REACTIVITY STUDIES OF MIXED-LIGAND DIORGANOTIN COMPLEXES, $R_2Sn(X)OSO_2Me$ (X = OMe, OH)

BY

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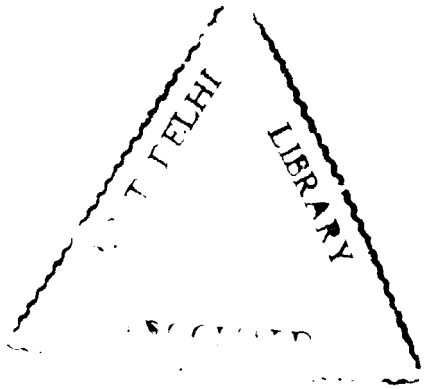

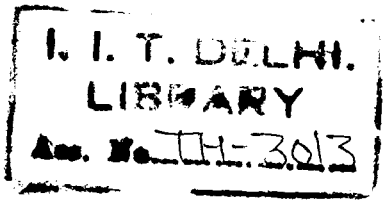

Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled, "***Reactivity Studies of Mixed-ligand Diorganotin Complexes, $R_2Sn(X)OSO_2Me$ (X = OMe, OH)***", being submitted by Mr. Mukesh Kumar to the Indian Institute of Technology, Delhi for the award of degree of Doctor of Philosophy is a bonafide research work carried out by him. Mr. Mukesh Kumar has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

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

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ABSTRACT

The work embodied in the present thesis is focussed on the synthesis and characterization of mixed-ligand diorganotin esters, $[R_2Sn(O_2CR')OSO_2Me]_n$. The synthetic protocol involving the reactions of precursor tin compounds, $R_2Sn(X)OSO_2Me$ [X = OMe (**1**), OH (**2**); R = n-Pr, n-Bu] with a variety of mono/dioic acids has been followed during the course of this study. Various factors which account the stability of these compounds are discussed by a critical analysis of the results obtained. It has been observed that the compounds derived from N-substituted aromatic carboxylic acids capable of {N, O} chelation are in general stable both in solid and solution state. On the other hand, analogous compounds derived from aliphatic dioic acids are unstable and undergo disproportionation to afford symmetrical diorganotin esters. Besides the spectroscopic data, structural motifs of these compounds have been elucidated from X-ray crystallography. Preliminary reactivity studies of the tin precursors, $R_2Sn(OH)OSO_2Me$ [R = n-Pr (**2a**), n-Bu (**2b**)] with ionic nucleophiles such as Bu_4NX (X = NO_3^-, F^-, OAc^-) and RLi (R = n-Bu, Me) are also described. These reactions proceed either via a nucleophilic addition on the tin center to yield trifunctional stannates or by ionic metathesis pathway which involves the cleavage of Sn-OSO_2Me bond.

A detailed account of the results is described in chapters III-V of the present dissertation. The contents of each chapter are summarized as follows:

Chapter III

Reactions of $R_2Sn(X)OSO_2Me$ [X = OMe (1), OH (2); R = n-Pr, n-Bu] with aromatic carboxylic acids—Isolation and characterization of $[R_2Sn(O_2CR')OSO_2Me]_n$ and $R_6Sn_3(O_2CC_5H_4N\text{-}2)_3(OSO_2Me)_3$

Chapter IV

Reactions of $R_2Sn(X)OSO_2Me$ [X = OMe (1), OH (2); R = n-Pr, n-Bu] with aliphatic and aromatic dicarboxylic acids--Isolation and characterization of $R_2Sn(O_2CR'COOH)_2$ and $R_2Sn(O_2CR'COOH)OSO_2Me$

Chapter V

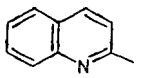
Reactions of $R_2Sn(OH)OSO_2Me$ (R = n-Pr, n-Bu) with Bu_4NX [X = NO_3, F, OAc] and RLi [R = n-Bu, Me] – Isolation and characterization of $[R_2Sn(\mu\text{-}OH)(OSO_2Me)(ONO_2)]_2 2Bu_4N$

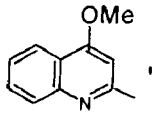
Chapter III

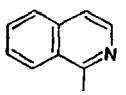
Reactions of $R_2Sn(OMe)OSO_2Me$ with 2-quinoline/4-methoxy-2-quinoline/1-isoquinoline carboxylic acids—Isolation and characterization of $[R_2Sn(O_2CR')OSO_2Me]_n$ (R = n-Pr, n-Bu)

Mixed-ligand diorganotin esters $[R_2Sn(O_2CR')OSO_2Me]_n$ (**3-8**) are accessible from the reactions of equimolar quantities of $R_2Sn(OMe)OSO_2Me$ (R = n-Pr, n-Bu) with 2-quinoline/4-methoxy-2-quinoline/1-isoquinoline carboxylic acid in acetonitrile under mild reaction conditions (RT, 12-15h). These reactions proceed by chemoselective cleavage of Sn-OMe bond in the precursor tin complexes in presence of carboxylic acid as shown in the equation below.

