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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDY OF Cu(II), Ni(II), Co(II) AND Zn(II) ALDIMINE METAL COMPLEXES

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ABSTRACT
Aldimine ligand 2-Hydroxy-5- bromo-benzylidene-4-hydroxy-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, thermal study, electrical conductivity and magnetic measurements. The results indicate that the ligand coordinate through azomithine nitrogen and oxygen of enolic group. The complexes were further screened for antimicrobial activity.

KEYWORDS: Aldimine, metal complexes, antimicrobial study.

1. INTRODUCTION
Aldimine are important class of ligand in coordination chemistry and their complex formation 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[1]. The aldimine metal complexes show antimicrobial[2], fungicidal[3] anti-cancer[4] and anti-inflammatory activity[5].Thus the present study describe synthesis, characterization and antimicrobial studies of some aldimine transition metal complexes.

Experimental
T he ligand 2-Hydroxy-5-bromo-benzylidene-4-hydroxy-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 antimicrobial activity of the investigated compound was tested by the paper diffusion method.

Synthesis of Aldimine
The aldimine was synthesized by reported procedure[6]. To the solution of 5-bromosalicyladehyde 0.112 (0.001 mole) in 25 ml ethanol and 0.109 gm (0.001 mol) p-amino phenol 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 recrystallized from ethyl alcohol and dried over calcium chloride in vacuum. The composition and yield of aldimine 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.

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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 x 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 3188.10 cm^{-1} assigned to –OH stretching, the lowering of normal free –OH stretching frequency from 3600- 3500 cm^{-1} to above value is expected due to the strong intramolecular hydrogen bonding.[9] A bond at 1618.20 cm^{-1} assigned to azomethine (C=N) stretching vibration. A bond at 12220.80 cm^{-1} is 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)	Scarlet	70	$C_{13}H_{10}BrNO_2$	292.13	53.34 (53.45)	3.36 (3.45)	--	4.67 (4.79)
$(L)_2Cu(H_2O)_2(NO_3)_2$	Black	55	$C_{26}H_{24}Br_2CuN_2O_6$	683.83	45.59 (45.67)	3.49 (3.54)	8.98 (9.29)	4.04 (4.10)
$(L)_2Ni(H_2O)_2(NO_3)_2$	Brown	69	$C_{26}H_{24}Br_2Ni\ N_2O_6$	676.96	46.06 (46.13)	3.19 (3.28)	8.42 (8.67)	4.07 (4.14)
$(L)_2Co(H_2O)_2(NO_3)_2$	Dark Brown	71	$C_{26}H_{24}Br_2CoN_2O_6$	679.22	45.91 (45.98)	3.41 (3.56)	8.38 (8.68)	4.06 (4.12)
$(L)_2Zn(H_2O)_2(NO_3)_2$	Brown	61	$C_{26}H_{24}Br_2ZnN_2O_6$	685.68	45.46 (45.54)	3.48 (3.53)	9.21 (9.54)	3.98 (4.09)

In the spectra of Ni(II) complexes the band at 3188.10 cm^{-1} disappears. The band at 1618.20 cm^{-1} is shifts to lower frequency (1609.67 cm^{-1}), indicating the co-ordination of azomethine nitrogen to metal atom. In spectra of complex the broad band at 3333.00 cm^{-1}, indicating the presence of coordinated water. The bands at 1222.80 cm^{-1} show upward shift (1236.02 cm^{-1}) suggest the bonding of enolic oxygen of aldimine base with metal during complexation[10,11], further confirmed by a new band. The new bands at 527.63 cm^{-1} and 476.67 cm^{-1} in the spectra of complex are assigned to stretching vibration of M-N and M-O bands respectively[12].

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

Ligand / Complex	ν (OH) Water	ν (OH) Phenoic	ν (C-O)	ν (C=N)	ν (M-N)	ν (M-O)
L	-	3188.10	1222.80	1618.20	-	-
L-Cu	3333.00	-	1236.02	1609.67	527.63	476.67

The UV-Visible spectra of copper complexes of ligand exhibit bands at 15037 cm^{-1}, 27027 cm^{-1} attributed to $^3Eg \rightarrow {}^2T_{2g}$ and charge transfer transition which indicate distorted octahedral geometry of Cu (II) complexes, which further supported by μ_{eff} value 1.90 B.M.[13].

The ligand field parameter values (Dq and LFSE) observed at 15037 cm^{-1} and 42.53 kcal $mole^{-1}$ respectively and these are in good agreement with the distorted octahedral Cu (II) complexes.

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The electronic spectra of Ni (II) complex exhibit bands in the three regions as 9746 cm^{-1} 16103 cm^{-1} and 24271 cm^{-1}. This pattern of absorption may be assigned to transition $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow T_{1g}$ (P) respectively. This may be assigned to characteristic three spin allowed transition of octahedral complexes[14], further supported by μeff value 2.98 B.M.

