

SOME TRIBENZYL TIN(IV) COMPLEXES WITH THIOHYDRAZIDES AND THIODIAMINES

Synthesis, characterization and thermal studies

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Abstract

Tribenzyl tin(IV) chloride complexes of morpholine N-thiohydrazide (L^1), aniline-N-thiohydrazide (L^2), N-(morpholine-N-thio)-1,3-propanediamine (L^3) and (aniline-N-thio)-1,3-propanediamine (L^4) of the type $(C_6H_5CH_2)_3Sn(L)Cl$ (where $L=L^1, L^2, L^3$ and L^4) have been synthesised in dioxane and in H_2O and acetone mixture. These were characterized by C,H,N-analysis, UV, IR and 1H NMR spectral studies. In both the complexes ligands act as bidentate, coordinating through sulphur and terminal nitrogen. The complexes are 1:1 metal ligand complexes. Various thermodynamic parameters have been calculated for the decomposition steps using TG/DTA curves in air as well as nitrogen atmosphere.

Keywords: synthesis, thermodynamic parameters, TG/DTA, tribenzyl tin(IV) complexes with thiohydrazides and thiodiamines

Introduction

The thiohydrazides are the hydrazine derivatives of dithioacids (RCS_2H^+) and thiodiamines are the diamine derivatives of dithioacids (RCS_2H^+). Many workers [1–7] prepared and characterised the thiohydrazides with different metals. The interest in organotin thiohydrazides has been stimulated as a result of their diversified applications. Thiohydrazides being derivatives of hydrazine must be tested for their performance as military/commercial explosives and solid rocket propellants. Performance as related to end use and safety, is determined by a number of factors mainly thermal stability, shock, friction and impact sensitivity, explosive power and detonation velocity [8, 9]. Organotin compounds find use in a wide range of products such as stabilizers for PVC [10–12], fungicides [10–14], agrochemicals [15–17], antifouling [18–20] paints, etc. because of their low toxicity and favourable environmental degradation [21] to nontoxic inorganic in residues.

Experimental

All the reagents used were of AR grade. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer and far IR recorded on Perkin Elmer FTIR 1710. The ^1H NMR spectra were recorded on Hitachi-R600, FT-NMR in d_6 -DMSO. The UV spectra were recorded on a Beckman DU-64 spectrophotometer. TG-DTA were simultaneously recorded on a Rigaku-model 8150 Thermaflex in static air at a heating rate of $10^\circ\text{C min}^{-1}$. Platinum crucibles were used with alumina as the reference material. Chlorine was determined gravimetrically as silver chloride, sulphur as BaSO_4 [22] and tin as SnO_2 [23].

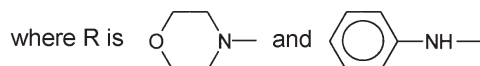
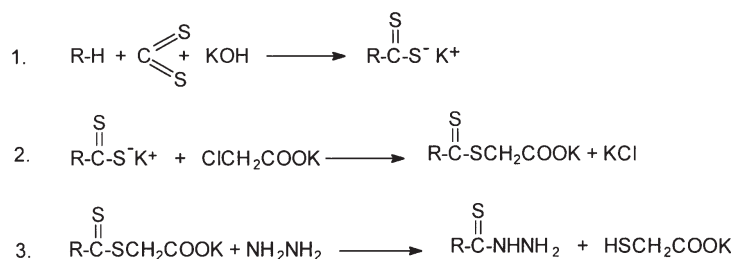
Preparation of tribenzyl tin chloride

$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnCl}$ was synthesised by the method given by Sisido *et al.* [24].

Preparation of ligands

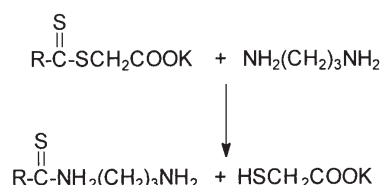
The ligands morpholine N-thiohydrazide and aniline N-thiohydrazide have been synthesized with some modifications in the method described by Kazakova *et al.* [24–27].

