



## Mn(II), Co(II), Ni(II), & Cu(II) COMPLEXES OF NITROGEN AND SULPHUR DONOR LIGAND: SYNTHESIS, SPECTRAL CHARACTERIZATION, MOLECULAR MODELING AND MICROBIOLOGY ACTIVITY

Sulekh Chandra\*<sup>1</sup>, Seema Gautam<sup>1</sup>, Amit Kumar<sup>2</sup>, Swati Agrawal<sup>3</sup>

<sup>1</sup>Department of Chemistry, Zakir Husain Delhi College (University of Delhi), JLN Marg, New Delhi-110002, India

<sup>2</sup>Department of Chemistry, Dayal Singh College (University of Delhi), New Delhi-110003, India

<sup>3</sup>Department of Chemistry, Moti Lal Nehru College (University of Delhi), Benito Juarez Road, New Delhi-110021, India

### ABSTRACT

Mn(II), Co(II), Ni(II) and Cu(II) complexes of nitrogen and sulphur donor atoms containing ligand i.e. 3,3'-thiodipropionic acid-bis(5-amino-1,3,4-thiodiazole-2-thiol) were synthesized and characterized by physical, analytical and spectroscopic methods. Elemental analysis indicated that metal complexes possessed general composition  $M(L)(NO_3)_2$  and  $M(L)(SO_4)$ , where  $M = Mn(II), Co(II), Ni(II), Cu(II)$  and  $L =$  ligand. The molar conductance value indicated that metal complexes  $[M(L)NO_3]NO_3$  and  $[M(L)SO_4]$  were electrolytic and non-electrolytic in nature, respectively. On the basis of IR Spectral study, it was concluded that ligand contain nitrogen and sulphur donor atoms and these donor atoms coordinated to metal ions and formed metal complexes. All complexes were found to have six-coordinated geometry i.e. Mn(II), Ni(II), Co(II) complexes possessed octahedral geometry, whereas Cu(II) complexes, distorted octahedral or tetragonal geometry. The covalency factor ( $\beta$ ) suggested that all complexes were covalent in nature. Ligand and metal complexes i.e. Mn(II), Co(II), Ni(II) and Cu(II) were screened for their microbiology activity against four fungi i.e. *Candida krusei*, *Candida tropicalis* and *Candida parapsilosis*.

**Keywords:** ligand, complexes, electrolytic, non-electrolytic, Spectral studies, covalency factor, six-coordinated geometry, microbiology.

### INTRODUCTION

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of multi donor ligands containing nitrogen, sulphur, and oxygen donor atoms<sup>1</sup>. Multi donor atom containing ligands are able to bind with transition metal ions to give stable complexes, which have various industrial and biological applications<sup>2</sup>. Presently, there is a growing interest in the coordination chemistry of structurally modified multi donor atom containing bio-ligands. Transition metal complexes of multi donor atom containing bio-ligands exhibit potential biological activity, are the focus of extensive investigations. These multi donor ligands are a class of important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial<sup>3-5</sup>, antifungal<sup>6-8</sup> and anticancer<sup>9-10</sup>. In order to exploit new type of multi donor atoms containing ligand and biological active compound, 3,3'-thiodipropionic acid was used in the present study to react with 5-amino-1,3,4-thiodiazole-2-thiol. Multi donor atoms containing novel ligand 3,3'-thiodipropionic acid-bis(5-amino-1,3,4-thiodiazole-2-thiol) and its Mn(II), Co(II), Ni(II), and Cu(II) metal complexes were synthesized. The chemical structures were confirmed by means of elemental analysis, IR, mass, UV-Visible, <sup>1</sup>H-NMR spectroscopy, molar conductivity measurement, magnetic moment, EPR, and theoretically by molecular modeling study. All

**Corresponding Author:**

**Email:** [seemachem.gautam@gmail.com](mailto:seemachem.gautam@gmail.com)

compounds were also screened for their microbiology activity.

## MATERIALS AND METHODS

### Materials

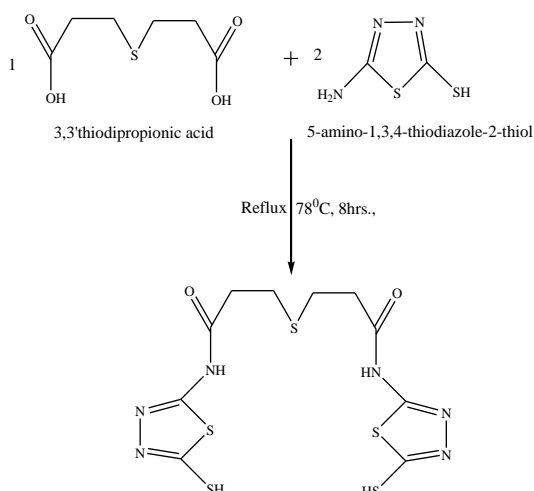
All the chemicals used were of Analytical grade and procured from Sigma-Aldrich, and Alfa Aesar. Metal salts were purchased from E. Merck and were used as received.

### Physical measurement methods

The microanalysis (CHN) was analyzed on a Carlo-Erba-1106 elemental analyzer. Magnetic susceptibility was measured at room temperature on a Gouy balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a calibrant. Molar conductance was measured on the ELICO (CM82T) conductivity bridge.  $^1\text{H-NMR}$  spectrum was recorded on a Hitachi FT-NMR, model R-600 spectrometer using DMSO as solvent. Chemical shifts are given in parts per million relative to tetramethylsilane. IR spectra were recorded using a FT-IR spectrum BX-II spectrophotometer on KBr pellets. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of complexes were recorded as polycrystalline sample and in DMSO at liquid nitrogen temperature on  $E_4$ -EPR spectrometer using the DPPH as the g-marker. Computational molecular modeling of the proposed structure of ligand and its complexes was modelled by using *Gaussian View 5.0* at Semi empirical PM6 level.

### Synthesis of ligand

A hot ethanolic solution (20 mL) of 3,3'-



**Fig. 1** Synthesis of nitrogen and sulphur donor ligand

thiodipropionic acid (0.001 mol) and a hot ethanolic solution (20 mL) of 5-amino-1,3,4-thiadiazole-2-thiol (0.002 mol) were mixed slowly with constant stirring. This mixture was refluxed at  $78^\circ\text{C}$  for 8 hrs. When the mixture was cooled in ice bath, a solid precipitate was formed, which was filtered off, washed with cold ethanol, and dried in a desiccator using silica gel as moisture absorbent. The synthetic route for ligand is shown in Fig. 1.

### Synthesis of complexes

A hot ethanolic solution of the ligand (0.001 mol) and hot ethanolic solution (20 mL) of corresponding metal salts (0.001 mol) were mixed with constant stirring. The mixture was refluxed for 10-15 hrs. at  $80^\circ\text{C}$ . Colored complex was precipitate out. This precipitate was filtered off, washed with ethanol and dried in a desiccator using silica gel as moisture absorbent. Physical data and elemental analysis for all synthesized complexes are shown in Table 1.

### Microbiology Activity

*Candida krusei*, *Candida tropicalis* and *Candida parapsilosis* were used to investigate microbiology activity (antifungal) of synthesized ligand and metal complexes. Stock solutions of tested compounds were prepared by dissolving the compounds in DMSO to get desired concentration i.e. 1000 ppm, 750 ppm, and 500 ppm. Bavastin and DMSO were used as commercial fungicide and as a control, respectively. Well diffusion method<sup>11</sup> was used for testing of antifungal activity. Sabouraud Dextrose Agar (SDA) media was used for testing antifungal activity. First of all, SDA was dissolved in distilled water, and antibacterial tetracycline was added in it to kill bacteria, if present, and autoclaved for 30 min. Now, autoclaved SDA media was poured into petri plates under aseptic conditions in a laminar flow hood. When media was solidified in petri plates, prepared broth of tested organism was rubbed on media surface, wells were prepared in each petri plate at equidistance, and tested compound of different concentration was poured in prepared wells. These treated petri plates were incubated at  $27 \pm 2^\circ\text{C}$  until fungal growth in the control petri plate was almost complete. All determination were made in duplicate for each of tested compound. The mycelial growth of fungi (mm) in each petri plate was measured diametrically and growth inhibition (I) were calculated by using the formula:  $I (\%) = (CT)/C \times 100$  Where I = % Inhibition, C = Radial diameters of

