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REVIEW

Structural chemistry of organotin carboxylates: a review of the crystallographic literature

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This review describes the structural chemistry of organotin carboxylates, covering data acquired for mono-, di- and tri-organotin compounds and complexes. A brief discussion is given for organotin amino-acid derivatives.

Keywords: Organotin, carboxylate, structure, X-ray, review

1 INTRODUCTION

Organotin carboxylates comprise an important class of compounds.[1-4] Certain derivatives have industrial applications, for example as homogeneous catalysts. Other uses relate to agricultural applications, where organotin carboxylates have been used as biocides and the like. More recently, the pharmaceutical properties of organotin carboxylates have been investigated with particular reference to their antitumour activity.[5,6] As a consequence of the important applications, and indeed potential uses, of organotin carboxylates[1-6] the structural chemistry of this class of compounds has received considerable attention. Central to the elucidation of the different structures adopted by organotin carboxylates are single-crystal X-ray crystallographic studies. Hence, there have to date been in excess of 100 crystal structures reported in the literature for compounds in this category. As will be demonstrated in this review, a large variety of structural types are known, even for seemingly closely related compounds. The aim of this review is to categorize each organotin carboxylate structure, as determined by crystallographic methods, and relate it to a common structural motif.

This review is organized so that mono-organotin carboxylates are collected in Section 2, diorganotin carboxylates in Section 3 and tri-organotin carboxylates in Section 4. In addition, a brief description of the known crystal structures of organotin derivatives of amino-acids is given in Section 5. For detailed discussion on individual structures the reader is referred to the original paper, as cited. All diagrams were drawn with the ORTEP program[7] using published fractional atomic coordinates and arbitrary thermal ellipsoids.

2 MONO-ORGANOTIN CARBOXYLATES

The smallest number of crystal structures reported for organotin carboxylates are those containing the monoorganotin moiety. These compounds, characterized primarily by Day, Holmes and co-workers,[8-11] fall neatly into two classes. One group, based on the formula $[RSn(O)(O_2CR')]_6$, adopt the so-called 'drum' structure as discussed in Section 2.1. The second class of compounds, based on the composition $\{[RSn(O)(O_2CR')]_2[RSn(O_2CR')_3]\}_2$, adopt a 'ladder' structure in the solid state as discussed in Section 2.2. The structural chemistry of both classes of compounds, including a discussion of the interconversion between the structural motifs, has been reviewed recently by the original authors in two separate accounts.[12,13]

Outside these two groups of compounds the only mention of other mono-organotin carboxylates found in the literature occur as references to unpublished work in Ref. 13, these being the structures of $[CH_3Sn(O_2CC_6H_5)_3]$, with three bidentate carboxylate ligands and thus a seven-coordinate tin (Sn) centre, and of

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$[(nBuSn)_3(S)(O)(O_2CC_6H_5)_5]$, which features octahedral Sn centres, a planar Sn_3O unit and a Sn–S–Sn bridge.

2.1 $[RSn(O)(O_2CR')]_6$

Six compounds of the general formula $[RSn(O)(O_2CR')]_6$ have been characterized crystallographically, although one of these with R = nBu, R′ = cC_6H_{11} is only of limited precision.[8] In addition to these, one mixed carboxylate/phosphate structure is also known, i.e. $\{[CH_3Sn(O)(O_2CCH_3)]\,[CH_3Sn(O)(O_2P(tBu)_2]\}_3$.[9] As can be seen from the two views shown for the $[CH_3Sn(O)(O_2CCH_3)]_6$ species[9] in Fig. 1, the hexameric compounds adopt a 'drum-like' structure in the solid state. In this description, the two lids of the 'drum' are defined by Sn_3O_3 hexagonal rings with alternate Sn and O_{hexa} atoms; these Sn_3O_3 rings are not planar but adopt 'chair' configurations. The two hexagonal rings are connected via Sn–O linkages implying that the lower hexagonal ring is rotated 60° relative to the upper ring. This has the consequence that the O atoms comprising the hexagonal rings, i.e. the 'framework' O atoms, are tri-coordinate. The six 'staves' thus formed may be thought of as Sn_2O_2 stannoxane groups. The Sn_2O_2 rectangles are not planar, however, because the O atoms which define the hexagonal rings are directed towards the centre of the 'drum' relative to the Sn atoms. The diagonally opposite Sn atoms of each rectangular face are bridged by a carboxylate ligand which forms essentially equivalent $Sn-O_{carb}$ bond distances which are longer than the other Sn–O bond distances in the structure. Important Sn–O bond distances are tabulated in Table 1, where the $Sn-O_{hexa}$ bonds are occurring within the hexagonal rings and the $Sn-O_{rect}$ are the Sn–O bonds that connect the two six-membered rings. The coordination about each Sn atom is completed by the organo function which occupies a position *trans* to a framework O atom. The O_5C coordination polyhedron about each of the six-coordinate Sn atoms is based on a distorted octahedron.

In three of the structures the hexameric rings have crystallographic S_6 symmetry and consequently there is one crystallographically unique Sn atom in the structure. The two remaining structures have $\bar{1}$ symmetry and have three crystallographically distinct Sn atoms which are, however, chemically equivalent; structural details for these compounds are given in Table 1.

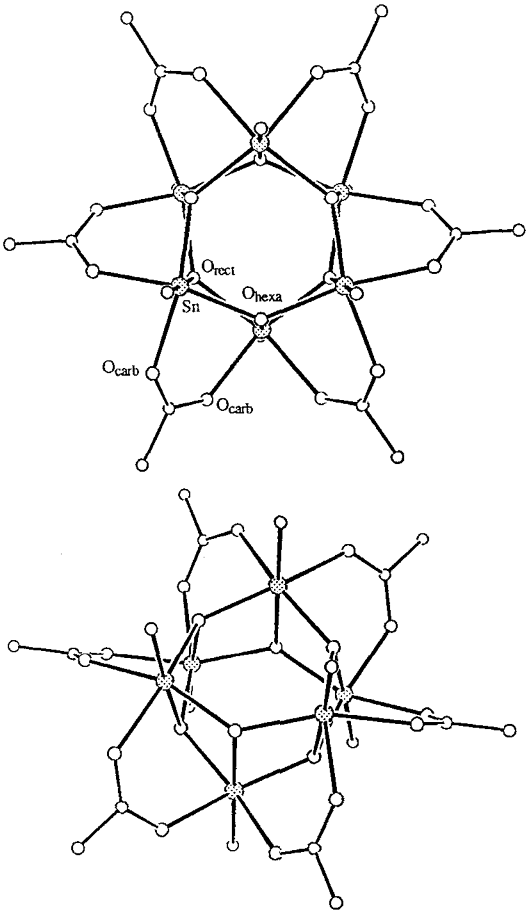


Figure 1 Two views of the structure of $[CH_3Sn(O)(O_2CCH_3)]_6$.[9]

2.2 $\{[RSn(O)(O_2CR')]_2[RSn(O_2CR')_3]\}_2$

The 'open-drum' or 'ladder' structures found for compounds of the general formula $\{[RSn(O)(O_2CR')]_2[RSn(O_2CR')_3]\}_2$ also comprise a total of six Sn atoms as for the 'drum' structures described in Section 2.1. However, in this class of compounds there are three chemically distinct Sn atoms, as opposed to those found for the 'drum' structures, where there was only one unique type of Sn atom in the structure. The three compounds that have been structurally characterized in this category have crystallographically imposed $\bar{1}$ symmetry and a representative structure, $\{[nBuSn(O)(O_2CC_6H_5)]_2[nBuSn(O_2CC_6H_5)_3]\}_2$,[10] for this category is shown in Fig. 2. Two structures, i.e. R = nBu, R′ = C_6H_{11}[8] and R = CH_3, R′ = C_6H_{11},[9] which adopt this structural motif were of limited accuracy and full details for these structures were not reported.

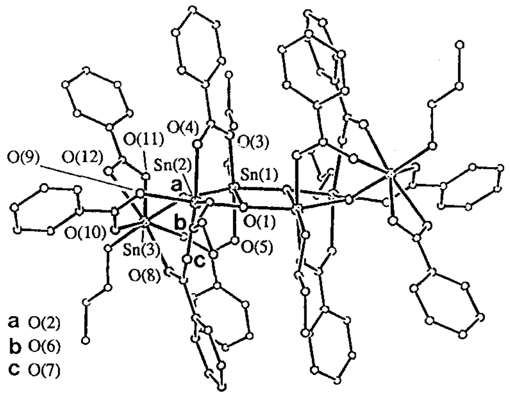


Figure 2 The structure of $\{[nBuSn(O)(O_2CC_6H_5)]_2[nBuSn(O_2CC_6H_5)_3]\}_2$.[10]

The structure is built up about a central Sn_2O_2 stannoxane ring which is centred about a site of symmetry $\bar{1}$. Linked to this central unit, via Sn–O bonds, are two pairs of Sn and O atoms. The disposition of these additional atoms, i.e. above and below the stannoxane unit, leads to a Sn_4O_4 'ladder' structure. The terminal bridging O atom of the 'ladder', i.e. the O(2) atom, also coordinates the exocyclic Sn atom, Sn(3), and is thus tricoordinate. Further links between the Sn atoms are provided by the carboxylate ligands.

Of the five unique carboxylate ligands in the structure, four are bridging. One, defined by the O(3) and O(4) atoms (see Fig. 2), bridges the Sn(1) and Sn(2) atoms; a bridge is similarly formed between the Sn(1) and Sn(3) atoms by the ligand with the O(5) and O(6) donor atoms, and two carboxylate ligands (with the O(7), O(8) and O(9), O(10) atoms) bridge the Sn(2) and Sn(3) atoms. The fifth carboxylate ligand (with the O(11) and O(12) atoms) only coordinates the exocyclic Sn atom. In two of the structures in this category, the Sn(3)–O bond distances of approximately 2.2 and 2.4 Å indicate that this fifth ligand is chelating (see Table 2). In the other structure,[14] i.e. R = Ph, R′ = CCl_3, the carboxylate ligand seems to coordinate in the monodentate mode with Sn–O bond distances of 2.08(1) and ≥4.0 Å; however, disorder associated with this ligand has been noted.[14]

The coordination about each Sn atom is completed by one organo group, which for the Sn(1) atom is *trans* to the O(1) atom, whereas for the Sn(2) and Sn(3) atoms the organo substituents are *trans* to the O(2) atom. The Sn(1) and Sn(2) atoms exist in distorted octahedral geometries with O_5C donor sets and the Sn(3) atom exists in a seven-coordinate O_6C environment based on a distorted pentagonal bipyramid with the C and O(2) atoms defining the axial positions in two of the compounds. For the R = Ph, R′ = CCl_3 compound mentioned above, i.e. with the monodentate carboxylate ligand, the Sn(3) atom also exist in a distorted octahedral geometry. Selected interatomic parameters for the compounds discussed in this section are listed in Table 2.

Also included in this section is the crystal structure of the closely related derivative, $\{[RSn(O)(O_2CR')]_2[RSnCl(O_2CR')_2]\}_2$.[8] In this compound the basic structure remains the same except that the terminal carboxylate ligand which coordinates the Sn(3) atom only has been replaced by a Cl atom; some parameters for this compound are also listed in Table 2.

3 DIORGANOTIN CARBOXYLATES

3.1 $[R_2Sn(O_2CR')]_2$

There are six crystal structures that are available in the literature for compounds of the general formula $[R_2Sn(O_2CR')]_2$.[15–18] This structural motif

Table 1 Structural parameters for $[RSn(O)(O_2CR')]_6$

R	R′	$Sn–O_{hexa}$	$Sn–O_{rect}$	$Sn–O_{carb}$	$C–Sn–O_r$	Ref.
CH_3[a]	CH_3	2.094(2), 2.081(2)	2.098(2)	2.155(2), 2.162(2)	177.6(2)	9
nBu[b]	c-C_5H_9	2.082(6), 2.086(7)	2.094(6)	2.167(7), 2.172(8)	176.1(4)	8
		2.093(7), 2.092(7)	2.082(7)	2.167(8), 2.173(8)	175.2(4)	
		2.088(7), 2.081(6)	2.075(7)	2.155(8), 2.161(9)	176.3(4)	
nBu[a]	$C_6H_4NO_2$-*o*	2.088(4), 2.097(4)	2.085(3)	2.197(4), 2.193(4)	177.8(2)	10
Ph[a]	CCl_3	2.095(7), 2.075(3)	2.089(3)	2.183(3), 2.191(3)	176.2(1)	14
Ph[b]	c-C_6H_{11}	2.083(3), 2.073(3)	2.124(3)	2.165(3), 2.155(4)	179.1(2)	11
		2.081(3), 2.089(3)	2.096(3)	2.153(4), 2.154(4)	178.9(2)	
		2.080(3), 2.069(3)	2.098(3)	2.139(4), 2.149(4)	177.0(2)	

[a] Molecule has crystallographic S_6 symmetry. [b] Molecule has crystallographic $\bar{1}$ symmetry.

