Organotin Biocides. Part 8.[1] The Crystal Structure† of Triphenyltin Formate and a Comparative Variable-temperature Tin-119 Mössbauer Spectroscopic Study of Organotin Formates and Acetates

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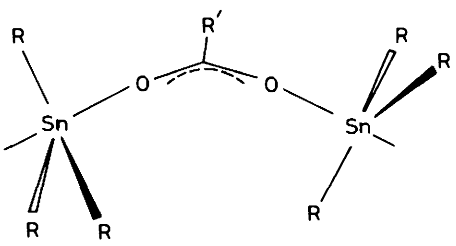
The structure of triphenyltin formate has been determined by an *X*-ray study. Crystal data: monoclinic, space group $B2_1/a$, $a = 20.176(8)$, $b = 15.539(6)$, $c = 21.952(10)$ Å, $\beta = 90.30(6)°$, $Z = 16$. The geometry about tin is trigonal bipyramidal with a *trans*-O_2SnR_3 stereochemistry (R = Ph), leading to a chain polymeric structure for the lattice. The geometric distortions which accompany polymer formation are assessed, and used to interpret variable-temperature Mössbauer spectroscopic data for triphenyl-, tricyclohexyl-, and trimethyl-tin formates and acetates.

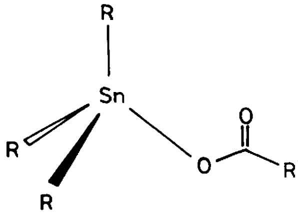
Our interest in the biocidal nature of organotin compounds embraces two themes, namely the synthesis of novel compounds incorporating SnR_n (R = alkyl or aryl) and independently active ligands,[1-3] and the structural analysis of phenyl- and cyclohexyl-tin compounds in general,[3-6] these classes forming the basis of many of the commercial tin-based fungicides and acaricides.[7] The latter area is typified by our structural studies of organotin carboxylates[8] and we have reported the structure of triphenyltin acetate[4] which is active against potato blight (*Phytophthora infestans*) and available as Brestan (Hoechst A G).

In addition to their biocidal importance, organotin carboxylates have occupied a pivotal position in the development of the understanding of structural organotin chemistry and our contributions cited above are only a few of the multitude of available reports embracing *ca.* 20 crystal structure determinations[9] and numerous spectroscopic studies.[10] The outcome of this is a clear preference for the carboxylate-bridged polymer architecture (**1**), while excessive steric bulk of the hydrocarbon groups bonded to tin[11] or of the carboxylic acid[12] can obviate bidentate ligand behaviour and result in the tetrahedral structure (**2**) for which there is only one clear-cut crystallographic report.[3] More recent structural work has made claims for the *cis*-O_2SnR_3 variation (**3**)[13-15] but the distinctions between this and (**2**) are often, in our view, too small to be unambiguous.[8]

Two important themes relating to these structures, however, remain unresolved. Firstly, what factors dictate the formation of (**1**)—(**3**), particularly those leading to the formation of the chelated monomer (**3**) rather than the bridged polymer (**1**)? This question is not merely of academic importance, since it has been shown in some instances that biocidal activity is significantly less for type (**3**) structures than either (**1**) or (**2**).[16] Secondly, how are polymers of type (**1**) formed; what geometric factors undergo distortions and by how much as a result of this process, and how do these distortions manifest themselves in the lattice dynamics of the solid? This report addresses itself to this latter question, and we present structural data for triphenyltin formate for comparison with the analogous acetate. In addition we have probed the lattice dynamics of a series of triorganotin formates and acetates (R = Me, Ph, or cyclo-C_6H_{11}) by variable-temperature Mössbauer spectroscopy (v.t.M.s.) and include our findings herein.



(**1**)



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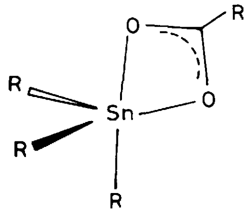

(**3**)

Experimental

Triphenyl- and tricyclohexyl-stannyl esters of acetic and formic acids were prepared by azeotropic dehydration of mixtures of organotin hydroxide and the carboxylic acid in refluxing toluene, as was trimethyltin formate. Trimethyltin acetate was prepared from the metathesis of sodium acetate and trimethyltin chloride in water. The product, which is insoluble in water, was isolated by filtration and recrystallised from boiling toluene. Full analytical data for all compounds are given in Table 1.

