

Structural studies of diorganotin(IV) sulphonates

The crystal structures of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\}_2]_n$ and its partially hydrolyzed product $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}]_n$

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Abstract

The X-ray crystal structures of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\}_2]_n$ (**1**) and $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}]_n$ (**2**) were determined to delineate the coordination behaviour of the sulphonate group with tin(IV) and to evaluate the metal sulphonate bonding interactions. The synthesis of **1** has been achieved by azeotropic dehydration of di-*n*-butyltin(IV) oxide and mesitylenesulphonic acid. **1** is polymeric containing six-coordinate tin and crystallizes from anhydrous toluene in the orthorhombic space group $P2_12_12$ with unit cell dimensions $a = 12.555(1)$, $b = 21.238(1)$, $c = 5.415(1)$ Å; $Z = 2$; R , 0.0236 and wR , 0.0607 for 1281 observed reflections. The structure exhibits highly symmetrical bridging bidentate mesitylenesulphonate groups and is made up of an infinite array of $(n\text{-C}_4\text{H}_9)_2\text{SnO}_4$ moieties. Compound **1** hydrolyzes very slowly to $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}]_n$ (**2**), when kept in $\text{CH}_3\text{OH}-\text{CHCl}_3$ mixture at room temperature for 35 days. Crystals of **2** are monoclinic with space group $P2_1/m$ and unit cell dimensions $a = 10.040(1)$, $b = 14.500(1)$, $c = 13.978(1)$ Å; $\beta = 91.58(1)^\circ$; $Z = 4$; R , 0.0226; wR , 0.0592 for 2725 observed reflections. The crystal structure is built of polymeric chains in which $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}]_n$ units are joined by bridging bidentate mesitylenesulphonate groups. The crystal lattice is stabilized by a network of hydrogen bonds running through the sheets, in which an oxygen atom of the sulphonate group and the hydroxyl group attached to tin participate in a symmetrical fashion. In DMSO solutions, chemical shift (^{119}Sn) and 1J ($^{119}\text{Sn}-^{13}\text{C}$) values for both **1** and **2** suggest a distorted octahedral geometry around tin in which DMSO may also be involved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Sulphonates; Diorganotin compounds

1. Introduction

Diorganotin(IV) carboxylates are known to exhibit a wide variety of structural arrangements with different coordination numbers and geometries around tin [1]. Crystallographic investigations on these compounds have revealed that the choice of structure depends on the steric bulk of the hydrocarbon groups bonded to tin or of the ligand and their electronic effects [2]. Generally, these compounds adopt a variety of structures exhibiting diverse modes of coordination/association of the carboxylate ligand. Surprisingly, only a very few studies are available on the structural chemistry of organotin(IV) compounds with another versatile ligand,

namely alkyl or arylsulphonates, although some spectroscopic studies have been reported [3–7]. Complexes of these anions with the organotin(IV) moiety, like the carboxylates, are expected to exhibit diverse structural patterns using different bonding modes such as monodentate, bidentate (chelating or bridging) or tridentate bridging. For example, the X-ray crystal structures of trimethyltin(IV) benzenesulphonate monohydrate [8] and $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{X})(\text{OSO}_2\text{CH}_3)$ ($\text{X} = \text{acac}$, bzbz , OH) [9] have shown the presence of monodentate and bridging bidentate sulphonate groups, respectively, in these compounds. Since only a few structural investigations are available on organotin(IV) sulphonates, any generalization of the preferential coordination modes of sulphonate anions and their structural patterns may be difficult. In this context, we report in this paper the preparation and X-ray crystal structures of $[(n\text{-$

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$[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\}_2]$ (**1**) and $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}_n]$ (**2**).

