

## Physico-chemical and Spectral Studies of Nickel(II) Complexes of 2-Substituted Benzaldehyde Semicarbazones and Thiosemicarbazones

BRAJESH KUMAR, S.K. SANGAL and ARUN KUMAR\*

*Department of Chemistry, Meerut College, Meerut-250 001, India*

Complexes of divalent nickel have been synthesized by refluxing the metal salts with the ligands, 2-chlorobenzaldehyde semicarbazone/thiosemicarbazone and 2-ethoxy benzaldehyde semicarbazone/thiosemicarbazone. All these complexes are characterized on the basis of elemental analysis, magnetic susceptibility measurements, infrared spectral and electronic spectral studies. Infrared spectral data of the complexes revealed bidentate complexing nature of the ligands coordinating through oxygen atom of carbonyl group/sulphur atom of thioketo form and azomethine nitrogen atom. High spin configuration has been indicated by magnetic moment measurements of these complexes. For all the metal complexes the probable structures are also reported here.

**Key Words:** Nickel(II), Complexes, Semicarbazones, Thiosemicarbazones.

### INTRODUCTION

The chemistry of the transition metal complexes of semicarbazones and thiosemicarbazones has been receiving considerable attention because of their pharmacological properties. It was found that the drugs when administered as metal chelates increase their activity<sup>1,2</sup> and a number of metal chelates were found to inhibit tumour growth<sup>3</sup>. The wide range of medicinal properties<sup>4</sup> of semicarbazones, thiosemicarbazones<sup>5</sup> and their metal complexes are emerging as a new class of experimental studies. Besides antitumour activity, these compounds have also been shown to possess antimalarial and antitubercular<sup>6,7</sup> activities. Complexes of transition metals and thiosemicarbazone ligands exhibit a broad spectrum of biological properties which include antimalarial<sup>8</sup>, antiviral<sup>9</sup> and antineoplastic activities<sup>10</sup>. In recent years, thiosemicarbazones have been used for the analytical determination of metals<sup>11</sup>. Nickel has been firmly established<sup>12</sup> as an essential nutritional requirement for any prokaryotic and eukaryotic organism. The study of nickel(II) complexes is due to the variety of stereochemical configurations attained and attending complications of interconversion of different structures. In the present study the complexes of divalent nickel with 2-chlorobenzaldehyde semicarbazone/thiosemicarbazone and 2-ethoxy benzaldehyde semicarbazone/thiosemicarbazone are synthesized and characterized on the basis of various physico-chemical techniques.

## EXPERIMENTAL

Analytical reagent grade chemicals and solvents were used.

### Preparation of ligands

The ligands, 2-ethoxy benzaldehyde semicarbazone (ebsc)/thiosemicarbazone (ebstc) and 2-chloro benzaldehyde semicarbazone (cbsc)/thiosemicarbazone (cbtsc) were prepared according to the literature method<sup>13</sup> by condensing the semicarbazide hydrochloride and thiosemicarbazide with 2-ethoxy benzaldehyde and 2-chloro benzaldehyde respectively and confirmed by elemental analysis and infrared spectral studies.

### General method for synthesization of metal complexes

A hot aqueous ethanolic solution (20 mL) of nickel(II) salt (0.05 mol) was mixed with a hot ethanolic solution (20 mL) of the respective ligand (0.10 mol) keeping the molar ratio 1 : 2. The contents were refluxed for about 5–6 h. The coloured complexes were separated out on cooling the refluxate. The same was filtered, washed with 50% ethanol, dried in an electric oven, analyzed and the data is reported in Table-1

The analyses of C, H and N were done by microanalytical techniques. Metal contents were determined<sup>14</sup> by the precipitation of nickel extract of dilute hydrochloric acid with dimethylglyoxime solution and weighed as  $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$ . The infrared spectral data of the ligands and their nickel(II) complexes were recorded on Perkin-Elmer 1600 FTIR automatic recording spectrophotometer in potassium bromide. Electronic spectra of complexes were scanned in ethonol on Shimadzu UV-Vis spectrophotometer 1601 CP. The magnetic moments of the complexes were determined by Gouy's method using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as calibrant.

