

Synthesis, Spectral, Thermal and Antimicrobial Investigation of Some New Co(II), Ni(II) and Cu(II) Schiff Base Complexes

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Abstract— Schiff base has been prepared by the condensation of 2-naphthylamine (NA) with 5-bromosalicylaldehyde (BSA). The ligand (NABSA) was isolated and characterized. Metal complexes have been synthesized by the interaction of NABSA with metal ions viz. Co(II), Ni (II), and Cu(II) in 1:2 molar ratio respectively. These complexes have been characterized by FT-IR, electronic spectroscopy, conductance measurements, magnetic moment, EPR, thermal analysis (TGA/DTA) and antimicrobial studies. IR spectra show that NABSA is coordinated to the metal ions in a bidentate manner through azomethine-N and phenolic-O-atom. The measured molar conductance values indicate that the complexes are nonelectrolytes. The thermal behavior of metal complexes reveals that the hydrated complexes lose water molecules of hydration in the first step, followed by decomposition of ligand molecule in the subsequent steps. The antimicrobial results indicate that the metal complexes have better activity compared to Schiff base ligand.

Keywords—Bidentate Schiff base ligand, Cobalt(II), Nickel(II), Copper(II), Biological activity.

I. INTRODUCTION

Schiff base compounds with the azomethine group ($-RC=N-$) are usually formed by the condensation of amine $-NH_2$ group with active $-C=O$ carbonyl group [1]. The field of Schiff base is fast evolving because of the wide variety and potential applications of their industrial, biological, analytical, medicinal, pharmaceutical and catalytical applications [2-5]. In particular, cobalt, nickel and copper complexes with Schiff base ligands have received considerable interest in the fields of medicinal chemistry for their antibacterial, antitumor, antifungal and herbicidal activities [4-7]. It has been suggested that azomethine linkage is responsible for biological activities of Schiff bases. Important results of studies concerning syntheses, spectral, magnetic and structural characteristics of complexes with Schiff bases derived from bromosalicylaldehyde and several amines were also reported [7,8]. Salen complexes have been used as catalytically active materials to develop surface modified electrodes for sensor applications [9]. Although during the recent years, considerable attention has been paid to the thermal behavior of transition metal Schiff base complexes containing substituted salicylaldehyde derivatives, which is one of the important properties of complexes indicating thermal stability and decomposition process under various conditions [10]. In this work, we synthesized a bidentate Schiff base bearing bromosalicyl and naphthyl groups. In order to investigate the coordination mode of this ligand, a new Cobalt(II), Nickel(II) and Copper(II) complexes were synthesized and characterized by using IR, UV, conductance measurements, magnetic moment, EPR, thermal analysis (TGA/DTA) and antimicrobial studies.

II. EXPERIMENTAL

A. Materials

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, 2-naphthylamine, 5-bromo-2-hydroxy benzaldehyde, Ethanol, Dimethyl formamide (DMF) have been purchased from Merck and used as such.

1) Physical measurements

Infrared spectra were recorded using KBr disks on a FT-IR Perkin-Elmer spectrophotometer in the range $4000-400\text{cm}^{-1}$. Molar conductances were measured in DMF (1×10^{-3} M) using Elico conductivity bridge and dip type conductivity cell. Electronic spectra of the complexes were recorded in DMF on a perkin-Elmer spectrophotometer. 1H and ^{13}C -NMR spectra of the ligand were recorded in $CDCl_3$ with a Bruker 400MHz using TMS as internal standard. Magnetic susceptibility measurements were carried out on solid compounds using Gouy balance at room temperature. Melting points of the ligand and their metal complexes were determined by open capillary method using vanaspathi bath and are uncorrected. Thermo gravimetric curves of the complexes were recorded on a Perkin Elmer analyser, (Diamond TGA/DTA) under nitrogen atmosphere (heating rate of $10^\circ\text{C}/\text{min}$) from $40-740^\circ\text{C}$. The EPR study was carried out in Bruker EMX Plus model at Liquid Nitrogen

Temperature (LNT). In vitro antibacterial and antifungal activities were studied at Kovai Medical College of Pharmaceutical sciences, Coimbatore.

