CRYSTAL AND MOLECULAR STRUCTURES OF BIS[(3-(2-FURANYL)-2-PROPENOATO)DI-N-BUTYLTIN] OXIDE AND TRIPHENYLTIN 3-(2-FURANYL)-2-PROPENOATE

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Abstract.

The crystal structures of the title compounds $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$ and $[Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)]$ have been determined at room temperature. In the structure of $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$ two nBu_2Sn units are connected to a centrosymmetric $nBu_4Sn_2O_2$ core at the bridging oxygen atoms. Each pair of tin atoms is linked further by a bidentate bridging carboxylate ligand and each of the two remaining ligands binds an exocyclic tin atom in the monodentate mode with the result that both of the independent tin atoms exist in a distorted trigonal bipyramidal geometry. A similar coordination geometry is found in the structure of $[Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)]$ which is polymeric owing to the presence of bidentate bridging carboxylate ligands. No evidence for tin to furan-oxygen interactions was found in either of the structures.

Introduction.

In connection with an earlier investigation of the biological activity of a variety of organotin esters of 3-(2-furanyl)-2-propenoic acid [1], the title compounds have been studied crystallographically. Organotin carboxylates are known to adopt a large range of structural types, sometimes for compounds with very similar chemical formulae [2, 3]. When the carboxylate residue contains additional potential donor atoms, such as oxygen and nitrogen, other structural possibilities arise. The present study was undertaken in order to determine whether the oxygen atom of the furan ring participates in coordination to tin in the solid state.

Experimental.

The $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$ and $[Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)]$ compounds were prepared as in the literature [1]. Intensity data for a colourless crystal of $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$ with dimensions 0.24 x 0.24 x 0.32 mm (0.08 x 0.16 x 0.29 mm; details for $[Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)]$ follow in parenthesis) were measured at room temperature on a Rigaku AFC6R four-circle diffractometer fitted with graphite monochromatized MoKα radiation, $\lambda = 0.71073$ Å. A total of 6929 (5205) data were measured with the ω:2θ scan technique to θ_{max} 25.0° (27.5°), 6663 (4911) were unique and of these 2475 (2722) satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis. The data were corrected for Lorentz and polarization effects [4] and for absorption employing the DIFABS program [5] which resulted in a range of transmission coefficients of 0.971 to 1.036 (0.967 to 1.016). Crystal data are listed in Table 1.

The structures were solved by direct methods [6, 7] and refined by a full-matrix least-squares procedure based on F [4]. In the refinement of $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$, only the Sn and O atoms were refined anisotropically owing to the generally high thermal motion associated with the remaining atoms. The H atoms were included in their calculated positions (C-H 0.97 Å) except for those in the C(51-54) residue. A more conventional refinement was employed for $[Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)]$ with anisotropic thermal parameters for non-H atoms and H atoms included in their calculated positions. At convergence $R = 0.054$ and $R_w = 0.059$ (0.037, 0.035) for sigma weights [4].* The final fractional atomic coordinates are listed in Tables 2 and 3 and the crystallographic numbering schemes used are shown in Figures 1 and 2, which were drawn with ORTEP [8]. Data manipulation was performed with the teXsan package [4] installed on an Iris Indigo workstation.

Table 1. Crystal data for $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$ (**1**) and for $[Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)]$ (**2**)

	1	**2**
Formula	$C_{60}H_{92}O_{14}Sn_4$	$C_{25}H_{20}O_3Sn$
Mol. wt.	1512.1	487.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	14.827(8)	9.690(8)
b, Å	11.128(6)	10.28(1)
c, Å	22.694(4)	21.48(2)

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* where $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$

β, deg.	107.63(2)	96.55(9)
V, Å^3	3568(2)	2125(3)
Z	2 (tetramers)	4
D_c, g cm^{-3}	1.407	1.522
$F(000)$	1528	976
μ, cm^{-1}	14.37	12.24
No. of data collected	6929	5205
No. of unique data	6663	4911
No. of unique reflections used with $I > 3.0\sigma(I)$	2475	2722
R	0.054	0.037
R_w	0.059	0.035
Residual ρ_{max}, e Å^{-3}	0.60	0.39

Table 2. Fractional atomic coordinates for $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$

