

# Synthesis and Characterization of $[(SnX_2)_2.L^1]$ ; $[(SnX_2)(MCl_2).L^1]$ ; $[SnX_2.L^2]$ and $[SnX_2.L^3]$ Compounds with Macrocyclic Ligands

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## ABSTRACT

$[(SnX_2)_2.L^1]$ ,  $[(SnX_2)(MCl_2).L^1]$ ,  $[SnX_2.L^2]$  and  $[SnX_2.L^3]$  (where X= Cl or Br;  $L^1= 3, 6, 9, 12, 20, 23, 26, 29, 35, 36$ -decaazatricyclo [29.3.1.1] hexatriaconta-1(34), 14, 16, 18(36) 31(35), 32-hexaene-2,13,19, 30-tetraone;  $L^2= 3,6,9,17,20,23,29,30$ -octaazatricyclo [23;3.1.1<sup>11,15</sup>] triaconta-1(28),11,13,15(30), 25(29), 26-hexaene-2,10,16,24-tetraone and  $L^3 = 3,7,15,19,25,26$ -hexaazatricyclo [19;3.1.1<sup>9,13</sup>] hexacosa 1(24),9,11,13(26),21(25),22-hexaene-2,8,14,20-tetraone) have been synthesized and characterized by elemental analysis, molar conductance, IR and X-ray photoelectron spectra(XPS) data and an octahedral geometry were established.

**Keywords:** Macrocyclic ligands, Tin(II) and XPS.

## I. INTRODUCTION

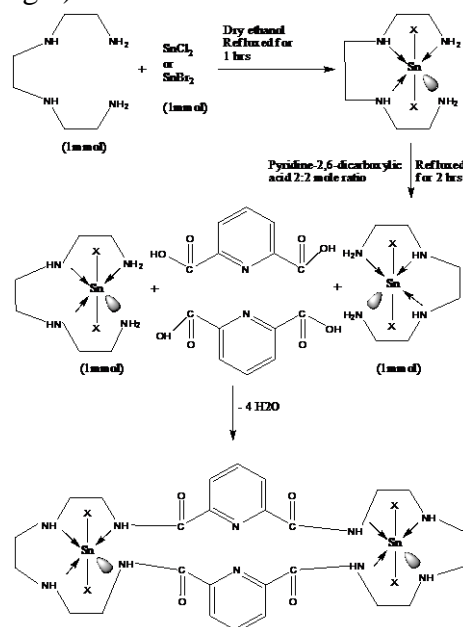
A literature survey reveals that many Sn(II) compounds with various monodentate, bidentate, tetradentate and Schiff base ligands have been synthesized and their structures have been also characterised by various physicochemical techniques<sup>1-2</sup>, but tin (II) compounds with macrocyclic ligands are very less known<sup>3-10</sup>. In this paper many tin(II) compounds with homobitin (II) and heteromonotin(II)-monometal(II) compounds (where metal (II)=Cu(II), Co(II), Mn(II), Ni(II), and Zn(II) ) with various macrocyclic ligands have been synthesized and characterized to establish their structure and geometry.

## II. METHODS AND MATERIAL

$SnCl_2$ ,  $SnBr_2$ , all chemicals and solvents were of AR grade.

**Preparation of  $[(SnX_2)_2.L^1]$  compounds with macrocyclic ligands ( $L^1$ ) i.e. 3, 6, 9, 12, 20, 23, 26, 29, 35, 36- decaazatricyclo [29.3.1.1<sup>14-18</sup>] hexatriaconta-1(34), 14, 16, 18(36) 31(35), 32-hexaene-2, 13, 19, 30-tetraone ligands.**

Triethylenetetraamine (1 mmol) was mixed with  $SnCl_2$  or  $SnBr_2$  (1 mmol) in dry ethanol and refluxed for 1 hr and then put dropwise pyridine 2, 6- dicarboxylic acid into this solution (2mmol :2mmol ratio) and again refluxed this solution for 2 hrs. The resulting precipitate was filtered and recrystallised into ether : ethanol (9:1 ratio) (Fig 1).



**Figure 1.** Proposed mechanism for homobimetallic compound  $[(SnX_2)_2.L^1]$

(ii) Preparation of  $[(SnX_2)(MCl_2)L^1]$  (Where M=Cu(II), Co(II), Mn(II), Ni(II) and Zn(II)] compounds with macrocyclic ligands  $L^1$  i.e. 3,6,9,12,20,23,26,29,35,36-decaazatricyclo[29.3.1.1<sup>14-18</sup>] hexatriaconta-1(34),14,16,18(36),31(35),32-hexaene-2, 13,19,30-tetraone ligands:

Triethylenetetraamine (1 mmol) was mixed with  $SnCl_2$  or  $SnBr_2$  (1mmol) in dry ethanol and refluxed for 1hr (**solution A**). Again triethylenetetraamine (1mmol) was mixed with  $MCl_2$  (where  $MCl_2=CuCl_2$  or  $CoCl_2$  or  $MnCl_2$  or  $NiCl_2$  or  $ZnCl_2$ ) (1mmol) in dry ethanol and refluxed for 1hr (**solution B**). In solution A then put dropwise pyridinedicarboxylic acid (2 mmol) and then put dropwise solution B into it (1mmol) and refluxed again for 2hrs. The resulting precipitate was filtered and recrystallized into ether: ethanol (9:1 ratio) (Fig 2).

