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Structural chemistry of organotin carboxylates

XVI *. Structural variation in dicarboxylato tetraorganostannoxanes: Crystal structure of $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$

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Abstract

The crystal structure of the title compound shows that it has the usual dicarboxylato tetraorganodistannoxane structure, based on a centrosymmetric Sn_2O_2 unit connected to exocyclic Sn atoms via two bridging carboxylate ligands; the remaining two carboxylate ligands are coordinated to the exocyclic Sn atom in the monodentate mode. There are no significant contacts between the Sn and S atoms.

Introduction

The chemistry of organotin carboxylates has attracted much attention owing to their industrial and agricultural importance [2–5]; and more recently to their anti-tumour activity [6,7]. Consequently there has been considerable interest in their strucutral characteristics. These compounds may adopt a variety of structural modes depending on the nature of the organic substituent on the Sn atom and/or the carboxylate ligand [8]. Attempts to predict structures, or indeed rationalize known structures of these systems have proved difficult, as seemingly small changes in chemical composition may result in a major change in the structure actually adopted, at least in the solid state. There have been numerous crystallographic studies of the dicarboxylato tetraorganostannoxanes, of formula $\{[R_2Sn(O_2CR')]_2O\}_2$, and there are at least five distinct types of structure known for them [8]; these are discussed in more detail below.

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* For Part XV see ref. 1.

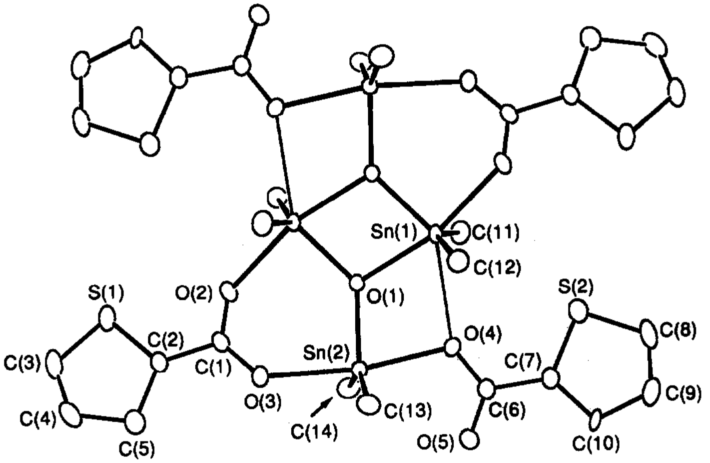


Fig. 1. Molecular structure and crystallographic numbering scheme employed for $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$ (illustrated for molecule b).

One reason for the large number of crystallographic investigations of compounds with this formula is that they are the readily generated by hydrolysis of compounds of the formula $[R_2Sn(O_2CR')_2]$. The title compound, $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$, for example, was isolated during the attempted recrystallization of monomeric $[Me_2Sn(O_2CC_4H_3S)_2]$ [9]. Interest in this structure arises not from the point of view of its chemistry, since it is a well characterized species [9], but rather because its availability allows comparison of a series of structures in which the carboxylate ligand remains the same while the organic substituents on the Sn atoms are varied.

Results and discussion

There are two molecules of $\{[R_2Sn(O_2CC_4H_3S)]_2O\}_2$ in the triclinic unit cell, but the crystallographic asymmetric unit is comprised of two independent half molecules, each located about a crystallographic centre of inversion; molecule a is centred about the position ($-x$, $1-y$, $-z$) and molecule b about ($-x$, $-y$, $1-z$). Only one molecule is shown in Fig. 1, i.e. molecule b, since both independent molecules have identical numbering schemes and similar molecular structures. Selected interatomic parameters are listed in Table 1.

The structure of $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$ conforms closely to that of related systems (see below), based on a centrosymmetric Sn_2O_2 unit connected to a pair of exocyclic Sn atoms via the bridging O atoms so that the bridging O atoms are tricoordinate. There are two distinct carboxylate ligands in the structure. The first, defined by the O(2) and O(3) atoms, symmetrically bridges the Sn(1) and Sn(2) atoms (Table 1). The second ligand is essentially monodentate, coordinating to the Sn(2) atom via the O(4) atom only. This ligand also shows a weak intramolecular interaction with the Sn(1) atom, via the O(4) atom, with a Sn · · · O distance of 2.683(7) Å for molecule a and 2.721(5) Å for molecule b; the O(5) atom does not participate in coordination to the Sn centres, being directed away from the central unit. There is no evidence of significant contacts between the Sn and S atoms (*vide infra*).

