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Synthesis and Crystal Structure of *Bis*[2-((E)-(*m*-tolylimino)methyl)-6-bromo-4-chlorophenol]copper(II)

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A new Schiff base complex CuL_2 [HL = 2-((E)-(*m*-tolylimino)methyl)-6-bromo-4-chlorophenol] is synthesized and characterized using single crystal X-ray diffraction analysis. The crystal belongs to the monoclinic system, space group C2/c, with a = 14.5521 (16), b = 8.6800 (10), c = 21.934 (2) Å, β = 100.0380 (10)°, V = 2728.1(5) $Å^3$, Z = 4, Dc = 1.730 g/cm^3, R(int) = 0.0505. The geometry around copper(II) is a flattened tetrahedron. The units of the complex are linked via the weak intermolecular Cu···Cl and Cl···O contracts, leading to the formation of one-dimension (1D) chains along the a axis, the multipoint Br···Br intermolecular interactions extend the 1D chain into a 2D (two-dimentional) layer.

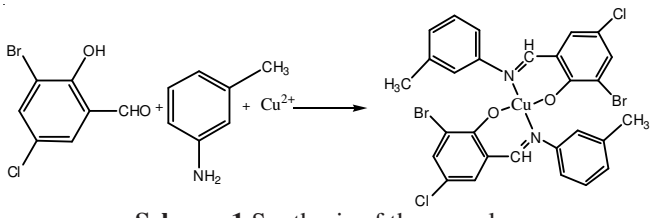
Key Words: Copper(II), Complexes, Single crystal X-ray analysis.

INTRODUCTION

Schiff bases and their metal complexes have attracted the attention of researchers for many decades[1-3]. This is not only because Schiff base complexes have preparative accessibility and structural variety, but also because they have extensive applications in industrial and biological fields. Copper(II) complexes with Schiff bases have been prepared and have proven to be very important in the area of electrochemistry and electromagnetic fields[4,5]. Nickle(II) and zinc(II) complexes with Schiff bases can be regarded as DNA secondary structure probes for their unusual binding properties and general photoactivity[6-7]. The role of the metal Schiff base complexes in these applications are related to molecular structure. Thus, it is quite important to have a good understanding of the structure of such metal complexes. In this paper, the complex, *bis*[2-((E)-(*m*-tolylimino)methyl)-6-bromo-4-chlorophenol] copper(II), is obtained from the reaction of 2-((E)-(*m*-tolylimino)methyl)-6-bromo-4-chlorophenol] and $CuCl_2·2H_2O$. Single crystal X-ray analyses of the complex is undertaken to elucidate the conformation and structure of the complex.

EXPERIMENTAL

Preparation: 3-Bromo-5-chloro-2-hydroxybenzaldehyde (0.002 mol) and *m*-toluidine (0.002 mol) were dissolved in ethanol to the resulting yellow mixture, $CuCl_2·H_2O$ (0.001 mol) was added until the mixture became brown clear. The resulting solution was stirred for 1 h, filtered and the filtrate was allowed to stand at room temperature. Brown crystals of the present copper(II) complex appeared after 2 weeks by slow evaporation of the ethanol solution (**Scheme-1**). The crystals was filtered, washed with cold ethanol and dried in vacuum desiccator using anhydrous $CaCl_2$ (yield 70 %).



Scheme-1 Synthesis of the complex

Crystal structure determination: A crystal having good morphology (0.48 mm × 0.43 mm × 0.31 mm) was chosen for the three-dimensional intensity data collection using a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated MoKα radiation (λ = 0.71073 Å) in the range of $2.74 \leq \theta \leq 25.02$ at 298 K. The structure was solved by direct methods using program SHELXS-97[8] and refined by full matrix least squares techniques on F2 with SHELXL-97[9]. Multi-scan absorption correction was applied. The crystal data and structure refinement parameters for the complex are summarized in Table-1. The main bond distances and bond angles are listed in Table-2. The structural data for the complex

was deposited in the Cambridge Crystallographic Data Center under the number CCDC 801071.

RESULTS AND DISCUSSION

The X-ray diffraction analysis of the complex shows that the central copper(II) atom is four coordinate and bonds to two nitrogen atoms and two oxygen atoms from two 2-((E)-(*m*-tolylimino)methyl)-6-bromo-4-chlorophenol Schiff bases in the usual *trans* arrangement(Fig.1). However, the phenylmethyl substituted complex has a distorted coordination at the Cu atom, displays as a flattened tetrahedron, where the dihedral angle between the two coordination planes defined by Cu1-O1-N1 to Cu1-O1A-N1A is 57.69°, whereas O1Cu1N1, N1ACu1N1 and O1ACu1O1 angles of 92.95(13), 131.3(2) and 148.4(2)°, respectively. [Symmetry code: A, -x, y, 1/2-z]. Such distortion may be compared with that engendered by the attachment of relatively bulky groups to the N-donor atoms. This distortion has been observed in the similar complex[10]. For the complex, the substituted amine ring of each ligand is rotated about the N1- C8 bond from the 3-bromo-5-chloro-salicylaldehyde plane. The dihedral angles between two rings are in the range 53.93°. The Cu-O bond distances are 1.870(3) Å, which is significantly shorter than in the similar Schiff base complexes reported by previous workers[11,12]. These bond shortenings presumably caused by the electron-withdrawing -Br and -Cl groups. The Cu-N (amine) distance (1.997(3) Å) is quite similar with other reported Cu-N distances, as reported by previous workers[4,13].

