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含 Schiff 碱配体的超分子 Co(Ⅱ)和 Cu(Ⅱ)配合物的合成、表征及晶体结构

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摘要：合成了 2 个含肟基 Schiff 碱 Co(Ⅱ)和 Cu(Ⅱ)配合物 $Co(L^1)_2$ (**1**)和 $Cu(L^2)_2$ (**2**)。X 射线单晶衍射分析结果表明,配合物 **1** 和 **2** 具有相似的结构,均由 1 个中心金属离子和 2 个双齿配体单元组成,且金属离子的配位数为 4,具有平面四边形结构。配合物 **1** 和 **2** 均属于三斜晶系,空间群均为 $P\bar{1}$。配合物 **1** 的晶胞参数为 a=1.156 40(11) nm,b=1.376 81(12) nm,c=1.388 59(13) nm,α=63.776 0(10)°,β=87.400(2)°,γ=84.280(2)°;配合物 **2** 的晶胞参数为 a=1.156 42(9) nm,b=1.372 19(13) nm,c=1.404 40(12) nm,α=63.683 0(10)°,β=87.227(2)°,γ=84.883 0(10)°。2 个配合物分子均通过分子间 C–H···O 和 C–H···π 氢键作用以及分子间 π···π 堆积作用相连接,形成了二维层状超分子结构。

关键词：钴(Ⅱ)配合物；铜(Ⅱ)配合物；晶体结构；Schiff 碱配体；超分子结构
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Supramolecular Cobalt(Ⅱ) and Copper(Ⅱ) Complexes with Schiff Base Ligand: Syntheses, Characterizations and Crystal Structures

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Abstract: Supramolecular cobalt(Ⅱ) and copper(Ⅱ) complexes, $Co(L^1)_2$ (**1**) and $Cu(L^2)_2$ (**2**), (HL^1=1-(4-{[(5-chlor-2-hydroxyphenyl)methylene]amino}phenyl)ethanone *O*-benzyloxime, HL^2=1-(4-{[(3,5-bromine-2-hydroxyphenyl)methylene]amino}phenyl)ethanone *O*-benzyloxime), have been synthesized and characterized structurally. X-ray structure showed that complexes **1** and **2** have the similar structure, consisting of one metal ion, two ligand units. The complexes **1** and **2** both crystallize in triclinic system, space groups are $P\bar{1}$ with the unit cell parameters for complex **1**: a=1.156 40(11) nm, b=1.376 81(12) nm, c=1.388 59(13) nm, α=63.776 0(10)°, β=87.400(2)°, γ=84.280(2)°, and for complex **2**: a=1.156 42(9) nm, b=1.372 19(13) nm, c=1.404 40(12) nm, α=63.683 0(10)°, β=87.227(2)°, γ=84.883 0(10)°. The Co(Ⅱ) and Cu(Ⅱ) atoms are both four-coordinated in a *trans*-CuN_2O_2 slightly distorted square-planar geometry by two hydroxyl O and two imine N atoms from two symmetry-related N,O-bidentate Schiff base ligands. Moreover, every Co(Ⅱ) or Cu(Ⅱ) complex molecule links some other molecules into an infinite 2D layer supramolecular structure via intermolecular C–H···O hydrogen bonding, C–H···π and π-π stacking interactions between neighboring benzene rings. CCDC: 1003361, **1**; 1473798, **2**.

Keywords: Co(Ⅱ) complex; Cu(Ⅱ) complex; crystal structure; oxime-type ligand; supramolecular

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0 Introduction

Schiff base compounds have been a research focus of coordination chemistry because of their potential application in catalysis[1-2], bioscience[3-4], new materials[5], magnetic properties[6-9] and constructing supramolecular structures[10-11]. At present, significant increases in the research of the transition metal complexes with these series Schiff base ligands have been observed. Herein, in order to further study the supramolecular structures of the transition metal complexes with the oxime-type Schiff base ligands, supramolecular Co(Ⅱ) and Cu(Ⅱ) complexes, $Co(L^1)_2$ (**1**) and $Cu(L^2)_2$ (**2**), with oxime-type Schiff base ligands (HL^1=1-(4-{[(5-chlor-2-hydroxyphenyl)methylene]amino}phenyl)ethanone *O*-benzyloxime, HL^2=1-(4-{[(3,5-bromine-2-hydroxyphenyl)methylene]amino}phenyl)ethanone *O*-benzyloxime) have been synthesized and characterized by elemental analyses, IR spectra, UV-Vis spectra and X-ray crystallographic analysis.

