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Crystal structure of the dimeric bis(*p*-fluoro- and pentafluorophenylacetato)tetra-n-butyldistannoxanes

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Abstract

The crystal structures of bis(pentafluorophenylacetato)tetra-n-butyldistannoxane, $\{[^nBu_2Sn(O_2CCH_2C_6F_5)]_2O\}_2$ (**1**) and bis(*p*-fluorophenylacetato)tetra-n-butyldistannoxane, $\{[^nBu_2Sn(O_2CCH_2C_6H_4F\text{-}p)]_2O\}_2$ (**2**) are reported. The compounds are shown to have different dimeric structures in the crystalline state despite their structural similarity. The structures each have a centrosymmetric $^nBu_4Sn_2O_2$ core to which are bonded two $^nBu_2Sn$ moieties. The main difference between the two structures involves the mode of attachment of one of the independent carboxylate ligands. In **1**, the ligand is bidentate, bridging a pair of endo- and exo-cyclic Sn atoms by using both O atoms, whereas in **2**, the comparable ligand bridges the Sn atoms by using one O atom only. The second independent carboxylate ligand is coordinated exclusively to the exocyclic Sn atom in each case. The great similarity of their NMR spectra reveals that compounds **1** and **2** have identical structures in $CDCl_3$ solution. The NMR data indicate also the existence of a dynamic process involving averaging of the carboxylate but not the diorganotin resonances, as observed previously; a process accounting for the fluxionality is proposed. A dissociation/reassociation mechanism involving an averaging equilibrium between dimeric and monomeric distannoxanes can be formally excluded.

Keywords: Tin; Distannoxanes; Crystal structure; Fluxionality; NMR

1. Introduction

Recent reviews of structures of organotin carboxylates have demonstrated that there are five types of structure that can be adopted in the crystalline state by the dimeric dicarboxylatotetraorganodistannoxanes, i.e. compounds of the general formula $\{[R_2Sn(O_2CR')]_2O\}_2$ [1]. Structure type A, shown in Fig. 1, is by far the predominant structural form and involves a centrosymmetric structure (usually crystallographically imposed) built up around a four-membered cyclic Sn_2O_2 core in which the two endocyclic Sn atoms are five-coordinate. Each of the two exocyclic five-coordinate Sn atoms is bound to one bridging O atom of the four-membered ring, making these O atoms tricoordinate. The two independent carboxylate groups are characterised by two distinct ligating modes. One ligand is unidentate and is coordinated exclusively to the exocyclic Sn atoms. The other ligand is bidentate, one O atom of the carboxylate group being coordinated to the exocyclic Sn atom and the other O atom to the endocyclic Sn atom.

One of the above-mentioned reviews [1b] indicates that 16 out of 23 dimeric dicarboxylato tetraorganodistannoxanes that have been characterised adopt this structural form. Since the compilation of that review, several other $\{[R_2Sn(O_2CR')]_2O\}_2$ compounds, including substituted dibenzoato- and disalicylato-tetrabutyldistannoxanes [2–7], have been shown to display the type A structural form, which can be considered as the reference structure for such compounds. Two other structure types can be considered as variants of the type A form. In the type C structure, adopted by the $\{[Me_2Sn(O_2CCH_3)]_2O\}_2$ compound [8], the inversion

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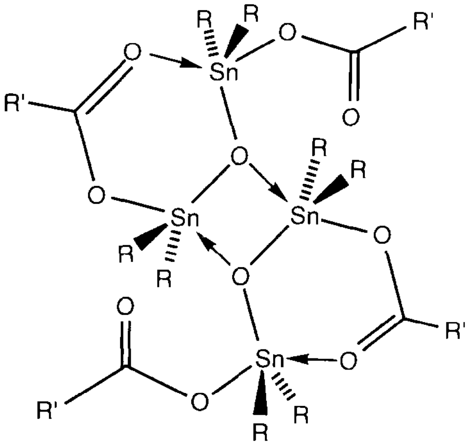

Fig. 1. General bonding pattern for structures of type A.

symmetry is removed by the presence of one additional bidentate, a bridging carboxylate group, leaving a single unidentate ligand. As a consequence, one endocyclic Sn atom becomes six-coordinate. Further, there is an intermolecular Sn–O interaction (i.e. 2.56(1) Å) involving the otherwise pendent O atom that leads to chains of loosely associated tetramers [8]. In the type D structure, found in $\{[Ph_2Sn(O_2CCCl_3)]_2O\}_2$ [9] and $\{[Me_2Sn(O_2CC^tBu)]_2O\}_2$ [10], the inversion symmetry is restored, and all four carboxylate groups span one exocyclic and one endocyclic Sn atom as bidentate bridging ligands; accordingly, the endocyclic Sn atoms are six-coordinate. The type B (see $\{[Me_2Sn(O_2CC_6H_4\text{-}NH_2)]_2O\}_2$ [11], $\{[Me_2Sn(O_2C(CH_2)_2C(O)C_6H_5)]_2O\}_2$ [12] and $\{[^nBu_2Sn(O_2C(CH_2)_2C(O)C_6H_5)]_2O\}_2$ [13]) and E structures (see $\{[^nBu_2Sn(O_2CC_5H_4N\text{-}2)]_2O\}_2$ [14]) retain the Sn_2O_2 core of the type A structure, but the two bidentate, bridging carboxylate ligands of type A now each utilise only one O atom in bridging the two Sn centres. The peculiar bonding of the carboxylate groups causes two of the opposite Sn–O bonds of the central four-membered ring to be adjacent to two other four-membered rings. Accordingly, the type B and E structures have a central core in common consisting of a ladder structure of three condensed four-membered rings. In the three type B structures, each of the two unidentate carboxylate ligands found in type A now chelate an exocyclic Sn atom, so that the exo- and endo-cyclic Sn atoms retain their five-coordinate geometries. In the structure of $\{[^nBu_2Sn(O_2CC_5H_4N\text{-}2)]_2O\}_2$ [14] there are also interactions between the pyridyl N atoms and the exocyclic Sn atom for two of the carboxylate ligands, so that these ligands may also be considered as chelating.

