"Synthesis, Spectroscopic and Thermal Analysis of Co(II), Ni(II), Cu(II), Cr(III), Fe(III) and VO(IV)Transition Metal Complexes of Pyrazoline Schiff Base Ligand"

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Abstract : Synthesis of Schiff base ligand has been carried out by the condensation of chalcone with isoaniazide in ethanolic solution. From this ligand new Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) complexes were synthesized. The Schiff base ligand and all metal complexes have been characterized on the basis of elemental analysis, IR spectra, ^{1}H-NMR spectra and mass spectra. The nonelectrolytic nature for all metal complexes confirmed on the basis of molar conductivity data. The Fremann-Caroll and Sharp-Wentworth methods have been employed to study the thermal behaviour of complexes and to calculate activation energy (Ea), thermal stability, order of reaction (n), entropy change (ΔS), free energy change (ΔF). The activation energy calculated with above two mentioned methods is in close agreement. The ligand and the complexes were also tested for their in vitro antibacterial activity.

IndexTerms **- Schiff base, Metal complexes, IR, Thermal, Antibacterial.**

I. INTRODUCTION

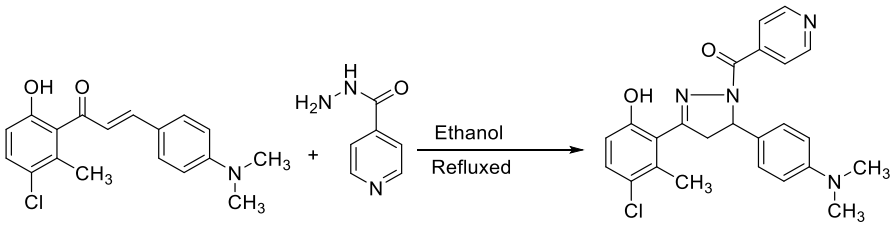
Coordination chemistry has been a challenge to the all chemist throughout the world ever since the first synthesis of coordination compound was observed in the nineteenth century.
These coordination compounds are also essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions. Schiff bases which are polydentate always coordinate to metal ions in such a way that to form a heterocyclic rings also known as chelate ring. They form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial, antifungal and antitumor activity. Schiff base contain pyrozoline ring easily form a complexes with transition metal ion having wide applications [1-5].

II. Material and Method

All chemicals used were of the analytical reagent (AR) grade and of highest purity available and purchased from SD-Fine Chem Limited. They included isoaniazide, P-dimethylaminobenzaldehyde, $Co(II)OAc_2.6H_2O$, $Ni(II)OAc_2.6H_2O$, $Cu(II)OAc_2$ $.6H_2O$, $Fe(III)Cl_3.6H_2O$, $Cr(III)Cl_3.6H_2O$, $VOSO_4.5H_2O$ were used. The chalcone required for synthesis of heterocyclic Schiff base ligand was synthesized according to literature method.
Melting points were determined with an Electro thermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 4300 spectrometer. NMR spectra were recorded with a Brucker 80 instrument using TMS as internal standard. Mass analyses of the products were conducted with a Finnigan-Matt 8430 GC-Mass instrument. Conductivity measurements were made on freshly prepared 10^{-3} molar solutions in DMF at room temperature with digital conductivity meter.

Synthesis of 3-(3-chloro-6-hydroxy-2-methylphenyl)-5-(4-dimethylamino-4,5-dihydro-1H-pyrazol-1-yl(pyridin-4-yl)methanone

A mixture of chalcone 3-chloro-6-hydroxy-2-methylphenyl)-3-(4-dimethyl aminophenyl)prop-2-en-1-one (3.15 g, 0.01mol) and isoaniazide (1.37 g, 0.01mol) was taken in a 250 ml R.B. flask containing ethanol as solvent. Whole reaction mixture was refluxed for about 8-10 hrs. The reaction mixture was cooled and poured into crushed ice to obtained solid product. Filter the solid residue and recrystalized by ethanol.
Yield- 59%, M. P.- 151^{0}C



