



## DONAR BEHAVIOUR OF N-(5-CHLORONAPHTHYL)-2-MERCAPTOPROPANAMIDE AND N-(5-HYDROXYNAPHTHYL)-2-MERCAPTOPROPANAMIDE WITH Fe(II) AND Zn(II) IONS

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### ABSTRACT

Some novel complexes of ligands N-(5-chloronaphthyl)-2-mercaptopropanamide (CMP-H) and N-(5-hydroxynaphthyl)-2-mercaptopropanamide (HMP-H) with Fe(II) and Zn(II) were prepared. The ligands and their metal complexes were characterized by physico-chemical spectroscopic techniques. The spectral data suggested the deprotonation of thiol(-SH) group and its coordination to the metal ion in complexes. It was also suggested to involve -NH group in coordination to the metal ion through nitrogen atom. Spectroscopic studies suggested tetrahedral Zn(II) complexes and octahedral Fe(II) complexes. The presence of water molecules in the Fe(II) complexes is confirmed by Thermogravimetric Analysis (TGA) studies.

**KEYWORDS :** N-(5-chloronaphthyl)-2-mercaptopropanamide, N-(5-hydroxynaphthyl)-2-mercaptopropanamide, Fe(II) and Zn(II) complexes.

### INTRODUCTION

Ligands containing sulphur and nitrogen donor are quite interesting and form an active field of current research in coordination chemistry. A large volume of work<sup>1-20</sup> has been reported on the complex formation behaviour of sulphur and nitrogen donor ligands. Yet donor characteristics of ligands N-(5-chloronaphthyl)-2-mercaptopropanamide and N-(5-hydroxynaphthyl)-2-mercaptopropanamide offer scope for further studies. In the present work, an attempt has been made to investigate the donor behaviour of above ligands with Fe(II) and Zn(II). Keeping all these minds in we reported the preparation and characterizations of Fe(II) and Zn(II) complexes of above ligands.

### EXPERIMENTAL

All the chemicals used were analytical grade: 1-amino-5-hydroxynaphthalene, 1-amino-5-chloronaphthalene, 2-mercaptopropanoic acid, Fe(II), Zn(II), Ethanol, KOH were purchased from the E.Merck (India) Limited.

#### Preparation

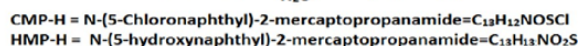
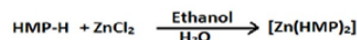
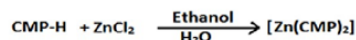
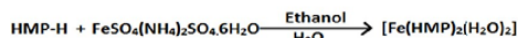
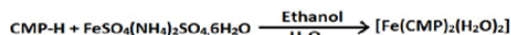
**(a) Preparation of N-(5-hydroxynaphthyl)-2-mercaptopropanamide:** This ligand was prepared in a manner analogous to the preparation of thioglycolanilide. For this equimolar proportion of 1-amino-5-hydroxynaphthalene and 2-mercaptopropanoic acid were mixed in 500 ml conical flask and heated in a glycerine bath at 110°C - 120°C for about 2-3 hours in the slow current of CO<sub>2</sub>. When the liquid was poured into a beaker of water, a solid mass was obtained. It was filtered, dried and crushed. It was purified by repeated recrystallisation from dilute alcohol. Finally, the obtained was dried in vacuum desiccators. The ligand obtained shows melting point 143°C-144°C.

**(b) Preparation of N-(5-chloronaphthyl)-2-mercaptopropanamide:** It was prepared as the ligand N-(5-hydroxynaphthyl)-2-mercaptopropanamide except that 1-amino-5-chloronaphthalene was used in place of 1-amino-5-hydroxynaphthalene. The ligand obtained has melting point 133°C - 134°C.

**(c) Preparation of Fe(II) complex:** The complexes of Fe(II) were prepared by mixing the aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.FeSO<sub>4</sub>.6H<sub>2</sub>O (Mohr's salt) and ethanolic solution of ligands (CMP-H) and (HMP-H) separately in the ratio of 2:1 whereby the colour of Mohr's salt solution disappeared immediately. The reaction mixture was shaken vigorously for 30 minutes as a result light yellow precipitate of Fe(II) complex appeared which was dried.

**(d) Preparation of Zn(II) complex:** For the preparation of Zn(II) complexes about 0.01 mole of ZnCl<sub>2</sub> was dissolved in 40-50 ml. aqueous ethanol and 0.02 mole of ligands (CMP-H) and (HMP-H) were dissolved separately in hot ethanol dioxane mixture. They were slowly mixed with constant stirring. The mixed solution was heated on a steam bath. The P<sup>H</sup> of Solution was raised by adding sodium acetate solution and a few drops of ammonia. From the hot solution of Zn(II) complexes were obtained as cream yellow products. The products were filtered, washed with cold aqueous ethanol and dried in a desiccator over anhydrous CaCl<sub>2</sub>. The sample was further dried in an air oven at 60°C - 70°C. The purity of complexes was checked by paper chromatography which developed on spot.

