



**SYNTHESIS, SPECTRAL EVALUATION, MOLECULAR MODELING STUDY AND MYCOLOGICAL SCREENING OF Mn(II), AND Ni(II) COMPLEXES OF POLYDENTATE LIGAND CONTAINING THIOSEMICARBAZIDE MOIETY**

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**ABSTRACT**

Complexes of Mn(II), and Ni(II) were synthesized with polydentate ligand i.e. isophthalic acid-bis(thiosemicarbazone) by using condensation reaction. The polydentate ligand was synthesized by the reaction of isophthalic acid and thiosemicarbazide in 1:2 ratio in alcoholic medium. Synthesized ligand was characterized by melting point, elemental analysis, infra-red, <sup>1</sup>H-NMR, mass, electronic spectra, and molecular modeling. Metal complexes of synthesized ligand were characterized by melting point, elemental analysis, molar conductance, magnetic moment, infra-red, uv-visible, electron paramagnetic resonance, and molecular modeling. On the basis of elemental analysis metal complexes possessed the general composition M(L)<sub>2</sub> where M = Mn(II), Ni(II) L = ligand, X = Cl<sup>-</sup>, CH<sub>3</sub>COO-(OAc), NO<sub>3</sub><sup>-</sup>. The IR data indicated that the ligand coordinated to metal ion through nitrogen and sulphur donor atoms. The spectral studies revealed that all complexes possessed monomeric composition. On the basis of spectral studies, complexes were found to have six coordinated octahedral geometry. The ligand field parameters were calculated using various energy level diagrams. In vitro ligand and metal complexes were examined against some pathogenic fungi to assess their mycological activity.

**Keywords:** polydentate ligand, Mn(II), Ni(II) complexes, electron paramagnetic resonance, molecular modeling, mycological activity

**INTRODUCTION**

Recently, the research concentrated on the synthesis and designing of nitrogen (N), oxygen (O), and sulphur (S) donor atoms containing ligands due to their good pharmacology activities<sup>1,2</sup>. Due to presence of N, O and S donor atoms in semicarbazide or thiosemicarbazide, chemists are interested to synthesize these moiety containing ligands<sup>3,6</sup>. The structure of the semicarbazide, or thiosemicarbazide moieties confer a good chelating capacity for targeted metal ion<sup>7,8</sup>. Chelation can be increased in semicarbazide, or thiosemicarbazide by introducing suitable aldehyde or ketone to isolate the polydentate ligand<sup>9</sup>. Polydentate ligands are used as antimicrobial agents. These agents act as drugs. These drugs kill or slow the growth of microbes<sup>10,11</sup>. Semicarbazide, or thiosemicarbazide moiety containing ligands and their complexes have received considerable attention because of their various activities in industry, medicinal chemistry and biological fields<sup>12,14</sup>. In biological fields these act as antiviral<sup>15</sup>, anticancer<sup>16</sup>, antibacterial<sup>17</sup>, antifungal<sup>18</sup>, anti-tuberculosis<sup>19</sup> drugs. The metal complexes of these ligands (Semicarbazide, or thiosemicarbazide containing ligands) show more antimicrobial activity as compared to the free ligand.

The aim of this study is to obtain the complexes of Mn(II) and Ni(II) with isophthalic acid and thiosemicarbazide moieties containing polydentate ligand and to determine the authenticity of structure and geometry by using various spectroscopic techniques and molecular modeling. As the

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application part of synthesized ligand and its metal complexes, these were examined for their mycological activity against some selected pathogenic fungi stain by using well diffusion method.

## MATERIAL AND METHODS

Isophthalic acid [ $C_8H_6O_4$ ] (99%) was purchased from Alfa Aesar, Heysham, England and thiosemicarbazide [ $CH_5N_2S$ ] (99%) of AR grade purchased from Sigma Aldrich, Bangalore, India. Metal salts were purchased from E. Merck, India and were used as received. Solvent were used of analytical grade. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. Elemental study (CHN) was analyzed on Carlo-Erba 1106 elemental analyzer.  $^1H$ -NMR spectra was recorded on a Bruker Advanced DPX-300 spectrometer using  $DMSO-d_6$  as a solvent at IIT Delhi. IR spectra were recorded on FT-IR spectrum BX-II spectrophotometer by using KBr pellets for near region, and CsI pellets for far region. Electronic impact mass spectrum was recorded on JEOL, JMS-DX-303 mass spectrometer. EPR spectra of Mn(II) complexes were recorded at room temperature on  $E_4$ -EPR spectrometer using the DDPH as the g-marker at SAIF, IIT Bombay. The UV-Visible spectra were recorded in DMSO on Shimadzu UV-visible mini-1240 spectrophotometer. Molecular modeling of the proposed structure of ligand and its Mn(II) complexes was done by using semiempirical (PM6) method of the *Gaussian 09 W* package, in gas phase.

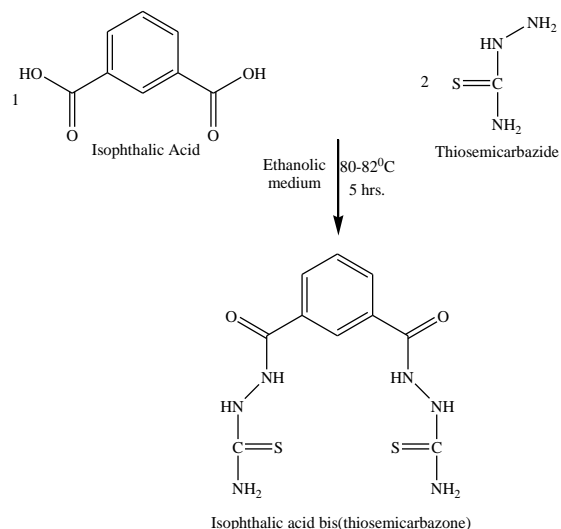
### Synthesis of polydentate Ligand

Hot ethanolic solution of thiosemicarbazide (2 mol) was added to hot ethanolic solution of isophthalic acid (1 mol) with continuous stirring and reaction solution was refluxed for 5 hrs. at  $80-82^\circ C$ . Now, reaction was allowed to stay at room temperature and kept in refrigerator for overnight. On cooling, the white color solid product was precipitated out. It was filtered, washed several times with distilled water, cold ethanol and then dried in a desiccator using silica gel in it as moisture absorbent. Synthesis and structure of polydentate ligand has been presented in **Figure 1**.

### Synthesis of Mn(II), Ni(II) complexes of polydentate ligand

A hot ethanolic solution (0.01 mol) of polydentate ligand was taken in a round bottom flask and gently warmed for about 10-15 min to

make clear solution. Then hot ethanolic solution (0.01 mol) of the corresponding metal salt was added with continuous stirring and then refluxed for about 12-15 hrs. On cooling at room temperature, the solid product was precipitated out. The resulting solid product was filtered, washed several times with ethanol, and dried in a desiccator using silica gel in it as moisture absorbent.