1 Experimental

1.1 Materials

3-Aminoacetophenone, *O*-benzylhydroxylamine, halogen substituted salicylaldehyde were purchased from Aladdin and used without further purification. The other solvents were analytical grade from Tianjin Chemical Reagent Factory.

1.2 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}). 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 a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

1.3 Synthesis of HL^1 and HL^2

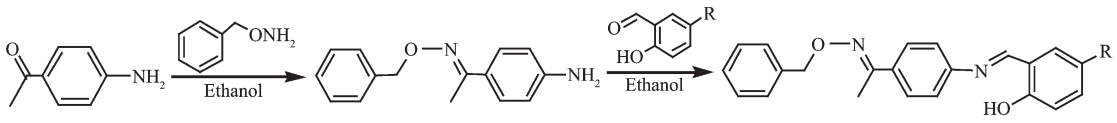
HL^1 and HL^2 were synthesized according to the analogous method[12-14]. The synthetic route is given in Scheme 1. HL^1: Yield 69.18%; m.p. 149~150 ℃. Anal. Calcd. for $C_{22}H_{19}ClN_2O_2$ (%): C, 69.75; H, 5.05; N, 7.39. Found (%): C, 70.23; H, 5.11; N, 7.28. HL^2: Yield 59.09%; m.p. 168~169 ℃. Anal. Calcd. for $C_{22}H_{19}BrN_2O_2$ (%): C, 62.42; H, 4.52; N, 6.62. Found (%): C, 62.56; H, 3.48; N, 6.42.

1.4 Synthesis of $Co(L^1)_2$ (1) and $Cu(L^2)_2$ (2)

A pale-pink ethanol solution (2 mL) of Co(Ⅱ) acetate tetrahydrate (0.50 mg, 0.002 mmol) was added dropwise to an acetone solution (2 mL) of HL^1 (1.70 mg, 0.004 mmol) 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. Red block single crystals suitable for X-ray structural determination were obtained. Anal. Calcd. for $C_{44}H_{36}Cl_2CoN_4O_4$(%): C, 64.87; H, 4.45; N, 6.88. Found(%): C, 64.72; H, 4.34; N, 6.78. The synthetic method of $Cu(L^2)_2$ (**2**) is similar with $Co(L^1)_2$ (**1**). Anal. Calcd. for $C_{44}H_{36}Br_2CuN_4O_4$(%): C, 58.19; H, 4.00; N, 6.17. Found(%): C, 58.53; H, 3.49; N, 6.25.

1.5 Crystal structure determination

The single crystals of complexes **1** and **2** with approximate dimensions of 0.30 mm×0.27 mm×0.15 mm and 0.21 mm×0.14 mm×0.08 mm were placed on a Bruker Smart 1000 CCD area detector. The diffraction data were collected using a graphite monochromated Mo *Kα* radiation (λ=0.071 073 nm) at 298(2) K. Empirical absorption correction was applied to the data using SADABS program[15]. The structures were solved by direct methods and refined by full-matrix leastsquares method on F^2 using the SHELXTL



HL^1: R= Cl; HL^2: R=Br

Scheme 1 Synthetic routes of HL^1 and HL^2

program[16]. 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.

CCDC: 1003361, **1**; 1473798, **2**.

