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Structural chemistry of organotin carboxylates

X *. Synthesis and characterization of $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ ($R = Me$, Et, ^nPr and ^nBu). X-Ray crystal structures of $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ ($R = Me$, Et)

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Abstract

Reaction of diorganotin(IV) oxide with trimethylacetic acid in 1/1 stoichiometry gives $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ ($R = Me$, Et, ^nPr and ^nBu). The IR and NMR (^1H, ^{13}C and ^{119}Sn) data indicate that these complexes adopt the dicarboxylato tetraorganodistannoxane structure. The crystal structures of the $R = Me$ and Et compounds confirm the spectroscopic assignments but reveal different solid state structures. For the $R = Et$ compound, each Sn atom of the central Sn_2O_2 stannoxane unit is linked to an exocyclic Sn atom via a carboxylate bridge; the remaining two carboxylate ligands coordinate the exocyclic Sn atom exclusively. By contrast, in the $R = Me$ compound each of the four carboxylate ligands bridges a pair of Sn atoms leading to both five- and six-coordinate Sn geometries compared to the five-coordinate Sn geometries found in the $R = Et$ compound.

Introduction

Tetraorganodistannoxanes are of current interest owing to their relevance in catalysis [2–4]. The reaction of R_2SnO with protic ligands or the partial hydrolysis of diorganotin compounds of the type R_2SnX_2 (X = anionic ligand) generally gives tetraorganodistannoxanes as isolable products. X-Ray structural analyses of several such molecules have revealed the predominance of 'ladder' or 'staircase' structures based on a planar, four-membered Sn_2O_2 ring [7–22]. Variation in the X ligand usually leads to structural diversity although the basic Sn_2O_2 skeleton is retained

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[7–22]. Despite the stability of the Sn_2O_2 unit, evidence for the existence of compounds with the closely related formula $R_2Sn(X)OSnR_2X$ has been provided recently [16]. Formation of these dimeric compounds with certain ligands has also been suggested earlier, however, no structural details are available to support the $R_2Sn(X)OSnR_2X$ formulation [23–26]. It was thought that sterically demanding X ligands may favour the formation of $R_2Sn(X)OSnR_2X$ and thus diorganotin compounds with $X = O_2C^tBu$ were prepared and characterized by IR, NMR and X-ray diffraction methods.

Results and discussion

Reactions of diorganotin(IV) oxides with trimethylacetic acid in 1/1 stoichiometry in refluxing benzene gave complexes of the type $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ (R = Me, Et, ^{n}Pr and ^{n}Bu) in 62–75% yield; see Table 1 for analytical data. The IR spectra of these complexes displayed two bands at 1610 ± 5 and 1545 ± 5 cm^{-1} which were assigned to asymmetric ν(COO). In the free acid this absorption appeared at 1640 cm^{-1} while in the sodium salt ν(COO) occurred at 1545 cm^{-1}. Strong bands at 630 and 480 ± 10 cm^{-1}, absent in ^{t}BuCOOH, were assigned to Sn–O–Sn and Sn–O modes [23,24,27–30], respectively. The Sn–C absorptions seem to be coupled with ligand vibrations in the region 500–600 cm^{-1}.

The ^{1}H NMR spectra showed the expected integration and peak multiplicities. The methyl groups of the carboxylate ligand appeared as a singlet at δ 1.0–1.13 ppm both in the complexes and the free acid. The dimethyltin complex displayed two resonances (δ 0.72 ppm, ^2J(Sn–H) 84 Hz exocyclic, and 0.78 ppm, ^2J(Sn–H) 90 Hz, endocyclic) for Me-Sn protons as expected for tetraorganodistannoxanes.

