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Synthesis, characterization and structural studies of mixed-ligand di-*n*-butyltin alkanesulfonate derivatives, [*n*-$Bu_2Sn(X)OS(O)_2R]_2$ [R = Et, *n*-Pr; X = acac, 4-OMe–$O_2CC_9H_5N$-2, $O_2CC_9H_6N$-2, $O_2CC_9H_6N$-1]

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Abstract

A number of stable mixed-ligand di-*n*-butyltin alkanesulfonates, [*n*-$Bu_2Sn(acac)OS(O)_2R]_2$ [R = Et (**1**), *n*-Pr (**2**)] as well as [*n*-$Bu_2Sn(X)OS(O)_2Et]_2$ [X = 4-OMe–$O_2CC_9H_5N$-2 (**3**), $O_2CC_9H_6N$-2 (**4**), $O_2CC_9H_6N$-1 (**5**) bearing a chelating co-ligand have been synthesized by reacting equimolar quantities of *n*-$Bu_2Sn(OR)OS(O)_2R$ (R = Et (**1a**) or *n*-Pr (**1b**)) with acetylacetone or 4-methoxy-2-quinoline/2-quinoline/1-isoquinoline carboxylic acid in dichloromethane/acetonitrile under mild conditions (rt, 10–12 h). The crystal structures of **1**–**3** reveal dimeric structural motif in each case by virtue of bridging bidentate mode of the ethane/propanesulfonate groups with distorted octahedral geometry around the tin atoms. The bonding between tin and the alkanesulfonate groups is largely covalent (2.2–2.3 Å) irrespective of the nature of the co-ligand.

Keywords: Acetylacetonate; Carboxylates; Di-*n*-butyltin; Mixed-ligand

1. Introduction

Synthetic protocols for di/triorganotin-esters derived from sulfonic acids have been known for a long time [1] and continue to remain the subject of interest owing to their potential applications as Lewis acid catalyst in organic synthesis [2]. These are generally prepared by dehydration reaction of the appropriate sulfonic acid with an organotin oxide, treatment of an organotin halide with the silver salt of the sulfonic acid or insertion reaction of SO_3 into Sn–C bond(s) of tetraalkyltin. Recently, a number of diorganotin bis(arene/perfluoroalkanesulfonate)s associated with organic substituents of varying electronic and steric attributes have been studied with respect to their hydrolysis behavior [3]. Due to the intrinsically weak nature of the Sn–O bond, these compounds often undergo hemi-hydrolysis to afford a variety of oxotin cations or hydroxo tin species with interesting associated structural motifs such as coordination polymers and supramolecular arrays. These studies have provided a better insight of the role of these species in the mechanistic implications of the hydrolysis of organotin halides/sulfonates [4,3d].

Nevertheless, prior reports on the synthesis of analogous tin-sulfonates derived from alkanesulfonic acids are scanty and their characterization is primarily based on elemental analysis and IR spectroscopy [1b]. Recently, we have undertaken a systematic study to explore the synthetic aspects as well as bonding and chemical behavior of these class of compounds. In this context, mixed-ligand diorganotin(methoxy)methanesulfonates, $R_2Sn(OMe)OSO_2Me$ [R = *n*-Pr, *n*-Bu, *i*-Bu, *c*-Hx] have been synthesized by a

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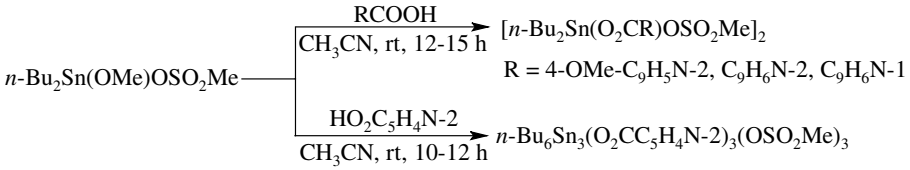
one pot reaction between diorganotin oxide and dimethylsulfite [5]. Their reactivity behavior towards a number of carboxylic acids have revealed the formation of structurally interesting class of mixed-ligand tin ester derivatives bearing the carboxylate and methanesulfonate ligands on the same tin center (Scheme 1) [6].



The bonding behavior of the methanesulfonate moiety in these compounds is found to be ubiquitous with the ligand acting as monodentate, bridging bidentate or μ_2-coordination mode. In a recent communication, we have also reported the utility of diethyl/di-*n*-propylsulfite as a synthon to afford the corresponding di-*n*-butyltin(alkoxy)alkanesulfonates (Eq. (1)) [7].

$$n\text{-}Bu_2SnO + ROS(O)OR + RI \xrightarrow[40-45h]{100-110\ ^\circ C} n\text{-}Bu_2Sn(OR)OSO_2R \quad (1)$$

R = Et,*n*-Pr

We envisioned that a rational understanding of the reactivity behavior of these tin derivatives may afford new mixed-ligand tin esters and their structural elucidation offer the possibility to get an insight into the coordination behavior and bonding features of higher alkanesulfonate moieties attached to the tin atom(s). In this context, we report herein the synthesis and characterization of a few mixed-ligand di-*n*-butyltin alkanesulfonates, *n*-$Bu_2Sn(X)OSO_2R$ [X = acac, R = Et (**1**), *n*-Pr (**2**); R = Et, X = 4-OMe–$O_2CC_9H_5N$-2 (**3**), $O_2CC_9H_6N$-2 (**4**), $O_2CC_9H_6N$-1 (**5**)].

