



Structural studies of diorganotin(IV) sulfonates: The synthesis of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_{2-2,5}\}_2]$ and $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{R}\}_2 \cdot 2(\text{hexamethylphosphoric triamide})]$ [R = CH₃, 4-C₆H₄CH₃, 2,5-C₆H₃(CH₃)₂, 2,4,6-C₆H₂(CH₃)₃] and crystal structures of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\mu\text{-OH})(\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_{2-2,5})]_2$ and $(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{R}\}_2 \cdot 2(\text{hexamethylphosphoric triamide})]$ [R = 4-C₆H₄CH₃, 2,5-C₆H₃(CH₃)₂, 2,4,6-C₆H₂(CH₃)₃]

Ramesh Kapoor^{a,*}, Anand Gupta^b, Paloth Venugopalan^b, Ajay Pal Singh Pannu^c, Maninder Singh Hundal^c, Pratibha Kapoor^{b,*}

^a Indian Institute of Science Education and Research Mohali, MGSIPI Complex, Sector 26, Chandigarh 160 019, India

^b Department of Chemistry, Panjab University, Chandigarh 160 014, India

^c Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India

ARTICLE INFO

Article history:

Received 7 October 2008

Received in revised form 3 November 2008

Accepted 13 November 2008

Available online 24 November 2008

Keywords:

Diorganotin(IV) sulfonate

Hexamethylphosphoric triamide

Crystal structures

NMR spectra

IR spectra

ABSTRACT

The syntheses of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_{2-2,5}\}_2]$ (**1**) and $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{R}\}_2 \cdot 2\text{HMPA}]$ [R = CH₃ (**3**), 4-C₆H₄CH₃ (**4**), 2,5-C₆H₃(CH₃)₂ (**5**), 2,4,6-C₆H₂(CH₃)₃ (**6**)] have been carried out to study their structures and to delineate the coordination behavior of the weakly coordinating sulfonate anions. Compound **1** hydrolyzes slowly to $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\mu\text{-OH})(\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_{2-2,5})]_2$ (**2**) when kept in CH₂Cl₂ for a few days. The crystal structure shows that **2** has a dimeric structure in which tin atoms are bridged by two hydroxy groups and each tin atom is further bonded to two *n*-Bu groups and a mono-coordinated sulfonate anion thus generating a trigonal bipyramidal geometry at tin atom. However, the coordination geometry at tin can be visualized as a severely distorted octahedron, if a relatively weak Sn–O bond of 2.690 Å between Sn and an O atom of the neighboring sulfonate anion is also considered. Compounds **3–6** are obtained by the consecutive reaction of $(n\text{-C}_4\text{H}_9)_2\text{SnO}$ with the appropriate sulphonic acid and hexamethylphosphoric triamide (HMPA). X-ray crystal structures of **4**, **5** and **6** show octahedral geometry around tin atom in the two compounds in which the sulfonate ligands are covalently bonded in a monodentate mode. Compounds **3–6** are nonionic in polar solvents. The Sn–O (sulfonate) bond distances 2.354(2), **2**: 2.233(2), **4**: 2.237(5), **5** and 2.227(3) Å, **6** suggest some degree of ionic character in the metal-anion bonds. These compounds have also been characterized by multinuclear (¹H, ¹³C and ¹¹⁹Sn) NMR studies.

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1. Introduction

Organotin(IV) ester derivatives of alkyl/arylsulphonic acids represent an important class of compounds with wide applications and structural diversity [1,2]. Their catalytic activity is attributed to weakly coordinating ability of anions, which leads to enhanced Lewis acidic nature of the organotin(IV) moiety. These compounds exhibit a wide variety of associated structures, primarily attributed

to the multidentate nature of the sulfonate anions and display supramolecular assemblies in solid state that are generated through extensive hydrogen bonding using one or more O donor atoms [3–12]. X-ray studies on diorganotin(IV) bis(alkyl or arylsulfonate) [R attached to sulfonate = CH₃, 4-C₆H₄CH₃, 2,4,6-C₆H₂(CH₃)₃] have revealed weak coordination of the sulfonate anions to the central tin atom [5–12]. The bond distances between tin and the sulfonate oxygens are observed to be longer than the normal Sn–O distance of 2.14 Å, and fall in the range 2.20–2.78 Å, indicating a fair degree of ionic character associated with this coordinate bond. Otera et al. [13,14] have reported the existence of discrete tin dications in the compounds $[\text{R}_2\text{SnOH}(\text{H}_2\text{O})]_2^{2+} [\text{OTf}^-]_2$ [OTf = CF₃SO₃⁻; R = *t*-Bu and 2-phenylbutyl]. These authors also observed that when R = *n*-Bu, a nonionic compound,

* Corresponding authors. Address: Indian Institute of Science Education and Research Mohali, MGSIPI Complex, Sector 26, Chandigarh 160 019, India.

E-mail address: rkapoor@pu.ac.in (R. Kapoor).