2) *Preparation of 4-bromo[2-naphthalen-2yliminomethyl] phenol [NABSA]*

The Schiff base (NABSA) was prepared by a stirred solution of 2-naphthylamine [1.43g, (0.01mol)] in 20ml ethanol was added drop wise a solution of 5-bromo-2-hydroxybenzaldehyde [2.01g, (0.01mol)] in 20ml ethanol. After the addition was complete, the mixture then refluxed with stirring for 1 hour. A pale yellow coloured solid was separated out, washed and dried over anhydrous CaCl_2 in a desiccator. The purity of the ligand was checked by melting point, TLC and spectral data. The ligand is partially soluble in Ethanol, acetonitrile, benzene and completely soluble in polar solvents viz. DMF, DMSO.

3) *Preparation of Schiff base complexes*

The schematic representation of synthesis of Schiff base is shown in Figure 1. The Schiff base complexes were synthesized by mixing 3 ml DMF with 10 ml ethanolic solution of the NABSA (1mmol, 0.326g), with 10 ml of the ethanolic solution of the metal salts (0.5mmol) in molar ratio [M:L=1:2], $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0119g)/ $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0118g)/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0852g) in the presence of few drops of triethylamine. The obtained mixtures were refluxed with stirring for 4-5 hours. The separated complexes were filtered off, washed several times with ethanol-pet ether mixture to remove any traces of unreacted starting materials, and then dried in a desiccator over anhydrous calcium chloride under vacuum. The yield ranged from 58% to 69%. The dried complexes were subjected to spectroscopic analysis.

III . RESULT AND DISCUSSION

Condensation of 2-naphthylamine with 5-bromosalicylaldehyde in ethanol under reflux afforded 4-bromo[2-naphthalen-2yliminomethyl]-phenol(NABSA). The complexes with formula $[\text{M}(\text{NABSA})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{NABSA})_2]$ where M=Co & Ni. The complexes were synthesized by reaction of Schiff base with metal(II) chlorides in 2:1 molar ratio in triethylamine presence. The complexes were characterized by thermal analyses, IR and UV-Vis spectral data as well as magnetic moment and EPR at LNT.

B. *^1H NMR and ^{13}C NMR spectra of 4-bromo[2-naphthalen-2yliminomethyl]-phenol*

The structure of the 4-bromo[2-naphthalen-2yliminomethyl] phenol was unequivocally supported by their ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of the ligand displayed one-proton singlet at δ 8.69 confirmed the azomethine (-CH=N) proton. The one phenolic -OH proton was observed in the offset region at 13.37 ppm as a broad singlet. The multiplets in the range of 7.53 - 7.91 ppm are assigned to the aromatic protons of both rings. The ^{13}C NMR spectrum of ligand showed the azomethine (-CH=N) carbon at δ 161.1 ppm, the hydroxyl group attached carbon at δ 160.2 ppm, the bromide group attached carbon at δ 110.6 ppm and all the aromatic carbons were observed at 119.4, 120.7,126.9, 128.1, 132.6, 134.3,135.8 & 145.3 ppm.

C. *Conductance and magnetic susceptibility measurements*

The molar conductance values of the prepared complexes with the mentioned metal ions under investigation were determined using 1×10^{-3} M DMF solution, are in the range of 10.3– 15.9 $\text{cm}^2 \text{mol}^{-1}$. These values indicated that, all synthesized complexes are nonelectrolyte [11]. The melting points of the complexes are higher than that of the ligand also confirms the complex formation. The room temperature magnetic moment values of the complexes are given in the Table 1. The magnetic moment of Co(II) complex was found at 3.89 B.M. at room temperature which supported the octahedral geometry [12]. The magnetic moment value 1.79 B.M. measured for the copper(II) complex lie in the range expected for a d^9 -system, which contains one unpaired electron. The measured value 3.24 B.M. for the nickel(II) complex suggests octahedral geometry [12]. Physical data and magnetic moment of complexes are listed in Table 1.

