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The synthesis, NMR (^1H, ^{13}C, ^{119}Sn) and IR spectral studies of some di- and tri-organotin(IV) sulfonates: X-ray crystal structure of $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2 \cdot 2H_2O]$

Ramesh Kapoor*, Anand Gupta, Pratibha Kapoor and Paloth Venugopalan

Center for Advanced Studies in Chemistry and Department of Chemistry, Panjab University, Chandigarh 160014, India

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A number of alkyltin(IV) paratoluenesulfonates, $R_nSn(OSO_2C_6H_4CH_3\text{-}4)_{4-n}$ ($n = 2$, 3; R = C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$), have been prepared and IR spectra and solution NMR (^1H, ^{13}C, ^{119}Sn) are reported for these compounds, including $(n\text{-}C_4H_9)_2Sn(OSO_2X)_2$ (X = CH_3 and CF_3), the NMR spectra of which have not been reported previously. From the chemical shift $\delta(^{119}Sn)$ and the coupling constants $^1J(^{13}C, ^{119}Sn)$ and $^2J(^1H, ^{119}Sn)$, the coordination of the tin atom and the geometry of its coordination sphere in solutions of these compounds is suggested. IR spectra of the compounds are very similar to that observed for the paratoluenesulfonate anion in its sodium salt. The studies indicate that diorganotin(IV) paratoluenesulfonates, and the previously reported compounds $(n\text{-}C_4H_9)_2Sn(OSO_2X)_2$ (X = CH_3 and CF_3), contain bridging SO_3X groups that yield polymeric structures with hexacoordination around tin and contain non-linear C–Sn–C bonds. In triorganotin(IV) sulfonates, pentacoordination for tin with a planar SnC_3 skeleton and bidentate bridging paratoluenesulfonate anionic groups are suggested by IR and NMR spectral studies. The X-ray structure shows $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2 \cdot 2H_2O]$ to be monomeric containing six-coordinate tin and crystallizes from methanol–chloroform in monoclinic space group *C2/c*. The Sn–O (paratoluenesulfonate) bond distance (2.26(2) Å) is indicative of a relatively high degree of ionic character in the metal–anion bonds. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: diorganotin(IV) sulfonates; triorganotin(IV) sulfonates; NMR; infrared; X-ray crystallography

INTRODUCTION

Our recent studies on the structural chemistry of diorganotin(IV) bis(alkyl- or aryl-sulfonates) have shown that the RSO_3^- groups exhibit a distinct preference to associate in a bidentate bridging mode, generating polymeric structures.[1,2] Organotin(IV) sulfonates may lead to the formation of a variety of supramolecular structures in organotin(IV) chemistry. However, the analogous diorganotin(IV) carboxylates[3] and diorganotin(IV) 1,1-dithiolates[4] show a definite preference to form monomeric chelating structures. The reasons for the adoption of different coordination polyhedra may be related to electronic, steric or crystal packing effects, or some combination of these factors. Until now, there have been only a few structural studies on organotin(IV) derivatives of alkyl or aryl sulfonic acids and, therefore, further structural investigations are required to establish the preferential coordination modes of the sulfonate anion and the nature of its bonding to the organotin(IV) moiety.

The synthesis of a number of alkyltin(IV) sulfonates, $R_nSn(OSO_2X)_{4-n}$ (n = 1 to 3; R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$; X = F, CF_3, CH_3, C_6H_5, 4-$CH_3C_6H_4$) has been reported in the literature.[5–14] On the basis of ^{119}Sn Mössbauer, vibrational data[5,6,9,10,12] and NMR (^1H, ^{13}C and ^{119}Sn),[14] polymeric structures containing six-coordinate and five-coordinate tin with bidentate bridging sulfonate anions were proposed for diorganotin(IV) and triorganotin(IV) sulfonates,[6,7,11,13,14] respectively. These proposals also find support from the

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*Correspondence to: Ramesh Kapoor, Center for Advanced Studies in Chemistry and Department of Chemistry, Panjab University, Chandigarh 160014, India.
E-mail: rkapoor@pu.ac.in

reported crystal structures of $Me_3Sn(OSO_2C_6H_5)\cdot H_2O$[11] and $Me_2Sn(OSO_2F)_2$.[12] In trimethyltin(IV) benzenesulfonate monohydrate the sulfonate anion is coordinated as a monodentate ligand, whereas the fluorosulfonate group is bonded in a bidentate bridging mode in $Me_2Sn(OSO_2F)_2$. Both these compounds exhibit fairly long Sn–O (sulfonate) bond distances, which were attributed to the existence of ionic structures. The X-ray crystal structures of the diorganotin(IV) sulfonates $[(n\text{-}C_4H_9)_2Sn\{\mu\text{-}OSO_2C_6H_2(CH_3)_3\}_2]_n$, $[(n\text{-}C_4H_9)_2Sn(\mu\text{-}OH)\{\mu\text{-}OSO_2C_6H_2(CH_3)_3\}]_n$[1] and $[(n\text{-}C_4H_9)_2Sn(X)(\mu\text{-}OSO_2CH_3)]_n$[2] (X = acac, bzbz, OH) have shown that the sulfonate anion acts as a bridging bidentate group, resulting in the formation of polymeric sheet structures. Continuing our work on the synthesis and the structural characterization of the organotin(IV) derivatives of sulfonic acids,[1] we have now synthesized and characterized organotin(IV) derivatives of paratoluenesulfonic acid. The organotin(IV) sulfonates are also of significant importance as biocides, because of their greater solubility in aqueous solution.[13] The ultimate aims of these studies are to contribute to the understanding of the coordination mode and of the structural arrangement of the sulfonate groups in organotin(IV) compounds.

