



# International Journal of Pharmaceutical Research and Development (IJPRD)

Platform for Pharmaceutical Researches & Ideas

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## SYNTHESIS, SPECTROSCOPIC AND ANTIMICROBIAL STUDIES OF 3D - BIVALENT METAL COMPLEXES DERIVED FROM 2-IMIDAZOLYL MERCAPTOACETO HYDRAZONE

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### ABSTRACT

A series of new Co(II), Ni(II), Cu(II) and Zn(II) complexes of the 2-imidazolyl mercaptoaceto hydrazones (LH<sub>2</sub>) have been prepared and characterized on the basis of analytical, Molar conductivity, Magnetic susceptibility, IR, Electronic and ESR spectral studies. Infrared spectra shows that the hydrazone behaves as a monobasic tridentate ligand in keto form in Co(II), Ni(II) and Zn(II) complexes except in Cu(II) complexes where they act as dibasic tridentate ligand exhibits in enol form with ONO donor sequence. From analytical data the stoichiometry of the complexes have been found to be 1:2 (metal:ligand) in Co(II) and Ni(II) complexes they can be represented by the general formula M(LH)<sub>2</sub> and in case of complexes Cu(II) and Zn(II) have been found to be 1:1 metal to ligand stoichiometry represented by the general formula Cu(L) and Zn(LH) respectively. Octahedral geometry of Co(II) and Ni(II) complexes, square planar geometry of Cu(II) complexes and tetrahedral geometry of Zn(II) complexes have been proposed. The thermal stabilities of the complexes have been studied by TGA. The hydrazones and their metal(II) complexes were screened for their in vitro antibacterial activity against *Salmonella paratyphi* and *Bacillus cirroflagellosus* and antifungal activity against *Aspergillus niger* and *Candida albicans*. The study of physiological activity has been found that zinc complexes are more reactive than other newly synthesized complexes.

**Key words:** Bivalent, Hydrazone, tridentate, spectral studies, thermal studies

### INTRODUCTION

The study of the complexes formed with hydrazones is very interesting because of the

tautomerism exhibited by these ligands. The chromophore group -CO-NH-N< of these ligands can enter the inner sphere of the complexes either

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in the keto or enol form. In the keto form they behave as monobasic tridentates whereas in enol form they act as dibasic tridentates. This tendency depends on a number of factors such as the *pH* of the medium employed in the synthesis of the complexes, the nature of the substituents attached to the carbonyl carbon atom,  $\beta$  - nitrogen atom, the anion of the metal salt and the metal ion. Varieties of substituent types are prepared to produce a range of hydrazone types. Hydrazones exhibited bactericidal, parasitical, leprosy, leukaemia, malignant neoplasm and tuberculositic antiactivity<sup>1</sup>. Aryl and heteroaryl hydrazones are described as antifungal agent<sup>2</sup> as well as active substances for the treatment of malaria or malignant tumours. Hydrazones have also found important applications as chromogenic reagents in

the spectrophotometric determination of transition metal ions (colorimetric agents) and metal extracts. The chemistry of transition metal complexes of hydrazones continues to be of interest on account of the interesting structural features presented by this class of compound and also because of their biological importance<sup>2-4</sup>. All this information stands as a testimony to the versatility of the hydrazones as chelating agents. The present work reports the synthesis, spectroscopic and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of hydrazone derived from the condensation of 2-imidazolyl mercaptoaceto hydrazide and *o*-hydroxy aromatic aldehyde, henceforth abbreviated as LH<sub>2</sub> and 3D- structure of L<sup>1</sup>H<sub>2</sub> is as shown below (I).



I. 3D-structure of the ligand (L<sup>1</sup>H<sub>2</sub>)

#### MATERIALS AND METHODS:

All chemicals used for the synthesis of ligands complexes were of reagent grade, the solvent were dried and distilled before use according to standard procedures. Carbon, Hydrogen and Nitrogen were determined on Carlo Erba CHN analyser. The metal content in all the complexes and chlorine in Zn(II) complexes were determined by using standard procedures<sup>5</sup>. Conductance measurements were made using 10<sup>-3</sup>M solutions of complexes in DMF using Elico conductivity bridge type CM-82 provided with a cell having cell constant 0.52 cm<sup>-1</sup>. The electronic spectra of complexes in DMF were recorded on Hitachi 2001 spectrophotometer and IR spectra were recorded on a Nicolet 170 SXFT-IR spectrophotometer in KBr pellets in the range 400-4000cm<sup>-1</sup>. Magnetic moment of the complexes were measured with a Faraday balance using

Mercury(II) tetrathiocyanatocobaltate(II) as celebrant. The EPR spectra of Cu(II) complexes at room temperature were recorded on Varian E-4X band EPR spectrophotometer using TCNE as the g marker. <sup>1</sup>H NMR spectra were recorded on a JEOL-AMX-400 NMR spectrometer. Thermograms were recorded on a Perkin Elmer analyser in N<sub>2</sub> atmosphere at a heating rate of 10 °C. Antimicrobial activities of the ligand (LH<sub>2</sub>) and its complexes along with the standard were carried out against the pathogenic bacteria *Escherichia coli* and *Bacillus cirroflagellatus* and antifungal activity against *Aspergillus niger* and *Candida albicans* by cup plate methods.

