



## THE SYNTHESIS AND IR AND NMR ( $^1\text{H}$ , $^{13}\text{C}$ AND $^{119}\text{Sn}$ ) SPECTRAL STUDIES OF SOME METHYLTIN(IV) SULPHONATES

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**Abstract**—Some methyltin(IV) sulphonates,  $\text{Me}_n\text{Sn}(\text{OSO}_2\text{X})_{4-n}$  ( $n = 1-3$  and  $\text{X} = 4\text{-tolyl}$  and  $2\text{-naphthyl}$ ) have been prepared. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra of these compounds and the previously reported compounds,  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$  ( $\text{X} = \text{CF}_3$ ,  $\text{CH}_3$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ) and  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{CH}_3)_2$ , in coordinating and non-coordinating solvents have been studied. From the chemical shifts  $\delta(^{119}\text{Sn})$  and the coupling constants  $^1J(^{13}\text{C}, ^{119}\text{Sn})$  and  $^2J(^1\text{H}, ^{119}\text{Sn})$ , coordination number of the tin atom and the geometry of its coordination sphere have been suggested. These observations have been complemented by IR spectroscopy. Synthesis of the ternary compounds,  $\text{MeSnCl}(\text{OSO}_2\text{X})_2$  ( $\text{X} = \text{CH}_3$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ), by reaction between  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$  and  $\text{Me}_2\text{SnCl}_2$  and subsequent cleavage of the tin-carbon bond is also discussed.

A number of trimethyltin(IV) sulphonates,  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$  ( $\text{X} = \text{CF}_3$ ,  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ) and dimethyltin(IV) bis(sulphonates),  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{X})_2$  ( $\text{X} = \text{F}$ ,  $\text{CF}_3$ ,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ), have been synthesized by acid solvolysis,<sup>1-4</sup> by metathetical reaction using the silver salt method,<sup>5,6</sup> by azeotropic dehydration of the organotin(IV) oxide and the arylsulphonic acid in benzene,<sup>7</sup> and by ligand redistribution reactions of methyltin(IV) chlorides and sulphonates.<sup>2</sup> Detailed Mössbauer and IR spectral studies by Aubke *et al.*<sup>3</sup> and Harrison *et al.*<sup>7</sup> have indicated that the tin atom in trimethyltin(IV) sulphonates achieves penta-coordination with bridging  $-\text{OSO}_2\text{X}$  groups at the axial sites giving polymeric compounds. The crystal structure of  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_5) \cdot \text{H}_2\text{O}$  has revealed the presence of planar  $\text{SnC}_3$  units, a unidentate benzenesulphonate group and a water molecule occupying the two apical positions.<sup>7</sup> In dimethyltin(IV) bis(sulphonates), the tin atom is hexacoordinated with two methyl groups at *trans*-octahedral positions and  $-\text{OSO}_2\text{X}$  groups acting as bidentate ligands,<sup>4</sup> with support from the reported crystal structure of  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{F})_2$ .<sup>8</sup>

In the present work,  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$ ,  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{X})_2$  ( $\text{X} = 4\text{-tolyl}$  and  $2\text{-naphthyl}$ ) and  $\text{MeSnCl}(\text{OSO}_2\text{X})_2$  ( $\text{X} = \text{methyl}$  and  $4\text{-tolyl}$ ) have been synthesized and characterized by multinuclear NMR and IR spectroscopy. In addition, NMR spectra of the known  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$  ( $\text{X} = \text{methyl}$  and trifluoromethyl) have been discussed. Caesium salts of the anions  $[\text{Me}_2\text{Sn}(\text{OSO}_2\text{X})_4]^{2-}$  ( $\text{X} = \text{methyl}$  and  $4\text{-tolyl}$ ) have been isolated.