Variable-temperature Mössbauer Spectroscopy.—Details of our Mössbauer spectrometer, cryostat, and temperature con-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Analytical and Mössbauer data for triorganotin acetates and formates

Compound	C[a]	H[a]	M.p.[b] (°C)	I.s.[c,d]	Q.s.[c,d]
(**4**) $SnPh_3(O_2CH)$	57.60 (57.75)	4.00 (4.10)	206—207 (201)[e]	1.48 (1.37)	3.48 (3.58)
(**5**) $SnPh_3(O_2CMe)$	58.35 (58.70)	4.40 (4.45)	120—121 (121—122)	1.28 (1.28)	3.35 (3.36)
(**6**) $Sn(C_6H_{11})_3(O_2CH)$	55.25 (55.25)	8.65 (8.30)	152—153	1.59	3.79
(**7**) $Sn(C_6H_{11})_3(O_2CMe)$	56.45 (56.25)	8.45 (8.50)	61—63 (61—63)	1.59 (1.57)	3.35 (3.27)
(**8**) $SnMe_3(O_2CH)$	22.90 (23.00)	4.85 (4.85)	148—150 (147—148)[f]	1.32	3.59
(**9**) $SnMe_3(O_2CMe)$	27.10 (26.95)	5.35 (5.45)	193—195 (197—198)	1.34 (1.30)	3.58 (3.57)

[a] Required values given in parentheses. [b] Literature values in parentheses taken from R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, **60**, 459, unless stated otherwise. [c] Values in mm s^{-1} (± 0.03 mm s^{-1}). [d] Literature values in parentheses taken from J. N. R. Ruddick, *Rev. Silicon, Germanium, Tin Lead Comp.*, 1976, **2**, 115. [e] Ref. 12. [f] Ref. 26.

Table 2. Final fractional positional parameters ($\times 10^5$ for Sn; $\times 10^4$ for remaining atoms) for (**4**) with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Sn(1)	33 627(3)	24 029(4)	32 243(3)	C(33)	3 801(8)	19(8)	4 205(6)
Sn(2)	41 378(3)	23 073(4)	6 976(2)	C(34)	4 386(7)	−276(7)	3 963(7)
O(1)	2 841(3)	2 321(4)	−910(3)	C(35)	4 697(7)	191(7)	3 519(6)
O(2)	3 705(3)	2 329(4)	−283(2)	C(36)	4 403(5)	928(6)	3 298(5)
O(3)	4 638(3)	2 406(4)	1 597(3)	C(41)	5 057(4)	2 648(5)	289(3)
O(4)	3 816(3)	2 206(4)	2 267(2)	C(42)	5 647(4)	2 426(6)	550(4)
C(1)	3 107(5)	2 251(7)	−395(4)	C(43)	6 249(5)	2 573(6)	289(5)
C(2)	4 371(5)	2 447(6)	2 108(4)	C(44)	6 267(5)	3 026(7)	−252(5)
C(11)	2 433(4)	2 203(5)	2 807(3)	C(45)	5 685(5)	3 256(6)	−540(5)
C(12)	1 878(5)	2 713(7)	2 947(5)	C(46)	5 081(4)	3 079(6)	−266(4)
C(13)	1 266(5)	2 519(8)	2 673(6)	C(51)	3 447(4)	3 283(5)	924(4)
C(14)	1 206(6)	1 864(8)	2 249(6)	C(52)	3 578(5)	4 129(7)	785(5)
C(15)	1 733(6)	1 379(8)	2 121(5)	C(53)	3 109(7)	4 752(7)	914(7)
C(16)	2 346(5)	1 531(7)	2 402(5)	C(54)	2 532(7)	4 555(7)	1 180(5)
C(21)	3 805(4)	3 627(5)	3 192(4)	C(55)	2 396(5)	3 737(8)	1 334(5)
C(22)	4 303(5)	3 872(7)	3 590(5)	C(56)	2 856(4)	3 086(6)	1 213(4)
C(23)	4 570(7)	4 720(9)	3 534(7)	C(61)	3 893(4)	988(5)	761(4)
C(24)	4 323(9)	5 264(8)	3 088(7)	C(62)	3 656(6)	633(6)	1 282(5)
C(25)	3 845(7)	5 041(7)	2 703(6)	C(63)	3 483(7)	−274(7)	1 300(7)
C(26)	3 587(5)	4 210(6)	2 753(5)	C(64)	3 562(8)	−728(8)	788(8)
C(31)	3 818(5)	1 238(5)	3 529(4)	C(65)	3 827(9)	−398(9)	289(7)
C(32)	3 519(5)	771(6)	3 989(5)	C(66)	3 968(8)	470(7)	254(5)

troller, along with the method of data acquisition and manipulation are given elsewhere.[4] In a typical experiment, spectra for a sample containing 0.5—1.0 mg ^{119}Sn cm^{-2} were collected in the temperature range 78—150 K, over a period of *ca.* 12 h. Data for $SnPh_3(O_2CR')$ ($R' = H$ or Me) are shown in Figure 1 and typify the quality obtained in all cases.

Crystal Structure of Triphenyltin Formate.—Crystals suitable for *X*-ray diffraction were obtained by slow cooling of a hot toluene solution.

