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The repeat distance in carboxylate-bridged triorganotin(IV) carboxylate polymers

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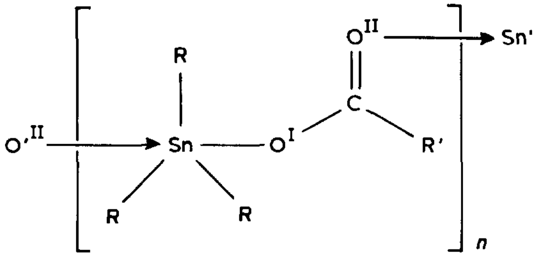
Abstract

An analysis of X-ray data for seventeen polymeric triorganotin(IV) carboxylates gives a repeat distance of 5.19 ± 0.21 Å for the carboxylate-bridged $R_3SnOC(O)R'$ unit that defines the crystal lattice. The repeat distance is insensitive to the organic substituents on either the tin or carboxylate group. Tricyclohexyltin acetate and tricyclohexyltin trifluoroacetate are reclassified as weakly associated polymers.

Introduction

Triorganotin(IV) carboxylates in which the carboxylate groups do not carry other basic sites are generally associated in the solid state through carboxylate bridging [1–4]. Their structures can be probed by ^{119m}Sn Mössbauer spectroscopy [5] and information on lattice dynamics can be obtained by recording the spectra at varying temperatures [6]. In the crystal lattice, the $Sn–O^I–C$ angle is generally 120°, but the $C–O^{II}–Sn'$ angle can open up to accommodate more bulky R' groups [7]:



This feature is exemplified in the following seventeen triorganotin esters which have been crystallographically characterized: trimethyltin formate [8], -acetate [9], trifluoroacetate [9], -4-amino- [10], -2-dimethylamino- [10], -2-methoxy- [11] and -2-chloro- [10] -benzoates, dimethylphenyltin acetate [12], trivinyltin acetate [13], -chloro-

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Table 1

Structural data for triorganotin carboxylate polymers

Triorganotin in Carboxylate	$Sn-O^I$ (Å)	O^I-C (Å)	$C-O^{II}$ (Å)	$Sn\cdots O^{II}$ (Å)	$Sn'-O^{II}$ (Å)	$Sn-O^I-C$ (°)	$C-O^{II}-Sn'$ (°)	$O^I-Sn-O'^{II}$ (°)	$\Sigma C-Sn-C$ (°)	Ref.
Me_3SnO_2CMe	2.205	1.269	1.240	3.23	2.391	122.5	136.6	171.6	359.5	9
$Me_3SnO_2CCF_3$	2.177	1.28	1.21	3.30	2.458	121	147	174.8	359.1	9
$Me_3SnO_2CC_6H_4$-4-$NH_2\cdot C_6H_6$	2.169	1.28	1.25	3.157	2.477			173.5	357.8	10
	2.168	1.28	1.25	3.357	2.416			174.1	358.8	
$Me_3SnO_2CC_6H_4$-2-NMe_2	2.201	1.271	1.243	3.224	2.426			170.0	358.8	10
$Me_3SnO_2CC_6H_4$-2-OMe	2.208	1.262	1.241	3.110	2.381	118.0		170.8	359.1	11
$Me_3SnO_2CC_6H_4$-2-Cl	2.200	1.277	1.219	3.143	2.414			174.2	359.2	10
Me_2PhSnO_2CMe	2.202	1.252	1.256		2.374	121.4	136.7	174.0	359.1	12
$(CH_2{=}CH)_3SnO_2CMe$	2.20				2.33	119	138	172.7	359.6	13
$(CH_2{=}CH)_3SnO_2CCH_2Cl$	2.21				2.34	119	137	174.3	359.6	13
$(CH_2{=}CH)_3SnO_2CCCl_3$	2.17	1.25	1.21	3.30	2.49	122.8	157.4	173.4	358.6	14
$(CH_2{=}CH)_3SnO_2C(C_5H_4FeC_5H_5)$	2.12	1.27	1.21	3.21	2.42	123	156	172.5	357	15
n-$Bu_3SnO_2CCH_2SC(S)NMePh$	2.190	1.248	1.253	3.199	2.393	121.5	142.6	173.9	359.2	16
Bz_3SnO_2CMe	2.14	1.31	1.21	3.23	2.65	123.9	131.7	168.6	357.4	17
Ph_3SnO_2CH	2.219	1.253	1.235	3.372	2.317	125.9	123.1	173.6	359.4	7
	2.219	1.248	1.232	3.513	2.318	127.3	125.5	173.1	359.5	
Ph_3SnO_2CMe	2.185	1.263	1.251	3.206	2.349	121.0	142.7	173.6	359.4	18
$Ph_3SnO_2CC_6H_4$-2-Cl	2.201	1.261	1.250	3.649	2.384	135.9		173.76	359.8	19

acetate [13], -trichloroacetate [14] and -ferrocenecarboxylate [15], tri-n-butyltin methylphenyldithiocarbamylacetate [16], tribenzyltin acetate [17], triphenyltin formate [7], -acetate [18] and -2-chlorobenzoate [19].

