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UV-VISIBLE, IR AND NMR SPECTRA ON COPPER (II) SCHIFF BASE COMPLEX

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ABSTRACT

Some copper (II) complexes with isatin or imine ligands derived from isatin were prepared and characterized by analytical and spectroscopic techniques [1]. Schiff base complex of Cu (II) from the ligands like 2-aminophenol and para dimethyl amino benzaldehyde have been synthesised. The molar conductance, IR, ^{1}H-NMR, ^{13}C NMR, UV-Visible spectroscopy have been carried out to suggest tentative structure of the complex.

INTRODUCTION

Metal Complexes of Schiff bases have played a central role in the development of coordination chemistry. From the survey of existing literature, it appears that benzyl monophenyl hydrazone and its related compounds have been extensively used as biologically active complexing agents and analytical reagents[2] .Schiff bases have been derived from a numbersss of Carbonyl compounds and amines have been used[3,4].Schiff bases were first synthesized by H.Schiff. Condensation of primary amines with carbonyl compounds yields Schiff bases[5,6]. The Schiff bases ligands are soluble in common organic solvents. But its metal complexes are generally soluble in DMF and DMSO[7]. In our work we have synthesized the Schiff's base from the 2-aminophenol and para dimethyl amino benzaldehyde and it was characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis. Metal Complexes with the stoichiometry ratio of 1:2 (where M= Co^{II}, Ni^{II}, Cd^{II} and Na^{II}) were isolated and characterized by chemical analysis, electrical conductivity and infrared spectra measurements.

MATERIAL & METHODS

Synthesis of a novel Schiff's Base Ligand:

A new Schiff's base was prepared by stirring 2-aminophenol and para dimethyl amino benzaldehyde dissolved in about 10 ml ethanol together into the beaker with continous stirring. This would give us the colourless solid product.

Synthesis of Metal complexes of novel Schiff's Base Ligand:

0.01 M each of Schiff's base and the Metal salt are dissolved in the ethanol respectively and mixed to get the complex crystallized out from the solution.

Characterization of the Metal Complex:22

The characterisation and the properties of the complex so formed are to be studied with the help of the UV, IR, SEM, TEM, TGA, DTA data. These data gives us the clear picture of the structure, the bond and the nature of the new complex.

EXPERIMENTAL TECHNIQUES

A Short account for the analytical methods employed in this work is presented. Elemental Analysis, Electrical conductance, Infrared spectral measurement and UV-Visible Spectral measurement where carried out to characterize the compounds prepared.

Molar Base Conductance Measurements for copper Schiff base (II)complex

Exactly 0.01 N KCl solution was prepared and was used to measure the cell constant of the conductivity cell. The cell constant of the conductivity cell was 0.092cm^{-1}. An approximately 10 M solution of the

copper(II) Schiff base complex was prepared in DMF and its conductivity was measured at $2.4*10^{-6}$ ohm^{-1}. Knowing the cell constant, the specific conductance of the solution was calculated using the relationship.

Specific conductance= cell constant*observed conductance

Further the molar conductance, was calculated employing the following equation.

Molar conductance = (1000*K)/C

Where, C is the molar concentration, K is the specific conductance

The observed molar conductance of the copper(II) Schiff base complex 1.74 ohm cm mole indicating the complex to be a non electrolyte in nature

Infra red spectral study

The infrared spectra of ligand and the complex were taken as KBr disc in the conventional region(4000-400cm^{-1}). The infrared measurements were done on a perkin Elmer-R×1 spectrophotometer. The IR Spectral study helps to decide the donar sites strength of bonding existence of any possible hydrogen bonding etc.

Electronic Spectral Measurement

The electronic spectrum of the black coloured complex of copper (II) in the region was measured using the EZ-301 spectrophotometer. The working range of the instrument 190-1100 nm spectrum of the copper(II)complex was recorded using a acetone as a solvent, due to the instrument action limitations absorptions in the near IR region was not recorded. The electronic spectral measurements are useful for assigning the stereochemistry of metal ions in the complexes based on the location and the number of d-d transitional bands.

