

Preparation and Characterization of Ni(II) and Mn(II) Complexes of Semicarbazone and Thiosemicarbazone of m- Hydroxy Benzaldehyde and p- Hydroxy Benzaldehyde

Kumari Sapna¹, Navin Kumar Sharma², Seema kohli¹

Abstract-- Ni(II) and Mn(II) complexes were synthesized with m- hydroxy benzaldehyde semicarbazone (L_1 = m-HBSC), m-hydroxy benzaldehyde thiosemicarbazone (L_2 = m-HBTSC), p-hydroxy benzaldehyde semicarbazone (L_3 =p-HBSC), p-hydroxy benzaldehyde thio-semicarbazone (L_4 =p-HBTSC). The ligands were characterized on the basis of elemental analysis, IR, ¹HNMR. While that of complexes were characterized by elemental analysis, molar conductance, magnetic moment, IR, electronic, ¹HNMR and EPR spectral studies. On the basis, the complexes were found to have general composition $[M(L)_2X_2]$ (where M =Ni(II), Mn(II), $L=L_1, L_2, L_3, L_4$ and $X=Cl^-, Br^-, NCS^-, SO_4^{2-}$). On the basis of IR, electronic and EPR spectra of complexes, octahedral geometries were found with planar coordination of ligand around metal ion and the anions occupies axial position.

Kew words – Semicarbazone and thiosemicarbazone, octahedral, Ni, Mn(II) complexes.

1. Introduction

The semicarbazone and thiosemicarbazone usually behave as chelating ligands and usually react with metallic cations giving complexes. They are versatile ligands in both neutral and anionic forms. Metal complexes of semicarbazone and thio-semicarbazone have gained special attention due to their importance in medicine and biological system¹. Nickel complexes occurred in several nickel-containing enzymes have been proposed to be involved in catalytic reaction².

Thiosemicarbazone are now well established as an important class of sulphur donor ligands particularly for transition metal ion³⁻⁵. This is due to remarkable biological activities observed for these compounds, which has since been shown to be related to their metal complexing ability. Thiosemicarbazone derivatives exhibit a great variety of biological activities, such as antitumor⁶, antifungal^{7,8}, antibacterial^{8,9} and antiviral¹⁰. In the present work we synthesized Ni (II) and Mn(II) complexes of semicarbazone (m-HBSC)/(p-HBSC) and thiosemicarbazone (m-HBTSC)/(p-HBTSC)

characterized through elemental analysis, IR, UV, and ¹HNMR etc.

2. Experimental

2.1 Materials

All the chemicals used were of Analytical R grade and procured from sigma- Aldrich and Flucka. Metal salts were purchased from E. Merck and were used as received. All solvents obtained commercially were distilled before use.

2.2 Synthesis of ligands

Hot ethanolic solution (50 ml) of, m-hydroxy benzaldehyde and p- hydroxy benzaldehyde (0.1 mol) was treated with ethanolic solution (50 ml) of semicarbazide and thiosemicarbazide. The resulting mixture was refluxed on water bath for 1-2 hour. On cooling the solution at 0°C, ligand is precipitated out. It was filtered and washed with hot water and dried over P₄O₁₀. For L_1 (m-HBSC) pale yellow long needles L_2 (m-HBTSC) long, sharp yellow needles, L_3 (p-HBSC) short whitish yellow needles, L_4 (p-HBTSC) short dark yellow needles. The proposed structure can be shown according to the following reaction;

1. Department of Chemistry, M. M. H. College (C.C.S. University, Meerut), Ghaziabad-201009, India
E-mail: thakur.sapna61@gmail.com