Corresponding amine (morpholine/aniline) (0.4 mol) was dissolved in about 140 ml methanol and to it 22.4 g KOH in 2 ml water and 38 ml methanol was added with constant stirring. The solution of 30 ml CS_2 in 40 ml methanol was added to the mixture. Temperature of the reaction mixture was kept below 10°C . A white crystalline precipitate of potassium salt of corresponding amine dithiocarbamate got separated. Its aqueous solution was treated with freshly prepared potassium chloroacetate (0.4 mol). Temperature of the reaction mixture was increased to about 40°C and maintained for about an h. The contents were then left for 24 h at room temperature. Then 25 ml methanolic solution of hydrazine hydrate was added and the reaction mixture heated on a water bath for about 1 h when the desired product separated out. It was cooled in ice for 24 h and filtered. Thiohydrazide so obtained was recrystallized from hot water and dried.



Preparation of *N*-thiodiamines

N-thiodiamines were prepared by the same method as in the case of *N*-thiohydrazide except that instead of adding hydrazine hydrate, 25 ml of 1,3-propanediamine (in 40 ml methanol) was added to the reaction mixture. The contents were then refluxed over water bath for one h and then evaporated to half of its original volume when the desired product began to separate. It was cooled in ice for 24 h and filtered. The desired product thus obtained was recrystallized from hot water and dried in desiccator.



Preparation of the complexes

$[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L})\text{Cl}]$, where $L=L^1, L^2, L^3$ and L^4

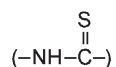
0.1 mol of tribenzyltin chloride was dissolved in 25 ml solvent in a round bottom flask; to it 0.1 mol of ligand in 25 ml solvent was added and stirred over a magnetic stirrer for 4 h. The solution obtained was filtered and the filtrate was reduced to 1/4 of its volume in rotary vacuum evaporator when the complex separated.

1,4-Dioxane was used as solvent for complexation of ligand L^1 and a mixture of water and acetone (1:7, v/v) for other ligands L^2, L^3 and L^4 .

Results and discussions

Elemental analysis vide Table 1 reveals that complexes are of good purity. All complexes are light yellow in colour. These are soluble in DMSO and acetone. From the analytical data, it is clear that tribenzyltin(IV) chloride reacts with the ligands in 1:1 molar proportion.

The ligands contain thioamide group



as potential bond forming site and coordination complexes of ligand containing thioamide-group have been extensively studied [23–32]. IR spectra of the free ligands show band around 3200 cm^{-1} due to $-\text{NH}$ -stretching vibrations of terminal $-\text{NH}_2$ group [28]. This band shifts to lower frequencies in the complexes and splits, which is attributed to the coordination of $-\text{NH}_2$ nitrogen to metal atom. A sharp band observed at $\sim 900 \text{ cm}^{-1}$ in the IR spectra of free ligands is due to the $\nu(\text{C}=\text{S})$. The lower shift of this band in complexes is attributed to bonding of thioamide group through thione sulphur to metal atom. Ligands also display a number of bands in near and far region

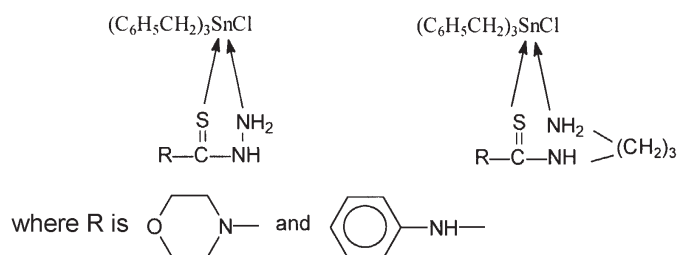
Table 1 Analytical data of complex

Complex	Melting point/ $^{\circ}\text{C}$	Elemental analysis found (calc.)/%					
		Sn	C	H	N	Cl	S
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^1)\text{Cl}$	134	20.00 (19.02)	49.94 (49.98)	5.45 (5.14)	6.60 (6.73)	5.71 (5.68)	5.09 (5.13)
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^2)\text{Cl}$	–	18.9 (17.82)	52.19 (52.33)	5.79 (5.70)	6.44 (6.30)	5.20 (5.32)	4.69 (4.80)
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^3)\text{Cl}$	138	19.42 (18.83)	52.98 (53.31)	4.63 (4.76)	6.80 (6.66)	4.80 (5.63)	4.09 (4.80)
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^4)\text{Cl}$	130	18.78 (18.14)	56.88 (56.86)	5.05 (5.50)	6.28 (6.42)	4.62 (5.43)	4.12 (4.89)