**Table 1 Physical data of synthesized ligand and metal complexes and their molar conductance in DMSO**

Compounds	Color	Mole- cular Weight	Meltin g Point (°C)	Molar Conduc- tance ( $\Omega^{-1}\text{cm}^2$ $\text{mol}^{-1}$ )	Yield (%)	Elemental Analysis Calculated(Found)			
						M	C	H	N
Ligand $\text{C}_{10}\text{H}_{12}\text{N}_6\text{O}_2\text{S}_5$	White	408	180	-					
$[\text{Mn}(\text{L})\text{NO}_3]\text{NO}_3$ $\text{MnC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	Brown	586.9	>320	86	50	9.35	20.44	2.04	19.08
$[\text{Mn}(\text{L})\text{SO}_4]$ $\text{MnC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_5$	White	558.9	>250	22					
$[\text{Co}(\text{L})\text{NO}_3]\text{NO}_3$ $\text{CoC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	Reddish Pink	590.9	>250	75	44	9.96	20.30	2.03	18.89
$[\text{Co}(\text{L})\text{SO}_4]$ $\text{CoC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_5$	Green	562.9	>320	25	52	10.46	21.31	2.03	14.21
$[\text{Ni}(\text{L})\text{NO}_3]\text{NO}_3$ $\text{NiC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	Parrot Green	590.7	>320	98	59	9.93	20.31	2.03	18.96
$[\text{Ni}(\text{L})\text{SO}_4]$ $\text{NiC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_5$	Prussian Blue	562.7	>250	15	64	10.43	21.32	2.13	14.92
$[\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$ $\text{CuC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	Green	595.5	>320	98	68	10.66	20.15-	2.01	18.80
$[\text{Cu}(\text{L})\text{SO}_4]$ $\text{CuC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_5$	Mehndi Green	567.5	>320	30	49	11.18	21.14	2.11	14.80

C-carbon, H-hydrogen, N-nitrogen, M-metal

the colony in control, T = Radial diameter of the colony in test compound.

## RESULTS AND DISCUSSION

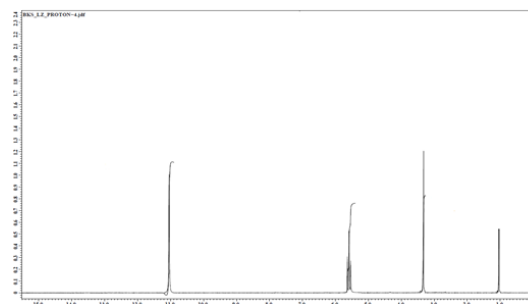
3,3'-thiodipropionic acid-bis(5-amino-1,3,4-thiodiazole-2-thiol) ligand was prepared by using condensation reaction between 2mol of 5-amino-1,3,4-thiodiazole-2-thiol and 1mol of 3,3'-thiodipropionic acid. Synthesized ligand further reacted with Mn(II), Co(II), Ni(II) and Cu(II) metal ions in the presence of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  anions gave rise to complexes with different composition. All the complexes were stable at room temperature and insoluble in nonpolar organic solvents but soluble in dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). Ligand act as multi donor ligand and coordinated through nitrogen and sulphur donor atoms. The elemental and analytical data of ligand and its complexes was given in Table 1. These data were in a good agreement with the proposed formula. The electrical molar conductivity value of the complexes in DMSO indicated non electrolytic nature for  $[\text{M}(\text{L})\text{SO}_4]$  complexes and electrolytic nature for  $[\text{M}(\text{L})\text{NO}_3]\text{NO}_3^-$  complexes. Molar

conductance value for all complexes are mentioned in Table 1.

## SPECTROSCOPIC CHARACTERIZATION

### $^1\text{H-NMR}$ spectrum of ligand

$^1\text{H-NMR}$  spectrum of ligand in  $\text{DMSO-d}_6$  displayed following signals: Signal at  $\delta$  3.0-3.5 for (s, 2H, 2SH) due to the presence of proton of SH group Fig. 2<sup>12</sup>. Multiplets at  $\delta$  5.7-5.9 ppm (m, 12H, 6CH<sub>2</sub>) due to the protons of six methylene groups, broad signal at  $\delta$  9.6 ppm (s, 2H, 2NH), corresponding to the two



**Fig. 2  $^1\text{H-NMR}$  spectrum of nitrogen and sulphur donor ligand**

**Table 2 : Selected IR bands of nitrogen and sulphur donor ligand and its complexes**

Compound	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C-S})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$	Anion Bands
$\text{C}_{10}\text{H}_{12}\text{N}_6\text{O}_2\text{S}_5$	1522	1609	754	-	-	-
$\text{MnC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	1475	1608	725	340	450	1401( $\nu_5$ ), 1310( $\nu_1$ ), 1057( $\nu_2$ )
$\text{MnC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_6$	1498	1608	744	325	450	972( $\nu_1$ ), 1127( $\nu_3$ )
$\text{CoC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	1499	1607	680	350	440	1397( $\nu_5$ ), 1322( $\nu_1$ ), 1068( $\nu_2$ )
$\text{CoC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_6$	1488	1612	709	327	434	980( $\nu_1$ ), 1120( $\nu_3$ )
$\text{NiC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	1492	1604	732	345	446	1425( $\nu_5$ ), 1320( $\nu_1$ ), 1070( $\nu_2$ )
$\text{NiC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_6$	1504	1610	701	319	452	988( $\nu_1$ ), 1135( $\nu_3$ )
$\text{CuC}_{10}\text{H}_{12}\text{N}_8\text{O}_8\text{S}_5$	1490	1601	740	339	458	1417( $\nu_5$ ), 1311( $\nu_1$ ), 1061( $\nu_2$ )
$\text{CuC}_{10}\text{H}_{12}\text{N}_6\text{O}_6\text{S}_6$	1501	1614	740	351	439	982( $\nu_1$ ), 1098 ( $\nu_3$ )

protons of two NH groups<sup>13-14</sup>.

### Mass Spectrum of ligand

The molecular ion peak for the ligand is observed at 409  $m/z$  which is in good agreement with the suggested molecular formula [ $\text{C}_{10}\text{H}_{11}\text{N}_6\text{O}_2\text{S}_5$ ]. The peaks at  $m/z = 375$  and 220 were due to the fragment of -SH group and the heterocyclic ring ( $\text{C}_5\text{N}_3\text{S}_2\text{H}_6$ ). Another high intensity peak at  $m/z = 160$  also appeared in the spectrum due to the (-CHNO) group. The fragmentation of the ligand is taken as a general scheme showing the main fragmentation paths involved and the fragmentation pattern is given in Fig. 3. The other positive ions gave peaks at 407, 291, 248, 188, 117 and 84.

### IR Spectrum

The IR spectrum of ligand displayed bands at 1609, and 1552  $\text{cm}^{-1}$ , which may be assigned to the  $\nu(\text{C=O})$  of amide group, and stretching vibration of  $\nu(\text{NH})$  group<sup>15</sup>. The band appearing at 754  $\text{cm}^{-1}$  in the spectrum corresponded to the  $\nu(\text{C-S})$  stretching vibration<sup>16</sup>. The bands which appeared in ligand at 1552  $\text{cm}^{-1}$ , and 754  $\text{cm}^{-1}$ , shifted downward in complexes spectra which indicated that the nitrogen atoms of NH groups and sulphur atoms of C-S-C group coordinated to the central metal ion. The coordination behavior of ligand through nitrogen, was also confirmed by the appearance of new bands in the spectra of complexes in 434-458  $\text{cm}^{-1}$  range. These bands may be assigned to  $\nu(\text{M-N})$  stretching vibrations, respectively<sup>17</sup>. However, the band corresponding to the C=O group remains almost unchanged on complexation, which indicated that the oxygen atom of carbonyl group was not involved in coordination. This discussion suggested that the ligand coordinated to metal ion in NNSSS ( $\text{N}_2\text{S}_3$ ) manner<sup>18</sup>.

### IR bands due to anions

The IR spectra of metal complexes also displayed the bands due to anions. In sulphato complexes, the two bands in the range 960-990  $\text{cm}^{-1}$  ( $\nu_1$ ) and strong band 1037-1137  $\text{cm}^{-1}$  ( $\nu_3$ ) were appeared Table 2. The splitting of ( $\nu_3$ ) band into two bands suggested the coordination of  $\text{SO}_4^{2-}$  ion was in unidentate manner<sup>19</sup>. The nitrate complexes showed bands in the range 1390-1427 ( $\nu_5$ ), 1310-1323 ( $\nu_1$ ) and 1050-1070  $\text{cm}^{-1}$  ( $\nu_2$ ) due to NO stretching vibration of the  $\text{NO}_3^-$  ion. The  $\Delta\nu$  i.e.  $\nu_5-\nu_1$  (93-95  $\text{cm}^{-1}$ ) indicated unidentate coordination of  $\text{NO}_3^-$  ion<sup>20</sup>. Appearance of a strong band at 1384  $\text{cm}^{-1}$ , suggested that one  $\text{NO}_3^-$  ion was not coordinated, means located outside of the coordination sphere<sup>21</sup>.

