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Synthesis and characterisation of $[SnX_2.L^{1-10}]$ complexes with some new macrocylic ligands

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Abstract: Thirty complexes of the type $[SnX_2.L^{1\ 10}]$ (where X = Cl or Br or CH_3COO and $L^{1\ 10}$ = macrocyclic ligands) have been synthsised and characterized by elemental analysis, molar conductance, IR and XPs data. A distorted octahedral geometry was also established.

In the continuation of synthesis of $[SnX_2.L^{1\ 10}]$ complexes (Where X = Cl or Br or CH_3COO and $L^{1\ 10}$ = macrocyclic ligands derived from condensation of trimestic acid i.e. Benzene 1,3,5–tricaboxylic acid and various diamines) [1]; in this research paper synthesis and characterisation of $[SnX_2.L^{1\ 10}]$ molecular adducts (where X = Cl or Br or CH_3COO and $L^{1\ 10}$ = macrocyclic Saciff base ligands) L^1 to L^{10} derived from condensation of p–thathalic acid i.e. terephthalic acid with different diamines i.e. in L^1= NH_2CH_2 $CH_2CH_2NH_2$; in L^2=$NH_2CH_2CH(CH_3)$ CH_2NH_2; in L^3=$NH_2CH_2NH(CH_2)_2NH_2$; in L^4 =NH_2 CH_2C $(CH_3)_2$ CH_2NH_2; in L^5=$NH_2(CH_2)_6NH_2$; in L^6=NH_2 $(CH_2)_7NH_2$; in L^7=$NH_2(CH_2)_8NH_2$; in L^8=NH_2 $(CH_2)_9$ NH_2; in L^9=$NH_2(CH_2)_{10}NH_2$; and L^{10}=NH_2 $(CH_2)_{12}$ NH_2; will be perform and their structure and geometry will be propose on basis of physicochemical methods.

(Keywords : Elemental analysis, molar conductivity, macrocyclic schiff base ligand, molar conductivity, X-ray and IR photoelectron spectra.)

Introduction

Tin is mentioned as a metal of value under the name bedill. The ancient Indian author Veda refers to tin as trapu. **T**in copper alloy bronze has been used from ancient times. Tin is found in nature as cassiterite or tin stone. True bronze are copper based tin alloys with a good combination of chemical resistance, mechanical strength and ease of manufacture.

Some Tin(II) and Tin(IV) Macrocyclic Schiff base complexes have been synthesised and characterised which are prepared by the reaction of Tindichloride, Tintetrachloride, and Tin methyltin dichloride with 1,3-diaminopropane and benzyl or m-phenylenediamine and acetylacetone in oxygen-free nitrogen atmosphere using THF as the reaction medium.

In the synthesis of $[SnX_2.L^{1-10}]$ (where X = Cl or Br Or CH_3COO and L^{1-10} = macrocyclic Schiff base ligands derived from condensation of trimastic acid lie benzene, 3,5–tricarboxylic acid and various diamines) the synthesis and characterisation of molecular adducts (where X = Cl or Br or and L macrocyclic Sciff base ligands derived from condensation of p–thathalic acid Lie terephthalic acid with different diamines lie in In , in in , in in in in in and in] will be performed and their structure and geometry will be proposed on the basis of physicochemical methods.

Experimental

Material and Method

Melting points were determined on melting point apparatus. The C, H, N and Cl or Br were carried out by CDRI, Lucknow, INDIA. Molar conductance was measured on Conductivity Bridge in acetone at room temperature. Infra-red spectra were recorded on Perkin – Elmer Infra-red spectrometer using CsI pellets. X-ray

photoelectron spectra were recorded on VG Scientific ESCA-II spectrometer using MgKα as X-ray source. p-thathalic acid i.e. terephthalic acid (2 m mol) in 50 ml dry methanol mixed with different diamines (2 m mol) i.e. $NH_2CH_2CH_2CH_2NH_2$ or $NH_2CH_2CH(CH_3)CH_2NH_2$ or $NH_2CH_2NH(CH_2)_2NH_2$ or $NH_2CH_2C(CH_3)_2CH_2NH_2$ or $NH_2(CH_2)_6NH_2$ or $NH_2(CH_2)_7NH_2$ or $NH_2(CH_2)_8NH_2$ or $NH_2(CH_2)_9NH_2$ or $NH_2(CH_2)_{10}NH_2$ or $NH_2(CH_2)_{12}NH_2$ in a refluxing flask and refluxed for three hours and then added SnX_2 (1 m mol) (Where X = Cl or Br or CH_3COO) solution in 50 ml methanol into above refluxing flask and refluxed another three hours. The precipitate was obtained, filtered and recrystallised by benzene: pet ether 9:1 and air-dried. (Fig1).

