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SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION STUDY OF CO(II), NI(II) AND CU(II) COMPLEXES OF HETEROCYCLIC SCHIFF BASE LIGAND

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ABSTRACT:

New Schiff base ligand has been synthesized by the condensation of 3-(3-chloro-6-hydroxy-2-methylphenyl)-5-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)(pyridin-4-yl)methanone with isoaniazide in ethanolic solution. This ligand is characterized on the basis of IR, ^{1}H-NMR and Mass Spectra. From this ligand new Co(II), Ni(II) and Cu(II) complexes were synthesized and characterized on the basis of elemental analysis, IR spectra and Electronic 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 is act as tridentate and square planar geometry is suggested to all metal complexes.[i-iii]

KEYWORDS: Schiff base, Metal complexes, IR, Thermal,

INTRODUCTION:

Coordination chemistry and its application have touched upon and made a mark in many areas of science and technology such as analytical chemistry, medicinal chemistry, metallurgy, industrial chemistry, etc.

These coordination compounds are important for various reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. 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.[i-iv]

EXPERIMENTAL

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, 4-methyl benzaldehyde, Co(II)OAc$_2$.6H$_2$O, Ni(II)OAc$_2$.6H$_2$O, Cu(II)OAc$_2$ .6H$_2$O 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. 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-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)(pyridin-4-yl)methanone (HMTA)

A mixture of chalcone 3-chloro-6-hydroxy-2-methylphenyl)-3-(p-tolyl)prop-2-en-1-one (2.86 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- 63%   M. P.- 159^{0}C

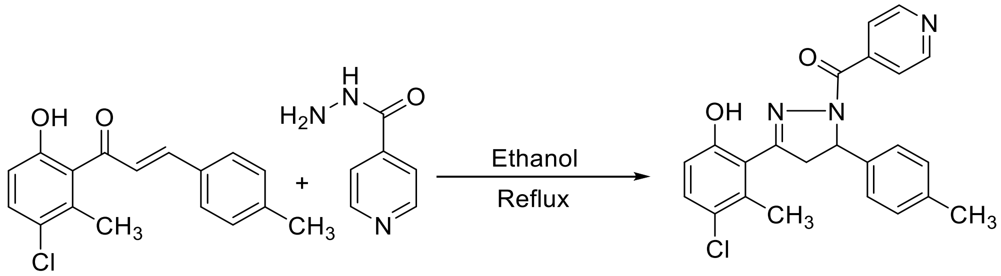

Fig 1: Synthesis of ligand HMTA

Synthesis of Metal Complexes

Hot ethanolic solution of cobalt(II) acetate tetrahydrate (0.002 M) or nickel(II) acetate tetrahydrate (0.002 M) or copper(II) acetate hydrate (0.002 M) mixed with the hot ethanolic solution of synthesized ligands(0.002 M) and refluxed for about 10 hours. The colored solids obtained were filtered, washed several times with petroleum ether and dried over calcium chloride.

Table 1: Analytical Data of ligand HMTA

Sr. No.	**Ligand**	**Molecular Formula**	**Molecular Weight**	**Color**	**Elemental Analysis**			
					C%	**H%**	**N%**	**Cl%**
1	HMTA	$C_{23}H_{20}ClN_3O_2$	405.88	Brown	68.06 **(68.12)**	4.97 **(5.02)**	10.35 **(10.32)**	8.73 **(8.71)**

Table 2: ^{1}H NMR data of ligand HMTA

Signal position (δ ppm)	**Relative number of Protons**	**Inference**	**Multiplicity**
11.49	1H	Singlet	-OH
7.71-8.54	10H	Multiplet	Aromatic Proton
2.24	6H	Singlet	-CH$_3$
3.19	1H	Double doublet	Pyrazoline proton
3.49	1H	Double doublet	Pyrazoline proton
5.21	1H	Double doublet	Pyrazoline proton

RESULTS & DISCUSSION

The desired Co(II), Ni(II) and Cu(II) complexes were obtained by the reaction of ligand HMTA 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.

IR Spectra

A characteristic strong band at 3360 cm^{-1} is in IR spectrum of ligand HMTA ascribed to ν(OH) which is disappeared in all metal complexes, confirming deprotonation and coordination of –OH group to metal ion. At the same time, the strong band at 1422 cm^{-1} due to ν (C-O) phenolic stretching in the ligand has been shifted to higher frequency by (16-23 cm^{-1}) in all metal complexes gives clear support to coordination of oxygen atom to metal ion [69,71].The band due to azomethine vibration in free ligand was appeared at 1599 cm^{-1} shifted to lower frequency in all metal complexes (by 18-29 cm^{-1}) after complexation, indicating the coordination of azomethine nitrogen to metal ion. A strong band in the region 1658 $cm^{-1}$is assigned to carbonyl stretch which is shifted to lower frequency in Co(II), Ni(II) and Cu(II) metal complexes. This indicates that carbonyl oxygen coordinate to these metal ion in complexes. The new bands in the region 432-457 cm^{-1} and 475-505 cm^{-1} found in all metal complexes are assigned to vibration of ν(M-N) and ν(M-O) bands respectively.[vii-ix]

Table 3: Proposed composition, formula weight, color, time of reflux and elemental analysis of HMTA complexes.