In this report, we show that the distinguishing feature in these structures is the constancy of the repeat distance, defined by the ratio of the unit cell length that is parallel to the axis of propagation of the polymer to the number of monomeric units this length covers.

Discussion

Table 1 lists the structural data and Table 2 the unit cell parameters and calculated repeat distances for the triorganotin carboxylate polymers.

The structures are characterized by a short Sn–O^I and a long intermolecular Sn′–O^{II} bond. The coordination polyhedron around the tin is essentially a trigonal bipyramid, with a planar C_3Sn girdle (sum of C–Sn–C angles ranges from 357 to 360°) and a near linear O^I–Sn–O'^{II} skeleton (range of angles is from 170 to 174°).

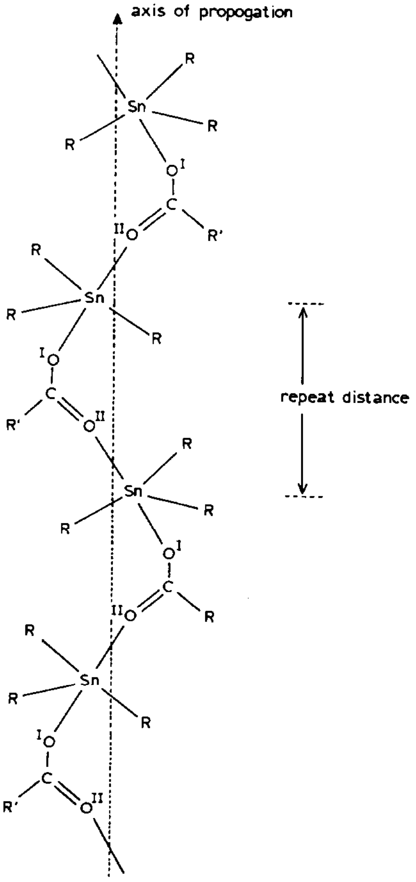


Fig. 1. Propagation of the triorganotin carboxylate polymer along the 2_1 screw axis.

Table 2

Repeat distance in triorganotin carboxylate polymers

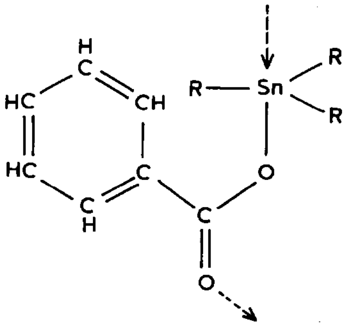
Triorganotin carboxylate	Space group	Parallel axis of propagation	Unit cell axial length (Å)	Number of monomeric units	Axial length per monomeric unit (Å)	Ref.
Me_3SnO_2CH		*a*	10.60	2	5.30	8
Me_3SnO_2CMe	*Pnma*	*a*	10.516	2	5.258	9
$Me_3SnO_2CCF_3$	*Pnma*	*a*	10.567	2	5.284	9
$Me_3SnO_2CC_6H_4$-4-$NH_2 \cdot C_6H_6$	$P2_1/n$	*b*	10.029	2	5.015	10
$Me_3SnO_2CC_6H_4$-2-NMe_2	$P2_1/n$	*b*	9.882	2	4.941	10
$Me_3SnO_2CC_6H_4$-2-CMe	$P2_1/n$	*b*	9.993	2	4.997	11
$Me_3SnO_2CC_6H_4$-2-Cl	$P2_1/n$	*b*	10.461	2	5.231	10
Me_2PhSnO_2CMe	*Pabc*	*a*	10.068	2	5.034	12
$(CH_2{=}CH)_3SnO_2CMe$	$P2_1/n$	*b*	10.027	2	5.014	13
$(CH_2{=}CH)_3SnO_2CCH_2Cl$	$P2_1/n$	*b*	10.137	2	5.069	13
$(CH_2{=}CH)_3SnO_2CCCl_3$	$I2/a$	*b*	10.267	2	5.134	14
$(CH_2{=}CH)_3SnO_2C(C_5H_4FeC_5H_5)$	$P2_1/a$	*b*	10.030	2	5.015	15
n-$Bu_3SnO_2CCH_2SC(S)MNePh$	$P2_1/c$	*b*	10.234	2	5.117	16
Bz_3SnO_2CMe	$P2_1/b$	*c*	10.943	2	5.472	17
Ph_3SnO_2CH	$B2_1/a$	*c*	21.952	4	5.488	7
Ph_3SnO_2CMe	$P2_1/c$	*b*	10.146	2	5.073	18
$Ph_3SnO_2CC_6H_4$-2-Cl	$P2_1/n$	*b*	11.407	2	5.704	19

