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# Cl 和 Br 取代基在晶体堆积中的交替排列：席夫碱及其铜配合物的合成与结构研究

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**摘要**：本文合成了 2 个新的席夫碱,*N*,*N*′-二 (5-氯水杨基)-1,3-二氨基戊烷 ($H_2CAP$) 和 *N*,*N*′-二 (5-溴水杨基)-1,3-二氨基戊烷 ($H_2BAP$),以及它们的铜(Ⅱ)配合物,[Cu(CAP)] (**1**),[Cu(BAP)] (**2**)和[$Cu(CAP)_{0.5}(BAP)_{0.5}$] (**3**),并通过元素分析、红外和电子光谱表征了它们的结构。对于配合物,还利用单晶 X-射线衍射进行了结构测试。在每个配合物中,铜原子都采取四面体畸变的平面四边形配位构型。通过将配合物 **1** 和 **2** 结合在一起形成了聚集体 **3**。在该聚集体中存在有趣的氯和溴取代基交替排列现象。

**关键词**：席夫碱；铜配合物；自组装；配合物聚集；单核配合物

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## Alternate Arrangement of Cl and Br Substituent Groups in Crystal Packing: Syntheses and Structures of Schiff Bases and Their Copper(Ⅱ) Complexes

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**Abstract:** Two new Schiff bases, *N*,*N*′-bis(5-chlorosalicylidene)-1,3-diaminopentane ($H_2CAP$) and *N*,*N*′-bis(5-bromosalicylidene)-1,3-diaminopentane ($H_2BAP$), and their copper(Ⅱ) complexes, [Cu(CAP)] (**1**), [Cu(BAP)] (**2**) and [$Cu(CAP)_{0.5}(BAP)_{0.5}$] (**3**), have been prepared and structurally characterized by elemental analysis, IR and electronic spectroscopy. The complexes have also been characterized by single-crystal X-ray diffraction studies. The Cu atom in each of the complexes is in a tetrahedrally distorted square planar coordination. By combination of complex **1** and **2**, a new aggregation **3** was formed. There are interesting alternate arrangement of Cl and Br substituent groups in the crystal packing of the aggregation. CCDC: 889058, **1**; 889059, **2**; 889057, **3**.

**Key words:** Schiff base; copper complex; self-assembly; complex aggregation; mononuclear complex

Schiff bases are a kind of versatile ligands which are readily synthesized from reactions of primary amines with carbonyl-containing compounds. In recent years, much work has been carried out on syntheses and properties of Schiff bases and their complexes. Schiff base complexes have been proved to have versatile structures[1-5], as well as catalytic, magnetic, fluorescence, and biological properties[6-10]. Recently, we have reported some Schiff base copper(Ⅱ) complexes with biological activities[11-13]. Detailed investigation on

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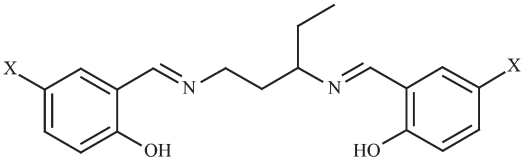
literatures of Schiff base complexes, we found that no complexes prepared by "aggregation of similar complexes" have been reported. As a further investigation on self-assembly and crystal packing of such complexes, in the present work, two new Schiff bases, *N*,*N*′-bis(5-chlorosalicylidene)-1,3-diaminopentane ($H_2CAP$; Scheme 1) and *N*,*N*′-bis(5-bromosalicylidene)-1,3-diaminopentane ($H_2BAP$; Scheme 1), and their copper(Ⅱ) complexes, [Cu(CAP)] (**1**) and [Cu(BAP)] (**2**), were prepared and structurally characterized. By mixing **1** and **2** in methanol, followed by recrystallization, a new aggregation of the two complexes, $[Cu(CAP)_{0.5}(BAP)_{0.5}]$ (**3**), was obtained for the first time.




$H_2CAP$: X=Cl; For $H_2BAP$: X=Br

Scheme 1 Schiff bases

## 1 Experimental

### 1.1 Materials and physical measurements

5-Chlorosalicylaldehyde, 5-bromosalicylaldehyde, and pentane-1,3-diamine with AR grade were purchased from Lancaster. Other reagents and solvents were purchased from Shanghai Chemical Reagent Company and used as received. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were measured with a Nicolet FT-IR 170-SX spectrophotometer. Electronic spectra in methanol (200~600 nm) were recorded in a Lambda 35 spectrophotometer. $^1$HNMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer with tetramethylsilane as the internal reference.

