A Reinvestigation of the Structures of Organotin Sulphates and Chromates, including the Crystal and Molecular Structure of Bis(trimethyltin) Sulphate Dihydrate†

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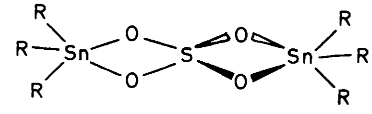
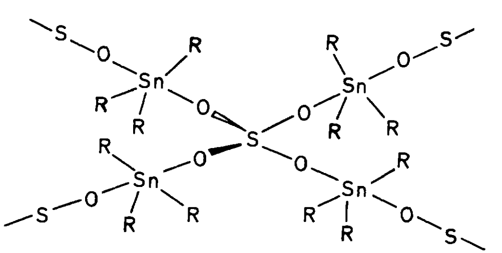
The structures of a group of triorganotin sulphates and chromates have been studied by ^{119}Sn n.m.r. and Mössbauer spectroscopies. All the compounds $(SnR_3)_2EO_4{\cdot}nH_2O$ (R = Me, E = Cr, n = 0; R = Me or Bu^n, E = S, n = 0; R = Me, E = S, n = 2) form polymeric lattices in the solid state, although for $(SnBu^n{}_3)_2SO_4$ an irregular lattice incorporating both four- and five-co-ordinate tin atoms is postulated. The structure of $(SnMe_3)_2SO_4{\cdot}2H_2O$ has been determined by an *X*-ray study. Crystal data: orthorhombic, space group *Pbcn*, a = 11.245(4), b = 12.695(5), c = 10.811(4) Å, Z = 4. The geometry about tin is trigonal bipyramidal with a *trans*-O_2SnC_3 stereochemistry about the metal, one of the axial sites being occupied by a molecule of hydration. Hydrogen bonding between oxygens of the anion and the solvate produces a three-dimensional network lattice.

Although organotin sulphates have been known since the early 1970s, detailed structural data for these systems are yet to be reported. There seems to be uniform agreement that $(SnMe_3)_2SO_4$ and its dihydrate are polymeric to some degree and that both anhydrous and hydrated species have similar co-ordination spheres at tin.[1] The structure of $(SnBu^n{}_3)_2SO_4$, however, has been the subject of some controversy,[2–4] primarily centred on the interpretation of variable-temperature Mössbauer spectroscopic (v.t.M.s.) data.[4] Mössbauer quadrupole splitting (q.s.) data are similar for $(SnBu^n{}_3)_2SO_4$ and $(SnMe_3)_2SO_4$, and led to the conclusion that the former has a polymeric structure of type (**I**).[3] On the other hand, the absence of an observable room-temperature Mössbauer spectrum, and the strong temperature dependence of the Mössbauer spectral area, has led other authors[2,4,5] to conclude that $(SnBu^n{}_3)_2SO_4$ has a monomeric structure, probably of type (**II**). Our own interest in the development of v.t.M.s. as a structural probe in organotin chemistry[6] has prompted us to reconsider the evidence central to this problem, and to study more fully the structures of organotin sulphates and the related chromates. We report our findings herein.



(**II**)



(**I**)

Experimental

Details of our Mössbauer spectrometer and the v.t.M.s. technique have been published elsewhere.[7] The compound $(SnMe_3)_2SO_4$, its dihydrate, and $(SnMe_3)_2CrO_4$ were prepared by published procedures.[1]

Synthesis of $(SnBu^n{}_3)_2SO_4$.—Silver sulphate (2.20 g, 7 mmol) and tri-n-butyltin chloride (4.59 g, 14 mmol) were stirred overnight at room temperature in dry methanol (50 cm^3), then for 1 h at reflux. After filtration and solvent evaporation, the resulting oil was titurated with hexane to yield a solid product which was recrystallised from CCl_4 (Found: C, 42.8; H, 8.0. Calc. for $C_{24}H_{54}O_4SSn_2$: C, 42.6; H, 8.1%). The m.p. of this sample (138—140 °C) is similar to that reported in the literature for a sample prepared from the oxidation of $(SnBu^n{}_3)_2S$ by H_2O_2 (140—144 °C),[2] but differs from that obtained by acetone crystallisation of the product of the reaction between $(SnBu^n{}_3)_2O$ and sulphuric acid (148—150 °C).[8]

The Structure of $(SnMe_3)_2SO_4{\cdot}2H_2O$.—Crystals of *X*-ray quality were obtained by slow evaporation of an aqueous solution.

Crystal data. $C_6H_{22}O_6SSn_2$, M = 459.7, orthorhombic, space group *Pbcn* (no. 60), a = 11.245(4), b = 12.695(5), c = 10.811(4) Å, U = 1 543.3 Å^3, Z = 4, Mo-K_α radiation, λ = 0.7107 Å, D_c = 1.98 g cm^{-3}, μ = 31.27 mm^{-1}, F(000) = 888.

