SYNTHESIS, CHARACTERIZATION AND STRUCTURAL STUDIES OF MIXED-LIGAND DIORGANOTIN(IV) BASED COORDINATION POLYMERS BEARING PHOSPHONATE/SULFONATE/ CARBOXYPHOSPHONATE LIGANDS

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by

ARCHANA JAIN

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the

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Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled "***Synthesis, characterization and structural studies of mixed-ligand diorganotin(IV) based coordination polymers bearing phosphonate/sulfonate/carboxyphosphonate ligands***" being submitted by Ms. Archana Jain 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 her.

Archana Jain 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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ABSTRACT

The work presented in this thesis relates to synthesis and structural studies of mixed ligand diorganotin based coordination polymers involving alkanesulfonate and phosphonate/carboxyphosphonate ligands in the structural frameworks. In view of paucity of literature precedence, major emphasis has been devoted to develop new synthetic methods for this class of organotin compounds and understand the role of ambidentate ligands in the construction of higher dimensional structural motifs. The thesis is divided into five chapters.

Chapter I - Introduction

This chapter deals with a survey of literature highlighting synthetic methods and structural aspects of organotin compounds derived from phosphonic/sulfonic acids. A brief account of the structural diversities among these organotin derivatives arising from different bonding modes of the ligands is presented.

Chapter II - Materials and methods

This chapter includes a detailed description of synthetic procedures which have been followed during the course of the work. In addition, various spectroscopic methods such as IR and multinuclear (^{1}H, $^{13}C\{^{1}H\}$, ^{31}P and ^{119}Sn) NMR as well as single crystal X-ray diffraction studies, which are routinely used for the characterization of the new compounds are summarized.

Chapter III – Synthesis, characterization and hydrolysis behavior of diorganotin(alkoxy)alkanesulfonates, $[R_2Sn(OR^1)OSO_2R^1]_n$

Synthesis of diorganotin(alkoxy)alkanesulfonates, $[R_2Sn(OR^1)OSO_2R^1]_n$ (R = Me, R^1 = Me (**1**), Et (**2**); R = Et, R^1 = Me (**3**), Et (**4**)) has been achieved from the reaction of an

appropriate diorganotin oxides with excess of dialkyl sulfite, $(R^1O)_2S{=}O$ (R^1 = Me, Et) in presence of an alkyl iodide.

$$R_2SnO + R^1O\text{-}S(O)\text{-}OR^1 + R^1I \xrightarrow[40\text{-}45\ h]{100\text{-}110\ ^oC} R_2Sn(OR^1)OSO_2R^1$$

R = Me, R^1 = Me (**1**), Et (**2**);
R = Et, R^1 = Me (**3**), Et (**4**)

Isolation of these compounds has expanded the scope of dialkyl sulfites as reagents in synthetic chemistry of organotin alkanesulfonates as already described in a few recent reports. The transformation of dialkyl sulfite into an alkanesulfonate moiety *via* S-centered Arbuzov-type rearrangement is evident in these reactions.

X-ray crystallographic studies of **1** and **2** present the first snapshot of the structural motifs among this family and reveal the formation of one-dimensional coordination polymer in each case featuring a unique disposition of alternate four-membered $-[Sn{-}O{-}]_2$ and eight-membered $-[Sn{-}O{-}S{-}O{-}]_2$ cyclic rings which are formed by μ_2-bonding of alkoxy and alkanesulfonate groups (figure 1). The Sn-O bond lengths lie in the range of 2.11-2.16 and 2.33-2.42 Å respectively. Each tin atom in the extended structures adopts