### 1.2 Preparation of $H_2CAP$ and $H_2BAP$

The two Schiff bases were prepared by mixing 1∶2 molar ratio of pentane-1,3-diamine with 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde, respectively, in methanol.

For $H_2CAP$: Yield: 93% . Anal. Calcd. for $C_{19}H_{20}Cl_2N_2O_2$(%): C, 60.2; H, 5.3; N, 7.4. Found(%): C, 60.0; H, 5.4; N, 7.4. IR data (KBr, $cm^{-1}$): 3 443 (w, $\nu_{O\text{-}H}$), 1 635 (s, $\nu_{C=N}$). $\lambda_{max}$ (nm) [$\varepsilon_{max}$ ($dm^3\cdot mol^{-1}\cdot cm^{-1}$)] (methanol): 221 ($7.4\times10^4$), 252 ($1.6\times10^4$), 330 ($5.6\times10^3$). $^1$H NMR ($d_6$-DMSO): δ: 0.88 (t, 3H), 1.71 (m, 2H), 2.05 (q, 2H), 3.24 (q, 1H), 3.61 (t, 2H), 6.90 (d, 2H), 7.16~7.28 (m, 4H), 8.23 (s, 1H), 8.25 (s, 1H), 13.38 (s, 2H). $^{13}$C NMR ($d_6$-DMSO): δ: 10.7, 29.4, 36.7, 56.5, 69.4, 118.7, 119.4, 119.5, 123.4, 130.4, 130.6, 132.3, 159.8, 159.9, 163.3, 164.3. For $H_2BAP$: Yield: 95%. Anal. Calcd. for $C_{19}H_{20}Br_2N_2O_2$ (%): C, 48.7; H, 4.3; N, 6.0. Found (%): C, 48.9; H, 4.3; N, 5.9. IR data (KBr, $cm^{-1}$): 3 435 (w, $\nu_{O\text{-}H}$), 1630 (s, $\nu_{C=N}$). $\lambda_{max}$ (nm) [$\varepsilon_{max}$ ($dm^3\cdot mol^{-1}\cdot cm^{-1}$)] (methanol): 222 ($7.9\times10^4$), 251 ($1.8\times10^4$), 330 ($5.4\times10^3$). $^1$H NMR ($d_6$-DMSO): δ: 0.88 (t, 3H), 1.71 (m, 2H), 2.05 (q, 2H), 3.24 (q, 1H), 3.59 (t, 2H), 6.86 (d, 2H), 7.26~7.41 (m, 4H), 8.23 (s, 1H), 8.25 (s, 1H), 13.41 (s, 2H). $^{13}$C NMR ($d_6$-DMSO): δ: 10.7, 29.4, 36.7, 56.5, 69.4, 110.2, 110.3, 119.2, 120.0, 120.2, 133.4, 133.6, 135.1, 160.3, 160.4, 163.2, 164.2.

### 1.3 Preparation of [Cu(CAP)] (1) and [Cu(BAP)] (2)

Copper complexes **1** and **2** were prepared by mixing 1∶1 molar ratio of $CuBr_2$ with $H_2CAP$ and $H_2BAP$, respectively, in methanol. Blue block-shaped single crystals of the complexes were obtained by slow evaporation of the solution in air.

For **1**: Yield: 63%. Anal. Calcd. for $C_{19}H_{18}Cl_2CuN_2O_2$(%): C, 51.8; H, 4.1; N, 6.4. Found(%): C, 51.6; H, 4.2; N, 6.3. IR data (KBr, $cm^{-1}$): 1 621 (s, $\nu_{C=N}$). $\lambda_{max}$ (nm) [$\varepsilon_{max}$ ($dm^3\cdot mol^{-1}\cdot cm^{-1}$)] (methanol): 234 ($9.1\times10^4$), 372 ($9.5\times10^3$). For **2**: Yield: 71%. Anal. Calc. for $C_{19}H_{18}Br_2CuN_2O_2$: C, 43.1; H, 3.4; N, 5.3. Found: C, 43.2; H, 3.4; N, 5.2%. IR data (KBr, $cm^{-1}$): 1 618 (s, $\nu_{C=N}$). $\lambda_{max}$ (nm) [$\varepsilon_{max}$ ($dm^3\cdot mol^{-1}\cdot cm^{-1}$)] (methanol): 232 ($1.5\times10^5$), 372 ($9.3\times10^3$).

