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Cleavage of Sn−C and S−C$_{alkyl}$ Bonds on an Organotin Scaffold: Synthesis and Characterization of a Novel Organotin-Sulfite Cluster Bearing Methyltin- and Dimethyltin Fragments

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Hydrolysis of the mixed-ligand dimethyltin(ethoxy)ethanesulfonate, $[Me_2Sn(OEt)(OSO_2Et)]_n$ (**1a**) in moist hexane proceeds via disproportionation and partial cleavage of Sn−C and S−C bonds to afford a novel oxo-/hydroxo-organotin cluster of the composition $[(Me_2Sn)(MeSn)_4(OSO_2Et)_2(OH)_4(O)_2(SO_3)_2]$ (**1**) bearing both mono- and dimethyltin fragments and in situ generated sulfite (SO_3^{2-}) anion in the structural framework. On the other hand, similar reactions with analogous mixed ligand diorganotin precursors, $[R_2Sn(OR^1)(OSO_2R^1)]_n$ (R=*n*-Bu, R^1=Et (**2a**); R=Et, R^1=Me (**3a**)), result in the formation of tetranuclear diorganotin clusters, $[\{(n\text{-}Bu_2Sn)_2(OH)(OSO_2Et)\}O]_2$ (**2**) and $[(Et_2Sn)_4(OH)(O)_2(OSO_2Me)_3]$ (**3**), respectively. The activation of the Sn−C or S−C bond is not observed in these cases. These findings provide a preliminary insight into the unusual reactivity of **1a** under hydrolytic conditions.

Introduction

Organotin based heterocyclic rings, cages, and clusters of varied nuclearity with oxo-/hydroxo groups as the constructing units have been extensively studied in the past.[1] A straightforward synthetic approach for these classes of molecular organotin-oxides involves controlled hydrolysis and condensation of reactive functional groups in mono/diorganotin derivatives such as $RSnX_3/R_2SnX_2$ (X = Cl, Br, OR^1, $C{\equiv}CR^1$, etc.).[2] Hydrolytic behavior of oligomethylene-bridged ditin complexes containing Sn−Cl bonds has been studied by Jurkschat and Dakternieks et al.[3] An alternate approach involves the reaction of organostannoic acid/diorganotin oxide with a protic ligand such as carboxylic, oxy-sulfur/oxy-phosphorus acids, and other related ligands.[4] The latter method allows the formation of oxo-/hydroxotin clusters bearing the complexing ligands which participate in the construction of structural frameworks. Under these conditions, molecular cluster entities formed by the cleavage of the Sn−C bond in di/triorganotin precursors is particularly noticeable.[5] The potential of these approaches can be gauged by the reported examples of organotin clusters with diverse structural motifs such as ladder, drum, butterfly, cube, among others.[6] The applications of these compounds as new materials and as mild Lewis acid catalyst in various organic transformations have been explored.[7]

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Recently, we have reported the utility of dialkyl sulfites in the synthetic domain of organotin chemistry by the isolation of a number of diorganotin(alkoxy)alkanesulfonates.[8a] Studies on the reactivity of these mixed-ligand tin complexes toward phosphonic acids, $RP(O)(OH)_2$ (R = Me, *t*-Bu, Ph) have unfolded a simple and mild approach to structurally diverse two-/three-dimensional organotin assemblies featuring $[Sn-O-P-O]_2$ and $[Sn-O-S-O]_2$ heterocyclic rings and clusters.[8b,c] As a part of our ongoing research in this area, the work reported herein describes hydrolysis studies of three diorganotin precursors, $[R_2Sn(OR^1)(OSO_2R^1)]_n$ (R = Me, R^1 = Et (**1a**); R = *n*-Bu, R^1 = Et (**2a**); R = Et, R^1 = Me (**3a**)) which result in the isolation of novel tetra-/pentanuclear oxo-tin clusters, $[(Me_2Sn)(MeSn)_4(OSO_2Et)_2(OH)_4(O)_2(SO_3)_2]$ (**1**), $[\{(n\text{-}Bu_2Sn)_2(OH)(OSO_2Et)\}O]_2$ (**2**), and $[(Et_2Sn)_4(OH)(O)_2(OSO_2Me)_3]$ (**3**), respectively, thus providing a new insight into the chemical behavior of these mixed ligand organotin complexes. In particular, the formation of the cluster entity **1** comprising mono- and dimethyltin fragments as well as an in situ generated dianionic sulfite ligand via cleavage of Sn−C(methyl) and S−C(ethanesulfonate) bonds, respectively, is quite revealing and provides the first example of the occurrence of this phenomenon on an organotin scaffold.

Results and Discussion

Dimethyltin(ethoxy)ethanesulfonate, **1a**, is obtained from a direct reaction between dimethyltin oxide and excess diethyl sulfite in the presence of ethyl iodide (eq 1). As reported earlier,[8a] this synthetic protocol involves sulfur-centered Arbuzov type rearrangement in diethylsulfite to afford in situ generation of ethanesulfonate moiety and formation of the desired mixed ligand diorgantin complex. The synthesis and characterization of analogous diorganotin precursors, $[R_2Sn(OR^1)(OSO_2R^1)]_n$ ($R = n\text{-Bu}$, $R^1 = Et$ (**2a**); $R = Et$, $R^1 =$ Me (**3a**) have been reported earlier.[8a,c]

$$Me_2SnO + EtOS(O)OEt + EtI \xrightarrow{100-110°C,\ 40-45h} \underset{\mathbf{1a}}{Me_2Sn(OEt)OS(O)_2Et} \qquad (1)$$

^1H NMR spectral data of **1a** is in conformity with the suggested composition and reveals $^2J_{Sn-H}$ coupling (102 Hz) associated with dimethyltin moiety. Because of poor solubility in non-coordinating solvent ($CDCl_3$), ^{13}C and ^{119}Sn NMR studies are performed in DMSO-d_6, and the relevant data is summarized in the Experimental Section. The ^{13}C resonances at δ 13.51 and 12.69 are devoid of J_{Sn-C} coupling information while ^{119}Sn NMR spectrum reveals four distinct signals at δ −176 to −288. By analogy with earlier studies on solution state behavior of related unsymmetrical diorganotin compounds,[9] the spectral data obtained herein suggests the existence of equilibrium between five- and six-coordinated diorganotin species in solution.

