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Studies on chelation behaviour of some azomethines with Nickel(II) and Copper(II) transition metals derived from 2- hydroxy-α - naphthaldehyde and thiosemicarbazide hydrochloride

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Abstract

The new complexes of Nickel(II) and Copper(II) with Schiff's bases obtained by the condensation of 2- hydroxy-α - naphthaldehyde dissolved in methanol and aqueous solution of thiosemicarbazide hydrochloride have been synthesized. The complexes formed have been characterized by elemental analysis, molar conductance, magnetic moment, thermogravimetric, electronic and infrared spectral analysis. The complexes were found to be non- electrolytes. Magnetic and spectral data indicate that Ni(II) and Cu(II) complexes are to be of octahedral geometry.

Key word: Schiff's bases, Aldehydes and Ketones, Amines, Transition metals, complexes.

Introduction

Due to interesting structural features and important applications metal complexes with Schiff's bases have occupied an important place in the development of co-ordination chemistry[1-5]. Schiff's bases are organic compounds having an azomethine group (>C=N-) and various studies[6,7] have shown that >C=N- group has considerable biological importance[8-10]. Schiff's base can be considered as useful chelating agent when a suitable functional group such as – OH, -SH, etc. is present sufficiently close to azomethine group.

Experimental

All the chemicals used were BDH, Fluka and E. Merck Anal aR grade. The Schiff's bases were prepared by the condensation of 2-hydroxy-α-naphthaldehyde dissolved in methanol with the solution of thiosemicarbazide hydrochloride in water.

The metal complexes of schiff's bases were prepared by adding methanol and water solution of metal (II) chloride with DMF solution of the ligand respectively and sodium acetate was added to it. Both the solutions were refluxed for about three hours and left to stand overnight. The red Ni (II) and reddish brown Cu (II) complexes precipitate obtained were filtered and washed with ice cold water followed by methanol and ethanol respectively and were made to dry.

Discussion

Schiff's base complexes of Ni(II) and Cu(II) were derived from derivatives of naphthaldehyde and thiosemicarbazide. The newly synthesized complexes are coloured crystalline solids and appear to be stable at atmospheric condition.

The elemental analysis are in good agreement with the presence of two water molecule in Cu(II) complex.

The low molar conductance values of the complexes ascribed to their non-electrolytic nature.

The μ_{eff} value of the Ni(II) and Cu(II) complexes are determined at room temperature and found to be 2.98 and 1.78 BM respectively. This indicates high spin octahedral stereochemistry for these Ni(II)[11] and Cu(II)[12] non-electrolyte complxes.

The interpretation of I.R. spectra is quite complicated due to the presence of various similar groups and hence many absorption bands. However, comparison of the spectral bands of the ligand with those of its Ni(II) and Cu(II) complexes gives some important information regarding the nature of the ligand as well as the co-ordination sites through which metal ion is co-ordinated with the ligand. The band at 3210 cm^{-1} in ligand assignable to phenolic O-H (hydrogen bonded) stretching frequency disappear in the Ni(II) complex, showing deprotonation of phenolic proton. The ligand also shows strong band at 1270 cm^{-1} which may be attributed to the phenolic C-O vibration. A shift of this band to higher frequency (~ 1300 cm^{-1}) in the complex indicate chelation of this ligand to metal ion through phenolic oxygen. The presence of a band near 3255 cm^{-1} in Cu(II) complex may be due to O-H of co-ordinated water molecules. This is further justified by the presence of a band around 1610 cm^{-1} as deformation band of water molecule[13].

The sharp band at ~1565 cm^{-1} in both the Ni(II) and Cu(II) complexes showing co-ordination through the nitrogen atom[14-20]. The ligand band at 1165 cm^{-1} may be assigned to vC=S group which shows downward shifting in mental complexes, indicating participation of this group in co-ordination.