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

Complex	**1**	**2**
Empirical formula	$C_{44}H_{36}Cl_2CoN_4O_4$	$C_{44}H_{36}Br_2CuN_4O_4$
Formula weight	814.60	908.13
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.156 40(11)	1.156 42(9)
b / nm	1.376 81(12)	1.372 19(13)
c / nm	1.388 59(13)	1.404 40(12)
α / (°)	63.776 0(10)	63.683 0(10)
β / (°)	87.400(2)	87.227(2)
γ / (°)	84.280(2)	84.883 0(10)
V / nm^3	1.973 4(3)	1.989 5(3)
Z	2	2
D_c / (g·cm^{-3})	1.371	1.516
μ / mm^{-1}	0.619	2.605
F(000)	842	918
θ range for data collection / (°)	2.31~25.02	2.33~25.02
Limiting indices	$-13 \leqslant h \leqslant 11$; $-13 \leqslant k \leqslant 16$; $-11 \leqslant l \leqslant 16$	$-13 \leqslant h \leqslant 13$; $-16 \leqslant k \leqslant 16$; $-11 \leqslant l \leqslant 16$
Reflections collected, unique	10 102, 6 866 (R_{int}=0.045 6)	10 568, 6 936 (R_{int}=0.047 8)
Completeness to θ / %	98.3 (θ=25.02°)	98.7 (θ=25.02°)
Data, restraints, parameters	6 866, 0, 562	6 936, 0, 562
GOF on F^2	1.084	1.068
Final R indices [$I>2\sigma(I)$]	R_1=0.057 3, wR_2=0.102 1	R_1=0.058 0, wR_2=0.138 0
R indices (all data)	R_1=0.118 4, wR_2=0.113 1	R_1=0.111 3, wR_2=0.152 7
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	480, −358	955, −726

2　Results and discussion

2.1　IR spectra analyses

The FT-IR spectra of HL^1, HL^2 and their corresponding complexes **1** and **2** exhibit various bands in the 400~4 000 cm^{-1} region. The most important FT-IR bands for HL^1, HL^2 and its Co(Ⅱ) and Cu(Ⅱ)complexes are listed in Table 2.

The characteristic C=N stretching bands of the free ligand HL^1 and HL^2 appear at 1 620 cm^{-1} and 1 618 cm^{-1}, respectively, while those of complex **1** and complex **2** are observed in the 1 613 cm^{-1} and 1 605 cm^{-1}, respectively. The C=N stretching frequencies are all shifted to lower frequencies by *ca.* 7 and 13 cm^{-1}

Table 2　Main bands in IR spectra of HL^1, HL^2 and its Co(Ⅱ) and Cu(Ⅱ) complexes

cm^{-1}

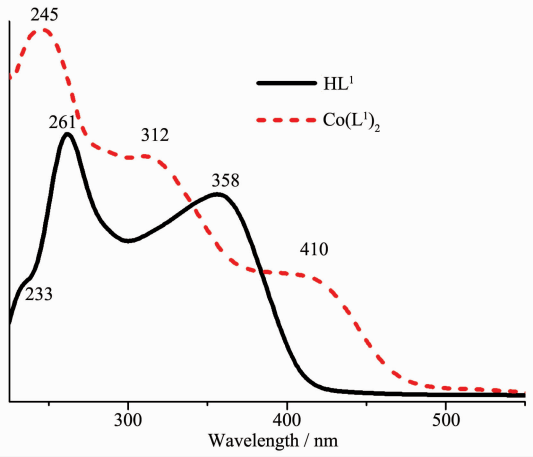
Compound	ν(O-H)	ν(C=N)	ν(Ar-O)	ν(M-N)	ν(M-O)
HL^1	3 445	1 620	1 167	—	—
$Co(L^1)_2$	—	1 613	1 160	512	470
HL^2	3 433	1 618	1 174	—	—
$Cu(L^2)_2$	—	1 605	1 159	522	476

upon complexation respectively, indicating a decrease in the C=N bond order due to the coordinated bond of the metal atom with the imino nitrogen lone pair[17]. The Ar-O stretching bands of the ligands HL^1 and HL^2 are observed at 1 167 cm^{-1} and 1 174 cm^{-1}, respectively, which are at 1 160 cm^{-1} and 1 159 cm^{-1} for complex **1** and complex **2**. The lower frequency of the Ar-O absorption shift indicates that M-O bond form between the metal ions and the oxygen atoms of the phenolic groups[18-19]. In addition, the broad O-H group absorption bands at 3 445 cm^{-1} and 3 433 cm^{-1} in the free ligands HL^1 and HL^2 disappear in the spectra of the complexes **1** and **2**, which further demonstrates the coordination of deprotonated phenolic oxygen atom to metal ion. The FT-IR spectrum of complex **1** shows ν(Co-N) and ν(Co-O) vibration absorption frequencies at 512 cm^{-1} and 470 cm^{-1} (or 522 cm^{-1} and 476 cm^{-1} for complex **2**), respectively. These assignments are consistent with the literature[20].