$$R_2Sn(OMe)OSO_2Me + R'COOH \xrightarrow[-\ MeOH]{CH_3CN,\ RT,\ 12\text{-}15h} \underset{\textbf{3-8}}{[R_2Sn(O_2CR')OSO_2Me]_n}$$

R' =  , R = n-Pr (**3**), n-Bu(**4**), n = ∞

 , R = n-Pr (**5**), n-Bu(**6**), n = 2

 , R = n-Pr (**7**), n-Bu(**8**), n = 2

The compounds **3-8** are white to pale yellow crystalline solids and are soluble in common organic solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$, CH_3OH, and DMSO etc. FAB mass spectra of these compounds reveal a few structurally diagnostic fragment ions at m/z 847 (for **3**), 908 (for **4**), 909(for **5**), 965(for **6**), 849(for **7**) and 905(for **8**) by the predominant loss of methanesulfonate group from the proposed dimeric structural unit [M]. IR spectra provide a qualitative bonding description of the carboxylate and methanesulfonate ligands bonded to the tin atoms. The compounds $[R_2Sn(O_2CC_9H_6N\text{-}2)OSO_2Me]_n$ (**3, 4**) exhibit a strong absorption at 1684 (for **3**) and 1652 cm^{-1} (for **4**) due to ν_aCO_2 mode while the corresponding absorption for $[R_2Sn(4\text{-}OMe\text{-}O_2CC_9H_5N\text{-}2)OSO_2Me]_2$ (**5, 6**) is discernable at 1667 and 1686 cm^{-1}. By analogy with the IR spectral data of previously known diorganotin esters derived from 2-pyridine carboxylic acid, the observed lowering of IR frequency in **4** is suggestive of tridentate coordination of the carboxylate ligand while bidentate {N, O} mode is suggested for **3**, **5** and **6**. On the other hand, IR spectra of $[R_2Sn(O_2CC_9H_6N\text{-}1)OSO_2Me]_2$ (**7, 8**) show two distinct absorptions at 1680-1670 (s) and 1620-1610(m) cm^{-1}. The former value is assigned to {N, O} chelation of the carboxylate ligand while the later corresponds to tridentate coordination mode featuring both {N, O} chelation and bridging carboxylate group. Characteristic absorptions due to νSO_3 mode appear at 1278-1240, 1180-1140 and 1044-990 cm^{-1}. The appearance of additional splitting in this region in **5-8** suggests bridging bidentate coordination mode of the methanesulfonate group. The identity of each compound is further corroborated by multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectral studies. Characteristic signals due to n-Pr_2Sn/n-Bu_2Sn, C_9H_6N-2/4-OMe-C_9H_5N-2/C_9H_6N-1 and SMe groups are distinctly observed in the ^1H NMR spectra with 1:1:1 integrated ratio. ^{119}Sn NMR spectra of these

compounds in $CDCl_3$ or DMSO-d_6 (for **5** and **6** only) show a sharp resonance ($w_{1/2}$ = 10-14Hz) in a narrow chemical shift range of δ –304 to –340 typical of six coordinated tin polyhedra.[58] The appearance of a single ^{119}Sn resonance in each compound suggests that tin atoms in these associated structures possess identical chemical environment. These spectroscopic findings have been further corroborated by X-ray crystal structure analysis of **4, 6** and **8**.

The compound [n-$Bu_2Sn(O_2CC_9H_6N$-2)$OSO_2Me]_n$ (**4**) crystallizes in space group I 4 [Tetragonal, a = b = 18.4020(16), c = 13.0580(16) Å, α = β = γ = 90°, Z = 8]. The molecular structure is polymeric in which both {N, O} chelation and intermolecular coordination of carboxylate oxygen [Sn(1)#1-O(3) = 2.780 Å]to the tin center of neighboring molecule are evident. The polymeric chains propagate along the c axis (Figure I). The methanesulfonate groups act in a monodentate mode. Interestingly, the neighboring molecules are associated in such a manner that the methanesulfonate and carboxylate ligands are disposed in a trans orientation in the polymeric chain.