In this paper, we report the synthesis, solution NMR (^1H, ^{13}C, ^{119}Sn) and IR spectra of $R_nSn(OSO_2C_6H_4CH_3\text{-}4)_{4-n}$ ($n = 2, 3$; $R = C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$). In addition, the NMR spectra of the previously known compounds $(n\text{-}C_4H_9)_2Sn(OSO_2X)_2$[6,9] ($X = CF_3$, CH_3,) and the X-ray crystal structure of $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2\cdot 2H_2O]$ has been investigated. Metal–oxygen (sulfonate) bond distances of structurally characterized compounds have been compared.

EXPERIMENTAL

Materials

Triethyltin(IV) chloride, diethyltin(IV) dichloride, tri-*n*-propyltin(IV) chloride, di-*n*-propyltin(IV) dichloride, tri-*n*-butyltin(IV) chloride, di-*n*-butyltin(IV) dichloride and di-*n*-butyltin(IV) oxide were obtained from Fluka and were used as supplied. Trifluoromethanesulfonic acid (Fluka AG), methanesulfonic acid (Fluka AG, 98%) and paratoluenesulfonic acid monohydrate (BDH) were purified before use. Silver paratoluenesulfonate was prepared by the reaction of Ag_2O (BDH) with an aqueous solution of the acid. The product was dried *in vacuo* at about 100 °C for 2–3 h before use. All reactions were carried out in anhydrous solvents under dry nitrogen atmosphere. Solvents were dried using standard methods (benzene, toluene and tetrahydrofuran (THF) were dried over and distilled from sodium–benzophenone ketyl under dry nitrogen).

Measurements

NMR spectra were measured using a Bruker AC-300 F spectrometer with tetramethylsilane (^1H), $CDCl_3$, dimethylsulfoxide-d_6 (DMSO-d_6) (^{13}C) and tetramethyltin (^{119}Sn) as standards. The compounds were practically insoluble in $CDCl_3$; as a result, their spectra were recorded in DMSO-d_6. IR spectra were recorded as KBr pellets on a Perkin–Elmer model 1430 ratio recording spectrometer. Elemental analyses (C, H) were performed on a Perkin–Elmer model 2400 CHN Elemental Analyzer and mass spectra were recorded using a VG Analytical 11-2505-70 SMS instrument at 70 eV at RSIC, Panjab University, Chandigarh. Tin was determined as SnO_2 and sulfur as $BaSO_4$ after fusing a known weight of the compound with a fusion mixture (K_2CO_3, KOH and KNO_3).[15]

Preparation of organotin(IV) sulfonates

Reactions of R_nSnCl_{4-n} ($n = 1, 2$) with $Ag^I(OSO_2C_6H_4CH_3\text{-}4)$ in THF in mole ratios of 1 : 1 and 1 : 2 at room temperature and on stirring for 8–10 h gave the desired products in almost quantitative yield after removal of the precipitated silver chloride. $(n\text{-}C_4H_9)_2Sn(OSO_2X)_2$ ($X = CF_3$, CH_3) were prepared by refluxing the suspension of di-*n*-butyltin(IV) oxide with the appropriate acid in 1 : 2 mole ratio in benzene in Dean and Stark apparatus. The clear solution in each reaction was evacuated to obtain a white crystalline solid. Di-*n*-butyltin(IV) bis(*p*-toluenesulfonate) dihydrate was prepared by a previously reported method.[5,8] The analytical results of the products are listed in Table 1.

The following tin-containing fragments were recorded in the mass spectra. For $Me_3Sn(OSO_2C_6H_4CH_3\text{-}4)$: *m/z* 321 $[M-Me]^+$ (100); 291 $[M-Me_3]^+$ (12.9); 241 $[M-Me-SO_3]^+$ (83); 211 $[M-Me_3-SO_3]^+$ (19); 165 $[M-OSO_2C_6H_4CH_3]^+$ (12); 135 $[M-Me_3-OSO_2C_6H_4CH_3]^+$ (11). For $Et_3Sn(OSO_2C_6H_4CH_3\text{-}4)$: *m/z* 349 $[M-Et]^+$ (100); 291 $[M-Et_3]^+$ (21); 269 $[M-Et-SO_3]^+$ (80); 240 $[M-Et_2-SO_3]^+$ (20); 211 $[M-Et_3-SO_3]^+$ (18); 149 $[M-Et_2-OSO_2C_6H_4CH_3]^+$ (50); 120 $[M-Et_3-OSO_2C_6H_4CH_3]^+$ (30). For $(n\text{-}Pr)_3Sn(OSO_2C_6H_4CH_3\text{-}4)$: *m/z* 377 $[M-(n\text{-}Pr)]^+$ (100); 297 $[M-(n\text{-}Pr)-SO_3]^+$ (36); 291 $[M-(n\text{-}Pr)_3]^+$ (30); 254 $[M-(n\text{-}Pr)_2\text{-}SO_3]^+$ (18).