## RESULTS AND DISCUSSION

All the nickel(II) complexes were insoluble in water and in most of the organic solvents with the exception of polar solvents such as DMF and DMSO. Analytical data of all the complexes correspond to 1 : 2 (M : L) stoichiometric ratio indicating coordination anions and have the composition  $\text{NiL}_2\text{X}_2$ , where L = ebsc, ebstc, cbsc, cbtsc and X =  $\text{Cl}^-$ ,  $\frac{1}{2}\text{SO}_4^{2-}$  and  $\text{NCS}^-$ . The complexes show different stereochemistry varying from four-coordinated tetrahedral, five-coordinated trigonal bipyramidal and six-coordinated octahedral.

A comparative infrared spectral study of complexes with free ligands gives informations regarding to the chelation sites of the ligand molecules. The ligands show main absorption bands in the region *ca.* 3030–3015  $\text{cm}^{-1}$  due to  $\nu(\text{C—H})$ , *ca.* 1610  $\text{cm}^{-1}$  due to  $\nu(\text{C=C})$ , 760–745  $\text{cm}^{-1}$  (*ortho*-substitution) diagnostic of aromatic character<sup>15</sup> and strong band at *ca.* 1660  $\text{cm}^{-1}$  is assignable to  $\nu(\text{C=O})$  stretching vibration<sup>16</sup> while the band at *ca.* 1532  $\text{cm}^{-1}$  is assignable to  $\nu(\text{C=N})$  stretching vibration<sup>16</sup>. The IR spectral data of free ligands exhibit absorption bands in the range 3370–3125  $\text{cm}^{-1}$  assigned to  $\nu(\text{NH})$  and  $\nu(\text{NH}_2)$  stretching vibrations<sup>17</sup>. These bands remain practically unaltered or shift to higher side

suggesting non-involvement of nitrogen atom of these groups in the complexation. The medium intensity bands at *ca.* 1000–995  $\text{cm}^{-1}$  are assigned to  $\nu(\text{N}=\text{N})$  vibration and the bands at *ca.* 815  $\text{cm}^{-1}$  are assigned to  $\nu(\text{C}=\text{S})$  vibrations<sup>16, 18</sup>. In all the complexes, IR spectral data indicate that the bands attributed to  $\nu(\text{C}=\text{S})$  shift to the lower region suggesting that the sulphur atom is taking part in the coordination with the metal ion. The absence of bands above 3400  $\text{cm}^{-1}$  or in the region 2600–2500  $\text{cm}^{-1}$ , which are attributed to  $\nu(\text{O}=\text{H})$  and  $\nu(\text{S}=\text{H})$  vibrations respectively, shows the presence of ligands in the thione/keto form<sup>19</sup>.

TABLE-I  
ANALYTICAL DATA OF NICKEL(II) COMPLEXES

Complexes	Colour	% found (Calculated)			
		Ni	C	H	N
$\text{Ni}(\text{C}_8\text{H}_8\text{N}_3\text{OCl})_2\text{Cl}_2$	Yellowish green	11.23 (11.19)	36.71 (36.60)	3.21 (3.05)	16.07 (16.00)
$\text{Ni}(\text{C}_8\text{H}_8\text{N}_3\text{OCl})_2\text{SO}_4$	Blackish green	10.70 (10.68)	34.83 (34.93)	3.00 (2.91)	15.21 (15.28)
$\text{Ni}(\text{C}_8\text{H}_8\text{N}_3\text{OCl})_2(\text{NCS})_2$	Brown	10.22 (10.30)	38.00 (37.91)	2.95 (2.81)	19.60 (19.66)
$\text{Ni}(\text{C}_8\text{H}_8\text{N}_3\text{SCl})_2\text{Cl}_2$	Light green	10.52 (10.54)	34.37 (34.49)	2.85 (2.87)	15.13 (15.09)
$\text{Ni}(\text{C}_8\text{H}_8\text{N}_3\text{SCl})_2\text{SO}_4$	Blackish green	10.11 (10.16)	33.27 (33.34)	2.70 (2.77)	14.59 (14.54)
$\text{Ni}(\text{C}_8\text{H}_8\text{N}_3\text{SCl})_2(\text{NCS})_2$	Yellowish green	9.88 (9.76)	35.99 (35.90)	2.72 (2.66)	18.52 (18.61)
$\text{Ni}(\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2)_2\text{Cl}_2$	Green	10.93 (10.80)	44.10 (44.14)	4.70 (4.78)	15.58 (15.45)
$\text{Ni}(\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2)_2\text{SO}_4$	Canry yellow	10.39 (10.32)	42.1 (42.20)1	4.51 (4.57)	14.89 (14.77)
$\text{Ni}(\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2)_2(\text{NCS})_2$	Brownish yellow	10.01 (9.97)	44.78 (44.84)	4.49 (4.42)	19.15 (19.02)
$\text{Ni}(\text{C}_{10}\text{H}_{13}\text{N}_3\text{OS})_2\text{Cl}_2$	Pale green	10.11 (10.20)	44.64 (41.69)	4.59 (4.52)	14.60 (14.59)
$\text{Ni}(\text{C}_{10}\text{H}_{13}\text{N}_3\text{OS})_2\text{SO}_4$	Light yellow	9.70 (9.77)	40.02 (39.95)	4.37 (4.33)	14.00 (13.98)
$\text{Ni}(\text{C}_{10}\text{H}_{13}\text{N}_3\text{OS})_2(\text{NCS})_2$	Duff yellow	9.53 (9.46)	42.55 (42.53)	4.30 (4.19)	18.18 (18.04)