Atom	*x*	*y*	*z*
Sn(1)	0.02695(6)	0.38880(8)	0.55155(4)
Sn(2)	0.20240(7)	0.47786(10)	0.47013(5)
O(1)	0.0803(5)	0.4791(6)	0.4909(3)
O(2)	0.1529(7)	0.2614(8)	0.5749(4)
O(3)	0.2666(7)	0.3557(10)	0.5512(5)
O(4)	0.1238(6)	0.6115(7)	0.4039(3)
O(5)	0.2422(8)	0.6187(9)	0.3672(4)
O(6)	0.4273(9)	0.0071(14)	0.6755(6)
O(7)	0.0264(9)	0.9461(11)	0.2497(5)
C(1)	0.2352(13)	0.2748(16)	0.5751(8)
C(2)	0.2991(11)	0.1770(13)	0.6113(6)
C(3)	0.3864(13)	0.1831(14)	0.6150(6)
C(4)	0.4576(15)	0.0970(19)	0.6488(9)
C(5)	0.5016(18)	-0.0684(19)	0.7058(9)
C(6)	0.5782(16)	-0.0096(20)	0.7063(9)
C(7)	0.5577(19)	0.0901(22)	0.6649(11)
C(8)	0.1679(12)	0.6560(13)	0.3683(7)
C(9)	0.1170(9)	0.7562(11)	0.3282(6)
C(10)	0.1521(9)	0.8076(13)	0.2902(6)
C(11)	0.1126(13)	0.9027(15)	0.2494(7)
C(12)	0.0011(16)	1.0446(21)	0.2080(11)
C(13)	0.0726(16)	1.0538(18)	0.1840(9)
C(14)	0.1396(11)	0.9724(15)	0.2092(7)
C(21)	0.0813(9)	0.4706(11)	0.6396(5)
C(22)	0.1701(10)	0.5387(12)	0.6516(6)
C(23)	0.1979(11)	0.6074(14)	0.7153(7)
C(24)	0.2801(14)	0.6880(18)	0.7225(9)
C(31)	-0.0511(9)	0.2334(11)	0.5079(5)
C(32)	-0.0260(10)	0.1878(13)	0.4526(6)

C(33)	-0.0953(11)	0.0848(14)	0.4220(7)
C(34)	-0.0664(13)	0.0388(17)	0.3672(9)
C(41)	0.1909(15)	0.3407(19)	0.4026(9)
C(42)	0.2418(31)	0.2416(45)	0.4241(21)
C(43)	0.2398(29)	0.1483(42)	0.3797(18)
C(44)	0.2571(26)	0.0465(37)	0.4156(19)
C(51)	0.3060(12)	0.6192(15)	0.5237(7)
C(52)	0.4011(23)	0.5849(30)	0.5201(16)
C(53)	0.4644(27)	0.7100(40)	0.5588(18)
C(54)	0.4556(27)	0.8000(38)	0.5256(18)

Table 3. Fractional atomic coordinates for [Ph$_3$Sn(O$_2$CC(H)=C(H)C$_4$H$_3$O)]

Atom	*x*	*y*	*z*
Sn	0.09141(4)	0.30840(3)	0.25493(2)
O(1)	0.2105(4)	0.4760(3)	0.2935(2)
O(2)	0.0429(4)	0.6222(3)	0.2747(2)
O(5)	0.3481(4)	0.7878(4)	0.4709(2)
C(1)	0.1538(6)	0.5834(5)	0.3053(2)
C(2)	0.2210(6)	0.6599(5)	0.3582(3)
C(3)	0.3379(6)	0.6237(5)	0.3908(3)
C(4)	0.4100(6)	0.6865(6)	0.4447(3)
C(6)	0.4390(7)	0.8257(7)	0.5211(3)
C(7)	0.5489(8)	0.7551(8)	0.5273(4)
C(8)	0.5302(7)	0.6642(7)	0.4788(4)
C(11)	0.1044(5)	0.3560(5)	0.1599(2)
C(12)	0.1154(6)	0.4822(5)	0.1395(3)
C(13)	0.1370(7)	0.5089(6)	0.0778(3)
C(14)	0.1490(7)	0.4094(8)	0.0372(3)
C(15)	0.1400(8)	0.2833(7)	0.0568(3)
C(16)	0.1171(6)	0.2571(6)	0.1176(3)
C(21)	0.2565(5)	0.1816(5)	0.2873(2)
C(22)	0.2441(6)	0.0900(6)	0.3335(3)
C(23)	0.3521(9)	0.0067(6)	0.3532(3)
C(24)	0.4735(8)	0.0129(7)	0.3269(4)
C(25)	0.4881(7)	0.1015(8)	0.2806(4)
C(26)	0.3809(6)	0.1855(7)	0.2620(3)
C(31)	-0.0570(5)	0.3438(4)	0.3179(3)
C(32)	-0.0114(6)	0.3604(6)	0.3808(3)
C(33)	-0.104(1)	0.3856(6)	0.4242(3)
C(34)	-0.2420(9)	0.3930(6)	0.4051(4)
C(35)	-0.2892(7)	0.3770(7)	0.3429(4)
C(36)	-0.1983(6)	0.3532(6)	0.2993(3)