2.2 UV-Vis absorption spectra analyses

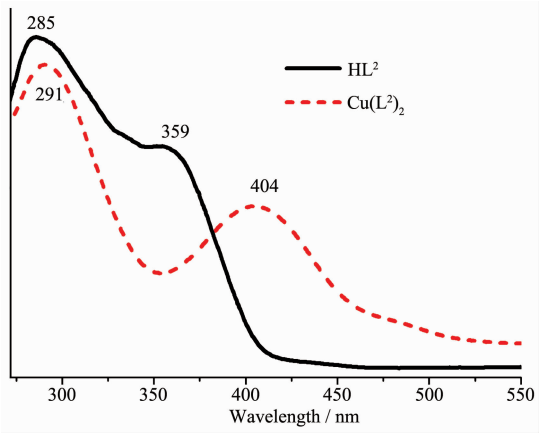
The UV-Vis absorption spectra of HL^1 and its corresponding Co(Ⅱ) complex in dilute CH_2Cl_2 solution are shown in Fig.1. The electronic absorption spectrum of free ligand HL^1 exhibits three absorption peaks at approximately 233, 261 and 358 nm. The former absorption peaks at 233 and 261 nm can be assigned to the π-π* transition of the benzene rings and the latter at 358 nm can be attributed to the intraligand π-π* transition of the C=N group[21]. Upon coordination of the ligand, the absorption at 358 nm disappears from UV-Vis spectra of the Co(Ⅱ) complex, indicating that the amino nitrogen is involved in coordination with Co(Ⅱ) ion[22]. The intraligand π-π* transition of the benzene ring is bathochromically shifted to 245 and 312 nm in the Co(Ⅱ) complex, indicating the coordination of Co(Ⅱ) ion with deprotonated L^- unit. The new peak at 410 nm of Co(Ⅱ) complex is assigned to L→M charge-transfer transition[23].

UV-Vis absorption spectra of the free ligand HL^2 and its corresponding Cu(Ⅱ) complex in the dilute CH_2Cl_2 solution is shown in Fig.2. The absorption of the Cu(Ⅱ) complex is obviously different from that of HL^2 owing to complexation. For the free ligand there are two intense peaks centered at around 285 and 359 nm, assigned to π-π* transitions of the benzene rings of the benzaldehyde and C=N groups, respectively[21]. Compared with the absorption peak of the free ligand, the absorption at 285 is slightly shifted bathochromically to 291 nm of the Cu(Ⅱ) complex, indicating the coordination of Cu(Ⅱ) ion with deprotonated L^- unit. Meanwhile, the absorption peak at 359 nm disappears from the UV-Vis spectrum of the Cu(Ⅱ) complex, which indicates that the amino nitrogen atom is involved in coordination to the metal atom[22]. In addition, a new absorption peak is observed at 404 nm in the Cu(Ⅱ) complex, which is assigned to the n-π* charge



c=5×10^{-5} mol·L^{-1}

Fig.1 UV-Vis absorption spectra of HL^1 and the Co(Ⅱ) complex in dilute CH_2Cl_2 solution at room temperature



c=5×10^{-5} mol·L^{-1}

Fig.2 UV-Vis absorption spectra of HL^2 and the Cu(Ⅱ) complex in dilute CH_2Cl_2 solution at room temperature

transfer from the filled $p\pi$ orbital of the bridging phenolic oxygen to vacant d-orbital of the Cu(Ⅱ) ions[24].

2.3 Crystal structures of complexes 1 and 2

The structures of complexes **1** and **2** are similar, which are all mononuclear structure and crystallize in the triclinic system, $P\bar{1}$ space group, and Z=2. Both of the complexes consist of one metal ion, two bidentate L^- units. The molecular structures of the complexes **1** and **2** are shown in Fig.3 and 4, respectively, and selected bond lengths and angles are listed in Table 3. In the molecule structures of the complexes **1** and **2**, the metal centers are tetra-coordinated slightly distorted square-planar geometry by two phenolic O and two imine N atoms from two deprotonated L^- units. In the complexes, the bond lengths of M-N bond (~0.201 nm) are longer than M-O bond (~0.188 nm), which indicates L^- has a little distortion probably as a result of the asymmetry.

