

2-[(*E*)-(3-氯苯胺基)甲基]-6-溴 4-氯苯酚 Schiff 碱的 铜及锌的配合物的合成及晶体结构

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摘要: 本文合成了 2 个以席夫碱 2-[(*E*)-(3-氯苯胺基)甲基]-6-溴 4-氯苯酚(HL)为配体的单核配合物 CuL_2 (**1**)和 ZnL_2 (**2**)。X-射线衍射分析表明两个配合物分别是一维与二维的高聚物形式的超分子体系。其中配合物 **1** 的几何构型是平面正方形, 依靠分子间的 $\text{C-H}\cdots\text{O}$ 与 $\text{C-H}\cdots\text{Br}$ 氢键作用联结成二维网状结构。配合物 **2** 展现的是畸变的四面体构型, 分子间的 $\text{C-H}\cdots\text{O}$ 的弱的相互作用将其联结成一维链状结构。两个配合物中, 氢键在高聚物链的形成中和配合物结构的稳定中起着很重要的作用。

关键词: 晶体结构; 2-[(*E*)-(3-氯苯胺基)甲基]-6-溴 4-氯苯酚; 铜配合物; 锌配合物

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Synthesis and Crystal Structure of Copper (II) and Zinc (II) Complexes with Schiff base 2-((*E*)-(3-Chlorophenylimino)methyl)-6-bromo-4-chlorophenol

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Abstract: Two mononuclear complexes with the Schiff base ligand 2-((*E*)-(3-chlorophenylimino)methyl)- 6-bromo-4-chlorophenol(HL), namely CuL_2 (**1**) and ZnL_2 (**2**), have been synthesized, aiming at the formation of extended coordination polymer with Cu(II) and Zn(II) ions. X-ray diffraction analyses of available single crystals revealed 1D and 2D polymeric patterns of supramolecular system. Among them, the coordination geometry in the Cu(II) complex is fairly square planar, and the unit CuL_2 is linked into a two-dimensional network structure by weak $\text{C-H}\cdots\text{Br}$ and $\text{C-H}\cdots\text{O}$ interactions. The Zn(II) complex is a distorted tetrahedral, and the neutral molecule unit ZnL_2 is connected by $\text{C-H}\cdots\text{O}$ hydrogen bonds to form a one-dimensional chain. In these two new complexes, hydrogen bonds play a very important role in building the bridged polymeric chain and stabilize the structure of the complexes. CCDC: 862453, **1**; 862451, **2**.

Key words: crystal structure; 2-((*E*)-(3-chlorophenylimino)methyl)-6-bromo-4-chlorophenol; copper(II) complex; zinc(II) complex

0 Introduction

The field of Schiff base complexes was fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines^[1-4]. Their complexes have

proved to be of significant interest in the areas of photoluminescence^[5], catalysis^[6], magnetism^[7] and molecular architectures^[8]. Hence, significant contemporary interests have grown gradually in this field to explore their physical, magnetic, optical and electronic properties through the variation of transition

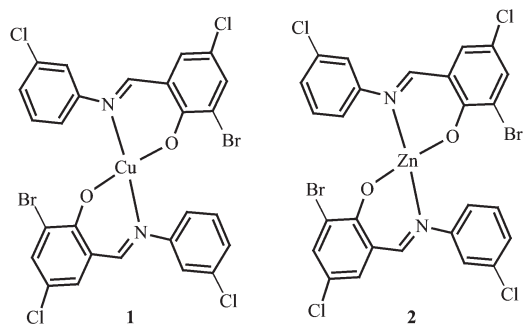
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metal ions like nickel(II), copper(II), zinc(II) and manganese(II/III) in different coordination environments with organic coligands and suitable bridging units. Among all the metals in the transition series, copper(II) and zinc(II) have been found to play the most important biochemical role^[9-10]. With these in mind, a variety of ligating systems has been employed to attain mimic the structural features of the active site. In particular, the Schiff base complexes with an N_2O_2 donor set have been extensively studied.