#### Synthesis Scheme



### RESULT AND DISCUSSION

All the complexes are stable at room temperature insoluble in water and most of the common organic solvent but soluble in DMF and DMSO. The analytical data and molar conductivity of the complexes (table no.01) indicates that their stoichiometry may be represented as 1:2 metal to ligand ratio. On the basis of elemental analysis the complexes were formulated as [Fe(CMP)<sub>2</sub>(H<sub>2</sub>O)], [Fe(HMP)<sub>2</sub>(H<sub>2</sub>O)], [Zn(CMP)<sub>2</sub>] and [Zn(HMP)<sub>2</sub>]. The molar conductance value of Fe(II) complexes in DMSO solvent represents octahedral geometry and their nonelectrolytic nature<sup>21</sup>. Due to completely filled d-orbital of Zn(II) ion, it exhibits diamagnetic nature. The magnetic moment of Fe(II) complexes has been found 4.31-4.42 BM at room temperature.

In high spin octahedral complexes of Fe(II) there are four unpaired electrons i.e. t<sub>2g</sub><sup>4</sup>e<sub>g</sub><sup>2,2,2</sup>. Hence the magnetic moment value due to four unpaired electrons is expected to be 4.9 BM. Here the experimental value of Fe(II) is slightly less than the magnetic moment value.

This may be attributed to 5T<sub>2g</sub> ⇌ A<sub>1g</sub> equilibrium i.e. equilibrium between high spin and low spin octahedral geometry of Fe(II) complexes<sup>23-28</sup>. The Zn(II) Complex has been suggested to possess a distorted tetrahedral structure.

**Table No.-01 Analytical data and Molar conductance**

S.No	Complexes	%M cal. (found)	%C cal. (found)	%H cal. (found)	%N cal. (found)	%S cal. (found)	%Cl cal. (found)	$\Delta m$ $Scm^2m$ $ol^{-1}$ $10^4$
1	[Fe(CMP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	9.02 (9.05)	50.24 (50.26)	4.18 (4.20)	4.50 (4.48)	10.31 (10.33)	11.43 (11.40)	12.04
2	[Fe(HMP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	9.58 (9.60)	53.42 (53.45)	4.79 (4.75)	4.79 (4.80)	10.96 (10.93)	-	14.05
3	[Zn(CMP) <sub>2</sub> ]	11.00 (11.05)	52.49 (52.45)	3.70 (3.71)	4.71 (4.72)	10.76 (10.75)	11.94 (11.93)	9.08
4	[Zn(HMP) <sub>2</sub> ]	11.73 (11.76)	55.79 (55.78)	4.30 (4.32)	5.02 (5.05)	11.48 (11.45)	-	11.09

Fe(II) complexes under investigation display no d-d transition because of strong charge-transfer bands, while no d-d transition is observed in Zn(II) complexes due to completely filled d-orbitals.

### Infra-red spectra

Infrared spectra of ligands (CMP-H) and (HMP-H) and its hitherto unknown complexes were recorded in region 4000-200  $cm^{-1}$  in KBr disc with the help of JASCO-FTIR spectrometer model 5300. The pertinent infrared data are listed in Table No. 02.

**Table No. 02 IR spectra of Fe(II) and Zn(II) complexes.**

S.No.	Ligand/complex	>NH $cm^{-1}$	>CO $cm^{-1}$	-SH $cm^{-1}$	M-S/M-N $cm^{-1}$
01	CMP-H	3260	1670	2565	-
02	HMP-H	3270	1675	2575	-
03	[Fe(CMP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3240s	1660s	-	320m/290m
04	[Fe(HMP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3245s	1665s	-	315m/285m
05	[Zn(CMP) <sub>2</sub> ]	3245s	1645s	-	300m/275m
06	[Zn(HMP) <sub>2</sub> ]	3250s	1655s	-	305m/270m

The broadband at 3300  $cm^{-1}$  (approx.) in the spectrum of the ligands points weak intermolecular hydrogen bonding in it. The spectra of all complexes exhibit new broad and strong bands in the region 3240-3250  $cm^{-1}$  suggests the coordination of ligands nitrogen atom of secondary amide (-CONH-) moiety. The band in the region 300-320  $cm^{-1}$  in the spectra of all mixed ligand complexes may be assigned to M-S frequency while medium bands in the region 270-290  $cm^{-1}$  is assigned M-N band frequency<sup>29-36</sup>. On the basis above observations following structures are suggested of prepared complexes.

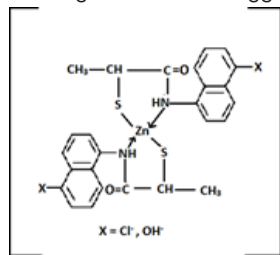


Figure 01

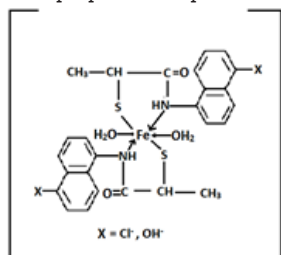


Figure 02

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