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2-[(2-溴苯胺基)甲基]-4-氯苯酚 Schiff 碱及其铜配合物的合成及晶体结构

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摘要:以 5-氯水杨醛和邻溴苯胺为原料合成了一种新的 Schiff 碱配体 2-[(2-溴苯胺基)甲基]-4-氯苯酚(**1**)($C_{13}H_9BrClNO$,H_2L),继而与过渡金属铜离子配合,得到其配合物 **2** ($[Cu(C_{13}H_8BrClNO)_2]$,CuL_2)。通过 X-射线衍射法对配体及其配合物进行了结构表征。化合物 **1** 属正交晶系,*Pbca* 空间群,晶胞参数 *a*=0.710 19(12) nm,*b*=1.308 2(2) nm,*c*=2.533 3(5) nm,M_r=310.57,*V*=2.353 6(7) nm^3,D_c=1.753 g·cm^{-3},*Z*=8,μ=3.700 mm^{-1},*Z*=8,*F*(000)=1 232,*R*=0.025 0,*wR*=0.055 5;化合物 **1** 依靠分子间的 C–H…N,C–H…O,C–H…Cl 氢键及 π-π 堆积作用进一步联结成二维网状结构。化合物 **2** 属单斜晶系,$P2_1/c$ 空间群, 晶胞参数 *a*=0.956 8(2) nm,*b*=1.085 3(3) nm,*c*=1.204 7(3) nm,β=105.965(7)°,M_r=682.67,*V*=1.202 8(6) nm^3,D_c=1.885 g·cm^{-3},*Z*=2,μ=4.481 mm^{-1},*F*(000)=670,*R*=0.045 0,*wR*=0.122 5。**2** 依靠分子间 C–H…π 作用及卤素…卤素作用进一步联结成三维网状结构。

关键词:5-氯水杨醛;Schiff 碱;合成;晶体结构
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Schiff Base 2-[(2-Bromo-phenylimino)-methyl]-4-chloro-phenol and Its Copper(Ⅱ) Complex:Synthesis and Crystal Structure

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Abstract: A Cu(Ⅱ) complex (**2**) of 2-[(2-bromo-phenylimino)-methyl]-4-chloro-phenol (**1**) generated from 5-chloro-salicylaldehyde and *o*-bromoaniline was synthesized and characterized by elemental analysis and single crystal X-ray diffraction. Compound **1** is in the orthorhombic system, space group *Pbca* with *a*=0.710 19(12) nm, *b*=1.308 2(2) nm, *c*=2.533 3 (5) nm, M_r=310.57, *V*=2.353 6 (7) nm^3, D_c=1.753 g·cm^{-3}, *F* (000)=1 232, μ=3.700 mm^{-1}, *Z*=8, *R*=0.025 0 and wR_2=0.055 5. Compound **2** belongs to the monoclinic system, space group $P2_1/c$ with *a*=0.956 8(2) nm, *b*=1.085 3(3) nm, *c*=1.204 7(3) nm, β=105.965(7)°, *V*=1.202 8(6) nm^3, M_r=682.67, D_c=1.885 g·cm^{-3}, *Z*=2, μ=4.481 mm^{-1}, *F*(000)=670, *R*=0.045 0 and wR_2=0.122 5. Compound **1** is stabilized by intermolecular C–H…N and intra-molecular C–H…O hydrogen bonds, C–H…Cl and π…π interaction and further linked into a 2D layer structure. But compound **2** is connected by halogen…halogen and C–H…π hydrogen bond to form a 3D network. CCDC: 803365, **1**; 803366, **2**.

Key words: 5-chlorosalicylaldehyde; Schiff base; synthesis; crystal structure

Hydrogen bondings, π…π stacking and halogen-halogen interactions are important in supramolecular chemistry and crystal engineering[1-2]. They play an important role in self-assembly[3-4], molecular reco-

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gnition[5-6] and the stability of inclusion complexes[7-9] as an auxiliary stabilizing short contact. Numerous experiments have been performed and several reviews have been documented for C–H···O interactions[10], C–H···Cl interactions[11] and $\pi\cdots\pi$ stacking interactions[12-13].

