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Disproportionation reactions of (methoxy/hydroxy)diorganotin(IV) methanesulfonates with carboxylic acids Synthesis and structure of new diorganotin(IV) carboxylates

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Abstract

Disproportionation reactions between equimolar quantities of $R_2Sn(X)OSO_2Me$ [X = OMe or OH] and ethylmalonic/maleic acid in acetonitrile under mild conditions afford new diorganotin dicarboxylates, $R_2Sn(O_2CR'COOH)_2$ [R′ = CHEt, R = *n*-Pr (**3a**), *n*-Bu (**3b**); R′ = CH=CH, R = *n*-Pr (**3c**), *n*-Bu (**3d**)] along with $R_2Sn(OSO_2Me)_2$ [R = *n*-Pr (**4a**), *n*-Bu (**4b**)]. Similar reactions of the tin precursors with pyridine-2-carboxylic acid provide an access to novel trinuclear tin complexes, $R_6Sn_3(O_2CC_5H_4N\text{-}2)_3(OSO_2Me)_3$ [R = *n*-Pr (**5a**), *n*-Bu (**5b**)]. These have been characterized by IR and multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectroscopies. The molecular structures of **3b**, **4b** and **5b** have been determined by X-ray crystallography. Compound **3b** is monomeric with bicapped tetrahedron geometry by virtue of anisobidentate coordination of one carboxylate group of each ligand, while the other carboxylic acid group remains free. The polymeric structure of **4b** features centrosymmetric eight-membered rings comprising bridging methanesulfonate groups and nearly perfect octahedral geometry around each tin atom. Compound **5b** crystallizes as **5b**$\cdot 2H_2O\cdot Et_2O$. Its molecular structure comprises 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 pyridine-2-carboxylate groups. A possible rationalization of these results are discussed in terms of the intermediacy of mixed ligand tin complexes, $R_2Sn(L)OSO_2Me$ (L = carboxylate) formed by the selective substitution of Sn–OMe group or by the dehydration of Sn–OH group in the tin precursors with the carboxylic acid.

Keywords: Disproportionation; Carboxylates; Diorganotin; Trinuclear tin

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1. Introduction

Diorganotin esters derived from monofunctional carboxylic acids have been studied extensively owing to their multifarious applications such as PVC stabilizers, biocides and metal-based drugs [1]. The complex formation equilibria between diorganotin(IV) species and carboxylic acids in aqueous solution have been investigated in order to understand their environmental fate and role in biological systems [2]. Tin carboxylates are commonly synthesized by classical azeotropic dehydration reaction between diorganotin oxide and the corresponding carboxylic acid [1a,3]. Davies et al. [4] have reported an alternate method, involving $R_2Sn(OPr)_2$ as the starting precursors, for the synthesis of diorganotin carboxylates under mild conditions. These compounds reveal a wide structural diversity depending upon the steric bulk of the alkyl/aryl substituents and/or of ligands and their electronic effect [5].

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By contrast, there are only a few systematic studies on analogous compounds derived from dioic acids [6–8]. Structurally authenticated examples in this family are limited and are polymeric in nature, e.g. $[Bu_2Sn(O_2CR\text{-}CO_2)]_x$ (R = alkyl/aryl) [6b,6c] and $[R_2Sn(O_2C)_2C_5H_3N\cdot H_2O]_x$ [7]. Diorganostannates derived from 2,6-pyridine dicarboxylic acid are also known [8].

We have been interested in the development of alternate synthetic methods for different structural variety of tin carboxylates which are otherwise inaccessible by the classical dehydration approach. In this context, a detailed study of the reactivity of mixed ligand diorganotin complexes such as $R_2Sn(X)OSO_2Me$ [R = *n*-Pr or *n*-Bu; X = OMe (**1**), OH (**2**)] [9] towards a number of carboxylic acids has been undertaken. The precursors **1** are chosen with a premise that the selective ability of reactive Sn–OMe/Sn–OSO_2Me groups to undergo substitution reactions may provide an access to a range of mixed ligand tin carboxylates. Similarly, the tin precursors **2** provide a case study to understand the competitive pathway involving substitution behavior of Sn–OSO_2Me group vis-à-vis dehydration reaction of Sn–OH group towards the carboxylic acids. The results obtained from these studies are reported herein.

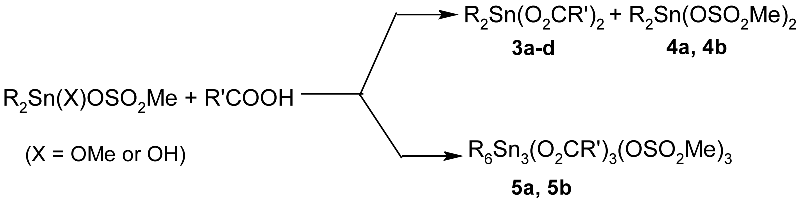
2. Results and discussion

2.1. Synthesis

As evident from Scheme 1, the reactions between equimolar quantities of $R_2Sn(X)OSO_2Me$ [X = OMe (**1**) or OH (**2**)] with ethylmalonic/maleic acid in acetonitrile gave the corresponding diorganotin dicarboxylates (**3a**–**3d**) and diorganotin bis(methanesulfonates) (**4a** and **4b**) [9] under mild conditions (RT, 8–10 h). On the other hand, analogous reactions of the tin precursors with pyridine-2-carboxylic acid led exclusively to the trinuclear tin compounds (**5a** and **5b**). The isolation of these complexes can be rationalized by assuming that the above reactions proceed by the formation of unstable mixed ligand tin complexes, $R_2Sn(L)OSO_2Me$ (L = carboxylate group), formed via selective substitution of the Sn–OMe bond (for **1**) or azeotropic dehydration of Sn–OH group (for **2**) with carboxylic acid. The resulting mixed ligand tin intermediate undergoes disproportionation to afford the new diorganotin esters. Strong evidence in support of this proposition comes from the crystal structure of the trinuclear tin compound **5b**.

