

IR Spectral Studies of Indole-3-Carboxaldehyde with Nickel-11 Complex

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Abstract

The Schiff base was successfully co-ordinated to the metal ions to form the complex. The stability of the metal Schiff base complex has been found to be maximum for five or six membered rings. Structural features were obtained from IR spectral studies. The data shows that the complex has composition of ML type.

Keywords: Indole-3-Carboxaldehyde, IR Spectra, L-Glutamic Acid, ML Complex, Nickel (II) Nitrate

1. Introduction

Schiff base was named after Hugo Schiff (1834-1915), German chemist, is a functional group that contains a carbon – nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen¹. Schiff bases are of the general formula $R_1R_2C=N-R_3$, where R_3 is a aryl or alkyl group that makes the Schiff base stable imine. A Schiff base derived from an aniline, where R_3 is a phenyl or substituted phenyl, can be called as an anil.

Schiff base can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine.

The possibility of having a lone pair of electrons in an sp^2 hybridized orbital on the imino nitrogen renders the azomethine group significant bio-chemically².

1.1 Important of Schiff Base Complexes

- Schiff base intermediates are found to have extensive application in the field of analytical chemistry, agriculture, polymer industry and medicine³⁻⁹.
- The Schiff base complexes of tin, lead and mercury used as fungicides and herbicides against plant enemies.

- Schiff base are used as chelating agents in many reactions. A polymeric chelate chain prepared by condensing glyoxal with di and tri-aminophenol can isolate copper and uranium upto 10% from samples of water containing 0.5-5 of metal ion per liter.
- Almost all the Schiff base complexes of the transition metals are coloured and hence they have been successfully used in dye and pigment industries.
- The rod and cone structure of the retina derived from vitamin A aldehyde and protein contain azomethine linkage.
- Polycondensation of nickel, cobalt and copper complexes of resorcinolaldehyde-o-phenylenediamine with diphenyldichlorosilane produces highly useful polymers.
- The Schiff bases and their complexes are used as antitumour reagents against sarcoma and leukemia.

1.2 Synthesis of Schiff Base Complexes

The general methods of preparations of Schiff base complexes of metal ions are given below.

- Reaction of the primary amine with bis-or-tris (carbonyl) compound metal complexes in solvents like ethanol or chloroform.
- Reaction of the metal ion and the Schiff base, usually

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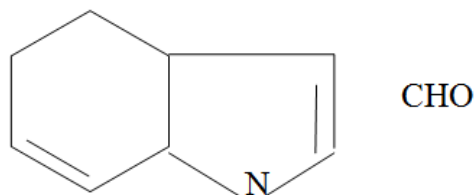
in alcoholic or aqueous alcoholic medium rendered basis by the addition of alkali acetate, alkali hydroxide or ammonia. This method is useful for the preparation of metal complexes of N-aryl-salicylaldiamines and β Ketoimines.

1.3 Role of Ligands and their Complexation with Metals

1.3.1 Importance of Ligands

- Ligands play a prominent role in the synthesis of complexes. The neutral molecule or ion which is attached with the central metal ion is called ligand. The central metal ion and the ligands act as Lewis acid and bases respectively. In most of the complexes, the ligand acts as donar.
- If the donar atoms belonging to the same type of ligand are bonded to the central metal ion, such compounds are known as 'Mixed donar complexes'. If the different groups belonging to different type of ligands are bonded to the central metal ion, such compounds are termed as 'Mixed Ligand Complexes'.
- The ligands are arranged around the metal ion inside the first sphere of attraction in preferred heometries. The common geometries are linear, equilateral triangular, tetrahedral, square planar, triangular bipyramidal, square pyramidal and octahedral.
- The Schiff base ligands usually contain both N and O donor atoms.

1.3.1.1 L-Glutamic Acid



Indole-3-carboxaldehyde (C_9H_7NO), is a yellow crystalline solid used as pharmaceutical intermediate. It is isolated from aqueous extracts of cotton plant parts by HPLC18. It is identified by its mass spectrum which is identical to that of an authentic sample of indole-3-carboxaldehyde.

1.3.2 Metal Complex Formation

The convenient method originally discovered by schiff19 and has been extensively used by Pfeiffer et al.20,21 for metal complex formation is the reaction of primary amine with bis or tris (salicylaldehyde) metal complexes in solvents like ethanol or chloroform.

The condensation of the metal ion and the preformed Schiff base usually in alcoholic or aqueous alcoholic medium rendered basis by the addition of alkali acetate or hydroxide for the metal complex formation of N-arylsalicylaldimines and β -Ketoimines.

