第 31 卷第 5 期 无 机 化 学 学 报 Vol.31 No.5
2015 年 5 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 1055-1062

含肟基 Schiff 碱配体及其 Cu(Ⅱ)配合物的合成及超分子结构

孙银霞* 陆瑞娥 李新然 赵亚元 李春宇
(兰州交通大学化学与生物工程学院,兰州 730070)

摘要: 合成了一个含肟基 Schiff 碱配体(HL,$C_{15}H_{16}N_2O$)及其 Cu(Ⅱ)配合物[CuL_2],采用元素分析、红外光谱、紫外光谱以及 X-射线单晶衍射分析进行了表征。结果表明,配体 HL 结构中,一对 HL 分子通过分子间的 Cl…Cl 卤键(Cl…Cl 的距离为 0.345 9(3) nm)链接形成了二聚体,每个二聚体通过分子间 C–H…π 作用链接其它 4 个相邻的二聚体形成了无限的三维超分子网状结构。Cu(Ⅱ)配合物为单核结构,由 1 个 Cu(Ⅱ)离子和 2 个双齿配体组成。Cu(Ⅱ)离子的配位数为 4,具有平面四边形结构。在 Cu(Ⅱ)配合物结构中每个配合物分子通过分子间 C–H…π 作用链接其它 4 个相邻的分子形成了二维层状超分子结构,这种层状结构通过 π…π 堆积作用而进一步连接。

关键词: Schiff 碱配体; 晶体结构; 铜(Ⅱ)配合物
中图分类号: O614.121 **文献标识码**: A **文章编号**: 1001-4861(2015)05-1055-08
DOI:10.11862/CJIC.2015.134

A Schiff Base Ligand Containing Oxime Group and its Cu(Ⅱ) Complex: Syntheses and Supramolecular Structures

SUN Yin-Xia* LU Rui-E LI Xin-Ran ZHAO Ya-Yuan LI Chun-Yu
(*School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou* 730070, *China*)

Abstract: A Schiff base chelating ligand containing oxime group, 1-(4-{[(*E*)-5-chloro-2-hydroxybenzylidene] amino}phenyl)ethanone *O*-benzyloxime (HL, $C_{15}H_{16}N_2O$) and its Cu(Ⅱ) complex ([CuL_2]) have been synthesized and characterized by elemental analyses, IR spectra, UV-Vis spectra and X-ray single crystal diffraction method. In the crystal structure of HL, the intermolecular Cl…Cl halogen bonding interaction links a pair of HL molecules to form a dimer unit with the Cl…Cl distance of 0.345 9(3) nm, and every dimer further links four other adjacent dimer units into an infinite 3D supramolecular networks structure containing 1D rectangle channels by intermolecular C–H…π interactions. The structure of the Cu(Ⅱ) complex is a mononuclear, consists of one Cu(Ⅱ) atoms, two bidentate L^- units. The Cu(Ⅱ) atom is in a square-planar geometry. And each Cu(Ⅱ) complex molecule links four other molecules into an infinite 2D layer supramolecular structure by intermolecular C–H…π interactions. This linkage is further stabilized by π…π stacking interactions with the centroid-centroid distances of 0.368 9(3) nm. CCDC: 1003553, HL; 1003552, Cu(Ⅱ) complex.

Key words: Schiff base ligand; crystal structure; Cu(Ⅱ) complex

Schiff bases have attracted much attention due to their tautomeric properties (and consequently proton transfer) and interesting biological properties. Schiff bases of *o*-hydroxybenzaldehydes and *o*-hydroxyacetophenones and, in many cases, the corresponding derivatives have been investigated in great detail[1-5]. It

收稿日期:2015-01-03。收修改稿日期:2015-03-28。
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)资助。
*通讯联系人。E-mail:sun_yinxia@163.com

is well-known that transition-metal complexes with the Schiff bases can themselves also act as ligands, which may be further coordinated through *cis*-oxygen atoms to other metal ions so that new bi- and trinuclear as well as one dimensional metal complexes are produced[6]. Schiff base compounds have long been used as chelating ligands in the synthesis of transition-metal complexes due to their ease of preparation and structural variety. These compounds can accommodate one, two or more metal centers and form homo- and heteronuclear metal complexes with interesting properties[7-11], such as excellent catalytic activity for epoxidation and aziridination[12]. In addition, they are also used as models for reaction centers in metalloenzymes[13], non-linear optical materials[14], and molecular recognition and biological activity[15]. What′s more, the oxime-type ligands should be stable enough to resist the metathesis of the C=N bonds[16]. In view of X-ray structural data on the free ligand based on *O*-benzylhydroxylamine and its corresponding Cu(Ⅱ) complex, we report here the preparation, spectroscopic characterization and X-ray crystal structure of the Cu(Ⅱ) complex with an oxime-type chelating ligand, together with the structure of the free ligand.

