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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-methoxy-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 Aldimine 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-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 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 0.123 gm (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 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

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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 2964.00 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 1616.20 cm^{-1} assigned to azomethine (C=N) stretching vibration. A bond at 1247.90 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)	Dark Brown	61	$C_{14}H_{12}ClNO_2$	261.7	64.12 (64.25)	4.54 (4.62)	--	5.28 (5.35)
$(L)_2Cu(H_2O)_2(NO_3)_2$	Dark Brown	57	$C_{28}H_{28}Cl_2CuN_2O_6$	622.98	53.81 (53.98)	4.41 (4.53)	9.93 (10.20)	4.47 (4.50)
$(L)_2Ni(H_2O)_2(NO_3)_2$	Green	54	$C_{28}H_{28}Cl_2N_2NiO_6$	618.13	54.49 (54.41)	4.49 (4.57)	9.19 (9.50)	4.46 (4.53)
$(L)_2Co(H_2O)_2(NO_3)_2$	Dark Brown	58	$C_{28}H_{28}Cl_2CoN_2O_6$	618.37	54.29 (54.38)	4.43 (4.56)	9.25 9.53)	4.46 (4.53)
$(L)_2Zn(H_2O)_2(NO_3)_2$	Brown	67	$C_{28}H_{28}Cl_2N_2O_6Zn$	624.83	53.79 (53.82)	4.46 (4.52)	10.12 (10.47)	4.32 (4.48)

In the spectra of Co(II) complexes the band at 2964.00 cm^{-1} disappears. The band at 1616.20 cm^{-1} is shifts to lower frequency (1598.68 cm^{-1}), indicating the co-ordination of azomethine nitrogen to metal atom. In spectra of complex the broad band at 3300.00 cm^{-1}, indicating the presence of coordinated water. The bands at 1247.90 cm^{-1} show upward shift (1285.70) suggest the bonding of enolic oxygen of aldimine with metal during complexation[10,11], further confirmed by a new band. The new bands at 550.00 cm^{-1} and 483.00 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	-	2964.00	1616.20	1247.90	-	-
L-Co	3300.00	-	1598.68	1285.70	550.00	483.00

The UV-Visible spectra of copper complexes of ligand exhibit bands at 14992 cm^{-1}, 27397 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 μ_{eff} value 2.10B.M.[13].

The ligand field parameter values (Dq and LFSE) observed at 14992 cm^{-1} and 42.80 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 9669 cm^{-1} 15873 cm^{-1} and 24509 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 μ_{eff} value 3.15 B.M.

The reduction of B values for the Ni(II) complexes (754.33 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 (0.732) in this case suggesting considerable amount of covalent character of the metal ligand bonds. The LFSE value (27.66 Kcal mole^{-1}) indicate considerable stability of Ni(II) complexes. The energy ratio ν_2/ ν_1 (1.638) being close to reported values (1.6-1.82) as well as the

10Dq (9689 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 9302 cm^{-1} , 17793 cm^{-1} and 21739 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 5.20 B.M.

The reduction in B values for all the Co(II) complexes (775.06 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 (0.798) and their %β values (25.31%) indicate partial covalent character in metal ligand bond. The LFSE value (24.33 Kcal mole^{-1}) indicates considerable stability of Co (II) complexes.

The electronic spectra of Zn (II) complex exhibits bands at 25641 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.The Co(II) complexes of ligand was subjected to X-ray powder diffraction studies. The X-ray powder diffractograms of these complexes are presented in figure-1. X-ray powder diffraction data of all the main peaks having relative intensity greater than 10% have been indexed by using computer software[17] by trial and error method. The indexed powder diffraction data, the unit cell data and crystal lattice parameters of complex are presented in table-3. The diffractogram of Co(II) complex have eleven reflections between 10 to 80°. The crystal volume is obtained from indexing of the diffraction pattern. The Z (number of molecules per unit cell) value were calculated and rounded up to the nearest whole number. The porosity percentage was calculated from the observed and calculated densities. The density calculated from diffraction data and the observed density was found to be very close to each other indicating the perfection in indexing. Such refined parameters were also used for finding out probable space group. These values are given in table-3. The crystallographic data of the complexes fit perfectly in monoclinic system with one molecule per unit cell the probable space group is P2/m.e in nature
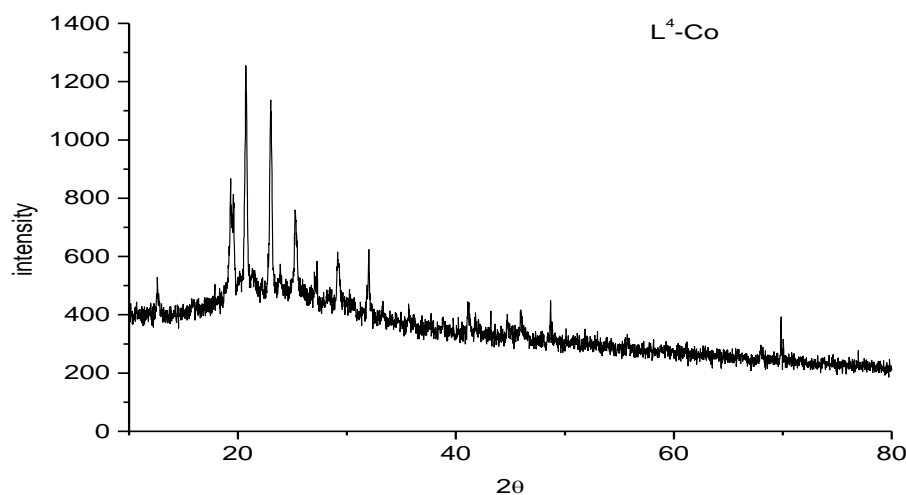
Figure-: X-Ray Diffractogram of L-Co

Table- 3 : XRD data of L^4-Co Complex

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS
0	1	1	0.028151	0.028165	-0.000014	19.318	19.323	4.5911
1	0	1	0.028896	0.028918	-0.000022	19.574	19.582	4.5315
2	0	0	0.032390	0.032356	0.000035	20.736	20.725	4.2801

0	2	0	0.039801	0.039685	0.000116	23.016	22.982	3.8611
1	2	0	0.047785	0.047774	0.000011	25.253	25.250	3.5238
-2	1	1	0.055491	0.055349	0.000142	27.250	27.214	3.2700
-1	2	1	0.063348	0.063432	-0.000084	29.155	29.175	3.0605
-1	0	2	0.076006	0.075892	0.000114	32.007	31.982	2.7941
-3	2	2	0.169922	0.169946	-0.000023	48.688	48.692	1.8687
-5	0	3	0.327633	0.327630	0.000003	69.834	69.834	1.3458
-1	2	4	0.329314	0.329331	-0.000017	70.040	70.042	1.3423

Crystal system: Monoclinic

a = 8.613687 ± 0.006657 A	α = 90.000000 ± 0.000000 DEG
b = 7.733519 ± 0.003881 A	β = 96.109390 ± 0.058171 DEG
c = 5.735569 ± 0.000940 A	γ = 90.000000 ± 0.000000 DEG
Density (ρobs) = 2.6536 g cm^{-3}	Z = 1
Density (ρcal) = 2.7020 g cm^{-3}	Unit Cell Volume =379.90 Å^3
Porosity % = 1.7912	Space group = P 2/m

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 aurous) 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°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	10
L-Cu	14	13
L-Ni	12	12
L-Co	14	11
L-Zn	13	11
Standard drug	**26**	**30**

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