Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

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To cite this article: Neeraj Sharma , Puneet Prem , Vipin Sharma , S. S. Bhatt & S. C. Chaudhry (1997) Synthesis, Characterization and Thermal Studies of Di- and Triphenyltin(IV) Complexes of p-Chloro- AND p-Nitrobenzohydroxamic Acids, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 27:9, 1381-1397, DOI: 10.1080/00945719708000166

To link to this article: http://dx.doi.org/10.1080/00945719708000166

SYNTH. REACT. INORG. MET.-ORG. CHEM., 27(9), 1381-1397 (1997)

SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF DI- AND TRIPHENYLTIN(IV) COMPLEXES OF p-CHLORO- AND p-NITROBENZOHYDROXAMIC ACIDS

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ABSTRACT

Di- and triphenyltin(IV) complexes of the compositions $Ph_2SnCl_n(XBHA)_{2-n}$ and $Ph_3Sn(XBHA)$ (where n=0 or 1, X=p-Cl or p-NO_2 and BHA=anion of the hydroxamic acid, BH_2A) have been synthesized by the reactions of Ph_2SnCl_2 or Ph_3SnCl with the potassium salts of the respective p-chloro or p-nitrobenzohydroxamic acids in a MeOH/THF mixture. The complexes have been characterized by elemental analyses, molar conductance, molecular weight determinations and IR spectra. The results indicate that the ligand is bidentate, coordinating through the carbonyl and hydroxylamine oxygens. The reactions of $Ph_2SnCl(XBHA)$ with sodium derivatives of acetylacetone, dibenzoylmethane and salicylaldehyde (NaL) have led to the formation of mixed ligand complexes of the type $Ph_2Sn(XBHA).L$ Thermal decomposition of the complexes in an air stream yielded pure SnO_2 at 700-800°C.

INTRODUCTION

The importance of hydroxamic acids as classical colorimetric and gravimetric reagents for many metals[1] and their ability to chelate metal centres has been proposed to be responsible for their inhibitory effect on several metal-containing enzymes[2-4]. General interest in their biochemical activity has led to a series of theoretical and experimental studies on the structure of hydroxamic acids[5-7] and their metal complexes[8,9]. Interestingly, the donor properties of hydroxamic acids[10] and aminohydroxamic acids[11] have been extensively reviewed, primarily involving the first row transition metal series. In contract, very little work has been reported on the synthesis of hydroxamates of main group elements. In the present work, tin(IV) complexes of two hydroxamic acids, namely p-chlorobenzohydroxamic acid (p-ClBH$_2$A) and p-nitrobenzohydroxamic acid (p-NO$_2$BH$_2$A) (Fig. 1) have been synthesized by reacting them with appropriate amounts of diphenyltin dichloride and triphenyltin chloride and attempts have been made to investigate their mode of coordination. The reactivity of some of these complexes with sodium derivatives of acetylacetone, dibenzoylmethane and salicylaldehyde have also been investigated to form mixed ligand complexes.

EXPERIMENTAL

MATERIALS

Ph_2SnCl_2 (Aldrich) and Ph_3SnCl (Fluka) were used as such without further purification. The purity of the materials

p-ClBHA p-NO_2BHA

Fig. 1. Structure of the Ligands

was, however, checked by their sharp melting points and chlorine analysis. *p*-Chlorobenzohydroxamic acid and *p*-nitrobenzohydroxamic acids were prepared via the ethyl ester of *p*-chlorobenzoic acid and *p*-nitrobenzoic acids by a literature method[12]. All solvents were AnalR grade. Methanol was dried by refluxing over magnesium methoxide while THF was dried over sodium. These were then distilled before use. The sodium derivatives of acetylacetone, dibenzoylmethane and salicylaldehyde were prepared by standard methods[13,14].