2. Results and discussion

The compound $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\}_2]$ (**1**) is obtained in 80% yield by azeotropic removal of water from the reaction between di-*n*-butyltin(IV) oxide and mesitylenesulphonic acid in the molar ratio 1:2 in toluene. It is a stable, white amorphous, non-hygroscopic solid. It shows limited solubility in benzene, toluene, chloroform, dichloromethane but is highly soluble in donor solvents such as dimethylformamide and dimethylsulphoxide. Crystallization of **1** was attempted in various solvents/mixtures and good single crystals were obtained from toluene. However, crystals which appeared to be visually different from **1** were also

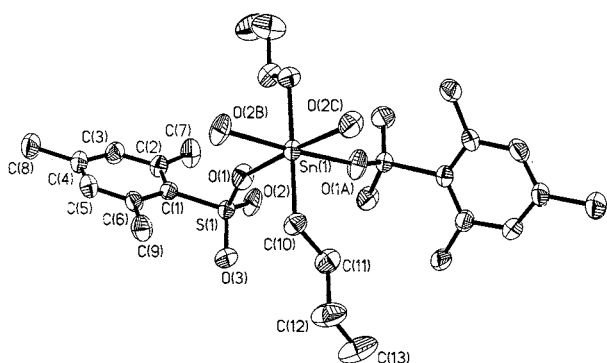


Fig. 1. A perspective view of a part of the polymer **1** with atom numbering scheme (thermal ellipsoids are at 40% probability level). The octahedral geometry around the tin is clear. The symmetry related oxygen atoms extend the polymer array and are labelled O(2B), O(2C) etc.

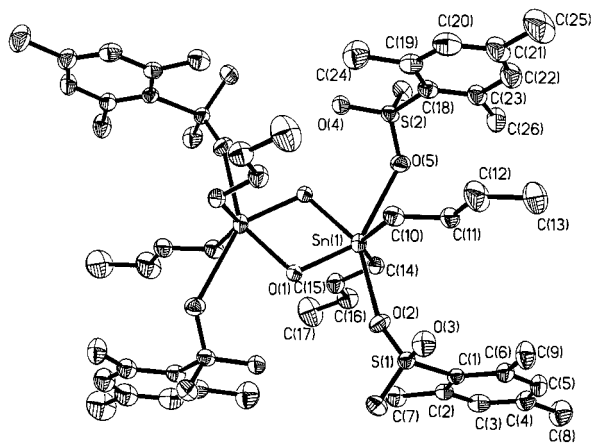
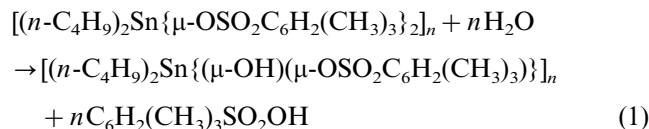


Fig. 2. A perspective view of a part of the infinite array of the polymer **2** with atom numbering scheme (thermal ellipsoids are at 40% probability level). Symmetry related O(2) and O(5) of both sulphonate groups bridge the next tin atom in the array.

obtained upon keeping a saturated solution of **1** for 35 days in $\text{CH}_3\text{OH}-\text{CHCl}_3$ mixture at $25 \pm 3^\circ\text{C}$. Analytical data from these crystals revealed that a partially hydrolyzed product, $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}_n]$ (**2**), was formed from **1** as shown below:



The ^{119}Sn -NMR spectra ($\text{DMSO}-d_6$) of **1** and **2** show sharp bands at -342.9 and -324.2 ppm, respectively. These values are well within the range -210 to -400 ppm observed for six-coordinate di-*n*-butyltin(IV) compounds [10]. Besides, the 1J (^{119}Sn , ^{13}C) coupling constants [909 (**1**) and 920 Hz (**2**)] give C–Sn–C angles corresponding to 165.8° and 167.7° respectively, by the use of the Holec equation [11]. These values and the chemical shift [δ (^{119}Sn)] strongly indicate a distorted octahedral arrangement around tin in both **1** and **2**.

The IR spectra of **1** and **2** are quite complex in the region 1400 to 400 cm^{-1} and show a splitting of both $\nu_4(\text{E})$ and $\nu_5(\text{E})$ modes [12]. Probably, C_{3v} symmetry for the CSO_3 group of the unperturbed ion is lowered to C_s in these compounds. This lowering of symmetry may arise from a form of coordination in which two oxygen atoms of each anion are bonded to tin and the third oxygen is free. This is consistent with the presence of bridging bidentate mesitylenesulphonate anions in **1** and **2** (as revealed by the X-ray analyses, see below).