Usually the divalent metal ion like cobalt (II) complexe of β -Ketoimines can be synthesized by the suspension of metal hydroxide in acetone solution with the Schiff base ligand. The stability of the metal Schiff base complexes has been found to be maximum for five or six membered rings. It is obvious that in metal complexes of the tridentate Schiff bases, the central metal ion increases its co-ordination number by forming solvated complexes.

1.4 Methods for Studying Schiff Base Complexes

The characterization of the Schiff base complex systems are usually carried out using different experimental techniques such as infrared, UV-Vis, EST, 1H -NMR, ^{13}C -NMR, TGA, DSC, SEM, ASS, elemental analysis, magnetic susceptibility, molar conductance, cyclic voltammetry. X-ray crystallography has played an important role in determining the molecular and crystal structure and certain other methods like ORD and CD spectra also been studied in specific cases.

2. Materials and Methods

Nitrates of Co(II), Ni(II) and Zn(II) used were AR grade from CDH. Indole-3-carboxaldehyde was purchased from Zigma Alrich and L-glutamic acid used in this work was AR grade from CDH.

2.1 Reagents

2.1.1 Ligands

Indole-3-carboxaldehyde and L-glutamic acid were used

in pure grade form as ligands. The solutions in the order of 0.05M were prepared and make up in 200ml SMF.

2.1.2 Metal Nitrates

Metal nitrates of Cu(II) of AR quality is weighed and prepared in the order of 0.05M and make up in 100ml SMF.

2.1.3 Solvent

The common solvents used in the study are water and ethanol in pure form.

2.1.4 Water

Distilled water was obtained by distilling ordinary tap water over alkaline permanganate. This distilled water was used in all the experiments.

2.2 Analytical Instruments

The infrared spectra of the solid samples were recorded using Perkin Elmer – 577 spectrophotometer in the range of $400\text{--}4000\text{cm}^{-1}$. For sample preparation potassium bromide disc method was used. Electronic absorption spectra were recorded using Double Beam Spectrophotometer using ethanol as solvent in the range of $200\text{--}600\text{nm}$. Conductance measurements were carried out in ethanol solvent using a ELICO conductivity meter.

2.3 Synthesis of Schiff Base Complexes Derived from Indole-3-Carboxaldehyde and L-Glutamic Acid

The synthesis of Schiff base complexes of divalent metal ion namely copper derived from the condensation of indole-3-carboxaldehyde.

2.3.1 Preparation of Schiff Base Complexes

2.3.1.1 Preparation of Indole-3-Carboxaldehydegutamate

The Schiff base is obtained by equimolar mixture of aqueous solution of 20ml of L-glutamic acid (0.05M) is added with the aqueous alcoholic solution of 20ml indole 3-carboxaldehyde (0.05M) and the mixture is heated to about 60°C on a water bath with constant stirring for about one hour. The solvent was evaporated and cooled

at room temperature, yellow crystals were separated out. It was washed with alcohol, ether and recrystallized from ethanol.

2.3.2 Preparation of Schiff Base Metal Complex

Washed the crystal with water followed by methanol and finally with ether. Then it is cooled in vacuum desiccators over fused anhydrous calcium chloride.

2.3.2.1 Preparation of Nickel (II) Complex

To about 20ml of the hot solution of Schiff base ligand (0.05M), 0.05M nickel nitrate is added drop wise and stirred. Temperature of the water bath is maintained at 60°C . The intensity of the colour of the solution increases after an hour and the solution becomes translucent. This confirmed the formation of complex. The solution is concentrated till the volume is one sixth of its initial volume without changing the temperature. The solution is allowed to crystallize for about 24 hours. Green crystals are formed and are separated by filtration using Buckner funnel.

Washed the crystal with water followed by methanol and finally with water. Then it is cooled in vacuum desiccators over fused anhydrous calcium chloride.

3. Characterization

The characterization of the Schiff base complex systems are usually carried out using different experimental techniques such as infrared, UV-Vis, ESR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, TGA, DSC, SEM, AAS, elemental analysis, magnetic susceptibility, molar conductance, cyclic voltammetry. X-ray crystallography has played an important role in determining the molecular and crystal structure and certain other methods like ORD and CD spectra also been studied in specific cases.

The stability constant measurements on Schiff base complex system was done using the batch wise p^{H} titration and the results are analysed using the computer program developed.