### EXPERIMENTAL

#### Chemicals

Tetramethyltin,<sup>9</sup> trimethyltin chloride<sup>10</sup> and dimethyltin dichloride<sup>11</sup> were prepared by literature methods. Trifluoromethanesulphonic acid (Fluka AG), methanesulphonic acid (Fluka AG, 98%) and *para*-toluenesulphonic acid monohydrate (BDH) were purified before use. 2-Naphthalenesulphonic acid monohydrate (m.p.  $124^\circ\text{C}$ ) was prepared by sulphonation of naphthalene and drying of the product over anhydrous  $\text{CaCl}_2$ . Silver sulphonates were prepared by the reaction of  $\text{Ag}_2\text{O}$  (BDH) with an aqueous solution of the appropriate acid. Reactions of  $\text{R}_{4-n}\text{SnCl}_n$  ( $n = 1, 2$ ) with  $\text{Ag}^+(\text{SO}_3\text{X})^-$

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(X = CF<sub>3</sub>, CH<sub>3</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 2-C<sub>10</sub>H<sub>7</sub>) in ethanol or THF at room temperature on stirring gave products in almost quantitative yield. Ternary derivatives, MeSnCl(OSO<sub>2</sub>X)<sub>2</sub> (X = CH<sub>3</sub> and 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) were prepared by stirring the appropriate Me<sub>3</sub>Sn(OSO<sub>2</sub>X) compound with Me<sub>2</sub>SnCl<sub>2</sub> in benzene at room temperature for 24 h. All operations were handled in a glove bag filled with dry N<sub>2</sub> gas.

Carbon and hydrogen analyses were carried out on a Carlo Erba Strumentazione Elemental Analyzer Model 1106. Tin was determined as SnO<sub>2</sub> and sulphur as BaSO<sub>4</sub> after fusing a known weight of the compound with a fusion mixture. NMR spectra were recorded on Bruker AC-300F. Tetramethylsilane (<sup>1</sup>H, 0 ppm), CDCl<sub>3</sub> (<sup>13</sup>C, 77.1 ppm), DMSO-*d*<sub>6</sub> (<sup>13</sup>C, 39.5 ppm), and tetramethyltin (<sup>119</sup>Sn, 0 ppm) served as reference materials. IR spectra were recorded as mulls in nujol and hexachlorobutadiene in KBr/CsI plates on a Perkin-Elmer 1430 ratio recording spectrophotometer and frequencies corrected using polyethylene film. Raman spectra were recorded using a Ramalab spectrometer and a Spectra Physics 1642 W argon-ion laser (5145 Å) with samples sealed in glass melting point capillaries.

## RESULTS AND DISCUSSION

The analytical results along with the melting or decomposition points are listed in Table 1. These compounds are white, microcrystalline solids, moderately hygroscopic, showing melting/decomposition points well above 200°C. The compounds have limited solubility in CHCl<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub>, but dissolve in stronger coordinating solvents such as DMSO, DMF etc. Molar conductances of their millimolar solutions in DMSO are much below the range generally expected for 1:1 electrolytes.<sup>12</sup>

### *Trimethyltin(IV) sulphonates*

The <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR parameters for compounds 1–4 in solutions of non-coordinating (CDCl<sub>3</sub>) and coordinating (DMSO-*d*<sub>6</sub>) solvents are summarized in Table 2. The observed range of δ(<sup>119</sup>Sn) for these compounds is in good agreement with those for other trimethyltin(IV) compounds with other monodentate bases.<sup>13</sup> The <sup>119</sup>Sn chemical shifts for the CDCl<sub>3</sub> solutions have values ranging from 75.5 to 165.3 ppm, which are typical of a quasitetrahedral arrangement of trimethyltin(IV) compounds with a four-coordinate tin atom.<sup>14</sup> The δ(<sup>119</sup>Sn) values for compounds 1–4 in coordinating solvent (DMSO-*d*<sub>6</sub>) show a large upfield shift, which is characteristic of the formation of a five-coor-

dinate complex with a donor molecule. We have been able to actually isolate the donor-acceptor complexes Me<sub>3</sub>Sn(OSO<sub>2</sub>CH<sub>3</sub>)·DMSO (5) and Me<sub>3</sub>Sn(OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)·DMSO (6) (Table 1).