2.2. Characterization

All compounds are white crystalline solids and are soluble in common organic solvents such as $CHCl_3$, CH_3CN, $C_6H_5CH_3$ and DMSO, etc. IR spectra (KBr) of **3a** and **3b** exhibit two strong bands at 1600–1605 and 1710–1715 cm^{-1} due to νCO_2 mode of coordinated and free carboxylic groups, respectively, while the corresponding absorptions for **3c** and **3d** appear at 1500–1505 and 1580–1590 cm^{-1}. These absorptions remain practically unaltered in dichloromethane solution. A broad band at ~ 3100 cm^{-1} is characteristic of νOH mode in each case. ^{1}H-NMR spectra of **3a**–**3d** 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-NMR spectra provide $^nJ(^{13}C-^{119/117}Sn)$ coupling values ($^1J = 540–570$ Hz). The carbonyl carbons appear as single resonance at $\delta = 165–175$ ppm, which suggests a rapid intermolecular/intramolecular carboxylate exchange in solution. These results are consistent with those of analogous tincarboxylates reported earlier [6b]. In **3b**, the accidental degeneracy of ^{13}C chemical shifts of $SnCH_2$ and CH_2(Et) carbons is substantiated by (^{1}H–^{13}C) HSQC NMR correlation spectrum which reveals cross-peak at $\delta = 25.5/(1.65-1.59)$. A close similarity of the $^1J(^{13}C-^{119/117}Sn)$ as well as ^{119}Sn-NMR chemical shifts δ (-151 to -140) for **3a**–**3d** suggest that these compounds adopt similar structural features in solution state. The IR spectra of **5a** and **5b** exhibit bands at 1650–1685 and 1294–1298 cm^{-1} due to coordinated



R' = CH(Et)COOH; R = n-Pr (**3a**), n-Bu(**3b**)
R' = CH=CHCOOH; n-Pr (**3c**), n-Bu (**3d**)
R = n-Pr (**4a**), n-Bu (**4b**)
R' = C_5H_4N-2; R = n-Pr (**5a**), n-Bu (**5b**)

Scheme 1.

ν_aCO_2 and ν_sCO_2 modes, respectively. ^{1}H-NMR spectrum of each compound identifies Pr_2Sn/Bu_2Sn, C_5H_4N-2 and SMe groups in 1:1:1 integrated ratio. The ^{119}Sn-NMR spectra ($CDCl_3$) of **5a** and **5b** show a close resemblance with the chemical shift values at $\delta = -216$, -346 and -418 (for **5a**) and -210, -346, -421 (for **5b**). However, these signals are broad and span over a large chemical shift range, thus suggesting structural changes in solution [10]. The identity of **5a** and **5b** is further established from the FAB mass spectra. Although M^+ ion corresponding to the trinuclear tin assembly is not discernable, structurally important ions such as $[M-2OSO_2Me-2H]^+$, $[M-R_2Sn(OSO_2Me)_3-2H]^+$, $[R_2Sn(O_2CC_5H_4N\text{-}2)]^+$, and $[RSn(O_2CC_5H_4N\text{-}2)_2]^+$ are evident from the spectra. The relevant data are summarized in Section 3.

2.3. *X-ray crystal structures*

The single crystals suitable for X-ray structure analysis were obtained upon cooling the solution of the compounds in dichloromethane (for **3b**), methanol/acetonitrile (70:30) (for **4b**) and dichloromethane/diethyl ether (80:20) (for **5b**). The molecular structures along with atomic labeling scheme are shown in Figs. 1–3, respectively. The relevant crystal data are given in Table 1, while selected bond lengths and angles are listed in Tables 2–4. The molecule **3b** adopts a centrosymmetric monomeric 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. The structure is best described as bicapped tetrahedron. The tetrahedron comprises of two Sn–C and two covalent Sn–O bonds [C(6)–Sn(1)–O(2)/C(6)#1–Sn(1)–O(2)#1, 105.3(6)°; C(6)#1–Sn(1)–O(2)/C(6)–Sn(1)–O(2)#1, 107.3(6)°], while O(1) and O(1)#1 form the caps of the bicapped tetrahedron [O(1)#1–Sn(1)–O(1), 173.5(7)°]. The effect of capping atoms is reflected in the narrow bond angles in C(6)–Sn(1)–C(6)#1 138.0(13)° and O(2)#1–Sn(1)–O(2) 77.1(6)°. The SnO_4 coordination sphere is planer ($360 \pm 1°$). The covalent Sn(1)–O(2)/Sn(1)–O(2)#1 as well as coordinated Sn(1)–O(1)/Sn(1)–O(1)#1 bond distances are 2.121(11) and 2.514(11) Å, respectively, and compare well with those of analogous tin carboxylates derived from monocarboxylic acids [11]. The presence of weak intermolecular (O...HO) hydrogen bonding (2.622 Å) is also manifested in the molecule. The crystal structure represents the first example of monomeric diorganotin dicarboxylate derived from dioic acid.

