CRYSTAL AND MOLECULAR STRUCTURES OF TWO POLYMERIC TRIORGANOTIN 2-(2-THIOPHENYL)ETHYLENE-1-CARBOXYLATE DERIVATIVES

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Abstract.

The crystal and molecular structures of [$Me_3Sn(TA)$] and [$Et_3Sn(TA)$], where TA is 3-(2-thiophenyl)-2-propenoate, are reported. The structures are polymeric owing to the presence of bidentate bridging carboxylate ligands; no evidence was found for Sn to S interactions. The Sn atom geometries are distorted trigonal bipyramidal with the organo substituents occupying equatorial positions. The structures found for the title compounds conform to the *trans*-R_3SnO_2 motif.

Introduction.

The diverse structures for carboxylic acid derivatives of tin compounds have been reviewed recently [1, 2]. In the solid state, very different structures are often observed, even for compounds with similar empirical formulae. In the context of the present report, it is noteworthy that compounds with the general formula [$R_3Sn(O_2CR')$] have been found to adopt at least three motifs [2]. Two extreme structures are represented by (I) and (II) below. In (I), the triorganotin moiety is coordinated by a carboxylate ligand which functions in the monodentate mode leading to a four-coordinate Sn centre. Higher coordination numbers for this motif are achieved as the pendent O atom approaches the Sn atom. Indeed, there are a small number of structures where the difference between the two Sn-O separations is approximately 0.5 Å [2]. The other extreme is represented in (II) where the carboxylate ligand is bidentate, bridging two Sn centres; the Sn atom in

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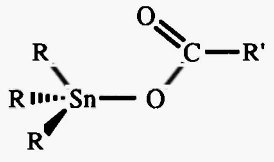
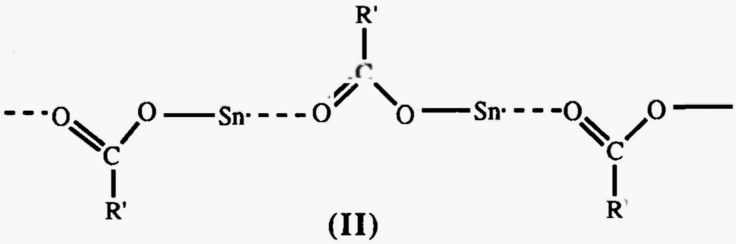
this motif exists in a distorted trigonal bipyramidal geometry. Different motifs are sometimes found when the carboxylate residue also carries additional potential donor atoms. In these circumstances the carboxylate group coordinates *via* one O atom only and the additional donor atom from the carboxylate residue (invariably an O or N atom) coordinates a symmetry related molecule leading to polymeric structures reminiscent to the *trans*-R_3SnO_2 motif (II). A systematic approach to examining structures of this type has been precluded owing to the unavailability of suitable crystals. In the few examples where the carboxylate ligand is unchanged and the triorganotin moieties varied, different results are obtained. Thus for the acetates, [$R_3Sn(O_2CCH_3)$], structure type (II) is found for both R = Me [3] and Ph [4] whereas for the thiophene carboxylates, structural type (I) is found for R = Ph [5] and type (II) for R = Me [6]; in neither case is evidence found for Sn to S interactions. The title compounds, [$Me_3Sn(TA)$] and [$Et_3Sn(TA)$] where TA is 3-(2-thiophenyl)-2-propenoate [7], have been characterized by X-ray crystallographic methods and the results of this study are reported herein as a continuation of previous studies in this field.



(I)



(II)

Crystallography.

Crystal data and refinement details for both determinations are collected in Table 1. In each case intensity data for a colourless crystal were measured at room temperature on a Rigaku AFC6R four-circle diffractometer fitted with nickel-filtered CuKα radiation, λ = 1.5418 Å employing the $\omega:2\theta$ scan technique to θ_{max} 60.0°. Each data set was corrected for Lorentz and polarization effects [8] and for absorption employing the DIFABS program [9]. Significant decomposition (*ca* 35 %) of the [$Et_3Sn(TA)$] crystal occurred during its data collection as monitored by the remeasurement of three control reflections after every 1 hr X-ray exposure time; correction was made for this intensity variation [8].

Each structure was solved by direct methods [10] and refined by a full-matrix least-squares procedure based on *F* [8]. Non-H atoms (excluding methyl C atoms in [$Et_3Sn(TA)$]) were refined with anisotropic thermal parameters and H-atoms were included in the model at their calculated positions (C-H 0.97 Å). Disorder in the positions of the ethyl group atoms and generally high thermal motion with all atoms were noted in the structure of [Et_3Sn(TA)]. One methyl group, C(11), was modeled over two positions with equal weight, however, only one position was found for the remaining groups. At convergence R = 0.045 and R_w = 0.043 (sigma weights [8]) for [Me_3Sn(TA)] and R = 0.047 and R_w = 0.050 for [Et_3Sn(TA)]. The final fractional atomic coordinates are listed in Table 2 and the crystallographic numbering schemes used are shown in Figure 1. Data manipulation was performed with the teXsan package [8] installed on an Iris Indigo workstation.

