

International Journal of Scientific Research and Reviews

Synthesis and Characterization of Co(II), Ni(II) and Cu(II) Complexes with bidentate Schiff base ligand

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ABSTRACT

A Series of transition metal complexes of Co (II), Ni (II) and Cu(II) were prepared from bidentate schiff base. The Schiff base ligand synthesized from the condensation of 5- bromo-2-hydroxy benzaldehyde and 3,4- dimethylaniline in an alcoholic medium. These metal complexes were characterized on the basis of their elemental analysis, molar conductance, electronic spectra, IR spectra, NMR spectra, electrical conductivity and magnetic susceptibility. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 2:1 (ligand : metal) ratio with coordination number 4 or 6. The IR spectra of the free ligand showed bands at 3314-3305 cm⁻¹. These are absent in the spectra of the metal complexes indicates the deprotonation of the hydroxyl group and coordinated through oxygen atom. The band 1615 cm⁻¹ due to the azomethine group of the Schiff base have shifted to lower frequency indicating the bonding of nitrogen of the azomethine group to the metal ion. The electronic spectra and magnetic moment data suggest the geometry for Co(II) complex is octahedral while complexes of Ni(II) and Cu(II) are square planar.

KEYWORDS :- Schiff base, 3,4-dimethylaniline, metal salt, 5-bromosalicylaldehyde.

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1. INTRODUCTION

Metal complexes have been receiving considerable attention for many years, due to their interesting characteristics in the field of material science and biological systems. Metal chelation is involved in many important biological processes where the coordination can occur between a variety of the metal ions and a wide range of ligands. Schiff base metal complexes have been widely studied because they have industrial, antifungal and biological applications. They serve as models for biological catalytic reactions. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. The synthesis of Schiff base ligands and their metal complexes have been extensively studied because of their interesting biological activities. Schiff bases have been reported to possess antimicrobial, antiviral, anticancer and anti-inflammatory activity. The imine functional group (HC=N) is believed to be responsible for the biological activity of Schiff base compounds. Schiff bases are one of the most prevalent and important of the mixed donor system in the field of coordination chemistry. Schiff bases are condensation products of primary amines with carbonyl compounds and they were first synthesized by Hugo Schiff in 1864. These compounds containing a general formula $RCH=N-R^1$ where R and R^1 are alkyl, aryl, cycloalkyl or heterocyclic groups are also known as anils, imines or azomethines. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerisable, while those of aromatic aldehydes having effective conjugation are more stable in general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are less sterically hindered than ketones. The extra carbon of ketones donate electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes. Schiff bases are generally bidentate, tridentate, tetradentate and polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordination ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reaction with a metal ion. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields like biological, inorganic and analytical chemistry. Schiff bases are used in optical and electrochemical sensors, as well as in various chromatographic methods to enable detection of enhanced selectivity and sensitivity. Schiff bases are widely applicable in analytical determination using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial and anticancer applications. Salicylaldehyde is a major precursor to aspirin, used in the synthesis and

technology of drug manufacturing and as an important intermediate in the manufacture of herbicides and pesticides. In this study, we report here the synthesis and characterization of metal (II) complexes with bidentate Schiff base ligand derived from 5-bromo-2-hydroxy benzaldehyde and 3,4-dimethyl aniline.

2. EXPERIMENTAL

2.1 Chemicals and Reagents :-

All the chemicals and reagents used were of analytical grade and were used without purification. They are benzaldehyde, Br₂, acetic acid, 5-bromo salicylaldehyde, CoCl₂ · 6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and solvents (methanol, ethanol, petroleum ether, benzene and acetone)

2.2 Physical Measurements :-

The percentage (%) of Co, Ni and Cu were determined by EDTA complexometric titration. The elemental analysis of C, H, and N was performed by using a perkin-Elmer elemental analyzer. The m.p of all compounds were determined using Griffin melting point apparatus. The solubility of the complexes was determined in some polar and non polar solvents like water, methanol, ethanol petroleum ether, benzene and acetone, Molar Conductivity were determined by using DMF as a solvent in digital conductivity meter at 25^oc. The IR. spectra of ligand and metal complexes were taken on perkin-Elmer model 577 spectrophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using Hg [Co(NCS)₄] as a calibrant, Electronic spectra of the complexes were recorded in DMF on Cary 2390 spectrophotometer.

