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# Structural investigation of mixed ligand complexes of Cu (II) and Ni (II) with salicylaldehyde semicarbazone and heterocyclic base

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## ABSTRACT

The mixed ligand complexes of Cu (II) and Ni (II) with schiff base derived from semicarbazone and heterocylic base pyridine have been synthesized and characterized on the basis of elemental analysis, IR, electronic, magnetic moment, conductance and thermogravimetric analysis. The complexes are colored and stable in air, having the general formula M(L)B.X[ metal: Ligand: base.  $H_2O]$ . The thermal behavior of complexes show that the hydrated complexes lose molecule of water first, followed by decomposition of ligand molecules in subsequent steps. The ligand and its complexes have also been tested for their antimicrobial behavior against various microorganisms and all complexes show a good activity.

Keywords: Salicylaldehyde Semicarbazone, Pyridine, TGA, Antimicrobial activity, Conductivity.

### INTRODUCTION

Shiff bases have found wide application in the field of coordination chemistry [1]. Salicylaldehyde amino acid Schiff base complexes [2] have been used to model N-pyridoxylidene amino acid which are considered to be an important intermediate in biological amination process[3]. Thermo chemical properties of Schiff bases have attracted much researcher attention in view of their ability to coordinate metal ions, acting as bidentate or tetradentate ligands in metal chelates involving a NO or N2O2-Schiff-base donor atom sets. The complexes with salen ligands derived from the condensation of salicylaldhyde with diamine are widely studied. [4-7]. Schiff base posses strong ability to form metal complexes[8] which deserve proper attention because of their biological properties[9-10]. The heterobinuclear alkali metal complexes of Cu (ll) and Ni(II) and Schiff base are also biologically active[11] and they enhance activity as compared to their parent ligands.

Copper is an essential element present in all organisms both land and marine and early literature is rich with investigation concerning the presence of copper in different form of life[12]. Several schiff base metal complexes have been studies because of their industrial and biological application[13-15]. Pyridine is the best known heterocyclic nitrogen ligand and its co-ordination chemistry has been studied in details. In view of the biological activity of transition metal complexes, we report the formation of some mixed ligand complexes using pyridine as an additional base and their structural characterization have also been described.

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#### MATERIALS AND METHODS

All the chemicals used were as AR grade obtained from the commercial source. Salicylaldehyde, semicarbazide hydrochloride (Aldrich) DMF, DMSO, ethanol, pyridine (E. merck) sodium acetate (BDH) metal salts in hydrated form (E. merck) were used .

#### Synthesis of the Schiff base ligand

Ligand was prepared by mixing together ethanolic solution of salicylaldehyde (0.1M, 10.5ml) and aquous solution of semicarbazide, (0.1M, 11.5gm) in equimolar ratio. The resulting mixture refluxed for 2-3hrs, when thick, white crystalline precipitate separated out. This was filtered, washed repeatedly with water, alcohol and finally with ether. It was recrystallized from DMF- Alcohol mixture and subsequently, dried over  $CaCl_2$  in a vaccum desicator. The purity of the ligand was checked by TLC, microanalysis, melting point determination, and IR analysis etc. The data are given in Table I. The ligand was insoluble in alcohol, acetone, ether, chloroform but dissolve in DMF and DMSO.

#### Synthesis of complexes

0.005 mol (0.895gm) solution of the ligand was throughly mixed with pyridine 0.005 mol (0.04ml) on a magnetic stirrer. An aquous solution of the metal salt 0.005 mol (0.99gm of Cu (CH<sub>3</sub>COO)<sub>2</sub>. H<sub>2</sub>O or 1.24gm of Ni (CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O was added to the above ligand-pyridine mixture drop wise with constant stirring and heating simultaneously for 2h. The reaction mixture was then refluxed for another 2-3 h on a heating mantle when the complexes began to separate out. The solid complexes were filtered, washed and dried. The relevant data included in the Table I. The yield of the complexes in the above order are 69.5% [Cu (L) M], 76.5%[Ni(L)M].

## Physical measurement

Microanalytical data of the complexes were obtained from Central Drug Research Institute, Lucknow. Standard methods were used for the determination of Cu(II) and Ni(II). The IR spectra of the ligand and their mixed ligand complexes were measured using Perkin-Elmer FT-IR Spectro-Photometer in the range 400-4000Cm<sup>-1</sup>. The electronic spectra were carried with Perkin-Elemer UV Win Lab Spectro Photometer. Magnetic susceptibilities measurement were carried out on a vibration sample magnetometer (VSM). The conductivity measurements were carried at room temperature with "systronics" conductivity meter (model no. 306) using dip type conductivity cell. Thermograviometric analysis were carried out on a Perkin-Elmer analyser at a heating rate  $10^{-0}$  C min<sup>-1</sup> in inert atmosphere of nitrogen.

#### **RESULTS AND DISCUSSION**

All the Cu (II) and Ni (II) complexes are coloured and stable towards air and moisture. They are insoluble in water and common organic solvents, but soluble in DMF, DMSO and dioxane . The ternary complexes react in the molar ration of 1:1:1 to yield mixed ligand complexes of the type  $[M(L)B.H_2O]$  where B= pyridine. The molar conductance values of these complexes is less than  $(650hm^{-1} cm^2 mol^{-1})$  in  $10^{-3}$  M DMF solutions shows their non-electrolytic nature

In order to study the binding mode of schiff base to metal in the complexes IR spectrum of the free ligand was compared with the spectra of the metal complexes.  $SSCH_2$  shows it characteristic absorption bands in the 3380,3060,1720,1500,1590,1010cm-1 region assignable to NH<sub>2</sub>, NH, C=O, C-C (phenolic), C=N, N-N vibration respectively.

