SYNTHESIS AND SPECTRAL STUDIES OF BIS{DIALKYL-[TRANS-3-(2-THIOPHENYL)-2-PROPENOATO]TIN} OXIDES: CRYSTAL STRUCTURE OF $\{[(CH_3)_2SnO_2C\text{-}CH{=}CH\text{-}C_4H_3S]_2O\}_2$

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ABSTRACT

Synthesis and multinuclear studies of stannoxane of 3-(2-thiophenyl)-2-propenoic acid have been performed. Crystal structure of bis[(3-(2-thiophenyl)-2-propenoato)-dimethyltin]oxide is presented. The unit cell is triclinic with space group $P\bar{1}$, Z=2. Out of 3050 reflections, 2273 were unique with $I \geq 2\sigma(I)$. The thiophene ring S1, C5, C6, C7 and C4 is staggered with an other ring containing S1a, C5a, C6a, C7a and C4a which describes the ring twist under the impact of radiation leading to disorder in the structural refinement. Of particular interest is the mode of O5 interactions. It forms an intra-molecular contact with Sn atom of the same molecule while an inter-molecular interaction with Sn atom of a symmetry related unit in the lattice. These intra- and inter-molecular interactions result in the formation of an infinite one dimensional polymer.

INTRODUCTION

Among organotin carboxylates, dimeric distannoxanes comprise the most interesting class with respect to their structural chemistry. Reports on crystallographic studies show that these compounds may adopt a variety of structural modes depending on the nature of organic substituents at the tin atom and/or carboxylate ligand.

Attempts to predict structures while comparing with already known structure of such systems have proved difficult, as seemingly a small change in chemical composition may result in a major change in the structure actually adopted, at least

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in the solid state. There have been numerous crystallographic reports on these compounds describing their dimeric nature and there are at least five distinct structural types known for them [1]. Here we discuss about the sixth structural type for which there exists only one example in literature [2].

EXPERIMENTAL

a) *Synthesis*

These stannoxanes were prepared by the reaction of R_2SnO with 3-(2-thiophenyl)-2-propenoic acid at reflux temperature of toluene; using a Dean-Stark apparatus, for azeotropic removal of water, according to the following equation;

$$4R_2SnO + 4HOOCCHCHC_4H_3S \longrightarrow [(R_2SnOOCCHCHC_4H_3S)_2O]_2 + 2H_2O$$

R = Me **(I)**, n-Bu **(II)**

(I) 1.64 g (0.01 mol) 3-(2-thiophenyl)-2-propenoic acid was refluxed with 1.647 g (0.01 mol)dimethyltin oxide as described above. Toluene was removed under reduced pressure and the residue was crystallized from dichloromethane/hexane (70/30 v/v), in 90% yield. mp = 134-135 °C.

(II) 3.28 g (0.02 mol) 3-(2-thiophenyl)-2-propenoic acid was refluxed with 4.96 g (0.02 mol)di-n-butyltin oxide as described above. Toluene was removed under reduced pressure and residue was crystallized from dichloromethane/hexane (70/30 v/v), in 83% yield. mp = 78-80 °C.

b) *Instrumentation*

Melting points were determined in a capillary tube using an electrothermal melting point apparatus modle MP-D Mitamura Riken Kogyo and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer, in $CDCl_3$ with reference to internal Me_4Si, while ^{119}Sn NMR spectra were obtained on a Bruker 250 ARX spectrometer with Me_4Sn as an external reference.

b) *Crystallography*

Crystal refinement data and selected interatomic parameters are given in Tables 1-4 (complete suplimentary data are available with the data bank). A colourless crystal of 0.3 x 0.3 x 0.2 mm was used for measurements. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2<\theta<22°$. 3050 reflections were collected out of which 2273 were unique with $I > 2\sigma(I)$. Data were corrected for Lorentz and polarization but not for absorption. The structure was solved by Patterson method and refined using SHELX suite of programs [3,4]. In the final least square cycles all atoms were allowed to vibrate anisotropically except for C6a, as anisotropic refinement afforded unsatisfactory thermal parameters. Hydrogen atoms were included at calculated positions on C8, C9, C10 and C11. The crystallographic numbering scheme is shown in Figure 1.