Proton NMR Spectrum of Ligand

The ^{1}H- NMR Spectrum of Ligand is shown in figure and the ^{1}H-NMR chemical shift data are provided in table. The ^{1}H-NMR Spectrum indicates the presence of mainly three types of protons in the ligand. A Signal seen at δ 3.039-3.104ppm is due to the protons of -N-CH_3 group. The Aromatic protons are seen at δ 6.695-7.803ppm. Then the signal seen at δ 8.8488ppm is due to the N=CH group.

Table 1.1

Proton NMR Chemical shifts of Ligands [in ppm]

Aromatic Protons	6.695-7.803
N-CH_3 Protons	3.039-3.104
-N=CH Protons	8.488

^{13}C- NMR spectrum of ligand

For the most organic molecules, ^{13}C-NMR spectral absorptions appear at low field for carbonyl carbons and at high field for methyl carbons in the range of 0 to 200ppm with reference to TMS. The spectrum detects total number of magnetically non-equivalent carbon atoms. The state of hybridisation is the dominating factor determining the chemical shift of a carbon atom.SP^3-hybrid carbon atoms absorb up field while SP^2 carbon atoms absorbs at lower field strength ie.SP^3>SP>SP^2

The ^{13} C –NMR spectrum of ligand is shown in fig. And the Spectral data are provided in table. The absorbtion of the aromatic carbons are observed at, δ 115.792 to 135.416

The Chemical shift observed at δ 43.832 to 45.508ppm due to the CH group. Then the another chemical shift observed at δ 82.54 to 83.431ppm, due to the >CH=N group and the Chemical shift observed at δ 149.309ppm due to the Ar -C-O group.

TABLE 1.2

^{13} C –NMR Chemical shifts of ligand (in ppm)

Methyl Carbons	43.83-45.508
Aromatic Carbons	115.792-135.516
>CH=N Carbon.	82.549-83.431
Ar-C-O-Carbon	149.309

Synthesis of Schiff Base Ligand

About 0.2183(0.02M) of 2-Aminophenol was dissolved in minimum amount of methanol and the solution was placed in a 100 ml beaker. Exactly 0.2984g (0.02M) of para dimethyl amino benzaldehyde was dissolved in a minimum amount of methanol and the solution was added drop by drop with the solution of 2-aminophenol in a 100ml beaker. The mixture of solution is stands for some times. After sometimes yellow coloured ligand was formed. Filtered, dried and recrystallized from hot methanol. The yield of the product is approximately 0.35g. Its melting point is noted at 149^0C.

Synthesis of Copper (II) Schiff Base Complex

Exactly 0.480g (0.02) of Schiff base ligand was weighed and placed into the 250 ml round bottom flask and added 20 ml of methanol to it. Exactly 0.1705g of Copper (II) chloride was weighed and placed into the 250 ml round bottom flask. Then the Copper (II) chloride solution was added into the Solution was added in to the Schiff base ligand solution and kept in a magnetic stirrer for an hour. The black coloured solid was separated out. Filtered, dried and crystallized from hot methanol.

Estimation of Metal

The metal content of the complex was estimated by Standard methods after decomposing them.

Preparation of Clear solution of the Metal from the complex

About 0.050 gms of the complex was accurately weighed and heated with a mixture of concentrated nitric acid (3ml) and (2ml) of hydrogen peroxide to dryness. This Process of heating was repeated for three times. After this is a suitable dilute acid was added in dilute acid was added in little amount to dissolve the residue to get the clear solution. The Solution was allowed to cool and made up to 100 ml.

RESULT AND DISCUSSION

Characterization of Ligand

The Schiff Base was prepared by facilating the condensation of 2-aminophenol and para dimethyl amino benzaldehyde in 1:1 ratio respectively. The IR spectrum of Ligand shows a peak at 3331 cm^{-1} corresponding to N-H stretching, the C-H stretching shows a peak at 2908cm, the –C-N-C stretching shows a peak at 1614cm^{-1} and the C-O stretching occurs at 1675cm,then the O-H stretching occurs at 3726 cm^{-1}.