Synthesis of Metal complex

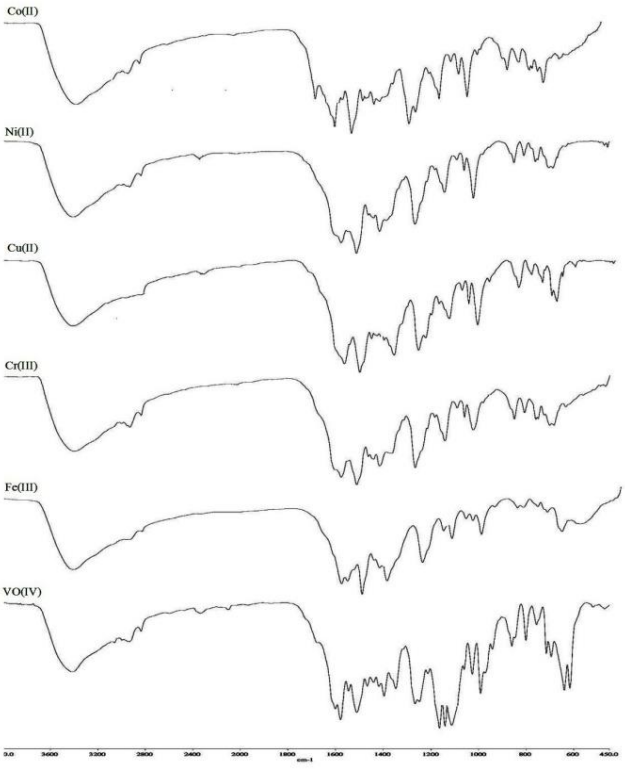
Hot ethanolic solution of metal salts (0.002 M) mixed with the hot ethanolic solution of the ligand (0.002 M) and refluxed for about 10 hrs. The colored solids obtained were filtered, washed several times with petroleum ether and dried over calcium chloride.

III. Results & Discussion

The desired Co(II), Ni(II), Cu(II), Cr(III) Fe(III) and VO(IV) complexes were obtained by the reaction of tridentate ligand with respective metal salts. The yields of the complexes were reasonable. All the complexes are stable and non-hygroscopic in nature, possess high decomposition temperature, insoluble in common organic solvents but soluble in DMSO and DMF.

Table 1: Elemental analysis and kinetic data for ligand and metal complexes

Sr. No.	Ligand	Formula weight g mol^{-1}	Colour	Time of reflux	Elemental Analysis		
					C%	H%	N%
1	$[Co(L)OAc].2H_2O$	587.92	Green	10 h	53.04 (53.12)	4.93 (4.97)	9.57 (9.53)
2	$[Ni(L)OAc].H_2O$	569.67	Red	11 h	54.80 (54.82)	4.75 (4.78)	9.87 (9.84)
3	$[Cu(L)OAc].H_2O$	574.52	Green	10 h	54.31 (54.36)	4.79 (4.74)	9.80 (9.75)
4	$[Cr(L)Cl_2(H_2O)].H_2O$	610.86	Brown	10 h	47.23 (47.19)	4.65 (4.62)	9.20 (9.17)
5	$[Fe(L)Cl_2(H_2O)].H_2O$	560.66	Green	11 h	51.37 (51.41)	3.92 (3.96)	9.95 (9.99)
6	$[VO(L)_2]$	934.76	Red	12 h	61.70 (61.67)	4.77 (4.74)	11.93 (11.99)



The values are in the range 8-12 $\Omega^{-1}cm^2mol^{-1}$ which indicates non-electrolytic nature of all the complexes. The result of elemental analysis of ligand and its complexes are in good agreement with those required by the proposed formulae giving in Table No 1. The analytical data of the complexes confirms 1:1 metal to ligand stoichiometry.

^{1}H NMR spectra of ligand

The ^{1}H NMR spectrum of Schiff base ligand (LH) was recorded to confirm its structure and it shows following signals. ^{1}H NMR (DMSO) δ ppm: 11.90(s, 1H, phenolic OH), 2.2(S, 3H, methyl), 5.23-5.29(dd,1H,CH Pyrazoline), 3.43-3.49(dd,1H, CH_2 Pyrazoline), 3.17-3.22(dd,1H, CH_2 Pyrazoline); 7.7(m, 10H, aromatic) [11-12].