Table 1 Crystal data for $\{[(CH_3)_2SnO_2CCHCHC_4H_3S]_2O\}_2$

Formula	$C_{36}H_{44}O_{10}S_4Sn_4$
Mol. Wt.	1239.8
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	7.709(2)
b, Å	11.372(2)
c, Å	14.054(2)
α, deg.	99.51(2)
β, deg.	97.37(2)
γ, deg.	106.61(1)
U, $Å^3$	1144.2
Z	2
D_c, g cm^{-3}	1.799
Crystal size, mm	0.3 x 0.3 x 0.2
F(000)	568
μ, cm^{-1}	23.9
λ, Å	0.7093
θ(max), deg.	22.0
No. of reflections collected	3050
No. of unique reflections with $I > 2\sigma(I)$	2273
R	0.0301
Rw	0.0338

RESULTS AND DISCUSSION

A clean structural refinement was heavily hampered by severe disorder in both thiophene rings. The ring composed of S1, C5, C6, C7 and C4 was seen staggered with an other ring containing S1a, C5a, C6a, C7a and C4a. The relative occupancy of these distorted rings refined to a ratio of 56:44. In the second thiophene, the disorder centered around the C16 and S2 positions and their counterparts C16a and

S2a with a relative occupancy ratio of 41:59. This disorder is a consequence of frequent twist of the thiophene ring around the C_4-C_3 single bond. It is imperative to point out that such a twist was also observed earlier in the case of 2-thiophene carboxylate derivatives [5], however, the relative occupancy of S and C on these positions was 72.7 : 27.3. If we compare this relative occupancy ratio with our present system it can be concluded that twist of the thiophene ring is much faster in present system as a consequence of longer chain of carboxylate part attached to the thiophene ring.

Unfortunately, all disordered atomic positions maintained higher than average positional error throughout the refinement and as a result all geometric data pertaining to the rings are poorly refined. Despite this ‘blot on the landscape’ nothing can be detracted from the interesting coordination spheres surrounding the metal atoms and extended lattice bonding in this structure.

The dimeric nature, ubiquitous in stannoxane chemistry, is shown in Figure 1. In the solid state, the two carboxylate ligands are quite distinct. The ligand based on C(1) bridges one half of the dimer in a relatively symmetrical manner [Sn(1)-O(2) = 2.251(7) Å; Sn(2)-O(3) = 2.221(7) Å], in what is conventional arrangement for carboxylate containing stannoxanes.

