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含 5-氯水杨醛 Schiff 碱配体的镍和铜配合物的合成及晶体结构

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摘要：合成了 2 个含三齿 Schiff 碱配体和单齿 *N*-杂环分子的多核过渡金属配合物：1 个含 5-氯水杨醛缩对硝基苯甲酰腙(H_2L_1)和吗啡啉(Mf)的镍(Ⅱ)配合物[Ni(L_1)(Mf)] (**1**)，1 个含 5-氯水杨醛缩水杨酰腙(H_2L_2)和吡啶(Py)的铜(Ⅱ)配合物[$Cu_2(L_2)_2(Py)_2$] (**2**)，并通过元素分析、红外光谱、紫外光谱以及单晶衍射等手段进行表征。在配合物 **1** 中，中心 Ni(Ⅱ)与酰腙配体(L_1^{2-})的酚氧、亚胺氮、去质子酰胺氧原子以及中性吗啡啉氮原子配位形成平面四方形的 N_2O_2 配位构型，相邻配合物通过分子间氢键作用构筑成一维超分子链状结构。配合物 **2** 中含有 2 个晶体学上独立的双核铜(Ⅱ)配合物，相邻配合物分子的酚氧原子分别桥联 2 个[Cu(L_2)(Py)]基本单元，形成 2 个含有 $Cu_2(\mu\text{-}O)_2$ 核心的配合物。每个 Cu(Ⅱ)原子具有五配位的 NONO(O)四角锥配位构型。

关键词：Schiff 碱；镍(Ⅱ)配合物；铜(Ⅱ)配合物；晶体结构
中图分类号：O614.81+3；O614.121 **文献标识码**：A **文章编号**：1001-4861(2012)01-0201-06

Syntheses and Crystal Structures of Nickel(Ⅱ) and Copper(Ⅱ) Complexes with Schiff Base Ligand of 5-Chlorosalicylaldehyde

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Abstract: Two polynuclear transition metal complexes with a monodentate heterocycle and tridentate Schiff base ligands have been synthesized and characterized by elemental analysis, IR, UV and X-Ray diffraction. One is nickel(Ⅱ) complex [Ni(L_1)(Mf)] (**1**) with 5-chlorosalicylaldehyde 4-nitrobenzoylhydrazone (H_2L_1) and morpholine (Mf), the other is copper(Ⅱ) complex [$Cu_2(L_2)_2(Py)_2$] (**2**) with 5-chlorosalicylaldehyde salicyloylhydrazone (H_2L_2) and pyridine (Py). In compound **1**, the Ni(Ⅱ) ion is coordinated by three donors (phenolate-O, imine-N and deprotonated amide-O atoms) from the ligand L_1^{2-} and the N atom of the neutral morpholine, forming a square-planar N_2O_2 coordination geometry. In the crystal, every two molecules related by centrosymmetric operation in compound **1** are connected through intermolecular hydrogen bonds, forming one-dimensional chain. There are two crystallographically binuclear copper(Ⅱ) units in complex **2**. The two metal centres are bridged by the phenolate O atoms of the neighboring ligand, forming two Cu_2O_2 quadrangle. Each Cu(Ⅱ) ion has a square-pyramidal geometry. CCDC: 846209, **1**; 846210, **2**.

Key words: Schiff base; Nickel(Ⅱ) complex; Copper(Ⅱ) complex; crystal structure

The study of transition metal-hydrazone complexes, in which the hydrazone ligands are formed by condensing hydrazine with β-diketones, salicylaldehyde and their derivatives, has attracted considerable

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attention because of the biological activity and chemical versatility of these complexes [1-3]. Tridentate Schiff-bases are regarded as a good type of chelating ligands for transition metal. For example, aroylhydrazones of salicylaldehyde and its derivatives can bind to a given metal ion through phenolate oxygen, imine nitrogen and amide oxygen atoms[4-5]. In addition, the phenolate-O site can function as a bridging site to furnish dinuclear complexes, which simultaneously having other ancillary ligands in their coordination positions [4,6-8]. Neutral *N*-donor pyridine or morpholine has been used as the ancillary ligand in those reported complexes[6-7,9-10]. In the following account, we have described the syntheses, characterizations and the crystal structures of a nickel complex and a binuclear copper complex with different aroylhydrazone ligands.