D. *Infrared spectra*

The tentative assignments of the important IR spectral bands for the Schiff base ligand as well as its complexes viz Co(II), Ni(II), and Cu(II) are listed in Table 2. The Schiff base ligand was compared with the spectra of the complexes. In the free Schiff base ligand (NABSA), the frequency of hydroxyl group was observed at about 3412 cm^{-1} , due to intramolecular hydrogen bonding between OH and the imine group [13]. The disappearance of this band in the spectra of the complexes indicates the deprotonation of the hydroxyl group and coordination through deprotonated phenolic OH group [14]. In Co(II) and Ni(II) complexes the coordinated water molecules are indicated by the appearance of a broad band at 3348 & 3404 cm^{-1} . The FT-IR spectrum of ligand exhibits a strong band of the azomethine (C=N) at 1564 cm^{-1} [15]. This band is shifted to the 1599 cm^{-1} in **1**, 1601 cm^{-1} in **2**, and 1599 cm^{-1} in **3**. In the free ligand, the high intensity band in 1273 cm^{-1} and 1399 cm^{-1} , assigned to the C-O and C-N stretching of the ligand. However after complexation of C-O and C-N group via oxygen and nitrogen to the metal ions these bands were observed at the regions of 1303 and 1381 for **1**, 1304 and 1387 for **2**, and 1302 and 1388 for **3**. In the far-IR region two new bands around 397 and 480 cm^{-1} assigned to (M-N) and (M-O), respectively [16]. These show the effect of complexation via phenolic oxygen and azomethine nitrogen. These overall data suggest that after complexation the azomethine-N and phenolic-O bands shifted to lower frequencies in all the complexes as compared to that of ligand.

E. *Electronic spectra*

The electronic spectra of the ligand & complexes were recorded in the range 250 – 800 nm in DMF. The ligand exhibits two absorption bands at 267(37453cm⁻¹) and 345(28985cm⁻¹) nm due to $\pi \rightarrow \pi^*$ transitions of the aromatic rings and $n \rightarrow \pi^*$ transitions of the C=N group respectively (Table 2). The cobalt complex in DMF solvent in 1×10^{-5} mol/cm³ showed that it has an octahedral feature. There are two detectable bands at 445(22472 cm⁻¹) and 361(27700cm⁻¹) due to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition, respectively [12]. The nickel complex exhibit two d-d transition bands at 429 & 414 (23310 & 24154cm⁻¹), while the third transition is not observed. These bands are assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ & ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition, respectively confirms the octahedral geometry [12, 17]. The copper complex show absorption band around 494(20242cm⁻¹) which is attributed due to ${}^2B_{1g} \rightarrow {}^2E_g$ which strongly indicates the square planar geometry around the Cu(II) ions [17, 18].

F. EPR studies

The EPR spectrum of copper complex (3) was recorded under N₂ atmosphere. The spectrum exhibits an anisotropic shape, and the hyperfine structure is not observed. The complex (3) shows rhombic spectra with give three g values [19]. The estimated spectral values $g_1 = 2.402$, $g_2 = 2.1033$ and $g_3 = 1.8041$. Here the g_3 value is less than 2.3 which is in agreement with the covalent character of M–L bonds [20].