Treatment of **1a**−**3a** with moist hexane for 2 days under atmospheric conditions affords the corresponding tetra/pentanuclear organotin assemblies, **1**−**3** respectively. These are obtained as white, air-stable solids and are readily soluble in polar coordinating solvents such as CH_3OH, CH_3CN, DMSO, and so forth. While the presence of organotin and alkanesulfonate groups in each compound is revealed by IR and ^1H NMR spectra, the ^{13}C resonances associated with dimethyl/diethyltin (for **1**,**3**) and ethanesulfonate (for **2**) groups reveal multiple resonances suggesting complex behavior of these compounds in solutions. An attendant argument that the solid state structure is not retained in solution comes from ^{119}Sn NMR spectra which reveal several resonances between δ −143 to −381. The chemical shift region is suggestive of penta-/hexacoordinated organotin species which remain in equilibrium in solution.[9] The relevant spectroscopic data is summarized in the Experimental Section.

Single crystals of **1**−**3** suitable for X-ray structure analysis were grown by slow evaporation of a solution of each compound in chloroform/methanol/toluene solvent mixture. The crystal data are summarized in Table 1, while selected bond lengths and angles are given in Tables 2, 3, and 4, respectively. As shown in Figure 1a, the structure of $[(Me_2Sn)(MeSn)_4(OSO_2Et)_2(OH)_4(O)_2(SO_3)_2]$ **1** is composed of a pentanuclear oxo-tin cluster bearing both mono- and dimethyl tin moieties as well as sulfite and ethanesulfonate ligands in the structural framework. These features provide a striking revelation of partial Sn−C and S−C bond cleavage on an organotin scaffold in the course of hydrolysis of **1a**. The molecule has Sn/S ratio of 5:4, and the basic structural framework consists of a puckered $[SnO]_4$ eight-membered cyclic ring containing four crystallographically unique tin (Sn2 to Sn5) and oxygen (O8 to O11) atoms. The μ_4-oxygen (O12) is tetrahedrally coordinated to each of these tin centers (Sn−O−Sn = 102.2−103.6°) and is responsible for puckering of the Sn_4O_4 ring. The role of the O7 atom is that of a μ_3- donor which provides connectivity to Sn2 and Sn3 atoms of the core structural framework as well as the exterior Sn1 atom of dimethyltin bis(ethanesulfonate). The geometry around O7 is planar with sum of Sn−O−Sn bond angles being 360°. The average Sn−O−Sn and O−Sn−O bond angles lies in the range of 105.2(3)−105.9(4)° and 74.2(3)−102.0(6)° with the exception of O9−Sn3−O10 and O11−Sn2−O8 which are significantly larger (146.1(4)°and 146.3(3)°). Further construction of the structural unit is realized by μ_3-O bonding modes of the two sulfite ligands (S3, S4) which cap the Sn2, Sn4, Sn5 and Sn3, Sn4, Sn5 atoms of the central core, respectively. The metrical parameters associated with sulfite ligands are consistent with those reported earlier in a few transition metal clusters.[10] The monomeric dimethytinbis(ethanesulfonate) adopts a distorted tbp geometry with SnC_2O arrangement forming the equatorial plane (Σ360°). Other tin atoms in the central core (Sn2 to Sn5) are hexacoordinated with SnO_4 basal plane (Σ360 ± 11.2−11.4°) and trans-arrangement of methyl group and the μ_4-oxygen (O12) atom [∠C−Sn−O 176.5(6)−178.9(5)°]. The average Sn−(μ_2)O, Sn−(μ_3)O and Sn−(μ_4)O bond lengths are 2.098, 2.079, and 2.138 Å respectively, and are consistent with those reported in literature for other oxo-/hydroxo tin clusters.[4a,6b,11] The Sn−O (sulfonate) bond lengths (2.201 Å) lie at the upper end of Sn−O covalent bond

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Table 1. Summary of Crystallographic Data for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{10}H_{32}O_{18}S_4Sn_5$	$C_{36}H_{86}O_{10}S_2Sn_4$	$C_{19}H_{49}O_{12}S_3Sn_4$
formula weight	1162.05	1217.93	1040.52
T (°C)	150(2)	150(2)	293(2)
λ	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	P 1 21/a 1	P 1 21/n 1
a	10.3510(5)	18.5182(11)	12.521(2)
b	11.2540(6)	12.3375(6)	15.424(3)
c	13.8090(6)	22.0960(14)	19.226(3)
α (deg)	87.615(2)	90.00	90.00
β (deg)	85.920(2)	93.224(3)	97.031(3)
γ (deg)	75.266(2)	90.00	90.00
V	1551.31(13)	5040.2(5)	3685.1(11)
Z	2	4	4
ρ_{calcd} (mg m^{-3})	2.488	1.605	1.875
μ (mm^{-1})	4.306	2.087	2.895
F(000)	1100	2456	2028
crystal size	0.015 × 0.01 × 0.01	0.30 × 0.30 × 0.02	0.53 × 0.31 × 0.12
reflections collected/unique	14353/14361	37180/8291	34775/6490
R(int)	0.0000	0.1299	0.0675
GOF	1.026	1.064	1.220
data/restraints/parameters	14361/0/344	8291/0/490	6490/3/376
final R indices [$I > 2\sigma(I)$]	R~1 = 0.0756, wR~2 = 0.1703	R~1 = 0.0764, wR~2 = 0.1458	R~1 = 0.0831, wR~2 = 0.1647
R indices (all data)	R~1 = 0.1191, wR~2 = 0.2046	R~1 = 0.1557, wR~2 = 0.1693	R~1 = 0.1039, wR~2 = 0.1756