Data collection was carried out at room temperature on a Hilger-Watts Y290 four-circle automatic diffractometer using Mo-K_α radiation. 1 197 Reflections were measured in the range $2 \leqslant \theta \leqslant 48°$, of which 960 had $I > 3\sigma(I)$ and were considered observed. Corrections were applied for Lorenz, polarisation,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

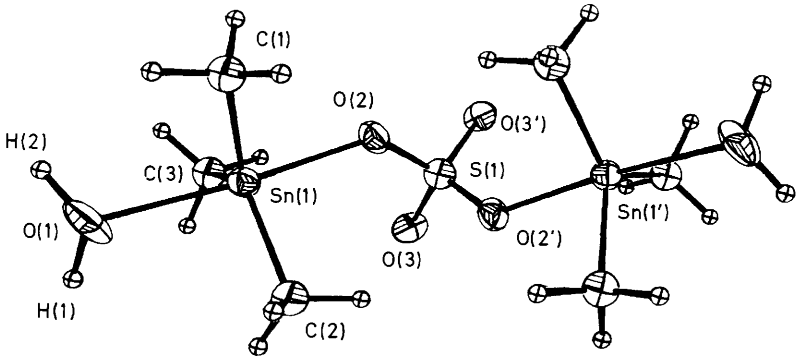

Figure 1. The asymmetric unit of $(SnMe_3)_2SO_4{\cdot}2H_2O$ showing the atomic labelling scheme. Primed atoms are related to their unprimed counterparts by $-x, y, \frac{1}{2} - z$. Labels for the hydrogen atoms attached to C(1) [H(11)–H(13)] and C(2) [H(21)–H(23)] have been omitted for clarity

Table 1. Fractional atomic co-ordinates for $(SnMe_3)_2SO_4{\cdot}2H_2O$

Atom	x	y	z
Sn(1)	0.244 35(3)	0.190 01(3)	0.323 94(4)
O(1)	0.401 2(5)	0.101 1(4)	0.419 4(5)
O(2)	0.100 2(4)	0.268 4(4)	0.214 6(4)
O(3)	0.031 0(4)	0.400 5(3)	0.358 7(4)
S(1)	0.0000	0.336 9(1)	0.2500
C(1)	0.274 0(7)	0.093 3(7)	0.169 3(7)
C(2)	0.340 1(7)	0.332 5(6)	0.344 1(8)
C(3)	0.128 9(7)	0.139 5(7)	0.463 5(7)

Table 2. Bond distances (Å) and angles (°) in $(SnMe_3)_2SO_4{\cdot}2H_2O$ *

Sn(1)–O(1)	2.335(4)	Sn(1)–O(2)	2.239(4)
Sn(1)–C(1)	2.101(8)	Sn(1)–C(2)	2.116(8)
Sn(1)–C(3)	2.091(8)	S(1)–O(2)	1.475(4)
S(1)–O(3)	1.468(4)		
O(2)–Sn(1)–O(1)	174.3(2)	C(1)–Sn(1)–O(1)	87.1(2)
C(1)–Sn(1)–O(2)	87.4(2)	C(2)–Sn(1)–O(1)	89.0(3)
C(2)–Sn(1)–O(2)	92.5(3)	C(2)–Sn(1)–C(1)	120.0(3)
C(3)–Sn(1)–O(1)	90.1(3)	C(3)–Sn(1)–O(2)	93.9(3)
C(3)–Sn(1)–C(1)	119.5(3)	C(3)–Sn(1)–C(2)	120.3(3)
O(3)–S(1)–O(2)	110.5(2)	O(2)–S(1)–O(2′)	107.6(4)
S(1)–O(2)–Sn(1)	132.7(3)		
O(3)–S(1)–O(3′)	112.9(4)		

* Primed atoms are related to their unprimed counterparts by $-x, y, \frac{1}{2} - z$.

and extinction effects, but not for absorption. The structure was solved using MULTAN[9] and refined using the SHELX[10] program suite. Hydrogen atoms were included in the final structure factor calculations at fixed, calculated positions (X–H 1.08 Å, X = C or O) with a common, fixed isotropic thermal parameter (U = 0.05 Å^2). Fifty-seven parameters were refined, ultimately using the weighting scheme $w = 1.000/[\sigma^2(F) + 0.001\ 500F^2]$. The final electron-density map contained no peaks greater than 0.5 e Å^{-3}. Final values for 960 observed reflections are R = 0.0337 and R' = 0.0427. Final fractional atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2 and refer to the asymmetric unit labelling scheme of Figure 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Discussion

The Structure of $(SnMe_3)_2SO_4{\cdot}2H_2O$.—Bis(trimethyltin) sulphate dihydrate consists of molecules in which a bidentate SO_4 unit binds two Me_3Sn moieties. The geometry at tin is a five-co-ordinate, *trans*-O_2SnC_3 framework in which one of the apical oxygen atoms arises from the sulphate ligand, the other from a molecule of hydration (Figure 1). The local geometry at each tin in the molecule is thus similar to that previously observed in the hydrates of trimethyltin nitrate,[11] benzenesulphonate,[12] and pyridine-2-carboxylate.[13] The bonds linking the water molecule to tin are typical of such a system (Table 3), being intermediate in the range of known $H_2O\!:\!\rightarrow Sn$ bonds.