From the above IR datas the ligand contains azomethane, phenolic and dimethyl amino groups. Examination of the structure of ligand shows that it can function as bidentate ligand in two ways. The –OH and –CH groups being present adjacently to each other in the benzene ring, may serve as chelating sites. On the other hand, the two azomethane groups may chelate with metal to form simple chelate. The Present study is undertaken to understand the preference of the metals between these two sites.

The complex of copper (II) prepared as given in the experimental section. For the preparation of complex metal salt and ligand are taken in mole ratio1:2

Characterization of Mononuclear Complex

Compound	(C-H)cm^{-1} aliphatic stretching	(C=N)cm^{-1} Stretching	(M-N)cm^{-1} Stretching	(N-H)cm^{-1} stretching	(O-H)cm^{-1} Stretching
O be ligand	2908	1614	-	3331	3726
Complex	2856	1587	589	33319	3451

In Copper complex a broad ppm IR band is observed at 3319 cm^{-1} corresponding to –OH stretching .The IR studies shows that >C=N stretching frequency of the complex occurs at1587 cm^{-1}group is involved in co-ordination with the metal center. The M-N stretching appears at 589 cm^{-1}.But in the ligand the stretching frequencies are absent.

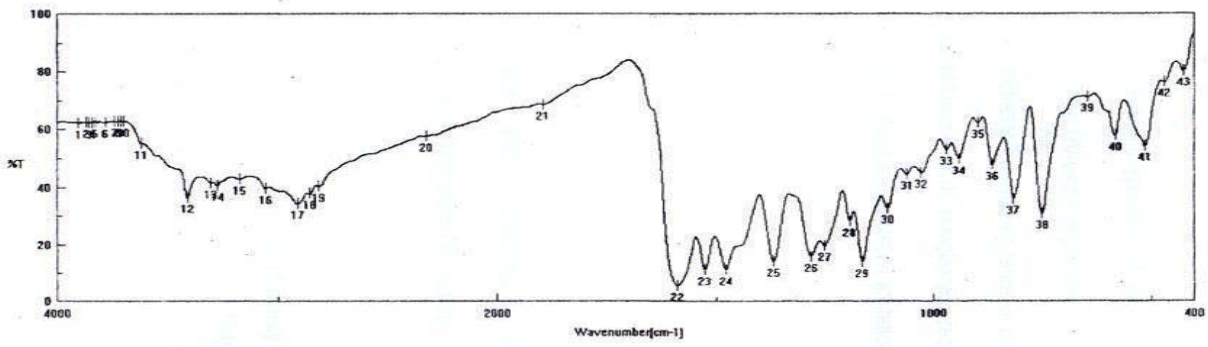
The electronic Spectrum of this complex a shoulder at ~425-450 nm. The molar conductance was found to be 1.74 mho cm^2 mho^{-1} thus revealing that the complex is non-electrolyte. This coupled with metal estimation that the complex may be formulated as$[CuL_2Cl_2]$.

In Copper complex the[1] H-NMR Spectrum indicates the presence of mainly three types of protons in the ligand.A Signal seen at δ 3.039-3.104ppm is due to the protons of –N-CH_3 group. The aromatic protons are seen to resonate at δ 6.695-7.803ppm.Then the Signal seen at δ 8.488ppm is due to the N=CH group. Then the another chemical shift observed at δ 82.54 to 83.431 ppm due to the >CH=N group and the chemical shift observed at δ 149.309 ppm due to the Ar-C-O group.

