

Synthesis and Characterization of Cu(II), Ni(II) and Co(II) Based Schiff Base Complexes

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ABSTRACT

N-(3-Bromo-4-hydroxy-5-methoxybenzylidene)-4-Bromobenzenamine was synthesized. This was further used to synthesize Co(II), Ni(II) and Cu(II) based metal complexes and characterized by FT-IR, Elemental analysis, ESI Mass and UV spectroscopy.

Keywords: Schiff Base; Metal Complexes

1. INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of an amino group [3], photochromic properties [4], and complexing ability towards some toxic metals [5]. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. The condensation of $>C=O$ group compound with varied primary amine or amino compound on elimination of water molecule forms a weakly basic compound known as an imine or an anil or an azomethine which is commonly known as Schiff base, named honor Schiff [6] who synthesized such compound. Extensive investigation in the field of Schiff bases, have been reported by Bayer [7].

Their preparation, chemical and physical properties have been described by Layer [8]. Many Schiff bases [9-11] were prepared by the condensation of salisaldehyde with aromatic amine. Several workers have reported that the Schiff bases formed from aromatic aldehyde or ketones and their derivatives are quite stable [12-14]. The new series of Thorium(IV) complexes with a Schiff bases derived from fluoroaniline and p-(N,N'-dicyanoethyl) amino benzaldehyde have been reported by Goyal et al. [15]. Schiff bases and their first row transition metal complexes such as Co(II), Ni(II), Cu(II), etc., were reported to exhibit fungicidal, bactericidal, antiviral and antitubercular activity [16-22].

In specially, Cu(II) complexes with diverse drugs have been the subject of a large number of research studies [23,24], presumably due to the biological role of Cu(II) and its synergetic activity with the drug [25]. The antifungal and antibacterial properties of a range of Cu(II) complexes have been evaluated against several pathogenic fungi and bacteria [26-28]. For many years it has been believed a trace of Cu(II) destroys the microbe, however,

recent mechanisms becomes activated oxygen in the surface of metal Cu kills the microbe because Cu(II) activity is weak.

2. EXPERIMENTAL

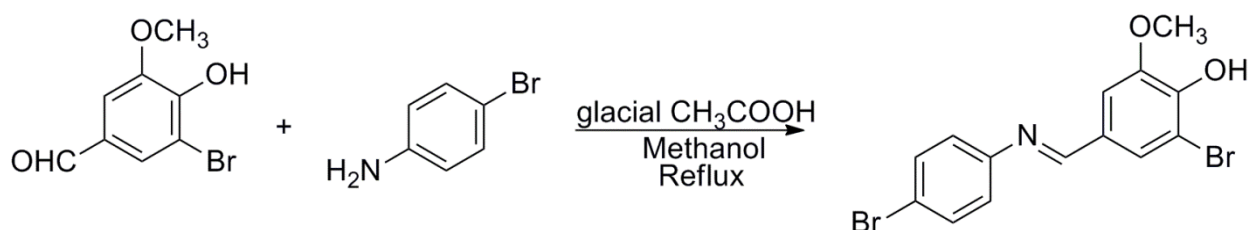
2. 1. Materials

All the chemicals were purchased from Loba chemical Pvt. Ltd. and used without purification.

2. 2. Method

Synthesis of N-(3-Bromo-4 hydroxy-5-methoxybenzylidene)-4-Bromobenzenamine: In R.B.F. 0.01 M of 3-bromo-4-hydroxy-5-methoxybenzaldehyde was dissolved in 10 ml methanol and then 0.01 M 4-bromo aniline was added with stirring and 4-5 drops of glacial acetic acid was added. Then reaction mixture was refluxed in water bath for 12 hours. Pour this reaction mixture in the crushed ice, Product is precipitated out. It was filtered and crystallized from methanol (Scheme 1).

Reaction Scheme 1



2. 3. Synthesis of metal complexes

Mixture of metal chloride solution (0.01 mole) and Schiff base (0.02 mole) was dissolved in methanol and stirred at 350 °C for about 48 hours. After completion of the reaction mixture was allowed to stand at room temperature for one hour. Then the product was filtered and washed with little quantity of methanol (Scheme 2).