The role of the two water molecules is crucial to the formation of the lattice, which is dominated by a network of hydrogen bonds. Figure 2 shows a projection of the unit cell along c, which for clarity only contains molecules in the range $0 \leqslant z \leqslant 0.5$. That is, all the sulphur atoms shown have z = 0.2500, while two molecules with sulphur at z = 0.7500 have been omitted. This perspective shows that one hydrogen atom on O(1) is hydrogen bonded to one of the unco-ordinated oxygens of the anion, O(3) [O(1)$\cdots$O(3) 2.74 Å], to produce a puckered sheet of molecules in the ab plane. Figure 3 shows the unit cell projected along b, thus allowing a view of the hydrogen-bonded planes in front and behind that shown in Figure 2. The two figures are easily related by identifying the sulphur atoms at x = 0.000, 1.000 in the two projections. From Figure 3, it can be seen that each of the hydrogen-bonded sheets in the ab plane is further linked to those sheets either side of it by a slightly weaker set of hydrogen bonds [O(1)$\cdots$O(3) 2.81 Å]. The second set of hydrogen bonds thus employs the second hydrogen atom of each of the co-ordinated water molecules, and requires each of the two oxygen atoms of the sulphate to form a pair of hydrogen bonds. The bifurcated nature of the hydrogen bonding at O(3) is a result of the molecular stoicheiometry, which has $H_2O:SO_4^{2-}$ at 2 : 1, *i.e.* four hydrogen atoms per two available oxygen atoms. The three-dimensional hydrogen-bonding network thus links each molecule to four molecules in the ab plane (Figure 2) and two others in each of the ab planes either side of it (Figure 3).

Spectroscopic Studies.—Mössbauer spectroscopic data for four organotin sulphates and chromates are given in Table 4. The quadrupole splitting (q.s.) for $(SnMe_3)_2SO_4{\cdot}2H_2O$ (4.11 mm s^{-1}) is in keeping with the *trans*-O_2SnC_3 geometry at tin and there can be little doubt that a similar environment about tin also exists in the anhydrous compounds $(SnMe_3)_2(EO_4)$ (E = S or Cr) with the axial molecule of hydration now

Table 3. Comparative structural data (distances in Å, angles in °) for organotin sulphates, chromates, and related species

Compound	$H_2O\!:\!\rightarrow Sn$	Sn–OE[a]	O–E	Sn–O–E	O···O[b]
$(SnMe_3)_2SO_4\cdot 2H_2O$[c]	2.335(4)	2.239(4)	1.468(4), 1.475(4)	132.7(3)	2.74, 2.81
$(SnMe_3)_3(OH)CrO_4$[d]	2.14(3), 2.17(4)[e]	2.16(4), 2.29(4)[f]	1.78(4), 1.70(4)[f]	129(2), 142(2)[f]	
		2.48(5), 2.51(4)[g]	1.56(4), 1.61(4)[g]	152(2), 153(2)[g]	
$(SiPh_3)_2CrO_4$[h]			1.51, 1.57	133.1, 162.7[i]	
$SnMe_3(O_3SPh)\cdot H_2O$[j]	2.30(1)	2.37(1)	1.45(1), 1.50(1), 1.48(1)	124.6(5)	2.54(2)
$SnMe_3(O_2SCH_2C{\equiv}CH)$[k]		2.31(1), 2.30(1)	1.54(1), 1.51(1)	125.3, 134.4	
$SnMe_3(O_2SMe)$[l]		2.21(3), 2.27(2)	1.47—1.56	130.4, 140.4 146.2, 169.2	
$SnMe_3(NO_3)\cdot H_2O$[m]	2.47(2)	2.22(3)			2.72(3)
$SnMe_3(O_2CC_5H_4N\text{-}2)\cdot H_2O$[n]	2.43	2.185		118.3, 125.2	2.65—2.88

[a] E = S, Cr, N, or C as appropriate. [b] Intermolecular contacts. [c] This work. [d] Ref. 15. [e] Sn–OH. [f] $CrO_4(Me_3Sn)CrO_4(Me_3Sn)$ chains. [g] $(OH)(Me_3Sn)CrO_4(Me_3Sn)$ chains. [h] B. Stensland and P. Kiekegaard, *Acta Chem. Scand.*, 1970, **24**, 211. [i] Si–O–E. [j] Ref. 12. [k] D. Ginderow and M. M. Huber, *Acta Crystallogr., Sect. B*, 1973, **29**, 560. [l] G. M. Sheldrick and R. Taylor, *Acta Crystallogr., Sect. B*, 1977, **33**, 135. [m] Ref. 11. [n] Ref. 13.

