy-1-naphthaldehyde were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory, and were used without further purification.

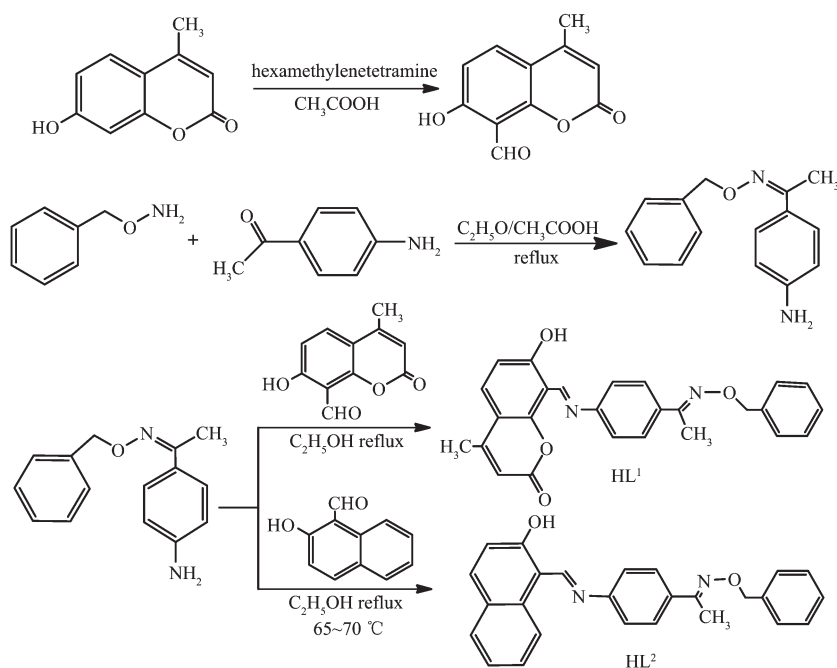
1.2 Instruments and methods

C, H and N analyses were carried out with a GmbH Vario EL V3.00 automatic elemental analyzer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (400~4 000 cm⁻¹) pellets. UV-Vis absorption spectra were recorded on a Shimadzu UV-3900 spectrometer. Luminescence spectra in solution were recorded on a Hitachi F-7000 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.

1.3 Syntheses of HL¹ and HL²

HL¹ and HL² were synthesized according to the following steps shown in Scheme 1.

HL¹: Firstly, 7-hydroxy-4-methyl-chromen-2-one 8.0 g (50 mmol) and hexamethylenetetramine 14.0 g (100 mmol) were dissolved in 50 mL glacial acetic



Scheme 1 Synthetic routes of HL¹ and HL²

acid, and the mixed solution was stirred and refluxed for 5~6 h. A 5% hydrochloric acid solution was added to adjust the pH value to about 4.5, and then refluxed and stirred for 30 min. The mixed solution was allowed to come to room temperature, then extracted with ether, washed with sodium chloride solution and dried with anhydrous MgSO_4 . After removing solvent and recrystallizing from absolute ethanol, 1.7 g crystalline solid of 7-hydroxy-4-methyl-2-oxo-2*H*-chromene-8-carbaldehyde was collected. Yield: 17%. m.p. 178~180 °C. Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{O}_4$ (%): C, 64.71; H, 3.95. Found(%): C, 65.04; H, 4.02.

Secondly, 1-(4-aminophenyl)ethan-1-one *O*-benzyl oxime was synthesized according to the reported method^[53] as yellow crystals. Yield: 874.3 mg, 80.6%. m.p. 80~81 °C. Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$ (%): C, 74.97; H, 6.71; N, 11.66. Found(%): C, 75.07; H, 7.35. N, 12.43.