IR Spectra

The IR spectrum of free Schiff base ligand HMDA shows strong and broad band at 3370 cm^{-1} assigned for ν(phenolic OH) vibration, Other bands at 1649, 1589 and 1423cm^{-1} corresponds to ν(C=O), ν(C=N) and ν(C-O) phenolic stretching vibrations respectively. On comparing IR spectrum of ligand with its metal complexes it was observed that the band due to intramolecular hydrogen bonded O-H disappeared in the spectra of all metal complexes indicating the involvement of phenolic O-H in coordination with the metal ion. This was again proved due to upward shift of ν(C-O) phenolic stretching frequency by 8-21 cm^{-1} in the spectra all the metal complexes. The band due to azomethine linkage ν(C=N) shifted to lower frequency (9-24 cm^{-1}) indicates the coordination of azomethine nitrogen to the metal ion.

The strong band due to ν(C=O) in the spectrum of free ligand shifted to lower wave number in the spectra of all the complexes except in VO(IV) confirming the participation of carbonyl oxygen atom in coordination with the central metal ion [6-8]. In the spectrum of VO(IV) complex, this band does not show any shift indicating non-involvement of carbonyl oxygen atom in coordination with VO(IV). The new weak bands in the range of 453-456 cm^{-1} and 470-478 cm^{-1} are assigned to ν(M-N) and ν(M-O) respectively.

Table 2: IR spectral data for Schiff base ligand and its metal complexes

Sr. No	Compound	ν(O-H) hydrogen bonded	ν(C=N) imine	ν(C=O) imine	ν(C-O) phenolic	ν(M-O)	ν(M-N)
1	HMDA (LH)	3370	1590	1649	1423	--	--
2	$[Co(L)OAc].2H_2O$	--	1567	1641	1439	478	453
3	$[Ni(L)OAc].H_2O$	--	1564	1632	1431	472	454
4	$[Cu(L)OAc].H_2O$	--	1579	1643	1442	475	456
5	$[Cr(L)Cl_2(H_2O)].H_2O$	--	1581	1642	1435	470	456
6	$[Fe(L)Cl_2(H_2O)].H_2O$	--	1567	1634	1437	471	455
7	$[VO(L)_2]$	--	1565	1648	1438	472	452