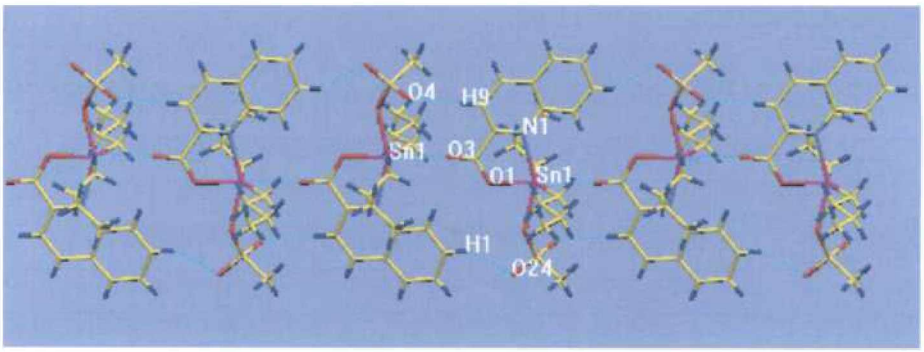


Figure I. Crystal structure of **4**

Secondary CH---O bonding interactions involving H-3, H-4 and H-7 atoms (IUPAC nomenclature) of the aromatic ring and oxygen atoms of methanesulfonate groups results in the formation of 3-D supramolecular assembly featuring square-grid type of structural

motif. [H(9)---O(4) = 2.467, C(9)-O(4) = 3.397 Å, C(9)-H(9)---O(4) = 176.3° ; H(1)---O(24) = 2.523, C(1)-O(24) = 3.220 Å, C(1)-H(1)---O(24) = 132.0°; H(10)---O(4) = 2.517, C(10)-O(4) = 3.394Å, C(10)-H(10)---O(4) = 157.4°]. The structure of [n-Bu_2Sn(4-OMe-$O_2CC_9H_5N$-2)OSO_2Me]$_2$ (**6**) [$P2_1/n$, Monoclinic, a = 14.1(13), b = 16.7(18), c = 20.3(19) Å, β = 107(4)°, Z = 8] reveals that the monomeric units are held together by weakly coordinating methanesulfonate groups acting in bridging bidentate mode [Sn(1A)-O(3B) = 3.010, Sn(1B)-O(3A) = 2.984Å] (Figure II). The carboxylate ligand is bonded to each tin atom by {N, O} chelation forming five membered ring while the other carboxylic oxygen [O(5A) and O(5B)] remains free.

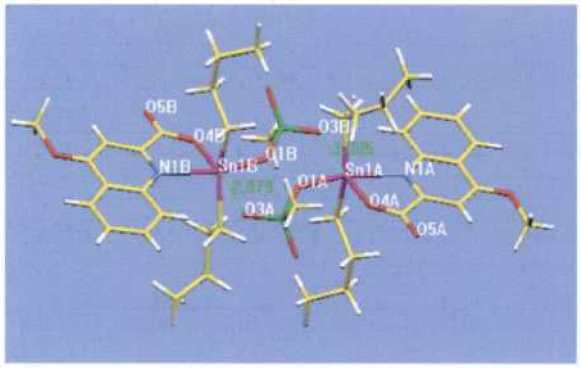


Figure II. Crystal structure of **6**

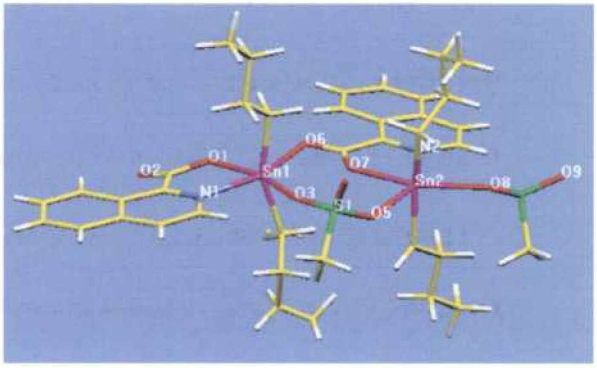


Figure III. Crystal structure of **8**

In contrast, the structure of [n-Bu_2Sn($O_2CC_9H_6$N-1)OSO_2Me]$_2$ (**8**) [Monoclinic, $P2_1/c$, a = 11.339(2), b = 14.806(3), c = 24.929(5) Å, β = 100.537(3)°, Z = 4] differs from **4** and **6** in respect of varying disposition of the ligands around the tin atoms (Figure III). Particularly noteworthy is the structural variation due to different bonding behavior of carboxylate and methanesulfonate groups associated with each monomeric entity in the molecule. While {N, O} chelation of the carboxylate groups is evident, the ligand at Sn(2) atom behaves in a tridentate fashion with O(6) atom forming a bridge between the

two tin centers [Sn(1)-O(6) = 2.507(2) Å]. The methanesulfonate groups at Sn(1) and Sn(2) atoms display bridging bidentate and monodentate coordination modes respectively [Sn(1)-O(3) = 2.366(2), Sn(2)-O(5) = 2.312(2), Sn(2)-O(8) = 2.300(2) Å].

Although varying bonding situations of the carboxylate and methanesulfonate ligands are evident from the X-ray crystal structures of **4, 6** and **8**, it is noteworthy to mention that structural similarities in respect of the coordination number of tin are evident. In each compound, the tin atoms possess a distorted octahedral geometry with SnO_3N core defining the equatorial plane while n-butyl groups occupy the trans-orientation.