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths (Å)			
Sn1—C1	2.084(15)	Sn1—C2	2.079(13)
Sn1—O7	2.022(7)	Sn1—O1	2.188(9)
Sn1—O4	2.215(9)	Sn2—C7	2.090(12)
Sn2—O11	2.094(8)	Sn2—O8	2.099(8)
Sn2—O7	2.114(8)	Sn2—O12	2.144(8)
Sn2—O13	2.156(9)	Sn3—C8	2.051(15)
Sn3—O7	2.100(7)	Sn3—O9	2.101(8)
Sn3—O10	2.105(8)	Sn3—O16	2.150(8)
Sn3—O12	2.164(8)	Sn4—O10	2.092(9)
Sn4—O17	2.098(8)	Sn4—O15	2.100(9)
Sn4—C9	2.100(14)	Sn4—O11	2.105(8)
Sn4—O12	2.118(8)	Sn5—C10	2.088(14)
Sn5—O18	2.089(8)	Sn5—O9	2.090(9)
Sn5—O8	2.100(8)	Sn5—O14	2.111(10)
Sn5—O12	2.126(8)		
Bond Angles (deg)			
C2—Sn1—C1	121.5(6)	O7—Sn1—C2	119.2(5)
O7—Sn1—C1	119.3(4)	O1—Sn1—O4	167.8(3)
C7—Sn2—O12	177.3(6)	O11—Sn2—O7	91.3(3)
O8—Sn2—O7	94.6(3)	O11—Sn2—O13	82.0(3)
O8—Sn2—O13	80.9(3)	O11—Sn2—O8	146.3(3)
O11—Sn2—O12	74.2(3)	O8—Sn2—O12	75.3(3)
O7—Sn2—O12	75.2(3)	O7—Sn2—O13	159.3(3)
O12—Sn2—O13	84.2(3)	C8—Sn3—O12	178.9(5)
O7—Sn3—O9	91.8(3)	O7—Sn3—O10	94.0(3)
O10—Sn3—O16	80.6(3)	O9—Sn3—O16	82.2(3)
O9—Sn3—O10	146.1(4)	O7—Sn3—O16	159.0(3)
O7—Sn3—O12	75.1(3)	O9 —Sn3—O12	74.3(3)
O10—Sn3—O12	75.0(3)	O16—Sn3—O12	84.0(3)
C9—Sn4—O12	176.8(5)	O10—Sn4—O11	84.7(3)
O15—Sn4—O11	90.6(3)	O17—Sn4—O15	88.1(4)
O10—Sn4—O17	89.0(3)	O10—Sn4—O15	159.7(3)
O17—Sn4—O11	158.2(3)	O10—Sn4—O12	76.2(3)
O17—Sn4—O12	83.7(3)	O15—Sn4—O12	83.4(3)
O11—Sn4—O12	74.5(3)	C10—Sn5—O12	176.5(6)
O8—Sn5—O14	87.4(3)	O18—Sn5—O14	89.5(4)
O18—Sn5—O9	90.5(3)	O9—Sn5—O8	85.0(3)
O18—Sn5—O8	159.1(3)	O9—Sn5—O14	158.5(3)
O18—Sn5—O12	83.4(3)	O9—Sn5—O12	75.3(3)
O8—Sn5—O12	75.7(3)	O14—Sn5—O12	83.4(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Bond Lengths (Å)			
Sn1—O1	2.379(7)	Sn1—O10	2.120(6)
Sn1—O20	2.029(6)	Sn1—C1	2.141(10)
Sn1—C5	2.132(10)	Sn2—O10	2.146(6)
Sn2—O20	2.054(6)	Sn2—O30	2.134(6)
Sn2—C11	2.103(10)	Sn2—C15	2.147(10)
Sn3—O20	2.131(6)	Sn3—O30	2.061(6)
Sn3—O40	2.185(7)	Sn3—C19	2.128(10)
Sn3—C23	2.109(13)	Sn4—O4	2.311(7)
Sn4—O30	1.993(6)	Sn4—O40	2.095(7)
Sn4—C27	2.129(10)	Sn4—C31	2.133(9)
Bond Angles (deg)			
C5—Sn1—C1	140.0(4)	O20—Sn1—C1	107.6(4)
O20—Sn1—C5	110.9(3)	O10—Sn1—O1	152.4(2)
O20—Sn2—C11	117.1(3)	O20—Sn2—C15	117.5(3)
O30—Sn2—O10	146.9(2)	C11—Sn2—C15	125.2(4)
O30—Sn3—C23	115.0(5)	O30—Sn3—C19	116.0(4)
C23—Sn3—C19	129.0(5)	O20—Sn3—O40	145.1(2)
O30—Sn4—C27	111.3(3)	O30—Sn4—C31	117.7(3)
O40—Sn4—O4	151.9(2)	C27—Sn4—C31	130.8(4)

distances and are in conformity with those reported earlier for related diorganotin alkanesulfonate derivatives.[12] To compensate for the charge neutrality in the molecular assembly, four additional H-atoms are required. Although these could not be located crystallographically, these are suggested to reside on the O8−O11 atoms based on strong intra- and intermolecular O---O contacts favoring OH---O type hydrogen bonding interactions with the sulfonate oxygen atoms [O8−O6 = 2.738 (13), O5−O9^{ii} = 2.725(13), O10−O3 = 2.716(12) Å, O2−O11^{i} = 2.734(12) Å] (Figure 1b). Further evidence of the presence of hydroxyl group in the core cluster framework comes from IR absorption at 3414 cm^{-1} as well as ES-MS spectrum which reveals an

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Table 4. Selected Bond lengths (Å) and Bond angles (deg) for **3**

Bond Lengths (Å)			
Sn1—O2	2.046(7)	Sn1—C1	2.098(12)
Sn1—C3	2.102(11)	Sn1—O1	2.110(7)
Sn1—O4	2.307(8)	Sn2—O2	2.073(7)
Sn2—O3	2.096(8)	Sn2—C5	2.100(13)
Sn2—C7	2.118(12)	Sn2—O5	2.336(8)
Sn3—O2	2.088(7)	Sn3—O1	2.125(7)
Sn3—C9	2.17(3)	Sn3—O3	2.164(8)
Sn3—C11	2.142(12)	Sn4—O1	1.989(7)
Sn4—C13	2.125(15)	Sn4—C15	2.172(17)
Sn4—O7	2.204(9)	Sn4—O10	2.305(8)
Bond Angles (deg)			
O1—Sn1—O4	164.2(3)	O2—Sn1—C1	106.1(4)
O2—Sn1—C3	108.3(5)	C1—Sn1—C3	144.2(5)
O3—Sn2—O5	160.5(3)	C5—Sn2—C7	140.4(7)
O2—Sn2—C5	107.8(5)	O2—Sn2—C7	110.7(4)
O1—Sn3—O3	147.4(3)	C9—Sn3—C11	135.5(10)
O2—Sn3—C9	110.6(10)	O2—Sn3—C11	113.9(4)
O7—Sn4—O10	161.7(3)	C13—Sn4—C15	143.0(7)
O1—Sn4—C13	110.5(5)	O1—Sn4—C15	106.2(6)

intense peak at *m*/*z* 812.6468 (calculated: 812.6345) attributed to $[M - (CH_3)_2Sn(OSO_2Et)_2 + H_3O]^+$.

