

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF
BIS[2-((E)-(P-TOLYLIMINO) METHYL)-6-BROMO-4-CHLOROPHENOL]COPPER(II)

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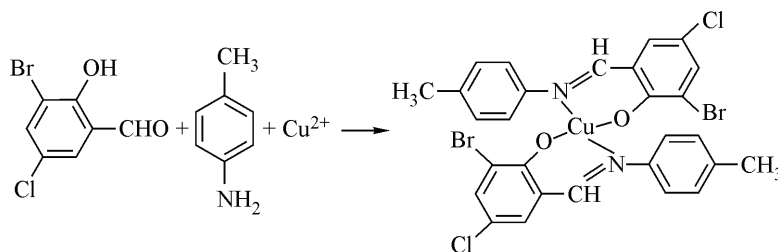
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A new complex CuL_2 1 [HL = 2-((E)-(p-tolylimino) methyl)-6-bromo-4-chlorophenol] is obtained and characterized using the single crystal X-ray diffraction analysis. The crystal belongs to the monoclinic system, $P2_1/c$ space group, with $a = 13.3203(13)$, $b = 12.3052(11)$, $c = 17.8664(17)$ Å, $\beta = 105.3420(10)^\circ$, $V = 2824.1(5)$ Å³, $Z = 4$, $D_c = 1.672$ g/cm³, $R_1 = 0.0686$. The geometry around copper(II) is intermediate between square planar and tetrahedral. The units of the complex are linked via weak inter-molecular Br...Br contracts, leading to the formation of one-dimension (1D) chains along the b axis; the multipoint Cu...Cl intermolecular interactions extend the 1D chain into a 2D layer.

Keywords: copper(II) complexes, single crystal X-ray analysis.

Copper is an important element that is essential for life; it exists in some native enzymes and is required by all organisms. Due to their important biological relevance, many copper complexes have been reported in recent years [1–4]. Among these complexes, Schiff's base complexes have been widely studied because of their industrial and biological applications [5–7]. In this paper, the complex bis[2-((E)-(p-tolylimino)methyl)-6-bromo-4-chlorophenol]copper(II) is obtained from the reaction of 2-((E)-(p-tolylimino)methyl)-6-bromo-4-chlorophenol] and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. A single crystal X-ray analysis of the complex is undertaken to elucidate its conformation and structure.

Experimental. To a solution of 3-bromo-5-chloro-2-hydroxybenzaldehyde (0.002 mol) in EtOH (10 cm³) a solution of *p*-toluidine (0.002 mol) in EtOH (10 cm³) was added followed by $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.001 mol) in EtOH (10 cm³). The mixture was stirred for about 30 min at room temperature to give a clear brown solution. After keeping this solution in air for 7 days, greenish brown block-shaped crystals were formed at the bottom of the vessel by slowly evaporating the solvent (scheme 1). The crystals was filtered, washed with cold EtOH, and dried in vacuum desiccator using anhydrous CaCl_2 (yield 70 %).



Scheme 1. Synthesis of the complex

Table 1

Selected bond lengths (Å) and bond angles (deg.)

Bond	Å	Bond	Å	Angle	deg.	Angle	deg.
Cu(1)—O(1)	1.885(6)	Cu(1)—N(1)	1.995(6)	O(1)—Cu(1)—O(2)	154.4(3)	O(1)—Cu(1)—N(2)	91.5(3)
Cu(1)—O(2)	1.893(6)	Br(1)—C(4)	1.892(9)	O(1)—Cu(1)—N(1)	93.5(3)	O(2)—Cu(1)—N(2)	93.0(3)
Cu(1)—N(2)	2.004(7)	Cl(1)—C(6)	1.772(10)	O(2)—Cu(1)—N(1)	92.0(3)	N(1)—Cu(1)—N(2)	157.6(3)

A crystal of CuL_2 with the dimensions of $0.47 \times 0.45 \times 0.40$ mm was mounted on a glass fiber in a random orientation. The data were collected by a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) in the range of $2.29 \leq \theta \leq 25.02$. The crystal belongs to the monoclinic system, $P2(1)/c$ space group, with $a = 13.3203(13)$, $b = 12.3052(11)$, $c = 17.8664(17)$ Å, $\beta = 105.3420(10)^\circ$, $V = 2824.1(5)$ Å³, $Z = 2$, $D_c = 1.672$ g/cm³, $\mu(\text{MoK}_\alpha) = 3.821$ mm⁻¹, $F(000) = 1404$, $S = 1.024$. Final values of the divergence factors were: $R_1 = 0.1415$, $wR_2 = 0.1987$ for all reflections and $R_1 = 0.0686$, $wR_2 = 0.1686$ for 4968 reflections with $I > 2\sigma(I)$ used in the calculations. Semi-empirical absorption correction was applied. The structure was solved using the direct methods and refined by full-matrix least-squares techniques on F^2 using the SHELXTL-97 program package [8]. The main interatomic distances and bond angles are listed in Table 1. The structural data for complex **1** were deposited in the Cambridge Crystallographic Data Center under the number CCDC 799982.