2. Department of Chemistry,
Inderprastha Engineering College, Sahibabad, India
E-mail: nkschemistry71in@rediffmail.com

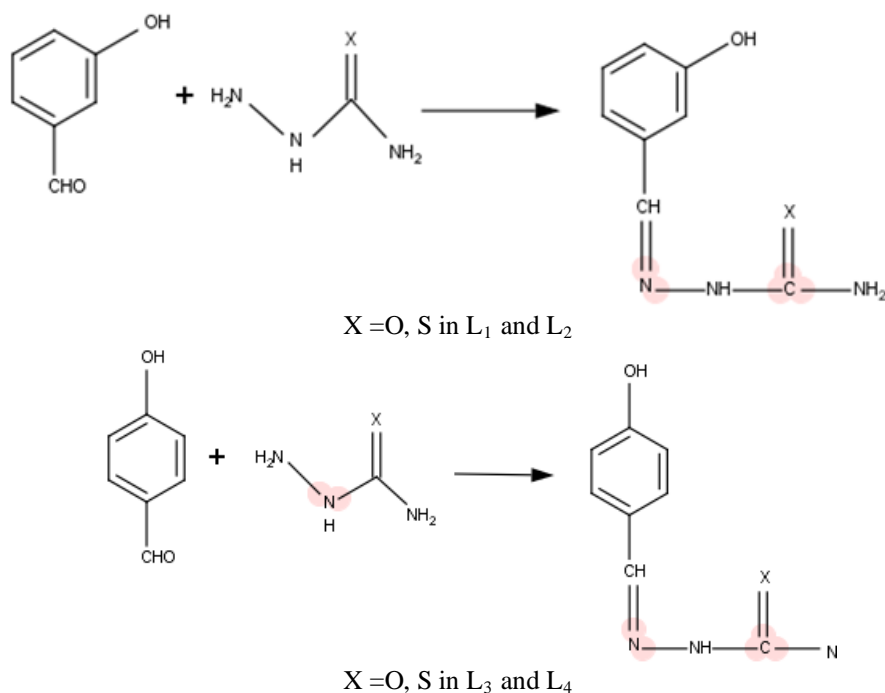


Figure 1.1 synthesis and structure of ligands

2.3 Synthesis of complexes

To a hot ethanolic solution (50ml) ligand L_1 , L_2 , L_3 , L_4 (0.1mol) dissolved in hot ethanolic solution (50ml) of corresponding metal salt (0.05mol) with mixed together with constant stirring. Then mixture was refluxed for 4 hour. On cooling a complex was precipitated out. The complexes were filtered washed with ethanol and dried in vacuum over P_4O_{10} .

2.4 Physical Measurement

C, H and N were analysed on a Carlo Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO conductivity bridge. Magnetic susceptibility was measured at room temperature on a Guoy balance using $CuSO_4 \cdot 5H_2O$ as calibrant. Infra-red spectra of ligand and their complexes have been recorded in KBr pellets on FTIR BX-11 spectrophotometer. 1H NMR spectra were recorded at room temperature on a Bruker Advance DPX-300 spectrophotometer using DMSO- d_6 as a solvent. Electronic spectra of the complexes were recorded in $CHCl_3$ with a perkin Elmer lamda 15UV/V is spectrophotometer.

The molar conductance (M) of the complexes has been studied using DMF as solvent at the concentration of 10^{-3} we observed non-electrolytic behaviour of complexes and conductivity values lay in the range $12-18 \text{ Ohm}^{-1}$

$\text{cm}^2 \text{ mol}^{-1}$ thus the complexes $[M(L_2)_2X_2]$ ($M = \text{Ni (II)}$ and Mn(II) , $X = \text{Cl}^-, \text{Br}^-, \text{NCS}^-, \text{SO}_4^{2-}$) (Table 1).

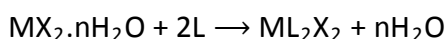
2.5 Magnetic Moment

All the complexes have composition $[\text{Ni}(\text{ligand})_2X_2]$ [$X = \text{Cl}^-, \text{Br}^-, \text{NCS}^-, \text{SO}_4^{2-}$] show magnetic behaviour of octahedral nickel(II) complexes relatively simple. Nickel (II) has the electronic configuration $3d^8$ and should exhibit a magnetic moment higher than expected for two unpaired electron in (2.8-3.2 BM) octahedral geometry.