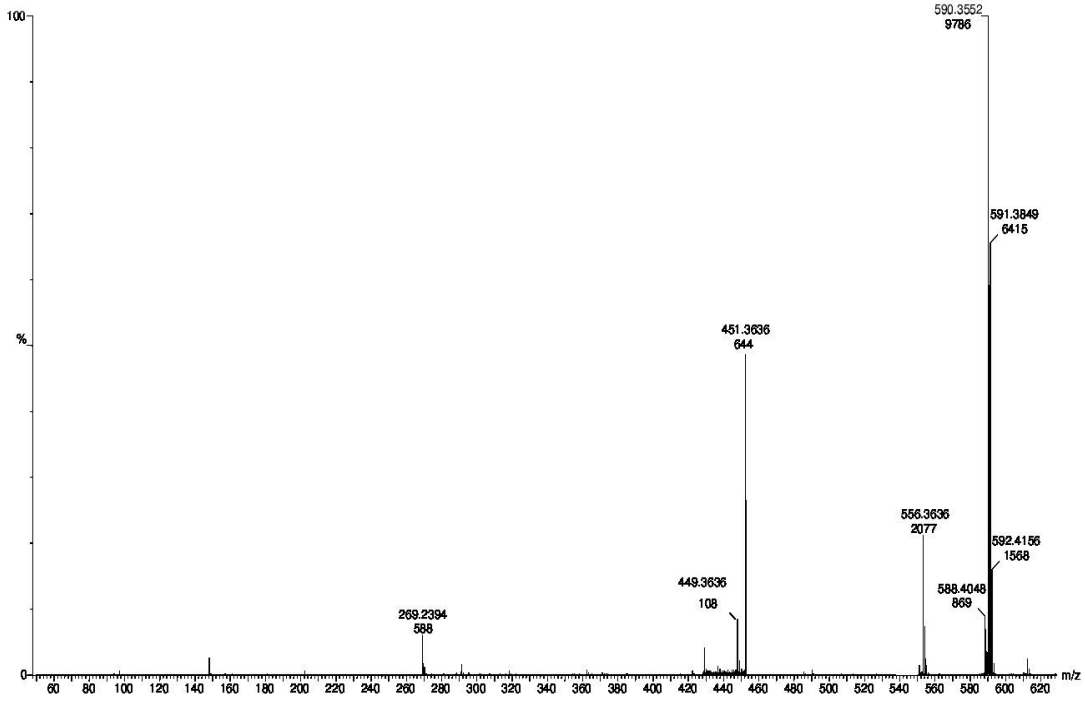


Fig: FAB mass spectrum of Schiff base ligand

Mass Spectra

The FAB mass spectrum of complexes of Schiff base ligand shows molecular ion peaks at m/z Co(II)- 590, Ni(II)- 570, Cu(II)- 573, Cr(III)- 610, Fe(III)- 560 and VO(IV)- 933. Various intense peaks which are obtained by further fragmentation of molecular ion are as follows.

$[Co(L)OAc].2H_2O$- { $[C_{26}H_{25}ClCoN_4O_4]^+$, $[C_{22}H_{17}ClCoN_3O_2]^+$, $[C_{11}H_{11}CoN_2O_2]^+$ }
$[Ni(L)OAc].H_2O$- { $[C_{23}H_{20}ClNiN_4O_2]^+$, $[C_{22}H_{17}ClNiN_3O_2]^+$, $[C_{16}H_{13}ClNiN_3O_2]^+$ }
$[Cu(L)OAc].H_2O$- { $[C_{24}H_{22}ClCuN_4O_2]^+$, $[C_{16}H_{14}CuN_3O_2]^+$, $[C_{17}H_{18}N_4O]^+$, $[C_8H_{11}N]^+$ }
$[Cr(L)Cl_2H_2O].H_2O$- { $[C_{11}H_{11}ClCrN_2O_3]^+$, $[C_{11}H_{11}ClCrN_2O_2]^+$, $[C_6H_6CrN_2O]^+$ }
$[Fe(L)Cl_2H_2O].H_2O$- { $[C_{24}H_{24}Cl_2FeN_4O_3]^+$, $[C_{24}H_{24}ClFeN_4O_3]^+$,$[C_{16}H_{13}ClFeN_3O_2]^+$ }

Table No 3: Thermal kinetic parameter for ligand and its metal complexes

Compounds	Half Decomposition Temp. (^{0}C)	Activation Energy Ea (K/J)		Order of Reaction (n)	Entropy Change ΔS (J/mol/K)	Free Energy Change ΔF (kJ/mol)	Apparent Entropy Change S* (kJ)
		FC	SW				
HMDA	240	17.00	17.13	0.96	-149.11	63.67	-62.24
[Co(L)OAc].2H_2O	500	18.66	17.22	0.97	-148.62	64.56	-25.70
[Ni(L)OAc].H_2O	360	16.04	18.20	0.99	-149.59	62.87	-25.55
[Cu(L)OAc].H_2O	400	18.49	18.26	0.93	-149.55	62.96	-25.74
[Cr(L)Cl_2(H_2O)].H_2O	370	17.36	16.90	0.99	-149.058	63.77	-25.95
[Fe(L)Cl_2.H_2O] H_2O	500	18.13	18.26	0.98	-148.38	64.63	-25.54
[VO($L)_2$].H_2O	430	24.98	24.82	0.93	-145.91	70.65	-25.32

