

“SYNTHESIS, CHARACTERIZATION AND MICROBIAL STUDY OF Cu(II), Ni(II), Co(II) AND Zn(II) COMPLEXES WITH 2-HYDROXY-4,5-DIODO-BENZYLIDENE-4-METHOXY-ANILINE”

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Abstract : Schiff base ligand 2-Hydroxy-4,5-diiodo-benzylidene-4-methoxy-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.

Key words: Schiff base, metal complexes, microbial study.

I. INTRODUCTION

Schiff bases are important class of ligands in coordination chemistry 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 importance¹. The Schiff base metal complexes show antimicrobial², fungicidal³ anti-cancer⁴ and anti-inflammatory activity⁵. Thus the present study describe synthesis, characterization and microbial studies of some schiff base transition metal complexes.

II. EXPERIMENTAL:

The ligand 2-Hydroxy-4,5-diiodo-benzylidene-4-methoxy-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 procedure⁶. To the solution of 2-hydroxy-4,5-diiodo-benzyldehyde 0.373 gm (0.001 mole) in 25 ml ethanol and 0.123gm (0.001 mol) p-anisidine 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 ligands 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.

III. 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^{7,8}. 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 3080.9 cm^{-1} assigned to $-OH$ stretching, the lower in of normal free $-OH$ stratching frequency from 3600 cm^{-1} to above value is expected due to the strong intramolecular hydrogen bonding⁹. A band at 1612.40 cm^{-1} assigned to azomethine ($C=N$) stretching vibration^{9,10,17}. A band at 1255.60 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)	Pale Orange	73	C ₁₄ H ₁₁ I ₂ NO ₂	479.05	35.02 (35.10)	2.24 (2.31)	--	2.79 (2.92)
(L) ₂ Cu(H ₂ O) ₂ (NO ₃) ₂	Dark Brown	61	C ₂₈ H ₂₆ CuI ₄ N ₂ O ₆	1057.68	31.72 (31.80)	2.36 (2.48)	5.75 (6.01)	2.56 (2.65)
(L) ₂ Ni(H ₂ O) ₂ (NO ₃) ₂	Yellow Brown	57	C ₂₈ H ₂₆ NiI ₄ N ₂ O ₆	1052.83	31.87 (31.94)	2.41 (2.49)	5.31 (5.57)	2.58 (2.66)
(L) ₂ Co(H ₂ O) ₂ (NO ₃) ₂	Dark Brown	67	C ₂₈ H ₂₆ CoI ₄ N ₂ O ₆	1053.07	31.86 (31.94)	2.42 (2.49)	5.32 (5.60)	2.53 (2.66)
(L) ₂ Zn(H ₂ O) ₂ (NO ₃) ₂	Yellow	71	C ₂₈ H ₂₆ ZnI ₄ N ₂ O ₆	1059.52	31.66 (31.74)	2.38 (2.47)	5.89 (6.17)	2.57 (2.64)

In the spectra of Ni complexes the band at 3080.9 cm⁻¹ disappears. The band at 1612.40 cm⁻¹ shifts to lower frequency (1592.10 cm⁻¹), indicating the co-ordination of azomethine nitrogen to metal atom. In spectra of complex the broad band at 3377.74 cm⁻¹, indicating the presence of coordinated water. The bands at 1255.60 cm⁻¹ show upper shift(1277.52 cm⁻¹), suggest the bonding of enolic oxygen of Schiff base with metal during complexation^{10,11,17}. The new bands at 493.53 cm⁻¹ and 520.18 cm⁻¹ in the spectra of complex are assigned to stretching vibration of M-O and M-N bands respectively^{12,17}.

Table-2: IR frequency (cm⁻¹) of ligand and complexes

Ligand / Complex	ν (OH) Water	ν (-OH)	ν (C=N)	ν (C-O)	ν (M-N)	ν (M-O)
L	--	3080.9	1612.40	1255.60	--	--
L-Ni	3377.7	--	1592.10	1277.52	520.18	493.53

The UV-Visible spectra of copper complexes of ligand exhibit bands at 15337 cm⁻¹, 27247 cm⁻¹ attributed to ³Eg→²T_{2g} and charge transfer transition which indicate distorted octahedral geometry of Cu (II) complexes, which further supported by μ_{eff} value 1.96 B.M.^{13,17}. The ligand field parameter values (Dq and LFSE) observed at 15337 cm⁻¹, and 43.79 kcal mole⁻¹ respectively and these are in good agreement with the distorted octahedral Cu (II) complexes.

The electronic spectra of Ni (II) complex exhibit bands in the three regions as 9615 cm⁻¹ 15673 cm⁻¹ and 23529 cm⁻¹. This pattern of absorption may be assigned to transition ³A_{2g}→³T_{2g}(F), ³A_{2g}→³T_{1g}(F) and ³A_{2g}→³T_{1g}(P) respectively. This may be assigned to characteristic three spin allowed transition of octahedral complexes^{14,17}, further supported by μ_{eff} value 3.33 B.M. The reduction of B values for the Ni(II) complexes (683.06 cm⁻¹) as compared to the free ion value for Ni (II) ion (1030 cm⁻¹) reveals complex formation. The Nephelauxetic ratio (β) obtained are less than unity (0.663) in this case suggesting considerable amount of covalent character of the metal ligand bonds. The LFSE value (27.45 Kcal mole⁻¹) indicate considerable stability of Ni (II) complexes. The energy ratio ν_2/ν_1 (1.630) being close to reported values (1.6-1.82) as well as the 10Dq (9615cm⁻¹) and percentage of β found (50.82) indicate that the Ni(II) complex is in octahedral geometry.

The electronic spectra of Co (II) complex exhibit bands at 9633, cm⁻¹, 18552 cm⁻¹ and 21739 cm⁻¹. These bands may be assigned to ⁴T_{1g}(F)→⁴T_{2g}, ⁴T_{1g}(F)→⁴A_{2g}, (F) and ⁴T_{1g}(F)→⁴T_{1g}, (p) respectively, suggesting a high spin octahedral geometry around the cobalt ion. Octahedral geometry around cobalt ion^{15,17} further supported by μ_{eff} value 4.88 B.M.

The reduction in B values for all the Co(II) complexes (759.46 cm⁻¹) as compared to the free ion value for Co(II) ion (971 cm⁻¹) reveals complexes formation thereby favoring the orbital overlap and delocalization of d orbitals. The Nephelauxetic ratio (β) in each case is less than unity (0.782) and their % β values (27.87 %) indicate partial covalent character in metal ligand bond. The LFSE value (25.46 Kcal mole⁻¹) indicates considerable stability of Co (II) complexes.

The electronic spectra of Zn (II) complex exhibits bands at 26666 cm⁻¹ attributed to charge transfer transition suggesting a octahedral environment^{16,17}. 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 on incubation period 24 h at 37°C and the results are presented in table 3. It was found that the metal complexes are more active than the free ligand.

Table 3: Antimicrobial activities of Schiff bases and their complexes

compound	Zone of inhibition	
	Staphylococcus aureus	Escherichia coli
L	14	12
L-Cu	18	14
L-Ni	17	15
L-Co	16	19
L-Zn	15	20
Standard drug	26	30

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