To gain further insight into the role of organic substituents on the tin and sulfur centers in bringing about the observed transformation in **1a**, a hydrolysis study of closely related mixed ligand di-*n*-butyltin(ethoxy)ethanesulfonate, **2a**, and diethyltin(methoxy)methanesulfonate, **3a**, was performed under identical conditions. The former is the di-*n*-butyltin analogue of **1a** while the latter bears organic substituents which are swapped on the tin and sulfonate centers with respect to **1a**. Interestingly, transformation of these precursors to diorganotin clusters, $[\{(n\text{-}Bu_2Sn)_2(OH)(OSO_2Et)\}O]_2$ **2** and $[(Et_2Sn)_4(OH)(O)_2(OSO_2Me)_3]$ **3**, respectively, proceeds without accompanying Sn−C or S−C bond cleavage. The unsymmetrically substituted distannoxane, **2** (Figure 2a) is composed of four crystallographically unique tin atoms and represents a ladder-like framework which is constructed on a central distannoxane (Sn_2O_2) unit with two bridging hydroxyl groups (O10, O40) providing connectivity between

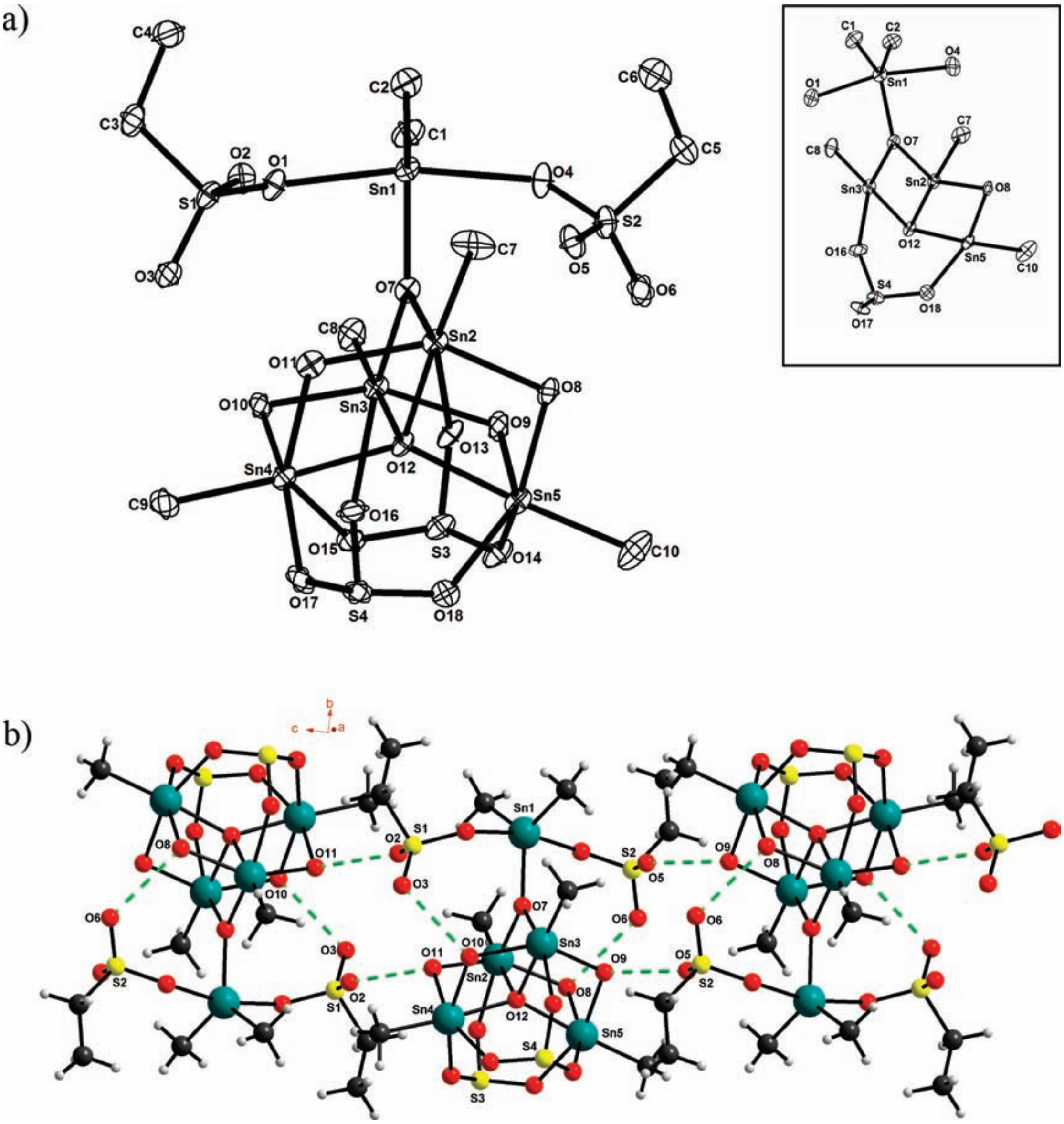


Figure 1. (a) ORTEP view of the molecular structure of **1**. The thermal ellipsoids are set at 30% probability, and the hydrogen atoms are omitted for clarity. Inset figure: An organotin fragment of **1** showing core-structure arrangement similar to that of **3**. (b) Intra- and intermolecular hydrogen bonding in **1** (view along *c*-axis).

