

Synthesis and Characterisation of Some New Anionic Complexes of Bis (pentafluorophenyl) tin (IV) Halides with Quaternary ammonium, -stibonium and -arsonium Salts

Isha Rizvi, Prof. Amarika Singh, Dharmendra K. Srivastava.

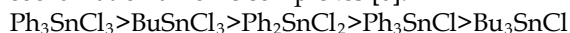
Abstract— A series of anionic complexes of bis(pentafluorophenyl)tin (IV) chloride; $(C_6F_5)_2SnCl_2$ with quaternary ammonium, -stibonium, -arsonium salts; R_4MY where $R = CH_3-, C_6H_5-$; $M = N, As, Sb$ and $Y = NCS^-, NCO^-, N_3^-$ have been synthesised. These newly synthesised anionic complexes are electrolyte in acetonitrile and are monomeric in benzene. The spectroscopic techniques (IR) and analytical data shows that Sn (IV) can expand their coordination sphere in presence of pentafluorophenyl group directly attached to tin with pseudohalide ligands. The ionic nature has been confirmed by conductance measurement and Van't Hoff factor 'i'.

Index Terms— Bis(pentafluorophenyl)tin (IV) chloride, Infrared, Pseudohalides, Anionic Complexes, Expansion of coordination sphere.

1 INTRODUCTION

There has been a considerable interest centered on the synthetic and structural chemistry of neutral $[R_nSnX_{4-n}L]$ and cationic $[R_nSnX_{n-1}]^+[Y]^-$ complexes of organotin compounds over the past two decades [1-4]. A relatively little work has been reported on the synthetic and structural chemistry of the anionic complexes [5]. Acceptor properties of tin (IV) halides and organo (C_6F_5-) substituted tin (IV) halides have not been studied to a considerable extent.

The system $R_{4-n}SnCl_n + R'_4NCl$ ($R = C_6H_5-, n-C_4H_9-, R' = CH_3-, C_2H_5-$ & $n = 2, 3$) has been studied by both potentiometrically and conductometrically in acetonitrile indicating that the ability to form complexes decreases in the given sequence for penta-coordination anionic complexes [6].



The Ph_2SnCl_2 has moderate tendency to form such type of complexes but it was observed by the present investigation that replacement of phenyl group form Ph_2SnCl_2 by pentafluorophenyl group; C_6F_5- enhances the complex forming tendency [7].

Grim and Seyferth [8] were the first to propose the halo bridged derivative structure for the anion $[(CH_3)_3SnBr_2]^-$ assuming that the tin atom could only have tetrahedral and octahedral arrangement. A Trigonal bipyramidal (TBP) has also been confirmed for the complexes of type $[Me_2SnCl_3]^-$ anion having more electronegative group on axial site.

Bhattacharya et al. [9] reported the formation of halo or pseudohalo complex organotin anion balancing organo group V (15th) metal cation $[R_4M]^+$.

The pentafluorophenyl group directly attached to tin enhances the acceptor property of tin to such an extent so as to facilitates the formation of anionic complexes from moderate to significant extent in which coordination number of central metal atom i.e. Sn get increased beyond four [10].

The present work deals with the synthesis and isolation of anionic complexes of $(C_6F_5)_2SnCl_2$ with quaternary organo ammonium, -arsonium and -stibonium salts; R_4MY where $R = CH_3-$ in case of R_4NY and $R = C_6H_5-$ in case of R_4SbY and R_4AsY . A series of complexes were obtained and are characterised by elemental analysis, molar conductance, molecular weight data and spectroscopic techniques (Infrared). The structure of the complexes has been assigned on the basis of spectroscopic techniques.

2 RESULTS AND DISCUSSION

Tetrakis (pentafluorophenyl) tin; $(C_6F_5)_4Sn$ and bis (pentafluorophenyl) tin (IV) chloride; $(C_6F_5)_2SnCl_2$ were obtained by Wurtz-Fittig reaction and redistribution reaction respectively (Eq. 1-2). The complex forming reactions were accompanied by derivatisation reaction by the reaction of bis (pentafluorophenyl) tin (IV) chloride with quaternary ammonium, -arsonium, -stibonium salts in acetonitrile as solvent.