Structure determination and refinement

Crystallization of $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2]$ (**3**) by slow evaporation of its saturated methanol–chloroform solution yielded good single crystals. Intensity data were collected on a Siemens P4 single-crystal diffractometer equipped with a molybdenum sealed tube ($\lambda = 0.710\,73$ Å) and a highly oriented graphite monochromator using crystals of dimensions $0.31 \times 0.26 \times 0.20\ mm^{-3}$ for $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2\cdot 2H_2O]$ (**4**) mounted in Lindemann glass capillaries. The lattice parameters and standard deviations were obtained by least-squares fit to 40 reflections ($9.8 < 2\theta < 32.0°$). Their intensities showed only statistical fluctuations during 51.04 h X-ray response time.

The structure was solved by direct methods using SHELX-97[16] and also refined on F^2 using the same program. All the non-hydrogen atoms were refined anisotorpically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their

Table 1. Physical and analytical data for di- and tri-organotin(IV) sulphonates

			Analysis [Found (Calc.)]			
Compound no.	Compounds	M.p. (°C)	C	H	S	Sn
1	$C_{18}H_{24}SnS_2O_6$		42.17	5.15	12.0	22.8
			(41.64)	(4.63)	(12.3)	(22.9)
2	$C_{20}H_{28}SnS_2O_6$		43.24	5.62	11.5	21.6
			(43.90)	(5.12)	(11.7)	(21.7)
3	$C_{22}H_{32}SnS_2O_6$		46.25	5.81	10.8	20.0
			(45.94)	(5.57)	(11.1)	(20.6)
4	$C_{22}H_{36}SnS_2O_7$	>290	43.18	5.62	10.4	19.3
			(43.23)	(5.59)	(10.5)	(19.4)
5	$C_{10}H_{18}SnS_2O_6F_6$	100–102	22.56	3.52	12.2	22.4
			(22.61)	(3.39)	(12.0)	(22.3)
6	$C_{10}H_{24}SnS_2O_6$	284–287	28.41	5.72	15.1	28.1
			(28.38)	(5.68)	(15.1)	(28.0)
7	$C_{10}H_{16}SnSO_3$	>230	36.22	4.87	8.8	35.0
			(35.85)	(4.78)	(9.5)	(35.4)
8	$C_{13}H_{22}SnSO_3$	170(dec.)	42.17	5.51	8.6	30.7
			(41.41)	(5.84)	(8.5)	(31.5)
9	$C_{16}H_{28}SnSO_3$	64	44.89	4.97	7.8	27.9
			(45.85)	(6.67)	(7.9)	(28.3)
10	$C_{19}H_{34}SnSO_3$	82	49.86	7.53	6.5	25.6
			(49.49)	(7.38)	(6.9)	(25.7)

respective non-hydrogen atoms. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ with $a = 0.056$ was used. The refinement converged to a final R value of 0.036 ($wR_2 = 0.085$) for 2050 reflections [$I > 2\sigma(I)$]. The final difference map was featureless. All other relevant information about the data collection and the refinement are presented in Table 2.

RESULTS AND DISCUSSION

Synthesis

Diorganotin(IV) and triorganotin(IV) paratoluenesulfonates (**1**–**10**) are obtained in good yield by a metathesis reaction between the appropriate diorganotin dichloride and triorganotin chloride and $Ag^I(OSO_2C_6H_4CH_3\text{-}4)$ in 1 : 2 and 1 : 1 mole ratios, respectively. Preparation of di-*n*-butyltin(IV) bis(*p*-toluenesulfonate) (**3**), was also attempted by another method,[5] but, in contrast to this report, a dihydrate (**4**) crystallized out of the methanol solution in the form of colourless needle-shaped crystals. Compounds **1**–**10** are white, microcrystalline, moderately hygroscopic solids. The compounds are practically insoluble in $CHCl_3$, CH_2Cl_2 and toluene, but they dissolve in polar solvents such as MeOH, DMSO, etc.

Dialkyltin(IV) paratoluenesulfonates (1–6)

Pertinent vibrational bands for **1** to **6**, along with that of Na^+ $(OSO_2C_6H_4CH_3\text{-}4)^-$, are given in Table 3. Their spectra in the range 1400–400 cm^{-1} exhibit very few unusually broad bands and are identical to the spectrum of paratoluenesulfonate anion in Na^+ $(-OSO_2C_6H_4CH_3\text{-}4)^-$. There is no evidence of splitting of the degenerate modes that may be expected from a further reduction in the C_s symmetry of the paratoluenesulfonate anion on coordination in a bidentate bridging mode. Either the splitting of these modes is masked due to the close overlap of the split bands, resulting in broad peaks, or the local symmetry (C_s) of the paratoluenesulfonate anion is not perturbed in these compounds. We suggest that the paratoluenesulfonate anions are either very weakly coordinated to the diorganotin(IV) moiety or are present as free ions.[†] The interaction between tin and the sulfonato ligand is weak; this was confirmed by the formation of ionic species, as suggested by conductivity results. The ionic dissociation of **4, 5** and **6** in methanol solution is evident from the large conductivity values,[‡] 111 Ω cm^2 mol^{-1}, 181 Ω cm^2 mol^{-1} and 158 Ω^{-1} cm^2 mol^{-1} respectively. Qualitatively, the IR spectra of **3** and **4** look quite similar, except for the fact that two additional bands at 3420 and 1600 cm^{-1}, attributed to coordinated water, are