Table 4. Mössbauer spectroscopic data (mm s^{-1}) for selected organotin sulphates, chromates, and related species

Compound	i.s.[a]	q.s.[a]	Γ[b]	χ^2	10^2a (r, points, T range)
$(SnMe_3)_2SO_4$	1.44	4.11	0.93, 0.94	502	2.40 (−0.999, 5, 78—120)
					2.72 (−0.994, 7, 78—140)
$(SnMe_3)_2SO_4\cdot 2H_2O$	1.43	4.09	1.12, 1.14	429	1.02 (−0.999, 9, 78—155)
$(SnMe_3)_2CrO_4$	1.43	3.81	1.02, 1.02	491	1.10 (−0.999, 8, 78—145)
$(SnBu^n{}_3)_2SO_4$	1.47[c]	3.90[c]	1.02, 1.02[c]	700[c]	
	1.48[d]	4.07[d]	0.88, 0.88[d]	473[d]	1.89 (−0.994, 8, 85—125)[e]
	1.40[d]	3.30[d]	0.99, 0.99[d]		1.94 (−0.991, 11, 78—135)[e]
$SnMe_3(O_3SPh)\cdot H_2O$[f]					1.71

[a] ±0.04 mm s^{-1}. [b] Full width at half height. [c] Single-doublet fit. [d] Two-doublet fit. [e] Total spectral area for two-doublet fit. [f] Ref. 12.

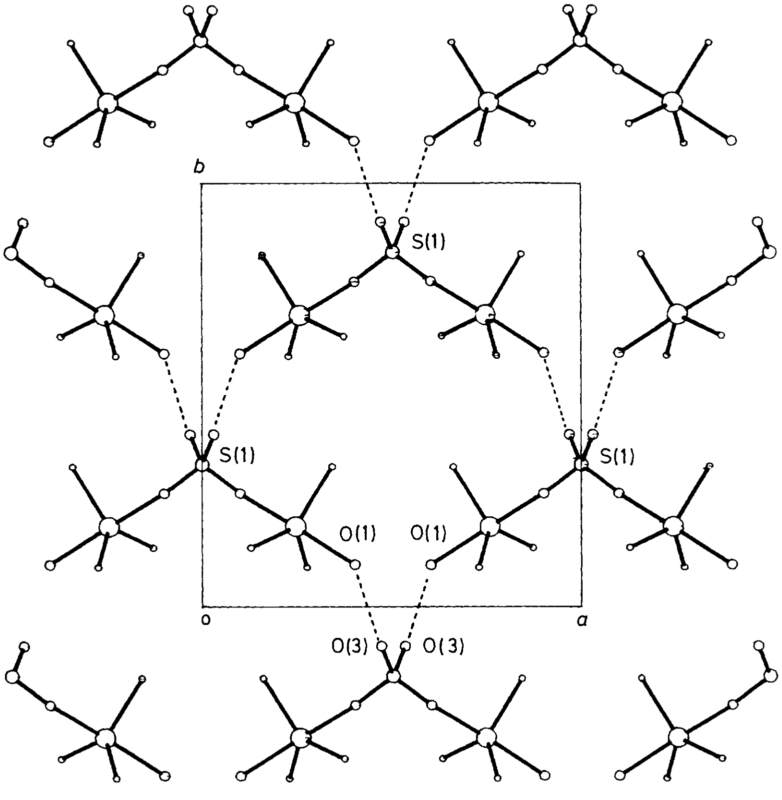

Figure 2. The unit-cell contents of $(SnMe_3)_2SO_4\cdot 2H_2O$ viewed along *c*. Dashed lines indicate hydrogen bonds

replaced by an oxygen of the $EO_4{}^{2-}$ ligand. However, the lattice structure of these three compounds shows considerable variation. Included in Table 4 are v.t.M.s. data for the four compounds studied, which are shown diagramatically in Figure 4 to indicate the quality of the data. We and others (ref. 6 and references therein) have shown that plots of ln *A*(*T*) *vs*. *T*,