At last, a solution of 1-(4-aminophenyl)ethan-1-one *O*-benzyl oxime (480.6 mg, 2.00 mmol) in ethanol (7.5 mL) was added to a solution of 7-hydroxy-4-methyl-2-oxo-2*H*-chromene-8-carbaldehyde (404.4 mg, 2.00 mmol) in ethanol (7.5 mL) and the mixture was heated to reflux at 65~70 °C for 7~8 h. After being cooled by ice-water bath, washed with an anhydrous ethanol solution and dried under reduced pressure, orange-red powder was obtained. Yield: 569.1 mg, 64.3%. m.p. 229~230 °C. Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4$ (%): C, 73.23; H, 5.20; N, 6.57. Found(%): C, 74.07; H, 6.05. N, 6.43.

HL^2 : The synthesis of HL^2 is similar to that of HL^1 except substituting 7-hydroxy-4-methyl-2-oxo-2*H*-chromene-8-carbaldehyde with 2-hydroxy-1-naphthaldehyde. The precipitate was filtered and washed successively with ethanol and ethanol/*n*-hexane (1:4, V/V), respectively. The product was dried in vacuum to obtain yellow powder. Yield: 79.43%. m.p. 127~129 °C. Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2$ (%): C, 79.17; H, 5.62; N, 7.10. Found(%): C, 80.03; H, 6.05. N, 7.46.

1.4 Syntheses of $[\text{Cu}(\text{L}^1)_2] \cdot (1,4\text{-dioxane})$ (**1**) and $[\text{Ni}(\text{L}^2)_2]$ (**2**)

Complex 1: A solution of copper (II) acetate monohydrate (0.51 mg, 0.002 5 mmol) in methanol (2 mL) was added dropwise to a solution of HL^1 (1.9 mg, 0.005 mmol) in 1,4-dioxane (2 mL) at room temperature. The color of the mixing solution turned to pale green immediately, and then the solution was filtered and the filtrate was allowed to stand at room temperature for about one week. Brown block-shape single crystals suitable for X-ray structural determination were obtained. Anal. Calcd. for $\text{C}_{56}\text{H}_{50}\text{CuN}_4\text{O}_{10}$ (%): C, 67.13; H, 5.03; N, 5.60. Found(%): C, 68.09; H, 5.64; N, 5.98.

Complex 2: The synthesis of complex **2** was same as above, and red-brown prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calcd. for $\text{C}_{52}\text{H}_{42}\text{NiN}_4\text{O}_4$ (%): C, 73.91; H, 5.01; N, 6.63. Found(%): C, 73.46; H, 4.68; N, 6.85.

1.5 X-ray crystallography of complexes **1** and **2**

The single crystals of complexes with approximate dimensions of 0.11 mm×0.16 mm×0.21 mm (**1**) and 0.28 mm×0.03 mm×0.02 mm (**2**) were placed on a Bruker Smart 1000 CCD area detector, respectively. The diffraction data of complexes **1** and **2** were collected using a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$) at 293.4(1) and 293.6(2) K, respectively. The Lp corrections were applied to the SAINT program^[60] and semi-empirical correction were applied to the SADABS program^[61]. The crystal structures were solved by the direct methods (SHELXS-2014)^[62]. All nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details of the data collection parameters and crystallographic information for complexes **1** and **2** are summarized in Table 1.

CCDC: 1542901, **1**; 1857932, **2**.

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

	1	2
Empirical formula	$\text{C}_{56}\text{H}_{50}\text{CuN}_4\text{O}_{10}$	$\text{C}_{52}\text{H}_{42}\text{NiN}_4\text{O}_4$
Formula weight	1 002.54	845.60