### 1.4 Preparation of $[Cu(CAP)_{0.5}(BAP)_{0.5}]$ (3)

Equimolar quantities (0.2 mmol each) of [Cu(CAP)] and [Cu(BAP)] were dissolved in 20 mL methanol. Block-like blue single crystals of complex **3** were obtained by slow evaporation of the solution in air. Anal. Calc. for $C_{19}H_{18}BrClCuN_2O_2$(%): C, 47.0; H, 3.7; N, 5.8. Found (%): C, 46.9; H, 3.8; N, 5.8. IR data (KBr, $cm^{-1}$): 1 623 (s, $\nu_{C=N}$). $\lambda_{max}$ (nm) [$\varepsilon_{max}$ ($dm^3\cdot mol^{-1}\cdot$

$cm^{-1}$)] (methanol): 234 ($5.6\times10^4$), 372 ($7.3\times10^3$).

### 1.5 X-ray crystallography

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART CCD detector with Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm). The collected data were reduced using SAINT program[14], and multi-scan absorption corrections were performed using SADABS program[15]. The structures were solved by direct method and refined against $F^2$ by full-matrix least-squares method using SHELXTL[16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The Cl and Br atoms in complex **3** are disordered, with occupancies of 0.5 and 0.5. A summary of the crystallographic data are given in Table 1. Coordinate bond lengths and angles are listed in Table 2.

CCDC: 889058, **1**; 889059, **2**; and 889057, **3**.

## 2 Results and discussion

### 2.1 Syntheses

$H_2$CAP and $H_2$BAP were prepared by the reaction of pentane-1,3-diamine with 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde, respectively, in methanol, with high yields and purity. Copper complexes **1** and **2** were readily prepared by mixing the Schiff bases with copper bromide in methanol. It is very interesting that the aggregation of complexes **1** and **2**, namely,

**Table 1　Crystallographic data for the complexes**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Chemical formula | $C_{19}H_{18}Cl_2CuN_2O_2$ | $C_{19}H_{18}Br_2CuN_2O_2$ | $C_{19}H_{18}BrClCuN_2O_2$ |
| Formula weight | 440.8 | 529.7 | 485.2 |
| Crystal shape / colour | Block / blue | Block / blue | Block / blue |
| Crystal size / mm | 0.17×0.15×0.15 | 0.18×0.17×0.17 | 0.20×0.20×0.17 |
| $T$ / K | 298(2) | 298(2) | 298(2) |
| $\lambda$ (Mo $K\alpha$) / nm | 0.071 073 | 0.071 073 | 0.071 073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ |
| $a$ / nm | 0.952 9(2) | 0.965 8(2) | 0.959 2(1) |
| $b$ / nm | 2.161 9(3) | 2.195 9(2) | 2.184 4(2) |
| $c$ / nm | 1.070 7(2) | 1.027 8(2) | 1.024 2(1) |
| $\beta$ / (°) | 119.996(2) | 114.997(2) | 114.549(1) |
| $V$ / $nm^3$ | 1.910 3(6) | 1.975 4(5) | 1.951 9(3) |
| $Z$ | 4 | 4 | 4 |
| $\mu$ (Mo $K\alpha$) / $cm^{-1}$ | 1.438 | 5.166 | 3.318 |
| $T_{min}$ | 0.792 0 | 0.456 5 | 0.556 6 |
| $T_{max}$ | 0.813 1 | 0.473 8 | 0.602 4 |
| $D_c$ / ($g\cdot cm^{-3}$) | 1.533 | 1.781 | 1.651 |
| Reflections | 10 246 | 10 955 | 10 189 |
| Independent reflections | 3 943 | 4 297 | 4 095 |
| Observed reflections ($I\geqslant2\sigma(I)$) | 2 749 | 2 296 | 3 095 |
| Parameters | 236 | 236 | 254 |
| Restraints | 0 | 0 | 4 |
| $R_{int}$ | 0.147 3 | 0.065 3 | 0.042 1 |
| Goodness of fit on $F^2$ | 1.011 | 0.947 | 1.097 |
| $R_1$ ($I\geqslant2\sigma(I)$) | 0.067 3 | 0.057 3 | 0.075 2 |
| $wR_2$ ($I\geqslant2\sigma(I)$) | 0.158 6 | 0.145 0 | 0.151 4 |
| $R_1$ (all data) | 0.090 0 | 0.123 9 | 0.105 7 |
| $wR_2$ (all data) | 0.177 5 | 0.180 1 | 0.168 1 |