#### Preparation of 2-imidazolyl mercaptoaceto hydrazone:

To an absolute ethanolic solution (100 ml) containing sodium metal (2.8 g) was added with stirring 2-mercapto imidazole (10 g) and the

resulting mercaptide was slowly treated with ethyl chloroacetate (30-40 ml). The mixture was refluxed on a steam bath for about an hour and filtered hot in a dry Buckner funnel. The alcoholic solution was concentrated to about 50% of its original volume and hydrazine hydrate was added. The solution was refluxed for about 20 h on a steam bath and cooled in ice. The separated solid was filtered, washed with water and crystallized from alcohol (yield 72-74%). Further to an ethanolic solution of 2-imidazolyl mercaptoaceto hydrazide (0.1 mol), salicylaldehyde / substituted salicylaldehyde (0.1mol) was added and the mixture was refluxed on a steam bath for about 3 h. The solution was filtered hot from the suspended impurities, concentrated and cooled. The separated solid was filtered, washed with water and crystallized from alcohol (yield 70–75%).

#### Preparation of the complexes:

An ethanolic solution of the ligand (0.02 mol) was added to an ethanolic solution of bivalent 3d-metal chloride. The resulting mixture was refluxed for about 3 h on a water bath. The

coloured complex thus obtained was filtered, washed with ethanol, dried and stored *in vacuo* over fused calcium chloride (yield 68–72%).

#### RESULTS AND DISCUSSION:

All the metal complexes are colored except zinc complexes, stable towards air and moisture at room temperature. The complexes are generally insoluble in water, ethanol and methanol but soluble in coordinating solvents like DMF and DMSO. The analytical data of the complexes (Table 1) reveal that the Co(II) and Ni(II) complexes are of 1:2 metal to ligand stoichiometry, and can be represented by the general formula  $M(LH)_2$ , Cu(II) complexes are of 1:1 metal to ligand stoichiometry, represented by the general formula  $CuL$  and Zn(II) complexes are of 1:1 metal to ligand stoichiometry and can be represented by the general formula  $Zn(LH)Cl$ . The molar conductance values of all the complexes at  $10^{-3} M$  in DMF fall in the range 5.2-12.6  $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ , indicating the non-electrolytic nature of the complexes<sup>6</sup>.

**Table 1:** Analytical, magnetic susceptibility and molar conductance data of the ligands and their transition metal (II) complexes

Compound (Mol For)	Mol.wt	Yield (%)	Elemental analysis Found / (Calcd) %				Molar conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	Magnetic Moment (BM)
			C	H	N	M		
$C_{12}H_{12}N_4O_2S$ ( $L^1H_2$ )	276	86	51.86 (52.17)	4.40 (4.34)	19.28 (20.30)	--	--	--
$[Co(C_{12}H_{11}N_4O_2S)_2]$ $[Co(L^1H)_2]$	608.93	72.8	48.06 (47.30)	3.72 (3.61)	18.42 (18.39)	9.74 (9.68)	11.4	5.04
$[Ni(C_{12}H_{11}N_4O_2S)_2]$ $[Ni(L^1H)_2]$	608.69	71.6	46.82 (47.31)	3.68 (3.61)	18.51 (18.4)	9.58 (9.64)	9.3	3.16
$[Cu(C_{12}H_{10}N_4O_2S)]$ $[Cu(L^1)]$	675.08	86.4	41.08 (42.66)	2.88 (2.96)	16.62 (16.59)	18.88 (18.82)	7.8	1.64
$[Zn(C_{12}H_{11}N_4O_2S)Cl]$ $[Zn(L^1H)Cl]$	376.22	82.2	37.93 (38.27)	2.95 (2.92)	20.32 (20.37)	17.53 (17.47)	10.2	--
$L^2H_2$ ( $C_{13}H_{14}N_4O_3S$ )	306	78	50.32 (50.98)	4.62 (4.57)	18.26 (18.31)	--	--	--
$[Co(C_{13}H_{13}N_4O_3S)_2]$ $[Co(L^2H)_2]$	668.93	66.3	45.34 (46.64)	3.92 (3.88)	16.82 (16.74)	8.84 (8.81)	12.6	4.98
$[Ni(C_{13}H_{13}N_4O_3S)_2]$ $[Ni(L^2H)_2]$	668.69	68.5	47.12 (46.65)	3.80 (3.89)	16.64 (16.75)	8.52 (8.78)	8.1	3.08
$[Cu(C_{13}H_{12}N_4O_3S)]$ $[Cu(L^2)]$	735.08	78.0	43.09 (42.44)	3.29 (3.26)	15.32 (15.24)	17.32 (17.29)	5.2	1.23