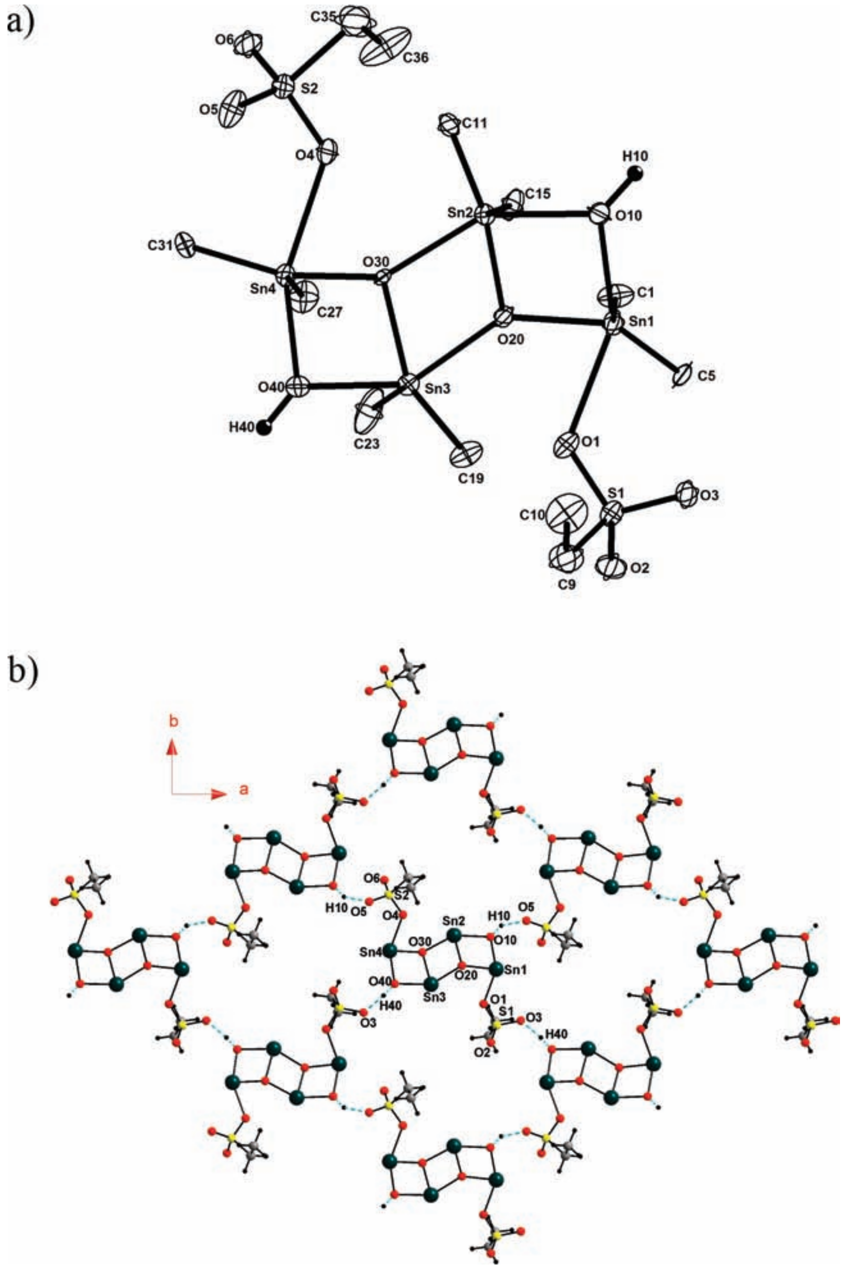
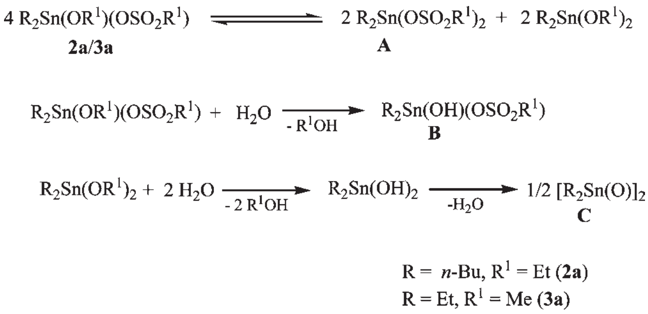


Figure 2. (a) ORTEP view of the molecular structure of **2**. The thermal ellipsoids are set at 30% probability, and the hydrogen (except O10 and O40) and *n*-butyl carbon (except Sn−C) atoms are omitted for clarity. (b) 2D structure of **2** in ab-plane. All the *n*-butyl groups on tin atoms are omitted for clarity.

Sn1 and 2, and Sn3 and 4, respectively (Sn−O = 1.993(6)−2.185(7) Å). Each tin atom in the molecule adopts a distorted trigonal bipyramidal geometry with SnC_2O (Σ360 ± 0.0−1.5°) core occupying the equatorial plane while the other two oxygen atoms are disposed axially in a trans manner [O1−Sn1−O10 = 152.4(2), O10−Sn2−O30 = 146.9(2), O20−Sn3−O40 = 145.1(2), O4−Sn4−O40 = 151.9(2) °]. The monodentate ethanesulfonate groups on Sn1 and Sn4 atoms (Sn1−O1 = 2.379(7); Sn4−O4 = 2.311(7) Å) are involved in OH---O hydrogen bonding. Thus each ladder structure is connected to four adjacent units via intermolecular hydrogen bonding interactions involving H10, H40 atoms of the hydroxyl groups and O5, O3 atoms associated with ethanesulfonate groups respectively [O10−H10 = 0.95, H10---O5 = 1.95, O10---O5 = 2.762(9) Å, O10−H10---O5 = 142°; O40−H40 = 0.95, H40---O3 = 1.86, O40---O3 = 2.738(9) Å, O40−H10---O3 = 153°]. This results in a sheet-like structure incorporating 28-membered macrocycle rings (Figure 2b). The Sn−O(ethanesulfonate) bond lengths (Sn1−O1 = 2.379(7); Sn4−O4 = 2.311(7) Å] are comparable with those reported earlier for related diorganotin compounds and suggest appreciable degree of ionic character.[8,12] The molecular structure of **3** is composed of two fused four-membered Sn_2O_2 rings which are constructed from Sn1, Sn2, Sn3 and O1, O2, O3 atoms [Sn−O = 2.046(7)−2.164(8) Å]. The oxygen atoms O1 and O2 are μ_3- donors, the former being associated with the exocyclic Sn4 atom of diethyltin bis(methanesulfonate) fragment [Sn1−O1 = 2.110(7)]. The Sn1 and Sn2 atoms are further associated with a bridging methanesulfonate (S1) group [Sn1−O4 = 2.307(8), Sn2−O5 = 2.336(8) Å]. Although one hydrogen atom which is essential to compensate for the charge neutrality could

Scheme 1. Proposed Intermediate Species Involved in the Formation of **2** and **3**



not be located crystallographically, its presence on the O3 atom has been suggested based on strong intermolecular O3---O11(S3) contacts [2.695(15) Å] suggesting the presence of hydrogen-bonding interactions. Each tin atom in the molecule adopts a trigonal bipyramidal geometry with SnC$_2$O (360 ± 0.0−1.4°) core occupying the equatorial plane while the other two oxygen atoms are placed in trans-disposition.