Continued Table 1

T / K	293.4(1)	293.6(1)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.990 6(3)	0.566 02(6)
b / nm	1.293 8(4)	1.058 5(2)
c / nm	1.958 3(5)	1.805 3(3)
$\alpha / (^{\circ})$	76.981(7)	76.312(17)
$\beta / (^{\circ})$	79.958(6)	89.215(11)
$\gamma / (^{\circ})$	81.130(5)	78.818(13)
V / nm^3	2.390 5(12)	1.030 3(3)
Z	2	1
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.393	1.363
μ / mm^{-1}	0.524	0.524
$F(000)$	1 046	442
θ range / $(^{\circ})$	2.2~25.0	3.800 0~20.172 0
Limiting indices	$-11 \leq h \leq 11, -15 \leq k \leq 15, -16 \leq l \leq 23$	$6 \leq h \leq 6, -12 \leq k \leq 13, -18 \leq l \leq 22$
Reflection collected, unique	12 625, 8 276 ($R_{\text{int}}=0.073$)	6 936, 1 749 ($R_{\text{int}}=0.081$ 3)
Completeness to $\theta / \%$	98.40 (25.0 $^{\circ}$)	99.86 (26.32 $^{\circ}$)
Max. and min. transmission	1.000 00 and 0.896	1.000 00 and 0.662 92
Data, restraint, parameter	8 276, 0, 645	4 034, 0, 278
GOF on F^2	1.015	1.025
$R_1, wR_2 [I > 2\sigma(I)]$	0.096 3, 0.235 0	0.086 6, 0.135 3
Largest diff. peak and hole / $(\text{e} \cdot \text{nm}^{-3})$	1 550 and -1 230	646 and -323

2 Results and discussion

2.1 IR spectra analyses

The FT-IR spectra of HL^1 , HL^2 and complexes **1** and **2** exhibited various bands in the 400~4 000 cm^{-1} region. The most important FT-IR bands for HL^1 , complex **1** and HL^2 , complex **2** are given in Table 2. HL^1 and HL^2 exhibited characteristic stretching bands of C=N group at 1 610 and 1 612 cm^{-1} , respectively^[63-69]. While those of complexes **1** and **2** were observed at the 1 580 and 1 597 cm^{-1} , respectively. Compared to the ligands, the C=N stretching frequencies of complexes **1** and **2** were both shifted to lower frequencies

by *ca.* 30 and 15 cm^{-1} , respectively, which indicated that the Cu(II) and Ni(II) ions coordinate with the oxime nitrogen lone pair^[70-72] in the C=N group, lowering the bond energy of the C=N bond. The stretching bands at 3 053 cm^{-1} (in HL^1) and 3 453 cm^{-1} (in HL^2) were assigned to the characteristic vibration of O-H in phenolic hydroxyl groups, respectively, which disappeared in complexes **1** and **2**, indicating that the phenolic hydroxyl groups in HL^1 and HL^2 are deprotonated and coordinate with Cu(II) and Ni(II) ions to form coordination bonds, respectively. The Ar-O stretching bands at 1 076 and 1 140 cm^{-1} of complexes **1** and **2** shifted toward lower frequencies by *ca.*

Table 2 Main bands in IR spectra of H_2L^1 , H_2L^2 and their Cu(II) and Ni(II) complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{O}-\text{H})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
HL^1	1 610	1 165	3 053	—	—
Complex 1	1 580	1 076	—	578, 517	458
HL^2	1 612	1 164	3 453	—	—
Complex 2	1 597	1 140	—	463	427

85 and 24 cm^{-1} compared with those of HL^1 and HL^2 at $1\ 165$ and $1\ 164\text{ cm}^{-1}$, respectively. The reason maybe is due to that coordination of Cu(II) and Ni(II) ions with the phenolic oxygen atoms of ligands result in reducing the Ar-O bond energy^[73]. The FT-IR spectrum of complex **1** showed $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibration frequencies at 578 , 517 and 458 cm^{-1} (or 463 and 427 cm^{-1} for complex **2**), respectively. These assignments are consistent with the literature^[49].

