

Research Article

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Synthesis, characterization and structure of Copper(II) complex involving chloride and tridentate NNS coordinate Schiff base ligand

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Abstract: Mononuclear copper(II) complex $[\text{CuLCl}_2]$ where L = (2-methylsulfanyl-phenyl)-(phenyl-pyridin-2-yl-methylene) amine, a tridentate NNS donor Schiff base ligand has been synthesized and characterized by microanalysis, IR, UV-Visible spectra and magnetic studies. Crystal structure of the complex has been solved by single crystal X-ray diffraction studies and shows the complex has distorted trigonal bipyramidal geometry.

Keywords: Copper(II); NNS donor ligand; five coordinate; IR; structure.

1. INTRODUCTION

Schiff base ligands and their coordination complexes with transition metals have been studied widely in the last few decades because of the ease of the preparation of ligand, formation of stable complexes with most transition metal ions. Nitrogen and sulfur donor atoms containing ligands and their transition metal complexes are used as model for many metalloenzymes. Copper is an important ion in the biological system and many copper containing metalloenzymes binds with N and S-coordinating ligand[1-5]. Transition metal complexes with N and S donor Schiff base ligand have catalytic as well as bioactivities. There are many reports on transition metal complexes with tridentate NNS donor Schiff bases and their bioactivities [6-10].

In the paper we report on the synthesis of the complex $[\text{CuLCl}_2]$ where L is (2-methylsulfanyl-phenyl)-(phenyl-pyridin-2-yl-methylene), a neutral NNS coordinate tridentate ligand and characterized by elemental analysis, IR, spectral data and crystal structure determination. Crystal structure of the complex has been solved by single crystal X-ray diffraction studies and shows it has distorted trigonal pyramidal geometry .

2. EXPERIMENTAL

All chemicals and solvents used were analytical grade reagents. 2-Methylthioaniline, benzoylpyridine (Aldrich) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

(Loba, India) were reagent grade and used as received.

The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyzer. The IR spectrum were recorded on a Perkin-Elmer FT-IR spectrometer RX1 spectrum using KBr pellets. UV-Vis spectra (1200- 190 nm) were recorded on a Shimadzu 3600 in CH_3CN solution. Room temperature magnetic susceptibility of powder sample was measured using Guoy balance. Solution conductivity was measured in CH_3CN solution ($\sim 10^{-3}$ M) using Equip-Tronics conductivity meter (model no. EQ-660A).

A mixture of 2-methylthioaniline (0.140 g, 1.0 mmol) and benzoylpyridine (0.185 g, 1.0 mmol) was taken in ethanol (20 ml) and refluxed for 3 hrs. To this solution, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g, 1.0 mmol) was added and reflux was continued for another 1 hr. The solution was filtered and the filtrate was kept for slow evaporation. Dark blue colored crystals were obtained after 3-4 days. Yield. 0.275 g (60%). Found %. C = 74.94, H = 5.30, N = 9.20 % Anal calc for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{SCuCl}_2$: C = 74.95, H = 5.31, N = 9.21; IR (KBr pellet) cm^{-1} ; 1592, 1467, 1443, 1326, 1257, 1161, 1071, 1021, 768, 745, 710. UV-Vis spectra(in CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{mol}^{-1}\text{cm}^{-1}$). 825(293), 331(17950), 280(25663) 249(30640), 220(34130), Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 10. μ_{eff} = 1.79 BM.

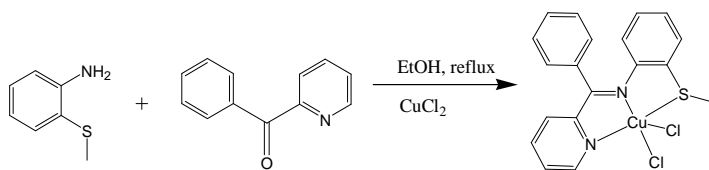
Crystals for X-ray diffraction of the compound obtained through slow evaporation of the solution. Single crystal X-ray diffraction intensity measurements were performed on Oxford X-CALIBUR-S diffractometer equipped with CCD detector using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The reflection was measured in the range of 2.17 to 28.22° . Data reduction was carried out using the program CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [11]. An absorption correction based on multi-scan method was applied [12]. The structure was solved by direct methods and refinement was performed by the full-matrix least-square technique on F^2 using the programs SHELXS-97 and

SHELXL-97 respectively [13]. All calculations were carried out using WinGX system Ver-1.64 [14]. All hydrogen atoms were located from difference Fourier map and treated as riding. All non hydrogen atoms were refined with anisotropic displacement coefficients.

The details of data collection and some important features of the refinement of the complex is given in Table S1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC 1472159.