1 Experimental

1.1 Materials

4-Aminoacetophenone, *O*-benzylhydroxylamine, 5-chloro salicylaldehyde 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

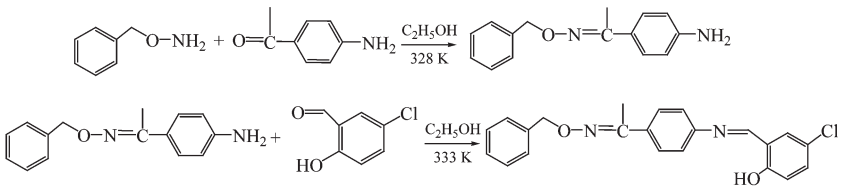
C, H and N analyses were carried out with a GmbH Vario EL V3.00 automatic elemental analyzer. Elemental analysis for Cu was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (400~4 000 cm^{-1}). 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 the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

1.3 Synthesis and characterization of the ligand HL

1-(4-{[(*E*)-5-Chloro-2 - hydroxybenzylidene]amino} phenyl)ethanone *O*-benzyl oxime was synthesized by *O*-benzylhydroxylamine, 4-aminoacetophenone and 5-chloro salicylaldehyde. To an ethanol solution (6 mL) of O-benzylhydroxylamine (369.45 mg, 3 mmol) was added an ethanol solution (12 mL) of 4-aminoacetophenone (405.53 mg, 3 mmol) and 3 drops of acetic acid. The reaction of mixture solution was stirred at 338 K for 24 h. The solvent was evaporated under vacuo. After cooling to room temperature, the formed precipitate was filtered and washed successively with ethanol and ethanol/water (1:4, *V*/*V*), respectively, resulting in 640.6 mg of ({4-amino}phenyl)ethanone *O*-benzyloxime as crystalline solid. Yield: 89.0%. m.p. 351~352 K. Anal. Calcd.(%) for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found (%): C, 74.68; H, 6.80; N, 11.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.38 (s, 3H, -CH_3), 4.97 (s, 2H, Ar-CH_2-O-), 5.23 (s, 2H, Ar-NH_2), 6.86 (dd, 2H, Ar-H), 7.43 (m, 5H, Ar-H), 7.65 (dd, 2H, Ar-H).

To an ethanol solution (4 mL) of ({4-amino} phenyl)ethanone *O*-benzyloxime (240.0 mg, 1 mmol) was add an ethanol (3 mL) of 5-chloro salicylaldehyde (156.5 mg, 1 mmol). The reaction of mixture solution was stirred at 333 K for 18 h. After cooling to room temperature, the formed precipitate was filtered and washed successively with ethanol and ethanol/*n*-hexane (1:4, *V*/*V*), respectively. The product was dried in vacuo and purified by recrystallization from ethanol to yield 261.84 mg of solid. Yield: 69.2 %. m.p. 422~423 K. Anal. Calcd.(%) for $C_{22}H_{19}ClN_2O_2$(%): C, 69.75; H, 5.06; N, 7.39. Found(%): C, 69.05; H, 5.01, N, 7.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.33 (s, 3H, -CH_3), 5.30 (s, 2H, Ar-CH_2-O-), 6.96 (d, 1H, Ar-H), 7.28 (s, 1H, Ar-H), 7.40 (m, 7H, Ar-H), 7.57 (d, 1H, Ar-H), 7.63 (d, 2H, Ar-H), 8.59 (s, 1H, -N=CH-Ar), 13.22 (s, 1H, ArO-H).

Pale-yellow block-shaped single crystals suitable



Scheme 1　Snthetic route of HL

for X-ray diffraction studies were obtained after about two weeks by slow evaporation from an ethanol/acetonitrile (2∶1, *V*/*V*) solution of HL.