The fragmentation pattern of **1** does not show the molecular-ion peak (M^+) at m/z 632. It undergoes a loss of C_4H_9 from the molecular-ion to form a stable trisubstituted tin(IV) ion at m/z 575. This is consistent with some earlier observations on organotin(IV) compounds [13], the loss is attributed to the non-existence of the Sn(V) oxidation state [14].

3. Solid state structural features of **1** and **2**

In order to understand structural details, single crystal X-ray diffraction study was carried out. A perspective view of structures of **1** and **2** with atom numbering scheme is given in Figs. 1 and 2, respectively. Selected bond lengths and angles of **1** and **2** are given in Table 1.

Examination of the bond lengths and angles around tin in **1** reveals that it adopts a near perfect octahedral geometry with *trans* disposition of atoms with bond angles greater than $176.5(2)^\circ$ (Table 1). It is worth mentioning that in a coordinating solvent like DMSO, the C–Sn–C angle is reduced to 165.8° [calculated using 1J (^{119}Sn , ^{13}C) value cited earlier], strongly pointing towards a different structural arrangement.

Table 1
Selected bond distances (Å) and angles (°) for compounds **1** and **2**^a

Compound 1			
Sn(1)–C(10)	2.114(4)	Sn(1)–C(10) # 1	2.114(4)
Sn(1)–O(1)	2.199(3)	Sn(1)–O(1) # 1	2.199(3)
Sn(1)–O(2) # 2	2.313(3)	Sn(1)–O(2) # 3	2.313(3)
S(1)–O(3)	1.418(3)	S(1)–O(2)	1.454(4)
S(1)–O(1)	1.455(4)		
C(10)–Sn(1)–C(10) # 1	176.5(2)	C(10)–Sn(1)–O(1)	89.9(2)
C(10) # 1–Sn(1)–O(1)	92.4(2)	C(10)–Sn(1)–O(1) # 1	92.4(2)
C(10) # 1–Sn(1)–O(1) # 1	89.9(2)	O(1)–Sn(1)–O(1) # 1	94.34(18)
C(10)–Sn(1)–O(2) # 2	86.8(2)	C(10) # 1–Sn(1)–O(2) # 2	90.8(2)
O(1)–Sn(1)–O(2) # 2	176.7(4)	O(1) # 1–Sn(1)–O(2) # 2	85.34(12)
C(10)–Sn(1)–O(2) # 3	90.8(2)	C(10) # 1–Sn(1)–O(2) # 3	86.8(2)
O(1)–Sn(1)–O(2) # 3	85.34(12)	O(1) # 1–Sn(1)–O(2) # 3	176.7(4)
O(2) # 2–Sn(1)–O(2) # 3	95.17(16)		
Compound 2			
Sn(1)–O(1)	2.0660(17)	Sn(1)–O(1) # 1	2.1073(17)
Sn(1)–O(2)	2.399(2)	Sn(1)–O(5) # 1	2.783(2)
Sn(1)–C(14)	2.115(3)	Sn(1)–C(10)	2.118(3)
S(1)–O(3)	1.425(3)	S(1)–O(2) # 2	1.461(2)
S(1)–O(2)	1.461(2)	S(2)–O(5)	1.454(2)
S(2)–O(5) # 2	1.454(2)	S(2)–O(4)	1.462(3)
O(1)–Sn(1)–O(1) # 1	70.08(9)	O(1)–Sn(1)–C(14)	107.40(9)
O(1) # 1–Sn(1)–C(14)	102.59(9)	O(1)–Sn(1)–C(10)	109.35(10)
O(1) # 1–Sn(1)–C(10)	104.18(10)	C(14)–Sn(1)–C(10)	140.03(12)
O(1)–Sn(1)–O(2)	76.07(7)	O(1) # 1–Sn(1)–O(2)	146.09(7)
C(14)–Sn(1)–O(2)	85.55(9)	C(10)–Sn(1)–O(2)	88.45(9)
O(1)–Sn(1)–O(5) # 1	143.52(7)	O(1) # 1–Sn(1)–O(5) # 1	73.44(6)
C(14)–Sn(1)–O(5) # 1	79.93(8)	C(10)–Sn(1)–O(5) # 1	79.91(9)
O(2)–Sn(1)–O(5) # 1	140.36(6)	Sn(1)–O(1)–Sn(1) # 1	109.92(9)