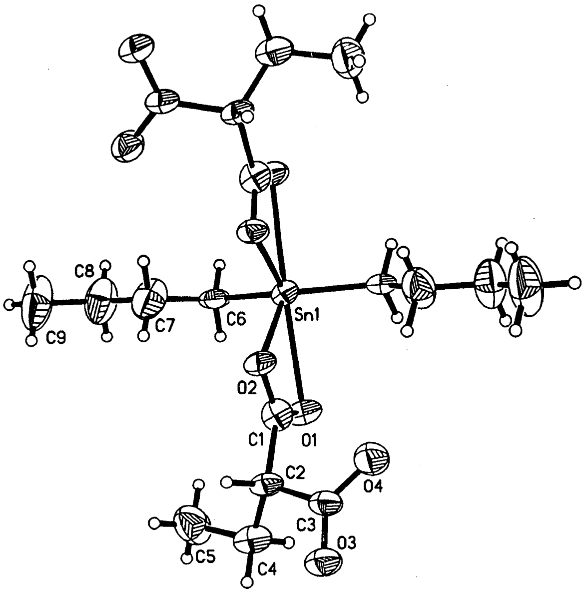


Fig. 1. The ORTEP view of **3b** with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability level.

The molecule **4b** adopts polymeric structure with centrosymmetric eight-membered rings comprising two bridging methanesulfonate groups between the two consecutive tin atoms. The linear chains propagate along $\bar{a}$ axis (1 0 0) but have no interaction with each other. The angles C(1)#1–Sn(1)–C(1) 180.0(2), O(1)#1–Sn(1)–O(1) 180.0(2) and O(2)#2–Sn(1)–O(2)#3 180.0(4)° propose nearly perfect octahedral geometry around each tin atom in this molecule. The *cis* angles around tin (C–Sn–O and O–Sn–O) vary between 86 and 94° (Table 3). The Sn–O (methanesulfonate) bond distances Sn(1)–O(1), Sn(1)–O(1)#1; 2.272(11) Å and Sn(1)–O(2)#2, Sn(1)–O(2)#3; 2.254(10) Å are longer than the normal covalent Sn–O (1.9–2.1 Å) bond length [12] and reflect some degree of ionic character. However, these are comparable with the corresponding Sn–O bond distances reported earlier for mixed ligand diorganotin methanesulfonates, $R_2Sn(X)OSO_2Me$ (X = OH, β-dik) [9] as well as dimethyltin bisfluorosulfonate [13].

The molecular structure of $\mathbf{5b}\cdot 2H_2O\cdot Et_2O$ reveals a self-assembly of the mixed ligand tin ester, n-$Bu_2Sn(O_2CC_5H_4N\text{-}2)OSO_2Me$ and its disproportionated products, i.e. 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 pyridine-2-carboxylate group. The O(1) and N(1) atoms of the ligand is bonded to Sn(1) in a chelating fashion [Sn(1)–O(1) = 2.109(6), Sn(1)–N(1) = 2.305(7) Å], while the other carboxylic oxygen, O(2) remains free. Such bonding behavior is previously observed in $Ph_2Sn(O_2CC_5H_4N\text{-}2)_2$ [14]. The tridentate coordination mode of O(7), N(2) and O(6) with Sn(2) atom is in agreement with that found in $Me_2Sn(O_2CC_5H_4N\text{-}2)_2$ [15]. However, the bonding situation involving intermolecular coordinative association of N(3) and O(10) to Sn(3) atom [Sn(3)–N(3) 2.329(7); Sn(3)–O(10), 2.214(6) Å] is unprecedented and likely to arise due to the adventitious entry of water molecule in the Sn(2) coordination sphere. This unusual bonding situation is reflected in narrow C(35)–O(9)–Sn(2) angle

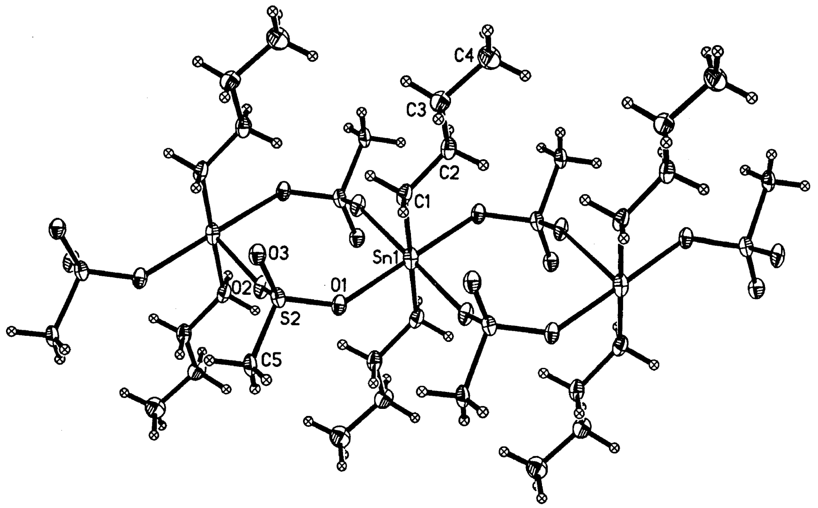


Fig. 2. The ORTEP view of **4b** with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability level.