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[†] The ionic nature of the tin–sulfonate bond has been suggested by the crystal structure of a number of sulfonate complexes (see Table 5). The distance between tin and the oxygen of the sulfonato ligand is significantly longer than the sum of the covalent radii of these atoms, i.e. 2.13 Å, but is shorter than the sum of their van der Waals radii of 3.7 Å.[17]

[‡] For an example of an A_2^+ B_2^- electrolyte, the molar conductivities of $Cu(OSO_2X)_2$ salts are 84.0 ($X = C_6H_4CH_3\text{-}4'$), 79.2 ($X = CH_3$), and 117.0 Ω^{-1} cm^2 mol^{-1} ($X = CF_3$) (10 mmol^{-1} in CH_3OH).

Table 2. Crystal data, data collection and structure refinement parameters for compound **4**

Empirical formula	$C_{22}H_{36}O_8S_2Sn$
Formula weight	611.32
Crystal system, space group	Monoclinic, $C2/c$
Unit cell dimensions	
a (Å)	31.768(7)
b (Å)	9.564(2)
c (Å)	9.265(2)
β (°)	93.8(1)
Volume (Å^3)	2808.8(10)
Z, calculated density (Mg m^{-3})	4, 1.446
Absorption coefficient (mm^{-1})	1.098
$F(000)$	1256
Max. and min. transmission	0.925, 0.780
θ range for data collection (°)	2.6 to 24.5
Reflections collected	2381
Independent reflection	2336 ($R_{\text{int}} = 0.035$)
Data/restraints/parameters	2336/0/151
Goodness-of-fit on F^2	1.105
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.056P)^2]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$
Data to parameter ratio	15.47 : 1
Final R indices, 2050 reflections [$I > 2\sigma(I)$]	$R_1 = 0.036$, $wR_2 = 0.085$
R indices (all data)	$R_1 = 0.044$, $wR_2 = 0.089$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.77 and −1.61
CCDC No.	190 224

observed in **4**. Interestingly, this was quite unexpected, as **4** contained paratoluenesulfonate groups coordinated in a monodentate mode (see crystal structure). Probably, the local symmetry of the anion is the same in **3** and **4**.

^{1}H, ^{13}C and ^{119}Sn NMR data for dialkyltin(IV) paratoluenesulfonates (**1**–**4**) and the previously known compounds $[(n\text{-}C_4H_9)_2Sn(OSO_2CF_3)_2]$[9] (**5**) and $[(n\text{-}C_4H_9)_2Sn(OSO_2CH_3)_2]$[6] (**6**), are given in Table 4. The $\delta(^{119}Sn)$ values are well within the range −210 to −400 ppm diagnostic of six-coordinate tin.[18,19] The $\delta(^{119}Sn)$ value for **4** shows significant upfield movement in comparison with the anhydrous salt **3**. The upfield movement in **4** may be attributed to a greater shielding of tin due to the presence of basic water molecules. The NMR results for **5** and **6** are consistent with the structure previously proposed on the basis of Mossbauer data.[9] As expected the $\delta(^{119}Sn)$ value for triflate **5** is observed at a lower field than the methanesulfonate derivative **6**. The C–Sn–C bond angles (θ) in these compounds in solution state in DMSO-d_6 have been deduced from $^1J(^{119}Sn, ^{13}C)$ coupling constant values (Table 4) using the equation reported by Holecek and Lycka.[19] The θ values ranging between 141 to 165° and the chemical shifts $\delta(^{119}Sn)$ are indicative of a distorted octahedral geometry. Additional coordination of a solvent molecule (DMSO) to the tin centre is suggested.

We thus envisage that anhydrous dialkyltin(IV) sulfonates possess polymeric structures wherein tin acquires hexacoordination with alkyl groups in nearly trans-octahedral positions and bidentate bridging anionic sulfonate groups coordinating through oxygen atoms. It appears that, on dissolution in donor solvents (DMSO), the polymeric structure of these compounds breaks down to give molecular species in which the solvent molecule may be coordinated to tin. Numerous attempts in our laboratory to grow single crystals of the anhydrous compounds suitable for a structural investigation have been unsuccessful.

Trialkyltin(IV) paratoluenesulfonates (7–10)

Pertinent vibrational bands are listed in Table 3. Surprisingly, in comparison with the IR spectra of $Me_3Sn(OSO_2X)$ (X = $-CH_3$, $-CF_3$),[7] $R_3Sn(OSO_2C_6H_4CH_3\text{-}4)$ (R = Me, Et, n-Pr, and n-Bu) compounds show only a few broad bands and their IR spectra apparently appear to be identical to the spectrum of paratoluenesulfonate anion. We envisage the presence of a paratoluenesulfonate group weakly coordinated to the R_3Sn moiety.