**FIGURE 1: Synthesis And Structure Of Polydentate Ligand**

### Mycological Screening of polydentate ligand and its complexes

The mycological activity of polydentate ligand and complexes was evaluated using well diffusion method<sup>20</sup>. A stock solution of 1000 ppm was prepared by dissolving  $1\text{ mg/cm}^3$  of each compound in DMSO. It was diluted up to three dilutions, giving the concentrations of 750 ppm, 500 ppm, and 250 ppm. Sabround Dextrose Agar (SDA) media plates were incubated for 24 hrs. at  $25-27^\circ C$ . Now, tested microorganism broth culture was rubbed on the surface of each plate, and four wells were made in each plate at equidistance. Tested compound solution at desired concentration was poured in marked wells i.e. 1000 ppm, 750 ppm, 500 ppm, 250 ppm. Now these petri plates were incubated in an incubator at  $27-30^\circ C$ . After 24 hrs. the zones of inhibition were measured.

### Molecular modeling

Molecular modeling of the proposed structure of polydentate ligand and its Mn(II) complexes was modelled by using Semi empirical (PM6) method. In

**Table 1: Analytical data, and molar conductance data of polydentate ligand and its metal complexes**

Compounds	M.P	Mol. Wt	Color	Elemental Analysis Calculated (Found) (%)					molar conductance
				C	H	N	S	M	
Polydentate ligand (L) C <sub>10</sub> H <sub>12</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	200	312	White	38.46 (38.44)	3.84 (3.85)	26.92 (26.91)	10.25 (10.27)	-	-
[Mn(L)Cl <sub>2</sub> ] C <sub>10</sub> H <sub>12</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub> MnCl <sub>2</sub>	>250	437.9	Cree-mish	27.40 (27.41)	2.74 (2.73)	19.18 (19.20)	14.61 (14.61)	12.53 (12.50)	10
[Mn(L)(OAc) <sub>2</sub> ] C <sub>14</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub> Mn	>250	484.9	Light brown	34.64 (34.65)	3.71 (3.70)	17.32 (17.30)	13.19 (13.20)	11.32 (11.33)	14
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ] C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> O <sub>8</sub> S <sub>2</sub> Mn	>250	496.9	White	24.14 (24.15)	2.41 (2.42)	22.53 (22.55)	25.75 (25.78)	12.77 (12.80)	10
[Ni(L)Cl <sub>2</sub> ] C <sub>10</sub> H <sub>12</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub> NiCl <sub>2</sub>	>250	441.7	Green	27.16 (27.20)	2.71 (2.70)	19.01 (19.00)	14.48 (14.48)	13.28 (13.28)	17
[Ni(L)(OAc) <sub>2</sub> ] C <sub>14</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub> Ni	>200	488.7	Mehndi Green	34.37 (34.35)	3.68 (3.65)	17.18 (17.18)	13.09 (13.10)	12.01 (12.00)	12
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ] C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> O <sub>8</sub> S <sub>2</sub> Ni	>250	500.7	Dark Green	23.96 (23.96)	2.39 (2.40)	22.36 (22.40)	12.78 (12.80)	11.72 (11.72)	09

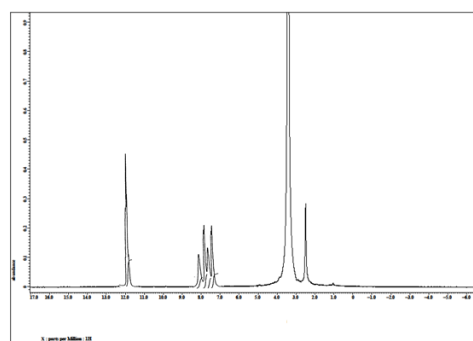
M.P-melting point, Mol. Wt.-molecular weight, C-carbon, H-hydrogen, N-nitrogen, S-sulphur, M-Mn(II), Ni(II) metal

order to obtain the structural information (bond length, bond order) for the ligand and its complexes, Geometry optimization was carried out for both, ligand and complexes, i.e. [Mn(L)Cl<sub>2</sub>], [Mn(L)(OAc)<sub>2</sub>] and [Mn(L)(NO<sub>3</sub>)<sub>2</sub>] by implementation of semi empirical (PM6) method of the *Gaussian 09 W* package, in the gas phase.

## RESULTS AND DISCUSSION

All metal complexes were insoluble in water, methanol, and ethanol but soluble in DMSO and DMF solvents. The analytical data of complexes indicated that all complexes possessed the general composition M(L)X<sub>2</sub> where M = Mn(II), Ni(II) L = isophthalicacid-bis(thiosemicarbazone), X = Cl<sup>-</sup>, OAc<sup>-</sup>, NO<sub>3</sub><sup>-</sup>. The molar conductance values of complexes in 10<sup>-3</sup> molar concentration in DMSO was in the range 10-17 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>, which revealed the non-electrolytic nature of metal complexes. IR data suggested that ligand behaved as tetradentate manner and coordinated to metal ion through sulphur and nitrogen donor atoms. The analytical data of ligand and its Mn(II) and Ni(II) complexes

with their physical properties are given in **Table 1** as supporting information, which indicates 1:1:2 metal: ligand: anion stoichiometry for all complexes.

