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Studies of newly synthesized Cu(ii) complex with ligand 2-hydroxy-5-methylbenzoic acid hydrazide

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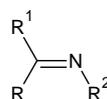
Abstract

The ligand 2-hydroxy-5-methylbenzoic acid hydrazide has been synthesized during the research work. Thereafter, a coordination compound with Transition metal Cu (II) has been prepared by the reaction between selected transition metal ions Cu (II) with newly synthesized acid hydrazide ligand. Thereafter, solubility, melting point, conductivity and spectral analysis have been studied. After analysis six coordinated distorted octahedral structure of the complex has been confirmed.

Keywords: Schiff base, acid hydrazide, Jahn-teller distortion.

Introduction

A Schiff base named after Hugo Schiff ^[1] is a compound with the general structure as:



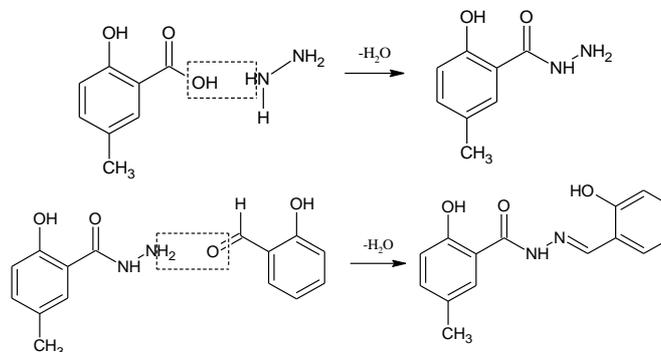
Schiff bases are common ligands in coordination chemistry. The imine nitrogen is basic and exhibits π -acceptor properties. The ligands are typically derived from alkyl diamines and aromatic aldehydes ^[2].

In this paper, we have reported, transition metal Cu (II) complex of Schiff base derived from salicylaldehyde and derivatives of benzoic acid hydrazide.

Materials and Methods

Preparation of Ligand

Reaction Scheme



Procedure

At first 2-hydroxy-5-methylbenzoic acid hydrazide was prepared. In order to obtain this acid hydrazide, stoichiometric amount of 5-chloro-2-hydroxybenzoic acid was carefully added to a stirred pre-warmed methanolic solution of hydrazine. The reaction mixture was refluxed at 70 °C for 2 h in a closed system. Consequently, the resultant mixture was cooled to room temperature and then concentrated to a volume of 20 ml.

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The solid product formed was recovered by filtration, washed with methanol and dried in a desiccator over anhydrous CaCl_2 at ambient temperature. The resulting pale yellow coloured solid was filtered. The solid was washed with ethanol three times repeatedly. The purity of ligand was checked by elemental analysis and melting point.

Preparation of 2-hydroxy-5-methylbenzoic acid hydrazide solution

A 0.05 M methanolic solution of 2-hydroxy-5-methylbenzoic acid hydrazide was prepared by adding 0.405 g of 2-hydroxy-5-methylbenzoic acid hydrazide in 50 ml of methanol.

Preparation of hydrazine solution

A 0.05 M methanolic solution of 2-hydroxybenzaldehyde (salicylaldehyde) was prepared in 50ml of methanol.

Preparation of ligand

Stoichiometric amount of 2-hydroxy-5-methylbenzoic acid hydrazide was carefully added to a stirred pre-warmed methanolic solution of 2-hydroxybenzaldehyde (salicylaldehyde).

The reaction mixture was refluxed at 70°C for ~2 h in a closed system. Consequently, the resultant mixture was cooled to room temperature and then concentrated to a volume of 20 ml. The solid product formed was recovered by filtration, washed with methanol and dried in a desiccator over anhydrous CaCl_2 at ambient temperature. The resulting yellow coloured solid was filtered. The solid was washed with ethanol three times repeatedly. The purity of ligand was checked by elemental analysis and melting point. It was also characterized by IR and ^1H NMR spectral studies.

Table 1: Elemental analysis of the compound

L^1	% of C	% of H	% of N
Calculated	66.67	5.18	10.37
Found	66.38	5.09	10.19

Characterization of ligand

IR spectrum of the ligand was recorded in a Perkin-Elmer FTIR spectrophotometer using KBR pellet method.

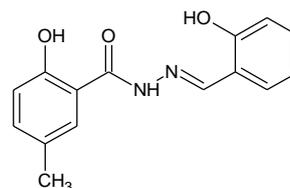
Table 2: The main IR spectral data of the ligands and their assignments

IR data of ligand in cm^{-1}					
Ar-OH	Ar-H	$\nu_{\text{C=O}}$	ν_{NH}	ν_{CN}	$\nu_{\text{C=O}}$
3558	830	1232	3274	1623	1695

The IR spectrum of ligand N^1 -salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide shows two strong absorption bands at 830 cm^{-1} indicating the presence of trisubstituted benzene [3]. There are three signals in the NMR spectrum of the ligand at the δ values 6.35 (s), 6.8(s) and 7.01(s), which further indicate [4] the presence of trisubstituted benzene in the ligand. The NMR spectrum of the ligand contains a singlet peak at 2.4 ppm indicating [5] the presence of methyl group attached to an aromatic ring. The spectrum of ligand contains a strong band at 1695 cm^{-1} attributed [6] to $>\text{C}=\text{O}$ group conjugated with benzene ring. The presence of a medium band at 3274 cm^{-1} indicating [7] the NH group conjugated with $\text{C}=\text{O}$ group, which shows [8] a singlet peak in NMR spectrum of the ligand at δ 5.01 ppm. The spectrum

of the ligand shows a peak at 3558 cm^{-1} indicating the phenolic hydroxyl group.