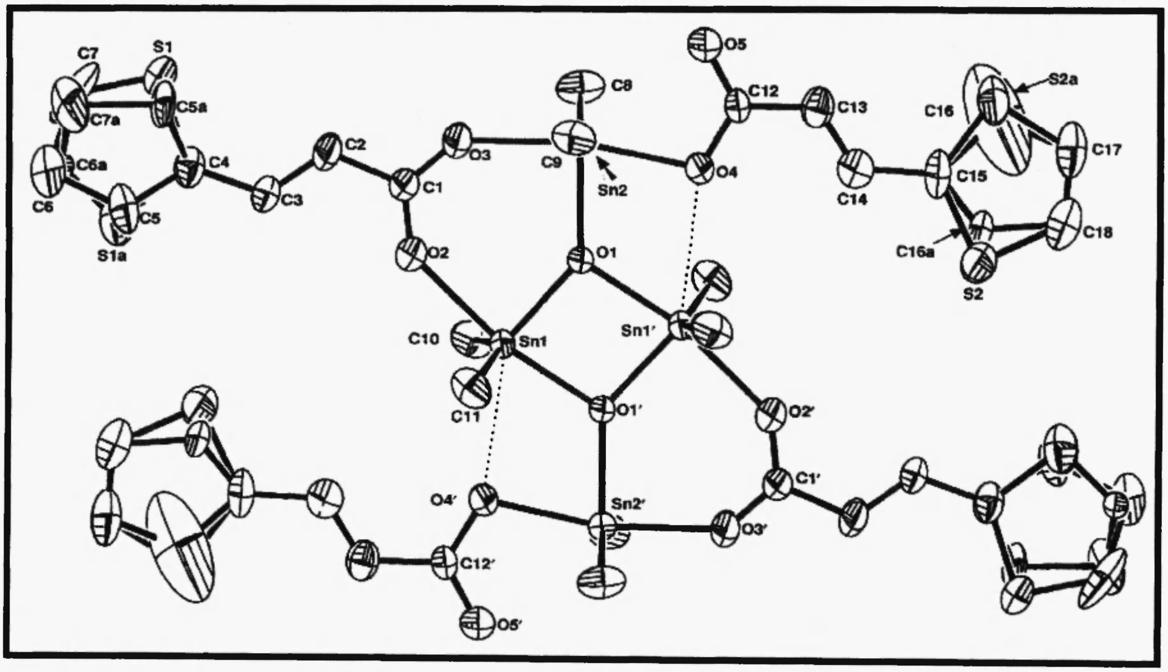


FIGURE 1:-Dimeric crystal structure of bis[(3-(2-thiophenyl)-2-propenoato)-dimethyltin]oxide.

The central four-membered Sn_2O_2 ring is relatively symmetrical, with the donor bond connecting the two halves of the dimer [Sn(1)-O(1$'$): 2.134(Å)] being only marginally longer than the Sn-O bonds with the component stannoxane units [Sn(1)-

O(1) = 2.037(5) Å: Sn(2)-O(1) = 2.039(5) Å]. The planarity of the central ring sets the pattern for the whole molecule which is essentially planar as a whole (except for the thiophene of the ligand) with methyl groups arranged above and below this plane. The environment about the Sn(1), the endocyclic metal, can be described as based on trigonal bipyramidal *cis*-Me_2SnO_3, with O(1) and O(2) in axial sites.An additional intramolecular interaction with $O(4^{\prime})$ [2.739 Å] expands this coordination number to effectively six, resulting in a distorted *trans*-Me_2SnO_4 arrangement. This latter bond has the effect of opening the C(10)-Sn-C(11) angle to $144.1(3)^{o}$, significantly wider than the 120^{0} expected for a perfect trigonal bipyramidal coordinate sphere. The coordination around the exocyclic Sn(2) can be descibed in a similar manner, with O(3) and O(4) occupying the axial sites of the *cis*-Me_2SnO_3 trigonal bipyramid [<OSnO = 168.4^{o}]. However, the coordination at Sn(2) is increased to seven by firstly a weak intermolecular bond from O(5) [2.850 Å] supported by a similar intermolecular bond from O(5) of an adjacent dimeric unit (Figure 2).