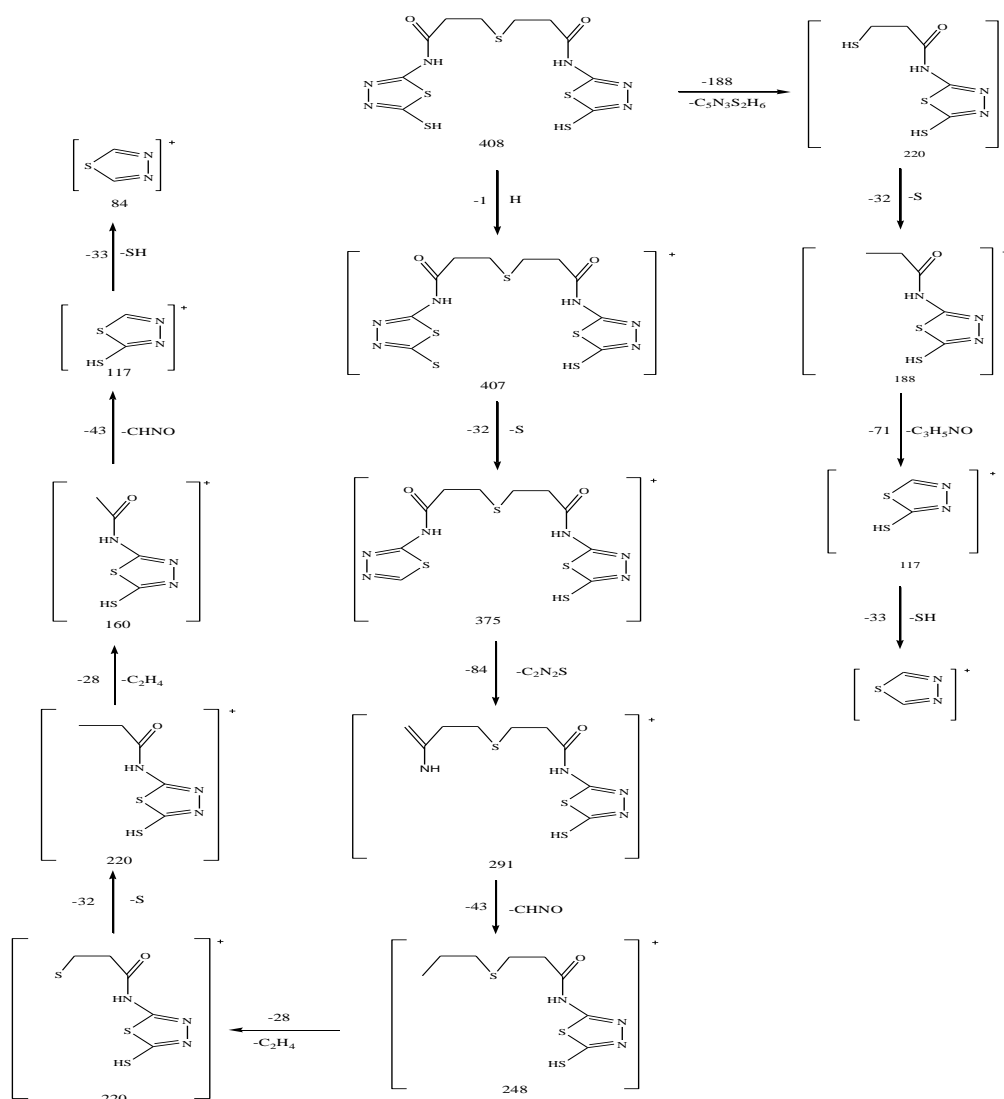
### Electronic spectra of metal complexes

#### Mn(II) Complex

Mn(II) complexes showed magnetic moment in the range 5.92-5.95 BM corresponding to five unpaired electrons. The electronic spectra of the complexes were recorded by using DMSO as solvent. All complexes showed the high energy absorption band in the region 36496-41322  $\text{cm}^{-1}$ . These higher energy absorption bands corresponding to charge transfer band<sup>22</sup>. The electronic spectra of the complex under study showed absorption bands, which were characteristic to an octahedral geometry. The complexes displayed four spectral bands in the range of 18621-23100  $\text{cm}^{-1}$ , 23100-24970  $\text{cm}^{-1}$ , 24970-28000  $\text{cm}^{-1}$  and 28000-29700  $\text{cm}^{-1}$  Table 3. These spectral bands may be assigned the following transitions  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ , and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ <sup>23</sup>. The EPR spectra were recorded as polycrystalline sample at room temperature Fig. 5 (a)(b). The polycrystalline spectra gave isotropic signal and exhibit g values in the range 1.05-2.18<sup>24</sup>.

**Table 3 : Electronic spectral band ( $\text{cm}^{-1}$ ) and Electron Paramagnetic Resonance spectra data of complexes**

Complexes	$\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ )	Electron Paramagnetic Resonance spectra data			
		$g_{  }$	$g_{\perp}$	$g_{\text{iso}}$	G
[Mn(L)NO <sub>3</sub> ]NO <sub>3</sub>	18621, 24472, 27489	-	-	2.18	-
[Mn(L)SO <sub>4</sub> ]	18962, 24768, 28020	-	-	2.06	-
[Co(L)NO <sub>3</sub> ]NO <sub>3</sub>	9310, 15300, 19125	2.16	2.00	2.5	-
[Co(L)SO <sub>4</sub> ]	9940, 15360, 18621	2.19	2.09	2.19	-
[Ni(L)NO <sub>3</sub> ]NO <sub>3</sub>	10834, 12816, 21413	-	-	-	-
[Ni(L)SO <sub>4</sub> ]	12108, 18623, 30322	-	-	-	-
[Cu(L)NO <sub>3</sub> ]NO <sub>3</sub>	12184, 16001, 25575	2.31	2.03	2.15	1.3
[Cu(L)SO <sub>4</sub> ]	15432, 17653, 27380	2.16	2.11	2.12	1.6


**Fig. 3 Mass fragmentation pattern of nitrogen and sulphur donor ligand**

 The ligand field parameter values  $Dq$ ,  $B$ ,  $C$ ,  $\beta$ ,  $F_2$ ,  $F_4$ ,

 $h_x$  for Mn(II) were calculated and given in Table 4.

**Table 4 : Ligand Field Parameters**

Complex	Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	$\beta$	C (cm <sup>-1</sup> )	$\nu_2/\nu_1$	F <sub>4</sub>	F <sub>2</sub>	hx	LFSE (KJ/mole)
[Mn(L)NO <sub>3</sub> ]NO <sub>3</sub>	1896	543	0.690	3867	1.305	110.48	1048.4	4.42	-
[Mn(L)SO <sub>4</sub> ]	1862	496	0.627	3902.4	1.314	111.49	1053.45	13.28	-
[Co(L)NO <sub>3</sub> ]NO <sub>3</sub>	994	344.06	0.30	-	1.545	-	-	-	142.67
[Co(L)SO <sub>4</sub> ]	931	433	0.386	-	1.64	-	-	-	133.63
[Ni(L)NO <sub>3</sub> ]NO <sub>3</sub>	1210	841	0.80	-	1.538	-	-	-	173.68
[Ni(L)SO <sub>4</sub> ]	1.182	115.13	0.11	-	1.182	-	-	-	155.45