The Sn(1) atom forms five close interactions as well as the weaker contact to the O(4) atom mentioned above. The coordination geometry about the Sn(1) atom may thus be regarded as based on a distorted octahedron with the four O atoms defining the basal plane. The C(11)–Sn–C(12) angle of 147.9(3)° (146.4(3)° for molecule b) is consistent with this description, but, as can be seen from Fig. 1(a), description based on a trigonal bipyramid would also be valid. In this latter description, the trigonal plane is defined by the two methyl groups and the O(1′) atom and the axial positions by the O(1) and O(2′) atoms, which form an angle of 167.0(2)°. The widening of the C(11)–Sn(1)–C(12) is consistent with the close approach of the O(4) atom. The Sn(2) exists in a distorted trigonal bipyramidal geometry with the basal plane defined by the O(1) atom and the C(13) and C(14) methyl groups; the axial sites are occupied by the O(3) and O(4) atoms which form an angle of 170.1(2)° at the Sn(2) atom (168.8(2)Å for molecule b). The O(5) atom is 2.988(6) Å (3.025(6) Å) from the Sn(2) atom, a distance too long to be considered as a significant bonding interaction. The Sn(2) atom in molecule b is involved in a weak intermolecular contact with an O(5)b′ atom (symmetry operation 1-*x*, -*y*, -1-*z*) at 3.211(6) Å; no such interaction is found for molecule a.

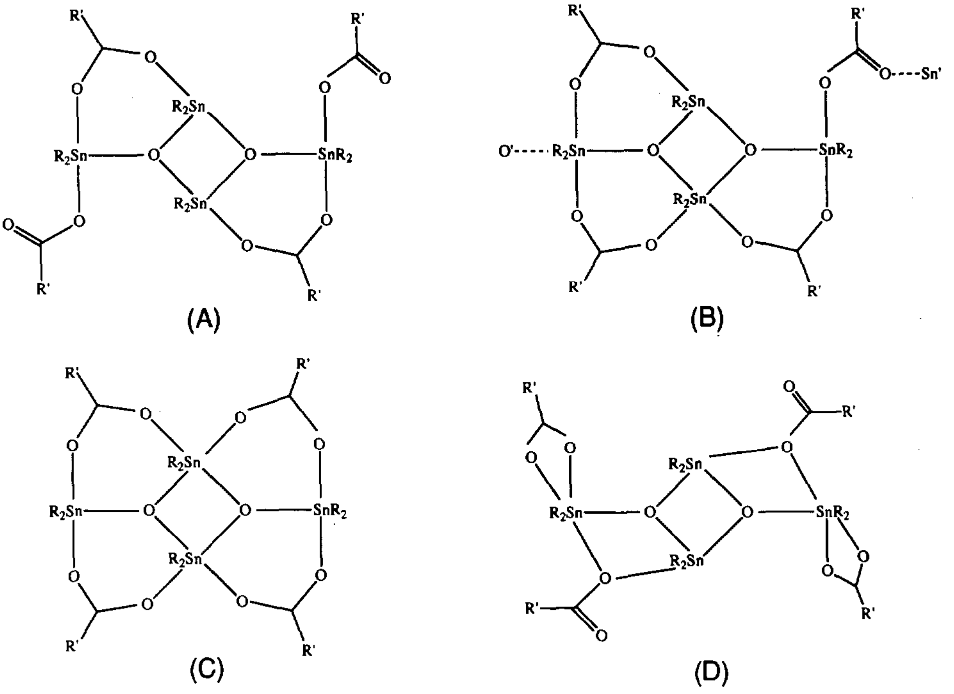
As detailed in the Experimental section (*vide infra*) positional disorder associated with the thiophene ring containing the S(1) atom was detected. This disorder was modelled successfully such that the site labelled S(1) in Fig. 1 contains 72.7(9)% S and 27.3(9)% C character for molecule a and a similar ratio was found for molecule b, *viz*. 70.6(8)% S character. As can be seen from Fig. 1 there is no hindrance to rotation about the C(1)–C(2) bond and thus the possibility of the disorder described above arises. The same is not true for the second thiophene ring, however. The S atom of this ring is relatively close to the Sn(1) atom, being separated from it by 3.726(6) Å (3.758(6) Å); this distance, while greater than the sum of the covalent radii of these atoms of 2.42 Å, is less than the sum of the relevant van der Waals radii *viz*. 4.0 Å. While not representing a significant interaction, the Sn(1)...S(2) contact is sufficient to preclude rotation about the C(6)–C(7) bond.