Preparation of Complexes

Triphenyltin(IV) *p*-Chlorobenzohydroxamate (VI). A solution of Ph_3SnCl (2.5 g, 6.49 mmole) in THF (20 mL) was reacted with an equimolar amount of potassium *p*-chlorobenzohydroxamate (1.36 g, 6.49 mmole) in methanol (25 mL). The reaction mixture was first stirred for 4-5 h at room temperature and then refluxed for another 5-6 h during which the formation of a white precipitate was observed. KCl thus formed was removed by filtration and the excess solvent (30 mL) was distilled off from the solution. On cooling the remaining solution overnight at room temperature, the complex was obtained as a fine solid. The complex was purified by repeated recrystallization from methanol. Yield: 2.89 g.

Triphenyltin(IV) p-Nitrobenzohydroxamate (V). Ph_3SnCl (2.8 g, 7.26 mmole) was dissolved in THF (20 mL) and reacted with potassium *p*-nitrobenzohydroxamate (1.6 g, 7.26 mmole) dissolved in methanol (20 mL). It was first stirred for 5 h at room temperature and then refluxed for another 5 h. The precipitated solid (KCl) formed during the course of the reaction was filtered off. The filtrate was then concentrated by distilling off the excess solvent (30 mL). It was then kept overnight at room temperature when a crystalline solid was obtained which was then recrystallized from methanol. Yield: 3.1 g.

Diphenylmonochlorotin(IV) p-Cl (I) and p-NO_2 (II) Benzohydroxamates. Ph_2SnCl_2 (1.8 g, 5.23 mmole) dissolved in THF (25 mL) was mixed with equimolar amounts of potassium *p*-Cl-benzohydroxamate (1.09 g, 5.23 mmole) or potassium *p*-NO_2-benzohydroxamate (1.15 g, 5.23 mmole), each dissolved separately in methanol (25 mL). The respective solutions were first stirred at room temperature and then refluxed for 8-10 h on a water bath. KCl formed during the course of the reaction was filtered and the filtrate was concentrated to about 15 mL by distilling off the excess solvent. The resulting solutions were left overnight at room temperature, when the complexes separated out as crystalline solids. These were then recrystallized from methanol. Yield: I, 2.10 g; II, 1.98 g.

Diphenyltin(IV) Bis-p-Cl (III) and Bis-p-NO_2 (IV) Benzohydroxamate. A solution of Ph_2SnCl_2 (1.8 g, 5.23 mmole) in THF (25 mL) was reacted with solutions of potassium p-Cl-benzohydroxamate (2.18 g, 10.46 mmole) or potassium p-NO_2 benzohydroxamate (2.3 g, 10.46 mmole), each dissolved separately in 25 mL of methanol. The reaction mixture was first stirred and then refluxed for 8-10 h on a water bath. After the resultant KCl was filtered, the filtrate was concentrated to about 20 mL by distilling off the solvent. The crystalline products were obtained on keeping the above solution undisturbed at room temperature and were recrystallized from methanol. Yield: III, 2.28 g; IV, 2.47 g.

Reactions of Ph_2SnCl(XBHA) with acacNa, dbmNa and salNa. To a solution of Ph_2SnCl(p-ClBHA) (1.5 g, 3.13 mmole) or Ph_2SnCl(p-NO_2BHA) (1.4 g, 2.86 mmole) in methanol (25 mL) in separate experiments, was added acacNa (0.382 g, 3.13 mmole) or (0.348 g, 2.86 mmole), respectively, in methanol (30 mL). The contents were, first stirred at room temperature and then refluxed for 6-8 h when formation of a white solid was observed. The resulting solid was filtered and the filtrate was concentrated to about one third of its volume. The solid complexes separated out slowly from this solution when left undisturbed. These were washed with petroleum ether and recrystallized from methanol.

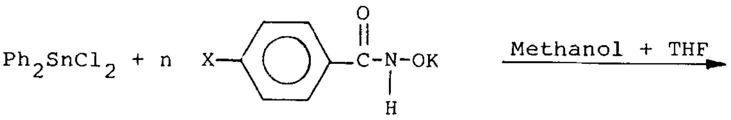
A similar procedure was adopted for carrying out the reactions with dbmNa and salNa.