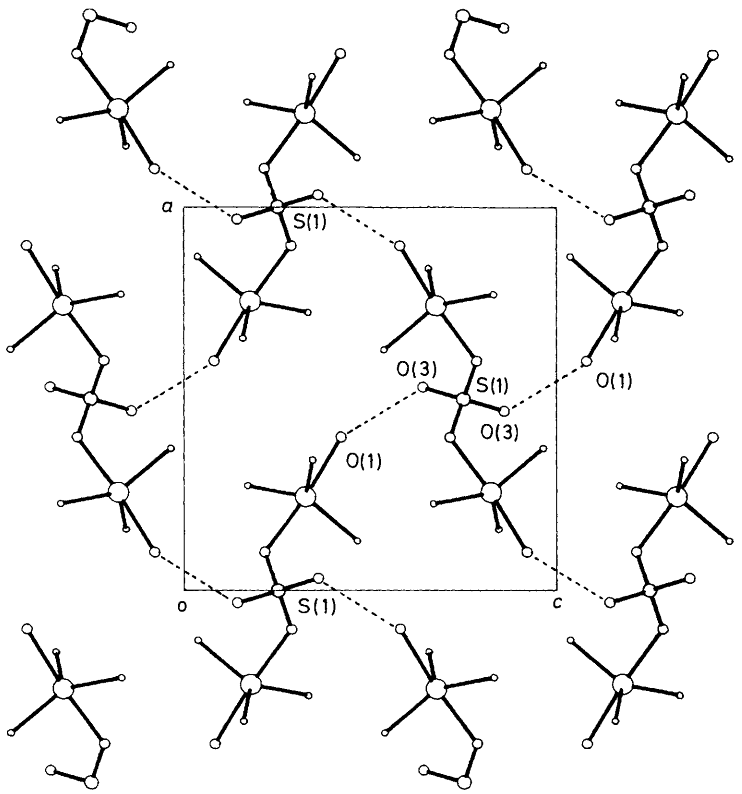

Figure 3. The unit cell of $(SnMe_3)_2SO_4{\cdot}2H_2O$ viewed along *b*. Dashed lines indicate hydrogen bonds

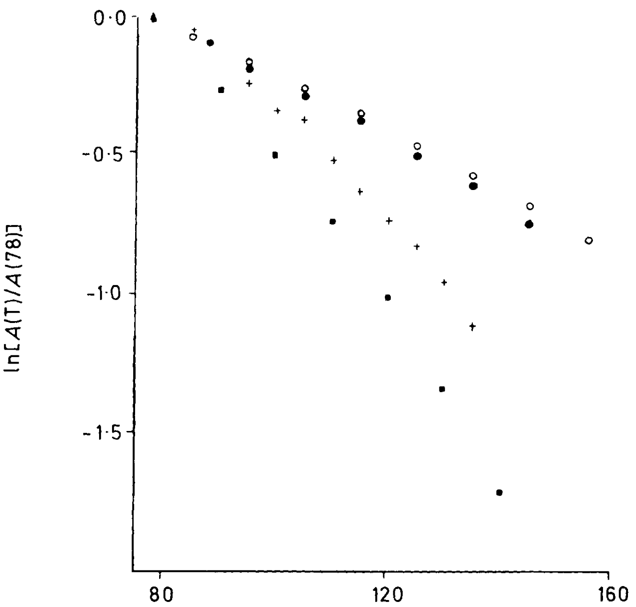

Figure 4. Variable-temperature Mössbauer spectroscopic data for (○) $(SnMe_3)_2SO_4{\cdot}2H_2O$, (●) $(SnMe_3)_2CrO_4$, (+) $(SnBu^n{}_3)_2SO_4$, and (■) $(SnMe_3)_2SO_4$. Numerical analysis of these data is given in Table 4

characterised by their slope $a = -\mathrm{d}\ln A(T)/\mathrm{d}T$, indicate the rigidity with which the Mössbauer nucleus (Sn) is held in the lattice. The relatively shallow slope ($10^2a = 1.02\ K^{-1}$) for $(SnMe_3)_2SO_4{\cdot}2H_2O$ indicates that the three-dimensional hydrogen-bonded lattice is of similar rigidity to one-dimensional Class 2 (zigzag)[6] polymers. More appropriate to this discussion is the similarity of the data to those for $SnMe_3(O_2CC_5H_4N\text{-}2){\cdot}H_2O$ ($10^2a = 1.27\ K^{-1}$)[14] which also forms a three-dimensional hydrogen-bonded lattice, with similar intermolecular contact distances.[13] V.t.M.s. data for $(SnMe_3)_2CrO_4$ ($10^2a = 1.10\ K^{-1}$) indicate a lattice of the same rigidity, and it seems reasonable to ascribe the network polymeric structure (**I**) to this compound. Sections of this framework can be found in the structure of $(SnMe_3)_3(OH)CrO_4$, a hydrolysis product of $(SnMe_3)_2CrO_4$.[15]

The structure of anhydrous $(SnMe_3)_2SO_4$ has been postulated as being similar to that of the corresponding chromate, but v.t.M.s. data (10^2a *ca.* $2.50\ K^{-1}$) suggest that significant differences exist. Detailed analysis of the d ln *A vs. T* plot shown in Figure 4 (■) is complicated by the line curvature, probably due to lattice anharmonicity. The slope data quoted in Table 4 are for both the most linear region (78—120 K) as well as for the complete data set, but in either case the conclusion is the same: the tin atom in anhydrous trimethyltin sulphate is vibrating with considerably greater amplitude than the same atom in either its dihydrate or $(SnMe_3)_2CrO_4$. The inability of others[1] to observe a room-temperature Mössbauer spectrum for $(SnMe_3)_2SO_4$ is in keeping with this assertion. We can only speculate at present as to the structural origin of the phenomenon, but three possible factors suggest themselves. Molecular models based upon structure (**I**) show significant crowding of the lattice cavities * by the methyl groups bonded to tin, and a misleading impression is given by Figure 1 of ref. 1 in this respect. The crowding in this sulphate is likely to be greater

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* Since the anhydrous material is produced by thermal dehydration of the dihydrate, our models are built using four Me_3Sn and four SO_4 units as this combination forms hydrogen-bonded rings in $(SnMe_3)_2SO_4{\cdot}2H_2O$ (Figure 2). Structures containing larger ring systems are possible, for example in $[Ph_3SnO_2P(OPh)_2]_6$,[16] but such arrays decrease in likelihood with increasing size, for 'chelate-effect' reasons.