**Table 5: Optimized geometry of pentadentate ligand and its metal complexes (bond length in angstrom)**

Parameters (bond length) [Mn(L)NO <sub>3</sub> ]NO <sub>3</sub>		Parameters (bond length) [Mn(L)SO <sub>4</sub> ]	
S <sub>1</sub> -C <sub>2</sub>	1.85928	S <sub>1</sub> -C <sub>2</sub>	1.85442
C <sub>2</sub> -C <sub>5</sub>	1.52327	C <sub>2</sub> -C <sub>5</sub>	1.51031
C <sub>5</sub> -C <sub>14</sub>	1.50461	C <sub>5</sub> -C <sub>14</sub>	1.50272
C <sub>14</sub> -O <sub>20</sub>	1.19300	C <sub>14</sub> -O <sub>20</sub>	1.19996
C <sub>14</sub> -N <sub>16</sub>	1.53262	C <sub>14</sub> -N <sub>16</sub>	1.50272
N <sub>16</sub> -C <sub>24</sub>	1.43583	N <sub>16</sub> -C <sub>24</sub>	1.43487
S <sub>27</sub> -C <sub>24</sub>	1.80671	S <sub>27</sub> -C <sub>24</sub>	1.78497
S <sub>27</sub> -C <sub>25</sub>	1.76905	S <sub>27</sub> -C <sub>25</sub>	1.74405
C <sub>24</sub> -N <sub>26</sub>	1.33140	C <sub>24</sub> -N <sub>26</sub>	1.33740
N <sub>26</sub> -N <sub>22</sub>	1.34214	N <sub>26</sub> -N <sub>22</sub>	1.34245
N <sub>22</sub> -C <sub>25</sub>	1.34633	N <sub>22</sub> -C <sub>25</sub>	1.35252
C <sub>25</sub> -S <sub>28</sub>	1.72893	C <sub>25</sub> -S <sub>28</sub>	1.72997
S <sub>28</sub> -H <sub>29</sub>	1.35587	S <sub>28</sub> -H <sub>29</sub>	1.35606
S <sub>1</sub> -C <sub>8</sub>	1.85927	S <sub>1</sub> -C <sub>8</sub>	1.85359
C <sub>8</sub> -C <sub>11</sub>	1.52327	C <sub>8</sub> -C <sub>11</sub>	1.52369
C <sub>11</sub> -C <sub>15</sub>	1.50463	C <sub>11</sub> -C <sub>15</sub>	1.51367
C <sub>15</sub> -O <sub>21</sub>	1.19300	C <sub>15</sub> -O <sub>21</sub>	1.19996
C <sub>15</sub> -N <sub>18</sub>	1.53255	C <sub>15</sub> -N <sub>18</sub>	1.50330
N <sub>18</sub> -C <sub>30</sub>	1.43585	N <sub>18</sub> -C <sub>30</sub>	1.43508
S <sub>33</sub> -C <sub>30</sub>	1.80676	S <sub>33</sub> -C <sub>30</sub>	1.78365
S <sub>33</sub> -C <sub>31</sub>	1.76897	S <sub>33</sub> -C <sub>31</sub>	1.74421
S <sub>34</sub> -C <sub>31</sub>	1.72895	S <sub>34</sub> -C <sub>31</sub>	1.72857
S <sub>34</sub> -H <sub>35</sub>	1.35587	S <sub>34</sub> -H <sub>35</sub>	1.35605
C <sub>31</sub> -N <sub>23</sub>	1.34634	C <sub>31</sub> -N <sub>23</sub>	1.35346
N <sub>23</sub> -N <sub>32</sub>	1.34211	N <sub>23</sub> -N <sub>32</sub>	1.34133
N <sub>32</sub> -C <sub>30</sub>	1.33140	N <sub>32</sub> -C <sub>30</sub>	1.33786
S <sub>1</sub> -M <sub>36</sub>	2.18809	S <sub>1</sub> -M <sub>36</sub>	2.18987
M <sub>36</sub> -O <sub>37</sub>	2.02444	M <sub>36</sub> -O <sub>37</sub>	1.74135
M <sub>36</sub> -N <sub>16</sub>	2.13257	M <sub>36</sub> -N <sub>16</sub>	2.16346
M <sub>36</sub> -N <sub>18</sub>	2.13239	M <sub>36</sub> -N <sub>18</sub>	2.16088
M <sub>36</sub> -S <sub>27</sub>	2.21744	M <sub>36</sub> -S <sub>27</sub>	2.29680
M <sub>36</sub> -S <sub>33</sub>	2.21741	M <sub>36</sub> -S <sub>33</sub>	2.29927
O <sub>37</sub> -N <sub>38</sub>	1.33647	O <sub>37</sub> -S <sub>38</sub>	1.77513
N <sub>38</sub> -O <sub>39</sub>	1.25038	S <sub>38</sub> -O <sub>39</sub>	1.47119
N <sub>38</sub> -O <sub>40</sub>	1.19077	S <sub>38</sub> -O <sub>40</sub>	1.47070
		1 <sub>38</sub> -O <sub>40</sub>	1.42633

The values of B and C were calculated from the

**Table 6: Optimized geometry of pentadentate ligand and its metal complexes (bond angle in degree)**

Parameters (bond angle) [Mn(L)NO <sub>3</sub> ]NO <sub>3</sub>		Parameters (bond angle) [Mn(L)SO <sub>4</sub> ]	
C <sub>8</sub> -S <sub>1</sub> -C <sub>2</sub>	104.64	C <sub>8</sub> -S <sub>1</sub> -C <sub>2</sub>	106.64
C <sub>2</sub> -C <sub>5</sub> -C <sub>14</sub>	110.44	C <sub>2</sub> -C <sub>5</sub> -C <sub>14</sub>	111.50
O <sub>20</sub> -C <sub>14</sub> -N <sub>16</sub>	114.57	O <sub>20</sub> -C <sub>14</sub> -N <sub>16</sub>	116.23
N <sub>16</sub> -C <sub>24</sub> -S <sub>27</sub>	112.06	N <sub>16</sub> -C <sub>24</sub> -S <sub>27</sub>	113.12
C <sub>24</sub> -N <sub>26</sub> -N <sub>22</sub>	112.46	C <sub>24</sub> -N <sub>26</sub> -N <sub>22</sub>	112.10
C <sub>25</sub> -S <sub>28</sub> -H <sub>29</sub>	96.95	C <sub>25</sub> -S <sub>28</sub> -H <sub>29</sub>	96.57
S <sub>1</sub> -C <sub>2</sub> -C <sub>5</sub>	103.61	S <sub>1</sub> -C <sub>2</sub> -C <sub>5</sub>	103.15
S <sub>1</sub> -C <sub>8</sub> -C <sub>11</sub>	103.62	S <sub>1</sub> -C <sub>8</sub> -C <sub>11</sub>	103.09
C <sub>8</sub> -C <sub>11</sub> -C <sub>15</sub>	110.44	C <sub>8</sub> -C <sub>11</sub> -C <sub>15</sub>	111.44
C <sub>15</sub> -N <sub>18</sub> -C <sub>30</sub>	116.18	C <sub>15</sub> -N <sub>18</sub> -C <sub>30</sub>	115.65
O <sub>21</sub> -C <sub>15</sub> -N <sub>18</sub>	114.57	O <sub>21</sub> -C <sub>15</sub> -N <sub>18</sub>	116.23
S <sub>33</sub> -C <sub>30</sub> -N <sub>32</sub>	112.45	S <sub>33</sub> -C <sub>30</sub> -N <sub>32</sub>	112.92
C <sub>30</sub> -N <sub>32</sub> -N <sub>23</sub>	112.46	C <sub>30</sub> -N <sub>32</sub> -N <sub>23</sub>	112.13
N <sub>32</sub> -N <sub>23</sub> -C <sub>31</sub>	117.22	N <sub>32</sub> -N <sub>23</sub> -C <sub>31</sub>	115.97
S <sub>33</sub> -C <sub>31</sub> -S <sub>34</sub>	123.44	S <sub>33</sub> -C <sub>31</sub> -S <sub>34</sub>	124.77
C <sub>31</sub> -S <sub>34</sub> -H <sub>35</sub>	96.95	C <sub>31</sub> -S <sub>34</sub> -H <sub>35</sub>	96.60
S <sub>1</sub> -M <sub>36</sub> -N <sub>37</sub>	165.56	S <sub>1</sub> -M <sub>36</sub> -N <sub>37</sub>	156.52
N <sub>18</sub> -M <sub>36</sub> -N <sub>16</sub>	104.28	N <sub>18</sub> -M <sub>36</sub> -N <sub>16</sub>	114.68
S <sub>27</sub> -M <sub>36</sub> -S <sub>33</sub>	101.07	S <sub>27</sub> -M <sub>36</sub> -S <sub>33</sub>	96.68
S <sub>27</sub> -M <sub>36</sub> -N <sub>37</sub>	77.08	S <sub>27</sub> -M <sub>36</sub> -N <sub>37</sub>	93.53
S <sub>33</sub> -M <sub>36</sub> -N <sub>18</sub>	76.62	S <sub>33</sub> -M <sub>36</sub> -N <sub>18</sub>	74.23
S <sub>33</sub> -M <sub>36</sub> -N <sub>16</sub>	76.60	S <sub>33</sub> -M <sub>36</sub> -N <sub>16</sub>	74.24

second and third transitions<sup>25</sup>. The numerical value of 786 cm<sup>-1</sup> for B for the Mn(II) free ion was used to calculate the value of  $\beta$ . The nephelauxetic parameter  $\beta$  was calculated by the relation:  $\beta = B(\text{complex})/B(\text{free ion})$  and the parameter B was calculated by the relation:  $B = 2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2/15\nu_2 - 27\nu_1$ . The  $\beta$  values indicate that there is an appreciable covalent character in the metal-ligand  $\sigma$  bond<sup>26</sup>.