In the past years, we have prepared a series of Schiff base complexes with an N_2O_2 donor set, and investigated their supramolecular architectures and some relative properties^[11-13]. As an extension of our comprehensive efforts towards synthesis and structural characterization of the new materials containing asymmetrical Schiff bases, we report herein the synthesis and crystallographic characterization of new copper(II) and zinc(II) complexes with the Schiff base ligand 2-((*E*)-(3-chlorophenylimino) methyl)-6-bromo-4-chlorophenol (HL). The structure of these complexes had been established accurately from the single crystal X-ray diffraction study. The results showed that the metal ion in the monomeric unit in the two complexes seems to reside in a four-coordinated environment with a N_2O_2 donor set from the chelating Schiff base ligands, while two oxygen atom and two nitrogen atom from the Schiff base. Not only **1** but also **2** were stabilized by intermolecular hydrogen bonds, and they were linked into a one-dimensional chain or two-dimensional network structure, respectively. These interactions play a very important role in the formation, stability and crystallization **1** and **2**.



Scheme 1 Structure of the complex **1** and **2**

1 Experimental

1.1 Physical measurements

C, H and N analyses were carried out with a Pekin-Elmer 2400 elemental analyzer. The X-ray crystal structure determination was carried out on a Bruker SMART 1000 CCD diffractometer.

1.2 Synthesis of the complex

To the vigorously stirred solution of 3-bromo-5-chlorosalicylaldehyde (0.2 mmol, 47.2 mg) in EtOH (5 cm³), was added dropwise a colourless solution of 3-chlorobenzenamine (0.2 mmol, 25.4 mg) in solution of EtOH (5 cm³) with stirring at room temperature for 1 h. To the resulting orange solution was added $Cu(NO_3)_2$ (0.1 mmol, 18.8 mg). The mixture was stirred for 1 h. Green block-shaped crystals of the complex **1** grew after two weeks. The product was filtered, washed with EtOH, and dried over anhydrous $CaCl_2$ in vacuo overnight. Yield: 70%. (Found(%): C, 41.9; H, 1.8; N, 3.4; $C_{26}H_{14}Br_2Cl_4CuN_2O_2$ Calcd.(%): C, 41.6; H, 1.9; N, 3.7).

Complex **2** can also be prepared by the reaction of $ZnCl_2$ with 3-bromo-5-chlorosalicylaldehyde and 3-chlorobenzenamine. Yield: 60%. (Found(%): C, 41.1; H, 2.1; N, 4.0; $C_{26}H_{14}Br_2Cl_4ZnN_2O_2$ Calcd.(%): C, 41.4; H, 1.9; N, 3.7).

1.3 X-ray single crystal structure determination

Suitable X-ray-quality crystals of **1** and **2** were grown by a solution growth method. The crystals were each mounted on a glass fiber in a random orientation. The data were collected on a Bruker SMART 1000 CCD diffractometer at different temperature. The unit cell parameters and data collections were performed using Bruker SMART program^[14] with graphite-monochromatic $Mo K\alpha$ radiation ($\lambda = 0.071\ 073\ nm$). Multi-scans absorption correction was applied by using the SADABS program^[15]. The structure was solved by direct methods and the refinements were carried out by using full-matrix least-squares techniques on F^2 using the SHELXTL-97 program package^[16], minimizing the function $w[(F_o^2 - F_c^2)^2]$ where the weight w , is defined as $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$, for complex **1** $a = 0.0435$, $b = 0$ and for complex