It is known that aromatic amines possessing primary amino groups react with carbonyl compounds to form the corresponding Schiff bases. Schiff base ligands containing N atoms can coordinate a variety of transition metals and N atoms also act as electron donor to form many intromolecular or intermolecular hydrogen bonds. Schiff bases possessing aromatic rings can form $\pi\cdots\pi$ stacking and C–H···π interaction, which play an important role for formation, stabilization and packing of the complex crystal. Based on the extensive application and flexibility of these intheractions in supramolecular network building[14] and the discovery of application prospect of Schiff base in catalysis[15], photoelectric and LCD[16]. We report herein the synthesis and characterisation of a new copper (Ⅱ) complex of Schiff base ligand synthesized from 5-chlorosalicylaldehyde and o-bromoaniline. The structure of the ligand and its Cu (Ⅱ) complex was established accurately from the single crystal X-ray diffraction study. The results show that the Cu(Ⅱ) ion in the monomeric unit resides in a distorted quadrilateral environment with a N_2O_2 donor set from the chelating Schiff base ligands. Not only **1** but also **2** were stabilized by intermolecular and intramolecular hydrogen bonds, $\pi\cdots\pi$ stacking interaction and halogen ··· halogen interactions and linked into a two- or three-dimentional network, respectively. These interactions play a very important role in the formation, stability and crystallization of **1** and **2**. Meanwhile, they also provide a unique case of a di- or poly-meric unit formed through these kinds of weak hydrogen bondings.

1 Experimental

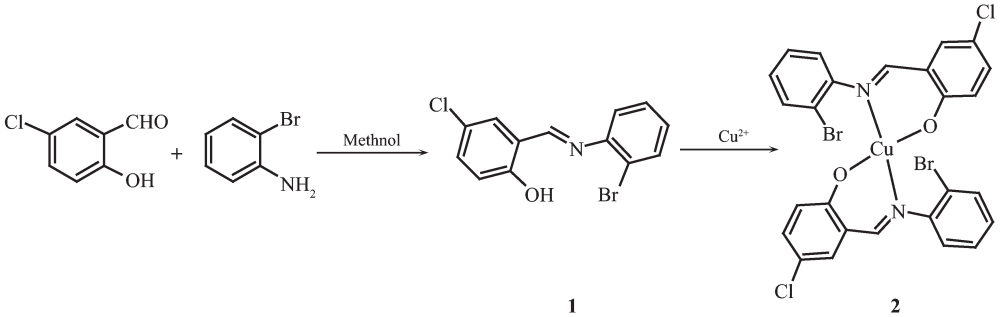
1.1 Reagents and physical measurements

Elemental analysis was performed on a Pekin-Elmer 2400 elemental analyzer. Crystal structure was determined on a Bruker Smart CCD-1000 diffractometer.

All reagents obtained from commercial sources were of AR grade and used without further purification.

1.2 Synthesis of 2-[(2-bromo-phenylimino)-methyl]-4-chloro-phenol (1)

As shown in Scheme 1, 1,2-[(2-bromo-phenylimino)-methyl]-4-chloro-phenol has been synthesized by dissolving 0.5 mmol of 5-chlorosalicylaldehyde and an equimolar quantity of 2-bromoaniline in 50 mL of methanol. The reaction mixture was stirred at room temperature for 30 min and allowed to stand in air. Yellow crystals were formed after 5 d. They were filtered and washed with small amounts of cooled methanol and recrystallized from methanol in good yield (73%). Yellow block single crystals suitable for single crystal X-ray diffraction were grown in methanol by slow evaporation. Anal. calcd. for $C_{13}H_9BrClNO$ (%): C, 50.27; H, 2.90; N, 4.51; Found(%): C, 50.22; H, 2.92; N, 4.46.