Crystal data. $C_{19}H_{16}O_2Sn$, $M = 395.0$, monoclinic, space group $B2_1/a$ (non-standard setting of $P2_1/c$), $a = 20.176(8)$, $b = 15.539(6)$, $c = 21.952(10)$ Å, $\beta = 90.30(6)°$, $U = 6\,882.2$ Å^3, $Z = 16$ (two independent molecules in the asymmetric unit), $D_c = 1.53$, $D_m = 1.54$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 1.36$ mm^{-1}, $F(000) = 3\,136$.

Data collection and refinement. A crystal of approximate dimensions 0.10 × 0.30 × 0.35 mm was used for data collection and was mounted with the *b* axis coincident with the rotation (ω) axis of a Stöe Stadi-2 two-circle diffractometer. 4 282 Unique reflections were collected with $2\theta < 45°$ of which 3 413 had $I > 3\sigma(I)$ and were considered as observed and used in the subsequent analysis. Corrections were made for Lorentz and polarisation effects, but not for absorption.

The structure was solved by conventional Patterson and Fourier methods. All the hydrogen atoms were located, and the ring hydrogens given ideal geometry (C–H 1.08 Å) while the formyl hydrogen positions were not refined. Scattering factors were calculated using an analytical expression[17] and the weighting scheme adopted was $w = 3.9417/[\sigma^2(F_o) + 0.0002(F_o)^2]$. The phenyl hydrogens were given common isotropic thermal parameters which refined to final values of $U =$

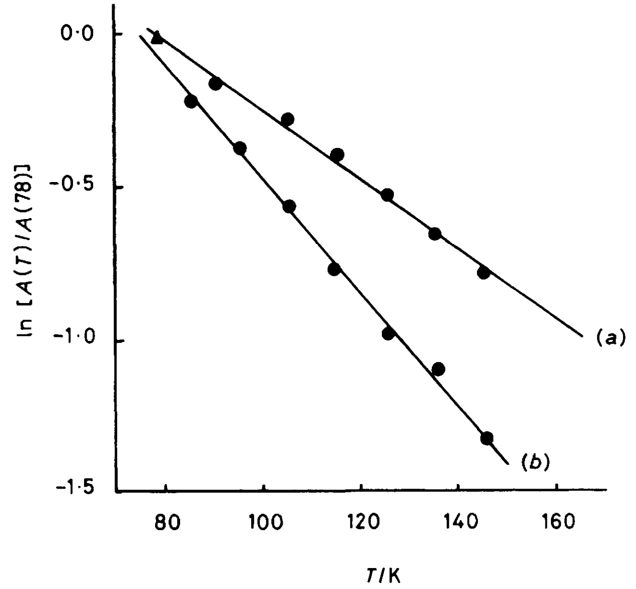


Figure 1. Variable-temperature Mössbauer spectroscopic data for (*a*) (**4**) and (*b*) (**5**). The point ▲ (78,0.0) is common to both plots

Table 3. Selected bond distances (Å) and angles (°) for (**4**) with e.s.d.s in parentheses[a]

Bond distances

Sn(1)–O(1′)	2.219(6)	Sn(2)–O(3)	2.219(6)	Sn(1)–C(31)	2.136(9)	Sn(2)–C(61)	2.113(8)
Sn(1)–O(4)	2.317(6)	Sn(2)–O(2)	2.318(5)	C(1)–O(1)	1.253(11)	C(2)–O(3)	1.248(11)
Sn(1)–O(2′)	3.372(6)	Sn(2)–O(4)	3.513(6)	C(1)–H(1)[b]	1.077	C(2)–H(2)[b]	0.876
Sn(1)–C(11)	2.105(8)	Sn(2)–C(41)	2.130(8)	C(1)–O(2)	1.235(11)	C(2)–O(4)	1.232(12)
Sn(1)–C(21)	2.102(9)	Sn(2)–C(51)	2.121(9)				

