SYNTHESIS, CHARACTERIZATION AND STRUCTURAL STUDIES OF MIXED-LIGAND DIORGANOTIN(IV) ESTERS DERIVED FROM OXY-SULFUR/OXY-PHOSPHOROUS/CARBOXYLIC ACIDS

BY

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Submitted

In fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
OCTOBER 2008

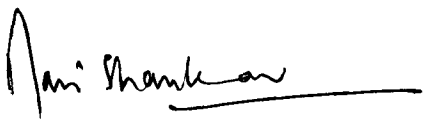
Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled "***SYNTHESIS, CHARACTERIZATION AND STRUCTURAL STUDIES OF MIXED-LIGAND DIORGANOTIN(IV) ESTERS DERIVED FROM OXY-SULFUR/OXY-PHOSPHOROUS/CARBOXYLIC ACIDS***" being submitted by **Mr. Atul Pratap Singh** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him.

Atul Pratap Singh has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.



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ATUL PRATAP SINGH

ABSTRACT

It has been well known that dimethyl sulfite undergoes isomerization to methylmethanesulfonate in presence of catalytic amount of tri-*n*-butylamine, featuring sulfur-centered Arbuzov rearrangement. However, the reactivity behavior of organic sulfites towards organometallic bases has not been explored until a recent report on the utility of dimethyl sulfite in the isolation of mixed-ligand diorganotin(methoxy)methanesulfonates, $R_2Sn(OMe)OSO_2Me$ (R = *n*-Pr, *n*-Bu, *c*-Hex).

$$R_2SnO + MeO\text{-}S(O)\text{-}OMe \xrightarrow[40\text{-}45\ h]{125\text{-}130\ ^oC} R_2Sn(OMe)OSO_2Me$$

R = *n*-Pr, *n*-Bu, *i*-Bu, *c*-Hx

The work presented in this thesis is devoted to the synthesis and characterization of mixed-ligand di-*n*-butyltin alkanesulfonates, [*n*-$Bu_2Sn(L)OSO_2R$] (R = Me, Et, *n*-Pr, L = alkoxy, acac, carboxylate, phosphonate) bearing a co-ligand (L) of ambidentate character on the same tin center. A consistent effort has been directed to develop new synthetic protocols for this family of tin-ester derivatives with particular emphasis on utilizing higher dialkyl sulfite, $(RO)_2SO$ (R = Et, *n*-Pr) as the reagent. The isomerization process in dialkyl sulfites via sulfur-centered Arbuzov rearrangement has been critically examined and aptly utilized to generate tin-alkanesulfonate bond(s).

A detailed account of the results is described in chapters 3-6 and summarized as follows:

Chapter 3 - Synthesis and characterization of di-*n*-butyltin(alkoxy)alkanesulfonates, [*n*-$Bu_2Sn(OR)OSO_2R]_n$ [R = Me, Et, *n*-Pr] and their reactivity behavior towards methyl/phenyl/*t*-butylphosphonic acid

The mixed-ligand di-*n*-butyltin(alkoxy)alkanesulfonates have been isolated from the direct reaction between di-*n*-butyltin oxide and the corresponding dialkyl sulfite in

presence of an alkyl iodide. The reaction in each case proceeds smoothly and provides a useful one pot synthetic route to the corresponding diorganotin(alkoxy)alkanesulfonates, **1-4**.

$$n\text{-}Bu_2SnO + RO\text{-}S(O)\text{-}OR + RI \xrightarrow[N_2,\ 40\text{-}45\ h]{100\text{-}110\ ^\circ C} n\text{-}Bu_2Sn(OR)OSO_2R$$

R = Et (**1**), *n*-Pr (**2**)

$$n\text{-}Bu_2SnO + RO\text{-}S(O)\text{-}OR + MeI \xrightarrow[N_2,\ 40\text{-}45\ h]{100\text{-}110\ ^\circ C} n\text{-}Bu_2Sn(OR)OSO_2Me$$

R = Et (**3**), *n*-Pr (**4**)

The identity of each compound has been established by IR, multinuclear (^1H, $^{13}C\{^1H\}$ and ^{119}Sn) NMR and FAB mass spectral studies. The presence of an alkanesulfonate group in **1-4** strongly suggests that these reactions proceed via the isomerization of dialkyl sulfites. The key mechanistic steps involved in this transformation and the role of alkyl iodide in the isomerization process have been proposed. All attempts to grow suitable quality crystals for X-ray structural analysis have not been successful.