We reported recently the X-ray structures of several bis(mono- or difluoro-benzoato)tetraorganodistannoxane compounds which were investigated as a part of a study of the biological activity of fluorinated organotin carboxylates [2,3]; these compounds exhibit the type A structure. The synthesis and characterisation of several classes of dicarboxylatotetraorganodistannoxanes in which the carboxylate ligand contains a pentafluorophenyl group, were also reported recently [3]. Subsequently, the novel compound, bis(pentafluorophenylacetato)tetra-n-butyldistannoxane, $\{[^nBu_2Sn(O_2CCH_2C_6F_5)]_2O\}_2$, compound **1** (and suitable crystals) was obtained and its structure has now been determined by an X-ray diffraction study, as has that of a structurally very similar compound, bis(*p*-fluorophenylacetato)tetra-n-butyldistannoxane, $\{[^nBu_2Sn(O_2CCH_2C_6H_4F\text{-}p)]_2O\}_2$, compound **2**, which was synthesised earlier [15]. The study reveals that **1** adopts the predominant structural form whereas **2** adopts structural type B, involving the presence of three condensed Sn_2O_2 rings in a ladder arrangement. The difference in the solid-state structures prompted an NMR study of the behaviour of **1** and **2** in solution.

The ^{119}Sn NMR data for these compounds in $CDCl_3$ lead us to conclude that compounds **1** and **2** have similar structures in solution. An intramolecular rearrangement process is suggested for dimeric dicarboxylatotetraorganodistannoxanes, $\{[R_2Sn(O_2CR')]_2O\}_2$, that provides a rationalisation for the systematic observation [2,10,16–20] of two sets of Sn–R resonances but only a single set of carboxylate resonances in the $^{13}C\{^1H\}$ spectra of such compounds [21].

2. Results and discussion

2.1. Synthesis and characterisation

Compound **1**, $\{[^nBu_2Sn(O_2CCH_2C_6F_5)]_2O\}_2$, was made in a manner similar to compound **2** [15], $\{[^nBu_2Sn(O_2CCH_2C_6H_4F\text{-}p)]_2O\}_2$, and other analogues (for example, Ref. 2]) by the reaction of equimolar amounts of di-n-butyltin oxide ($^nBu_2SnO$) and pentafluorophenylacetic acid ($C_6F_5CH_2COOH$). The compound was characterised by ^{1}H, ^{13}C, ^{19}F, ^{119}Sn NMR, Mössbauer spectroscopy, X-ray diffraction and elemental analysis.

2.2. X-Ray structure determination

The molecular structure of $\{[^nBu_2Sn(O_2CCH_2C_6F_5)]_2O\}_2$ (**1**) is shown in Fig. 2 and selected interatomic parameters are listed in Table 1. The lattice is comprised of discrete molecular entities, with no significant intermolecular contacts; the closest non-H contact, of 2.78(2) Å, is that between centrosymmetrically related pairs of F(28) atoms (symmetry operation: $1-x$, $-1-y$, $1-z$) The structure adopted by **1** in the crystalline state is of the form commonly found for compounds of this type [1], and is essentially as shown in Fig. 1. To the centrosymmetric $^nBu_4Sn_2O_2$ core are

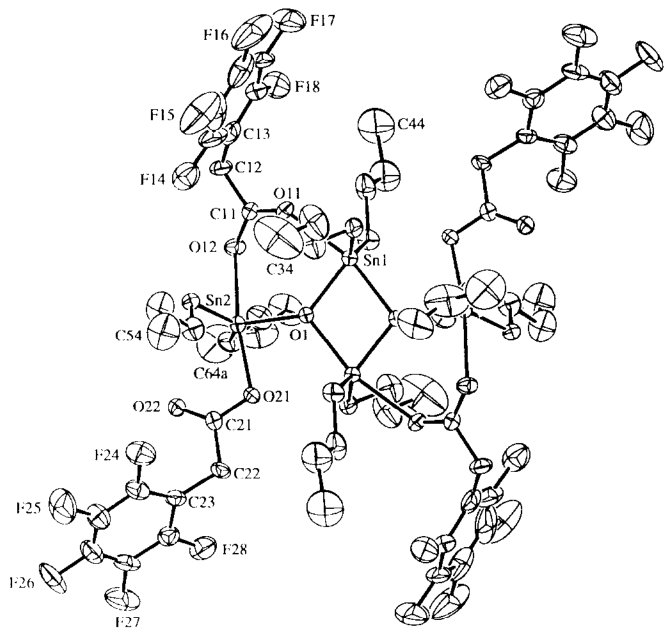

Fig. 2. Molecular structure and crystallographic numbering scheme for compound **1**.