[113.2(5)°] and a long Sn(2)–O(9) bond distance 2.374(6) Å as compared with other analogous metrical parameters in the molecule [C(21)–O(7)–Sn(2) = 120.3(5)°, C(6)–O(1)–Sn(1) = 121.1(5)°; Sn(1)–O(1) = 2.109(6) Å, Sn(2)–O(7) = 2.179(6) Å]. The average covalent and coordinate Sn–O bond distances are comparable with those of previously reported for diorganotin dicarboxylates derived from pyridine-2-carboxylic acid [14,15]. The average Sn–O (methanesulfonate) bond distance (2.311 Å) is relatively large and suggests some degree of ionic character [9].

In summary, isolation of new diorganotin carboxylates such as **3a**–**3d** and **5a** and **5b** is achieved from chemoselective reactivity of Sn–OMe/Sn–OH groups in the mixed ligand tin precursors towards the carboxylic acids. The structure of **5b**$\cdot 2H_2O \cdot Et_2O$ represents the first crystallographic signature of the disproportionation phenomena [16], wherein the mixed ligand tin intermediate, n-$Bu_2Sn(O_2CC_5H_4N\text{-}2)OSO_2Me$ and its disproportionated products, i.e. n-$Bu_2Sn(O_2CC_5H_4N\text{-}2)_2$ and n-$Bu_2Sn(OSO_2Me)_2$ form a self-assembly by the coordinative association of pyridine-2-carboxylate groups.

3. Experimental

All reactions were conducted in an inert atmosphere of nitrogen. Solvents were dried using standard techniques (acetonitrile, dichloromethane and n-hexane over P_2O_5). Glassware was dried in an oven at 110–120 °C and further flame-dried under vacuum prior to use. (Methoxy/hydroxy)diorganotin(IV) methanesulfonates and n-Pr_2SnO were prepared using literature methods [9,17]. ^1H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded on BRUKER DPX-300 at 300, 75.46 and 111.88 MHz, respectively. ^1H-NMR and ^{13}C-NMR chemical shifts are quoted with respect to the residual protons of the solvent, while ^{119}Sn-NMR data are given using tetramethyltin as internal standard. The IR spectra were

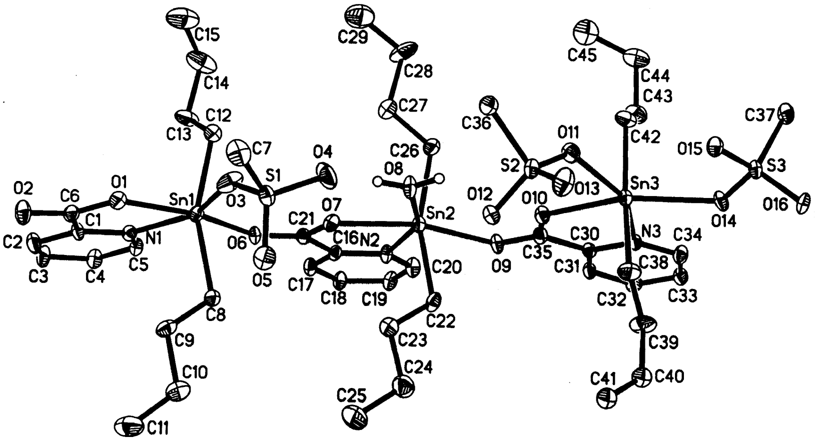


Fig. 3. The ORTEP view of **5b**$\cdot 2H_2O \cdot Et_2O$ with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms, lattice water and diethyl ether molecule are omitted for clarity.

Table 1
Summary for crystallographic data for compounds **3b**, **4b** and **5b**$\cdot 2H_2O \cdot Et_2O$[a]

	3b	**4b**	**5b**$\cdot 2H_2O \cdot Et_2O$
Empirical formula	$C_{18}H_{30}O_8Sn$	$C_5H_{12}O_3SSn_{1/2}$	$C_{49}H_{87}N_3O_{18}S_3Sn_3$
Formula weight	493.11	211.55	1458.47
T (°C)	23(2)	−100	−100
λ (Å)	1.54178	0.71069	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	C_2/c (no. 15, C_{2h}^6)	$P1$ (no. 2, C_i^1)	$P2_1/c$ (no. 14, C_{2h}^5)
a (Å)	22.130(4)	5.321(2)	20.5774(16)
b (Å)	5.0110(10)	8.762(3)	17.4931(14)
c (Å)	21.535(4)	10.792(3)	18.9046(15)
α (°)	90	64.30(2)	90
β (°)	102.74(3)	73.308(13)	103.790(2)
γ (°)	90	74.432(11)	90
V (Å^3)	2329.3(8)	428.2(2)	6608.8(9)
Z	4	2	4
ρ_{calcd} (mg m^{-3})	1.406	1.641	1.466
μ (mm^{-1})	9.045	1.751	1.282
Final R Indices [$I > 2\sigma(I)$]	$R1 = 0.0775$, $wR2 = 0.2057$	$R1 = 0.0829$, $wR2 = 0.2007$	$R1 = 0.0560$, $wR2 = 0.12$
R indices (all data)	$R1 = 0.1195$, $wR2 = 0.2431$	$R1 = 0.1081$, $wR2 = 0.2178$	$R1 = 0.1073$, $wR2 = 0.1423$