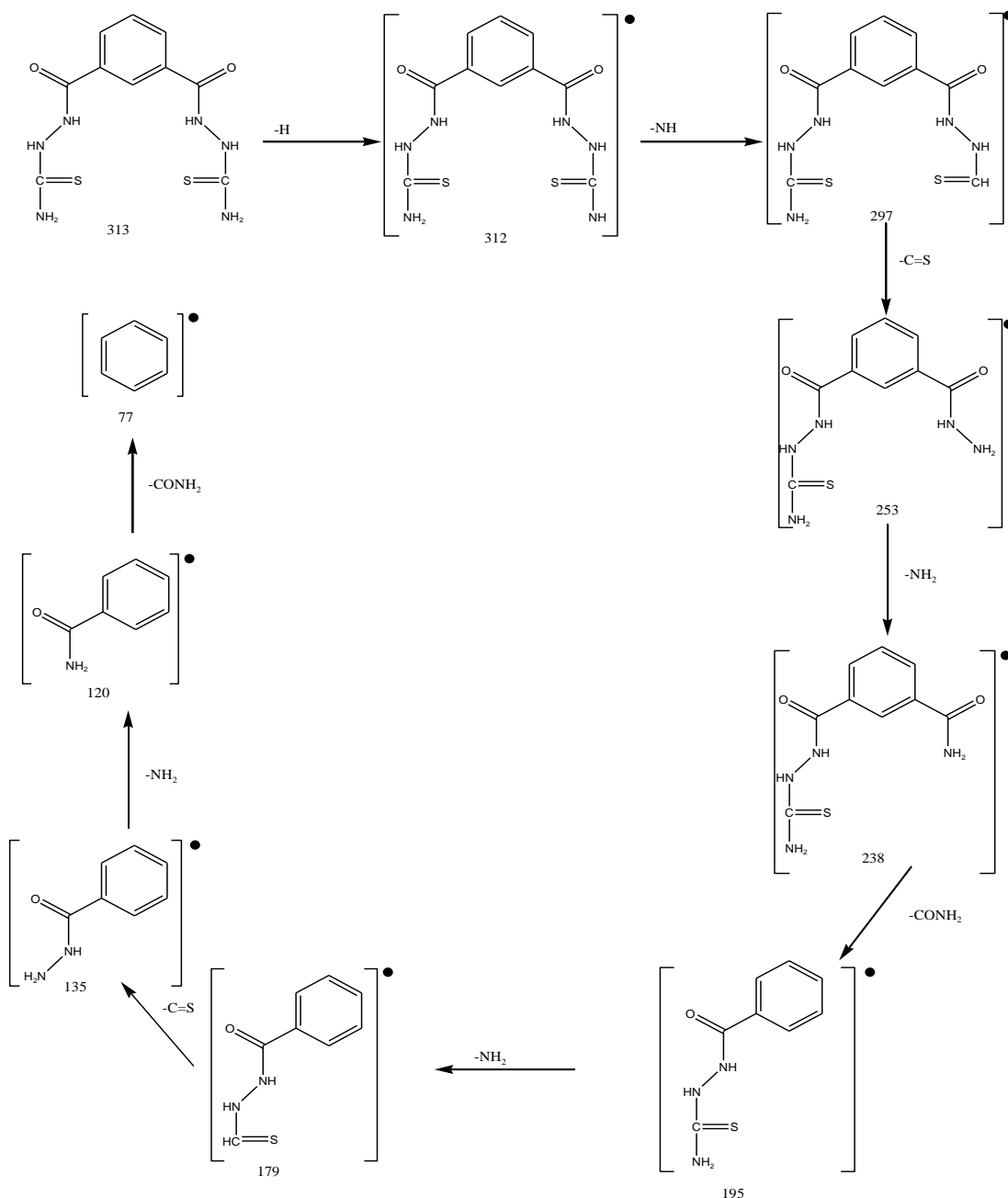


**FIGURE 3: <sup>1</sup>H-NMR SPECTRUM OF POLYDENTATE LIGAND**

### Characterization of polydentate ligand

#### Mass Spectrum, <sup>1</sup>H-NMR

The electron impact mass spectrum of polydentate ligand confirms the proposed formula



**FIGURE 2: Mass Fragmentation of Polydentate Ligand**

by showing a peak at 312amu corresponding to the moiety  $[(C_{10}H_{12}N_6S_2O_2)^+]$ , calculated atomic mass 313amu]. The series of peaks in the range i.e. 297, 253, 238, 195, 179, 135, 120, and 77 amu may be corresponded to fragments i.e.  $C_{10}H_{11}N_5S_2O_2$ ,  $C_9H_{11}N_5SO_2$ ,  $C_9H_{10}N_4SO_2$ ,  $C_8H_9N_3SO$ ,  $C_8H_7N_2SO$ ,  $C_7H_7N_2O$ ,  $C_7H_6NO$ , and  $C_6H_6$  moiety respectively. Their intensity gave an idea of stability of fragments given in Figure 2. The <sup>1</sup>H-NMR spectrum of the ligand (L) in DMSO-d<sub>6</sub> give signals which are attributed to

aromatic proton Ar-H (6H) at  $\delta$  7.89 ppm (m)<sup>21</sup>, NH (4H) at  $\delta$  12 ppm<sup>22</sup>, and NH<sub>2</sub> (4H) at 4.28 ppm<sup>23</sup>. This data support to the presence of different protons in ligand **Figure 3**.

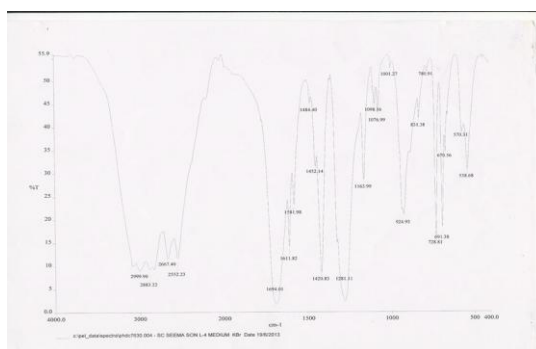
#### IR Spectra

The IR absorption bands, which provide information about the formation of polydentate ligand and the mode of coordination in its complexes, are given in **Table 2**. The infrared

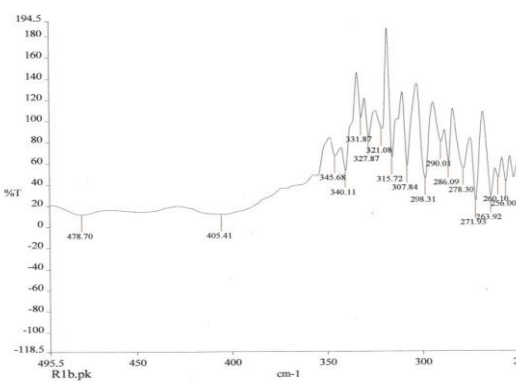
**TABLE 2: RELEVANT IR SPECTRAL PEAKS (cm<sup>-1</sup>) AND THEIR ASSIGNMENT**

Compounds	$\nu(-NH)$	$\nu(C=O)$	$\nu(C-S)$	$\nu(M-N)$	Bands due to anions
Polydentate ligand (L)	2999	1694	780	-	-
[Mn(L)Cl <sub>2</sub> ]	3362	1693	796	405	325
[Mn(L)(OAc) <sub>2</sub> ]	3273	1690	792	402	1485( $\nu_5$ ), 1330( $\nu_3$ )
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	3370	1692	794	408	1430( $\nu_5$ ), 1302( $\nu_1$ ), 1006( $\nu_2$ )
[Ni(L)Cl <sub>2</sub> ]	3299	1693	797	404	318
[Ni(L)(OAc) <sub>2</sub> ]	3301	1695	796	408	1492( $\nu_5$ ), 1340( $\nu_3$ )
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	3372	1690	794	407	1436( $\nu_5$ ), 1300( $\nu_1$ ), 1028( $\nu_2$ )

spectrum of ligand does not exhibit any band corresponding to free -NH and -OH groups. The appearance of bands which are characteristics to amide group, at 1694  $\nu(C=O)$  amide I, 1611  $\nu(CS-NH)$  amide II, 1581  $\nu(C-N)+\delta(N-H)$  amide III, 1281  $\delta(N-H)$  and 647  $\nu(C=O)$  amide IV, appeared in spectra<sup>24</sup> **Figure 4(a)**. A sharp band observed in the region



(a)

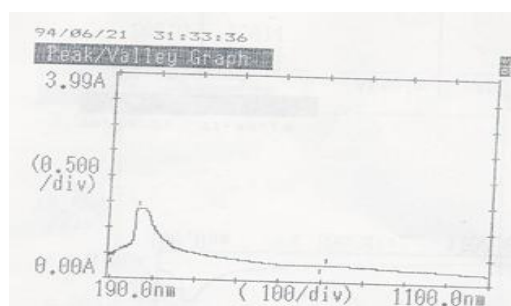


(b)

