Asian Journal of Chemistry Vol. 9, No. 1 (1997), 75–77

Mixed Chelate Complexes of Nickel(II) and Copper(II)

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

Mixed ligand complexes of Ni^{2+} and Cu^{2+} containing bis-salicylaldehyde ethylene diamine or salicylaldehyde semicarbazone and neutral monodentate ligands of the type [Cu(SB)L_1], [Cu(SB)L_2], [Cu(SB)L_3] and [Ni(SB)L_1], [Ni(SB)L_2] and [Ni(SB)L_3] were synthesised. The compounds were characterised on the basis of their elemental analyses, molecular weight, conductivity, magnetic moment, infrared and electronic spectral data.

INTRODUCTION

In the present investigation, bi-negative tridentate or tetradentate Schiff bases and neutral monodentate ligands have been reacted with divalent nickel and copper. The preference of coordination number and stabilisation of stereochemistry of Ni(II) and Cu(II) when provided with such a mixed ligand field have been studied.

EXPERIMENTAL

Synthesis of Ligands: All the chemicals used were of AR grade. The Schiff bases bis-salicylaldehyde ethylene diamine and salicylaldehyde semicarbazone were prepared by literature method[1].

Synthesis of complex To a weighed amount of $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ was added a calculated amount of bis-salicylaldehyde ethylene diamine/salicylaldehyde semicarbazone in 1 : 1 molar ratio in ethanolic medium and stirred vigorously. To this, ethanolic solution of γ-picoline/pyridine/γ-picoline-N-oxide were added in excess with constant stirring. The complexes so formed were suction filtered, washed with ethanol and dried in vacuum.

Metals were estimated by standard methods[2]. I.R. spectra were recorded on a Shimadzu 408 and electronic spectra were recorded on a Elico-CL-54 spectrophotometers. The conductance measurement was carried out in *ca.* 10^{-3} M solution of nitrobenzene 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[3] constants. The molecular weights were determined by Rast's biphenyl method.

RESULTS NAD DISCUSSION

The compounds formed are micro-crystalline solids. The analytical data are consistent with the formulation of the compounds. The conductance measurement values [2.1–6.2 ohm^{-1} cm^2 mol^{-1}] show that the compounds are non-electrolytes. The molecular weight measurement indicates that the compounds are monomeric.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compounds (colour)	m.p. (°C)	M(%) Found/Calcd.	μ_{eff} (B.M.)	Λ_m (Ω^{-1} cm^2 mol^{-1})
[Cu(Sal$_2$en)(γ-Pic)] (Dirty green)	>200	14.60 (15.02)	2.31	5.706
[Cu(Sal$_2$en) (γ-Pic-NO)] (Deep green)	>200	10.98 (11.59)	2.65	4.530
[Cu(Sal$_2$en)(Py)$_2$] (Bottle green)	>200	12.83 (13.02)	2.37	6.229
[Cu(Sal.sc)(γ-Pic)$_3$] (Light green)	>200	12.26 (12.70)	1.89	5.012
[Cu(Sal.sc)(γ-Pic-NO)$_3$] (Green)	>200	11.07 (11.65)	1.78	4.932
[Cu(Sal.sc)(Py)$_3$] (Light blue)	>200	12.79 (13.26)	1.99	6.118
[Ni(Sal$_2$en)(γ-Pic)] (Orange)	>200	13.12 (13.98)	2.24	5.695
[Ni(Sal$_2$.en)(γ-Pic-NO)$_2$] (Brick red)	>200	10.23 (10.80)	2.18	4.524
[Ni(Sal$_2$.en)(Py)$_2$] (Buff)	>200	11.92 (12.14)	2.40	2.160
[Ni(Sal.sc)(γ-Pic)$_3$] (Blue)	>200	11.62 (11.85)	2.34	2.671
[Ni(Sal.sc)(Py)$_3$] (Sky blue)	>200	11.93 (12.37)	3.37	2.931

Infrared spectra: The Schiff base bis-salicylaldehyde ethylene-diamine exhibits a sharp band at *ca.* 1630 cm^{-1} due to ν(C═N). This band shifts to a lower frequency by 5–15 cm^{-1} on complexation which is due to the reduction of electron density in the azomethine links. The absence of stretching and bending modes of OH groups in spectra indicated the deprotonation of the ligands in the complexes. These observations were supported by the shift of ν(C—O) of free ligands from 1300 cm^{-1} to lower wave number of 1285 ± (5–15) cm^{-1}. Thus the Schiff base bis-salicylaldehyde-ethylene-diamine behaves as bifunctional tertradentate (ONNO)[4–6] ligands. The Schiff base salicylaldehyde semicarbazone exhibits a sharp band at *ca.* 1620 cm^{-1} due to ν(C═N). The complexes with this ligand show a downward shift by (5–15) cm^{-1}. This is due to the reduction of electron density in the azomethine links. The absence of stretching and bending modes of OH group in spectra indicated the deprotonation of the ligands in the complexes. These observations were supported by the shift of ν(C—O) of the free ligand from *ca.* 1380 cm^{-1} to lower wave number by (5–15) cm^{-1}. Thus, the Schiff base salicylaldehyde semicarbazone is coordinated through its two oxygen and one nitrogen atoms[7, 8]. The presence of coordinate γ-picoline and pyridine in the complexes was known from their ν(C—C) + ν(C—N) bands found at *ca.* 1550