attached two $^{n}Bu_2Sn$ units, making the O(1) atoms three-coordinate. Two carboxylate ligands bridge in bidentate fashion, each linking a pair of endo- and exo-cyclic Sn atoms to give rise to slightly different Sn(1)–O(11) and Sn(2)–O(12) bond distances of 2.241(6) and 2.271(7) Å, respectively. The second independent carboxylate ligand is coordinated exclusively to the exocyclic Sn(2) atom, and gives rise to the shortest Sn–O(carboxylate) bond distance of 2.157(6) Å. The coordination modes of the carboxylate ligands lead to five-coordinate geometry about each of the Sn atoms. As in other structures of this type there are relatively close intramolecular Sn · · · O interactions. Thus, the Sn(1) · · · O(21)′ separation is 2.872(6) Å and the Sn(2) · · · O(22) separation 2.890(7) Å. These distances, while within the sum of the van der Waals radii for these atoms [22], are not indicative of significant bonding interactions between the respective pairs of atoms. The relatively close approach of the O(21)′ and O(22) atoms to the Sn(1) and Sn(2) atoms, respectively do, however, cause some distortion from the ideal geometries. In compound **1**, both Sn atoms have distorted trigonal bipyramidal geometries. The Sn(1) atom lies 0.1209(8) Å out of the trigonal plane defined by the O(1), C(31) and C(41) atoms in the direction of the O(1)′ atom and the Sn(2) atom lies 0.1224(7) Å out of the plane defined by O(1), C(51) and C(61) in the direction of the O(21) atom.

Table 1
Selected interatomic bond distances (Å) and angles (°) for compound **1** [a]

Sn(1)–O(1)	2.004(5)	Sn(1)–O(1)′	2.154(5)
Sn(1)–O(11)	2.241(6)	Sn(1)–C(31)	2.08(1)
Sn(1)–C(41)	2.13(1)	Sn(2)–O(1)	2.015(5)
Sn(2)–O(12)	2.271(7)	Sn(2)–O(21)	2.157(6)
Sn(2)–C(51)	2.08(1)	Sn(2)–C(61)	2.12(1)
O(1)–Sn(1)–O(1)′	75.9(2)	O(1)–Sn(1)–O(11)	88.6(2)
O(1)–Sn(1)–C(31)	114.5(4)	O(1)–Sn(1)–C(41)	105.7(4)
O(1′)–Sn(1)–O(11)	162.7(2)	O(1′)–Sn(1)–C(31)	97.3(3)
O(1′)–Sn(1)–C(41)	101.2(3)	O(11)–Sn(1)–C(31)	82.0(3)
O(11)–Sn(1)–C(41)	90.2(4)	C(31)–Sn(1)–C(41)	138.7(4)
O(1)–Sn(2)–O(12)	90.7(2)	O(1)–Sn(2)–O(21)	81.1(2)
O(1)–Sn(2)–C(51)	109.9(4)	O(1)–Sn(2)–C(61)	115.2(4)
O(12)–Sn(2)–O(21)	171.4(2)	O(12)–Sn(2)–C(51)	85.6(3)
O(12)–Sn(2)–C(61)	84.5(4)	O(21)–Sn(2)–C(51)	99.4(3)
O(21)–Sn(2)–C(61)	96.7(4)	C(51)–Sn(2)–C(61)	133.9(5)
Sn(1)–O(1)–Sn(1)′	104.1(2)	Sn(1)–O(1)–Sn(2)	134.0(3)
Sn(1)′–O(1)–Sn(2)	121.2(3)	Sn(1)–O(11)–C(11)	132.1(7)
Sn(2)–O(12)–C(11)	124.6(7)	Sn(2)–O(21)–C(21)	109.9(6)
O(11)–C(11)–O(12)	126.2(9)	O(11)–C(11)–C(12)	121(1)
O(12)–C(11)–C(12)	112(1)	O(21)–C(21)–O(22)	125(1)
O(21)–C(21)–C(22)	111.6(9)	O(22)–C(21)–C(22)	123.3(9)

[a] Primed atoms are related by a centre of inversion.

The molecular structure of $\{[^{n}Bu_2Sn(O_2CCH_2C_6H_4F\text{-}p)]_2O\}_2$ (**2**) is shown in Fig. 3 and selected bond distances and angles are listed in Table 2. The crystal consists of discrete molecules, the closest contact between non-H atoms being 3.26(1) Å for F(16) · · · C(27)′ and F(16) · · · C(28)′ (symmetry operation: 1 + *x*, *y*, *z*). The central, centrosymmetric $(^{n}Bu_2Sn)_2O_2(^{n}Bu_2Sn)_2$ framework is the same as in **1**, but the mode of association of the two independent carboxylate ligands is different. The bidentate bridging ligand of **1** still bridges a pair of endo- and exo-cyclic Sn atoms but utilises one O atom only. The bridge is not symmetric, Sn(1)–O(11) being 2.206(4) Å and Sn(2)–O(11) equal to 2.498(5) Å. The pendent O(12) atom is 3.141(6) Å away from the Sn(1) atom, a distance too long for a bonding interac-