1 Experimental

1.1 Reagents and physical measurements

The Schiff base ligands 5-chlorosalicylaldehyde 4-nitrobenzoylhydrazone (H_2L_1) and 5-chlorosalicylaldehyde salicyloylhydrazone (H_2L_2) were synthesized according to the reported method[10]. All starting chemicals were of analytical grade and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried with an Elementar Vario EL Ⅲ microanalyser. IR spectra were recorded on a Perkin-Elmer spectrum 2000 spectrophotometer with KBr pellets in the range of 4 000~400 cm^{-1}. Electronic spectra were recorded on a UV-1900 UV/VIS spectrophotometer using ethanol as the solvent.

1.2 Synthesis of complex [Ni(L_1)(Mf)] (1)

H_2L_1 (0.1 mmol) and $NiCl_2 \cdot 2H_2O$ (0.1 mmol) were dissolved in methanol (10 mL). After stirring for 15 min, morpholine (Mf, 1 mL) was added to the solution, which was then stirred for another 1 h and filtered. Red single crystals of (**1**) were obtained after one week. Anal. Calcd. for $C_{18}H_{17}ClN_4NiO_5$(%): C 46.60, H 3.67, N 12.08; found(%): C 46.72, H 3.63, N 12.01.

1.3 Synthesis of complex [$Cu_2(L_2)_2(Py)_2$] (2)

To H_2L_2 (0.1 mmol) in methanol (5 mL) was added an equimolar amount of $CuCl_2 \cdot 2H_2O$ (0.1 mmol) in methanol (5 mL). After stirring for 15 min, 3 mL pyridine (Py) was added to the solution. The resulting mixture was stirred at room temperature for an additional period of 1 h and then filtered. Dark-blue prism-shaped crystals of (**2**) were obtained from the solution after two weeks. Anal. cald. for $C_{38}H_{28}Cl_2Cu_2N_6O_6$(%): C 53.13, H 3.98, N 9.39; found(%): C 52.86, H 3.25, N 9.74.

1.4 Crystal structure determination

Single crystals with suitable dimensions of 0.16 mm×0.24 mm×0.48 mm for complex **1** and 0.13 mm×0.28 mm×0.51 mm for complex **2** were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at a Rigaku RAPID Weissenberg IP diffractometer with graphitemonochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) and the φ-ω scan mode. Both structures were solved by direct method with SHELXS-97[11] and refined by fullmatrix least squares calculations with SHELXL-97[12]. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located from the geometrical calculation and refined isotropically. Crystallographic data and structure refinement data for both complexes are listed in Table 1.

CCDC: 846209, **1**; 846210, **2**.

Table 1 Crystallographic data for complexes 1 and 2

Complex	**1**	**2**
Formula	$C_{18}H_{17}ClN_4NiO_5$	$C_{38}H_{28}Cl_2Cu_2N_6O_6$
Molecular weight	463.52	862.64
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	0.861 2(4)	1.860 3(17)
b / nm	0.993 1(4)	0.754 2(7)
c / nm	1.171 2(5)	2.628(2)

Continued Table 1

α / (°)	74.884(16)	
β / (°)	79.307(19)	91.885(12)
γ / (°)	82.55(2)	
V / nm^3	0.946 7(7)	3.685(6)
Z	2	4
D_c / (g·cm^{-3})	1.626	1.555
μ / mm^{-1}	1.206	1.355
F(000)	476	175 2
θ_{min}, θ_{max} / (°)	3.25, 26.50	2.19, 26.00
Index range (h, k, l)	−10~10, −12~12, −14~14	−22~22, −9~9, −32~32
Goodness of fit on F^2	1.121	0.884
R	0.058 0	0.080 1
wR	0.102 9	0.141 8
$(\Delta/\sigma)_{max}$	0.000	0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm^{-3})	314, −371	783, −950

2　Results and discussion

2.1　Crystal structure of complex 1

The selected bond lengths and angles of complex **1** are given in Table 2. As shown in Fig.1, the nickel(Ⅱ) ion lies in a square-planar coordination environment with the hydrazone ligand (H_2L_1) coordinated to it as a tridentate chelating agent via the phenolic O2 atom, the imine N2 atom and the deprotonated amide O1 atom.