The absorption band at 3390 cm^{-1} due

Table 1.Elemental analysis and general charaterisation of Schiff's base and its complexes with Ni(II) and Cu (II)

S. No.	Name /Molecular formula/Mol.wt.		Colour	MP/DT (0^0C)	% C	%H	%N	%Cl	% M (Metal)	% S	Molar conductance (in Ohm^{-1} cm^2 $mole^{-1}$) solubility	Magnetic moment (in BM)
1.	Ligand	(HN-TS) = ($C_{12}H_{10}N_3OS$) mol.wt. = 244	Crude White	220	57.38	5.27 (4.49)	16.73	-	-	12.65 (13.10)		
2.	Complexes	(Ni(HN-TS)$_2$) mol.wt. = 546.69	Red	258	51.21 (52.66)	4.37 (3.66)	14.69 (15.36)	-	9.79 (10.73)	11.01 (11.74)	19.5 (Non electrolytic)	2.98
3.		[Cu(HN-TS) Cl.2H_2O] mol.wt. = 379	Reddish brown	240	36.27 (37.98)	4.79 (3.69)	10.68 (11.08)	8.75 9.36	15.31 (16.75)	7.83 (8.47)	11.4 (Non electrolytic)	1.78

Table 2. Infra Red Spectral data (in cm^{-1}) of [Ni(HNTS)$_2$] and [Cu(HNTS)$_2$ Cl.2H_2O]

S.N.	Name of compound		ν(C=N)	ν(C=S)	ν(O-H)	ν(C-O)	ν(M-N)	ν(M-O)	ν(M-S)
1.	Ligand	(HN-TS)	1590	1165	3210	1270			
2.	Complex	Ni(HN-TS)$_2$	1575	1145	-	1290	545	485	335
3.		(Cu(HN-TS) Cl.2H_2O	1575	1140	3255	1295	545	505	305

On the basis of above facts the octahedral geometry could be assigned for these Bis(2-hydroxy- -naphthyl thiosemicarbazone) Nickel (II) and Monochloridodiaqua (2-hydroxy- -naphthyl thiosemicarbazone) Copper (II) complexes.

to vN-H group in the free ligand remains unaltered in the complexes indicating non-participation of this group in co-ordination.

Thus, we come to a conclusion that the ligand, 2-hydroxy-α - naphthyl thiosemicarbazone. (HN-TS) behaves as a tridentate ligand for the mental ions, co-ordinating through phenolic oxygen(C – O), (I); nitrogen atom of a azomethine group C=N, (II) and ketonic sulphur of C=S, (II), of eholic group. Similar kind of situation has been reported by S.K. Thampy and others[21 - 24].

This ligand is biprotonic in both Ni (II) and Cu(II) complexes.