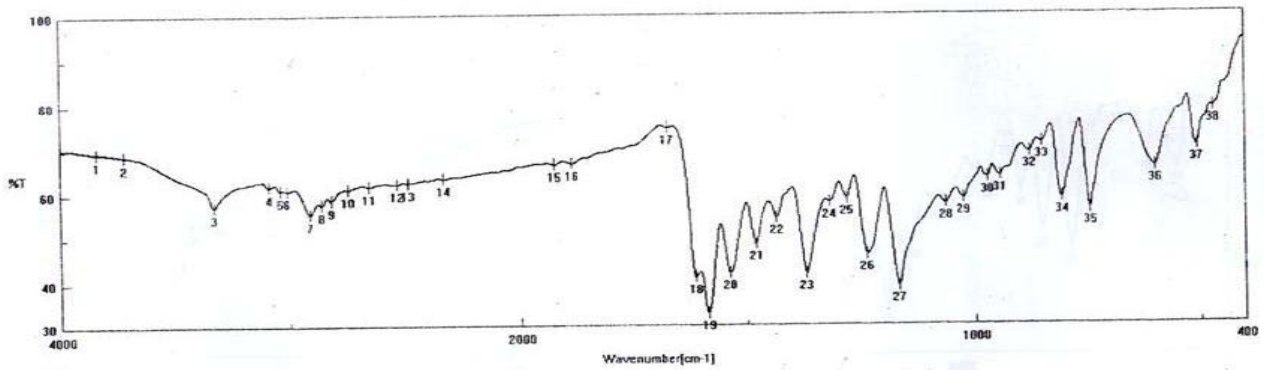
SUMMARY AND CONCLUSION

This dissertion embodies the result of investigation carried out on the synthesis and charecterization of a new schiff base derived from 2-aminophenol and p- dimethyl amino benzaldehyde and it co ordination with copper(II)chloride. Experimental techniques which were employed to charecterized the ligand and its co ordination complex are outlined in chapter II. The physical methods described in chapter II are electrical conductance, electronic and infrared spectral measurement determination. Chapter III describes the Schiff base condensation from 2-aminophenol and p-dimethyl benzaldehyde in 1:1 ratio to form Schiff base. The Elemental analysis were used to determine the empirical formula and the structural elucidation was made with the use of the Infrared data.

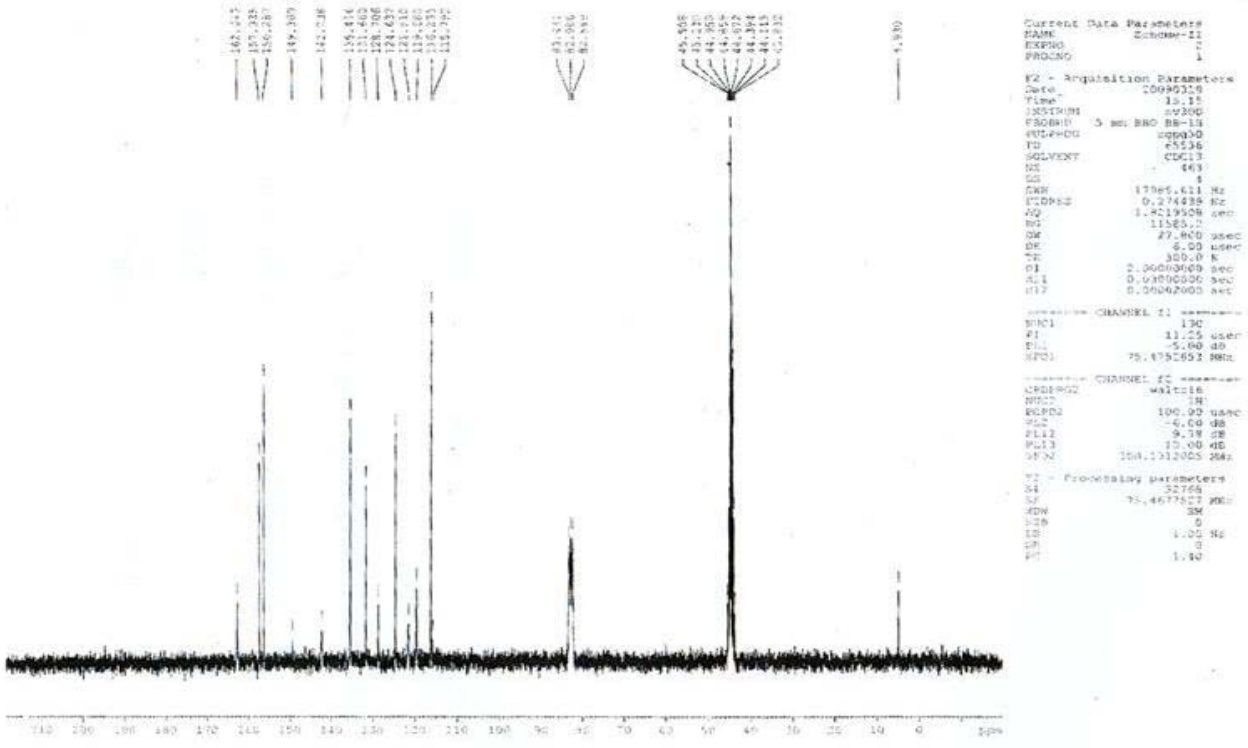
Preparation of the Schiff base complex with Copper (II) chloride and the charecterization of the complex are outlined in Chapter III. The Copper was estimated by gravimetrically. The results of the investigation are summarized in chapter IV. Electriconductance values indicate that the anions have co ordinate to the metal atoms. Further on the basis of elemental analysis, infrared spectral measurent and UV-Visible Spectra indicates copper(II) Schiff's base is tentatively proposed to have an octahedral stereochemistry.