[Zn(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>3</sub> S)Cl] [Zn(L <sup>2</sup> H)]Cl	406.32	86.0	39.16 (38.40)	3.22 (3.20)	13.83 (13.78)	16.24 (16.18)	11.6	--
L <sup>3</sup> H <sub>2</sub> (C <sub>13</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S)	290	69.2	52.86 (53.79)	4.86 (4.83)	19.32 (19.31)	--	--	--
[Co(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub> ] [Co(L <sup>3</sup> H) <sub>2</sub> ]	636.63	70	47.72 (48.98)	4.07 (4.08)	17.66 (17.58)	9.26 (9.25)	9.4	4.76
[Ni(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub> ] [Ni(L <sup>3</sup> H) <sub>2</sub> ]	636.69	68.6	48.34 (49.0)	4.05 (4.08)	17.63 (17.59)	9.24 (9.22)	8.6	2.92
[Cu(C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S)] [Cu(L <sup>3</sup> )]	703.08	80	44.49 (44.38)	3.44 (3.41)	15.59 (15.93)	18.12 (18.07)	10.6	1.52
[Zn(C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S)Cl] [Zn(L <sup>3</sup> H)]Cl	390.22	76.2	39.12 (39.97)	3.31 (3.33)	14.31 (14.75)	16.91 (16.84)	9.4	--

### Infrared spectra

The data of the IR spectra are listed in Table 2, by comparing the characteristic peaks in the spectra of the ligands and their complexes in order to determine the involvement of coordination sites in chelation. The infrared spectra of ligands show a broad band around 3380–3345 cm<sup>-1</sup> due to the intramolecular hydrogen bonded –OH. The ligands show bands in the regions 3200–3185, 3050–3030 and 1690–1665 cm<sup>-1</sup> assigned to  $\nu(\text{N-H})^7$  of hydrazide,  $\nu(\text{N-H})$  of imidazole moiety and  $\nu(\text{C=O})^7$  respectively. The bands due to  $\nu(\text{C-O})$  and  $\nu(\text{C=N})$  are located in the regions 1520–1490 and 1640–1625 cm<sup>-1</sup> respectively<sup>8</sup>. The ligands exhibit two

different types of coordinating patterns. In Co(II), Ni(II) and Zn(II) complexes, the band due to  $\nu(\text{OH})$  disappears indicating clearly the involvement of oxygen of the phenolic group in coordination after deprotonation. The band due to  $\nu(\text{N-H})$  of hydrazide remains unaltered. Non-shifting of  $\nu(\text{N-H})$  clearly suggests coordination of the ligand in keto form. The band due to  $\nu(\text{C=O})$  shifts to lower frequency by 15–22 cm<sup>-1</sup> indicating the involvement of coordination of carbonyl oxygen to the metal ion. The band due to  $\nu(\text{C=N})$  also suffers a negative shift by 18–25 cm<sup>-1</sup> indicating the involvement of azomethine nitrogen in the coordination<sup>9,10</sup>.

**Table 2:** Important spectral IR bands (cm<sup>-1</sup>) of the ligands and their metal (II) complexes

Ligand/Complex	$\nu(\text{N-H})$ imidazole	$\nu(\text{N-H})$ Hydrazine	$\nu(\text{C=O})$	$\nu(\text{C=N})$ azomethine	$\nu(\text{C-O})$ Phenolic	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L <sup>1</sup> H <sub>2</sub>	3032	3192	1686	1638	1508	--	--
[Co(L <sup>1</sup> H) <sub>2</sub> ]	3034	3194	1665	1616	1527	541	458
[Ni(L <sup>1</sup> H) <sub>2</sub> ]	3035	3198	1662	1622	1525	548	443
[Cu(L <sup>1</sup> )]	3031	-	-	1624	1523	532	452
[Zn(L <sup>1</sup> H)]Cl	3029	3199	1672	1630	1532	542	452
L <sup>2</sup> H <sub>2</sub>	3048	3186	1679	1627	1503	-	-
[Co(L <sup>2</sup> H) <sub>2</sub> ]	3046	3185	1662	1608	1522	539	462
[Ni(L <sup>2</sup> H) <sub>2</sub> ]	3051	3189	1660	1605	1519	541	455
[Cu(L <sup>2</sup> )]	3045	-	-	1614	1521	538	462
[Zn(L <sup>2</sup> H)]Cl	3049	3188	1661	1615	1523	540	465
L <sup>3</sup> H <sub>2</sub>	3034	3185	1672	1631	1494	-	-
[Co(L <sup>3</sup> H) <sub>2</sub> ]	3031	3187	1651	1612	1509	547	457
[Ni(L <sup>3</sup> H) <sub>2</sub> ]	3036	3183	1656	1651	1516	539	442
[Cu(L <sup>3</sup> )]	3033	-	-	1616	1511	541	453
[Zn(L <sup>3</sup> H)]Cl	3035	3189	1652	1608	1518	548	461

