



Synthesis and characterization of anionic complexes of diorganotin mixed halides with tetraammonium, arsonium and stibonium salts

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ABSTRACT

A series of complexes of type $[R_4M_2] [(p-FC_6H_4)_2SnClBr(Y)_2]$ were prepared and characterized by melting point, elemental analysis, infrared and solution studies data showing $(p-FC_6H_4)_2Sn(IV)$ can expand their coordination number six in the presence of halide or pseudohalide ligands and the stereochemical studies assigned octahedral structure to the anionic complex.

Keywords: diorganotin mixed halides, anionic complexes, electro-chemical property, IR spectroscopy.

INTRODUCTION

In comparison to the well studied synthetic and structural aspects of neutral $[R_nSnX_{4-n}XL]$ and cationic $[R_nSnX_{n-1}]^+[Y]^-$ complexes of organotin compounds relatively little work has so far been reported on the anionic complexes. Organotin anionic complexes with ligands such as halogens and pseudohalogens [1-4] and the environment of the tin atoms in species such as $[R_3SnX_2]^-$ and $[R_2SnX_4]^{2-}$ (X = halogens and pseudohalogens) are expected to correspond to that of the related polymeric neutral derivatives R_3SnX [5-7] or R_2SnX_2 [8]. Seyferth and Grim [1] as early as 1961 reported some anionic complexes of the type $[Et_4N]^+[Me_3SnBr_2]^-$ during the course of their studies on nucleophilic displacement of halide ion in the metal halides by triphenyl phosphine methylene and mentioned briefly that the stability of the hexacoordinated tin anions fall as the number of electronegative substituents decreases.



The system $[R_{4-n}SnCl_n + R'_4NCl]$ (R=Ph, Bu, R' = Me, Et and n =2, 3) has been studied both potentiometrically and conductometrically in acetonitrile indicating that the ability to form complexes decreases in the following sequence for pentacoordinated anionic complexes [9].



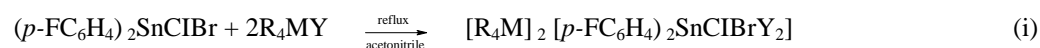
Seyferth and Grim [1] were the first to propose the halogen bridged, derivative structures for the anions $[Me_3SnBr_2]^-$, assuming that the tin atom could only have, tetrahedral and octahedral configuration. Later on Wilkins and Hendler [10] also reported a comparative investigation of the infrared spectra of the complexes of fluoride and propose the trans configuration for the anions of the type $[(CH_3)_2SnF_4]^{2-}$.

A trigonal bipyramidal structure has also been confirmed for the complexes of the type $[Me_2SnCl_3]^-$ anion having more electronegative group on axial sites [11]. A part from a large number of patented compounds of triorgano tin anions with tetraorgano phosphonium compounds [12]. Few tri- and diorganotin pseudohalo and mixed pseudohalo complex anions with tetralkyl ammonium and tetralkyl arsonium cations have been reported and their probable structures established from Mossbauer, infrared and conductance measurement [3, 2]. Bhattacharya et al. [13] have

reported the formation of halo or pseudohalo complex organotin anions with balancing organo group V metal cations $[R_4M]^+$.

EXPERIMENTAL SECTION

A general method (i) was employed for preparation of anionic complexes of di-(*p*-fluorophenyl)tin (IV) halo, pseudohalo anions employing stoichiometric amounts of the reactants (eq.(i)).



where M = N, As, Sb, R = CH₃, C₆H₅, Y = NCS, N₃, NCO.

The complex of type $[R_4M]_2 [(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(Y)_2]$ were prepared by refluxing for several hrs 1 mmole of (*p*-FC₆H₄)₂SnClBr and 2 mmole R₄MY in acetonitrile or absolute alcohol. After concentrating and cooling the solution a white crystalline solid precipitated. The compound was once again crystallized by acetonitrile. The melting point, elemental analysis, infrared and solution studies data are given in table 1 and 2.