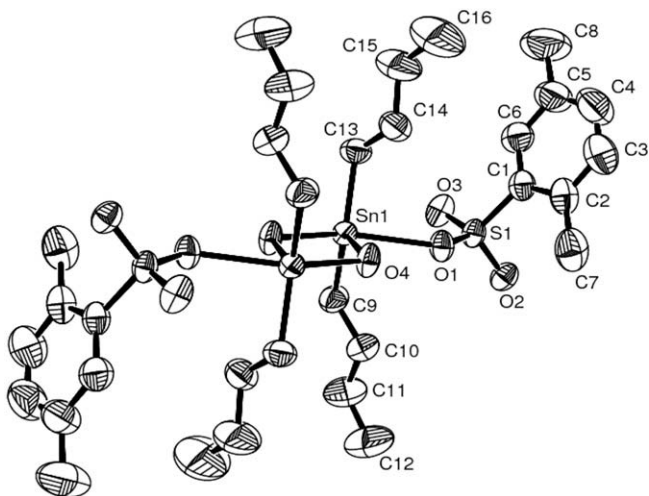


Fig. 1. ORTEP view of **2** showing the centrosymmetric dimer.

$[\text{R}_2\text{SnOH}(\text{OTf})(\text{H}_2\text{O})_2]_2$, is obtained in the solid state which dissociates into ionic species in solutions of CH_3CN . The interaction between Sn and the triflate ligand is weak as the Sn–O (triflate) distance was observed to be 2.622 Å. Beckmann et al. [15] reported the synthesis of $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+} [\text{OTf}^-]_2$ (R = Me and *n*-Bu) and the existence of diorganotin dicationic species was attributed to the stability provided by the neutral donor ligands.

The general consensus emerging out of these studies is that the Sn–O(sulfonate) bond is weakly coordinating with a relatively large Sn–O distance, and generation of discrete ionic species from alkyl/aryl substituted tin and sulfonate moiety would be tedious if not impossible. Our studies [5,6] with ligands like $(2,4,6\text{-C}_6\text{H}_2(\text{CH}_3)_3\text{SO}_3)^-$, $(4\text{-C}_6\text{H}_4\text{CH}_3\text{SO}_3)^-$ and $(\text{CH}_3\text{SO}_3)^-$ and by others [7] also vouch for this observation. To probe deep into the nature of the product formation and to augment the hypothesis that RSO_3^- (R = non-fluorinated alkyl or aryl group) is indeed weakly coordinating, we synthesized a number of di-*n*-butyltin(IV) sulfonate: $(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2\text{-}2,5\}_2$ (**1**) and $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{R}\}_2 \cdot 2\text{HMPA}]$ [R = CH_3 (**3**), $4\text{-C}_6\text{H}_4\text{CH}_3$ (**4**), $2,5\text{-C}_6\text{H}_3(\text{CH}_3)_2$ (**5**), $2,4,6\text{-C}_6\text{H}_2(\text{CH}_3)_3$ (**6**)] and investigated the X-ray crystal structures of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}\{(\mu\text{-OH})(\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)_2\}]_2$ (**2**) and $(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{R}\}_2 \cdot 2\text{HMPA}$ [R = $4\text{-C}_6\text{H}_4\text{CH}_3$ (**4**), $2,5\text{-C}_6\text{H}_3(\text{CH}_3)_2$ (**5**), $2,4,6\text{-C}_6\text{H}_2(\text{CH}_3)_3$ (**6**)].

2. Results and discussion

2.1. Synthesis of $(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2\}_2$ (**1**), $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\mu\text{-OH})(\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2\text{-}2,5)]_2$ (**2**) and $(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{X}\}_2 \cdot 2\text{HMPA}$ [X = CH_3 (**3**), $4\text{-C}_6\text{H}_4\text{CH}_3$ (**4**), $2,5\text{-C}_6\text{H}_3(\text{CH}_3)_2$ (**5**), $2,4,6\text{-C}_6\text{H}_2(\text{CH}_3)_3$ (**6**)]

The compound $(n\text{-C}_4\text{H}_9)_2\text{Sn}\{\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2\}_2$ (**1**) is obtained in about 80% yield by azeotropic removal of water from the reaction between di-*n*-butyltin(IV) oxide and 2,5-dimethylbenzenesulfonic acid in 1:2 molar ratio in anhydrous benzene. It is a stable, white amorphous, non-hygroscopic solid and shows limited solubility in hot CH_2Cl_2 , CHCl_3 but can be easily dissolved in polar solvents, e.g., in CH_3OH , DMSO, DMF etc. Its millimolar solutions in CH_3OH and CH_3CN are non-conducting thus suggesting that sulfonate anion is not ionized on dissolution in these solvents. Crystallization of **1** from CH_2Cl_2 yielded good single crystals on keeping at room temperature for a few days but the analytical results on these crystals revealed that compound **1** had undergone partial hydrolysis on long standing and coordination by water even when only trace amounts of water were probably present in the solvent. The result-

Table 1
NMR (119 Sn, ^1H , ^{13}C) data of complexes 1–6.