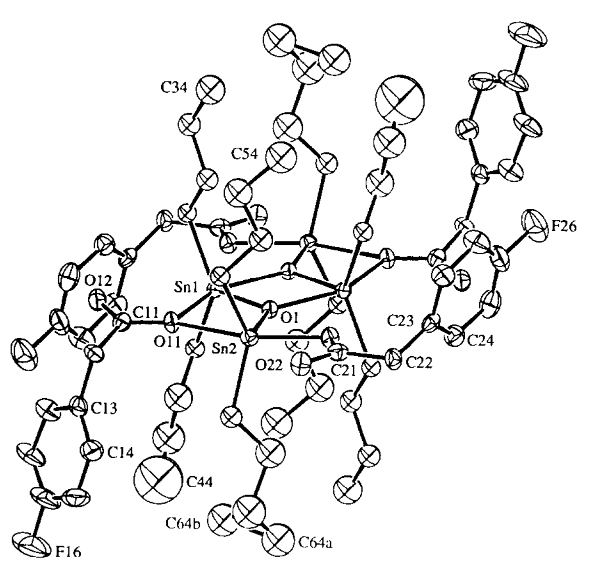

Fig. 3. Molecular structure and crystallographic numbering scheme for compound **2**.

Table 2
Selected interatomic bond distances (Å) and angles (°) for compound **2** [a]

Sn(1)–O(1)	2.021(4)	Sn(1)–O(1')	2.148(4)
Sn(1)–O(11)	2.206(4)	Sn(1)–C(31)	2.097(8)
Sn(1)–C(41)	2.078(8)	Sn(2)–O(1)	2.003(4)
Sn(2)–O(11)	2.498(5)	Sn(2)–O(21)	2.093(5)
Sn(2)–C(51)	2.089(8)	Sn(2)–C(61)	2.093(9)
O(1)–Sn(1)–O(1')	74.0(2)	O(1)–Sn(1)–O(11)	74.6(2)
O(1)–Sn(1)–C(31)	115.3(2)	O(1)–Sn(1)–C(41)	115.3(3)
O(1')–Sn(1)–O(11)	148.6(2)	O(1')–Sn(1)–C(31)	96.4(2)
O(1')–Sn(1)–C(41)	96.1(2)	O(11)–Sn(1)–C(31)	97.9(2)
O(11)–Sn(1)–C(41)	96.2(2)	C(31)–Sn(1)–C(41)	129.3(3)
O(1)–Sn(2)–O(11)	68.5(2)	O(1)–Sn(2)–O(21)	84.2(2)
O(1)–Sn(2)–C(51)	109.3(2)	O(1)–Sn(2)–C(61)	110.8(3)
O(11)–Sn(2)–O(21)	152.7(2)	O(11)–Sn(2)–C(51)	85.5(2)
O(11)–Sn(2)–C(61)	86.5(3)	O(21)–Sn(2)–C(51)	105.1(3)
O(21)–Sn(2)–C(61)	103.1(3)	C(51)–Sn(2)–C(61)	132.6(3)
Sn(1)–O(1)–Sn(1')	106.0(2)	Sn(1)–O(1)–Sn(2)	120.8(2)
Sn(1)–O(1)–Sn(2)	133.1(2)	Sn(1)–O(11)–Sn(2)	95.9(2)
Sn(1)–O(11)–C(11)	119.8(5)	Sn(2)–O(11)–C(11)	143.8(5)
Sn(2)–O(21)–C(21)	108.7(5)	O(11)–C(11)–O(12)	121.9(7)
O(11)–C(11)–C(12)	117.6(7)	O(12)–C(11)–C(12)	120.4(8)
O(21)–C(21)–O(22)	121.0(8)	O(21)–C(21)–C(22)	119.0(7)
O(22)–C(21)–C(22)	119.9(7)		

[a] Primed atoms are related by a centre of inversion.

tion. Similarly, the intramolecular Sn(1) · · · O(21') interaction is weak at 3.301(6) Å. The geometry about the Sn(1) atom is thus distorted trigonal bipyramidal with the Sn(1) atom lying 0.0132(6) Å out of the trigonal plane [defined by the O(1), C(31) and C(41) atoms] in the direction of the O(11) atom. The second independent carboxylate ligand is coordinated exclusively to the exocyclic Sn(2) atom, at an Sn(2)–O(21) bond distance of 2.093(5) Å. The second O(22) atom of this ligand is 2.746(6) Å from the Sn(2) atom, and it is debatable whether or not this represents a significant interaction. In the three other $\{[\mathrm{R}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CR'})]_2\mathrm{O}\}_2$ structures that conform to this form, viz. $\{[\mathrm{Me}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CC}_6\mathrm{H}_4\text{–}\mathrm{NH}_2)]_2\mathrm{O}\}_2$ [11], $\{[\mathrm{Me}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{C}(\mathrm{CH}_2)_2\mathrm{C}(\mathrm{O})\mathrm{C}_6\mathrm{H}_5)]_2\mathrm{O}\}_2$ [12] and $\{[{}^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{C}(\mathrm{CH}_2)_2\mathrm{C}(\mathrm{O})\mathrm{C}_6\mathrm{H}_5)]_2\mathrm{O}\}_2$ [13], the corresponding separations are 2.573(6), 2.734(4) and 2.746(7) Å, respectively. If this interaction is considered significant, the Sn(2) atom would be best described as based on a skew-trapezoidal bipyramidal geometry with the ^{n}Bu groups disposed over the weaker Sn–O bonds, i.e. Sn(2)–O(11) and Sn(2)–O(22). If the Sn(2) · · · O(22) interaction is not considered significant, the geometry about the Sn(2) atom would be one based on a distorted trigonal bipyramid with the Sn(2) atom lying 0.3192(6) Å out of the trigonal plane defined by the O(1), C(51) and C(61) atoms in the direction of the more tightly bound O(21) atom; the O(11)–Sn(2)–O(21), i.e. the axial angle in this description, is 152.7(2)°.