^a Symmetry transformations used to generate equivalent atoms for **1**: (# 1) $-x, -y, z$; (# 2) $-x, -y, z+1$; (# 3) $x, y, z+1$. Symmetry transformations used to generate equivalent atoms for **2**: (# 1) $-x+1, -y, -z$; (# 2) $x, -y+1/2, z$.

Due to the twofold symmetry of the molecule, only two sets of Sn–O(mesitylenesulphonate) bond lengths are observed, one being relatively longer, 2.313(3) Å [Sn(1)–O(2)] than the other, 2.199(3) Å [Sn(1)–O(1)]. These bond lengths in **1** (2.19–2.31 Å) are comparable with similar Sn–O(sulphonate) bond distances (2.25–2.65 Å) [9] and may be considered to constitute strong covalent bonds. The molecular geometry of the sulphonate group is normal in terms of bond lengths, angles and planarity [8,9,15].

The crystal structure of **1** is built from an infinite array of polymeric sheets resulting out of a 2_1 screw operation and are stacked perpendicular to the bc plane (Fig. 3). Within the individual sheets, that are placed parallel to the c -axis, the mesitylenesulphonate groups are bridging and isobidentate. As a consequence, an eight-membered ring structure sharing a common tin atom in the middle is generated (Fig. 3) and the n -butyl groups are positioned almost perpendicular to it. These rings have the stable chair–chair configuration in the solid state.

The crystal structure of **2** can be visualized as an infinite array of four-membered [$\{(n\text{-C}_4\text{H}_9)_2\text{Sn}\}_2(\text{OH})_2$] moieties, that are successively bridged by mesitylene-

sulphonate groups. These rings are generated by a centre of inversion and are comparable to similar $\text{Sn}_2(\text{OH})_2$ rings observed in other compounds [9,16–18]. As a consequence, each tin atom is associated with two mesitylenesulphonate groups (Fig. 4) but, interestingly, both are quite different in their coordination behaviour. These are strictly isobidentate due to their crystallographic mirror symmetry, but their bond lengths are significantly different, Sn(1)–O(2) = 2.399(2) and Sn(1)–O(5) = 2.783(2) Å, respectively. Notably, their angular relationships are also much varied, Sn(1)–O(2)–S(1) being 153.05° in the first case and 132.78° for Sn(1)–O(5)–S(2), clearly pointing out their asymmetry in coordination behaviour. An increase of about 0.38 Å in the Sn–O(mesitylenesulphonate) bond length reflects the weak nature of this tin–sulphonate bond and may be attributed to the presence of appreciable ionic character. The tin atoms are separated by 3.4171(5) Å which is comparable to Sn⋯Sn distances in existing organotin(IV) analogues [9,18].

The coordination geometry around tin in **2** can be visualized as a severely distorted octahedron [C(10)–Sn(1)–C(14) = 140.03°] with C(10) and C(14) occupying the apical positions. In the case of **1**, this distortion

is just marginal, the three atoms are almost collinear, the C–Sn–C value being $176.5(2)^\circ$. Thus it is striking that though considerable structural differences exist between **1** and **2** in the solid state, the C–Sn–C angular difference is only 1.9° (165.8 for **1** and 167.7 for **2**), in the coordinating solvent. This very similar reduction of angles from the ideal value of 180° in solution strongly suggests that DMSO has approached the metal atom in the coordination polyhedra of these compounds.