The structure found here for $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$ is virtually identical to that of the n-butyl analogue [9]. In the context of the disorder associated with the thiophene ring found in $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$, it is noteworthy that in $\{[{}^nBu_2Sn(O_2CC_4H_3S)]_2O\}_2$ the S atom in both thiophene residues is directed away from the Sn_2O_2 moiety. This feature represents the most significant difference between the two structures.

Both $\{[R_2Sn(O_2CC_4H_3S)]_2O\}_2$, R = Me and ^{n}Bu, compounds adopt structures based on the most common mode found for compounds of the general formula $\{[R_2Sn(O_2CR')]_2O\}_2$; see (A) (Scheme 1) [8]. Variations on this basic structure are shown in (B), (C) and (D). In (B) three of the carboxylate ligands are bridging (e.g. R = Me; R′ = Me [10]) and in (C) each of the four carboxylate ligands bridge a pair of Sn atoms (e.g. R = Ph; R′ = CCl_3 [11] and R = Me; R′ = ^{t}Bu [12]). A fourth structural type is found for the R = Me; R′ = $C_6H_4NH_2$-*p* compound [13], in which two ligands are bridging and two are chelating. A fifth structural type (not illustrated) is found in the compound with R = ^{n}Bu and R′ = C_5H_4N-*o* in which the N atom participates in coordination to the Sn atoms [14]. This last example

Table 1. Selected interatomic parameters (Å, deg.) for $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$.

	Molecule a	Molecule b
Sn(1)–O(1)	2.043(3)	2.140(4)
Sn(1)–O(1′)	2.154(3)	2.037(4)
Sn(1)–O(2′)	2.245(7)	2.265(5)
Sn(1)–C(11)	2.106(8)	2.104(6)
Sn(1)–C(12)	2.103(7)	2.110(6)
Sn(1)–O(4)	2.683(7)	2.721(5)
Sn(2)–O(1)	2.007(4)	2.029(4)
Sn(2)–O(3)	2.212(7)	2.300(4)
Sn(2)–O(4)	2.183(5)	2.207(4)
Sn(2)–C(13)	2.105(9)	2.096(6)
Sn(2)–C(14)	2.093(9)	2.111(8)
O(2)–C(1)	1.24(1)	1.251(9)
O(3)–C(1)	1.242(9)	1.249(9)
C(1)–C(2)	1.47(1)	1.482(9)
O(4)–C(6)	1.289(8)	1.270(9)
O(5)–C(6)	1.21(1)	1.232(9)
C(6)–C(7)	1.49(1)	1.487(9)
O(1)–Sn(1)–O(1′)	76.8(2)	77.1(2)
O(1)–Sn(1)–O(2′)	90.2(2)	88.1(2)
O(1)–Sn(1)–C(11)	106.3(2)	103.6(2)
O(1)–Sn(1)–C(12)	105.0(2)	108.8(2)
O(1)–Sn(1)–O(4)	142.7(2)	142.2(2)
O(1′)–Sn(1)–O(2′)	167.0(2)	164.5(2)
O(1′)–Sn(1)–C(11)	96.3(2)	99.0(2)
O(1′)–Sn(1)–C(12)	97.3(3)	97.3(2)
O(1′)–Sn(1)–O(4)	66.0(2)	65.6(2)
O(2′)–Sn(1)–C(11)	86.2(3)	88.7(2)
O(2′)–Sn(1)–C(12)	87.0(3)	83.1(2)
O(2′)–Sn(1)–O(4)	127.1(2)	129.5(2)
C(11)–Sn(1)–C(12)	147.9(3)	146.4(3)
C(11)–Sn(1)–O(4)	80.2(3)	79.4(3)
C(12)–Sn(1)–O(4)	79.1(3)	80.8(3)
O(1)–Sn(2)–O(3)	91.5(2)	91.6(2)
O(1)–Sn(2)–O(4)	79.1(2)	78.2(2)
O(1)–Sn(2)–C(13)	109.9(3)	108.6(2)
O(1)–Sn(2)–C(14)	112.0(3)	106.0(2)
O(3)–Sn(2)–O(4)	170.1(2)	168.8(2)
O(3)–Sn(2)–C(13)	88.8(3)	86.6(3)
O(3)–Sn(2)–C(14)	86.6(3)	91.6(3)
O(4)–Sn(2)–C(13)	96.9(3)	93.1(2)
O(4)–Sn(2)–C(14)	94.4(3)	95.7(2)
C(13)–Sn(2)–C(14)	137.9(4)	145.4(3)
Sn(1)–O(1)–Sn(1′)	103.2(2)	102.9(2)
Sn(1)–O(1)–Sn(2)	136.7(2)	136.0(2)
Sn(1′)–O(1)–Sn(2)	119.9(2)	120.7(2)
Sn(1)–O(2)–C(1)	138.7(5)	133.4(4)
Sn(1)–O(4)–Sn(2′)	95.0(2)	94.1(2)
Sn(1)–O(4)–C(6)	151.2(5)	147.8(5)
Sn(2)–O(3)–C(1)	138.7(6)	129.9(6)
Sn(2)–O(4)–C(6)	112.9(5)	114.1(4)
O(2)–C(1)–O(3)	124.0(8)	125.6(6)
O(2)–C(1)–C(2)	116.5(6)	115.6(6)
C(2)–C(1)–C(3)	119.5(8)	118.8(6)
O(4)–C(6)–O(5)	123.8(7)	123.2(6)
O(4)–C(6)–C(7)	115.5(7)	117.9(6)
O(5)–C(6)–C(7)	120.7(6)	118.8(7)