All the complexes have composition have composition $[\text{Mn}(\text{ligand})_2X_2]$ [$X = \text{Cl}^-, \text{Br}^-, \text{NCS}^-, \text{SO}_4^{2-}$] show a very good agreement with standard magnetic moment value 5.81 to 5.91 B.M. of complexes having five unpaired electrons at room temperature given in table. In the high spin octahedrally coordinated Mn^{2+} complexes, the lowest configuration $(t_{2g})^3 (e_g)^2$ gives rise to the ground states.

3. Results and Discussion

The reaction of ethanolic solution of m-HBSC/m-HBTSC, p-HBSC/p-HBTSC with metal salts gave complexes of the general formula $[M(\text{ligand})_2X_2]$ where $X = \text{Cl}^-, \text{Br}^-, \text{NCS}^-, \text{SO}_4^{2-}$ respectively, as established on the basis of microanalysis and conductance values. The general reaction can be expressed by the following equation.



Where $L = L_1, L_2, L_3, L_4$ and $M = Ni(II)$ and $Mn(II)$

All the complexes are thermally and hydrolytically stable and could be stored for several for several months, and most of them have sharp melting point. They are poorly soluble in water, ethanol and methanol and in other common organic solvents, but are soluble in DMF and DMSO.

3.1 Infra-red spectra

A study and comparison of infra- red spectra of free ligands (m-HBSC), (m-HBTSC), (p-HBSC) and (p-HBTSC) and their metal complexes imply that all ligands behave as bidentate behave as metal is coordinated through nitrogen of azomethine group (Table-2).

3.2 With Ligand L_1 : The position of ligand band due to $\nu(>C=N)$, 1560 cm^{-1} is shifted towards lower side by $10\text{-}80\text{ cm}^{-1}$ on complexation¹¹. Indicate that the coordination takes place through the nitrogen atom of imine groups. The position of ligand band due to $\nu(>C=O)$, 1630 cm^{-1} is also shifted to lower wave number by $10\text{-}40\text{ cm}^{-1}$ this indicate that the coordination takes place through oxygen atom of $>C=O$ group. Thus it is implied that ligand L_1 behave as bidentate.

3.3 With Ligand L_2 : The position of ligand band 1510 cm^{-1} due to $\nu(>C=N)$ is shifted towards lower side by $10\text{-}20\text{ cm}^{-1}$ on complexation¹². This indicates that the coordination takes place through the nitrogen atoms of imine group and the shifting $\nu(>C=S)$ 780 cm^{-1} towards lower side by $20\text{-}30\text{ cm}^{-1}$ suggest involvement of sulphur in coordination. Thus, it is implied that ligand L_2 behaves as bidentate.

3.4 With Ligand L_3 : The position of ligand band due to $\nu(>C=N)$, 1590 cm^{-1} is shifted towards lower side by $10\text{-}80\text{ cm}^{-1}$ on complexation¹³. The position of ligand band due to $\nu(>C=O)$, 1680 cm^{-1} is also shifted to lower wave number by 10-

40 cm^{-1} coordination takes place through the nitrogen atom of imine groups and oxygen atom of $>C=O$ group. Thus it is implied that ligand L_3 behave as bidentate.

3.5 With Ligand L_4 : The position of ligand band 1550 cm^{-1} due to $\nu(>C=N)$ is shifted towards lower side by $10\text{-}20\text{ cm}^{-1}$ on complexation, coordination takes place through the nitrogen atoms of imine group and the shifting $\nu(>C=S)$ 805 cm^{-1} towards lower side by $20\text{-}30\text{ cm}^{-1}$ suggest involvement of sulphur in coordination. Thus, it is implied that ligand L_4 behaves as bidentate.

The ligands have been found to bidentate in nature and coordination is confirmed by (M-O) at $520\text{-}460\text{ cm}^{-1}$, $\nu(M-N)$ at $420\text{-}390\text{ cm}^{-1}$ and $\nu(M-Cl)$ at $450\text{-}590\text{ cm}^{-1}$ vibration in L_1, L_3 respectively¹⁴⁻¹⁵. In thiosemicarbazone complexes (L_2, L_4) $\nu(M-N)$ at $450\text{-}465\text{ cm}^{-1}$ and $380\text{-}395\text{ cm}^{-1}$ due to $\nu(M-S)$ ^{16,17}. The IR spectrum of $Ni(L_4)Cl_2$ shown in fig.(1).