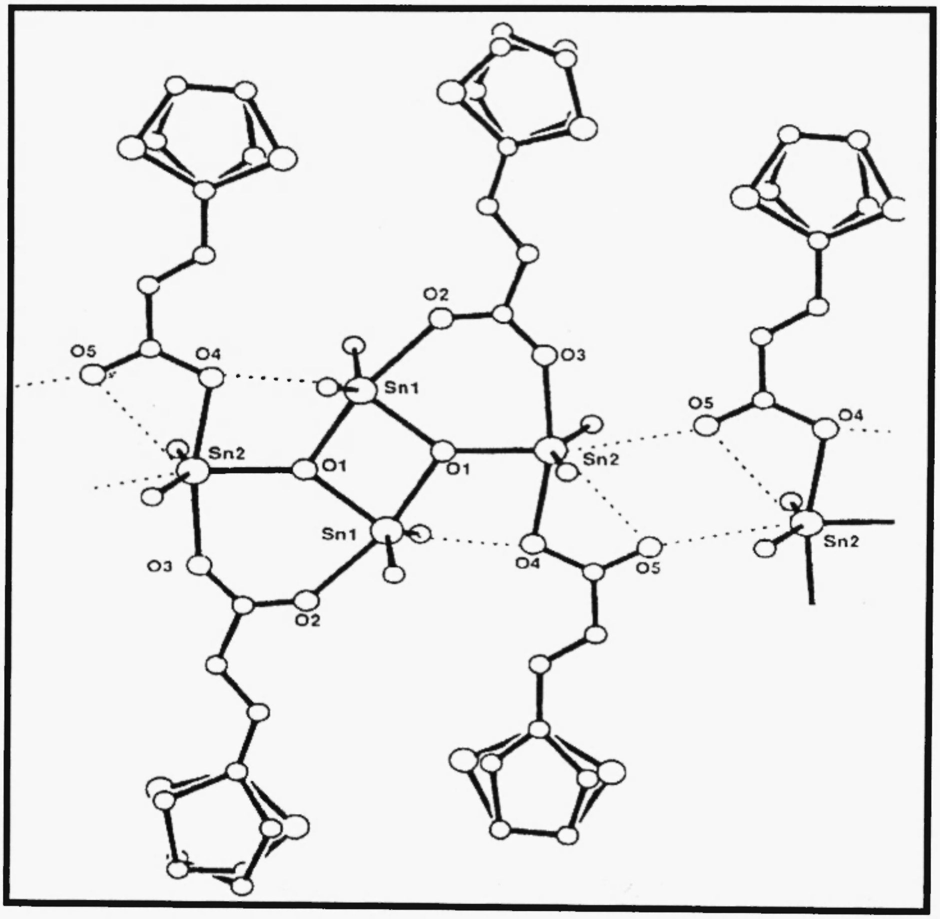


FIGURE 2:-One dimensional polymeric crystal structure of bis[(3-(2-thiophenyl)-2-propenoato)dimethyltin]oxide.

Table 2:- Selected fractional atomic coordinates.

atom	x	y	z
Sn(1)	627(1)	44(2)	6161(3)
Sn(2)	177(1)	3008(3)	5436(4)
S(1)	2305(10)	4686(4)	10996(3)
S(2)	-2350(34)	408(20)	9(15)
O(1)	108(5)	1177(3)	5254(3)
O(2)	1382(11)	1652(6)	7468(4)
O(3)	836(12)	3246(5)	7055(4)
C(1)	1298(10)	2694(6)	7667(5)
C(8)	-2473(10)	3003(6)	5619(6)
C(9)	2901(9)	3978(6)	5413(6)
C(10)	3472(9)	283(6)	6387(5)
C(11)	-1810(11)	-689(7)	6662(6)

Table 3:- Selected inter atomic distances (Å).

O(1)-Sn(1)	2.037(5)	O(2)-Sn(1)	2.251(7)
O(1)-Sn(2)	2.039(5)	O(3)-Sn(2)	2.221(7)
C(8)-Sn(2)	2.090(9)	C(9)-Sn(2)	2.082(9)
C(10)-Sn(1)	2.107(9)	C(11)-Sn(1)	2.087(9)
C(1)-O(2)	1.194(9)	C(1)-O(3)	1.220(9)
Sn(1)-Sn($1'$)	3.258(4)	C(2)-C(1)	1.489(9)

Key to symmetry operations relating designated atoms to referene atoms at (x,y,z):
(a) -x, -y, 1.0-z

The resulting geometry is thus distorted *trans*-Me_2SnO_5 pentagonal bipyramidal, with the C(8)-Sn(2)-C(9) angle [150.4(2)°] more open than the analogous angle about Sn(1). This observation is antiparallel with many earlier reports [5, 6] where the (C-Sn-C) angle around endocyclic tin is larger than that for exocyclic tin atom. Crystal data show that dimeric distannoxanes in which one of the carboxylate groups (usually linked with exocyclic tin atom) is acting as a bidentate chelate with an additional inter- or intra-molecular interaction through one of the carboxylate oxygens, the larger C-Sn-C angle is associated with exocyclic tin atom. However this observation parallels many cases where carboxylate group is bidentate, and further chelation is achieved though both the oxygens or only one oxygen executes this behaviour [5, 7-11].