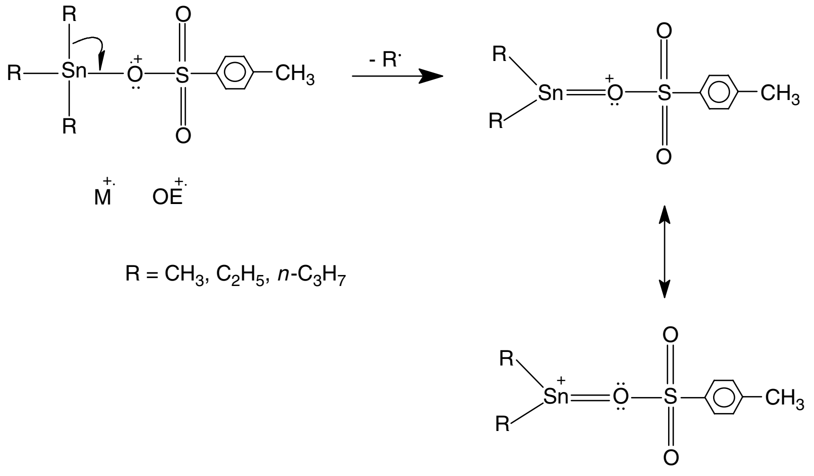
^{1}H, ^{13}C and ^{119}Sn NMR parameters for compounds **8** to **10** in DMSO-d_6 solutions are summarized in Table 4. The observed range of $\delta(^{119}Sn)$ for these compounds is in good agreement with five-coordinate triorganotin(IV) complexes.[20,21] Substitution of CH_3 by C_2H_5 results in the $\delta(^{119}Sn)$ value moving upfield. Since no structural changes are expected to occur, this upward shift can only be attributed to an increase in the electron-releasing power of C_2H_5 over that of CH_3. Only a small upfield shift is observed on substituting the C_2H_5 group by an n-C_3H_7 or n-C_4H_9 group. The chemical shift values $\delta(^{13}C)$ and the coupling constants $^nJ(^{119}Sn-^{13}C)$ for **1**–**4** are also in the range suggested for five-coordinate complexes ($^1J = 441$–509 and $^3J = 73$–80 Hz).[20,21] The polymeric structure appears to break down into individual molecules when these compounds are dissolved in DMSO. The retention of coordination number five by tin (see NMR results) suggests participation of DMSO in the form of a donor–acceptor complex of the type $R_3Sn(OSO_2C_6H_4CH_3\text{-}4)\cdot OS(CH_3)_2$ with paratoluenesulfonate anion coordinating as a monodentate ligand.

The fragmentation patterns of compounds **7** to **9** do not show the molecular ions (M^+). Each compound, however, shows the loss of an R group (R = CH_3, C_2H_5, n-C_3H_7) due to the stereoelectronic factors from the molecular ion to form resonance-stabilized ions at m/z 321, 349 and 377 for **7**, **8** and **9** respectively (Scheme 1). This is consistent with the fragmentation patterns observed for some other organotin(IV) compounds[22] and the loss is attributed to the non-existence of the tin(V) oxidation state.[23] The low abundance of tin fragment at m/z 120 suggests that the species representing the base peaks are very stable.

Table 3. IR data (cm^{-1}) of anhydrous di- and tri-organotin(IV) sulfonates

	Assignment								
Compound	ν(SO$_2$) asym. stretch	ν(SO$_2$) sym. stretch	ν(S–O) stretch	ν(S–X)	ν(SO$_2$) bend	ν(SO$_2$) rock	ν(S–O) wag	δ CH$_3$–C$_6$H$_4$ torsion	Internal vibration
Na$^+$ (OSO$_2$C$_6$H$_4$CH$_3$-4)$^{-}$ [a]	1240s,br	1190s	1128s	680s	568s	500s	395s	—	815s
1	1240s,br	1140s	1105m	680s	568s	490w	300m	1035s 1005s	—
2	1265s,br	1155s	1125m	685s	565s	495w	310m	1040s 1010s	815s
3	1260s,br	1125s	1098m 1074s	680s	560s	490w	390m	1028m 1003m	815s
5	1265s,br	1175s	1030s	640s	570s	520w	—	—	790m 865m
6	1230s,br	1184s	1090m	680m	552s	525w	—	—	874s
7	1240s,br	1120s	1040m 1015m	688s	565s	500w	400m	—	820s 790m
8	1290s,br 1215m	1120s	1030m 1005m	680s	565s	495w	395s 358m	—	815m
9	1260s,br 1220m	1118s	1030m 1005m	680s	560s	480w	396m 365w	—	810s
10	1270s,br 1215w	1120s	1030m 1005m	680s	565s	495w	395m 330m	880m	820s

[a] Based on C_s symmetry for the –OSO$_2$C$_6$H$_4$CH$_3$-4$^-$ moiety.



Scheme 1.