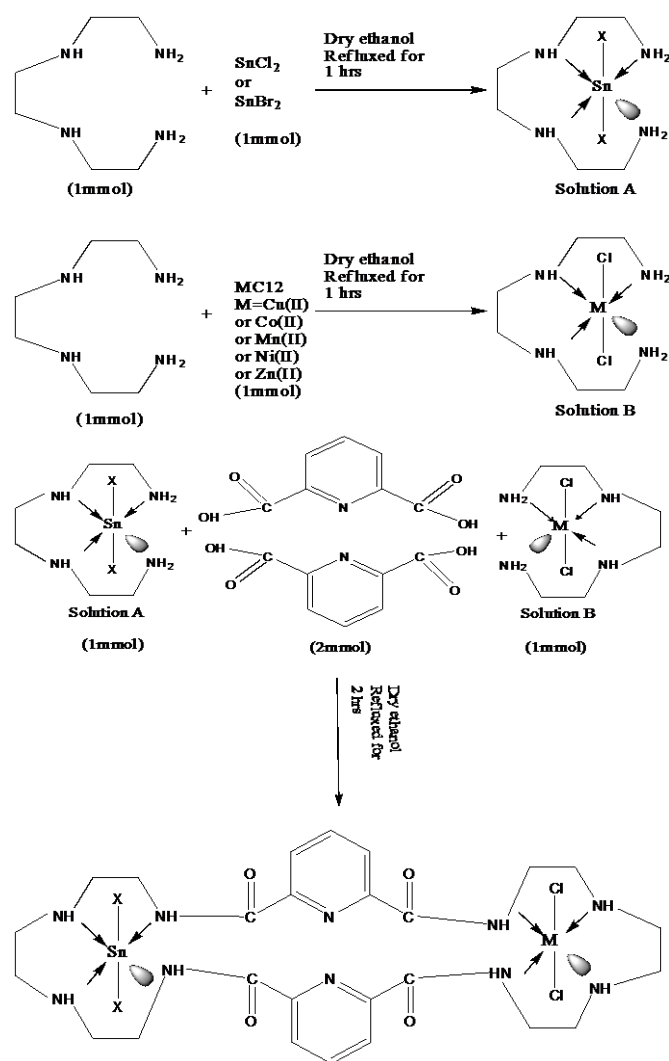


Figure 2 : Proposed mechanism for  $[(SnX_2)(MCl_2)L^1]$

(iii) Preparation of  $[SnX_2L^2]$  compounds with macrocyclic ligands ( $L^2$ ) i.e. 3,6,9,17,20,23,29,30-octaazatricyclo [23;3.1.1<sup>11,15</sup>] triaconta-1(28),11,13,15(30), 25(29), 26-hexaene-2,10,16,24-tetraone:

The diethylenetriamine (2 mmol) was mixed with  $SnCl_2$  or  $SnBr_2$  (1 mmol) in dry ethanol and refluxed for 2 hr and then pyridine-2, 6- dicarboxylic acid (2 mmol : 1mmol ratio) is mixed into above solution and refluxed for 2hrs. The resulting precipitate was filtered and recrystallised by benzene- pet ether 9:1 ratio solution (**Fig3**).

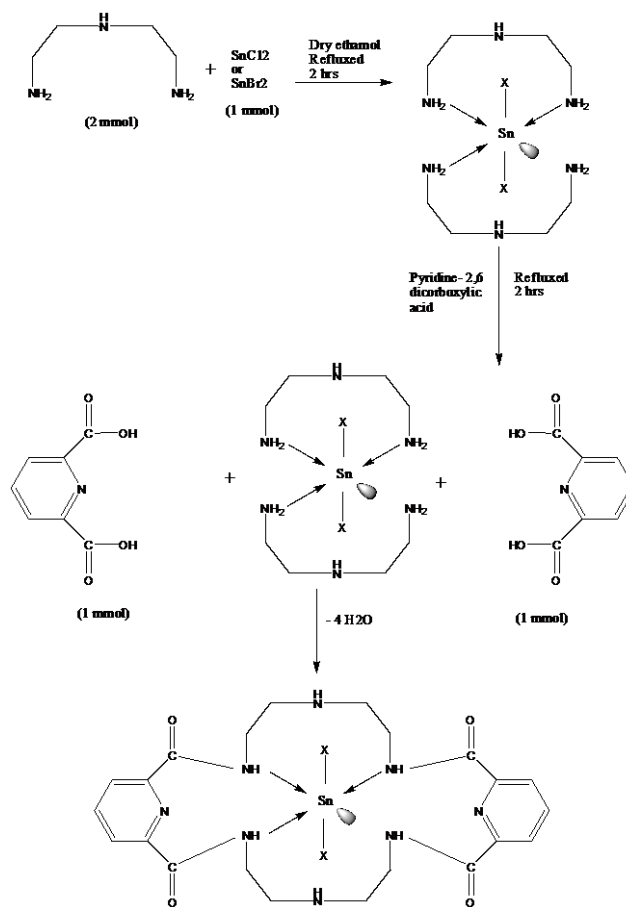


Figure 3 : Proposed mechanism of  $[SnX_2.L^2]$  Compounds

(iv) Preparation of  $[SnX_2L^3]$  compounds with macrocyclic ligands ( $L^3$ ) i.e. 3,7,15,19,25,26-hexaazatricyclo [19;3.1.1<sup>9,13</sup>] hexacosa 1(24),9,11,13(26),21(25),22-hexaene-2,8,14,20-tetraone:

The 1, 3 diaminopropane (2mmol) was mixed with  $SnCl_2$  or  $SnBr_2$  (1mmol) in dry ethanol and refluxed for 1hr and then into this solution pyridine 2, 6-dicarboxylic acid (2mmol : 1mmol ratio) was mixed and again refluxed for 3hrs. The resulting precipitate was filtered and recrystallised by

benzene : pet ether 9:1 ratio solution (Fig 4).