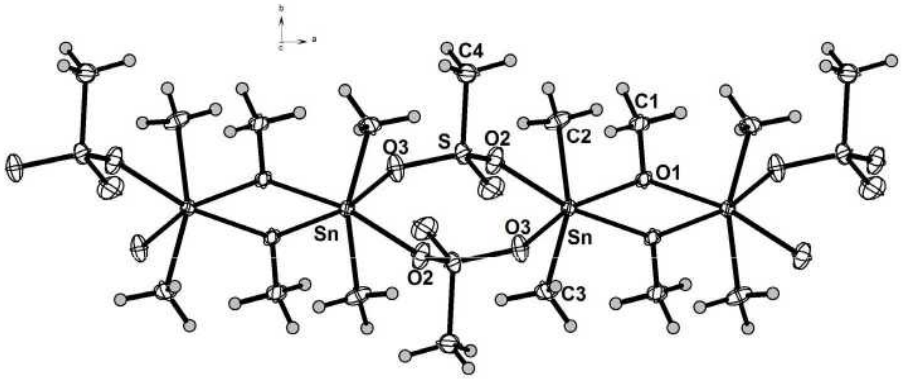

Figure 1. ORTEP view of 1D polymeric chain of $[Me_2Sn(OMe)OSO_2Me]_n$.

distorted octahedral geometry with SnO_4 basal plane and trans disposition of two alkyl groups. Intrestingly, the alkanesulfonate groups also function as both H-donor and acceptor and exhibit strong CH---O hydrogen bonding interactions. These secondary interactions provide inter-chain connectivity and result in the formation of three- and two-dimensional structural motifs for **1** and **2**, respectively.

A study of hydrolysis behavior of these tin precursors under controlled conditions offers a new route to construct novel organotin clusters bearing oxo-/hydroxo- and alkanesulfonate ligands. Controlled hydrolysis of dimethyltin(ethoxy)ethanesulfonate, **2** in moist hexane (hexane:water = 95:5v/v) proceeds at room temperature *via* partial cleavage of Sn-C and S-C bonds to afford the formation of a novel pentanuclear tin cluster, $[(Me_2Sn)(MeSn)_4(OSO_2Et)_2(OH)_4(O)_2(SO_3)_2]$ bearing both methyltin and dimethyltin moieties as well as sulfite and ethanesulfonate ligands (figure 2). The cluster entity can be considered as a self-assembly of simple molecular constructs, $Me_2Sn(OSO_2Et)_2$, $[MeSn(OH)(SO_3)]_2$ (designated by Sn4 and Sn5) and

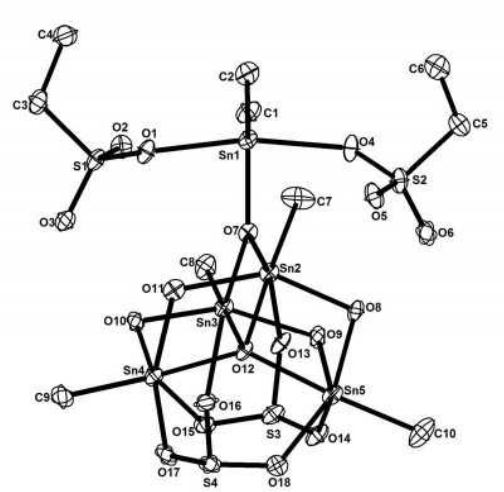

Figure 2. ORTEP view of the molecular structure of $[(Me_2Sn)(MeSn)_4(OSO_2Et)_2(OH)_4(O)_2(SO_3)_2]$.