In case of Cu(II) complexes, the mode of coordination remains the same except that the bands due to  $\nu(\text{NH})$  and  $\nu(\text{C=O})$  disappear due to

enolization of the ligand followed by coordination of carbonyl oxygen to the metal ion via deprotonation. Thus the ligands exhibit a

tridentate dibasic nature. This is further supported by the appearance of a new band<sup>11</sup> around 1612  $\text{cm}^{-1}$  due to  $>\text{C}=\text{N}-\text{N}=\text{C}<$ . The  $\nu(\text{C}=\text{N})$  shifts to lower frequency region by 12-18  $\text{cm}^{-1}$  indicating the involvement of azomethine nitrogen in the coordination. A noticeable change in the IR spectra of these complexes is the shift of phenolic (C-O) to higher energy side by 16-22  $\text{cm}^{-1}$ . This large shift and the coordination pattern of the ligand suggest the formation of phenolic oxygen bridge in the copper complexes.

In the present complexes, the non ligand bands appearing in the regions 550-520 and 465-440  $\text{cm}^{-1}$  are assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  modes respectively<sup>10,12</sup>. In general,  $\nu(\text{M}-\text{N})$  band is usually sharp and strong and the  $\nu(\text{M}-\text{O})$  band is broad and strong since a large dipole moment change is involved in the vibration of the M-O bond in comparison to that of the M-N bond. Hence it is expected that the  $\nu(\text{M}-\text{O})$  band should appear at a higher energy in comparison to that of the  $\nu(\text{M}-\text{N})$  band. The M-O bond length is usually shorter than the M-N bond length and this also supports the occurrence of the  $\nu(\text{M}-\text{O})$  band at a higher energy in comparison to that of the  $\nu(\text{M}-\text{N})$  band. The band due to  $\nu(\text{Zn}-\text{Cl})$ <sup>12</sup> were observed in the 364-352  $\text{cm}^{-1}$  region and is characteristic of chlorine atom in Zn(II) complex, further confirmed by quantitative chloride estimation.

#### Electronic spectra and magnetic moments:

The electronic spectra of Co(II) complexes display two bands in the ranges 7600-8800  $\text{cm}^{-1}$  and 20400-21200  $\text{cm}^{-1}$ . These have been assigned to  ${}^4\text{T}_{2g(\text{F})} \leftarrow {}^4\text{T}_{1g(\text{F})}$  ( $\nu_1$ ) and  ${}^4\text{T}_{1g(\text{P})} \leftarrow {}^4\text{T}_{1g(\text{F})}$  ( $\nu_3$ ) respectively<sup>12-14</sup>. The  $\nu_2$  transition in spectra of complexes is not observed but calculated from Konig equation. The values of magnetic moments for Co(II) fall in the range 4.76-5.04 B.M. The observed magnetic moments and transitions are consistent with octahedral geometry around the metal ions for the Co(II) complexes<sup>15</sup>. The electronic spectra of all the Ni(II) complexes show three bands in the ranges 8600-10400  $\text{cm}^{-1}$ , 15150-16300  $\text{cm}^{-1}$  and 23200-24900  $\text{cm}^{-1}$  which are assignable to the transitions  ${}^3\text{T}_{2g(\text{F})} \leftarrow {}^3\text{A}_{2g(\text{F})}$  ( $\nu_1$ ),  ${}^3\text{T}_{1g(\text{F})} \leftarrow {}^3\text{A}_{2g(\text{F})}$  ( $\nu_2$ ) and  ${}^3\text{T}_{1g(\text{P})} \leftarrow {}^3\text{A}_{2g(\text{F})}$  ( $\nu_3$ )

respectively. The observed magnetic moments values (2.92-3.16 BM) which agree well with the known values for Ni(II) complexes, suggest that octahedral geometry<sup>16,17</sup>.