3.6 IR spectra of thiocyanato complexes

Thiocyanate anion may co-ordinate in different ways. It can show linkage isomerism and may act as a bridging anion or as a purely ionic species. $Ni(II)$ and $Mn(II)$ complexes under study show a single strong sharp band at both thiocyanate groups are N bonded¹⁸ and are in similar environment. A six coordinate structure with two bidentate semicarbazone /thiosemicarbazone compounds and two N- coordinated thiocyanate groups is suggested for these complexes.

3.7 IR spectra of sulphato complexes

IR spectra of these complexes show bands corresponding to bidentate sulphate group. For a bidentate sulphate group the symmetry is C_{2v} and each ν_3 and ν_4 band is split into three components. In the complexes the four S-O stretching bands are observed near at $1100\text{-}1108$, $1090\text{-}1076$, $1060\text{-}1065$ and $980\text{-}990\text{ cm}^{-1}$ indicate the bidentate nature of sulphate group¹⁹.

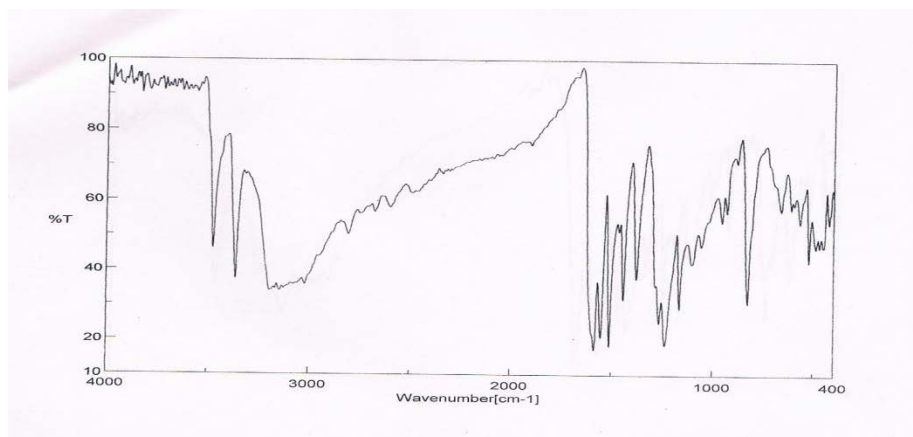


Figure 1: IR spectrum of Ni(L₄)₂Cl₂

3.8 Electronic Spectra:

The Ni(II) complexes exhibit three bands in the regions, 11700-11100 cm⁻¹, 18400-18100 cm⁻¹ and 24700-24000 cm⁻¹ which may be assigned to ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F), ³A_{2g}(F) → ³T_{1g}(P) transitions respectively, which indicate octahedral²⁰ geometry for all the Ni(II) complexes, which is further supported^{21,22} by the μ_{eff} value in the range 3.11-3.23 BM, for all the Ni(II) complexes

Electronic spectra of the complexes display weak absorption bands in the range 9681-18635, 18450-27100 cm⁻¹, 21475-30860, 27300-34950 cm⁻¹ which are characteristics of octahedral geometry. These bands may be assigned as ⁶A_{1g} → ⁴T_{2g}(⁴G) ν₁, ⁶A_{1g} → ⁴E_g, ⁴A_{1g}(⁴G) (10B+5C) ν₂, ⁶A_{1g} → ⁴E_g(⁴D) (17B+5C) ν₃ and ⁶A_{1g} → ⁴T_{2g}(⁴P)(ν₄) transitions respectively (Table 3)