Scheme 1

1.3 Synthesis of the Cu(Ⅱ) complex (2)

0.2 mmol of **1** was dissolved in 20 mL methanol and mixed with 0.2 mmol of $Cu(NO_3)_2$ in 10 mL methanol. A brown solution was obtained after stirring in air at room temperature for 2 h and then filtered. The filtrate was left in air to evaporate the solvent and brown

crystals were obtained after 7 d. The product was collected by filtration, washed with cool methanol and then dried in air. Yield: 56% . Brown plate single crystals suitable for single crystal X-ray diffraction were grown in methanol by slow evaporation. Anal. calcd. for $C_{26}H_{16}Br_2Cl_2CuN_2O_2$(%): C, 45.73; H, 2.34; N, 4.10. Found(%): C, 45.70; H, 2.40; N, 4.05.

1.4 X-ray crystal structure determination of 1 and 2

In the determination of the structures of the crystals **1** and **2**, X-ray data were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ =0.071 073 nm) using φ-ω scan technique at 103 (2) K. The structures were solved using direct methods with SHELXTL program [17] and refined on F^2 by full-matrix least-squares techniques. The structures were solved by direct method and refined by full matrix least-squares with the SHELXL program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. The crystals used for the diffraction study showed no decomposition during the data collection. The crystals data, experimental details, and refinement results are summarized in Table 1. The selected bond lengths and angles are given in Table 2.

CCDC: 803365, **1**; 803366, **2**.

Table 1 Crystallographic data and structure refinement summary for 1 and 2

Compound	**1**	**2**
Empirical formula	$C_{13}H_9BrClNO$	$C_{26}H_{16}Br_2Cl_2CuN_2O_2$
Formula weight	310.57	682.67
Crystal size / mm	0.32×0.29×0.27	0.40×0.32×0.09
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a / nm	0.710 19(12)	0.956 8(2)
b / nm	1.308 2(2)	1.085 3(3)
c / nm	2.533 3(5)	1.204 7(3)
β / (°)		105.965(7)
V / nm^3	2 353.6(7)	1 202.8(6)
D_c / (g·cm^{-3})	1.753	1.885
Z	8	2
μ / mm^{-1}	3.7	4.481
F(000)	1 232	670
Index ranges	$-9 \leqslant h \leqslant 9, -16 \leqslant k \leqslant 16, -32 \leqslant l \leqslant 32$	$-9 \leqslant h \leqslant 12, -14 \leqslant k \leqslant 14, -12 \leqslant l \leqslant 15$
θ range / (°)	3.1 to 27.5	3.1 to 27.50
Reflections collected / unique	17 077/ 2 703	9 176 / 2 686
R, *wR* ($I \geqslant 2\sigma(I)$)	0.025 0, 0.055 5	0.045 0, 0.122 5
R, *wR* (all data)	0.032 0, 0.058 1	0.056 0, 0.128 5
GOF on F^2	1	1.001
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	371, −231	1 429, −1 727

Final weighting scheme: $w=1/[\sigma^2(F_o^2)+(0.029\ 6P)^2+1.620P]$, where $P=(F_o^2+2F_c^2)/3$ for **1**; $w=1/[\sigma^2(F_o^2)+(0.069\ 9P)^2+1.396P]$, where $P=(F_o^2+2F_c^2)/3$ for **2**.

Table 2 Selected bond lengths (nm) and angles (°) complex 2

Cu(1)-O(1)$^{\#1}$	0.188 4(3)	Cu(1)-N(1)$^{\#1}$	0.201 8(4)	Cu(1)-N(1)	0.20 18(4)
O(1)$^{\#1}$-Cu(1)-O(1)	180.0	O(1)$^{\#1}$-Cu(1)-N(1)	90.47(14)	C(7)-N(1)-Cu(1)	123.0(3)
O(1)$^{\#1}$-Cu(1)-N(1)$^{\#1}$	89.53(14)	O(1)-Cu(1)-N(1)	89.53(14)		
O(1)-Cu(1)-N(1)$^{\#1}$	90.47(14)	N(1)$^{\#1}$-Cu(1)-N(1)	180.0		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, -y+1, -z+1$.