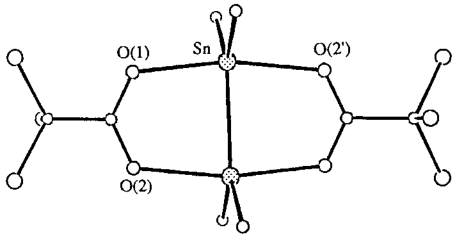


Figure 3 The structure of $[(CH_3)_2Sn(O_2CCF_3)]_2$.[15]

features a Sn–Sn bond formed between two R_2Sn centres such that the resultant R_2Sn—SnR_2 unit is planar. The Sn–Sn bond distances are all slightly less than 2.80 Å, being the sum of the covalent radii for two Sn atoms; see Table 3 for selected interatomic parameters. The Sn–Sn vector is bridged by two carboxylate ligands which lie above and below the R_2Sn–SnR_2 plane as shown for $[(CH_3)_2Sn(O_2CCF_3)]_2$[15] in Fig. 3. The Sn atoms exist in distorted trigonal bipyramidal geometries with the O atoms occupying the axial positions; the *trans* angles are approximately 168° in each structure. Distortions from the ideal geometry arise partly as a result of the inability of the carboxylate ligands to span the Sn–Sn vector owing to the restricted bite distance of the ligand. It is worth noting that these structures have a high degree of inherent symmetry with all but the $R = CH_3$, $R' = CF_3$[15] and $CHCl_2$[16] derivatives (which have $2/m$ symmetry) having crystallographic $\bar{1}$ symmetry. The $R = Ph$, $R' = CH_3$ compound has been the subject of two independent structure determinations.[17,19] However, only the interatomic parameters from the latter determination (using contemporary methods) are listed in Table 3.

3.2 $[R_2Sn(O_2CR')X]_n$

There are two structurally characterized compounds of the general formula $[R_2Sn(O_2CR')X]_n$ reported in the literature.[20,21] The structure of the first compound, i.e. $R = CH_3$, $R' = CH_3$ and $X = Cl$, is polymeric as a result of bridging acetate groups as shown in Fig. 4.[20] The Sn atom exists in a distorted trigonal bipyramidal geometry with the two methyl groups and the Cl (Sn–Cl 2.375(2) Å) atom defining an approximate trigonal plane. The axial positions are occupied by O atoms (Sn–O(1) 2.165(6) and Sn–O(2') 2.392(7) Å) derived from two acetate groups such that O(1)—Sn—O(2') is 170.1(2)°. The intramolecular Sn···O(2) separation of 2.782(7) Å is

Table 2 Structural parameters for $\{[RSn(O)(O_2CR')]_2[RSn(O_2CR')_3]\}_2$

Parameter	$R = nBu$ $R' = CH_3$	$R = nBu$ $R' = C_6H_5$	$R = Ph$ $R' = CCl_3$	$R = nBu$[a] $R' = C_6H_5$
Sn(1)–O(1)	2.049(7)	2.051(4)	2.03(1)	2.055(3)
Sn(1)–O(1')	2.061(7)	2.079(5)	2.094(9)	2.068(3)
Sn(1)–O(2)	2.140(7)	2.161(4)	2.124(9)	2.123(7)
Sn(1)–O(3)	2.169(9)	2.210(4)	2.21(1)	2.178(3)
Sn(1)–O(5)	2.166(8)	2.161(4)	2.16(1)	2.181(3)
Sn(2)–O(1)	2.054(7)	2.060(4)	2.02(1)	2.053(3)
Sn(2)–O(2)	2.072(7)	2.067(4)	2.10(1)	2.066(3)
Sn(2)–O(4)	2.159(8)	2.149(5)	2.16(1)	2.179(3)
Sn(2)–O(7)	2.143(8)	2.130(5)	2.15(1)	2.116(3)
Sn(2)–O(9)	2.148(9)	2.147(5)	2.13(1)	2.148(3)
Sn(3)–O(2)	1.983(7)	1.985(4)	1.99(1)	2.012(3)
Sn(3)–O(6)	2.230(9)	2.242(5)	2.21(1)	2.162(3)
Sn(3)–O(8)	2.244(9)	2.232(4)	2.13(1)	2.234(3)
Sn(3)–O(10)	2.194(9)	2.189(5)	2.29(1)	2.127(3)
Sn(3)–O(11)	2.23(1)	2.218(5)	2.08(1)	2.422(1)[b]
Sn(3)–O(12)	2.42(1)	2.407(5)	≥4.0	—
C—Sn(1)—O(1)	176.4(4)	174.5(2)	166.6(5)	173.6(2)
C—Sn(2)—O(2)	178.3(4)	174.4(3)	173.3(6)	175.8(2)
C—Sn(3)—O(2)	174.9(5)	175.2(3)	168.6(6)	168.6(2)
Ref.	10	10	14	8

[a] Compound is $\{[nBuSn(O)(O_2CC_6H_5)]_2[nBuSnCl(O_2CC_6H_5)_2]\}_2$ [b] Sn(3)–Cl.

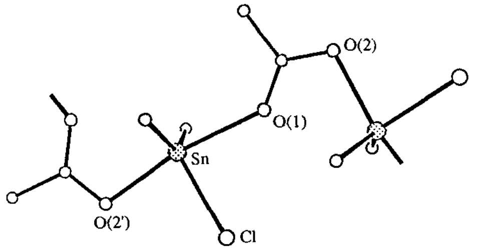


Figure 4 The structure of $[(CH_3)_2Sn(O_2CCH_3)Cl]_n$.[20]

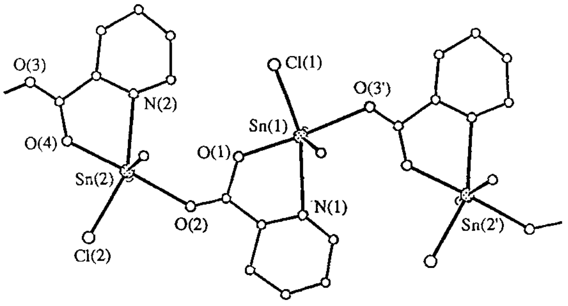


Figure 5 The structure of $[(CH_3)_2Sn(O_2CC_5H_4N\text{-}o)Cl]_n$.[21]

not considered to be a significant bonding interaction between these atoms. In many respects the structure found for $[(CH_3)_2Sn(O_2CCH_3)Cl]_n$ resembles those found for the *trans*-O_2SnR_3 structures described below (see section 4.1.4) in which the Cl atom is replaced by a third R group.

The second structure of this general formula is found for the $R = CH_3$, $R' = 2\text{-}C_5H_4N$ and $X = Cl$ derivative.[21] This structure is also polymeric and is represented in Fig. 5. There are two unique Sn atoms in the asymmetric unit. The polymeric structure arises as a result of the presence of bridging 2-pyridinecarboxylate ($O_2CC_6H_4$-*o*) ligands. Both Sn atoms exist in distorted octahedral geometries, each defined by two *cis*-CH_3 groups, a Cl atom, the N and O atoms derived from a chelating $O_2CC_6H_4N$-*o* ligand and an O′ atom from a neighbouring $O_2CC_6H_4N$-*o* ligand (which is *trans* to the O atom). The 2-pyridinecarboxylate ligands coordinate in the tridentate mode utilizing both O atoms and the heterocyclic N atom. Important interatomic parameters for the Sn(1) atom are: Sn(1)–O(1) 2.08(3), Sn(1)–O(3′) 2.38(3), Sn(1)–N(1) 2.51(3) and Sn(1)–Cl(1) 2.409 Å; O(1)—Sn(1)—O(3′) 175.3(8) and N(1)—Sn(1)—Cl(1) 161.3(7)°. For the Sn(2) atom: Sn(2)–O(2) 2.29(3), Sn(2)–O(4) 2.13(3), Sn(2)–N(2) 2.47(2) and Sn–Cl(2) 2.43(1) Å; O(2)—Sn(2)—O(4) 175.9(8) and N(2)—Sn(2)—Cl(2) 154.5(8)°.

3.3 $\{[R_2Sn(O_2CR')]_2O\}_2$

3.3.1 Type I

The predominant structural type adopted by compounds of the general formula $\{[R_2Sn(O_2CR')_2]O\}_2$, the dicarboxylato tetraorganodistannoxanes,[14,22–30] is illustrated for the $\{[nBu_2Sn(O_2CCCl_3)]_2O\}_2$ compound[14] in Fig. 6. No less than 11 of the 15 structures known for this formulation adopt this structural type; the four exceptions are discussed below in Sections 3.3.2–3.3.5. In addition there is a partially determined structure of this type, namely $\{[(H_2C{=}CH)_2Sn(O_2CCF_3)]_2O\}_2$; however, severe disorder in the light atom positions precluded a full refinement of the model.[31] Selected interatomic parameters for the compounds discussed in this category are listed in Table 4.

The structure is built up around a planar Sn_2O_2 unit (invariably centred about a crystallographic site of symmetry $\bar{1}$) with Sn—O(1)—Sn′ angles in the range 102–105° and O(1)—Sn—O(1′) angles in the range 75–81°. The two exocyclic Sn atoms are connected to the bridging O atoms of the Sn_2O_2 unit. There are two distinct carboxylate groups in the structure. One carboxylate ligand is bidentate bridging and bridges both the endocyclic and exocyclic Sn atoms via the O(2) and O(3)

Table 3 Structural parameters for $[R_2Sn(O_2CR')]_2$

R	R′	Sn–Sn	Sn–O(1)	Sn–O(2)	O(1)—Sn—O(2)	Ref.
CH_3	CF_3	2.707(1)	2.319(4)	2.345(4)	168.5(1)	15
CH_3	CH_2Cl	2.692(3)	2.241(7)	2.349(7)	168.7(2)	16
CH_3	CCl_3	2.711(1)	2.285(6)	2.332(5)	168.5(1)	18
Ph[a]	CH_3	2.691(1)	2.261(3)	2.278(3)	168.2(1)	17
		2.696(1)	2.259(3)	2.274(3)	168.4(1)	
Ph[a]	CF_3	2.718(1)	2.305(5)	2.309(5)	168.9(1)	17
		2.720(2)	2.288(7)	2.324(7)	168.8(2)	
Ph	CCl_3	2.711(1)	2.295(3)	2.322(3)	168.3(4)	17

[a] Two molecules in asymmetric unit each situated about $\bar{1}$.

