

*Journal of Organometallic Chemistry*, 365 (1989) 103–110  
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands  
 JOM 09638

## The crystal structure of dimethylphenyltin(IV) acetate

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(Received June 30th, 1988)

### Abstract

Dimethylphenyltin(IV) acetate,  $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{SnOC}(\text{O})\text{CH}_3$ , crystallizes in the orthorhombic space group *Pbca* with  $a$  10.068(3),  $b$  15.065(7),  $c$  14.976(5) Å;  $Z = 8$ ;  $V$  2271(2) Å<sup>3</sup>. The structure was determined from 1793 observed out of 2348 unique reflections and refined to an  $R$  factor of 0.034. The geometry at tin is trigonal bipyramidal, with the oxygen atom of the acetate and the carbonyl oxygen of the adjacent symmetry-related ( $\frac{1}{2} + x$ ,  $\frac{1}{2} - y$ ,  $1 - z$ ) acetate occupying the axial positions of the *trans*- $\text{C}_3\text{SnO}_2$  polyhedron to result in a polymer whose backbone, formed by the repetition of  $\text{Sn}-\text{O}-\text{C}(\text{O})$  fragment, adopts a conformation that is closer to the zig-zag configuration of trimethyltin acetate than to the helical form of triphenyltin acetate.

### Introduction

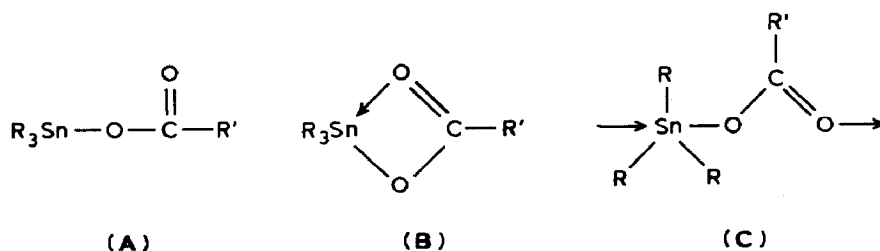
A central question in the structural chemistry of triorganotin(IV) carboxylates (**A**) is whether the carboxylate group will chelate (as in **B**) to form monomers of five-coordinate tin or bridge (as in **C**) through its carbonyl oxygen to result in five-coordinate repeat  $\text{R}_3\text{SnOC}(\text{O})\text{R}'$  units, or, instead, do neither, in which case the solid will be made up of monomers with four-coordinate tin (as in **A**).

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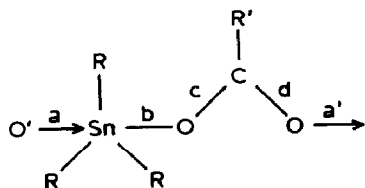
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Structure **A** will be favored for *R* groups which are bulky or branched at the carbon  $\alpha$  to the tin. Structures **B** and **C** will be favored by electron-withdrawing groups at tin which will enhance its acceptor power. The bridging **C** structure will also be favored by *R* and *R'* groups which are sterically less demanding. Structure **C** is expected to be trigonal bipyramidal at tin with the oxygen atoms in the axially-most-electronegative configuration. Electron-withdrawing *R'* groups in the carboxylate residue will be expected to diminish the Lewis basicity of the carbonyl oxygen separated from it by two bonds, but will increase the Lewis acidity of the tin atom linked three bonds away. Which effect predominates is only revealed by experimental results on crucial examples. These choices were revealed in the first pair of triorganotin carboxylate structures determined twenty years ago, namely, tribenzyltin acetate [1] and tricyclohexyltin acetate [2].

The structural criteria, a, b, c and d, for deciding among **A**, **B** and **C** are depicted below:



The interatomic distance *a* establishes the intra- (as in **B**) or inter- (as in **C**) molecularity of the triorganotin carboxylate. Coordination by the carboxylate oxygen will have the effect of increasing the lengths of all bonds made by the tin as well as the length of the carbon-oxygen double bond, *d*. In the extreme, symmetrization of structure **C** will flatten the  $R_3Sn$  group into planarity with carbon-tin-carbon angles equal to  $120^\circ$ , straighten the O-Sn-O' skeleton and make lengths *a* equal to *b* and *c* equal to *d*. The opposite extreme, a perfectly tetrahedral tin in **A** will not, however, be realized owing to the operation of isovalent hybridization on the  $C_3SnO$  unit. The more electronegative oxygen will tend to open the carbon-tin-carbon angles from the ideal  $109.5^\circ$  value in the four-coordinate monomer, making the distinction between **A** and **B** more difficult to discern. Structure **B** requires a four-membered chelate ring. The distance *a*, established intramolecularly, is critical to an argument supported by the distances and angles in the  $R'C(=O)O$  group. In the absence of close contacts from the carbonyl oxygen of a neighboring molecule, structure **B** must be considered, but distinguishing it from **A** has proved difficult, and even the rich variety of data generated from spectroscopic methods (infrared and Raman absorption frequencies, tin-119 Mössbauer isomer shifts (IS) and quadrupole splittings (QS), as well as NMR chemical shifts and coupling constants from solution proton-1, carbon-13 and tin-119 spectra) fail to rule out one or the other decisively.

We are aware of no authenticated examples of simple compounds adopting structure **B** at this writing [3,4]. Triorganotin carboxylates are currently thought to adopt **A** or **C** geometries, but simple examples of the former crystallizing into solids comprising monomers with unidentate carboxylato ligands and four-coordinate tin atoms may be better considered as weakly bridged, one-dimensional polymers, **C**, unless special features are present. Tricyclohexyltin acetate [2] and tricyclohexyltin trifluoroacetate [5] carry bulky R groups at tin. However, although the intermolecular tin–oxygen distances are in the Van der Waals limit for these two compounds, the structures have been assigned configuration **C** on the basis of Mössbauer [6] and crystallographic [7] data.

The claim of the first *cis*, five-coordinated triorganotin carboxylate, triphenyltin 2-(2-hydroxy-5-methylphenylazo)benzoate, with the carboxylate group spanning axial and equatorial sites of the trigonal bipyramid [6], has been discounted [8], although the tin–carbonyl oxygen distance is well within the Van der Waals range. Triphenyltin arylcarboxylates are generally monomeric molecules with tetrahedral tin [8,9]; the aryl group prefers to be conjugated to the carboxylate group so that these two planes can remain coplanar, but this orientation prevents the carbonyl oxygen from approaching the tin [7]. As exemplified by triphenyltin thiophene-2-carboxylate [10], the intramolecular oxygen–tin–oxygen angle is much less than the 90° required for a *cis* trigonal bipyramidal geometry. Triphenyltin acetate is claimed to be six-coordinate owing to the presence of a somewhat weak intramolecular carbonyl oxygen–tin interaction, and the argument rests on the widening of the carbon–tin–carbon angle that is closest to the carbonyl oxygen [11]. However, a comparison of the structure of triphenyltin acetate with that of the chloroacetate [12] reveals no significant change in either the contact distance or the carbon–tin–carbon angle.

In compounds capable of hydrogen-bonding, one-dimensional lattices predominate even at the expense of abandoning conventional donor–acceptor tin–oxygen interactions and unidentate carboxylate groups are the result, as in trimethyltin glycinate [13], in tricyclohexyltin 3-indolylacetate [14] as well as in the hydrated trimethyltin pyridine-2-carboxylate [15] and triphenyltin 8-quinoloxylacetate [16]. With tricyclohexyltin *N*-methyl-3-indolylacetate, the nitrogen is blocked and hydrogen-bonding through the indolyl nitrogen is precluded [17]. In the hydrogen-bonded lattice of triphenyltin 2-chlorobenzoate hydrate-etherate, dimers containing two different five-coordinate  $C_3SnO_2$  units, one carboxylate bridged and one with a terminal water molecule, are found. One carboxylate group is free [18].

Competition by other donor atoms in the carboxylate residue of the molecule can also alter the structural choice. The effect of the combination of hydrogen-bonding plus the potential for nitrogen donor activity is seen in trimethyltin glycinate, in which the tin atoms are connected by four atom,  $-O-C-C-N-$  bridges [13]. Five atom,  $-O-C-C-C-N-$  bridges are found in triphenyltin pyridine-3-carboxylate and the one-dimensional lattice is flat [19].

While these more complicated systems capable of sundry bonding modes shed light on the controlling parameters, the basic question raised twenty years ago remains: what is the crossover point among structure **A**, **B** and **C** for simple triorganotin carboxylate solids? As a contribution to this answer, we report the results for dimethylphenyltin acetate.