2. Results and discussion

2.1. Synthesis

Following our earlier approach [6], the reaction between equimolar quantities of *n*-$Bu_2Sn(OEt)OSO_2Et$ (**1a**) or *n*-$Bu_2Sn(OPr)OSO_2Pr$ (**2a**) with acetylacetone in dichloromethane proceeds under mild conditions (rt, 10–12 h) via chemoselective cleavage of Sn–OEt/Sn–OPr bond to afford the corresponding mixed-ligand tin complexes, **1** and **2**, respectively (Eq. (2)).

$$2n\text{-}Bu_2Sn(OR)OS(O)_2R \xrightarrow[CH_2Cl_2,rt,10-12h]{2Hacac} [n\text{-}Bu_2Sn(acac)OS(O)_2R]_2 + 2ROH \quad (2)$$

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

Analogous reactions of **1a** with 4-methoxy-2-quinoline/2-quinoline/1-isoquinoline carboxylic acid afford the corresponding mixed-ligand tin derivatives, **3**–**5** (Eq. (3)).

$$2n\text{-}Bu_2Sn(OEt)OSO_2Et \xrightarrow[CH_3CN,rt,10-12h]{2RCOOH} [n\text{-}Bu_2Sn(O_2CR)OSO_2Et]_2 + 2EtOH \quad (3)$$

R = 4-OMe–C_9H_5N-2(**3**), C_9H_6N-2(**4**), C_9H_6N-1(**5**)

2.2. Characterization

The compounds **1**–**5** are obtained as white crystalline solids and are soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, methanol, etc. IR spectra of these compounds are particularly useful in providing qualitative information concerning the coordination mode of the alkanesulfonate and acac/carboxylate groups. The bonding behavior of ethane/propanesulfonate moiety can be gleaned by IR absorptions at 1250–1260, 1190–1180 and 1060–1000 cm^{-1} due to νSO_3 mode. The presence of additional splitting of the bands in these regions is suggestive of bridging bidentate character of the alkanesulfonate groups [8]. For **1** and **2**, the characteristic νCO absorption at 1510–1525 cm^{-1}suggests bidentate chelating behavior of the acetylacetonate group. The spectra of **3** and **4** exhibit a strong absorption at 1687–1655 cm^{-1} due to $\nu_a CO_2$ mode similar to those previously reported for $Ph_2Sn(O_2CC_5H_4N$-2)$_2$ [9] and $Bu_2Sn(O_2CC_5H_4N$-2)$_2 \cdot H_2O$ [10] in which chelation through {N, O} coordination has been identified by X-ray crystal structure analysis. On the other hand, the spectrum of **5** reveals two distinct $\nu_a CO_2$ absorptions at 1675 and 1620 cm^{-1} and suggest the possibility of tridentate coordination mode featuring N,O chelation and bridging carboxylate group [11]. Similar behavior has been previously observed for analogous mixed-ligand tin esters derived from 1-isoquinoline carboxylic acid and other related diorganotin carboxylates [6].

^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$ solution display distinct signals associated with di-*n*-butyltin, ethane/propanesulfonate and acetylacetonate (for **1** and **2**) or quinaldate (for **3**–**5**) moieties (see Section 3) and are in accord with the suggested composition. From the observed tin satellites in the ^{13}C NMR spectra, the $^1J(^{13}C–^{119}Sn)$ value for **1** and **2** has been calculated as 630 and 633 Hz, respectively. Although, the corresponding tin satellites have eluded detection in the spectra of **3**–**5**, the observed ^2J and ^3J ($^{13}C–^{119}Sn$) data are found to be quite similar to those calculated for **1** and **2**. From the ^1J ($^{13}C–^{119}Sn$) data, the C–Sn–C angles (θ) in solution for **1** and **2** have been determined as 137.75° and 138.05°, respectively, by using the

empirical correlation as reported by Holecek and Lycka [12]. These values differ significantly from those obtained in the solid state (163.76° and 156.70°) by X-ray crystal structure analysis (*vide infra*). It must however be mentioned that relevant data on the solution state studies for asymmetrically substituted di-*n*-butyl tin derivatives are scarce and any reliable structural information for **1** and **2** in solution is thus warranted on the basis of the observed C–Sn–C angles alone. Furthermore, exceptions to the existing empirical (J, θ) correlation have also been reported earlier for a few symmetrically substituted diorganotin derivatives [13]. The ^{119}Sn NMR spectrum of each compound displays a single resonance at δ −235 to −241 (for **1**, **2**) and −334 to −340 (for **3**–**5**). These results are consistent with hexacoordinate environment around the tin center [14]. FAB mass spectra (in 3-nitrobenzyl alcohol matrix) of **1** and **2** reveal structurally important fragment ions at m/z 726/754 $[M-acac-Bu]^+$ and m/z 685/713 $[M-2acac+H]^+$ associated with the dimeric entity while the fragment ions in **3**–**5** originate from the predominant loss of the ethanesulfonate moiety (see Section 3).

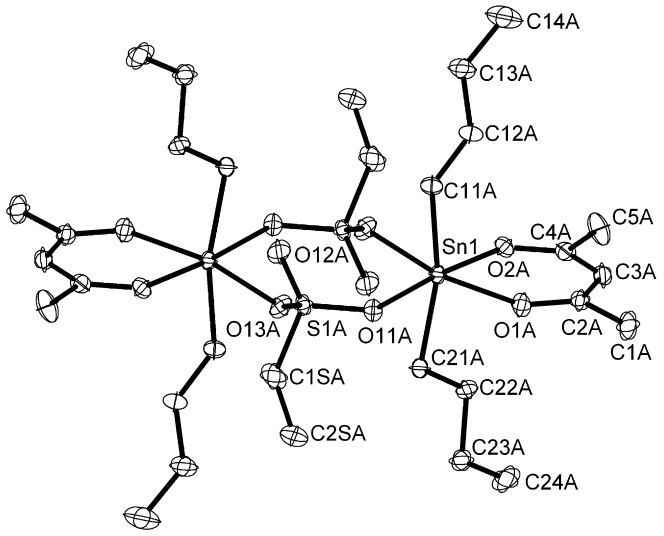


Fig. 1. Molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability level.