2.2 UV-Vis absorption spectra analyses

The absorption spectra of HL^1 and its corresponding Cu(II) complex **1**, ligand HL^2 and its corresponding Ni(II) complex **2** were determined in diluted DMSO solution as shown in Fig.1 and 2, respectively. UV-Vis spectrum of HL^1 exhibited two absorption peaks at *ca.* 281 and 328 nm. The former at 281 nm can be assigned to the $\pi\text{-}\pi^*$ transition of the benzene rings, which blue-shifted to high energy region by *ca.* 23 nm in complex **1**, indicating Cu(II) ion coordinated with the O and N atoms of deprotonated (L^-) ligand. The later at 328 nm attributed to the intra-ligand $\pi\text{-}\pi^*$ transition of C=N bonds^[74] was absent in complex **1**, indicating the oxime nitrogen atom is involved in the coordination with Cu(II) ion^[75]. However, a new absorption peak observed at 410 nm in complex **1** can be ascribed to the *d-d* forbidden transition of Cu(II) ion.

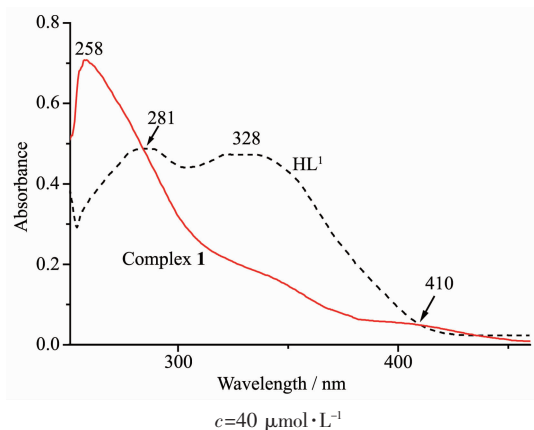


Fig.1 UV-Vis absorption spectra of HL^1 and complex **1** in diluted DMSO solution at room temperature

It can be seen that the absorption peaks of complex **2** are obviously different from those of HL^2 upon coordination (Fig.2). Compared with complex **2**, an important feature of the absorption spectrum of HL^2

was that three absorption peaks were observed at 390, 446 and 470 nm attributed to the intra-ligand $\pi\text{-}\pi^*$ transition of C=N bonds and conjugated aromatic chromophore, which are absent in the spectrum of complex **2**. A new absorption peak owing to L \rightarrow M charge-transfer transitions^[75] was observed at 426 nm in complex **2**, which are characteristic of the transition metallic coordination compounds with N_2O_2 coordination spheres. And the absorption peak at 324 nm assigned to the $\pi\text{-}\pi^*$ transitions of phenyl rings in HL^2 was shifted to 323 nm in complex **2** indicating the coordination of Ni(II) ion with HL^2 .

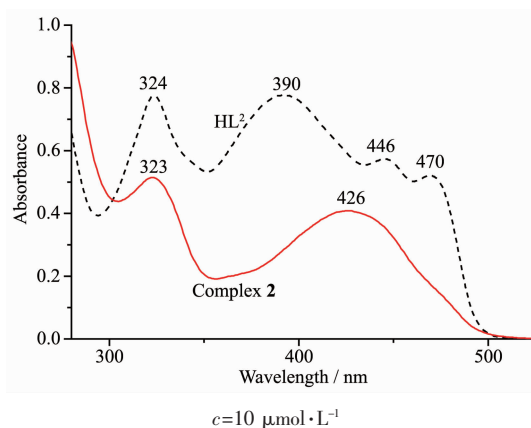


Fig.2 UV-Vis absorption spectra of HL^2 and complex **2** in diluted DMF solution at room temperature