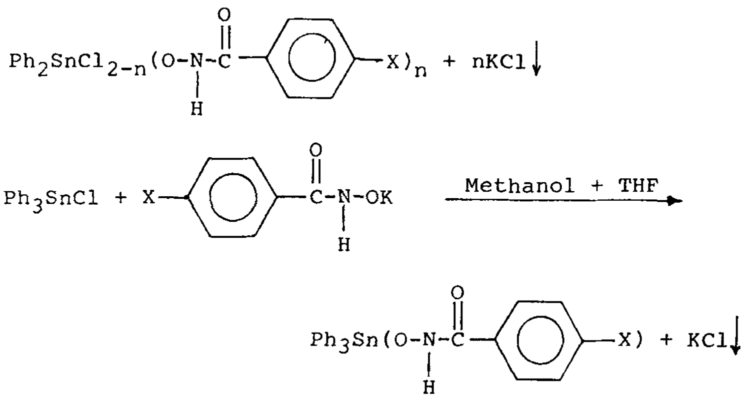
Physico-chemical Measurements

Analyses for C and H were carried out with a Coleman C-H-N analyzer. The tin content of the complexes was determined by treating the complex with a mixture of concentrated nitric acid (3 volumes) and concentrated sulphuric acid (2 volumes) and then heating strongly with a Meker burner for 2-3 h till a constant weight for SnO_2 was obtained[15]. Chlorine was determined by Volhard's method. The conductivities of 10^{-3} M solutions of the complexes in methanol were measured on an Elico Conductivity Bridge type CM-82T. The molecular weights were determined by Rast's camphor method. The IR spectra were recorded as KBr pellets as well as in Nujol mulls on a Beckman spectrophotometer IR-4250. The thermograms were recorded on a DTG-40 (simultaneous DTA-TG module, Shimadzu Corporation) at a heating rate of 20°C/minute in air using a Pt crucible and Pt/Pt:Rh thermocouple.

RESULTS AND DISCUSSION

Potassium p-chloro- and p-nitrobenzohydroxamates (p-XBHAK) react with Ph_2SnCl_2 or Ph_3SnCl according to the following equations:





(where n=1 and 2; X=p-Cl, p-NO_2)

The elemental analyses of the complexes confirm their stoichiometry and are listed in Table I. The complexes are light yellow to light brown solids and fairly stable in air. They are insoluble in CCl_4, $CHCl_3$, C_6H_6 and CH_2Cl_2 but are soluble in polar solvents. The molar conductances in 10^{-3} M MeOH solution are in the range 31.5-48.5 ohm^{-1} cm^2 $mole^{-1}$ indicating the non-electrolytic nature of the complexes[16]. The molecular weight determinations of the complexes in camphor (175° C) by the Rast method show that they exist as monomers.

IR Spectra

The IR spectra of hydroxamic acids and their complexes are generally very complex, though some characteristic bands for different ligand structures have been suggested. Several important changes are observed in the structure of the

Table I. Analytical and IR Spectral Data (cm^{-1}) of Di- and Triphenyltin(IV) Hydroxamates