2.3. X-ray crystal structures

The structures of **1**–**3** have been further corroborated by X-ray crystallography. The structures of **1** and **2** comprise of two independent molecules in the unit cell of which only one is shown in Figs. 1 and 2, respectively. The crystal data are summarized in Table 1 while selected bond lengths and angles are given in Tables 2 and 3, respectively. The primary structural motif in these compounds is quite similar and is reminiscent of eight membered –[Sn–O–S–O–]$_2$ ring formed by virtue of bridging bidentate ethane/propanesulfonate groups while the acetylacetonate moiety acts in a chelating bidentate fashion. The centrosymmetric dimers thus formed possess a distorted octahedral geometry around each tin atom with planar SnO_4 core occupying the equatorial position (360 ± 0.1°). The *n*-butyl groups adopt a trans disposition with average C–Sn–C angle of 163.76° and 156.70° for **1** and **2**, respectively. The covalent Sn–O bond lengths associated with the alkanesulfonate moieties [Sn(1)–O(11A) 2.476(14), Sn(2)–O(11B) 2.275(15) Å (for **1**); Sn(1)–O(3) 2.259(4), Sn(2)–O(8) 2.224(3) Å (for **2**)] are found to be comparable with that of analogous mixed-ligand tin derivative, *n*-$Bu_2Sn(acac)OSO_2Me$ (2.379 Å) [5]. Interestingly, these values are much shorter than those observed previously for hexa-coordinated tetra-*n*-butyldistannoxane

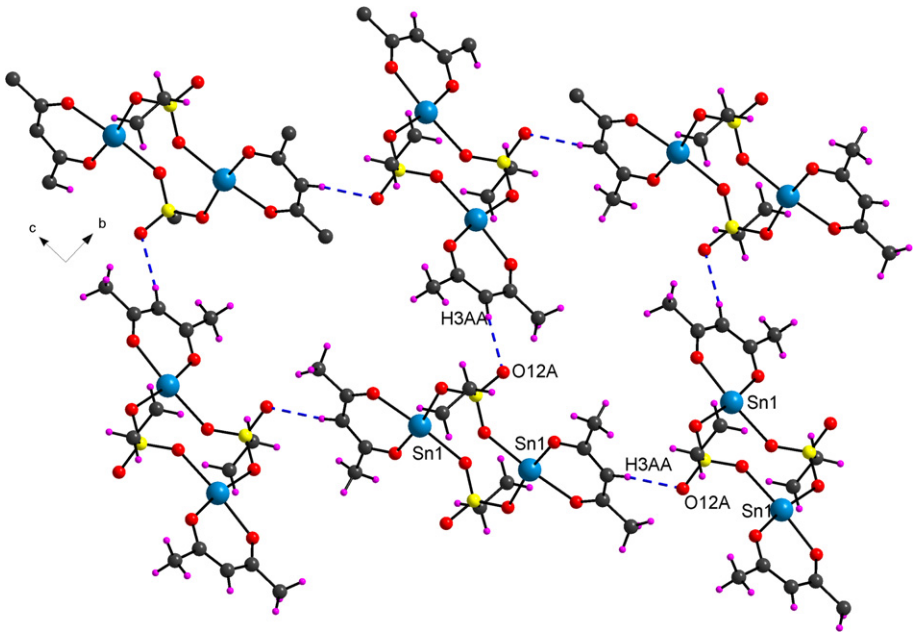


Fig. 1a. Structure of **1** (*bc* plane) showing C–H–O contacts.

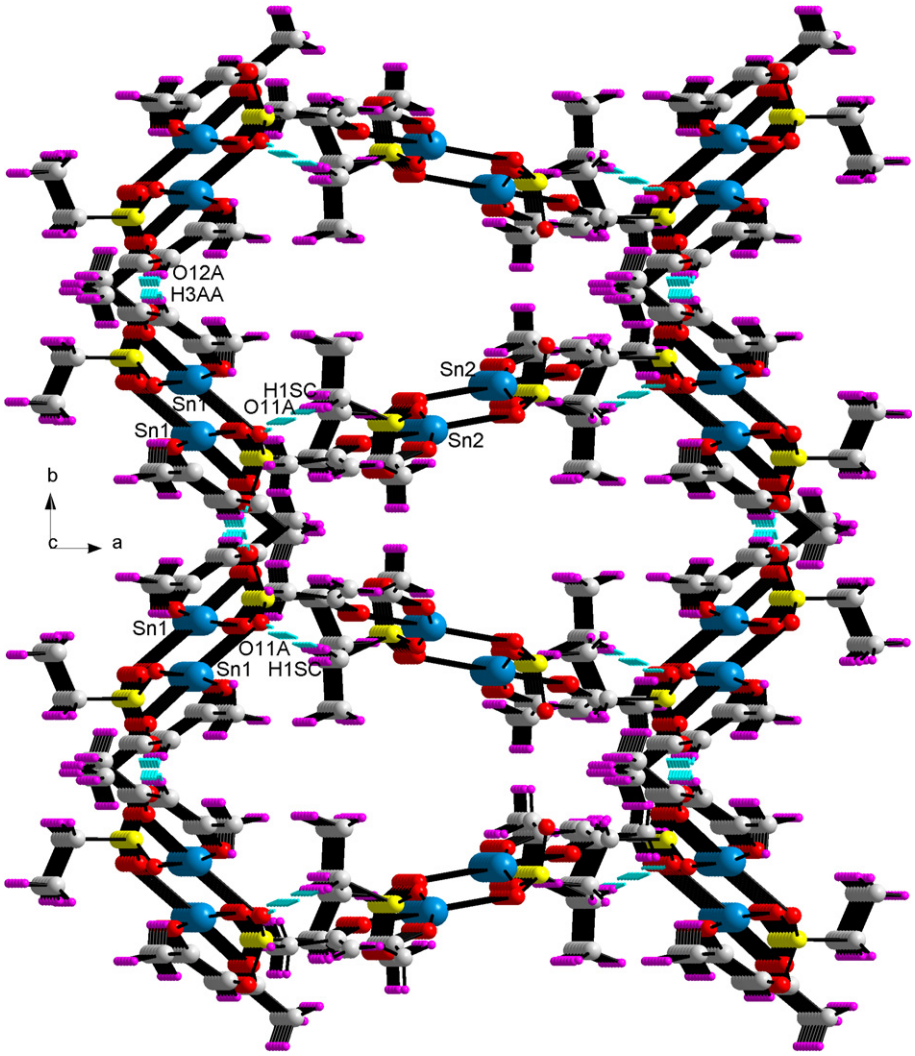


Fig. 1b. 3-D structure of **1** (*ab* plane). *n*-Butyl groups are omitted for clarity.