$[MeSn(O)(OH)]_2$. Controlled hydrolysis of related mixed ligand tin precursors, $[Et_2Sn(OMe)OSO_2Me]_n$ and $[n\text{-}Bu_2Sn(OEt)OSO_2Et]_n$ under identical conditions affords products of compositions, $[(Et_2Sn)_4(OH)(O)_2(OSO_2Me)_3]$ and $[\{(n\text{-}Bu_2Sn)_2(OH)(OSO_2Et)\}O]_2$ respectively which have been structurally characterized by X-ray crystallography. The former is composed of three molecular sub-entities, $[Et_2SnO]_2$, $Et_2Sn(OH)OSO_2Me$ (designated by Sn1, Sn3 and Sn2 atoms respectively) and $Et_2Sn(OSO_2Me)_2$ in 1:1:1 stoichiometry (figure 3a). On the other hand, the later represents a ladder-like framework (figure 3b) which is constructed on a central distannoxane (Sn_2O_2) unit. The bridging hydroxyl groups (O10, O40) of di-*n*-butyltin(hydroxy)ethanesulfonate provide connectivity between Sn1, Sn2 and Sn3, Sn4 atoms, respectively. The role of alkanesulfonate groups in the execution of hydrogen bonding interactions (OH---O) is evident in the structures. A plausible mechanism is put -

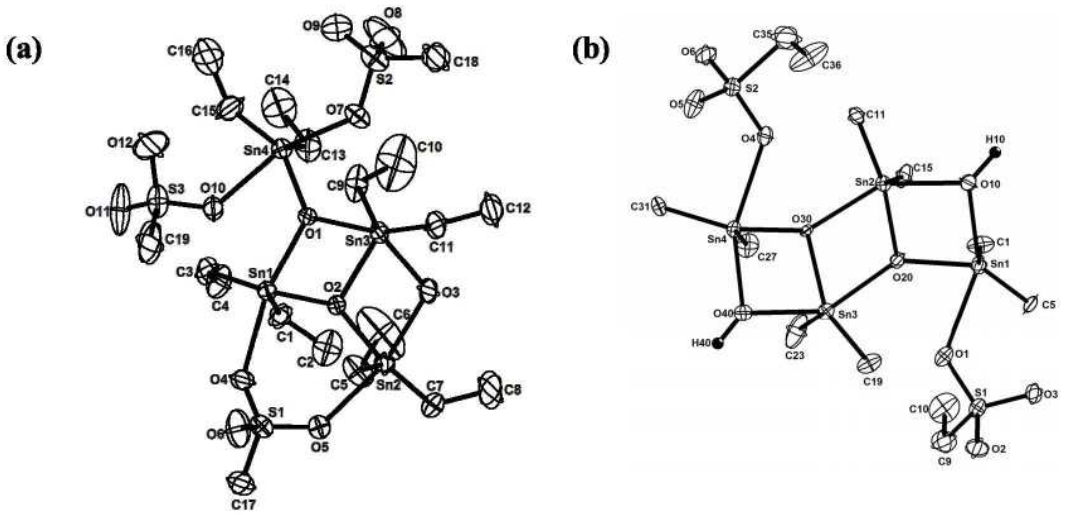

Figure 3. ORTEP view of the molecular structures of (a) $[(Et_2Sn)_4(OH)(O)_2(OSO_2Me)_3]$ and (b) $[\{(n\text{-}Bu_2Sn)_2(OH)(OSO_2Et)\}O]_2$

forth to rationalize the formation of simple constructs which self-assemble to form these coordination assemblies. $^{13}C\{^1H\}$ and ^{119}Sn NMR spectral data in DMSO-d_6 suggest complex dynamic behavior of these complexes in solution as a result of associative-dissociative phenomena. The summary of crystallographic data as well as selected bond lengths and angles for the compounds discussed in this chapter are given in tables A-1 to A-7 (see Appendix).

Chapter IV – Synthesis and characterization of diorganotin-based coordination polymers incorporating alkanesulfonate and phosphonate ligands

This chapter deals with a detailed study on the reactivity behavior of diorganotin(alkoxy)alkanesulfonates towards phosphonic acids. Using this approach, synthesis of new organotin based metal-organic frameworks (MOFs)/coordination polymers comprising of trinuclear tin-phosphonate clusters, $[(R_2Sn)_3(O_3PR^2)(OSO_2R^1)_2]$ as well as $-[Sn-O-S-O-]_2$ and $-[Sn-O-P-O-]_2$ cyclic rings has been achieved. The reactions of precursor tin complexes, **1-3** with equimolar quantity of *t*-butyl-/methylphosphonic acid proceed under mild conditions (dry CH_2Cl_2, rt, 8-10 h) to afford three dimensional coordination polymers. Inclusion of solvent molecules in these compounds appears from the solvent of crystallization.