#### Co(II) Complex

Co (II) complexes showed magnetic moment

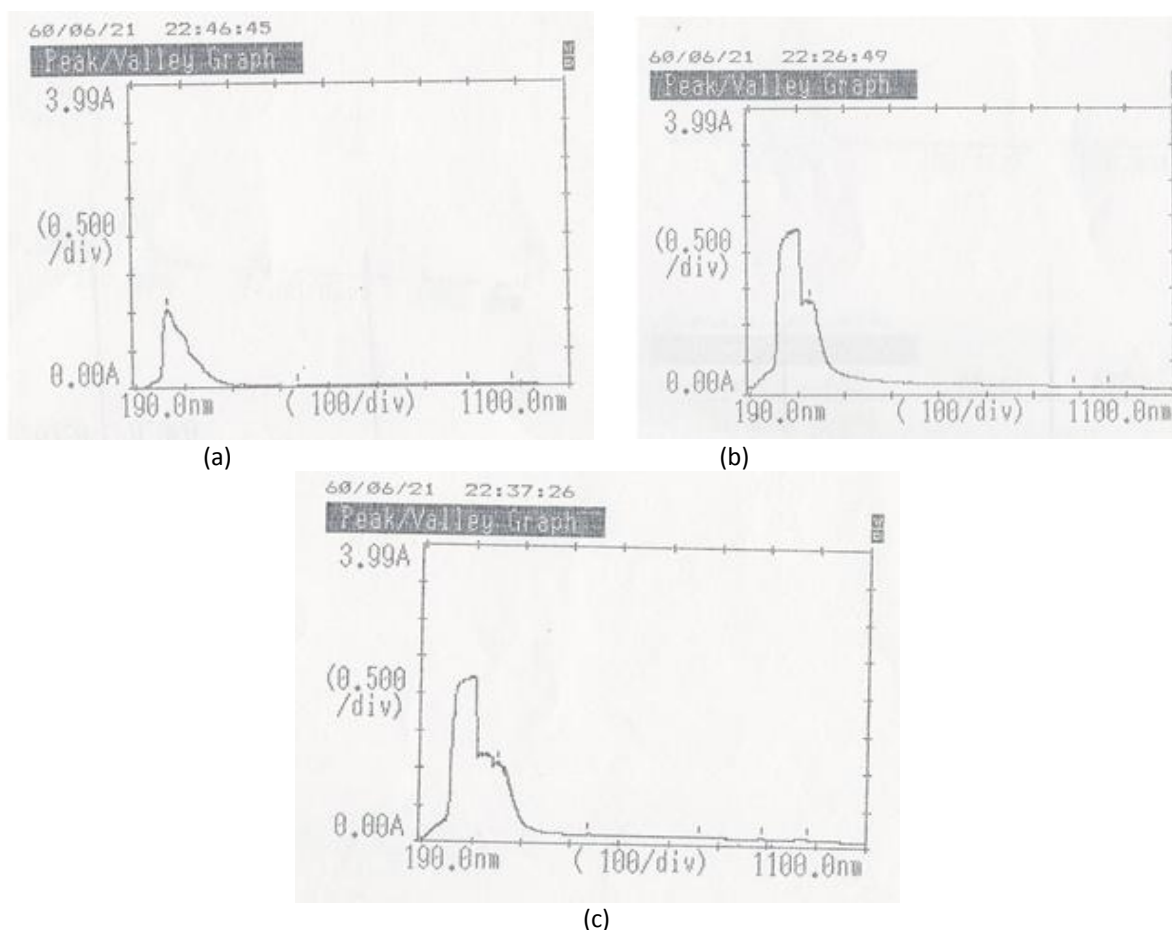


Fig. 4 Electronic Spectra of (a)  $[\text{Ni}(\text{L})\text{SO}_4]$  (b)  $[\text{Cu}(\text{L})\text{SO}_4]$  (c)  $[\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$  Complexes

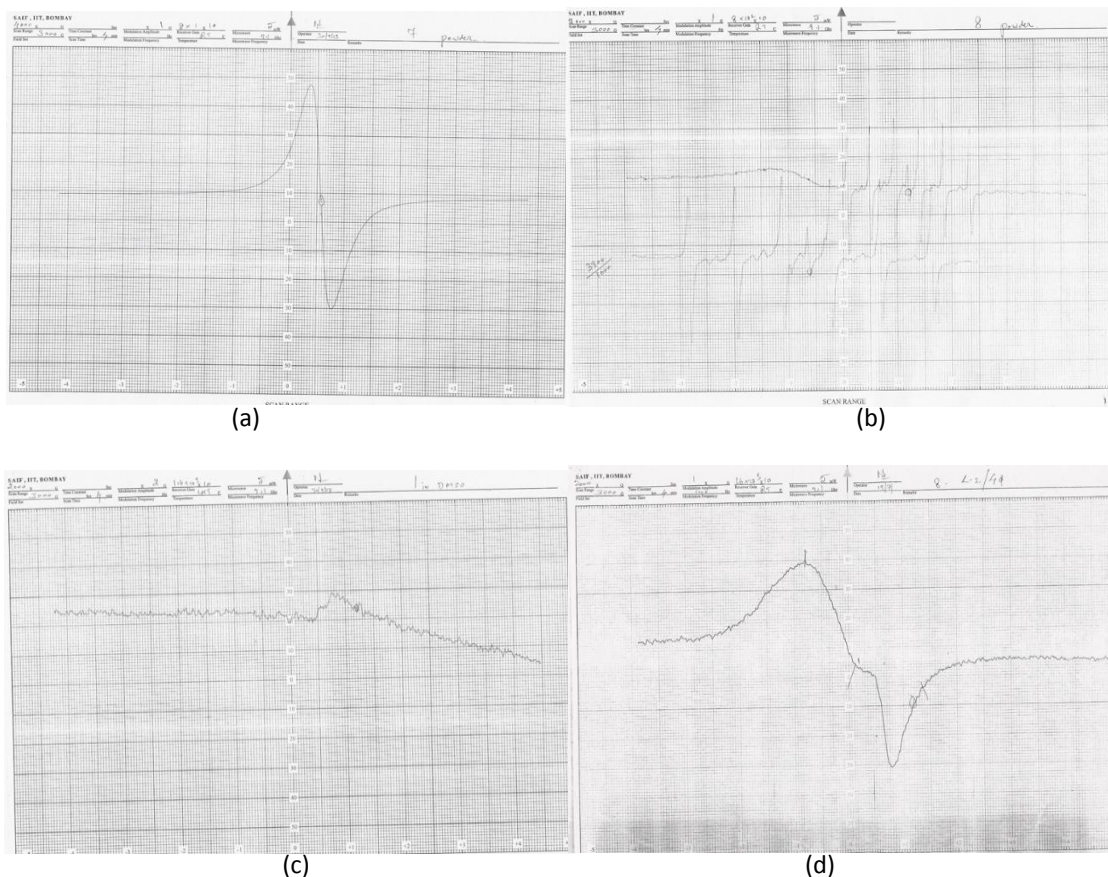
value in the range 4.79-4.92 BM corresponding to four unpaired electrons. The electronic spectra of Co(II) complexes under study displayed the absorption bands in the range of  $9310\text{-}9940\text{ cm}^{-1}$ ,  $13262\text{-}16290$ ,  $16,290\text{-}19,143\text{ cm}^{-1}$  and  $20,510\text{-}22,339\text{ cm}^{-1}$ . These transitions may be assigned to the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ ,  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ , and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$ . These transitions were corresponding to the octahedral geometry of the Co(II) complexes<sup>27</sup>. Various ligand field parameters, i.e. Dq, B,  $\beta$  and LFSE were calculated and reported in Table 4. The Dq values were evaluated using the Orgel diagram<sup>28</sup>. The value for B(free ion) for Co(II) is  $1120\text{ cm}^{-1}$ . The parameter B was calculated by the relation:  $B = u_2 + u_3 - 3u_1/15$ . The values of  $\beta$  lie in the range 0.29-0.40, indicated an appreciable covalent character in the complexes. The EPR spectra of the Co(II) complexes were recorded as polycrystalline samples at liquid nitrogen temperature (LNT), because the rapid spin lattice relaxation of Co(II) broaden the lines at higher temperatures. The g values lie in the range 2.20-2.50 Table 3.

#### Ni(II) Complex

Ni(II) complexes showed magnetic moment in the range 2.96-2.98 BM corresponding to two unpaired electrons. The electronic spectra of Ni(II) complexes were displayed three absorption bands in the ranges of  $9870\text{-}9337\text{ cm}^{-1}$ ,  $14577\text{-}14124\text{ cm}^{-1}$ , and  $25700\text{-}24100\text{ cm}^{-1}$  Fig. 4 (a). The ground state Ni(II) in an octahedral coordination is  ${}^3\text{A}_{2g}$ <sup>29</sup>. Various ligand field parameters, were calculated by Orgel diagrams and calculated, reported in Table 4.