Table 4 Structural parameters for $\{[R_2Sn(O_2CR')]_2O\}_2$, Type I

Parameter	$R = CH_3$ $R' = CF_3$	$R = CH_3$ $R' = CH_2Cl$	$R = CH_3$ $R' = CCl_3$	$R = CH_3$[a] $R' = C_6H_4NH_2$-*o*	$R = nPr$ $R' = CH_2SPh$
Sn(1)-O(1)	2.039(5)	2.07(1)	2.07(1)	2.029(5); 2.049(5)	2.062(5)
Sn(1)-O(1′)	2.137(4)	2.10(1)	2.12(1)	2.162(6); 2.135(6)	2.166(5)
Sn(1)-O(2)	2.367(5)	2.36(2)	2.24(1)	2.254(7); 2.29(1)	2.300(6)
Sn(1)-O(4)	2.727(5)	2.66(2)	2.74(1)	2.877(5); 2.886(7)	2.631(6)
Sn(2)-O(1)	2.040(4)	2.03(1)	2.03(1)	2.007(5); 2.004(5)	2.011(5)
Sn(2)-O(3)	2.215(5)	2.20(2)	2.24(1)	2.260(7); 2.34(1)	2.230(6)
Sn(2)-O(4)	2.253(4)	2.17(1)	2.262(9)	2.154(5); 2.200(7)	2.193(6)
$Sn(2)\text{-}O(5)_{intra}$	3.164(7)	3.09(2)	3.12(1)	2.909(6); 2.746(7)	3.044(7)
$Sn(2)\text{-}O(5)_{inter}$	2.996(6)	3.18(2)	3.24(1)	≥3.5	≥3.5
Sn(1)···Sn(1′)	3.257(1)	3.266(2)	3.276(2)	3.292(1); 3.307(1)	3.319(1)
Sn(1)—O(1)—Sn(1′)	102.5(2)	102.9(7)	103.4(7)	103.5(2); 104.4(2)	103.4(2)
O(1)—Sn(1)—O(1′)	77.5(2)	77.1(7)	76.7(7)	76.5(2); 75.6(2)	76.6(2)
Reference	22	23	24	25	26

[a] Two molecules in asymmetric unit each situated about $\bar{1}$.

atoms as shown in Fig. 6. This carboxylate ligand forms asymmetric Sn–O bonds (Δ(Sn—O) 0.2–0.3 Å) which reflects the restricted bite distance of the ligand. The other ligand coordinates the Sn(2) atom in the monodentate mode via the O(4) atom and at the same time forms a weaker interaction to Sn(1) (also via the O(4) atom) in the range 2.6–2.9 Å. The Sn(1)···O(4) distances are not considered to fall in the range expected for significant bonding interactions between these atoms. However, these contacts play an important role in determining the coordination geometry about the Sn(1) atom. The non-coordinating atom of the second carboxylate ligand, O(5), is orientated so that it is directed away from the rest of the molecule but nevertheless does form weak intramolecular interactions with the Sn(2) atom (Table 4). In the case of three of the $R = CH_3$ derivatives, the O(5) atom also forms weak intermolecular interactions with the Sn(2) atoms of neighbouring molecules such that O(5)···Sn(2)′ contacts of >3.0 Å are found.[22–24] The presence of bulkier R groups residing on the Sn atoms (and/or on the carboxylate ligands) in the remaining structures apparently precludes close intermolecular contacts of this type. While the weak intra- and inter-molecular contacts between Sn(2) and O(5) are not indicative of substantial bonding interactions, they would be expected to be stereochemically important for the

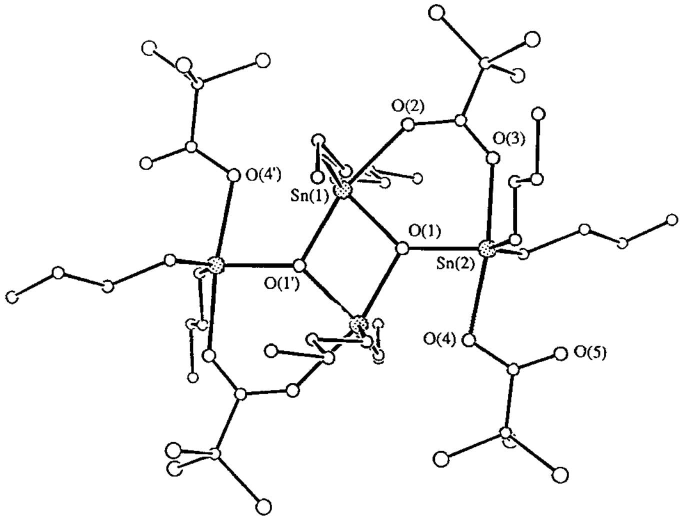


Figure 6 The structure of $\{[nBu_2Sn(O_2CCCl_3)]_2O\}_2$.[14]

R = Bu[a] R′ = $C_6H_4NH_2$-*o*	R = nBu R′ = CCl_3	R = nBu R′ = C_4H_3S	R = nBu R′ = CH_2SPh	R = nBu[a] R′ = C_6H_4OMe-*o*	R = Ph R′ = CCl_3
2.09(1); 2.01(1)	2.03(2)	2.034(7)	2.055(7)	2.161(6); 2.034(7)	2.154(4)
2.17(2); 2.01(1)	2.12(2)	2.177(7)	2.165(7)	2.041(6); 2.163(7)	2.062(5)
2.29(2); 2.28(2)	2.32(2)	2.275(9)	2.295(9)	2.286(6); 2.297(6)	2.323(6)
2.72(1); 2.79(2)	2.68(2)	2.830(8)	2.770(9)	2.781(7); 2.787(7)	2.866(5)
1.97(1); 2.05(1)	2.05(2)	2.023(7)	2.018(7)	2.036(6); 2.036(6)	2.031(5)
2.26(2); 2.22(2)	2.20(2)	2.234(8)	2.27(1)	2.275(8); 2.281(6)	2.250(5)
2.23(2); 2.15(2)	2.22(2)	2.166(7)	2.168(9)	2.160(7); 2.182(6)	2.212(5)
3.11(2); 2.84(1)	3.06(2)	2.867(8)	2.97(1)	2.861(7); 2.736(7)	2.901(5)
≥ 3.5	≥ 3.5	≥ 3.5	≥ 3.5	≥ 3.5	≥ 3.5
3.299(2); 3.315(2)	3.287(3)	3.314(1)	3.314(1)	3.327(2); 3.330(1)	3.314(1)
102(1); 105(1)	105(1)	103.8(2)	103.5(2)	104.7(2); 105.0(2)	103.6(2)
78(1); 81(1)	75(1)	76.2(2)	76.5(2)	75.3(2); 75.0(2)	76.4(2)
27	28	29	26	30	14

Sn(2) atom. The endocyclic tin atom, Sn(1), forms five significant bonds in these structures and exists in a distorted trigonal bipyramidal geometry with O(1) and carboxylate O(2) atoms occupying *trans* positions. If the weak Sn(1)···O(4) interaction were taken into account then the geometry would be best described as being based on a distorted octahedron with a basal plane defined by four O atoms. A coordination number of five is found for the exocyclic tin atom, Sn(2), which exists in a distorted trigonal bipyramidal geometry with the carboxylate O atoms in *trans* positions.

It is noteworthy that in the R = CH_3, R′ = $C_6H_4NH_2$-*o*,[25] R = nPr, R′ = CH_2SPh[26] and R = nBu, R′ = CH_2SPh,[26] $C_6H_4NH_2$-*o*,[27] C_4H_3S,[29] and $C_6H_4OCH_3$-*o*[30] structures there are no significant intra- or inter-molecular interactions involving the Sn atom and the non-carboxylate hetero atoms in contrast to the R = nBu, R′ = C_5H_4N-*o* compound described below in Section 3.3.5.[33]

3.3.2 Type II

The second structure type found for the $\{[R_2Sn(O_2CR')]_2O\}_2$ formulation is that of the R = CH_3, R′ = $C_6H_4NH_2$-*p* compound[25] which is illustrated in Fig. 7; selected interatomic parameters are listed in Table 5. The basic centrosymmetric framework described in Section 3.3.1 is retained in this compound, except that the O(2),O(3) carboxylate ligand now functions in the bidentate ligand (through one O atom only) rather than in the bidentate bridging mode and the O(4),O(5) carboxylate ligand chelates the Sn(2) atom. The Sn(1) atom exists in a distorted trigonal bipyramidal geometry as described for

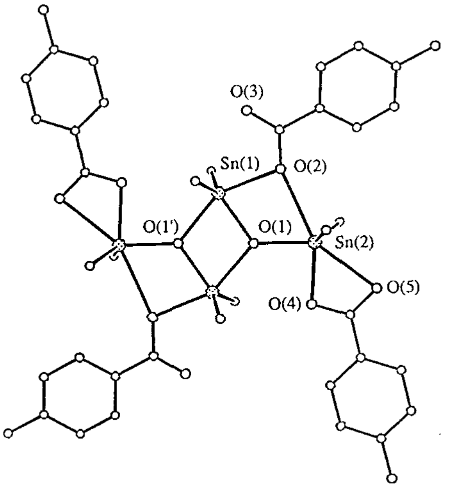


Figure 7 The structure of $\{[(CH_3)_2Sn(O_2CC_6H_4NH_2\text{-}p)]_2O\}_2$.[25]

the Sn(1) atom in the Type I structures. With the Sn(2) atom the situation is a little more complicated. Considering the four close contacts about the Sn(2) atom only, the coordination polyhedron would be based on a distorted tetrahedron. However, there are two other relatively close contacts to take into consideration, i.e. Sn(2)–O(5), 2.573(6) and Sn(2)–O(2) 2.688(5) Å, which are probably close enough to be considered as being significant. The original authors suggested that the coordination geometry about the Sn(2) atom was akin to that found for the $[R_2Sn(O_2CR')_2]$ structures (described in Section 3.5), i.e. as being based on a skew-trapezoidal bipyramidal geometry with C—Sn—C

Table 5 Structural parameters for $\{[R_2Sn(O_2CR')]_2O\}_2$, Types II–V

$\{[(CH_3)_2Sn(O_2CC_6H_4NH_2\text{-}p)]_2O\}_2$[25]			
Sn(1)-O(1)	2.036(5)	Sn(2)-O(1)	2.009(5)
Sn(1)-O(1′)	2.166(5)	Sn(2)-O(2)	2.688(5)
Sn(1)-O(2)	2.202(6)	Sn(2)-O(4)	2.104(6)
Sn(1)-O(3)	2.935(6)	Sn(2)-O(5)	2.573(6)
Sn(1)-O(4′)	3.315(6)	Sn(1)-Sn(1′)	3.358(1)
Sn(1)—O(1)—Sn(1′)	106.1(2)	O(1)—Sn(1)—O(1′)	74.0(2)
$\{[(CH_3)_2Sn(O_2CCH_3)]_2O\}_2$[32]			
Sn(1)-O(1)	2.15(2)	Sn(2)-O(1)	2.07(2)
Sn(1)-O(2)	2.07(2)	Sn(2)-O(2)	2.12(2)
Sn(1)-O(3)	2.34(2)	Sn(2)-O(8)	2.28(2)
Sn(1)-O(5)	2.38(2)	Sn(2)-O(9)	2.89(1)
Sn(3)-O(1)	2.01(2)	Sn(4)-O(2)	2.00(2)
Sn(3)-O(6)	2.24(1)	Sn(4)-O(4)	2.24(2)
Sn(3)-O(7)	2.25(2)	Sn(4)-O(9)	2.26(1)
Sn(3)-O(10)′	2.56(1)	Sn(4)-O(10)	2.92(2)
Sn(1)—O(1)—Sn(2)	101.8(7)	Sn(1)—O(2)—Sn(2)	102.6(6)
O(1)—Sn(1)—O(2)	77.3(6)	O(1)—Sn(2)—O(2)	77.9(2)
$\{[Ph_2Sn(O_2CCCl_3)]_2O\}_2$[14]			
Sn(1)-O(1)	2.14(1)	Sn(2)-O(1)	2.21(1)
Sn(1)-O(1′)	2.131(8)	Sn(2)-O(3)	2.21(1)
Sn(1)-O(2)	2.43(1)	Sn(2)-O(5)	2.20(1)
Sn(1)-O(4)	2.40(1)	Sn(1)-Sn(1′)	3.360(2)
Sn(1)—O(1)—Sn(1′)	103.9(4)	O(1)—Sn(1)—O(1′)	76.1(4)
$\{[nBu_2Sn(O_2CC_5H_4N\text{-}o)]_2O\}_2$[33]			
Sn(1)-O(1)	2.110(4)	Sn(2)-O(1)	2.055(4)
Sn(1)-O(1′)	2.047(4)	Sn(2)-O(2)	2.474(4)
Sn(1)-O(2)	2.303(4)	Sn(2)-O(9)	2.134(4)
Sn(1)-Sn(1′)	3.290(1)	Sn(2)-N(2)	2.550(5)
Sn(1)—O(1)—Sn(1′)	104.7(1)	O(1)—Sn(1)—O(1′)	75.3(1)

135.3(4)°. Thus to a first approximation the structure contains two bidentate carboxylate ligands that each coordinate via one oxygen atom only and two bidentate, chelating carboxylate ligands.