Isolation and characterization of [n-Bu_2Sn($O_2CC_9H_6N$-2)-O-Sn(OSO_2Me)n-Bu_2]$_2$ (9)

The formation of tetraorgano distannoxane (**9**) is accessible from the hydrolysis of mixed-ligand tin ester, [n-Bu_2Sn($O_2CC_9H_6N$-2)OSO_2Me]$_n$ (**4**). It is believed that n-Bu_2Sn(OH)OSO_2Me and n-Bu_2Sn(OH)$O_2CC_9H_6N$-2 are the key intermediates in the hydrolysis pathway which upon subsequent condensation affords the tetraorgano distannoxane **9**. ^{1}H NMR spectrum of **9** exhibits characteristic resonances due to n-Bu_2Sn, SMe and aromatic ring protons in 2:1:1 integrated ratio. ^{119}Sn NMR spectrum ($CDCl_3$) shows two resonances at δ -221 and –278 which are attributed to the endocyclic (pentacoordinated) and exocyclic (hexacoordinated) tin atoms respectively. IR spectrum both in solid and dichloromethane solution reveals a strong absorption at 1684 cm^{-1} due to $\nu_a CO_2$ mode arising from (N, O) chelation of the carboxylate ligand. Characteristic absorption due to νSn-O-Sn mode appears at 605 cm^{-1}. The structural motifs of the distannoxane, **9** has been established by X-ray crystallography

The molecule **9** [Monoclinic, C2/c, a = 21.152(3), b = 13.307(2), c = 26.060(4) Å, β = 110.02(10)°, Z = 8] adopts a centrosymmetric dimeric structure by virtue of μ_3- oxo atoms [Sn(1)-O(3) = 2.066(5); Sn(2)-O(3)#1 = 2.068(5) Å] which form the central $R_4Sn_2O_2$ core with planer Sn_2O_2 ring (Figure IV). The methanesulfonate group associated with each endocyclic tin atom is uniquely coordinated to Sn(1) and Sn(1)#1 atoms (exocyclic) in a μ_2- fashion [Sn(2)-O(6) = 2.603(4), Sn(1)-O(6) = 2.632(4) Å] and is

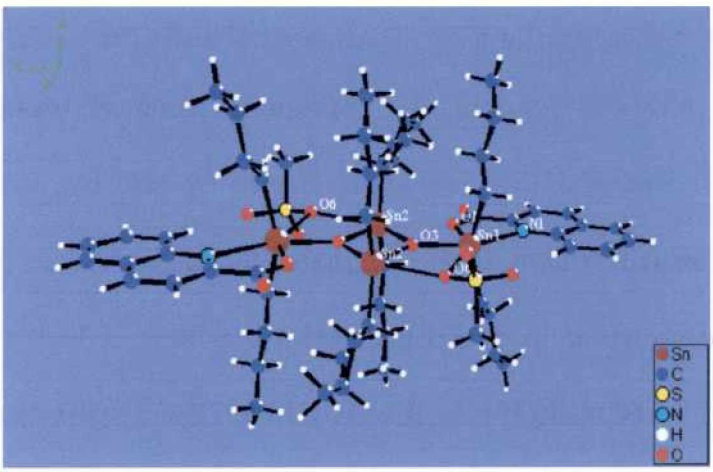


Figure IV. Crystal structure of **9**

unprecedented in the related tin derivatives. This results in a ladder-type structural motif. Each exocyclic tin atom is also bonded to the carboxylate ligand via {N, O} chelation mode. The coordination geometry around the endocyclic tin atoms is distorted trigonal bipyramidal with trigonal plane being defined by C_2O donor set in each case. The axial positions are occupied by O(6) and O(3)#1 atoms. Each exocyclic tin atom adopts distorted octahedral geometry with equatorial disposition of O(6), O(3), O(1) and N(1) atoms (sum of angles = 360±0.2°).

Disproportionation reactions of (methoxy/hydroxy)diorganotin methanesulfonate with 2-pyridine/2-thiophene/2-furoic carboxylic acid

Reactions of $R_2Sn(X)OSO_2Me$ [X = OMe (**1**) or OH (**2**)] with equivalent amount of 2-pyridine carboxylic acid in acetonitrile at room temperature afford the corresponding trinuclear tin compounds as shown in equation below.

$$3\ R_2Sn(X)OSO_2Me + 3\ HOOCC_5H_4N\text{-}2 \xrightarrow{CH_3CN,\ RT,\ 10\text{-}12\ h} R_6Sn_3(O_2CC_5H_4N\text{-}2)_3(OSO_2Me)_3$$

(X = OMe, OH) n-Pr(**10**), n-Bu(**11**)