$$3n\ R_2Sn(OR^1)OSO_2R^1 \ (\textbf{1-3}) + 2n\ R^2P(O)(OH)_2 \xrightarrow[\text{rt, 8h}]{CH_2Cl_2} [(R_2Sn)_3(O_3PR^2)_2(OSO_2R^1)_2.L]_n + 3n\ R^1OH + n\ R^1SO_3H$$

R = R^1 = Me, Et; R^2 = *t*-Bu, Me
L = $CHCl_3/CH_3OH$

All the compounds thus obtained have been characterized by spectroscopic methods [IR and multinuclear (^1H, $^{13}C\{^1H\}$, ^{31}P and ^{119}Sn) NMR] as well as X-ray crystallography.

The NMR spectroscopic data [$^{13}C\{^1H\}$: δ 25.12-9.31 (Me_2Sn/Et_2Sn; $^1J_{Sn-C}$ = 920-998 Hz)] in DMSO-d_6 suggest hexacoordinated tin environment in each case while the observed $^2J_{Sn-O-P}$ coupling constants (222-242 Hz) indicate the retention of tin-phosphonate bonds in solution state. As evident from X-ray crystallography, the asymmetric unit of each compound is quite similar and represents a trinuclear tin-phosphonate core with two of the tin atoms being covalently bonded to sulfonate groups. An illustrative example of the asymmetric unit of $[(Me_2Sn)_3(O_3PBu^t)_2(OSO_2Me)_2.2CHCl_3]_n$ is shown in figure 4. The ability of sulfonate side arm functionalties to act as μ_1, μ_2, or μ_3-coordination modes allows the primary structure to transform into three-dimensional metal organic frameworks, featuring rectangular voids which are occupied by solvent ($CHCl_3$) molecules.

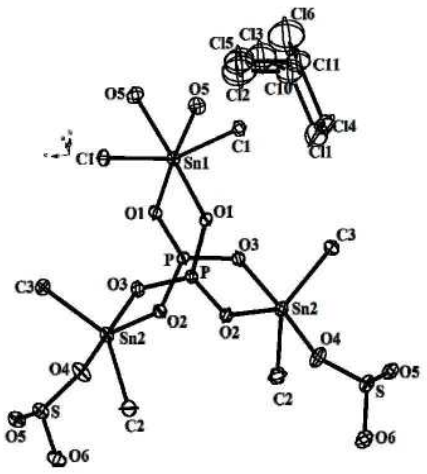

Figure 4. ORTEP view of the asymmetric unit of $[(Me_2Sn)_3(O_3PBu^t)_2(OSO_2Me)_2.2CHCl_3]_n$

A similar reaction of diethyltin(ethoxy)ethanesulfonate, **4** with methylphosphonic acid affords a product of the composition, $[(Et_2Sn)_4(O_3PMe)_2(O_2P(OH)Me)_2$-

$(OSO_2Et)_2.2H_2O]_n$. The asymmetric unit (figure 5) resembles a ladder-like motif comprising of $Sn_4P_4O_{10}$ core with two appended ethanesulfonate groups on each Sn2 atom and also contains two solvated water molecules which exhibit strong (P)O-H---O hydrogen bonding interactions. The ethanesulfonate groups act in a bridging bidentate fashion and results in the construction of one-dimensional polymeric chains. These chains are connected to one another via intermolecular OH---O hydrogen bonding involving the lattice water molecules, P(OH) and sulfonate moieties and thus provide layered connectivity in two-dimensional motif.