These compounds react with a number of phosphonic acids under mild conditions to afford mixed-ligand diorganotin derivatives, **5-13** bearing both alkanesulfonate and phosphonate groups on the same tin center. The chemoselective reactivity of the precursor tin complexes towards phosphonic acids is in accord with the more basic character of the alkoxide group as compared to the alkanesulfonate.

$$n\text{-}Bu_2Sn(OR)OSO_2R + R^1P(O)(OH)_2 \xrightarrow[rt,\ 6\text{-}8\ h]{DCM} [n\text{-}Bu_2Sn(OP(O)(OH)R^1)OSO_2R]_n$$

R^1 = Me, R = Me (**5**), Et (**6**), *n*-Pr (**7**)

R^1 = Ph, R = Me (**8**), Et (**9**), *n*-Pr (**10**)

R^1 = *t*-Bu, R = Me (**11**), Et (**12**), *n*-Pr (**13**)

All the mixed-ligand tin esters isolated above are quite stable and soluble in common organic solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$ and DMSO etc. The identity of each

compound is established by IR, multinuclear (^{1}H, $^{13}C\{^{1}H\}$ and ^{119}Sn) NMR as well as X-ray crystallography (for **5**, **6**, **8**, **10** and **11**). The molecular structures of **5**, **6**, **10** and **11** correspond to a centrosymmetric dimer based on an eight-membered -(Sn-O-P-O-)$_2$ ring, formed by bridging bidentate mode of the hydrogenmethyl/hydrogenphenyl/hydrogen-*t*-butylphosphonate groups. However, significant structural differences are discernible as a result of varying disposition of the alkanesulfonate groups around the tin atoms. For **6, 10** and **11**, the monomeric units are associated with one another by virtue of bridging bidentate mode of methane/ethane/*n*-propanesulfonate groups and form one-dimensional polymeric chain comprising of alternate -(O-S-O-Sn-)$_2$ and -(O-P-O-Sn-)$_2$ eight-membered rings (figure 1). On the other hand, the structure of **5** represents a two-dimensional motif (figure 2) in which the methanesulfonate groups provide layer connectivity and result in the formation of centrosymmetric 24-membered hexa-tin macrocyclic rings.