3. RESULTS AND DISCUSSION

Mononuclear copper(II) complex $[\text{CuLCl}_2]$ was synthesized in two steps. The ligand was not isolated separately. The tridentate NNS donor Schiff base L ligand solution was prepared by refluxing in 1:1 mole ratio of benzoyl pyridine and 2-methylthioaniline in ethanol and finally CuCl_2 in ethanol was added in the Schiff base and refluxed was continued for another 1 hr [scheme 1]. The molecular composition of the complex was confirmed by micro analysis, IR and crystal structure determination. Molar conductivity measurement in CH_3CN solution ($\sim 10^{-3}\text{M}$) shows that the complex has very low molar conductivity ($\Lambda_M \sim 10 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$), indicating non ionic nature of the complex. Single crystal X-ray diffraction study of the complex shows that the copper atom has distorted trigonal bipyramidal geometry in the complex. The complex has moderate solubility in acetonitrile, methanol, ethanol, dichloromethane, acetone etc.



Scheme 1. Synthesis of the complex

IR spectrum of complex $[\text{CuLCl}_2]$ exhibits several strong bands. Among these, the absorbance band at 1592 cm^{-1} may be assigned to the coordination of copper(II) by the azomethine (C=N) nitrogen atom to the copper(II) center [15]. IR spectra of the complexes were supported by the crystal structure of the complex.

The UV-Vis spectrum of complex $[\text{CuLCl}_2]$ was recorded in the range of 200-1100 nm in CH_3CN . The high intensity bands appeared at less than 400 nm are due to intra ligand $n-p^*/p-p^*$ transition. A broad absorption band observed at 825 nm with molar extinction coefficient $\epsilon = 293 \text{ mol}^{-1}\text{cm}^{-1}$ was due to d-d transition. Room temperature magnetic susceptibility measurement of the complex shows magnetic moment with μ_{eff} (spin only) is 1.78 BM indicating one electron paramagnetism of copper(II) complex.

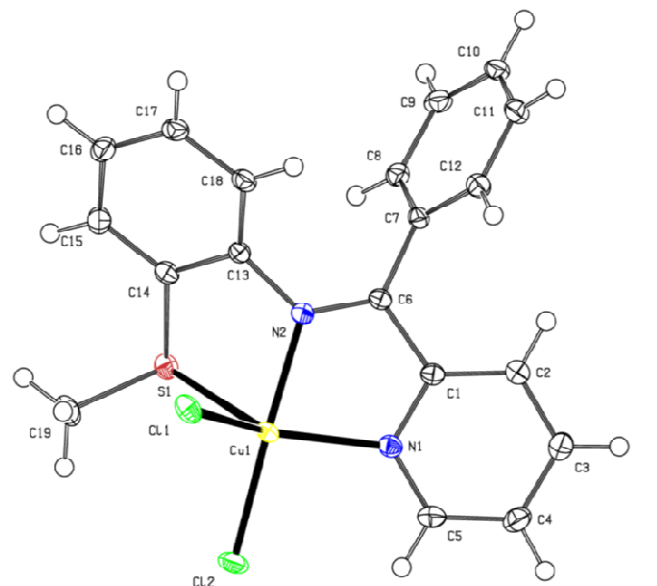


Figure 1a. ORTEP diagram of the complex $[\text{CuLCl}_2]$ (50% probability factor for the thermal ellipsoids).

Description of crystal structure:

The ORTEP diagram of the complex and atom-labeling scheme is shown in Fig. 1a and crystal parameters in Table S1 and selected bond lengths and angles are given in Table 1. The packing diagram of the complex is shown in Fig.1(b) and it indicates there are four molecule in the crystal packing. Complex $[\text{CuLCl}_2]$ is crystallized in the monoclinic crystal system with $P2_1/c$ space group. The Schiff base ligand (2-methylsulfanyl-phenyl)(phenyl-pyridin-2-yl-methylene)amine (L) act as NNS donor tridentate ligand and being bonded through two nitrogen atoms N(1) and N(2) and one sulfur atom S(1). The central Cu(II) ion has five coordination with $\text{N}_2\text{Cl}_2\text{S}$ environment and coordinated by two nitrogen atoms N(1) and N(2) and one sulfur atom S(1) from tridentate ligand L and two chloride ions Cl(1) and Cl(2). The coordination geometry around copper center is best described as distorted trigonal bipyramidal or square pyramidal which is revealed by the magnitude of the trigonality index ($\tau = 0.52$). For the perfect square pyramidal and trigonal bipyramidal geometries, the values are zero and one, respectively [16]. The equatorial positions are occupied by nitrogen N(1) atom of pyridine ring and one sulfur S(1) atom of ligand L atom and one chloride ion Cl(1). The axial positions are occupied by another chloride ion Cl(2) and nitrogen atom N(2) of imine group of Schiff base ligand L. The equatorial bond lengths Cu(1)-N(1) [2.0256(13)], Cu(1)-S(1) [2.6127(4)] and Cu(1)-Cl(1) [2.2863(4) Å] are not equal. The Cu(1)-S(1) bond distance is very long but comparable with reported compounds.[17].