The structural analysis provides a scope to delineate hydrolysis pathways of the mixed-ligand diorganotin precursors **1a**−**3a** and also the genesis of the simplest constructs forming the organotin clusters **1**−**3**. As shown in Scheme 1, a common trait of all the tin precursors is their tendency to exist in equilibrium with the corresponding disproportionated products, R$_2$Sn(OSO$_2$R^1)$_2$ (**A**) and R$_2$Sn(OR^1)$_2$ under hydrolytic conditions. For **2a** and **3a**, selective hydrolysis of the Sn−OR^1 bonds in the equilibrated diorganotin species yields stable R$_2$Sn(OH)OSO$_2$R^1 and [R$_2$SnO]$_2$ complexes, designated as **B** and **C**, respectively, in Scheme 1. It is imperative to mention that similar monomeric cyclo- stannoxanes such as **C** are known with bulky substituents on the tin atoms,[13] while analogous hydroxo diorganotin alkanesulfonate such as **B** has been reported earlier by us.[9d] The structural motif of **2** (Figure 2a) is thus viewed as comprising of a coordination self-assembly formed by association of the corresponding **B** and **C** subunits in 2:1 ratio. On the other hand, the genesis of **3** results from the coexistence of the subunits, **A**, **B**, and **C** in 1:1:1 ratio which involves Sn4, Sn2 and Sn1, Sn3 atoms, respectively (Figure 3a). Interestingly, an insight into the molecular structure of compound **1** identifies a molecular fragment whose core atom arrangement is similar to that observed for **3** (Figure 1a, inset). This leads one to speculate that the initial stage of hydrolysis of the tin precursors, **1a** and **3a**, is similar and generates analogous intermediate species (Scheme 2). For **1a**, a tentative reaction pathway involving the formation of the intermediate [CH$_3$Sn(OH)(SO$_3$)] (**E**) is proposed which involves concurrent Sn−C(methyl) and S−C(ethanesulfonate) bond cleavage in (CH$_3$)$_2$Sn(OH)(OSO$_2$Et) with the formation of propane as the byproduct which could not be identified. This speculation is based on extensive studies on C−C bond formation involving organosulfur reagents in the presence of an organotin and transition metal species as catalysts (Stille-type coupling reaction).[14] Sporadic reports are also available for the synthesis of diorganotin-sulfites, R$_2$SnSO$_3$ involving the insertion reaction of SO$_2$ into diorganotin oxide.[15] The formation of the cyclic stannoxane, [CH$_3$Sn(O)(OH)]$_2$ (**F**) may result from the partial hydrolysis and condensation of the tin species, **E**. The formation of the cluster **1** is realized by association of the species **D**, **E**, and **F** in a 1:2:1 ratio by coordinative association of oxo-/hydroxo-/sulfite ligand sets. The tin atoms representing these species in the structure are Sn1, Sn4 and Sn5, Sn2 and Sn3, respectively.

On the basis of these studies, it is apparent that Sn−C and S−C bond activation and formation of **1** is a cooperative phenomenon, and the key determinant to bring about this transformation is the nature of organic substituents on the tin and sulfur centers in the precursor mixed-ligand diorganotin-(alkoxy)alkanesulfonate. In particular, the observed S−C$_{\text{alkyl}}$ bond cleavage in the ethanesulfonate moiety bound on an organotin scaffold without the aid of a transition metal complex may open new opportunities in organotin cluster chemistry.

Experimental Section

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere unless otherwise stated. Solvents were freshly distilled over phosphorus pentoxide (chloroform and hexane). Glasswares were dried in an oven at 110−120 °C and further flame-dried under vacuum prior to use. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a BRUKER DPX-300 spectrometer at 300, 75.47, and 111.88 MHz, respectively. ^{1}H and ^{13}C chemical shifts are quoted with respect to the residual protons of the solvent while ^{119}Sn NMR data are given using tetramethyltin as external standard. IR spectra were recorded on Nicolet protege 460 ESP spectrophotometer using KBr optics. Elemental analysis (C, H) was performed on a Perkin-Elmer model 2400 CHN elemental analyzer. HRMS were recorded with AB Sciex, 1011273/A model using ESI technique. Compounds **2a** and **3a** were prepared by following the literature procedure.[8a,c]

Synthesis of 1a. The reaction between dimethyltin oxide (0.36 g, 2.18 mmol) and excess of diethyl sulfite (3.04 g, 21.8 mmol) was performed under refluxed conditions (100−110 °C, 40−45 h) in presence of ethyl iodide (0.34 g, 2.18 mmol). The clear solution thus obtained was cooled and *n*-hexane was added to precipitate a white solid which was filtered and dried under vacuum. The compound was identified as **1a**.

1a. [Me$_2$Sn(OEt)(OSO$_2$Et)]$_n$. Yield: 60%. ^{1}H NMR (DMSO-d_6): δ 3.29 (q, $^3J_{\mathrm{H-H}} = 6.9$ Hz, 2H, OCH_2CH$_3$), 2.36 (q, $^3J_{\mathrm{H-H}} = 7.5$ Hz, 2H, SCH_2CH$_3$), 1.28 (t, $^3J_{\mathrm{H-H}} = 7.5$ Hz, 3H, SCH$_2$CH_3), 1.16 (t, $^3J_{\mathrm{H-H}} = 6.9$ Hz, 3H, OCH$_2$CH_3), 0.82 ($^2J_{\mathrm{Sn-H}} = 102$ Hz, 6H, SnCH_3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 60.61 (OCH$_2$CH$_3$), 45.75 (SCH$_2$CH$_3$), 18.35 (OCH$_2$CH$_3$), 13.51, 12.69 (SnCH$_3$), 8.48 (SCH$_2$CH$_3$). ^{119}Sn NMR (DMSO-d_6): δ −176, −182, −248, −288. IR (KBr, cm^{-1}): 1258, 1188, 1128, 1057 (νSO$_3$), 778 (νSCH$_2$CH$_3$). Anal. Calcd for C$_6$H$_{16}$O$_4$SSn: C, 23.79; H, 5.32. Found: C, 23.73; H, 5.44.