3.3.3 Type III

The third structural type for the $\{[R_2Sn(O_2CR')]_2O\}_2$ compounds is found for the $R = CH_3$, $R' = CH_3$ derivative[32] as illustrated in Fig. 8. This molecule does not possess any crystallographically imposed symmetry. The basic framework of Type I is retained and the difference between the two structures arises as a result of the different coordination of the carboxylate ligands. Whereas in Type I there are two bidentate and two monodentate ligands, in Type III this ratio has been altered to 3:1. Selected parameters for this structure are given in Table 5. Of particular interest is the coordination of the monodentate carboxylate ligand O(9)—C—O(10). The O(9) atom forms a close contact with the Sn(4) atom and a weaker contact of 2.89(1) Å with Sn(2) reminiscent of that

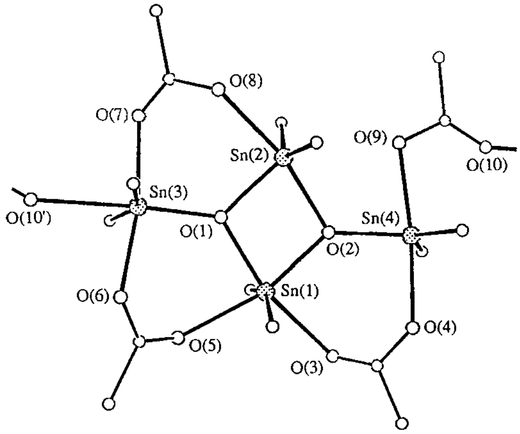


Figure 8 The structure of $\{[(CH_3)_2Sn(O_2CCH_3)]_2O\}_2$.[32]

observed in the Type I structures. The non-coordinating O(10) atom forms a weak contact of 2.92(2) Å with the Sn(4) atom. More importantly, the O(10) atom forms a significant intermolecular contact with a symmetry-related Sn(3) atom of 2.56(1) Å and thus the crystal lattice may be considered as being composed of chains of $\{[(CH_3)_2Sn(O_2CCH_3)]_2O\}_2$ molecules. A consequence of this structural type is that the Sn(1) and Sn(3) atoms are six-coordinate, distorted octahedral and that the Sn(2) and Sn(4) atoms are five-coordinate, distorted trigonal bipyramidal.

3.3.4 Type IV

A fourth structural type, illustrated in Fig. 9, was reported recently for R = Ph and R′ = CCl_3.[14] This compound is an isomer of one of the compounds which was shown to be of Type I (see Table 4). This fact indicates that there is little energy difference between structural Types I and IV (and Types II and III for that matter) and that the structure ultimately adopted in the solid state may depend largely on the crystallization conditions employed. From Fig. 9 it is evident that for Type IV all four carboxylate ligands are bridging. The molecule has $\bar{1}$ symmetry; therefore there are two distinct Sn atom geometries. The Sn(1) atom is distorted octahedral with four O atoms defining the basal plane and the Sn(2) atom is distorted trigonal bipyramidal as described above. Important parameters are summarized in Table 5.

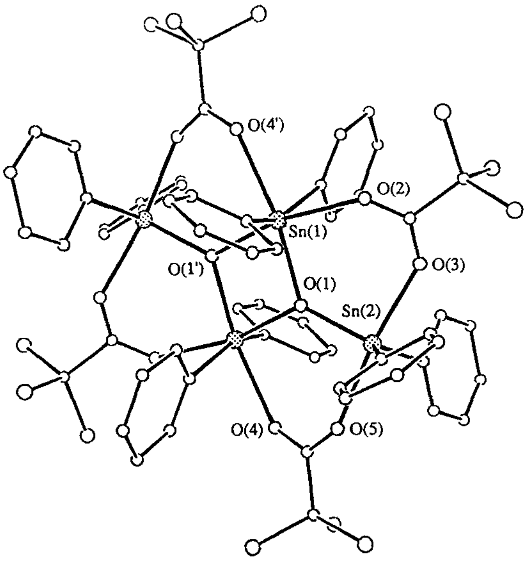


Figure 9 The structure of $\{[Ph_2Sn(O_2CCCl_3)]_2O\}_2$.[14]

3.3.5 Type V

The fifth structural type found for this class of compounds arises as a result of the interaction of an additional donor atom, residing on the R′ group (i.e. other than the carboxylate O atoms) with the Sn atom. The crystal structure of this compound, with R = nBu and R′ = C_5H_4N-*o*, in which the additional donor atom is a pyridine N atom, was reported recently.[33] The structure, which has crystallographic $\bar{1}$ symmetry, features the basic $R_8Sn_4O_2$ framework described above and two distinct carboxylate ligands; see Fig. 10 and Table 5. The first carboxylate ligand bridges the Sn(1) and Sn(2) atoms via the O(2) atom; the pendant O(3) atom does not form a close interaction with the Sn atoms. The N donor atom from the R′ group of this carboxylate ligand also forms

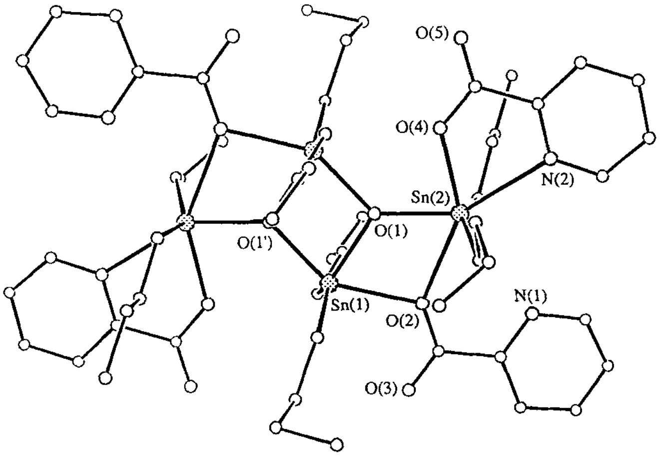


Figure 10 The structure of $\{[nBu_2Sn(O_2CC_5H_4N\text{-}o)]_2O\}_2$.[33]

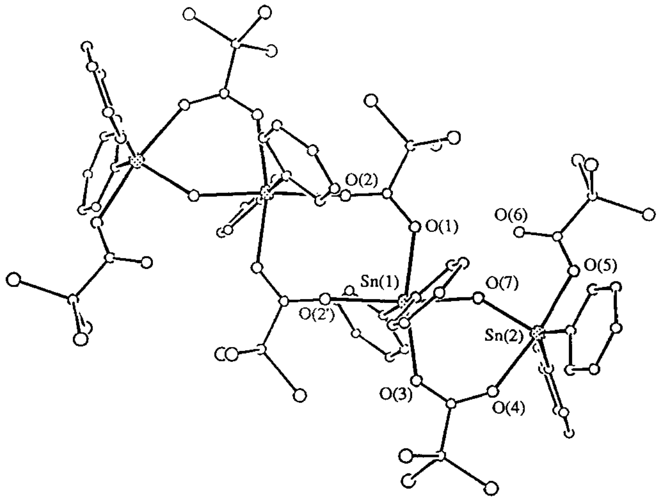


Figure 11 The structure of $[Ph_8Sn_4(O_2CCCl_3)_6(OH)_2]$.[14]

a relatively long interaction to the Sn(2) atom of 3.150(5) Å, which is not indicative of a bonding interaction. The second ligand chelates the exocyclic Sn(2) atom via the O(4) and N(2) atoms and simultaneously forms a weak interaction between the O(4) atom and the Sn(1) atom of 3.066(5) Å. The O(5) atom does not coordinate either of the Sn atoms. The endocyclic Sn(1) atom may therefore be considered as five-coordinate and to exist as a distorted trigonal bipyramidal geometry with the O(1′) and O(2′) atoms in approximate axial positions; O(1′)—Sn(1)—O(2) 146.8(4)°. The Sn(2) atom is six-coordinate and exists in a distorted octahedral geometry with an O_3N basal plane; C—Sn—C 148.4(3)°.

3.4 $[R_8Sn_4(O_2CR')_6X_2]$

The structure of $[Ph_8Sn_4(O_2CCCl_3)_6(OH)_2]$[14] features a centrosymmetric tetramer with two distinct Sn atoms, bridging hydroxyl groups, and three distinct carboxylate ligands as shown in Fig. 11. The linkage of the endocyclic Sn atoms, Sn(1), via two bridging carboxylate ligands results in the formation of an eight-membered ring. This carboxylate ligand forms disparate Sn–O bonds (Sn(1)–O(1) 2.185(6) and Sn(1)–O(2′) 2.361(7) Å). The second carboxylate ligand bridges the endocyclic and exocyclic Sn atoms with distances Sn(1)–O(3) 2.277(6) and Sn(2)–O(4) 2.212(6) Å. The Sn(1) and Sn(2) atoms are also linked by a hydroxyl bridge such that Sn(1)–O(7) is 2.155(6) Å, Sn(2)–O(7) is 2.021(5) Å and Sn(1)—O(7)—Sn(2) is 137.8(3)°. The third carboxylate ligand functions as a monodentate ligand forming a Sn(2)–O(5) bond distance of 2.157(6) Å. As a result of an intramolecular hydrogen bond the O(6) and O(7) atoms are separated by only 2.61 Å. The Sn(1) atom geometry is distorted octahedral with the phenyl groups approximately *trans*; C—Sn—C 167.6(4)°. In contrast the geometry about the Sn(2) atom is based on a trigonal bipyramid with the two phenyl groups and the hydroxyl group defining the trigonal plane and two carboxylate O atoms occupying axial positions; O—Sn—O 172.1(3)°.

3.5 $[R_2Sn(O_2CR')_2]$

There are seven X-ray structures of the general formula $[R_2Sn(O_2CR')_2]$ available in the literature.[25,26,34–37] Structural details for six of these compounds, which are monomeric, are listed in Table 6. It is noteworthy that four of the monomeric species possess crystallographically imposed two-fold symmetry. The Sn atoms exist in skew-trapezoidal bipyramidal geometries with each basal plane being defined by two asymmetrically chelating carboxylate groups (Sn–O(1) $\leq$ 2.2 and Sn–O(2) $\geq$ 2.5 Å) as shown in Fig. 12 for the

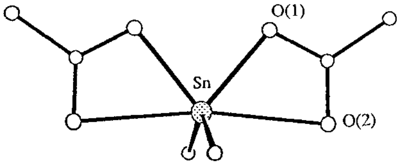


Figure 12 The structure of $[(CH_3)_2Sn(O_2CCH_3)_2]$.[34]

Table 6 Structural parameters for $[R_2Sn(O_2CR')_2]$

R	R′	Sn-O(1)	Sn-O(2)	O(1)—Sn—O(1′)	O(2)—Sn—O(2′)	C—Sn—C	Ref.
CH_3[a]	CH_3	2.106(2)	2.539(2)	79.5(1)	170.3(1)	135.9(2)	32
CH_3	C_6H_5	2.156(9) 2.128(9)	2.51(1) 2.510(9)	84.4(4)	165.3(3)	147.2(7)	37
CH_3	$C_6H_4NH_2$-*p*	2.077(3) 2.097(3)	2.556(3) 2.543(3)	81.8(1)	168.0(1)	134.7(2)	25
nPr[a]	$CH_2SC_6H_5$	2.114(3)	2.587(4)	79.5(1)	172.5(1)	136.7(1)	26
nBu[a]	C_6H_4Br-*p*	2.075(3)	2.635(4)	81.1(1)	171.1(1)	130.6(2)	35
nBu[a]	$CH_2SC_6H_5$	2.134(4)	2.559(4)	79.5(2)	170.5(2)	140.7(1)	36

[a] Molecule has two-fold symmetry.

$R = CH_3$, $R' = CH_3$ compound.[34] The axial positions are occupied by the two organo substituents such that the R groups are disposed over the longer Sn–O vectors with the C—Sn—C angles in the range 130–150°. This coordination geometry is described as skew-trapezoidal bipyramidal.

A second structural type for this general formula is found for the $R = CH_3$ and $R' = C_5H_4N$-*o* compound, i.e. $[(CH_3)_2Sn(O_2CC_6H_4\text{-}o)_2]_n$.[38] This structural type arises as a result of the participation of the heterocyclic N atoms in bonding to the Sn atoms. The Sn atom in this polymeric compound (see Fig.13) is seven-coordinate. In addition to the two CH_3 groups and two sets of N,O donor atoms (Sn–N 2.477(4), 2.507(4) Å; Sn–O 2.199(4), 2.393(4) Å) derived from two 2-pyridinecarboxylate groups, the Sn atom is coordinated by a symmetry related O(2′) atom at 2.340(3) Å. There are two crystallographically distinct carboxylate groups in the structure, one being bidentate chelating whilst the other is tridentate, chelating one Sn atom via the N atom and one O atom and simultaneously bridging a neighboring Sn atom via the second O atom. The coordination geometry about the Sn atom may be best described as pentagonal bipyramidal with the two CH_3 groups occupying axial positions such that C—Sn—C is 174.5(3)°.