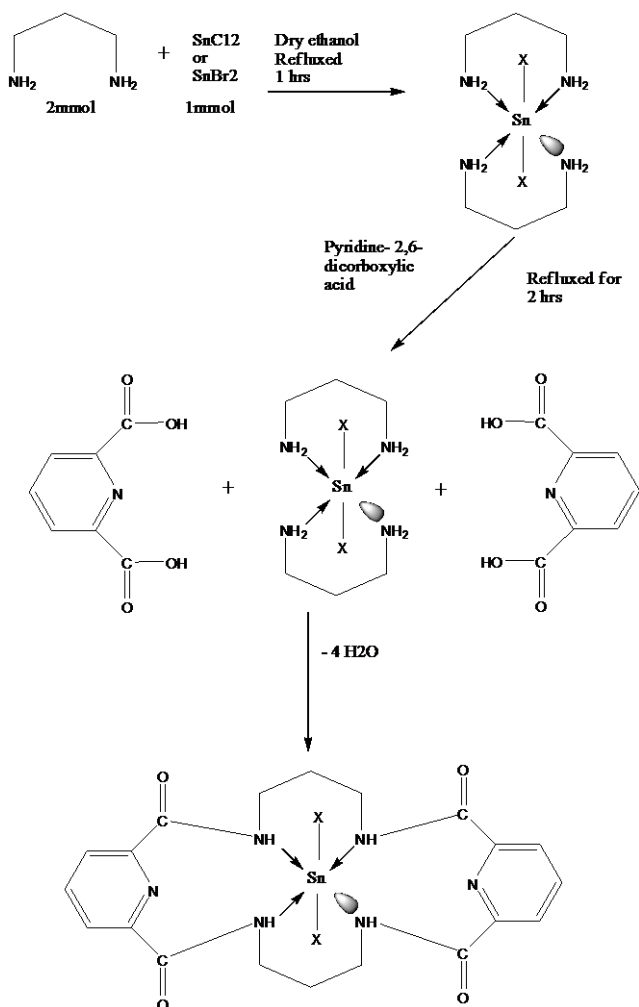


Figure 4 : Proposed mechanism for  $[\text{SnX}_2.L^3]$  Compounds

### III. RESULTS AND DISCUSSION

All these newly synthesized compounds  $[(\text{SnX}_2)_2.L^1]$ ;  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$  (where  $\text{M} = \text{Cu(II)}$ ,  $\text{Co(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$ );  $[\text{SnX}_2.L^2]$  and  $[\text{SnX}_2.L^3]$  are light yellow coloured solids. They are soluble in common organic solvents and stable towards atmospheric oxygen and moisture. They all are stable at room temperature even on long standing.

The elemental analysis for C, H, N and Sn were within  $\pm 0.5\%$  range. Molar conductance values ranges from 20-30  $\text{ohm}^{-1}$

$\text{cm}^2 \text{mol}^{-1}$  in acetone and 0.82 to 1.02  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  in nitrobenzene indicating absence of ionic species<sup>11</sup>.

Infrared frequency associated with fundamental modes of vibration of  $\nu_{\text{Sn-N}}$  and  $\nu_{\text{Sn-Cl}}$  was observed in the range 436-480  $\text{cm}^{-1}$  and 485-964  $\text{cm}^{-1}$  respectively<sup>37</sup>. In these all prepared compounds  $\nu_{\text{Cu-Cl}}$  in  $[(\text{SnX}_2)(\text{CuCl}_2)L^1]$ ;  $\nu_{\text{Co-Cl}}$  in  $[(\text{SnX}_2)(\text{CoCl}_2)L^1]$ ;  $\nu_{\text{Mn-Cl}}$  in  $[(\text{SnX}_2)(\text{MnCl}_2)L^1]$ ;  $\nu_{\text{Ni-Cl}}$  in  $[(\text{SnX}_2)(\text{NiCl}_2)L^1]$  and  $\nu_{\text{Zn-Cl}}$  in  $[(\text{SnX}_2)(\text{ZnCl}_2)L^1]$  compounds were observed in ranges 485-496  $\text{cm}^{-1}$ .<sup>12</sup>