The $^{13}C\{^1H\}$ NMR spectra (Table 2) exhibited two sets of Sn–R resonances except for the $^n Bu_2Sn$ complex where overlapping signals were observed. Ligand carbons appeared as singlets in all cases. The quaternary carbon and the methyl carbon of the ^{t}Bu group are slightly deshielded compared to the free ligand whereas the carbonyl carbon resonance is almost unaffected. It is interesting to note that in the $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$ compound there are two types of carboxylate ligands as revealed by X-ray diffraction data (see below), but in solution only a single resonance is detected for each of the ligand carbon atoms. It is possible that in

Table 1

Analytical and melting point data for $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ [a]

Compound	M.p. (°C)	Analyses (Found (calc.) (%))		
		C	H	Sn
$\{[Me_2Sn(O_2C^tBu)]_2O\}_2$	197–200	33.16 (32.60)	5.89 (5.86)	45.98 (46.02)
$\{[Et_2Sn(O_2C^tBu)]_2O\}_2$	204–206	37.75 (37.80)	7.04 (6.70)	41.34 (41.51)
$\{[^nPr_2Sn(O_2C^tBu)]_2O\}_2$	145	41.92 (42.08)	6.48 (7.38)	37.48 (37.80)
$\{[^nBu_2Sn(O_2C^tBu)]_2O\}_2$	120	46.53 (45.65)	8.23 (7.96)	34.62 (34.70)

[a] Compounds recrystallized from diethyl ether in 62–75% yield.

Table 2

$^{119}Sn\{^1H\}$ and $^{13}C\{^1H\}$ NMR data (ppm) for $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ [a]

Compound	$\delta(^{119}Sn)$	$\delta(^{13}C)$						
		ligand carbons			Sn–R			
		CO_2	C	CH_3	C(1)	C(2)	C(3)	C(4)
^tBuCOOH	–	185.5	38.3	26.7	–	–	–	–
$\{[Me_2Sn(O_2C^tBu)]_2O\}_2$	−188, −194	186.0	39.1	27.6	8.8, 6.8	–	–	–
$\{[Et_2Sn(O_2C^tBu)]_2O\}_2$	−211, −229	185.6	39.3	27.7	21.2, 20.4	9.8, 9.4	–	–
$\{[^nPr_2Sn(O_2C^tBu)]_2O\}_2$	−216, −231	185.4	39.3	27.7	31.4, 30.9	18.9, 18.6	18.3	–
$\{[^nBu_2Sn(O_2C^tBu)]_2O\}_2$ [b]	−194, −210	185.4	39.3	27.7	27.3	26.8	26.7	13.4

[a] Recorded in $CDCl_3$ solution. [b] Overlapping signals for C(1), C(2) and C(3) were observed.

solution a dynamic equilibrium exists between various tetraorganodistannoxanes leading to the equivalence of the carboxylate ligands [31].

The $^{119}Sn\{^1H\}$ NMR of these complexes showed two well separated resonances, characteristic of the tetraorganodistannoxane structure [31]. The low- and high-field resonances observed for these complexes have been attributed to the exocyclic and endocyclic tin atoms, respectively. Two of the complexes (R = Me and R = Et) yielded colourless crystals suitable for X-ray diffraction analysis and hence their structures were determined. Consistent with the spectroscopic studies, both compounds were shown to adopt the dicarboxylato tetraorganodistannoxane structure in the solid state.

The molecular structures of $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ R = Et, are shown in Fig. 1 and selected interatomic parameters are listed in Table 3. The availability of two $\{[R_2Sn(O_2CR')]_2O\}_2$ structures in which the R′ group remains constant but the R groups bound to the Sn atom are varied enables the effect of the R group on the overall structure to be examined. A similar comparison has been reported recently for the R = ^{n}Pr and ^{n}Bu, R′ = CH_2SPh compounds which were shown to adopt essentially the same structures in the solid state [15]. In contrast, the two compounds reported here adopt different structures in the solid state.

The $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$ compound adopts the most common structural type found for compounds of the general formula $\{[R_2Sn(O_2CR)]_2O\}_2$ [22]. The compound is molecular there being no significant intermolecular contacts in the crystal lattice. The molecule is centred about a Sn_2O_2 group located about a crystallographic centre of inversion located at 1/2 1/2 1/2; two Et_2Sn moieties are connected via Sn–O bonds to the Sn_2O_2 group. There are two unique carboxylate ligands in the structure. One is bidentate bridging, linking the *endo*- and *exo*-cyclic Sn centres forming disparate Sn–O bond distances (Sn(1)–O(2) 2.226(4) and Sn(2)–O(3) 2.280(4) Å). As would be expected, this disparity is reflected in the associated C–O bond distances. The second carboxylate ligand coordinates the exocyclic Sn atom in the monodentate mode. The pendant O atom, O(5), is 2.746(4) Å from the Sn(2) atom, a distance that is too long to be considered a significant interaction. Support for this conclusion is found in the C–O bond distances. The C(6)–O(5) bond distance of 1.215(8) Å indicates substantial multiple bond character in this bond and is significantly shorter than 1.296(7) Å being the distance of the C(6)–O(4) bond. As can be seen from Fig. 1(b), the O(5) atom is directed away from the endocyclic Sn atom and the O(4) atom is in close proximity to the Sn(1′) atom being