Complex	Empirical formula	Yield (%)	Colour	M.P. (°C)	ELEMENTAL ANALYSIS % Found (Calcd.)				Mol.wt. Found (Calcd)	Molar Conductance in Methanol $ohm^{-1}\ cm^2\ mole^{-1}$	IR Spectral Band (cm^{-1})			
					Sn	Cl	C	H			$\nu_{C=O}$	$\nu_{C=N}$	ν_{N-O}	ν_{Sn-O}
Ph_2SnCl(p-ClBHA) (I)	$SnC_{19}H_{15}Cl_2NO_2$	84	Brownish Pink	210	24.38 (24.84)	14.38 (14.82)	48.2 (47.6)	3.0 (3.13)	491 (479)	48.6	1570	1375	925	465
Ph_2SnCl(p-NO_2BHA (II)	$SnC_{19}H_{15}ClN_2O_4$	77	Yellow	128	23.79 (24.33)	7.84 (7.25)	47.1 (46.6)	3.01 (3.06)	458 (489)	46.1	1575	1370	935	460
Ph_2Sn(p-ClBHA)$_2$ (III)	$SnC_{26}H_{20}Cl_2N_2O_4$	71	Light green	161	18.93 (19.38)	12.01 (11.56)	50.6 (50.81)	3.1 (3.25)	589 (614)	37.8	1545	1372	910	470
Ph_2Sn(p-NO_2BHA)$_2$ (IV)	$SnC_{26}H_{20}N_4O_8$	74	Yellow	210^d	18.21 (18.74)	-	49.3 (49.1)	3.18 (3.14)	580 (635)	35.9	1575	1370	915	465
Ph_3Sn(p-ClBHA) (V)	$SnC_{25}H_{20}ClNO_2$	85	Brown	89	23.01 (22.86)	6.25 (6.82)	57.2 (57.7)	3.7 (3.84)	488 (520)	32.2	1580	1365	935	460
Ph_3Sn(p-NO_2BHA) (VI)	$SnC_{25}H_{20}N_2O_4$	80	Brown	187^d	22.93 (22.41)	-	56.2 (56.5)	3.6 (3.7)	481 (531)	31.6	1560	1360	930	450

d = Decomposition

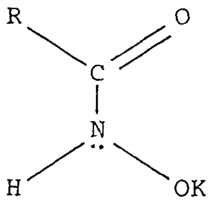
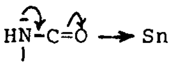


Fig. 2. Keto Form of Hydroxamic Acid Salt

hydroxamate ligating groups when they undergo complexation. The IR spectra of the complexes have been rationalized by camparing them with the spectra of p-ClBHAK and p-NO_2BHAK. The ν(C=O) vibrations appear at 1590 and 1600 cm^{-1} in the spectra of pure p-ClBHAK and p-NO_2BHAK, respectively, while in their corresponding organotin complexes these bands are significantly lowered by 15-45 cm^{-1} on complexation. The ν(C-N) bands which occur at 1320 and 1315 cm^{-1} in the respective ligands appeared in the region 1340-1360 cm^{-1} in the complexes. The lowering of ν(C=O) and the shift of ν(C-N) to higher wave numbers is in agreement with the electronic shift  $\text{HN}-\text{C}=\text{O}\rightarrow\text{Sn}$ resulting from donation of electrons from the carbonyl oxygen to the metal atom accompanied by the strengthening of the C-N bond, as expected from the hydroxamide structure, thereby suggesting coordination through the carbonyl oxygen. The ν(N-O) mode present at ∼910 cm^{-1} in the free ligands appears at ∼930 cm^{-1} in the spectra of the complexes, indicating that complexation occurs through an oxygen atom of the hydroxylamine group, in accordance with the formation of a