## Experimental

**Synthesis.** Dimethylphenyltin acetate was prepared from dimethylphenyltin iodide and silver acetate in methanol in 80% yield, m.p. 159–160 °C. The starting organotin halide was prepared through tin-phenyl cleavage by elemental iodine. Carbon, hydrogen and tin analyses for  $C_{10}H_{14}O_2Sn$  (found (calcd.) (%)) C, 42.15; (42.17); H, 4.76 (4.95); Sn, 40.25 (41.79). Mössbauer data: IS 1.44, QS 3.39 mm s<sup>-1</sup>. Mass spectrum (12 eV):  $m/e$  271 (100%)  $CH_3C_6H_5SnOC(O)CH_3^+$ . In the infrared spectrum [Raman], the tin-carbon  $\nu$ (asymmetric) mode absorbs at 550(m) [550(w)] and the tin-carbon  $\nu$ (symmetric) at 515(w) [520(w)] cm<sup>-1</sup>. In the proton NMR, in deuteriochloroform, deuterobenzene and deuteromethanol solutions, the methyltin signals appear at 0.75, 0.50 and 0.67 ppm, respectively and the two-bond coupling tin-119 coupling constants are 60.0, 60.0 and 71.0 Hz, respectively. In the carbon-13 NMR, the methyl carbons appear at -3.9, -4.2 and -2.8 ppm, respectively and only the one-bond coupling constant in deuteromethanol could be observed (at 543 Hz). The tin-119 chemical shifts are 42.6, 40.4 and -57.0 ppm, relative to tetramethyltin (concentration 10% wt./vol.)

**X-ray crystallography.** A colorless parallelepiped shaped crystal with approximate dimensions 0.28 × 0.30 × 0.43 mm, air stable at room temperature, was used for the crystallographic measurements. Unit cell parameters were calculated with 24 reflections from all octants of reciprocal space (Table 1). The data were collected at room temperature on an Enraf-Nonius CAD4 automatic diffractometer (Mo- $K_\alpha$ , graphite monochromator) (scan technique:  $\theta$ -2 $\theta$ ; 2 $\theta$  range 0–53°). 2348 unique reflections were measured of which 1793 were observed ( $I > 2\sigma(I)$ ). Normal Lorentz-polarization and absorption corrections were applied [20]. The structure was solved by the Patterson method and refined with full-matrix least squares to an  $R$  factor of 0.034 and an  $R_w$  factor of 0.038 using the SHELX program [20]; scattering factors were obtained from the International Tables for X-ray Crystallography [21]. The positions of the hydrogen atoms were found from the difference Fourier map. The hydrogen temperature factors were constrained to 0.05 Å<sup>2</sup> whereas those of the other atoms were refined anisotropically. The maximum and minimum heights in the final difference Fourier map were 0.96 and -0.62 eÅ<sup>-3</sup>, located near

Table 1

Crystal data for dimethylphenyltin acetate,  $(CH_3)_2(C_6H_5)SnOC(O)CH_3$ 

|                |                                               |
|----------------|-----------------------------------------------|
| Formula        | $C_{10}H_{14}O_2Sn$                           |
| Formula weight | 284.91                                        |
| $a$            | 10.068(3) Å                                   |
| $b$            | 15.065(7) Å                                   |
| $c$            | 14.976(5) Å                                   |
| crystal system | orthorhombic                                  |
| space group    | $Pbca$                                        |
| $Z$            | 8                                             |
| $V$            | 2271(2) Å <sup>3</sup>                        |
| $\rho_{X-ray}$ | 1.666 gm cm <sup>-3</sup>                     |
| $\mu$          | 20.43 cm <sup>-1</sup> ( $\lambda$ 0.71069 Å) |

Table 2

Atomic positions for dimethylphenyltin acetate,  $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{SnOC}(\text{O})\text{CH}_3$ 

| Atom  | x          | y          | z          |
|-------|------------|------------|------------|
| Sn    | 0.05105(3) | 0.28989(2) | 0.46670(2) |
| O(1)  | -0.1117(3) | 0.3847(2)  | 0.4435(2)  |
| O(2)  | -0.2582(3) | 0.2995(2)  | 0.5106(2)  |
| C(1)  | 0.1753(4)  | 0.3695(3)  | 0.3830(3)  |
| C(2)  | 0.2782(5)  | 0.3334(4)  | 0.3344(4)  |
| C(3)  | 0.3622(6)  | 0.3850(4)  | 0.2835(3)  |
| C(4)  | 0.3433(6)  | 0.4752(4)  | 0.2790(4)  |
| C(5)  | 0.2411(7)  | 0.5121(4)  | 0.3260(5)  |
| C(6)  | 0.1584(5)  | 0.4604(3)  | 0.3768(4)  |
| C(7)  | 0.0620(5)  | 0.3169(4)  | 0.6051(4)  |
| C(8)  | -0.0431(6) | 0.1827(4)  | 0.4025(5)  |
| C(9)  | -0.2285(4) | 0.3669(3)  | 0.4655(3)  |
| C(10) | -0.3330(6) | 0.4314(4)  | 0.4374(5)  |