That different structures are found in the crystalline state for **1** and **2** is of interest but not unprecedented for closely related compounds [1]. Furthermore, the structures of $\{[{}^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CC}_6\mathrm{F}_5)]_2\mathrm{O}\}_2$ and $\{[{}^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CC}_6\mathrm{H}_4\mathrm{F}\text{-}p)]_2\mathrm{O}\}_2$, which differ only in the absence of a bridging methylene group, both adopt the predominant structural type [3]. To investigate the structures of **1** and **2** further, a multinuclear magnetic resonance study was performed.

2.3. NMR data in solution

The ^{1}H and ^{13}C data for compound **1**, given in the Experimental section, and those of compound **2**, previously reported [15], reveal the general spectral patterns observed for dicarboxylato tetraorganodistannoxanes investigated earlier by us and by others [2,4–6,10,16–21]. The presence of two sets of ^{13}C and, in part, ^{1}H butyl resonances, is in agreement with the pairwise heterotopic non-equivalence of the exocyclic and endocyclic ^{n}Bu$_2$Sn moieties. In contrast, the presence of only one single set of aromatic ^{13}C resonances, as well as the straightforward appearance of the ^{19}F spectrum in terms of a single type of pentafluorophenyl group, indicates that the four carboxylate moieties are equivalent on the ^{13}C and ^{19}F NMR time scales. The single ^{1}H resonance for the methylene group of the pentafluorophenylacetate moiety confirms this view. These observations are in agreement with all previous NMR data on dicarboxylato tetraorganodistannoxanes [2,4–6,10,16–21].

The ^{119}Sn NMR data for compound **1** are given in Table 3. Those reported previously for **2** [15] are given for comparison. The well-separated high- and low-frequency ^{119}Sn resonances were assigned as previously to the exocyclic and endocyclic Sn atoms, respectively [10,21]. These data confirm the usual non-equivalence of the ^{n}Bu$_2$Sn moieties in solution [2,4–6,10,16–21]. The only slight difference in the ^{119}Sn chemical shifts, well accounted for by the stronger electron-withdrawing nature of the pentafluorophenyl group of compound **1** as compared to the p-fluorophenyl group of compound **2**, and the close similarity of the $^2J(^{119}\mathrm{Sn\text{–}O\text{–}}^{119/117}\mathrm{Sn})$ coupling constants for compounds **1** and **2** suggest that they have similar structures in solution. This shows that the different structures in the crystalline state arise mainly from packing effects, the preferred solution structure being of the usual type A.

The existence of the ^{1}H, ^{13}C and ^{119}Sn resonances in pairs for each atom type of the ^{n}Bu$_2$Sn moieties, con-

Table 3
^{119}Sn NMR data for compounds **1** and **2** [a]

	Compound 1	Compound 2
$\delta(^{119}\mathrm{Sn})_{\mathrm{exo}}$	−204.6	−207.9
$\delta(^{119}\mathrm{Sn})_{\mathrm{endo}}$	−209.3	−215.8
$^2J(^{119}\mathrm{Sn\text{–}O\text{–}}^{119/117}\mathrm{Sn})$	121	121

[a] Taken from Ref. [10] for compound **2**; exo = exocyclic Sn atom; endo = endocyclic Sn atom; $\delta(^{119}\mathrm{Sn})$ in ppm; $^2J(^{119}\mathrm{Sn\text{–}O\text{–}}^{119/117}\mathrm{Sn})$ = unresolved $^2J(^{119}\mathrm{Sn\text{–}O\text{–}}^{119}\mathrm{Sn})$ and $^2J(^{119}\mathrm{Sn\text{–}O\text{–}}^{117}\mathrm{Sn})$ couplings in Hz.

sidered along with the uniqueness of the ^1H, ^{13}C and ^{19}F resonances for the atoms in the four pentafluorophenylacetate groups, indicates the existence of a dynamic exchange process, as pointed out previously [10,21]. The latter must be such that non-equivalence of the endocyclic and exocyclic $^nBu_2Sn$ moieties is preserved on all the NMR time scales, while the carboxylate moieties undergo site-exchange averaging. Indeed, the structure of type A compounds indicates that there is no reason to expect all the carboxylate moieties to be equivalent on the NMR time scale if the complex is non-fluxional, as they are pairwise and heterotopic as are the $^nBu_2Sn$ moieties. This holds especially for the ^{13}C carboxy resonances, which should display pairwise different chemical shifts, the carboxylate groups being bidentate and unidentate. We suggest in Fig. 4 a fluxionality mechanism that fulfils the requirement of exchanging the chemical environments of the unidentate and bidentate carboxylates while preserving the exocyclic and endocyclic nature of the $^nBu_2Sn$ moieties. It requires that, prior to the rearrangement, the pendant O atom of the carboxylate ligand that, at least in the solid state, seems to be weakly coordinated to the exocyclic tin atom, is orientated towards the endocyclic tin atom through internal rotation about the Sn–O(carboxylate) bond. The NMR data formally exclude a dissociation reassociation mechanism between possible dimeric and monomeric distannoxanes, since this would necessarily lead to exchange-averaging of the endocyclic and exocyclic $^nBu_2Sn$ moieties.