In the case of diorganotin dicarboxylates or triorganotin carboxylates the mode of COO interaction is not uniform. For example in the case of $[Et_2Sn(O_2CCH_4H_3S)_2]$ [12], C(1)-O(1) = 1.291(8) Å, C(1)-O(2) = 1.237(8) Å. Similarly the carboxylate part chelates the tin atom in an asymmetric way, and this asymmetry is reflected in the associated C-O bond distances; as expected the larger C-O bond distances are associated with shorter Sn-O bonds. However in the case of some dimeric distannoxanes the carboxylate interaction is quite uniform when it is acting as bidentate ligand e.g. in case of $[Me_2SnO_2CC_4H_3S)_2O]_2$,C(1)-O(2) = 1.240(1) Å, C(1)-O(3) = 1.242(9) Å [5]. Similarly if the carboxylate group is acting as monodentate or has further contact through an already bonded oxygen atom, the C-O bond distances are also uniform. For example bond distances of C(6)-O(4) = 1.296(7) Å, C(6)-O(5) = 1.215(8) Å for $[(Et_2SnO_2C^tBu_2)_2O]_2$,[10] and C(6)-O(4) = 1.289(8) Å, C(6)-O(5) = 1.21(1) Å are observed for $[(Me_2SnO_2CC_4H_3S)_2O]_2$, [5].

In the present case the double bond character of the caboxylate is more evenly spread over the two C-O bonds [1.194(9) Å, 1.220(9) Å]. In constrast, the ligand centre around C(12) is remarkable because O(4) and O(5) form bifurcated bond to two metal centers. O(4) which is part of the C-O group based on the C-O bond length [C(12)-O(4): 1.298(8) Å] forms a normal covalent bond to Sn(2) [2.204(6) Å] while bridging intramolecularly to Sn(1′) [2.739(6) Å] to generate a new Sn_2O_2 ring. On the other hand, O(5), nominally forms a C=O function [C(12)-O(5): 1.225(8) Å] and bridges intermolecularly to Sn(2) of the adjacent dimer [2.953 Å] whilst simultaneously chelating the Sn(2) from which the ligand emanates [2.850 Å].The bridging behaviour generates a one-dimensional polymeric stannoxane strand (Figure 2). Although the bridging/chelating mode for O(5) has been precedented in certain triorganotin and related carboxylates such as $Ph_3Sn(OAc)$,[13]; $[Me_3SnO_2CC_4H_3O]_n$, [14] and $Me_2(Cl)Sn(OAc)$,[15] though in no previous case is the dual bonding role so evenly embraced. For example, in $Ph_3Sn(OAc)$, [13] the bridging and chelating bonds are quite dissimilar [2.349(3) Å, and 3.206(3) Å].

Table 4:- Selected bond angles (°).

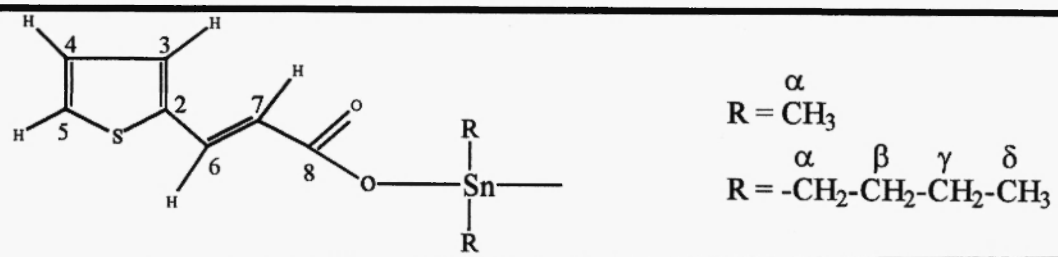
O(1)-Sn-(1)-O(2)	90.5(3)	O(1)-Sn(2)-O(3)	90.5(3)
C(1)-O(3)-Sn(2)	139.8(5)	C(1)-O(2)-Sn(1)	139.0(5)
C(8)-Sn(2)-O(1)	105.5(3)	O(3)-C(1)-O(2)	123.5(7)
C(9)-Sn(2)-O(1)	104.0(3)	C(8)-Sn(2)-O(3)	86.6(4)
C(9)-Sn(2)-O(3)	90.7(4)	C(9)-Sn(2)-C(8)	150.4(2)
C(10)-Sn(1)-O(1)	108.2(3)	C(10)-Sn(1)-O(2)	84.6(4)
C(11)-Sn(1)-C(10)	144.1(3)	C(11)-Sn(1)-O(1)	106.7(3)
C(11)-Sn(1)-O(2)	87.2(4)		