Bond angles

O(4)–Sn(1)–O(1′)	173.6(2)	O(2)–Sn(2)–O(3)	173.1(2)	C(21)–Sn(1)–C(31)	126.5(3)	C(51)–Sn(2)–C(61)	121.6(3)
O(4)–Sn(1)–O(2′)	144.9(2)	O(2)–Sn(2)–O(4)	147.2(2)	Sn(1)–O(1′)–C(1′)	125.9(6)	Sn(2)–O(3)–C(2)	127.3(6)
O(4)–Sn(1)–C(11)	86.6(3)	O(2)–Sn(2)–C(41)	86.0(3)	Sn(1)–O(2′)–Sn(2′)	168.0(1)	Sn(2)–O(4)–Sn(1)	163.6(1)
O(4)–Sn(1)–C(21)	85.4(3)	O(2)–Sn(2)–C(51)	87.8(3)	Sn(1)–O(2′)–C(1′)	67.9(6)	Sn(2)–O(4)–C(2)	62.3(6)
O(4)–Sn(1)–C(31)	90.1(3)	O(2)–Sn(2)–C(61)	89.3(3)	O(1)–C(1)–H(1)[b]	111.4	O(3)–C(2)–H(2)[b]	110.5
O(1′)–Sn(1)–O(2′)	40.5(2)	O(3)–Sn(2)–O(4)	38.3(2)	O(1)–C(1)–O(2)	125.8(9)	O(3)–C(2)–O(4)	129.6(9)
O(1′)–Sn(1)–C(11)	88.6(3)	O(3)–Sn(2)–C(41)	88.0(3)	O(2)–C(1)–H(1)[b]	121.2	O(4)–C(2)–H(2)[b]	115.9
O(1′)–Sn(1)–C(21)	93.3(3)	O(3)–Sn(2)–C(51)	92.2(3)	Sn(1)–C(11)–C(12)	122.0(6)	Sn(2)–C(41)–C(42)	121.3(6)
O(1′)–Sn(1)–C(31)	95.8(3)	O(3)–Sn(2)–C(61)	96.5(3)	Sn(1)–C(11)–C(16)	120.1(6)	Sn(2)–C(41)–C(46)	121.6(6)
O(2′)–Sn(1)–C(11)	128.2(3)	O(4)–Sn(2)–C(41)	126.1(3)	Sn(1)–C(21)–C(22)	122.4(7)	Sn(2)–C(51)–C(52)	120.2(7)
O(2′)–Sn(1)–C(21)	80.6(3)	O(4)–Sn(2)–C(51)	71.2(3)	Sn(1)–C(21)–C(26)	118.7(7)	Sn(2)–C(51)–C(56)	121.1(7)
O(2′)–Sn(1)–C(31)	73.4(3)	O(4)–Sn(2)–C(61)	81.3(3)	Sn(1)–C(31)–C(32)	119.0(7)	Sn(2)–C(61)–C(62)	122.2(7)
C(11)–Sn(1)–C(21)	119.8(3)	C(41)–Sn(2)–C(51)	119.7(3)	Sn(1)–C(31)–C(36)	123.3(7)	Sn(2)–C(61)–C(66)	119.1(7)
C(11)–Sn(1)–C(31)	113.1(3)	C(41)–Sn(2)–C(61)	118.2(3)				

[a] Primes indicate atoms at *x*, 0.5 − *y*, 0.5 + *z*. [b] No errors are given for bond distances and angles involving the formyl hydrogens, whose positions were not refined.

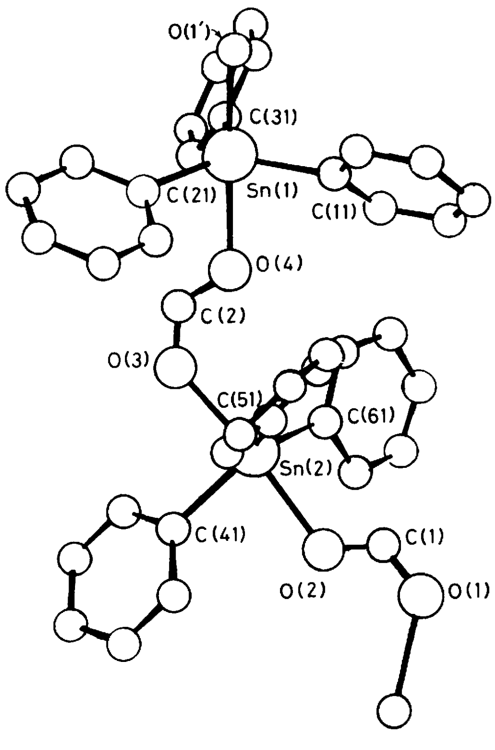


Figure 2. The asymmetric unit (two molecules) of (**4**) showing the labelling scheme used. Hydrogen atoms have been omitted for clarity

0.091(11) and 0.144(16) $\mathring{A}^2$ for H(12)—H(36) and H(42)—H(66) respectively. Isotropic thermal parameters applied to the formyl hydrogens refined to final values of $U = 0.104(40)$ and 0.041(22) $\mathring{A}^2$ for H(2) and H(1) respectively. All other atoms were given anisotropic thermal parameters and least-squares refinement gave final values of $R = 0.047$ and $R' = 0.047$. Scattering factors were taken from ref. 17. All calculations were performed on an IBM 4341 computer using SHELX.[18] Final fractional atomic co-ordinates for non-hydrogen atoms are given in Table 2, bond distances and angles in Table 3. Tables of hydrogen atom positions, thermal parameters, and structure factors are available upon request from the authors (I. W. N.). The asymmetric unit, including the labelling scheme employed, is shown in Figure 2.