δ ^{119}Sn (ppm)	^1H NMR (ppm)		^{13}C NMR (ppm)		δ (anion)	δ (base)	δ (anion)
	δ (Sn-R)	δ (base)	δ (anion)	δ (Sn-R)			
1 –337.2	0.78, 1.15–1.26, 1.51–1.60	–	2.27, 2.49 7.00, 7.59	34.22(C1), 26.95(C2), 25.48(C3), 13.24(C4)	19.46, 20.42 127.15, 130.31, 130.91 132.56, 134.08, 142.42	–	–
2 –119.9	0.81, 1.28, 1.65, 1.76	–	2.31, 2.60 7.09, 7.83	34.00(C1), 26.86(C2), 25.36(C3), 13.14(C4)	19.41, 20.37 127.05, 130.04, 130.76, 132.42, 133.91, 143.20	–	–
3 –296.5	0.94, 1.42, 1.83, 1.92	2.68–2.71	2.42	32.04(C1), 26.69(C2), 26.37(C3), 13.61(C4)	35.09	36.84	35.09
4 –334.1	0.87, 1.23–1.31, 1.74, 1.85	2.62–2.66	2.36 7.17–7.19 7.69–7.72	33.22(C1), 26.78(C2), 26.53(C3), 13.42(C4)	21.09, 125.84, 128.48, 140.32, 141.19	36.60	21.09, 125.84, 128.48, 140.32, 141.19
5 –318.3	0.75, 1.22, 1.58, 1.68	2.64	2.24, 2.47	35.19(C1), 26.73(C2), 26.44(C3), 13.61(C4)	19.90, 20.86	36.86	19.90, 20.86
6 –309.2	0.74, 1.20, 1.65, 1.84	2.64–2.68	2.24, 2.59, 6.82	32.87(C1), 26.28(C2), 26.11(C3), 13.23(C4)	127.83, 131.12, 131.40, 134.70, 141.78 20.48, 22.69 130.45, 137.13, 138.14, 139.13	34.85–36.51	127.83, 131.12, 131.40, 134.70, 141.78 20.48, 22.69 130.45, 137.13, 138.14, 139.13

Table 2

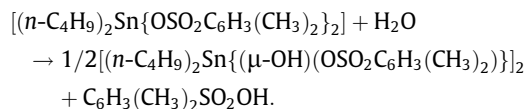
Selected bond distances [Å] and angles [°] in [(*n*-C₄H₉)₂Sn(μ-OH)(OSO₂C₆H₃(CH₃)₂)]₂ (**2**); [(*n*-C₄H₉)₂Sn{(CH₃)₂N₃PO}₂(OSO₂C₆H₄CH₃-4)₂] (**4**); [(*n*-C₄H₉)₂Sn{(CH₃)₂N₃PO}₂(OSO₂C₆H₄(CH₃)₂-2,5)₂] (**5**); [(*n*-C₄H₉)₂Sn{(CH₃)₂N₃PO}₂(OSO₂C₆H₄(CH₃)₂-2,4,6)₂] (**6**).

Compound 2			
Sn(1)–O(4)	2.059(2)	Sn(1)–C(9)	2.109(4)
Sn(1)–C(13)	2.111(3)	Sn(1)–O(4) ^{#1}	2.134(2)
Sn(1)–O(1)	2.354(2)	Sn(1)–O(2)	2.690(2)
S(1)–O(2)	1.449(2)	S(1)–O(3)	1.450(2)
S(1)–O(1)	1.467(2)		
O(4)–Sn(1)–C(9)	107.17(13)	O(4)–Sn(1)–C(13)	107.43(12)
O(4)–Sn(1)–O(4) ^{#1}	144.06(15)	O(4)–Sn(1)–O(4) ^{#1}	70.38(10)
C(9)–Sn(1)–O(4) ^{#1}	100.92(14)	C(13)–Sn(1)–O(4) ^{#1}	99.48(13)
O(4)–Sn(1)–O(1)	76.52(8)	C(9)–Sn(1)–O(1)	88.22(13)
C(13)–Sn(1)–O(1)	90.58(13)	O(4) ^{#1} –Sn(1)–O(1)	146.90(8)
O(2)–S(1)–O(3)	113.45(15)	O(2)–S(1)–O(1)	111.54(15)
O(3)–S(1)–O(1)	111.56(14)	O(2)–S(1)–C(1)	107.46(16)
Sn(1)–O(4)–Sn(1) ^{#1}	109.62(10)		
Compound 4			
Sn–C(1)	2.113(3)	S–O(4)	1.430(3)
S–C(11)	1.769(4)	Sn–O(1)	2.215(2)
S–O(2)	1.481(3)	Sn–O(2)	2.233(2)
S–O(3)	1.430(3)		
C(1)–Sn–O(2) ^{#1}	93.02(13)	O(1)–Sn–O(2) ^{#1}	92.83(10)
C(1)–Sn–O(2)	86.98(13)	C(1)–Sn–C(1) ^{#1}	180.00(18)
C(1)–Sn–O(1)	90.20(13)	O(1)–Sn–O(2)	87.17(10)
C(1) ^{#1} –Sn–O(1)	89.80(13)	C(1)–Sn–O(1) ^{#1}	89.80(13)
O(2) ^{#1} –Sn–O(2)	180.00(6)	C(1) ^{#1} –Sn–O(1) ^{#1}	90.20(13)
Compound 5			
Sn–C(1)	2.111(7)	S–O(3)	1.427(6)
Sn–O(1)	2.212(5)	S–O(4)	1.440(6)
Sn–O(2)	2.237(5)	S–O(2)	1.480(5)
C(1)–Sn–O(2)	90.6(2)	O(1)–Sn–O(2)	86.1(2)
C(1)–Sn–O(2) ^{#1}	89.4(2)	C(1)–Sn–C(1) ^{#1}	180.0(3)
C(1)–Sn–O(1)	89.1(2)	O(1)–Sn–O(2) ^{#1}	93.9(2)
C(1) ^{#1} –Sn–O(1)	90.9(2)	O(2)–Sn–O(2) ^{#1}	180.000(1)
Compound 6			
Sn(1)–C(10)	2.113(6)	Sn(1)–O(4)	2.214(3)
Sn(1)–O(1)	2.227(3)	S(1)–O(3)	1.429(6)
S(1)–O(2)	1.371(6)	S(1)–O(1)	1.442(4)
C(10)–Sn(1)–C(10) ^{#1}	180.0(4)	C(10)–Sn(1)–O(4)	90.63(19)
C(10) ^{#1} –Sn(1)–O(4)	89.37(19)	C(10) ^{#1} –Sn(1)–O(4) ^{#1}	190.63(19)
O(4)–Sn(1)–O(4) ^{#1}	180.00(18)	O(4)–Sn(1)–O(1) ^{#1}	89.00(13)
O(4) ^{#1} –Sn(1)–O(1) ^{#1}	191.00(13)	O(1)–Sn(1)–O(1) ^{#1}	180.0(3)