Solid-state structural features of [(n-C$_4$H$_9$)$_2$Sn(OSO$_2$C$_6$H$_4$CH$_3$-4)$_2$·2H$_2$O (4)]

A perspective view of the structure of **4** with the atom numbering scheme is given in Fig. 1, and selected bond lengths and angles are given in Table 5. Examination of bond lengths and angles around tin reveals that it adopts a nearly perfect octahedral configuration with trans disposition of atoms with bond angles greater than 175(2)° (Table 5). It may be mentioned that, in a donor solvent like DMSO, the C–Sn–C angle is reduced to 165° [calculated using $^1J(^{119}$Sn, ^{13}C) value cited earlier; Table 3], strongly suggesting a different structural arrangement in which DMSO has approached the metal atom in the coordination polyhedra. The molecule resides on a crystallographic two fold axis passing through tin and water molecules. The Sn–O (paratoluenesulfonate) bond length of 2.26(2) Å is significantly longer than the normal covalent Sn–O (1.9–2.1 Å) bond length[17] and reflects some degree of ionic character. This bond distance is comparable with Sn–O (sulfonate) bond distances of (2.25–2.65 Å)[1,2,11] observed in other organotin(IV) sulfonates. The Sn–O (H$_2$O)

Table 4. NMR (^{1}H, ^{13}C, ^{119}Sn) data for di- and tri-organotin(IV) sulfonates in DMSO-d_6 solutions

Compound	δ^{119}Sn (ppm)	^{1}H NMR δ (ppm)		^{13}C NMR δ (ppm)		$\vert {}^nJ \vert$ (Hz)	θ(°)
		Sn–R	Ligand	Sn–R	Ligand		
1	−285.0	1.2–1.3(m)	2.3(s)	29.0 C(1)	20.8, 125.5, 128.1, 137.8, 139.2	—	—
			7.1–7.5(m)	10.8 C(2)			
2	−255.0			36.5 C(1)	20.7, 125.5, 128.2, 137.6, 139.1	—	—
		0.8–1.2(m)	2.4(s)	18.5 C(2)			
			7.1–7.6(m)	17.7 C(3)			
3	−258.0	0.9(t)	2.3(s)	36.7 C(1)	21.3, 126.1, 128.6, 139.9, 142.1	664.0 (^{1}J)	141.2
		1.3–1.4(m)	7.1–7.5(m)	27.5 C(2)		40.0 (^{2}J)	
		1.6–1.7(m)		26.1 C(3)		115.0 (^{3}J)	
				13.7 C(4)			
4	−376.4	0.8(t)	2.4(s)	34.0 C(1)	21.2, 125.8, 128.6, 140.3, 141.5	902.0 (^{1}J)	165.1
		1.2–1.3(m)	7.2–7.7(m)	26.8 C(2)		44.0 (^{2}J)	
		1.5–1.7(m)		25.9 C(3)		169.0 (^{3}J)	
				13.6 C(4)			
5	−353.4	0.9(t)		34.1 C(1)	114.7, 119.0, 123.2, 127.5(q)	859.1 (^{1}J)	160.8
		1.3–1.4(m)	—	27.9 C(2)		46.6 (^{2}J)	
		1.6–1.8(m)		26.3 C(3)		161.4 (^{3}J)	
				14.0 C(4)			
6	−380.4	0.9(t)	2.8(s)	34.4 C(1)	39.5	895.5 (^{1}J)	164.5
		1.3–1.4(m)		26.9 C(2)		46.6 (^{2}J)	
		1.7–1.8(m)		25.8 C(3)		166.0 (^{3}J)	
				13.6 C(4)			
7	23.3	0.6(s)	2.3(s)	0.8	20.7, 122.4, 128.2, 138.5, 144.1	512.3	121.5
			7.1–7.6(m)				
8	11.8	1.0–1.7(m)	2.3(s)	11.8 C(1)	21.1, 125.8, 128.8, 139.3, 143.9	—	—
			7.1–7.6(m)	10.2 C(2)			
9	5.0	1.0(t)	2.3(s)	22.4 C(1)	20.8, 125.5, 128.3, 139.3, 143.9	—	—
		1.3–1.8(m)	7.1–7.6(m)	18.8 C(2)			
				18.3 C(3)			
10	4.7	1.0(t)	2.3(s)	19.6 C(1)	20.8, 125.5, 128.3, 139.0, 143.5	465.7 (^{1}J)	—
		1.3–1.8(m)	7.1–7.6(m)	27.4 C(2)		27.42 (^{2}J)	
				26.3 C(3)		76.46 (^{3}J)	
				23.4 C(4)			

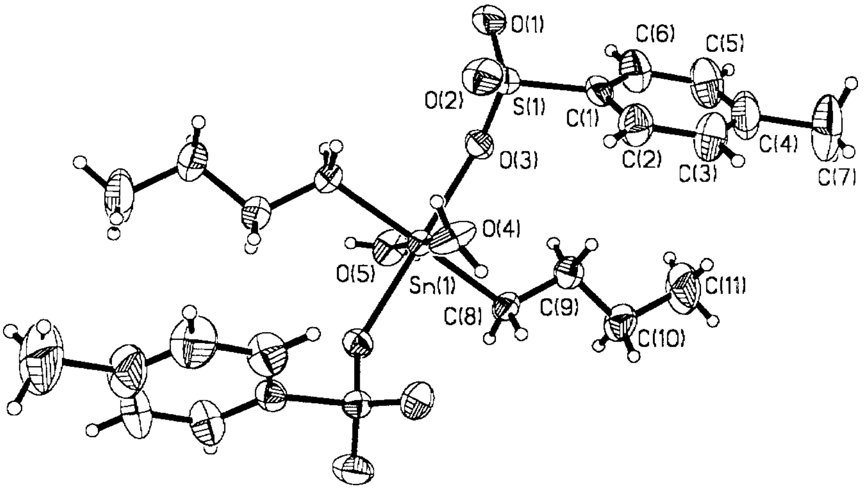


Figure 1. Molecular structure and crystallographic numbering scheme employed for $(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2 \cdot 2\ H_2O$ (**4**).