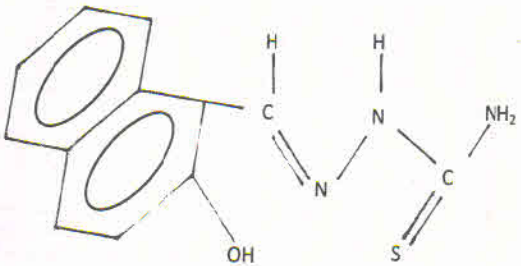

Fig. 1.0
2 – hydroxyl nephthyl thiosemicarbazone

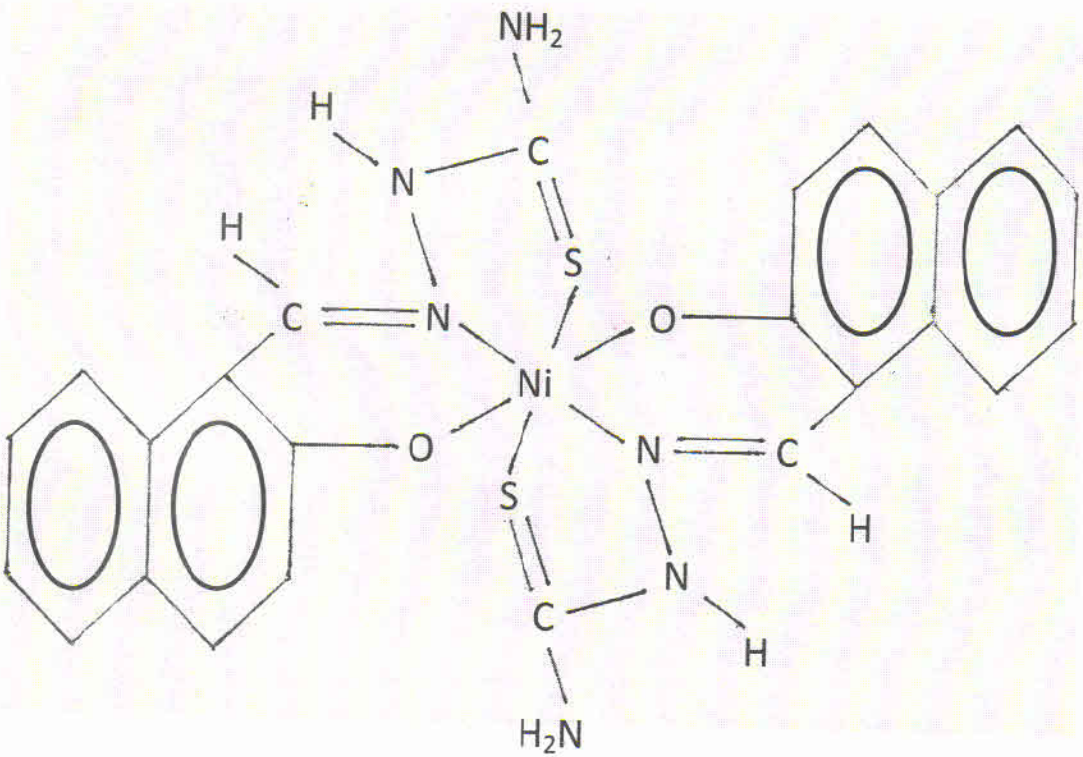

Fig. 2
Bis 2 – hydroxy naphthyl thiosemicarboze Ni(II)

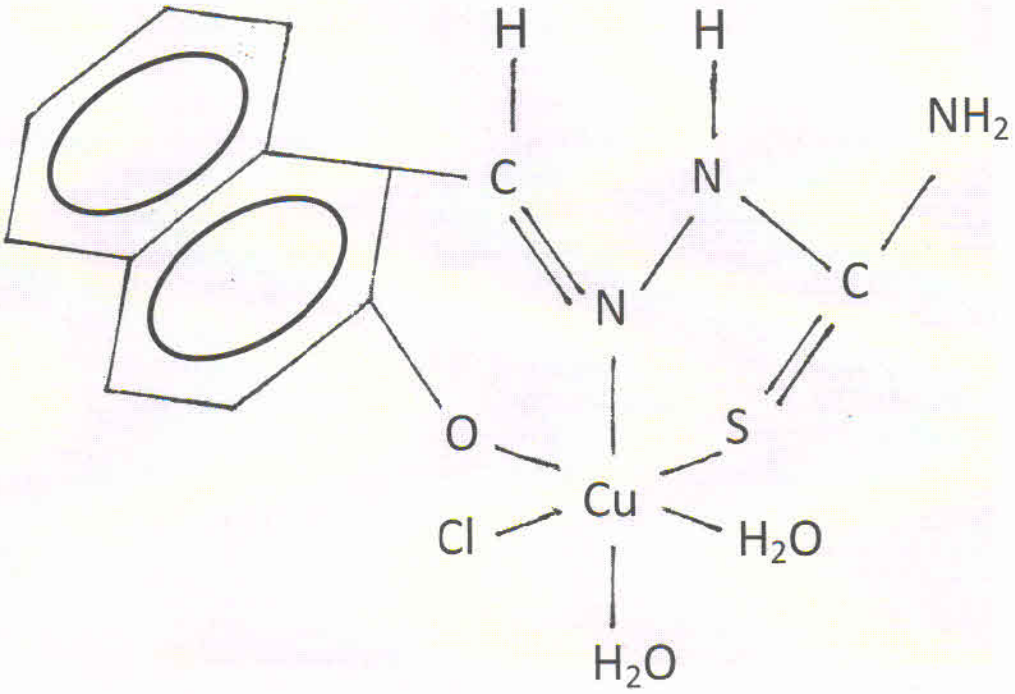

Fig. 3
Di aqua monochlorido Bis (2 – hydroxy naphthyl thiosemicarboze) Cu (II)

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