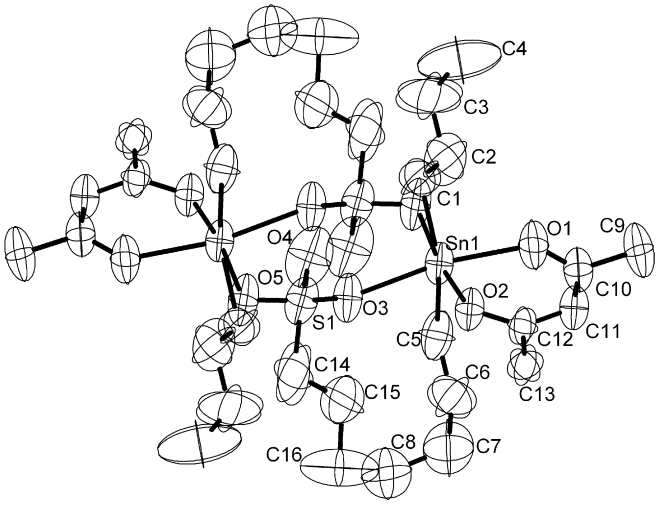


Fig. 2. Molecular structure of **2**. Thermal ellipsoids are drawn at 30% probability level.

associated with trifluoromethanesulfonate group [Sn–O 2.69–2.74 Å] where appreciable degree of ionic character has been suggested [3b,3c]. The Sn–O (acetylacetonate) bond lengths lie in the range of 2.10–2.16 Å. The O–Sn–O bite angles subtended by the alkanesulfonate moieties [104.61(5)° for **1**, 103.53(17)° for **2**] are shorter than those observed for structurally similar tin–methanesulfonate analog (111.60(2)°). Other metrical parameters associated with acetylacetonate/alkanesulfonate group are consistent with those found in related organotin derivatives [5,15]. To our knowledge, the structure of **2** represents the first crystallographically authenticated example of a tin-ester associated with propanesulfonate ligand.

The primary structure of **1** extends into 3D supramolecular motif by virtue of CH–O hydrogen bonding interactions. As shown in Fig. 1a, a view along the crystallographic *a*-axis reveals that one of the asymmetric molecules designated with Sn1 atom involves the enolic hydrogen (H3AA) of acet-

Table 1
Summary of crystallographic data for **1**–**3**

	1	**2**	**3**
Empirical formula	C_{15} $H_{30}O_5SSn$	$C_{16}H_{32}O_5SSn$	$C_{21}H_{31}NO_6SSn$
M_r	441.14	455.20	544.22
T (K)	273(2)	273(2)	93(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$C2/c$
a (Å)	16.9524(12)	11.043(5)	20.716(2)
b (Å)	14.3409(10)	11.490(5)	16.5468(18)
c (Å)	17.3213(12)	18.723(5)	14.3900(15)
α (°)	90.00	88.837(5)	90.00
β (°)	111.9600(10)	74.299(5)	105.722(2)
γ (°)	90.00	75.863(5)	90.00
V (Å^3)	3905.5(5)	2215.1(15)	4748.2(9)
Z	8	4	8
ρ calcd (g cm^{-3})	1.501	1.365	1.523
$F(000)$	1808	936	2224
Crystal size (mm)	$0.79 \times 0.44 \times 0.44$	$0.18 \times 0.16 \times 0.13$	$0.85 \times 0.85 \times 0.55$
θ Range for data collection (°)	1.30–30.75	1.83–28.48	1.60–28.32
Reflections collected	43 258	25 946	17 857
Independent reflections	11 390	10 520	5722
R_{int} value	0.0429	0.0363	0.0273
Data/restraints/parameters	11 390/0/407	10 520/33/469	5722/0/276
Goodness-of-fit on F^2	1.021	0.958	1.247
R_1, wR_2 [$I > 2\ \sigma\ (I)$]	$R_1 = 0.0281$	$R_1 = 0.0522$	$R_1 = 0.0300$
	$wR = 0.0626$	$wR_2 = 0.1444$	$wR_2 = 0.0672$
R_1, wR_2 (all data)	$R_1 = 0.0386$	$R_1 = 0.1075$	$R_1 = 0.0331$
	$wR_2 = 0.0673$	$wR_2 = 0.1888$	$wR_2 = 0.0681$