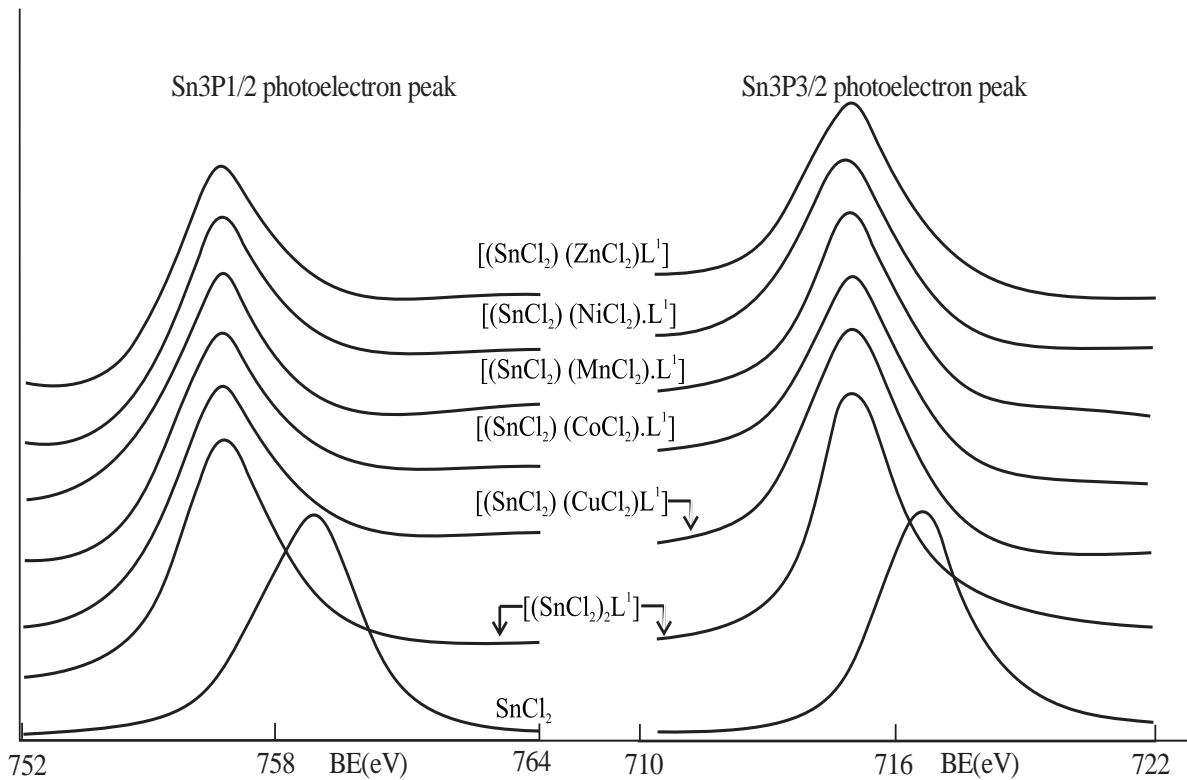
The binding energies (eV) of  $\text{SnX}_2$ ;  $[(\text{SnX}_2)_2.L^1]$ ;  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$  (Where  $\text{M} = \text{Cu(II)}$ ,  $\text{Co(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$ );  $[\text{SnX}_2.L^2]$  and  $[\text{SnX}_2.L^3]$  for Sn  $3p_{1/2, 3/2}$  and N1s photoelectron peaks are listed in table 1-2 (Fig 5). It was observed that the binding energies of Sn  $3p_{1/2, 3/2}$  in starting material  $\text{SnCl}_2$  or  $\text{SnBr}_2$  was higher than their prepared molecular adducts i.e.  $[(\text{SnX}_2)_2.L^1]$ ;  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$ ;  $[\text{SnX}_2.L^2]$  and  $[\text{SnX}_2.L^3]$ . These observations suggested that electron density on the Tin(II) metal ion has increased due to coordination of ligands with Sn(II) metal ion<sup>38</sup>. (Fig 5-7). It was also observed in  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$  compounds that M  $2P_{1/2, 3/2}$  binding energies in starting material ( $\text{MCl}_2$ ) ( $\text{M} = \text{Cu(II)}$ ,  $\text{Co(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$ ); were higher than in prepared  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$  compounds, suggesting that electron density on metal ion in  $\text{MCl}_2$  has increased due to coordination of metal ion<sup>38</sup>. (table1) (Fig.8). Moreover, N1s photoelectron spectra have shown two N1s photoelectron peaks with intensity ratio 4:6 in  $[(\text{SnX}_2)_2.L^1]$ ; 3:7 in  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$ ; 5:3 in  $[\text{SnX}_2.L^2]$  and 3:3 in  $[\text{SnX}_2.L^3]$  at 399.6 eV and at 403.2 eV suggested in  $[(\text{SnX}_2)_2.L^1]$  four nitrogen atoms are uncoordinated and six are coordinated; in  $[(\text{SnX}_2)(\text{MCl}_2)L^1]$  three nitrogen are uncoordinated and seven are coordinated; in  $[\text{SnX}_2.L^2]$  five nitrogen atoms are uncoordinated and three nitrogen atoms are coordinated and in  $[\text{SnX}_2.L^3]$  three nitrogen are uncoordinated and three coordinated<sup>13</sup>. (Fig 9) (Table 2).

**Table 1:** Sn  $3p_{1/2, 3/2}$  and M  $2p_{1/2, 3/2}$  binding energies (eV) in  $[\text{SnX}_2]$  (X= Cl, Br),  $[(\text{SnX}_2)_2.L^1]$ ,  $[(\text{SnX}_2).L^2]$  and  $[(\text{SnX}_2).L^3]$  compounds

Sr. No.	Compounds	Sn $3p_{1/2, 3/2}$		M=	
		Sn $3p_{1/2}$	Sn $3p_{3/2}$	M $2p_{1/2}$	M $2p_{3/2}$
1.	SnCl <sub>2</sub>	758.8	716.8	-	-
2.	SnBr <sub>2</sub>	758.6	716.6	-	-
3.	$[(\text{SnCl}_2)_2.L^1]$	756.8	714.8	-	-
4.	$[(\text{SnBr}_2)_2.L^1]$	756.6	714.6	-	-
5.	CuCl <sub>2</sub>	-	-	952.8	932.8
6.	$[(\text{SnCl}_2)(\text{CuCl}_2).L^1]$	756.8	714.8	951.8	931.8
7.	$[(\text{SnBr}_2)(\text{CuCl}_2).L^1]$	756.6	714.6	951.8	931.8
8.	CoCl <sub>2</sub>	-	-	795.8	781.8
9.	$[(\text{SnCl}_2)(\text{CoCl}_2).L^1]$	756.8	714.8	794.8	780.8
10.	$[(\text{SnBr}_2)(\text{CoCl}_2).L^1]$	756.6	714.6	794.6	780.6
11.	MnCl <sub>2</sub>	-	-	653.8	642.8
12.	$[(\text{SnCl}_2)(\text{MnCl}_2).L^1]$	756.8	714.8	652.8	641.8
13.	$[(\text{SnBr}_2)(\text{MnCl}_2).L^1]$	556.6	714.6	652.6	641.6
14.	NiCl <sub>2</sub>	-	-	873.8	856.8
15.	$[(\text{SnCl}_2)(\text{NiCl}_2).L^1]$	756.8	714.8	872.8	855.8
16.	$[(\text{SnBr}_2)(\text{NiCl}_2).L^1]$	756.6	714.6	872.6	855.6
17.	ZnCl <sub>2</sub>	-	-	1045.8	1022.8
18.	$[(\text{SnCl}_2)(\text{ZnCl}_2).L^1]$	756.8	714.8	1044.8	1021.8
19.	$[(\text{SnBr}_2)(\text{ZnCl}_2).L^1]$	756.6	714.6	1044.6	1021.6
20.	SnCl <sub>2</sub> .L <sup>2</sup>	756.8	714.8	-	-
21.	SnBr <sub>2</sub> .L <sup>2</sup>	756.6	714.6	-	-
22.	SnCl <sub>2</sub> .L <sup>3</sup>	756.8	714.8	-	-
23.	SnBr <sub>2</sub> .L <sup>3</sup>	756.6	714.6	-	-