The coupling constants <sup>1</sup>J(<sup>13</sup>C, <sup>119</sup>Sn) and <sup>2</sup>J(<sup>1</sup>H, <sup>119</sup>Sn) have been used to determine the value of the C—Sn—C angle in the coordination polyhedron of each compound in the solution phase.<sup>15–18</sup> The |<sup>2</sup>J| values in CDCl<sub>3</sub> (Table 2) indicate a quasitetrahedral arrangement for Me<sub>3</sub>Sn(OSO<sub>2</sub>X) (1–4) compounds with four-coordinate tin. Both |<sup>1</sup>J| and |<sup>2</sup>J| values show a positive upward shift in DMSO-*d*<sub>6</sub>, indicating a change in coordination number of tin from four to five.

Pertinent vibrational bands along with approximate assignments on the basis of C<sub>3v</sub> local symmetry for the free XSO<sub>3</sub><sup>-</sup> ion are listed in Table 3. Vibrational spectra of Me<sub>3</sub>Sn(OSO<sub>2</sub>X) (X = F, CF<sub>3</sub> and CH<sub>3</sub>) and their assignments are reported in the literature.<sup>2,3</sup> Surprisingly, in comparison to the spectra of Me<sub>3</sub>Sn(OSO<sub>2</sub>X) (X = F, CF<sub>3</sub> and CH<sub>3</sub>), the IR spectra of Me<sub>3</sub>Sn(OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4) and Me<sub>3</sub>Sn(OSO<sub>2</sub>C<sub>10</sub>H<sub>7</sub>-2) show very few bands which are very broad and are identical to the spectra of their free anions. It appears that the local symmetry of the CSO<sub>3</sub> moiety is not lowered below C<sub>3v</sub> in these compounds as no splitting of the ν<sub>4</sub>(E) and ν<sub>5</sub>(E) modes is observed. The presence of free XSO<sub>3</sub><sup>-</sup> ion (X = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and 2-C<sub>10</sub>H<sub>7</sub>) in these compounds is ruled out on the basis of Λ<sub>M</sub><sup>1000</sup> data (Table 1), which suggest that 3 and 4 remain undissociated in solution. Possibly, the splitting of the ν<sub>4</sub>(E) and ν<sub>5</sub>(E) modes is masked due to the close overlap of the split bands and results in broad peaks. The compounds containing bidentate bridging OSO<sub>2</sub>X (X = 4-tolyl and 2-naphthyl) groups are associated in the solid state, which is probably responsible for the broad nature of the bands. Similar evidence for the presence of bidentate bridging fluorosulphate groups has been obtained from the crystal structure of Me<sub>2</sub>Sn(OSO<sub>2</sub>F)<sub>2</sub>.<sup>8</sup> The observed bond parameters for the fluorosulphate group are identical to those observed in the crystal structure of K<sup>+</sup>SO<sub>3</sub>F<sup>-</sup> salt,<sup>19</sup> suggesting that the fluorosulphate group does not deviate from C<sub>3v</sub> symmetry. The highly ionic nature of the tin-sulphonate bond has also been indicated by the crystal structure of Me<sub>3</sub>Sn(OSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)·H<sub>2</sub>O.<sup>7</sup> We thus envisage a similar situation for Me<sub>3</sub>Sn(OSO<sub>2</sub>X) (X = 4-tolyl and 2-naphthyl) compounds which may contain weakly bridging sulphonate groups with a planar Me<sub>3</sub>Sn moiety. The presence of a symmetric Sn—C<sub>3</sub> stretching mode at 520 cm<sup>-1</sup> in their Raman spectra and its absence in their IR spectra is good evidence of the planar nature of the Me<sub>3</sub>Sn moiety. The asymmetric Sn—C<sub>3</sub> stretching mode which is gen-