The dihedral angle between the axial plane [defined by Sn(1), C(10) and C(14)] and the equatorial one (defined by the four tin bonded oxygens) is $89.72(9)^\circ$, the deviation of tin from this best equatorial plane is only $-0.049(1)$ Å, both features expected for an octahedral geometry. However, the bond angles that are subtended between the tin and oxygen atoms are far

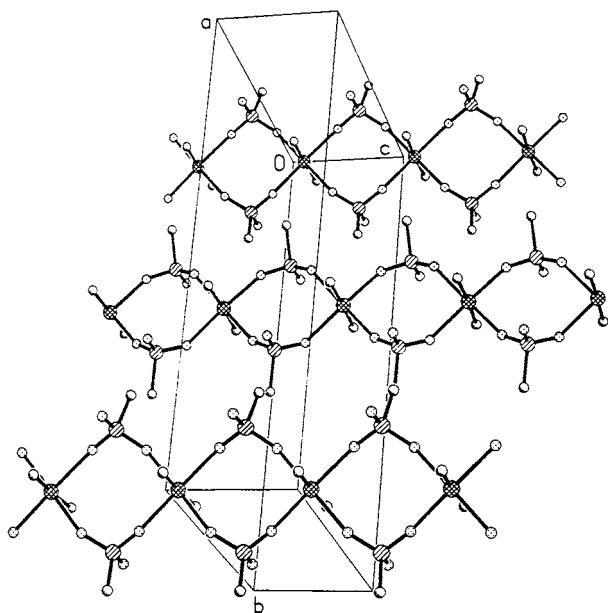


Fig. 3. Formation of the polymeric sheets of **1** in the crystal lattice. These sheets consisting of eight-membered rings run parallel to the *c* axis and stack perpendicular to the *bc* plane (see text). Only the tin bonded atom of the *n*-Bu group and the sulphur bonded C atom of the ligand are shown for clarity.

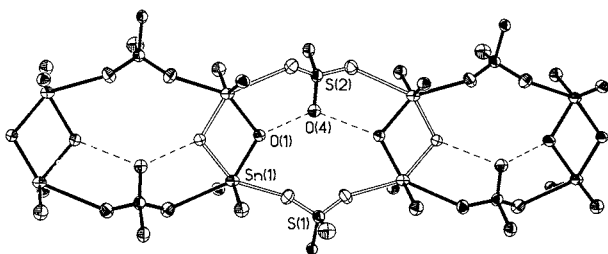


Fig. 4. Formation of polymeric sheets of **2** by intertwined 12-membered rings (one such ring is shown in open bond type) in which the mesitylenesulphonate group acts as strict isobidentate ligand. Note the parallel arrangement of Sn_2O_2 rings within the sheet (only the first carbon of *n*-Bu and ligand is shown). The dotted lines represent the symmetrical hydrogen bond that stabilizes the sheet.

away from 90° (see Table 1), showing a considerable amount of deviation. Another noteworthy feature is that the relatively weak coordinating oxygen of the sulphonate group [i.e. O(5)] approaches the metal in such a way that it bisects the C(10)–Sn(1)–C(14) angle almost in a symmetrical fashion [the distances of O(5) from C(10) and C(14) are $3.188(2)$ and $3.187(2)$ Å, respectively]. Probably, due to this, the linearity of the C–Sn–C angle is considerably reduced.

The crystal structure of **2** contains polymeric sheets parallel to (010) with mesitylenesulphonate groups acting as strict isobidentate ligands due to its crystallographically imposed mirror symmetry. These sheets can be thought of as intertwined 12-membered rings (Fig. 4) and upon stacking build the crystal structure exhibiting interesting structural features. The entire structure can be visualized as starting from the $n\text{-Bu}_4\text{Sn}_2(\text{OH})_2$ part of the molecule, which upon bridging by mesitylenesulphonate groups and lying in a plane generates an infinite sheet. In this type of arrangement, the $\text{Sn}_2(\text{OH})_2$ rings are themselves parallel and lie perpendicular to the length of the sheet. The *n*-Bu groups are placed like supporting poles for these sheets and provide depth. By this way of packing, it is interesting to note that the hydrophobic alkyl chains are proximal and provide the maximum interaction. The stability of the structure is derived from a network of hydrogen bonds running through the sheets, in which O(4) of the sulphonate group and the hydroxyl group attached to tin [i.e. O(1)] participate in a symmetrical fashion [$\text{O}(4)\cdots\text{O}(1) = 2.775(2)$ Å, $\text{H}(1\text{A})\cdots\text{O}(4) = 2.021$ Å and $\text{O}(1) - \text{H}(1\text{A})\cdots\text{O}(4) = 147.2^\circ$ (Fig. 4)]. To the best of our knowledge, this may be the first report of a sulphonate complex of tin in which the same ligand adopts different coordination behaviour.