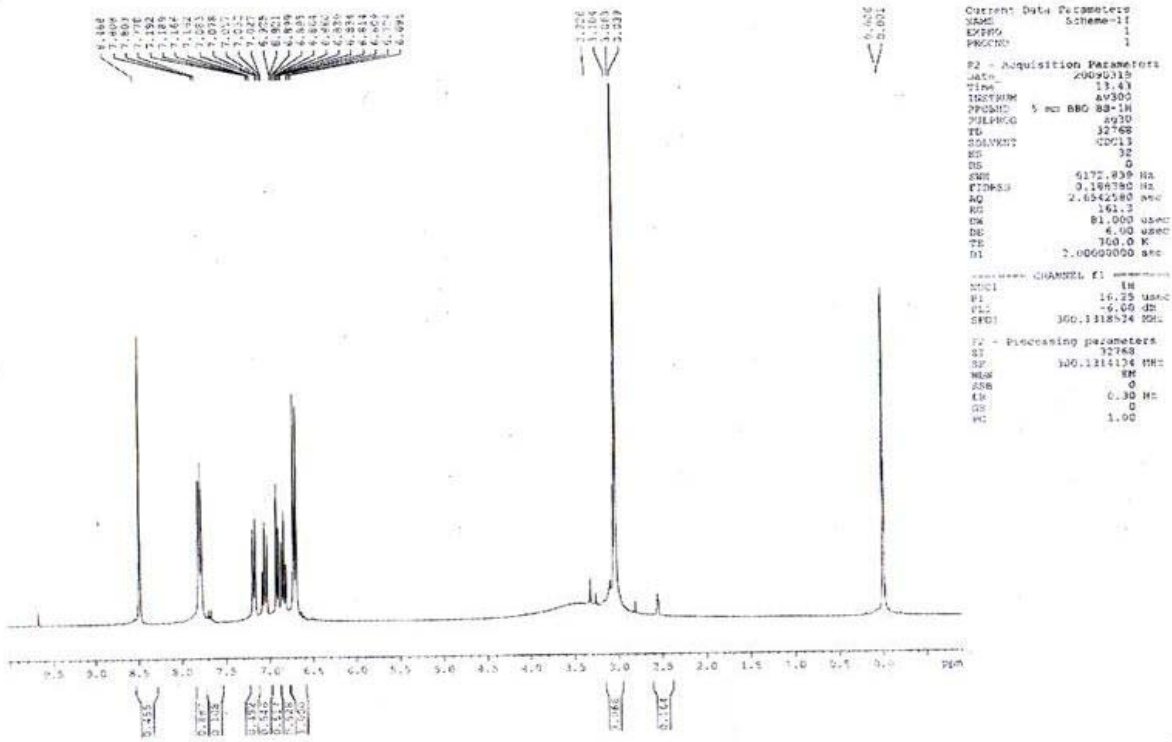
IR SPECTRUM OF COMPLEX



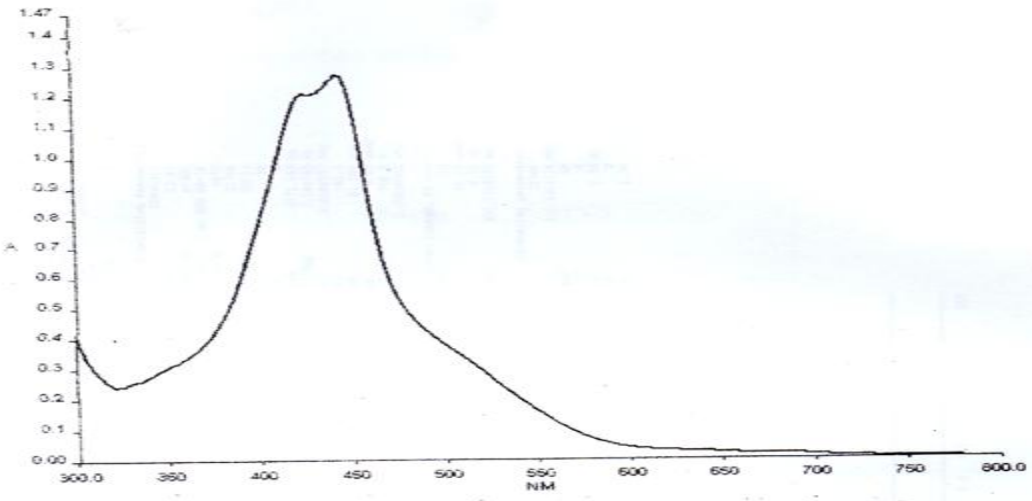
IR SPECTRUM OF LIGAND



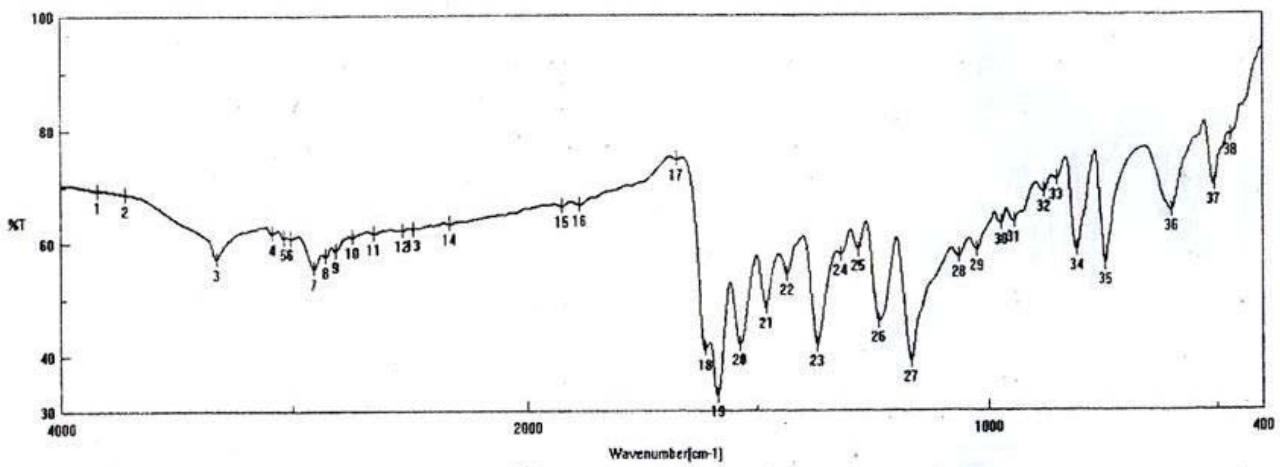
^{13}C-NMR of the schiff base ligand



Proton NMR of the schiff base ligand



UV Spectrum of copper complex



IR SPECTRUM OF LIGAND

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