Results and Discussion.

The molecular structure of $\{[nBu_2Sn(O_2CC(H){=}C(H)C_4H_3O)]_2O\}_2$ is shown in Figure 1 and selected interatomic parameters are listed in Table 4.

Table 4. Selected bond distances (Å) and angles (°) for $\{[nBu_2Sn(O_2CC(H){=}C(H)C_4H_3O)]_2O\}_2$

Sn(1)-O(1)	2.047(7)	Sn(1)-O(1)'[a]	2.165(7)
Sn(1)-O(2)	2.276(9)	Sn(1)-C(21)	2.12(1)
Sn(1)-C(31)	2.15(1)	Sn(2)-O(1)	2.004(7)
Sn(2)-O(3)	2.254(9)	Sn(2)-O(4)	2.183(8)
Sn(2)-C(41)	2.13(2)	Sn(2)-C(51)	2.28(2)
C(1)-O(2)	1.23(2)	C(1)-O(3)	1.21(2)
C(8)-O(4)	1.28(1)	C(8)-O(5)	1.18(1)
C(4)-O(6)	1.32(2)	C(5)-O(6)	1.39(2)
C(11)-O(7)	1.37(2)	C(12)-O(7)	1.42(2)
C(1)-C(2)	1.51(2)	C(2)-C(3)	1.27(2)
C(8)-C(9)	1.49(2)	C(9)-C(10)	1.27(1)
O(1)-Sn(1)-O(1)'	75.4(3)	O(1)-Sn(1)-O(2)	90.3(3)
O(1)-Sn(1)-C(21)	108.0(4)	O(1)-Sn(1)-C(31)	110.4(4)
O(1)'-Sn(1)-O(2)	165.2(3)	O(1)'-Sn(1)-C(21)	98.4(4)
O(1)'-Sn(1)-C(31)	97.0(4)	O(2)-Sn(1)-C(21)	89.8(4)
O(2)-Sn(1)-C(31)	84.0(4)	C(21)-Sn(1)-C(31)	141.1(5)
O(1)-Sn(2)-O(3)	90.0(3)	O(1)-Sn(2)-O(4)	79.9(3)
O(1)-Sn(2)-C(41)	107.0(6)	O(1)-Sn(2)-C(51)	112.4(5)
O(3)-Sn(2)-O(4)	168.0(3)	O(3)-Sn(2)-C(41)	94.4(7)
O(3)-Sn(2)-C(51)	86.0(5)	O(4)-Sn(2)-C(41)	94.8(6)
O(4)-Sn(2)-C(51)	91.7(5)	C(41)-Sn(2)-C(51)	140.6(7)
Sn(1)-O(1)-Sn(1)'	104.6(3)	Sn(1)-O(1)-Sn(2)	135.7(3)
Sn(1)-O(1)-Sn(2)'	119.6(3)	Sn(1)-O(2)-C(1)	132(1)
Sn(2)-O(3)-C(1)	133(1)	Sn(2)-O(4)-C(8)	115.4(9)
O(2)-C(1)-O(3)	127(2)	O(2)-C(1)-C(2)	112(2)
O(3)-C(1)-C(2)	121(2)	C(1)-C(2)-C(3)	117(2)
C(2)-C(3)-C(4)	124(2)	O(4)-C(8)-O(5)	122(1)
O(4)-C(8)-C(9)	114(1)	O(5)-C(8)-C(9)	124(2)
C(8)-C(9)-C(10)	121(1)	C(9)-C(10)-C(11)	128(2)

[a] primed atoms related by symmetry operation: $-x$, $1-y$, $1-z$.