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Sn(1)–C(11A)	2.117(2)	Sn(1)–C(21A)	2.115(2)
Sn(1)–O(13A)^{i}	2.289(14)	Sn(1)–O(11A)	2.476(14)
Sn(1)–O(1A)	2.164(14)	Sn(1)–O(2A)	2.132(14)
Sn(2)–C(11B)	2.112(2)	Sn(2)–C(21B)	2.112(2)
Sn(2)–O(11B)	2.275(15)	Sn(2)–O(13B)^{i}	2.574(2)
Sn(2)–O(1B)	2.171(16)	Sn(2)–O(2B)	2.125(16)
Bond angles			
C(21A)–Sn(1)–C(11A)	163.76(8)	O(13A)^{i}–Sn(1)–O(11A)	104.61(5)
O(1A)–Sn(1)–O(11A)	87.42(5)	O(2A)–Sn(1)–O(1A)	84.91(5)
O(2A)–Sn(1)–O(13A)^{i}	82.99(5)	O(2A)–Sn(1)–O(11A)	172.30(5)
O(13A)^{i}–Sn(1)–O(1A)	167.04(5)		
C(21B)-Sn(2)–C(11B)	160.66(9)	O(13B)^{ii}–Sn(2)–O(11B)	109.20(5)
O(13B)^{ii}–Sn(2)–O(1B)	85.16(6)	O(2B)-Sn(2)–O(1B)	83.68(6)
O(2B)–Sn(2)–O(11B)	81.83(6)	O(11B)–Sn(2)–O(1B)	165.27(6)
O(13B)^{ii}–Sn(2)–O(2B)	168.59(6)		

ylacetonate group to form strong intermolecular CH···O hydrogen bonding [16] with oxygen atom O(12A) of the adjacent sulfonate groups. The bond parameters involved in this interaction are as follows [O(12A)···H(3AA) 2.410(2) Å, O(12A)···C(3A) 3.332(3) Å, O(12A)–H(3AA)–C(3A) 171.01(14)°]. The structure is reminiscent of 2D polymeric tape along the ab plane. These chains are held together by additional intermolecular CH···O hydrogen bonding involving the SCH_2 proton of the other independent molecule designated with Sn2 atom [O(11A)···H(1SC) 2.454(2) Å, O(11A)···C(1SB) 3.408(3) Å, O(11A)–H(1SC)–C(1SB) 167.87(13)°]. This results in a 3D supramolecular motif as shown in Fig. 1b.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Sn(1)–C(1)	2.098(7)	Sn(1)–C(5)	2.133(7)
Sn(1)–O(3)	2.259(4)	Sn(1)–O(5)^{ii}	2.597(10)
Sn(1)–O(1)	2.146(4)	Sn(1)–O(2)	2.099(4)
Sn(2)–C(17)	2.101(7)	Sn(2)–C(21)	2.076(8)
Sn(2)–O(8)	2.224(3)	Sn(2)–O(9)^{i}	2.732(11)
Sn(2)–O(6)	2.074(4)	Sn(2)–O(7)	2.174(4)
Bond angles			
C(1)–Sn(1)–C(5)	156.70(3)	O(2)–Sn(1)–O(1)	83.80(16)
O(2)–Sn(1)–O(3)	83.52(15)	O(3)–Sn(1)–O(5)^{ii}	103.53(17)
O(5)^{ii}- Sn(1)–O(1)	89.13(16)	O(1)–Sn(1)–O(3)	167.02(17)
O(2)–Sn(1)–O(5)^{ii}	172.92(16)		
C(21)–Sn(2)–C(17)	154.30(3)	O(6)–Sn(2)–O(7)	83.57(16)
O(6)–Sn(2)–O(8)	82.08(14)	O(8)–Sn(2)–O(9)^{i}	100.83(13)
O(9)^{i}–Sn(2)–O(7)	93.48(14)	O(7)–Sn(2)–O(8)	165.44(16)
O(6)–Sn(2)–O(9)^{i}	176.87(14)		

The molecular structure of **3** is shown in Fig. 3 and relevant crystal data as well as selected bond lengths and angles are summarized in Tables 1 and 4, respectively. The structure finds an analogy with those of **1** and **2** in respect of the bridging bidentate mode of the ethanesulfonate/propanesulfonate group which forms a dimeric entity with centrosymmetric eight membered ring. The carboxylate ligand is bonded to each tin atom by {N, O} chelation while the other carboxylate oxygen (O2) remains free. Thus, the coordination geometry around each tin atom is a distorted octahedron with planar SnO_3N core occupying the equatorial position (360 ± 0.07°). The *n*-butyl groups adopt trans disposition with an average C–Sn–C angle of 154.59°. Notably, the observed Sn–O bond lengths associated with ethanesulfonate [Sn–O(11) 2.190(15) Å] and carboxylate [Sn–O(1) 2.085(16) Å] groups are quite comparable and lie at the upper end of the normal range excepted for the Sn–O covalent bond (1.9–2.1 Å) [17]. A comparison of the Sn–O (ethanesulfonate) bond length with those observed for **1** and **2** reveal no significant variations with the nature of the co-ligand. Other metrical parameters of the carboxylate ligand involved in chelation [Sn–O(1) 2.085(16) Å, Sn–N 2.332(18) Å] are consistent with those of di-*n*-butyltin methanesulfonate analog [6a]. In addition, strong hydrogen bonding interaction between the hydrogen atoms associated with aromatic ring/OMe group and the oxygen atoms of carboxylate/sulfonate groups are evident [O(2)···H(11A) 2.385(2) Å, O(2)···C(11) 3.112(3) Å, C(2)-H(11)-C(11) 130.38(16)°; O(13)···H(7A) 2.375(2) Å, C(7)···O(13) 3.309(4) Å, C(7)-H(7A)-O(13) 167.71(14)°].

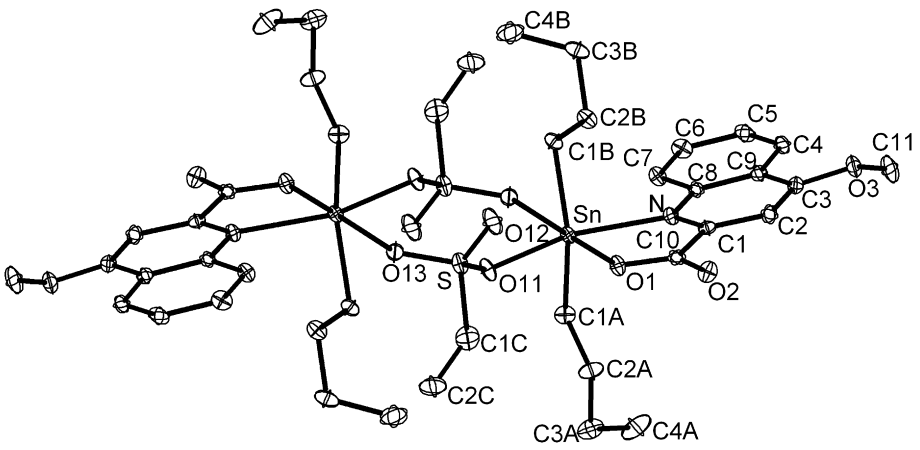


Fig. 3. Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level.