Table I. Physical and analytical data<sup>a</sup>

Compound	Analysis (%) <sup>b</sup>				M.p. (°C)	$\Lambda_M^{1000}$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
	C	H	S	Sn		
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{CF}_3)$ (1)	15.1 (15.3)	2.5 (2.9)	10.0 (10.2)	38.0 (38.9)	—	22.6 (DMSO) 4.3 ( $\text{C}_6\text{H}_5\text{NO}_2$ )
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{CH}_3)$ (2)	18.1 (18.5)	4.2 (4.6)	12.0 (12.4)	45.6 (45.9)	144	0.6 ( $\text{C}_6\text{H}_5\text{NO}_2$ )
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-4})^c$ (3)	36.2 (35.8)	4.9 (4.8)	8.8 (9.5)	35.0 (35.4)	230	26.0 (DMSO) 5.5 ( $\text{CH}_3\text{CN}$ )
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{C}_{10}\text{H}_7\text{-2})$ (4)	41.7 (42.1)	4.7 (4.3)	8.7 (8.6)	30.5 (32.0)	156	—
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{CH}_3) \cdot \text{DMSO}$ (5)	20.2 (21.3)	5.3 (5.3)	18.6 (18.9)	35.0 (35.5)	—	—
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-4}) \cdot \text{DMSO}$ (6)	36.5 (36.7)	5.0 (5.6)	16.1 (16.3)	30.2 (30.6)	—	—
$\text{Me}_2\text{Sn}(\text{OSO}_2\text{CH}_3)_2$ (7)	13.9 (14.2)	3.2 (3.5)	18.3 (18.9)	34.6 (35.0)	230	—
$\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-4})_2$ (8)	38.4 (39.1)	4.2 (4.1)	12.8 (13.0)	24.0 (24.2)	—	21.0 (DMSO)
$\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_{10}\text{H}_7\text{-2})_2$ (9)	47.5 (46.9)	3.3 (3.5)	10.9 (11.4)	20.3 (21.1)	—	—
$\text{Cs}_2[\text{Me}_2\text{Sn}(\text{OSO}_2\text{CH}_3)_4]$ (10)	9.0 (9.1)	2.2 (2.3)	15.2 (16.1)	14.6 (14.9)	—	—
$\text{Cs}_2[\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-4})_4]$ (11)	32.4 (33.8)	3.1 (3.1)	10.8 (11.6)	9.8 (10.8)	—	82.0 (DMSO)
$\text{MeSn}(\text{Cl})(\text{OSO}_2\text{CH}_3)_2$ (12)	10.6 (10.0)	2.6 (2.5)	17.9 (17.7)	32.3 (33.2)	138	—
$\text{MeSn}(\text{Cl})(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-4})_2$ (13)	35.1 (35.1)	3.1 (3.3)	12.3 (12.5)	22.6 (23.4)	230	—

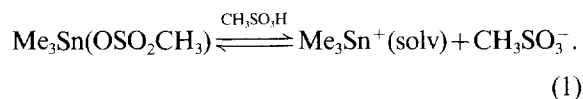
<sup>a</sup>Calculated results are given in parentheses.

<sup>b</sup>Compounds 1, 2 [3], 3 [7] and 7 [5] have been prepared by literature methods.

<sup>c</sup>Mass spectrum of 3 showed a base peak at  $m/z$  321  $[\text{M} - \text{Me}]^+$ . The mass spectrum exhibited the presence of only tri- and monovalent organotin species (even electron ions).

erally observed in the region 540–560  $\text{cm}^{-1}$  in the IR<sup>3</sup> is obscured by the presence of a  $\nu_s$  band at 565  $\text{cm}^{-1}$ . The absence of this band in their Raman spectra also suggests a planar arrangement of the  $\text{Me}_3\text{Sn}$  moiety. It appears from these studies that the trimethyltin(IV) sulphonates in the solid state consist of trigonal planar  $\text{Me}_3\text{Sn}$  groups containing weakly coordinated bidentate bridging  $\text{SO}_3\text{X}^-$  ions. The polymeric structure seems to break down in non-coordinating solvents and tin acquires quasi-tetrahedral geometry.