Table 3

Selected interatomic parameters for $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ (R = Et, Me) [a]

R = Et		R = Me	
Sn(1)–O(1)	2.176(3)	Sn(1)–O(1)	2.110(5)
Sn(1)–O(1′)	2.036(3)	Sn(1)–O(1′)	2.088(5)
Sn(1)–O(2)	2.226(4)	Sn(1)–O(2)	2.353(7)
Sn(1)–O(4′)	2.863(4)	Sn(1)–O(4′)	2.330(7)
Sn(1)–C(11)	2.135(7)	Sn(1)–C(11)	2.10(1)
Sn(1)–C(13)	2.124(6)	Sn(1)–C(12)	2.12(1)
Sn(2)–O(1)	2.024(3)	Sn(2)–O(1)	2.005(5)
Sn(2)–O(3)	2.280(4)	Sn(2)–O(3)	2.228(8)
Sn(2)–O(4)	2.162(4)	Sn(2)–O(5)	2.243(6)
Sn(2)–O(5)	2.746(4)	–	
Sn(2)–C(15)	2.147(8)	Sn(2)–C(13)	2.100(9)
Sn(2)–C(17)	2.127(9)	Sn(2)–C(14)	2.121(8)
C(1)–O(2)	1.204(7)	C(1)–O(2)	1.27(1)
C(1)–O(3)	1.223(8)	C(1)–O(3)	1.20(1)
C(1)–C(2)	1.521(8)	C(1)–C(2)	1.50(2)
C(6)–O(4)	1.296(7)	C(6)–O(4)	1.23(1)
C(6)–O(5)	1.215(8)	C(6)–O(5)	1.28(1)
C(6)–C(7)	1.529(9)	C(6)–C(7)	1.52(1)
O(1)–Sn(1)–O(1′)	76.6(2)	O(1)–Sn(1)–O(1′)	76.6(2)
O(1)–Sn(1)–O(2)	92.9(2)	O(1)–Sn(1)–O(2)	86.9(2)
O(1)–Sn(1)–O(4′)	140.7(2)	O(1)–Sn(1)–O(4′)	164.0(2)
O(1)–Sn(1)–C(11)	108.5(3)	O(1)–Sn(1)–C(11)	97.2(4)
O(1)–Sn(1)–C(13)	109.6(3)	O(1)–Sn(1)–C(12)	99.0(3)
O(1′)–Sn(1)–O(2)	169.4(2)	O(1′)–Sn(1)–O(2)	163.2(2)
O(1′)–Sn(1)–O(4′)	64.2(2)	O(1′)–Sn(1)–O(4′)	87.4(2)
O(1′)–Sn(1)–C(11)	95.8(3)	O(1′)–Sn(1)–C(11)	99.2(3)
O(1′)–Sn(1)–C(13)	95.5(2)	O(1′)–Sn(1)–C(12)	100.5(3)
O(2)–Sn(1)–O(4′)	126.4(2)	O(2)–Sn(1)–O(4′)	109.1(2)
O(2)–Sn(1)–C(11)	88.6(3)	O(2)–Sn(1)–C(11)	85.8(3)
O(2)–Sn(1)–C(13)	86.8(2)	O(2)–Sn(1)–C(12)	78.7(4)
O(4′)–Sn(1)–C(11)	75.5(3)	O(4′)–Sn(1)–C(11)	86.2(3)
O(4′)–Sn(1)–C(13)	76.8(3)	O(4′)–Sn(1)–C(12)	82.8(3)
C(11)–Sn(1)–C(13)	142.3(3)	C(11)–Sn(1)–C(12)	156.9(5)
O(1)–Sn(2)–O(3)	89.5(2)	O(1)–Sn(2)–O(3)	91.4(3)
O(1)–Sn(2)–O(4)	81.7(1)	O(1)–Sn(2)–O(5)	91.3(2)
O(1)–Sn(2)–O(5)	133.0(2)	–	
O(1)–Sn(2)–C(15)	110.3(2)	O(1)–Sn(2)–C(13)	113.6(3)
O(1)–Sn(2)–C(17)	109.8(3)	O(1)–Sn(2)–C(14)	113.4(3)
O(3)–Sn(2)–O(4)	171.1(2)	O(3)–Sn(2)–O(5)	177.1(3)
O(3)–Sn(2)–O(5)	137.4(2)	–	
O(3)–Sn(2)–C(15)	85.4(3)	O(3)–Sn(2)–C(13)	93.8(4)
O(3)–Sn(2)–C(17)	84.9(3)	O(3)–Sn(2)–C(14)	87.6(3)
O(4)–Sn(2)–C(14)	96.8(3)	O(5)–Sn(2)–C(13)	86.1(3)
O(4)–Sn(2)–C(17)	98.4(3)	O(5)–Sn(2)–C(14)	90.4(3)
O(4)–Sn(2)–O(5)	51.4(2)	–	
O(5)–Sn(2)–C(15)	77.9(3)	–	
O(5)–Sn(2)–C(17)	82.8(3)	–	
C(15)–Sn(2)–C(17)	138.7(4)	C(13)–Sn(2)–C(14)	133.0(4)
Sn(1)–O(1)–Sn(2)	121.4(2)	Sn(1)–O(1)–Sn(2)	127.0(3)
Sn(1)–O(2)–C(1)	137.3(5)	Sn(1)–O(2)–C(1)	124.2(7)
Sn(2)–O(3)–C(1)	138.7(5)	Sn(2)–O(3)–C(1)	126.1(8)
O(2)–C(1)–O(3)	123.3(6)	O(2)–C(1)–O(3)	121(1)
Sn(2)–O(4)–C(6)	106.5(4)	Sn(1)–O(4′)–C(6′)	124.0(6)

