

## Spectral and Antifungal Activity of Fe(II) and Cu(II) Mixed Ligand Complexes with Oxygen, Nitrogen and Sulphur Donor Ligands

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Mixed ligand complexes of the type  $[M(LH_2)B_2]$  where M = Fe(II) or Cu(II), L = 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7,9-decapentene ( $LH_2$ ), B = water, ammonia, phenyl isocyanide, quinoline, pyridine or  $\alpha$ ,  $\beta$  and  $\gamma$ -picolines. The ligand as well as metal complexes were characterized on the basis of elemental analyses, IR, electronic spectra, molar conductance, magnetic moment data. On the basis of above observations the complexes were proposed to be octahedral in nature. The  $LH_2$  behaves as binegative tetradentate ligand. The remaining coordination sites are satisfied by neutral molecules. The ligand as well as their metal complexes were also screened for antifungal activity.

**Key Words:** Fe(II), Cu(II), Complexes, Spectroscopy, Antifungal activity.

### INTRODUCTION

Recently the metal complexes of mixed ligand with N, O and S donor sites is of great importance due to their wide application in laser technology, biological science<sup>1-5</sup> and industry. There has been a growing interest in the structural study of the chelates derived from organic compounds containing N, O and S donor with antimicrobial activity. Hence, in continuation of our earlier work<sup>6-12</sup> on the mixed ligand complexes on N, O and S donor sites, herein the synthesis and characterization of Fe(II) and Cu(II) complexes of 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7-decapentene are reported.

### EXPERIMENTAL

All the reagents used were either B.D.H. or E. Merck quality. The metal contents were determined using standard procedures<sup>13</sup>. Molar conductance values were made on systronics conductivity meter model 303 using DMF as a solvent. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The electronic spectral values recorded with Hitachi-320 spectrophotometer. Magnetic susceptibility of the complexes were determined by Guoy method using mercury tetrakisothiocyanatocobaltate as the calibrant.

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**Preparation of the ligand:** The ligand 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7,9-decapentene were synthesized in two steps. 12.1 g of 2-amino benzaldehyde were dissolved in ethanol is treated with 10.9 g of 2-amino phenol dissolved in ethanol. The resulting solution were refluxed for 2 h on water bath. The resulting solution after cooling furnish faint yellow colour 1-hydroxy-6-amino-1,2:5,6-dibenzo-3-aza-1,3,5-hexane. 21.2 g ethanolic solution of 1-hydroxy-6-amino-1,2:5,6-dibenzo-3-aza-1,3,5-hexane were treated with 13.8 g *ortho* mercapto benzaldehyde dissolved in ethanol. The resulting mixture was heated under reflux on water bath for 1 h. After cooling, the refluxed solution furnish yellow colour solid which was separated by filtration, washed and finally dried and crystallized with tetrahydro furan to furnish 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7,9-decapentene as yellow silky prismatic needles m.p.  $276 \pm 1$  °C, yield 60-65 %.

**Preparation of the complexes:** The ethanolic solution of metal acetates/chlorides (0.01 m) was allowed to react with ethanolic solution of ligand LH<sub>2</sub> (0.01 m) in molar ratio 1:1. The resulting mixtures was refluxed on water bath 2-3 h. The solution was then cooled and treated with neutral bases water/ammonia/quinoline/phenyl isocyanide/pyridine/ $\alpha$ -,  $\beta$ - or  $\gamma$ -picolines separately. The resulting mixtures were again heated on water bath for 1-2 h. The procedure carried out in each case were similar with slight variation of timing of reflux. On cooling solid coloured complexes separated out which was filtered, washed with ethanol, dried and recrystallized with tetrahydrofuran (Yield in all cases 60-65 %).

## RESULTS AND DISCUSSION

The analytical data, colour, magnetic susceptibility, molar conductance data and electronic spectra have been recorded in Table-1.