G. Thermal studies

Thermal analysis techniques are usually employed for determining the thermal stability and composition of complexes. Thermal behaviors (TGA–DTA) of the ligand and its metal complexes have been performed in the temperature range from 40 to 700 °C under N₂ atmosphere with a heating rate of 10°C min⁻¹. The mass losses (experimental and calculated) as a function of temperature of the Co(II) complex **1** decompose mainly in three steps. The first step appeared within the temperature range 115-190°C was due to the elimination of coordinated water molecules [21]. The second step within the temperature range 220-310°C was associated with an endothermic. This peak was due to the partial decomposition of the ligand. The final decomposition step appeared above 450°C corresponding to the complete thermal decomposition of the complex and the loss of their organic portion resulting in the formation of CoO as final products. The Ni(II) complex **2** decompose in three steps. The first step appeared within the temperature range 130 – 190°C was due to the elimination of coordinated water molecules [22]. The second step within the temperature range 310 – 345 °C was associated with an endothermic. This peak was due to the partial decomposition of the ligand. The final decomposition step appeared above 500°C corresponding to the complete thermal decomposition of the complex and the loss of their organic portion resulting in the formation of NiO as final products. The Cu(II) complex **3** exhibits thermal stability up to 230 °C, which confirms that this complex is free from any types of water molecules. The second step within the temperature range 250-300°C was associated with an endothermic. This peak was due to the partial decomposition of the ligand. The final decomposition step appeared above 550°C corresponding to the complete thermal decomposition of the complex and the loss of their organic portion resulting in the formation of CuO as final products.

H. Antimicrobial activity

The analysis regarding the antimicrobial activities of the newly synthesized compounds was studied against the various gram positive and gram negative bacterial organisms such as Gram negative bacteria *Pseudomonas aeruginosa*, *E.coli* Gram positive bacteria *Staphylococcus aureus*, *Bacillus subtilis* and fungi *Candida albicans*, and *Aspergillus fumigates* were used to find out the antimicrobial activity. Comparisons of the biological activity of the synthesized compounds are presented in Figure 2. The results compared with standard drug (ciprofloxacin 5 µg/ disc for bacteria; Nystatin 100 units/ disc for fungi) have indicated that complexes were active but activity was lesser than the standard drugs. All the new complexes showed a remarkable biological activity against bacteria and fungus. From the results it is clear that the some metal complexes are found to have more antimicrobial activity than the parent ligand. Co²⁺, Ni²⁺ and Cu²⁺ complexes showed tremendous activity when compared to the ligands activity against *Candida albicans* which is shown in Figure 2 & 3. The greater activity can be explained on the basis of particle size and size of metal ion [23] and on chelation theory [24].

IV. CONCLUSION

A new series of Co(II), Ni(II), and Cu(II) Schiff base complexes have been synthesized and characterized. From the analytical data and the physical studies the ligand has been shown to act as a bidentate manner and coordination through the phenolic oxygen and azomethine nitrogen. It forms complexes in 2:1 ratio. The coordination numbers of the complexes **1** & **2** are 6 while that of complex **3** is 4. The thermal decomposition provided information concerning the presence of both crystallization and coordination water molecules. The final product of decomposition was stable metallic oxide. The complexes decompose in three or two steps and display a complex thermal behavior. The antibacterial activity has been explained on the basis of chelation theory. In general metal complexes possess antibacterial and antifungal activity against the selected species of bacteria and fungi more than the free Schiff base ligand.