RESULTS AND DISCUSSION

In the present work, some hitherto unknown di-(*p*-fluoro phenyl)tin(IV) halo, mixed halo or pseudohalo anions $[(p\text{-FC}_6\text{H}_4)_2\text{SnBrClX}]^-$ (X=N₃, NCS, NCO) were isolated in combination with balancing tetra ammonium, arsonium and stibonium cations, $[R_4M]^+$ (R = CH₃, C₆H₅, M = N, As, Sb). Surprisingly, there is no reference regarding the synthesis of substituted aryl tin (IV) anion which are expected to display significant biocidal activity in the light of reported observation [14]. The probable solid state structures of these complexes derived on the basis of analytical, conductance and infrared studies were also reported. The compounds prepared (Table 1) were characterized to be the organo ammonium, arsonium and stibonium salts of the di organo tin(IV) anions by analytical data showing (*p*-FC₆H₄)₂ Sn(IV) can expand their coordination number six in the presence of halide or pseudohalide ligands. The constancy in the melting points of the products obtained on repeated crystallization excluded any possibility of the presence of mixture of the reactants. The compounds were white crystalline solids soluble in polar organic solvents. They were studied spectroscopically in the infrared region 400-4000 cm⁻¹, and their, ionic nature has been confirmed from conductance measurements and Van't Hoff's factor 'i' value.

1. Solution Studies:

The values of molar conductance of the complexes (1-9) are in the range of 263-295 ohm⁻¹ cm² mol⁻¹ in acetonitrile and this shows the compounds to be 2:1 electrolytes [3] (Table 1). The observed molecular weights of the compounds (1-9) were approximately one third of the formula molecular weights, indicating that the complexes were dissociated into three or two ions in the solutions. The calculated values of Van't Hoff's factor 'i' further confirmed that the complexes are 2:1 electrolytes.

2. Infrared Spectra:

The infrared absorptions due to (*p*-fluorophenyl) group [15] bound to tin correspond to these reported in the literature, while the vibrations due to cations also agree well, with reported values [16]. These absorption assignments, therefore have not been discussed further, characteristic absorption together with their possible assignments of the pseudohalide group are listed in Table 2. In the anionic complexes having thiocyanate group the possibility of the group being either -N or -S bonded to tin have been a matter of controversy over a long period [3, 6, 17]. However, the isothiocyanate group (-NCS) which is attached to tin through the nitrogen atom can readily be distinguished from the position, intensity and shape of the asymmetric -NCS band [18]. In the anions containing isothiocyanate group, the vibrations occur as a strong and broad band around 2040 ± 5 cm⁻¹ suggesting it to be N bonded to tin, whereas the thiocyanate bonding is indicated by very sharp well formed N-C stretching band above 2100 cm⁻¹ [3]. Similarly in case of isocyanate derivatives NCO was found to be N- bonded to Sn on the basis of IR data.

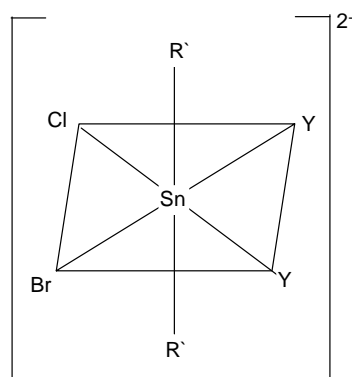


Figure 1: Octahedral structure of complexes, where $R' = (p\text{-FC}_6\text{H}_4)$ and $Y = \text{NCS}, \text{N}_3, \text{NCO}$

The most prominent absorptions in the infrared spectra of the organotin anions containing an azide group are asymmetric stretching frequency observed in the range $2030 \pm 10 \text{ cm}^{-1}$ and a much weaker symmetric mode at 1260 cm^{-1} [19]. The position of asymmetric band is more in favour of covalently binded -N_3 group to the central tin atom. However, a band observed at 650 cm^{-1} is being assigned suggest the presence of a covalently bonded linear -N=N=N group.

From the above experimental data and taking into consideration the stereochemical studies reported so far on similar compounds an octahedral structure may be assigned to anion (figure 1). This seems to be a general trend and expectations are few.