The infrared spectra from the interpretation of the IR spectra of the ligand, it is expected that two protons, one from OH group and one from SH group present in the ligand molecule will be deprotonated and dianioning tetradentate donor molecule is formed as shown in Fig. 1.

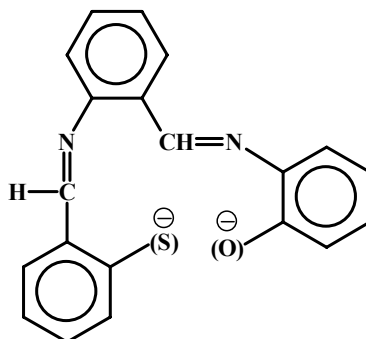


Fig.-1

TABLE-1  
ANALYTICAL COLOUR, MAGNETIC SUSCEPTIBILITY, ELECTRONIC SPECTRA AND  
CONDUCTIVITY MEASUREMENT DATA FOR LIGAND AND ITS METAL COMPLEXES

Compounds (colour)	Elemental analysis (%):				$\mu_{\text{eff}}$ (BM)	$\lambda_{\text{max}}$ (electronic $\text{cm}^{-1}$ )	$\Omega_m$ ( $\text{ohm}^{-1}$ $\text{cm}^2 \text{mol}^{-1}$ )
	Found (Calcd.)						
	M	C	H	N			
LH <sub>2</sub> (Yellow)	–	72.15 (72.28)	4.85 (4.81)	8.47 (8.43)	–	–	–
[Fe(LH <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ] (Light green)	13.11 (13.24)	56.72 (56.88)	4.30 (4.26)	6.66 (6.63)	5.20	10540, 29800, 39200	8.7
[Fe(LH <sub>2</sub> )(NH <sub>3</sub> ) <sub>2</sub> ] (Faint green)	13.16 (13.31)	56.98 (57.15)	4.80 (4.76)	13.36 (13.33)	5.16	10560, 30400, 39400	8.9
[Fe(LH <sub>2</sub> )(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ] (Yellowish, green)	8.52 (8.63)	70.65 (70.81)	4.36 (4.34)	8.73 (8.69)	5.05	10600, 30200, 39350	8.3
[Fe(LH <sub>2</sub> )(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ] (Brownish green)	9.30 (9.44)	68.80 (68.93)	4.07 (4.05)	9.48 (9.46)	5.10	10300, 30600, 39450	10.4
[Fe(LH <sub>2</sub> )(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ] (Brownish white)	10.10 (10.20)	66.04 (66.18)	4.44 (4.41)	10.32 (10.29)	5.14	10400, 30300, 39600	11.6
[Fe(LH <sub>2</sub> )( $\alpha$ -pic) <sub>2</sub> ] (Brownish white)	9.65 (9.77)	67.01 (67.14)	4.92 (4.89)	9.93 (9.79)	5.12	10350, 30400, 39250	11.3
[Fe(LH <sub>2</sub> )( $\beta$ -pic) <sub>2</sub> ] (Greenish brown)	9.60 (9.77)	66.98 (67.14)	4.91 (4.89)	9.85 (9.79)	4.90	10450, 30500, 39750	11.9
[Fe(LH <sub>2</sub> )( $\gamma$ -pic) <sub>2</sub> ] (Greenish brown)	9.62 (9.77)	66.96 (67.14)	4.93 (4.89)	9.82 (9.79)	4.98	10250, 30450, 39300	12.3
[Cu(LH <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ] (Light green)	14.66 (14.78)	55.80 (55.87)	4.22 (4.19)	6.56 (6.51)	1.90	14900, 25500	12.7
[Cu(LH <sub>2</sub> )(NH <sub>3</sub> ) <sub>2</sub> ] (Light green)	14.74 (14.83)	56.08 (56.14)	4.70 (4.67)	13.15 (13.09)	1.94	15400, 25200	13.9
[Cu(LH <sub>2</sub> )(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ] (Faint green)	9.66 (9.74)	69.87 (69.99)	4.34 (4.29)	8.64 (8.59)	1.88	15000, 25900	14.3
[Cu(LH <sub>2</sub> )(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ] (Greenish white)	10.50 (10.59)	67.95 (68.05)	4.04 (4.00)	9.40 (9.34)	1.92	15200, 25800	15.01
[Cu(LH <sub>2</sub> )(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ] (Pale green)	11.42 (11.51)	65.20 (65.27)	44.40 (4.35)	10.20 (10.15)	1.95	15300 25400	16.3
[Cu(LH <sub>2</sub> )( $\alpha$ -pic) <sub>2</sub> ] (Faint green)	10.82 (10.95)	66.18 (66.26)	4.89 (4.83)	9.70 (9.66)	1.98	15600 25100	16.3
[Cu(LH <sub>2</sub> )( $\beta$ -pic) <sub>2</sub> ] (Light green)	10.80 (10.95)	66.16 (66.26)	4.86 (4.83)	9.78 (9.66)	1.96	15500, 25600	18.9
[Cu(LH <sub>2</sub> )( $\gamma$ -pic) <sub>2</sub> ] (Pale green)	10.84 (10.95)	66.14 (66.26)	4.88 (4.83)	9.74 (9.66)	1.90	15100 25700	20.3