Result and Discussion:

By the refluxing of p–thathalic acid with different diamines i.e. or $NH_2CH_2CH_2CH_2NH_2$ or $NH_2CH_2CH(CH_3)CH_2NH_2$ or $NH_2CH_2NH(CH_2)_2NH_2$ or $NH_2CH_2C(CH_3)_2CH_2NH_2$ or $NH_2(CH_2)_6NH_2$ or $NH_2(CH_2)_7NH_2$ or $NH_2(CH_2)_8NH_2$ or $NH_2(CH_2)_9NH_2$ or $NH_2(CH_2)_{10}NH_2$ or $NH_2(CH_2)_{12}NH_2$ in 2:2 molar ratio, provided ten macrocyclic Schiff base ligands i.e. L^1 or L^2 or L^3 or L^4 or L^5 or L^6 or L^7 or L^8 or L^9 or L^{10} (Fig1). When SnX_2 (1m mol) (Where X = Cl or Br or CH_3COO) was added in each prepared ligand and again refluxed, a precipitate was obtained called molecular adduct.

Molecular adducts $[SnX_2.L^{1\,10}]$ where yellow solid and stable. The elemental analysis for C, H, N and Cl was observed within $\pm 0.5\%$ .The molar conductance of each molecular adducts were observed below 30$ohm^{-1}cm^2mol^{-1}$ in acetone at room temperature, suggesting non-ionic[2]. Fundamental frequency of IR for νSn-Cl and νSn-N in these molecular adducts were in the range 485-496cm^{-1} and 436-480 respectively[3-4].

The Sn 3p1/2,3/2 and N1s photoelectron peaks binding energies (eV) for ligands, SnX_2 and $[SnX_2.L^{1\,10}]$ molecular adducts are listed in Table I. During the comparative observation of Sn 3p1/2,3/2 photoelectron peaks binding energies (eV) in SnX_2 and $[SnX_2.L^{1\,10}]$ it was found that 3p1/2,3/2 photoelectron peaks binding energies (eV) are more in SnX_2 than $[SnX_2.L^{1\,10}]$ from these observation one can conclude that electron density is increased on Tin (II) metal ion in $[SnX_2.L^{1\,10}]$ than SnX_2 due to coordination of ligand [5] (Fig2) (Table I).

Furthermore, comparative observation of N1s photoelectron peaks binding energies (eV) in each ligand with their each $[SnX_2.L^{1\,10}]$ molecular adducts have shown two N1s photoelectron peaks in $[SnX_2.L^{1\,10}]$ 1:3 Intensity ratio, one N^1s photoelectron peak with high intensity was observed at higher binding energy side than N^1s photoelectron peak of each ligand; while one N^1s photoelectron peak with low intensity was observed at the same position as in the ligand N^1s Photoelectron peak. One can conclude from these XPS N1s data that out of four nitrogen atoms in $[SnX_2.L^{1\,10}]$, these are coordinated with Tin (II) metal ion while one nitrogen atom is uncoordinated [5] (Table I & fig3). Furthermore, Sn 3s photoelectron peak of all each molecular adduct have shown a single symmetrical peak suggesting diamagnetic nature of all each $[SnX_2.L^{1\,10}]$ [5].

Conclusion

On the basis of elemental analysis, molar conductance, IR and XPS data, the structure of $[SnX_2.L^{1\,10}]$ may be proposed as given in Fig 1 and a distorted octahedral geometry may be proposed.