**Table 2 Coordinate bond lengths (nm) and angles (°) for the complexes**

| | | | | | |
|---|---|---|---|---|---|
| | | | **1** | | |
| Cu1-O1 | 0.189 8(3) | Cu1-O2 | 0.188 0(3) | Cu1-N1 | 0.193 0(3) |
| Cu1-N2 | 0.195 0(3) | | | | |
| O2-Cu1-O1 | 89.8(1) | O2-Cu1-N1 | 156.3(1) | O1-Cu1-N1 | 94.1(1) |
| O2-Cu1-N2 | 95.0(1) | O1-Cu1-N2 | 152.3(1) | N1-Cu1-N2 | 92.3(1) |
| | | | **2** | | |
| Cu1-O1 | 0.187 8(4) | Cu1-O2 | 0.190 3(4) | Cu1-N1 | 0.194 6(5) |
| Cu1-N2 | 0.193 0(5) | | | | |
| O1-Cu1-O2 | 90.2(2) | O1-Cu1-N2 | 155.4(2) | O2-Cu1-N2 | 94.4(2) |
| O1-Cu1-N1 | 94.6(2) | O2-Cu1-N1 | 152.4(2) | N2-Cu1-N1 | 92.5(2) |
| | | | **3** | | |
| Cu1-O1 | 0.187 6(4) | Cu1-O2 | 0.190 7(4) | Cu1-N1 | 0.195 4(4) |
| Cu1-N2 | 0.193 8(5) | | | | |
| O1-Cu1-O2 | 90.0(2) | O1-Cu1-N2 | 156.4(2) | O2-Cu1-N2 | 94.0(2) |
| O1-Cu1-N1 | 94.6(2) | O2-Cu1-N1 | 152.5(2) | N2-Cu1-N1 | 92.4(2) |

complex **3**, was obtained by recrystallization of 1∶1 molar ratio of complexes **1** and **2** in methanol.

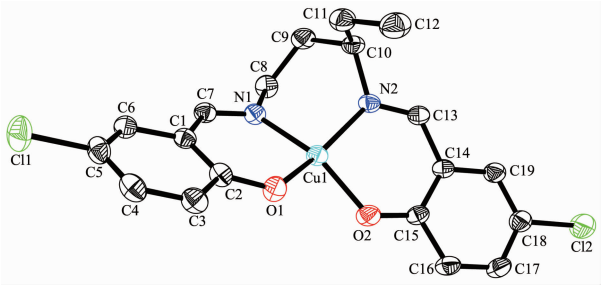
## 2.2 IR and electronic spectra

IR spectra of the Schiff bases and their complexes provide information about the metal-ligand bonding. In the IR spectra of $H_2$CAP and $H_2$BAP, there exist broad and weak O-H vibrations at about 3 440 $cm^{-1}$. Several weak peaks observed for HL[1] and the complexes in the range 3 180~2 860 $cm^{-1}$ are due to the aromatic and aliphatic C-H stretches. The strong absorption bands at about 1 635 $cm^{-1}$ in the spectra of the Schiff bases are assigned to azomethine groups, $\nu$(C=N)[17]. These bands are shifted to lower wave numbers in the complexes, 1 621 $cm^{-1}$ for complex **1**, 1 618 $cm^{-1}$ for complex **2**, and 1 623 $cm^{-1}$ for complex **3**. This phenomenon can be attributed to the coordination of the nitrogen atoms of the azomethine groups to the Cu atoms. The phenolic $\nu$(Ar-O) in the Schiff bases exhibit strong bands at about 1 188 $cm^{-1}$. However, in the complexes, the bands appear at 1 175 $cm^{-1}$ **1**, 1 168 $cm^{-1}$ **2**, and 1 173 $cm^{-1}$ **3**, which may be assigned to the skeletal vibration related to the phenolic oxygen atoms of the ligands, and the bands are known to shift to lower frequencies when the phenolic oxygen atoms coordinate to metal atoms[18]. The weak bands in the region 400 ~560 $cm^{-1}$ for the complexes can be assigned to the Cu-O and Cu-N vibrations[19-20].