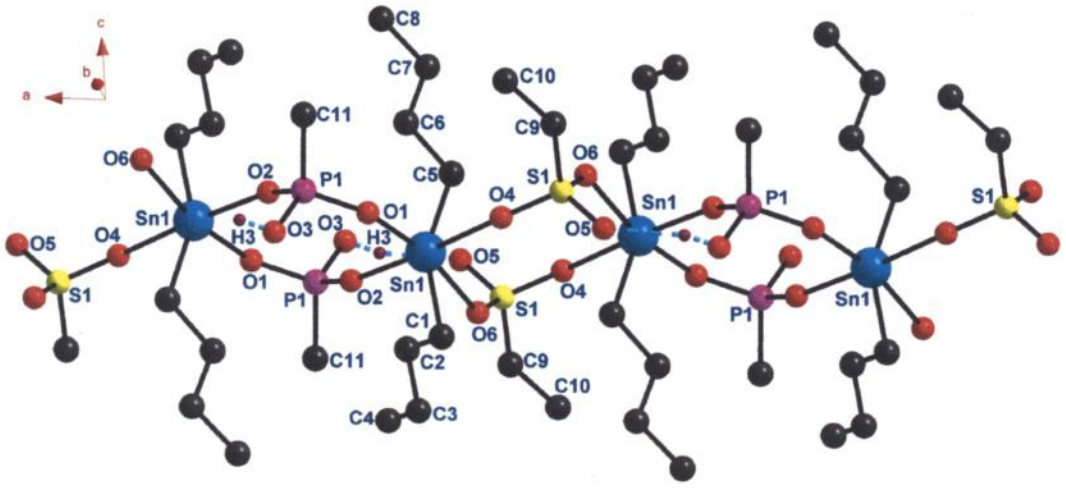

Figure 1. 1D structure of **6.**

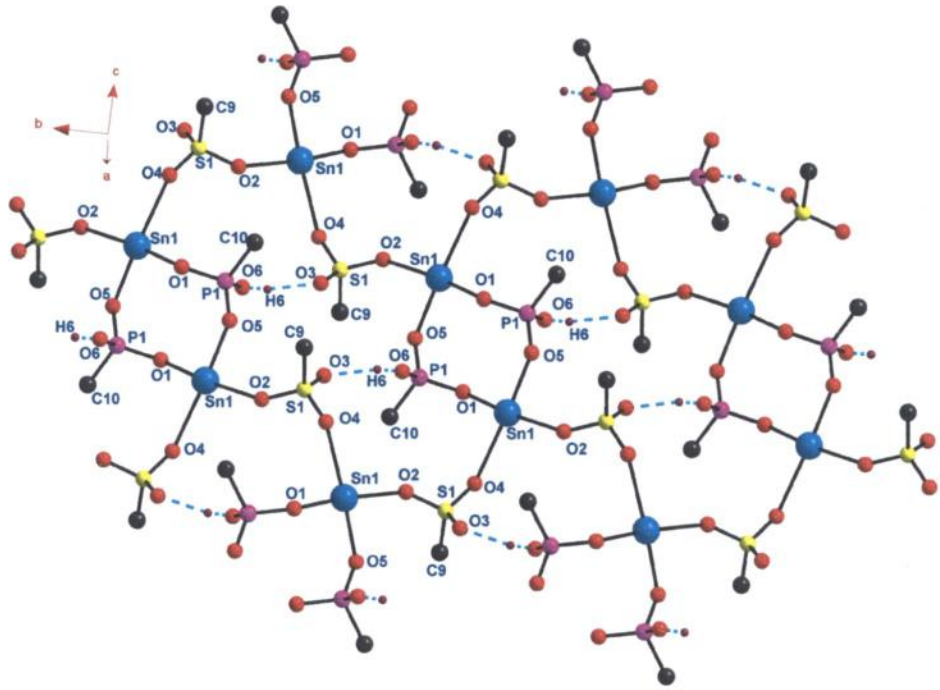

Figure 2. 2D structure of **5**.

The tin atoms in these compounds adopt a distorted octahedral geometry with basal plane defined by SnO_4 core. The Sn-O_P and Sn-O_S bond lengths lie in the range of 2.06-2.09 and 2.46-2.62 Å, respectively.

The structure of $[n\text{-}Bu_2Sn(OP(O)(OH)Ph)OSO_2Me]_n$ (**8**) adopts a 3-D motif by virtue of varying coordination modes of methanesulfonate (μ_1, μ_3) and hydrogenphenylphosphonate (μ_2) groups. The asymmetric unit is comprised of a tetramer with four crystallographically unique tin atoms (figure 3a). The structure reveals a central eight-membered -(Sn-O-S-O-)$_2$ cyclic ring with two exocyclic tin atoms (Sn1 and Sn4) which results from μ_3-binding mode of the two methanesulfonate groups (S2 and S3). The remaining two methanesulfonate groups (S1 and S4) on the exocyclic tin atoms are

monodentate and contribute in (P)O-H---O hydrogen bonding. The structure is extended into three-dimensional coordination polymer with the aid of hydrogenphenylphosphonate group on each tin atom acting in μ_2-O_2P mode and forming a series of eight-membered -(Sn-O-P-O-)$_2$ rings in the structural framework (figure 3 b).