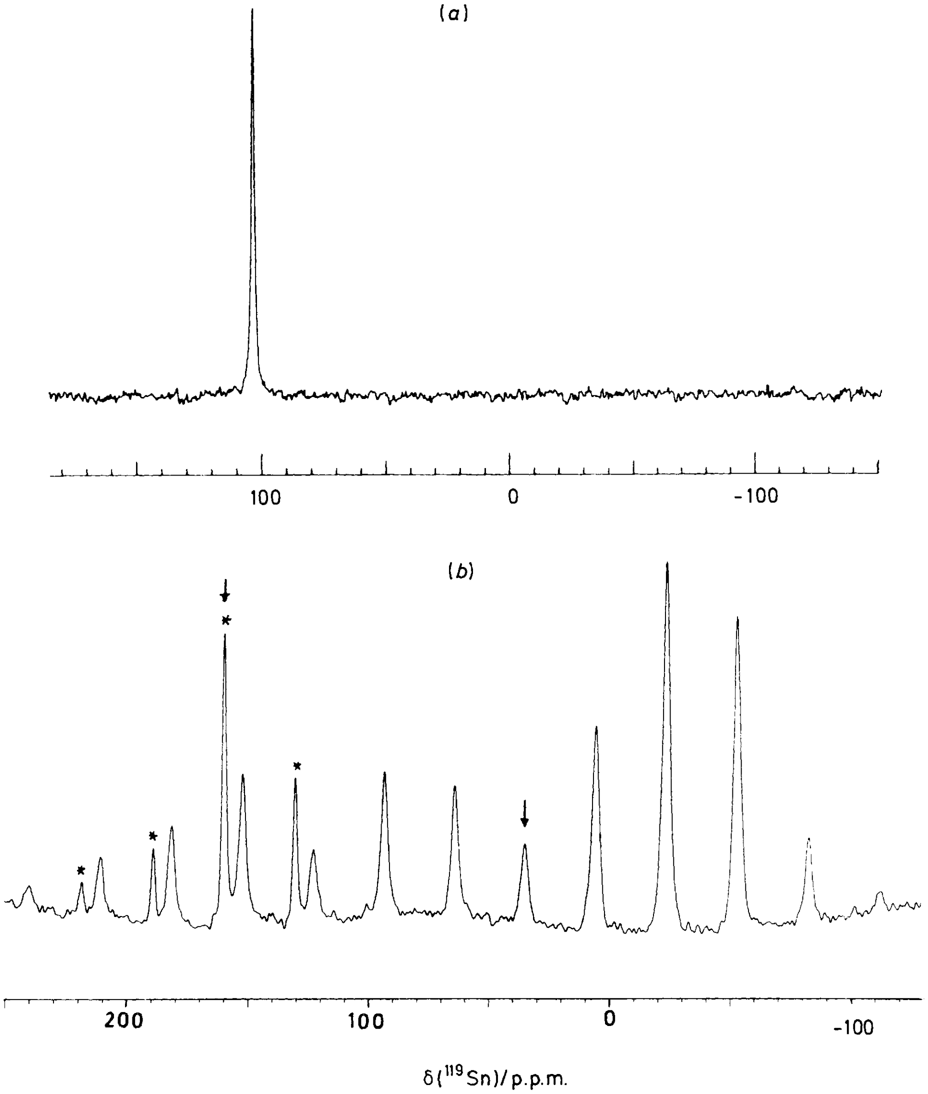

Figure 5. ^{119}Sn N.m.r. data for $(SnBu^n_3)_2SO_4$ (*a*) at room temperature, for a saturated solution in $CDCl_3$, and (*b*) in the solid state. Centre-band positions are marked by arrows. The asterisks denote those bands belonging to the low-field resonance envelope. Instrumental settings for solid-state spectrum: frequency = 111.86 MHz, acquisition time = 0.15 s, relaxation delay = 5.0 s, pulse width = 90°, repetitions = 150, contact time = 1.0 ms, decoupler power levels = 140 (contact) and 150 (dipolar), and spin rate = 2 100 Hz. A second spectrum recorded at 2 900 Hz was used to identify the centre bands

than in the corresponding chromate, since S–O bonds are *ca.* 10—20 pm shorter than Cr–O bonds (Table 3). Steric crowding within the cavities of $(SnMe_3)_2SO_4$ can be relieved by (*i*) isotropic swelling of the lattice by lengthening *all* the Sn-O bonds, (*ii*) lengthening only two of the Sn-O bonds to produce an array of two-dimensional sheets held weakly in stacks by the now longer Sn–O bonds, or (*iii*) distortions in the polymer framework, most likely by bending of the angle Sn–O–S. In the last respect, considerable variation in Sn–O–E can be found in these systems (Table 3) and we have shown that structural changes of this type bring about quite different lattice dynamics in the case of $SnPh_3(O_2CR)$ (R = H or Me).[17] One or more of these three structural modifications would account for the differing lattice structures of trimethyltin sulphate and chromate.