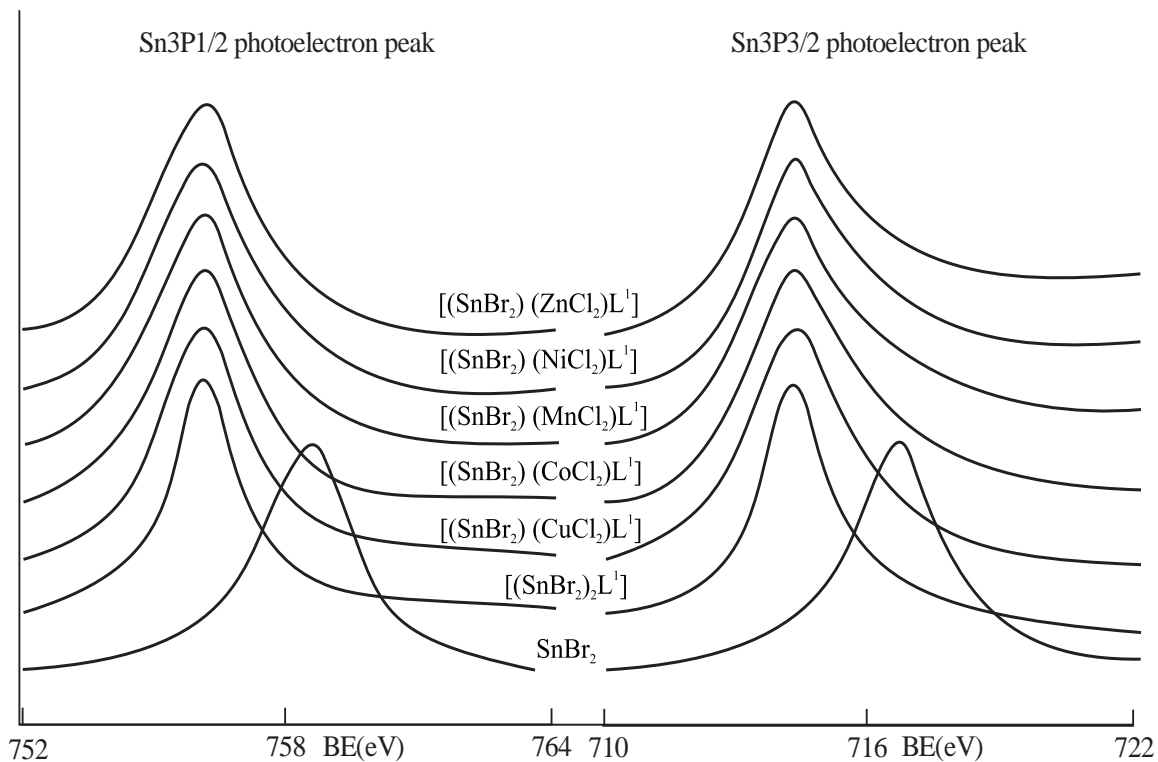
**Table 2** : N 1s binding energies (eV) in [(SnX<sub>2</sub>)<sub>2</sub>.L<sup>1</sup>], [(SnCl<sub>2</sub>)(MCl<sub>2</sub>).L<sup>1</sup>], [(SnX<sub>2</sub>) L<sup>2</sup>] and [(SnX<sub>2</sub>) L<sup>3</sup>] compounds.

Sr. No.	Compounds	N1s(399 eV)	
		Uncoordinated	Coordinated
1.	[(SnCl <sub>2</sub> ) <sub>2</sub> .L <sup>1</sup> ]	399.6	403.2
2.	[(SnCl <sub>2</sub> )(CuCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
3.	[(SnCl <sub>2</sub> )(CoCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
4.	[(SnCl <sub>2</sub> )(MnCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
5.	[(SnCl <sub>2</sub> )(NiCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
6.	[(SnCl <sub>2</sub> )(ZnCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
7.	[(SnBr <sub>2</sub> ) <sub>2</sub> .L <sup>1</sup> ]	399.6	403.2
8.	[(SnBr <sub>2</sub> )(CuCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
9.	[(SnBr <sub>2</sub> )(CoCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
10.	[(SnBr <sub>2</sub> )(MnCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
11.	[(SnBr <sub>2</sub> )(NiCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
12.	[(SnBr <sub>2</sub> )(ZnCl <sub>2</sub> ).L <sup>1</sup> ]	399.6	403.2
13.	[(SnCl <sub>2</sub> ).L <sup>2</sup> ]	399.6	403.4
14.	[(SnBr <sub>2</sub> ).L <sup>2</sup> ]	399.6	403.4
15.	[(SnCl <sub>2</sub> ).L <sup>3</sup> ]	399.6	403.4
16.	[(SnBr <sub>2</sub> ).L <sup>3</sup> ]	399.6	403.4