Discussion

The Structure of Triphenyltin Formate.—The asymmetric unit of triphenyltin formate consists of two independent molecules of virtually identical structure (Figure 2), which is similar to that of the corresponding acetate.[4] The geometry about tin is that of a mildly distorted trigonal bipyramid, with the ligands disposed in a *trans*-O_2SnR_3 manner. The α-carbons of the phenyl rings occupy the equatorial positions [Σ(C–Sn–C) = 359.4°, Sn(1); 359.5°, Sn(2)] with the more electronegative oxygen atoms in the axial sites. This arrangement demands bidentate, bridging behaviour from the formate ligand leading to a chain polymeric structure propagating along *c* (Figure 3). As with triphenyltin acetate the three-dimensional structure of the polymer chain can be described as a flattened helix, but differences are discernible in the two chain structures which are highlighted by the v.t.M.s. experiment, discussed in detail below.

The formate ligands bridge in an anisobidentate fashion [Sn(1)–O(1′) 2.219(6), Sn(1)–O(4) 2.317(6), Sn(2)–O(3) 2.219(6), Sn(2)–O(2) 2.318(5) Å]; this is the most symmetrical arrangement yet observed in carboxylate-bridged triorganotin species (Table 4). The two C–O bonds within each of the pair of formyl groups are essentially equal [$d(\text{C–O}) - d(\text{C=O}) < 3\sigma(d)$] implying complete delocalisation of π-electron density over the CO_2– moiety, in full accord with the pattern of Sn–O bond distances (see above). In contrast to $SnPh_3(O_2CMe)$, there is no evidence for co-ordination expansion at tin to six, which in the acetate arises from weak chelation by the formally bridging oxygen to the metal from which the ligand emanates.[4] This manifests itself in a large C–Sn–C opening (135.2°) in the vicinity of the chelating oxygen and an equalising of C–O bond lengths in the acetate ligand despite a markedly anisobidentate arrangement of Sn–O bonds. In $SnPh_3(O_2CH)$ (**4**) the chelating

Table 4. Collected structural data for carboxylate-bridged triorganotin compounds $SnR_3(O_2CR')$

R	R′	Sn–O(1)/Å	Sn–O(2) (inter)/Å	Sn–O(2) (intra)/Å	O(1)–C(1)–O(2)/Å	α/°	β/°
Me	Me[a]	2.205(3)	2.391(4)	3.23	1.269(5), 1.240(6)	122.5(3)	136.6(3)
Me	CF_3[a]	2.177(14)	2.458(15)	3.30	1.28(2), 1.21(2)	121(1)	147(1)
Me	$CH_2CO_2SnMe_3$[b]	2.19(1)	2.46(2)	3.16	1.27(3), 1.22(3)	121(1)	152(1)
		2.17(1)	2.44(2)	3.12	1.28(3), 1.28(3)	121(1)	139(1)
$CH=CH_2$	Me[c]	2.20(1)	2.33(1)			119	138
$CH=CH_2$	CH_2Cl[c]	2.21(1)	2.34(1)			119	137
$CH=CH_2$	CCl_3[d]	2.17(2)	2.49(1)	3.30	1.25(2), 1.21(2)	122.8(8)	157.4(7)
$CH=CH_2$	$Fe(C_5H_5)(C_5H_4)$[e]	2.12(1)	2.42(1)	3.21	1.27(1), 1.21(2)	123(1)	156(1)
Ph	H[f]	2.219(6)	2.317(6)	3.372(6)	1.253(11), 1.235(11)	125.9(6)	123.1
		2.219(6)	2.318(5)	3.513(6)	1.248(11), 1.232(12)	127.3(6)	125.5
Ph	Me[g]	2.185(3)	2.349(3)	3.206(3)	1.263(5), 1.251(5)	121.0(2)	142.7(2)
$PhCH_2$	Me[h]	2.14(2)	2.65(2)	3.23(3)	1.31(4), 1.21(4)	123.9	131.7
C_6H_{11}	Me[i]	2.12(3)	3.84	2.95(4)	1.39(8), 1.25(9)	124.9	146.9
C_6H_{11}	CF_3[j]	2.08(4)	3.70	3.11	1.28(4), 1.20(5)	122(2)	159

[a] Ref. 24. [b] U. Schubert, *J. Organomet. Chem.*, 1978, **155**, 285. [c] G. Valle, V. Peruzzo, D. Marton, and P. Ganis, *Cryst. Struct. Commun.*, 1982, **11**, 595. [d] S. Calogero, D. A. Clemente, V. Peruzzo, and G. Tagliavini, *J. Chem. Soc., Dalton Trans.*, 1979, 1172. [e] R. Graziani, U. Casellato, and G. Plazzogna, *J. Organomet. Chem.*, 1980, **187**, 381. [f] This work. [g] Ref. 4. [h] N. W. Alcock and R. E. Timms, *J. Chem. Soc. A*, 1968, 1873. [i] Ref. 22. [j] Ref. 23.