#### Cu(II) Complex

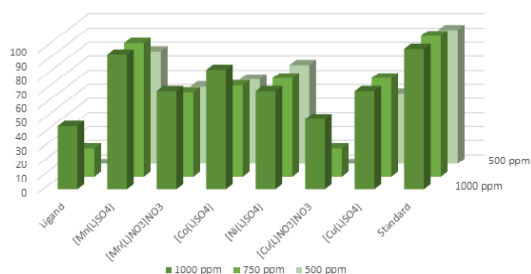
Cu(II) complexes showed magnetic moments in the range 1.24-1.28 BM corresponding to one unpaired electron. The electronic spectra of Cu(II) complexes displayed bands in the ranges of  $12180\text{-}15432\text{ cm}^{-1}$ ,  $15432\text{-}17667\text{ cm}^{-1}$  and  $25575\text{-}27380\text{ cm}^{-1}$  Fig. 4 (b)(c). These bands were corresponded to the transitions  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ , and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ . Therefore, the complexes may be considered to possess a tetragonal geometry<sup>30</sup>. The EPR spectra of the



**Fig. 5** Electron Paramagnetic Resonance spectra of (a)  $[Mn(L)SO_4]$  (b)  $[Mn(L)NO_3]NO_3$  (c)  $[Cu(L)SO_4]$  (d)  $[Cu(L)NO_3]NO_3$

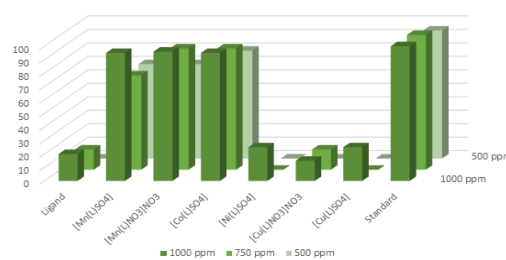
complexes under study recorded as polycrystalline sample at room temperature Fig. 5 (c)(d). The observed  $g_{||}$  values for the complexes are less than 2.4 in agreement with the covalent character of the metal ligand bond. The trend  $g_{||} > g_{\perp} > 2.0023$  observed for the complexes was indicated that unpaired electron was localized in  $d_{x^2-y^2}$  orbital of the Cu(II) ion and the spectral features were

exchange interaction between the metal centres in a polycrystalline solid, were calculated. According to Hathaway<sup>31</sup> if  $G > 4$ , the exchange interaction was negligible, but  $G < 4$  indicates considerable exchange interaction in the solid complexes. The calculated G value found in the range 1.3-1.6. These values were less than 4, so these values indicated the exchange interaction in solid complexes.



**Fig. 8** Graph showing effect of concentration on antifungal activity of compounds against *Candida parapsilosis*

characteristic of axial symmetry. Thus, a tetragonal geometry was confirmed for the aforesaid complexes.  $G = (g_{||} - 2)/(g_{\perp} - 2)$ , which measured the

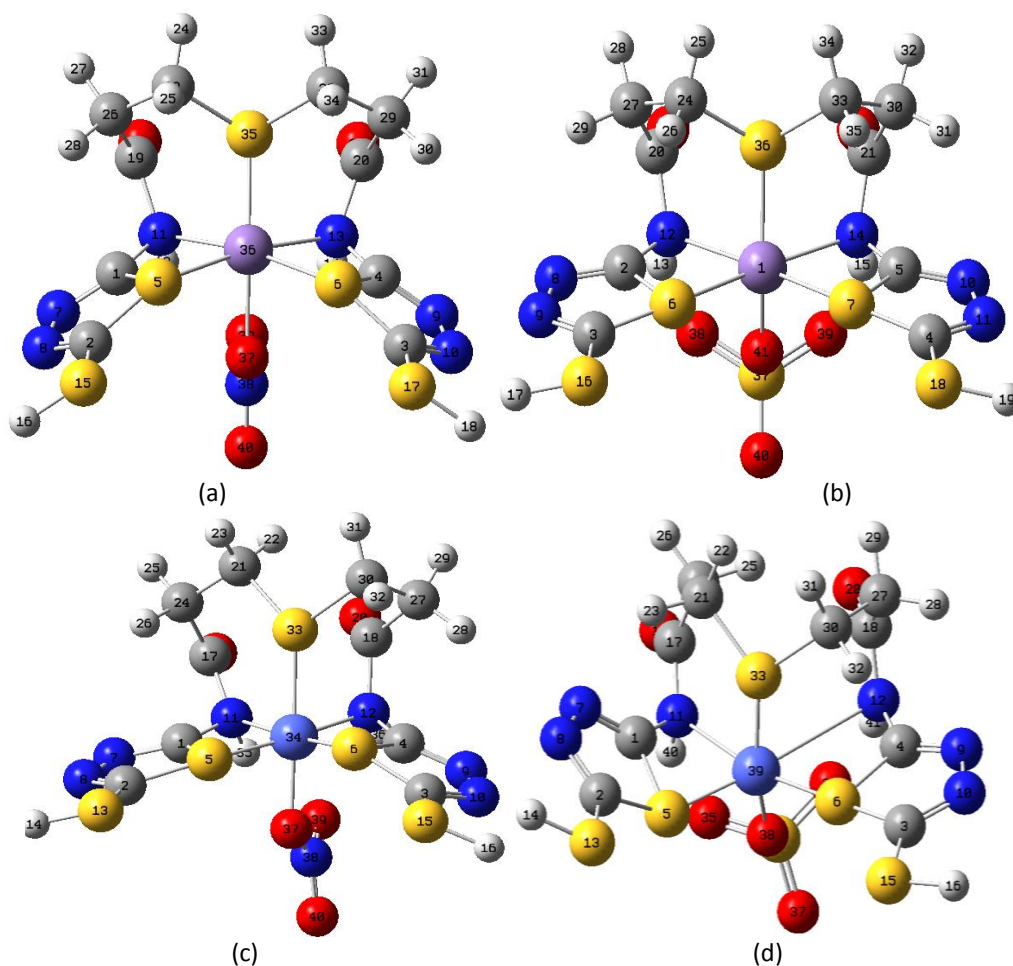


**Fig. 9** Graph showing effect of concentration on antifungal activity of compounds against *Candida tropicalis*

### Molecular Modeling

Geometry optimization was done to obtain the structural information for the ligand and its





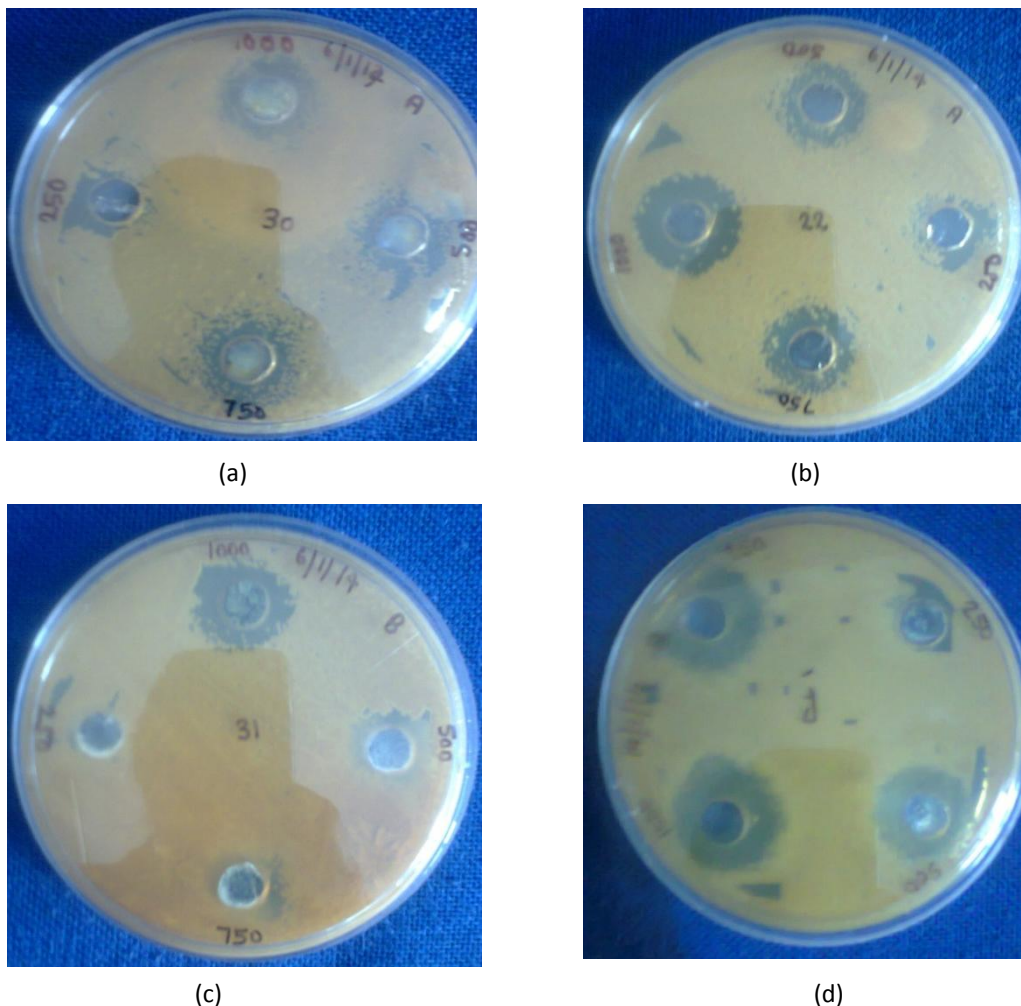
**Fig. 6** The optimized molecular structure of (a)  $[\text{Mn}(\text{L})\text{NO}_3]\text{NO}_3$  (b)  $[\text{Mn}(\text{L})\text{SO}_4]$  (c)  $[\text{Co}(\text{L})\text{NO}_3]\text{NO}_3$  (d)  $[\text{Co}(\text{L})\text{SO}_4]$  Color indication [Purple-Mn(II), light blue-Co(II), red-oxygen, yellow-sulphur, blue-nitrogen, grey-carbon, white-hydrogen]

