



# Synthesis, Spectroscopic Characterisation and Biological Studies of Copper (II) Complex Derived from Salicyloyl Hydrazone with Furfuraldehyde

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## Abstract

A Cu(II) complex of a ligand [L] derived from salicyloyl hydrazone and furfuraldehyde has been prepared. The ligand and metal complex were characterised by elemental analysis, magnetic measurement, molar conductance, FTIR, UV-Vis spectra, ESR and mass spectral studies. Analytical data suggests the molecular formula of the complex as  $[CuL_2]Cl_2$ . The IR spectral data suggest that the [L] is acting as neutral bidentate ligand towards Cu(II) in its complex. IR, ESR and magnetic susceptibility of the sample taken in the solid state, electronic and mass spectra are taken in the ethanolic solution and the conductance is measured in the solution state. The electronic spectral data and magnetic moment value agrees to the tetrahedral geometry of the complex. The electrolytic nature is evidenced from the high conductance data. The biological screening activity of the ligand and its copper(II) complex against the bacteria *Escherichia Coli*, *Vibrio Cholerae* and fungi *Aspergillus Niger*, and *Penicillium Crysogenum* are also reported. The complex exhibit increased activity than the ligand.

**Keywords:** Furfuraldehyde, IR spectra, ESR, Cu(II).

## Introduction

The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes of these ligands have been investigated<sup>1</sup>. The development in the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species<sup>2-4</sup>. Schiff base which are considered as privileged ligands have the ability to stabilise different metals in different oxidation states and thus regulate the performance of metals in a large variety of catalytic transformations. The catalytic activity of the schiff base complexes are highly dependant on the environment about the metal centre and their conformational flexibility. Therefore it is to be expected that the introduction of bulky substituents near the coordination sites might lead to low symmetry complexes with enhanced catalytic properties. The azomethine group present in them makes a wide scope. Schiff bases possess excellent structural similarities with natural biological substances relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties. Their structural features were obtained from elemental analysis, FT-IR, ESR, UV-Visible spectra, mass spectra, magnetic susceptibility and electrolytic conductance

**Reagent and Instruments:** All the reagents were Merck, Aldrich, Lancaster or BDH and solvents used were purified by standard methods<sup>5</sup>. The copper content of the prepared complex was determined iodometrically following standard procedure<sup>6</sup>. The halogen content of the complex also done by the standard procedure<sup>6</sup>. The carbon, hydrogen and nitrogen contents of the

ligand and complex were performed using vario EL-III CHN elemental analyser. The infra red spectra were recorded on a Perkin-Elmer spectrum 65 infra red spectrometer using KBr pellet in the region 400-4000 $cm^{-1}$ . The electronic absorption spectra of the ligand and the complexes in methanol was measured using a Perkin-Elmer UV-visible spectrophotometer  $\lambda$  25. The X band EPR spectra of polycrystalline samples were recorded in solid state, solution and frozen states on a varian-E-112 spectrometer using TCNE as marker at 9.1GHz microwave frequency. The magnetic susceptibility measured at room temperature employing Sherwood Scientific Magnetic Susceptibility Balance. Molar conductivity measurements were made using Systronics direct reading conductivity meter. Mass spectra of the ligand taken from NIIST, Thiruvananthapuram.

## Methodology

**Synthesis of ligand [L] and Cu(II) complex:** The ligand [L] is synthesized by adding hydrazine hydrate (0.01M) to an ethanolic solution of methylsalicylate (0.01M) drop wise with stirring at room temperature. After complete addition of hydrazine hydrate, the resulting clear solution was refluxed for 5 hrs on a water bath. The pale yellow solid thus filtered, washed with cold ethanol and recrystallised from aqueous ethanol. The compound obtained is salicyloyl hydrazone. Salicyloyl hydrazone (0.01M) is dissolved in ethanol and is mixed with (0.01M) furfuraldehyde in ethanol. It is then refluxed for 5 hrs. The reddish brown precipitate is filtered, washed and recrystallised<sup>7</sup>.

Solid complex synthesized by addition of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.01mol) in methanol to methanolic solution of [L] (0.01mol). Resulting mixture was refluxed for 3-4 hrs. After concentrating the solution was filtered and washed several times with ethanol and dried in dessicator over  $\text{CaCl}_2$ .

### Results and Discussion

The ligand and its Cu (II) complex are air stable soluble in DMSO, DMF and methanol but less soluble in ethanol and chloroform. The elemental analysis shows that Cu (II) complex has stoichiometry of type  $[\text{CuL}_2] \text{Cl}_2$  (table-1).

**Mass spectra:** The mass spectra of complex was recorded and agrees with its stoichiometry. The molecular ion peak is observed at 568, corresponds to that of the  $[\text{CuL}_2] \text{Cl}_2$ .