The electronic spectra of Cu(II) complexes exhibit a very broad but of low intensity in the region 15900-16900  $\text{cm}^{-1}$ , which can be assigned to a  $d-d$  transition. The complexes exhibit another strong band in the region 23850-24890  $\text{cm}^{-1}$ , which is due to the ligand to metal charge transfer transition rather than due to a bimetallic species. The electronic spectra of the complexes indicate a four coordinated environment characteristic of CuONOO coordination species<sup>18</sup>. The Cu(II) complexes have subnormal magnetic moments in the range 1.23-1.65 B.M. The observed magnetic moment values are less than the spin only value (1.73 to 2.20 BM) for Cu(II) ( $3d^9$ ) mononuclear complexes having no major interactions between two copper moieties. The low magnetic moment in Cu(II) complexes are usually attributed to spin-coupling within a dimer brought about by the bridging of monomeric units of paramagnetic centers through the phenolic or enolic oxygen atoms. This oxygen bridging often leads to change in electronic structure of the attached atoms resulting in reduction of paramagnetism partially or completely of the metal atoms bridged. So the subnormal magnetic moments observed for the present Cu(II) complexes may be accounted by assuming dimeric structure in the solid state, in which considerable antiferromagnetic exchange occurs through a super-exchange mechanism as there is little possibility of a direct interactions. The low magnetic moment values and the IR data indicate the presence of oxygen bridged structure, in which Cu(II) exhibits coordination number four. Zinc (II) complexes are diamagnetic in nature.

#### ESR spectra

The ESR spectra of polycrystalline Cu(II) complex possess a characteristic spectrum having asymmetric bands with two 'g' values ( $g_{\parallel}$  and  $g_{\perp}$ ). These values are computed from the spectrum using 'g' marker TNCE ( $g=2.0027$ ). The analysis of spectra gives  $g_{\parallel}=2.1776$ ;  $g_{\perp}=2.0924$ . The  $g_{\parallel}$  is less than 2.3 suggest that the covalent character of

metal – ligand bond<sup>19</sup>. The value of G is less than 4 indicating the interaction of copper centers which is also supported by subnormal magnetic moment. The trend  $g_{||} > g_{\perp} > g_e$  (free ion value = 2.0023) for the complex shows that the unpaired electron is in the  $d_{x^2-y^2}$  orbital of Cu(II) ion<sup>20</sup>.

### <sup>1</sup>H NMR spectra

Spectrum of <sup>1</sup>H NMR in DMSO-d<sub>6</sub> solvent used. The ligand (L<sup>1</sup>H<sub>2</sub>) show a multiplet between 7.32-8.02 ppm due to aromatic protons, singlet at 3.68ppm due to –CH<sub>2</sub>- protons, singlet at 8.36 ppm due to azomethine proton. The singlets at 12.04, 11.02 and 12.76 ppm are assigned to phenolic –OH, –NH (hydrazine) and –NH (imidazole) respectively. But in the case of Zn(II) complex the signal of phenolic –OH has been disappeared indicating the involvement of phenolic oxygen in the coordination via deprotonation<sup>21</sup>. The peak appears at  $\delta$  8.36 (s, 1H, –CH=N) due to the azomethine group in ligand but in case of its Zn(II) complex the peak observed at 8.66 (s, 1H, –CH=N). This downshifting results from coordination through the nitrogen of azomethine group to the Zn (II) ion. In complex the downshifting of –CH<sub>2</sub>- peak (4.26ppm) suggest that the coordination of the adjacent carbonyl group to the metal ion.

### Thermal studies

The TG curves of the Co(L<sup>1</sup>H)<sub>2</sub>, Ni(L<sup>2</sup>H)<sub>2</sub> and Cu(L<sup>3</sup>) complexes show a stable plateau upto 390K indicating that the complexes are stable upto this temperature. The complexes do not show the presence of water molecules either in or out of the coordination sphere. The complexes then undergo the first stage of decomposition in the range 390-525 K, the weight loss corresponds to the loss of one molecule of ligand while the second stage of decomposition occurs in the range 525-770 K, indicating the loss of another ligand molecule. A plateau is obtained, which indicate the formation of stable metal oxides. The weight of residues obtained agrees well with the calculated values.

The TG curve of the Zn(L<sup>1</sup>H)Cl complex shows a stable plateau upto 415K indicating that the complex is stable up to this temperature. The complex does not show the presence of water

molecule either in or out of the coordination sphere. The complex undergoes the first stage of decomposition in the range 415-545 K, the weight loss corresponds to the loss of one coordinated chloride while the second stage of decomposition occurs in the range 545-790 K, indicating the loss of one ligand molecule. A plateau is obtained, which indicates the formation of stable metal oxide. The weight of residue obtained agrees well with the calculated value.