Symmetry transformations used to generate equivalent atoms:

#1 $-x, -y, -z + 1$; #2 $-x, y - 1/2, 1.5 - z$ (**2**); #1 $-x + 1, -y, 1 - z$ (**4**); #1 $-x + 1, -y, -z + 1$ (**5**); #1 $-x, -y, -z$ (**6**).

ing compound was [(*n*-C₄H₉)₂Sn{(μ-OH)(OSO₂C₆H₃(CH₃)₂)}]₂ (**2**) (Fig. 1).



Compounds **3–6** were easily obtained on reaction of di-*n*-butyltin(IV) oxide, 2 mol of the appropriate sulphonic acid and 2 mol of HMPA in CH₃CN. It was observed that even if 4 mol of HMPA were used the product corresponded to the composition observed for **3–6**. The compounds are stable in air and are easily recrystallized from CH₃CN. Conductivity studies on these compounds revealed their non-ionic nature.

2.2. Spectral studies

The identity of **1–6** has been established by IR and multinuclear (¹H, ¹³C and ¹¹⁹Sn) NMR spectral studies. The data are summarized in Table 1. The ¹H NMR spectrum of each compound reveals distinct signals at δ 0.7–1.9, 2.0–2.7 and 7.0–7.9 arising from *n*-C₄H₉/HMPA/sulfonate protons, respectively. The observed integral ratios of these groups support the composition of compounds **1–6**. The ¹¹⁹Sn NMR shifts recorded for **1** and **2** in CDCl₃/DMSO-*d*₆ show a sharp peak at δ = –337.2 and –119.2 ppm, respectively. The δ value for **1** falls within the region (–210 to –400 ppm) generally assigned to indicate 6-coordinate Sn, while the value for **2** suggests 5-coordinate Sn consistent with the range (–90 to –190) generally observed in di-*n*-butyltin(IV) compounds [16]. Besides, the ¹J (¹¹⁹Sn–¹³C) coupling constant, 896 Hz for **1** gives C–Sn–C angle corresponding to 164.5° by the use of Holecek equation [17]. The ¹J and the δ ¹¹⁹Sn values suggest severely distorted octahedral and trigonal bipyramidal geometries for **1** and **2**, respectively. Thus, the NMR data give evidence for breakdown of the polymeric structure of compound **2** to give discrete molecular structure in solution (see solid state structure of **2**). ¹¹⁹Sn NMR spectra for **3–6** show a single peak for each compound in the region –290 to –340 ppm (**1**), which are indicative of hexacoordinate tin [16]. This data clearly suggest that sulfonate ligands are bonded to Sn in a monodentate coordination mode.

The question whether the sulfonate anions are bonded to the Sn atoms or not, is unambiguously answered on the basis of IR spectra

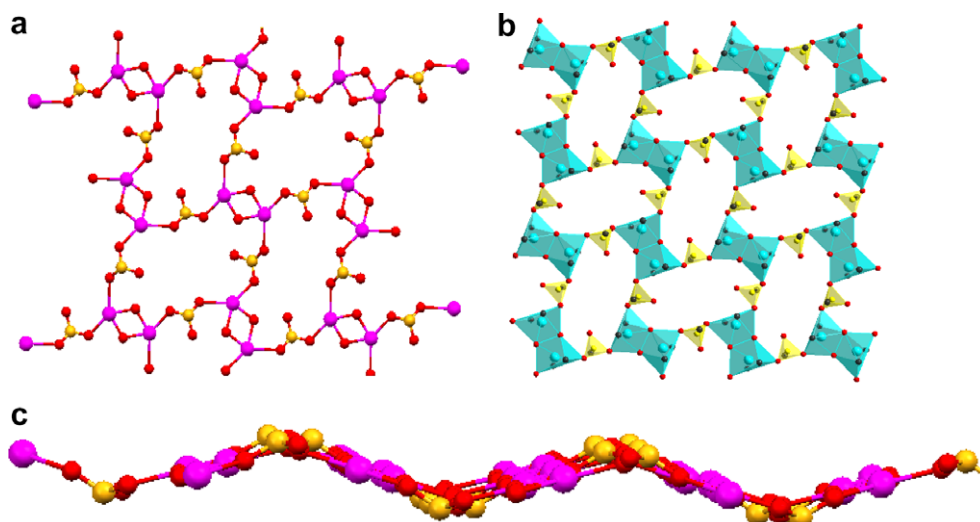


Fig. 2. (a) and (b) The formation of macrocyclic corrugated sheet structure through Sn–O coordinate bonds. Four such 20 membered rings are shown. (c) The side view of the sheet indicating the corrugated nature of the sheet. The carbon atoms bonded to Sn and sulfonate moiety are not shown in these figures. The carbon atoms which are perpendicular to the sheet have been removed from the figure.