The ligand (LH<sub>2</sub>) act as tetradentate molecule through deprotonated oxygen (OH), sulphur (SH) and two aldimine N atoms with metal ion.

A careful interpretation of IR spectral bands of the ligand LH<sub>2</sub> and the complexes [M(L)B<sub>2</sub>] reveals that there are certain bands of the ligand which are appreciable affected after the complex formation indicating the donor atoms of coordination sites of the ligand to form the linkage with metal ions. Some new bands, which are totally absent in the ligand appears in the complexes also indicate the formation of bond between the metal and donor atoms of the ligand.

The ligand exhibit a band at  $3260\text{ cm}^{-1}$  which assignable to  $\nu(\text{OH})^{14}$  and disappears in almost all the complexes and a new band is obtained in the far IR region at  $550\text{ cm}^{-1}$  due to  $\nu(\text{M-O})$  vibration<sup>15</sup> indicating deprotonation of phenolic OH and linkage with oxygen atom in the formation of the complex with the metal ions.

A broad and sharp band appeared at  $2460\text{ cm}^{-1}$  in the ligand assignable to  $\nu(\text{S-H})$  vibration. This band disappears in almost all the complexes indicating deprotonation of (SH) group and a new band appears<sup>16</sup> in the far ir region at  $380\text{ cm}^{-1}$  has been obtained in the complexes due to coordination of (SH) sulphur atom of ligand with metal ion. The bands due to  $\nu(\text{C-O})$  and  $\nu(\text{C-S})$  vibrations have been reduced by  $25\text{-}30\text{ cm}^{-1}$  suggesting the deprotonation of OH and SH group present in the ligand.

The next IR band of the ligand shows a broad and strong band at  $1650\text{ cm}^{-1}$  assignable<sup>17</sup> to  $\nu(\text{C=N})$  vibrations. This band has been reduced by  $30\text{-}40\text{ cm}^{-1}$  in complexes proposes the linkage of both azomethine nitrogen atoms present in the ligand molecule in the complex formation.

Thus on the basis of IR spectral data it is proposed that ligand ( $\text{LH}_2$ ) behaves as bidentate tetradentate manner and coordination takes place with deprotonated phenolic oxygen sulphur and two azomethine nitrogen atoms. The remaining two coordination sites are satisfied by neutral molecules like water, ammonia, quinoline, phenyl isocyanide, pyridine and  $\alpha$ ,  $\beta$  and  $\gamma$ -picolines.