### ANTIMICROBIAL ACTIVITY:

Antimicrobial activity was carried out using the cup-plate method<sup>22</sup>. The antimicrobial activity results of the screened compounds are given in the Table 3. The ligands and their Cu(II), Co(II), Ni(II) and Zn(II) complexes have been tested for their antibacterial activity<sup>23</sup> against *B.cirroflagellosus* and *S.paratyphi* and antifungal activity<sup>24</sup> against *A. niger* and *C.albicans* at 100  $\mu\text{g}/0.1 \text{ cm}^3$  concentration. The standard drugs contrimoxazole and fluconazole were also tested for their antibacterial and antifungal activity at the same concentration under the conditions similar to that of the test compounds. The antibacterial activity results (Table 3) revealed that the ligand and its complexes show weak to good activity. The ligand and its Cu(II) and Ni(II) complexes shows weakly active with the zone of inhibition 12-14 mm against the both organisms when compared to the standard drug contrimoxazole. The Co(II) complexes shows active and moderate activity as compared to its ligand with zone of inhibition 14-16 mm. The Zn(II) complexes have exhibited good activity with the zone of inhibition 17 to 19 mm when compared to the standard drug contrimoxazole (Fig. 1). The antifungal activity results (Table 3) revealed that the ligand and its Cu(II), Co(II), Ni(II) and Zn(II) complexes have exhibited weak to good activity. The ligand and its Cu(II) and Co(II) complexes shows weak activity when compared to the standard drug fluconazole. The Ni(II) complexes shows active and moderate activity as compared to its ligand with the zone of inhibition 13-14 mm respectively. The Zn(II) complexes have exhibited good activity with the zone of inhibition 18-20 mm when compared to

the standard drug flucanazole (Fig.2). The higher inhibition zone of metal complexes then those of

the ligands can be explained on the basis of Overtones concept and chelation theory.

**Table 3:** Antimicrobial activity of the ligand and their metal (II) complexes (Zone of inhibition in mm)

Sl.No.	Compounds	Antibacterial		Antifungal	
		B.c	S.p	A.n	C.a
1	L <sup>1</sup> H <sub>2</sub>	12	11	11	12
2	Co(L <sup>1</sup> H) <sub>2</sub>	15	14	14	15
3	Ni(L <sup>1</sup> H) <sub>2</sub>	14	12	13	14
4	Cu(L <sup>1</sup> )	13	14	12	13
5	Zn(L <sup>1</sup> H)Cl	17	18	18	20
6	L <sup>2</sup> H <sub>2</sub>	12	13	12	11
7	Co(L <sup>2</sup> H) <sub>2</sub>	14	16	14	13
8	Ni(L <sup>2</sup> H) <sub>2</sub>	13	14	15	14
9	Cu(L <sup>2</sup> )	13	14	13	15
10	Zn(L <sup>2</sup> H)Cl	18	19	20	18
11	L <sup>3</sup> H <sub>2</sub>	13	12	11	12
12	Co(L <sup>3</sup> H) <sub>2</sub>	16	15	14	13
13	Ni(L <sup>3</sup> H) <sub>2</sub>	14	13	13	15
14	Cu(L <sup>3</sup> )	14	13	12	12
15	Zn(L <sup>3</sup> H)Cl	18	18	17	19
16	Contrimoxazole	28	31	-	-
17	Flucanazole.	-	-	29	28

Bc=Bacillus cirroflagellosus; Sp=Salmonella paratyphi; An=Aspergillus niger;

Ca=Candida albican.