Multinuclear NMR data are given in Table 5. Different resonances were assigned by their multiplicity and intensity pattern as well as by their coupling constants and/or the tin satellites. The ligand's carbon resonances were assigned by the comparison of experimental chemical shifts with those calculated from incremental method [16]. The $^{n}J[^{119}Sn\text{-}X]$ (where $X = {}^{1}H$ or ^{13}C), suggests a coordination number in between 5 and 6 for the tin atom, in contrast with the hexa or hepta coordination state in the solid phase. This is similar to a common behaviour of most triorganotin carboxylates that they exist as polymers as solids [1, 17] while as monomeric entities in non coordinating solvents [18], as a consequence of the cleavage of intermolecular interactions.

Hence, in solution the possibility of hexa or hepta coordination state can be easily excluded because a higher coordination or the polymeric lattice due to intra- or intermolecular interactions via O(4) and O(5) will no longer persist.

The resolution of two tin environments, in both the ^{1}H and ^{13}C NMR spectra allows us to test the available model for estimating the angle C-Sn-C based on $^{2}J[^{119}Sn\text{-}^{1}H]$ and $^{1}J[^{119}Sn\text{-}^{13}C]$ coupling constants (Table 5). The C-Sn-C angle (140.7°, 145.8° from ^{2}J and 144.1°, 150.4° from ^{1}J) from the Lockhart formulae [19] are in close agreement with crystal data (144.1° and 150.4°, Table 4).

Table 5:- ^{1}H and ^{13}C NMR data of dimeric tetraorganodicarboxylato distannoxanes [a-d]



$\overset{\alpha}{R = CH_3}$

$R = -\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-\overset{\gamma}{CH_2}-\overset{\delta}{CH_3}$

^{1}H NMR data			^{13}C NMR data		
Proton	**R = Me**	**R = n-Bu**	**Carbon**	**R = Me**	**R = n-Bu**
2	-----	-----	**2**	135.53	135.81
3	7.40 (d, 7.0)	7.00 (d, 7.0)	**3**	128.41	127.71
4	7.08 (dd, 3.5, 3.5)	6.7 (dd, 3.5, 3.5)	**4**	128.32	127.53
5	7.30 (d, 3.5)	6.90 (d, 3.5)	**5**	129.94	129.79
6	7.68 (d, 15.6)	7.43 (d, 15.6)	**6**	140.33	139.82
7	6.21 (d, 15.6)	6.00 (d, 15.6)	7	120.22	120.24
8	-----	-----	**8**	173.15	173.51
α	0.93,0.85, [90.5],[87.2]	1.43 (tq, 7.3, 7.3)	α	10.11, 6.23 [830.0], [761.0]	29.21, 27.34 [735.0], 698.0]
β	-----	1.29 (tq, 8.3, 8.3)	β	-----	27.50, 27.28 [25.0], [22.0]
γ	-----	1.08 (tq, 7.29, 7.29)	γ	-----	27.25, 26.64 [130.0], [117.0]
δ	-----	0.58, 0.55 (t, 7.0) (t, 7.0)	δ	-----	13.45

[a] Chemical shifts (δ) in ppm, $^3J(^1H-^1H)$ in Hz, $^nJ[^{119}Sn-X]$ (where X = ^1H, ^{13}C) in Hz.

[b] Multiplicity is given by, d = doublet, dd = doublet of doublet, t = triplet and tq = triplet of quartet.

[c] Theoretically H^3 shold give a doublet of doublet but in the spectra only one well defined doublet is observed. The same is the case with H^5.

[d] δ ^{119}Sn for **(I)** = -176.0, -194.7 ppm; ^2J[Sn-O-Sn = 103.7 Hz], δ ^{119}Sn for **(II)** = -205.4, -216.8 ppm; ^2J[Sn-O-Sn = 116.0 Hz].

CONCLUSION

Like triorganotin carboxylates, distannoxanes may also adopt a polymeric form in the solid phase. In the case where the carboxylate ligand contains a five membered heterocyclic ring, there exists a possibility of ring twist. The ring twist becomes more and more frequent with an increase in the carboxylate chain.

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