Table 5. Bond distances and bond angles in compound **4**[a]

Bond distances (Å)		Bond angles (°)	
Sn(1)–O(4)	2.21(4)	C(8)$^{\#1}$–Sn(1)–C(8)	175(2)
Sn(1)–O(3)	2.26(2)	C(8)–Sn(1)–O(4)	93(11)
Sn(1)–O(5)	2.29(4)	C(8)–Sn(1)–O(3)	93(12)
Sn(1)–C(8)	2.11(3)	O(3)–Sn(1)–O(3)$^{\#1}$	178(12)
C(1)–C(2)	1.36(6)	O(4)–Sn(1)–O(3)$^{\#1}$	91(6)
C(2)–C(3)	1.38(7)	C(8)$^{\#1}$–Sn(1)–O(5)	87(11)
C(4)–C(5)	1.39(9)	O(4)–Sn(1)–O(5)	180
C(5)–C(6)	1.38(7)	O(3)$^{\#1}$–Sn(1)–O(5)	89(6)
C(9)–C(10)	1.53(6)	O(2)–S(1)–O(3)	111(17)
C(10)–C(11)	1.50(7)	O(2)–S(1)–C(1)	107(18)
C(8)–C(9)	1.50(5)	O(3)–S(1)–C(1)	105(16)
C(1)–C(6)	1.38(6)	C(2)–C(1)–C(6)	121(4)
C(3)–C(4)	1.35(9)	C(6)–C(1)–S(1)	120(3)
C(4)–C(7)	1.53(7)	C(4)–C(3)–C(2)	121(5)
S(1)–O(1)	1.44(3)	C(3)–C(4)–C(7)	121(7)
S(1)–O(2)	1.44(3)	C(6)–C(5)–C(4)	120(5)
S(1)–O(3)	1.48(3)	C(9)–C(8)–Sn(1)	119(3)
S(1)–C(1)	1.79(4)	C(11)–C(10)–C(9)	112(5)
		C(8)$^{\#1}$–Sn(1)–O(3)	87(12)
		O(4)–Sn(1)–O(3)	91(6)
		O(2)–S(1)–O(1)	115(2)
		O(1)–S(1)–O(3)	111(17)
		O(1)–S(1)–C(1)	107(18)
		S(1)–O(3)–Sn(1)	137(15)
		C(2)–C(1)–S(1)	120(3)
		C(1)–C(2)–C(3)	120(5)
		C(3)–C(4)–C(5)	119(5)
		C(5)–C(4)–C(7)	120(7)
		C(1)–C(6)–C(5)	119(5)
		C(8)–C(9)–C(10)	114(4)

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

distances [Sn(1)–O(4) = 2.21(4) and Sn(1)–O(5) = 2.29(4) Å] are normal and closer to the Sn–O (H_2O) distance of 2.30(1) Å in $Me_3Sn(OSO_2Ph){\cdot}H_2O$.[11] The molecular geometry of the paratoluenesulfonato group is normal in terms of bond lengths, angles and planarity.[1,11,24]

The molecules of $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2{\cdot}2H_2O]$ (**4**) occupy the two fold axis of the $C2/c$ space group, resulting in an interesting network of hydrogen bonds. It is pertinent that both the oxygen atoms of water molecules, along with the tin atom, occupy the special positions and, therefore, are involved in degenerate hydrogen bonds spanning to the opposite side of the O(5)–Sn(1)–O(4) axis (see the mid region of Fig. 2 with named atoms). In such an association, four molecules of the complex form macromolecular 24-membered rings that share this axis (one such ring is shown in open bonds in Fig. 2). All the four hydrogen atoms of the coordinated water molecules are involved in hydrogen bonding with the oxygen of the sulfonate moiety, but their associations are different. The two symmetry-equivalent hydrogen atoms, H(4A) and H(4AA), bonded to the water molecule at the bottom form an indefinite corrugated sheet [H(4A)···O(2) = 1.83(3) Å, O(4)–H(4A)···O(2) = 166(1)°] parallel to the *bc* plane (see bottom part of Fig. 2). The role of the hydrogen atoms on the other water molecule [H(5B) and H(5BA)] is to stabilize these sheets through interlinking them [H(5B)···O(1) = 1.91(3) Å, O(5)–H(5B)···O(1) = 176(1)°] almost perpendicular to these sheets. Interestingly, during this network stabilization, a 12-membered ring is generated within the macrocyclic 24-membered outer ring (see middle part of the 24-membered ring shown in open bonds). The inner 12-membered ring has two water molecules as hydrogen bond donors and four sulfonate oxygen atoms as acceptors, thus taking the form $R^4_2(12)$. Interestingly, the outer macrocycle $R^4_4(24)$ is stabilized by five other rings, the central 12-membered ring and the four surrounding 12-membered rings. Thus, an infinite two-dimensional layer of corrugated ribbons interconnected through a network of hydrogen bonds brings overall stability to the crystal lattice. The hydrocarbon regions of the molecule (i.e. *p*-tolyl moiety and *n*-butyl groups) are placed as inter-layer space-filling moieties, which brings