Table 3 (continued)

R = Et		R = Me	
Sn(2)–O(5)–C(6)	80.8(4)	Sn(2)–O(5)–C(6)	125.0(6)
O(4)–C(6)–O(5)	121.4(6)	O(4)–C(6)–O(5)	122.6(7)
Sn(2)–O(4)–Sn(1)	92.5(2)		

[a] The table has been arranged such that common interatomic parameters between the structures occur in the same row.

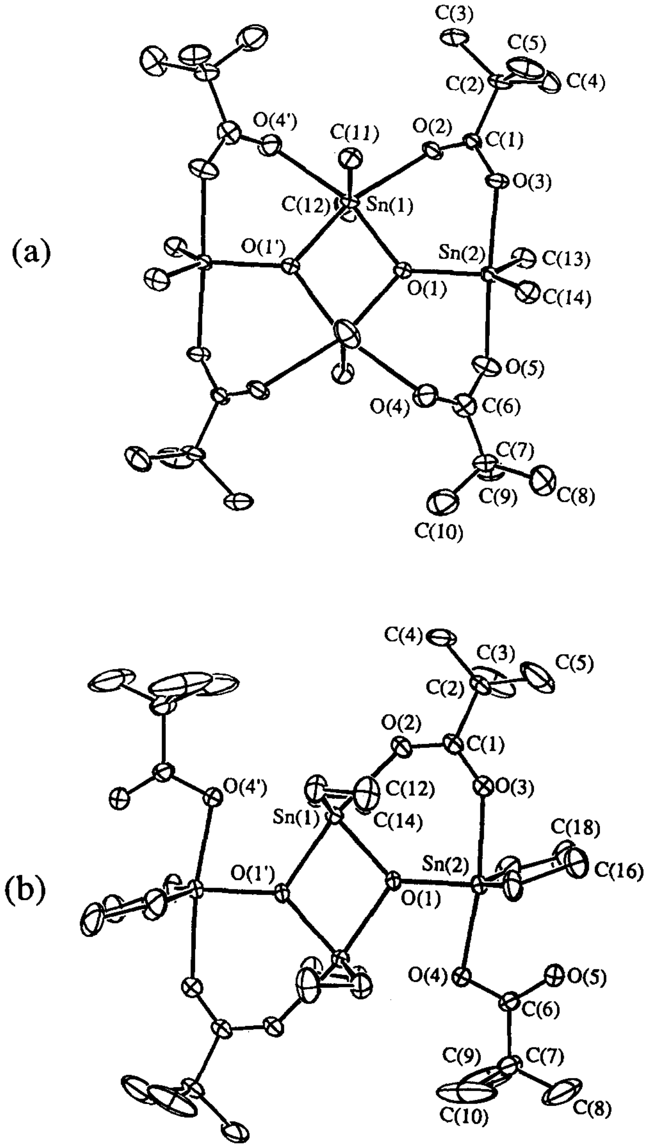

Fig. 1. Molecular structure and crystallographic numbering scheme employed for $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ (a) R = Me, (b) R = Et. For the R = Et compound, only one position of the disordered C(18) atom i shown.

separated by 2.863(4) Å. This distance is not indicative of a significant interaction between these atoms. The close approach of the O(4) atom to the Sn(1) atom and the O(5) atom to the Sn(2) atom does influence significantly the individual coordination geometries about the Sn atoms.

The geometry about the Sn(1) atom is based on a distorted trigonal bipyramid with the two ethyl substituents and the O(1′) atom defining the basal plane. The Sn(1) atom lies 0.0394(4) Å out of this plane in the direction of the O(1) atom. The proximity of the O(4′) atom causes the C–Sn(1)–C angle to be opened to 142.3(3)° and consequently the two O(1)–Sn(1)–C angles are contracted to approximately 109° so that the sum of the trigonal angles is 360.4° supporting the postulate that the O(4′) atom does not coordinate the Sn(1) atom. The deviation from 180° found for the axial angle (169.4(2)°) also reflects the steric influence of the O(4′) atom. A similar coordination geometry is found for the Sn(2) atom. The sum of the trigonal angles in this case is 358.8° (the Sn(2) atom lies 0.1303(4) Å out of the basal plane in the direction of the O(4) atom) and again the C–Sn–C angle is opened up to 138.7(4)° owing to the steric influence of the O(5) atom; the axial angle, O(3)–Sn(2)–O(4), is 171.2(2)°. Whereas the structure of $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$ has several precedents in the literature [22], the structure of the dimethyltin analogue, $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$, is different from these and has only one precendent [10].