3. Experimental details

3.1. Synthesis

Compound **1** was synthesised by reaction of pentafluorophenylacetic acid and di-n-butyltin oxide in the molar ratio 1 : 1. The acid was dissolved in a 4 : 1 mixture of toluene and ethanol, and the solution refluxed for 4–6 h. The ternary water/ethanol/toluene azeotrope, followed by the binary ethanol/toluene azeotrope, was taken off with a Dean–Stark apparatus up to 50% reduction of the initial volume. The solvent was evaporated with a Rotavapor. The crude solid was recrystallised from ethanol/light petroleum; m.p. 76–77°C, yield, 85%. Anal.: Found (Calc.): C, 41.2 (41.24); H, 4.4 (4.33); F, 20.4 (20.38); Sn, 25.2 (25.47)%.

3.2. Characterisation

Mössbauer data: QS, quadrupole splitting; IS, isomer shift; Γ_1 and Γ_2, line widths, all in mm s^{-1}: QS, 3.39; IS, 1.29; Γ_1 and Γ_2, 0.96 and 0.99.

NMR data: all spectra were recorded for $CDCl_3$ solutions and referenced to the residual C^1HCl_3 resonance at 7.24 ppm for the ^1H spectrum, to the central $^{13}CDCl_3$ resonance at 77.0 ppm for the ^{13}C spectrum, to $\Xi(^{119}Sn) = 37.290665$ and $\Xi(^{19}F) = 94.094003$ for the ^{119}Sn and ^{19}F spectra, respectively [23].

Abbreviations for coupling patterns: s = singlet; d = doublet; t = triplet; td = triplet of doublets; tq = triplet of quartets; b = broad resonance; m = complex pattern; nv = non-visible; coupling constants are given in Hz between brackets: $^nJ(^1H–^1H)$ for ^1H spectra, $^nJ(^{13}C–^{19}F)$ ($n = 1$, 2 or 3) for ^{13}C spectra. Other coupling constants are indicated explicitly.

^1H NMR: CH_2CO: s, 3.56; α- and β-CH_2: m, 1.44–1.54; γ-CH_2: tq, 1.27 [7,7]; tq, 1.29 [7,7]; CH_3: t, 0.86 [7]; t, 0.89 [7].

^{13}C NMR: C-1: tt, 109.9 [17,4]; C-2 and C-6: bd: 145.3 [247]; C-3 and C-5: bd, 137.4 [253]; C-4: bd, 140.3 [249]; CH_2CO: 29.6; CO: 173.9; α-C: 29.5 [$^1J(^{13}C–^{119/117}Sn)$: nv]; 29.1 [$^1J(^{13}C–^{119/117}Sn)$: nv]; β-C: 27.2 [$^2J(^{13}C–^{119/117}Sn)$: 32]; 27.6 [$^2J(^{13}C–^{119/117}Sn)$: 37]; γ-C: 26.6 [$^3J(^{13}C–^{119/117}Sn)$: 125]; 26.8 [$^3J(^{13}C–^{119/117}Sn)$: nv]; CH_3: 13.2, 13.3.

^{19}F NMR: F-2 and F-6: dddd, −143.4 [$^nJ(^{19}F–^{19}F)$:

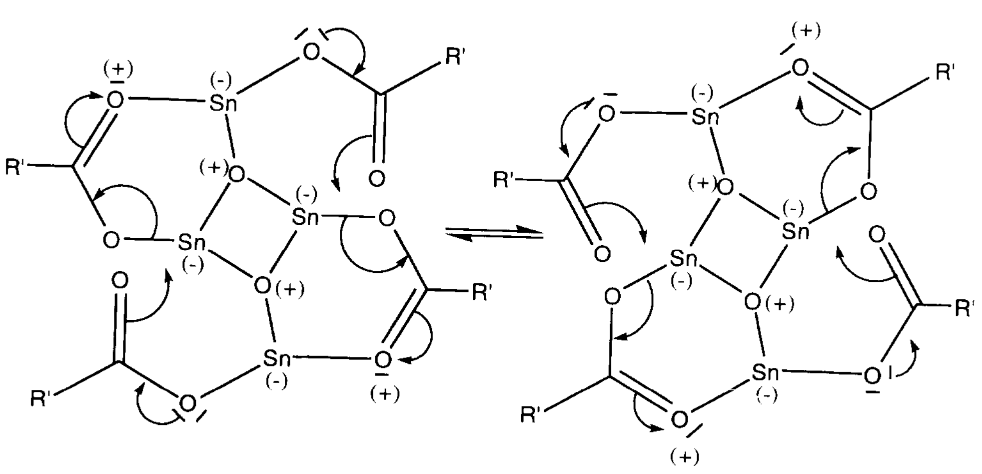

Fig. 4. Proposed exchange mechanism in dicarboxylato tetraorganodistannoxane. The tin-bound R groups (see Fig. 1) have been omitted for clarity.

