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TIN- AND ORGANOTIN (IV) COMPLEXES OF THYMOL DERIVATIVE DERIVED FROM ALANINE: SYNTHESIS AND CHARACTERISTIC SPECTRAL STUDIES

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ABSTRACT

A new series of tin- and organotin(IV) complexes of general formula $Sn(OPr^i)_2$(hbal) (1), $Sn(OPr^i)_2$(Hhbal)$_2$ (2), Bu_3Sn(Hhbal) (3), Ph_3Sn(Hhbal) (4), $(Ph_3Sn)_2$(hbal) (5) were synthesized by the reacting of tin- and triorganotin(IV) chloride with the ligand, with the aid of sodium iso-propoxide in appropriate stiochiometric ratios (1:1, 1:2 and 2:1). These complexes were characterized by elemental analysis, IR, ^{1}H nuclear magnetic resonance. On the basis of spectral evidence it has been found, the complex 1, 3, 4 and 5 incorporated with a pentacoordinated derivative and carboxylate oxygen atom coordinated to tin in bidentate manner.

Keywords: organotin complexes, alanine derivative, spectroscopic studies

INTRODUCTION

Organotin (IV) compounds are well known by their application in the chemical industry, agriculture and other field of human activities[1-3]. It has been found that the biological activities of organotin (IV) derivatives are believed to be greatly dependent on the coordination mode between tin metal and the ligand[4-20]. Organotin (IV) complexes with amino acid derivative containing the Sn-O, Sn-N and Sn-C linkage display significant and important biological activity. Therefore we report herein the synthesis and characterization of tin- and organotin(IV) complexes with amino acid derivative and illustrated their geometrical structure by using spectral analysis. The studies are likely to be a meaningful addition in the area of work now being pursued on the reactivity of tin and organotin alkoxide.

EXPERIMENTAL

All the reagents, viz., tin (Merck), Bu_3SnCl (Merck), Ph_3SnCl (Merck), thymol (Merck), alanine (Merck) wera used as received. All the chemicals and solvents used were dried and purified by standard methods, and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes.

Synthesis of ligand (H_2hbal)

The ligand of amino acid derivative was prepared adopting procedure almost identical to those described by Mehrotra et al.[21].An equimolar mixture of thymol (11.86 gm, .05 mole), alanine (3.75 gm, .05 mole), sodium acetate crystals (6.8 gm, .05 mole) were dissolved in glacial acetic acid (25 ml). Formaline solution (4.05 ml) was added to it drop wise with stirring and the contents were heated at 60-80^{0}C, till a viscous mass was obtained. The viscous mass was then poured drop wise with brisk stirring in excess of water. The crude product thus obtained was purified by dissolving it in a requisite quantity of sodium hydroxide solution followed by its reprecipitation by 50% hydrochloric acid. It is further purified by recrystalisation from alcohol.

Synthesis of tin complexes

In the first step $SnCl_4$ was prepared by the action of chlorine gas on pure tin metal in a specially designed apparatus (bubbler). A pale yellow liquid of $SnCl_4$ thus obtained was purified by distillation. A solution of tin(IV) tetrachloride (2.471 gm, 0.0095 mole) in benzene (10 ml) was treated with sodium isopropoxide (3.116 gm, 0.038 mole) to produce tin(IV) tetraisopropoxide and sodium chloride.

The sodium chloride precipitate was removed by filtration and the solvent was removed by distillation. The solution of tin(IV) tetraisopropoxide and ligand was refluxed in benzene, in appropriate stoichiometric ratios, for 8-10 h (Scheme I). These reactions proceed with the liberation of isopropanol, which is removed azeotropically with benzene. Evaporation of the solvent gave yellow brown solid, which was purified by recrystallisation from alcohol at room temperature to furnish yellow brown crystals and dried under vacuum.

Synthesis of organotin complexes

A solution of triorganotin(IV) chloride (0.0095 mole) in benzene (10 ml) was treated with sodium isopropoxide to produce triorganotin(IV) isopropoxide and sodium chloride. The sodium chloride precipitate was removed by filtration and the solvent was removed by distillation. The solution of triorganotin(IV) isopropoxide and ligand was refluxed in benzene, in appropriate stoichiometric ratios, for 8-10 h (Scheme-1). These reactions proceed with the liberation of isopropanol, which is removed azeotropically with benzene. The complexes was purified by recrystallisation from alcohol at room temperature and dried under vacuum.