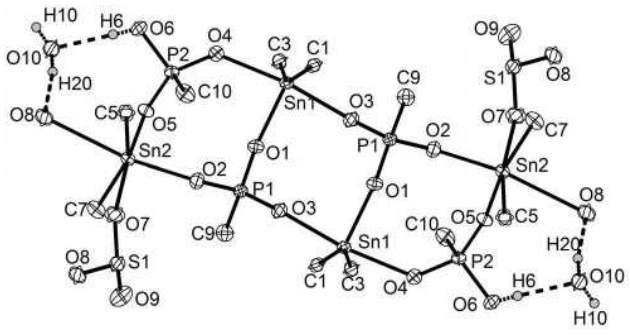

Figure 5. ORTEP view of the asymmetric unit of $[(Et_2Sn)_4(O_3PMe)_2(O_2P(OH)Me)_2$-$(OSO_2Et)_2.2H_2O]_n$.

The reactions of the tin precursors **1-4** with phenylphosphonic acid invariably result in the formation of one-dimensional coordination polymers of composition, $[R_2Sn(O_2P(OH)Ph)OSO_2R^1]_n$.

$$n\ R_2Sn(OR^1)OSO_2R^1 + n\ PhP(O)(OH)_2 \xrightarrow[\text{rt, 8 h}]{CH_2Cl_2} [R_2Sn(O_2P(OH)Ph)OSO_2R^1]_n + n\ R^1OH$$

1-4 $\qquad\qquad$ $R = R^1 = Me, Et$

The spectroscopic data [IR and multinuclear NMR] in DMSO-d_6 are in conformity with the composition of each compound. X-ray crystal structure analysis of

$[Et_2Sn(O_2P(OH)Ph)OSO_2Me]_n$ (figure 6) reveals that both sulfonate and hydrogenphosphonate ligands act in μ_2-coordination mode and form 1D polymer featuring alternate –[Sn–O–S–O–]$_2$ and –[Sn–O–P–O–]$_2$ eight-membered rings.

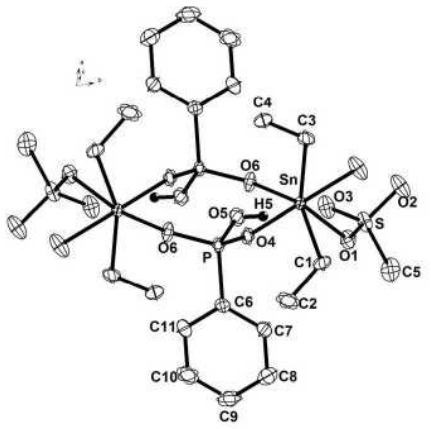

Figure 6. ORTEP view of the asymmetric unit of $[Et_2Sn(O_2P(OH)Ph)OSO_2Me]_n$.

As part of this synthetic study, we have examined the effect of solvent medium and presence of trace amount of water during the reactions of diorganotin(alkoxy)alkanesulfonates with *t*-butylphosphonic acid. Such variations in the reaction conditions allowed the formation of new secondary building units which are capable of forming novel coordination-driven self-assemblies. It is observed that the reactions of dimethyltin precursors, $[Me_2Sn(OR^1)OSO_2R^1]_n$ (R^1 = Me (**1**), Et (**2**)) with equimolar amount of *t*-butylphosphonic acid (rt, 8-10 h) in dry methanol result in the formation of identical products of composition, $[(Me_2Sn)_3(O_3PBu^t)_2(O_2P(OH)Bu^t)_2]_n$ [^{31}P NMR: δ 30.54 (br), 25.73 ($^2J_{Sn\text{-}O\text{-}P}$ = 248 Hz)].

$$3n\ Me_2Sn(OR^1)OSO_2R^1 \ (\mathbf{1, 2}) + 4n\ t\text{-}BuP(O)(OH)_2 \xrightarrow[rt,\ 8h]{CH_3OH} [(Me_2Sn)_3(O_3PBu^t)_2(O_2P(OH)Bu^t)_2]_n + 3n\ R^1OH + 3n\ R^1SO_3H$$