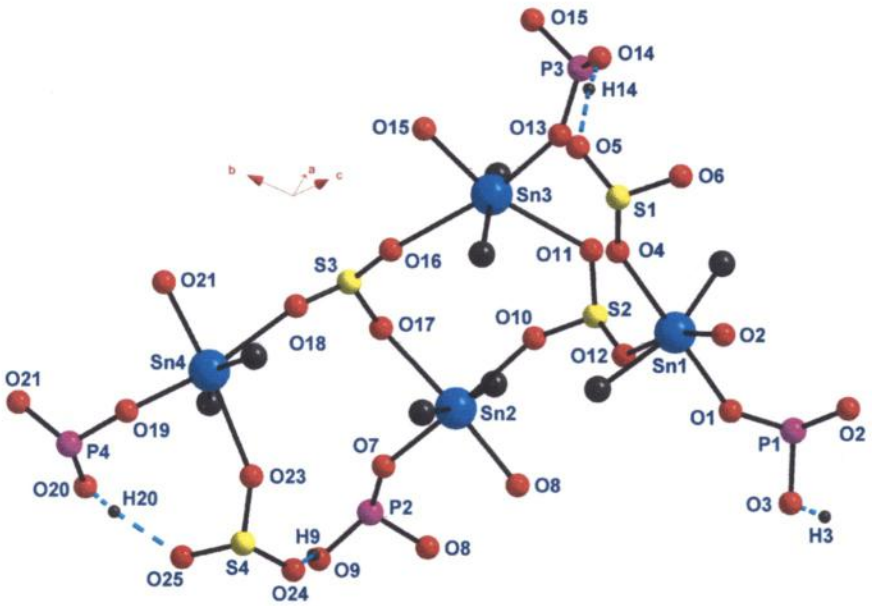

Figure 3a. Asymmetric unit of **8**

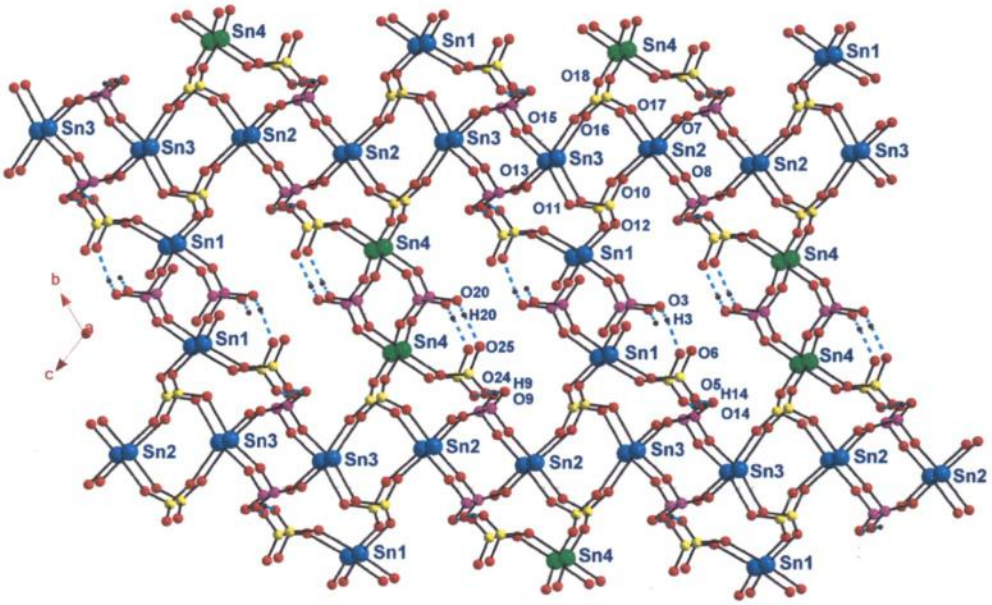

Figure 3b. 3D structure of **8**

Each tin atom in the extended structure adopts a distorted octahedral geometry. The mean Sn-O_S (2.35-2.64 Å) bond lengths across the four methanesulfonate groups are found to be much larger than those observed for Sn-O_P bonds (2.09-2.12 Å).