**FIGURE 4. INFRARED SPECTRUM OF (a) POLYDENTATE LIGAND (b) [Ni(L)Cl<sub>2</sub>] COMPLEX**

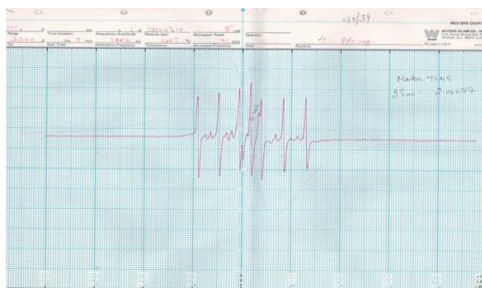
3379-2999  $\text{cm}^{-1}$  may be assigned to  $\nu(N-H)$  of the secondary amino group. A strong to medium intensity band in the region of 750-780  $\text{cm}^{-1}$  has been assigned to  $\nu(C-S)$ <sup>25</sup>. The  $\nu(C-S)$  band is shifted

by 30  $\text{cm}^{-1}$  in the complexes clearly indicated that sulphur also takes place in coordination. The complexes show the new bands in the range 390-408  $\text{cm}^{-1}$  which may be assigned to  $\nu(M-N)$ <sup>26</sup>. It supports the involvement of nitrogen and sulphur in coordination. The chloro complexes displayed bands in the region 320-345  $\text{cm}^{-1}$  corresponding to  $\nu(M-Cl)$  bond formation **Figure 4(b)**<sup>27</sup>. In IR spectra of acetato complexes showed at 1471-1490 ( $\nu_5$ )  $\text{cm}^{-1}$ , and 1327-1340 ( $\nu_3$ )  $\text{cm}^{-1}$ , differences between two frequencies is 148-152  $\text{cm}^{-1}$  strongly supported that both acetato anions coordinated to metal ion in monodentate fashion. The IR spectra of nitrate complexes of Mn(II) and Ni(II) showed bands at 1427-1438 ( $\nu_5$ ) 1298-1306( $\nu_1$ ) and 1005-1035 ( $\nu_2$ )  $\text{cm}^{-1}$ , indicated that nitrate group coordinated to the metal ion as an unidentate manner<sup>28</sup>.

**FIGURE 5: ELECTRONIC SPECTRA OF [Ni(L)(NO<sub>3</sub>)<sub>2</sub>] COMPLEX OF POLYDENTATE LIGAND**

#### **Molar conductance and magnetic moment measurement**

The molar conductance values for the complexes were found in the range 10-17  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  in DMSO, which indicated their non-electrolytic nature **Table 1**. Thus, the complexes can be formulated as  $[M(L)X_2]$ . The magnetic moment for Mn(II) and Ni(II) complexes were found in the range 5.82-5.96 B.M



**FIGURE 6: EPR SPECTRA OF THE [Mn(L)Cl<sub>2</sub>] COMPLEX OF POLYDENTATE LIGAND**

and 2.91-2.97 B.M respectively (Table 3), suggested octahedral geometry for all complexes.

### Electronic spectra

#### Manganese(II) complexes

The electronic spectra of Mn(II) complexes displayed the absorption bands in the range of 17,850-18,518 cm<sup>-1</sup>, 23,034-24,096 cm<sup>-1</sup>, and 26,809-28188 cm<sup>-1</sup>, 34,482-37,735 cm<sup>-1</sup> Figure 5. These transitions may be assigned to the <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>, <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>, <sup>4</sup>A<sub>1g</sub>, <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub> (4D) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>. These transitions revealed the octahedral geometry for the

These parameters indicate significant covalent character in metal ligand bonds.

#### Nickel(II) complexes

The electronic spectra of the Ni(II) complexes show bands in the range 9725-9870 cm<sup>-1</sup>, 15,800-17,600 cm<sup>-1</sup> and 22,950-24,520 cm<sup>-1</sup> characteristic to an octahedral geometry and may be assigned to the <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>, <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> transitions, respectively. Band at 36,800-39,420 cm<sup>-1</sup> corresponded for charge transfer.

Various ligand field parameters i.e. Dq, β and B, for complexes were calculated and given in Table 4. The nephelauxetic parameter β is obtained by using the relation: β = B(complex)/B(free-ion), where B is the Racah inter-electronic repulsion parameter. The value of B(free-ion), for Ni(II) complexes is (1041cm<sup>-1</sup>). The lowering in the B value suggests 24-37% covalent character in the bonding. The β lies in the range of 0.66-0.81. These values indicate the appreciable covalent character of metal ligand σ bond.

#### Electronic paramagnetic Resonance (EPR)

**TABLE 3: ELECTRONIC SPECTRAL AND MAGNETIC SPECTRAL MOMENT DATA OF COMPLEXES**

Compounds	μ <sub>eff</sub> (B.M)	Spectral bands (cm <sup>-1</sup> )	Geometry
[Mn(L)Cl <sub>2</sub> ]	5.82	17,850, 23,945, 27,809, 35,590	octahedral
[Mn(L)(OAc) <sub>2</sub> ]	5.96	17,502, 24,034, 26,802, 36, 856	octahedral
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	5.88	18,518, 24096, 28,188, 37,735	octahedral
[Ni(L)Cl <sub>2</sub> ]	2.91	9,725, 17,268, 24,529, 36,800	octahedral
[Ni(L)(OAc) <sub>2</sub> ]	2.94	9,870, 15,800, 22,950, 38,540	octahedral
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	2.97	9,858, 17,600, 23,900, 39,420	octahedral