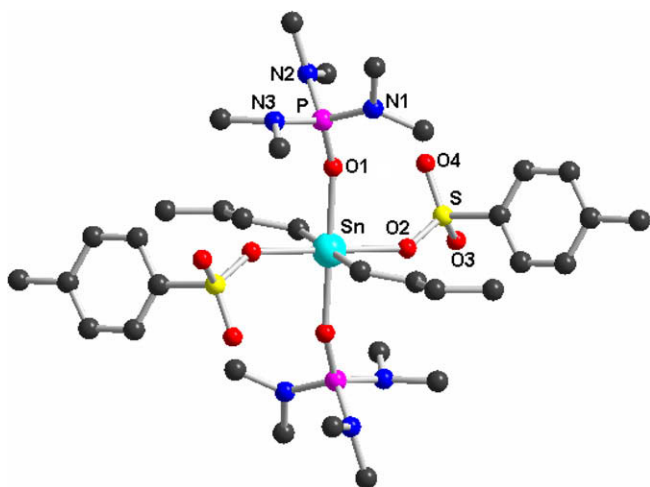


Fig. 3. Showing the structure of **4** and the labeling scheme used in the structure analysis.

of these compounds. For free sulfonate anion, the CSO_3 moiety has C_{3v} symmetry and the asymmetric stretching vibration $\nu_{\text{asym}} \text{SO}_3$ is doubly degenerate. However, on coordination the axial symmetry is reduced to C_s and the asymmetric SO_3 stretching vibration splits into two bands. Accordingly, for **1–6** the sulfonate anions give rise to split bands in the region $1300\text{--}1000\text{ cm}^{-1}$ and apparently suggest coordination of sulfonate groups to tin.

2.3. X-ray crystal structures of **2**, **4**, **5** and **6**

A perspective view of structure of **2** with atom numbering scheme is given in Fig. 1. Selected bond lengths and angles are given in Table 2. In the crystal lattice compound **2** exists in the dimeric form, which can be considered as built from the four-

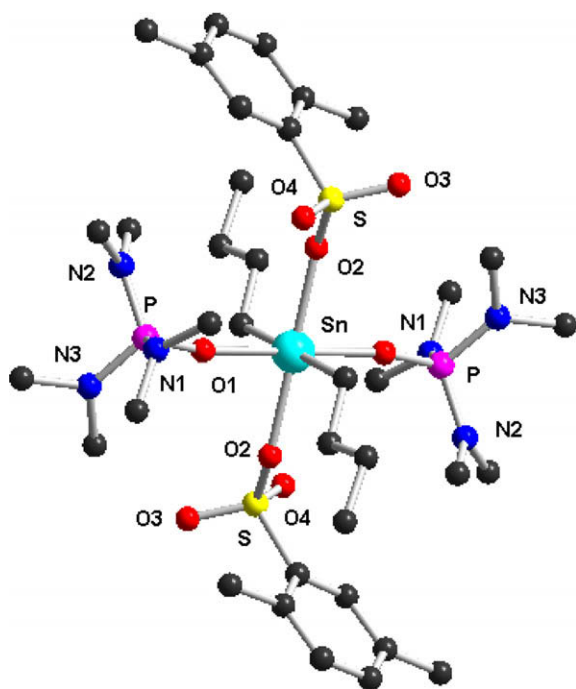


Fig. 4. Showing the structure of **5** and the labeling scheme used in the structure analysis.

membered $[\text{Sn}(\mu_2\text{-OH})_2\text{Sn}]$ core. This core is similar in geometry and conformation as observed in other reported structures [10,18–25]. The five primary bonds to tin in **2** are to the two *n*-butyl groups [$\text{Sn}\text{--C}(9) = 2.109(4)\text{ \AA}$; $\text{Sn}\text{--C}(13) = 2.111(3)\text{ \AA}$], and to O of the sulfonate anion [$\text{Sn}\text{--O}(1) = 2.354(2)\text{ \AA}$], besides the two bridging hydroxo groups [$\text{Sn}\text{--O}(4) = 2.059(2)\text{ \AA}$; $\text{Sn}\text{--O}(4)^\# = 2.134(2)\text{ \AA}$], thus generating a distorted trigonal bipyramidal geometry at tin. In addition there is a very weak intermolecular $\text{Sn}\text{--O}$ interaction [$\text{Sn}\text{--O}(2) = 2.69(1)\text{ \AA}$], the geometry at Sn becomes a highly distorted 6-coordinate octahedral with the two $\text{Sn}\text{--}n\text{-butyl}$ groups in trans orientation [$\text{C}(9)\text{--Sn}(1)\text{--C}(13) = 144.1^\circ$]. The $\text{Sn}\text{--O}(1)$ ($2.354(2)\text{ \AA}$) and $\text{Sn}\text{--O}(2)^\#$ ($2.690(2)\text{ \AA}$) bond distances in **2** are longer than the sum of the covalent bond radii of Sn and O of 2.06 \AA [26–28], but are considerably shorter than the sum of their van der Waals radii of 3.71 \AA [29]. Intramolecular $\text{Sn}\cdots\text{O}$ distances in the range $2.263(6)\text{--}3.071$ have been reported to suggest $\text{Sn}\text{--O}$ bonding [30]. However, such an elongation of an $\text{Sn}\text{--O}$ bond from the normal covalent bond distance point to a considerable ionic character associated with $\text{Sn}\text{--O}$ (sulfonate) bonds. The $\text{Sn}\text{--O}(2)^\#$ interaction is easily broken down in solution to give the dimeric structure (cf. ^{119}Sn NMR value). Along with this relatively weak coordination to the central metal atom, the O3 atom of the sulfonate moiety also forms a strong hydrogen bond with the hydroxyl hydrogen of the $\text{Sn}(\mu_2\text{-OH})_2\text{Sn}$ core ($\text{O3}\cdots\text{H4A} = 1.850\text{ \AA}$; $\text{O4}\text{--H4A}\cdots\text{O3} = 159.5^\circ$). Due to the centrosymmetric structure of the $\text{Sn}(\mu_2\text{-OH})_2\text{Sn}$ core, two of these hydrogen bonds are spanning to opposite sides of the central core.