1.4　Synthesis of the Cu(Ⅱ) complex [CuL_2]

Cu(Ⅱ) acetate monohydrate (1.90 mg, 0.01 mmol) dissolved in methanol (5 mL) was added dropwise to an acetone solution (3 mL) of HL (7.98 mg, 0.01 mmol) at room temperature under vigorous stirring. The resulting turned to red-brown solution, which was stirred for an additional 30 min and the solution was left at room temperature for slow evaporation. Upon standing at room temperature for about two weeks, the solvent partially evaporated and massive brown block-shaped single crystals suitable for X-ray crystallography were obtained. Anal. Calcd. for $C_{44}H_{36}Cl_2CuN_{44}$ (%): C, 40.17; H, 2.76; N, 46.85, Cu, 4.83. Found(%): 40.03; H, 2.68; N, 46.76, Cu, 4.69.

1.5　X-ray crystallography of HL and its Cu(Ⅱ) complex

The single crystals with approximate dimensions of 0.37 mm×0.35 mm×0.13 mm (H_2L) and 0.34 mm×0.18 mm×0.16 mm (Cu(Ⅱ) complex) were placed on a Bruker Smart 1000 CCD area detector. The diffraction data of HL and its Cu(Ⅱ) complex were collected using a graphite monochromated Mo $K\alpha$ radiation (λ = 0.071 073 nm) at 298(2) K. The structures were solved by direct method using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package[17]. Hydrogen atoms were added geometrically and refined using the riding model. Details of the data collection parameters and crystallographic information for HL and Cu(Ⅱ) complex are summarized in Table 1.

CCDC: 1003553, HL; 1003552, Cu(Ⅱ) complex.

2　Results and discussion

2.1　IR spectra of HL and its Cu(Ⅱ) complex

The FT-IR spectra of HL and its corresponding Cu(Ⅱ) complex exhibit various bands in the 400~4 000

Table 1　Crystal data and structure refinement for HL and its Cu(Ⅱ) complex

Compound	HL	[CuL_2]
Formula	$C_{22}H_{19}ClN_2O_2$	$C_{44}H_{36}Cl_2CuN_{44}$
Formula weight	378.84	819.21
T / K	293	298(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	4.267 8(5)	1.152 70(11)
b / nm	0.722 97(9)	1.371 60(12)
c / nm	0.613 09(6)	1.391 30(13)
α / (°)	90.00	63.993 0(10)
β / (°)	91.498(9)	87.479(2)
γ / (°)	90.00	84.417 0(10)
V / nm^3	1.891 0(4)	1.967 6(3)
Z	4	2
D_c / ($g\cdot cm^{-3}$)	1.331	1.383
μ / mm^{-1}	0.221	0.739
F(000)	792	846

Continued Table 1

θ range for data collection / (°)	2.86~25.01	2.41~25.02
Limiting indices	$-50 \leqslant h \leqslant 47$, $-8 \leqslant k \leqslant 8$, $-7 \leqslant l \leqslant 7$	$-8 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 15$
Reflections collected / unique	11 238 / 3 294 (R_{int}=0.082 8)	10 084 / 6 853 (R_{int}=0.041 5)
Completeness to θ / %	98.4	98.5
Data / restraints / parameters	3 294 / 0 / 245	6 853 / 0 / 571
GOF on F^2	1.036	1.049
Final R indices ($I>2\sigma(I)$)	R_1=0.064 6, wR_2=0.134 3	R_1=0.058 1, wR_2=0.094 4
R indices (all data)	R_1=0.084 7, wR_2=0.147 8	R_1=0.080 0, wR_2=0.105 4
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	424, −496	396, −342

cm^{-1} region, and are given in Fig.1. The O-H stretching band of the free ligand HL appears at 3 038 cm^{-1}, which disappears in the Cu(Ⅱ) complex, indicating the oxygen atoms in the phenolic hydroxyl groups have been completely deprotonated and coordinated to Cu(Ⅱ) ion. The free ligand HL exhibits characteristic C=N stretching band at 1 611 cm^{-1}, while that of the Cu(Ⅱ) complex is observed in the 1 582 cm^{-1}. The C=N stretching frequency shift is *ca.* 29 cm^{-1} upon complexation, indicating a decrease in the C=N bond order due to the coordination of the Cu(Ⅱ) ion to the oxime nitrogen lone pair[18-19]. The Ar-O stretching frequency occurs at 1 273 cm^{-1} for the ligand HL, and at 1 296 cm^{-1} for the Cu(Ⅱ)) complex. The higher frequency of the Ar-O absorption shift is 23 cm^{-1} indicating that Cu-O bond is formed between the Cu(Ⅱ) ion and the oxygen atoms of the phenolic groups.