3.9 NMR Spectra

In the ¹H NMR spectrum of semicarbazone ligands and the thiosemicarbazone ligands

multiplets between δ 6.80 and δ 7.70 ppm are all due to the aromatic protons of phenyl rings. The signals of the =N-NH protons were observed as singlets at δ 11.21-11.53. The signals of the HC=N protons which appear as singlet at δ 8.03-8.17 in the ligands show a shift to downfield in δ 0.003-0.80 after complexation. This shift indicates the coordination of imine nitrogen to the metal centre²³. The NH₂ signal in the ligands L₁, L₂, L₃, L₄ appear as doublets at δ 7.98-8.45 due to the non-equivalence of amine protons. Suggesting the involvement of azomethine group in the bond formation. The broad band at 10.02 ppm in the ¹H NMR spectrum of ligands assigned to OH proton, appear in the spectra of metal complexes suggesting -OH group not upon coordination to metal ion. The peaks around 3.5 and 2.5 are for water and solvent i.e. DMSO respectively. The ¹H NMR spectrum of ligand L₂ and [Mn(L₄)Cl₂] shown in fig(2) and (3).

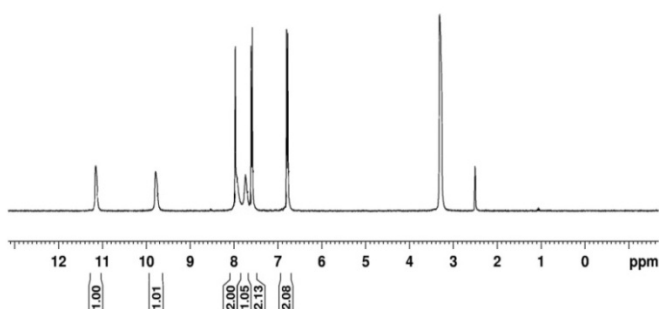


Figure 2: ¹H NMR spectrum of ligand (L₂)

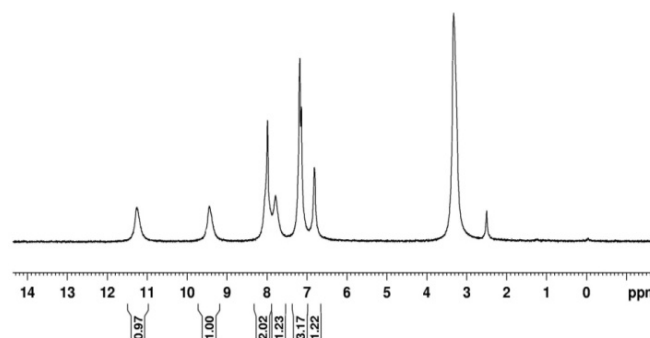


Figure 2: ¹H NMR spectrum of metal complex Mn(L₄)₂Cl₂

4. Acknowledgments

The authors are thankful to IIT Delhi for recording ¹H NMR and ARBRO Pharmaceutical LTD.

Analytical Division, Kirti Nagar, New Delhi for recording IR and UV spectra.