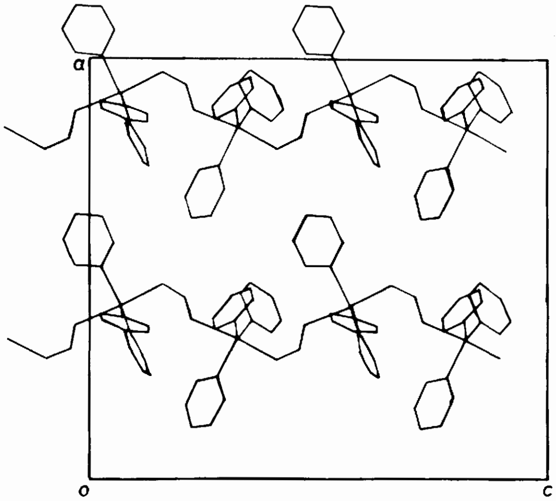
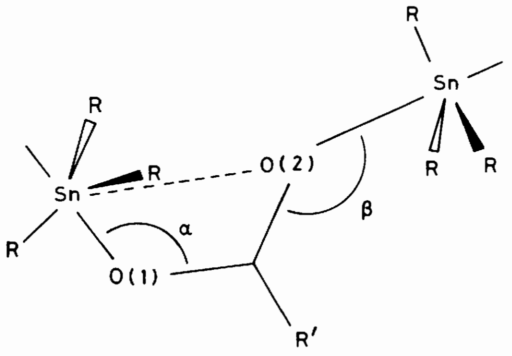


Figure 3. The unit-cell contents of (**4**) viewed along *b*, showing polymer propagation along *c*



Sn–O interactions [3.372(6), 3.513(6) Å] are significantly longer than the same bond in the acetate [3.206(3) Å];[4] moreover the largest angles C–Sn–C [126.5(3), 121.6(3)°] indicate that any bonding interaction of a chelating nature is, at best, marginal.

Mössbauer quadrupole splitting (q.s.) values for triphenyltin formate and acetate (Table 1) are larger for the former, in line with trends observed for trimethyl- and triphenyl-tin halogenoacetates in which an increase in q.s. occurs with increasing strength of the carboxylic acid.[19,20] It has been suggested that this trend arises from an increase in asymmetry of the two Sn–O bonds with increasing σ* (Taft inductive factor) of the carboxylate group, *i.e.* increasing acid strength. The structural results presented here show that this is not the case, and that although formic acid is stronger than acetic (pK_a = 3.75 and 4.76 respectively) the Sn–O bonds are *more* symmetrical in $SnPh_3(O_2CH)$. An alternative rationale for the trends in q.s. values lies not in the relationship with Sn–O bond asymmetry, but with the electronegativity of the acid. The stronger acids, being more electron withdrawing, cause greatest rehybridisation of bonding electron density in the orbitals about tin, concentrating *p*-character in the axially directed orbitals. It is the balance of *s,p,d*-character of the hybrid orbitals at tin which is most polarised with strongly electron-withdrawing ligands that leads to increases in q.s. The correlation with Sn–O bond asymmetry, which has been supported by numerous examples (Table 4) is purely fortuitous, and arises because of the increased steric demands of the stronger acids studied, *e.g.* CH_3CO_2H *vs.* CCl_3CO_2H, which inhibit close approach of molecules, thus leading to unusually long bridging Sn–O bonds. In the present study, acid strength is increased without increasing the steric requirements of the ligand, and the underlying cause of the q.s. trend revealed.

Variable-temperature Mössbauer Spectroscopy.—This provides a probe of the vibrational freedom of the Mössbauer-active atom (in this case ^{119}Sn) and hence indirectly the state of lattice association. Equations (1) and (2) underlie the theory, in which $f(T)$ is the recoil-free fraction of the absorber at temperature T, $\langle x(T)^2 \rangle$ the mean-square amplitude of vibration of the tin, λ the wavelength of the Mössbauer transition divided by 2π, E_R the Mössbauer recoil energy, and θ_D the Debye temperature of the lattice.

$$f(T) = \exp[-\langle x(T)^2 \rangle / \lambda^2] \qquad (1)$$

$$\mathrm{d}f(T)/\mathrm{d}T = \mathrm{d}\exp(-6E_R T/k\theta_D{}^2)/\mathrm{d}T \qquad (2)$$

For 'thin absorbers', $A(T)$, the area under the spectral envelope, and $f(T)$ are linearly related and plots of ln $[A(T)/A(78)]$ *vs.* T are linear. Normalisation of data to 78 K is merely to facilitate intersample comparison. The slope of these plots, $a = -\mathrm{d} \ln A(T)/\mathrm{d}T$, characterises the degree of lattice associ-

Table 5. Variable-temperature Mössbauer spectroscopic data for triorganotin formates and acetates

Compound	Range of T/K	$-r^a$	10^2a/K^{-1}
(**4**) $SnPh_3(O_2CH)$	78—145	0.997 (7)	1.15
(**5**) $SnPh_3(O_2CMe)$	78—145	0.998 (8)	1.91
(**6**) $Sn(C_6H_{11})_3(O_2CH)$	78—150	0.992 (10)	0.93
(**7**) $Sn(C_6H_{11})_3(O_2CMe)$	78—145	0.997 (7)	1.59
(**8**) $SnMe_3(O_2CH)$	78—140	0.998 (8)	1.90^b
(**9**) $SnMe_3(O_2CMe)$	78—140	0.996 (8)	1.62

[a] Correlation coefficient for stated number of data points (in parentheses). [b] Quoted as 2.15 K^{-1} in S. Matsubara, M. Katada, K. Sato, I. Motoyama, and H. Sano, *J. Phys. Coll.*, 1979, C2.