The shifting of characteristic absorption bands of the free ligands in the complex formation indicates the bidentating behaviour of the ligands in all the

divalent nickel complexes. The strong band observed at *ca.* 1660  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  vibration<sup>16</sup> is affected upon coordination and shifted to lower wavenumber by *ca.* 30–55  $\text{cm}^{-1}$  in all the complexes suggesting the involvement of oxygen atom in coordination. The band at *ca.* 1532  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$ <sup>16</sup> also shifts to lower wavenumber side by *ca.* 25–60  $\text{cm}^{-1}$  in all the complexes showing that the azomethine nitrogen is involved in the coordination with metal ion.

The IR spectral data of the thiocyanato complexes of semicarbazone and thiosemicarbazone ligands show only one absorption and at *ca.* 2075–2085  $\text{cm}^{-1}$  which is in favour of coordination through N of both NCS groups<sup>20</sup> in trans position. The infrared spectrum of sulphato complexes exhibit bands at 1055–1038  $\text{cm}^{-1}$ , 1156–1125  $\text{cm}^{-1}$ , *ca.* 982  $\text{cm}^{-1}$  and *ca.* 558  $\text{cm}^{-1}$  suggesting monodentate behaviour of the sulphate group<sup>21</sup>.

The observed magnetic moments at room temperature for Ni(II) complexes reported here lie in the range 2.96–3.12 B.M. (Table-2) and have been used as a criterion to determine the type of geometry<sup>22</sup> around the metal ion. The magnetic moment values of the complexes exclude the possibility of square-planar geometry<sup>22,23</sup>. The electronic spectra of thiocyanato complexes show bands in the range 10500–9755, 16348–15308 and 24108–24065  $\text{cm}^{-1}$  which may be assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  transitions respectively<sup>21</sup>. These bands are characteristic of six-coordinated octahedral geometry<sup>21</sup> with the two NCS groups occupying axial positions in the  $\text{NiL}_2$  plane. The electronic spectra of semicarbazone (cbsc, ebcs) chloro complexes show the bands at 9078, 8480  $\text{cm}^{-1}$ , 14500, 15200  $\text{cm}^{-1}$  and 24175, 21095  $\text{cm}^{-1}$  respectively. These bands are assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  respectively and characteristic of octahedral geometry<sup>21</sup>. Electronic spectra of thiosemicarbazone (cbtsc, ebtsc) chloro complexes exhibit absorption bands at ( $\nu_1$ ) 8980, 8670  $\text{cm}^{-1}$ , ( $\nu_2$ ) 14385, 15250  $\text{cm}^{-1}$  and ( $\nu_3$ ) 23065  $\text{cm}^{-1}$  with  $\nu_1$  absorption weaker than  $\nu_2$  suggesting five-coordinated trigonal bipyramidal geometry<sup>21</sup>. The electronic spectra of the semicarbazone (cbsc, ebcs) sulphato complexes