Table 1: Analytical, magnetic moment, and Physical properties of metal complexes

Complexes	Colour	Molar conductance $\text{ohm}^{-1} \text{cm}^{-2} \text{mol}^{-1}$	m.p $^{\circ}\text{C}$	%Analysis found (Cal.)			
				M	C	H	N
$[\text{Ni}(\text{L}_1)_2\text{Cl}_2]$	Green	12	307	16.45 (16.47)	46.05 (46.07)	4.79 (4.77)	15.12 (14.14)
$[\text{Ni}(\text{L}_2)_2\text{Cl}_2]$	Canary Green	18	312	5.33 (5.35)	43.03 (43.05)	4.58 4.17	15.37 (16.55)
$[\text{Ni}(\text{L}_3)_2\text{Cl}_2]$	Pale Green	16	293	14.69 (14.71)	42.15 (42.13)	3.50 (3.52)	14.38 (14.40)
$[\text{Ni}(\text{L}_4)_2\text{Cl}_2]$	Light Yellow	16	306	16.94 (16.81)	41.05 (41.07)	4.32 (4.34)	14.37 (14.39)
$[\text{Mn}(\text{L}_1)_2\text{Br}_2]$	White	20	293	15.66 (15.45)	43.45 (43.43)	4.51 (4.50)	14.34 (14.43)
$[\text{Mn}(\text{L}_2)_2\text{Br}_2]$	Milky white	21	306	13.56 (13.43)	40.03 (40.01)	3.54 (3.34)	14.45 (14.42)
$[\text{Mn}(\text{L}_3)_2\text{Br}_2]$	Milky white	20	301	14.69 (14.65)	46.05 (46.07)	4.62 (4.64)	14.28 (14.26)
$[\text{Mn}(\text{L}_4)_2\text{SO}_4]$	Off white	20	295	14.75 (14.77)	45.11 (45.13)	4.68 (4.80)	14.24 (14.22)
$[\text{Ni}(\text{L}_4)_2(\text{NCS})_2]$	Light Yellow	20	294	14.95 (14.97)	44.11 (44.09)	4.54 (4.52)	14.16 (14.18)
$[\text{Mn}(\text{L}_4)_2(\text{NCS})_2]$	Off white	21	291	14.85 (14.10)	43.12 (43.14)	4.26 (4.23)	14.18 (14.23)

Table-2: IR spectral data of the ligands and their complexes

Compounds	V(OH)	V(NH)	V _{C=O}	V _{C=N}	V _{C=S}	V _{M-O}	V _{M-S}	V _{M-N}
L ₁	3335m	3500-3000	1630	1460				350
L ₂	3332m	3372-3100		1510	780			355
L ₃	3436m	3270-3100	1650	1490				360
L ₄	3537m	3273-3160		1592	680			355
L ₅	3437m	3272-3180	1680	1432				362
L ₆	3556m	3171-3165		1453	740			372
$[\text{Ni}(\text{L}_1)_2\text{Cl}_2]$		3500-3000	1621	1490		750		365
$[\text{Ni}(\text{L}_2)_2\text{Cl}_2]$		3500-3000		1491	750		405	350
$[\text{Ni}(\text{L}_3)_2\text{Cl}_2]$		3500-3000	1639	1493		460		350
$[\text{Ni}(\text{L}_4)_2\text{Cl}_2]$		3500-3000		1587	652		400	340
$[\text{Mn}(\text{L}_1)_2\text{Br}_2]$		3200-3000	1660	1583		465		360
$[\text{Mn}(\text{L}_2)_2\text{Br}_2]$		3270-3001		1584	720		410	350
$[\text{Mn}(\text{L}_3)_2\text{Br}_2]$		3273-3000	1630	1581		462		350
$[\text{Ni}(\text{L}_4)_2(\text{NCS})_2]$		3271-3000		1502	743		400	340
$[\text{Mn}(\text{L}_1)_2(\text{NCS})_2]$		3261-3000	1632	1541		443		355
$[\text{Ni}(\text{L}_4)_2\text{SO}_4]$		3251-3000		1561	732		413	360

Table 3: Electronic spectral data of the complexes

Complexes	μ_{eff} (B.M.)	$\lambda_{\text{max}}(\text{cm}^{-1})$
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		ν_1	ν_2	ν_3	ν_4
[Ni(L ₁) ₂ Cl ₂]	3.01	11300	18150	24700	
[Ni(L ₂) ₂ Cl ₂]	2.95	10100	18625	24000	
[Ni(L ₃) ₂ Cl ₂]	2.98	11320	1800	24300	
[Ni(L ₄) ₂ Cl ₂]	3.01	11500	20400	24000	
[Ni(L ₂) ₂ (NCS) ₂]	3.91	10681	1896	24300	
[Mn(L ₂) ₂ Br ₂]	5.08	12520	20620	24020	28176
[Mn(L ₃) ₂ Br ₂]	5.11	16600	18400	24000	30765
[Mn(L ₄) ₂ Br ₂]	5.23	9681	18760	24600	30654
[Mn(L ₂) ₂ SO ₄]	5.34	9570	18720	24520	32178
Mn(L ₄) ₂ (NCS) ₂]	5.81	12000	18418	26708	34380

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