The relatively weak $\text{Sn}\text{--O}$ coordination around the central metal atom and the two symmetrical hydrogen bonds from the basic $\text{Sn}(\mu_2\text{-OH})_2\text{Sn}$ unit generates a corrugated sheet structure parallel to the *bc* plane of the lattice (Fig. 2a). In this sheet structure, four $\text{Sn}(\mu_2\text{-OH})_2\text{Sn}$ moieties are interlinked through four sulfonate groups and thus form cyclic rings that consist of 20 atoms. Four such rings are illustrated in Fig. 2a. A noteworthy feature in such an arrangement is that the most hydrophobic part of the structure consisting of the tertiary butyl groups and the aromatic moieties project ‘up’ and ‘down’ from these sheets. In this way of building the lattice, all the hydrocarbon part of the structure seems to cluster and get sandwiched in between the most hydrophilic part of the structure, which are the corrugated sheets (Fig. 2b). Such type of lattice stabilization achieved through the close proximity of the hydrocarbon regions point towards the cooperative effect of the very weak hydrophobic interactions amid the so-called strong coordinate and hydrogen bonds and also makes us aware of the necessity to consider the total effect of such interactions in crystal packing. To best of our knowledge this is a second report of a sheet type structure based on $\text{Sn}(\mu_2\text{-OH})_2\text{Sn}$ building block. In literature there is a report of a sheet based on 22 member ring consisting of four $\text{Sn}(\mu_2\text{-OH})_2\text{Sn}$ subunits [10].

Bond lengths and bond angles around tin reveal that the compounds **4**, **5** and **6** (Figs. 3–5) adopt octahedral geometry with the trans disposition of sulfonate groups with bond angles of 180.0° (Table 2). The sulfonate groups are covalently bonded in a monodentate mode with $\text{Sn}\text{--O}(\text{sulfonate})$ bond lengths varying in the range $2.227(3)\text{--}2.237(5)\text{ \AA}$ which are longer than the normal $\text{Sn}\text{--O}$ covalent bond distance and reflect some degree of ionic character. These three structures can best be described as a Sn octahedral sharing four opposite corners with four tetrahedra obtained from two sulfonate and two phosphoric triamide moieties (Fig. 5b).

An earlier report [5] on structure of $\text{Sn}(\text{IV})$ complex of ligand mesitylenesulfonato- O,O' indicates that the ligand used in complex **6** coordinates as unsymmetrical bridging bidentate (i.e., through two oxygens) or unsymmetrical bridging monodentate (ie through one O). Our earlier studies [5] indicate that when the ligand acts as a bridging bidentate between two $\text{Sn}(\text{IV})$ centers, the $\text{Sn}(\text{IV})\text{--O}(\text{sulfonate})$ distance distance of $2.3999(1)$ and

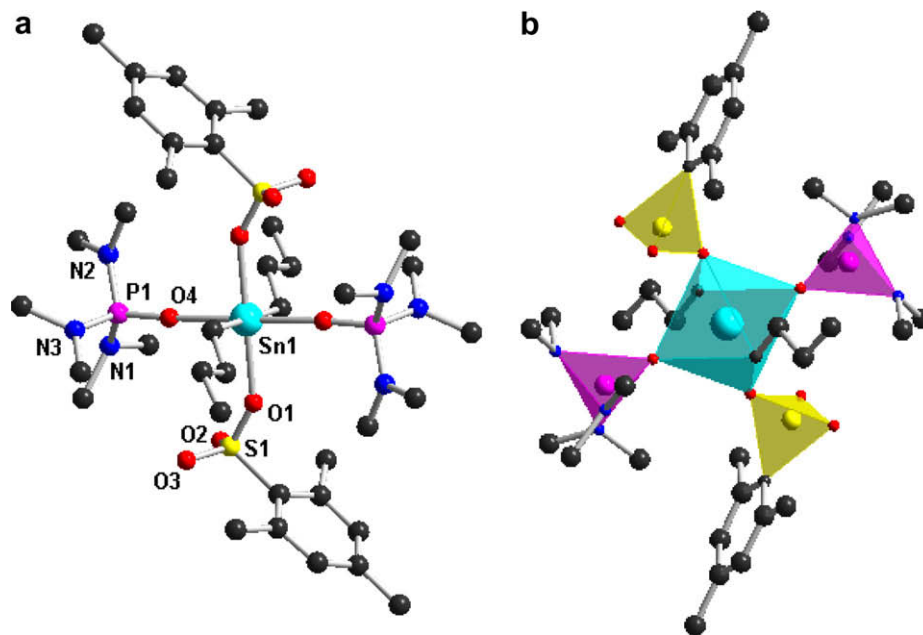


Fig. 5. Showing the structure and the labeling scheme in compound 6.