Chapter 4. Reactivity behavior of di-*n*-butyltin(alkoxy)alkanesulfonates, [*n*-$Bu_2Sn(OR)OSO_2R$] [R = Et, *n*-Pr] towards acetylacetone and 4-methoxy-2-quinoline/2-quinoline/1-isoquinoline carboxylic acid

In chapter 3, it has been shown that di-*n*-butyltin(alkoxy)alkanesulfonates, *n*-$Bu_2Sn(OR)OSO_2R$ (R = Et, *n*-Pr) are excellent precursors for the synthesis of mixed-ligand diorganotin esters bearing both alkanesulfonate and hydrogenphosphonate groups on the same tin center. It was of interest to understand the structural features and bonding behavior of related tin-alkanesulfonate derivatives bearing a co-ligand which has an affinity for chelation towards the metal center. The present chapter describes the synthesis, characterization and structural studies of *n*-$Bu_2Sn(L)OSO_2R$ (R = Et, *n*-Pr, L = acac, quinaldates). These are obtained from the reaction between di-*n*-butyltin(alkoxy)alkanesulfonates, *n*-$Bu_2Sn(OR)OSO_2R$ (R = Et, *n*-Pr) and acetylacetone or 4-methoxy-2-quinoline/2-quinoline/1-isoquinoline carboxylic acid under mild conditions.

$$2\ n\text{-}Bu_2Sn(OR)OSO_2R \xrightarrow[CH_2Cl_2,\ rt,\ 10\text{-}12\ h]{2\ Hacac} [n\text{-}Bu_2Sn(acac)OSO_2R]_2 + 2ROH$$

R = Et (**14**), *n*-Pr (**15**)

$$2\ n\text{-}Bu_2Sn(OR)OSO_2R \xrightarrow[CH_3CN,\ rt,\ 10\text{-}12\ h]{2\ R^1COOH} [n\text{-}Bu_2Sn(O_2CR^1)OSO_2R]_2 + 2ROH$$

R^1 = 4-OMe-C_9H_5N-2, R = Et (**16**), *n*-Pr (**17**)
R^1 = C_9H_6N-2, R = Et (**18**), *n*-Pr (**19**)
R^1 = C_9H_6N-1, R = Et (**20**), *n*-Pr (**21**)

All the compounds obtained above are white crystalline solids and are soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, methanol, etc. The spectroscopic data [IR, multinuclear (^{1}H, $^{13}C\{^{1}H\}$ and ^{119}Sn) NMR, FAB mass] in solution are in conformity with the composition of each compound and suggest associated structural motifs. Further corroboration of the structural features has been established by X-ray crystal structures of the compounds, **14-16**.

The structures of $[n\text{-}Bu_2Sn(acac)OSO_2R]_2$ (R = Et (**14**), *n*-Pr (**15**)) comprise of two independent molecules in the unit cell. The primary structural motif in these molecules is quite similar and is reminiscent of eight-membered -(Sn-O-S-O-)$_2$ ring formed by virtue of bridging bidentate ethane/*n*-propanesulfonate groups while acetylacetonate moiety acts in chelating bidentate fashion (figure 4a). The centrosymmetric dimers thus formed possess a distorted octahedral geometry around each tin atom with the basal plane defined by SnO_4 core (360 ± 0.1°). The covalent Sn-O_S bond lengths lie in the range of 2.22-2.48 Å.

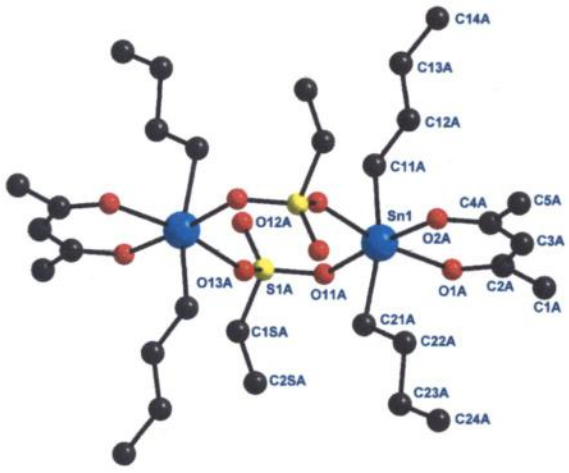

Figure 4a. Molecular structure of **14**.