Finally, we return to the structure of $(SnBu^n_3)_2SO_4$ which originally prompted our interest in these systems. V.t.M.s. data for this compound show deviations from linearity, particularly at $T > 125$ K, as indicated previously.[4] Analysis of these data yields 10^2a *ca.* 1.90 K^{-1}, compared with *ca.* 1.60 K^{-1} estimated from the data of ref. 4. This high value of *a* has been used by Herber[4] as evidence against polymeric structure (**I**), and more in keeping with the monomeric assembly (**II**). However, our analysis of the electronic factors which control the structures of triorganotin compounds would suggest that, with groups of such differing electronegativity as C_4H_9 and SO_4 bonded to the metal, the *trans*-O_2SnC_3 geometry will be preferred over the *cis*-O_2SnC_3 isomer,[18] and given the similar q.s. data for all four sulphates and chromates studied (Table 4) we have no reason to doubt that $(SnBu^n_3)_2SO_4$ has the former co-ordination sphere about tin. The similarity of v.t.M.s. data for $(SnBu^n_3)_2SO_4$ and $SnBu^n_3(O_2CMe)$ has led to the assertion that these compounds are structurally similar, and reference is made to a proposed trimeric structure for the carboxylate.[4] However, such a thesis is tenuous, given that the common Class 3 polymer structure for organotin carboxylates also exhibits similar v.t.M.s. behaviour to those of molecular species.[6,7] Indeed, we have recently determined the structure of tri-n-butyltin indole-3-acetate and found it to be polymeric.[19]

The factors which influence the lattice structure of

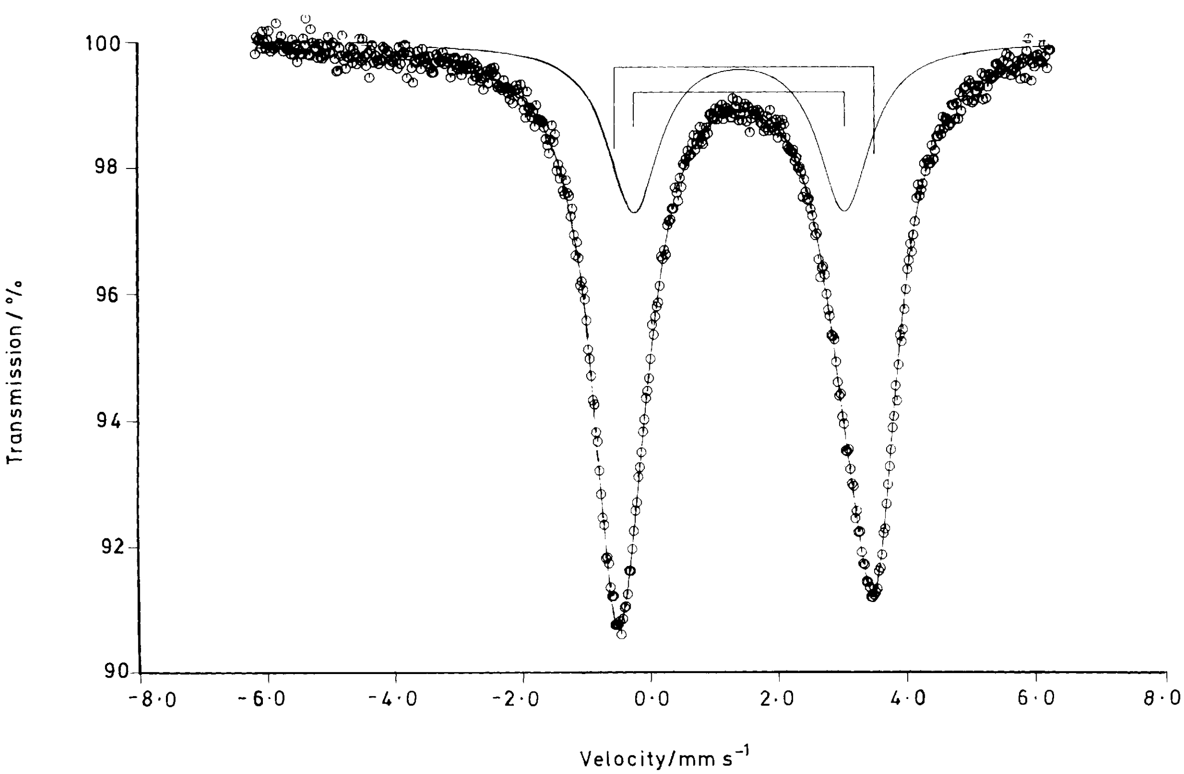

Figure 6. ^{119}Sn Mössbauer spectrum for $(SnBu^n{}_3)_2SO_4$ fit to two quadrupole-split doublet sites. The overall spectral envelope along with that for the minor component of the spectrum is marked

