



SYNTHESIS AND CHARACTERIZATION OF SOME MIXED LIGAND COMPLEXES OF SN(II) AND PB(II) IONS.

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ABSTRACT The study of co-ordination chemistry of tin(II) and lead (II) metals was under taken with a view to find out their complexing ability towards various organic moiety. Complexes of N-(5-hydroxynaphthyl)-2-mercaptopropanamide and N-(5-chloronaphthyl)-2-mercaptopropanamide have been prepared with Sn(II) and Pb(II) having molecular formula $ML_2 \cdot nH_2O$ and $ML_2 \cdot nH_2O$. These complexes have been characterized on the basis of analytical, infrared, electronic spectra studies, and measurement of magnetic moment. On the characterization all the complexes have been found to be tetrahedral geometry. Metal ligands vibration in far infrared region have also been assigned.

KEYWORDS : N-(5-hydroxynaphthyl)-2-mercaptopropanamide and N-(5-chloronaphthyl)-2-mercaptopropanamide, tin(II) and lead (II) complexes.

INTRODUCTION

Of all p-block elements tin(II) and lead(II) have a particular fascination for co-ordination chemists as it can adopt many different geometry in its complexes allowing a degree of tolerance for ligand configuration. The present investigation was under taken to make a systematic study on the co-ordination chemistry of p-block heavy elements i.e. Sn^{2+} and Pb^{2+} .

After 1925, there were many evidences regarding the complex formation of S-block alkali and alkaline earth metals despite the absences of d-orbitals in them¹⁻¹⁰.

The above facts enabled us to investigate the complexing abilities of P-block metals¹¹⁻¹⁵. We are especially interested with the preparation and characterization of mixed ligand complexes of tin and lead metals in lower oxidation state e.g. +2 state¹⁶⁻¹⁸.

The present investigation was under taken to examine the possible complex formation of Sn(II) and Pb(II) with N-(5-hydroxynaphthyl)-2-mercaptopropanamide and N-(5-chloronaphthyl)-2-mercaptopropanamide. Co-ordination site in our ligands are oxygen and sulphur atom and act as bidentate double faced ligands.

Experimental

All the chemicals used were analytical grade. 1-amino-5-hydroxynaphthalene, 1-amino-5-chloronaphthalene, 2-mercaptopropanoic acid, $Sn(CH_3COO)_2$, $Pb(CH_3COO)_2$, ethanol, KOH were purchased from the E. Merck. (India) Limited.

- Preparation N-(5-hydroxynaphthyl)-2-mercaptopropanamide and N-(5-chloronaphthyl)-2-mercaptopropanamide:** Preparation of N-(5-hydroxynaphthyl)-2-mercaptopropanamide: This ligand was prepared in a manner analogous to the preparation of the 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 glycerin bath at 110°C-120°C for about 2-3 hours in slow current of CO_2 . When liquid was poured into a beaker of water a solid mass is obtained. It is filtered, dried and crushed. It was purified by repeated recrystallization from dilute alcohol. Finally the ligand obtained is dried in a vacuum desiccator. The ligand obtained shows melting point 143°C-144°C.
- Preparation of N-(5-Chloronaphthyl)-2-mercaptopropanamide:** It was prepared as ligand N-(5-hydroxynaphthyl)-2-mercaptopropanamide except that 1-amino-5-chloronaphthalene was used 1-amino-5-hydroxynaphthalene. The ligand obtained has melting point 133°C-135°C.
- Synthesis of tin(II) and lead(II) complexes:** Tin (II) complexes were synthesized by the reaction of tin(II) acetate and CMP-H and HMP-H separately in 1:2 molar ratio in dry ethanol reaction medium. The resulting was stirred on magnetic stirrer for about two hours. The solvent was removed under pressure and the product was finally dried in vacuum at 40-50°C. Lead(II) complexes were prepared as the preparation of Sn(II) complexes.