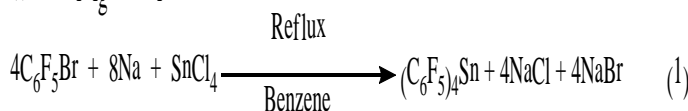
In the present work a series of unreported bis (pentafluorophenyl) tin dichloro pseudohalo anions; $[(C_6F_5)_2SnCl_2Y_2]^{2-}$ ($Y = N_3^-, NCO^-, NCS^-$) were synthesised and isolated in combination with balancing tetra ammonium, -arsonium and -stibonium cation $[R_4M]^+$ ($R = CH_3-$ in case of $M = N$, $R = C_6H_5-$ where $M = As, Sb$).

Under anhydrous oxygen free condition neutral adduct of type $[R_4M]_2^+[(C_6F_5)_2SnCl_2Y_2]^{2-}$ could be obtained by the interaction of bis (pentafluorophenyl) tin (IV) chloride with tetraorgan ammonium, -arsonium and -stibonium salts (Eq.

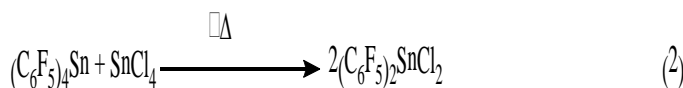
- Author names are Isha Rizvi, Prof. Amarika Singh from Institute of Engineering & Technology, a constituent college of G. B. T. U., Sitapur Road Lucknow and Dharmendra K. Srivastava, Chem. Dept. Lucknow University.
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3), (Fig. 1).

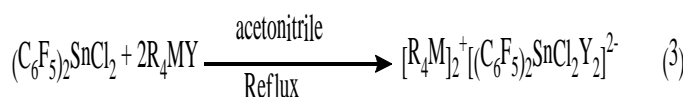
Wurtz-Fittig Reaction:



Redistribution Reaction:



Derivatisation Reaction (Complex Formation):



[Where M = N, As, Sb; R = CH₃, C₆H₅; Y = NCS⁻, N₃⁻, NCO⁻]

The probable solid state structure of these complexes was derived on the basis of analytical, conductance and spectroscopic (Infrared) studies.

The newly synthesised complexes (Table-1) were characterised to be the organoammonium, -arsonium, -stibonium salts of the diorganotin (IV) anion by analytical data showing that bis (pentafluorophenyl) tin (IV) chloride can expand their coordination sphere due to enhancement of acceptor property by pentafluorophenyl organic group directly attached to Sn in presence of pseudohalide as ligands such as N₃⁻, NCO⁻, NCS⁻. The constancy in the melting point of the products obtained on repeated crystallisation excludes any possibility of the presence of mixture of reactants. The compounds were white crystalline solid soluble in polar organic solvents. They were studied spectroscopically in infrared region 400-4000cm⁻¹ and their ionic nature has been confirmed from conductance measurements and Van't Hoff factor 'i' values.

2.1 SOLUTION PHASE STUDY

The values of molar conductance of the complexes (1 to 9) are in the range of 265-290 ohm⁻¹ cm² mol⁻¹ in acetonitrile and this shows the compounds to be 2:1 electrolyte [11] (Table-1). The observed molecular weight of the compounds 1-9 were approximately one third of the formula molecular weights, indicating that the complexes were dissociated in to three or two ions in the solution. The calculated values of Van't Hoff factor 'i' further confirmed that the complexes are 2:1 electrolyte.