21, 3, 2, −9]; F-3 and F-5: bs, −163.3; F-4: bs, −156.8.

^{119}Sn NMR: −204.6, −209.3 [$^{2}J(^{119}\mathrm{Sn{-}O{-}}^{117/119}\mathrm{Sn})$: 121].

3.3. Instrumentation

All NMR spectra were recorded on a Bruker AC250 instrument, using a QNP probe tuned at 250.13, 62.93, 93.28 and 235.36 MHz for ^{1}H, ^{13}C, ^{119}Sn and ^{19}F nuclei, respectively. Mössbauer spectra were obtained as described previously [7].

3.4. X-ray crystallography

Intensity data for colourless crystals were measured at room temperature on a Rigaku AFC6R diffractometer fitted with Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å); in each case the $\omega : 2\theta$ scan technique was employed and $\theta_{\max}$ was 25°. No decomposition of the crystals occurred during data collection and the data sets were corrected for Lorentz and polarisation effects [24] and for absorption by an empirical procedure [25] Crystal data are summarised in Table 4.

The structures were solved by direct methods [26] and each refined by a full-matrix least-squares procedure based on F [24]. In compound **1** all non-hydrogen atoms were refined with anisotropic thermal parameters, but for compound **2** the butyl atoms were refined isotropically owing to high thermal motion; the hydrogen atoms were included in the models in their calculated positions except for the disordered atoms. In both refinements disorder was noted in the position of the terminal C(64) methyl group and in each case these were refined over two sites with equal weight. The refinements were continued until convergence, and final refinement details are given in Table 4. Final fractional atomic coordinates for the non-hydrogen atoms are listed in Tables 5 and 6 and the numbering schemes employed are shown in Figs. 2 and 3, which are drawn with ORTEP at 20% probability ellipsoids [27]. Data

Table 4
Crystallographic data for compounds **1** and **2**

	Compound **1**	Compound **2**
Formula	$C_{32}H_{40}F_{10}O_5Sn_2$	$C_{32}H_{48}F_2O_5Sn_2$
Mol. wt.	932.0	788.1
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	13.430(5)	15.203(1)
b (Å)	13.906(4)	12.147(3)
c (Å)	11.918(4)	19.537(1)
α (°)	93.16(3)	90
β (°)	111.70(3)	108.23(1)
γ (°)	66.03(2)	90
V (Å^3)	1877(1)	3426.8(8)
Z	1 (tetramer)	2 (tetramers)
D_c (g cm^{-3})	1.648	1.527
F(000)	924	1592
μ (cm^{-1})	14.15	15.04
No. of data collected	7177	6868
No. of unique data	6857	6608
No. of reflections with $I \geq 3.0\sigma(I)$	3902	3850
R	0.059	0.042
R_w	0.061	0.046
Residual $\rho_{\max}$ (e Å^{-3})	0.90	0.67

Table 5
Fractional atomic coordinates for compound **1**

Atom	x	y	z
Sn(1)	−0.13214(6)	0.08878(6)	−0.01777(5)
Sn(2)	0.05306(6)	−0.07259(6)	0.28086(5)
F(14)	−0.1719(9)	0.2791(9)	0.3718(9)
F(15)	−0.2605(18)	0.4839(13)	0.3239(16)
F(16)	−0.4833(15)	0.5965(7)	0.1625(13)
F(17)	−0.6092(11)	0.4927(10)	0.0517(11)
F(18)	−0.5205(9)	0.2894(11)	0.0940(10)
F(24)	0.4897(7)	−0.1393(6)	0.5862(7)
F(25)	0.6519(9)	−0.2337(9)	0.8000(8)
F(26)	0.7605(7)	−0.4420(7)	0.8394(6)
F(27)	0.7109(8)	−0.5568(6)	0.6624(9)
F(28)	0.5534(7)	−0.4630(6)	0.4433(7)
O(1)	0.0137(5)	−0.0164(5)	0.1105(5)
O(11)	−0.2039(6)	0.1505(5)	0.1267(6)
O(12)	−0.1393(6)	0.0117(6)	0.2564(6)
O(21)	0.2263(5)	−0.1489(5)	0.2749(5)
O(22)	0.2782(6)	−0.2065(6)	0.4633(6)
C(11)	−0.2053(9)	0.1061(9)	0.2102(9)
C(12)	−0.2960(11)	0.1599(10)	0.2651(11)
C(13)	−0.3476(19)	0.2698(20)	0.2333(17)
C(14)	−0.2886(36)	0.3233(19)	0.2867(33)
C(15)	−0.3179(29)	0.4197(63)	0.2761(24)
C(16)	−0.4220(25)	0.4860(17)	0.1985(21)
C(17)	−0.4953(14)	0.4461(10)	0.1337(14)
C(18)	−0.4578(17)	0.3390(16)	0.1530(16)
C(21)	0.3012(9)	−0.1996(8)	0.3782(9)
C(22)	0.4278(9)	−0.2441(10)	0.3826(9)
C(23)	0.5139(10)	−0.2966(10)	0.5051(11)
C(24)	0.5448(11)	−0.2438(10)	0.6024(13)
C(25)	0.6275(14)	−0.2899(15)	0.7094(14)
C(26)	0.6809(13)	−0.3929(16)	0.7325(13)
C(27)	0.6579(12)	−0.4510(11)	0.6444(16)
C(28)	0.5743(11)	−0.4020(11)	0.5307(12)
C(31)	−0.1375(11)	0.2401(9)	−0.0269(9)
C(32)	−0.0497(16)	0.2543(12)	0.0882(15)
C(33)	−0.0556(22)	0.3583(19)	0.0835(18)
C(34)	0.0237(30)	0.3723(20)	0.1828(33)
C(41)	−0.2487(9)	0.0130(8)	−0.0834(9)
C(42)	−0.3751(13)	0.0804(13)	−0.0970(11)
C(43)	−0.4538(18)	0.0338(18)	−0.1573(17)
C(44)	−0.5725(18)	0.0961(23)	−0.1567(21)
C(51)	0.0792(9)	0.0380(9)	0.03996(9)
C(52)	0.1808(13)	0.0625(11)	0.4117(11)
C(53)	0.1863(16)	0.1484(16)	0.4923(15)
C(54)	0.2781(22)	0.1759(19)	0.4996(19)
C(61)	0.0297(12)	−0.2125(9)	0.2954(11)
C(62)	−0.0741(13)	−0.2224(15)	0.2060(14)
C(63)	−0.0883(35)	−0.3274(19)	0.2114(37)
C(64a) [a]	−0.0542(60)	−0.3685(42)	0.3105(63)
C(64b) [a]	−0.1893(32)	−0.3383(33)	0.1198(37)