2 Results and discussion

As shown in Fig.1 and 2, both **1** and **2** contain Schiff base ligands. Compound **1** is built up only by Schiff base molecules, but compound **2** built up by Cu (Ⅱ) ion and Schiff base ligands, within which all bond lengths and bond angles of ligand are in normal ranges. **1** and the ligand of **2** assign to be *E* configuration with respect to the azomethine -CH=N- bond on the basis of the crystal data. The C(7)=N(1) distance of **2** (0.129 2(5) nm) is longer than that of **1** (0.128 7(2) nm). The dihedral angle of two phenyl rings (ring A, C(1)~C(6); ring B, C(8)~C(13)) of 2 is 45.52°, which is much bigger than that of **1** (9.58°). It can be interpreted in terms of coordination ceffect. Moreover, the whole molecule of **1** is nearly coplanar with the dihedral angles of 9.59(1)° (A and B), which is interpreted by conjugation effect and the stabilization of ring from intramolecular hydrogen bond. But **2** is not coplanar with the dihedral angles of 45.56 (15)° (A and B) due to coordination ceffect and steric effect.

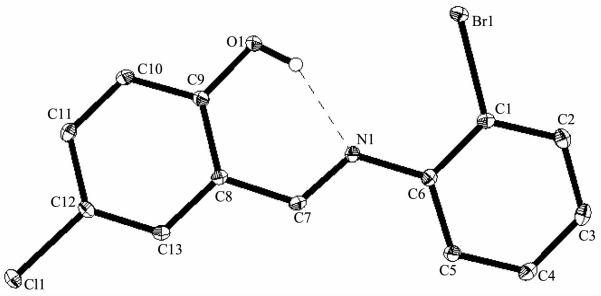
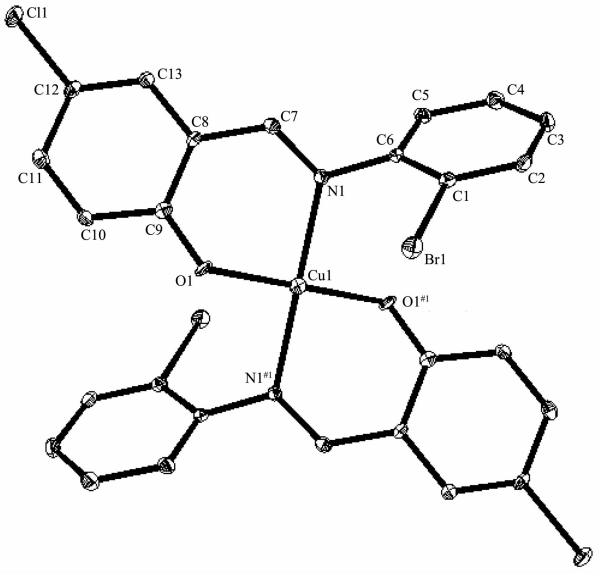


Fig.1 Molecular structure of **1** with displacement ellipsoids are drawn at the 30% probability level

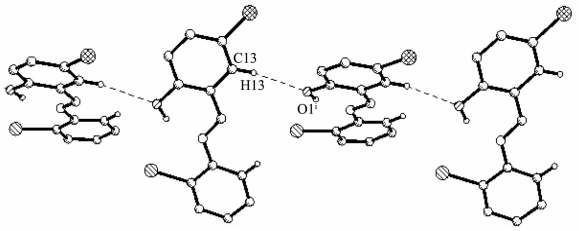


Symmetrycode: #1 −*x*+1, −*y*+1, −*z*+1

Fig.2 Molecular structure of **2** with displacement ellipsoids are drawn at the 30%probability level and the hydrogen atoms are omitted for clarity