**Important IR spectral bands of [L] and its Cu (II) complex:** Ligand shows strong band at  $1581\text{cm}^{-1}$  corresponding to azomethine  $\nu_{\text{C=N}}$ . On complexation it exhibit a shift to lower frequency  $1539\text{cm}^{-1}$ , an evidence for C=N participation in bonding<sup>8</sup>. The  $\nu_{\text{C=O}}$  bands at  $1633\text{cm}^{-1}$  corresponds to C=O exhibit a shift to lower value of  $1616\text{cm}^{-1}$  on complex formation. The appearance of new band in  $532\text{cm}^{-1}$  due to  $\nu_{\text{M-O}}$  supports the coordination of C=O group to metal ion<sup>9</sup>. A new band appears at  $418\text{cm}^{-1}$  corresponds to  $\nu_{\text{M-N}}$  stretching frequency<sup>10</sup>. The  $\nu_{\text{O-H}}$  of both ligand and complex remain unaltered at  $3361\text{cm}^{-1}$ , indicating nonparticipation of OH group in complexation. The IR spectral evidences indicate that the ligand is coordinated to the Cu (II) ion in a neutral bidentate manner.

**Electronic spectral data of the ligand and  $[\text{Cu L}_2]\text{Cl}_2$  complex:** The electronic spectra of SHF shows two absorption maxima at 375nm and 321nm corresponding to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The electronic spectra of Cu complex shows a broad band at 384nm and 335nm corresponds to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The principal maxima centered around 448nm due to d-d transitions<sup>11,12</sup>.

**Molar conductance and effective magnetic moment of Cu (II) complex:** Molar conductance measurement values of the complex in methanol ( $172.00\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ), acetonitrile ( $235.00\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) and nitrobenzene ( $53.00\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) shows that the complex is a 1:2 electrolyte<sup>13</sup>. The effective magnetic moment value of the Cu complex is found to be 2.207 BM corresponds to that for tetrahedral geometry (table-2).

**ESR spectra:** The ESR spectra of metal chelates provide information about hyperfine and super hyperfine structures which are important in studying the metal ion environment in the complexes. The X band ESR spectra of Cu complex in polycrystalline state at room temperature has been evaluated to give  $g_{\text{avg}}$  value as 2.132. The spectrum lacks hyperfine structure which suggest the predominant effect due to exchange interaction among the Cu(II) ions. ESR parameters of the complex coincide well with related systems which suggest that complex has tetrahedral geometry<sup>14</sup>.

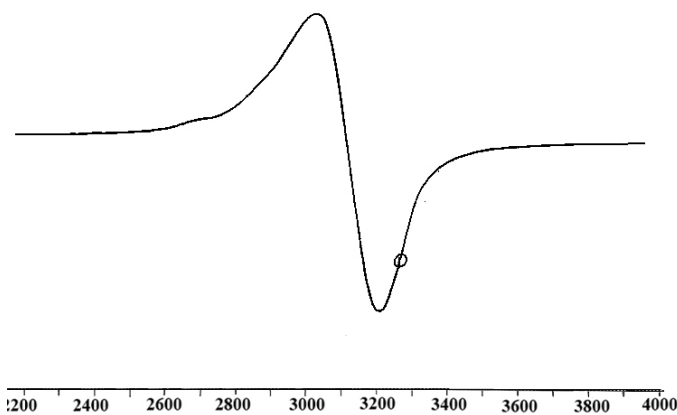


Figure-1  
ESR spectra of Cu(II) complex

**Biological Activity:** The compound was tested against gram positive and gram negative bacteria. The antifungal activity of the ligand and the complex evaluated by screening them against two fungi. It was found that the complex has got more activity than ligand<sup>15,16</sup>.

Table-1  
Elemental analytical data of [L] and Cu (II) complex observed (calculated)

complex	colour	Metal%	Cl%	C%	N%	H%
[L]	Reddish brown	-	-	62.60 (62.62)	12.17 (12.20)	4.35 (4.36)
$[\text{CuL}_2] \text{Cl}_2$	Red	10.69 (10.54)	11.92 (11.78)	48.45 (48.52)	9.42 (9.51)	3.36 (3.39)

Table-2  
Magnetic moment and conductance value

compound	$\mu_{\text{eff}}$ (BM)	Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )		
		methanol	Acetonitrile	nitrobenzene
$[\text{CuL}_2] \text{Cl}_2$	2.207	172	235	53

## Conclusion

The present study confirmed tetrahedral geometry of Cu (II) complex with [L] as a bidentate neutral ligand and two chlorine atoms outside the coordination sphere. The spectral techniques also suggest the tetrahedral nature of complex, which is supported by the electrolytic nature and the magnetic susceptibility value.

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