Solutions of  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{CH}_3)$  in pure methanesulphonic acid are quite stable, unlike those of  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{F})$  in  $\text{HSO}_3\text{F}$ <sup>3</sup> which decompose slowly to give methane. Conductance values of  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{CH}_3)$  in anhydrous methanesulphonic acid up to 0.06 m are significantly lower than the standard monoprotic base  $\text{K}^+\text{CH}_3\text{SO}_3^-$ .<sup>20</sup> This may suggest that the equilibrium in eq. (1) lies predominantly towards the left:



#### Dimethyltin(IV) disulphonates

<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR data for the compounds  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{X})_2$  (X = CH<sub>3</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and 2-C<sub>10</sub>H<sub>7</sub>) are given in Table 2. Due to their poor solubility in non-coordinating solvents, these studies could not be carried out in CDCl<sub>3</sub>. Their  $\delta(^{119}\text{Sn})$ ,  $|^1J|$  and  $|^2J|$  values fall in the region expected for other octahedral dimethyltin(IV) complexes.<sup>15,16,18</sup> Their IR spectra are very similar to each other (Table 3) and are identical to their respective sodium salts. The absence of a  $\nu_s(\text{Sn}-\text{C}_2)$  band in their IR spectra and its observation around 520  $\text{cm}^{-1}$  in their Raman spectra suggests a linear C—Sn—C arrangement.

These compounds act as  $\text{SO}_3\text{X}^-$  ion acceptors.

Table 2.  $^{19}\text{Sn}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for compounds

Compound	Solvent	$^1\text{H}$ NMR data				$^{13}\text{C}$ NMR data			
		$\delta$ ( $^{19}\text{Sn}$ ) (ppm)	$\delta$ (Sn—R) (ppm)	$\delta$ (ligand—hydrogen) (ppm)	$^2J$ (Hz)	Estd. R—Sn—R angle ( $^\circ$ )	$\delta$ (ligand—carbon) (ppm)	$^1J$ (Hz)	Estd. R—Sn—R angle ( $^\circ$ )
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{CF}_3)$ (1)	DMSO- $d_6$	35.5	0.56	-77.7 ( $^{19}\text{F}$ )	68.0	118.1	—	510.3	121.5
	$\text{CDCl}_3$	165.3	0.74	—	62.8	116.0	139.8, 125.8, 111.7, 97.6	432.0	114.6
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{CH}_3)$ (2)	DMSO- $d_6$	16.9	0.54	2.50	70.8	120.6	39.85	517.8	122.2
	$\text{CDCl}_3$	75.5	0.70	2.74	64.0	114.8	40.15	456.0	116.7
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3-4)$ (3)	DMSO- $d_6$	23.3	0.55	2.3, 7.1-7.9	69.0	118.9	20.65, 122.4, 128.2, 138.5, 144.1	512.3	121.7
	$\text{CDCl}_3$	103.6	0.66	2.4, 7.1-7.9	63.0	114.1	—	440.2	115.4
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{C}_{10}\text{H}_7-2)$ (4)	DMSO- $d_6$	30.9	0.60	7.6-8.4	68.0	118.1	123.6, 124.3, 126.5, 126.7, 127.5, 128.5, 132.1, 132.9, 144.2	510.3	121.5
	$\text{CDCl}_3$	87.9	0.70	7.4-8.3	65.0	115.6	—	—	—
$\text{Me}_3\text{Sn}(\text{OSO}_2\text{CH}_3) \cdot \text{DMSO}$ (5)	$\text{CDCl}_3$	71.0	—	—	—	—	—	—	—
	$\text{CDCl}_3$	102.4	—	—	—	—	—	—	—
	DMSO (6)	—	—	—	—	—	—	—	—
$\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_3)_2$ (7)	DMSO- $d_6$	-347	1.10	2.80	110.0	183.0	39.99	1064	170.0
	$\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3-4)_2$ (8)	-349	1.13	2.40, 7.03-7.90	110.0	183.0	20.96, 125.65, 128.56, 138.86, 144.18	1054	169.2
$\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_{10}\text{H}_7-2)_2$ (9)	DMSO- $d_6$	-332	1.16	7.40 8.40	110.0	183.0	123.60, 124.30, 126.60, 126.80, 127.60, 128.60, 132.10, 132.90, 144.50	1024	166.5
	$\text{CDCl}_3$	—	—	—	—	—	—	—	—
$\text{Cs}_2[\text{Me}_2\text{Sn}(\text{OSO}_2\text{CH}_3)_4]$ (10)	DMSO- $d_6$	-204	0.22	1.79	110.0	183.0	—	—	—
	$\text{Cs}_2[\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3-4)_4]$ (11)	-201	0.21	1.39, 6.24-6.68	108.0	178.6	—	—	—
$\text{MeSn}(\text{Cl})(\text{OSO}_2\text{CH}_3)_2$ (12)	DMSO- $d_6$	-211	1.16	2.83	—	—	38.09	—	—
	$\text{MeSn}(\text{Cl})(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3-4)_2$ (13)	-201	1.16	2.36, 7.1-7.9	—	—	20.78, 125.47, 128.34, 138.65, 144.19	—	—