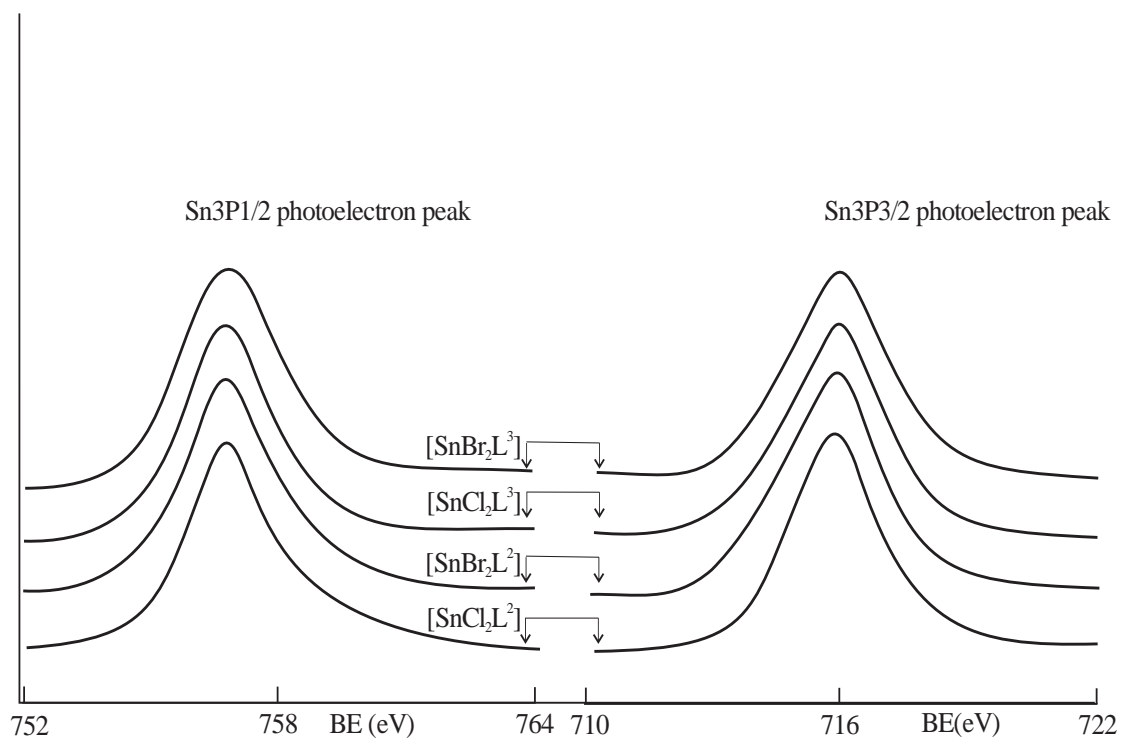
**Figure 5a :** Sn3P<sub>1/2</sub> binding energies (eV) in SnCl<sub>2</sub>, [(SnCl<sub>2</sub>)<sub>2</sub> L<sup>1</sup>] & [(SnCl<sub>2</sub>)(MCl<sub>2</sub>)L<sup>1</sup>]

**Figure 5b :** Sn3P<sub>3/2</sub> binding energies (eV) in SnCl<sub>2</sub>, [(SnCl<sub>2</sub>)<sub>2</sub> L<sup>1</sup>] & [(SnCl<sub>2</sub>)(MCl<sub>2</sub>)L<sup>1</sup>]



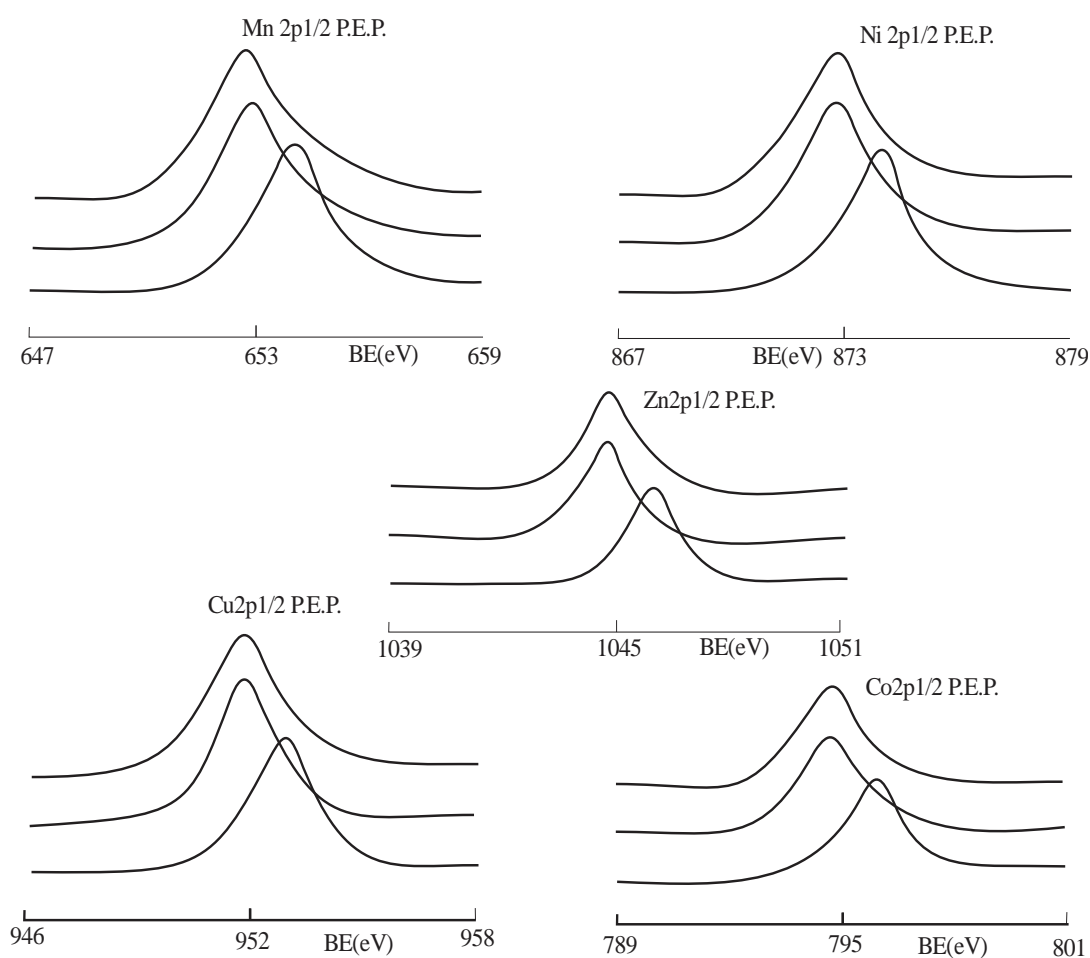
**Figure 6a:** Sn3P<sub>1/2</sub> binding energies (eV) in SnBr<sub>2</sub>, [(SnBr<sub>2</sub>)<sub>2</sub> L<sup>1</sup>] & [(SnBr<sub>2</sub>)(MCl<sub>2</sub>)L<sup>1</sup>]