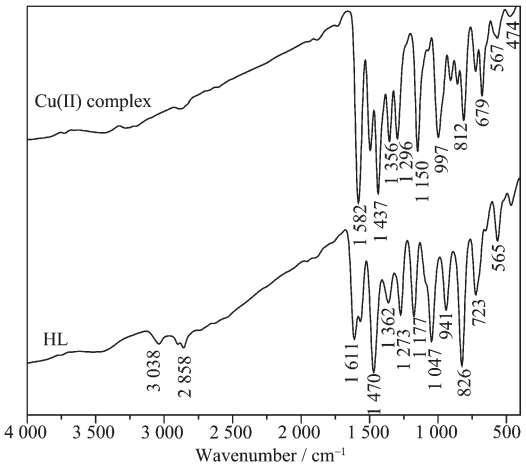


Fig.1 IR spectra of HL and its Cu(Ⅱ) complex

2.2 UV-Vis absorption spectra of HL and its Cu(Ⅱ) complex

The absorption spectra of HL and its corresponding Cu(Ⅱ) complex (Fig.2), in diluted DMSO solution show that the spectrum of the Cu(Ⅱ) complex is different from the spectrum of the free ligand HL. The UV-Vis spectrum of the free ligand HL exhibits two absorption peaks at *ca.* 275 and 390 nm, which can be assigned to the π-π* transition of the benzene rings and the intra-ligand π-π* transition of the C=N bonds[20], respectively.

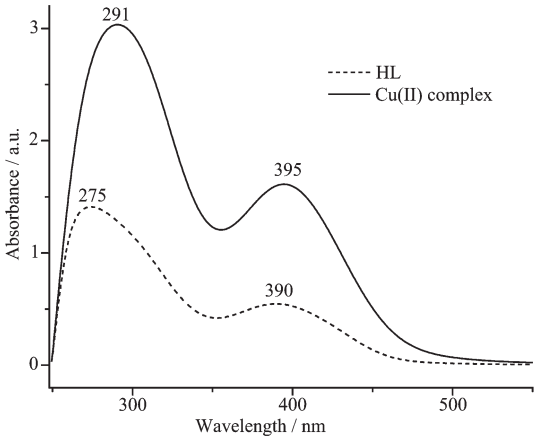


Fig.2 UV-Vis absorption spectra of HL and its Cu(Ⅱ) complex in DMSO (0.1 mmol·L^{-1})

Compared with the absorption peak of the free ligand HL, a corresponding absorption peak at 291 nm is observed in the Cu(Ⅱ) complex, which bathochromically shifted for *ca.* 16 nm, indicating the coordination of Cu(Ⅱ) ions with the free ligand. Meanwhile, the absorption band at about 390 nm disappears from the UV-Vis spectrum of the Cu(Ⅱ) complex, which indicates that the oxime nitrogen atom is involved in the coordination to the Cu(Ⅱ) atom[21-22]. In addition, the new bands observed at 395 nm for the Cu(Ⅱ) complex is assigned to the n-π* charge transfer transition from the filled $p\pi$ orbital of the phenolic oxygen to the

vacant-orbital of the Cu(Ⅱ) ions, which are characteristic of the transition metal complexes with N_2O_2 coordination spheres[23].

2.3 Structural description of HL and its Cu(Ⅱ) complex

The molecular structure of the free ligand HL is shown in Fig.3, and selected bond lengths and angles of HL are listed in Table 2. The crystal structure of HL is only built up by the $C_{88}H_{76}Cl_4N_8O_8$ molecule, within all bond lengths are in normal ranges. The dihedral angle between the two terminal benzene rings (C10-C15 and C17-C22) is 46.01(3)°.