The reactions of tin (II) acetate and lead(II) acetate with ligands are as:

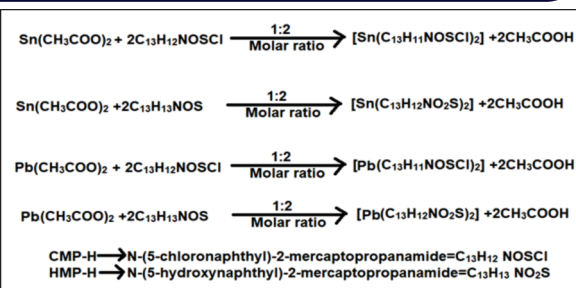


Table 01 Analytical table

S. N	Complexes	% M cal. (found)	% C cal. (found)	% H cal. (found)	% N cal. (found)	% S cal. (found)	% Cl cal. (found)
1	[Sn(CMP) ₂]	18.36 (18.35)	48.15 (48.16)	3.4 (3.5)	4.32 (4.30)	9.70 (9.81)	10.95 (10.92)
2	[Sn(HMP) ₂]	19.47 (19.48)	51.06 (581.02)	3.60 (3.61)	4.58 (4.56)	10.47 (10.48)	-
3	[Pb(CMP) ₂]	28.13 (28.15)	42.39 (42.37)	2.99 (3.01)	3.80 (3.81)	8.69 (8.66)	9.64 (9.66)
4	[Pb(HMP) ₂]	29.61 (29.63)	44.63 (44.60)	3.43 (3.41)	4.00 (4.03)	9.15 (9.13)	-

RESULT AND DISCUSSION

The complexes of Tin(II) - [Sn(CMP)₂], [Sn(HMP)₂] and Lead(II)- [Pb(CMP)₂], [Pb(HMP)₂] have been isolated. The molecular compositions have derived on the basis of analytical result which is given in the Table 01. The magnetic measurements show the diamagnetic nature and hence square planar. These complexes are soluble in organic solvents such as methanol, benzene, DMF and DMSO. The molar conductance value of the complexes fall in range 15 to 20 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that these chelates are non-electrolyte. These complexes are yellow and cream solid. The complexes containing chlorine were shaken with aqueous Na_2CO_3 solution thoroughly and the aqueous extract was filtered, acidified with dilute HNO_3 and AgCl occurred indicating the presence of covalent chloride. Other complexes contain covalently bonded hydroxyl group because they do not give brown precipitate of Ag_2O when shaken with $AgNO_3$ solution. Hence covalently bonded chloride and hydroxyl group was assumed.

Infrared spectra: Infrared spectra of the ligands and its mixed ligand Sn(II) and Pb(II) complexes were recorded in region 4000-200 cm^{-1} in KBr phase with the help of spectrometer. Pertinent IR data for these compounds were recorded in the Table 02.

Table 02 IR Spectra Table

Compounds	>NH cm^{-1}	>C=O cm^{-1}	-S-H cm^{-1}	M-S/M-O cm^{-1}
LH(CMP-H)	3260	1670	2565	-
L'H(HMP-H)	3270	1675	2575	-
[Sn(CMP) ₂]	3240	1650	-	400w/(455w)
[Sn(HMP) ₂]	3255	1655	-	420w/(460w)

[Pb(CMP) ₂]	3235	14640	-	350w/(420w)
Pb(HMP) ₂]	3240	1645	-	340w/(460w)

Structure and bonding: On the basis of elemental analysis, the general formula of mixed ligand complexes of Sn(II) and Pb(II) metal chelates with LH and L'H ligands, the infrared spectra of these complexes suggest metal through hydroxyl oxygen as well as sulphur atom of -SH group. The structure of complexes are shown in the Figure 01.

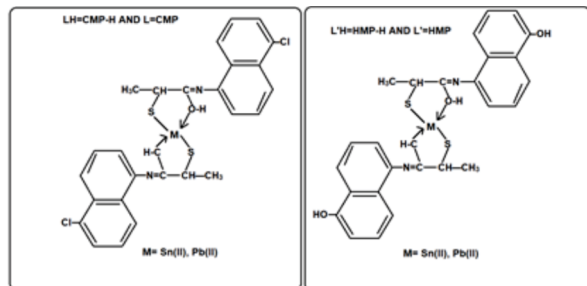


Figure 01 Structure and bonding

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