Table 1 Crystal data and structure refinement parameters

Properties	Complex 1	Complex 2
Empirical formula	C ₂₆ H ₁₄ Br ₂ Cl ₄ CuN ₂ O ₂	C ₂₆ H ₁₄ Br ₂ Cl ₄ ZnN ₂ O ₂
Formula weight	751.55	753.38
Temperature / K	173(2)	163(2)
Crystal shape / color	Block / green	Prism / orange
Crystal size / mm	0.37×0.30×0.29	0.38×0.22×0.19
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.994 5(3)	1.063 5(3)
<i>b</i> / nm	1.112 9(3)	1.133 4(3)
<i>c</i> / nm	1.252 6(4)	1.300 7(4)
α / (°)		105.613(2)
β / (°)	108.569(5)	110.505(2)
γ / (°)		102.224(3)
<i>V</i> / nm ³	1.314 1(7)	1.330 5(6)
<i>Z</i>	2	2
<i>D_c</i> / (g·cm ⁻³)	1.899	1.881
μ / mm ⁻¹	4.308	4.357
<i>F</i> (000)	743	736
θ range / (°)	2.16/29.17	2.12/29.12
Index range (<i>h</i> , <i>k</i> , <i>l</i>)	-12/12, -15/15, -12/17	-13/14, -15/12, -17/17
Absorption correction	Muti-scan	Muti-scan
Max. and min. transmission	0.367 1 and 0.296 4	0.486 8 and 0.291 2
Measured reflections	3 449	6 956
Observed reflections (<i>I</i> ≥ 2σ(<i>I</i>))	2 781	4 580
Data / restraints / parameters	3 449 / 0/ 169	6 956 / 0 / 334
Goodness-of-fit on <i>F</i> ²	0.999	1.001
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> ≥ 2σ(<i>I</i>))	0.030 7 / 0.073 2	0.037 1 / 0.069 0
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.043 6 / 0.077 3	0.061 7 / 0.072 3
Large diff. peak and hole / (e·nm ⁻³)	689 and -359	1 156 and -691

2 *a*=0.021 0, *b*=0.106. In the final cycles refinement of all the non- hydrogen atoms were refined anisotropically, and hydrogen atoms were located at their idealized positions. Crystal data, additional data collection parameters and refinement details are given in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 862453, **1**; 862451, **2**.

2 Results and discussions

2.1 Description of the crystal structure of complex **1**

The X-ray diffraction analysis of complex **1** (Fig. 1) shows that the four-coordinated copper ion are

bonded to the oxygen and nitrogen donor atoms of the two bidentate ligand molecules in the usual trans arrangement. The geometry around copper(II) is fairly square planar, where the dihedral angle between the two coordination planes defined by O(1)ACu1N(1) and O(1A)Cu1N(1A) (symmetry code: A: -*x*+1, -*y*+1, -*z*+1) is nearly 0°. It is interesting to note that the similar complex bis-[(diphenylmethyl)-[(3-oxo-2H-naphth-2-ylidene) methyl]-aminato]copper(II) [17], show a similar dihedral angle between O-Cu-N of 0°. This indicated that the phenyl substituent having a similar steric effect with the diphenylmethyl substituent on the geometry of these kinds of complex[17]. Thus the angles O(1A)-Cu(1)-N(1) and O(1)-Cu(1)-N(1A) are lesser or