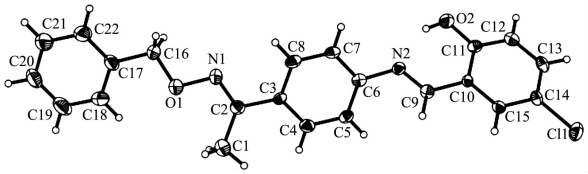


Fig.3　Molecular structure of the free ligand HL showing 30% probability displacement ellipsoids

The ORTEP representation of the Cu(Ⅱ) complex is shown in Fig.4. Selected bond lengths and bond angles are summarized in Table 3. The Cu(Ⅱ)complex consists of one Cu(Ⅱ) ion and two bidentate L^- units. It can be described as centrosymmetric mononuclear Cu(Ⅱ) complex, and the Cu(Ⅱ) ion lying on the inversion centre, is four-coordinated in a trans-CuN_2O_2 square-planar geometry, with two phenolate O and two N atoms from two N,O-bidentate oxime-type ligands.

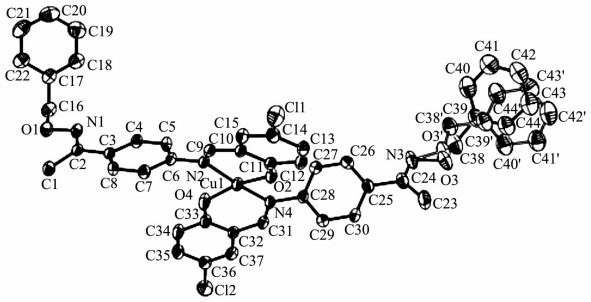


Fig.4　Molecular structure of the Cu(Ⅱ) complex showing 30% probability displacement ellipsoids

Table 2　Selected bond lengths (nm) and bond angles (°) for HL

Cl(1)-C(14)	0.172 9(8)	C(13)-C(14)	0.140 2(1)	C(4)-C(5)	0.139 8(1)
O(1)-C(16)	0.141 8(9)	C(16)-C(17)	0.150 8(1)	C(6)-C(7)	0.137 4(1
N(1)-C(2)	0.128 7(9)	C(17)-C(22)	0.139 4(1)	C(9)-C(10)	0.146 7(9)
N(2)-C(9)	0.128 0(9)	C(19)-C(20)	0.137 4(1)	C(10)-C(15)	0.139 8(9)
C(2)-C(3)	0.149 8(1)	C(21)-C(22)	0.138 3(1)	C(12)-C(13)	0.138 5(1)
C(3)-C(8)	0.140 1(9)	O(1)-N(1)	0.141 7(6)	C(14)-C(15)	0.137 7(1)
C(5)-C(6)	0.139 1(9)	O(2)-C(11)	0.135 9(9)	C(17)-C(18)	0.138 7(1)
C(7)-C(8)	0.137 4(1)	N(2)-C(6)	0.143 2(9)	C(18)-C(19)	0.137 0(1)
C(10)-C(11)	0.141 2(8)	C(1)-C(2)	0.148 1(1)	C(20)-C(21)	0.137 2(1)
C(11)-C(12)	0.139 2(1)	C(3)-C(4)	0.139 9(1)		

N(1)-O(1)-C(16)	108.6(5)	Cl(1)-C(14)-C(15)	120.1(5)	C(3)-C(8)-C(7)	120.9(7)
C(6)-N(2)-C(9)	120.8(5)	C(10)-C(15)-C(14)	120.4(6)	C(9)-C(10)-C(11)	120.9(5)
N(1)-C(2)-C(3)	113.4(6)	C(16)-C(17)-C(18)	123.5(7)	C(11)-C(10)-C(15)	119.3(6)
C(2)-C(3)-C(4)	121.8(6)	C(18)-C(17)-C(22)	118.5(8)	O(2)-C(11)-C(12)	118.6(6)
C(4)-C(3)-C(8)	118.3(7)	C(18)-C(19)-C(20)	119.9(9)	C(11)-C(12)-C(13)	121.3(6)
C(4)-C(5)-C(6)	120.2(7)	C(20)-C(21)-C(22)	121.2(8)	Cl(1)-C(14)-C(13)	119.1(6)
N(2)-C(6)-C(7)	118.2(6)	O(1)-N(1)-C(2)	110.8(6)	C(13)-C(14)-C(15)	120.7(7)
C(6)-C(7)-C(8)	121.0(6)	N(1)-C(2)-C(1)	124.7(7)	O(1)-C(16)-C(17)	109.2(6)
N(2)-C(9)-C(10)	120.7(5)	C(1)-C(2)-C(3)	121.8(7)	C(16)-C(17)-C(22)	117.9(7)
C(9)-C(10)-C(15)	119.8(5)	C(2)-C(3)-C(8)	119.9(7)	C(17)-C(18)-C(19)	121.4(8)
O(2)-C(11)-C(10)	122.1(7)	C(3)-C(4)-C(5)	120.2(6)	C(19)-C(20)-C(21)	119.6(8)
C(10)-C(11)-C(12)	119.3(6)	N(2)-C(6)-C(5)	122.2(7)	C(17)-C(22)-C(21)	119.3(8)
C(12)-C(13)-C(14)	119.0(8)	C(5)-C(6)-C(7)	119.4(8)		