[a] For **3b**, **4b** and **5b**$\cdot 2H_2O \cdot Et_2O$: $R1 = (\Sigma \| \|F_0\| - \|F_c\| \| / \Sigma \|F_0\|)$, $wR2 = \Sigma w(F_0^2 - F_c^2)^2 / \Sigma w[(F_0^2)^2]^{1/2}$, $s = [\Sigma w(F_0^2 - F_c^2)^2/(n-p)]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **3b**[a]

Bond lengths			
Sn(1)–C(6)	2.06(2)	Sn(1)–C(6)#1	2.06(2)
Sn(1)–O(2)#1	2.121(11)	Sn(1)–O(2)	2.121(11)
Sn(1)–O(1)#1	2.514(11)	Sn(1)–O(1)	2.514(11)
Sn(1)–C(1)#1	2.66(2)	Sn(1)–C(1)	2.66(2)
O(1)–C(1)	1.28(2)	O(2)–C(1)	1.21(2)
O(3)–C(3)	1.26(2)	O(4)–C(3)	1.25(2)
Bond angles			
C(6)–Sn(1)–C(6)#1	138.0(13)	C(6)–Sn(1)–O(2)#1	107.3(6)
C(6)#1–Sn(1)–O(2)#1	105.3(6)	C(6)–Sn(1)–O(2)	105.3(6)
C(6)#1–Sn(1)–O(2)	107.3(6)	O(2)#1–Sn(1)–O(2)	77.1(6)
C(6)–Sn(1)–O(1)#1	85.7(5)	C(6)#1–Sn(1)–O(1)#1	91.9(5)
O(2)#1–Sn(1)–O(1)#1	54.9(4)	O(2)–Sn(1)–O(1)#1	131.6(4)
C(6)–Sn(1)–O(1)	91.9(5)	C(6)#1–Sn(1)–O(1)	85.7(5)
O(2)#1–Sn(1)–O(1)	131.6(4)	O(2)–Sn(1)–O(1)	54.9(4)
O(1)#1–Sn(1)–O(1)	173.5(7)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

Table 3
Selected bond lengths (Å) and angles (°) for **4b**[a]

Bond lengths			
Sn(1)–C(1)#1	2.10(2)	Sn(1)–C(1)	2.10(2)
Sn(1)–O(2)#2	2.254(10)	Sn(1)–O(2)#3	2.254(10)
Sn(1)–O(1)#1	2.272(11)	Sn(1)–O(1)	2.272(11)
S(2)–O(3)	1.436(12)	S(2)–O(1)	1.477(11)
S(2)–O(2)	1.490(11)	S(2)–C(5)	1.77(2)
Bond angles			
C(1)#1–Sn(1)–C(1)	180.0(2)	C(1)#1–Sn(1)–O(2)#2	93.8(5)
C(1)–Sn(1)–O(2)#2	86.2(5)	C(1)#1–Sn(1)–O(2)#3	86.2(5)
C(1)–Sn(1)–O(2)#3	93.8(5)	O(2)#2–Sn(1)–O(2)#3	180.0(4)
C(1)#1–Sn(1)–O(1)#1	87.8(5)	C(1)–Sn(1)–O(1)#1	92.2(5)
O(2)#2–Sn(1)–O(1)#1	85.9(4)	O(2)#3–Sn(1)–O(1)#1	94.1(4)
C(1)#1–Sn(1)–O(1)	92.2(5)	C(1)–Sn(1)–O(1)	87.8(5)
O(2)#2–Sn(1)–O(1)	94.1(4)	O(2)#3–Sn(1)–O(1)	85.9(4)
O(1)#1–Sn(1)–O(1)	180.0(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$; #2 $-x, -y+1, -z+1$; #3 $x+1, y, z$; #4 $x-1, y, z$.

recorded on Nicolet protégé 460 E.S.P. spectrophotometer using KBr optics. FAB mass spectra were recorded on a VG analytical 70-S and JEOL SX 102/DA-6000 spectrometer. Elemental analysis (C, H and N) was performed on a Perkin–Elmer model 2400CHN elemental analyzer. Sulfur and tin were estimated by gravimetric methods [18].