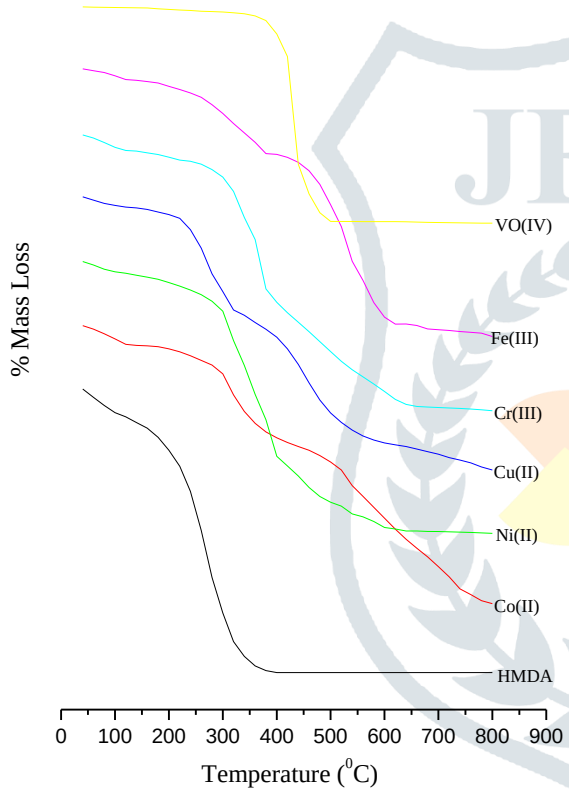


Fig: Thermogram of metal complexes

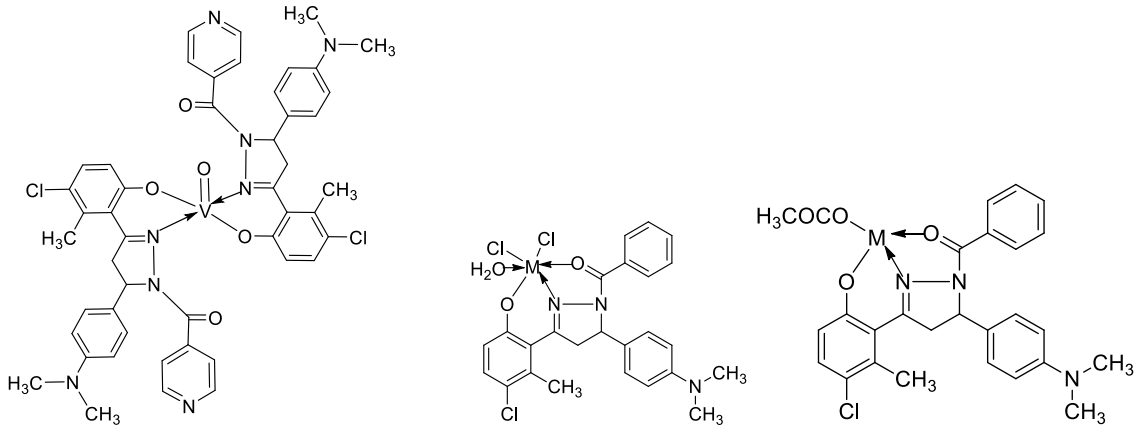
Thermal Analysis

Thermogram of Schiff base ligand and its metal complexes shows that Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) complexes decomposed in three stages while ligand in two stages and VO(IV) complex in one stage. Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) complexes are stable upto 60^{0}C. Above 60^0 C there occurs a loss of one lattice water molecule from Ni(II), Cu(II) and Fe(III) complexes with a mass loss obs/calcd. Ni(II): 3.93/3.16, Cu(II): 3.27/3.13, Fe(III): 3.51/3.21. While Co(II) and Cr(III) complexes shows a loss of two lattice water molecule %wt loss obs/calcd. Co(II): 6.09/6.12, Cr(III): 5.60/5.90.

In case of Cr(III) and Fe (III) complexes there is further loss occurs upto 220^{0}C indicates the presence of coordinate water molecule (wt% obs/calcd. Cr(III): 3.04/2.95, Fe(III): 3.11/3.21. In Co(II), Ni(II) and Cu(II) complexes no mass loss observed upto 220^{0}C showing the absence of coordinated water molecule in these complexes. In VO(IV) complex no mass loss observed upto 260^{0}C indicates the absence of lattice and coordinate water molecule. In all the complexes above 260^{0}C loss of free part of ligand occurs followed by loss of actual coordinate part of ligand [9&10]. All the complexes do not decomposed completely and finally converted into their respective metal oxides. The relative thermal stability on the basis of half decomposition temperature for all the compounds was found to be,

Fe(III) = Co(II) > VO(IV) > Cu(II) > Cr(III) > Ni(II) > HMDA

The decomposition data of complexes and basic kinetic parameter are given in Table No 3.



M= Cr(III) and Fe(III) M= Co(II), Ni(II) and Cu(II)

Fig: Suggested Structure of Metal Complexes

IV. ACKNOWLEDGMENT

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