Twelve of the structures listed in Table 2 possess a 2_1 screw axis around which the the polymer propagates. The helix is better defined for those cases where the difference between the Sn–O^I and Sn′–O^{II} bond lengths is minimal, whereas for larger differences, the helix becomes stretched into an *S* configuration [6,7]. For cases in which the screw axis is absent, the planar Sn–O–C(=O) unit propagates in a zig-zag manner on a mirror plane. The flexibility of the helices is reflected in the slope of the variable-temperature Mössbauer plots [6]. The average repeat distance of the polymers (Table 2) is 5.185 Å for the seventeen structures (standard deviation 0.211 Å), with a minimum of 4.941 and a maximum of 5.704 Å.

The constancy of the repeat distance shows that the propagation of the polymer is insensitive to the substituents on either the tin or the carboxylate group. Space to accommodate bulky R′ groups must therefore be provided by elongation of the other two axes of the unit cell. Trimethyltin acetate and trimethyltin trifluoroacete are isostructural, crystallizing in the space group *Pnma*. Although the *a* axial lengths are nearly identical (10.516 and 10.567 Å, respectively), the area of the *b*–*c* plane is 77.77 for the former and 92.23 $Å^2$ for the latter [9]. The *b*-axes of the unit cells of trivinyltin acetate and trivinyltin chloroacetate are also nearly identical (10.516 and 10.567 Å, respectively) [13] and replacement of the methyl or chloromethyl group by the ferrocenyl group [15] has minimal effect on the repeat distance.

Figure 1 is a representation of the propagating polymer whose monomeric units are related by the 2_1 screw axis symmetry element.

If the carboxylate group is conjugated, as for example, in the benzoate anion, the tin atom will lie in the plane of conjugation:



The polymeric lattice is destabilized and a monomer results, as in the case of triphenyltin benzoate [20]. However, bridging by the acyl oxygen can be facilitated if the benzene ring is twisted with respect to the carboxyl group, and this is actually favored for steric reasons in trimethyltin 2-methoxybenzoate [11] and triphenyltin 2-chlorobenzoate [19], both of which are polymeric, with the 2-chlorophenyl plane in the last-named compound being twisted by 60.6° [19]. When the methoxy group is replaced by the smaller hydroxyl group, the structure readily slips into the hydroxyl-bridged polymer instead [11].

The intermolecular $Sn'-O^{II}$ bonds in tricyclohexyltin acetate [21] and tricyclohexyltin trifluoroacetate [22] are long (3.84 and 3.70 Å, respectively, i.e. almost equal to the sum of the Van der Waals' radii of 3.70 Å). Interestingly, the $O^{I}-Sn-O'^{II}$ angles in these compounds are 167.8 and 172°, respectively. The space group is *Pcmn* for both crystal lattices and the planar axial carboxyl groups appear to be linked to the triorganotin units in a zig-zag fashion. The calculated repeat distance along the *c*-axis is 5.712 Å for the acetate and 5.758 Å for the trifluoroacetate. We do not consider these two values to be substantially larger than average of 5.19 Å for the structures in Table 2, and so the two compounds should be regarded as borderline cases among polymeric triorganotin carboxylates.

To illustrate the use of the repeat distance in triorganotin carboxylates, we consider the structure of trimethyltin glycinate, a compound which exhibits an ambient temperature Mössbauer spectrum, and which must therefore be polymeric [23]. The unit cell constants for this compound were published in 1973 ($a = b = 7.839$, $c = 14.659$ Å) [24]. None of the axial distances divided by 2 (or 4) yields a value close to 5.19 Å. A bridging interaction by the amino group could therefore be inferred, and the presence of this interaction was, in fact, demonstrated in 1980 by a full X-ray structural determination [23].

Acknowledgements

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