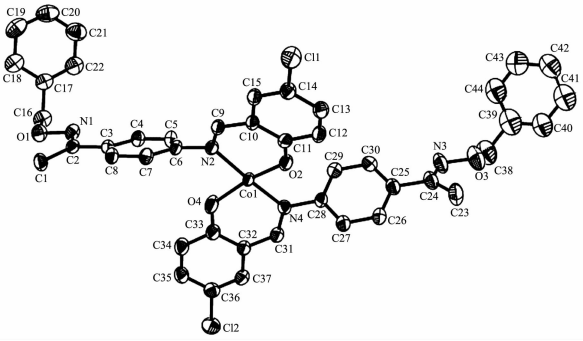


Fig.3　Molecular structure of complex **1** showing 30% probability displacement ellipsoids

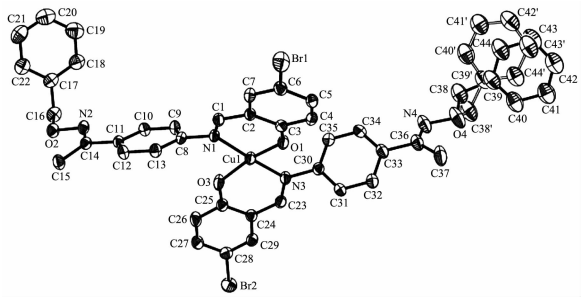


Fig.4　Molecular structure of complex **2** showing 30% probability displacement ellipsoids

In addition, complexes **1** and **2** have the same intermolecular weak interaction. As shown in Fig.5 and Table 4, in the crystals of complexes **1** and **2** there are all two slipped π-π stacking between adjacent complexes, which involve the chelating rings and benzene rings. The interplanar centroid separation distance of π-π stacking interactions of $Cg1\cdots Cg2$ in **1** (or $Cg3\cdots Cg4$ in **2**) is 0.375 9(3) nm (or 0.377 5(3) nm), with a dihedral angle of 1.52° (or 2.25°). The interplanar centroid separation distance of π-π stacking interactions of $Cg2\cdots Cg2^i$ in **1** (or $Cg4\cdots Cg4^i$ in **2**) is 0.370 5(3) nm (or 0.366 2(4) nm), with a dihedral angle of 0° (or 0°). These π-π stacking interactions link the adjacent molecules into a dimeric polymer.

Table 3　Selected bond lengths (nm) and bond angles (°) of the complex 1

			1		
Co1-O4	0.188 5(3)	Co1-O2	0.189 6(3)	Co1-N4	0.201 1(4)
Co1-N2	0.201 2(4)				
O4-Co1-O2	165.57(15)	O4-Co1-N4	92.03(15)	O2-Co1-N4	87.99(14)
O4-Co1-N2	88.70(15)	O2-Co1-N2	92.39(14)	N4-Co1-N2	175.58(15)
C9-N2-Co1	123.4(3)	C6-N2-Co1	119.6(3)	C31-N4-Co1	123.5(3)
C28-N4-Co1	120.8(3)	C11-O2-Co1	129.8(3)	C33-O4-Co1	129.7(3)
			2		
Cu1-O1	0.188 00	Cu1-O3	0.188 80	Cu1-N1	0.201 50
Cu1-N3	0.201 60				
O1-Cu1-O3	166.61(19)	O1-Cu1-N3	87.6(2)	O3-Cu1-N3	92.2(2)
O3-Cu1-N1	88.74(19)	O1-Cu1-N1	92.16(19)	N1-Cu1-N3	176.8(2)
C1-N1-Cu1	123.5(4)	C8-N1-Cu1	119.9(4)	C23-N3-Cu1	123.1(4)
C30-N3-Cu1	121.2(4)	C3-O1-Cu1	130.5(4)	C25-O3-Cu1	130.0(4)

Table 4 Putative π-π stacking interactions for complexes 1 and 2*

nm

Ring (I)	Ring (J)	*Cg*-*Cg*	*Cg*(I)-perp	*Cg*(J)-perp	Slippage
Complex **1**					
*Cg*1	*Cg*2	0.375 9(3)	−0.341 4(2)	−0.337 2(2)	0.157 3
*Cg*2	*Cg*2^{i}	0.370 5(3)	−0.339 8(2)	−0.339 8(2)	0.147 7
Complex **2**					
*Cg*3	*Cg*4	0.377 5(3)	−0.341 0(2)	−0.334 4(3)	0.161 9
*Cg*4	*Cg*4^{i}	0.366 2(4)	−0.338 5(3)	−0.338 5(3)	0.139 7