Sr. No	Ligand	Formula weight g $mole^{-1}$	Color	Time of Reflux	Elemental Analysis Found (Calcd.) M%	C%	H%	N%	Cl%
1	$[Co(L)OAc].2H_2O$	558.88	Green	10 h	10.75 (10.54)	52.97 (53.73)	4.41 (4.69)	7.67 (7.52)	6.49 (6.34)
2	$[Ni(L)OAc].H_2O$	540.63	Red	11 h	11.19 (10.86)	54.70 (55.54)	4.17 (4.47)	7.95 (7.77)	6.71 (6.56)
3	$[Cu(L)OAc].H_2O$	545.48	Green	10 h	11.98 (11.65)	54.27 (55.05)	4.20 (4.44)	7.87 (7.70)	6.70 (6.50)

Table 4: IR data of ligand and its 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)	H_2O
1	Ligand	3360	1599	1658	1422	--	--	--
2	$[Co(L)OAc].2H_2O$	--	1573	1639	1444	475	453	3420,1610
3	$[Ni(L)OAc].H_2O$	--	1581	1637	1444	505	457	3419,1613
4	$[Cu(L)OAc].H_2O$	--	1577	1640	1438	481	444	3412,1608

Table 5: Magnetic moments and assignments of electronic spectra of complexes.

Sr. No.	Complex	μ_{eff} B.M.	Absorption Band (nm)	(cm^{-1})	Assignment	Λ_M $\Omega^{-1}cm^{-3}mole^{-1}$
1	Co(II)	2.34	376 512	26595 19531	LNCT $^1A_{1g}\rightarrow{}^1B_{1g}$	6.90
2	Ni(II)	Dia	529 598 711	18903 16722 14064	$^1A_{1g}\rightarrow{}^1A_{2g}$ $^1A_{1g}\rightarrow{}^1B_{2g}$ $^1A_{1g}\rightarrow{}^1E_g$	8.32
3	Cu(II)	1.63	302 645 549	33112 15503 18214	LNCT JTD $^2B_{1g}\rightarrow{}^2A_{1g}$	9.41

ELECTRONIC SPECTRA:

The magnetic moment values of Co(II) complex is found to be very closed to 2.32 B. M. corresponding to presence of two unpaired electron that indicating low spin square planar configuration of Co(II) in its complex. UV Spectrum of Co(II) complexes shows band at 26595 and 19531 cm^{-1} assigned to LMCT and $^1A_{1g}\rightarrow{}^1B_{1g}$ transition respectively. These bands clearly suggest square planar geometry for Co(II) complex.

The magnetic moment values of Ni(II) complex is found to($\mu_{eff} = 0$) that confirms the square planar environment around Ni(II) ion. Electronic spectra of all the Ni(II) complexes shows bands at 18903, 16722 and 14064 cm^{-1} attributed to spin forbidden, $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1A_{1g}\rightarrow{}^1B_{2g}$ and $^1A_{1g}\rightarrow{}^1E_g$transition respectively.

Cu(II) complex having magnetic moment value in range 1.63 B. M. respective to single electron and characteristic of square planar geometry. Electronic spectra of Cu(II) complexes display first bands at 33112 cm^{-1}, second broad band in region 15503 cm^{-1} and third at 18214 cm^{-1} assigned to charge transfer, Jahn-Teller distortion and $^2B_{1g}\rightarrow{}^2A_{1g}$ transition respectively suggesting square planar geometry around Cu(II) ion.[iv-vi]

THERMAL ANALYSIS

Thermogram of ligand and its metal complexes shows that complexes Co(II), Ni(II) and Cu(II) complexes shows three stage decomposition pattern while ligand shows two stage decomposition pattern.Co(II), Ni(II) and Cu(II) are stable upto 60^{0}C and further decomposed. From Ni(II) and Cu(II) complexes there occurs a loss of one lattice water molecule at 120^{0}C (Wt. loss obs/calcd. Ni(II): 3.46/3.33, Cu(II): 3.53/3.30, and for Co(II) complexes loss observed corresponding to two lattice water molecule at the same temperature (Wt. loss obs/calcd. Co(II): 6.40/6.45. The Co(II), Ni(II) and Cu(II) complexes are free with coordinate water molecule as there no weight loss observed further. The complexes do not decomposed completely, at the end of decomposition they are converted to their corresponding metal oxides. The relative thermal stability of all complexes and ligand calculated on the basis of their half decomposition temperature.[x-xii]

Co(II) > Cu(II) > Ni(II) > HMTA

Table 6: Decomposition data of complexes of ligand HMTA

Complexes	Temp. Range (^{0}C)	% Mass Loss **Obs**/Calcd	Probable assignment
[Co(L)OAc].2H_2O	60-120	**6.40**/6.45	2 lattice water
	280-480	**36.39**/35.92	Non-coordinate organic part
	480-700	**34.40**/34.58	Actual Coordinate part
[Ni(L)OAc].H_2O	60-120	**3.46**/3.33	1 lattice water
	220-440	**38.26**/39.89	Non-coordinate organic part
	440-540	**35.88**/35.74	Actual Coordinate part
[Cu(L)OAc].H_2O	60-120	**3.53**/3.30	1 lattice water
	220-480	**39.78**/39.53	Non-coordinate organic part
	480-640	**35.64**/35.41	Actual Coordinate part

Table 6: Thermodynamicdata of ligand HMTA and its complexes.