The structure is tetrameric and is arranged about a centrosymmetric Sn_2O_2 unit (i.e. containing endocyclic tin atoms) with two exocyclic tin atoms connected at the oxygen atoms with the result that these O(1) atoms are triply bridging. Each pair of endo- and exo-cyclic tin atoms is linked by a bidentate bridging carboxylate ligand and the two remaining carboxylate ligands are monodentate, coordinating the exocyclic tin atom exclusively. The bridging ligand forms almost equivalent interactions with tin, i.e. Sn(1)-O(2) is 2.276(9) Å and Sn(2)-O(3) is 2.254(9) Å, and these distances are longer, as expected, than the Sn(2)-O(4) separation of 2.183(8) Å. Within this arrangement there are several intramolecular Sn...O interactions. Hence, the Sn(1) atom is 2.718(9) Å from the centrosymmetrically related O(4)' atom and Sn(2)...O(5) is 3.017(9) Å (it is noteworthy that the O(5) atom is directed away from the Sn(1) atom). Neither of these interactions are considered as significant bonding contacts, however, these are partly responsible for the distortions from the ideal geometries about each of the independent tin atoms. The coordination geometries are based on trigonal bipyramids with

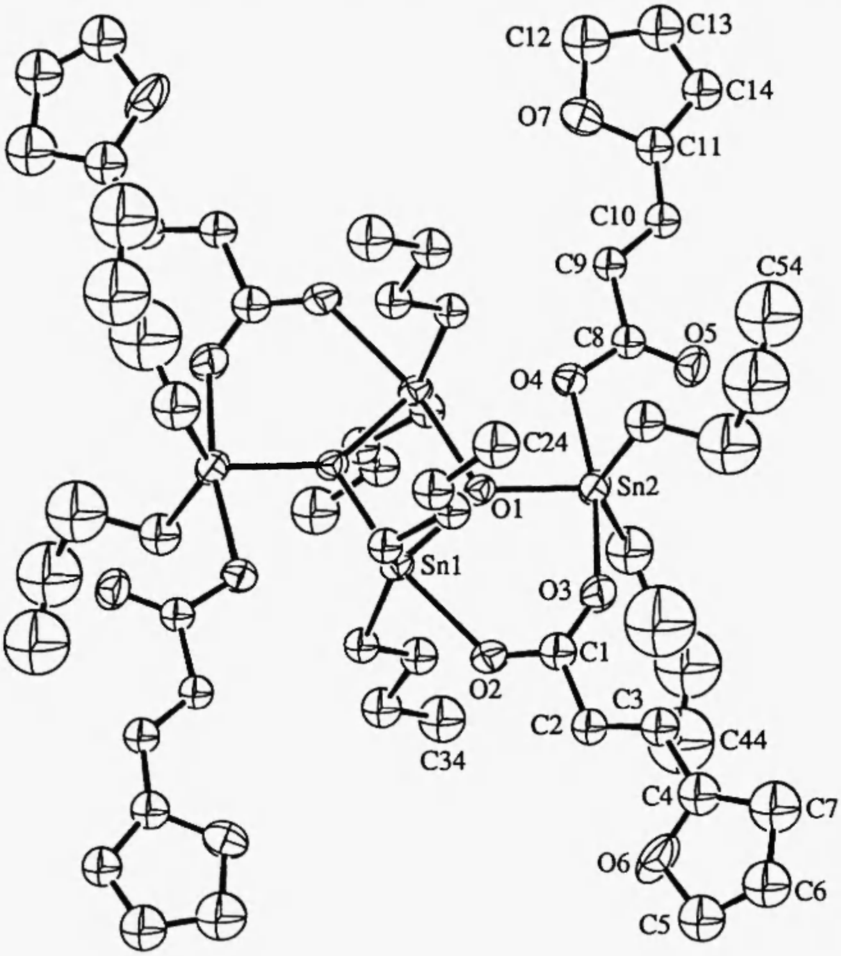

Figure 1. Molecular structure and crystallographic numbering scheme for $\{[nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$.