3.6 $[R_2Sn(O_2CR')_2L_2]$

There is one example in the literature of a crystal structure with the above formula, this being $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2(bipy)]$;[39] see Fig. 14. The Sn atom exists in a distorted octahedral geometry defined by a chelating 2,2′-bipyridyl ligand (Sn–N 2.34(1), 2.34(2) Å), two vinyl organo groups which are *trans* to each other (C—Sn—C 174.4(8)°) and two O atoms derived from two monodentate carboxylate ligands (Sn–O(1) 2.18(1), Sn–O(3) 2.25(1) Å). The pendant O atoms do not coordinate the Sn atom (Sn–O(2) 3.47(1), Sn–O(4) 3.01(1) Å).

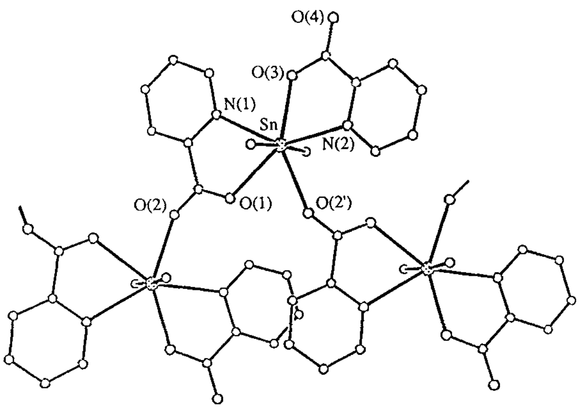


Figure 13 The structure of $[(CH_3)_2Sn(O_2CC_6H_4N\text{-}o)_2]_n$.[38]

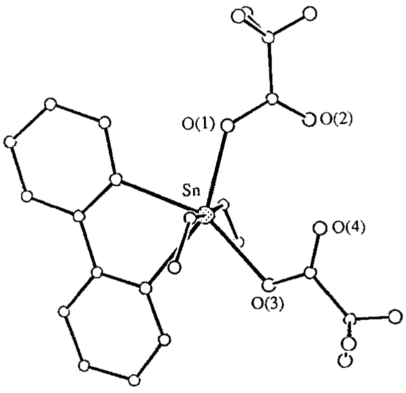


Figure 14 The structure of $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2(bipy)]$.[39]

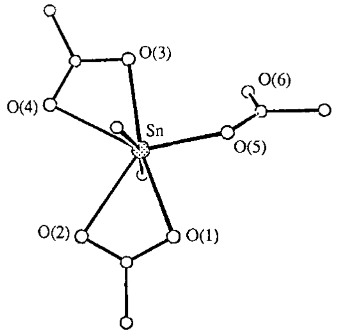


Figure 15 The structure of $[(CH_3)_2Sn(O_2CCH_3)_3]^-$.[34]

3.7 $[R_2Sn(O_2CR')_3]^-$

The facile 1/1 reaction of $(CH_3)_2Sn(O_2CCH_3)_2$ with $[(CH_3)_4N]^+[O_2CCH_3]^-$ yields the crystalline complex $[(CH_3)_2Sn(O_2CCH_3)_3]^-$.[34] The monomeric complex features a seven-coordinate Sn atom (Fig. 15) which is coordinated by two CH_3 groups and three carboxylate ligands. Two of the acetate ligands are bidentate and coordinate the Sn atom with asymmetry in their Sn–O bonds; Sn–O 2.291(9), 2.525(9) and 2.271(8), 2.520(9) Å. The third acetate ligand is monodentate and forms the shorter Sn–O bond of 2.113(9) Å. The five O donor atoms form an approximate pentagonal plane (±0.06 Å) and the two CH_3 groups occupy axial positions (C—Sn—C 165.8(6)°) thereby defining a pentagonal bipyramidal geometry about the Sn atom.

3.8 $[R_2Sn((O_2C)_2R')]$

A crystal structure determination of a nBu_2Sn compound containing the ligand *N* (2-hydroxyethyliminodiacetate) has shown that the dicarboxylate ligand functions in the tetradentate mode in this monomeric species.[40] The Sn atom (see Fig. 16) is coordinated by two O atoms derived from each of the carboxylate residues (Sn–O(1) 2.16(1), Sn–O(3) 2.17(1) Å and O(1)—Sn—O(3) 147.8(4)°), the imino N atom (2.32(1) Å) and the hydroxy O atom O(5) at 2.18(1) Å. The geometry about the Sn atom is based on a distorted octahedron with *cis* n-butyl groups; C—Sn—C 112.0(8)°.

3.9 $[R_2Sn((O_2C)_2R')L]_n$

There are four crystal structures of diorganotin compounds that contain dicarboxylate ligands and an additional ligand coordinated to the Sn atom.[41–43] For three of the structures the dicarboxylate ligand is derived from 2,6-pyridinedicarboxylic acid[41, 42] while for the fourth structure the anion is iminodiacetate.[43] a representative structure for three of the compounds (i.e. with $n = 2$)[42, 43] is shown in Fig. 17 and selected interatomic parameters are collected in Table 7. The structures of these are each situated about a crystallographic centre of symmetry. The Sn atoms are seven-coordinate, being coordinated by two organo groups, two O atoms (one from each CO_2 residue) and one N atom of the carboxylate ligand, an O atom from the symmetry-related carboxylate ligand and an O atom from a coordinated water molecule. The dicarboxylate ligand is thus tetradentate, forming three bonds to one Sn atom and at the same time bridging a second Sn atom. However, only two of the possible four carboxylate O atoms are involved in coordination to the Sn atoms (the other two O atoms do not form a close interaction with Sn) owing to the fact that the O(1) atom bridges two Sn centres. The planar Sn_2O_2 unit is not symmetrical, containing two different Sn–O bond distances (see Table 7), with one Sn–O bond being significantly longer than the other. The coordination polyhedron for the seven-coordinate Sn atoms is based on a

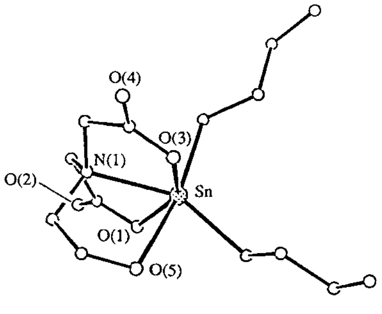


Figure 16 The structure of $[nBu_2Sn((O_2CCH_2)_2N(CH_2CH_2OH))]$.[40]

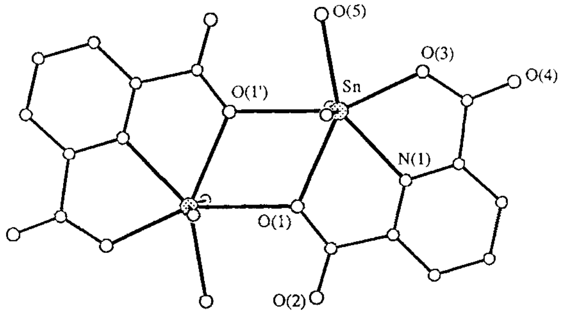


Figure 17 The structure of $[(CH_3)_2Sn((O_2C)_2C_5H_3N)(OH_2)]_2$.[42]

Table 7 Structural parameters for $[R_2Sn((O_2C)_2R')L]_n$

R	Sn–O(1)	Sn–O(1′)	Sn–N	Sn–O(3)	Sn–O(5)	Sn–O(2′)	C—Sn—C	Ref.
CH_3[a,b]	2.471(3)	2.593(3)	2.301(4)	2.206(4)	2.312(3)	—	166.2(2)	42
nBu[a,b]	2.422(4)	2.783(4)	2.265(5)	2.176(5)	2.352(5)	—	162.2(3)	42
CH_3[b,c]	2.371(3)	2.790(3)	2.290(4)	2.199(3)	2.376(4)	—	161.0(3)	43
Ph[a,d]	2.446(3)	—	2.338(3)	2.214(3)	2.271(3)	2.380(3)	172.4(2)	41

[a] With 2,6-pyridinedicarboxylate. [b] $n = 2$. [c] With iminodiacetate. [d] $n = \infty$.

pentagonal bipyramid, with the plane being defined by an NO_4 donor set and the organo substituents occupying the axial positions. For the $R = CH_3$ derivative (with the pyridine-based ligand) one of the non-coordinating Sn atoms is hydrogen-bonded to a water molecule of crystallization.[42]

The fourth compound of this type, $[Ph_2Sn((O_2C)_2C_5H_3N)(OH_2)]$ (shown in Fig. 18), forms a polymeric structure, i.e. with $n = \infty$.[41] The 2,6-pyridinedicarboxylate ligand coordinates the Sn atom as described above; however, in this example there is no intermolecular bond formed between the O(1) atom and the centrosymmetrically related Sn′ atom. The intermolecular links in this case are formed via the O(2) atoms and Sn atoms of neighbouring molecules; this generates a zig-zag polymeric chain. The fifth position of the pentagonal plane about the Sn atom is again occupied by a water molecule of crystallization, leading to a pentagonal bipyramidal coordination polyhedron as described above. Selected intermolecular parameters are given in Table 7.

3.10 $[R_2Sn(O_2CR')]_6$

The crystal structure of $[nBu_2Sn(O_2CCH_2CH_2S)]_6$ has been determined recently in which the carboxylate ligand is dinegative by virtue of the presence of a uninegative thiolate function as well as the carboxylate group.[44] The compound was shown to crystallize as a cyclic hexamer, as illustrated in Fig. 19, such that there are two distinct molecules in the asymmetric unit each disposed about a crystallographic centre of inversion. The hexamer may be thought of as comprising six R_2SnSR' entities bridged by carboxylate ligands. In this respect the structure resembles those found for the polymeric *trans*-R_3RnO_2 compounds, as discussed in Section 4.1.4, except that in the former six molecules aggregate to form a hexamer rather than an infinite polymer as found in the latter compounds. The Sn atoms exist in distorted trigonal bipyramidal geometries with the two n-butyl groups and the S atom (Sn–S

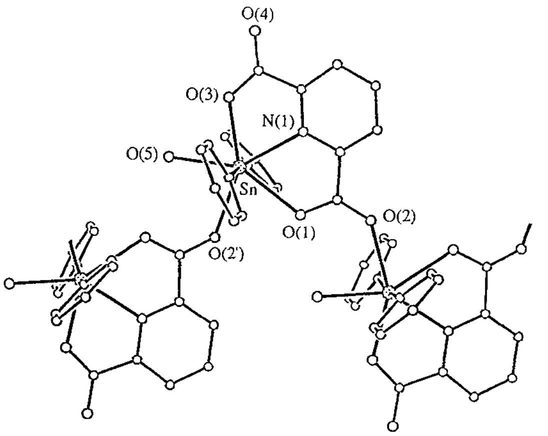


Figure 18 The structure of $[Ph_2Sn((O_2C)_2C_5H_3N)(OH_2)]_n$.[41]

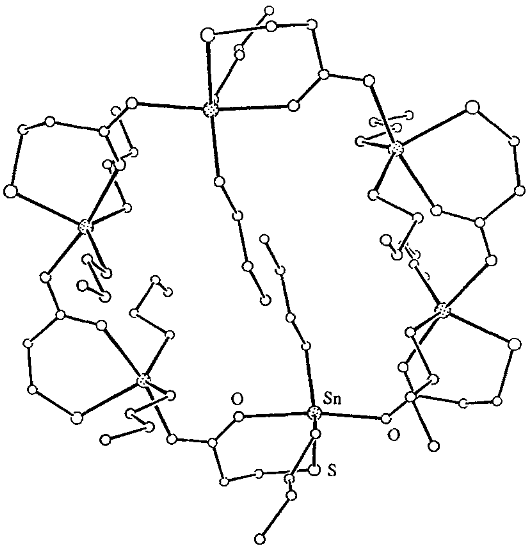


Figure 19 The structure of $[nBu_2Sn(O_2CCH_2CH_2S)]_6$.[44]

2.379(5)–2.398(4) Å) defining the trigonal plane, and two O atoms, derived from different carboxylate ligands, occupying the axial sites (Sn–O 2.17(1)–2.31(1) Å; O—Sn—O 169.6(3)–172.1(4)°).