The bromine atom at phenyl ring is slightly twisted out of the ring with the torsion angle Br (1)-C (1)-C(2)-C(3) 179.89(14)° in the structure of **1** and with the torsion angle Br (1)-C (1)-C (2)-C (3) 176.3 (3)° in the structure of **2**. The hydroxyl group nearly oriented out of the oriented phenyl ring, as indicated by the torsion angle C(13)-C(8)-C(9)-O(1) 179.62(17)° in the structure of **1** and by the torsion angle C(13)-C(8)-C(9)-O(1) 174.4(4)° in structure of **2**. All are due to the *p*-π conjugate effect of atoms possessing unshared electron pairs and phenyl rings.

In the structure of **1**, there are some intermolecular interaction C–H⋯Cl, C–H⋯O hydrogen bonds and π ⋯ π stacking interaction in the lattice structure. Discrete monomeric molecules are held together by intermolecular hydrogen bond C(13)–H(13)⋯O(1), which connect the molecules to form a 1D zig-zag chain along *b* axis (Fig.3, Table 3).



C–H⋯O hydrogen bond was showed as dashed lines, hydrogen atomes were omitted for clarity; #1 −*x*+3/2, 1/2+*y*, *z*

Fig.3 A one-dimentional zig-zag chain of **1** along *b*-axis

A striking feature of this complex is that the zig-zag chains were linked to form a 2D nextwork through C–H⋯Cl hydrogen bonding and π⋯π interactions. Atom C (5) acts as hydrogen bonding acceptor and the Cl(1) atom of a neighboring molecule functions as the hydrogen bonding donor to form C(5)–H(5)⋯Cl(1) hydrogen bondings. As the current interests in crystal engineering and supramolecular chemistry, there is now a new insight into weak hydrogen bonding interactions.

Table 3　Parameters of hydrogen bonds, C–H···π and halogen-halogen interaction of 1 and 2

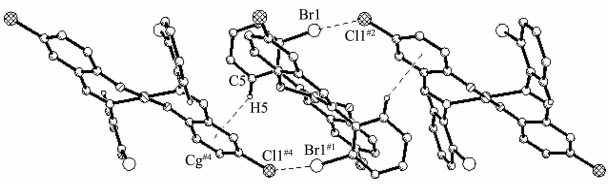
Compound	D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠(DHA) / (°)
1	O(1)–H(1O)···N(1)	0.083 2	0.186 4	0.261 4	149.3
	C(13)–H(13)···O(1)$^{\#1}$	0.095 0	0.260 4	0.353 7	167.0
	C(5)–H(5)···Cl(1)$^{\#2}$	0.095 0	0.289 7	0.362 1	133.8
2	C(1)–Br(1)···Cl(1)$^{\#2}$	0.191 1	0.353 4		154.1
	C(1)–Br(1) ···Br(1)$^{\#3}$	0.191 1	0.360 0		135.8
	C(5)–H(5)···Cg$^{\#4}$	0.095 0	0.282 6	0.346 4	125.4

Cg is center of the plane of the C8~C13 ring; Symmetrycodes: **1**: $^{\#1}$ $-x+3/2$, $1/2+y$, z; $^{\#2}$ $x-1/2$, $-y+3/2$, $z+1$; **2**: $^{\#2}$ $-x+1$, $y-1/2$, $-z+1/2$; $^{\#3}$ $-x+2$, $-y+1$, $-z+1$; $^{\#4}$ x, $-y+1/2$, $-z+1/2$.