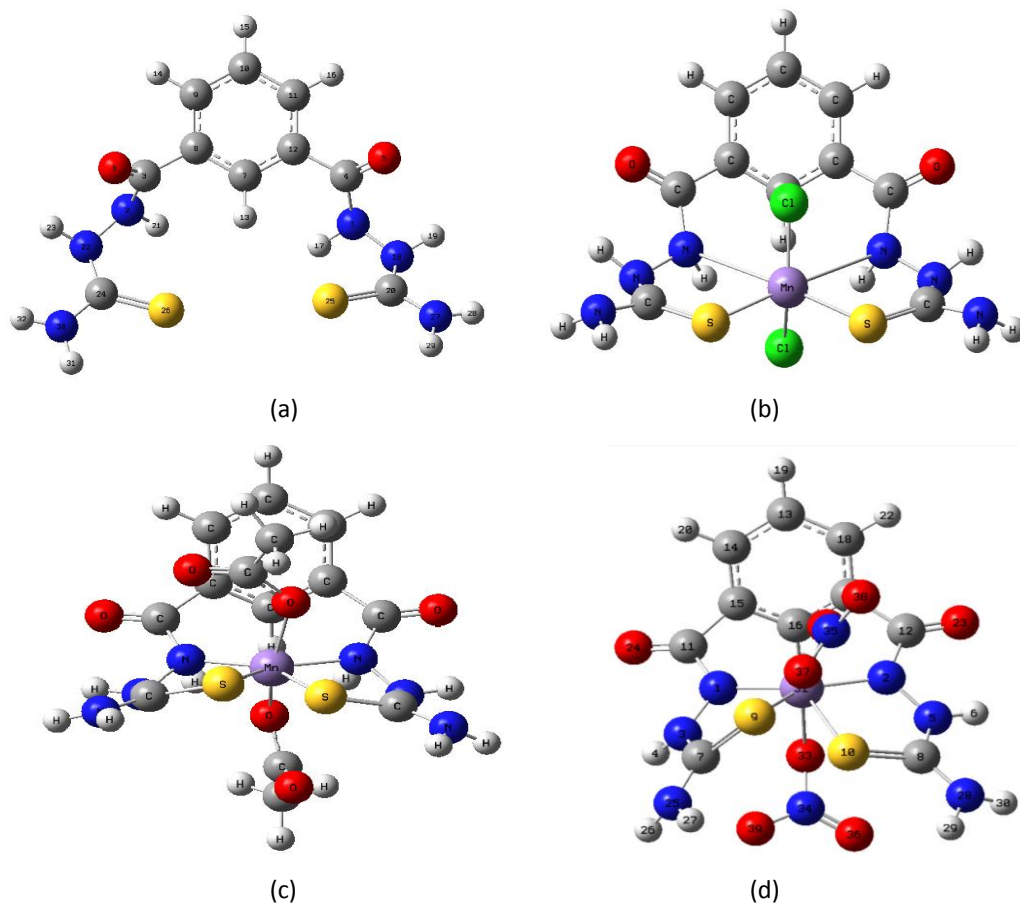
Mn(II) complexes<sup>29</sup>. Band at 35,482-37,735 cm<sup>-1</sup> corresponded for charge transfer.

Various ligand field parameters for Mn(II) complexes i.e. Dq, β and B, C, F<sub>2</sub>, F<sub>4</sub>, and hx were calculated<sup>30</sup> and their values are given in Table 4.

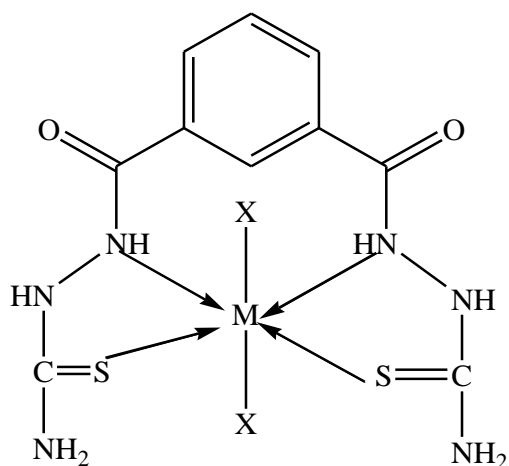
EPR spectra of the Mn(II) complexes were reordered as polycrystalline sample shown in Figure 6. An isotropic signal was obtained and g<sub>iso</sub> values found in the range of 2.02-2.07, which is almost equal to free electron value (i.e. 2.0023)<sup>31</sup> Table 4.

**TABLE 4: LIGAND FIELD PARAMETERS AND EPR SPECTRAL DATA OF THE COMPLEXES**

Compounds	Dq	u <sub>2</sub> /u <sub>1</sub>	B (cm <sup>-1</sup> )	β	C	F <sub>2</sub>	F <sub>4</sub>	hx	LFSE	g <sub>iso</sub>
[Mn(L)Cl <sub>2</sub> ]	1385	1.34	583.56	0.74	3673	1100.55	103.51	3.71	-	2.02
[Mn(L)(OAc) <sub>2</sub> ]	1750	1.37	639.53	0.81	3528	1139	100.8	2.71	-	2.00
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1851	1.30	521	0.66	3777	1060	107.91	4.85	-	2.07
[Ni(L)Cl <sub>2</sub> ]	972	1.77	841.46	0.80	-	-	-	-	139.52	-
[Ni(L)(OAc) <sub>2</sub> ]	987	1.60	609.33	0.58	-	-	-	-	139.52	-
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	985	1.78	795.06	0.76	-	-	-	-	141.38	-



**Figure 7: OPTIMIZED GEOMETRY OF (a) POLYDENTATE LIGAND, (b) [Mn(L)Cl<sub>2</sub>] (c) [Mn(L)(OAc)<sub>2</sub>] (d) [Mn(L)(NO<sub>3</sub>)<sub>2</sub>] COMPLEX OF POLYDENTATE LIGAND**



**FIGURE 9: CHEMICAL STRUCTURE OF METAL COMPLEX OF POLYDENTATE LIGAND [M = Mn(II), Ni(II) AND X = Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>]**

### Molecular modeling Analysis

Because the single crystals could not be obtained for ligand and complexes, it was thought worthwhile to obtain structural information. So for obtaining structural information, geometry optimization of compounds (ligand and Mn(II) complexes) was done by using the *Gaussian 09W* programme in gas phase. Molecular modeling analysis enables to calculate the actual bond lengths, and bond angles of molecule in terms of deviations from reference unstrained bond lengths, angles, and torsions plus non-bonded interactions. The fully optimized geometry of the polydentate ligand, and its Mn(II) complexes were shown in **Figure 7**. The molecular structure of Mn(II) complexes showed an octahedral geometry around the Mn(II) center as revealed from the calculated bond lengths and bond angles (**Tables 5 and 6**) respectively.