3.1. Reactions of (methoxy)diorganotin methanesulfonate with ethylmalonic/maleic acid

To a stirred solution of n-$Pr_2Sn(OMe)OSO_2Me$ (0.44 g, 1.34 mmol)/n-$Bu_2Sn(OMe)OSO_2Me$ (0.56 g, 1.55 mmol) in acetonitrile was added ethylmalonic acid (0.17 g, 1.34 mmol)/(0.21 g, 1.55 mmol) or maleic acid (0.15 g, 1.34 mmol)/(0.18 g, 1.55 mmol). The contents were stirred for 10–12 h at room temperature. A white precipitate formed in each case was filtered, dried and characterized as n-$Pr_2Sn(OSO_2Me)_2$ (**4a**) and n-$Bu_2Sn(OSO_2Me)_2$ (**4b**). The filtrates from the above reactions were concentrated and n-hexane was added. A white solid thus obtained in each case was filtered, washed with n-hexane and dried under vacuum. Recrystallization of the products from dichloromethane/toluene afforded the corresponding diorganotin dicarboxylates **3a**–**3d**.

Table 4
Selected bond lengths (Å) and angles (°) for **5b**·$2H_2O$·Et_2O

Bond lengths			
Sn(1)–O(1)	2.109(6)	Sn(1)–O(3)	2.282(6)
Sn(1)–N(1)	2.305(7)	Sn(1)–O(6)	2.440(5)
Sn(2)–O(7)	2.179(6)	Sn(2)–O(8)	2.248(5)
Sn(2)–N(2)	2.296(7)	Sn(2)–O(9)	2.374(6)
Sn(3)–O(10)	2.214(6)	Sn(3)–O(14)	2.289(6)
Sn(3)–N(3)	2.329(7)	Sn(3)–O(11)	2.331(6)
Bond angles			
C(8)–Sn(1)–C(12)	158.5(4)	O(1)–Sn(1)–N(1)	73.8(2)
O(1)–Sn(1)–O(3)	79.8(2)	N(1)–Sn(1)–O(6)	82.4(2)
O(3)–Sn(1)–O(6)	123.9(2)	C(26)–Sn(2)–C(22)	159.9(4)
O(7)–Sn(2)–N(2)	72.8(2)	O(7)–Sn(2)–O(8)	80.0(2)
O(8)–Sn(2)–O(9)	128.4(2)	N(2)–Sn(2)–O(9)	78.8(2)
C(42)–Sn(3)–C(38)	167.6(4)	O(14)–Sn(3)–N(3)	78.1(2)
O(10)–Sn(3)–N(3)	71.9(2)	O(10)–Sn(3)–O(11)	81.5(2)
O(14)–Sn(3)–O(11)	128.4(2)	C(6)–O(1)–Sn(1)	121.1(5)
C(21)–O(7)–Sn(2)	120.3(5)	C(35)–O(9)–Sn(2)	113.2(5)

3.2. Reactions of (hydroxy)diorganotin methanesulfonate with ethylmalonic/maleic acid

The reactions between *n*-$Pr_2Sn(OH)OSO_2Me$ (1.55 mmol)/*n*-$Bu_2Sn(OH)OSO_2Me$ (1.60 mmol) and equivalent amount of the corresponding acid in acetonitrile were carried under similar conditions as described above. The compounds **4a** and **4b** were isolated as the precipitated products while **3a**–**3d** were obtained from the filtrates.

*3.2.1. n-Pr₂Sn(O₂CCH(Et)COOH)₂ (**3a**)*

Yield: (0.27 g, 44%), m.p. 120–123 °C. ^{1}H-NMR ($CDCl_3$): δ 1.01 (m, 12H, CH_3-Et+Sn(CH_2)$_2$CH_3), 3.36 (t, 2H, CH), 1.75 (m, 8H, CH_2-Et+SnCH_2CH_2), 1.97 (m, 4H, SnCH_2) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 11.9 (CH_3-Et), 53.1 (CH), 22.7 (CH_2-Et), 28.6 (C_1, $^1J(^{13}C-^{119/117}Sn) = 567/542$ Hz), 18.1 (C_2 $^2J(^{13}C-^{119}Sn) = 33$ Hz), 17.6 (C_3, $^3J(^{13}C-^{119}Sn) = 95$ Hz), 177.6 (C=O) ppm. ^{119}Sn-NMR ($CDCl_3$): δ −150.1 ppm. IR (KBr, cm^{-1}): 3100 (νOH), 1714, 1601 ($\nu_a CO_2$), 1290 ($\nu_s CO_2$). Anal. Calcd. for $C_{16}H_{28}O_8Sn$: C, 41.02; H, 5.98; Sn, 25.64. Found: C, 40.80; H, 5.76; Sn, 25.44%.

*3.2.2. n-Bu₂Sn(O₂CCH(Et)COOH)₂ (**3b**)*

Yield: (0.36 g, 47%), m.p. 130–132 °C. ^{1}H-NMR ($CDCl_3$): δ 0.94 (t, 6H, CH_3-Et), 3.29 (t, 2H, CH), 1.61 (m, 8H, SnCH_2+CH_2-Et), 1.91 (m, 4H, SnCH_2CH_2), 1.37 (m, 4H, Sn(CH_2)$_2$CH_2), 0.96 (t, 6H, Sn(CH_2)$_3$CH_3) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 10.9 (CH_3-Et), 52.0 (CH), 25.5 (CH_2-Et+C_1, $^1J(^{13}C-^{119}Sn) = 549$ Hz), 21.7 (C_2), 25.2 (C_3, $^3J(^{13}C-^{119}Sn) = 100$ Hz), 12.4 (C_4), 176.1 (C=O) ppm. ^{119}Sn-NMR ($CDCl_3$): δ −144.5 ppm. IR (KBr, cm^{-1}): 3100 (νOH), 1712, 1601 ($\nu_a CO_2$), 1289 ($\nu_s CO_2$). Anal. Calcd. for $C_{18}H_{32}O_8Sn$: C, 43.54; H, 6.45; Sn, 24.19. Found: C, 43.50; H, 6.62; Sn, 24.10%.