cm^{-1} for salicylaldehyde ethylene diamine and *ca.* 1450 cm^{-1} for salicylaldehyde semicarbazone. The shifting of ν(N—O) band of γ-picoline-N-oxide from *ca.* 1215 cm^{-1} band to *ca.* 1190 cm^{-1} and δ(N—O) band from *ca.* 840 cm^{-1} to *ca.* 850 cm^{-1} indicated its bending to the metal ions through the oxygen atom[9].

Magnetic Moments and Electronic Spectra

The five coordinated nickel(II) compounds exhibited normal magnetic moment values where as the six coordinated nickel(II) complexes exhibited lower magnetic moment values[10] as observed for Schiff base compounds. The magnetic moment values for copper(II)[11] are consistent with that of $3d^9$ system.

One [Cu(SB)L] compound was found to exhibit absorption band at 16129 cm^{-1} which supports the pentaco-ordinated stercochemistry[12, 13]. Bands due to other Cu(II) compounds obtained at 13698 cm^{-1}, 17699–17121 cm^{-1}, 23892–22201 cm^{-1} support octahedral configuration.[14–16]

One [Ni(SB)L] compound exhibits absorption bands in the region 13245–16393 cm^{-1} which support penta-coordinated geometry.[17] Absorption bands due to the four $[Ni(SB)L_2]$ compounds obtained at 13386 cm^{-1}, 17543 cm^{-1} and 23809–21881 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^2T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, for octahedral stereochemistry for the compounds[18].

Thus, through this communication penta-coordinated Ni(II), Cu(II) and hexa coordinated Ni(II), Cu(II) compounds containing bifunctional tetradentate Schiff base and tridentate Schiff base and netural N, O donor ligands are reported.

REFRENCES

1. M. Tripathy, R.V. Singh and J.P. Tandon, *Indian J. Chem.*, **20A**, 90 (1981).
2. A.I. Vogel, A. Text Book of Quantitative Inorganic Analysis, ELBS, London, pp. 479, 497, 436 (1961).
3. P.W. Selwood, Magneto Chemistry, 2nd Ed., pp. 78, 92, 93 (1956).
4. K. Kawakani, Miya-uchi and T. Tanaka, *J. Inorg, Nucl. Chem.*, **33**, 3773 (1971).
5. K. Uno and A.E. Martelli, *J. Phys. Chem.*, **60**, 1270 (1956).
6. T.N. Srivastava, A.K. Chauhan and G.K. Mehrotra, *Indian J. Chem.*, **24A**, 708 (1985).
7. S. Kato, A. Hori, H. Shiotone and M. Mizula, *J. Organometal. Chem.*, **82**, 223 (1974).
8. B. Samual, R. Snaith, C. Summerford and K., Wade, *J. Chem. Soc. (A)*, **43**, 1755 (1981).
9. I.S. Ahuja and R. Singh, *J. Inorg. Nucl. Chem.*, **35**, 561 (1973).
10. Richard L. Carlin, *Transition Metal Chem.* (A series of advances), **4**, 200 (1968).
11. R.L. Dutta and M.M. Hossain, *Indian. J. Chem.*, **23A**, 30 (1984).
12. T.R. Rao, M. Sahaya and R.C. Agarwal, *Indian J. Chem.*, **23A**, 214 (1984).
13. P.S. Rakita, S.J. Kopperi and J.P. Fackler, *J. Inorg, Nucl. Chem.*, **30**, 2139 (1968).
14. M. Kelton, A.B.P. Lever and B.S. Ramaswamy, *Can. J. Chem.*, **48**, 3185 (1970).
15. B. Sing, P.L. Maurya, B.V. Agarwal and A.K. Dey, *J. Indian Chem. Soc.*, **58**, 541 (1981).
16. D.A. Baldwin, A.B.P. Lever and R.V. Parish, *Inorg. Chem.*, **8**, 107 (1969).
17. I. Bertini and F. Mani, *Inorg Chem.*, **9**, 248 (1970).
18. R.D. Gillard and G.L. Wilkinson, *J. Chem. Soc.*, 5399 (1963).

(*Received*: 21 May 1996 ; *Accepted*: 9 September 1996) AJC-1157