Table 3

Interatomic distances (Å) and angles ( $^\circ$ ) in dimethylphenyltin acetate,  $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{SnOC}(\text{O})\text{CH}_3$ 

|                 |          |                |          |                 |          |
|-----------------|----------|----------------|----------|-----------------|----------|
| Sn–C(1)         | 2.139(4) | Sn–C(7)        | 2.115(6) | Sn–C(8)         | 2.105(6) |
| Sn–O(1)         | 2.201(3) | Sn–O(2)'       | 2.370(3) | O(1)–C(9)       | 1.250(5) |
| O(2)–C(9)       | 1.256(5) | C(9)–C(10)     | 1.493(8) | C(1)–C(2)       | 1.378(7) |
| C(2)–C(3)       | 1.379(8) | C(3)–C(4)      | 1.374(9) | C(4)–C(5)       | 1.365(9) |
| C(1)–C(6)       | 1.383(6) | C(5)–C(6)      | 1.371(8) |                 |          |
| C(1)–Sn–C(7)    | 115.8(2) | C(1)–Sn–C(8)   | 115.2(2) | C(7)–Sn–C(8)    | 128.2(3) |
| C(1)–Sn–O(1)    | 88.8(1)  | C(1)–Sn–O(2)'  | 85.9(1)  | C(7)–Sn–O(1)    | 93.9(2)  |
| C(7)–Sn–O(2)'   | 85.8(2)  | C(8)–Sn–O(1)   | 95.2(2)  | C(8)–Sn–O(2)'   | 89.7(2)  |
| O(1)–Sn–O(2)'   | 174.0(1) | Sn–C(1)–C(2)   | 121.9(3) | Sn–C(1)–C(6)    | 121.5(3) |
| C(2)–C(1)–C(6)  | 116.6(4) | C(1)–C(2)–C(3) | 122.1(5) | C(2)–C(3)–C(4)  | 120.0(5) |
| C(3)–C(4)–C(5)  | 118.8(5) | C(4)–C(5)–C(6) | 120.8(5) | C(5)–C(6)–C(1)  | 121.7(5) |
| Sn–O(1)–C(9)    | 121.3(3) | O(1)–C(9)–O(2) | 122.6(4) | O(1)–C(9)–C(10) | 116.7(4) |
| O(2)–C(9)–C(10) | 120.7(4) | Sn–O(2)'–C(9)' | 136.9(3) |                 |          |

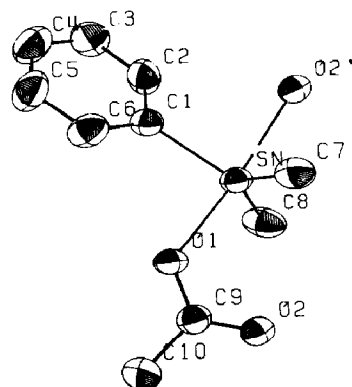


Fig. 1. Asymmetric unit of dimethylphenyltin acetate, with atomic labeling.

the tin atom. The atomic positions are listed in Table 2 and the bond lengths and angles in Table 3. The estimated standard deviation with respect to the last digit is shown in parentheses. The coordination geometry of the tin is shown in Fig. 1. The thermal parameters and hydrogen positions are available from the authors.