These reactions proceed via disproportionation of unstable mixed-ligand tin intermediate $R_2Sn(O_2C_5H_4N\text{-}2)OSO_2Me$, formed by selective substitution of Sn-OMe bond (for **1**) or dehydration of Sn-OH group (for **2**) in presence of the carboxylic acid. X-Ray crystal structure of **11**.$2H_2O.Et_2O$ [Monoclinic, $P2_1/c$, a = 20.5774(16), b = 17.4931(14), c = 18.9046(15) Å, β = 103.790(2)°, z = 4] reveals a self assembly of mixed-ligand tin ester n-$Bu_2Sn(O_2CC_5H_4N\text{-}2)OSO_2Me$ and its disproportionated products n-Bu_2Sn $(O_2CC_5H_4N\text{-}2)_2$ and n-$Bu_2Sn(OSO_2Me)_2$ which are coordinatively associated by varying bonding modes of 2-pyridine carboxylate ligand (Figure V). Each tin atom

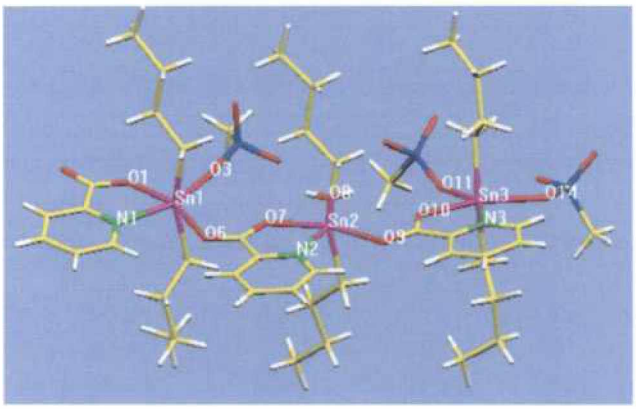


Figure V. Crystal structure of **11**.$2H_2O.Et_2O$

possesses a distorted octahedral geometry with equatorial SnO_3N core. Thus an intrinsic tendency of the mixed-ligand tin ester towards disproportionation is clearly evident from the crystal structure. Elemental analysis, IR and FAB mass spectral data of **10** and **11** are in accord with the trinuclear tin compounds. Although M^+ ion corresponding to the trinuclear tin assembly is not discernable in the FAB mass spectra, structurally important ions such as $[M\text{-}2OSO_2Me\text{-}2H]^+$, $[M\text{-}R_2Sn(OSO_2Me)_3\text{-}2H]^+$, $[R_2Sn(O_2CC_5H_4N\text{-}2)]^+$, and $[RSn\ (O_2CC_5H_4N\text{-}2)_2]^+$ are evident. IR spectra (KBr pellet) of **10** and **11** exhibit bands at 1680-1685, 1610-1620 and 1338 cm^{-1} due to ν_aCO_2 and ν_sCO_2 modes respectively. ^1H NMR spectrum of each compound in $CDCl_3$ identifies Pr_2Sn/Bu_2Sn, C_5H_4N-2 and SMe groups in 1:1:1 integrated ratio. ^{119}Sn NMR spectra show a close resemblance with chemical shift values at -216, -346, –418 (for **10**) and –210, -346, -421 (for **11**). However, these signals are broad and span over a large chemical shift range which are normally attributed to five and six coordinated tin atoms.[58]

To better understand the disproportionation phenomena as observed above, it was desired to extend the reactions of $n\text{-}Bu_2Sn(OMe)OSO_2Me$ with 2-thiophene and 2-furoic carboxylic acid. As shown in the equation below, symmetrical diorganotin esters, $n\text{-}Bu_2Sn(O_2CR)_2$ [R = C_4H_3S (**12**), C_4H_3O (**13**)] and $n\text{-}Bu_2Sn(OSO_2Me)_2$ are formed in these reactions suggesting complete disproportionation of the mixed-ligand tin intermediates.

$$2\ n\text{-}Bu_2Sn(OMe)OSO_2Me + 2RCOOH \xrightarrow[CH_3CN,\ RT,\ 8\text{-}10h]{} n\text{-}Bu_2Sn(O_2CR)_2 + n\text{-}Bu_2Sn(OSO_2Me)_2$$

R = C_4H_3S (**12**), C_4H_3O (**13**)

Although the compounds **12** and **13** are reported previously by direct reaction of di-n-butyltin oxide and the corresponding carboxylic acid, a critical evaluation of the

results obtained herein is significant to throw light on the factors which govern the stability of the mixed-ligand tin ester derivatives.