Scheme 1.

aside, it is clear that there is a simple relationship between the four structural types found for the $\{[R_2Sn(O_2CR')]_2O\}_2$ compounds.

Attempts to rationalize the preference for one structure over another have proved difficult. Although, as mentioned above, structure (A) is the most common structural type, there are several examples of $\{[R_2Sn(O_2CR')]_2O\}_2$ compounds with the other structures. If the R′ group on the carboxylic acid is kept constant and the Sn-bound R substituent is varied, as in the present study, different structures may be adopted. Whereas the compounds $\{[R_2Sn(O_2CC_4H_3S)]_2O\}_2$, R = Me and ^{n}Bu [9] and $\{[R_2Sn(O_2CCH_2SPh)]_2O\}_2$, R = ^{n}Pr and ^{n}Bu [15] have essentially the same structure, i.e. one based on (A), for the compounds $\{[R_2Sn(O_2C^tBu)]_2O\}_2$ the species with R = Me adopts structure (C), and the R = Et derivative structure (A) [12]. If the R substituent is kept constant and the carboxylate ligand is varied, different structures are again found, as can be seen from the examples mentioned above.

On the basis of the above discussion, it would appear that there is little energy difference between the structural forms adopted by compounds of the formula $\{[R_2Sn(O_2CR')]_2O\}_2$. To further illustrate this point we note (i) compounds with R = Ph, R′ = CCl_3 exists as isomers, representing structural types (A) and (C) [11], and (ii) many compounds of this general formula exist with two centrosymmetric molecules in the crystallographic asymmetric unit [8]. The overwhelming structural evidence suggests that crystal packing effects, which are difficult to assess quantitatively, play an important role in determining the nature of the molecular structure actually adopted in the solid state.

Table 2

Crystal data and refinement details for $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$

Formula	$C_{28}H_{36}O_{10}S_4Sn_4$
Mol. wt.	1135.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.637(2)
b (Å)	20.914(2)
c (Å)	8.597(2)
α (deg)	90.28(1)
β (deg)	99.32(2)
γ (deg)	77.80(1)
V (Å^3)	2017.1
Z	2
D_c (g cm^{-3})	1.870
$F(000)$	1096
μ (cm^{-1})	24.95
T (K)	293
Max/min transmission factors	0.919, 0.761
No. of data collected	5801
No. of unique data	5287
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	3549
R	0.025
k	0.998
g	0.0004
R_w	0.026
Residual ρ_{max} (e Å^{-3})	0.39

Experimental

Crystallography

Intensity data for $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$ were measured at 293 K 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°. The data set was corrected for Lorentz and polarization effects and for absorption by use of an analytical procedure [16]. Relevant crystal data are given in Table 2.