Disappearance of the v(C=O) frequency, present at 1720 in the ligand, in complexes spectra and presence of v(C-O) at ~ 1330 only in the complexes [16] confirm that enolization of the ligand, takes place during complex formation.

Positive shift of v (C=N) at ~1590 in the ligand by ~300cm<sup>-1</sup> and presence of new band at ~1600 only in the complexes due to v(C=N-N=C) moiety predicts that azomethine nitrogen takes active part in coordination[17]. Higher shift of v(C-O) in complexes from 1500 in ligand to 1540 in complexes confirm this fact presence of v(M-O) band in the far infrared region in the complex spectra confirm this coordination site[18]. Presence of v (M-O) and v (M-N) band at 530-590cm<sup>-1</sup> and 400-500cm<sup>-1</sup>[19] also pertain it's to the enol structure of ligand in complex and the enolic oxygen as coordination site.

[Ni(SSC)Py.2H<sub>2</sub>O]

Presence of specific bands due to coordinated pyridine are observed at ~1620, 1260, 1040, 630, and 515 cm<sup>-1</sup>.

v(OH) of H<sub>2</sub>O,  $\delta$ H<sub>2</sub>O and y(H<sub>2</sub>O) of coordination is present in the region ~ 3130, 1640,640, respectively in the complex of Ni.

Electronic absorption spectra are often helping in the evaluation of result furnished by other methods of structural investigation. The electron spectral measurement were used for assigning the stereochemistry of metal ions in the complex based on the positions and number of d-d transitions peaks. The electron absorption spectra of the schiff base and its Cu(II) and Ni(II) complexes were recorded at room temperature. Only one broad band is observed at 16,638 cm<sup>-1</sup> in the electronic spectrum of Cu (II) complex assigned to  $2Eg \rightarrow 2A_{\perp}g$  transition which is in conformity with square planner geometry. The appearance of a band at 19,240 cm<sup>-1</sup> due to  $3A_2 g(f) \rightarrow 3T_1 g(p)$  transition favours an octahedral geometry[20] in the Ni complex.

The magnetic moment value of Cu(II) complex 1.92 BM which suggest a square planner complex.

The Ni (II) complex has magnetic moment value of 3.23 BM indicating a octahedral complex.

Thermogravimetric analytical data shows no loss in weight up to ~  $200^{\circ}$ C for Ni-SSC complex. Then gradual weight loss occurs up to  $700^{\circ}$ C at which a final stable product is formed. The weight loss between 240-700°C corresponds to the elimination of two coordinated water molecule. The Cu-complex is stable up to  $160^{\circ}$ C and steep loss of weight occurs up to  $680^{\circ}$ C it shows no coordinates water molecule present in this complex.

The antibacterial studies of ligand and these complexes were determined by disk diffusion method (filter paper disk) against microorganisms klebesiella pneumoniae, staphylococcus aureus and Escherichia coli. Ligand shows mild activity but both the complexes displayed good antibacterial activity. Thus it can be said that complexation increases the antibacterial activity[21-23].

Proposed composition of the complexes	Color	M.P. ( <sup>0</sup> C )	Time of Reflux (hrs)	Yield(%)	Elemental Analysis ( % ) found(Calculated)			Metal	Water	Molar Conductance
					С	Н	Ν	(%)	(%)	(ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
SSCH <sub>2</sub>	White	173	3	88.6	53.60	4.80	22.96			
					(53.93)	(4.49)	(23.59)	-	-	—
[Cu(SSC)Py]	Dark	300	5-6	69.5	43.46	3.51	18.13	19.68		4.224
	Green				(48.8)	(3.75)	(17.52)	(19.86)	-	
[Ni(SSC)Py 2H <sub>2</sub> O]	Light	299	5-6	76.6	37.67	4.56	16.86	14.29	10.0	44 88
		477	.,-0	/0.0						

Table - I Analytical data and general behaviour of mixed ligand in complexes

SSCH<sub>2</sub> - Salicylaldehyte semicarbazone

76.6

Green

#### CONCLUSION

(44.48)

(4.56)

(15.86)

(16.74)

(10.26)

Synthesis of the schiff base ligand salicylaldehyde semicarbazone carried out and it is employed in the preparation of ternary complexes with two positive cation Ni (II) and Cu (II). The primary ligand is the SSCH<sub>2</sub> and the secondary ligand is heterocyclic base pyridine. From the analytical, spectral and antibacterial data, it can be concluded that the synthesized complexes are stable and the biological activity of the ligand is enhanced when it is present in the form of metal complex. In view of the foregoing discussions, the high melting points and insolubility in common organic solvents, also concluded that the three common coordinate sites are phenolic oxygen, azomethine nitrogen and enolic oxygen. It is observed that the complex [Cu(SSCH<sub>2</sub>) Py ] has 4 coordination geometry with no water molecule in its coordination sphere where as the complex [Ni (SSCH<sub>2</sub>)Py.2H<sub>2</sub>O] contain two molecule of water and posses an octahedral geometry.

The structure proposed for these complexes are:



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