The close resemblance of the shape and the positions of the absorption bands suggest similar coordination modes for the complexes. IR spectra of the complexes are consistent with the X-ray structural results.

## 2.3 Structure description of complexes 1, 2 and 3

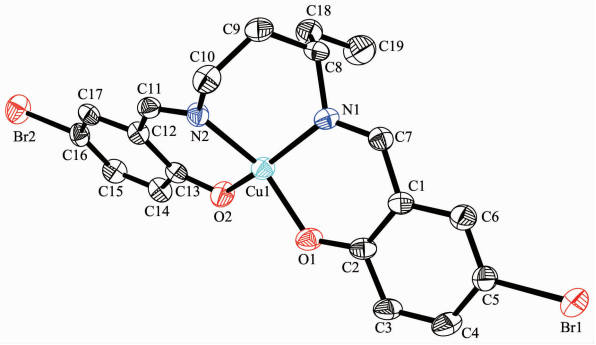
The molecular structures of complexes **1**, **2** and **3** are shown in Fig.1, 2, and 3, respectively. Complex **3** is an aggregation of complexes **1** and **2** with 1∶1 molar ratio. The three complexes are structurally similar mononuclear copper compounds. The Cu atom in each




Hydrogen atoms are omitted for clarity

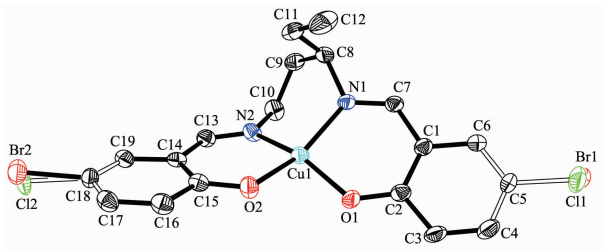
Fig.1 Molecular structure of **1** with 30% thermal ellipsoids

of the complexes is coordinated by two imino N and two phenolate O atoms of the Schiff base ligand, forming a tetrahedrally distorted square planar geometry. The distortion is mainly observed from the coordinate bond angles. The perpendicular bond angles are range from 89.8(1)° to 95.0(1)° for complex **1**, 92.5(2)° to 94.6(2)° for complex **2**, and 92.4(2)° to 94.6(2)° for complex **3**. The trans bond angles are 152.3(1)° and 156.3(1)° for complex **1**, 152.4(2)° and 155.4(2)° for complex **2**, and 152.5(2)° and 156.4(2)° for complex **3**. The bond lengths in the complexes are comparable to each other, and similar to those