$(SnBu^n{}_3)_2SO_4$ will be those described above in connection with $(SnMe_3)_2SO_4$, and the general appearance of the v.t.M.s. data for these two compounds indicates that they will be of generally similar structural type. However, steric crowding within the cavities of a network polymer (**I**) will be more acute when R = n-C_4H_9 than CH_3. In order to accommodate the *trans*-O_2SnC_3 stereochemistry at tin within a polymeric array, severe lattice distortions can be anticipated. The ^{119}Sn n.m.r. data for $(SnBu^n{}_3)_2SO_4$ are shown in Figure 5. In $CDCl_3$ solution a single resonance at *ca.* 110 p.p.m. is observed. This is consistent with a co-ordination number of four at tin, resulting from break-up of the proposed solid-state polymeric structure upon dissolution. The concentration dependence of the chemical shift, linewidth (28—45 Hz), and $^1J(^{13}C-^{117,119}Sn)$ (380, 370 Hz) all correlate with a solution equilibrium between four- and five-co-ordinate tin atoms. In the solid-state ^{119}Sn n.m.r. spectrum recorded under cross-polarisation magic angle spinning conditions two resonance envelopes are observed. While most of the lines in the spectrum are due to spinning sidebands, recording of spectra at different spinning rates enables the centre bands to be identified, at 159.6 and 34.8 p.p.m. In this case, the low-field resonance arises from tin with co-ordination number four, while the major resonance, at high field, arises from tin with co-ordination number five. That is, even in the solid state, tin atoms with both co-ordination numbers (4, 5) exist. Quantitative estimates of site populations by spectral integration are complicated by the rolling baseline, but the 5:1 ratio of high:low co-ordination numbers measured gives a good guide. The presence of only one signal in the solution-state n.m.r. spectrum rules out compound impurities as the origin of the resonance observed at 159.6 p.p.m. in the solid-state n.m.r. spectrum.

Though much less sensitive, ^{119}Sn Mössbauer data corroborate the solid-state n.m.r. results. Superficially, the spectrum (Figure 6) consists of a doublet, with isomer shift (i.s.) = 1.47, q.s. = 3.90, and Γ = 1.02 mm s^{-1} and the 'goodness of fit' χ^2 = 700 for 505 degrees of freedom. When a second tin site (quadrupole-split doublet) is included in the least-squares fit, χ^2 drops to 473 (for 501 degrees of freedom), which is a significantly more statistically acceptable result. The parameters now obtained are given in Table 4. Data for the high-co-ordination site are not appreciably altered from those for the simple single-doublet fit, while the second tin site has q.s. = 3.30 mm s^{-1}. Although this may appear high for a co-ordination number of four at tin, it must be remembered that electronegativity inbalance will also influence q.s. values as well as geometry. For example, the q.s. values for the five-co-ordinate organotin sulphates and chromate reported here (*ca.* 4.0 mm s^{-1}) are higher than normally associated with the *trans*-O_2SnC_3 geometry[20] (*e.g.* $SnMe_3(OH)$, q.s. = 2.94 mm s^{-1}, $SnMe_3(O_2CMe)$, q.s. = 3.57 mm s^{-1})[21,22] but in line with other compounds of this structure incorporating highly electronegative ligands, *e.g.* $SnMe_3(O_2CCF_3)$, q.s. = 4.18 mm s^{-1}.[22] Using spectral areas as an estimate of site populations now gives 3:1 for high:low co-ordination numbers.

The structural picture which emerges from this compendium of data is a lattice which consists of a network polymer in which voids are created within the lattice to accommodate the bulky n-C_4H_9 groups on tin, and this is achieved by 'defect sites' in which tin has a co-ordination number of four. Triorganotin derivatives of other oxyanions (*e.g.* $CO_3{}^{2-}$ and $PhPO_3{}^{2-}$)[23–25] also incorporate both four- and five-co-ordinate tin atoms but in a structurally regular arrangement, *e.g.* 1:1. Although we cannot be certain of this at this time, it would appear that in $(SnBu^n{}_3)_2SO_4$, the low-co-ordination site is of much lower concentration within the solid, and thus more likely to occur in an irregular manner. Attempts to grow crystals of this compound by us and others[4,8] have been unsuccessful. Lattice parameters have been reported, but diffuse reflections arising from '*different kinds of structural defects*' precluded full structural analysis.[8] In our hands, slow evaporation of $CHCl_3$ solutions yield large hexagonal crystals, but these include large volumes of solvent and have 'soft centres.' The range of melting points reported for this compound (see Experimental section) also suggests that the distribution of defect sites within the lattice is non-stoicheiometric.

Conclusions

The compounds $(SnMe_3)_2CrO_4$, $(SnMe_3)_2SO_4$ and its dihydrate have all been shown to form polymeric lattices, with a local *trans*-O_2SnC_3 co-ordination sphere about tin. However, contrary to previous inferences,[1] the hydrated compound has water molecules directly bonded to tin. The compound $(SnBu^n{}_3)_2SO_4$ also forms a polymeric lattice, but structural irregularities are required to accommodate the bulkier butyl groups, and four-co-ordinate tin sites also occur in this lattice.

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