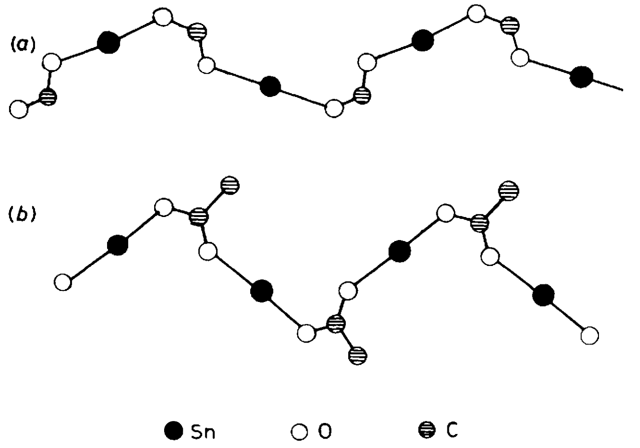


Figure 4. Polymer propagation for (*a*) (**4**) and (*b*) (**5**). Only atoms forming the polymer backbone are shown to highlight the more linear character of the formate chain

ation and is dependent upon (*i*) monomer *vs.* polymer formation, (*ii*) the strength of bridging bonds within the polymer, and (*iii*) the spacial distribution (tertiary structure[21]) of the polymer, with smaller a corresponding to a more rigid lattice. We have found[21] that helical (Class 4) or S-shaped (Class 3) polymers afford tin a vibrational freedom akin to that of a monomer, but this is sequentially restricted in zig-zag (Class 2) or rod (Class 1) polymers which are more linear in nature.

Variable-temperature Mössbauer data for three organotin formate/acetate pairs are given in Table 5, and shown pictorially for the triphenyltin derivatives in Figure 1. For both triphenyl- and tricyclohexyl-tin pairs [(**4**)/(**5**) and (**6**)/(**7**) respectively] the lattice formed by the formate is significantly stiffer than the acetate, as evidenced by a lower a value in each case. The value of $10^2a = 1.91$ K^{-1} for (**5**) is typical of a Class 3 polymer in keeping with its own structure.[4] The structure of (**4**) is ostensibly similar to that of the acetate, and while the shorter bridging Sn–O bond for the former [2.317(6), 2.318(5) *vs.* 2.349(3) Å] would be expected to lead to a reduction in a, it does not appear significant enough a difference to lower a (more rigid lattice) to the value observed ($10^2a = 1.15$ K^{-1}). We believe that the rigidity of the polymer derives substantially from its more linear character (Figure 4) and can be best described as having Class 2 (zig-zag) characteristics. Typical 10^2a values for Class 2 triphenyltin compounds are 1.49 (fluoride), 1.10 (hydroxide), and 1.04 K^{-1} (1,2,4-triazol-1-yl).[21]

Consideration of the collected structural data for polymeric triorganotin carboxylates (Table 4) reveals those parameters which are most variable as a result of polymer formation and hence underlie the v.t.M.s. behaviour. Clearly the bulkier hydrocarbon moieties bonded to tin inhibit close approach of molecules, and hence long intermolecular Sn–O linkages result. Tricyclohexyltin acetate[22] and trifluoroacetate[23] demonstrate this phenomenon markedly, and represent a well advanced position along the polymer–monomer dissociation pathway. Indeed, previous authors have considered these species (erroneously[13]) to be non-associated. Steric bulk of the substituents on the α-carbon of the carboxylate group also causes a lengthening of the intermolecular Sn–O bond, but this effect does not manifest itself at long Sn–O distances, *cf.* $Sn(C_6H_{11})_3(O_2CCX_3)$ (X = H or F), Table 4. Within the carboxylate group the α angle (Table 4) is largely insensitive (119—127.3°) and it is the β angle which accommodates the steric requirements of the carboxylate substituents. This angle varies between 123 and 159° for the available data, and is a minimum (123.1, 125.5) for triphenyltin formate. Moreover, it is the steric requirements of the methyl group in $SnPh_3(O_2CMe)$, which opens β to 142.7°, that induces the flexibility into the polymer chain, as reflected in the v.t.M.s. experiment.