Table 4
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Sn–C(1A)	2.113(2)	Sn–C(1B)	2.115(2)
Sn–O(11)	2.190(15)	Sn–O(13)^{i}	2.711(2)
Sn–O(1)	2.085(16)	Sn–N	2.332(18)
Bond angles			
C(1A)–Sn–C(1B)	154.59(9)	O(13)^{i}–Sn–O(11)	97.72(6)
O(1)–Sn–O(11)	84.81(6)	O(1)–Sn–N	74.16(6)
N–Sn–O(13)^{i}	103.23(6)	O(11)–Sn–N	158.82(7)
O(13)^{i}–Sn–O(1)	177.09(6)		

In summary, mixed-ligand di-*n*-butyltin esters, **1**–**5** are accessible under mild conditions by the reaction of *n*-$Bu_2Sn(OR)OSO_2R$ (R = Et, *n*-Pr) with acetylacetone or an appropriate carboxylic acid. X-ray crystal structures of **1**–**3** reveal a dimeric structural motif in each case by virtue of bridging bidentate character of ethane/propanesulfonate groups. The bonding between tin and alkanesulfonate group is largely covalent (Sn–O 2.2–2.3 Å) irrespective of the nature of the co-ligand. These results along with previous reports on related tin–methanesulfonate derivatives [5,6] clearly suggest that the chemistry of tin esters derived from alkanesulfonic acids may differ from that of the corresponding class of tin esters associated with triflate/arenesulfonate moieties. This aspect is currently being explored.

3. Experimental

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere. Solvents were freshly distilled over phosphorous pentaoxide (dichloromethane, acetonitrile and hexane). Glasswares were dried in an oven at 110–120 °C and further flame dried under vacuum prior to use. ^{1}H, $^{13}C\{^{1}H\}$ and ^{119}Sn NMR spectra were recorded in $CDCl_3$ solution on BRUKER DPX-300 and BRUKER AVANCE II 400 spectrometers at 300, 75.48 and 149.19 MHz, respectively. ^{1}H and $^{13}C\{^{1}H\}$ 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 FAB mass spectra were recorded in 3-nitrobenzyl alcohol (NBA) matrix at room temperature on JEOL SX 102/DA-6000 mass spectrometer/Data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The assignments of the observed fragment ions have been made by using Chem Draw Ultra 7.0.1 program. IR spectra were recorded on Nicolet protege 460 E.S.P. spectrophotometer using KBr optics. Elemental analysis (C, H, and N) was performed on a Perkin–Elmer model 2400 CHN elemental analyzer.

3.1. Synthesis of [*n*-$Bu_2Sn(acac)OS(O)_2R]_2$ [R = Et (**1**), *n*-Pr (**2**)]

To a stirred solution of di-*n*-butyltin(ethoxy)ethanesulfonate (**1a**) (0.51 g, 1.32 mmol) or di-*n*-butyltin(propoxy)propanesulfonate (**2a**) (0.55 g, 1.32 mmol) in dichloromethane was added acetylacetone (0.13 g, 1.32 mmol) and the clear solution was stirred for 10–12 h at room temperature. Thereafter, the solvent was removed under vacuum and *n*-hexane (10 mL) was added. The resulting clear solutions upon cooling gave **1** and **2**, respectively, as white solids which were filtered and dried under vacuum.

3.1.1. For compound **1**

Yield: (0.45 g, 78%), ^{1}H NMR ($CDCl_3$): δ 5.52 (s, 1H, C*H* of acac), 2.97 (q, $^{3}J_{H-H} = 7.3$ Hz, 2H, S–CH_2), 2.09 (s, 6H, CH_3 of acac), 1.77–1.61 (m, 8H, Sn(CH_2)$_2$), 1.35-1.40 (m, 7H, $Sn(CH_2)_2CH_2 + SCH_2CH_3$), 0.94 (t, $^{3}J_{H-H} = 7.1$ Hz, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 194.40 (CO), 101.80 (*C*H of acac), 46.10 (S*C*H$_2$), 27.50 (*C*H$_3$ of acac), 26.97 (Sn*C*H$_2$, $^{1}J(^{13}C–^{119}Sn) = 630$ Hz), 26.42 ($SnCH_2CH_2$, $^{2}J(^{13}C–^{119}Sn) = 43$ Hz), 26.20 ($Sn(CH_2)_2CH_2$, $^{3}J(^{13}C–^{119}Sn) = 103$ Hz), 13.43 ($Sn(CH_2)_3CH_3$), 8.98 (SCH_2CH_3). ^{119}Sn NMR ($CDCl_3$): δ −241 ppm. FAB mass (*m*-nitrobenzyl alcohol): *m*/*z* 726 $[M-acac-Bu]^+$, 685 $[M-2acac+H]^+$, 647 $[M-acac-OS(O)_2Et-2Me+3H]^+$, 590 $[M-acac-OS(O)_2Et-2Me-Bu+3H]^+$, 476 $[M-acac-OS(O)_2Et-2Me-3Bu+3H]^+$. IR (KBr, cm^{-1}): 1518 (ν CO),

1251, 1187, 1060 (ν SO_3). Anal. Calc. for $C_{15}H_{30}O_5SSn$: C, 40.84; H, 6.85. Found: C, 40.71; H, 7.13%.