Table 3. IR data (cm<sup>-1</sup>) of sulphonates

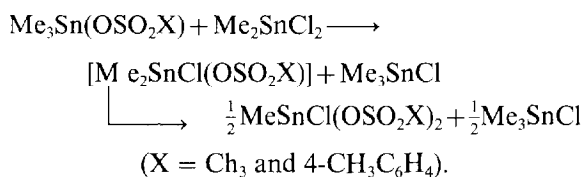
Assignments <sup>b</sup> (C <sub>3v</sub> )	Compounds <sup>a</sup>										
	3 <sup>a</sup>	4 <sup>a</sup>	8 <sup>a</sup>	9 <sup>a</sup>	10 <sup>b</sup>	11 <sup>b</sup>	12 <sup>b</sup>	13 <sup>b</sup>	Assignments <sup>c</sup> (C <sub>s</sub> )		
$\nu_4(E)$ SC <sub>3</sub> asym. str.	1240br	1270br 1200m	1235br	1275s	1270s	1260m	1215s	1270s 1205w 1130s	$\nu(\text{SO}_2)$ asym. str.		
$\nu_1(A_1)$ SO <sub>3</sub> sym. str.	1120s	1030s	1152s	1025s	1020m	1080m 1030m	1085s 810s	1085s	$\nu(\text{SO}_2)$ sym. str.		
$\nu_2(A_1)$ S—X str.	688s	820m	680s	815m	770m	820s	780s	690s	$\nu(\text{S} \rightarrow \text{X})$		
$\nu_5(E)$ SO <sub>3</sub> asym. defn.	565s	560s	530br	545m	530m	550m	550m	560m	$\nu(\text{SO}_2)$ bend		
$\nu_3(A_1)$ SO <sub>3</sub> sym. defn.	500w	470m 420w	490w	470w	430w 375m	410w 370w	450w 375s	410w 370w	$\nu(\text{SO}_2)$ rock $\nu(\text{S} \rightarrow \text{O})^d$ wag. $\nu(\text{S} \rightarrow \text{X})$ torsion		
$\nu_6(E)$ S—X defn. int. vib	1040m 1015m 820s 790m 400m	350w 320w	1035m 1005m 815s 305m	350w	1010m 800m	1010s 810m	1020s 720m	1010s 720s	$\nu(\text{S} \rightarrow \text{X})$ wag CH <sub>3</sub> $\delta$ 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> int. vib.		