Table 2 Selected bond lengths and bond angles for complex 1 and 2

Complex 1					
Cu(1)-O(1)	0.1903 8(2)	Cl(1)-C(4)	0.175 5(2)	C(1)-C(6)	0.140 9(3)
Cu(1)-O(1A)	0.1903 8(2)	Cl(2)-C(12)	0.174 1(3)	C(1)-C(2)	0.141 8(3)
Cu(1)-N(1A)	0.199 9(2)	O(1)-C(1)	0.130 3(3)	C(2)-C(3)	0.137 7(3)
Cu(1)-N(1)	0.199 9(2)	N(1)-C(7)	0.129 3(3)	C(3)-C(4)	0.138 0(3)
Br(1)-C(2)	0.188 1(2)	N(1)-C(8)	0.145 2(3)		
O(1)-Cu(1)-O(1A)	180.0 0	N(1A)-Cu(1)-N(1)	180.0 0	O(1)-C(1)-C(6)	123.7(2)
O(1)-Cu(1)-N(1A)	88.70(8)	C(1)-O(1)-Cu(1)	128.95(15)	O(1)-C(1)-C(2)	120.5(2)
O(1A)-Cu(1)-N(1A)	91.30(8)	C(7)-N(1)-C(8)	113.1(2)	C(6)-C(1)-C(2)	115.8(2)
O(1)-Cu(1)-N(1)	91.30(8)	C(7)-N(1)-Cu(1)	123.73(16)	C(3)-C(2)-Br(1)	118.71(18)
O(1A)-Cu(1)-N(1)	88.70(8)	C(8)-N(1)-Cu(1)	122.83(15)		
Complex 2					
Zn(1)-O(1)	0.190 9(2)	Cl(1)-C(4)	0.175 0(3)	N(1)-C(7)	0.130 8(3)
Zn(1)-O(2)	0.192 1(2)	Cl(2)-C(12)	0.173 6(3)	N(1)-C(8)	0.144 1(3)
Zn(1)-N(1)	0.200 3(2)	Cl(3)-C(17)	0.175 2(3)	N(2)-C(20)	0.130 0(3)
Zn(1)-N(2)	0.200 7(2)	Cl(4)-C(25)	0.174 4(3)	N(2)-C(21)	0.143 4(4)
Br(1)-C(2)	0.188 9(3)	O(1)-C(1)	0.130 5(3)	Br(2)-C(15)	0.190 3(3)
O(2)-C(14)	0.130 3(3)				
O(1)-Zn(1)-O(2)	119.40(9)	C(1)-O(1)-Zn(1)	124.72(19)	C(20)-N(2)-Zn(1)	120.0(2)
O(1)-Zn(1)-N(1)	96.43(9)	C(14)-O(2)-Zn(1)	124.89(19)	C(21)-N(2)-Zn(1)	120.13(18)
O(2)-Zn(1)-N(1)	109.62(9)	C(7)-N(1)-C(8)	120.2(2)	O(1)-C(1)-C(2)	119.4(3)
O(1)-Zn(1)-N(2)	109.62(9)	C(7)-N(1)-Zn(1)	119.07(19)	O(1)-C(1)-Cl(6)	124.0(3)
O(2)-Zn(1)-N(2)	96.88(9)	C(8)-N(1)-Zn(1)	120.47(17)	N(1)-Zn(1)-N(2)	126.82(9)
C(20)-N(2)-C(21)	119.7(2)				

Symmetry code: 1: A: $-x+1, -y+1, -z+1$.

greater than the ideal value of 90° and the trans angles N(1A)-Cu(1)-N(1) and O(1)-Cu(1)-O(1A) exactly equal to the ideal bond angle 180° , which are also consistent with the conclusion of the geometry. The Cu-N and Cu-O distances are 0.190 38(16) and 0.199 9(2) nm, which are also consistent with the corresponding Cu-N and Cu-O distance in bis-{2-[(2-bromo-phenylimino)-methyl]-4-chloro-phenol} copper (II)^[13]. In the structure of **1**, there are some intermolecular interactions C-H \cdots Br and C-H \cdots O hydrogen bonds in the lattice structure. Discrete monomeric molecules are held together by intermolecular hydrogen bond from the adjacent molecule, which connect the molecules to form a one-dimensional chain, and then a two-dimensional network (Fig.2, Table 3).