The molecular structure of $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$ is shown in Fig. 1(a); there are no close intermolecular contacts in the lattice. As for $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$, the molecule is situated about a crystallographic centre of inversion (located at 1/2 1/2 0). The basic tetraorganodistannoxane framework of $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$ is retained in the structure of $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$, the difference arises in the mode of attachment of the four carboxylate ligands to the common $R_2SnOSn_2OSnR_2$ framework. In the R = Me compound all four carboxylate ligands are bidentate bridging in contrast to the two bidentate bridging and two monodentate carboxylate ligands in the R = Et compound. The $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$ structure is derived from $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$ by a rotation about the the Sn(2)–O(4) bond in the latter which brings the O(5) atom to within bonding distance of the Sn(1) atom. As a consequence of the different modes of coordination of the carboxylate ligands the coordination geometry about the Sn(1) atom is quite different from that observed in $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$.

The Sn(1) atom exists in a distorted octahedral geometry with four O atoms defining the basal plane; the axial positions are occupied by the methyl substituents which define a C–Sn(1)–C angle of 156.9(5)°. The disposition of the methyl groups is such that they lie over the two longer Sn–O bonds i.e. those formed by the bridging carboxylate ligands. The Sn(2) atom exists in a trigonal bipyramidal geometry with the Sn(2) lying 0.318(6) Å out of the trigonal plane defined by the O(1), C(13) and C(14) atoms (the sum of the trigonal angles is 360°) in the direction of the O(3) atom. It is notable that in the absence of weak Sn $\cdots$ O interactions (as was found in the structure of $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$) the C–Sn–C angle is still large at 133.0(4)°. The axial angle, O(3)–Sn(2)–O(5), is 177.1(3)°.