**Fig:1** Antibacterial activity of Ligands and their complexes.

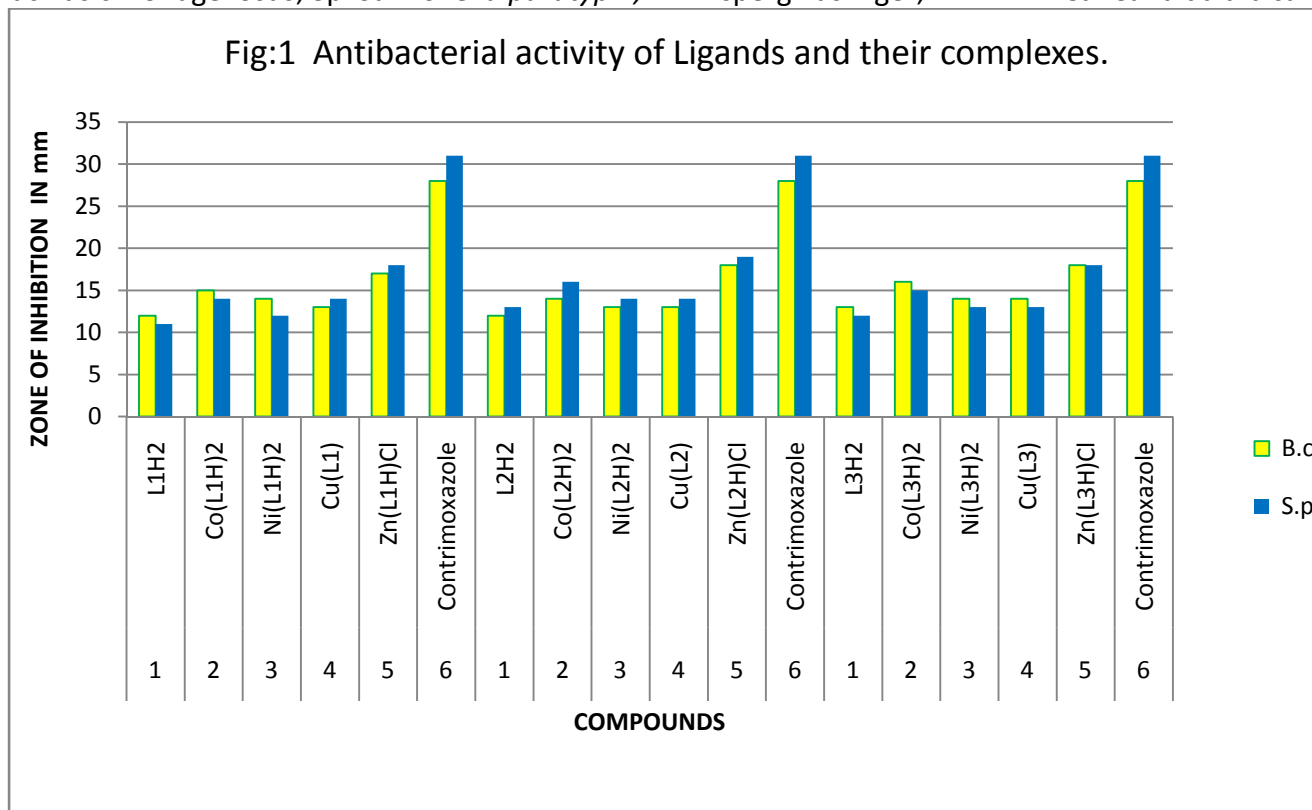
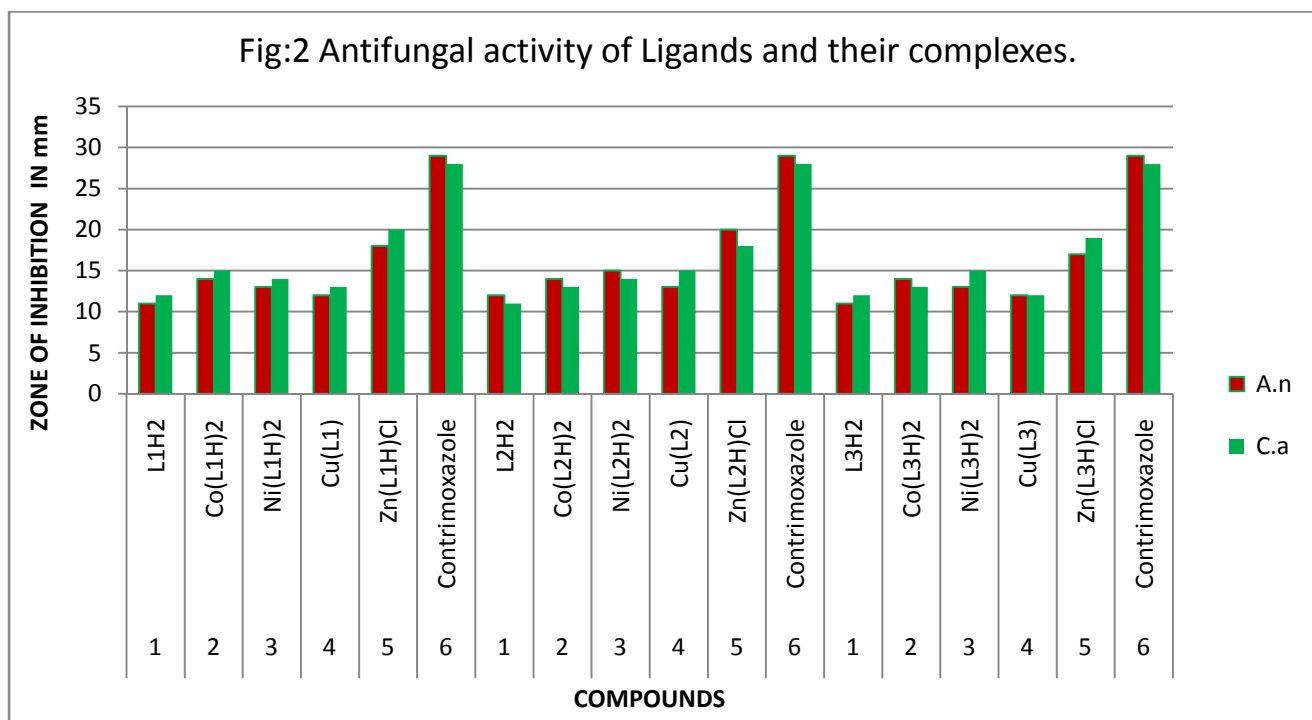