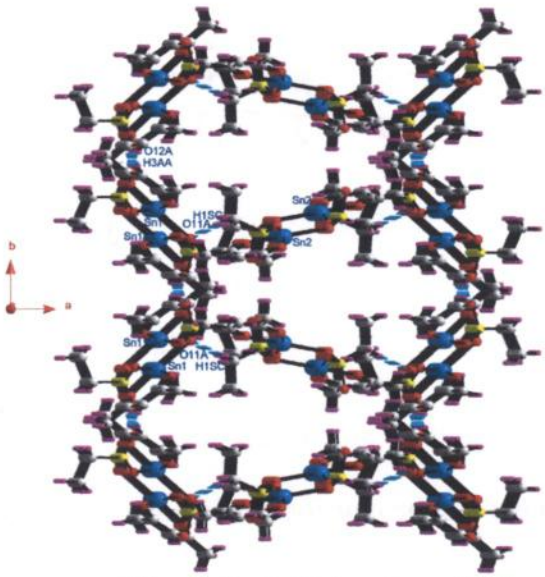

Figure 4b. 3-D structure of **14**.

The primary structure of **14** extends into 2-D supramolecular motif by virtue of CH…O hydrogen bonding interactions between the enolic hydrogen (H3AA) of acetylacetonate and oxygen atom (O12A) of the adjacent sulfonate groups. The 2D polymeric tape like structure (ab-plane) is further extended to a 3D motif by intermolecular CH---O hydrogen bonds involving the SCH_2 protons of the other independent molecule designated with Sn2 atom (figure 4b).

The molecular structure of $[n\text{-}Bu_2Sn(4\text{-}OMe\text{-}O_2CC_9H_5N\text{-}2)OSO_2Et]_2$ (**16**) is shown in figure 5. The structure finds an analogy with that of **14** in respect of the bridging bidentate mode of the ethanesulfonate group and the dimeric entity thus formed is comprised of centrosymmetric -(Sn-O-S-O-)$_2$ eight-membered ring. The carboxylate ligand is bonded to each tin atom by {N, O} chelation while other carboxylate oxygen remains free.

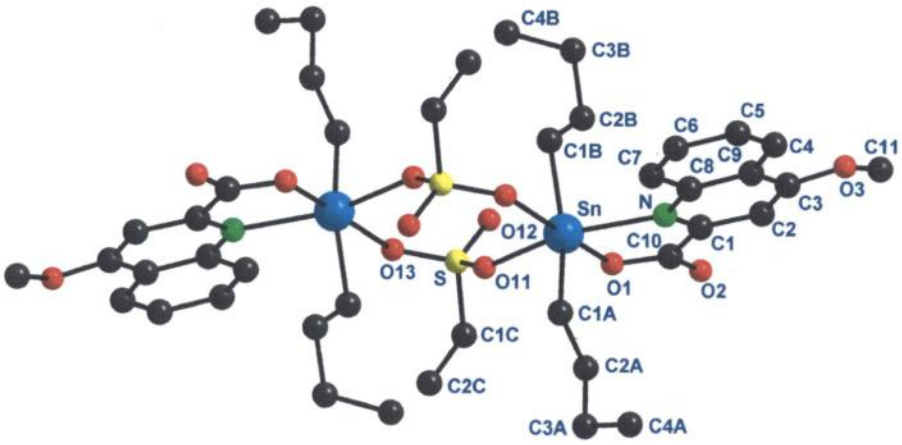

Figure 5. Crystal structure of **16**.