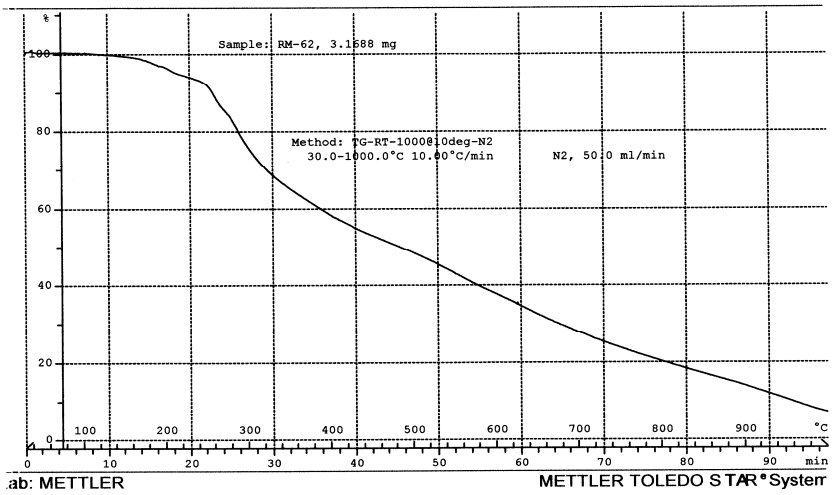
The reduction of B values for the Ni(II) complexes (742.40 cm^{-1}) as compared to the free ion value for Ni(II) ion (1030 cm^{-1}) reveals complex formation. The Nephelauxetic ratio (β) obtained are less than unity (0.720) in this case suggesting considerable amount of covalent character of the metal ligand bonds. The LFSE value (27.83 Kcal $mole^{-1}$) indicate considerable stability of Ni(II) complexes. The energy ratio ν_2/ν_1 (1.652) being close to reported values (1.6-1.82) as well as the 10Dq (9746 cm^{-1}) and percentage of β found (38.88) indicate that the Ni (II) complex is in octahedral geometry.

The electronic spectra of Co (II) complex exhibit bonds at 9541 cm^{-1} , 17761 cm^{-1} and 22421 cm^{-1}. These bands may be assigned to 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[15] further supported by μ_{eff} value 4.87 B.M.

The reduction in B values for all the Co(II) complexes (770.60 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 orbital. The Nephelauxetic ratio (β) in each case is less than unity (0.793) and their %β values (26.19 %) indicate partial covalent character in metal ligand bond. The LFSE value (23.47 Kcal $mole^{-1}$) indicates considerable stability of Co (II) complexes.

The electronic spectra of Zn (II) complex exhibits bands at 27173 cm^{-1} attributed to charge transfer transition suggesting an octahedral environment[16]. This complex is diamagnetic in nature.

The Ni (II) complex was screened for thermal study. The TG curve of complex shows that the complex was stable up to 140°C. There after the complex start decomposing up to 220°C.The percentage weight loss is about 5.32 % (cal 5.30). The weight corresponding to two moles of water molecules. The loss of water molecule in complex is a two step process, indicated by two endothermic peaks in the DTA curve, which occurs at 180°C and 210°C.



TG Curve of Ni complex

After this, complex show decrease in weight, indicating decomposition of complex, further confirmed by endothermic nature of peaks obtained in DTA curve organic part content of the metal complex is removed during this loss, leading to formation of stable residue of metal oxide.

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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 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.

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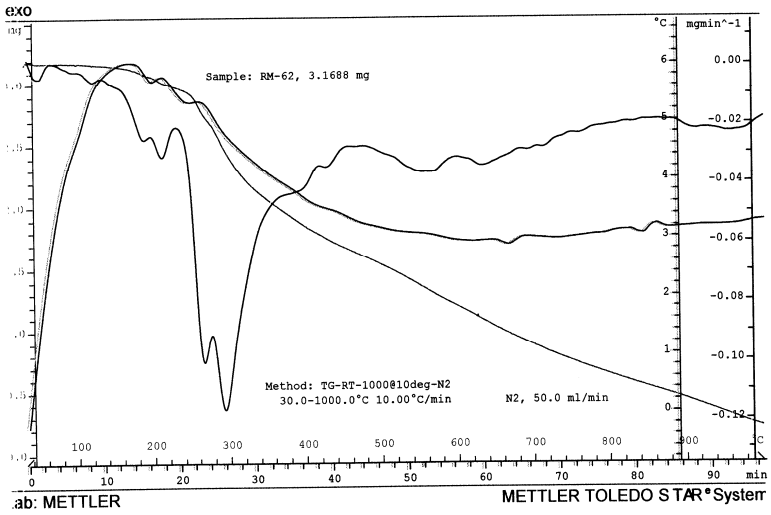

TG-DTA DTG Curve of Ni complex

Table 3: Antimicrobial activities of Schiff bases and their complexes

compound	Zone of inhibition	
	Staphylococcus aureus	Escherichia coli
L	10	11
L-Cu	14	15
L-Ni	16	13
L-Co	13	14
L-Zn	14	12
Standard drug	**26**	**30**

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