2.3 Structural description of complexes **1** and **2**

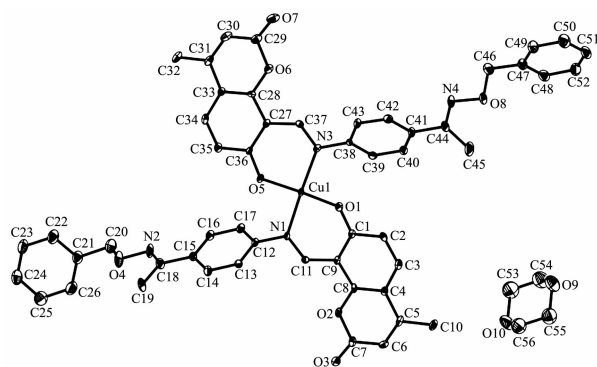
The molecular structures of complexes **1** and **2** are shown in Fig.3 and 4, respectively, and selected bond lengths and angles are listed in Table 2. Complexes **1** and **2** are all mononuclear structures and crystallize in the triclinic system, $P\bar{1}$ space group. Both of complexes **1** and **2** consist of one metal ion M(II) (M=Cu or Ni), two bidentate L^- units, in which the difference is that complex **1** contains a crystallizing 1,4-dioxane molecule. In the molecular structures of complexes **1** and **2**, the metal centers M(II) (M=Cu for **1** and Ni for **2**) are tetra-coordinated in a *trans*- MN_2O_2 slightly distorted square-planar geometries, with two phenolic O and two imino N atoms from two N,O-bidentate oxime-type Schiff ligands (HL^1 and HL^2). In complex **1**, the four atoms of the donor set (N1, N3, O1, O5) and Cu1 approximately lie in a plane with the distance being 0.000 7 nm and 0.017 3~0.017 4

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

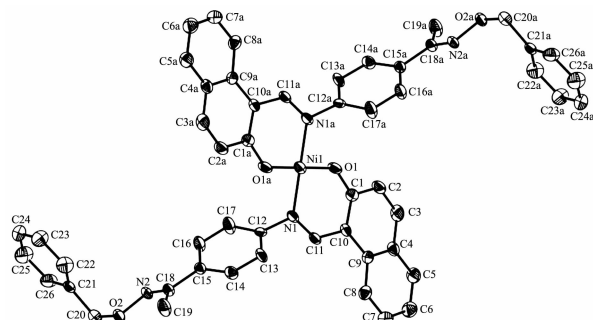
Complex 1					
Cu1-O1	0.189 3(5)	Cu1-O5	0.188 4(6)	Cu1-N1	0.203 3(6)
Cu1-N3	0.202 1(6)				
O1-Cu1-O5	169.0(2)	O1-Cu1-N1	91.7(2)	O1-Cu1-N3	89.4(2)
O5-Cu1-N1	88.3(2)	O15-Cu1-N3	92.4(2)	N1-Cu1-N	170.6(2)
Complex 2					
Ni1-O1	0.182 8(4)	Ni1-N1	0.189 0(5)		
O1a-Ni1-O1	180.0	O1-Ni1-N1a	87.51(19)	O1a-Ni1-N1	87.51(19)
O1-Ni1-N1	92.49(19)	O1a-Ni1-N1a	92.50(19)	N1-Ni1-N1a	180.0

Symmetry codes: a: $-x, -y, -z$.

nm of Cu(II) and N/O atoms to the square plane. The dihedral angle between the coordination plane of N1-Cu1-O1 and that of N3-Cu1-O5 is 14.22° , indicating slight distortion toward tetrahedral geometry from the square planar structure. And the four atoms of the donor set (N1, N1a, O1, O1a) and Ni1 are completely



Hydrogen atoms are omitted for clarity

Fig.3 Molecular structure of complex **1** showing 30% probability displacement ellipsoidsHydrogen atoms are omitted for clarity; Symmetry codes: a: $-x, -y, -z$ **Fig.4** Molecular structure of complex **2** showing 30% probability displacement ellipsoids

coplanar. In addition, the bond lengths of M-N (0.203 3(6) and 0.202 1(6) nm for Cu-N, 0.189 0(5) nm for Ni-N) are longer than M-O bond (0.188 4(6) and 0.189 3(5) nm for Cu-O, 0.182 8(4) nm for Ni-O) in complexes **1** and **2**, which is probably due to the weakening of the coordination abilities of coordinating nitrogen atoms by the larger electronegativity of oxygen atoms of phenolic hydroxyl groups. The significant elongation has been observed in other metal complexes with Schiff ligands^[47].