## Results and discussion

Dimethylphenyltin acetate is a one-dimensional polymer with five-coordinate tin with the electronegative oxygen atoms occupying the apical positions of the trigonal bipyramid, a feature common in five-coordinate triorganotin compounds [3,4]. The tin–oxygen bond lengths of 2.202(3) and 2.370(3) Å attest to the unevenness in bonding. The oxygen–tin–oxygen skeleton is bent ( $174.0(1)^\circ$ ) and the distortion from idealized geometry is also seen in the sum of the carbon–tin–carbon angles ( $359.2(7)^\circ$ ). Apparently to minimize steric interactions, the phenyl ring is twisted by  $59.8(2)^\circ$  with respect to the equatorial plane. The tin atom does not lie in this plane, but is displaced by 0.104(1) Å in the direction of O(1). The largest carbon–tin–carbon angle is the dimethyltin angle ( $128.2(3)^\circ$ ) which is opened by the intramolecular acyl oxygen (Sn  $\cdots$  O(2) 3.185(3) Å) and the methyl carbon of the adjacent ( $\frac{1}{2} + x$ ,  $\frac{1}{2} - y$ ,  $1 - z$ ) acetate. The dimethyltin angle is larger than the angle in trimethyltin acetate. In these two triorganotin acetates and in triphenyltin acetate, the carbonyl oxygen is seen to open up the carbon–tin–carbon angle nearest it, the angle increasing from  $121.9^\circ$  in trimethyltin acetate [22] to  $128.1(3)^\circ$  in dimethylphenyltin acetate to  $135.1^\circ$  in triphenyltin acetate [11]. The tin atom in these three acetates lie on the side of the equatorial plane opposite to the bridging carboxylate group with the atom being displaced by 0.090 Å in trimethyltin acetate and by 0.094 Å in triphenyltin acetate.

The trialkyltin carboxylates that have been authenticated encompass trimethyltin [22,23], trivinyltin [24–26], tri-*n*-butyltin [17,27] and tribenzyltin [1], but the triaryltins are limited to the triphenyltin carboxylates [11,12,18,28] only. The carboxylate unit is more varied, with the R' radical being hydrogen [28], methyl [1,11,22,24], chloromethyl [12,24], trifluoromethyl [22], trichloromethyl [25], 2-methoxyphenyl [23], ferrocenyl [26], 3-indolylmethyl [17], *N,N*-methylphenyldithiocarbamylmethyl [27] and 2-chlorophenyl [18]. Only a preliminary account of the simplest triorganotin carboxylate, trimethyltin formate, has appeared [29]. The polymer backbone of the two trimethyltin alkanoates is flat, a condition that is crystallographically imposed. With the bulkier phenyl groups on the tin, the principal atoms of the repeat unit generally propagate in the unit cell through a  $2_1$  screw axis translation and the backbone adopts a distorted helical conformation. As a point of interest, with organogermanium compounds, the expansion of the coordination number above four for germanium is relatively uncommon [30] and triphenylgermanium trifluoroacetate is monomeric [31].

With the triphenyltin carboxylates, the phenyl groups generally do not orient themselves around the tin in a propeller-like fashion as this configuration is of high potential energy. Some support for this observation comes from the structures of triarylphosphine oxides, which appear to undergo a Walden-type of inversion at the phosphorus center [32]. In the five-coordinate transition state, one phenyl ring is coplanar with the equatorial plane and the second is tilted at less than  $90^\circ$  to this plane; the last ring is tilted at an angle greater than  $90^\circ$ . Indeed, the expansion of

coordination number of a triorganotin carboxylate can be viewed simply as an  $S_N2$  [33] type of reaction, analogous to the bimolecular nucleophilic substitution reactions of tetrahedral carbon chemistry. The donor oxygen from the adjacent carboxylate unit can be viewed as the 'nucleophilic reagent' and the sigma-bonded oxygen the 'leaving group'. Viewed from this perspective, it comes as no surprise that the tin atom in the carboxylates always get displaced out of the incipient equatorial plane, in the direction of the latter atom. The three phenyl rings in four-coordinate triphenyltin chloride are arranged in a propeller-like manner around the Sn-Cl vector [34]. In the five-coordinate triphenyldichlorostannate anion, the dihedral angles with respect to the equatorial plane are calculated, from the atomic coordinates [35], to be 12.1, 46.2 and 119.5°. The calculated dihedral angles for triphenyltin acetate are -8.3, 42.3 and 49.9°.

We note in the title compound, which carries only one phenyl group, that the phenyl group occupies the equatorial position farthest away from the intramolecular carbonyl oxygen. If the Sn-O-C(O) fragment were flat, the phenyl ring must be perpendicular to the equatorial plane. This configuration imposes energy constraints, and the ring twists by about 60° instead. The  $z$  atomic coordinates for these four atoms are spread around the  $z = 0.5$  plane. The flat character of the fragment is relatively retained, and dimethylphenyltin acetate is seen to resemble trimethyltin acetate more than triphenyltin acetate.

### Acknowledgements

This work is supported by the Office of Naval Research and the National Science Foundation. We thank the University of Oklahoma for providing computer time.

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