The geometry around each tin atom is distorted octahedron with planer SnO_3N core occupying the equatorial position (360 ± 0.07 Å) with trans *n*-butyl groups. Notably, the observed covalent Sn-O bond lengths associated with carboxylate (Sn-O1 = 2.085(16) Å)

and ethanesulfonate (Sn-O11 = 2.190(15) Å) groups are quite comparable and lie at the upper end of the normal range expected for the Sn-O covalent bond (1.9-2.1 Å).

Chapter 5. Synthesis and characterization of diorganostannates, $[R_2Sn(OSO_2R^1)_4].2[R^2{}_4N]$ (R = *n*-Pr, *n*-Bu, Ph; R^1 = Me, Et, *n*-Pr; R^2 = alkyl)

In chapter 3, it has been demonstrated that the affinity of dialkyl sulfites to isomerize into the corresponding alkanesulfonate moiety in presence of an alkyl iodide has led to the isolation of novel class of mixed-ligand di-*n*-butyltin(alkoxy)alkanesulfonates, **1-4**. As a part of continued interest in the development of new synthetic protocols involving dialkyl sulfites as the reagent in organotin chemistry, we initiated the reactivity of diorganotin oxide with various dialkyl sulfites in presence of triethyl amine or tetraalkylammonium iodide. These reactions proceed under ambient conditions (110-120 °C, 20 h) via sulfur-centered Arbuzov rearrangement in dialkyl sulfite to afford the corresponding dianionic tetraalkanesulfonato diorganostannates, **22-30** respectively.

$$R_2SnO + 4MeO\text{-}\overset{\overset{O}{\|}}{S}\text{-}OMe + 2Et_3N \xrightarrow[20\ h]{110\text{-}120\ ^\circ C} [R_2Sn(OSO_2Me)_4].2[Et_3NMe] + MeOMe$$

R = *n*-Pr (**22**), *n*-Bu (**23**), Ph (**24**)

$$n\text{-}Bu_2SnO + 4R^1O\text{-}\overset{\overset{O}{\|}}{S}\text{-}OR^1 + 2R^2{}_4NI \xrightarrow[20\ h]{110\text{-}120\ ^\circ C} [n\text{-}Bu_2Sn(OSO_2R^1)_4].2[R^2{}_4N] + 2R^1I + R^1OR^1$$

R^1 = Me, R^2 = Et (**25**), *n*-Bu (**26**)
R^1 = Et, R^2 = Et (**27**), *n*-Bu (**28**)
R^1 = *n*-Pr, R^2 = Et (**29**), *n*-Bu (**30**)

The identity of these compounds has been established by IR, multinuclear (^1H, $^{13}C\{^1H\}$ and ^{119}Sn) NMR spectral studies in $CDCl_3$ solution. The ESI (negative ion) mass spectrum of each compound in acetonitrile solution shows an isotopic cluster pattern corresponding to penta-coordinated tin species $[R_2Sn(OSO_2R^1)_3]^-$ as the predominant

peak. The formation of these species in solution has been further supported by comparison of the $^{119/117}$Sn NMR data both in solution and solid state.

X-ray crystal structures of $[R_2Sn(OSO_2Me)_4].2[Et_3NMe]$ [R = *n*-Bu (**23**), Ph (**24**)] as well as $[n\text{-}Bu_2Sn(OSO_2Me)_4].2[Et_4N]$ (**25**) have revealed that the structural motifs of the dianion in each case is identical and consists of a discrete monomer in which the tin atom adopts a distorted octahedron geometry by virtue of four uniquely disposed monodentate methanesulfonate groups with SnO_4 core defining the basal plane (360 ± 0.11°). The Sn-O_S bond lengths (2.19-2.29 Å) suggest a predominantly covalent character in all the stannates under study. The molecular structures of **23** and **24** are shown in figures 7 and 8 respectively.