A view of the crystal cell of the complex is shown in Figs. 2 and 3. The 1-D infinite chain structure is formed with the weak Cu…Cl and Cl…O intermolecular contacts linkages along the a axis. In addition, each 1-D wavelike chain is connected by weak intermolecular Br...Br contracts into a 2D layers with its neighboring chains along the *b* axis, spreading out along the *ac* plane.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS

Properties	Complex
Empirical formula	$C_{28}H_{20}N_2O_2Br_2Cl_2Cu$
Formula weight	710.72
Temperature/K	298 (2)
Radiation (MoKα), λ (Å)	0.71073
Crystal shape/colour	Block/brown
Crystal size (mm^3)	0.48 × 0.43 × 0.31 mm
Crystal system	Monoclinic
Space group	C2/c
a (Å)	14.5521(16)
b (Å)	8.6800(10)
c (Å)	21.934(2)
β (°)	100.0380(10)
V ($Å^3$)	2728.1(5)
Z	4
D_c (g/cm^3)	1.730
μ (mm^{-1})	3.955
F(0 0 0)	1404
θ range (°)	2.74/25.02
Index range (h, k, l)	-17/17, -7/10, -26/21
Measured reflections	6582
Observed reflections [I≥2 σ(I)]	2411
Data/restraints/parameters	2411/0/168
Goodness-of-fit on F^2	1.039
R_1, wR_2 [I≥2σ(I)]	0.037/0.0836
R_1, wR_2 (all data)	0.0679/0.0942
Large diff. peak and hole(e $Å^{-3}$)	0.682 and -0.452

Note: $R_1 = \sum||F_o|-|F_c||/|F_o|$, $wR_2 = [\sum w(Fo^2-Fc^2)^2/\sum w(Fo^2)]^{1/2}$, where w = 1/ [Č $\sigma^2(Fo^2) + (0.0386P)^2 + 2.33520P$, $P = (Fo^2 + 2Fc^2)/3$

Table 2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Å	Angle	°
Cu(1)-O(1)	1.870(3)	O(1)-Cu(1)-O(1A)	148.4(2)
Cu(1)-O(1A)	1.870(3)	O(1A)-Cu(1)-N(1)	99.94(13)
Cu(1)-N(1A)	1.997(3)	O(1)-Cu(1)-N(1)	92.95(13)
Cu(1)-N(1)	1.997(3)	O(1)-Cu(1)-N(1A)	99.94(13)
Br(1)- C(4)	1.884(4)	O(1A)-Cu(1)-N(1A)	92.95(13)
Cl(1)-C(6)	1.752(4)	N(1)-Cu(1)-N(1A)	131.3(2)

Symmetry code: A, -x, y, 1/2-z

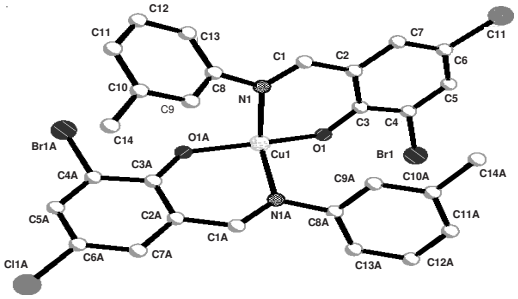


Fig. 1. View of the complex, showing 50% probability displacement ellipsoids (H atoms are omitted for clarity, Symmetry code: A -x, y, 1/2-z)

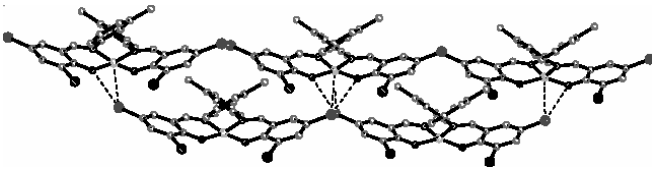


Fig.2. The 1D chain of complex along the a axis. (The dash lines represent the weak intermolecular Cl…O interactions and Cu…Cl interactions)

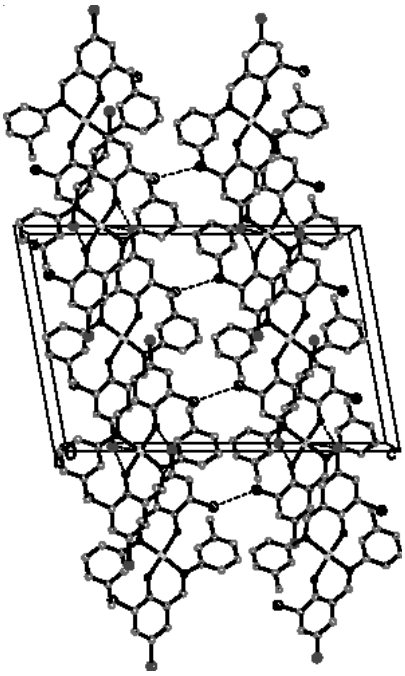


Fig. 3. The packing structure of the complex along the b-axis, showing the formation of column by weak intermolecular Br…Br interactions

Conclusion

In summary, we have designed and synthesized a 2D layer compound which is constructed from 2-((E)-(*m*-tolylimino)-methyl)-6-bromo-4-chlorophenol and Co(II). In this compound, it possesses extensive weak Cu···Cl, Cl···O, Br···Br intermolecular contacts which connect the 1D chain to form the 2D layer and stabilize the structure.

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