the Sn(1) atom lying 0.0834(9) Å out of the equatorial plane defined by the O(1), C(21) and C(31) atoms in the direction of the O(1)' atom. Similarly, the Sn(2) atoms lies 0.005(1) Å above the O(1), C(41) and C(51) plane in the direction of the O(3) atom. Each of the carboxylate ligands is effectively planar as seen in the O(2)/C(1)/C(2)/C(3), C(1)/C(2)/C(3)/C(4) and C(2)/C(3)/C(4)/O(6) torsion angles of -179(1), 179(1) and 2(3)°, respectively; the comparable angles for the second carboxylate ligand are -179(1), 180(1) and 0(2)°, respectively. No evidence was found for an interaction between the furan oxygen atom and tin and indeed there are no significant intermolecular interactions in the lattice with the closest non-hydrogen contact of 3.25(2) Å occurring between the O(5) and C(14) atoms (symmetry operation: 0.5-*x*, -0.5+*y*, 0.5-*z*).

The structure of [$Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)$] is shown in Figure 2 and selected geometric parameters are given in Table 5. The structure is polymeric owing to the presence of a bidentate bridging carboxylate ligand with forms disparate Sn-O(1) and Sn-O(2)' (symmetry operation: -*x*, -0.5+*y*, 0.5-*z*) distances of 2.184(4) and 2.361(5) Å, respectively. This coordination mode leads to a trigonal bipyramidal geometry about the tin atom which lies 0.0726(3) Å out of the trigonal plane defined by the three ipso carbon atoms of the phenyl substituents, in the direction of the more tightly bound O(1) atom; the dihedral angles between the three C(11-16), C(21-26) and C(31-36) phenyl groups are 63.9, 87.3 and 54.7°, respectively. The carboxylate ligand is planar, but marginally less so compared with the ligands in the structure of {[$nBu_2Sn(O_2CC(H)=C(H)C_4H_3O)]_2O\}_2$, as seen in the three O(1)/C(1)/C(2)/C(3), C(1)/C(2)/C(3)/C(4) and C(2)/C(3)/C(4)/O(5) torsion angles of 3.0(8), -177.0(5) and 7(1)°, respectively. In the lattice the closest non-hydrogen contact of 3.038(7) Å occurs between the O(2) and C(31) atoms (symmetry operation: -*x*, 0.5+*y*, 0.5-*z*) and no evidence of a contact between tin and the O(5) atom was found.

Table 5. Selected bond distances (Å) and angles (°) for [$Ph_3Sn(O_2CC(H)=C(H)C_4H_3O)$]

Sn-O(1)	2.184(4)	Sn-O(2)'[a]	2.361(5)
Sn-C(11)	2.117(5)	Sn-C(21)	2.119(6)
Sn-C(31)	2.116(5)	C(1)-O(1)	1.271(6)
C(1)-O(2)	1.259(6)	C(4)-O(5)	1.356(7)
C(6)-O(5)	1.368(7)	C(1)-C(2)	1.471(7)
C(2)-C(3)	1.315(7)		
O(1)-Sn-O(2)'	173.3(1)	O(1)-Sn-C(11)	95.5(2)
O(1)-Sn-C(21)	90.9(2)	O(1)-Sn-C(31)	89.4(2)
O(2)'-Sn-C(11)	91.1(2)	O(2)'-Sn-C(21)	87.8(2)
O(2)'-Sn-C(31)	85.3(2)	C(11)-Sn-C(21)	109.4(2)

C(11)-Sn-C(31)	134.2(2)	C(21)-Sn-C(31)	116.0(2)
Sn-O(1)-C(1)	122.7(3)	Sn-O(2)'-C(1)'	144.0(3)
O(1)-C(1)-C(2)	122.2(5)	O(1)-C(1)-C(2)	117.1(5)
O(2)-C(1)-C(2)	120.7(5)	C(1)-C(2)-C(3)	122.5(5)
C(2)-C(3)-C(4)	127.7(5)		

a primed atoms related by symmetry operation: -*x*, -0.5-*y*, 0.5-*z*.

