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## ABSTRACT

Schiff base ligand 2-Hydroxy-4,5-diiodo-benzylidene-4-nitro-aniline (L) and its complexes with Cu (II), Ni (II), Co (II) and Zn (II) were prepared and characterized by analytical, spectroscopic (IR, UV-Vis) techniques, electrical conductivity and magnetic measurements. The results indicate that the ligand coordinate through azomithine nitrogen and phenolic oxygen to the metal ions. The complexes were further screened for microbial activity.

**KEYWORDS:** Schiff base, metal complexes, microbial study.

## 1. INTRODUCTION

In coordination chemistry Schiff bases are important class of ligands and their complexing ability containing different donor atom is widely reported. The chemistry of transition metal complexes containing heterocyclic donor continues to be of interest on account of their biological importance<sup>1</sup>. The Schiff base metal complexes show antimicrobial<sup>2</sup>, fungicidal<sup>3</sup> anti-cancer<sup>4</sup> and anti-inflammatory activity<sup>5</sup>. Thus the present study describe synthesis, characterization and microbial studies of some schiff base transition metal complexes.

**Experimental**

The ligand 2-Hydroxy-4,5-diiodo-benzylidene-4-nitro-aniline (L) has been characterized by infrared spectral studies. The complex characterized by infrared spectral studies, electronic spectral studies, magnetic moment, thermal analysis and conductivity measurement. The microbial activity of the investigated compound was tested by the paper diffusion method.

**Synthesis of Schiff bases**

The Schiff base was synthesized by reported procedure<sup>6</sup>. To the solution of 2-hydroxy-4,5-diiodo-benzyldehyde 0.373 gm (0.001 mole) in 25 ml ethanol and 0.138 gm (0.001 mol) p-nitro aniline in 25 ml ethanol was added. The solution was refluxed for 5-6 hrs. The solution was monitored on TLC, on completion of reaction the solution was concentrated, cooled and poured in water the separated solid was filtered, washed with water and recrystallised from ethyl alcohol and dried over calcium chloride in vacuum. The composition and yield of Schiff base have shown in Table no 1.

**Synthesis of metal complexes**

The metal complexes of Cu (II), Ni (II), Co (II) and Zn (II) with ligand were prepared by refluxing the ethanolic solution of metal nitrate and ligand in 1:2 molar ratios. The pH of solution was adjusted by alcoholic ammonia.

Ligand (0.02 mole) in slight excess was taken in a round bottom flask containing 30 ml anhydrous ethanol and refluxed for few minutes with constant stirring to ensure complete dissolution, A solution of the appropriate metal nitrate (0.01 M) in 20 ml of anhydrous ethanol was then added drop by drop with constant-stirring in the hot

solution of ligand. The content was refluxed five hours. After cooling, the pH of the mixture was maintained by the addition of alcoholic ammonia solution. The resultant precipitate was digested for one hour. The precipitate was filtered, washed with hot ethanol and dried in vacuum desiccators over anhydrous granular calcium chloride. The composition and yield of metal complexes have shown in table no 1.

## 2. RESULT AND DISCUSSION

The metal complexes are colored and stable to air and moisture. They are insoluble in water, sparingly soluble in benzene, chloroform, carbon tetrachloride etc. and completely soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). Elemental analysis suggests that the complex have 1:2(metal-ligand) stoichiometry. The conductivity value in DMF ( $1 \times 10^{-3}M$ ) reveals their electrolyte nature <sup>7,8</sup>. Based on elementary chemical analysis the formula,  $ML_2(H_2O)_2(NO_3)_2$  were suggested for all compounds.

In IR spectrum of ligand, shows band at  $3288.40\text{ cm}^{-1}$  assigned to  $-OH$  stretching, the lowering of normal free  $-OH$  stretching frequency from  $3600\text{ cm}^{-1}$  to above value is expected due to the strong intramolecular hydrogen bonding<sup>9</sup>. A band at  $1601.60\text{ cm}^{-1}$  assigned to azomethine ( $C=N$ ) stretching vibration <sup>9,10</sup>. A band at  $1338.50\text{ cm}^{-1}$  assigned to enolic- $C-O$  stretching frequency.

**Table 1: Analytical data of ligand and metal complexes**

Compound	Colour	Yield (%)	Formula	Mol Wt.	% Analysis Found(Calculated)			
					C	H	M	N
Ligand(L)	Violet	61	$C_{13}H_8I_2N_2O_3$	494.02	31.54 (31.61)	1.54 (1.63)	--	5.59 (5.67)
$(L)_2Cu(H_2O)_2(NO_3)_2$	Green	73	$C_{26}H_{20}Cu_4N_4O_8$	1087.62	28.64 (28.71)	1.79 (1.85)	5.60 (5.84)	5.10 (5.15)
$(L)_2Ni(H_2O)_2(NO_3)_2$	Yellow	59	$C_{26}H_{20}Ni_4 N_4O_8$	1082.77	28.78 (28.84)	1.79 (1.86)	5.29 (5.42)	5.09 (5.17)
$(L)_2Co(H_2O)_2(NO_3)_2$	Brown	52	$C_{26}H_{20}Co_4N_4O_8$	1083.01	28.74 (28.83)	1.81 (1.86)	5.19 (5.44)	5.10 (5.17)
$(L)_2Zn(H_2O)_2(NO_3)_2$	Yellow	53	$C_{26}H_{20}Zn_4 N_4O_8$	1089.47	28.58 (28.66)	1.76 (1.85)	5.78 (6.00)	5.08 (5.14)

In the spectra of Co complexes the band at  $3288.40\text{ cm}^{-1}$  disappears. The band at  $1601.60\text{ cm}^{-1}$  is shifts to lower frequency ( $1594.70\text{ cm}^{-1}$ ), indicating the co-ordination of azomethine nitrogen to metal atom. In spectra of complex the broad band at  $3435.72\text{ cm}^{-1}$ , indicating the presence of coordinated water. The bands at  $1338.50\text{ cm}^{-1}$  show upper shift( $1358.33\text{ cm}^{-1}$ ), suggest the bonding of enolic oxygen of Schiff base with metal during complexation<sup>10,11</sup>. The new bands at  $454.15\text{ cm}^{-1}$  and  $557.14\text{ cm}^{-1}$  in the spectra of complex are assigned to stretching vibration of M-O and M-N bands respectively<sup>12</sup>.