The earlier structures of diorganotin(IV) sulphonates [8,9] and our present studies clearly demonstrate that these compounds preferably adopt polymeric sheet structures while their carboxylate analogues often exhibit monomeric (chelating) structures [19–27] besides only a few polymeric structures [28,29]. This significant conclusion, that organotin(IV) sulphonates prefer polymeric sheet structures in the solid state, may provide the means to construct a variety of supramolecular architectures in organotin(IV) chemistry [30].

4. Experimental

All reactions were carried out in an inert atmosphere of pure dry nitrogen gas. Solvents were dried using standard techniques (*n*-hexane over calcium hydride, chloroform, benzene, toluene and dichloromethane over P_2O_5). Di-*n*-butyltin(IV) oxide (Fluka) and 2-mesitylenesulphonic acid dihydrate (Aldrich) were used as supplied.

Glassware was dried in an oven maintained around 250°C and further flame dried under vacuum before setting the reaction.

NMR spectra were recorded in DMSO- d_6 solutions on a Bruker AC-300F spectrometer with TMS (^1H), DMSO- d_6 (^{13}C) and tetramethyltin (^{119}Sn) as standards. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer model 1430 ratio recording spectrometer. Mass spectrum of **1** (EI, 70 eV) was obtained on a VG Analytical 11-2505-70 SMS mass spectrometer. Elemental analyses (C, H) were performed on a Perkin–Elmer model 2400 CHN elemental analyser. Sulphur was determined by gravimetric method [31].

4.1. Preparation of

$(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\}_2\}_n$ (**1**)

To a solution of di-*n*-butyltin(IV) oxide (2.487 g, 10 mmol) in toluene (60 cm³) was added 2-mesitylenesulphonic acid dihydrate (4.725 g, 20 mmol). The reaction mixture was heated under reflux conditions (110°C) for about 8–10 h, with a Dean–Stark apparatus used for the azeotropic removal of water. After the reaction mixture was allowed to attain room temperature, a white amorphous powder separated out which was removed by filtration and vacuum dried. Yield 5.10 g, 80%; m.p. 168°C. Anal. Found: C, 49.62; H, 6.43; S, 9.8. Calc. for $\text{C}_{26}\text{H}_{40}\text{O}_6\text{S}_2\text{Sn}$: C, 49.47; H, 6.34; S, 10.1%. $^1\text{H-NMR}$: δ , 0.80 (m), 1.23 (m), 1.56 (m), 1.64 (m) (18H, *n*-C₄H₉Sn); 2.23 (s) (6H, mes-CH₃), 2.59 (12H, mes-(CH₃)₂); 6.80 (s) and 7.60 (s) ppm (4H, C₆H₂). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ , 13.54 C(4), 25.66 C(3), 27.07 C(2), 33.43 C(1); 20.36, 22.74, 130.12, 136.28, 137.05 and 141.7 ppm (ligand). The values for coupling constants, nJ (^{119}Sn , ^{13}C) are 1J , 909; 2J , 45.2 and 3J , 173.6 Hz. $^{119}\text{Sn-NMR}$: δ , -342.9 ppm. IR (KBr, cm⁻¹): 1240 m, 1200 sh, 1170 vs [$\nu_4(\text{E})\text{SO}_3$ as. str.]; 1130 m [$\nu_1(\text{A}_1)\text{SO}_3$ sym. str.]; 675 s [$\nu_2(\text{A}_1)\text{SX}$ str.]; 580 m, 545 w [$\nu_5(\text{E})\text{SO}_3$ as. defn.]; 515 w [$\nu_3(\text{A}_1)\text{SO}_3$ sym. defn.]; 1090 m, 1020 m, 870 w, 840 m, 795 w, 440 w, 390 w [$\nu_6(\text{E})\text{SX}$ defn., mesitylene group int. vib.]. The following tin containing fragments have been recorded in its mass spectrum m/z : 575 [$\text{M} - \text{C}_4\text{H}_9$]⁺ (90); 495 [$\text{M} - \text{C}_4\text{H}_9 - \text{SO}_3$]⁺ (24); 433 [$\text{M} - \text{OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$]⁺ (52); 375 [$\text{M} - \text{OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3 - \text{C}_4\text{H}_{10}$]⁺ (36); 319 [$\text{M} - \text{OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3 - \text{C}_4\text{H}_{10} - \text{C}_4\text{H}_8$]⁺ (59); 239 [$\text{M} - \text{OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3 - \text{C}_4\text{H}_{10} - \text{C}_4\text{H}_8 - \text{SO}_3$]⁺ (22); 120 [$\text{M} - 2\{\text{OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\} - \text{C}_4\text{H}_{10} - \text{C}_4\text{H}_8$]⁺ (65).