R^1 = Me (**1**), Et (**2**)

X-ray crystal structure of the compound reveals that peripheral functionalization of the otherwise rigid trinuclear tin-phosphonate core framework with $-O_2P(OH)t$-Bu ligand in the primary structure (figure 7) allows coordinative association as well as H-bonding interactions to facilitate the formation of a novel 3D supramolecular assembly. These results are quite unique in view of the fact that analogous reactions when carried out in dry CH_2Cl_2 medium (*vide supra*) provide access to mixed ligand diorganotin compounds, $[(Me_2Sn)_3(O_3PBu^t)_2(OSO_2R^1)_2.L]$ (R^1 = Me, Et; L = $2CHCl_3$, CH_3OH).

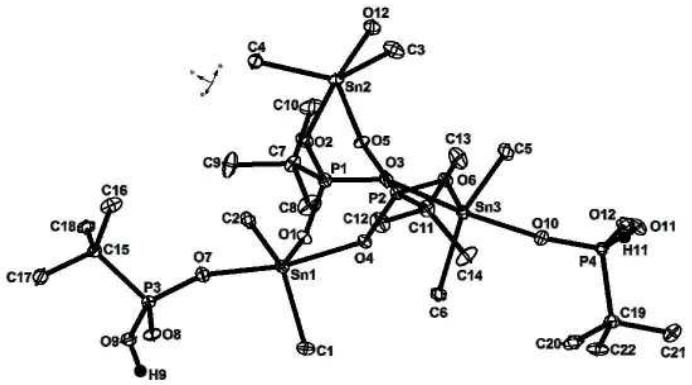

Figure 7. ORTEP view of the asymmetric unit of $[(Me_2Sn)_3(O_3PBu^t)_2(O_2P(OH)Bu^t)_2]_n$.

The reactions of $[Et_2Sn(OMe)OSO_2Me]_n$ with an equimolar quantity of *t*-butylphosphonic acid in presence of trace amount of water have been studied in dichloromethane and methanol medium separately. This has resulted in the isolation of new coordination driven self-assemblies, $[(Et_2Sn)_6(O_3PBu^t)_4(OSO_2Me)_4.L]_n$ (L = CH_2Cl_2, $2H_2O$) respectively. Despite similarities in their compositions, a marked variation is discernible in the organization of the simple molecular constructs, $(Et_2Sn)_3(O_3PBu^t)_2(OSO_2Me)_2$, $[Et_2SnO_3PBu^t]_2$ and $Et_2Sn(OSO_2Me)_2$ which co-crystallize in different spatial dispositions. The availability of active donor sites of the sulfonate

groups in the primary structures (figure 8) results in coordinative association to form three-dimensional self-assemblies. The summary of crystallographic data as well as selected bond lengths and angles for the compounds discussed in this chapter are given in tables A-8 to A-18 (see Appendix).