2.3 Synthesis of 5-bromo-2-hydroxy benzaldehyde-

Salicylaldehyde (1.22g, 0.01 mol) was suspended in acetic acid (15 ml) in a flask and was cooled in an ice bath. To this solution bromine in acetic acid (25%v, 6.4 ml) was added slowly drop by drop with constant stirring. The mixture was stirred to get a clear solution. After complete addition of bromine the stirring was stopped, solution was allowed to solidify. The solid mass was filtered washed repeatedly with water to remove excess of bromine and recrystallized from alcohol to get white crystalline solid

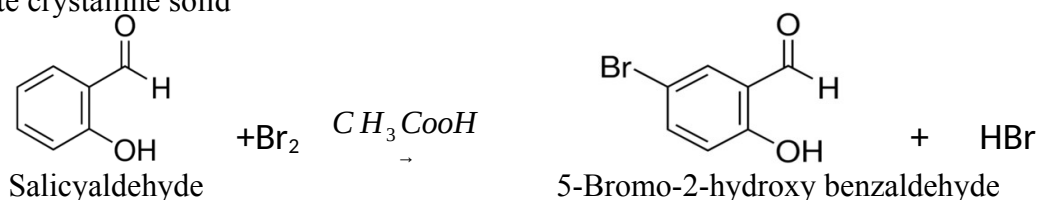


Fig 1 : Synthesis of 5-bromo-2-hydroxy benzaldehyde

2.4 Synthesis of schiff base ligand (HL) :-

The ligand 5-bromosalicylidene-3,4-dimethylaniline (HL) was prepared by condensation of equimolar ratio of 5-bromo-2-hydroxy benzaldehyde (4g, 0.021mol) with 3,4-dimethyl aniline

(2.541g, 0.021mol) in 50 ml ethanol (1:1 molar ratio). The reaction mixture was refluxed for 4h. A brown precipitate was obtained. This precipitate was filtered, washed with cold ethanol and finally recrystallized from ethanol and ether and dried in air at room temperature and preserved in desiccator containing CaCl_2 .

2.5 Synthesis of the metal (II) complexes :-

The complexes of metal (II) were synthesized by mixing 25 ml of ethanolic solution of Schiff base (1.824 g, 6mmol) with 25ml of ethanolic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.714g, 3mmol) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.512g, 3mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.713g, 3mmol). Keeping ligand-metal (II) ratio (2:1). The reaction mixture was refluxed for 4 h on water bath. The precipitate formed was filtered and washed with distilled water and ether. Finally, the precipitate was dried in a vacuum over CaCl_2 .

3. RESULTS AND DISCUSSION

The Co(II), Ni(II) and Cu(II) complexes were obtained with moderate yields (64-69%, table-1). The complexes vary in colour depending on metal (II) ions and are soluble in most organic solvents. The observed value of molar conductivity of the complexes in DMSO, which indicates non electrolytic nature of metal (II) complexes, the analytical data of the ligands and their metal (II) complexes are presented in table-2. Elemental analysis revealed the observed and calculated values for H, C and N compositions of the Schiff base and its metal complexes are in good agreement with the proposed structure.

IR Spectra of Schiff base ligand :-

The IR spectrum of free ligand was compared with that of complexes in order to determine the coordination sites in chelation. (table-3). A very strong band at 1615cm^{-1} is characteristics of the azomethine nitrogen ($>\text{C}=\text{N}$) present in the schiff base ligand. This was shifted to $1592\text{-}1602\text{cm}^{-1}$ in the complexes, which indicates the bonding of the metal to the azomethine nitrogen. The ligand spectra showed bands at $3314\text{-}3305\text{ cm}^{-1}$ due to the stretching and deformation of the phenolic -OH. These are absent in the spectra of complexes indicates the deprotonation of the hydroxyl group and coordinated through oxygen. The phenolic $\nu(\text{C-O})$ stretching vibration that appeared at 1250 cm^{-1} in schiff base ligand shift towards higher frequencies ($25\text{-}30\text{ cm}^{-1}$) in the complexes which indicates the participation of oxygen in The C-O-M bond. The appearance of broad bands around at ($3386\text{-}3422\text{ cm}^{-1}$) in the spectra of complexes may be due to water molecules. Two new bands appearing in the low frequency range $535\text{-}547\text{ cm}^{-1}$ and $486\text{-}496\text{ cm}^{-1}$ are indicate the formation of M-O and M-N bond in the complexes.