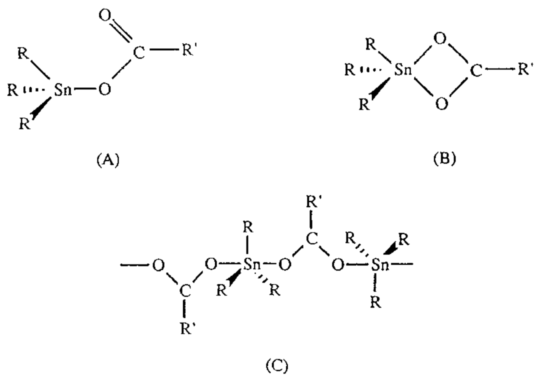
4 TRIORGANOTIN CARBOXYLATES

4.1 [$R_3Sn(O_2CR')$]

4.1.1 Preamble

There has been considerable interest in compounds of the empirical formula [$R_3Sn(O_2CR')$], owing in part to the diversity of structures that have been found in the solid state for these compounds.[45–70] The structures are, however, closely related to each other and there is a clear progression from monomeric species to infinite polymeric chains. Basically, there are three ideal structures that may be adopted as shown in Scheme 1. Structure **A** incorporates a four-coordinate Sn atom and features a monodentate carboxylate ligand. For structure **B**, a bidentate carboxylate ligand chelates the Sn atom, which is now five-coordinate. In contrast to the monomeric structures **A** and **B**, a polymeric structure is represented by **C**. Here, the carboxylate ligands are bidentate bridging and the five-coordinate Sn atoms exist in distorted trigonal bipyramidal geometries. The monomeric species as represented by **A** and **B** probably do not exist but structures somewhere in between these extremes are known. There are numerous examples of structure type **C** in the literature.

Some generalizations may be made concerning the steric or electronic requirements that may favour one structural motif over another. Organotin compounds with bulky R groups coordinated to tin would tend to favour the monomeric structures, whereas sterically less demanding R groups would favour structural type C. Electron-withdrawing R groups coordinated to Sn would be expected to favour five-coordinate species as the acceptor character at the Sn atom would be enhanced. Less clear, however, is the effect on the [$R_3Sn(O_2CR')$] structures adopted when the R′ is altered. In Section 4.1.2 the structures that lie in between the **A** and **B** motifs are discussed and the **C** type structures are dealt with in Section 4.1.4.



Scheme 1 Three ideal structures for compounds of the empirical formula [$R_3Sn(O_2CR')$]

4.1.2 Type I

Compounds of the general formula [$R_3Sn(O_2CR')$] in this category exist as monomeric compounds in the solid state and, as mentioned above, their structures lie somewhere in between structures **A** and **B** shown in Scheme 1. Table 8 lists 13 structures in this grouping in order of increasing coordination at the Sn atom in accord with the length (and hence strength) of the Sn–O(2) bond. It is noteworthy that only tricyclohexyl- and triphenyl-tin compounds are represented in this category, although it is noted that triphenyltin compounds are also known to adopt the *trans*-R_3SnO_2 structure (see Section 4.1.4).

The compound [(c-hexyl)$_3$Sn(O_2CF_3)][45] is judged to resemble most closely structure **A** in Scheme 1 (owing to disorder associated with the CF_3 groups in this compound; the acetate analogue[47] is shown in Fig. 20). The Sn atom in the [(c-hexyl)$_3$Sn(O_2CF_3)] compound is essentially four-coordinate, distorted tetrahedral. The

Table 8 Structural parameters for [$R_3Sn(O_2CR')$]

R	R′	Sn–O(1)	Sn–O(2)	Ref.
c-Hexyl	CF_3	2.08(4)	3.11(4)	45
Ph	C_6H_4OH-*o*	2.083(2)	3.071(2)	46
c-Hexyl	CH_3	2.12(3)	2.95(4)	47
c-Hexyl	$CH_2(C_8H_6N)$[a]	2.086(3)	2.929(4)	48
Ph	C_6H_4Cl-*p*	2.048(4)	2.861(4)	49
Ph	$C_6H_4NH_2$-*o*	2.043(3)	2.823(3)	50
Ph	$C_6H_4SCH_3$-*p*	2.060(2)	2.783(3)	46
Ph	$C_6H_4OCH_3$-*o*	2.054(3)	2.781(3)	46
c-Hexyl	$CH_2(C_8H_6NCH_3)$[b]	2.05(1)	2.78(1)	51
Ph	C_4H_3S	2.076(4)	2.768(4)	52
Ph	$C_6H_4N(CH_3)_2$-*p*	2.072(2)	2.629(2)	50
Ph	$C_6H_4N(CH_3)_2$-*o*	2.115(6)	2.564(7)	50
Ph	$C_6H_4(N_2C_6H_3(OH)(CH_3))$[c]	2.070(5)	2.463(7)	53

[a] Indole-3-acetic acid. [b] *N*-methylindole-3-acetic acid. [c] *o*-(2-Hydroxy-5-methylphenylazo)benzoate.

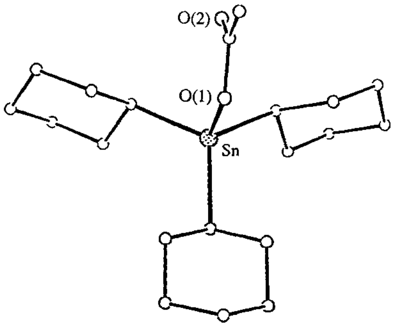


Figure 20 The structure of $[(c\text{-hexyl})_3Sn(O_2CCH_3)]$.[47]

Sn–O(2) separation of 3.11(4) Å is not considered to be a substantial interaction between these atoms. However, the O(2) atom exerts a steric influence and contributes to the distortion of the geometry about the Sn atom. Similarly an intermolecular O(2)···Sn′ interaction of 3.70 Å is not indicative of a significant interaction. If the O(2)···Sn′ interaction was significant, the structure would conform to the *trans*-R_3SnO_2 structural motif described in Section 4.1.4; however, this is not the case.

The other limiting structure in this category is represented by $[Ph_3Sn((o\text{-2-hydroxy-5-methylphenylazo})benzoate)]$[53] and is illustrated in Fig. 21. The two Sn–O distances of 2.070(5) and 2.463(7) Å indicate significant bonding interactions and therefore the Sn atom must be thought of as being five-coordinate. The geometry is based on a distorted *cis*-trigonal bipyramid with the two oxygen atoms occupying both apical and equatorial positions. The distortion in the coordination polyhedron is manifested by the acute O—Sn—O angle imposed by the restricted bite distance of the carboxylate ligand.

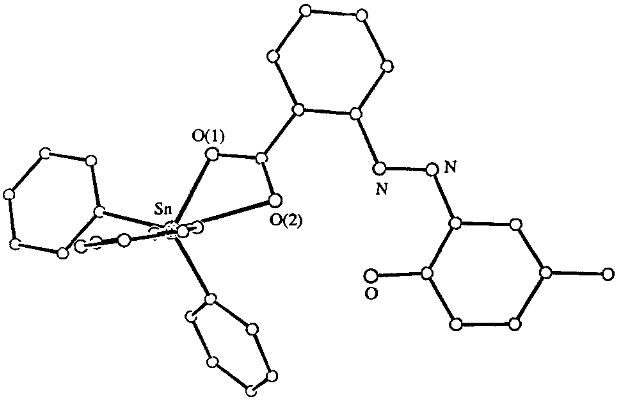


Figure 21 The structure of $[Ph_3Sn((o\text{-2-hydroxy-5-methylphenylazo})benzoate)]$.[53]

A systematic X-ray study of structures falling in between structures **A** and **B** shown in Scheme 1 has been reported by Day and co-workers in which a series of triphenyltin carboxylates, containing functionalized aryl groups, were structurally characterized and distortions about the Sn atom examined.[46, 49, 50] In particular the transformation from tetrahedral Sn to trigonal bipyramidal Sn, arising from the close approach of the O(2) atom (i.e. the less strongly bound O atom), was investigated. In order for the Sn atom to be considered trigonal bipyramidal in these compounds, it was necessary to define the trigonal plane by the O(1) atom and two phenyl groups and the apical positions by the O(2) atom and the remaining phenyl ring. Support for this assignment was found in the dihedral angle between the trigonal plane and the axial plane which were all found to be near 90°. However, as noted in the original articles, the Sn atom lies at least 0.5 Å out of the trigonal plane (in all examples), consistent with a tetrahedral coordination geometry about the Sn atom. While the O(2) atom may not occupy a formal coordination site in the Sn atom geometry, its presence has a marked stereochemical effect in that the C—Sn—C angle opposite is opened up to approximately 120°. Worthy of particular mention are three structures containing NH_2 or $N(CH_3)_2$ substituents on the R′ groups which illustrate the importance of hydrogen-bonding effects in organotin carboxylate structures.[50]

In the $[Ph_3Sn(O_2CC_6H_4NH_2\text{-}o)]$ compound[50] the Sn–O(2) separation was found to be quite long at 2.823(3) Å, owing, in part, to the presence of an intramolecular hydrogen bond between O(2) and an N-bound H atom of 2.04(6) Å. In the $N(CH_3)_2$ analogue, $[Ph_3Sn(O_2CC_6H_4N(CH_3)_2\text{-}o)]$, where no such intramolecular hydrogen bond is possible, the Sn–O(2) interaction contracts to 2.564(7) Å. Again, in $[Ph_3Sn(O_2CC_6H_4NH_2\text{-}p)]$, where there is a significant intermolecular hydrogen bond between the O(2) atom and a symmetry-related amino hydrogen atom of 2.16(4) Å, which is weaker than found in the *ortho* compound, the Sn–O(2) distance is shortened to 2.629(2) Å i.e. a distance that is intermediate between the two examples cited above.

4.1.3 Type II

The crystal structure of $[(CH_3)_3Sn(O_2CC_6H_4\text{-}OH\text{-}o)]$ is shown in Fig. 22.[54] The immediate environment about the Sn atom comprises three methyl groups and the O(1) atom, Sn–O(1)

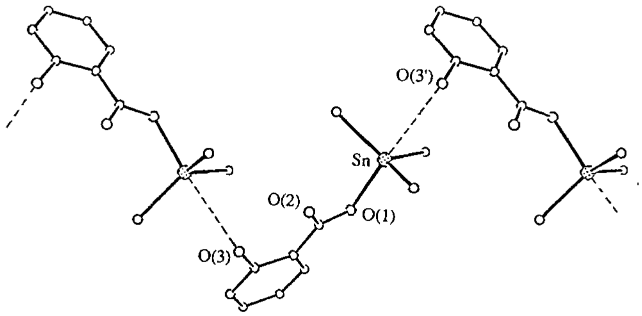


Figure 22 The structure of $[(CH_3)_3Sn(O_2CC_6H_4OH\text{-}o)]$.[54]

2.114(7) Å, derived from a monodentate carboxylate ligand. The Sn···O(2) separation is 3.029(8) Å. The OH function of salicylic acid forms a weak intermolecular contact with a neighbouring Sn atom such that Sn···O(3') is 3.08(1) Å. The resultant O(1)—Sn—O(3') angle is 173.4(2)° so that the Sn atom environment may be thought of as being based on a trigonal bipyramidal geometry. However, it is noted that the Sn atom lies 0.35 Å out of the plane of the methyl groups, in the direction of the O(1) atom, in contrast to the *trans*-R_3SnO_2, i.e. Type III, structures discussed in Section 4.1.4 in which the R_3Sn atoms are coplanar. The length of the Sn···O(3') separation indicates that there is not a significant bonding interaction between these atoms. Therefore, on the structural evidence, the Sn atom geometry is best described as being based on a distorted tetrahedron. That the O(3) atom influences the Sn atom geometry is seen in the nature of the distortion from the ideal tetrahedral geometry. The presence of the O(3) atom accounts for the opening up of the C—Sn—C angles to 116.7(2), 118.9(2), and 123.5(2)° and the concomitant contraction of the O(1)—Sn—C angles to 88.8(1), 92.7(1) and 98.0(1)°. The $[(CH_3)_3Sn(O_2CC_6H_4OH\text{-}o)]$ compound represents an intermediate structure between the Type I and Type III structures (Section 4.1.4).

