

Study on Spectral property of Cu(II) Complex with Ligand 2-hydroxy-5-chlorobenzoic acid hydrazide

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ABSTRACT

A methanolic solution of Cu(II) chloride of 0.5 M strength was prepared by mixing 0.672g of Cu(II) chloride in 10 ml of ethanol in a dried beaker with continuous stirring. A methanolic solution of ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L^1) of 0.5 M strength was prepared by mixing 0.932 g of ligand with 10 ml of ethanol in a dried beaker with continuous stirring. Both solutions were filtered to remove any insoluble residue left.

Keywords : Copper (II), Methanolic solution, Chloride solution,

Introduction :

A warm stirred methanolic solution (30 ml) of the ligand (0.01mol) was added in a 250 ml round bottom flask containing the copper (II) chloride solution and fitted with a water condenser in a dropwise manner. The mixture was stirred vigorously for 20 minutes and refluxed over a steam bath at 70 °C for 2 hours. Consequently, the resultant solution was left overnight in a fume cupboard at ambient temperature until all traces of the solvent had evaporated. The solid formed, washed with methanol and dried over anhydrous calcium chloride in a vacuum desiccator. The violet precipitate was washed successively with distilled water, ethanol, and diethyl ether.

A solubility test of this complex was performed. It was found soluble in dimethyl sulphoxide (DMSO), dimethyl formamide (DMF). It was sparingly soluble in water and insoluble in alcohol, ether and acetone.

The thin layer chromatography of this complex was performed by using aluminium plates coated with silica gel-60GF254 as the stationary phase. The solvent system was consisted of butyl acetate:glacial acetic acid:methanol:water (5:2.5:2.5:1, V/V) as mobile phase. The R_f value was found 0.42 ± 0.02 .

Its melting point was determined using open capillary tube in kjeldal flask filled with concentrated sulphuric acid. Its melting point was $\sim 240^\circ\text{C}$.

The analytical data for the ligand and its metal complex was analyzed through Cario Erba 1108 elemental analyzer. The elemental analysis data is given as:

Table : 1.1

Elemental analysis of the compound by legend L₁ (Cu)

	% of Cu	% of C	% of H	% of N
Calculated	14.61	33.66	2.76	12.89
Found	14.34	33.28	2.71	12.73

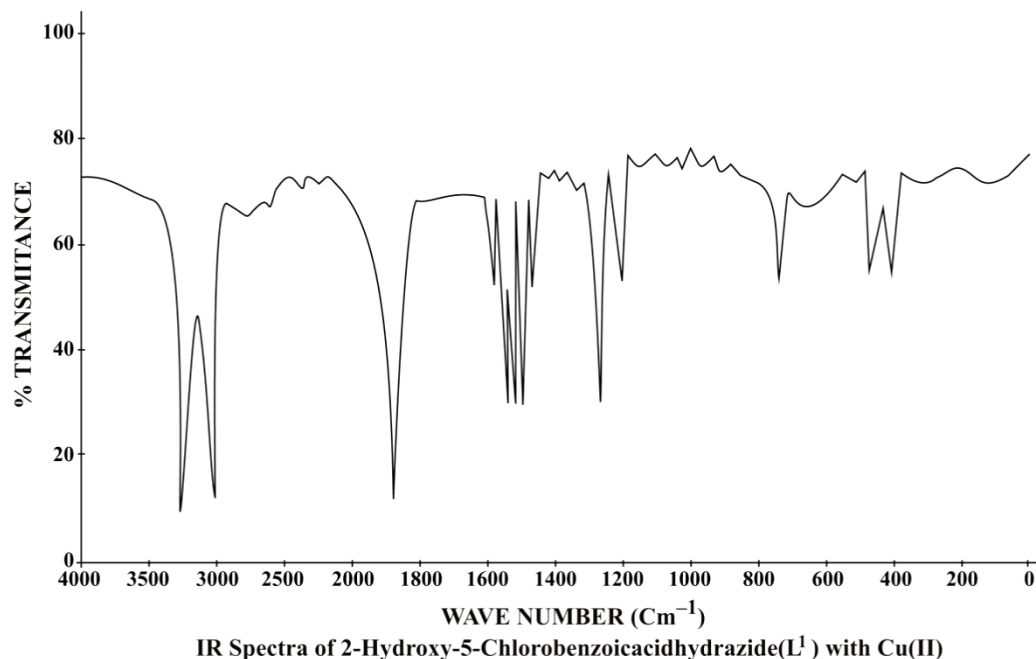


Fig. : 1.1

Results and Discussion:

The transition metal *Cu*(II) complex of ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L¹) is anhydrous as supported by analytical and spectral studies. The complex is soluble in acetone, DMSO and DMF and insoluble in Water, alcohol and ether.

The molar conductance of the complex has been recorded in nitrobenzene in digital systonic conductivity meter-304. The complex is non-electrolytic in nature because it showed very low value of its molar conductance. Magnetic moment of the complex is in good agreement with the theoretical value calculated by Van-Vleck. Analytical data, magnetic moment, molar conductance and colour of the complex are given in following table.