Synthesis of 1−3. Dimethyltin(ethoxy)(ethanesulfonate) (**1a**), di-*n*-butyltin(ethoxy)(ethanesulfonate) (**2a**), or diethyltin(methoxy)-(methanesulfonate) (**3a**) (~1.5 mmol) was added in ~50 mL of moist hexane (hexane/water = 95:5 v/v) and the heterogeneous solution in each case was stirred under atmospheric conditions for 48 h. Thereafter, the white solid thus obtained was filtered, washed with dry diethyl ether, and dried under

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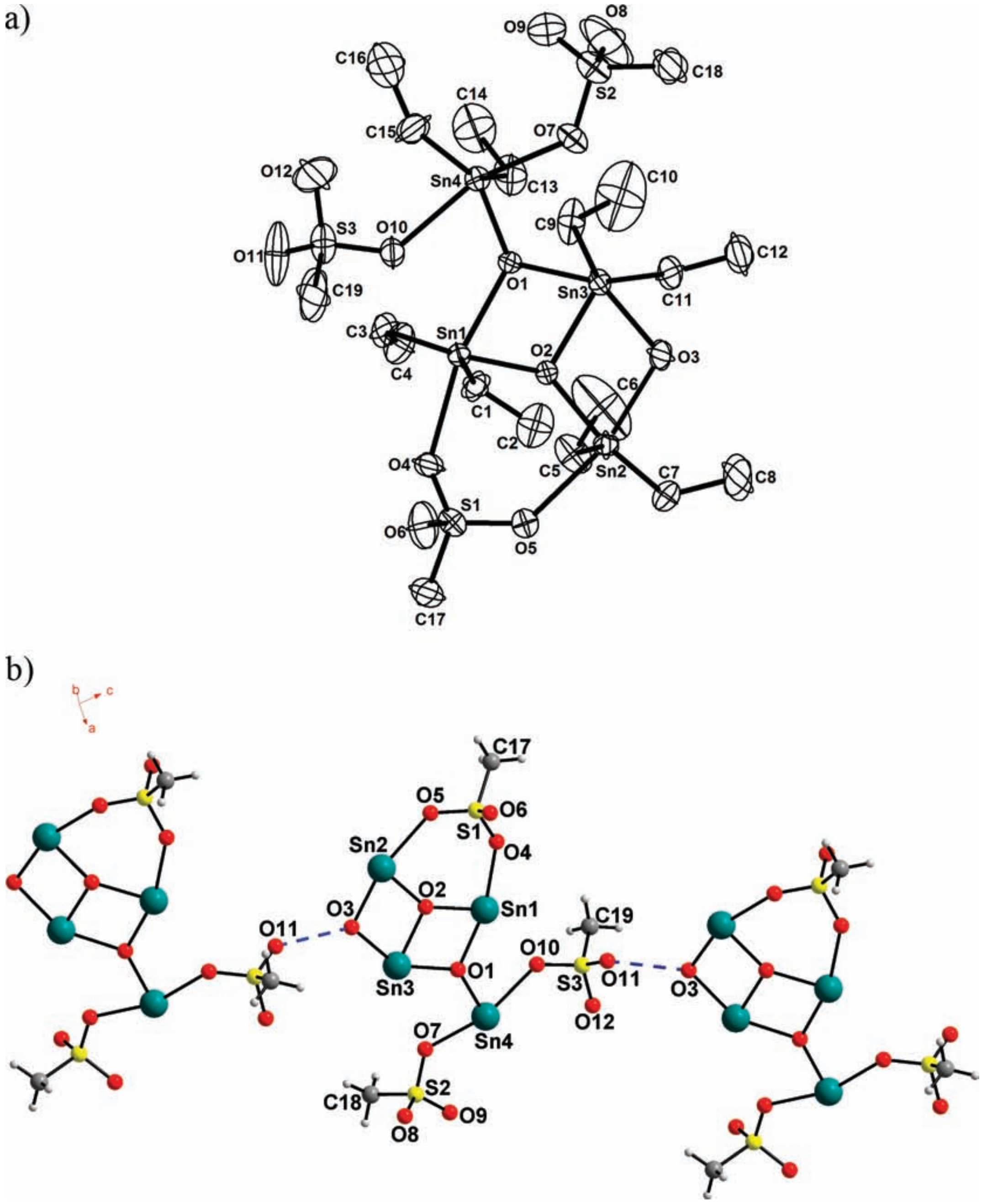


Figure 3. (a) ORTEP view of the molecular structure of **3**. The thermal ellipsoids are set at 30% probability, and the hydrogen atoms are omitted for clarity. (b) 1D chain of **3** along *c*-axis showing intermolecular hydrogen bonding interactions. The ethyl groups on tin atoms are omitted for clarity.

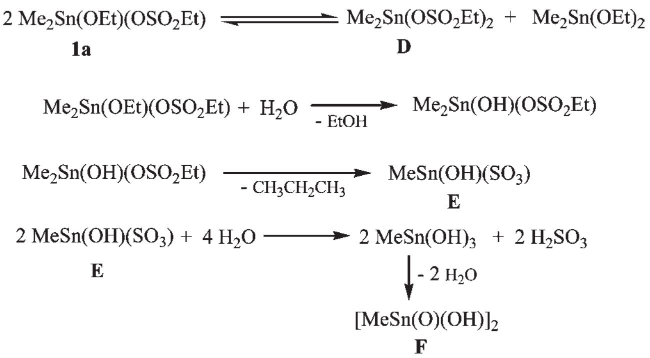
vacuum. The product in each case was crystallized from chloroform/methanol/toluene mixture to obtain the organotin clusters, **1**−**3** respectively in analytically pure form.

1 **[(Me$_2$Sn)(MeSn)$_4$(OSO$_2$Et)$_2$(OH)$_4$(O)$_2$(SO$_3$)$_2$].** Yield: 55%. ^{1}H NMR (DMSO-d_6): δ 2.53 (q, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, 4H, SCH_2CH$_3$), 1.09 (t, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, 6H, SCH$_2$$CH_3$), 0.90 (br, 6H, Sn($CH_3$)$_2$), 0.53 (br, 12H, Sn$CH_3$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 45.68 (SCH$_2$CH$_3$), 14.34 (Sn(CH$_3$)$_2$), 9.53, 8.73 (SCH$_2$$CH_3$), 1.22 (Sn$CH_3$, $^1J_{\mathrm{Sn-C}}$ = 513 Hz) . ^{119}Sn NMR (DMSO-d_6) = δ −151, −199, −345. IR (KBr, cm^{-1}): 1260, 1227, 1188, 1137 (νSO$_3$), 3414 (br, νOH). Anal. Calcd for $C_{10}H_{32}O_{18}S_4Sn_5$: C, 10.33; H, 2.78. Found: C, 10.30; H, 2.98.