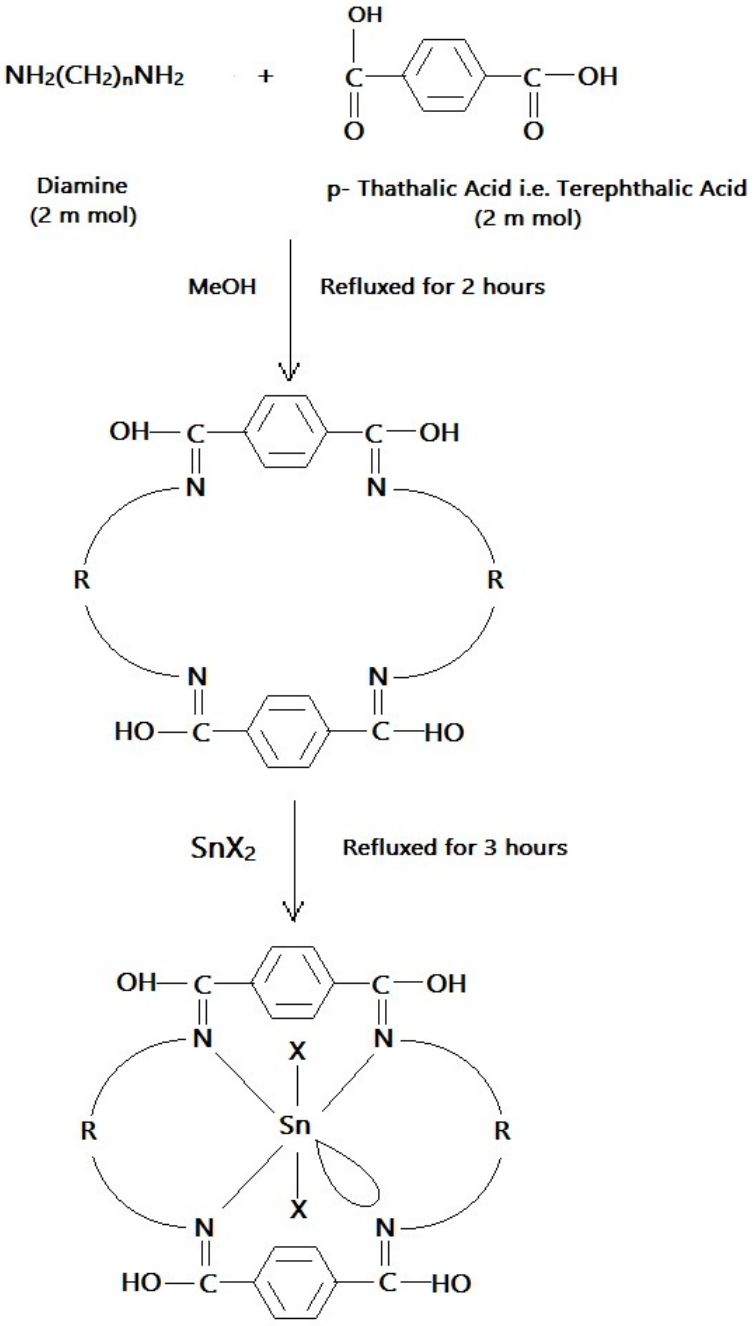

Fig 1: Preparation of [$SnX_2.L$] where X= Cl or Br or CH_3COO and R= $-CH_2CH_2CH_2-$; $-CH_2CH(CH_3)CH_2-$; $-CH_2NH(CH_2)_2-$; $-CH_2C(CH_3)_2CH_2-$; $-(CH_2)_6-$; $-(CH_2)_7-$; $-(CH_2)_8-$; $-(CH_2)_9-$; $-(CH_2)_{10}-$; and $-(CH_2)_{12}-$

Table I: $Sn3p_{1/2,3/2}$ and N1s binding energies (eV) in ligand, SnX_2 and $[SnX_2.L]$ complexes