*3.1.2. For compound **2***

Yield: (0.50 g, 83.33%), ^{1}H NMR ($CDCl_3$): δ 5.42 (s, 1H, C*H* of acac), 2.84 (t, $^3J_{H-H} = 7.7$ Hz, 2H, SCH_2), 1.99 (s, 6H, CH_3 of acac), 1.84–1.67 (br, 10H, Sn(CH_2)$_2$ + SCH_2CH_2), 1.34 (br, 4H, $Sn(CH_2)_2CH_2$), 0.97 (t, $^3J_{H-H} = 7.4$ Hz, 3H, $SCH_2CH_2CH_3$), 0.87 (t, $^3J_{H-H} = 6.1$ Hz, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 194.22 (CO), 101.65 (*C*H of acac), 53.71 (S-*C*H_2), 27.44 (*C*H_3 of acac), 27.17 (Sn*C*H_2, $^1J(^{13}C–^{119}Sn) = 633$ Hz), 26.40 ($SnCH_2$-*C*H_2, $^2J(^{13}C–^{119}Sn) = 39$ Hz), 26.07 ($Sn(CH_2)_2CH_2$, $^3J(^{13}C–^{119}Sn) = 103$ Hz), 17.93 (SCH_2CH_2), 13.35 (Sn-$(CH_2)_3CH_3$), 13.01 ($S(CH_2)_2CH_3$). ^{119}Sn NMR ($CDCl_3$): δ −235. FAB mass (*m*-nitrobenzyl alcohol): *m*/*z* 754 [M−acac−Bu]$^+$, 713 [M−2acac+H]$^+$, 334 [M/2−OSO_2Pr+H]$^+$. IR (KBr, cm^{-1}): 1525 (ν CO), 1261, 1181, 1060 (ν SO_3). Anal. Calc. for $C_{16}H_{32}O_5SSn$: C, 42.22; H, 7.09. Found: C, 42.13; H, 7.18%.

*3.2. Synthesis of [n-Bu$_2$Sn(OOCR′)OS(O)$_2$Et]$_2$ [R′ = 4-OMe–C$_9$H$_5$N-2 (**3**), C$_9$H$_6$N-2 (**4**), C$_9$H$_6$N-1 (**5**)]*

4-Methoxy-2-quinolidic acid (0.27 g, 1.32 mmol)/2-quinolidic acid (0.23 g, 1.32 mmol)/1-isoquinolidic acid (0.23 g, 1.32 mmol) was added separately into a solution of di-*n*-butyltin(ethoxy)ethanesulfonate (**1a)** (0.51 g, 1.32 mmol) in CH_3CN. The contents were stirred for 10–12 h at room temperature. Thereafter, the solvent was removed under vacuum and *n*-hexane was added to precipitate a white solid in each case. The solid thus obtained was filtered, washed with *n*-hexane and dried under vacuum. These compounds were identified as **3**–**5**, respectively.

*3.2.1. For compound **3***

Yield: (0.61 g, 84.72%), ^{1}H NMR ($CDCl_3$): δ 8.43 (br, 1H, H-5), 8.40 (br, 1H, H-8), 8.0 (t, $^3J_{H-H} = 6.9$ Hz, 1H, H-7), 7.89 (s, 1H, H-3), 7.79 (t, $^3J_{H-H} = 7.9$ Hz, 1H, H-6), 4.29 (3H, s, OMe), 3.09 (q, $^3J_{H-H} = 7.4$ Hz, 2H, SCH_2), 1.93 (br, 8H, Sn(CH_2)$_2$), 1.45 (t, $^3J_{H-H} = 7.4$ Hz, 3H, SCH_2CH_3), 1.26 (br, 4H, $Sn(CH_2)_2CH_2$), 0.75 (br, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.69 (CO_2), 149.66, 143.76, 133.44, 128.87, 128.29, 125.02, 123.28, 122.52, 100.52 (aromatic carbons), 57.41 (OMe), 46.42 (S*C*H_2), 29.81 (Sn*C*H_2), 26.76 ($SnCH_2$-*C*H_2, $^2J(^{13}C–^{119}Sn) = 47$ Hz), 25.93 ($Sn(CH_2)_2CH_2$, $^3J(^{13}C–^{119}Sn) = 129$ Hz), 13.38 ($Sn(CH_2)_3CH_3$), 9.29 (SCH_2CH_3). ^{119}Sn NMR ($CDCl_3$): δ −339. FAB mass (*m*-nitrobenzyl alcohol): *m*/*z* 683 [M−2(4-OMe–quinoldate)−H]$^+$, 436 [M/2−OSO_2Et]$^+$, 321 [Sn(4-OMe–quinoldate)−H]$^+$, 229 [Sn(OS(O)$_2$Et)]$^+$. IR (KBr, cm^{-1}): 1687 ($\nu_a CO_2$), 1339 ($\nu_s CO_2$), 1584 (ring vibration), 1262, 1137, 1009 (ν SO_3). Anal. Calc. for $C_{21}H_{31}NO_6SSn$: C, 46.34; H, 5.74; N, 2.57. Found: C, 46.31; H, 5.81; N, 2.51%.