Electronic Spectra of Metal Complexes :-

The electronic spectral data of the metal complexes in DMSO solution are given in Table-4. The nature of the ligand field around the metal ion has been deduced from the electronic spectra. The electronic spectra of $[Co(L)_2(H_2O)_2]$ exhibited three bands in the region of 9426, 15258 and 19610 cm^{-1} which have tentatively been assigned to $4T_{1g} \rightarrow 4T_{2g}$, $4T_{1g} \rightarrow 4A_{2g}$ and $4T_{1g} \rightarrow 4T_{1g}(P)$ transitions, respectively. The values of magnetic moment for these complexes are 5.07 and 5.12 B.M. respectively which suggested octahedral geometry of the complexes.

The absorption spectra of the $[Ni(L)_2]2H_2O$ exhibited bands 12110 and 21645 cm^{-1} which have tentatively been assigned to the transitions $1A_{1g} \rightarrow 1E_g$ and $1A_{1g} \rightarrow 1B_{2g}$ respectively, these are diamagnetic complex, therefore square planar geometry has been suggested.

The electronic spectra of the $[Cu(L)_2]2H_2O$ showed bands at 12876 and 18540 cm^{-1} which showed transitions $2B_{1g} \rightarrow 2B_{2g}$ and $2B_{1g} \rightarrow 2E_g$ respectively. The magnetic moment for these complexes found 1.93 and 1.98 B.M. which suggested square planar geometry for Cu(II) complex.

¹H-NMR Spectra :-

The proton NMR spectra of the Schiff base ligand were recorded in DMSO-d₆ solution using TMS as internal standard. The ¹H-NMR Spectra of the ligand showed multiplet at δ 7.126-7.654 ppm due to aromatic protons while the azomethine proton resonates as singlet at δ 8.462 ppm. The phenolic -OH group have signal at δ 12.241 ppm, which is disappeared on deuteration.

Table No.1 : Physical properties of Schiff base and metal (II) complexes

Compounds	Colour	Yield(%)	Molar conductivity ($\Omega^{-1} cm^2 mol^{-1}$)
L=C ₁₅ H ₁₄ NOBr	Brown	74	0
[Co(L) ₂ (H ₂ O) ₂]	Yellowish Brown	69	15.1
[Ni(L) ₂]2H ₂ O	Dark Brown	64	12.4
[Cu(L) ₂] 2H ₂ O	Yellowish Green	68	9.5

Table No. 2 : Analytical data of Synthesized ligands and their metal complexes

Compounds	% Analysis Found (cal)			
	C	H	N	M
L=C ₁₅ H ₁₄ NOBr	59.15 (59.21)	4.58(4.65)	4.51(4.61)	-
[Co(L) ₂ (H ₂ O) ₂]	51.25 (51.39)	4.24 (4.32)	3.81 (3.98)	8.34 (8.42)
[Ni(L) ₂]2H ₂ O	51.4 (51.5)	4.26(4.33)	3.97 (4.01)	8.36 (8.39)
[Cu(L) ₂] 2H ₂ O	51.1 (51.08)	4.22 (4.29)	3.91 (3.96)	8.91 (9.02)

Table No. 3 : IR Spectra data of Schiff base and their metal complexes.

Compounds	ν (O-H) cm^{-1}	ν (C-O) cm^{-1}	ν (C=N) cm^{-1}	ν (H ₂ O) cm^{-1}	ν (M-N) cm^{-1}	ν (M-O) cm^{-1}
L=C ₁₅ H ₁₄ NOBr	3310	1250	1615	-	-	-
[Co(L) ₂ (H ₂ O) ₂]	-	1276	1602	3386, 810	486	535
[Ni(L) ₂]2H ₂ O	-	1280	1596	3422	490	541
[Cu(L) ₂] 2H ₂ O	-	1279	1592	3392	496	447