*3.2.3. n-Pr₂Sn(O₂CCH=CHCOOH)₂ (**3c**)*

Yield: (0.27 g, 46%), m.p. 135–136 °C. ^{1}H-NMR ($CDCl_3$): δ 6.38 (s, 4H, CH=CH), 1.77 (m, 8H, Sn(CH_2)$_2$$CH_3$), 1.04 (t, 6H, CH_3) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 130 (CH=CH), 30.1 (C_1), 17.4 (C_2, $^2J(^{13}C-^{119}Sn) = 31$ Hz), 16.9 (C_3, $^3J(^{13}C-^{119}Sn) = 117$ Hz), 169.0 (C=O) ppm. ^{119}Sn-NMR δ −148.9 ppm. IR (KBr, cm^{-1}): 3050 (νOH), 1587, 1508 ($\nu_a CO_2$), 1240 ($\nu_s CO_2$). Anal. Calcd for $C_{14}H_{20}O_8Sn$: C, 38.53; H, 4.58; Sn, 27.52. Found: C, 39.10; H, 5.05; Sn, 26.48%.

*3.2.4. n-Bu₂Sn(O₂CCH=CHCOOH)₂ (**3d**)*

Yield: (0.31 g, 43%), m.p. 146–148 °C. ^{1}H-NMR ($CDCl_3$): δ 6.33 (s, 4H, CH=CH), 1.70 (m, 8H, Sn(CH_2)$_2$$CH_2$$CH_3$), 1.38 (m, 4H, Sn($CH_2$)$_2CH_2$$CH_3$), 0.91 (t, 6H, Sn($CH_2$)$_3CH_3$) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 129.6 (CH=CH), 25.8 (C_1, $^1J(^{13}C-^{119}Sn) = 551$ Hz), 25.7 (C_2, $^2J(^{13}C-^{119}Sn) = 29$ Hz), 26.5 (C_3, $^3J(^{13}C-^{119}Sn) = 99$ Hz), 13.5 (C_4), 169.0 (C=O) ppm. ^{119}Sn-NMR δ −140.7 ppm. IR (KBr, cm^{-1}): 3050 (νOH), 1585, 1505 ($\nu_a CO_2$), 1239 ($\nu_s CO_2$). Anal. Calcd for $C_{16}H_{24}O_8Sn$: C, 41.37; H, 5.17; Sn, 25.86. Found: C, 41.12; H, 5.15; Sn, 25.40%.

*3.3. Preparation of R₆Sn₃(O₂CC₅H₄N-2)₃(OSO₂Me)₃ (**5a** and **5b**)*

To a stirred solution of *n*-$Pr_2Sn(OMe)OSO_2Me$ (0.45 g, 1.35 mmol)/*n*-$Bu_2Sn(OMe)OSO_2Me$ (0.62 g, 1.72 mmol) in dry acetonitrile (~50 ml) was added pyridine-2-carboxylic acid (0.16 g, 1.35 mmol)/(0.21 g, 1.72 mmol). After 10–12 h, the clear solution was concentrated and *n*-hexane was added. Compounds **5a** and **5b** were isolated as white solids. These compounds were also obtained from analogous reactions of (hydroxy)di-*n*-propyl/*n*-butyltin methanesulfonate with pyridine-2-carboxylic acid under similar conditions as above.

*3.3.1. n-Pr₆Sn₃(O₂CC₅H₄N-2)₃(OSO₂Me)₃ (**5a**)*

Yield: (0.50 g, 81%), ^{1}H-NMR ($CDCl_3$): δ [7.79 (t, 1H), 8.15 (t, 1H), 8.46 (d, 1H), 9.25 (br, s, 1H) pyridine ring protons], 2.89 (s, 3H, SMe), 1.70 (m, 4H, SnC$H_2$$CH_2$$CH_3$), 1.35 (m, 4H, Sn$CH_2CH_2$$CH_3$), 0.75 (t, 6H Sn($CH_2$)$_2CH_3$) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ [126.2, 128.4, 141.3, 147.0, 148.0 (pyridine ring carbons)], 39.8 (SMe), 32.3 (C_1), 18.8 (C_2), 17.5 (C_3, $^3J(^{13}C-^{119}Sn) = 169$ Hz), 166.5 (C=O) ppm. ^{119}Sn-NMR ($CDCl_3$): δ −210, −346, −421 ppm. FAB mass [(*m*-nitrobenzyl alcohol): [M^+, 1269]], *m/z* 1077 $[M-2OSO_2Me-2H]^+$, 776 $[M-Pr_2Sn(OSO_2Me)_3-2H]^+$, 690 $[M-Pr_2Sn(OSO_2Me)_3-2Pr-2H]^+$, 407 $[PrSn(O_2CC_5H_4N\text{-}2)_2]^+$ and 328 $[PrSn(O_2CC_5H_4N\text{-}2)]^+$. IR (KBr, cm^{-1}): 1676 ($\nu_a CO_2$), 1296 ($\nu_s CO_2$), 1240, 1148, 1046 (νSO_3). Anal. Calcd for $C_{39}H_{63}N_3O_{15}S_3Sn_3$: C, 36.87; H, 4.96; N, 3.30; S, 7.56;

Sn, 28.36. Found: C, 36.50; H, 5.05; N, 3.15; S, 7.31; Sn, 27.72%.