Compound **1** offers a good example of C –H ··· Cl hydrogen bonding. Meanwhile, it is interesting that there is one type of π···π stacking interaction exists between the adjacent molecules in an antiparallel manner. The center-to-center distance of two rings B in two neighboring molecules is 0.365 6 nm and the perpendicular interplane distance is 0.331 3 nm. Obviously, both of them lie in the normal range of 0.33~0.38 nm[18] indicating of π···π stacking interactions in the crystal structure of **1**. Combination of the C (5)–H (5) ···Cl(1) and the aromatic π···π stacking interactions linked the zig-zag chains to generate a 2D network structure. These interactions also mutually strengthen and solidify the molecule.

In the structure of **2**, the central copper(Ⅱ) atom is four coordinate and bonds to two nitrogen atoms and two oxygen atoms from two **1** in the usual trans arrangement. Each ligand acts as a bidentate ligand. The geometry around copper(Ⅱ) in **2** is in a slightly distorted tetrahedral environment, where the dihedral angle between the two coordination planes defined by O(1)Cu(1)N(1) and O(1)$^{\#1}$Cu(1)N(1)$^{\#1}$ is 89.53(14)°, nearly perpendicular. It can be interpreted in terms of the phenyl substituent having a bigger steric effect. The phenyl ring plane (ring B) and the chelate ring (O(1)/Cu(1)/N(1)/C(7)/C(8)/C(9), Rms deviation of fitted atoms is 0.177 2) are nearly coplanar with a dihedral angle of 10.15(13)°. This is true of the corresponding planes which are generated by symmetry. Bond angles also show that the coordination geometry about the copper atom in **2** is a slightly distorted tetrahedral structure with O(1)Cu(1)N(1), N(1)Cu(1)N(1)$^{\#1}$ and O(1)Cu(1)O(1)$^{\#1}$ angles of 89.53(14)°, 180.0° and 180.0°, respectively. The distances of Cu(1)-O(1) and Cu(1)-N(1) are 0.188 4(3) and 0.201 8(4) nm, respectively. The distances are approaching to the values found in reported copper complexes[19-20].

In crystal structure of **2**, discrete monomeric molecules are held together by halogen-halogen (Br··· Cl and Br ··· Br) interactions and C –H ··· π hydrogen bonding (Fig.4). The hydrogen bonding data are summarized in Table 3. First, the Br(1) ··· Cl(1)$^{\#2}$ distance of 0.353 4 nm and H ···π distance of 0.2826 nm indicate the formation of halogen-halogen interaction and C –H ···π hydrogen bonding between the neighboring molecules, which connect the molecules to form a 2D network. Furthermore, such 2D networks are linked by another Br(1) ··· Br(1)$^{\#3}$ halogen-halogen interaction (Table 3) to generate 3D framework. The results reveal that the halogen-halogen interaction and C –H ··· π hydrogen bonding not only play a very important role in the formation, stability and crystallization of **2**, but also connect the independent molecular to a three-dimentional network.



Other hydrogen atoms are omitted forclarity; Symmetrycode: $^{\#1}$ $-x+1$, $-y+1$, $-z+1$; $^{\#2}$ $-x+1$, $y-1/2$, $-z+1/2$; $^{\#4}$ x, $-y+1/2$, $-z+1/2$

Fig.4　Part of the crystal structure of **2**, showing the formation of the C–H···π and halogen-halogen interactions

3　Conclusion

In sumary, a new Cu(Ⅱ) complex (**2**) of 2-[(2-

bromo-phenylimino)-methyl]-4-chloro-phenol (**1**) generated from 5-chlorosalicylaldehyde and *o*-bromoaniline was synthesized. The structure of the ligand and complex were determined by X-ray crystallography diffraction. **1** was stabilized and linked into a two-dimentional layer structure by intermolecular C–H···N, intramolecular C–H···O, C–H···Cl hydrogen bonds and $\pi \cdots \pi$ stacking interaction. But **2** was connected by halogen···halogen and C–H···π hydrogen bond to form a three-dimentional network. Meanwhile, these interactions play a very important role in the formation, stabilization and crystallization of **1** and **2**.

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