Physical measurements

The melting points were determined in open capillaries with electronic melting point apparatus and were uncorrected. C, H and N analysis of these compounds were carried on a VarioEL, CHNS elemental analyzer. The tin content in the synthesized compounds was determined gravimetrically as SnO_2. Infrared spectra of the solid compounds were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer in the range 4000-400 cm^- from KBr discs. ^1H NMR spectra were recorded on a Bruker DRX 300 (300 MHz FT NMR) spectrometer at the central drug research institute, Lucknow, India, using DMSO or MeOD as a solvent and TMS as the internal standard.

$$SnCl_4 + 4NaOPr^i \xrightarrow[\text{reflux}]{\text{Benzene/isopropanol}} Sn(OPr^i)_4 + 4NaCl$$

$$Sn(OPr^i)_4 + H_2hbal \xrightarrow[\text{Benzene}]{\text{1:1/1:2 ratios}} (OPr^i)_2Sn(hbal)/\ (OPr^i)_2Sn(Hhbal)_2 + 2(CH_3)_2CHOH$$

$$R_3SnCl + NaOPri \longrightarrow R_3Sn(OPri) + NaCl$$
(R= Ph, Bu)

$$Bu_3Sn(OPri) + H_2hbal \xrightarrow[\text{Benzene}]{\text{reflux}} Bu_3Sn(Hhbal) + (CH_3)_2CHOH$$

$$Ph_3Sn(OPri) + H_2hbal \xrightarrow[\text{Benzene}]{\text{1:1/1:2 ratios}} Ph_3Sn(Hhbal)/\ (Ph_3Sn)_2(hbal) + n(CH_3)_2CHOH$$

Scheme-1

RESULTS AND DISCUSSION

All the newly synthesized complexes are coloured solids and soluble in common organic solvents. The colour, melting point, elemental analysis of the ligand and their complexes are presented in Table-1.

Infrared Spectra

The characteristic infrared frequencies of the tin (IV) complexes are given in table-2. The infrared data of tin- and organotin complexes are used to predict their solid state structure. The IR spectra of the tin- and organotin derivatives display a vibrational band at 3400 **2**, 3455-3000 **3**, 3438 **4**,[22-23], which are assignable to the unbonded –OH stretching of the phenolic group. The IR stretching frequency of the carboxylate groups are very important for determining their structures *viz*., when there are interaction between the carbonyl oxygen atoms of the carboxylate groups and the tin atom. The magnitude of ν_{as}- ν_s ($\Delta\nu$) separation has been used to explain the type of boding of carboxylate group to the tin metal[24]. The

magnitude of ν_{as}- ν_s ($\Delta\nu$) for **2**, **3**, **4** and **5** are below 200 cm^{-1}, indicating the bridged tin- and organotin carboxylate (fig.1a and 1b). For the complex **1**, $\Delta\nu$ value of ~200 cm^{-1} has been attributed to the bidentate carboxyl group[25]. The presence of ν(Sn–O) in the range of 500-556 cm^{-1} [26-29], indicates deprotonation of the carboxylic acid group and consequent coordination of the carboxylate group with the tin metal. The proposed coordination of the complexes **5** is further supported by the appearance of a band in the region of ~400 cm^{-1} due to the ν(N→Sn)[31].

^{1}H NMR Spectra

Table-3 shows the chemical shifts (δ in ppm) of various protons in ligand and metal complexes. The absence of a signal due to the –OH proton at δ =12.00-13.00 suggests deprotonation of the carboxylic oxygen atom of the ligand on complexation[30]. A signal at δ =7.97 -8.44, indicating the presence of hydrogen bonded phenolic –OH group[32]. In the complexes, the $-NH_2$ resonances is observed either as a broad weak signal at δ =7.76 or in conjugation with phenyl protons[33]. The butyl protons attached to the tin in complex **3**, observed at appropriate position in accordance to the previously reported values[26]. In the complex **4** and **5**, the signals for the phenyl group attached to tin are observed in the range of 7.30- 7.57, in conjugation with phenyl protons of the ligand.