**Figure 6b:** Sn3P<sub>3/2</sub> binding energies (eV) in SnBr<sub>2</sub>, [(SnBr<sub>2</sub>)<sub>2</sub> L<sup>1</sup>] & [(SnBr<sub>2</sub>)(MCl<sub>2</sub>)L<sup>1</sup>]



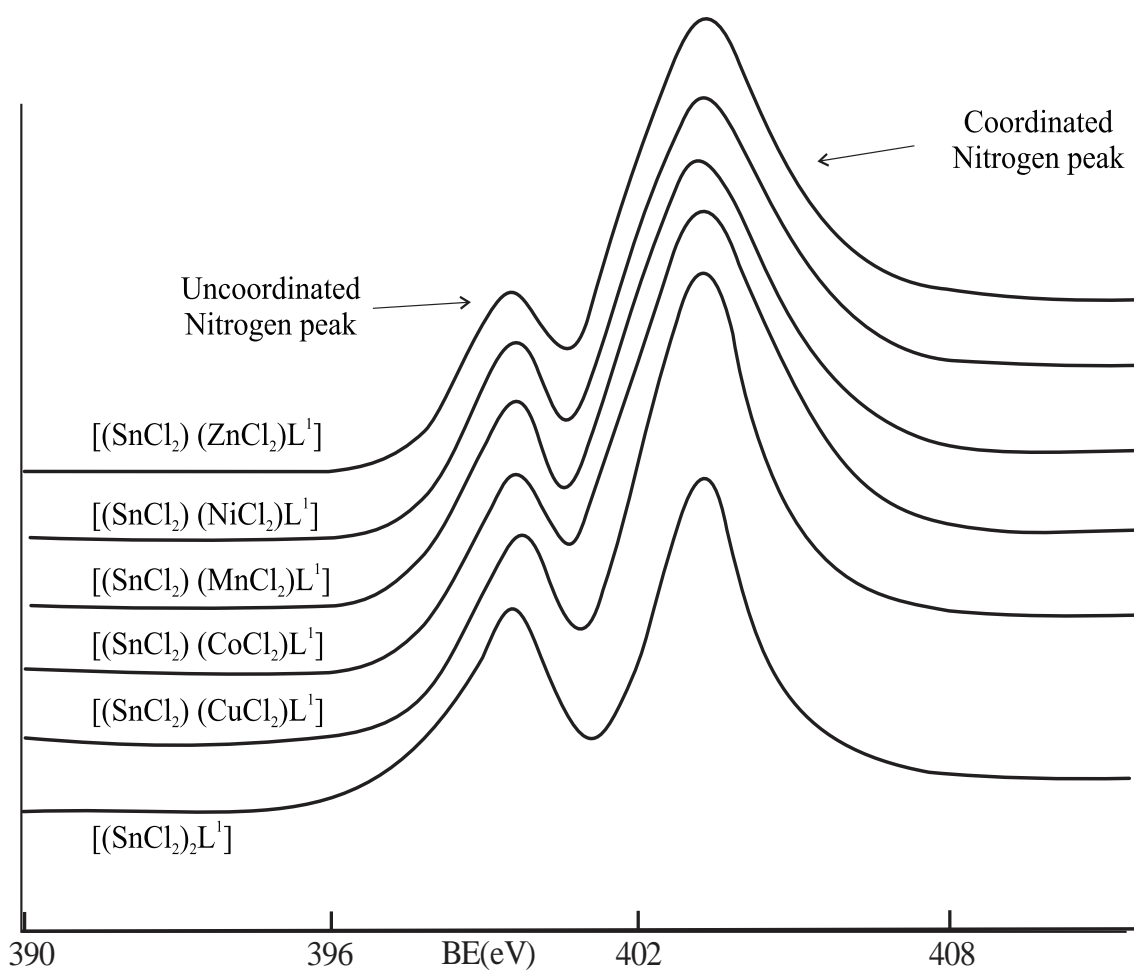
**Figure 7a:** Sn3P<sub>1/2</sub> binding energies (eV) in [SnX<sub>2</sub>L<sup>2</sup>] & [SnX<sub>2</sub>L<sup>3</sup>]

**Figure 7b:** Sn3P<sub>3/2</sub> binding energies (eV) in [SnX<sub>2</sub>L<sup>2</sup>] & [SnX<sub>2</sub>L<sup>3</sup>]