3.3.2. *n*-$Bu_6Sn_3(O_2CC_5H_4N\text{-}2)_3(OSO_2Me)_3$ (**5b**)

Yield: (0.62 g, 75%), ^{1}H-NMR ($CDCl_3$): δ [7.89 (t, 1H), 8.27 (t, 1H), 8.54 (d, 1H), 9.3 (br, s, 1H) pyridine ring protons], 2.99 (s, 3H, SMe), 1.85 (m, 8H, $Sn(CH_2)_2CH_2CH_3$), 1.39 (m, 4H, $Sn(CH_2)_2CH_2CH_3$), 0.75 (6H, t, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ [125.9, 128.2, 141.4, 146.0, 147.5 (pyridine ring carbons)], 39.8 (SMe), 32.5 (C_1), 27.1 (C_2, $^2J(^{13}C-^{119}Sn) =$ 38 Hz), 25.8 (C_3, $^3J(^{13}C-^{119}Sn) = 159$ Hz), 13.3 (C_4) ppm. ^{119}Sn-NMR ($CDCl_3$): δ −216, −346, −418 ppm. FAB mass [(*m*-nitrobenzyl alcohol): (M^+, 1353)], *m*/*z* 1161 $[M-2OSO_2Me-2H]^+$, 832 $[M-Bu_2Sn(OSO_2Me)_3-2H]^+$, 718 $[M-Bu_2Sn(OSO_2Me)_3-2Bu-2H]^+$, 421 $[BuSn(O_2CC_5H_4N\text{-}2)_2]^+$, 356 $[BuSn(O_2CC_5H_4N\text{-}2)]^+$. IR (KBr, cm^{-1}): 1680 (ν_aCO_2), 1295 (ν_sCO_2), 1260, 1146, 1046 (νSO_3). Anal Calcd. for $C_{45}H_{75}N_3O_{15}S_3Sn_3$: C, 39.91; H, 5.54; N, 3.10; S, 7.09; Sn, 26.60. Found: C, 39.51; H, 5.38; N, 3.05; S, 6.91; Sn, 25.92%.

3.4. X-ray crystallography

The crystals of **3b**, **4b** and **5b** were mounted along with the largest dimension in sealed capillaries and were used for data collection. The intensity data for **3b** were collected on Rigaku AFC6R diffractometer equipped with a copper rotating anode and a highly oriented graphite monochromator at 23 °C. Rigaku AFC8 coupled with mercury-CCD detector (for **4b**) and Bruker SMART APEX diffractometers (for **5b**) equipped with molybdenum sealed tube and a highly oriented graphite monochromator were used for data collection at −100 °C. All calculations were done on an IBM compatible PC using programs TEXAN [19], Crystal Clear [20], SHELXL-97 [21], and SMART (VER 5.624) [22]. For compound **3b**, the systematic absences ($h\ k\ l$, $h+k+l=2n+1$; and $0\ k\ 0$, $k=2n+1$) indicated a choice between the space group $C2$ and $C2/c$. The latter space group was chosen and later confirmed by successful refinement of the structure. The structure was solved by Patterson method. No systematic absences were observed in **4b**. The structure was solved by direct method using SHELXL-97. The crystals of **5b** crystallizes as solvates. Asymmetric unit content: **5b**$\cdot 2H_2O\cdot Et_2O$. The systematic absences ($0\ k\ 0$, $k=2n+1$; and $h\ 0\ l$, $l=2n+1$) for **5b**$\cdot 2H_2O\cdot Et_2O$ indicated the space group $P2_1/c$. The structure was solved by direct methods using SHELXTL-PC. There appears to be considerable disorder on two *n*-butyl groups bonded to Sn(3). Two separate positions for the carbon atoms of these butyl groups were therefore refined. The atoms C38 to C41 were found with exact 0.5 occupancy (occupancy values 0.494(11) and 0.506(11)). The lattice also contains disordered solvent ether and a water molecule. In each case, all non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The function minimized was $\Sigma w(\|F_0\| - \|F_c\|^2)$. Hydrogen atoms were included in the ideal position with fixed isotropic U-values. A weighting scheme of the form $w = 1/[\sigma^2(F_0)^2+(aP)^2+bP]$ with $a = 0.141$, $b = 20.86$ (for **3b**), $a = 0.1176$, $b = 3.123$ (for **4b**) and $a = 0.0552$, $b = 0.00$ (for **5b**$\cdot 2H_2O\cdot Et_2O$) was used. An extinction correction was also applied to the data. The refinement converged to the R indices given in Table 1. The final difference map was devoid of significant features.

4. Supplementary material

Crystallographic data for the structural analysis (as.CIF format) have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 198700 (for **3b**), 198699 (for **4b**) and 189370 (for **5b**$\cdot 2H_2O\cdot Et_2O$). Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1233-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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