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Characterization of newly synthesized schiff base complex of cu (II) ion

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Abstract

In this paper, we have reported the synthesis of Schiff base ligand derived from anthranilic acid and p-dimethylaminobenzaldehyde. The synthesized Schiff base ligand p-dimethylaminobenzaldehyde was characterized by elemental analysis, solubility, Melting point and spectral analyses say IR, NMR. Thereafter, a Schiff base complex with transition metal Cu (II) was prepared. The synthesized Schiff base Cu (II) complex was characterized by elemental analysis, solubility, Melting point, Conductivity Measurements, Magnetic Susceptibility Measurement and spectral analyses like IR, NMR and electronic spectral studies.

Keywords: Schiff Base, IR, NMR.

Introduction

There are various chemical species, which behave as ligands. Most ligands have significant properties [1, 2] in the point of therapeutical view. Out of them, Schiff base ligands have significant therapeutical importance.

With this regard, we have selected Schiff bases derived from anthranilic acid and p-dimethylamino benzaldehyde has been selected to prepare some Schiff base complexes with transition metal (II) complexes.

Preparation of Ligand 2-{[dimethylamino)benzylidene]amino}benzoic acid:

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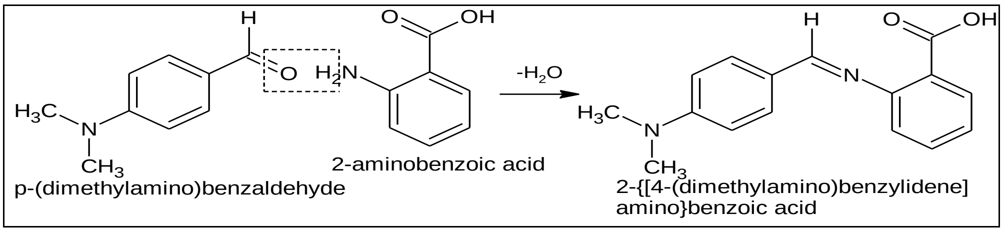

Procedure

A 0.4 M ethanolic solution of p-dimethylbenzaldehyde was prepared by adding 1.492g of p-dimethylbenzaldehyde in 25 ml of ethanol.

An ethanolic solution of anthranilic acid of 0.4 M strength was prepared by adding 1.3714 g in 25 ml ethanol.

Preparation of Ligand

A solution of p-dimethylbenzaldehyde (0.4M) in 25 ml of ethanol was added to an ethanolic solution (0.04M, 25ml) of anthranilic acid.

The reaction mixture was refluxed on a water bath for 6 hrs. The reaction mixture was poured in crushed ice, whereby orange precipitate was obtained. It was filtered by suction pump. The solid was washed with water and cold ethanol three times respectively and repeatedly. It was crystallized from dimethylformamide (DMF) and dried in an oven at 60 ^{0}C. The pure Schiff base was recrystallized from distilled water.

The purity of ligand was checked by elemental analysis and melting point (m.p.; 186 ^{0}C, yield; 71%). Elemental analysis of the compound is given as

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Table 1: Elemental analysis of the compound

BFMH	% of C	% of H	% of N
Cal.	71.64	5.97	10.45
Found	71.32	5.91	10.24

Preparation of Cu (II) Complex

All chemicals such as copper (II) chloride and ethanol, etc used in this study were of analytical grade. These chemicals were purchased from CDH or Merck and used as such.

Preparation of Solution of ligand 2-{[dimethylamino)benzylidene]amino}benzoic acid

An aqueous solution of Schiff base of 0.2M of volume 20 ml was prepared by taking 0.254 g of the ligand 2-{[dimethylamino)benzylidene]amino}benzoic in hot distilled water in a dried beaker with continuous stirring.

Preparation of Solution of Cu (II) salt

An aqueous solution of Cu (II) chloride of 0.1 M strength was prepared by mixing 0.127 g of Cu (II) chloride in 20 ml of ethanol in a dried beaker with continuous stirring.

Both solutions were filtered to remove any insoluble residue left.

Preparation of complex

The aqueous solution of Cu (II) chloride solution (0.1M, 20ml) was mixed with continuous stirring with a clear aqueous solution of the ligand 2-{[dimethylamino)benzylidene]amino}benzoic (0.2M, 20ml) in a dried beaker of 100 ml. After mixing, the reaction mixture was taken in a conical flask.

The elemental analysis of the complex is given as:

Elemental analysis

Table 2: The elemental analysis of the complex

	% of Cu	% of C	% of H	% of N
Cal.	10.63	64.27	5.02	4.69
Found	10.48	63.98	4.97	4.58

Results and Discussion

Molar conductance of the complexes was measured by Systronics digital conductivity meter model-304 in 1×10^{-3}M DMF solution. Magnetic moment of the complexes were measured by Gouy's method in B.M. unit at room temperature using $Hg[Co(NCS)_4]$ as the calibrant at CDRI Lucknow.