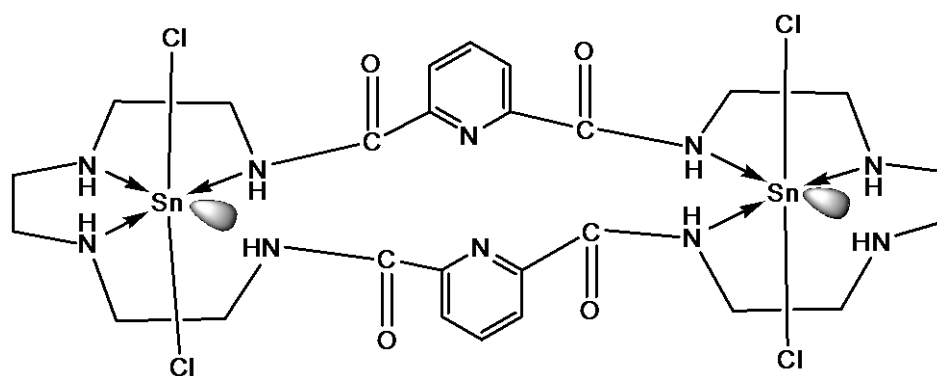


**Figure 8:** M2P<sub>1/2</sub> binding energies (eV) in [(SnX<sub>2</sub>)(MCl<sub>2</sub>)L<sup>1</sup>] Compounds

N1s photoelectron peak

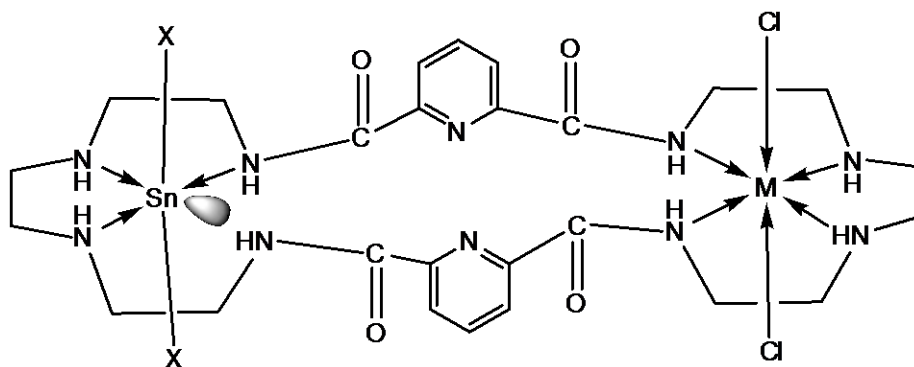


**Figure 9:** N1s binding energies (eV) in  $[(\text{SnCl}_2)_2\text{L}^1]$  and  $[(\text{SnCl}_2)(\text{MCl}_2)\text{L}^1]$  compounds

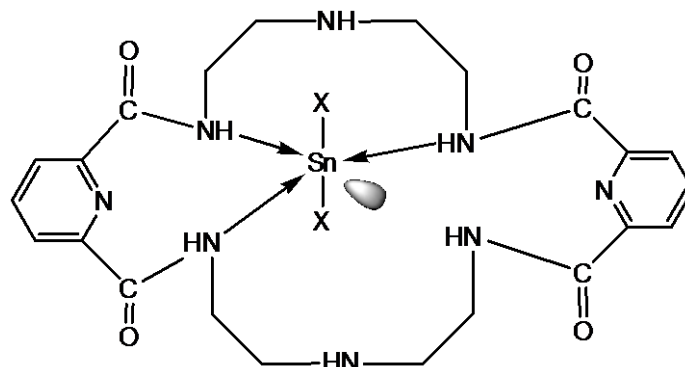


**Figure 10 :**  $[(\text{SnCl}_2)_2\text{L}^1]$

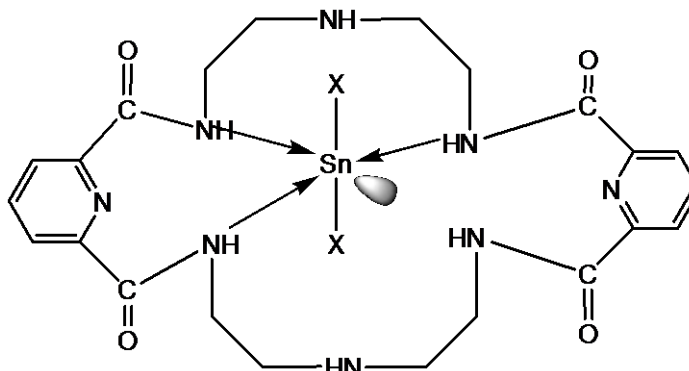




**Figure 11 :**  $[(\text{SnX}_2)(\text{MCl}_2)\cdot\text{L}^1]$  [Where  $\text{M}=\text{Cu}(\text{II}), \text{Co}(\text{II}), (\text{Mn}(\text{II}), \text{Ni}(\text{II})$  and  $\text{Zn}(\text{II})$ ] [Where  $\text{X}=\text{Cl}$  or  $\text{Br}$ ]



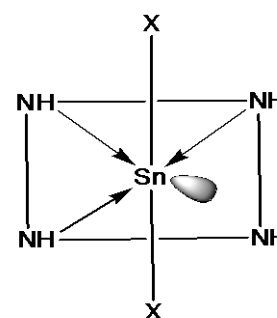
**Figure 12 :**  $[\text{SnX}_2\cdot\text{L}^2]$  [Where  $\text{X}=\text{Cl}$  or  $\text{Br}$ ]



**Figure 13 :**  $[\text{SnX}_2\cdot\text{L}^3]$  [Where  $\text{X}=\text{Cl}$  or  $\text{Br}$ ]

#### IV. CONCLUSION

On the basis of elemental analysis, molar conductivity data showing that all these molecular adducts are nonionic and IR and X-ray Photoelectron spectra (XPS) results, showing the site of coordination, it is possible to assign a structure for each adduct as shown in fig 10-13. With octahedral geometry hybridization as shown below (Fig 14 a,b,and c).



**Figure 14(a) :** Geometry of  $[(\text{SnX}_2)_2\cdot\text{L}^1]$

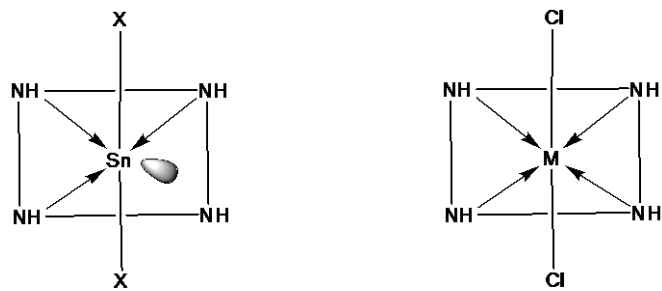


Figure 14(b): Geometry of  $[(\text{SnX}_2)(\text{MCl}_2)\cdot\text{L}^1]$

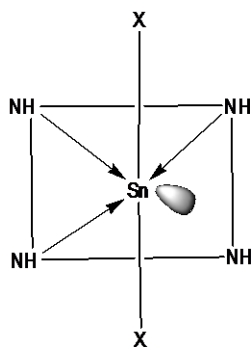


Figure 14(c): Geometry of  $[\text{SnX}_2\cdot\text{L}^2]$  or  $[\text{SnX}_2\cdot\text{L}^3]$

## V. ACKNOWLEDGEMENT

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