exhibit bands at ( $\nu_1$ ) 10300, 8968  $\text{cm}^{-1}$ , ( $\nu_2$ ) 16100, 15500  $\text{cm}^{-1}$  and ( $\nu_3$ ) 23062  $\text{cm}^{-1}$  ( $\nu_1$  absorption weaker than  $\nu_2$ ), suggesting five-coordinated geometry<sup>24,25</sup>. Also the electronic spectra of these complexes are quite similar to those of already reported trigonal bipyramidal geometry<sup>26</sup>. The electronic spectra of the complex  $\text{Ni}(\text{cbtsc})_2\text{SO}_4$  shows bands at 10315, 16078 and 24108  $\text{cm}^{-1}$  transitions corresponding to five-coordinated trigonal bipyramidal geometry<sup>24,26</sup> whereas the complex  $\text{Ni}(\text{ebtsc})_2\text{SO}_4$  displays three well defined absorption bands at 5085, 8220 and 15382  $\text{cm}^{-1}$  which may be assigned to  $\nu_1(3\text{T}_1 \rightarrow 3\text{T}_2)$ ,  $\nu_2(3\text{T}_1 \rightarrow 3\text{A}_2)$ , and  $\nu_3[3\text{T}_1 \rightarrow 3\text{T}_1(\text{P})]$  respectively<sup>27</sup>. These are transitions for the tetrahedral<sup>28</sup> Ni(II). The splitting in  $\nu_3$  may be attributed either to ground state geometrical distortion<sup>29</sup> or to Jahn-Teller splitting of excited state<sup>30</sup>.

On the basis of elemental analysis, magnetic moment, electronic and infrared spectral studies six-coordinated octahedral geometry is proposed for thiocyanato complexes and semicarbazone chloro complexes whereas five-coordinated trigonal bipyramidal for thiosemicarbazone chloro complexes and all the sulphato complexes except  $\text{Ni}(\text{ebtsc})_2\text{SO}_4$  complex for which four-coordinated tetrahedral geometry is suggested.

TABLE-2  
ELECTRONIC SPECTRAL BANDS AND MAGNETIC  
MOMENTS OF Ni(II) COMPLEXES

Complexes	Spectral bands (cm <sup>-1</sup> )			$\mu_{\text{eff}}$ (B.M.)
	$\nu_1$	$\nu_2$	$\nu_3$	
Ni(ebsc) <sub>2</sub> Cl <sub>2</sub>	8480	15200	21095	3.02
Ni(ebsc) <sub>2</sub> SO <sub>4</sub>	8968	15500	—	3.00
Ni(ebsc) <sub>2</sub> (NCS) <sub>2</sub>	9755	15308	—	2.96
Ni(cbse) <sub>2</sub> Cl <sub>2</sub>	9078	14500	24175	3.06
Ni(cbse) <sub>2</sub> SO <sub>4</sub>	10300	16100	23062	3.07
Ni(cbse) <sub>2</sub> (NCS) <sub>2</sub>	10500	16348	24065	3.12
Ni(ebtsc) <sub>2</sub> Cl <sub>2</sub>	8670	15250	—	3.02
Ni(ebtsc) <sub>2</sub> SO <sub>4</sub>	5085	8220	15382	2.99
Ni(ebtsc) <sub>2</sub> (NCS) <sub>2</sub>	9400	15675	—	3.04
Ni(cbtsc) <sub>2</sub> Cl <sub>2</sub>	8980	14385	23065	3.01
Ni(cbtsc) <sub>2</sub> SO <sub>4</sub>	10315	16078	24108	3.08
Ni(cbtsc) <sub>2</sub> (NCS) <sub>2</sub>	10050	15870	24072	2.99

### ACKNOWLEDGEMENTS

The authors are thankful to Dr. S.K. Agarwal, Principal, Meerut College, Meerut for providing laboratory facilities and to Department of Chemistry, Indian Institute of Technology Roorkee for instrumental measurements.