Table-1

S. No.	Ligand/Complex	Colour	m.p. (^{0}C)	Elemental Analysis % Obsd. (Calcd.)			
				C%	H%	N%	Sn%
1	H_2hbal	Dull brown	74^{0}C	66.89(66.85)	8.40(8.36)	5.51(5.57)	.....
2	$Sn(OPr^i)_2$(hbal)	Cream	158^{0}C	49.40(49.37)	6.84(6.79)	2.95(2.98)	24.46(24.41)
3	$Sn(OPr^i)_2(Hhbal)_2$	brown	163^{0}C	55.37(55.33)	7.36(7.32)	3.85(3.90)	16.14(16.09)
4	Bu_3Sn(Hhbal)	Brown	> 300^{0}C	57.86(57.81)	8.75(8.71)	2.56(2.60)	22.02(21.99)
5	Ph_3Sn(Hhbal)	Yellow	> 300^{0}C	64.06(64.03)	5.88(5.84)	2.30(2.34)	19.83(19.79)
6	$(Ph_3Sn)_2$(hbal)	Yellow	> 300^{0}C	63.22(63.27)	5.19(5.16)	1.42(1.47)	25.08(25.03)

Table-2

S.No.	Ligand/Complex	*v*(OH)	*vas*(OCO)	*vs*(OCO)	Δ *v*	*v*(Sn-O)	*v*(Sn-C)
1	H_2hbal	3395 br	1590	1422			
2	$Sn(OPr^i)_2$(hbal)	……	1616	1414	202		
3	$Sn(OPr^i)_2(Hhbal)_2$	3400	1617 s*	1419 m	198	500 m	
4	Bu_3Sn(Hhbal)	3455-3000 br*	1600 s br*	1418	182	510 m	530
5	Ph_3Sn(Hhbal)	3438	1612 s*	1422 m	190	556 m	205 s
6	$(Ph_3Sn)_2$(hbal)	…..	1610	1418	192	556 m	

Table-3

S. No.	Ligand/Complex	Phenolic -OH	Isopropyl Substituent protons	Aromatic proton	Sn-C_4H_9/ Sn-CH_3/ Sn-C_6H_5
1	H_2hbal	8.30 (s,1H)	1.02-1.13 (dd, 6H)	6.35-6.84 (dd,2H)	
2	$Sn(OPr^i)_2$(hbal)	…..	1.11-1.16 (dd, 6H)	6.65-6.68 (d, 1H) 7.01-7.03 (d, 1H)	
3	$Sn(OPr^i)_2(Hhbal)_2$	7.99 (s,1H) 8.44 (s, 1H)	1.09-1.19(m, 12H)	6.45-6.87 (m, 4H)	
4	Bu_3Sn(Hhbal)	8.05 (s, 1H)		6.54-6.58 (d, 1H) 6.89-6.91(d, 1H)	0.65 and 1.32-0.82 (t, m)
5	Ph_3Sn(Hhbal)	7.97 (s, 1H)		7.30-7.56(m, 4H)	7.30-7.56 (m)
6	$(Ph_3Sn)_2$(hbal)			7.32-7.57 (m, 4H)	7.32-7.57 (m)

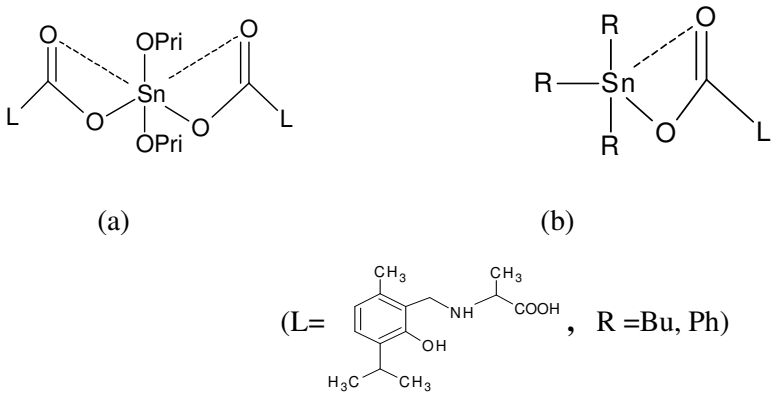

Fig.-1: Proposed structure of tin- and triorganotin complexes

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