complexes, geometry optimization was carried out for ligand,  $[\text{Mn}(\text{L})\text{NO}_3]\text{NO}_3$ ,  $[\text{Mn}(\text{L})\text{SO}_4]$ ,  $[\text{Co}(\text{L})\text{NO}_3]\text{NO}_3$ ,  $[\text{Co}(\text{L})\text{SO}_4]$  complexes at semi empirical (PM6) level of theory using the *Gaussian 09* package, in the gas phase. Reported values of bond length and bond angle are given in table 5, and Table 6, respectively. These obtained values were closed to earlier reported data<sup>32</sup>. The central metal ions lie in the mid center of the three chelating sulphur atoms and two chelating nitrogen atoms. All complexes were found to possess six coordinated octahedral geometry with slightly distortion Fig. 6. Several attempts were done to optimized the molecular structure of Cu(II) and Ni(II) complexes, but were not found successful.

### Microbiology activity

The *in-vitro* microbiology activity (antifungal activity) of the synthesized ligand and its complexes

were tested by using well diffusion method against *Candida krusei*, *Candida tropicalis* and *Candida parapsilosis* Fig. 7. The tested compounds in measured quantities were dissolved in DMSO to get concentrations of 1000 ppm, 750 ppm, and 500 ppm Fig. 8. An average of two independent readings for each compound was recorded. On the basis of this figure, it was suggested, that among all complexes  $[\text{Mn}(\text{L})\text{SO}_4]$  complex exhibited higher inhibition zone than others. Fig. 9 is showing antifungal activity of tested compounds against fungi *Candida tropicalis*. On the basis of this figure, it was suggested, that among all complexes  $[\text{Mn}(\text{L})\text{NO}_3]\text{NO}_3$  complex exhibited higher inhibition zone than others. It also observed that ligand exhibited higher activity than  $[\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$  complex. Fig. 10 is showing antifungal activity of tested compounds against fungi *Candida krusei*. It was concluded that  $[\text{Co}(\text{L})\text{SO}_4]$  exhibited maximum inhibition that other complexes. From figs.



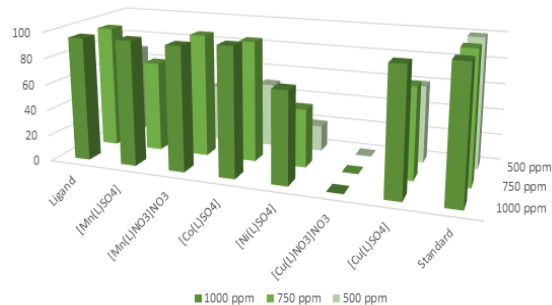
**Fig. 7** Photograph showing antifungal screening of (a)  $[\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$ , (b)  $[\text{Mn}(\text{L})\text{SO}_4]$  complex against *Candida parapsilosis* and (c)  $[\text{Cu}(\text{L})\text{SO}_4]$ , (d)  $[\text{Mn}(\text{L})\text{SO}_4]$  complexes against *Candida tropicalis*

8, 9, 10 it was observed that standard drug (Bavastin) showed 100% inhibition zone. The activity of the metal complexes may be retained to the lipophilic nature of the complexes which arose from the chelation. This elevation is probably due to faster diffusion of the chelates as a whole through the cell membrane. The chelated metal may block the enzymatic activity of the cell or it may catalyze the toxic reactions among cellular constituents<sup>33</sup>.

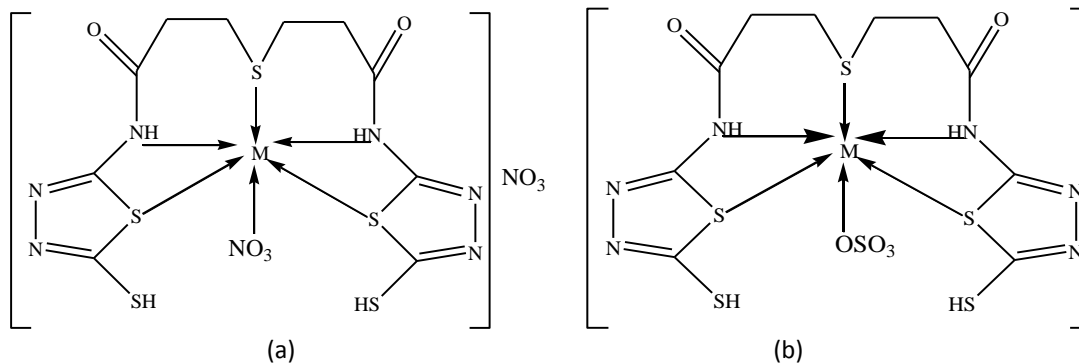
The activity order of tested compounds against *Candida parapsilosis* at 1000 ppm was found to be-Standard (Bavastin) >  $[\text{Mn}(\text{L})\text{SO}_4]$  >  $[\text{Co}(\text{L})\text{SO}_4]$  >  $[\text{Ni}(\text{L})\text{SO}_4]$ ,  $[\text{Cu}(\text{L})\text{SO}_4]$  >  $[\text{Mn}(\text{L})\text{NO}_3]\text{NO}_3$  >  $[\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$  > Ligand

The order of activity of against *Candida tropicalis* at 1000 ppm was found to be-Standard (Bavastin) >

$[\text{Mn}(\text{L})\text{NO}_3]\text{NO}_3 > [\text{Mn}(\text{L})\text{SO}_4]$ ,  $[\text{Co}(\text{L})\text{SO}_4] > [\text{Ni}(\text{L})\text{SO}_4]$   
 =  $[\text{Cu}(\text{L})\text{SO}_4] > \text{Ligand} > [\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$



**Fig. 10** Graph showing effect of concentration on antifungal activity of compounds against *Candida kursei*



**Fig. 11 Structure of complexes (a)  $[M(L)NO_3]NO_3$ , (b)  $[M(L)SO_4]$ , where  $M = Mn(II), Co(II), Ni(II)$  and  $Cu(II)$   $L =$  Ligand**

The activity order of compounds against *Candida kursei* at 1000 ppm was found to be-

Standard (Bavastin) >  $[Co(L)SO_4]$  >  $[Mn(L)SO_4]$  >  $[Mn(L)NO_3]NO_3$  >  $[Cu(L)SO_4]$  = Ligand >  $[Ni(L)SO_4]$  >  $[Cu(L)NO_3]NO_3$

## CONCLUSION

Based on the above observations i.e. elemental analysis, molar conductivity, UV-Visible, magnetic moment, IR and EPR, it is possible to determine the type of coordination of ligand to metal ions. The spectral study data showed that ligand exist as NNSSS type by bonding to metal ion through the nitrogen and sulphur donor atoms. The remaining center of the metal ions was satisfied by negative ions such as  $NO_3^-$ , and  $SO_4^{2-}$ .  $Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$  complexes possessed octahedral geometry, whereas  $Cu(II)$  complexes tetragonal geometry, as shown in Fig. 11. Microbiology screening indicated that the metal complexes inhibited higher fungus growth than free ligand but less active than standard drug bavastin. The compounds also inhibited the growth of fungi to a greater extent as the concentration was increased. Comparing their activity, we found that  $Mn(II)$  complexes inhibited the growth of fungi to a greater extent than other complexes.