S.No.	Ligand andCompound	$Sn3p_{1/2,3/2}$		N1s	
		$Sn3p_{1/2}$	$Sn3p_{3/2}$	uncoord	coord
01.	L1	-	-	400.0	-
02.	L2	-	-	400.0	-
03.	L3	-	-	400.0	-
04.	L4	-	-	400.0	-
05.	L5	-	-	400.0	-
06.	L6	-	-	400.0	-
07.	L7	-	-	400.0	-
08.	L8	-	-	400.0	-
09.	L9	-	-	400.0	-
10.	L10	-	-	400.0	-
11.	$SnCl_2$	758.8	516.8	-	-
12.	$[SnCl_2.L^1]$	757.4	515.4	400.0	404.4
13.	$[SnCl_2.L^2]$	757.4	515.4	400.0	404.4
14.	$[SnCl_2.L^3]$	757.4	515.4	400.0	404.4
15.	$[SnCl_2.L^4]$	757.4	515.4	400.0	404.4
16.	$[SnCl_2.L^5]$	757.4	515.4	400.0	404.4
17.	$[SnCl_2.L^6]$	757.4	515.4	400.0	404.4
18.	$[SnCl_2.L^7]$	757.4	515.4	400.0	404.4
19.	$[SnCl_2.L^8]$	757.4	515.4	400.0	404.4
20.	$[SnCl_2.L^9]$	757.4	515.4	400.0	404.4
21.	$[SnCl_2.L^{10}]$	757.4	515.4	400.0	404.4
22.	$SnBr_2$	758.6	516.6	-	-
23.	$[SnBr_2.L^1]$	757.2	515.2	400.0	404.2
24.	$[SnBr_2.L^2]$	757.2	515.2	400.0	404.2
25.	$[SnBr_2.L^3]$	757.2	515.2	400.0	404.2
26.	$[SnBr_2.L^4]$	757.2	515.2	400.0	404.2
27.	$[SnBr_2.L^5]$	757.2	515.2	400.0	404.2
28.	$[SnBr_2.L^6]$	757.2	515.2	400.0	404.2
29.	$[SnBr_2.L^7]$	757.2	515.2	400.0	404.2
30.	$[SnBr_2.L^8]$	757.2	515.2	400.0	404.2
31.	$[SnBr_2.L^9]$	757.2	515.2	400.0	404.2
32.	$[SnBr_2.L^{10}]$	757.2	515.2	400.0	404.2
33.	$Sn(CH_3COO)_2$	758.2	516.2	-	-
34.	$[Sn(CH_3COO)_2.L^1]$	757.0	515.0	400.0	403.8
35.	$[Sn(CH_3COO)_2.L^2]$	757.0	515.0	400.0	403.8
36.	$[Sn(CH_3COO)_2.L^3]$	757.0	515.0	400.0	403.8
37.	$[Sn(CH_3COO)_2.L^4]$	757.0	515.0	400.0	403.8
38.	$[Sn(CH_3COO)_2.L^5]$	757.0	515.0	400.0	403.8
39.	$[Sn(CH_3COO)_2.L^6]$	757.0	515.0	400.0	403.8
40.	$[Sn(CH_3COO)_2.L^7]$	757.0	515.0	400.0	403.8
41.	$[Sn(CH_3COO)_2.L^8]$	757.0	515.0	400.0	403.8
42.	$[Sn(CH_3COO)_2.L^9]$	757.0	515.0	400.0	403.8
43.	$[Sn(CH_3COO)_2.L^{10}]$	757.0	515.0	400.0	403.8

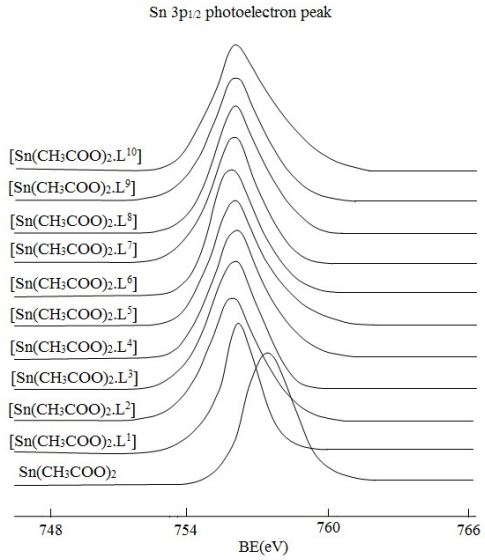

Fig2: Sn $3p_{1/2}$ binding energies (eV) in $Sn(CH_3COO)_2$ & [$Sn(CH_3COO)_2.L^{1-10}$] complexes

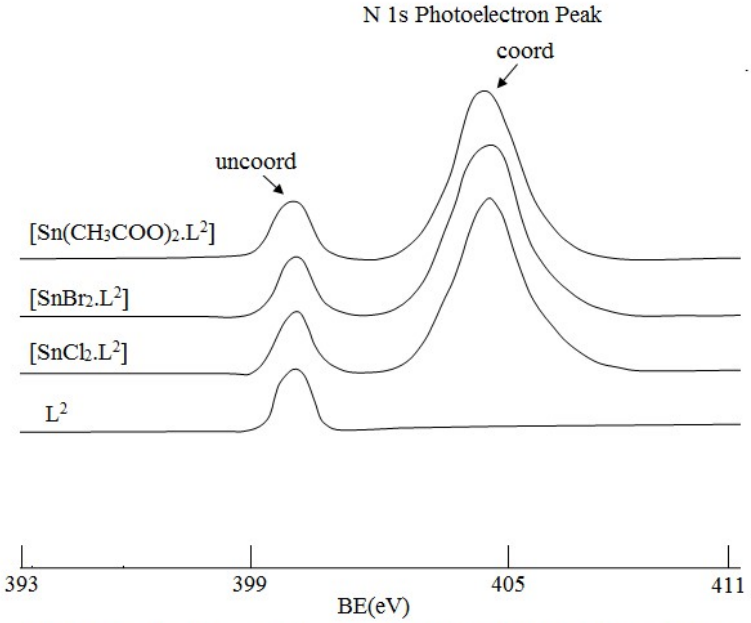

Fig3: N1s binding energies (eV) in L^2 and [$SnX_2.L^2$] complexes

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