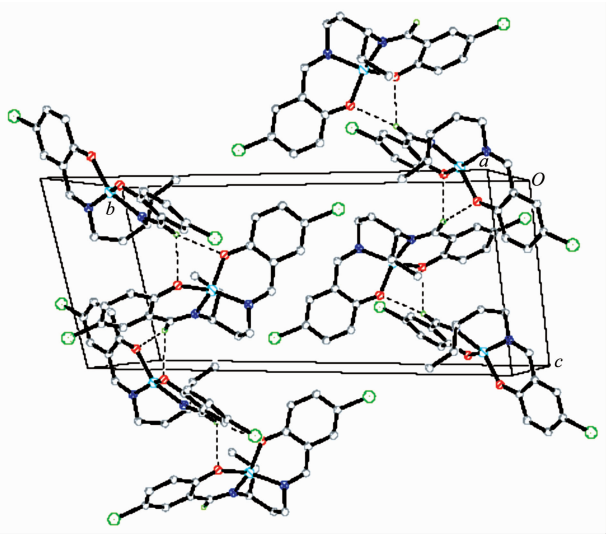

Hydrogen atoms are omitted for clarity

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



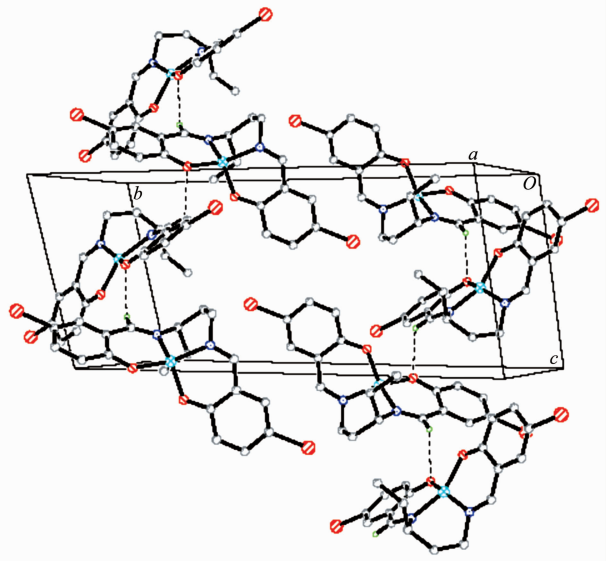

Hydrogen atoms are omitted for clarity

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




Hydrogen bonds are shown as dashed lines

Fig.4　Molecular packing of **1**, viewed along the *a* axis




Hydrogen bonds are shown as dashed lines

Fig.5　Molecular packing of **2**, viewed along the *a* axis

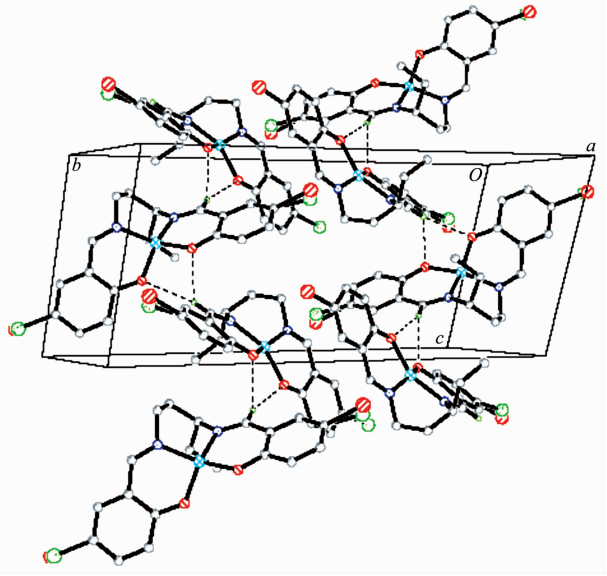
**Table 3　Hydrogen-bond geometry of the complexes**

| D–H···A | *d*(D-H) / nm | *d*(H···A) / nm | *d*(D···A) / nm | ∠DHA / (°) |
|---|---|---|---|---|
| **1** | | | | |
| C13–H13···O1#1 | 0.093 | 0.251(2) | 0.340 6(8) | 162 |
| C13–H13···O2#1 | 0.093 | 0.240(2) | 0.301 9(8) | 123 |
| **2** | | | | |
| C7–H7···O1#2 | 0.093 | 0.244(2) | 0.304 5(9) | 123 |
| C7–H7···O2#2 | 0.093 | 0.259(2) | 0.348 3(9) | 162 |
| **3** | | | | |
| C7–H7···O1#3 | 0.093 | 0.241(2) | 0.303 0(8) | 124 |
| C7–H7···O2#3 | 0.093 | 0.254(2) | 0.344 0(8) | 162 |

Symmetry codes: #1: −1/2+*x*, 1/2−*y*, −1/2+*z*; #2: −1/2+*x*, 3/2−*y*, −1/2+*z*; #3: 1/2+*x*, 1/2−*y*, 1/2+*z*.

observed in other copper(Ⅱ) complexes with Schiff bases[21-22]. The dihedral angles between the two benzene rings in the complexes are 41.4(3)° for complex **1**, 43.5(3)° for complex **2**, and 43.0(3)° for complex **3**.

In the crystal structures of the three complexes (Fig.4 for **1**, Fig.5 for **2**, Fig.6 for **3**), molecules are linked through intermolecular C –H ··· O hydrogen bonds (Table 3), to form 1D chains.




Hydrogen bonds are shown as dashed lines

Fig.6 Molecular packing of **3**, viewed along the *a* axis

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