Table No. 4 : Electronic absorption spectral data of metal complexes

Compounds	Absorption (cm ⁻¹)	Assignments	Geometry
[Co(L) ₂ (H ₂ O) ₂]	9426 15258 19610	4 T _{1g} → 4 T _{2g} 4 T _{1g} → 4 A _{2g} 4 T _{1g} → 4 T _{1g} (P)	Octahedral
[Ni(L) ₂]2H ₂ O	12110 21645 -	1 A _{1g} → 1 E _g 1 A _{1g} → 1 B _{2g}	Square Planar
[Cu(L) ₂] 2H ₂ O	12876 18540	2 B _{1g} → 2 B _{2g} 2 B _{1g} → 2 E _g	Square Planar

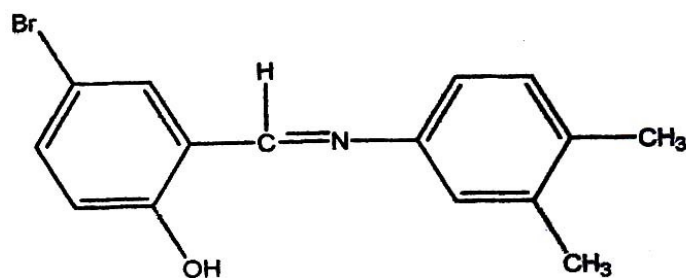


Fig 2 : Structure of Schiff base ligand (5-bromosalicylidene-3, 4-dimethylaniline)

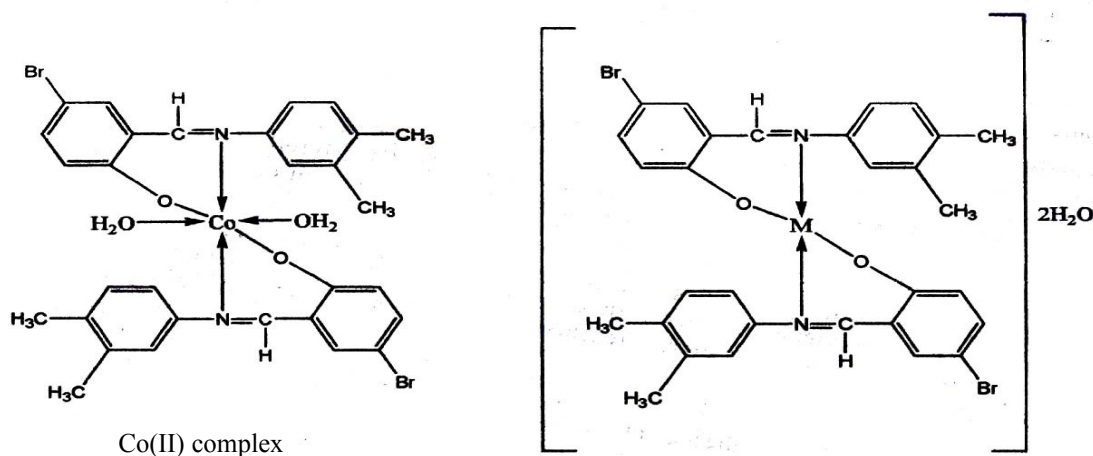


Fig 3 : Proposed structure of M(II) complexes M= Ni & Cu

4. CONCLUSION

A novel Schiff base ligand was synthesized by the reaction of 5-bromo salicylaldehyde and 3,4-dimethylaniline in equimolar ratio with a molecular formula of C₁₅H₁₄NOBr. The complexes of Co(II), Ni(II) and Cu(II) were synthesized by direct reaction of the synthesized ligand with metal salt both in 2:1 ratio. In the present work Co(II), Ni(II) and Cu(II) complexes were synthesized and characterized by analytical and spectroscopic techniques. The Schiff base acts as bidentate ligand. The Metal(II) ion Coordinated through the phenolic oxygen and nitrogen atom of azomethine group. This is supported by infrared spectral data. The electronic spectral band observed are consistent with an octahedral geometry for Co(II) complex. On the basis of absorption spectral data of Ni(II) and Cu(II) complexes therefore square planar geometry has been suggested. The molar conductivity data of the complexes in methanol indicated that they are non electrolytes. All the complexes are air

stable and soluble in protic solvents like methanol and ethanol. They in vitro antimicrobial study shows that the metal complexes have higher biological activities compared to the free ligand.

ACKNOWLEDGEMENTS :-

The authors are grateful thank to Department of Chemistry R.C Chapra for providing laboratory facilities.

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