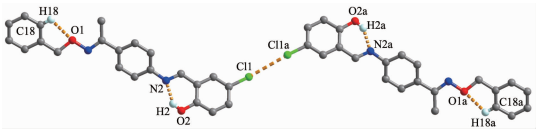
Table 3 Selected bond lengths (nm) and bond angles (°) for the Cu(Ⅱ) complex

Cu(1)-O(2)	0.188 8(3)	Cu(1)-N(2)	0.201 2(4)	Cu(1)-O(4)	0.188 4(4)
Cu(1)-N(4)	0.200 3(4)				
O(2)-Cu(1)-O(4)	166.1(1)	Cu(1)-N(2)-C(6)	119.8(3)	N(2)-Cu(1)-N(4)	175.3(2)
O(2)-Cu(1)-N(4)	87.4(2)	Cu(1)-N(4)-C(28)	121.3(3)	Cu(1)-O(4)-C(33)	129.8(3)
O(4)-Cu(1)-N(4)	92.6(2)	O(2)-Cu(1)-N(2)	92.7(2)	Cu(1)-N(2)-C(9)	123.2(3)
Cu(1)-O(2)-C(11)	129.4(3)	O(4)-Cu(1)-N(2)	88.5(2)	Cu(1)-N(4)-C(31)	123.2(3)

In the Cu(Ⅱ) complex, two N atoms of C=N group 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 coordinated bonds, Cu-O and Cu-N, indicates weaker interaction of L^- unit with the Cu(Ⅱ) center, 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 Cu(Ⅱ) complex with the salen-type ligands.

2.4 Supramolecular interaction of HL and its Cu(Ⅱ) complex

The main hydrogen bond data of HL and its Cu(Ⅱ) complex are given in Table 4. In the crystal structure of HL, a strong O2–H2···N2 and a weak C18–H18···O1 intramolecular hydrogen bonds generate six-membered ring motifs and establish the molecular conformation. Meanwhile, the intermolecular Cl···Cl halogen bonding interaction linked a pair of compound molecules to form a dimer unit with the Cl···Cl distance of 0.345 9(3) nm (Fig.5). Furthermore, every dimer further links four other adjacent dimer units into an infinite 3D supramolecular networks structure containing 1D rectangle channels along the *c* axis by five pairs of intermolecular C–H···π interactions (Fig. 6 and 7).



Symmetry code: a: 1–*x*, 1–*y*, 2–*z*

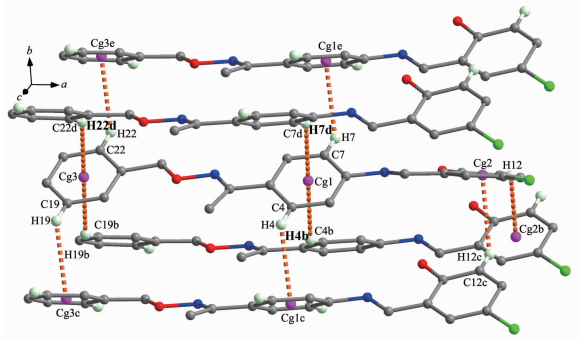
Fig.5 Part of intramolecular O2–H2···N2, C18–H18···O1 hydrogen bonds and intermolecular Cl···Cl halogen bonding interactions of HL

