

# Anionic Complexes of Nickel (II) and Copper (II) Containing Schiff Bases

Savita<sup>1</sup>, Kumari Sweeti<sup>2</sup>, Rajesh Kumar<sup>3</sup> and Priyanka Priya<sup>4</sup>

Department of Chemistry

<sup>1 and 2</sup> Ph.D. (Chemistry), B. N. Mandal, University, Madhepura (Bihar),

<sup>3</sup>Assistant Professor, B. P. S. College, Desari (Vaishali),

<sup>4</sup> Ph.D. (Chemistry), B. R. A. Bihar University, Muzaffarpur (Bihar)

**ABSTRACT:** A series of complexes of the type  $M'[M(B.B')]$  where  $M =$  tetramethyl ammonium ( $Me_4N^+$ ) or cetylpyridinium chloride ( $Cepy^+$ ),  $M = Ni(II)$ ,  $Co(II)$ ,  $BB' =$  bi-negative tridentate ligands such as salicylaldehyde thiosemicarbazone, salicylaldehyde *o*-amino phenol and salicylaldehyde anthranilic acid have been isolated in non-aqueous medium. The compounds were characterised on the basis of their elemental analyses, molecular weight, conductivity, magnetic moment, infrared and electronic spectra data.

Under the present investigation, an attempt has been made to study the preference and stabilisation of coordination number and stereochemistry by nickel (II) and copper (II) when provided with N, O, S donor bi-negative tridentate chelates.

**Synthesis of ligands:** All the chemicals used were of AR grade. The Schiff bases salicylaldehyde semicarbazone (Stse), salicylaldehyde *O*-amino phenol (Sal, OAP) and salicylaldehyde anthranilic acid (Sal.anth. acid) were prepared by literature method.

**Synthesis of complexes:** An ethanolic solution of tetramethyl ammonium chloride or cetylpyridinium chloride was mixed with excess of an ethanolic solution of salicylaldehyde thiosemicarbazone/salicylaldehyde *o*-amino phenol/salicylaldehyde anthranilic acid in 2:2 molar ratio and the resulting solution was added to nickel(II) chloride or copper(II) chloride in ethanol medium with constant stirring. The resulting solution was neutralized with  $NH_3$  and refluxed for 0.5 h. The solid products thus formed were separated out and were suction filtered, washed with ethanol, ether and dried in vacuum.

Metals and sulphur were estimated by standard methods. IR spectra were recorded on a Shimadzu-408 and electronic spectra were recorded on an Elico-CL-54 spectrophotometer. The conductance measurement was carried out in  $Ca. 10^{-3}$  M solution of DMF with Systronics-303 direct reading conductivity meter. Magnetic susceptibility measurements were carried out at room temperature by a Gouy balance. Diamagnetic corrections were made by Pascal's constants.

The compounds are microcrystalline in nature and are quite stable. They do not possess sharp melting points and decompose above  $200^\circ C$ . The complexes are soluble in dimethyl formamide. The analytical data revealed a stoichiometry of 2: 1:2. The molar conductance values in DMF [ $20-50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ] show that the compounds are 1: 1 electrolytes.

Salicylaldehyde thiosemicarbazone behaves as a dibase tridentate ligand.

Deprotonation of phenolic  $-OH$  and coordination through oxygen is indicated by the occurrence of  $\nu(C-O)$  at  $1340-1320 \text{ cm}^{-1}$ . A sharp band at  $1600 \text{ cm}^{-1}$  indicates the coordination of the chelate through azonmethine nitrogen atom. The Schiff base has undergone keto  $\rightleftharpoons$  enol tautomerism in alkaline medium. Hence, deprotonation of  $C-SH$  group is indicated by the absence of bands in the region  $2800-2650 \text{ cm}^{-1}$ . An additional band due to  $\nu(C=N)$  (found by thio-enolisation of the Schiff base) appearing at  $1470 \text{ cm}^{-1}$  indicates the thio-enol co-ordination of the ligand. Hence, it can be concluded that the ligand salicylaldehyde thiosemicarbazone is coordinated as a bi-negative tridentate (O, N, S) chelate.

The IR spectra of salicylaldehyde anthranilic acid shows a broad band in the region  $3400-3200 \text{ cm}^{-1}$  due to  $\nu(OH)$  mode of carboxylic and phenolic OH groups. A sharp band at  $ca. 1680 \text{ cm}^{-1}$  is found to be

absents in the complexes indication the absence of free—COOH group in the complexes.  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  vibrations of the  $\text{COO}^-$  group in the complexes appeared at  $1865\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  respectively.  $\Delta\nu$  value of  $225\text{ cm}^{-1}$  indicates unidentate coarboxylate co-ordination. The deprotonation of phenolic OH and coordination through oxygen is indicated by the occurrence of  $\nu(\text{C—O})$  at  $1320\text{--}1300\text{ cm}^{-1}$ . The sharp band at  $1600\text{ cm}^{-1}$  of the ligand was found to be shifted to  $1600\text{ cm}^{-1} \pm 10\text{ cm}^{-1}$  on complexation, indicating the coordination of the chelate through azomethine nitrogen. Hence, it can be concluded that the ligand salicylaldehyde anthranilic acid is coordinated as a binegative tridentate (O, N, O) chelate.

