NOTE

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

Ms MINATI SATPATHY and B. PRADHAN*
Department of Chemistry
Regional Engineering College, Rourkela-769 008, India

A series of complexes of the type M′[M(BB′)] where M = tetramethyl ammonium (Me_4N^+) or cetylpyridinium chloride ($Cepy^+$), M = Ni(II), Cu(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 spectral 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 (Stsc), 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 neutralised 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.[1] 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.[2]

The compounds are microcrystalline in nature and are quite stable. They do not possess sharp melting points and decompose above 200°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 ohm^{-1} cm^2 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 v(C—O) at 1340–1320 cm^{-1}. A sharp band at 1600 cm^{-1} indicates the coordination of the chelate through azomethine nitrogen atom. The Schiff base has undergone keto$\rightleftarrows$ enol tautomerism in alkaline medium. Hence, deprotonation of C—SH group is indicated by the absence of bands[3] in the region 2800–2650 cm^{-1}. An additional band due to v(C=N) (found by thio-enolisation of the Schiff base) appearing at 1470 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 cm^{-1} due to v(OH) mode of carboxylic and phenolic OH groups. A sharp band at *ca.* 1680 cm^{-1} is found to be absent in the complexes indicating the absence of free —COOH group in the complexes.[4, 5] v_{asym} and v_{sym} vibrations of the COO$^-$ group in the complexes appeared at 1865 cm^{-1} and 1640 cm^{-1} respectively. Δv value of 225 cm^{-1} indicates unidentate carboxylate co-ordination.[6, 7] The deprotonation of phenolic OH and coordination through oxygen is indicated by the occurrence of v(C—O) at 1320–1300 cm^{-1}. The sharp band at 1600 cm^{-1} of the ligand was found to be shifted to 1600 cm^{-1} ± 10 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 shows a strong band at 1630 cm^{-1} due to azomethane v(C=N) linkage. This band was found to be shifted to lower energy by 20–10 cm^{-1} in the complexes indicating co-ordination through azomethine nitrogen. In the complexes, the v(C—O) is indicated by a band at 1530 ± 10 cm^{-1} indicating the coordination of phenolic oxygen atom to the metal ion.[8] The Schiff base exhibits a medium intense band at 2700 cm^{-1} due to intra-molecular hydrogen bond (OH).[8] 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 cm^{-1} in the hexachlorobutadiene mull is assigned to the N—H streching of cetyl-pyridinium complexes.[9] The presence of (Me$_4$N) group is indicated by the appearance of bands at 940 cm^{-1} and 760 cm^{-1} in the complexes.[10]

The μ_{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 μ_{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 15384–16666 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 cm^{-1} (v_1), 15300 cm^{-1} (v_2) and 22222 cm^{-1} (v_3). These may be assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$(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.)		μ_{eff} (B.M.)	$\Lambda_m \, \Omega^{-1}$ $cm^2 \, mol^{-1}$
		M	S		
[Me$_4$N]$_2$[Cu(Stsc)$_2$] (Reddish brown)	>200	10.12 (10.58)	10.02 (10.68)	2.2	50.02
[Me$_4$N]$_2$Cu(Sal.OAP)$_2$] (Brown)	>200	9.50 (10.00)	—	1.8	21.14
[Me$_4$N]$_2$[Cu(Sal.anth.acid)$_2$] (Brown)	>200	8.80 (9.20)	—	2.1	30.09
[Cepy]$_2$[Cu(Stsc)$_2$] (Green)	>200	5.50 (6.00)	5.75 (6.05)	2.2	30.00
[Cepy]$_2$[Cu(Sal.OAP)$_2$] (Blue)	>200	5.20 (5.80)	—	1.9	20.01
[Cepy]$_2$[Cu(Sal.anth.acid)$_2$] (Brown)	>200	5.00 (5.50)	—	2.3	30.22
[Me$_4$N]$_2$[Ni(Stsc)$_2$] (Green)	>200	9.20 (9.85)	10.23 (10.76)	2.6	30.70
[Me$_4$N]$_2$[Ni(Sal.OAP)$_2$] (Green)	>200	8.91 (9.32)	—	2.9	40.09
[Me$_4$N]$_2$[Ni(Sal.anth.acid)$_2$] (Brown)	>200	7.90 (8.56)	—	3.5	30.00
[Cepy]$_2$[Ni(Stsc)$_2$] (Brown)	>200	5.10 (5.50)	5.72 (6.08)	2.8	20.03
[Cepy]$_2$[Ni(Sal.OAP)$_2$] (Red)	>200	6.00 (6.69)	—	3.0	40.02
[Cepy]$_2$[Ni(Sal.anth.acid)$_2$] (Green)	>200	4.90 (5.13)	—	2.6	20.06

REFERENCES

1. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS, London, pp. 474, 497, 436 (1961).

2. P.W. Selwood, Magneto Chemistry, 2nd Edn., pp. 78, 92, 93 (1956).

3. S.N. Poddar and N. Saha, *J. Indian Chem. Soc.*, **52**, 57 (1975).

4. R.M. Silverstein, G.C. Besseler and T.C. Morill, Spectrophotometric Identification of Organic Compounds, John Wiley and Sons, New York (1981).

5. L.J. Bellamy, Advances in Infrared Group Frequencies. Methuen, London (1968).

6. U. Casselleto, P.A. Vigato and M. Vidali, *Canad Chem. Rev.* **26**, 85 (1978).

7. G.B. Deacan and R.J. Philips; *Canad. Chem. Rev.*, **33**, 227 (1988).

8. G.C. Besseler and R.M. Silverstein, Spectrophotometric Identification of Organic Compounds, 3rd Edn., John Wiley and Sons Inc., New York.

9. A.K. Das and D.V. Ramana Roy, *Chem. & Ind.*, **186** (1973).

10. _____, *J. Indian Chem. Soc.*, **48**, 823 (1971).