4.2. Preparation of

$(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\mu\text{-OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)\}_n$ (**2**)

The partially hydrolysed product **2** crystallized as fine needles from a saturated solution of compound **1** in 50:50 v/v CH₃OH–CHCl₃ upon keeping it for 35 days at 25 ± 3°C. The excess solvent was slowly decanted

and product dried by applying mild vacuum. M.p. > 220°C. Anal. Found: C, 45.11; H, 6.32; S, 6.9. Calc. for $\text{C}_{17}\text{H}_{30}\text{O}_4\text{SSn}$: C, 45.46; H, 6.69; S, 7.1%. $^1\text{H-NMR}$: δ , 0.88 (m), 1.36 (m), 1.62 (m), 1.70 (m), (18H, *n*-C₄H₉Sn); 2.25 (s) (3H, mes-CH₃), 2.60 (s) (6H, mes-(CH₃)₂); 4.80 (s) (br, 1H, OH); 6.82 (s) and 7.60 (s) ppm (2H, C₆H₂). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ , 13.26 C(4), 24.84 C(3), 26.62 C(2), 32.46 C(1); 21.02, 23.12, 130.80, 136.02, 137.84 and 142.10 ppm (ligand). 1J (^{119}Sn , ^{13}C), 920 Hz. $^{119}\text{Sn NMR}$: δ , -324.1 ppm. IR (KBr, cm⁻¹): 3450 [$\nu(\text{OH})$]; 1260 m, 1190 [$\nu_4(\text{E})\text{SO}_3$ as. str.]; 1100 s [$\nu_1(\text{A}_1)\text{SO}_3$ sym. str.]; 680 s [$\nu_2(\text{A}_1)\text{SX}$ str.]; 585 m, 540 m [$\nu_5(\text{E})\text{SO}_3$ as. defn.]; 510 w [$\nu_3(\text{A}_1)\text{SO}_3$ sym. defn.]; 1080 s, 1015 s, 880 m, 855 m, 805 w, 755 w [$\nu_6(\text{E})\text{SX}$ defn. mesitylene group int. vib.].

4.3. Crystal structure determinations and refinements

Crystallization of **1** by slow evaporation of its saturated toluene solution and **2** from a mixed solvent CH₃OH–CHCl₃ (50:50, v/v) yielded good single crystals. Intensity data were collected on a Siemens P4 single crystal diffractometer equipped with molybdenum sealed tube ($\lambda = 0.71073$ Å) and highly oriented graphite monochromator using crystals of dimensions 0.30 × 0.24 × 0.21 mm for **1** and 0.31 × 0.27 × 0.21 mm for **2** mounted in Lindmann glass capillaries. For **1**, the lattice parameters and standard deviations were obtained by least squares fit to 40 reflections ($10.48 < 2\theta < 28.94^\circ$). The data were collected by 2θ – θ scan mode with a variable scan speed ranging from 2.0° to a maximum of 45.0° min⁻¹. Three reflections were used to monitor the stability and orientation of the crystal and were remeasured after every 97 reflections. Their intensities showed only statistical fluctuations during 23.68 h X-ray response time. The data were collected for Lorentz and polarization factors and an empirical absorption correction based on psi scan method was applied. All other relevant information about the data collection and the refinement are presented in Table 2.