Table 2 TG and DTA of the complexes

Complex	Step No.	n	TG				DTA	
			Coats-Redfern		Horowitz Metzger		Thermal effect	$\Delta H/\text{J g}^{-1}$
			$E_a/\text{K mol}^{-1}$	$S^*/\text{J K}^{-1}\text{ml}^{-1}$	$E_a/\text{K mol}^{-1}$	$S^*/\text{J K}^{-1}\text{ml}^{-1}$		
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^1)\text{Cl}$	1	1	36	9	40	9	exothermic	92
	2	1	96	9	93	9	exothermic	159
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^2)\text{Cl}$	1	1	115	8	117	8	exothermic	115
	2	1	191	9	186	9	exothermic	361
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^3)\text{Cl}$	1	1	29	9	27	9	exothermic	171
	2	1	32	10	31	10		
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{L}^4)\text{Cl}$	1	1	29	8	33	9	exothermic	156
	2	1	77	10	81	9	exothermic	824

due to morpholine ring, aniline ring, NH-NH_2 and $\text{NH}(\text{CH}_2)_3\text{NH}_2$ part. Due to withdraw of electron density from donor atom towards metal atom, IR band positions of the co-ordinating groups are shifted. The metal complexes also show the following bands $\nu(\text{Sn-S})$ at $\sim 350 \text{ cm}^{-1}$, $\nu(\text{Sn-N})$ [33] at $\sim 660 \text{ cm}^{-1}$ and $\nu(\text{Sn-Cl})$ [34] at $\sim 360 \text{ cm}^{-1}$. All facts indicate that ligands are coordinated to the metal through sulphur and terminal nitrogen as shown below:



In the electronic spectra the absorption band is due to chromophore $\text{N}=\text{C}=\text{S}$ group which are assigned to $\pi-\pi^*$ intraligand transition [36–38]. This band at $\sim 295 \text{ nm}$ corresponding to free ligands shifts to lower wavelength $\sim 268 \text{ nm}$ on complexation showing the involvement of $\text{C}=\text{S}$ group in complexation.

The $^1\text{HNMR}$ spectra of ligand L^1 gives the following signals $\delta 3.5\text{--}3.7$ (t, 8H, CH_2); $\delta 3.15$ (s, 2H, terminal $-\text{NH}_2$), L^2 gives signals $\delta 3.0\text{--}3.25$ (t, 14H, CH_2), L^3 gives signals $\delta 2.3\text{--}2.5$ (t, 2H, NH_2) and L^4 gives signals at $\delta 5.70\text{--}7.2$ (5H, aniline); $\delta 3.1$ (t, 2H terminal NH_2) $\delta 3.0$ (t, 6H, CH_2). On complexation, additional peaks in the region $\delta 7.0\text{--}7.5$ (ArH) and $2.2\text{--}2.5$ (s, $-\text{CH}_2$ group) corresponding to the benzyl groups also appear in the $^1\text{HNMR}$ spectra of the complexes. The signal due to terminal $-\text{NH}_2$ experiences a downfield shift indicating coordination through nitrogen of $-\text{NH}_2$ group to tin.

Thermal studies

TG-DTA data for complexes in air and nitrogen atmosphere are shown in Figs 1, 1(a), 2, Tables 2 and 3.

In air the complexes decompose in two steps. The first step (423–685 K) involves the loss of three benzyl groups and chlorine atom, and the second step (763–1023 K) corresponds to the formation of SnO_2 .

In nitrogen atmosphere the complexes decompose in a single step (423–973 K) corresponding to the formation of tin sulphides.

From the TG curves, the reaction order (n) activation energy (E_a) and entropy of activation (S^*) for the two thermal decomposition steps have been determined by the methods of Coats-Redfern [39] and Horowitz-Metzger [40] (Table 2).