2 **[{(*n*-Bu$_2$Sn)$_2$(OH)(OSO$_2$Et)}O]$_2$.** Yield: 60%. ^{1}H NMR (CDCl$_3$): δ 2.78 (q, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, 4H, SCH_2CH$_3$), 1.65−1.56 (m, 32H, SnCH_2CH_2), 1.33−1.15 (m, 22H, Sn(CH$_2$)$_2$-CH_2 + SCH$_2$$CH_3$), 0.87 (t, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, 24H, Sn(CH$_2$)$_3$$CH_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 46.05, 45.97 (SCH$_2$CH$_3$), 27.48, 27.29, 27.04, 26.90, 26.77, 26.62, 25.94, 24.96, 23.93, 23.77 (Sn(CH$_2$)$_3$), 13.59 (Sn(CH$_2$)$_3$$CH_3$), 9.23, 8.57 (SCH$_2$$CH_3$). ^{119}Sn NMR (CDCl$_3$): δ −143, −148, 154, −174, −192. IR (KBr, cm^{-1}): 1262, 1138, 1084 (νSO$_3$), 742 (νSCH$_2$CH$_3$). Anal. Calcd for $C_{36}H_{86}O_{10}S_2Sn_4$: C, 35.50; H, 7.12. Found: C, 35.23; H, 7.50.

3 **[(Et$_2$Sn)$_4$(OH)(O)$_2$(OSO$_2$Me)$_3$].** Yield: 62%. ^{1}H NMR (CDCl$_3$): δ 4.24 (br, 1H, OH), 2.76 (br, 9H, SCH_3), 1.59 (br, 16H, SnCH_2), 1.42 (br, 24H, SnCH$_2$$CH_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 39.46 (SCH$_3$), 20.59 (SnCH$_2$CH$_3$, $^1J_{\mathrm{Sn-C}}$ = 640 Hz), 9.47, 9.35, 9.21 (SnCH$_2$$CH_3$). ^{119}Sn NMR (CDCl$_3$): −151, −161, −174, −198, −207, −248. ^{119}Sn NMR (DMSO-d_6): δ −165, −168, −217, −240, −381. IR (KBr, cm^{-1}): 1220, 1157, 1048 (νSO$_3$), 3273 (νOH). Anal. Calcd for $C_{19}H_{49}O_{12}S_3Sn_4$: C, 21.93; H, 4.75. Found: C, 21.58; H, 5.01.

Scheme 2. Proposed Intermediate Species Involved in the Formation of **1**



$$\underset{\mathbf{1a}}{2\,Me_2Sn(OEt)(OSO_2Et)} \rightleftharpoons \underset{\mathbf{D}}{Me_2Sn(OSO_2Et)_2} + Me_2Sn(OEt)_2$$

$$Me_2Sn(OEt)(OSO_2Et) + H_2O \xrightarrow[\text{- EtOH}]{} Me_2Sn(OH)(OSO_2Et)$$

$$Me_2Sn(OH)(OSO_2Et) \xrightarrow[\text{- }CH_3CH_2CH_3]{} \underset{\mathbf{E}}{MeSn(OH)(SO_3)}$$

$$\underset{\mathbf{E}}{2\,MeSn(OH)(SO_3)} + 4\,H_2O \longrightarrow 2\,MeSn(OH)_3 + 2\,H_2SO_3$$

$$2\,MeSn(OH)_3 \xrightarrow{\text{- }2\,H_2O} \underset{\mathbf{F}}{[MeSn(O)(OH)]_2}$$

X-ray Crystallography. The intensity data of **1** and **2** were collected on Nonius Kappa CCD diffractometer equipped with a molybdenum sealed tube (Mo Kα radiation, $\lambda = 0.71073$ Å) and a graphite monochromator at $T = 150(2)$ K. Cell parameters, data reduction and absorption corrections were performed with Nonius software (DENZO and SCALEPACK).[16] The structures were solved by direct methods using SIR97,[17] and refined by full matrix least-squares method on F^2 using SHELXL-97.[18] All calculations were performed using WinGx.[19] Partial atoms were refined isotropically. X-ray diffraction studies of **3** mounted on a capillary were carried out on a BRUKER AXS SMARTAPEX diffractometer with a CCD area detector (KR) 0.71073 Å, monochromator: graphite).[20] Frames were collected at $T = 293$ K by ω, φ, and 2θ-rotation at 10 s per frame with SAINT.[20] The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[21] Structure solution, refinement, and data output were carried out with the SHELXTL program.[22] Images were created with the Diamond program.[23] Hydrogen bonding interactions in the crystal lattice were calculated with SHELXTL and Diamond.[22,23] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model unless stated otherwise. The crystals of **1** were exceptionally small, and diffraction fall off was evident at higher Bragg angles. Pseudo-merohedral twinning (180° rotation about the 0,1,0 reciprocal lattice direction) accounted for in the refinement. This twinning may also have impacted on the diffracting power of the sample, and data were consequently truncated at a Bragg angle of 25.24°. Four hydrogen atoms (one attached to each of O8, O9, O10, and O11) could not be reliably located and, hence, were omitted from the final-least-squares cycles. However, intra- (for O8 and O10) and intermolecular contacts (for O7 and O9) to proximate oxygens in the structure suggest the presence of strong hydrogen-bonding involving these hydrogens, as discussed in the text. Similarly, this crystal was also a poor diffractor with 92% data completeness up to 25°. Despite this, the framework of the molecule can be unambiguously identified, which would be impossible by any spectroscopic technique. In addition, the compound **2** shows disorder in two *n*-Bu groups attached to Sn, based on C23−C26 (ratio 1:1) and C31−C34 (ratio 2:1). As a result, C26A, C32−C34 and C32A-C34A were refined isotropically. Hydrogen atoms for two OH groups (O10 and O40) had to be assigned as they did not appear in the difference Fourier map but whose position is strongly suggested by the close approach of potential hydrogen-bonding partners. For **3**, there is disorder in two of the ethyl groups bonded to Sn, namely, C5, C6, C6A (75:25) and C9, C10, C9A, C10A (60:40). C9A was refined isotropically, and bond restraints were required for C5−C6A, C13−C14 and C15−C16 of this ligand.

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Note Added after ASAP Publication. This paper was published on the Web on April 21, 2010, with an error in eq 1. The corrected version was reposted on April 26, 2010.

Supporting Information Available: Crystallographic data (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **1** (CCDC-763217), **2** (CCDC-763218), and **3** (CCDC-763219) have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44−1233−336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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