The ligand salicylaldehyde *o*-amino phenol show a strong band at  $1630\text{ cm}^{-1}$  due to azomethane  $\nu(\text{C=N})$  linkage. This band was found to be shifted to lower energy by  $20\text{--}10\text{ cm}^{-1}$  in the complexes indication co-ordination through azomethine nitrogen. In the complexes, the  $\nu(\text{C—O})$  is indicated by a band at  $1530 \pm 10\text{ cm}^{-1}$  indicating the coordination of phenolic oxygen atom to the metal ion. The Schiff base exhibits a medium intense band at  $2700\text{ cm}^{-1}$  due to intra-molecular hydrogen bond (OH). The absence of this band in the complexes indicates the deprotonation of the phenolic groups and coordination of oxygen atoms to metal ion. Thus, the ligand salicylaldehyde *o*-amino phenol acts as binegative tridentate ligand (ONO).

In addition to these bands, a sharp band obtained at  $3060\text{ cm}^{-1}$  in the hexachlorobutadiene mull is assigned to the N—H stretching of cetylpyridinium complexes. The presence of (Me<sub>4</sub>N) group is indicated by the appearance of bands at  $940\text{ cm}^{-1}$  and  $760\text{ cm}^{-1}$  in the complexes.

The  $\mu_{\text{eff}}$  values of copper (II) complexes lie in the range (1.8-2.3 B.M), as expected for octahedral compounds. For the Ni (II) complexes, the  $\mu_{\text{eff}}$  values are in the range (2.6-3.5 B.M) which is consistent with a  $3d^8$  configuration.

The studies of the electronic spectra of copper (II) complexes are consistent with the octahedral nature of the compounds. A broad band obtained at  $15384\text{--}16666\text{ cm}^{-1}$  is due to  ${}^3E_g \rightarrow {}^2T_{2g}$  transition for distorted octahedral stereochemistry for the hexa-coordinated complex of Ni(II), the electronic spectral bands are found at  $12900\text{ cm}^{-1}$  ( $\nu_1$ ),  $15300\text{ cm}^{-1}$  ( $\nu_2$ ) and  $22222\text{ cm}^{-1}$  ( $\nu_3$ ). These may be assigned to the transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (f),  ${}^3A_{2g} \rightarrow {}^3A_{1g}$  (F) and  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (P) respectively. These values are in agreement with octahedral geometry for the complexes.

#### Physical and Analytical Data of Cu(II) and Ni(II) Complexes

Compounds (colour)	m.p (°C)	% Analysis Found(Calcd.)		$\mu_{\text{eff}}$ (B.M. )	$\Lambda_m \Omega^{-1}\text{ cm}^2$ $\text{Mol}^{-1}$
		M	S		
[Me <sub>4</sub> N] <sub>2</sub> [Cu(Stsc) <sub>2</sub> ] (Reddish brown)	>200	10.12 (10.58)	10.02 (10.68)	2.2	50.02
[Me <sub>4</sub> N] <sub>2</sub> [Cu(Sal. OAP) <sub>2</sub> ] (Brown)	>200	9.50 (10.00)	--	1.8	21.14
[Me <sub>4</sub> N] <sub>2</sub> [Cu(Sal.anth.acid) <sub>2</sub> ] (brown)	>200	8.80 (9.20)	--	2.1	30.09
[Cepy] <sub>2</sub> [Cu(Stsc) <sub>2</sub> ] (Green)	>200	5.50 (6.00)	5.75 (6.05)	2.2	30.00
[Copy] <sub>2</sub> [Cu(Sal. OAP) <sub>2</sub> ] (Blue)	>200	5.20 (5.80)	--	1.9	20.01
[Cepy] <sub>2</sub> [Cu(Sal.anth.acid) <sub>2</sub> ] (brown)	>200	5.00 (5.50)	--	2.3	30.22
[Me <sub>4</sub> N] <sub>2</sub> [Ni(Stsc) <sub>2</sub> ] (Green)	>200	9.20	10.23	2.6	30.70

[Me <sub>4</sub> N] <sub>2</sub> [Ni(Sal. OAP) <sub>2</sub> ] (Green)	>200	(9.85) 8.91	(1076) --	2.9	40.09
[Me <sub>4</sub> N] <sub>2</sub> [Ni(Sal.anth.acid) <sub>2</sub> ] (brown)	>200	(9.32) 7.90	--	3.5	30.00
[Cepy] <sub>2</sub> [Ni(Stsc) <sub>2</sub> ] (brown)	>200	(8.56) 5.10	5.72	2.8	20.03
[Cepy] <sub>2</sub> [Ni(Sal. OAP) <sub>2</sub> ] (Red)	>200	(5.50) 6.00	(6.08) --	3.0	40.02
[Cepy] <sub>2</sub> [Ni(Sal.anth.acid) <sub>2</sub> ] (Green)	>200	(6.69) 4.90	--	2.6	20.06
		(5.13)			

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