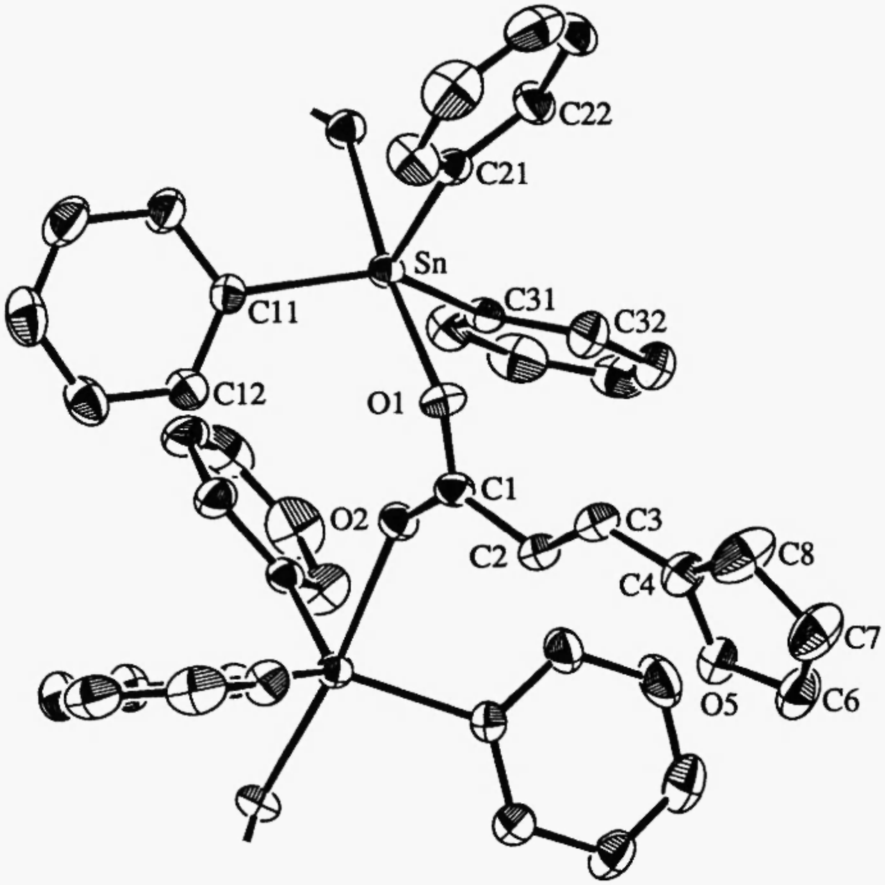

Figure 2. A portion of the polymeric structure showing the crystallographic numbering scheme for [$Ph_3Sn(O_2CC(H){=}C(H)C_4H_3O)$].

The structure of {[$nBu_2Sn(O_2CC(H){=}C(H)C_4H_3O)]_2O\}_2$ conforms to the common motif for compounds with the general formula {[$R_2Sn(O_2CR')]_2O\}_2$ [2, 3]. Other motifs arise as a result of different modes of attachment of the carboxylate ligands, however, there is one example in which a potential donor atom resident on the R' residual coordinates to tin. In the structure of {[$nBu_2Sn(O_2CC_5H_4N\text{-}2)]_2O\}_2$ each exocyclic tin atom is chelated by a carboxylate ligand via the pyridine nitrogen atom and one of the oxygen atoms of the carboxylate group [9]. No evidence of tin to oxygen coordination, where the oxygen atom forms a part of the carboxylate R' residual, has been shown crystallographically. The structure of [$Ph_3Sn(O_2CC(H){=}C(H)C_4H_3O)$] also conforms to a frequently observed motif for compounds of the general formula [$R_3Sn(O_2CR')$], i.e. the *trans*-R_3SnO_2 motif. The closely related sulfur analogues, i.e. [$R_3Sn(O_2CC(H){=}C(H)C_4H_3S)$], R = Me and Et [10], adopt essentially the same structure in the solid state and common with the present R = Ph compound, show no evidence of additional interactions involving the tin atom and the carboxylate R' residual.

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