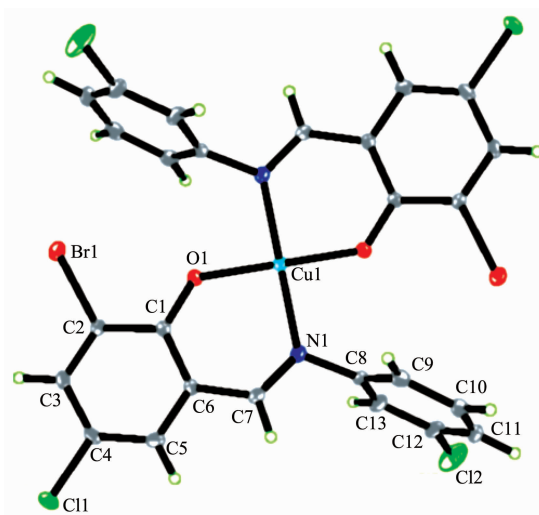
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Fig.1 Molecular structure of complex 1 with displacement ellipsoids are drawn at the 30% probability level

Table 3 Parameters of some hydrogen bonds of **1** and **2**

Complex	D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / ^\circ$
1	C(5)-H(5)...O(1)	0.095 0	0.256	0.344 18	155
	C(7)-H(7)...Br(1)	0.095 0	0.290	0.367 26	139
2	C(13)-H(13)...O(2)	0.095 0	0.259	0.343 68	148
	C(22)-H(3)...O(1)	0.095 0	0.242	0.318 55	138

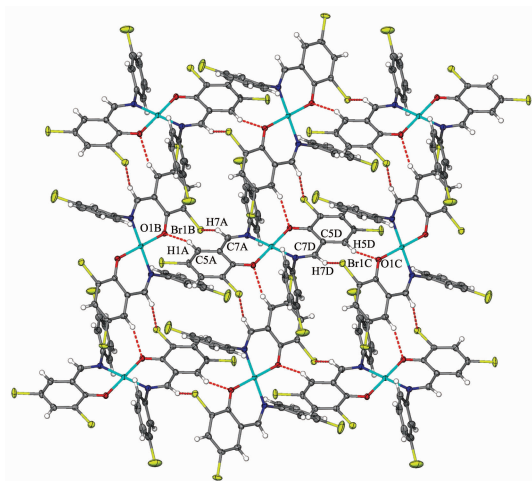
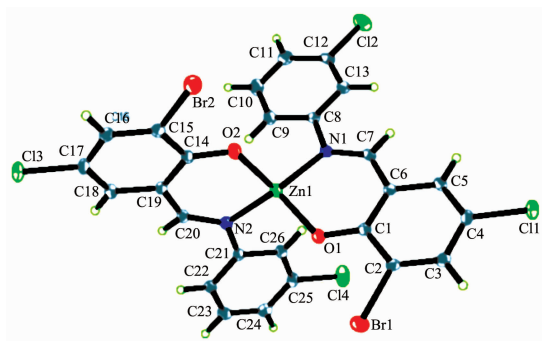

 Symmetry code: A: $-x+1, -y+1, -z+1$; B: $1-x, 1/2+y, 1/2-z$; C: $x, 1/2-y, 1/2+z$; D: $1-x, 1-y, 1-z$

 Fig.2 Packing structure of the complex **1**, hydrogen bonds were showed as dashed lines

2.2 Description of the crystal structure of complex **2**

The crystal structure of **2** consists of a mononuclear complex (Fig.3). The central zinc(II) atom is four coordinate and bonds to two nitrogen atoms and two oxygen atoms from two bidentate ligand molecules in the usual trans arrangement. The geometry around zinc (II) is in a slightly distorted tetrahedral environment, where the dihedral angle between the two coordination planes defined by O(1)Zn(1)N(1) and


 Fig.3 Molecular structure of complex **2** with displacement ellipsoids are drawn at the 30% probability level