*Cg1 and Cg2 are the centroids of chelating rings (Co1, O2, N2 and C9~C11) and benzene ring C10~C15 of complex **1**, respectively. Cg3 and Cg4 are the centroids of chelating rings (Cu1, O1, N1 and C1~C3) and benzene ring C2~C7 of complex **2**, respectively. Symmetry codes: ^{i} −*x*, 1−*y*, 1−*z*

Table 5 Hydrogen bonding Hydrogen-bonding for the complexes 1 and 2

D−H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D−H···A / (°)
Complex **1**				
C27−H27···O2^{i}	0.093	0.255	0.343 5(7)	160
C1−H1^{ii}···$\pi_{centroid(C3\sim C8)}$	0.096	0.291	0.372 9(5)	144
C4−H4^{iii}···$\pi_{centroid(C39\sim C44)}$	0.093	0.295	0.369 0(5)	138
Complex **2**				
C31−H31···O1	0.093	0.256	0.345 0(8)	160
C15−H15B···$\pi_{centroid(C8\sim C13)}$	0.096	0.294	0.374 3(7)	141
C10−H10···$\pi_{centroid(C39\sim C44)}$	0.093	0.296	0.371 0(5)	139

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

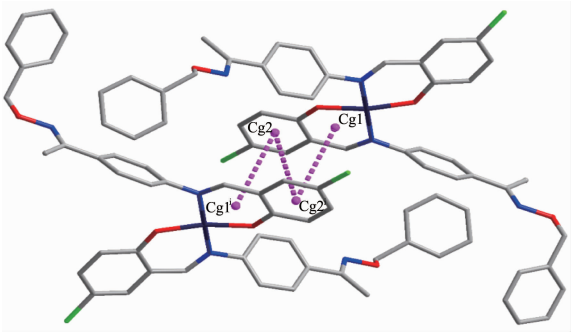


Fig.5 π···π stacking interactions in the complexes **1** and **2**

Furthermore, this linkage is further linked into a 1D chains by a pairs of intermolecular C−H···O hydrogen bond formed between the -CH group of the benzene rings and the phenolic oxygen atom of adjacent molecules (Fig.6 and Table 5). In addition, 1D chains are further linked by two pairs of intermolecular C−H ···π hydrogen bonds interactions (Fig.7) to form a 2D supramolecular networks structure (Fig.8).

2.4 Fluorescence spectra

The emission spectrum of the ligands and

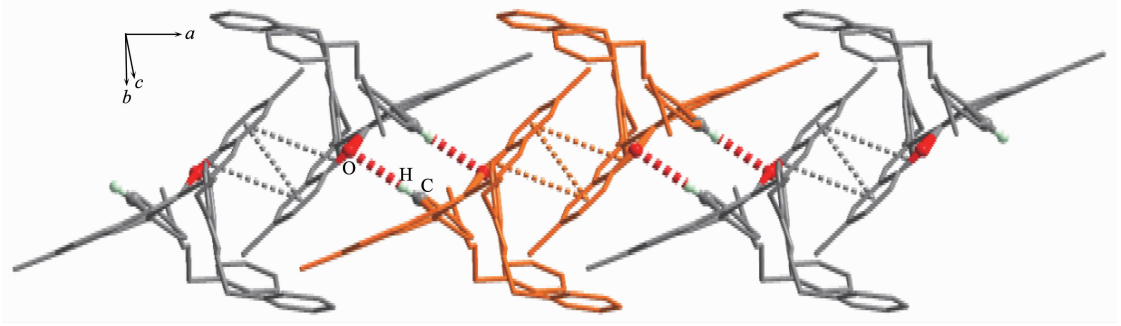


Fig.6 1D infinite chain supramolecular structure of the complexes via intermolecular C−H···O hydrogen bonding interactions and π-π stacking interactions