Table 1. Crystal data for [Me_3Sn(TA)] and [Et_3Sn(TA)]

	[Me_3Sn(TA)]	[Et_3Sn(TA)]
Formula	$C_{10}H_{14}O_2SSn$	$C_{13}H_{20}O_2SSn$
Mol. wt.	317.0	359.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (C^5_{2h}, No. 14)	$P2_1/n$ (C^5_{2h}, No. 14)
a, Å	10.366(4)	11.607(3)
b, Å	9.886(3)	10.478(1)
c, Å	12.493(4)	14.211(3)
β, deg.	99.39(3)	108.70(1)
V, Å^3	1263.0(7)	1637.0(5)
Z	4	4
D_c, g cm^{-3}	1.667	1.457
Crystal size, mm	0.03 x 0.06 x 0.32	0.11 x 0.12 x 0.26
F(000)	624	720
μ, cm^{-1}	174.71	135.46
No. of data collected	2132	2734
No. of unique reflections used with $I > 3.0\sigma(I)$	1280	866
R	0.045	0.047
R_w	0.043	0.050
Residual ρ_{max}, e Å^{-3}	0.76	0.36

Table 2. Fractional atomic coordinates

$[Me_3Sn(TA)]$

Atom	x	y	z
Sn	-0.44900(7)	0.16861(7)	0.70322(6)
S(1)	-0.0272(3)	0.7866(4)	0.6681(3)
O(1)	-0.3167(6)	0.3309(8)	0.6747(6)
O(2)	-0.4140(7)	0.4740(7)	0.7725(6)
C(1)	-0.3321(10)	0.4490(11)	0.7152(9)
C(2)	-0.2419(11)	0.5597(11)	0.6911(10)
C(3)	-0.1771(11)	0.5563(12)	0.6107(10)
C(4)	-0.0903(9)	0.6594(12)	0.5817(10)
C(5)	0.0587(12)	0.8533(13)	0.5734(12)
C(6)	0.0367(12)	0.7802(14)	0.4819(12)
C(7)	-0.0446(10)	0.6698(14)	0.4866(9)
C(8)	-0.3386(11)	0.0342(12)	0.6221(11)
C(9)	-0.6143(10)	0.2628(11)	0.6120(8)
C(10)	-0.4070(12)	0.1729(14)	0.8748(11)

$[Et_3Sn(TA)]$

Atom	x	y	z
Sn	0.7282(1)	0.07172(9)	0.29299(9)
S(1)	0.6650(6)	0.6621(6)	0.5714(6)
O(1)	0.6908(12)	0.2294(11)	0.3779(9)
O(2)	0.7281(12)	0.3796(11)	0.2799(10)
C(1)	0.7048(18)	0.3450(21)	0.3553(17)
C(2)	0.6868(18)	0.4430(19)	0.4247(20)
C(3)	0.6686(16)	0.4119(17)	0.5069(20)
C(4)	0.6605(15)	0.5016(18)	0.5795(20)
C(5)	0.6576(25)	0.6836(29)	0.6916(19)
C(6)	0.6442(30)	0.5659(46)	0.7257(22)
C(7)	0.6515(23)	0.4701(17)	0.6736(20)
C(8)	0.9166(17)	0.1148(22)	0.3161(21)
C(9)	0.9769(39)	0.1644(35)	0.4001(29)
C(10)	0.6901(27)	-0.0593(17)	0.3911(17)
C(11a)[a]	0.6625(56)	-0.0057(53)	0.4679(44)
C(11b)[a]	0.5499(38)	-0.0614(33)	0.3756(31)
C(12)	0.5865(31)	0.1002(24)	0.1484(20)
C(13)	0.5039(42)	0.1576(38)	0.1438(33)