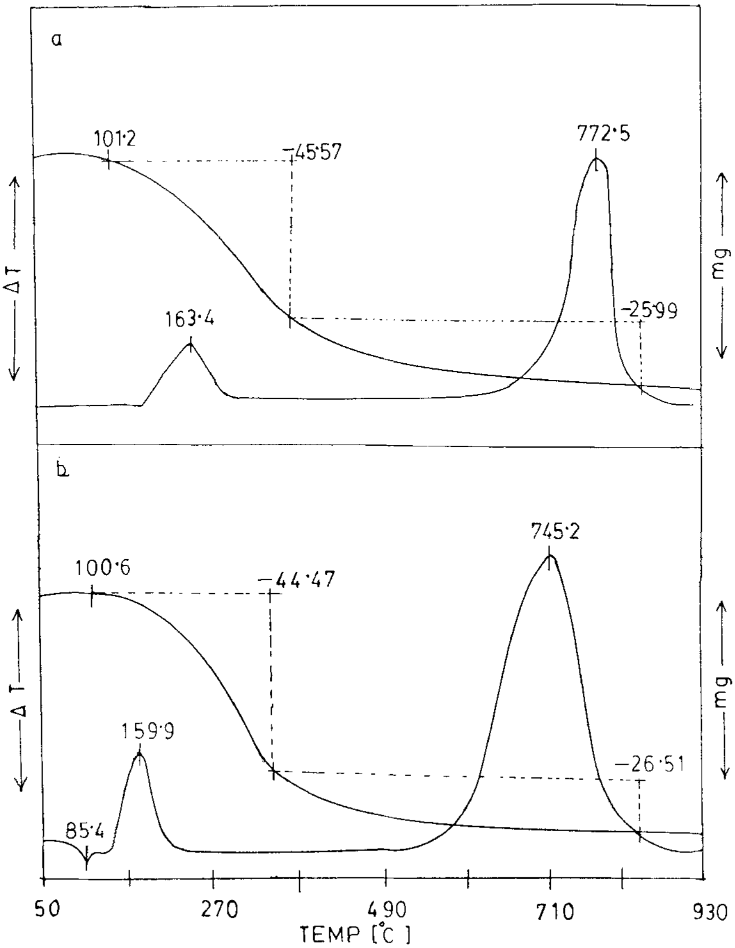


Fig. 3. Thermograms of a. $Ph_3Sn(ONHCOC_6H_4\text{-}NO_2\text{-}p)$ [VI]
b. $Ph_3Sn(ONHCOC_6H_4\text{-}Cl\text{-}p)$ [V]

metal-oxygen bond of the type N-O-Sn. It may, therefore, be concluded that the ligands are mainly coordinating in the keto form <u>i.e.</u>, the hydroxamide structure shown in Fig. 2. The ν(N-H) and other vibrational bands of the ligands remain practically unchanged upon complexation; this result excludes NH coordination of the ligand to the metal ion.

In the Far-IR spectra of the complexes, bands located in the regions 450-480 cm^{-1} and $\sim$230 cm^{-1} have been assigned to ν(Sn-O) and ν(Sn-Ph) modes while the observance of bands in the region 320-350 cm^{-1} (in I and II only) have been ascribed to ν(Sn-Cl) vibrations.

The above observations thus suggest a five-coordinate monomeric structure for $Ph_3Sn(XBHA)$ (V and VI) and Ph_2SnCl-(XBHA) (I and II) and a six-coordinate environment in Ph_2Sn-$(XBHA)_2$ (III and IV) [X=p-Cl and p-NO_2] around tin, involving bonding through carbonyl and hydroxylamine oxygens of the hydroxamate ligand.

Thermal Studies

The DTA/TG curves of the complexes Ph_3Sn(p-ClBHA) (V) and Ph_3Sn(p-NO_2BHA) (VI) presented in Fig. 3 show that they are stable upto 100° C, after which a continuous weight loss in the temperature range 100-850° C is revealed in the thermogravimetric curve. The decomposition of the complexes amounting to a total loss of 70·98% and 71.56% for (V) and (VI), respectively, indicates the complete breakdown of the organic matter leaving behind only the metallic oxide (SnO_2) as the ultimate residue. Interestingly, a careful examination of the TG curves of both complexes shows a small inflexion around 380° C arising due to the rapid weight losses of 44.47% and 45.57% for (V) and (VI), respectively, in the temperature range 101-380° C followed by slowing down of the