The carboxylate ligands form asymmetric Sn–O bonds such that those involving the Sn(1) atom are longer than those involving the Sn(2) atom. Consequently the C–O bond distances associated with the weaker of the Sn–O bonds are shorter than the remaining C–O bonds. The different Sn–O bond distances are in accord with the increased coordination number of the Sn(1) atom over that of the Sn(2) atom.

Only one other crystal structure in the literature has a structure similar to that reported here for $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$ namely that of $\{[Ph_2Sn(O_2CCl_3)]_2O\}_2$ [10]. In the latter compound, the carboxylate groups again coordinate the Sn atoms with disparate Sn–O bond distances, although the difference between the Sn–O bond distances is greater in this compound, i.e. $\geqslant 0.20$ Å cf. $\geqslant 0.10$ Å in $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$. This observation may reflect the different steric profile of the Ph_2Sn units compared with the Me_2Sn units. While the structure of $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$ is different to that found for the R = Et analogue, a simple relationship exists between the two structures.

Pertinent to this comparison is the crystal structure of second isomer of $\{[Ph_2Sn(O_2CCl_3)]_2O\}_2$ [10] which was shown to adopt the structural motif found for the $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$ compound reported herein. This suggests that there is a small energy difference between both structural forms and that variations found between the $\{[R_2Sn(O_2C^tBu)]_2O\}_2$, R = Me and Et, structures may reflect crystallization conditions rather than the different steric or electronic effects of the Sn-bound R groups. While it is not possible to exclude, absolutely, the different steric profiles of the Me_2Sn and Et_2Sn moieties as a factor, an examination of the structures shown in Fig. 1 suggest no obvious steric reasons to preclude the adoption of either of the two structures shown.

Experimental

Trimethylacetic acid and dibutyltin oxide were obtained from Fluka. Other diorganotin oxides were prepared in the laboratory. Dried analytical grade solvents were used in all experiments. The IR spectra were recorded as nujol/fluorolube mulls on a Perkin–Elmer 577 spectrophotometer. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian FT-80A NMR spectrometer operating at 79.54, 20.00 and 29.63 MHz, respectively. The ^1H NMR spectrum of $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$ was recorded on a Bruker 200 spectrometer. Chemical shifts are reported in ppm from internal chloroform peak (7.26 for ^1H and 77.0 ppm for ^{13}C) and external 33% Me_4Sn in C_6D_6 for ^{119}Sn. Tin was estimated as SnO_2. Microanalyses were performed by the Bio-organic Division of B.A.R.C.

Preparation of $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$

To a benzene suspension of Et_2SnO (2.00 g, 10.4 mmol) was added a benzene solution of ^tBuCOOH (1.06 g, 10.4 mmol). The mixture was refluxed for 4 h, with water formed during the reaction removed azeotropically with a Dean and Stark apparatus. The clear solution thus obtained was evaporated under vacuum to leave a white solid (2.80 g, 97%), which was recrystallized from diethyl ether (70% yield). Similarly other distannoxanes were prepared. Pertinent data for these compounds are given in Tables 1 and 2.

Crystallography

Intensity data for both compounds were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with graphite-monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The ω–2θ scan technique was employed to measure data up to a maximum Bragg angle of 22.5° in each case. The data sets were corrected

Table 4

Crystal data and refinement details for $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ (R = Me, Et)

	R = Me	R = Et
Formula	$C_{28}H_{60}O_{10}Sn_4$	$C_{36}H_{76}O_{10}Sn_4$
Mol. wt.	1031.5	1143.7
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a, Å	25.458(5)	10.308(1)
b, Å	11.792(1)	10.354(2)
c, Å	14.811(4)	23.328(5)
β, °	111.46(2)	96.74(1)
V, Å^3	4138.0	2472.6
Z	4 (tetramers)	2 (tetramers)
D_c, g cm^{-3}	1.656	1.536
$F(000)$	2032	1144
μ, cm^{-1}	22.42	18.80
Max./min trans. factors	0.708; 0.381	0.689; 0.468
No. of data collected	3422	4754
No. of unique data	2708	4364
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	2114	2793
R	0.044	0.030
k	1.0	0.63
g	0.0054	0.0014
R_w	0.048	0.034
Residual ρ_{max}, e Å^{-3}	1.73	0.67