a atom has 50% site occupancy factor

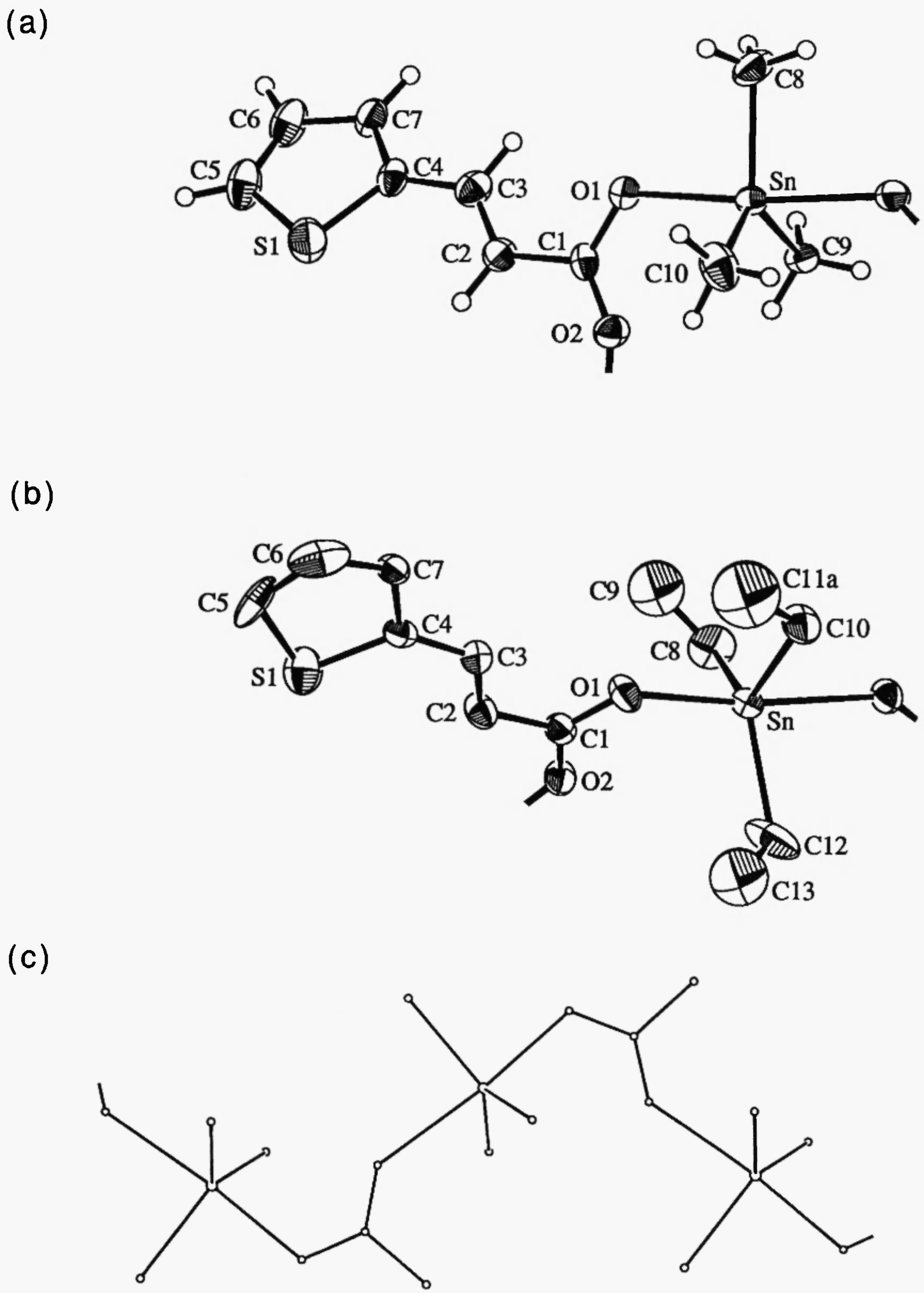


Figure 1. Immediate Sn atom environments and crystallographic numbering schemes for (a) $[Me_3Sn(TA)]$ and (b) $[Et_3Sn(TA)]$ (non-H atoms shown only). (c) The polymeric structure of $[R_3Sn(TA)]$ with terminal groups removed for clarity.

Results and Discussion.

The immediate environment about the Sn atom in [$Me_3Sn(TA)$] is shown in Fig. 1(a) and selected interatomic parameters are listed in Table 3. The Sn atom exists in a distorted trigonal bipyramidal geometry with the trigonal plane being defined by the three methyl substituents. The axial positions are occupied by O atoms (175.2(3)°) which are derived from symmetry related carboxylate residues. The carboxylate ligand is bidentate, coordinating one Sn atom intramolecularly via the O(1) atom and another intermolecularly via the O(2´) atom; the Sn-O(2) intramolecular contact of 3.145(7) Å is not indicative of a significant interaction between these atoms. The bidentate, bridging ligand forms different Sn-O(1) and Sn-O(2´) bond distances of 2.178(7) and 2.439(7) Å, respectively (see Table 3 for symmetry operation) with the disparity in the Sn-O bond distances being reflected in the associated C-O separations. The Sn atom lies 0.1188(7) Å out of the trigonal plane in the direction of the more strongly bound O(1) atom. The carboxylate residue is essentially planar as seen in the C(1)/C(2)/C(3)/C(4) torsion angle of 179(1)° and coordinates the Sn atoms via the carboxylate O atoms exclusively, there being no evidence for Sn to S interactions. The structure reported here for [$Me_3Sn(TA)$] is essentially the same as that found for the triethyl analogue [$Et_3Sn(TA)$], which is the first reported triethyltin carboxylate structure.