The structure was solved by direct methods [17] and refined by a block-matrix least-squares procedure based on F [16]. The crystallographic asymmetric unit in the structure is comprised of two half molecules, each located about a crystallographic centre of inversion. Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model in their calculated positions. Examination of the geometric and thermal parameters associated with the S(1) and C(5) atoms for both molecules comprising the asymmetric unit indicated the presence of positional disorder. These sites were refined with composite scattering factor curves comprised of those of S and C; the weight given to each type of atom was determined by the refinement of the site occupancy factors. Subsequent refinement revealed the percentage occupancy of the S(1) site to be 72.7(9)% S for

Table 3

Fractional atomic coordinates for $\{[Me_2Sn(O_2CC_4H_3S)]_2O\}_2$

Atom	*x*	*y*	*z*
Sn(1)a	0.03441(4)	0.44138(2)	0.13706(5)
Sn(2)a	−0.28280(4)	0.53623(2)	0.04251(5)
S(1)a	−0.1055(3)	0.3308(1)	0.5563(3)
S(2)a	−0.2373(3)	0.6945(1)	−0.3882(3)
O(1)a	−0.1079(3)	0.5109(2)	0.0328(5)
O(2)a	−0.0812(5)	0.4066(3)	0.2892(7)
O(3)a	−0.2641(5)	0.4640(3)	0.2370(8)
O(4)a	−0.2680(4)	0.6051(2)	−0.1395(5)
O(5)a	−0.4632(5)	0.6379(3)	−0.1602(7)
C(1)a	−0.1857(7)	0.4205(4)	0.3120(8)
C(2)a	−0.2149(7)	0.3837(3)	0.4403(8)
C(3)a	−0.2030(12)	0.3118(5)	0.6589(11)
C(4)a	−0.3129(11)	0.3422(6)	0.6183(11)
C(5)a	−0.3403(7)	0.3950(4)	0.4807(8)
C(6)a	−0.3694(7)	0.6409(3)	−0.2011(8)
C(7)a	−0.3656(7)	0.6874(3)	−0.3302(9)
C(8)a	−0.3057(13)	0.7527(5)	−0.5236(12)
C(9)a	−0.4231(12)	0.7678(5)	−0.5242(12)
C(10)a	−0.4681(8)	0.7324(3)	−0.4121(8)
C(11)a	0.0274(7)	0.3553(3)	0.0109(10)
C(12)a	0.1081(7)	0.4853(4)	0.3387(8)
C(13)a	−0.3754(8)	0.4774(4)	−0.1073(11)
C(14)a	−0.3202(9)	0.6083(4)	0.2078(10)
Sn(1)b	0.03343(4)	0.04835(2)	−0.35770(5)
Sn(2)b	0.28090(4)	−0.02188(2)	−0.55581(5)
S(1)b	−0.1011(3)	0.1896(1)	0.0572(3)
S(2)b	0.2239(2)	0.1517(1)	−0.1253(3)
O(1)b	−0.1058(3)	0.0097(2)	−0.4613(5)
O(2)b	−0.0806(5)	0.0929(3)	−0.1735(5)
O(3)b	0.2723(5)	−0.1098(2)	−0.7157(6)
O(4)b	0.2591(4)	0.0574(2)	−0.3856(5)
O(5)b	0.4517(5)	0.0520(3)	−0.3692(6)
C(1)b	−0.1872(7)	0.1221(3)	−0.1890(8)
C(2)b	−0.2218(6)	0.1747(3)	−0.0752(7)
C(3)b	−0.1852(10)	0.2487(4)	0.1340(10)
C(4)b	−0.2988(10)	0.2623(4)	0.0655(12)
C(5)b	−0.3334(4)	0.2204(2)	−0.0645(6)
C(6)b	0.3562(7)	0.0720(3)	−0.3222(8)
C(7)b	0.3543(6)	0.1139(3)	−0.1821(8)
C(8)b	0.2945(10)	0.1882(4)	0.0252(10)
C(9)b	0.4139(9)	0.1728(4)	0.0325(10)
C(10)b	0.4545(6)	0.1279(3)	−0.0829(8)
C(11)b	0.0005(7)	0.1413(3)	−0.4691(8)
C(12)b	0.1278(7)	−0.0129(3)	−0.1639(8)
C(13)b	0.3801(6)	−0.0911(3)	−0.3830(8)
C(14)b	0.2882(7)	0.0387(4)	−0.7480(9)

molecule a and 70.6(8)% S for molecule b. After the inclusion of a weighting scheme of the form $w = k/[\sigma^2(F) + |g|F^2]$, the refinement was continued until convergence; final refinement details are listed in Table 2. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed, common to both molecules, is shown in Fig. 1 and was drawn with ORTEP [18] at 25% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [16] and the refinement was performed on a SUN4/280 computer. Other crystallographic details comprising thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors are available from E.R.T.T.

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