The crystal structure of the Cu(Ⅱ) complex is stabilized by intermolecular C29–H29···O2a hydrogen bonds (Fig.8). Meanwhile, the Cu(Ⅱ) complex is linked by C4–H4···π (Cg4) and C1–H1A···π (Cg5) hydrogen bonds into a infinite 2D layer supramolecular structure. This linkage is further stabilized by π···π stacking interactions of between benzene rings (Cg6···Cg6c) of

Table 4 Putative hydrogen bonds (nm) in HL and its Cu(Ⅱ) complex*

Compound	D–H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠DHA
HL	O2–H2···N2	0.082	0.186	0.259 0(6)	147
	C18–H18···O1	0.093	0.246	0.277 7(1)	100
	C4–H4···Cg1	0.093	0.293	0.361 5(8)	131
	C7–H7···Cg1	0.093	0.285	0.352 0(7)	130
	C12–H12···Cg2	0.093	0.292	0.356 2(8)	127
	C19–H19···Cg3	0.093	0.289	0.358 3(1)	132
	C22–H22···Cg3	0.093	0.281	0.352 2(1)	134
Cu(Ⅱ) complex	C29–H29–O2a	0.093	0.255	0.243 9(6)	160
	C4–H4···Cg4	0.093	0.290	0.372 7(5)	144
	C1–H1A···Cg5	0.096	0.294	0.366(5)	136

*Cg1, Cg2 and Cg3 are the centroids of benzene ring C3~C8, C10~C15 and C17~C22 of HL, respectively; Cg4, Cg5 and Cg6 are the centroids of benzene ring C39~C44, C3~C8 and C10~C15 of the Cu(Ⅱ) complex; Symmetry code: a: 1–*x*, 1–*y*, 1–*z*



Symmetry code: b: x, 0.5−y, −0.5+z; c: x, 0.5−y, 0.5+z; d: x, 1.5−y, 0.5+z; e: x, 1.5−y, −0.5+z

Fig.6　Part of intermolecular C−H$\cdots\pi$ interactions of HL

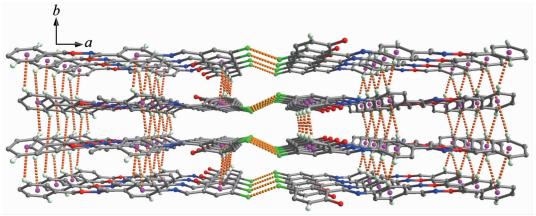
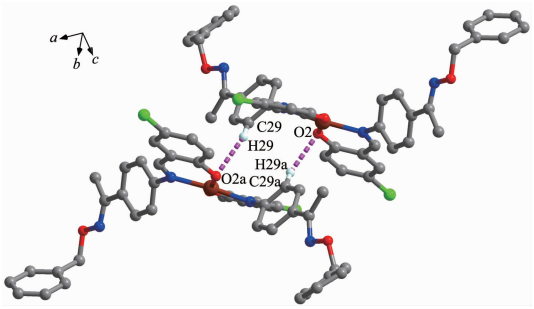


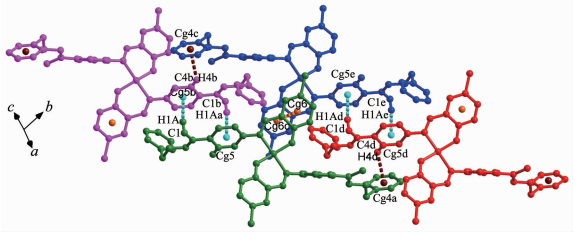
Fig.7　Part of 3D supramolecular networks with the 1D rectangle channels along the c axis in HL



Symmetry code: a: 1−x, 1−y, 1−z

Fig.8　Part of intermolecular C−H$\cdots$O interactions in the Cu(Ⅱ) complex

the adjacent Cu (Ⅱ) complex molecules with the centroid-centroid distances of 0.368 9 (3) nm and the dihedral angle of the two neighboring benzene rings is 0° (Fig.9). Consequently, the intermolecular non-classical hydrogen-bonding (Cl$\cdots$Cl halogen bonding, C−H$\cdots\pi$ hydrogen bonding and $\pi\cdots\pi$ stacking interactions) plays a very important role in the construction of supramolecular networks structure.