On the basis of above studies, a few important conclusions emerge which are mentioned as follows:

The compounds $[R_2Sn(O_2CR')OSO_2Me]_n$ [n = ∞, R' = C_9H_6N-2, n-Pr (**3**), n-Bu (**4**); n = 2, R' = 4-OMe-C_9H_5N-2, n-Pr (**5**), n-Bu (**6**); R' = C_9H_6N-1, n-Pr (**7**), n-Bu (**8**)] represent a new family of mixed-ligand tin esters which possess ambidentate ligands derived from carboxylic and methanesulfonic acids. Analogous compounds derived from 2-pyridine/2-thiophene/2-furoic carboxylic acid are unstable and undergo disproportionation to afford symmetrical tin derivatives. The stability of **3-8** may thus partly be attributed to strong {N, O} chelation effect of the carboxylate ligands as well as ability of the co-ligand (methanesulfonate) in providing coordinative saturation around the tin atoms in the associated structural motif. The formation of distannoxane **9** represents the first example in which two different hemi-labile functional groups (2-quinoline carboxylate and methanesulfonate) bonded to tin atom in the compound **4** undergo hydrolysis in a selective manner. The distannoxane **9** adopts a ladder type structure by virtue of unique μ_2- coordination of covalent oxygen atoms [O(6) and O(6)#1] of methanesulfonate group.

Chapter IV

Reactions of $R_2Sn(X)OSO_2Me$ (X = OMe, OH; R = n-Pr, n-Bu) with ethylmalonic/ maleic/succinic/adipic acid—Isolation and characterization of $R_2Sn(O_2CR'COOH)_2$ and $R_2Sn(OSO_2Me)_2$

The reactions between equimolar quantities of $R_2Sn(X)OSO_2Me$ [X = OMe (**1**) or OH (**2**)] with ethylmalonic/maleic acid in acetonitrile afford the corresponding diorganotin

structure in which one carboxylate unit of each ligand is bonded to the tin atom in anisobidentate fashion, while the other carboxylic group remains free (Figure VI). The

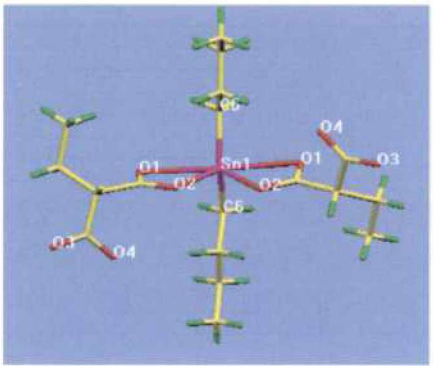


Figure VI. Crystal structure of **15**

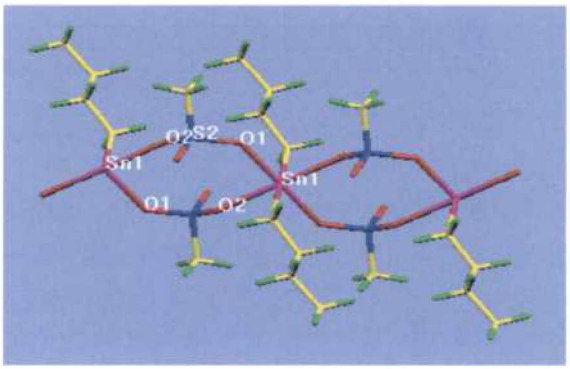


Figure VII. Crystal structure of **19**

coordination geometry around the tin atom is best described as bicapped tetrahedron. The presence of weak intermolecular (O…HO) hydrogen bonding (2.622 Å) is also manifested in the molecule. The molecular structure of n-$Bu_2Sn(OSO_2Me)_2$ (**19**) [Triclinic $P\bar{1}$, a = 5.321(2), b = 5.321(2), c = 10.792(3) Å, α = 64.30(2), β = 73.308(13), γ = 74.432(11)°, Z = 2] is polymeric with centrosymmetric eight member rings comprising of bridging methanesulfonate groups between the two consecutive tin atoms (Figure VII). The geometry around each tin atom is octahedral as evident from the metrical parameters.

On the other hand, disproportionation reactions between n-$Bu_2Sn(OMe)OSO_2Me$ and succinic or adipic acid afford the known diorganotin esters, $[n\text{-}Bu_2Sn(O_2CRCO_2)]_x$ [R = $(CH_2)_2$, $(CH_2)_4$] and n-$Bu_2Sn(OSO_2Me)_2$.

$$2n\text{-}Bu_2Sn(OMe)OSO_2Me + R(COOH)_2 \xrightarrow{CH_3CN,\ RT,\ 8\text{-}10h} [n\text{-}Bu_2Sn(O_2CRCO_2)]_x + nBu_2Sn(OSO_2Me)_2$$

[R = $(CH_2)_2$ (**20**), $(CH_2)_4$ (**21**)]

dicarboxylates (**14-17**) and diorganotin bis(methanesulfonate)s (**18, 19**) under mild conditions (RT, 8-10h).

$$2R_2Sn(X)OSO_2Me + 2R'(COOH)_2 \xrightarrow{CH_3CN,\ RT,\ 8\text{-}10h} R_2Sn(O_2CR'COOH)_2 + R_2Sn(OSO_2Me)_2$$

14-17 **18, 19**

(X = OMe, OH)

R' = CHEt, R = n-Pr (**14**), n-Bu(**15**)
R' = CH=CH, R = n-Pr (**16**), n-Bu (**17**)
R = n-Pr (**18**), n-Bu (**19**)

By analogy with the results discussed in chapter III, the above reactions can also be envisioned to proceed in two steps. In the initial step, the mixed-ligand diorganotin esters, $R_2Sn(O_2CR'COOH)OSO_2Me$ are formed by cleavage of Sn-OMe or dehydration of Sn-OH group in the precursor tin complexes. Subsequent disproportionation of these unstable mixed-ligand tin intermediates afford the tin carboxylates, **14-17** and diorganotin bis(methanesulfonate) (**18, 19**).