**Electronic spectra and magnetic susceptibility of the complexes:** The electronic spectra of Fe(II) complexes exhibits a band at  $10600\text{ cm}^{-1}$  in visible region and two broad band with low intensity at  $30700$  and  $39600\text{ cm}^{-1}$ , respectively corresponding to the  ${}^5\text{E}_g(\text{D}) \leftarrow {}^5\text{T}_{2g}(\text{D})$ ,  ${}^3\text{T}_{1g}(\text{H}) \leftarrow {}^5\text{T}_{2g}(\text{D})$  and  ${}^3\text{E}_g(\text{H}) \leftarrow {}^5\text{T}_{2g}(\text{D})$  transition, respectively.  ${}^3\text{T}_{1g}(\text{D}) \leftarrow {}^5\text{T}_{2g}(\text{D})$  and  ${}^3\text{E}_g(\text{H}) \leftarrow {}^5\text{T}_{2g}(\text{D})$  transitions are spin forbidden and are possibly due to  $n\text{-}\pi$  and  $n\text{-}\pi^*$  transitions of the ligands or due to the merger of both the transitions. The electronic spectral data for all Fe(II) complexes proposed an octahedral<sup>18,19</sup> geometry which is further supported<sup>20,21</sup> by  $\mu_{\text{eff}}$  4.90-5.20 BM. The electronic spectra of Cu(II) complexes  $1500\text{ cm}^{-1}$  and another band at  $25000\text{ cm}^{-1}$  assignable to  ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$  and charge transfer band which is characteristic of octahedral<sup>18,19</sup> stereochemistry. The magnetic moment of Cu(II) complexes lies in the range of 1.88-1.98 BM.

**Conductivity measurement:** Molar conductance values were recorded on systronic conductivity meter model 303 using DMF as a solvent. All the complexes were found to be non-electrolytic<sup>22</sup> in nature giving conductivity value in the range  $8.3\text{-}20.3\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ . The molar conductance data of the complexes also supports the assigned structure on the basis of elemental analysis spectral data, magnetic susceptibility value.

**Antifungal activity:** Fungicidal activity of the ligand and their metal complexes were carried out by disc method<sup>23</sup> on *Aspergillus flavus* and *Penicillin notatum*. The ligand and their corresponding metal complexes in DMF were screened antifungal activity. The ligand exhibited 20-25 and 30-35 % inhibition per 125 to 250 ppm concentration, respectively. It is observed that the metal complexes show enhanced

antifungal activity than ligand. This is due to chelation which reduces the polarity of metal ion due to partial sharing of its positive charge with ligand. The chelation increases lipophilic character in the complexes and results in the enhancement of fungicidal activity. The inhibition of metal complexes has been increased by 30-65 and 40-70 % for 125 and 250 ppm concentration. The Cu complex exhibit greater fungicidal activity than Fe complexes.

### Conclusion

On the basis of elemental analysis, IR, UV spectral study magnetic susceptibility value and molar conductance data the ligands LH<sub>2</sub> acts in bidentate tetradentate manner and linkage takes place through deprotonated phenolic oxygen and two azomethine N atoms. The remaining two coordination sites are satisfied by neutral molecules like water, ammonia, quinoline phenylisocyanide, pyridine and  $\alpha$ ,  $\beta$  and  $\gamma$ -picolins. The geometry of the complexes were proposed to be octahedral in nature as shown in Fig. 2.

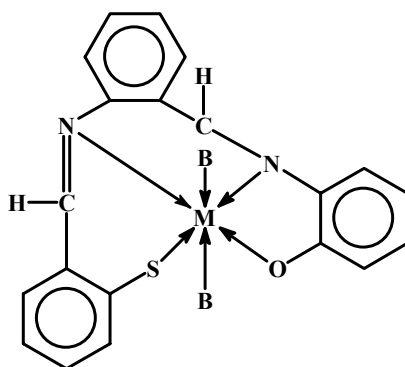


Fig. 2. [M(LH<sub>2</sub>)B<sub>2</sub>]; M = Fe(II) and Cu(II)

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