Results and discussion. The X-ray diffraction analysis of complex **1** shows, that the copper ion is bonded to the oxygen and nitrogen donor atoms of two bidentate ligand molecules in the usual *trans* arrangement (Fig. 1). The geometry around copper(II) in **1** is intermediate between square planar and tetrahedral, where the dihedral angle between the two coordination planes defined by O(1)—Cu(1)—N(1) and O(2)—Cu(1)—N(2) is 33.4° . It is interesting to note that a similar complex bis- $\{(\text{diphenylmethyl})[(2\text{-oxo-1H-benzo-1-yl-idene})\text{-methyl}]\text{aminato}\}$ copper(II) shows a similar dihedral angle between O—Cu—N of 38.6° . The difference indicates that the phenylmethyl substituent has a smaller steric effect than the diphenylmethyl substituent on the geometry of these complexes [9]. Bond angles also show that the coordination geometry about the copper atom in **1** is distorted square planar, with O1—Cu1—N1, N1—Cu1—N2 and O1—Cu1—O2 angles of $93.5(3)^\circ$, $157.6(3)^\circ$, and $154.4(3)^\circ$ respectively. The Cu—N (amine) distance in **1** is quite similar to other reported Cu—N distances in the $1.995(6)$ — $2.004(7)$ Å range, as in bis- $\{(\text{diphenylmethyl})[(2\text{-oxo-1H-benzo-1-yl-idene})\text{-methyl}]\text{aminato}\}$ copper(II) and bis- $\{(\text{diphenylmethyl})[(2\text{-oxo-1H-naphth-1-ylidene})\text{-methyl}]\text{aminato}\}$ copper(II) [9]. The Cu—O distances are 1.886 Å and 1.894 Å, which are also consistent with the corresponding Cu—O distance in bis(N-*i*-propylsalicylideneaminato)copper(II) [10] and bis(N-*i*-Pr-1,2-naphthaldiminato)copper(II) [11]. In the ligands, the lengths of N=C bonds are different on average by 0.005 Å; the lengths of N—C bonds are different on average by 0.02 Å, while the C—C bonds of the phenyl rings are different by 0.10 Å. The phenyl rings A and C of the ligands are nearly coplanar with the chelating rings. This is probably a result of the coordination of N and O atoms to copper(II). To avoid steric conflicts, the phenyl rings B and D of the

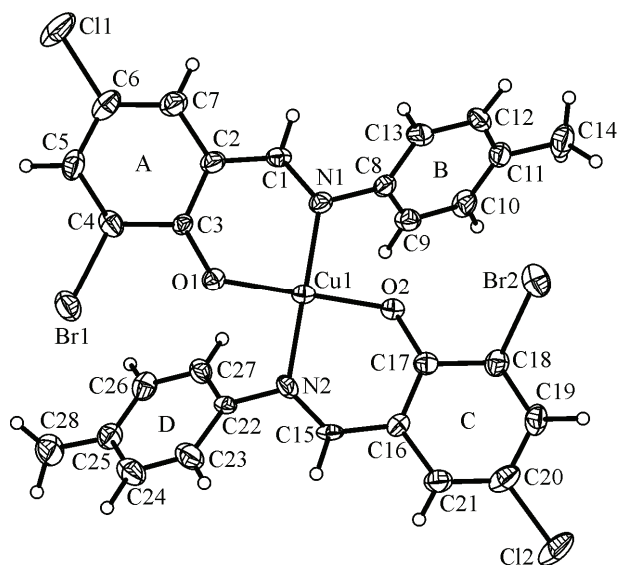


Fig. 1. View of the complex, showing 30 % probability displacement ellipsoids (arbitrary spheres for the H atoms)

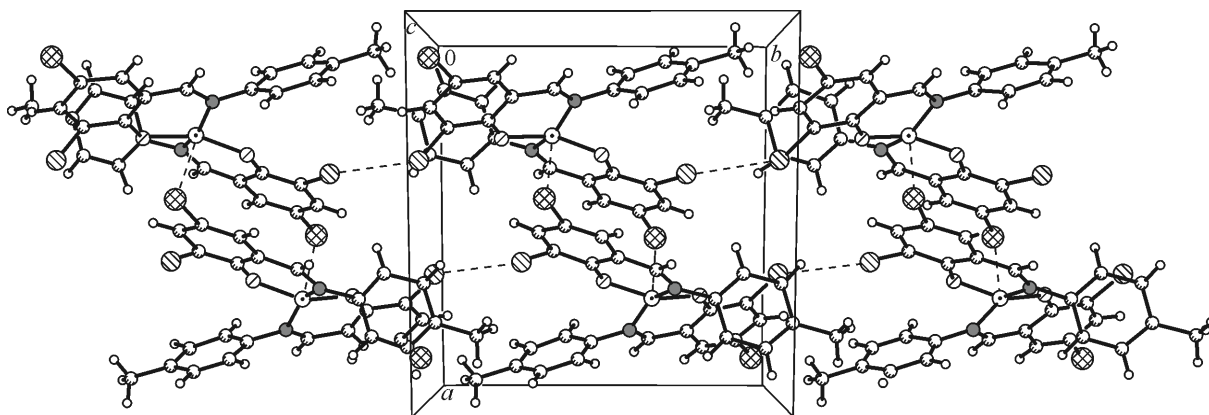


Fig. 2. Packing structure of the complex along the *c* axis, showing the formation of a column by weak intermolecular Br...Br interactions and Cu...Cl interactions

ligands, are rotated with respect to the corresponding chelating rings with the dihedral angles of 51.7° and 50.1° .

Weak intermolecular Br...Br contacts are 3.521 \AA ; they connect the molecules to form a one-dimensional chain. The complexes are packed into layers perpendicular to the *c* axis, where they are linked by Cu...Cl intermolecular contacts of 3.843 \AA (Fig. 2).

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