Table 3
The crystallographic data.

	2	4	5	6
Empirical formula	C ₁₆ H ₂₈ O ₄ SSn	C ₃₄ H ₆₈ N ₆ O ₈ P ₂ S ₂ Sn	C ₃₆ H ₇₂ N ₆ O ₈ P ₂ S ₂ Sn	C ₃₈ H ₇₄ N ₆ O ₈ P ₂ S ₂ Sn
Formula weight	435.13	466.85	961.75	493.89
Crystal size (mm)	0.28 × 0.21 × 0.19	0.20 × 0.19 × 0.15	0.25 × 0.22 × 0.20	0.19 × 0.14 × 0.12
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>Pbca</i>	<i>P1</i>
<i>a</i> (Å)	14.778(2)	9.964(5)	10.297(5)	10.897(1)
<i>b</i> (Å)	12.302(1)	15.814(5)	21.065(5)	11.724(1)
<i>c</i> (Å)	12.145(1)	15.033(5)	22.584(5)	12.447(1)
α (°)	90.0	90.0	90.0	111.31(1)
β (°)	114.22(1)	105.770(5)	90.0	99.51(1)
γ (°)	90.0	90.0	90.0	112.90(1)
<i>V</i> (Å ³)	2013.6(4)	2279.6 (16)	4899(3)	1274.61(19)
<i>Z</i>	4	4	4	2
ρ_{calc} (Mg m ⁻³)	1.435	1.360	1.304	1.287
<i>F</i> ₀₀₀	888	980	2024	520
Temperature (K)	293(2)	293(2)	293(2)	293(2)
μ (mm ⁻¹)	1.385	0.773	0.721	0.695
θ (°)	2.24–23.99	1.91–24.99	1.80–25.50	1.88–24.00
Number of reflections	3309	4171	4022	4016
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0255 <i>wR</i> ₂ = 0.0588	<i>R</i> ₁ = 0.0339 <i>wR</i> ₂ = 0.0910	<i>R</i> ₁ = 0.0557 <i>wR</i> ₂ = 0.1504	<i>R</i> ₁ = 0.0441 <i>wR</i> ₂ = 0.1154
CCDC No.	674140	674142	674143	674141

2.783(1) Å is observed. However, when sulfonate group is bridging monodentate the two observed distances are 2.199(1) and 2.313(1) Å. In the present study (complex **6**) the sulfonate is non bridging monodentate and Sn(IV)–O distance is 2.227(3) Å.

3. Conclusions

It is evident from these studies that di-*n*-butyltin(IV) alkyl/aryl sulfonate (R/Ar = –CH₃, –C₆H₄CH₃–4, –C₆H₃(CH₃)₂–2,5, –C₆H₂(CH₃)₃–2,4,6) are non-ionic compounds containing covalently bonded sulfonate anions though the bonding is weak. It is clear that these sulfonate anions are fairly basic and may be classified as coordinating ligands when interacting with R₂Sn²⁺ moiety. In comparison the more electronegative triflate ligand is crucial for the generation of the cationic moiety.

4. Experimental

4.1. General

All additions and manipulations were carried out under dry nitrogen environment unless otherwise stated. All solvents were distilled prior to use (benzene, toluene over P₄O₁₀ and acetonitrile from calcium hydride). *n*-Bu₂SnO, sulphonic acids, hexamethylphosphoric triamide (HMPA), were obtained from Aldrich and used without any purification. The solution NMR were measured using a JEOL 300 MHz-spectrometer and were referenced against Me₄Si and Me₄Sn. The spectra were recorded in CDCl₃ containing 1–2 drops of DMSO-*d*₆ to improve the solubility of the compounds. Elemental analyses (C, H, N) were performed on a Perkin–Elmer model 2400 CHN analyzer. IR spectra were recorded as KBr pellets on a

Perkin–Elmer RX-1 FTIR spectrophotometer. Only strong to medium intensity bands are listed for each compound.

4.2. Preparation of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)_2]$ (**1**) from $n\text{-Bu}_2\text{SnO}$ and $2,5\text{-C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_3\text{H}$

To the suspension of di-*n*-butyltin(IV) oxide (2.50 g, 10 mmol) in dry benzene (60 cm³) was added 2,5-dimethylbenzenesulphonic acid dihydrate (4.44 g, 20 mmol). The mixture was heated under reflux conditions for about 10 h, with a Dean–Stark apparatus used for the azeotropic removal of water. The solution was filtered to remove any unreacted di-*n*-butyltin(IV) oxide. The clear solution was evacuated at room temperature to give a white amorphous solid. Yield: 5.4 g, 80%; m.p. >240 °C. Anal. Found: C, 47.42; H, 5.56%. Calc. for C₂₄H₃₆SnS₂O₆: C, 47.78; H, 5.97. IR (KBr, cm⁻¹): 1260, 1214 (ν_{asym}SO₃), 1168, 1096, 1028, 994, 882, 815, 772, 696, 629, 550, 523.