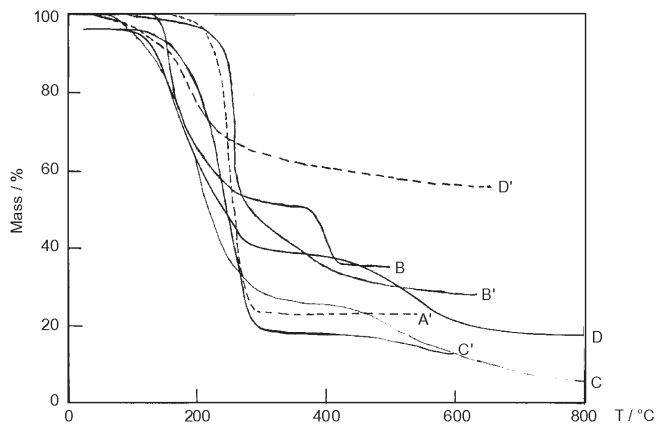


Fig. 1 TG curves for complexes in air: B – $(C_6H_5CH_2)_3Sn(L^2)Cl$; C – $(C_6H_5CH_2)_3Sn(L^3)Cl$; D – $(C_6H_5CH_2)_3Sn(L^3)Cl$; A', B', C', D' – in N_2 atm

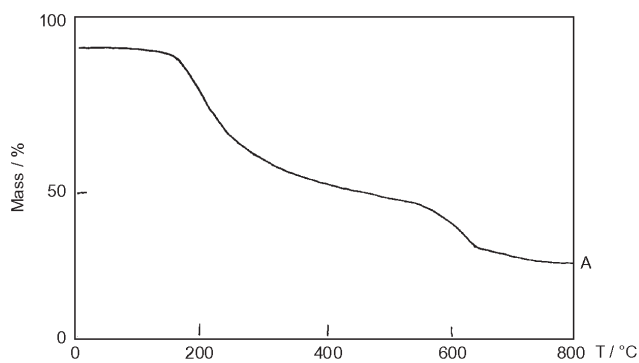


Fig. 1a TG curve for complex $(C_6H_5CH_2)_3Sn(L^1)Cl$ in air atmosphere

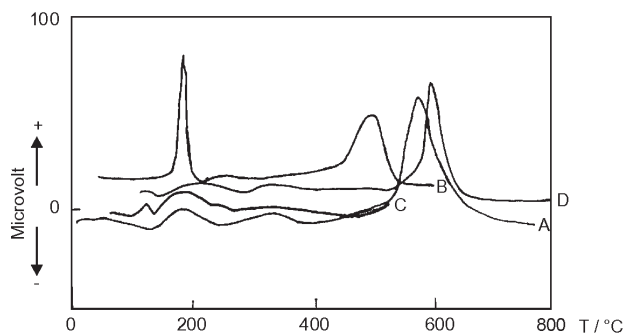


Fig. 2 DTA curves for complexes: A – $(C_6H_5CH_2)_3Sn(L^1)Cl$;
B – $(C_6H_5CH_2)_3Sn(L^2)Cl$; C – $(C_6H_5CH_2)_3Sn(L^3)Cl$; D – $(C_6H_5CH_2)_3Sn(L^4)Cl$

Table 3 Mass loss data

Complex	Step No.	Temp. range/K	Mass loss found (calc.)/%	Nature of loss
(C ₆ H ₅ CH ₂) ₃ Sn(L ¹)Cl	1	423–685	50.0 (49.43)	loss of three benzyl groups and chlorine atom
	2	763–1023	74.0 (74.09)	formation of SnO ₂
(C ₆ H ₅ CH ₂) ₃ Sn(L ²)Cl	1	420–573	50.0 (51.11)	loss of three benzyl group and chlorine atom
	2	723–793	75.8 (76.0)	formation of SnO ₂
(C ₆ H ₅ CH ₂) ₃ Sn(L ³)Cl	1	423–813	40.0 (41.2)	loss of three benzyl group
	2	823–1023	47.4 (48.0)	loss of chlorine
(C ₆ H ₅ CH ₂) ₃ Sn(L ⁴)Cl	1	398–593	55.32 (56.32)	loss of three benzyl groups
	2	263–923	77.5 (77.2)	formation of SnO ₂

The order of reaction (n) in each case is one. The mass loss data of complexes is given in Table 3. On the basis of thermal data, following conclusion have been drawn. Sn–C₆H₅CH₂ bond and Sn–Cl bond are weaker than Sn–L bond (where L=L¹, L², L³ and L⁴) so these bonds cleave before Sn–L bond and hence, the activation energy (E_a) value for step I is lower than step II because of greater steric hindrance initially in the complexes.

The ΔH (J g⁻¹) values for the first and second decomposition steps of the complexes have been taken from DTA curves, where the first thermal effect is due to the melting of complexes, the ΔH values have been calculated for the next steps.

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