4.1.4 Type III

The largest class of compounds of the general formula $[R_3Sn(O_2CR')]$ are those best described as the *trans*-R_3SnO_2 type.[49,51,54–67] These structures are polymeric, associating via bridging carboxylate ligands as shown for the $[Ph_3Sn(O_2CCH_3)]_n$ compound[54] in Fig. 23. Important interatomic parameters are listed in Table 9. The Sn atoms in these structures exist in distorted trigonal bipyramidal environments with the three organo substituents defining the trigonal planes so that the C_3Sn groups are very nearly planar. The more electronegative O atoms, from symmetry-related carboxylate ligands, occupy the axial positions. The carboxylate ligands bridge two Sn atoms forming different Sn–O bond distances: the shorter Sn–O(1) bonds fall in the range 2.12(1)–2.266(1) Å and the longer Sn–O(2) bonds in the overlapping range 2.246(1)–2.65(2) Å. The O(1)—Sn—O(2') *trans* angles lie in the range 168.6(8)–176.2(8)°. In two of the compounds in this class, namely $[nBu_3Sn(O_2CC_9H_8N)]$[51] and $[(PhCH_2)_3Sn(O_2CCH_3)]$,[66] the Sn–O(2) bond distance is in excess of 2.5 Å. It is clear, however, that from an examination of the Sn atom geometries these structures fall neatly into this category of compounds. The intramolecular Sn···O(2) separations are ≥3.0 Å in all of the structures. In a recent survey of structures of this type, it was noted that there was a constancy of the repeat distance of the polymers, which are invariably aligned along a crystallographic unit-cell edge, such that the average repeat distance was found to be 5.2(2) Å per monomeric entity.[70] Furthermore, the authors noted that the polymeric structures were propagated along a crystallographic 2_1-screw axis in most cases; in the remaining structures the zig-zag array is aligned along a mirror plane.[70]

Particularly noteworthy in this class of compounds is the structure determination of $[(CH_3)_3Sn(O_2CC_5H_4N)].H_2O$,[56] which crystallizes with four molecules in the crystallographic asymmetric unit. Furthermore, this is the only compound among the organotin carboxylates in which the carboxylate ligand contains a pyridine N atom that does not coordinate the Sn atom (except for the zwitterions discussed in Section 4.2). Each pyridine-N atom is, however, connected to a water molecule of crystallization via hydrogen bonds.

As has been noted previously, the factors which dictate whether compounds of the general

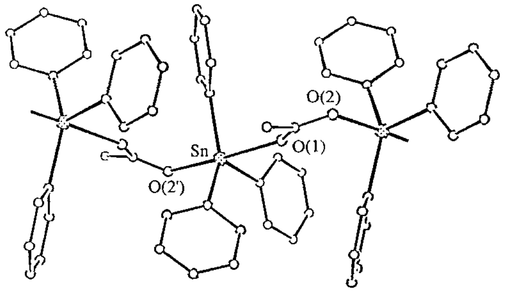


Figure 23 The structure of $[Ph_3Sn(O_2CCH_3)]_n$.[63]

Table 9 Structural parameters for $[R_3Sn(O_2CR')]_n$

R	R′	Sn–O(1)	Sn–O(2′)	O(1)—Sn—O(2′)	Ref.
CH_3	CH_3	2.205(3)	2.391(4)	171.6(1)	55
CH_3	CF_3	2.18(1)	2.46(2)	174.8(5)	55
CH_3[a]	C_5H_4N	2.21(1)	2.44(4)	176.2(8)	56
		2.18(2)	2.43(2)	177.5(9)	
		2.15(2)	2.41(2)	173.5(9)	
		2.20(2)	2.44(2)	171.3(9)	
CH_3	C_4H_3O	2.191(3)	2.430(4)	172.3(2)	57
CH_3	C_4H_3S	2.149(8)	2.482(8)	173.4(3)	58
CH_3	$C_6H_4OCH_3$-*o*	2.208(2)	2.381(2)	170.8(1)	54
$CH{=}CH_2$	CH_3	2.20(1)	2.33(1)	172.7(5)	59
$CH{=}CH_2$	$CHCl_2$	2.21(1)	2.34(1)	174.3(2)	59
$CH{=}CH_2$	CCl_3	2.17(2)	2.49(1)	173.4(3)	60
$CH{=}CH_2$	$C_5H_4FeC_5H_5$	2.12(1)	2.42(1)	172.5(2)	61
nBu	C_9H_8N[b]	2.199(3)	2.524(3)	173.5(2)	51
Ph[c]	H	2.219(6)	2.317(6)	173.6(2)	62
		2.219(6)	2.318(5)	173.1(2)	
Ph	CH_3	2.185(3)	2.349(3)	173.6(1)	63
Ph	CH_2Cl	2.201(2)	2.372(2)	174.8(1)	64
Ph	C_6H_4Cl-*o*	2.201(3)	2.384(3)	173.8(1)	49
Ph	$C_6H_4C(O)(CH_2)_2$	2.266(1)	2.246(1)	174.6(1)	65
CH_2Ph	CH_3	2.14(2)	2.65(2)	168.6(8)	66
$(CH_3)_2Ph$[d]	CH_3	2.201(3)	2.370(3)	174.0(1)	67

[a] Four molecules in crystallographic asymmetric unit. [b] Indole-3-acetic acid. [c] Two molecules in crystallographic asymmetric unit. [d] $[(CH_3)_2PhSn(O_2CCH_3)]$.

formula $[R_3Sn(O_2CR')]$ adopt one structural type over another are yet to be fully understood. As can be seen from Table 8, bulky R groups bound to the Sn atom seem to favour monomeric complexes; however, there are several examples of triphenyltin compounds adopting the $[R_3Sn(O_2CR')]_n$ motif as well. Similarly, the range of carboxylate groups in these structures is wide and there is no obvious trend to account for the different structural types. An interesting comparison was made recently for the $(CH_3)_3Sn$ and Ph_3Sn complexes containing the thiophene-2-carboxylate anion. For the $[Ph_3Sn(O_2CC_4H_3S)]$ compound[52] a monomeric structure was reported, whereas a polymeric *trans*-R_3SnO_2 type of structure was found for the $(CH_3)_3Sn$ analogue.[58] For the related pair of acetate structures, i.e. $[(CH_3)_3Sn(O_2CCH_3)]$[55] and $[Ph_3Sn(O_2CCH_3)]$,[63] only the polymeric motif has been demonstrated by X-ray crystallography. This result would seem to suggest that other factors, such as crystal packing effects, may have to be taken into account when attempting to explain the structures adopted in the solid state for these compounds. The importance of hydrogen-bonding contacts in determining the structures adopted in the solid state has already been mentioned in the work of Day *et al.*[49, 50, 54] and of Molloy *et al.*[51]

4.1.5 Type IV

The polymeric structure found for $[Ph_3Sn(O_2CC_5H_4N)]_n$ is illustrated in Fig. 24.[68] This structure resembles those of the *trans*-R_3SnO_2 type described in Section 4.1.4 in that the Sn atom exists in a trigonal bipyramidal geometry and the carboxylate ligand is bidentate bridging, leading to a polymeric structure. In this example, however, the two donor atoms of the 3-pyridinecarboxylate ligand are the O(1) atom and the pyridine N atom; Sn–O(1) 2.137(6) and Sn–N(1′) 2.568(7) Å. The O(2) atom does not

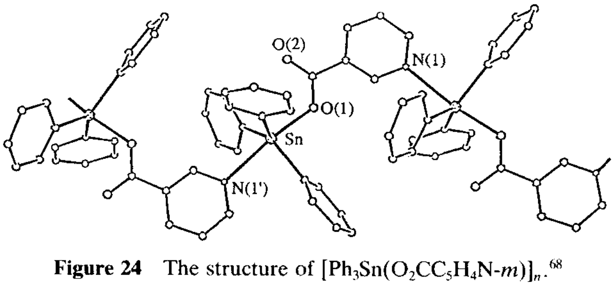


Figure 24 The structure of $[Ph_3Sn(O_2CC_5H_4N\text{-}m)]_n$.[68]

form a significant interaction with the Sn atom, this separation being 3.271(6) Å. The O(1)—Sn—N(1′) angle is 173.1(2)°, reminiscent of the Type III structures described above in Section 4.1.4.

4.2 $[R_3Sn(O_2CR'H)X]$

The zwitterionic forms of two carboxylic acids, each containing an *N*-heterocyclic function, have been characterized in three separate structure determinations;[71-73] one example, i.e. of $[Ph_3Sn(O_2C_5H_4NH)Cl]$,[71] is shown in Fig. 25. The monomeric compounds of the general formula $[R_3Sn(O_2CR'H)X]$ contain trigonal bipyramidal Sn atoms. The three organo substituents occupy positions in the trigonal plane and the O(1) atom and the X atom (Cl or NCS) in axial positions; see Table 10 for selected interatomic parameters. In these structures the electrically neutral carboxylic acid ligands coordinate in the monodentate mode via one O atom. The site of protonation has been determined unambiguously in each of the three determinations as being at the heterocyclic N atom. The second O atom of the carboxylic acid does not coordinate to the Sn atom; the Sn···O(2) separation for the R = Ph, R′ = $C_5H_4N^+H$ and X = Cl compound[71] being approximately 3.8 Å whilst in the other two compounds this separation is approximately 3.3 Å.[72,73] This major difference between the structures may be rationalized in terms of hydrogen-bonding effects. In the latter two compounds, two molecules of water of crystallization link two centrosymmetrically related molecules via a network of hydrogen bonds involving the water molecules, the two O(2) atoms, and the N-bound H atoms. For the first compound,[71] which crystallizes free of solvent H_2O, there is a close intramolecular contact of 2.17 Å between the O(2) atom and the N-bound H atom, as well as an intermolecular O(2)···H—N contact of 1.73 Å between centrosymmetrically related molecules. The net result of the different hydrogen-bonding schemes is that for $[Ph_3Sn(O_2CC_5H_4NH)Cl]$ the O(2) atom is directed further away (by about 0.5 Å) from the Sn atom.[71]

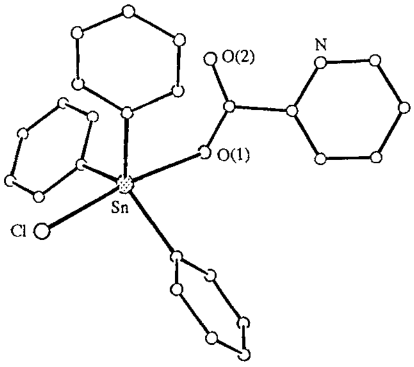


Figure 25 The structure of $[Ph_3Sn(O_2CC_5H_4NH)Cl]$.[71]

4.3 $[(R_3Sn)_2(O_2CR')_2L]$

An interesting structure is found for $[(Ph_3Sn)_2(O_2CC_6H_4Cl\text{-}o)_2(OH_2)]$[49] as shown in Fig. 26. The structure comprises two Ph_3Sn entities which are linked by a bidentate bridging carboxylate ligand. The Sn(1) atom exists in a distorted trigonal bipyramidal geometry with the three phenyl groups defining the trigonal plane. The axial sites are occupied by the O(1) atom derived from the bridging carboxylate ligand and the O(3) atom from a coordinated water molecule. The Sn(1)-O(1) and Sn(1)-O(3) bond distances are 2.162(4) and 2.335(5) Å, respectively and the O(1)—Sn(1)—O(3) angle is 175.9(2)°. The Sn(2) atom also exists in a trigonal bipyramidal geometry as for the Sn(1) atom, the terminal axial site in this case being occupied by the O(4) atom derived from a monodentate carboxylate ligand. Important parameters are: Sn(2)–O(2) 2.636(5), Sn(2)-O(4) 2.147(5) Å, and O(2)—Sn(2)—O(4) 176.9(2)°. The O(5) atom is 3.223(5) Å from the Sn(2) atom and is connected via a hydrogen bond to a symmetry-related O(3′) atom. While the Sn(2)—O(2) bond is in the upper range of Sn–O bond distances for R_3Sn com-

Table 10 Structural parameters for $[R_3Sn(O_2CR'H)X]$

R	R′	X	Sn–X	Sn–O(1)	X—Sn—O(1)	Ref.
Ph	$C_5H_4N^+$	Cl	2.515(1)	2.347(3)	172.8(1)	71
Ph	$C_5H_4N^+$	NCS	2.284(3)	2.221(2)	175.8(2)	72
Ph	$C_9H_6N^+$	Cl	2.526(1)	2.350(5)	177.3(2)	73

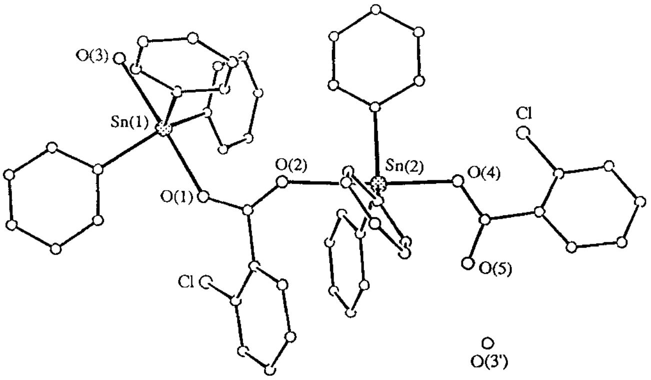


Figure 26 The structure of $[(Ph_3Sn)_2(O_2CC_6H_4Cl\text{-}o)_2(OH_2)]$.[49]

pounds (perhaps for steric reasons), it is considered a significant bonding interaction on the basis of the geometry about the Sn(2) atom, in particular the near-planarity of the R_3Sn unit.