Compounds	**Half Decomposition Temperature (^{0}C)**	**Activation Energy Ea (kJ/mole)**		**Order of Reaction (n)**	**Entropy Change ΔS (J/mol/K)**	**Free Energy Change ΔF (kJ/mol)**	**Apparent Entropy Change S^* (kJ)**
		FC	**SW**				
HMTA	230	20.52	20.41	0.97	-147.55	66.70	-60.28
[Co(L)OAc].2H_2O	500	17.44	17.29	0.98	-148.90	64.05	-88.77
[Ni(L)OAc].H_2O	460	17.94	18.05	0.96	-148.67	64.47	-88.43
[Cu(L)OAc].H_2O	480	20.37	20.53	0.93	-147.61	66.57	-88.68

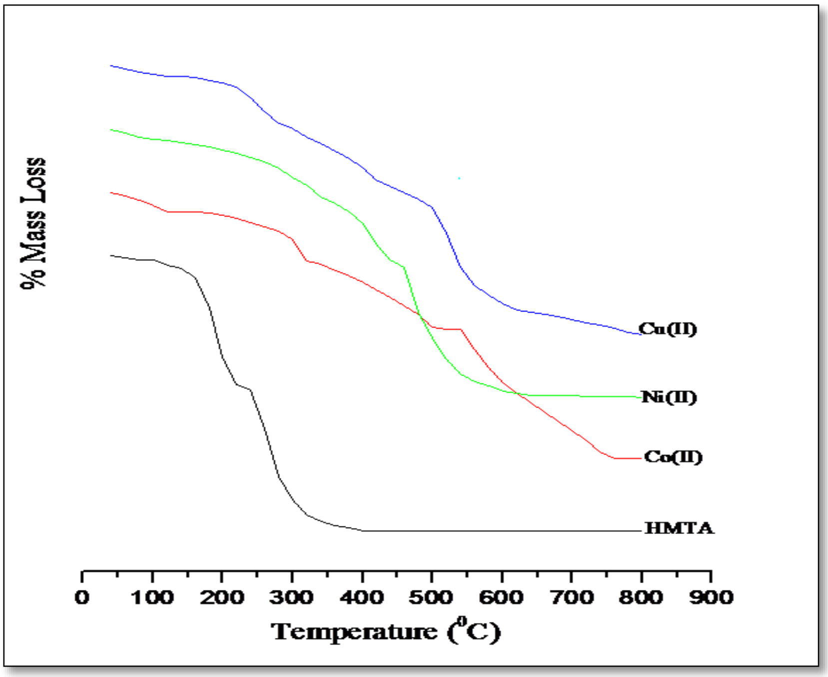

Fig 2: Thermogram of ligand HMTA and its Complexes

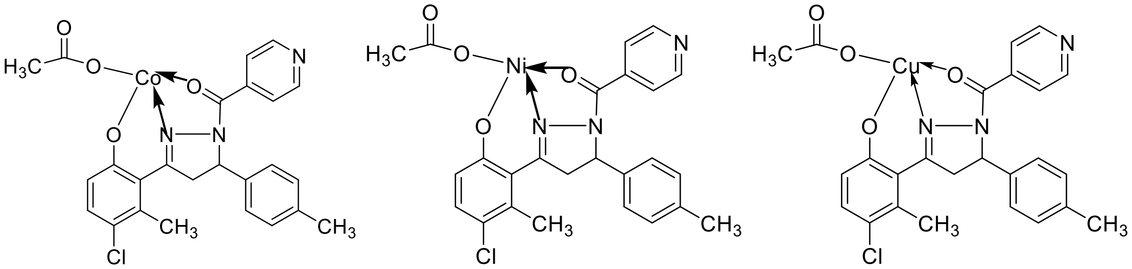

Fig: Suggested Structure of Metal Complexes

CONCLUSION:

A new series of Co(II), Ni(II) and Cu(II) complexes were prepared from the ligand3-(3-chloro-6-hydroxy-2-methylphenyl)-5-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)(pyridin-4-yl)methanone. The synthesized Schiff base act as tridentate towards metal ion. The bonding of ligand to metal is confirmed by spectral, magnetic and thermal studies. The stability of complexes explained and all the kinetic parameters have been evaluated by using Fremann-Caroll and Sharp-Wentworth methods.

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