On the basis of spectral analyses and elemental analysis, following structure of the complex has been confirmed.



Preparation of complex

Preparation of solution

A methanolic solution of transition metal Cu (II) chloride of 0.5 M strength was prepared by mixing appropriate amount of Cu (II) chloride in 10 ml of ethanol in a dried beaker with continuous stirring.

A methanolic solution of ligand N^1 -salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide (L^2) of 0.5 M strength was prepared by mixing 1.35 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.

Preparation of complex

A warm stirred methanolic solution (30 ml) of the ligand (0.01mol) was added in a 250 ml round bottom flask containing the metal (II) salt 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 yellowish blue precipitate was washed successively with distilled water, ethanol, and diethyl ether.

Table 3: Elemental analysis

	% of Cu	% of C	% of H	% of N
Calculated	10.56	59.85	4.32	9.31
Found	10.21	59.48	4.28	9.13

Results and Discussion

The transition metal Cu (II) complex of ligand N^1 -salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide 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.

Table 4: Analytical data, magnetic moment, molar conductance and color of the complexes

Complex ith L^2	Colour	Boiling point ($^\circ\text{C}$)	Δ_m ($\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	μ_{eff} (in B.M.)
[Cu(L^2) $_2$]	Yellowish blue	215	10.3	1.75

IR spectral analysis

The infrared spectrum of the ligand *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide showed that the vibrational frequency due to the phenolic OH group that appeared in the spectrum of the ligand at 3558 cm⁻¹ for *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide had disappeared in the spectrum of the complex. This may be due to the displacement of its proton during the condensation process of complex formation^[9]. The $\nu(\text{NH})$ of the uncoordinated NH groups appeared as a shoulder at 3274 cm⁻¹ in spectra of the ligands *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide and at 3358 cm⁻¹ in spectra of the Cu (II) complex^[10]. The IR spectra of the free ligand show the characteristic >C=N (azomethine group) bands in the 1623 cm⁻¹ region which are shifted to lower frequencies in the spectra of the metal complex (1588 cm⁻¹)^[11]. This $\nu(\text{C=N})$ shift to in the complex by about 35 cm⁻¹ indicates the involvement of azomethine nitrogen in the coordination sphere with the metal ions for all the complexes as well as lack of carbonyl group from original substituted benzohydrazide compound^[12]. The stretching vibration of the phenolic $\nu(\text{C-O})$ observed at regions 1232 cm⁻¹ in the free ligands undergo a hypochromic shift to 1311 cm⁻¹ regions in the complexes upon complexation. This shifts further confirms the coordination of the phenolic oxygen leading to the formation of C-O-M bond^[13] (where M= Cu²⁺). The vibrational frequency at 1695 cm⁻¹, is due to carbonyl stretching vibration in the ligand *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide molecule. This carbonyl frequency is shifted downwards in the spectra of transition metal Cu (II) complex indicating the coordination has taken place through oxygen atom of C=O group^[14].

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, respectively^[15]. The bands observed at ~1576 cm⁻¹ is due to the $\nu(\text{C-C})$ stretching of the aromatic ring systems. In the metal Schiff base complex, most of the bands shift observed in the wave number region 1379-1436 cm⁻¹ and 1240-1259 cm⁻¹ are in agreement with the structural changes observed in the molecular carbon skeleton after complexation^[16], which cause some changes in (C-C) bond lengths. Valuable evidence concerning the environment of the functional group's coordination to the metal atoms through azomethine nitrogen and phenolic oxygen atoms has been obtained from the FT-IR spectra.

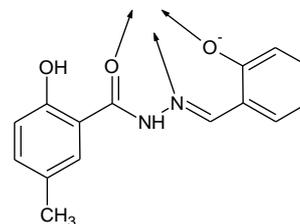
Electronic spectra

The Cu (II) complexes are known in a wide variety of structures. In present research work, The Cu (II) complex with ligand *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide molecule show absorptions 17,200 cm⁻¹, 18,400 cm⁻¹ and 20,500 cm⁻¹ respectively. They are labeled as ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ indicating the tetragonal geometry of the complex^[17]. The increased bonding partner of the $d_{x^2-y^2}$ copper atomic orbital then leads to larger splitting of the ground state ${}^2\text{E}_g$ than we would anticipate from a purely ionic model. The approximate positions of the ${}^2\text{E}_g$ and ${}^2\text{B}_g$ states can be estimated from the *g*-factor obtained from electron paramagnetic spectra^[18].

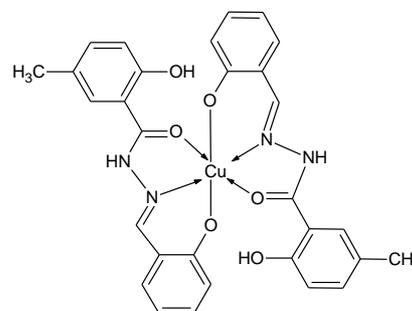
Thus six coordinated Cu (II) complex is distorted from a regular octahedral with the axial ligands of the octahedron further away from the metal ion than the equatorial ligands due to Jahn-Teller distortion.

Conclusion

IR analysis of the ligand indicates that the ligand *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide behaves as uninegative tridentate ligand having coordinating sites phenolic oxygen, carbonyl oxygen and azomethine nitrogen. The coordination sites may be shown as:



The analysis of electronic spectrum of the complex formed by the ligand *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide with Cu (II) ion indicates that the complex is six coordinated tetragonal geometry. Further, elemental analysis indicates that the complex is formed by 1:2 ratios of the metal Cu (II) and ligand *N*¹-salicylidene-5-methyl-2-hydroxybenzoic acid hydrazide. Thus the structure of the newly synthesized complex may be shown as:



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