Both the structures were solved by direct methods using SHELX-97 [32] and also refined on F^2 using the same one. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their respective non-hydrogen atoms. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $a = 0.0370$ and $b = 0.00$ was used. The refinement converged to a final R value of 0.0236 ($wR_2 = 0.0607$ for 1281 reflections) [$I > 2\sigma(I)$]. The final difference map was featureless.

The data collection procedure, structure solution and refinement for **2** were essentially the same as that for **1**; 40 reflections ($14.71 < 2\theta < 35.53^\circ$) for accurate cell parameter determination, a total of 45.54 h of X-ray exposure time, $R = 0.0226$, $wR = 0.0592$, $a = 0.030$ and

Table 2
Crystal data and structure refinement details for compounds **1** and **2**

	1	2
Empirical formula	C ₂₆ H ₄₀ O ₆ S ₂ Sn	C ₁₇ H ₃₀ O ₄ SSn
Formula weight	631.39	449.16
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2	Monoclinic, <i>P</i> 2 ₁ / <i>m</i>
Unit cell dimensions		
<i>a</i> (Å)	12.555(1)	10.040(1)
<i>b</i> (Å)	21.238(1)	14.500(1)
<i>c</i> (Å)	5.415(1)	13.978(1)
<i>α</i> (°)	90	90
<i>β</i> (°)	90	91.58(1)
<i>γ</i> (°)	90	90
Volume (Å ³)	1443.9(3)	2034.1(3)
<i>Z</i> , calculated density (Mg m ⁻³)	2, 1.452	4, 1.467
Absorption coefficient (mm ⁻¹)	1.066	1.374
<i>F</i> (000)	652	920
Maximum and minimum transmission	0.925, 0.865	0.840, 0.593
<i>θ</i> range for data collection (°)	1.88–23.99	2.02–23.00
Scan type	2 θ – θ	2 θ – θ
Scan speed (° min ⁻¹)	Variable, 2.0–45.0 in ω	Variable, 2.0–30.0 in ω
Scan range (ω) (°)	1.20 plus <i>K</i> α separation	0.92 plus <i>K</i> α separation
Index ranges	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 24, –6 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 15, –15 ≤ <i>l</i> ≤ 15
Reflections collected	1355	3141
Independent reflections	1355	2950 [<i>R</i> _{int} = 0.0152]
Data/restraints/parameters	1355/0/159	2950/0/242
Goodness-of-fit on <i>F</i> ²	1.108	1.061
Weighting scheme	1/[$\sigma^2(F_o^2) + (0.0370P)^2 + 0.00P$], <i>P</i> = (max(<i>F</i> _o ² , 0) + 2 <i>F</i> _o ²)/3	1/[$\sigma^2(F_o^2) + (0.0300P)^2 + 1.14P$], <i>P</i> = (max(<i>F</i> _o ² , 0) + 2 <i>F</i> _o ²)/3
Data to parameter ratio	8.52:1	12.19:1
Final <i>R</i> indices, 1281 reflections [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0236, <i>wR</i> ₂ = 0.0607	<i>R</i> ₁ = 0.0226, <i>wR</i> ₂ = 0.0592 (reflections 2725)
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0262, <i>wR</i> ₂ = 0.0626	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0609
Largest difference peak and hole (e Å ⁻³)	0.245 and –0.501	0.457 and –0.368

b = 1.14 [in the weighting scheme] were the parameters associated with this structure. Full details are presented in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146941 for compound [(*n*-C₄H₉)₂Sn{ μ -OSO₂C₆H₂(CH₃)₃}₂]_{*n*} (**1**) and CCDC no. 147052 for compound [(*n*-C₄H₉)₂Sn{(μ -OH)(μ -OSO₂-C₆H₂(CH₃)₃)}]_{*n*} (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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