*3.2.2. For compound **4***

Yield: (0.54 g, 79.41%), ^{1}H NMR ($CDCl_3$): δ 8.66 (d, $^3J_{H-H} = 7.3$ Hz, 1H, H-3), 8.55 (d, $^3J_{H-H} = 7.6$ Hz, 1H, H-4), 8.12 (d, $^3J_{H-H} = 7.9$ Hz, 1H, H-8), 8.04 (br, 2H, H-5 and H-6), 7.86 (t, $^3J_{H-H} = 7.2$ Hz, 1H, H-7), 3.12 (q, $^3J_{H-H} = 7.2$ Hz, 2H, S–CH_2), 1.97 (br, 8H, Sn(CH_2)$_2$), 1.47 (t, $^3J_{H-H} = 7.2$ Hz, 3H, SCH_2CH_3), 1.26 (br, 4H, $Sn(CH_2)_2CH_2$), 0.72 (br, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.71 (CO_2), 147.75, 142.80, 141.93, 133.19, 130.18, 129.91, 128.79, 125.91, 121.28 (aromatic carbons), 46.43 (S*C*H_2), 30.15 (Sn*C*H_2), 26.75 ($SnCH_2$ *C*H_2, $^2J(^{13}C–^{119}Sn) = 47$ Hz), 25.81 ($Sn(CH_2)_2CH_2$, $^3J(^{13}C–^{119}Sn) = 131$ Hz), 13.27 ($Sn(CH_2)_3CH_3$), 9.23 (SCH_2CH_3). ^{119}Sn NMR ($CDCl_3$): δ −336. FAB mass (*m*-nitrobenzyl alcohol): *m*/*z* 919 [M−OSO_2Et]$^+$, 405 [M/2−OSO_2Et−H]$^+$, 342 [M/2−(2-quinoldate)−H]$^+$. IR (KBr, cm^{-1}): 1655 ($\nu_a CO_2$), 1339 ($\nu_s CO_2$), 1570 (ring vibration), 1265, 1186, 1061 (νSO_3). Anal. Calc. for $C_{20}H_{29}NO_5SSn$: C, 46.71; H, 5.68; N, 2.72. Found: C, 46.10; H, 5.99; N 2.46%.

*3.2.3. For compound **5***

Yield: (0.51 g, 75%), ^{1}H NMR ($CDCl_3$): δ 10.11 (d, $^3J_{H-H} = 7.7$ Hz, 1H, H-4), 9.12 (br, 1H, H-3), 8.22 (d, $^3J_{H-H} = 5.8$ Hz, 1H, H-8), 8.05 (t, $^3J_{H-H} = 7.4$ Hz, 1H, H-6), 7.98 (t, $^3J_{H-H} = 8.6$ Hz, 1H, H-7), 7.94 (d, $^3J_{H-H} = 6.7$ Hz, 1H, H-5), 3.08 (q, $^3J_{H-H} = 7.2$ Hz, 2H, S–CH_2), 1.96 (br, 4H, SnCH_2), 1.46 (m, 7H, $SnCH_2CH_2$ + SCH_2CH_3), 1.26 (br, 4H, $Sn(CH_2)_2CH_2$), 0.75 (br, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.41 (CO_2), 145.90, 138.87, 138.31, 133.55, 130.76, 129.43, 128.02, 127.68, 127.05 (aromatic carbons), 46.49 (SCH_2), 32.36 ($SnCH_2$), 27.11 ($SnCH_2$-*C*H_2, $^2J(^{13}C–^{119}Sn) = 47$ Hz), 25.85 ($Sn(CH_2)_2CH_2$, $^3J(^{13}C–^{119}Sn) = 152$ Hz), 13.25 ($Sn(CH_2)_3CH_3$), 9.28 (SCH_2CH_3). ^{119}Sn NMR ($CDCl_3$): δ −339. FAB mass (*m*-nitrobenzyl alcohol): *m*/*z* 919 [M−OSO_2Et]$^+$, 864 [M−OSO_2Et−Bu+2H]$^+$, 808 [M−2OSO_2Et −2H]$^+$, 405 [M/2−OSO_2Et−H]$^+$. IR (KBr, cm^{-1}): 1675, 1620 ($\nu_a CO_2$), 1586 (ring vibrations), 1302 ($\nu_s CO_2$), 1258, 1188, 1038 (ν SO_3). Anal. Calc. for $C_{20}H_{29}NO_5SSn$: C, 46.71; H, 5.68; N, 2.72. Found: C, 46.34; H, 5.91; N, 2.51%.

3.3. X-ray crystallography

The crystals of **1**–**3** were mounted along the largest dimension and were used for data collection. The intensity data were collected on a BRUKER AXS SMART-APEX CCD diffractometer equipped with a molybdenum sealed tube (MoKα radiation, $\lambda = 0.71073$ Å) and a graphite monochromator. Frames were collected at $T = 273$ K (**3** at 93 K) by ω, ϕ and 2θ-rotation at 10 s per frame with SMART [18].The measured intensities were reduced to $F^2$and corrected for absorption [19].The structures were solved by direct methods using SIR92 [20] (for **2**) and SHELXS-97 (for **1** and **3**), and refined by full matrix least-square method on

F^2 using SHELXTL [21]. All calculations were performed using WINGX-32 [22] (for **2**) and SHELXTL (for **1** and **3**).

For compound **2**, a total of 25946 reflections were measured of which 10520 were unique and 4721 were considered observed [$I > 2\sigma$ (I)]. There were two crystallographically independent molecules in the unit cell and both of them showed moderate to high degree of disorder in terms of high thermal parameters and unusual bond lengths. This disorder was either been resolved partially or completely for the *n*-butyl chains and completely for the *n*-propyl chains of the sulfonate groups in both the molecules. Thus C4, C8, C14, C15, C16, C18 C19, C20, C22, C23, C24, C30, C31 and C32 atoms have been split at two atomic sites (occupancy defined by free variables) with total site occupancy of 1.00 for each one of them. All disordered atoms belonging to *n*-butyl or propanesulfonate group have been assigned one free variable for site occupancy and one for the U_{iso} value. The bond distances involving these atoms have been fixed at C–C 1.510(3) and C–S 1.720(3) Å and each atom pair was assigned with same U_{iso} values. All atoms were refined anisotropically. All hydrogen atoms were attached geometrically and were not refined. The final R and wR obtained are 0.0522 and 0.1444 for observed reflections and 0.1075 and 0.1888 for all reflections, respectively, and final residual peak in the difference Fourier being only 0.660 e Å^3.

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Appendix A. Supplementary material

CCDC 648005, 648006 and 648007 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.045.

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