2.4 Supramolecular interaction of complexes **1** and **2**

The main hydrogen bond and $\pi \cdots \pi$ stacking interactions parameters of complexes **1** and **2** are given in Table 4 and Table 5. As shown in Fig.5, a pair of intermolecular non-classical hydrogen bonds C13-H13 \cdots O7a have stabilized a pair of complex **1** molecules to form a dimer unit. Synchronously, this dimer unit is further stabilized via two hydrogen bonds C22-H22 \cdots O9 and C34-H34 \cdots O10 between the crystallizing 1,4-dioxane molecule and complex **1**

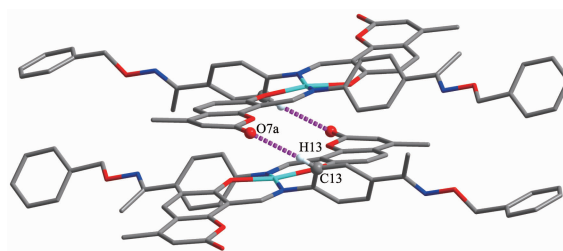
Symmetry codes: a: $-x, 1-y, 1-z$ **Fig.5** View of dimer unit stabilized by hydrogen bonds of complex **1**

Table 4 Hydrogen bonds parameters for complex **1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
C13-H13...O7a	0.093	0.257	0.350 0(10)	176
C27-H27...O9b	0.093	0.256	0.342 6(13)	156
C34-H34...O10b	0.093	0.247	0.336 6(11)	163
C6c-H6c...O3	0.093	0.254	0.343 2(10)	160
C51d-H51d...O3	0.093	0.247	0.338 5(11)	169

Symmetry codes: a: $-x, 1-y, 1-z$; b: $1-x, 1-y, 1-z$; c: $2-x, -y, 1-z$; d: $-1+x, y, 1+z$.

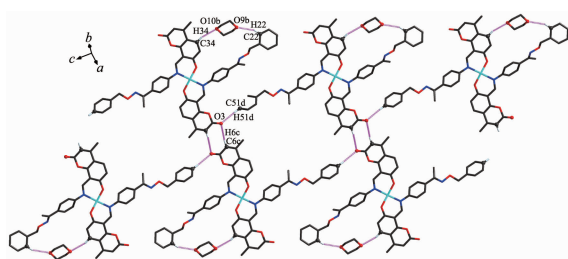
Table 5 π - π stacking interactions parameters for complexes **1** and **2**

Ring(<i>i</i>)	Ring(<i>j</i>)	$d(\text{Cg}\cdots\text{Cg}) / \text{nm}$	Dihedral angle / ($^\circ$)	$d(\text{Cg}(i)\text{-perp}) / \text{nm}$	$d(\text{Cg}(j)\text{-perp}) / \text{nm}$	Slippage / nm
Complex 1						
Cg1	Cg2a	0.351 8(4)	8.0(3)	0.329 8(3)	0.339 1(3)	0.093 3
Cg3	Cg1a	0.382 2(4)	9.5(3)	0.302 9(3)	0.335 3(3)	0.183 4
Cg4	Cg1a	0.346 4(4)	8.6(2)	0.320 8(3)	0.330 7(3)	0.102 9
Cg5	Cg5a	0.330 9(4)	0.0(3)	0.327 3(3)	0.327 3(3)	0.049 0
Cg5	Cg6b	0.382 3(4)	16.0(3)	0.343 3(3)	0.357 9(3)	0.134 2
Cg3	Cg6b	0.363 6(5)	14.0(4)	0.323 5(3)	0.352 5(3)	0.089 0
Cg2	Cg7c	0.385 1(5)	13.5(4)	0.337 4(3)	0.363 7(3)	0.126 6
Cg8	Cg9d	0.381 2(5)	6.4(4)	0.334 4(4)	0.352 5(4)	0.145 1
Complex 2						
Cg10	Cg10e	0.394 1(4)	0.0(3)	0.371 8(3)	0.371 8(3)	0.130 7