Table 2　Selected bond lengths (nm) and angles (°) for complexes 1 and 2

			1		
Ni1-O2	0.181 7(2)	Ni1-N2	0.183 0(3)	Ni1-O1	0.183 9(2)
Ni1-N4	0.194 2(3)	O1-C7	0.130 6(4)	O2-C10	0.131 3(4)
N1-C7	0.130 8(4)	N1-N2	0.140 2(4)	N2-C8	0.128 4(4)
O2-Ni1-N2	96.26(12)	O2-Ni1-O1	178.82(11)	N2-Ni1-O1	84.17(12)
O2-Ni1-N4	86.17(11)	N2-Ni1-N4	176.44(13)	O1-Ni1-N4	93.45(11)
			2		
Cu1-O3	0.191 4(4)	Cu1-N2	0.195 2(5)	Cu1-O2	0.196 3(4)
Cu1-N3	0.202 9(5)	Cu2-O6	0.191 8(4)	Cu2-O5	0.194 2(4)
Cu2-N5	0.195 9(5)	Cu2-N6	0.205 2(5)	O1-C2	0.137 4(7)
O2-C7	0.130 1(6)	N1-C7	0.135 0(7)	N1-N2	0.142 2(6)
N2-C8	0.131 2(7)	O3-C10	0.135 2(6)	O4-C21	0.136 8(7)
N4-C26	0.134 7(7)	N4-N5	0.141 5(6)	N5-C27	0.130 6(7)
O6-C29	0.134 9(7)	Cu1-O3^{ii}	0.277 5(4)	Cu2-O6^{iii}	0.277 5(4)
O3-Cu1-N2	93.24(18)	O3-Cu1-O2	172.47(16)	N2-Cu1-O2	81.41(18)
O3-Cu1-N3	92.85(18)	N2-Cu1-N3	169.25(17)	O2-Cu1-N3	93.28(17)
O3-Cu1-O3^{ii}	86.90(16)	O2-Cu1-O3^{ii}	88.49(14)	N2-Cu1-O3^{ii}	97.05(16)
N3-Cu1-O3^{ii}	92.11(15)	O6-Cu2-O5	172.72(16)	O6-Cu2-N5	92.9(2)
O5-Cu2-N5	81.5(2)	O6-Cu2-N6	93.63(19)	O5-Cu2-N6	92.73(19)
N5-Cu2-N6	168.43(19)	O6-Cu2-O6^{iii}	88.73(15)	O5-Cu2-O6^{iii}	88.03(14)
N5-Cu2-O6^{iii}	102.42(16)	N6-Cu2-O6^{iii}	87.28(16)		

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

The fourth coordination position is occupied by N4 atom of the morpholine ligand. There is nearly no deviation of the mental center from the N_2O_2 square-plane. The maximum and minimum deviations from the mean plane constituted by O1, O2, N2, N4 and Ni1 is 0.003 4(2) and 0.001 0(1) nm, respectively.

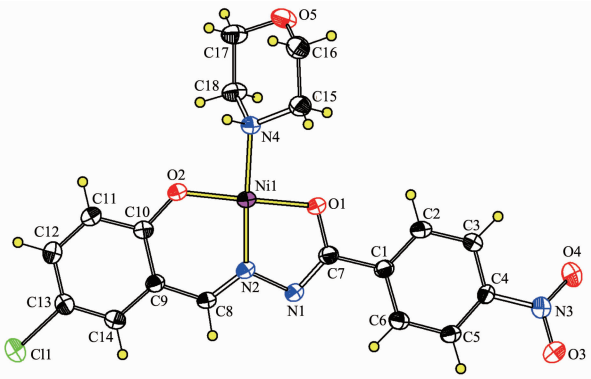
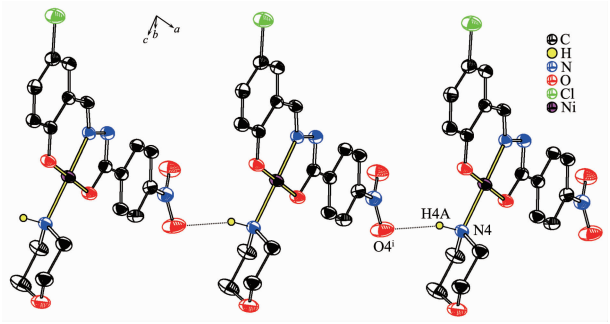