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

The partially hydrolyzed product **2** crystallized as fine crystalline material from a dichloromethane solution of compound **1** upon keeping it at room temperature for a few days. The excess solvent was decanted and product dried by keeping it over P₄O₁₀ in a desiccator. M.p. >240 °C. Anal. Found: C, 44.08; H, 6.31%. Calc. for C₁₆H₂₈O₄Sn: C, 44.13; H, 6.43. IR (KBr, cm⁻¹): 3390(OH), 1297, 1203(ν_{asym}SO₃), 1068, 985, 860, 811, 744.

4.4. Preparation of $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3)_2\text{N}_3\text{PO}]_2(\text{OSO}_2\text{X})_2$ [$\text{X} = \text{-CH}_3$ (**3**), $\text{-C}_6\text{H}_4\text{CH}_3$ (**4**), $\text{-C}_6\text{H}_3(\text{CH}_3)_2$ (**5**), $\text{-C}_6\text{H}_2(\text{CH}_3)_3$ (**6**)]

To the suspension of *n*-Bu₂SnO in CH₃CN (30 mL), 2 equiv. of the appropriate arylsulphonic acid and four equivalents of HMPA were added with stirring. The mixture was heated for about 4–6 h around 60 °C. The clear solutions on evacuation yielded a white solid in each case. The compounds were recrystallised from CH₃CN solution on cooling in an ice bath.

4.4.1. $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3)_2\text{N}_3\text{PO}]_2(\text{OSO}_2\text{CH}_3)_2$ (**3**)

M.p. 82 °C. Anal. Found: C, 36.61; H, 7.90; N, 11.46%. Calc. for C₂₂H₆₀N₆O₈P₂S₂Sn: C, 36.73; H, 8.35 and N, 11.69. IR (KBr, cm⁻¹): 1263, 1186(ν_{asym}SO₃), 1098, 1073, 1029, 1002, 882, 852, 814, 692, 681, 559.

4.4.2. $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3)_2\text{N}_3\text{PO}]_2(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3)_2$ (**4**)

M.p. >200 °C. Anal. Found: C, 43.46; H, 7.04; N, 8.79%. Calc. for C₃₄H₆₈N₆O₈P₂S₂Sn: C, 43.70; H, 7.28 and N, 9.00%. IR (KBr, cm⁻¹): 1298, 1270(ν_{asym}SO₃), 1160, 1109, 1069, 1028, 985, 887, 846, 814, 748, 678.

4.4.3. $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3)_2\text{N}_3\text{PO}]_2(\text{OSO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)_2$ (**5**)

M.p. 97–99 °C. Anal. Found: C, 44.80; H, 7.12; N, 8.26%. Calc. for C₃₆H₇₂N₆O₈P₂S₂Sn: C, 44.92; H, 7.49 and N, 8.74. IR (KBr, cm⁻¹): 1300, 1187(ν_{asym}SO₃), 1097, 1031, 987, 813, 750, 708, 630, 561, 525, 479.

4.4.4. $[(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3)_2\text{N}_3\text{PO}]_2(\text{OSO}_2\text{C}_6\text{H}_2(\text{CH}_3)_3)_2$ (**6**)

M.p. 118–120 °C. Anal. Found: C, 46.04; H, 7.23; N, 8.34%. Calc. for C₃₈H₇₆N₆O₈P₂S₂Sn: C, 46.12; H, 7.69 and N, 8.50. IR (KBr, cm⁻¹): 1299, 1278, 1202(ν_{asym}SO₃), 1097, 1068, 1024, 986, 878, 850, 750, 676, 579.

4.5. X-ray data collection and structure analyses

Intensity data were collected with a Siemens P4 single crystal X-ray diffractometer using a graphite monochromatized molyb-

denum Kα (λ = 0.71069 Å). Table 3 shows the unit cell parameters and data measurement details. The lattice parameters and standard deviations were obtained by least squares fit to 40 reflections 20° < θ < 25°. The data were collected by the θ–2θ scan mode with a variable scan speed ranging from 2.0 to a maximum of 60° per minute. Three reflections were used to monitor the stability and orientation of the crystal and were measured after 97 reflections. Their intensities showed only statistical fluctuations during exposure time. The data were collected for Lorentz and polarization factors. The data were corrected for absorption correction by psi scan. The structure was solved by direct methods using SIR97 [31] and also refined on F² using SHELX-97 [32]. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding on their respective non-hydrogen atoms. The final difference map was featureless in all the cases. The mean plane calculations were performed using PARST [33].

The C4 atom in structure of **4** is disordered. During the refinement the disorder was resolved. The terminal methyl groups attached to N1, N2 and N3 atoms in the structure of **5** are disordered. Because of the disorder the platon check gives some A level errors in case of **4** and **5** because of the constraints used during refinement. However, attempts to resolve the disorder were not successful. All the methyl groups attached to these atoms were refined by fixing N–C distances at 1.470(3) Å.

Acknowledgement

Ajay Pal Singh Pannu thanks Department of Science and Technology and University Grants Commission, New Delhi for research fellowship.

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