3.1 Infrared Spectra

The study of IR stretching frequencies of the ligand and metal complexes will give an idea about the mode of bonding in complexes and they also indicate the

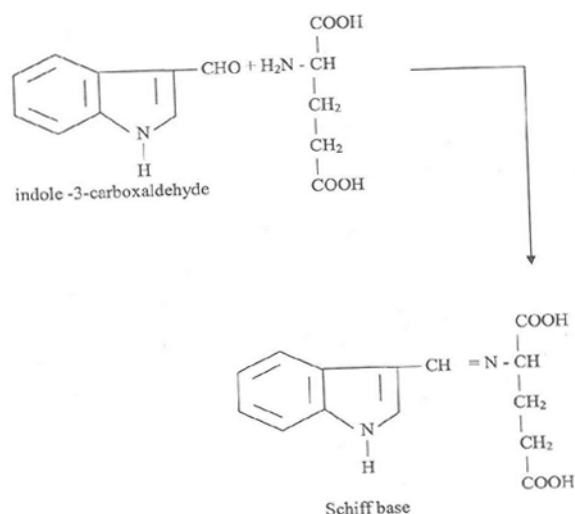
arrangement of atoms in space and the bond angles. Most of the assignments of IR absorptions frequencies have been based on the concept of group frequency. The approximate vibrational frequency of a like A-B is determined primarily by the elasticity of the bond and measured by the force constant, and by the masses of A and B. In large molecule, factors, both external as well as internal, influence the force constant and determine the precise position of the infrared absorption bands.

On complexation with metal ions, the characteristic IR frequencies of the coordinating groups are influenced by the force constant of the metal ligand bond resulting in shifting of the group frequencies. These shifts are useful in identifying the coordination sites. The important vibrating group in a free Schiff base is naturally the imino group. The strong absorption band due to this found to lie in the region $1600\text{--}1640\text{cm}^{-1}$. However, on complexation the group frequency of the free azomethine group is altered.

In external environment, some factors are influenced such as solvent effects, changes in phases or crystalline form and presence of hydrogen bonding. Changes in molecular geometry, masses of substituent groups, electrical and steric influences of the substituent groups, coupling one vibration with another are some of the internal factor influencing the position of the absorption bands.

4. Results and Discussion

4.1 Schiff Base Derived from Indole-3-Carboxaldehyde and L-Glutamic Acid



The pale yellow indole-3-carboxaldehydegutamate is obtained by the action of indole-3-carboxaldehyde and L-glutamic acid. Indole-3-carboxaldehyde is insoluble in both cold and hot water but soluble in alcohol. L-glutamic acid is soluble in cold water.

In the present study, the Schiff base derived from the condensation of indole-3-carboxaldehyde and L-glutamic acid function as tridentate ligand with their ONO donor set.

4.2 Infrared Spectra

The infra-red frequencies of the Schiff base ligand and its complexes are reported in Table 1.

4.2.1 Ni (II) Complex

Green indole-3-carboxaldehydegutamate to nickel (II) complex is obtained from Ni (II) nitrate and Schiff base. The complex is soluble in alcohol.

The infrared spectra of this complex show a broad band centered around 3165.13cm^{-1} , which is assigned to the co-ordinated water molecule. The infrared spectrum of the Schiff base ligand shows a strong band at 1630.48cm^{-1} , which is assigned to the C=N stretching vibration. On complexation this band is shifted to 1628.07cm^{-1} (Figure 1). This indicates that the azomethine nitrogen is co-ordinated to the metal ion.

The asymmetric carboxyl stretching is shifted to lower frequency in the 1519.40cm^{-1} range and the symmetric carboxyl stretching is shifted to lower frequency in the 1333.53cm^{-1} range, indicating the formation of a linkage between the metal ion and carboxyl to oxygen. The characteristic absorption frequencies of the individual complexes and their assignments are given in Table 1.



Figure 1. IR spectra of indole-3-carboxaldehydegutamatecopper (II) complex.

Table 1. Infrared absorption frequencies indole-3-carboxaldehyde glutamine to nickel (II) complex

Name of the Complex	Functional Group	Frequencies in cm^{-1}
indole-3-carboxal-	O-H	3165.13cm^{-1}
dehyde glutamine to	C=N	1628.07cm^{-1}
nickel	sym COO-	1333.53cm^{-1}
(II) complex	asym COO-	1519.40cm^{-1}

5. Summary and Conclusion

Importance of Schiff base and its metal complexes have been well documented. Schiff base of indole-3-carboxaldehyde and L-gutamic acid has been isolated in the solid state. It is a tridentate ligand. It form complex with Nickel (II) and metal ions. The present work was undertaken with a view on studying the synthesis and spectral data of Schiff base and its metal complexes.

The Schiff base complex of Nickel (II) metal is green coloured and Copper (II) metal is dark blue coloured. The IR spectra of all these complexes clearly indicate the co-ordination site.

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