IR spectra of **14-17** reveal the presence of coordinated and free carboxylic acid in the region of 1700-1500 cm^{-1}. A broad band at ~3100cm^{-1} is attributed to νOH mode. ^1H NMR spectra of these compounds are quite straightforward and manifest 1:2 integrated ratio of R_2Sn and CHEt or CH=CH groups. The observed $^{119/117}Sn$ satellites in $^{13}C\{^1H\}$ NMR spectra provide $^nJ(^{13}C\text{-}^{119/117}Sn)$ coupling values (^1J = 540-570 Hz). The carbonyl carbons appear as single resonance at δ 165-175 which suggests a rapid inter/intramolecular carboxylate exchange in solution. A close similarity of $^1J(^{13}C\text{-}^{119/117}Sn)$ data as well as ^{119}Sn NMR chemical shifts δ -151 to -140 suggests that these compounds adopt identical structural features in solution state.

X-Ray crystal structure of $n\text{-}Bu_2Sn(O_2CCHEtCOOH)_2$(**15**) [Monoclinic, C_2/c, a = 22.130(4), b = 5.0110(10), c = 21.535(4) Å, β = 102.74(3)°, Z = 4] reveals a monomeric

The formation of polymeric compounds can be rationalized on the basis of lower pk2 values of succinic acid (5.48) and adipic acid (5.62) as compared to those of ethylmalonic acid (5.83) and maleic acid (6.34).

Reactions of $R_2Sn(OMe)OSO_2Me$ (R = n-Pr, n-Bu) with 2, 3-pyridine/6-methyl-2,3-pyridine dicarboxylic acid-Isolation and characterization of $R_2Sn(O_2CR')OSO_2Me$

Synthesis of stable mixed-ligand diorganotin carboxylates, $R_2Sn(O_2CR')OSO_2Me$ (**22-25**) is achieved by appropriate choice of the N-substituted aromatic dioic acids.

$$R_2Sn(OMe)OSO_2Me + RCOOH \xrightarrow{CH_3CN,\ RT,\ 8\text{-}10h} R_2Sn(O_2CR')OSO_2Me$$

R' = C_5H_3N-2,3-COOH, R = n-Pr (**22**), n-Bu (**23**)

R' = C_5H_2N-2,3-COOH-6-Me, R = n-Pr (**24**), n-Bu (**25**)

In the absence of single crystal structure, these compounds have been characterized by FAB mass, IR and multinuclear NMR spectral studies. FAB mass spectra reveal the highest m/z ions corresponding to the fragment $[M\text{-}3OSO_2Me]^+$ (where M corresponds to trimeric entity). Other structurally important fragment ions are also discernable which corroborate with the isotopic cluster pattern arising from di/tritin species. IR spectra of **22-25** exhibit a band at 1610-1630 cm^{-1} due to ν_aCO_2 mode analogous to those observed in **7** and **8** where tridentate coordination mode of the carboxylate ligand has been subscribed. An additional band at 1700-1730 cm^{-1} in the spectra of each compound is assigned to ν_aCO_2 mode of free COOH group

^1H NMR spectra of these compounds show characteristic resonances due to n-Pr_2Sn/n-Bu_2Sn, SMe and aromatic groups in 1:1:1 integrated ratio and conform to the structural composition. ^{119}Sn NMR ($CDCl_3$) spectrum of each compound reveals a single

resonance between δ - 340 to -355 and suggestive of hexacoordination around tin atom. On the basis of cumulative spectroscopic data, a trimeric structure involving coordinative association of the carboxylate ligand has been proposed.

