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

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Abstract:

Aldimine ligand 2-Hydroxy-5-Chloro-benzylidene-4-methyl-aniline (L) and its complexes with Cu (II), Ni (II), Co (II) and Zn (II) were prepared and characterized by analytical, infrared spectral studies, electronic spectral studies, electrical conductivity and magnetic measurements. The results indicate that the ligands coordinate through azomithine nitrogen and oxygen of enolic group. The complexes were further screened for microbial activity.

Key works: Aldimine, ligand, transition metal, metal complexes, microbial study.

Introduction:

Aldimine are important class of ligands in coordination chemistry and their complex formation ability containing different donor atom is mostly reported. The chemistry of transition metal complexes containing heterocyclic donor continues to be of interest on account of their biological importance[1]. The Schiff base metal complexes show antimicrobial[2], fungicidal[3] anti-cancer[4] and anti-inflammatory activity[5].Thus the present study describe synthesis, characterization and microbial studies of some aldimine transition metal complexes.

Experimental:

The ligand 2-Hydroxy-5-chloro-benzylidene-4-methyl-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 Aldimine:

The aldimine was synthesized by reported procedure[6]. To the solution of 5-chlorosalicyladehyde 0.157 (0.001 mole) in 25 ml ethanol and 0.108 gm (0.001 mol) P- toludine in 25 ml ethanol was added. The solution was refluxed for 4-5 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 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 ethanol 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.

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 3026.00 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 1612.00 cm^{-1} assigned to azomethine (C=N) stretching vibration. A bond at 1278.00 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)	Yellow	72	$C_{14}H_{12}ClNO$	245.70	68.29 (68.44)	4.85 (4.92)	--	5.58 (5.70)
$(L)_2Cu(H_2O)_2(NO_3)_2$	Dark Brown	63	$C_{28}H_{28}Cl_2CuN_2O_4$	590.98	56.84 (56.90)	4.65 (4.78)	10.49 (10.75)	4.63 (4.74)
$(L)_2Ni(H_2O)_2(NO_3)_2$	Deep Yellow	59	$C_{28}H_{28}Cl_2N_2NiO_4$	586.13	57.22 (57.38)	4.76 (4.82)	9.73 (10.01)	4.66 (4.78)
$(L)_2Co(H_2O)_2(NO_3)_2$	Pink	64	$C_{28}H_{28}Cl_2CoN_2O_4$	586.37	57.42 (57.35)	4.76 (4.81)	9.78 (10.05)	4.63 (4.78)

$(L)_2Zn(H_2O)_2(NO_3)_2$	Yellow	56	$C_{28}H_{28}Cl_2N_2O_4Zn$	592.83	56.67 (56.73)	4.69 (4.76)	10.76 (11.03)	4.65 (4.)

In the spectra of Zn(II) complexes the band at 3026.00 cm^{-1} disappears. The band at 1612.00 cm^{-1} is shifts to lower frequency (1602.00 cm^{-1}), indicating the co-ordination of azomethine nitrogen to metal atom. In spectra of complex the broad band at 3219.70 cm^{-1}, indicating the presence of coordinated water. The bands at 1278.00 cm^{-1} show upward shift (1301.00) suggest the bonding of enolic oxygen of aldimine with metal during complexation[10,11] , further confirmed by a new band. The new bands at 547.42 cm^{-1} and 498.65 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=N)	ν (C-O)	ν (M-N)	ν (M-O)
L	-	3026.00	1612.00	1278.00	-	-
L-Co	3219.70	-	1602.00	1301.00	547.42	498.65

The UV-Visible spectra of copper complexes of ligand exhibit bands at 15383 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 1.98 B.M.[13].

The ligand field parameter values (Dq and LFSE) observed at 15383 cm^{-1} and 43.92 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 9433 cm^{-1} 15822 cm^{-1} and 23696 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 3.20 B.M.

The reduction of B values for the Ni(II) complexes (747.93 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 (0.726) in this case suggesting considerable amount of covalent character of the metal ligand bonds. The LFSE value (27.93 Kcal mole^{-1}) indicate considerable stability of Ni(II) complexes. The energy ratio ν_2/ν_1 (1.677) being close to reported values (1.6-1.82) as well as the 10Dq (9433 cm^{-1}) and percentage of β found indicate that the Ni(II) complex is in octahedral geometry.

The electronic spectra of Co (II) complex exhibit bonds at 9345 cm^{-1} , 17605 cm^{-1} and 21834 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 5.10 B.M.

The reduction in B values for all the Co(II) complexes (760.26 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 (0.782) and their %β values (227.87 %) indicate partial covalent character in metal ligand bond. The LFSE value (23.58 Kcal mole^{-1}) indicates considerable stability of Co (II) complexes.

The electronic spectra of Zn (II) complex exhibits bands at 28490.00 cm^{-1} attributed to charge transfer transition suggesting an octahedral environment[16]. 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

Microbial 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 aurous) 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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Table 3: Antimicrobial activities of Schiff bases and their complexes

compound	Zone of inhibition	
	Staphylococcus aureus	Escherichia coli
L	12	11
L-Cu	17	18
L-Ni	15	14
L-Co	14	13
L-Zn	14	12
Standard drug	**26**	**30**

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