Table : 1.2

Analytical Data, Mainatic moment (Cu) and colour of the complex

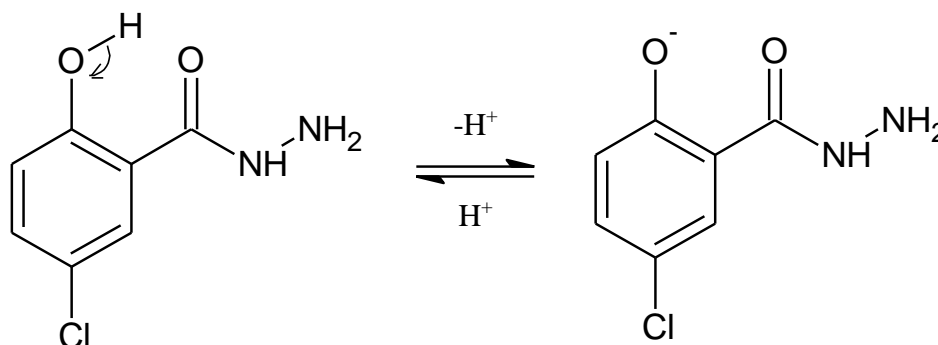
Complex with L ²	Colour	Boiling point (^o C)	Λ_m ($\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	μ_{eff} (in B.M.)
[Cu(L ²) ₂]	Yellowish blue	215	10.3	1.73

IR Spectral Analysis:

The ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L¹) expected to act as tridentate one, the possible coordination sites being phenolic oxygen, carbonyl of amide and NH₂ groups. The infrared frequencies in the present ligand associated with amide group (carbonyl-oxygen), NH₂ group and phenolic oxygen are expected to lie influenced on complex formation with metal ions have been discussed.

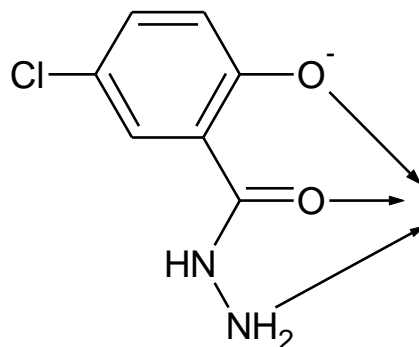
Generally, all amides show two absorption bands¹⁻⁴ at $\sim 1640\text{ cm}^{-1}$ related to C=O, group known as amide-I band and $1600\text{--}1500\text{ cm}^{-1}$ known as amide-II band. The amide-I band in the ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L¹) appears at 1660 cm^{-1} . The complexes show a considerable negative shift from 1660 to 1580 in $\nu_{\text{C=O}}$ indicating a decrease in the stretching frequency due to the decrease in force constant of C=O as a consequence of coordination through the carbonyl oxygen⁵⁻⁷ atom of the ligand (L¹). The amide-II band appears at the normal position in the NH-deformation rather than C–N link. In the ligand (L¹), the absorption in 1560 cm^{-1} reason has been assigned to amide-II absorption. The NH stretching absorption in free ligand occurs at 3290 and 3220 cm^{-1} which remains unaffected after complexation, it excludes the possibility of coordination through imine nitrogen⁸⁻⁹. In spectra of the complex, the band occurs in the range of $\sim 3200\text{ cm}^{-1}$ attributed to NH₂ group (ν_{NH_2}), shifted to lower wave number and appears in 3170 cm^{-1} indicating the involvement of nitrogen atom of NH₂ group in coordination¹⁰⁻¹¹. The strong bands observed at 1520 and 1000 cm^{-1} are tentatively assigned¹²⁻¹³ to asymmetric and symmetric $\nu_{\text{C=C}} + \nu_{\text{C=C}}$ of aromatic ring stretching and deformations remain practically unchanged in frequency and band intensities.

The infrared spectrum of the ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L¹) showed that the vibrational frequency due to the phenolic OH group that appeared in the spectrum of the ligand at 3558 cm^{-1} for 2-hydroxy-5-chlorobenzoic acid hydrazide (L¹) had disappeared in the spectrum of the complex. This may be due to the displacement of its proton during the condensation process of complex formation¹⁴⁻¹⁶.



Further, the appearance of new bands at 839 cm^{-1} and 815 cm^{-1} suggests $\nu(\text{M-O})$ and $\nu(\text{M-N})$ linkage, respectively¹⁷⁻²⁰.

Thus the ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L^1) behaves as uninegative monodentate ligand having coordinating sites phenolic oxygen, carbonyl oxygen and amine (NH_2) group. The coordination sites may be shown as:



Electronic Spectra:

The Cu(II) complexes are known in a wide variety of structures. In present research work, The Cu(II) complex with ligand 2-hydroxy-5-chlorobenzoic acid hydrazide (L^1) show absorptions $17,000\text{ cm}^{-1}$, $18,000\text{ cm}^{-1}$ and $20,000\text{ cm}^{-1}$ respectively. They are labeled as ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ indicating the tetragonal geometry of the complex²¹⁻²⁵. The increased bonding partner of the $d_{x^2-y^2}$ copper atomic orbital then leads to larger splitting of the ground state 2E_g than we would anticipate from a purely ionic model²⁶⁻²⁷. The approximate positions of the 2E_g and 2B_g states can be estimated from the g-factor obtained from electron paramagnetic spectra.

Conclusion :

Thus, six coordinated Cu(II) complex is distorted from a regular octahedral with the axial ligands of the octahedron further away from the metal ion than the equatorial ligands due to Jahn-Teller distortion.

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