Cg1, Cg2, Cg3, Cg4, Cg5, Cg6, Cg7, Cg8 and Cg9 are the centroids of the rings Cu1-O1-C1-C9-C11-N1, O6-C28~C30-C32-C33, C32~C37, O6-C28~C30-C32-C34~C36, Cu1-O5-C36~C38-N3, O2-C4~C8, C1~C4-C8~C9, C39~C44, C48~C53; Cg10 is the centroids of benzene ring C21~C26; Symmetry codes: a: $-x, 1-y, 1-z$; b: $1-x, 1-y, 1-z$; c: $-x, 1-y, 1-z$; d: $-x, 1-y, 2-z$ for **1**; e: $2-x, -1-y, 1-z$ for **2**.

molecule (Fig.6). Furthermore, this linkage is linked via two pairs of intermolecular C6c-H6c...O3 and C51d-H51d...O3 hydrogen bonds to form an infinite 1D band-like supramolecular structure (Fig.6). Thus, complex **1** molecules are linked together into an infinite 2D-layer supramolecular structure via intermolecular non-classical C-H...O hydrogen bonds interactions (Fig.7). In addition, this adjacent 2D-layer

are further held together by the intermolecular complicated $\pi\cdots\pi$ stacking interactions to form 3D network supramolecular structure (Table 5)^[76-80]. Consequently, the intermolecular non-classical hydrogen-bonding plays a very important role in the construction of supramolecular networks structure^[81-85]. Whereas, in complex **2**, the molecules linked only via a intermole-



Symmetry codes: b: $1-x, 1-y, 1-z$; c: $2-x, -y, 1-z$; d: $-1+x, y, 1+z$

Fig.6 View of infinite 1D band-like supramolecular structure linked by hydrogen bonds of complex **1**

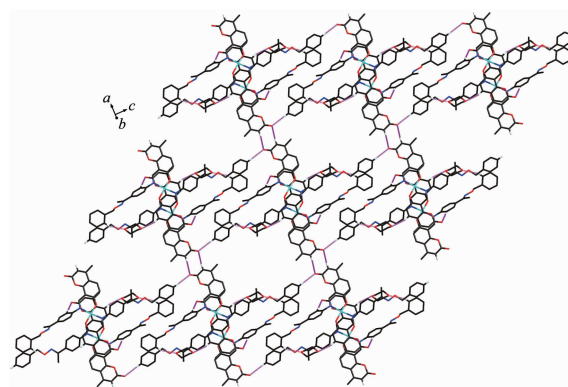


Fig.7 View of 2D-layer supramolecular stabilized by hydrogen bonds of complex **1**

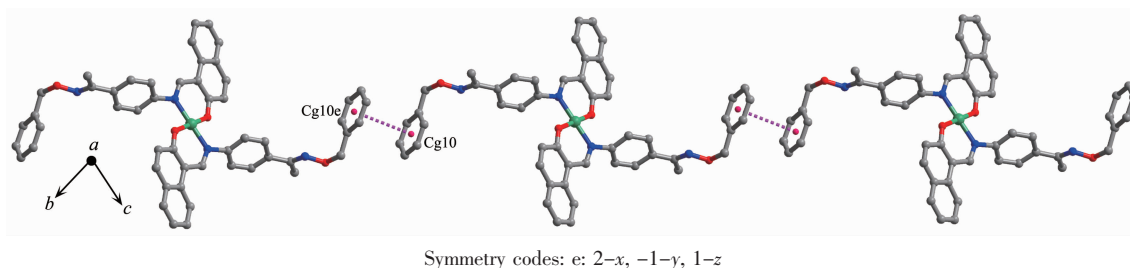


Fig.8 View of 1D infinite supramolecular chain linked by $\pi\cdots\pi$ stacking interaction of complex **2**

cular $\pi_{\text{centroid}}(\text{C21}\sim\text{C26})\cdots\pi_{\text{centroid}}(\text{C21e}\sim\text{C26e})$ stacking interactions of benzene rings of the neighboring molecules to form a 1D infinite chain parallel to the *a* axis (Fig.8, Table 5).