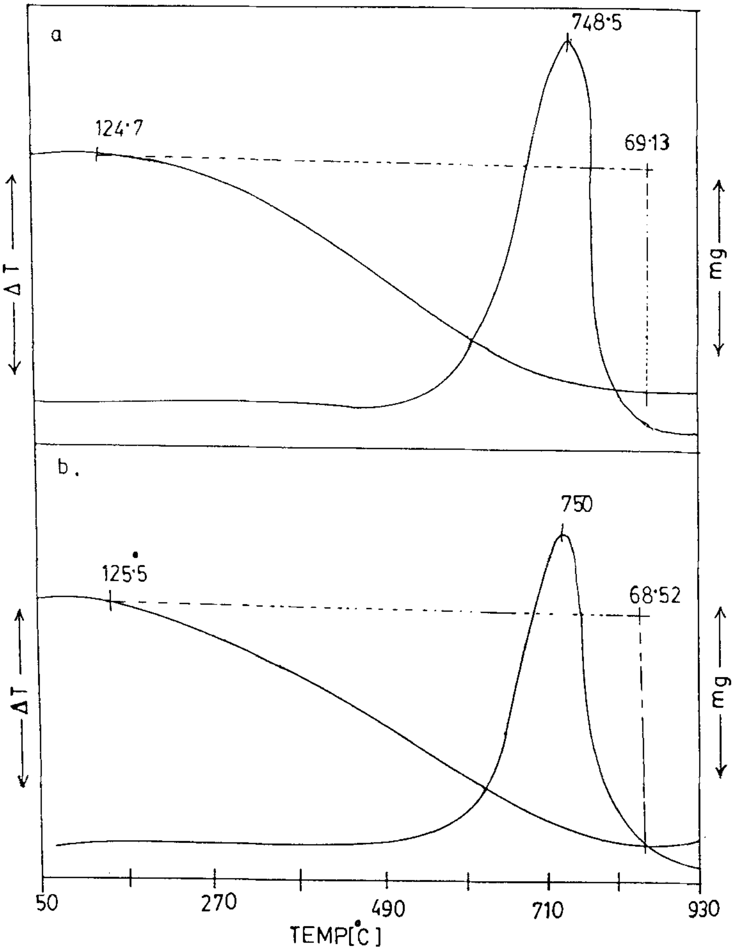


Fig. 4. Thermograms of a. $Ph_2SnCl(ONHCOC_6H_4\text{-}No_2\text{-}p)$ [II]
b. $Ph_2SnCl(ONHCOC_6H_4\text{-}Cl\text{-}p)$ [I]

rate of decomposition. This inflexion has been attributed to the formation of Ph_2SnO as the probable intermediate which is also supplemented by the appearance of an exothermic peak at 159.9° C for (V) and at 163.4° C for (VI) in the DTA. It may

Table II. Analytical Data of the Reaction Products of $Ph_2SnCl(XBHA)$ with Chelating Ligands.

Complex	Empirical Formula	Yield (%)	M.P. (° C)	ELEMENTAL ANALYSES % Found (Calcd)				Molecular weight Found (Calcd)
				Sn	Cl	C	H	
Ph_2Sn(p-ClBHA).acac	$SnC_{24}H_{22}ClNO_4$	70	184	22.4 (21.9)	5.8 (6.5)	52.5 (53.1)	3.19 (4.05)	525 (542)
Ph_2Sn(p-NO_2BHA).acac	$SnC_{24}H_{22}N_2O_6$	73	124	21.8 (21.5)	-	51.7 (52.1)	4.3 (3.9)	528 (552)
Ph_2Sn(p-ClBHA).dbm	$SnC_{34}H_{26}ClNO_4$	69	205	18.4 (17.8)	6.1 (5.3)	60.7 (61.2)	4.5 (3.9)	635 (666)
Ph_2Sn(p-NO_2BHA).dbm	$SnC_{34}H_{26}N_2O_6$	71	180^d	18.0 (17.6)	-	59.2 (60.3)	2.9 (3.8)	642 (676)
Ph_2Sn(p-ClBHA).sal	$SnC_{26}H_{20}ClNO_4$	59	85	20.7 (21.09)	6.9 (6.3)	54.9 (55.3)	3.0 (3.5)	583 (564)
Ph_2Sn(p-NO_2BHA).sal	$SnC_{26}H_{20}N_2O_6$	76	110^d	21.1 (20.7)	-	53.1 (54.3)	4.7 (3.5)	558 (574)