Table 1: Analytical Data of Anionic Complexes of Diorganotin mixed halides

S. No	Complex(a, b) (2:1) ($\text{Ph} = \text{C}_6\text{H}_5$)	Empirical formula	Analysis Found (Caled.) %				M.p. ($^\circ\text{C}$)	Yield (%)
			C	H	N	Sn		
1	$[(\text{CH}_3)_4\text{N}]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCS})_2]$	$\text{C}_{22}\text{H}_{32}\text{SnClBrN}_4\text{S}_2\text{F}_2$	38.35 (38.38)	4.60 (4.64)	8.09 (8.13)	17.20 (17.24)	170	80
2	$[(\text{CH}_3)_4\text{N}]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{N}_3)_2]$	$\text{C}_{20}\text{H}_{32}\text{SnClBrN}_8\text{S}_2\text{F}_2$	36.58 (36.60)	4.83 (4.87)	17.01 (17.06)	18.06 (18.08)	178	85
3	$[(\text{CH}_3)_4\text{N}]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCO})_2]$	$\text{C}_{22}\text{H}_{32}\text{SnClBrN}_4\text{O}_2\text{F}_2$	40.21 (40.25)	4.82 (4.87)	8.51 (8.53)	18.05 (18.08)	210	78
4	$[(\text{Ph}_4\text{As})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCS})_2]$	$\text{C}_{62}\text{H}_{48}\text{SnClBrN}_4\text{As}_2\text{S}_2\text{F}_2$	56.92 (56.98)	3.63 (3.67)	2.11 (2.14)	9.02 (9.08)	230	80
5	$[(\text{Ph}_4\text{As})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCO})_2]$	$\text{C}_{62}\text{H}_{48}\text{SnClBrN}_2\text{O}_2\text{As}_2\text{F}_2$	58.40 (58.42)	3.72 (3.76)	2.15 (2.19)	9.30 (9.31)	240	85
6	$[(\text{Ph}_4\text{As})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{N}_3)_2]$	$\text{C}_{60}\text{H}_{48}\text{SnClBrN}_6\text{As}_2\text{F}_2$	56.51 (56.53)	3.74 (3.76)	6.57 (6.59)	9.28 (9.31)	140	80
7	$[(\text{Ph}_4\text{Sb})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCS})_2]$	$\text{C}_{62}\text{H}_{48}\text{SnClBrN}_4\text{S}_2\text{Sb}_2\text{F}_2$	53.14 (53.17)	3.40 (3.42)	1.95 (1.99)	8.45 (8.47)	1.48	65
8	$[(\text{Ph}_4\text{Sb})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCO})_2]$	$\text{C}_{62}\text{H}_{48}\text{SnClBrN}_2\text{O}_2\text{Sb}_2\text{F}_2$	54.40 (54.42)	3.47 (3.50)	2.01 (2.04)	8.65 (8.67)	152	80
9	$[(\text{Ph}_4\text{Sb})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{N}_3)_2]$	$\text{C}_{60}\text{H}_{48}\text{SnClBrN}_6\text{Sb}_2\text{F}_2$	52.61 (52.66)	3.45 (3.50)	6.11 (6.13)	8.63 (8.67)	148	75

^aMolar conductances were found corresponding to 2:1 electrolyte and ^bThe value of Van't Hoff factor was approximately 1/3.

Table 2: Infrared Spectra of the Mixed Pseudohalide Complexes

S.No.	Complex	$\nu_{\text{asym}}(\text{Ps})^*$	$\nu_{\text{sym}}(\text{Ps})$	$\delta(\text{Ps})$
1	$[(\text{CH}_3)_4\text{N}]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCS})_2]$	2045	840	470
2	$[(\text{CH}_3)_4\text{N}]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{N}_3)_2]$	2040	1260	650
3	$[(\text{CH}_3)_4\text{N}]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCO})_2]$	2110	880	450
4	$[(\text{Ph}_4\text{As})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCS})_2]$	2040	840	470
5	$[(\text{Ph}_4\text{As})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCO})_2]$	2095	880	465
6	$[(\text{Ph}_4\text{As})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{N}_3)_2]$	2030	1260	650
7	$[(\text{Ph}_4\text{Sb})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCS})_2]$	2035	840	475
8	$[(\text{Ph}_4\text{Sb})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{NCO})_2]$	2090	810	460
9	$[(\text{Ph}_4\text{Sb})_2]_2[(p\text{-FC}_6\text{H}_4)_2\text{SnClBr}(\text{N}_3)_2]$	2020	1260	650

Ps = pseudohalide group.

CONCLUSION

The study reflected that $(p\text{-FC}_6\text{H}_4)_2\text{Sn}(\text{IV})$ expanded their coordination number six in the presence of halide/pseudohalide ligands and the stereochemical studies assigned octahedral structure to the anionic complex.

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