Fig.1 Molecular structure of complex **1** with 30% thermal ellipsoids

The N-N, N-C and C-O bond distances in the =N-NC(O^-)- fragment of L_1^{2-} are consistent with the enolate form of the amide functionalities[9-10,13]. The Ni1-O1 (amide), Ni1-O2 (phenolic) and Ni1-N2 (imine) bond distances are similar to those observed in nickel (Ⅱ) complexes having the same coordinating atoms [9,10,13]. The Ni1-N4 (morpholine) bond length is comparable to the value observed in the only three examples of a tetracoordinated Ni (Ⅱ) complex containing monodentated neutral morpholine moiety[9-10,13]. Both the six-membered chelating ring (r.m.s deviation=0.000 6(2) nm) and the five-membered chelating ring (r.m.s deviation=0.001 5(4) nm) are close to planar, and the dihedral angle between them is 0.6(2)°. The dihedral angle between the two benzene rings of the hydrazone ligand is 5.8(2)°, indicating a slight twist of the whole ligand.

In the crystal structure, the asymmetric units are linked by a week intermolecular N4–H4A(morpholine)⋯O4^{i} (nitro) (symmetry code: ^{i} $x-1$, $y+1$, z) hydrogen bonds, leading to a one-dimensional chain (Fig.2). The N4⋯O4 distance and N4–H4A⋯O4 angle are 0.335(4) nm and 161.68°, respectively. The Ni⋯Ni distance in this uniform arrangement is 1.23 (1) nm, which is longer than that (0.853 3(3) nm) in the similar complex[10].

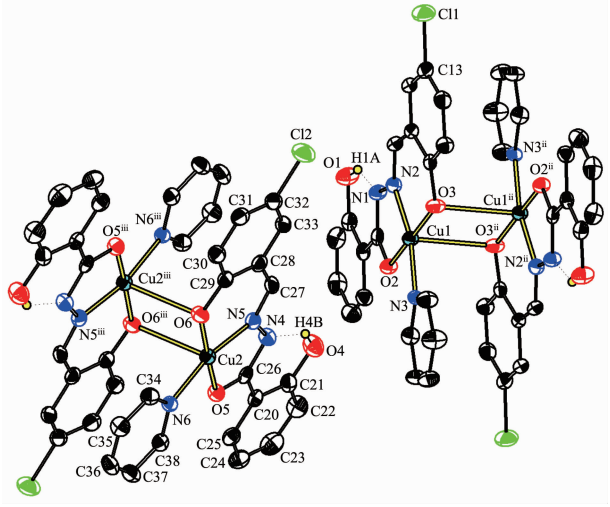


Symmetry code: ^{i} $x-1$, $y+1$, z; H atoms not involved in hydrogen bonding have been omitted

Fig.2 One-dimensional chain structure of complex **1**

2.2 Crystal structure of complex 2

The selected bond lengths and angles of complex **2** are given in Table 2. Single crystal X-ray diffraction analysis reveals that in compound **2** each unit cell consists of two molecules $[Cu(L_2)(Py)]_2$ (named molecule A and molecule B), which are crystallographically independent but chemically similar as shown in Fig.3. Either A or B has a coplanar $Cu_2(\mu\text{-}O)_2$ fragment with the Cu1⋯Cu1^{ii} (symmetry code: ^{ii} $1-x$, $2-y$, $-z$) and Cu2⋯Cu2^{iii} (symmetry code: ^{iii} $-x$, $-y$, $-z$) separations of 0.345 2(3) nm and 0.340 7(3) nm, respectively. The environment around Cu1 and Cu2 in molecules A and B, respectively, are a (4+1) distorted square-pyramidal geometry, as evidenced by the structural index parameter τ[14] which are 0.06 and 0.07, respectively. The value is consistent with that of 0.012 in the copper



Symmetry codes: ^{ii} $1-x$, $2-y$, $-z$; ^{iii} $-x$, $-y$, $-z$; H atoms not involved in hydrogen bonding have been omitted for clarity