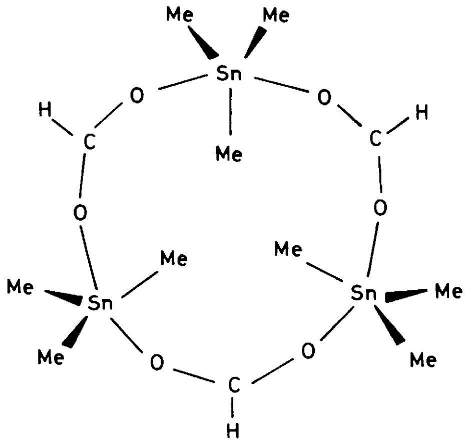
It is likely that the rationale provided above for the pair of triphenyltin carboxylates also holds for the tricyclohexyltin analogues, and that it is the tertiary structure of the polymer that determines the v.t.M.s. behaviour in these systems, not, as we had previously speculated,[21] a strengthening of the intramolecular, chelating Sn–O interaction [Table 4, Sn–O(2) (intra)].

In contrast, v.t.M.s. data for the trimethyltin formate/acetate pair are less easy to rationalise; here the acetate ($10^2a = 1.62$ K^{-1}) shows a more rigid lattice than the formate ($10^2a = 1.90$ K^{-1}). Trimethyltin acetate is polymeric and of Class 3 architecture,[24] and its a value is consistent with this, although it is somewhat lower than might have been anticipated from the a value for $SnPh_3(O_2CMe)$. To the extent to which this difference is significant, it may be due to the more linear nature of the trimethyltin acetate as measured by the α and β angles which are 122.5(3), 136.6(3)° and 121.0(2), 142.7(2)° respectively for the methyl and phenyltin compounds. On the basis of the v.t.M.s. behaviour of $SnR_3(O_2CH)$ (R = Ph or C_6H_{11}), the structure of *polymeric* $SnMe_3(O_2CH)$ should show a more, not less, rigid lattice than the corresponding acetate. The resolution of this paradox must lie in the observation that solid trimethyltin formate can exist in two markedly different forms: one form is virtually insoluble in organic solvents while the second form is very soluble, *ca.* 200 mg cm^{-3} in chloroform.[25,26] Both forms are sublimable in a high vacuum, reportedly without interconversion. It has been proposed[26] that the soluble form exists in solution (*e.g.* chloroform or cyclohexane) in a cyclic, associated form in equilibrium with free monomer, and that the cyclic form, such as the cyclic trimer (**10**), persists in the solid state. A linear polymeric structure, on the other hand, has been attributed to the insoluble form (ref. 26 and refs. therein) and an incomplete *X*-ray structure for trimethyltin formate[27] shows planar $SnMe_3$ groups and O_2CH groups arranged alternately along a helical chain.

The sample of trimethyltin formate used in the present v.t.M.s. experiment was very readily soluble in chloroform at room temperature, and, on the basis of v.t.M.s. systematics,[21,28] its high a value is entirely consistent with the hypothesis[26] that the soluble form exists as small cyclic systems in the solid state.

Trimethyltin acetate has also been observed in two forms, one relatively insoluble, the other soluble in organic solvents such as chloroform.[26] The sample examined in the present study was only sparingly soluble in chloroform and thus probably has the one-dimensional, helical polymeric structure reported in the crystallographic study.[24]

The insoluble form of $SnMe_3(O_2CH)$ was originally prepared by mixing stoicheiometric quantities of $SnMe_3(OH)$ and formic



(10)

acid and purified by sublimation,[25,26] and was converted to soluble trimethyltin formate by heating in a sealed ampoule with cyclohexane at 90 °C for 12—24 h.[26] The material used in the present study was prepared by refluxing reagents in toluene in a Dean and Stark apparatus. The formation of small cyclic systems rather than a polymer is favoured because of an increase in entropy[26] and is free to occur in higher temperature preparations as in the literature method or the preparation used herein (refluxing toluene). $SnMe_3(O_2CMe)$ was obtained in its insoluble and soluble forms in the same manner as the formate,[26,27] and the material in the present study was prepared from aqueous solutions of sodium acetate and trimethyltin chloride at room temperature followed by recrystallisation from toluene. It would seem reasonable to assume that the low-temperature route to $SnMe_3(O_2CMe)$ used in this study would parallel the mixing of neat reagents and yield the insoluble (polymeric) form of the compound.

Conclusions

Triphenyltin formate is a carboxylate-bridged polymer with a similar structure to that of the corresponding acetate. Variable-temperature Mössbauer spectroscopy highlights differences in the detail of polymer construction between the two compounds, and results underline the importance of considering the tertiary structure of the polymer in assessing data from this spectroscopic method.

Acknowledgements

We gratefully acknowledge financial support from the National Board for Science and Technology (Ireland), and the S.E.R.C. (U.K.) for equipment grants (to I. W. N.).

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Received 27th January 1986; *Paper* 6/187