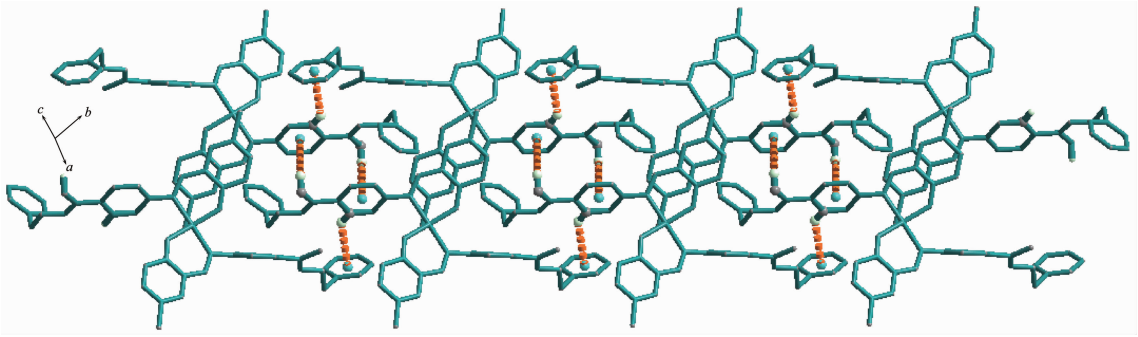


Fig.7　1D infinite chain supramolecular structure of the complexes via C–H···π hydrogen bonding interactions

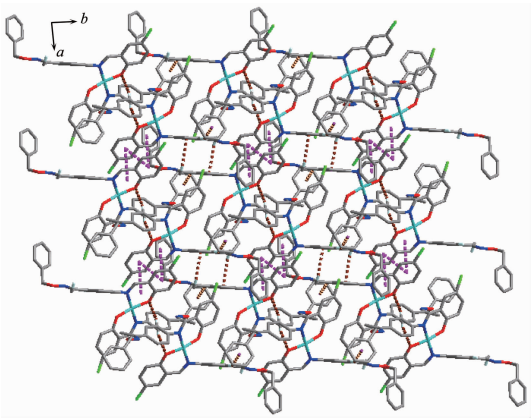
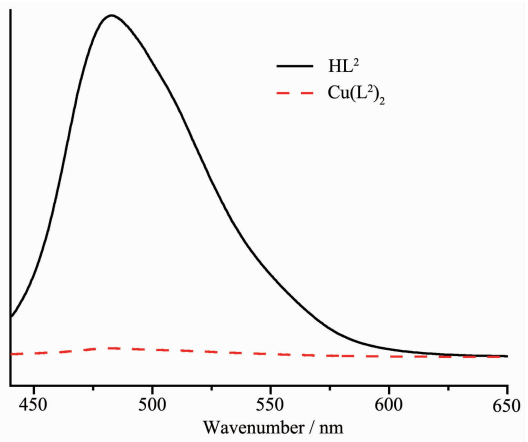


Fig.8　2D layer supramolecular structure of the complexes

complex **2** in dilute DMF solution at room temperature are shown in Fig.9. The ligand (HL^2) exhibits an intense emission at 482 nm upon excitation at 300 nm, which should be assigned to intraligand π-π* transition. Compared with the free ligand, an extremely weak fluorescence intensity of the Cu(Ⅱ) complex is observed, indicating that fluorescent characteristic has been influenced by the introduction of the Cu(Ⅱ) ion. However, compared with the ligand HL^2, the ligand HL^1 and its Co(Ⅱ) complex show no fluorescence. It indicated that the substituted groups on the ligands could play a small impact on the fluorescence properties of complexes **1** and **2**, which also give rise to the variations in IR and UV-Vis spectra in complexes **1** and **2**.



c=5.00×10^{-5} mol·L^{-1}

Fig.9　Emission spectra of HL^2 (λ_{ex}=300 nm, λ_{em}=482 nm) and complex **2** in dilute DMF at room temperature

3　Conclusions

Two Schiff base mononuclear Co(Ⅱ) and Cu(Ⅱ) complexes have been synthesized and characterized structurally. The structures of complexes **1** and **2** are similar, although the two ligands with different substituents. The Co(Ⅱ) and Cu(Ⅱ) complexes are all tetra-coordinated by two nitrogen atoms and two oxygen atoms of two deprotonated L^- units defining the N_2O_2 basal plane. The coordination environment around Co(Ⅱ) and Cu(Ⅱ) atoms are best regarded as the square-planar geometry. Complexes **1** and **2** also form a 2D-layer supramolecular structure by different intermolecular interaction, $\pi\cdots\pi$ interaction and C–H···O, C–H···π hydrogen bond interactions, respectively. Consequently, the intermolecular non-classical hydrogen-bonding plays a very important role in the construction of supramolecular networks structure.

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