V. ACKNOWLEDGEMENT

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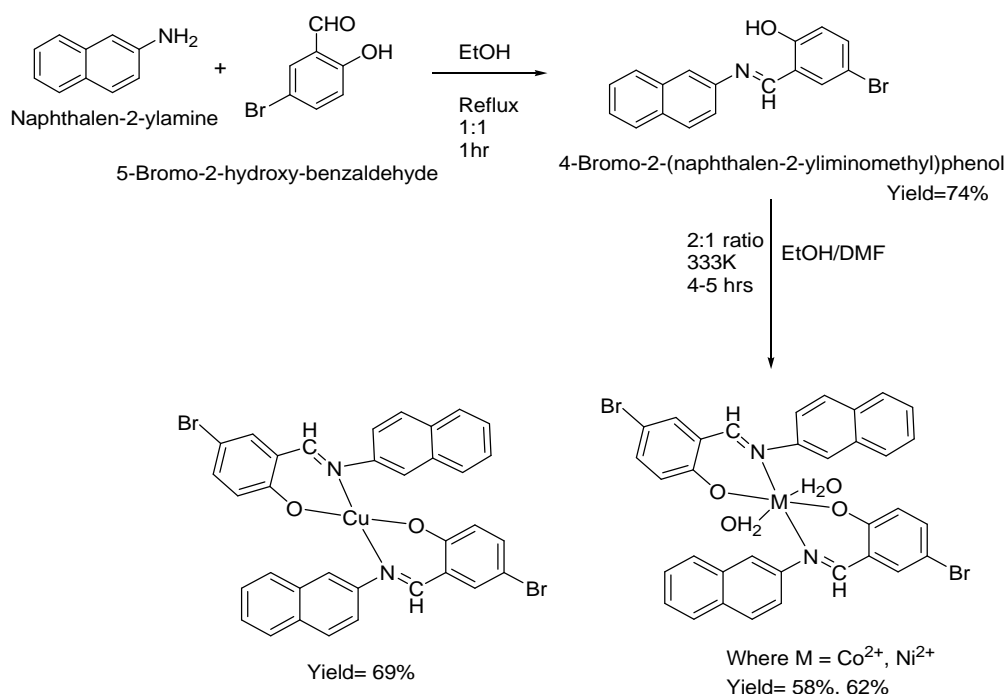


Figure 1. Schematic representation of synthesis of Schiff base complexes

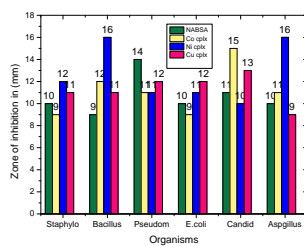


Figure 2. Biological activities of the ligand (NABSA) and its cobalt, nickel and copper complexes against various organisms.



Figure 3. Biological activities of the ligand NABSA and its cobalt, nickel and copper complexes against candida albicans.

Table 1. Physical data and magnetic moment of title compounds.

Compound	Composition	Colour	Yield %	Melting Point (°C)	Molecular weight	Molar conductance ($\text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (BM) at RT
NABSA	$\text{HL}/\text{C}_{17}\text{H}_{12}\text{BrNO}$	Yellow	74	146	326	-	-
Complex 1	$[\text{Co}(\text{HL})_2(\text{H}_2\text{O})_2]/[\text{CoC}_{34}\text{H}_{26}\text{Br}_2\text{N}_2\text{O}_4]$	Brown	58	174	745	10.3	3.89
Complex 2	$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]/[\text{NiC}_{34}\text{H}_{26}\text{Br}_2\text{N}_2\text{O}_4]$	Olive green	62	285	745	15.9	3.24
Complex 3	$[\text{Cu}(\text{HL})_2]/[\text{CuC}_{34}\text{H}_{22}\text{Br}_2\text{N}_2\text{O}_2]$	Dark brown	69	>320	713	14.4	1.79

Table 2. Selective FT-IR & Electronic data for NABSA and its metal complexes (cm^{-1})

Compound	IR Spectral bands in cm^{-1}							Electronic spectral bands (max) in cm^{-1}	
	(C=N)	(C-O)	(C-N)	(M-N)	(M-O)	Ph ring C=C	(OH/ H ₂ O)		
NABSA	1564	1273	1399	-	-	1472	3412	267/37453 cm^{-1} 345/28985 cm^{-1}	- n- *
Complex 1	1599	1319	1381	397	480	1453	3348	445/22472 cm^{-1} & 361/27700 cm^{-1}	⁴ T _{1g} ⁴ A _{2g} ⁴ T _{1g} ⁴ T _{1g} (P)
Complex 2	1601	1304	1387	397	479	1455	3404	414/24154 cm^{-1}	³ A _{2g} (F) ³ T _{1g} (P)
Complex 3	1599	1302	1388	398	479	1454	-	494/20242 cm^{-1}	² B _{1g} ² E _g