d=Decomposition

be mentioned here that although it is difficult to account for the formation of an intermediate, unless it is actually identified, yet the nature of the curves shown in Fig. 3 is broadly consistent with the presence of Ph_2SnO as an intermediate. The subsequent weight loss of 26.51% and 25.99% beyond 380° C for (V) and (VI), respectively, has been ascribed to the oxidative decomposition of Ph_2SnO to give SnO_2. The second exothermic peak in the DTA curves at 742.5° C for Ph_3Sn(p-ClBHA) and at 772.5° C for Ph_3Sn(p-NO_2BHA) has been attributed to the decomposition of organic matter. These observations can be tentatively rationalized in terms of the following scheme of decomposition:

$$Ph_3Sn(XBHA) \longrightarrow Ph_2SnO + \text{organic moiety}$$

$$Ph_2SnO + \tfrac{1}{2}O_2 \longrightarrow SnO_2 + \text{organic matter}$$

The TG curves of Ph_2SnCl(p-ClBHA) (I) and Ph_2SnCl(p-NO_2BHA) (II) (Fig. 4) have revealed that the complexes are fairly stable upto 125° C beyond which a continuous loss of weight in the temperature range 125-800° C is observed. The weight loss of 68.52% and 69.13%, for (I) and (II), respectively, corresponds exactly to the formation of SnO_2 as the final residue. No intermediate has been proposed. This one-step decomposition may be represented as:

$$Ph_2SnCl(XBHA) \longrightarrow SnO_2 + \text{organic matter}$$

This is further substantiated by the appearance of only one exothermic peak observed around 750° C in these complexes.

Reactions of $Ph_2SnCl(XBHA)$ with acacNa, dbmNa and salNa

The reactions of $Ph_2SnCl(XBHA)$ (I) and (II) with NaL [where L is the anion of acetylacetone (acacH), dibenzoylmethane (dbmH) and salicylaldehyde (salH)] lead to the formation of mixed ligand complexes of the type $Ph_2Sn(XBHA).L$, according to the reaction:

$$Ph_2SnCl(XBHA) + NaL \longrightarrow Ph_2Sn(XBHA).L + NaCl\downarrow$$

It is important to mention here that the direct reaction of diphenylchlorotin (p-chloro/p-nitrobenzohydroxamates) with the chelating ligands acetylacetone, dibenzoylmethane and salicylaldehyde neither leads to the evolution of HCl gas nor yields any compound of definite composition. Under these circumstances, an alternative route involving the reaction of the parent complexes with the sodium salts of the chelating ligands was adopted as it allowed the desired replacement of chlorine in the form of NaCl (quantitative separation) to yield the mixed ligand complexes.

The elemental analyses of the complexes agree very well with the proposed stoichiometric compositions. They are moisture sensitive, fine-crystalline solids and are fairly soluble in common organic solvents while the parent complexes are soluble only in polar solvents. The molar conductances suggest that they are non-electrolytes while cryoscopic molecular weights are commensurate with their monomeric character (Table II).

A comparison of the IR spectra of the mixed ligand complexes with those of the parent complexes reveals that the bands attributed to the νSn-Cl mode in the parent hydroxamates are completely missing in the complexes containing secondary ligands. Though the characteristic vibrations of the chelating ligands in the region 1300-1600 cm^{-1} generally show significant changes on complexation but in the complexes under investigation, these could not be clearly distinguished, perhaps because of the mixing or overlapping of C=C or C=O stretching bands of the mixed ligand complexes. The other important bands due to the ν N-H and ν C-N modes of the hydroxamate group are shifted only slightly in the mixed ligand complexes.

Thus, it can be inferred from the above studies that a change in geometry from a five-coordinate structure in the parent complexes to an octahedral environment around Sn in the mixed ligand complexes can tentatively be proposed.

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Received: 13 May 1996 Referee I: R. A. Geanangel
Accepted: 14 July 1997 Referee II: L. R. Sita