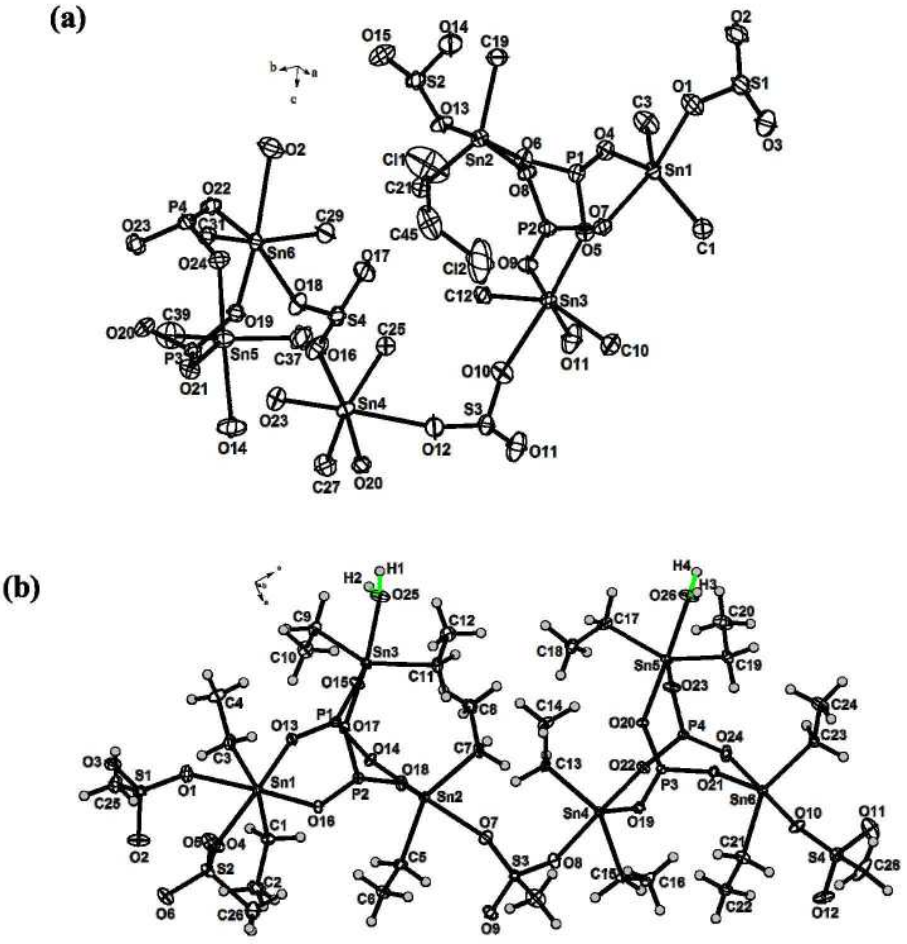

Figure 8. ORTEP view of the asymmetric units of (a) $[(Et_2Sn)_6(O_3PBu^t)_4(OSO_2Me)_4.CH_2Cl_2]_n$ and (b) $[(Et_2Sn)_6(O_3PBu^t)_4(OSO_2Me)_4.2H_2O]_n$

Chapter V – Reactivity behavior of diorganotin(alkoxy)alkanesulfonates towards 3-phosphonopropionic acid

This chapter describes the synthesis and characterization of coordination polymers of compositions, $[(Me_2Sn)_3(O_3PCH_2CH_2COOMe)_2(OSO_2R^1)_2]_n$ (R^1 = Me, Et) and $[R_2Sn(O_2P(OH)CH_2CH_2COOMe)OSO_2R^1]_n$ (R = Et, *n*-Bu; R^1 = Me, Et). These are accessible by reacting appropriate diorganotin precursors, $[R_2Sn(OR^1)OSO_2R^1]_n$ with 3-phosphonopropionic acid in dry methanol (rt, 8-10 h).

$$3n\ Me_2Sn(OR^1)OSO_2R^1 + 2n\ (HO)_2(O)PCH_2CH_2COOH \xrightarrow[8\ h,\ rt]{CH_3OH,} [(Me_2Sn)_3(O_3PCH_2CH_2COOMe)_2(OSO_2R^1)_2]_n + 3n\ MeOH + n\ MeSO_3H + 2n\ H_2O$$

R^1 = Me, Et

$$n\ R_2Sn(OR^1)OSO_2R^1 + n\ (HO)_2(O)PCH_2CH_2COOH \xrightarrow[8\ h,\ rt]{CH_3OH,} [R_2Sn(O_2P(OH)CH_2CH_2COOMe)OSO_2R^1]_n + n\ R^1OH + n\ H_2O$$

R = Et, *n*-Bu; R^1 = Me, Et

The formation of methylpropionate functionality on the phosphorus center in these compounds results from *in situ* esterification of the carboxylic groups. These have been characterized by IR and multinuclear [^1H, $^{13}C\{^1H\}$, ^{31}P and ^{119}Sn] NMR spectroscopy as well as X-ray crystallography in a few select cases.