The Sn atom geometry in [$Et_3Sn(TA)$] is shown in Fig. 1(b) and selected interatomic parameters are collected in Table 3. The Sn atom lies 0.242(1) Å out of a trigonal plane defined by the three ethyl substituents in the direction of the O(1) atom; the O(1)-Sn-O(2´) axial angle in the distorted trigonal bipyramidal geometry is 171.7(4)°. The Sn-O(1) and O(2´) bond distances of 2.17(1) and 2.39(1) Å, respectively indicate more symmetry in the bridging mode of coordination of the carboxylate ligand; the Sn...O(2) separation is 3.23(1) Å. The carboxylate residue is planar, as for [$Me_3Sn(TA)$], with the C(1)/C(2)/C(3)/C(4) torsion angle being 175(2)°. There are no Sn-S interactions of note.

The structures found for [$Me_3Sn(TA)$] and [$Et_3Sn(TA)$] conform to the *trans*-R_3SnO_2 structural motif as represented in Fig. 3(c); as discussed in the *Introduction*, this motif is one of the major motifs for compounds of this type. The reduced asymmetry in the Sn-O interactions in the [$Et_3Sn(TA)$] compound may be correlated with the enhanced Lewis acidity of the Sn atom in the Et_3Sn moiety compared with Me_3Sn. Of interest is the absence of Sn to S interactions in the structures. This behaviour is consistent with other triorganotin carboxylates having S atoms in the R´ groups of the $^-O_2CR'$ ligands, but contrasts several structures containing N or O potential donor atoms in the carboxylate residues which have different structural types [1, 2].

Table 3. Selected interatomic parameters (Å, deg.) for [$\mathrm{Me_3Sn(TA)}$] and [$\mathrm{Et_3Sn(TA)}$]

[$\mathrm{Me_3Sn(TA)}$]		[$\mathrm{Et_3Sn(TA)}$]	
Atoms	Parameter	Atoms	Parameter
Sn-O(1)	2.178(7)	Sn-O(1)	2.17(1)
Sn-O(2´)[a]	2.439(7)	Sn-O(2´)[b]	2.39(1)
Sn-C(8)	2.12(1)	Sn-C(8)	2.15(2)
Sn-C(9)	2.11(1)	Sn-C(10)	2.10(2)
Sn-C(10)	2.12(1)	Sn-C(12)	2.20(3)
S(1)-C(4)	1.72(1)	S(1)-C(4)	1.69(2)
S(1)-C(5)	1.72(1)	S(1)-C(5)	1.75(2)
C(1)-O(1)	1.29(1)	C(1)-O(1)	1.28(2)
C(1)-O(2)	1.22(1)	C(1)-O(2)	1.24(2)
O(1)-Sn-O(2´)[a]	175.2(3)	O(1)-Sn-O(2´)[b]	171.7(4)
O(1)-Sn-C(8)	88.8(4)	O(1)-Sn-C(8)	97.5(7)
O(1)-Sn-C(9)	93.7(4)	O(1)-Sn-C(10)	90.4(7)
O(1)-Sn-C(10)	96.9(4)	O(1)-Sn-C(12)	101.1(7)
O(2´)[a]-Sn-C(8)	86.3(4)	O(2´)[b]-Sn-C(8)	84.1(7)
O(2´)[a]-Sn-C(9)	88.7(3)	O(2´)[b]-Sn-C(10)	81.8(7)
O(2´)[a]-Sn-C(10)	85.3(4)	O(2´)[b]-Sn-C(12)	84.8(7)
C(8)-Sn-C(9)	118.2(5)	C(8)-Sn-C(10)	117(1)
C(8)-Sn-C(10)	117.4(5)	C(8)-Sn-C(12)	122(1)
C(9)-Sn-C(10)	123.5(5)	C(10)-Sn-C(12)	117(1)
Sn-O(1)-C(1)	118.6(6)	Sn-O(1)-C(1)	121(1)
Sn-O(2´)[a]-C(1´)[a]	135.0(7)	Sn-O(2´)[b]-C(1´)[b]	139(1)
Sn/O(1)/C(1)/O(2)	3(1)	Sn/O(1)/C(1)/O(2)	8(3)
Sn/O(1)/C(1)/C(2)	-178.1(7)	Sn/O(1)/C(1)/C(2)	-175(1)
O(1)/C(1)/C(2)/C(3)	20(2)	O(1)/C(1)/C(2)/C(3)	6(3)
C(1)/C(2)/C(3)/C(4)	179(1)	C(1)/C(2)/C(3)/C(4)	175(2)

* Indicated atoms are related by the symmetry operations: a -1-*x*, -0.5+*y*, 1.5-*z*; and b 1.5-*x*, -0.5+*y*, 0.5-*z*

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