Chapter V

Reactions of $R_2Sn(OH)OSO_2Me$ with Bu_4NNO_3 – Synthesis and characterization of $[R_2Sn(\mu\text{-}OH)(OSO_2Me)(ONO_2)]_2Bu_4N$ [R = n-Pr (26), n-Bu (27)]

The synthesis of trifunctional stannates, $[R_2Sn(\mu\text{-}OH)(OSO_2Me)(ONO_2)]_2Bu_4N$ [R = n-Pr (**26**), n-Bu (**27**)] involves the reaction of (hydroxy)diorganotin methane sulfonates, (**2a** or **2b**) with one equivalent of tetra-n-butylammonium nitrate in dichloromethane as shown in equation below. These reactions proceed via nucleophilic addition of NO_3^- ion to the Lewis acidic tin center.

$$2R_2Sn(OH)OSO_2Me + 2Bu_4NNO_3 \xrightarrow[CH_2Cl_2]{RT/8\text{-}10h} [R_2Sn(\mu\text{-}OH)(OSO_2Me)(ONO_2)]_2Bu_4N$$

R = n-Pr (**26**), n-Bu (**27**)

The solid-state structure of di-n-butyltin derivative (**27**) is elucidated by X-ray crystallography. The compound crystallizes as two independent molecules in the unit cell [Triclinic, $P\bar{1}$, a = 11.9775(18), b = 13.610(2), c = 22.857(3) Å, α = 81.360(2), β = 75.527(3), γ = 67.153(2)°, Z = 4]. The anion in each molecule adopts a centrosymmetric hydroxyl-bridged dimeric structure with highly distorted octahedral geometry around each tin atom (Figure VIII). The coordination sphere around the tin atom is formed by C_2SnO_4 core with two bridging OH, a monodentate methanesulfonate and a nitrate group lying in the equatorial position (360±1°). Principle differences between the two molecules in the unit cell appear in the Sn-O (methanesulfonate and nitrate) bond distances and O-Sn-O/C-Sn-C angles.

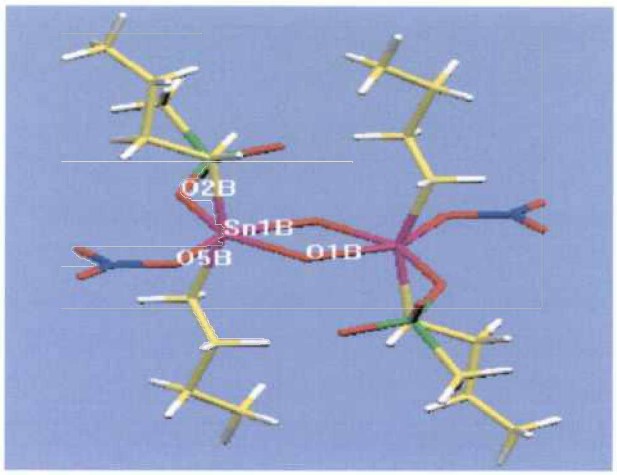


Figure VIII. Crystal structure of **27**

Selected spectroscopic data are as follows: [IR (KBr, cm^{-1}): 1485-1490 ($\nu_a NO_2$), 1384-1388 ($\nu_s NO_2$), 1205-1210, 1050-1060 (νSO_3); ^{119}Sn NMR ($CDCl_3$): δ -155, -159, -191, -234 (for **24)** –157, -159, -194, -234 (for **25**)]. It is conceived that the ^{119}Sn NMR signals between δ –155 to –194 and their relative intensities are similar to those of the tin precursors. However, an additional upfield signal at δ -234 in the spectrum of each compound is attributed to the stannate derivative. It is thus suggested that a fast equilibrium between the tin precursor **2a** or **2b** and the product exists in solution.

The complexation of the NO_3^- ion can be rationalized by considering coordinative dissociation of bridging bidentate methanesulfonate in the tin precursors. It appears that the nucleophilicity of NO_3^- and $MeSO_3^-$ ions being comparable inhibits the ionic metathesis pathway.

Reactions of n-Bu_2Sn(OH)OSO_2Me with n-Bu_4NX (X = OAc, F) and RLi (R = n-Bu, Me) – Synthesis and characterization of [n-Bu_2Sn(X)]$_2$O and [n-Bu_2Sn(R)]$_2$O

The reactions of n-Bu_2Sn(OH)OSO_2Me with strong nucleophilic reagents such as Bu_4NX (F, OAc) and RLi (n-Bu, Me) invariably proceed via an ionic metathesis pathway

involving the cleavage of Sn-OSO_2Me bond. The products obtained are either tetraorgano distannoxanes or unsymmetrical triorganotin oxides.

$$2n\text{-}Bu_2Sn(OH)OSO_2Me + 2Bu_4NX \xrightarrow[8\text{-}10h]{CH_2Cl_2,\ RT} [n\text{-}Bu_2Sn(X)]_2O + 2n\text{-}Bu_4NOSO_2Me + H_2O$$

X = F (**28**), OAc (**29**)

$$2n\text{-}Bu_2Sn(OH)OSO_2Me + 2RLi \xrightarrow[8\text{-}10h]{Et_2O,\ RT} (n\text{-}Bu_2RSn)_2O + 2\ LiOSO_2Me + H_2O$$

R = n-Bu (**30**), Me (**31**)

The identity of these products has been confirmed by IR, ^1H, and ^{119}Sn NMR spectral data. The use of organometallic reagents such as RLi may be of significant synthetic utility in the formation of novel mixed triorganotin oxide.

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