Table 6. Sn–O bond distances observed in different organotin(IV) sulfonates

Compound	Sn–O bond length (Å)	Ref.
$(CH_3)_3SnOSO_2Ph{\cdot}H_2O$	2.37(1)	11
$(CH_3)_2Sn(OSO_2F)_2$	2.24(1)	12
$(n\text{-}C_4H_9)_2Sn\{\mu\text{-}OSO_2C_6H_2(CH_3)_3\}_2$	2.31(3), 2.20(3)	1
$(n\text{-}C_4H_9)_2Sn\{(\mu\text{-}OH)\mu\text{-}OSO_2C_6H_2(CH_3)_3\}$	2.40(2), 2.78(2)	1
$(n\text{-}C_4H_9)_2Sn\{(acac)(OSO_2CH_3)\}$	2.43(4), 2.38(5)	2
$(n\text{-}C_4H_9)_2Sn\{(bzbz)(OSO_2CH_3)\}$	2.38(7), 2.46(8)	2
	2.25(7), 2.65(7)	
$(n\text{-}C_4H_9)_2Sn\{(OH)(OSO_2CF_3)H_2O\}_2$	2.62(4)	24
$(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2{\cdot}2\ H_2O$	2.26(2)	Present work
$(n\text{-}C_4H_9)_2Sn(OSO_2CH_3)_2$	2.27(11), 2.25(10)	26

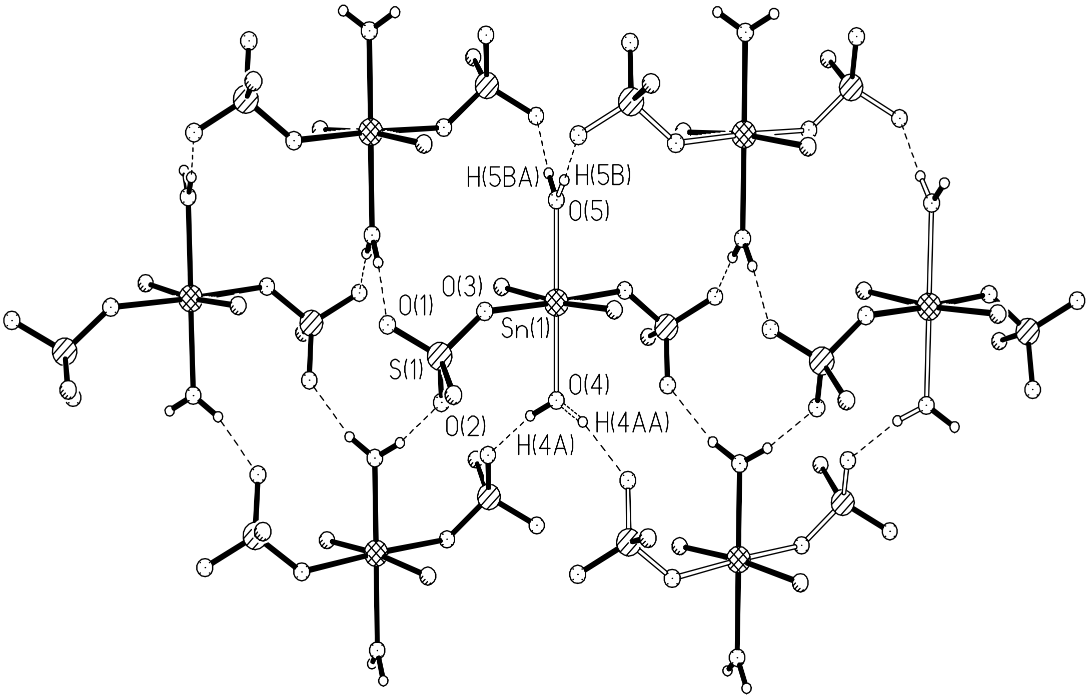


Figure 2. Part of corrugated sheets of **4** formed parallel to the *bc* plane showing 24-membered rings (one such ring is shown in open bond type). Only the octahedral surroundings of tin and sulfonate moieties are shown for clarity.

an additional overall stabilization to the three-dimensional lattice. The intermolecular O···O contacts lie between 2.67(3) and 2.76(4) Å, which are in the same range for similar interactions in $Me_3Sn(ONO_2)\cdot H_2O$ (2.72 Å).[25]

The interactions between tin and the various sulfonate groups (Table 6) are very weak, since the distance between tin and the sulfonato oxygen is always observed to be longer than the normal Sn–O covalent bond distance of 2.13 Å[17] (the sum of the covalent radii of tin and oxygen). Intramolecular Sn···O distances in the range of 2.20(3)–2.78(2) Å (Table 6) are shorter than the sum of van der Waals radii (3.70 Å)[17] and are in the range that has been confidently reported to indicate Sn–O bonding.[4,27–30] We feel that the Sn–O (sulfonato) bonds reflect a relatively high degree of ionic character, consistent with the fact that these anions are weakly basic, being anions of strong acids.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis of $[(n\text{-}C_4H_9)_2Sn(OSO_2C_6H_4CH_3\text{-}4)_2\cdot 2H_2O$, (**4.**) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 190 224.

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