Elemental analysis of the complex was carried out at CDRI Lucknow. Nitrogen content was estimated using elemental analyzer Heraeus Carlo Erba-1108 at CDRI, Lucknow. IR spectra of the ligand and complexes were recorded in a Perkin-Elmer FTIR spectrophotometer using KBr pellet method at CDRI Lucknow *(given in appendix-I)*. Molecular weights of the complexes were determined by Camphor-Rast Method. Electronic spectra of the complexes were recorded by the courtesy of CDRI, Lucknow.

For Cu (II) complex

From the result of elemental analysis and conductivity measurement it has been found that Cu (II) forms complex of the type $[CuL_2]$ Where L= deprotonated ligand.

The μ_{eff} value of the complex was found to be 1.93 B.M indicating the paramagnetic in nature of the complex. The complex is stable up to 300 ^{0}C and it neither change colour nor lose weight.

Discussion of Magnetic behavior of Cu (II) complexes

On the basis of studies on several Cu (II) complexes Ray and Sen[3] have categorized them into following two sub groups.

a. Complexes having magnetic moments between 1.73 and 1.83 B.M.
b. Those having magnetic moment values between 1.94 and 2.20 B.M.

They assigned the former to be square Planar with dsp [2] hybridization and the later tetrahedral sp [3] or octahedral with sp^3d^2 hybridization.

The absence of orbital contribution in former category has been explained by the author [4] on the assumption of greater quenching effect of the crystal field in the orbital moments.

The Pauling's valance bond theory [5] assumed that the tetrahedral complexes of Cu (II). Owing to their own symmetries tetrahedral complexes have a greater crystal contribution to the magnetic moment than the square planar complexes.

The CFSE for a square planar configuration is much higher (12.28 Dq) than for octahedral (6 Dq) or tetrahedral (-2.66 Dq) configurations. The higher value of CFSE indicates greater stability of the resulting structure.

The orbital contribution to the magnetic moment is greater in the case of tetrahedral Cu (II) complexes since the ground state is triply degenerated [6]. The nine 3d electrons of cupric ion are distributed among the five 3d orbitals in such a way that the energy of the system is minimum. Therefore, the stabilization energy due to the crystal field will be greater for a square planar geometry than that for a tetrahedral structure. Furthermore, a perfectly tetrahedral copper complex is triply degenerate.

So in accordance with Jahn-Teller Theorem, it is unstable and it must distort. These considerations account for the rarely of the tetrahedral copper complexes. A square planar complex is not degenerated; it should have μ_{eff} values approximately equal spin only value e.g. 1.7 B.M. A slight excess value above the spin only value can be visualized from splitting of d-orbitals in planar field.

The unpaired electron of the d [9] configuration is in the b_{1g} orbital giving a $^2B_{1g}$ ground term (non degenerate) in the case of square planar. In such circumstances, the $\mu_{\mathbf{eff}}$ is expected to be 15% above the spin only value.

A tetrahedral Cu (II) complex has a degenerate ground state and should have a large orbital contribution. In this case the magnetic moment should be varied with the temperature and at room temperature, it should be 2.20 B.M. where as a distorted tetrahedral complex should have a lower magnetic moment value.

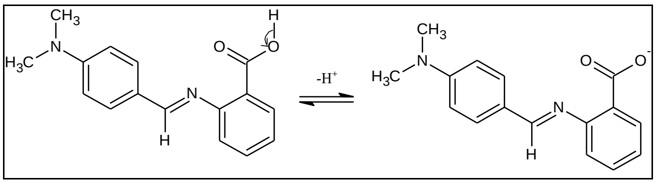
Kettle [7], suggested the square planar Cu (II) complexes have magnetic moments in the range of 1.83-1.86 B.M where as for tetrahedral configuration, the moments are large than 2.00 B.M.

In the present investigation the magnetic moment value of the complex $[CuL_2]$ was 1.93 B.M. suggesting them an octahedral geometry with orbital contribution.

Infrared Spectral Analysis

The Ir spectra of the complex $[CuL_2]$ with ligands 2-{[dimethylamino)benzylidene]amino}benzoic acid the same position of the strong band at 750 cm^{-1} indicating the aromatic ring remains same [5] even after the formation of complex. The characteristic weak band of aromatic ring at 1600 and 1500-1430 cm^{-1} also remain almost unaffected [6] even after the formation of complex.

The IR spectrum of complex with ligand 2-{[dimethylamino)benzylidene]amino}benzoic acid, shows the absence of strong and very broad band at 3010 and 3020 cm^{-1}, which indicates [8] the participation of carboxyl group in complexation with Cu(II) ion. It further indicates that ligand molecule undergo deprotonation during condensation before complexation.