The asymmetric unit of $[(Me_2Sn)_3(O_3PCH_2CH_2COOMe)_2(OSO_2Me)_2]_n$ shown in figure 9 resembles a trinuclear tin cluster comprising of $Sn_3P_2O_6$ framework which is

constituted by μ_3-coordination of the phosphonate groups. Each Sn1 atom of the core structural unit is functionalized with dangling methanesulfonate group. It is believed that the formation of methyl-ester moiety seems to be significant in protecting the otherwise potentially active donor sites of the carboxlylate groups and allows the construction of 2D assemblies with the aid of sulfonate moieties.

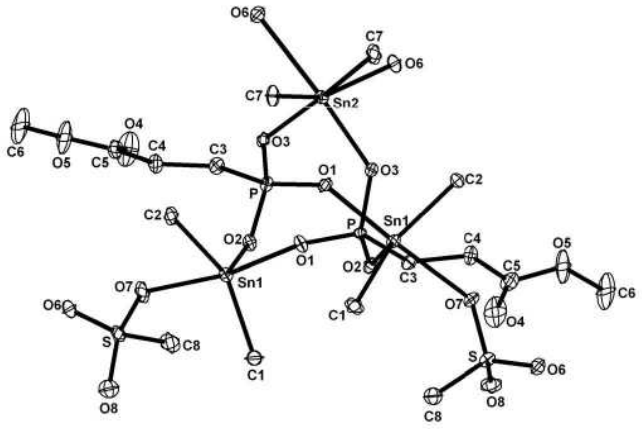

Figure 9. ORTEP view of the asymmetric unit of $[(Me_2Sn)_3(O_3PCH_2CH_2COOMe)_2(OSO_2Me)_2]_n$.

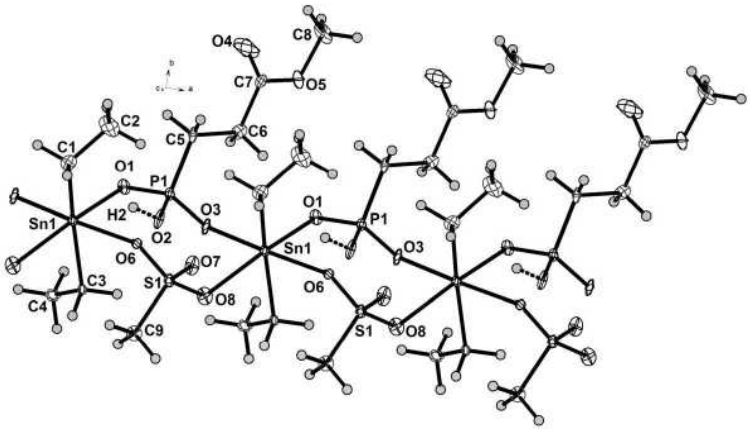

Figure 10. ORTEP view of 1D polymeric chain of $[Et_2Sn\text{-}(O_2P(OH)CH_2CH_2COOMe)OSO_2Me]_n$.

The construction of 1D coordination polymer in $[Et_2Sn\text{-}(O_2P(OH)CH_2CH_2COOMe)OSO_2Me]_n$ (figure 10) is unique in terms of repeating eight-membered cyclic rings containing Sn, O, P and S heteroatoms. The contribution from (P)O-H---O(S) hydrogen bonding interactions is found to be significant in the construction of two dimensional motif. The summary of crystallographic data as well as selected bond lengths and angles for the compounds discussed in this chapter are given in tables A-19 to A-22 (see Appendix).

CONTENTS

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