### Mycological Activity



**TABLE 5: BOND LENGTHS IN ANGSTROMS FOR OPTIMIZED GEOMETRY OF THE LIGAND AND ITS Mn(II) COMPLEXES**

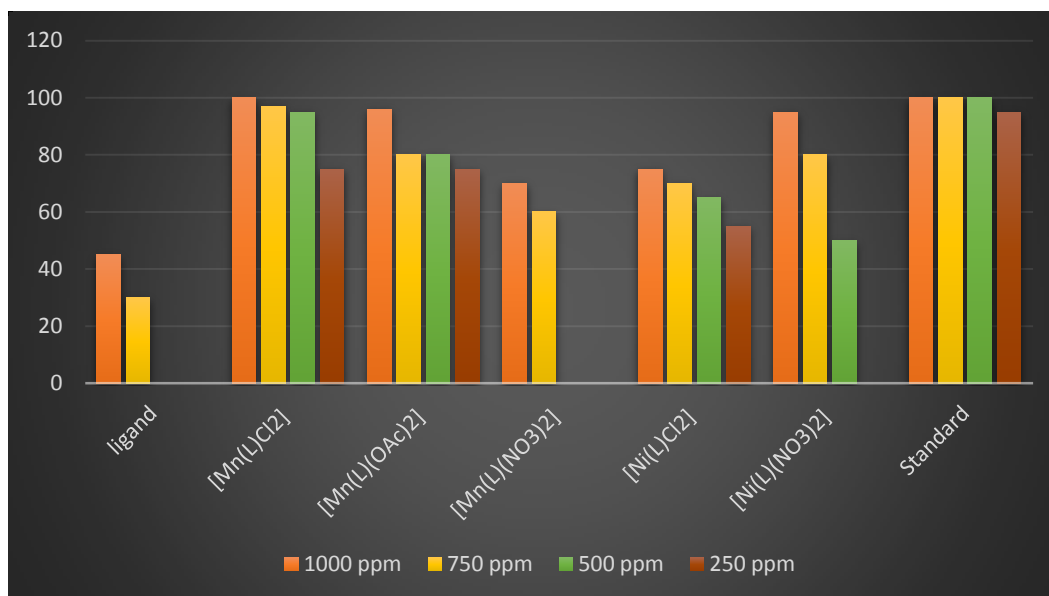
Bond Length	Ligand	[Mn(L)Cl <sub>2</sub> ]	[Mn(L)(OAc) <sub>2</sub> ]	[Mn(L)NO <sub>3</sub> ]
N <sub>1</sub> -C <sub>4</sub>	1.43521	1.44442	1.41447	1.41636
N <sub>2</sub> -C <sub>3</sub>	1.43708	1.44442	1.42344	1.42538
C <sub>4</sub> -O <sub>5</sub>	1.21429	1.21674	1.22053	1.21584
C <sub>3</sub> -O <sub>6</sub>	1.21133	1.21674	1.21675	1.20836
C <sub>3</sub> -C <sub>8</sub>	1.49329	1.48998	1.49341	1.49854
C <sub>4</sub> -C <sub>12</sub>	1.49181	1.48998	1.49414	1.49789
C <sub>8</sub> -C <sub>9</sub>	1.40129	1.40558	1.40056	1.39932
C <sub>9</sub> -C <sub>10</sub>	1.39799	1.39870	1.40215	1.40277
C <sub>10</sub> -C <sub>11</sub>	1.39700	1.39870	1.40147	1.40307
C <sub>11</sub> -C <sub>12</sub>	1.40397	1.40558	1.40019	1.39968
C <sub>12</sub> -C <sub>7</sub>	1.40000	1.40022	1.40230	1.40593
C <sub>8</sub> -C <sub>7</sub>	1.40051	1.40022	1.40170	1.40711
N <sub>2</sub> -N <sub>22</sub>	1.40772	1.42895	1.41244	1.40585
N <sub>1</sub> -N <sub>18</sub>	1.40815	1.42895	1.41226	1.40519
N <sub>22</sub> -C <sub>24</sub>	1.42447	1.44267	1.42348	1.36651
N <sub>18</sub> -C <sub>20</sub>	1.42562	1.44267	1.41492	1.36072
C <sub>24</sub> -S <sub>26</sub>	1.66829	1.65242	1.66453	1.77682
C <sub>20</sub> -S <sub>25</sub>	1.66607	1.65242	1.66861	1.74179
N <sub>30</sub> -H <sub>31</sub>	1.00684	1.01494	1.00451	1.01608
N <sub>30</sub> -H <sub>32</sub>	1.01576	1.01827	1.01142	1.01099
N <sub>27</sub> -H <sub>28</sub>	1.00676	1.01494	1.00856	1.01626
N <sub>27</sub> -H <sub>29</sub>	1.01547	1.01827	1.01466	1.00878
M <sub>33</sub> -Cl <sub>34</sub>	-	1.96653	1.99808	2.07216
M <sub>33</sub> -Cl <sub>35</sub>	-	2.22946	1.94709	2.12190
M <sub>33</sub> -N <sub>1</sub>	-	2.95197	1.92314	1.90507
M <sub>33</sub> -N <sub>2</sub>	-	2.95197	1.89045	1.85251
M <sub>33</sub> -S <sub>25</sub>	-	2.19667	2.32551	2.32653
M <sub>33</sub> -S <sub>26</sub>	-	2.19667	2.29948	2.40311

Synthesized ligand and its Mn(II) and Ni(II) complexes were screened for their mycological activity against *C. parapsilosis*, and *C. tropicalis* fungi at 1000 ppm, 750 ppm, 500 ppm, 250 ppm. The standard drug amphotericin B was also tested for mycological activity at the same concentration and similar conditions as for tested compounds concentration. Mycological property was related to the ability of the metal ion to form complexes with ligand containing sulphur, and nitrogen donor atoms. The increased activity of the metal chelates can be explained on the basis of chelation theory<sup>32,33</sup>. The mycological screening data showed that compounds exhibit antifungal properties, and it is also important to note that some of the metal complexes exhibited inhibitory zone than the polydentate ligand (**Figure 9 and 10**).

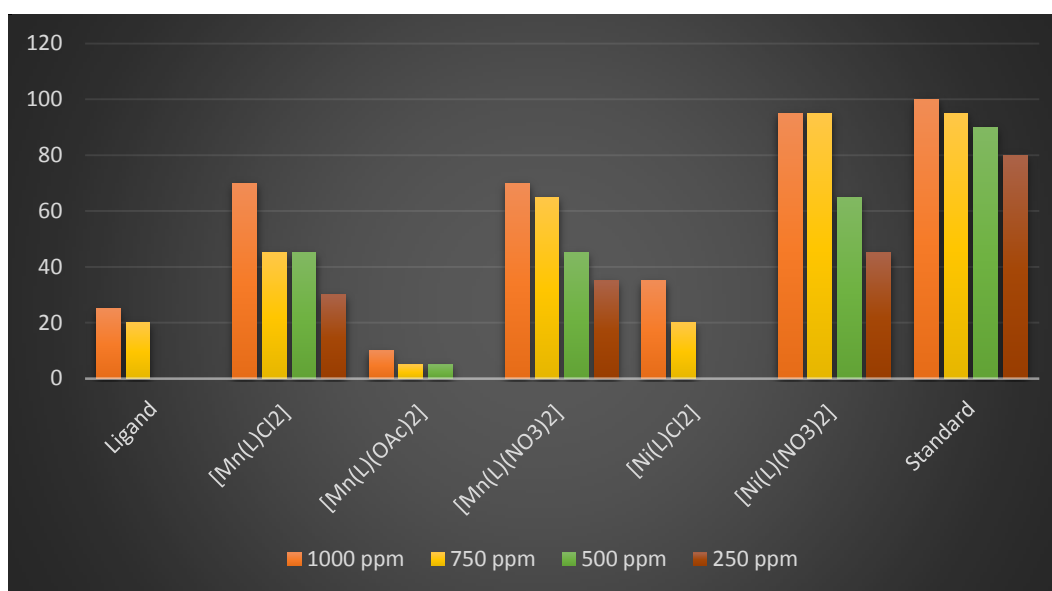
## CONCLUSION:

This research paper describes synthesis and characterization of novel polydentate ligand and its Mn(II), Ni(II) complexes based on thiosemicarbazide moiety. The synthesis procedure is simple and efficient. The complexes were non-electrolytic in nature on the basis of molar conductance analyses. The spectral studies reasonably proved that complexation of the metal and ligand took place via nitrogen and sulphur donor atoms present in polydentate ligand, and anions (Cl<sup>-</sup>, OAc<sup>-</sup>, NO<sub>3</sub><sup>-</sup>). All the above investigations revealed hexa-coordinated stereochemistry around the metal ions Mn(II) and Ni(II) **Figure 10**. The compounds studied for mycological study, concentration factor influence the mycological property. Complexes showed better





(a)



(b)

**FIGURE 8: GRAPHICAL REPRESENTATION OF MYCOLOGICAL ACTIVITY OF PPOLYDENTATE LIGAND, ITS Mn(II), AND Ni(II) COMPLEXES AT CONCENTRATION 1000 ppm, 750 ppm, 500 ppm, 250 ppm AGAINST FUNGI (a) *C. parapsilosis*, AND *C. tropicalis***

activity than parent ligand. Among all Complexes [Mn(L)Cl<sub>2</sub>], and [Ni(L)(NO<sub>3</sub>)<sub>2</sub>] exhibited good results for *C. parapsilosis*, and *C. tropicalis* fungi respectively.

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**TABLE 6: BOND ANGLE IN DEGREE FOR OPTIMIZED GEOMETRY OF Mn(II) COMPLEXES**

Bond Angles	[Mn(L)Cl <sub>2</sub> ]	[Mn(L)(OAc) <sub>2</sub> ]	[Mn(L)NO <sub>3</sub> ]
C <sub>8</sub> -C <sub>7</sub> -C <sub>12</sub>	120.47	117.38	117.26411
C <sub>7</sub> -C <sub>8</sub> -C <sub>3</sub>	120.46	115.56	114.81942
C <sub>8</sub> -C <sub>3</sub> -O <sub>6</sub>	124.41	128.43	129.62647
O <sub>6</sub> -C <sub>3</sub> -N <sub>2</sub>	120.38	122.41	124.86019
C <sub>3</sub> -N <sub>2</sub> -N <sub>22</sub>	116.70	116.11	118.32146
N <sub>2</sub> -N <sub>22</sub> -C <sub>24</sub>	112.07	111.24	115.60898
N <sub>22</sub> -C <sub>24</sub> -S <sub>26</sub>	129.16	115.43	115.80394
N <sub>22</sub> -C <sub>24</sub> -N <sub>30</sub>	113.26	120.52	121.70550
C <sub>24</sub> -N <sub>30</sub> -H <sub>31</sub>	116.46	123.54	122.21616
C <sub>24</sub> -N <sub>30</sub> -H <sub>32</sub>	114.34	119.24	118.05152
N <sub>30</sub> -C <sub>24</sub> -S <sub>26</sub>	117.46	123.68	121.88488
C <sub>7</sub> -C <sub>12</sub> -C <sub>4</sub>	120.46	115.32	114.86530
C <sub>12</sub> -C <sub>4</sub> -O <sub>5</sub>	124.41	127.68	128.48571
O <sub>5</sub> -C <sub>4</sub> -N <sub>1</sub>	120.38	122.83	123.84457
C <sub>4</sub> -N <sub>1</sub> -N <sub>18</sub>	116.70	115.91	115.37699
N <sub>1</sub> -N <sub>18</sub> -C <sub>20</sub>	112.07	112.36	117.42340
N <sub>18</sub> -C <sub>20</sub> -S <sub>25</sub>	129.16	116.10	116.14570
N <sub>18</sub> -C <sub>20</sub> -N <sub>27</sub>	113.26	119.75	121.48441
C <sub>20</sub> -N <sub>27</sub> -H <sub>28</sub>	116.41	121.09	122.23106
C <sub>20</sub> -N <sub>27</sub> -H <sub>29</sub>	114.34	117.23	117.44494
N <sub>27</sub> -C <sub>20</sub> -S <sub>25</sub>	117.46	123.89	122.31260
Cl <sub>34</sub> -M <sub>33</sub> -Cl <sub>35</sub> *	140.52	159.26	163.16034
N <sub>1</sub> -M <sub>33</sub> -N <sub>2</sub>	102.71	142.97	146.47597
N <sub>1</sub> -M <sub>33</sub> -S <sub>25</sub>	71.59	80.37	81.97390
S <sub>25</sub> -M <sub>33</sub> -S <sub>26</sub>	112.75	56.20	56.97139
S <sub>26</sub> -M <sub>33</sub> -N <sub>2</sub>	71.59	81.03	80.60225
S <sub>26</sub> -M <sub>33</sub> -Cl <sub>35</sub> *	95.47	124.21	111.18399
S <sub>25</sub> -M <sub>33</sub> -Cl <sub>34</sub> *	105.84	73.97	87.37209
N <sub>1</sub> -M <sub>33</sub> -Cl <sub>35</sub> *	74.97	81.34	83.22014
N <sub>2</sub> -M <sub>33</sub> -Cl <sub>34</sub> *	80.72	105.12	114.80219
M <sub>33</sub> -O <sub>35</sub> -C <sub>39</sub>	-	121.79	124.64702
M <sub>33</sub> -O <sub>34</sub> -C <sub>38</sub>	-	125.23	127.51604
O <sub>35</sub> -C <sub>39</sub> -O <sub>36</sub>	-	121.97	-
O <sub>34</sub> -C <sub>38</sub> -O <sub>37</sub>	-	122.41	-
O <sub>35</sub> -C <sub>39</sub> -C <sub>40</sub>	-	112.50	-
O <sub>34</sub> -C <sub>38</sub> -O <sub>41</sub>	-	113.67	-

In case of nitrate Cl<sub>35</sub> is O<sub>35</sub>**REFERENCES**

- Rai BK, and Kumar R, Synthesis, Structural, spectroscopic and antibacterial studies of schiff base ligands and their metal complexes containing nitrogen and sulphur donor atom Ori. J. Chem., 29 (2013) 1163.
- Ali MA, Mirza AH, Mei CC, Bernhardt PV, and Karim MR, Synthesis, spectroscopy and x-ray crystal structures of some zinc(II) and cadmium(II) complexes of the 2-pyridinecarboxaldehyde Schiff bases of S-methyl- and S-benzylthiocarbazates Polyhedron, 49 (2013) 277.
- Chandra S, and Pundir M, Spectroscopic characterization of chromium(III), manganese(II) and nickel(II) complexes with a nitrogen donor tetradentate, 12-membered azamacrocyclic ligand, Spectrochim. Acta Part A, 69 (2008) 1.
- Chandra S, and Gautam A, Spectroscopic and biological approach in the characterization of Cr(III), Mn(II) and Co(II) complexes with a novel hexaaza macrocyclic ligand derived from semicarbazide, J. Serb. Chem. Soc., 74 (2009) 1413.
- Chandra S, and Gupta LK, Spectroscopic approach in characterization of chromium(III), manganese(II), iron(III) and copper(II) complexes with a nitrogen donor tetradentate, 14-membered azamacrocyclic ligand, Spectrochim. Acta Part A, 61 (2005) 2549.
- Chandra S, Bargujar S, Nirwal R, Qanungo K, and Sharma SK, Spectroscopic evaluation of manganese(II) complexes derived from semicarbazones and thiosemicarbazones, Spectrochim. Acta Part A, 113 (2013) 164.
- Tyagi M, Chandra S, and Tyagi P, Mn(II) and Cu(II) complexes of a bidentate Schiff's base ligand: Spectral, thermal, molecular modelling and mycological studies Spectrochim. Acta Part A, 117 (2014) 1.
- Chandra S, Vandana, and Kumar S, Synthesis, spectroscopic, anticancer, antibacterial and antifungal studies of Ni(II) and Cu(II) complexes