The position of strong band [9] at 1250 cm^{-1} and 1255 cm^{-1} was shifted to the lower frequency at 1190 cm^{-1} and 1180 cm^{-1} in the spectrum of complex. It also indicates the participation of carboxyl group in complexation with Cu(II) ion.

A medium band appears at 1150 cm^{-1} of N-CH_3 group remains unaffected after the complexation [10]. A band of medium intensity at 1580 cm^{-1} of ligand 2-{[dimethylamino)benzylidene]amino}benzoic acid and 2-{[diethylamino)benzylidene]amino}benzoic acid was shifted to 1510 to 1500 cm^{-1} indicating the participation[11] of C=N group in complexation.

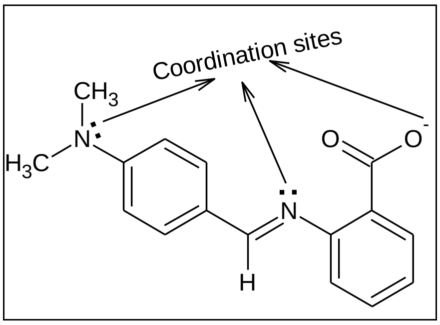
Further, the band corresponding to Ar-N shifted to lower frequency, which indicates the absence of conjugation of lone pair of electrons of nitrogen of amine group. It is possible only when nitrogen participate [12] in complexation through its lone pair of electrons.

In the IR spectra of complexes, carbonyl stretching vibrations of ligand exhibits a medium sharp intensity band [13] in the region 1675 cm^{-1}. This band has shifted towards negative region 1640 to 1645 cm^{-1} in the metal complexes indicating the coordination of the ligand with the metal ion through oxygen of the carboxyl group.

The appearance of new band in the IR spectra of metal chelates in the region 550-520 cm^{-1} is probable due to formation of M-O bonds [14].

The appearance of new band in the IR spectra of metal chelates in the region 810 and 805 cm^{-1} is probable due to formation of M-N bonds [15].

On the basis of above facts, it has been concluded that the proposed ligands 2-{[dimethylamino)benzylidene]amino}benzoic acid behave as uninegative tridentate ligand. The coordination site of the ligands may be shown as:



NMR Spectral analysis

The singlet peaks at δ 11.2 and 11.5 ppm are absent in the ^{1}HNMR spectrum [16] of the complex [CuL_2] indicating the deprotonation of the ligands before the participation of the ligands in complexation as it was also confirmed by IR analyses.

The NMR peak of aromatic proton at 7.2 ppm remains almost unaffected [17]. The singlet NMR signal of methyl protons attached to nitrogen at 2.4 ppm is shifted to downfield at δ 2.8 ppm indicating [17] the participation of lone pair of nitrogen in coordination with Cu (II) ion. The singlet signal of imine hydrogen at 6.5ppm is shifted to downfield at 6.8 ppm. It indicates the participation[18] of imine nitrogen in complexation.

Thus NMR spectrum also suggests that there is three coordination sites in ligands 2-{[dimethylamino) benzylidene]amino}benzoic acid.

Electronic Spectrum

Electronic spectral data for the Cu (II) complex are given in following Table.

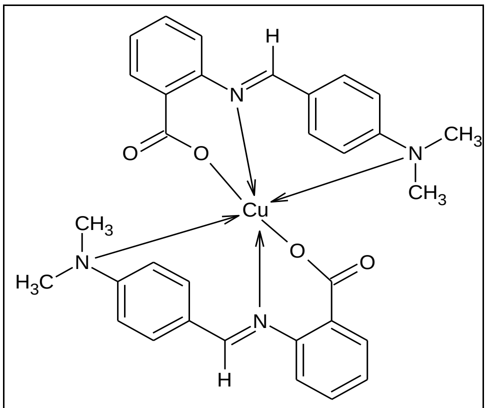
Table 3: Electronic spectral data along with band-assignment (in cm^{-1}) of "[CuL_2]" complexes

[CuL_2]	$^4E_g \rightarrow {}^2B_{2g}$, $^2B_{1g}$ and $^4A_{1g}$	14540, 13130 and 12460

Conclusion

The coordination ability of Schiff bases with Cu (II) ion afford the study of the metals in such system keeping the above facts. The results of our investigations on the synthesis, spectral and theoretical studies of Cu (II) complexes with ligands 2-{[dimethylamino)benzylidene]amino}benzoic acid in alcoholic medium. The complexes were characterized through elemental analysis, spectral, magnetic susceptibility and conductivity measurements.

On the basis of above facts, octahedral geometry of the complex has been predicted. The structure may be shown as:



Structure of the complex [CuL_2]
L = deprotonated p=dimethylaminobenzaldehyde

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