4.4 $[R_3Sn(O_2CR')L]$

The structure of $[Ph_3Sn(O_2CCCl_3)(CH_3OH)]$[14] is monomeric as shown in Fig. 27. The Sn atom exists in a distorted trigonal bipyramidal geometry with the axial positions occupied by the O(1) atom (Sn–O(1) 2.172(2) Å) and the O(3) atom (2.400(3) Å) derived from a coordinated methanol molecule of solvation; the O(1)—Sn—O(3) angle is 178.3(1)°. The carboxylate ligand coordinates in the monodentate mode with a Sn···O(2) separation of 3.264(3) Å. The Sn atom lies 0.128(2) Å out of the trigonal plane, in the direction of the O(1) atom, indicating a tendency towards a tetrahedral distortion.

4.5 $[(R_3Sn)_2((O_2C)_2R')]_n$

A series of compounds of the general formula $[(R_3Sn)_2((O_2C)_2R')]_n$, i.e. containing dicarboxylate ligands, were prepared recently and two of these, i.e. $R = CH_3$, $R' = C_2$ (represented in Fig. 28) and $R' = C_6H_4$, were examined crystallographically.[74] Each of the four carboxylate O atoms (per dicarboxylate ligand) is involved in coordination to a Sn atom, which has the result that each triorganotin moiety is bonded to two O atoms and each Sn atom is five-coordinate. The mode of coordination of the dicarboxylate in this category leads to a polymeric network, a portion of which is shown in Fig. 28. The carboxylate moieties form disparate Sn–O bonds. Thus for the $R' = C_2$ compound, Sn(1)-O(1), O(2)-Sn(1'), Sn(2)-O(3) and O(4)-Sn(2') are 2.239(4), 2.408(4), 2.219(4) and 2.401(4) Å, respectively and for the $R' = C_6H_4$ compound,

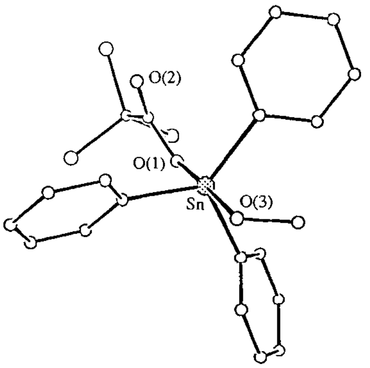


Figure 27 The structure of $[Ph_3Sn(O_2CCCl_3)(CH_3OH)]$.[14]

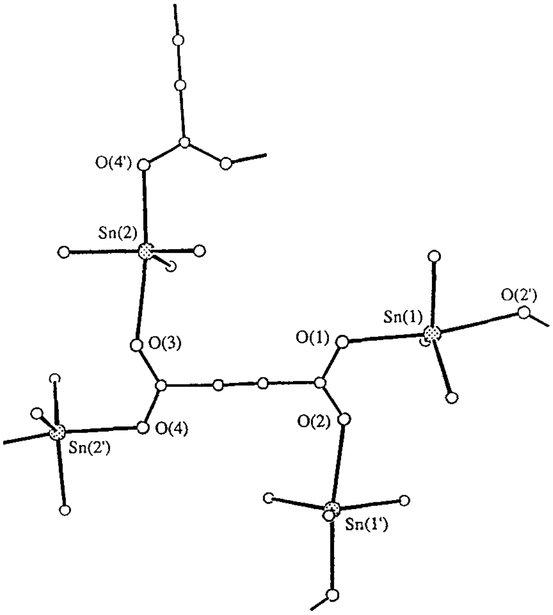


Figure 28 The structure of $[((CH_3)_3Sn)_2((O_2C)_2C_2)]_n$.[74]

which is situated about a crystallographic two-fold axis, the two unique Sn–O bond distances are Sn(1)–O(1) 2.140(3) and O(2)–Sn(1′) 2.506(3) Å. The coordination geometry about the Sn atoms in both compounds is based on a trigonal bipyramid with the three organo substituents defining the trigonal plane; the O—Sn—O angles are 172.2(1) and 171.5(1)° about the Sn(1) and Sn(2) atoms in the $R' = C_2$ compound and 174.6(1)° for the $R' = C_6H_4$ compound. A consequence of the tetradentate mode of coordination of the dicarboxylate ligands is the formation of 22-membered and 26-membered rings for the $R' = C_2$ and C_6H_4 compounds, respectively which are connected to form two-dimensional polymeric networks.

4.6 $[(R_3Sn)_2(O_2CR')]$

A recent crystal structure determination on $[Ph_3Sn(O_2CC_6H_4S)SnPh_3]$, Fig. 29, shows that the dinegative carboxylate ligand coordinates one Ph_3Sn entity via the carboxylate function and the other Ph_3Sn group via the thiolate atom.[75] Both Sn centres exist in distorted tetrahedral geometries. The Sn(1) atom is coordinated by three phenyl groups and the O(1) atom, with the Sn(1)–O(1) bond distance being 2.079(3) Å. The O(2) atom is 2.766(3) Å from Sn(1), a distance not indicative of a significant bonding interaction between these atoms. Support for this conclusion is found in the distance that the Sn(1) atom lies out of the plane defined by the three phenyl groups. This was calculated to be 0.554 Å, which is consistent with a tetrahedral geometry about the Sn(1) atom. This Sn(1)···O(2) contact does, however, introduce a distortion in the coordination polyhedron about the Sn(1) atom in that the C(8)—Sn(1)—C(20) angle is opened up to 120.5(1)°. The range of remaining tetrahedral angles about the Sn(1) atom is 95.6(1)–112.9(1)°. The Sn(2) atom is coordinated by three phenyl groups and the S atom (Sn(2)–S 2.414(1) Å). The O(2) atom is 3.015(1) Å from Sn(2) and distorts the S–Sn(2)–C(32) angle to 119.1(1)° as described above for the Sn(1) atom; the remaining tetrahedral angles lie in the range 101.6(1)–112.2(1)°.

5 ORGANOTIN COMPLEXES WITH AMINO-ACIDS

There are six crystal structures available that describe the solid-state structures of organotin complexes with amino-acids (or peptides).[76–81] Three conform to the general formula $[R_2Sn(O_2CR')]$; one example of these, i.e. $[Me_2Sn(glycylmethionate)]$, is illustrated in Fig. 30.[76] The dinegative ligand in each of these complexes coordinates the Sn atom in the tridentate mode and thereby leads to a five-coordinate Sn centre. The Sn atom exists in a distorted trigonal bipyramidal geometry with the trigonal plane being defined by the two methyl groups and the imino N atom (Sn–N(1) 2.071(4) Å). The axial positions are occupied by the carboxylate O atom (Sn–O(1) 2.161(4) Å) and the amino N atom (Sn–N(2) 2.249(4) Å) such that the O(1)–Sn–N(2) angle is 153.0(2)°. Analogous structures were found for $[Ph_2Sn(glycylglycinate)]$[77] (Sn–O(1) 2.157(8), Sn–N(1)

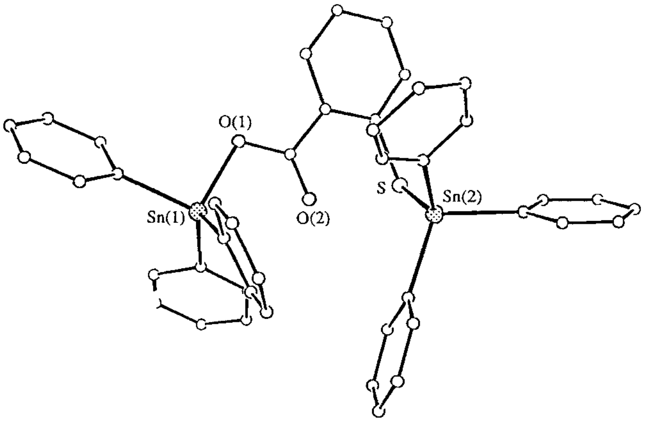


Figure 29 The structure of $[Ph_3Sn(O_2CC_6H_4S)SnPh_3]$.[75]

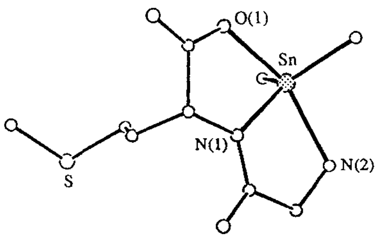


Figure 30 The structure of $[(CH_3)_2Sn(glycylmethionate)]$.[76]

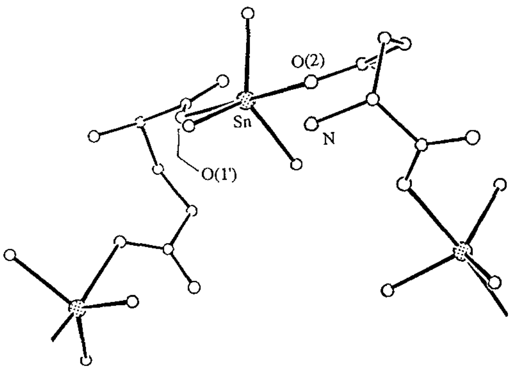


Figure 31 The structure of $[(CH_3)_3Sn(glutamate)]_n$.[81]

2.082(8), Sn–N(2) 2.273(9) Å and O(1)–Sn–N(2) 153.2(3)°) and for $[Bu_2Sn(glycylglycinate)]$[78] (Sn–O(1) 2.196(7), Sn–N(1) 2.085(8), Sn–N(2) 2.293(8) Å and O(1)–Sn–N(2) 149.6(3)°).

A crystal structure for $[nBu_2Sn(mono\text{-}chloroacetyl\text{-}L\text{-}phenylalaninate)_2]$ has been determined recently.[79] This structure conforms to that described for the $[R_2Sn(O_2CR')_2]$ compounds discussed in Section 3.5; important parameters are: Sn–O(1) 2.140(4), Sn–O(2) 2.506(5) Å and C—Sn—C 138.3 (2)°; the molecule has two-fold symmetry.

Two structures containing triorganotin moieties are also known. The first is that of $[(CH_3)_3Sn(glycinate)]_n$, which was found to be polymeric.[80] The $(CH_3)_3Sn$ centres are bridged by O and N donor atoms (Sn–O(1) 2.21(1), Sn–N 2.46(2) Å, O(1)—Sn—N 169.2(6)°C) in a mode similar to that described in Section 4.1.5.

The second triorganotin structure in this category, i.e. $[Ph_3Sn(glutamate)]_n$,[81] is illustrated in Fig. 31. The glutamate anion in this structure was found to exist as a zwitterion $[^{-}O_2CCH_2CH_2(NH_3^+)CO_2^-]$. The structure is polymeric with bridging coordination to Sn occurring via the O(1) and O(2) atoms derived from the α and β carboxylate residues, respectively. The Sn atom geometry is based on a trigonal bipyramid as found in the *trans*-R_3SnO_2 structures discussed in Section 4.1.4; important parameters are: Sn–O(1′) 2.222(3), Sn–O(2) 2.301(3) Å; O(1′)—Sn—O(2) 174.8(2)°.

6 CONCLUSION

From the foregoing discussion it is clear that organotin carboxylates have a rich diversity of structural motifs. Despite the large number of different structures found for this class of compound there is a relatively limited range of coordination geometries about the Sn atoms. Thus four-coordinate Sn is invariably distorted tetrahedral, five-coordinate Sn is distorted trigonal bipyramidal, six-coordinate Sn is distorted octahedral and seven-coordinate Sn is distorted pentagonal bipyramidal. The Sn atom in mono-organotin carboxylates has only been demonstrated to exist in distorted octahedral geometries (the single exception being a pentagonal bipyramidal geometry; see Section 2). A larger range has been observed for diorganotin carboxylate structures, where five-, six-, and seven-coordinate geometries have been reported. Whereas for triorganotin carboxylates, both four- and five coordinate geometries are known.

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