### REFERENCES

1. D.R. Williams, *Chem. Rev.*, **72**, 203 (1972).
2. A. Frust and R.T. Haro, *Prog. Egpt. Tumor Res.*, **12**, 102 (1969).
3. F.P. Dwyer, E. Mayhe, E.M.F. Roe and A. Shulama, *Brit. J. Cancer*, **19**, 195 (1965).
4. D.X. West, S.B. Padhye and P.B. Sonaware, *Struct. Bonding*, **1**, 29 (1991) and references therein.
5. S.B. Padhye and G.B. Kauffman, *Coord. Chem. Rev.*, **12**, 63 (1985).
6. N.C. Kasuga, K. Sckino, C. Koumo, N. Shimda, M. Ishikawa and K. Nomiya, *J. Inorg. Biochem.*, **84**, 55 (2001) and references therein.
7. N.C. Kasuga, K. Sckino, M. Ishikawa, A. Honda, M. Yokoyana, S. Nakano, N. Shimada, C. Koumo and K. Nomiya, *J. Inorg. Biochem.*, **96**, 298 (2003).
8. P. Anita, *Synth. React Inorg. Met.-Org. Chem.*, **25**, 1885 (1995).
9. A. Singh, R. Dhakarey and G.C. Sexana, *J. Indian Chem. Soc.*, **73**, 339 (1996).
10. A. Castineiras, R. Carballo and T. Perez, *Polyhedron*, **20**, 441 (2001).
11. H. Nishioka, T. Kumajai and T. Nagahiro, *Microchem. J.*, **50**, 88 (1994).
12. R.K. Thakur, G. Diekert and P. Sehonheit, *Trend Biochem. Soc.*, 304 (1980).
13. A.I. Vogel, *Practical Organic Chemistry*, 4th Edn., Longman-ELBS, London, (1973).
14. A.I. Vogel, *Quantitative Inorganic Analysis*, 3rd Edn., Longman-ELBS, London (1962).
15. R.M. Silverstein and G.C. Bassler, *Spectrometric Identifications of Organic Compounds*, John Wiley, New York, p. 1367 (1968).

16. S.I. Mostafa and M.M. Bekheit, *Chem. Pharm. Bull. (Japan)*, **48**, 266 (2000).
17. P. Karla, A. Das, B. Surjit, Dixit and B. Jayaram, *Indian J. Chem.*, **39A**, 262 (2000).
18. H. Beraldo, L.P. Boyd and D.X. West, *Transition Met. Chem.*, **23**, 67 (1998).
19. M.P. Teotia, J.N. Gurtu and V.B. Rana, *Indian J. Chem.*, **19A**, 133 (1980).
20. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience Publication, New York (1978).
21. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier Publication Company, Amsterdam-New York (1968).
22. R.A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, New York (1962).
23. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, Interscience Publishers, p. 737 (1962).
24. M. Ciampalini and N. Nardi, *Inorg. Chem.*, **6**, 445 (1967).
25. L. Sacconi and G.F. Sperori, *Inorg. Chem.*, **7**, 295 (1968).
26. M. Mathew and G.J. Palenik, *J. Am. Chem. Soc.*, **91**, 4923 (1969).
27. G.R. Boston and P. Smith, *J. Am. Chem. Soc.*, **85**, 1006 (1963).
28. L. Sacconi, in: R.L. Carlin (Ed.), *Transition Metal Chemistry*, Vol. 4, Marcel-Dekker Inc., New York, p. 244 (1968).
29. C. Furlani and G.Z. Morpurgo, *Physio. Chem. (Frankfurt)*, **28**, 93 (1961).
30. H.A. Weakleim and D.S. McClure, *J. Appl. Phys. Suppl.*, **33**, 347 (1962).

(Received: 19 January 2006; Accepted: 30 June 2006)

AJC-4991

**XXIII INTERNATIONAL CONFERENCE ON  
PHOTOCHEMISTRY**

**JULY 29 TO AUGUST 3, 2007**

**COLOGNE, GERMANY**

*Contact:*

E-mail: [info@icp2007.net](mailto:info@icp2007.net)

**XXV INTERNATIONAL CONFERENCE ON  
PHOTONIC, ELECTRONIC AND ATOMIC COLLISIONS**

**JULY 25 - 31, 2007**

**FREIBURG, GERMANY**

*Contact:*

Website: <http://www.mpi-hd.mpg.de/ICPEAC2007/index.php>