2.2 INFRARED SPECTRA

The infrared absorptions due to pentafluorophenyl group bound to tin correspond to these reported in our previous paper published in IJSER [7, 10], while the vibrations due to cations also agree well with reported values [12]. The absorption assignments, therefore have not been discussed further, characteristic absorptions together with their possible assignments of the pseudohalide groups are mentioned 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 [11-13]. However, the isothiocyanate group (-NCS) which is attached to tin through the nitrogen can readily be distinguished from the position, intensity and shape of the symmetrical -NCS band [14]. In the anion containing isothiocyanate group, the vibrations occurs as a strong and broad band around 2035±5 cm⁻¹ suggesting it to be N bonded to tin [11] whereas the isothiocyanate bonding was indicated by very sharp N-C stretching band above 2050cm⁻¹ [11]. Similarly in case of isocyanate derivatives NCO was found to be N-bonded to Sn on the basis of Infrared data.

The most prominent absorption in the infrared spectra of the organotin anions containing an azide group are the asymmetric stretching frequency observed in the range 2025±10 cm⁻¹ and a much weaker symmetric mode at 1250 cm⁻¹ [15]. The position of asymmetric band is more in favour of covalently bonded -N₃ group to the central tin atom. However, a band observed at 675 cm⁻¹ is being assigned suggest the presence of a covalently bonded linear -N=N=N group. From the above experimental data and taking in to consideration the stereochemical studies reported so far on similar compounds an octahedral structure (Fig. 1) may be assigned to anion. This seems to be a general trend and exceptions are few.

3 EXPERIMENTAL

A general method as described below was employed for the preparation of anionic complexes of bis (pentafluorophenyl) tin (IV) chloride with pseudohalides employing stoichiometric amounts of the reactant (Eq. 1-3). Further details are given in Table-1

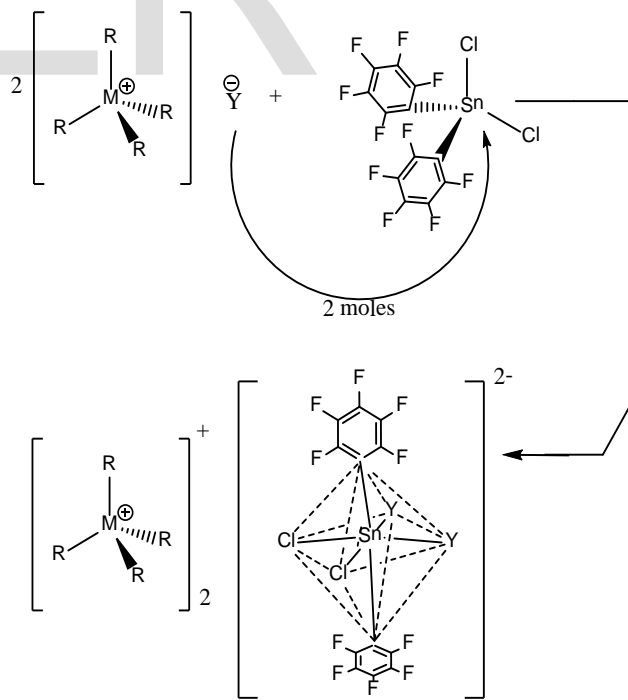
3.1 Synthesis of bis (pentafluorophenyl) tin anionic complexes

The complexes of type [R₄M]₂[(C₆F₅)₂SnCl₂Y₂] were prepared by refluxing for several hours 1mmole of (C₆F₅)₂SnCl₂ and 2 mmole R₄MY in acetonitrile or absolute alcohol. After concentrating and cooling the solution, a white crystalline solid was precipitated. The compounds was once again crystallised by acetonitrile. The melting points, elemental analysis, Infrared spectroscopic and solution studies are given in Table 1 to 3.

4 TABLES

5 FIGURES

Figure 1: Schematic Representation of Mechanistic view:



Anionic complex balanced with cationic quaternary cation

CONCLUSION

The replacement of phenyl group by pentafluorophenyl group

enhances the acceptor property to such an extent as to facilitate the formation of anionic complexes of R_2SnCl_2 type compounds. These newly synthesised anionic complexes have an octahedral disposition around central atom i. e. Sn

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