Table 5

Fractional atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for $\{[Me_2Sn(O_2C^tBu)]_2O\}_2$

Atom	x	y	z
Sn(1)	24827(2)	30415(5)	10142(4)
Sn(2)	38940(2)	25512(5)	9335(4)
O(1)	3049(2)	2483(5)	364(4)
O(2)	3283(3)	3568(7)	2361(5)
O(3)	3896(4)	2288(7)	2425(6)
O(4)	3327(2)	1461(6)	−1305(4)
O(5)	3936(3)	2785(6)	−541(4)
C(1)	3673(5)	2889(9)	2835(9)
C(2)	3894(5)	2854(9)	3922(7)
C(3)	3471(7)	3382(16)	4208(11)
C(4)	4427(5)	3535(11)	4406(12)
C(5)	3981(6)	1644(11)	4294(8)
C(6)	3706(3)	2133(8)	−1266(6)
C(7)	3962(4)	2146(9)	−2048(7)
C(8)	4461(5)	1328(11)	−1715(9)
C(9)	4170(7)	3263(11)	−2180(10)
C(10)	3515(6)	1715(17)	−3012(9)
C(11)	2485(4)	1554(11)	1793(7)
C(12)	2517(4)	4808(11)	780(10)
C(13)	4215(4)	4207(8)	1226(7)
C(14)	4284(4)	939(8)	1058(7)

Table 6

Fractional atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for $\{[Et_2Sn(O_2C^tBu)]_2O\}_2$

Atom	x	y	z
Sn(1)	59066(3)	62686(4)	52123(2)
Sn(2)	65686(4)	48506(4)	38379(2)
O(1)	5522(3)	4863(4)	4520(2)
O(2)	6049(5)	7485(5)	6004(2)
O(3)	4455(7)	7013(7)	6480(3)
O(4)	7390(4)	6577(4)	4258(2)
O(5)	8504(6)	6423(5)	3517(2)
C(1)	5463(7)	7611(7)	6418(3)
C(2)	5960(7)	8595(7)	6876(3)
C(3)	6849(13)	7921(15)	7323(5)
C(4)	6692(19)	9606(13)	6628(5)
C(5)	4843(13)	9170(15)	7168(6)
C(6)	8262(6)	6998(6)	3946(3)
C(7)	8955(7)	8262(8)	4132(4)
C(8)	10122(16)	8459(16)	3887(10)
C(9)	8129(11)	9315(11)	4100(10)
C(10)	9421(22)	8171(18)	4759(7)
C(11)	5000(8)	7858(7)	4739(3)
C(12)	3761(9)	8316(10)	4928(4)
C(13)	7763(6)	5511(8)	5538(3)
C(14)	7851(9)	4939(10)	6131(3)
C(15)	8271(8)	3658(8)	4020(4)
C(16)	8809(10)	3127(11)	3503(5)
C(17)	5473(10)	5738(12)	3114(3)
C(18) [a]	5828(24)	5574(31)	2576(7)
C(18′) [a]	5441(22)	7023(16)	3020(10)

[a] The C(18) and C(18′) atoms were refined with 50% site occupancy factors.

for Lorentz and polarization effects and an analytical absorption correction was applied [32]. Relevant crystal data are compiled in Table 4.

The structures were solved by direct methods [33] and each refined by a full-matrix least-squares procedure based on F [32]. All non-H atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in each model at their calculated positions (except for the C(18) atoms). For the R = Et compound the methyl group, $C(18)H_3$, was found to be disordered over two positions such that the site occupancy factor for each site was fixed at 50%. After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$, the refinements were continued until convergence; final refinement details are listed in Table 4. The analysis of variance showed no special features in either of the refinements, indicating that appropriate weighting schemes had been applied in each case. Fractional atomic coordinates are listed in Tables 5 and 6 and the numbering schemes employed are shown in Fig. 1 which was drawn with ORTEP [34] at 15% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [32] and the refinements were performed on a SUN4/280 computer. Other crystallographic details (available from E.R.T.T.) comprise thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

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