O(2)Zn(1)N(2) is $82.97(6)^\circ$ nearly perpendicular, which could be interpreted in terms of the phenyl substituent having a bigger steric effect. The phenyl ring plane (C(1)C(2)C(3)C(4)C(5)C(6): ring A) and the chelate ring (O(1)/Zn(1)/N(1)/C(7)/C(6)/C(1), Rms deviation of fitted atoms is 0.087 3 are nearly coplanar with a dihedral angle of $6.74(15)^\circ$. The phenyl ring plane (C(14)C(15)C(16)C(17)C(18)C(19): ring B) and the chelate ring (O(2)/Zn(1)/N(2)/C(20)/C(19)/C(14)), Rms deviation of fitted atoms is 0.047 1 are nearly coplanar with a dihedral angle of $6.27(18)^\circ$. This indicated that the corresponding planes which did not generate by symmetry, but have good axisymmetry. Bond angles also show that the coordination geometry about the zinc atom is a slightly distorted tetrahedral structure, with O(1)Zn(1)N(1), O(2)Zn(1)N(1) and N(1)Zn(1)N(2) angles of $96.45(9)^\circ$, $119.45(9)^\circ$ and $126.83(9)^\circ$, respectively. The Zn-N bond length (0.2003(2) and 0.2007(2) nm) and Zn-O bond length (1.909(2) nm and 1.921(2) nm) are quite different from other reported Zn-N and Zn-O distances, as in 2-((2-(dimethylamino)ethylimino)methyl)-phenol^[18] and 2,4-diiodo-6-[(2-morpholin-4-yl-ethylimino)-methyl]-phenolato-zinc(II)^[19]. The packing of complex **2** in the crystal lattice are worth mentioning. As shown in Fig.4, each neutral molecular unit interacts with two neighbouring

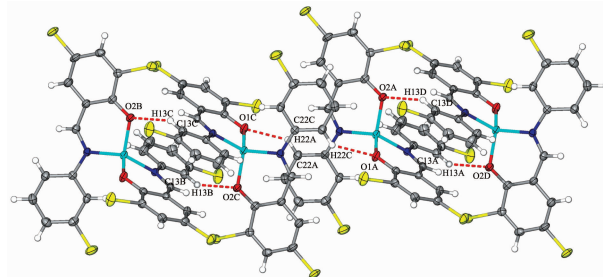

 Symmetry code: A: $-x+1, -y+1, -z+1$; B: $x, y, 1+z$; C: $1-x, 1-y, 1-z$; D: $1-x, 1-y, -z$

 Fig.4 Packing structure of the complex **2**, hydrogen bonds were showed as dashed lines

ones via intermolecular hydrogen bonding involving C13–H13···O1 and C22–H22···O2 (Table 3), leading to the formation of one-dimensional chain, which also mutually strengthen and solidify the molecule.

2.3 Comparison between complex 1 and 2

Due to the Jahn-Teller effect, copper(II) as a d^9 ion is expected to be stable in a square planar for the ligand field is strong enough to cause spin pairing, which is low spin complex and have excellent stability, whereas zinc(II) as a d^{10} ion is expected to be stable in tetrahedral environment, which is high spin complex and have low stability. Thus the phenyl rings of the ligands from aldehyde are all close to the plane of the complexes, whereas the phenyl rings of the ligands from amine are all rotated certain angle. This is probably a result of some conjugation between the aromatic system of phenyl group and pseudoaromatic system of chelating fragment.

Complex **1** and **2** are stabilized by weak intermolecular C–H···O and C–H···Br hydrogen bonds, and the molecule were linked into a one-dimensional chain or two dimensional network structure by them. Meanwhile, these interactions play a very important role in the formation, stability and crystallization of **1** and **2**.

3 Conclusions

In this paper, two new complexes CuL₂ and ZnL₂, which from 2-((E)-(3-chlorophenylimino)methyl)-6-bromo-4-chlorophenol have been synthesized. The complexes were determined by X-ray crystallography diffraction. Complex CuL₂ appears to be a two-dimensional network of the monomeric units formed by the involvement of several interesting intermolecular hydrogen bonds, whereas complex ZnL₂ displays a one-dimensional network. Such type of complexes are expected to be very much useful as the precursor complexes to prepare different complexes having potential application on the biology, the medicine and

so on many domains.

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