- with hydrazine carboxamide, 2-[3-methyl-2-thienyl methylene] Spectrochim. Acta Part A, 135 (2015) 356.
9. Rai BK, Kumar R, and Thakur A, Antimicrobial screening of Co(II), Ni(II) and Cu(II) Complexes with nitrogen and oxygen containing schiff base Ori. J. Chem. 28 (2015) 943.
  10. Sawant NV, Biswal J, & Garje SS, Synthesis, structural and thermal studies of some biologically active antimony semicarbazones and thiosemicarbazones, J. Coord. Chem., 64 (2011) 1758.
  11. Al-Amiery AA, Al-Majedy YK, Abdulreazak H, & Abood H, Synthesis, Characterization, Theoretical Crystal Structure, and Antibacterial Activities of Some Transition Metal Complexes of the Thiosemicarbazone (Z)-2-(pyrrolidin-2-ylidene)hydrazinecarbothioamide Bioinorg. Chem. Appl., (2011) 1. doi:10.1155/2011/483101.
  12. Parmar KC, Vora J J, & Vasava S B, Synthesis, Spectral and microbial studies of some novel schiff base derivatives of 2-amino pyridine, Journal of Chemical and Pharmaceutical Research, 6 (2014) 259.
  13. Kumar U, & Chandra S, Synthesis, Characterization and in vitro Antifungal Screening of Manganese(II) and Copper(II) Complexes of Hexaaza [N6] Macrocylic Ligand J. Nepal Chem. Soc., 25 (2010) 46.
  14. Rao Y.S., Prathima B., Hariprasad O., Reddy N.N., Jagadeesh M., & Reddy A.V., Synthesis, characterization and bioactivities of Ni(II) and Co(II) complexes of benzyloxybenzaldehydethiosemicarbazone J. Chem. Pharm. Res, 2(2010) 292.
  15. Prakash A, & Adhikari D, Application of Schiff bases and their metal complexes-A Review Int. J. Chem Tech Res., 3(2011) 1891.
  16. Chandra S, & Vandana, Synthesis, spectroscopic, anticancer and antibacterial studies of Ni(II) and Cu(II) complexes with 2-carboxybenzaldehyde thiosemicarbazone Spectrochim. Acta Part A, 129 (2014) 333.
  17. Chandra S & Gautam S, Antibacterial and antifungal activity of Schiff base ligands and their metal complexes-A Review Int. J. Chem. Pharma. Sci., 5 (2014) 27.
  18. Chandra S, & Agrawal S, Spectroscopic characterization of Lanthanoid derived from a hexadentate macrocyclic ligand: Study on antifungal capacity of complexes Spectrochim. Acta Part A, 124 (2014) 564.
  19. Kumar S, Dhar DN & Saxena PN, Applications of metal complexes of Schiff bases-A review J. Sci. Ind. Res.,; 68 (2009) 181.
  20. Chandra S, Gautam S, Kumar A & Madan M, Coordination mode of pentadentate ligand derivative of 5-amino-1,3,4-thiadiazole-2-thiol with nickel(II) and copper(II) metal ions: Synthesis, spectroscopic characterization, molecular modeling and fungicidal study Spectrochim. Acta Part A, 136 (2015) 672.
  21. Rani S, Kumar S & Chandra S, Spectroscopic and biological approach in the characterization of a novel 14-membered [N4] macrocyclic ligand and its palladium(II), platinum(II), ruthenium(III) and iridium(III) complexes Spectrochim. Acta Part A, 118 (2014) 244.
  22. Chandra S, Singh D & Sarkar A, PVC Membrane Selective Electrode for Determination of Cadmium(II) Ion in Chocolate Samples Chin. J. Chem. Eng., 22 (2014) 480.
  23. Sharma AK & Chandra S, Complexation of nitrogen and sulphur donor Schiff's base ligand to Cr(III) and Ni(II) metal ions: Synthesis, spectroscopic and antipathogenic studies Spectrochim. Acta Part A, 78 (2011) 337.
  24. Chandra S, Ruchi, Qanungo K & Sharma SK, New hexadentate macrocyclic ligand and their copper(II) and nickel(II) complexes: Spectral, magnetic, electrochemical, thermal, molecular modeling and antimicrobial studies Spectrochim. Acta Part A, 94 (2012) 317.
  25. Chandra S, Goel S & Dwivedi SD, Spectroscopic and biological studies on newly synthesized copper (II) and nickel (II) complexes with p-dimethylaminobenzaldehyde semicarbazone and p-dimethylaminobenzaldehyde

- thiosemicarbazone Int. J. Appl. Bio. Pharma. Tech., 3 (2012) 1.
26. Chandra S, Gautam S & Kumar A, Antifungal screening of nitrogen and sulphur donor atom containing ligand 3,3'-thiodipropionicacid-bis(5-amino-1,3,4-thiodiazole-2-thiol) and its Mn(II), Co(II) complexes: synthesis, spectroscopic approach, molecular modeling World J. Pharma. Res., 3 (2012) 576.
  27. Nakamoto N, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., John Wiley & Sons, New York, NY, USA, 1978.
  28. Chandra S & Verma S, Spectroscopic studies of transition metal complexes with a N-donor tetradentate(N<sub>4</sub>) 12-membered macrocyclic ligand Spectrochim. Acta Part A, 71 (2008) 458.
  29. Lever ABP, Crystal field spectra, in: Inorganic Electronic Spectroscopy, first ed., Elsevier, Amsterdam, 1968.
  30. Chandra S & Pipil P, Ir electronic and epr spectral studies on cobalt(II) complexes of macrocyclic ligand J. Saudi Chem. Soc., 11 (2007) 41.
  31. Hathaway BJ, Bradley JN & Gillard RD, Essays in Chemistry, Academic Press, New York, 1971.
  32. Chandra S, Gautam S, Rajor HK & Bhatia R, Syntheses, spectroscopic characterization, thermal study, molecular modeling, and biological evaluation of novel Schiff's Base benzil bis(5-amino-1,3,4-thiodiazole-2-thiol) with Ni(II), and Cu(II) metal complexes Spectrochim. Acta Part A, 137 (2015) 749.
  33. Chandra S & Gupta LK, EPR mass IR electronic and magnetic studies on copper(II) complexes of semicarbazones and thiosemicarbazones Spectrochim. Acta Part A, 61 (2005) 1181.