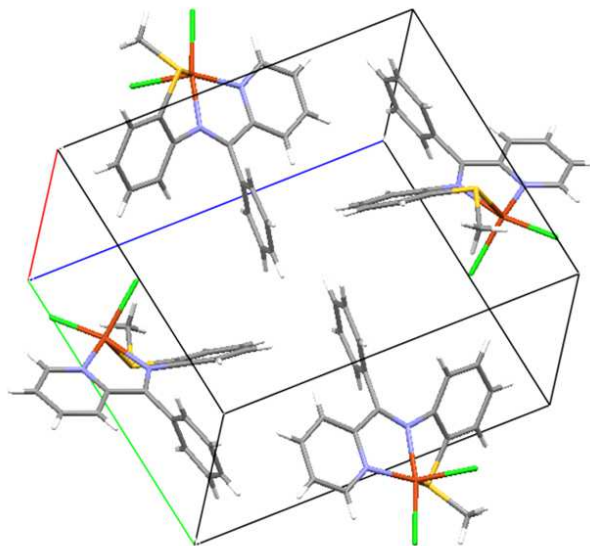


Figure 1b. Packing diagram of the complex

Two axial bond lengths Cu(1)-Cl(2)[2.2194(4)] and Cu(1)-N(2) [2.0115(12) Å] are not equal. The equatorial Cu(1)-Cl(1) [2.2863(4) Å] bond distance is nearly similar to axial Cu(1)-Cl(2) [2.2194(4) Å] bond distance and comparable with reported compounds [18]. The equatorial bond angles Cl(1)-Cu(1)-S(1), N(1)-Cu(1)-S(1) and N(1)-Cu(1)-Cl(1) are 96.841(14), 125.18(4) and 132.83(4)°, respectively and axial bond angle N(2)-Cu(1)-Cl(2) is 166.43(4)° which is deviated from ideal 180°.

Table 1. Bond length (Å) and Bond angles(°) of the complex

Bond Length (Å)		Bond Angles (°)	
Cu(1) – N(2)	2.011(12)	N(2) - Cu(1) - N(1)	79.57(5)
Cu(1) – N(1)	2.026(13)	N(2) - Cu(1) - Cl(2)	166.43(4)
Cu(1) – Cl(2)	2.219(4)	N(1) - Cu(1) - Cl(1)	132.83(4)
Cu(1) – Cl(1)	2.286(4)	N(1) – Cu(1) – S(1)	125.18(4)
Cu(1) – S(1)	2.613(4)	N(2) - Cu(1) - N(1)	79.57(5)
		N(1) - Cu(1) - Cl(2)	96.64(4)
		N(2) - Cu(1) - Cl(1)	97.77(4)
		N(2) - Cu(1) - S(1)	74.87(4)

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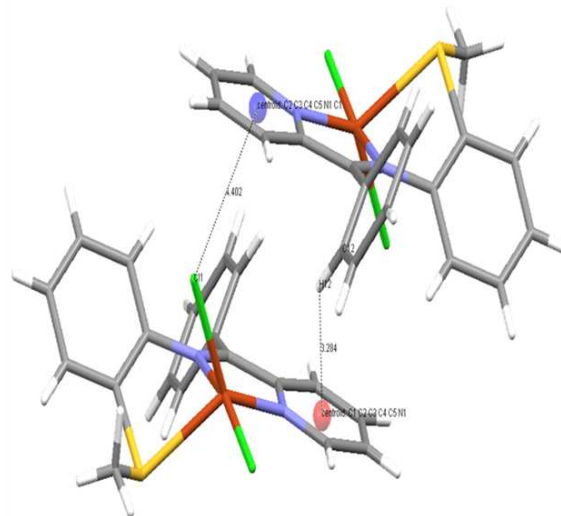


Figure 1c. Short intermolecular interaction in the complex.

Two molecules are connected by Cl-p interaction between Cl(1) of one molecule and centroid of benzene ring [C(2)C(3)C(4)C(5)N(1)C(1)] of another molecule with distance 4.402Å and CH-p interaction between H(2) atom of C(2)H(2) of one molecule and centroid of benzene ring [C(2)C(3)C(4)C(5)N(1)C(1)] of another molecule with a distance of 3.284Å [Figure 1C].

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