2.4 Fluorescence spectra

The fluorescence emission spectra of HL¹, HL² and complexes **1** and **2** in diluted DMSO and DMF solution at room temperature are shown in Fig.9 and Fig.10, respectively. With excitation at 350 nm, HL¹ exhibited an intense emission at 530 nm and show a

strong yellow-green fluorescence, which may be assigned to the intra-ligand $\pi\text{-}\pi^*$ transition^[86-87]. In comparison with HL¹, an extremely weak fluorescence intensity of complex **1** was observed, indicating that the change of fluorescence is due to the coordination of Cu(II) ion to HL¹. However, both HL² and complex **2** show strong fluorescence emission at 502 and 511 nm with the excitation at 323 nm, respectively. Compared with HL², the emission peak of complex **2** is slightly red shifted *ca.* 9 nm, indicating that Ni(II) ion coordinates with the N and O atoms and occurs electron transition.

3 Conclusions

Two Schiff base mononuclear complexes **1** and **2** have been synthesized and characterized structurally. Complexes **1** and **2** are tetra-coordinated by two nitrogen atoms and two oxygen atoms of two deprotonated (L¹)⁻ units defining the N₂O₂ basal plane. The coordination environment around the metal ions M(II) (M=Cu for **1** and Ni for **2**) are best regarded as the slightly distorted square-planar geometries. Complex **1** forms a 3D network supramolecular structure by intermolecular non-classical C-H \cdots O hydrogen bonds and $\pi\cdots\pi$ stacking interactions. Whereas, complex **2** just forms a 1D infinite chain held together by intermolecular $\pi\cdots\pi$ stacking interaction. The fluorescence of complex **1** was quenched by Cu(II) but that of complex **2** was red-shifted *ca.* 9 nm upon complexation compared to HL¹ and HL², respectively.

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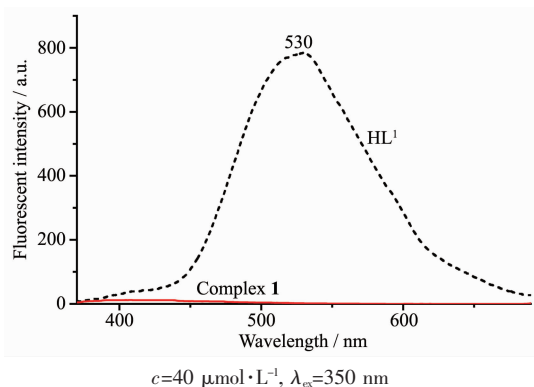


Fig.9 Emission spectra of HL¹ and complex **1** in diluted DMSO at room temperature

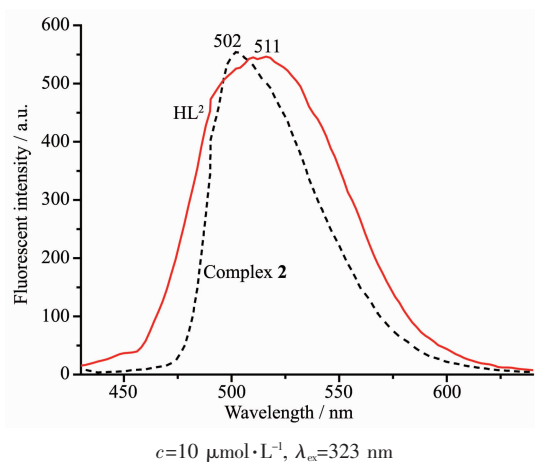


Fig.10 Emission spectra of HL² and complex **2** in diluted DMF at room temperature

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