Fig.3 Molecular structure of complex **2** with 30% thermal ellipsoids

(Ⅱ) complex [Cu(HSBzh)(HPz)Cl]·H_2O[15] with the same coordination geometry. The basal plane is defined by the phenolic oxygen atom, the imine nitrogen atom and the deprotonated amide oxygen atom from the tridentate dinegative ligand (L_2^{2-}) and pyridine nitrogen atom. The average deviations from the mean planes in A and B are 0.011 93 nm and 0.011 95 nm, respectively with the Cu(Ⅱ) atoms 0.003 9(2) nm and 0.005 3(2) nm out of the relevant planes. The corresponding r.m.s. deviation from the mean plane is 0.006 6 nm [16]. Another phenolate oxygen atom O3^{ii} or O6^{iii} of the neighboring hydrazone ligand completes the five-coordinated square pyramidal geometry in the axial direction, respectively, resulting the Cu1^{ii}-O3, Cu1-O3^{ii} bonds of 0.277 5(4) nm and Cu2^{iii}-O6, Cu2-O6^{iii} bonds of 0.277 5 (4) nm. The long Cu-O bonds may be explained by Jahn-Teller effect[17]. The torsion angle Cu1-O3-Cu1^{ii}-O3^{ii} and Cu2-O6-Cu2^{iii}-O6^{iii} are 0.00°.

The bond distances, Cu-N and Cu-O, are comparable to those found in the similar compound [$Cu_2(C_{16}H_{14}O_4N_2)_2(C_5H_5N)_2$]·$2CH_4O$ [16]. Double-bond character is present in C7-N1, C8-N2, C26-N4 and C27-N5, as judged from their bond lengths (0.135 0(6), 0.131 2(6) nm, 0.134 9(6) nm, 0.130 8(6) nm), which is in agreement with an enolic form of H_2L[18-19]. The C7-O2 and C26-O5 bond lengths of 0.129 9(6) nm and 0.131 6(6) nm are a little longer than the value of 0.127 3 nm expected for an enolic form of the hydrazone ligand[19].

Each tridentate hydrazone ligand combines with one Cu(Ⅱ) atom resulting in one planar five-membered and one planar six-membered chelating rings, with mean devition of 0.000 84~0.001 86 nm and 0.003 87~0.005 72 nm, respectively. The two phenyl rings in each ligand, C1-C6 and C9-C15, C20-C25 and C28-C33, make dihedral angles of 5.5(3)° and 1.5(3)°, respectively, indicating each ligand in complex **2** is planar with mean devition of 0.003 66~0.007 74 nm.

In the crystal structure there are intramolecular O1–H1A⋯N1 and O4–H4B⋯N4 hydrogen bondings between the uncoordinated phenolate O atom and hydrazine N atom of the hydrazone ligand. The O⋯N distances and the O–H⋯N angles are 0.262 8(5) nm, 0.263 5(6) nm and 145.55°, 146.39°, respectively.

2.3 IR spectra

IR spectra of the ligand show stretching bands attributed to PhO-H, C=O and N-H at 3 445~3 427, 1 679~1 671 and 3 329~3 302 cm^{-1}, respectively[17]. Bands at 1 231~1 225 cm^{-1} are assigned to the stretching vibration of ν(Ph-O). For the title complexes, the absence of the N-H and C=O stretching vibration bands suggested the deprotonation and enolization of the CONH group and coordination to the metal ions[20]. A new band appearing in 1 246 cm^{-1} in the complex was assigned to the ν(C-O) (enolate) mode[21]. The deprotonation and coordination can also be confirmed by the bands at 563~686 cm^{-1} (M-O linkages) and 419~626 cm^{-1} (M-N linkages)[17,22], respectively.

2.4 Electronic spectra

The electronic spectra were recorded in ethanol solution for the title complexes (Fig.4). They both have absorptions locating in the range of 300~350 nm corresponding to n-π* transitions[23]. The bands between 200 and 300 nm are assigned to π-π* transitions of the phenyl ring[23] ligands. They also display an electronic spectral bands at ca. 400 nm, which may be assigned to the ligand-to-metal charge transfer (LMCT) transition[10].

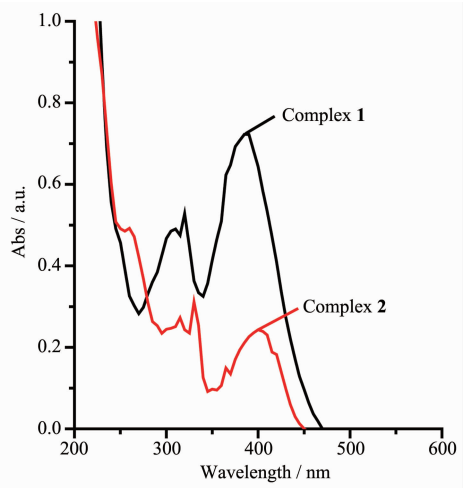


Fig.4 UV spectra of complexes **1** and **2**

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