[a] Atom has a site occupancy factor of 0.5.

Table 6
Fractional atomic coordinates for compound **2**

Atom	x	y	z
Sn(1)	0.10281(3)	0.01360(4)	0.06263(3)
Sn(2)	0.00435(4)	0.26793(4)	−0.00347(3)
F(16)	0.5349(6)	0.3407(7)	−0.0008(5)
F(26)	−0.4912(5)	0.0186(5)	−0.1777(4)
O(1)	−0.0007(3)	0.1032(3)	−0.0043(3)
O(11)	0.1481(3)	0.1866(4)	0.0816(3)
O(12)	0.2666(4)	0.1415(5)	0.1722(3)
O(21)	−0.1261(3)	0.2559(4)	−0.0813(3)
O(22)	−0.1126(4)	0.4354(4)	−0.0701(3)
C(11)	0.2236(6)	0.2097(6)	0.1303(4)
C(12)	0.2605(5)	0.3251(6)	0.1319(4)
C(13)	0.3338(6)	0.3275(7)	0.0942(5)
C(14)	0.3288(7)	0.4000(8)	0.0408(6)
C(15)	0.3980(12)	0.4019(12)	0.0076(7)
C(16)	0.4716(11)	0.3326(13)	0.0321(9)
C(17)	0.4791(8)	0.2620(10)	0.0862(8)
C(18)	0.4100(7)	0.2595(8)	0.1154(6)
C(21)	−0.1578(6)	0.3529(7)	−0.0985(5)
C(22)	−0.2484(6)	0.3667(6)	−0.1575(5)
C(23)	−0.3135(6)	0.2723(6)	−0.1619(4)
C(24)	−0.3112(6)	0.1838(8)	−0.2021(5)
C(25)	−0.3715(9)	0.0976(8)	−0.2088(6)
C(26)	−0.4309(8)	0.1045(10)	−0.1721(7)
C(27)	−0.4359(7)	0.1888(10)	−0.1294(6)
C(28)	−0.3763(7)	0.2723(8)	−0.1263(5)
C(31)	0.0896(5)	−0.0187(6)	0.1644(4)
C(32)	0.0091(6)	0.0299(7)	0.1813(5)
C(33)	0.0005(7)	−0.0054(7)	0.2520(5)
C(34)	−0.0806(9)	0.0377(10)	0.2688(7)
C(41)	0.2057(5)	−0.0358(6)	0.0200(4)
C(42)	0.2526(9)	0.0415(10)	−0.0088(6)
C(43)	0.3245(11)	−0.0150(13)	−0.0435(9)
C(44)	0.3592(21)	0.0499(26)	−0.0727(15)
C(51)	−0.0214(5)	0.3266(6)	0.0890(4)
C(52)	−0.1216(7)	0.3212(8)	0.0863(5)
C(53)	−0.1345(9)	0.3463(10)	0.1563(7)
C(54)	−0.2377(10)	0.3438(11)	0.1506(7)
C(61)	0.0886(6)	0.3249(7)	−0.0626(5)
C(62)	0.0647(9)	0.3003(11)	−0.1379(7)
C(63)	0.1417(13)	0.3369(14)	−0.1755(10)
C(64a) [a]	0.1302(22)	0.3023(26)	−0.2333(18)
C(64b) [a]	0.2077(22)	0.2906(26)	−0.1617(17)

[a] Atom has a site occupancy factor of 0.5.

manipulation were performed with the teXsan program [24] installed on an Iris Indigo work station. Tables of thermal parameters and H-atom coordinates, and complete lists of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

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