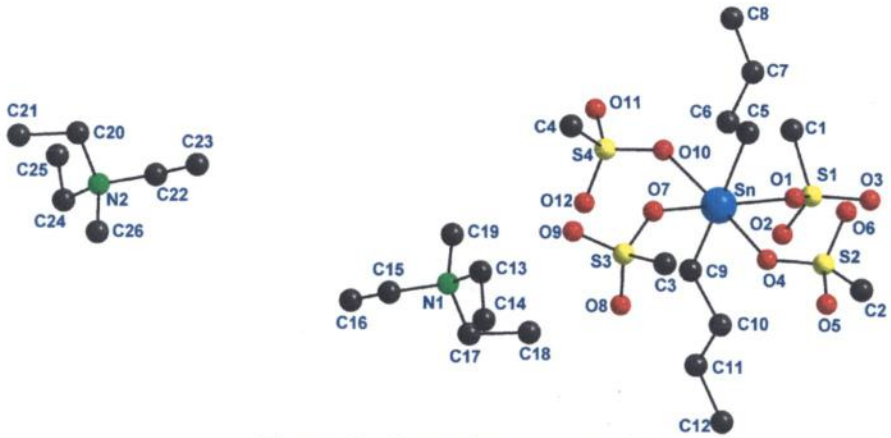

Figure 7. Crystal structure of **23**.

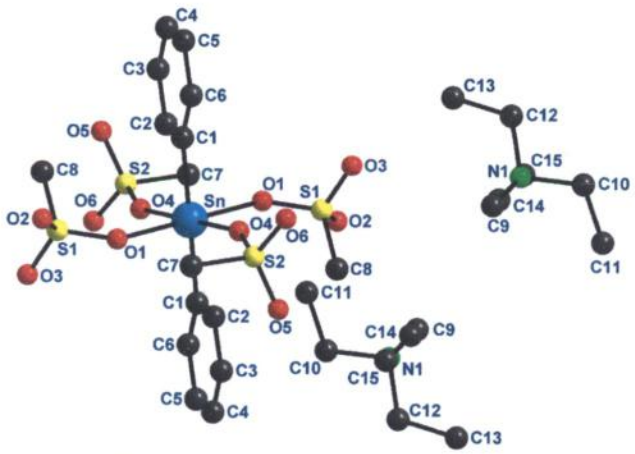

Figure 8. Crystal structure of **24**.

Chapter 6. Synthesis and characterization of diorganotin bis(alkylsulfite)s, $R_2Sn(OS(O)OR^1)_2$ (R = *n*-Pr, *n*-Bu, R^1 = Me, Et, *n*-Pr, *i*-Pr)

This chapter describes the synthesis and characterization of a series of diorganotin bis(alkylsulfite)s, $R_2Sn(OS(O)OR^1)_2$ (R = *n*-Pr, *n*-Bu, R^1 = Me, Et, *n*-Pr, *i*-Pr) (**31-38**). These are accessible by reaction of diorganotin oxide (2 equivalent) with excess of the corresponding dialkyl sulfite (12 equivalent) in presence of iodine (1 equivalent) under mild conditions (50-60 °C, 20 h, N_2).

$$R_2SnO + R^1O\text{-}S(O)\text{-}OR^1 \xrightarrow[50\text{-}60\ ^\circ C,\ 20\ h]{I_2} R_2Sn(OS(O)OR^1)_2$$

R^1 = Me, R = *n*-Bu (**31**), *n*-Pr (**32**)
R^1 = Et, R = *n*-Bu (**33**), *n*-Pr (**34**)
R^1 = *n*-Pr, R = *n*-Bu (**35**), *n*-Pr (**36**)
R^1 = *i*-Pr, R = *n*-Bu (**37**), *n*-Pr (**38**)

The isolation of these compounds represents yet another potential application of organic sulfites in synthetic organotin chemistry of oxy-sulfur acids. The role of I_2 in selective C-O bond cleavage in dimethyl sulfite and the stabilization of methyl sulfite ion in the form of charge transfer complex, $[D\text{-}I]^+[MeOS(O)O]^-$ (D = dimethyl sulfite) have been studied by UV/Vis spectroscopy. All the tin sulfites obtained have been characterized by IR, multinuclear (^1H, $^{13}C\{^1H\}$ and ^{119}Sn) NMR spectroscopy and thermogravimetric analysis (TGA).

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