**Table-2: IR frequency ( $\text{cm}^{-1}$ ) of ligand and complexes**

Ligand / Complex	$\nu$ (OH) Water	$\nu$ (-OH)	$\nu$ (C=N)	$\nu$ (C-O)	$\nu$ (M-N)	$\nu$ (M-O)
L	--	3288.40	1601.60	1338.50	--	--
L-Co	3435.72	--	1594.70	1358.33	557.14	545.15

The UV-Visible spectra of copper complexes of ligand exhibit bands at  $15432\text{ cm}^{-1}$ ,  $27624\text{ cm}^{-1}$  attributed to  ${}^3E_g \rightarrow {}^2T_{2g}$  and charge transfer transition which indicate distorted octahedral geometry of Cu (II) complexes, which further supported by  $\mu_{\text{eff}}$  value 1.85 B.M.<sup>13</sup>.

The ligand field parameter values ( $Dq$  and  $LFSE$ ) observed at  $15432\text{ cm}^{-1}$ , and  $44.06\text{ kcal mole}^{-1}$  respectively and these are in good agreement with the distorted octahedral  $\text{Cu(II)}$  complexes.

The electronic spectra of  $\text{Ni(II)}$  complex exhibit bands in the three regions as  $9746\text{ cm}^{-1}$ ,  $16129\text{ cm}^{-1}$  and  $23866\text{ cm}^{-1}$ . This pattern of absorption may be assigned to transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  respectively. This may be assigned to characteristic three spin allowed transition of octahedral complexes<sup>14</sup>, further supported by  $\mu_{\text{eff}}$  value 3.31 B.M.

The reduction of  $B$  values for the  $\text{Ni(II)}$  complexes ( $717.13\text{ cm}^{-1}$ ) as compared to the free ion value for  $\text{Ni(II)}$  ion ( $1030\text{ cm}^{-1}$ ) reveals complex formation. The Nephelauxetic ratio ( $\beta$ ) obtained are less than unity (0.696) in this case suggesting considerable amount of covalent character of the metal ligand bonds. The  $LFSE$  value ( $27.82\text{ Kcal mole}^{-1}$ ) indicate considerable stability of  $\text{Ni(II)}$  complexes. The energy ratio  $\nu_2/\nu_1$  (1.654) being close to reported values (1.6-1.82) as well as the  $10Dq$  ( $9746\text{ cm}^{-1}$ ) and percentage of  $\beta$  found (43.67) indicate that the  $\text{Ni(II)}$  complex is in octahedral geometry.

The electronic spectra of  $\text{Co(II)}$  complex exhibit bands at  $9478\text{ cm}^{-1}$ ,  $17543\text{ cm}^{-1}$  and  $22271\text{ cm}^{-1}$ . These bands may be assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$  respectively, suggesting a high spin octahedral geometry around the cobalt ion. Octahedral geometry around cobalt ion<sup>15</sup> further supported by  $\mu_{\text{eff}}$  value 5.25 B.M.

The reduction in  $B$  values for all the  $\text{Co(II)}$  complexes ( $758.66\text{ cm}^{-1}$ ) as compared to the free ion value for  $\text{Co(II)}$  ion ( $971\text{ cm}^{-1}$ ) reveals complexes formation thereby favoring the orbital overlap and delocalization of  $d$  orbitals. The Nephelauxetic ratio ( $\beta$ ) in each case is less than unity (0.781) and their  $\% \beta$  values (28.04 %) indicate partial covalent character in metal ligand bond. The  $LFSE$  value ( $23.02\text{ Kcal mole}^{-1}$ ) indicates considerable stability of  $\text{Co(II)}$  complexes.

The electronic spectra of  $\text{Zn(II)}$  complex exhibits bands at  $25188\text{ cm}^{-1}$  attributed to charge transfer transition suggesting a octahedral environment<sup>16</sup>. This complex is diamagnetic in nature.

The simultaneous use of TG and DTA show that the metal complexes are thermally quite stable. Thermograms of all the complexes indicate the presence of coordinated water molecules.

X-Ray powder pattern investigation suggests that all the complexes are crystalline in nature

### Antimicrobial Activity

The ligand and their metal complexes were tested for antibacterial activity Mueller Hinton agar was used for testing the susceptibility of microorganism by well diffusion method, using DMSO as solvent, at a concentration of 0.01 M against gram positive (*staphylococcus aureus*) and gram negative (*Escherichia coli*) bacteria.

The zones inhibition against the growth of microorganisms was determined at the end of an incubation period 24 h at  $37^\circ\text{C}$  and the results are presented in table 3. It was found that the metal complexes are more active than the free ligand.

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Table 3: Antimicrobial activities of Schiff bases and their complexes

compound	Zone of inhibition	
	Staphylococcus aureus	Escherichia coli
L	15	14

L-Cu	19	18
L-Ni	16	15
L-Co	17	16
L-Zn	16	17
Standard drug	<b>26</b>	<b>30</b>

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