¹H NMR spectra were recorded on BRUCKER Av spectrophotometer (300MHz) using TMS as an internal reference. FT-IR spectra were recorded on SHIMADZU FT – IR 8400 spectrophotometer on KBr pellets. Mass spectra were recorded on GCMS QP-2010 gas Chromatograph SHIMADZU. UV -Visible spectra were recorded in DMSO Solution on a SHIMADZU UV mini - 1240 Spectrophotometer. TLC was performed on silica gel-G using ethyl acetate: hexane solvent system.

Reaction Scheme 2

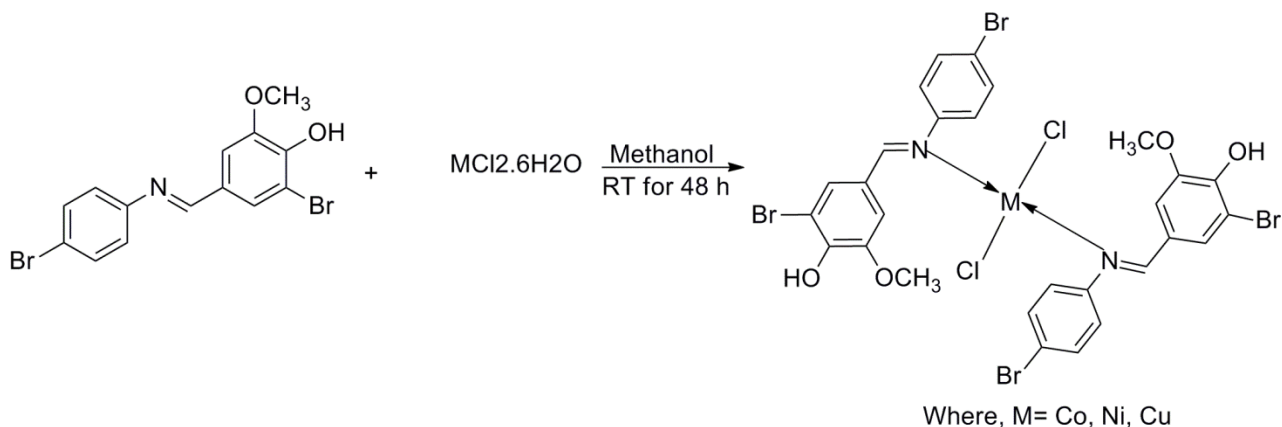


Table 1. Physical Data of Synthesized Compound.

Compound Code	Metal	Reaction time in hour	Yield (%)	M.P. °C
AB-1	Co	62	77	310
AB-2	Ni	65	81	350
AB-3	Cu	55	67	288

3. RESULTS AND DISCUSSION

The ligands have reacting system containing N and O situated as to form heterocyclic ring with metal ion.

The absorption spectra of ligand in UV visible region show three bands at 215-235, 264-280 nm and 340-368 nm. These are attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition. Cu complex is insoluble in water and difficultly soluble in alcohol, chloroform and carbon tetrachloride. Cu complex show all the three characteristics of the ligand system and two bands due to d-d transition of the metal ion. The position of the ligand bands are shifted which may be due to their interaction of the ligand with metal ion. Thus three spin allowed transition are expected. All are d-d transitions and hence would be Laporteforbidden. The band corresponding to ${}^2E_g \leftarrow {}^2B_{1g}$ transition would have overlapped with the strong charge transfer band of the spectra. Thus it indicates D_{4h} .

The magnetic moment of the Cu complex is 2.05 B.M. This value is greater than spin only value for unpaired electron (1.73 B.M.) The excess value is considered to be due to spin orbital coupling.

Ni complex is insoluble in water and difficultly soluble in alcohol. The absorption band at 540-580. It is fully filled up to a_{1g} orbital. The excitation of one of the a_{1g} electron to

b_{1g} orbital leads to ${}^3B_{1g}$ and ${}^1B_{1g}$ terms but the transition from to is spin forbidden and hence band at 640-685 nm is attributed to the transition. The other band at 540-580 nm is attributed to the extinction coefficient of these two bands are large in spite of the Laporte –forbidden. It is the because of the extensive mixing of the metal ‘d’ orbitals and the ligand orbitals.

4. CONCLUSION

In the present work, coordination chemistry of a Schiff base ligand obtained from the reaction of 3-bromo-4-hydroxy-5-methoxybenzaldehyde and 4-bromoaniline is described. The metal complexes of Cu, Co and Ni have been synthesized using the Schiff base ligand in good to moderate yield. The synthesized metal complex are characterized by spectral and analytical data.

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