<sup>a</sup>Numbers refer to the serial number of the compounds in Table 1.<sup>b</sup>Assignments refer to compounds 3, 4, 8 and 9.<sup>c</sup>Assignments refer to compounds 10-13.<sup>d</sup>Coordinating oxygen atom of the sulphonate group.

Compounds **7** and **8** combine with their caesium salts to give  $\text{Cs}_2[\text{Me}_2\text{Sn}(\text{OSO}_2\text{CH}_3)_4]$  (**10**) and  $\text{Cs}_2[\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3)_4]$  (**11**), respectively (Table 1). Their IR spectra show splitting of  $\nu_4(E)$   $\text{SO}_3$  asymmetric stretching and  $\nu_5(E)$   $\text{SO}_3$  asymmetric deformation modes. The increased number of bands suggests that the local symmetry of the  $-\text{OSO}_2\text{X}$  groups is reduced from  $C_{3v}$  to  $C_s$  and the  $-\text{OSO}_2\text{X}$  groups are coordinated in unidentate mode. The  $\delta(^{119}\text{Sn})$  values are also quite high, suggesting octahedral geometry around tin.

#### *Ternary sulphonates*

The ternary sulphonate,  $\text{Me}_2\text{SnCl}(\text{OSO}_2\text{F})$ , has been prepared by a ligand redistribution reaction employing  $\text{Me}_2\text{SnCl}_2$  and  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{F})_2$ .<sup>2</sup> Our attempts to prepare  $\text{Me}_2\text{SnCl}(\text{OSO}_2\text{X})$  ( $\text{X} = \text{CH}_3$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ) by reactions of  $\text{Me}_2\text{SnCl}_2$  with  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{CH}_3)_2$  and  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3)_2$  did not yield any definite products. However, reactions of  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$  ( $\text{X} = \text{Me}$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ) with  $\text{Me}_2\text{SnCl}_2$  yield white flaky solids,  $\text{MeSnCl}(\text{OSO}_2\text{CH}_3)_2$  (**12**) and  $\text{MeSnCl}(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3)_2$  (**13**) (Table 1). The sequence of reactions may be visualized as:



The formation of  $\text{Me}_3\text{SnCl}$  was confirmed. Both  $\text{Me}_2\text{SnCl}(\text{OSO}_2\text{F})$  and  $\text{MeSnCl}(\text{OSO}_2\text{F})_2$  are known,<sup>2</sup> but analogous compounds containing the  $-\text{OSO}_2\text{CF}_3$  group could not be isolated using similar reaction.<sup>2</sup> It was suggested that the bulkier  $-\text{CF}_3$  group provides steric hindrance and makes the uncoordinated oxygen atom of the bridging  $-\text{OSO}_2\text{CF}_3$  group less accessible. It appears that this argument may be valid for reactions of  $\text{Me}_2\text{Sn}(\text{OSO}_2\text{X})_2$  ( $\text{X} = \text{CF}_3$ ,  $\text{CH}_3$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ) which contain six-coordinated tin and do not undergo ligand redistribution reactions due to steric crowding. However, such reactions are feasible between  $\text{Me}_3\text{Sn}(\text{OSO}_2\text{X})$  ( $\text{X} = \text{CH}_3$  and  $4\text{-CH}_3\text{C}_6\text{H}_4$ ) (coordination number of tin = 5) and  $\text{Me}_2\text{SnCl}_2$ .

Both compounds **12** and **13** are soluble only in polar donor solvents. The  $\delta(^{119}\text{Sn})$  are observed at high fields (Table 2), in the range normally expected for five- or six-coordinated tin. Their IR spectra contain split bands, which suggest that the  $\text{XSO}_3^-$  group has reduced local symmetry. These compounds probably contain bridging ( $-\text{OSO}_2\text{X}$ ) groups.

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