## ACKNOWLEDGEMENT

The author express sincere thanks to the University Grant Commission (UGC) New Delhi, for financial assistance, USIC, University of Delhi for spectroscopic characterization, IIT Bombay for recording EPR spectra, and Head, Microbiology Department, Swami Vivekananda Subharti University, Meerut. Authors also express sincere thank to the Principal, Zakir Husain Delhi College, University of Delhi.

## REFERENCE

1. Pandya J H & Saha M K, Synthesis and antimicrobial properties of transition metal complexes of novel schiff base ligand derived from 5-bromosalicylaldehyde, *Journal of Indian Council Chemistry*, 26 (2009) 109-112.
2. Chandra S & Gautam A, Epr, ir, and electronic spectral studies on  $Ni(II)$ , and  $Cu(II)$  complexes with N-donor tetradentate  $[N_4]$  macrocyclic ligand, *Spectrochimica Acta part A*, 70 (2008) 1001-1005.
3. Sharma A K & Chandra S, Synthesis, structural and fungicidal studies of hydrazine based coordination compounds, *Spectrochimica acta part A*, 103 (2013) 96-1001.
4. Chandra S & Gautam, S, Antibacterial and antifungal activity of schiff base ligands and their metal complexes-a review, *International Journal of Chemical and Pharmaceutical Sciences*, 5 (2014) 27-41.
5. Chandra S, Gautam S, Rajor H K & Bhatia R, Syntheses, spectroscopic characterization, thermal study, molecular modeling, and biological evaluation of novel schiff's base benzil bis(5-amino-1,3,4-thiadiazole-2-thiol) with  $Ni(II)$ , and  $Cu(II)$  metal complexes, *Spectrochimica Acta Part A* 137 (2015) 749-760.
6. Chandra S, Bargujar S, Nirwal R & Yadav N, Synthesis, spectral characterization and biological evaluation of copper(II) and nickel(II) complexes with thiosemicarbazones derived from a bidentate schiff base, *Spectrochimica Acta Part A*, 106 (2013) 91-98.

7. Chandra, S & Agrawal S, Spectroscopic characterization of lanthanoid derived from a hexadentate macrocyclic ligand: study on antifungal capacity of complexes, *Spectrochimica Acta Part A*, 124 (2014) 564-570.
8. 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 modelling and fungicidal Study, *Spectrochimica acta part A* 136 (2015) 672-681.
9. Chandra S & Vandana, Synthesis, spectroscopic, anticancer and antibacterial studies of Ni(II) and Cu(II) complexes with 2-carboxybenzaldehyde thiosemicarbazone, *Spectrochimica Acta Part A*, 129 (2014) 333-338.
10. Youssef N S, El Zahany E A & Ali M M, Synthesis, spectral, characterization, and anticancer activity of some binary and mixed ligand complexes of 4-methyl-2-pentanone thiosemicarbazone and some amino acids. Phosphorus, Sulfur, and Silicon, 185 (2010) 2171-2181.
11. Collins C H, Lyne P M & Grange J M, Microbiological Methods, *Butterworths Oxford UK*, 6th edition (1989).
12. Avaji P G, Patil S A & Badami P S, Synthesis, spectral, thermal, solid state, electrical conductivity and biological studies of Co(II), Ni(II) and Cu(II) complexes with 3-substituted-4-amino (indole-3-aldehyde)-5-mercapto-1,2,4-triazole schiff bases. *Journal of Coordination Chemistry*, 61 (2008) 1884-1896.
13. Chandra S and Ruchi, Synthesis, spectroscopic characterization, molecular modeling and antimicrobial activities of Mn(II), Co(II), Ni(II), Cu(II) complexes containing the tetradentate aza schiff base ligand, *Spectrochimica Acta Part A*, 103 (2013) 338-348.
14. Chandra S, Tyagi M & Agarwal S, Synthesis and characterization of a tetraaza macrocyclic ligand and its cobalt(II), nickel(II) and copper(II) complexes, *Journal of Serbian Chemical Society*, 75 (2010) 935-941.
15. Chandra S & Gupta L K, Modern spectroscopic and biological approach in the characterization of a novel 14-membered [N<sub>4</sub>] macrocyclic ligand and its transition metal complexes, *Transition Metal Chemistry*, 32, (2007) 240-245.
16. Chandra S & Ballabh P, Synthesis, characterization and physicochemical studies of Ni(II) and Cu(II) complexes with some nitrogen-oxygen and nitrogen sulphur donor ligands, *International Journal of Pharmaceutical Science and Research*, 4 (2013) 2393-2399.
17. Singh D P, Grover V, Kumar K & Jain K, Synthesis and characterization of divalent metal complexes of the macrocyclic ligand derived from isatin and 2-diaminobenzene. *Journal of Serbian Chemical Society* 76 (2011) 1-9.
18. Chandra S, Jain D, Sharma A K & Sharma P, Coordination modes of a schiff base pentadentate derivative of 4-aminoantipyrine with cobalt(II), nickel(II) and copper(II) metal ions: synthesis, spectroscopic and antimicrobial studies, *Molecules* 14 (2009) 174-190.
19. Chandra S, Gupta L K & Sangeetika, Spectroscopic, cyclic voltammetric and biological studies of transition metal complexes with mixed nitrogen-sulphur (NS) donor macrocyclic ligand derived from thiosemicarbazide, *Spectrochimica Acta Part A*, 62 (2005) 453-460.
20. Nakamoto K, Infrared and raman spectra of coordination compounds. *Wiley Interscience, New York* (1970).
21. Chandra S, & Gupta L K, Spectroscopic studies on Co(II), Ni(II) and Cu(II) complexes with a new macrocyclic ligand: 2,9-dipropyl-3,10-dimethyl-1,4,8,11-tetraaza-5,7:12,14 dibenzocyclotetradeca-1,3,8,10-tetraene, *Spectrochimica Acta Part A*, 61 (2005) 1181-1188.
22. Tyagi M and Chandra S, Synthesis and spectroscopic studies of biologically active tetraazamacrocyclic complexes of Mn(II), Co(II), Ni(II), Pd(II) and Pt(II), *Journal of Saudi Chemical Society*, 18 (2014) 53-58.
23. Sunitha M, Jogi P, Ushaiah B & Kumar C G, Synthesis, characterization and antimicrobial

- activity of transition metal complexes of schiff base ligand derived from 3-ethoxy salicylaldehyde and 2-(2-aminophenyl) 1-H-benzimidazole, *E-Journal of Chemistry* 9 (2012) 2516-2523.
24. Tyagi M, Chandra S & Choudhary S K, Tetraaza macrocyclic complexes: synthesis, spectral and antifungal studies, *Journal of Chemical and Pharmaceutical Research*, 3 (2011) 56-63.
  25. Chandra S & Pipil P, Spectral and magnetic studies on manganese(II) complexes of macrocyclic ligands, *Journal of Saudi Chemical Society*, 11 (2007) 41-46.
  26. Lever A B P, *Inorganic Electronic Spectroscopy, 1st Edn. Elsevier, Amsterdam*, 249 (1968).
  27. Kumar U & Chandra S, Synthesis, spectral and antifungal studies of some coordination compounds of cobalt(II) and copper(II) of a novel 18-membered octaaza [N<sub>8</sub>] tetradentate macrocyclic ligand, *Journal of Saudi Chemical Society*, 15 (2011) 187-193.
  28. Chandra S & Kumar U, Spectral and magnetic studies on manganese(II), cobalt(II) and nickel(II) complexes with schiff bases, *Spectrochimica Acta Part A*, 61 (2005) 219-224.
  29. Chandra S & Sharma A K, Nickel(II) and copper(II) complexes with base ligand 2,6-diacetylpyridine bis(carbohydrazone): synthesis and IR, mass, <sup>1</sup>H-nmr, electronic and epr spectral studies, *Spectrochimica Acta Part A*, 72 (2009) 851-857.
  30. Chandra S, Ruchi, Qanungo K, & Sharma S K, Synthesis, molecular modeling and spectroscopic characterization of nickel(II), copper(II), complexes of new 16-membered mixed-donor macrocyclic schiff base ligand incorporating a pendant alcohol function, *Spectrochimica Acta Part A*, 79 (2011) 1326-1330.
  31. Hathaway B J, Bradley J N & Gillard R D, *Essays in Chemistry, Academic Press, New York* (1971).
  32. 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 Journal of Pharmaceutical Research*, 3 (2014) 576-595.
  33. Sharath N, Naik H S B, Kumar B V & Hoskeri J, Antibacterial, molecular docking, dna binding and photo cleavage studies on novel heterocyclic pyrazoles. *British Journal of Pharmaceutical Research* 1 (2011) 46-65.