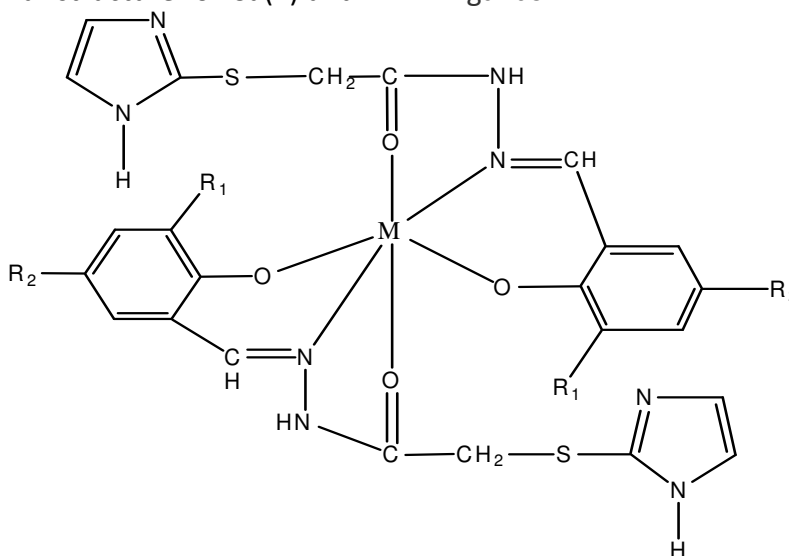
Fig:2 Antifungal activity of Ligands and their complexes.



### CONCLUSION

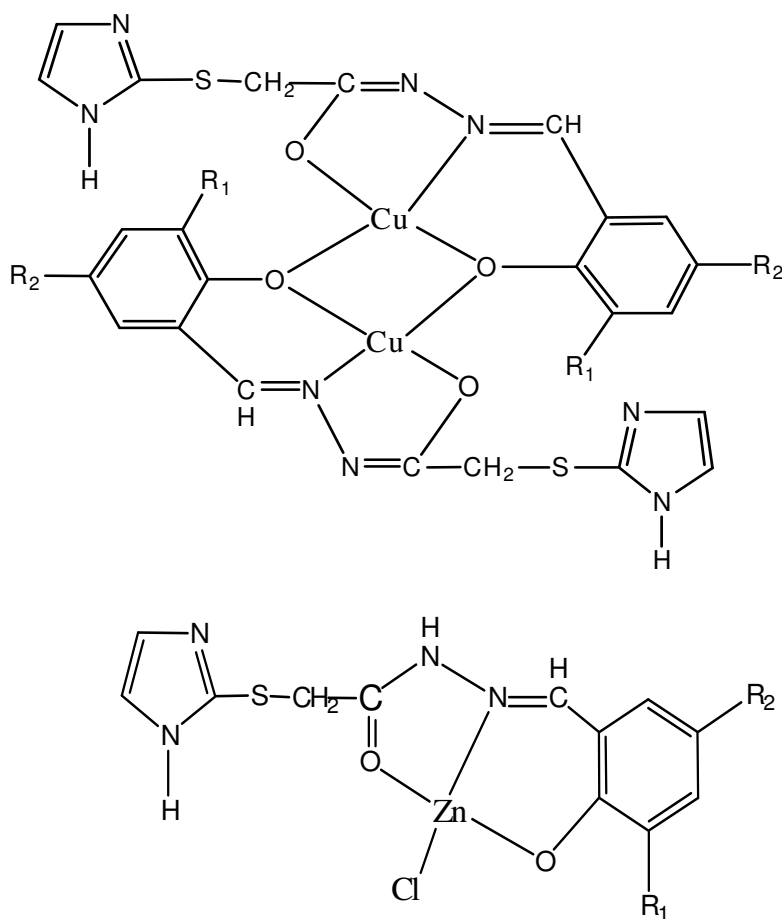
From the above discussion, it is concluded that the ligands behave in a monobasic tridentate manner in all the complexes except in Cu(II) complexes, where they act as dibasic tridentate ligands with ONO donor sequence. The six coordinate octahedral structure for Co(II) and Ni(II), dimeric square planar structure for Cu(II) and

tetrahedral structure for Zn(II) complexes (II) have been proposed. On comparing the biological activity of the ligands and their complexes with the standard bactericide and fungicide, it is observed that the metal complexes have moderate activity as compared to the standard but all the complexes are more active than their respective ligands.



M= Co (II) and Ni (II)





II. Proposed structures of metal (II) complexes of LH<sub>2</sub>

#### ACKNOWLEDGEMENT:

The author would like to thank Department of Biotechnology, Basaveshwar Engineering college, Bagalkot. for providing necessary facilities for interpretation of antimicrobial activity.

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