Symmetry code: a: 1−x, 1−y, 1−z; b: −x, −y, 2−z; c: −1+x, y, z; d: x, 1+y, −1+z; e: −x, 1−y, 1−z

Fig.9　Digram showing C−H$\cdots\pi$ and π-π stacking interactions in the Cu(Ⅱ) complex

3　Conclusions

An oxime-type ligand and its mononuclear Cu(Ⅱ) complex have been synthesized and characterized structurally. The Cu(Ⅱ) complex is tetracoordinated by two nitrogen atoms and two oxygen atoms of two deprotonated L^- units defining the N_2O_2 basal plane. The coordination environment around Cu(Ⅱ) atom is best regarded as the square-planar geometry, and every Cu(Ⅱ) complex molecule links four other molecules into an infinite 2D-layer supramolecular structure via intermolecular C−H$\cdots\pi$ hydrogen-bonding interactions and $\pi\cdots\pi$ stacking interactions. Consequently, the intermolecular non-classical hydrogen-bonding plays a very important role in the construction of supramolecular networks structure.

References:

[1] Kim J, Chen B, Reineke T M, et al. *J. Am. Chem. Soc.*, **2001**,**123**(34):8239-8247

[2] Lacroix P G. *Eur. J. Inorg. Chem.*, **2001**(2):339-348

[3] Sharma A K, Lloret F, Mukherjee R N. *Inorg. Chem.*, **2007**, **46**(13):5128-5130

[4] Percy G C, Thornton J. *J. Inorg. Nucl. Chem.*, **1973**,**35**:2319-2327

[5] Adhikary C, Sen R, Bocelli G, et al. *J. Coord. Chem.*, **2009**, **62**(22):3573-3582

[6] Rajasekar M, Sreedaran S, Prabu R. et al. *J. Coord. Chem.*, **2010**,**63**:136-146

[7] Dong W K, Sun, Y X, Zhang Y P, et al. *Inorg. Chim. Acta*, **2009**,**362**(1):117-124

[8] Dong W K, He X N, Yan H B, et al. *Polyhedron*, **2009**,**28** (8):1419-1428

[9] Dong W K, Zhao C Y, Sun Y X, et al. *Inorg. Chem. Comm.*, **2009**,**12**(3):234-236

[10]Dong W K, Duan J G, Guan Y H, et al. *Inorg. Chim. Acta*, **2009**,**362**(4):1129-1134

[11]Katsuki T. *Coord. Chem. Rev.*, **1995**,**140**:189-214

[12]Summers M F, Marzilli L G, Bresciani-Pahor N, et al. *J. Am. Chem. Soc.*, **1984**,**106**:4478-4485

[13]Lacroix P G. *Eur. J. Inorg. Chem.*, **2001**(2):339-348

[14]Sun S S, Stern C L, Nguyen S T, et al. *J. Am. Chem. Soc.*, **2004**,**126**:6314-6326

[15]Koehler K, Sandstrom W, Cordes E H. *J. Am. Chem. Soc.*, **1964**,**86**(13):2413-2419

[16]DONG Wen-Kui(董文魁), TANG Xiao-Lu(唐晓璐), HE Xue-Ni(何雪妮), et al. *Chinese. J. Inorg. Chem.*(无机化学学报), **2009**,**25**(3):528-532

[17]Sheldrick G M. *SHELXS* 97, *Program for Refinement of Crystal* Structures, University of Göttingen, Germany, **1997**.

[18]Wu H L, Yuan J K, Bai Y, et al. *Transition Met. Chem.*, **2011**,**36**:819-827

[19]Wu H L, Li K, Sun T, et al. *Transition Met. Chem.*, **2011**, **36**:21-28

[20]Ghosh T, Mondal B, Ghosh T, et al. *Inorg. Chim. Acta*, **2007**,**360**:1753-1761

[21]Smith H E. *Chem. Rev.*, **1983**,**83**:359-377

[22]Dong W K, Sun Y X, Liu G H, et al. *Z. Anorg. Allg. Chem.*, **2012**,**638**(9):1370-1377

[23]Akine S, Taniguchi T, Nabeshima T. *Chem. Lett.*, **2001**,**30**: 682-683