Journal of Organometallic Chemistry, 393 (1990) 195–200
Elsevier Sequoia S.A., Lausanne
JOM 20934

Structural chemistry of organotin carboxylates

V *. X-ray crystal structure of polymeric trimethylstannyl thiophene-2-carboxylate

G.K. Sandhu, S.P. Verma

Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005 (India)

and E.R.T. Tiekink

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

(Received March 7th, 1990)

Abstract

The crystal structure of the title compound, $[Me_3Sn(O_2CC_4H_3S)]_n$, has been determined at 205 K. The structure features bidentate bridging thiophene-2-carboxylate ligands and five-coordinate Sn atoms, and represents an additional example of the *trans*-R_3SnO_2 structural type found for related systems.

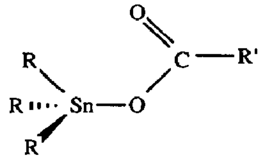
Introduction

The study of the structural chemistry of triorganotin carboxylates has received considerable attention owing to the various structural types that may be adopted in the solid state [1–3]. There are at least three limiting structures for compounds of the empirical formula $R_3Sn(O_2CR')$. The first of these is represented by **A** in which the carboxylate ligand functions in the monodentate mode, there being no significant interaction between the tetrahedral Sn atom and the pendant O atom. A closely related structure is shown in **B**, in which the monomeric species contains a bidentate chelating carboxylate ligand with five-coordinate tin. The third structural type found in the solid state is that shown in **C**, in which the carboxylate ligand is again bidentate, but this time bridging, so that a polymeric species is generated and the Sn atom is five-coordinate, trigonal bipyramidal.

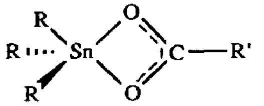
---

* For part IV, see Ref. 6.

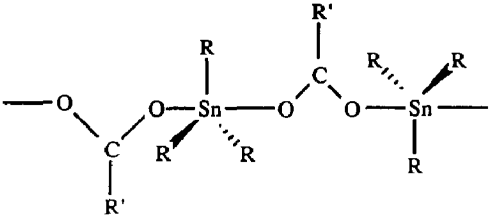
0022-328X/90/$03.50



(A)



(B)



(C)

Despite the interest in this field it is still not clear what properties determine whether structures **A**, **B**, or **C** (or structures somewhere between these limiting forms) are adopted in the solid state. The crystal structure of $Ph_3Sn(O_2CC_4H_3S)$, in which the carboxylate ligand is derived from thiophene-2-carboxylic acid as in the title compound, was determined recently [4], and in the former, the compound shown to be monomeric with the Sn atom essentially four-coordinate, distorted tetrahedral. Continuing our interest in the solid state structures of organotin carboxylates (in particular in circumstances where the carboxylate ligand contains an additional potential donor atom in R′ [5,6]) we thought it of interest to examine the structure of the trimethyl analogue [7] and to compare it with that found for the triphenyltin species [4].

Results and discussion

The molecular structure of $[Me_3Sn(O_2CC_4H_3S)]_n$ is shown in Fig. 1 and selected interatomic parameters are given in Table 1. As can be seen from Fig. 1, the structure adopted in the solid state is of the *trans*-R_3SnO_2 structural type. The Sn atom exists in a distorted trigonal bipyramidal geometry with the three methyl groups defining the trigonal plane such that the sum of the trigonal C–Sn–C angles is 358.2°. The axial sites are occupied by the O(1) atom, Sn–O(1) 2.149(8) Å, and the O(2′) atom at 2.482(8) Å (where O(2′) is related by the symmetry operation: $1-x$, $1-y$ $0.5+z$); the O(1)–Sn–O(2′) angle is 173.4(2)°. The Sn atom lies 0.1684(4) Å out of the least-squares plane through the methyl groups, in the direction of the O(1) atom. The carboxylate ligand is bidentate and bridges two symmetry-related Sn atoms, giving rise to unequal Sn–O bond distances. This inequality is reflected in the C(1)–O bond distances, the longer C(1)–O(1) bond being associated with the shorter Sn–O(1) bond. The Sn–O(2) separation of 3.227(8) Å is not indicative of a significant interaction between these atoms. However, the close proximity of the O(2) atom influences the coordination geometry about the Sn atom by opening up the C(7)–Sn–C(8) angle to 125.2(6)°. The carboxylate ligand $^{-}O_2CC_4H_3S$ is essentially planar (to within ±0.038(4) Å), there being a dihedral

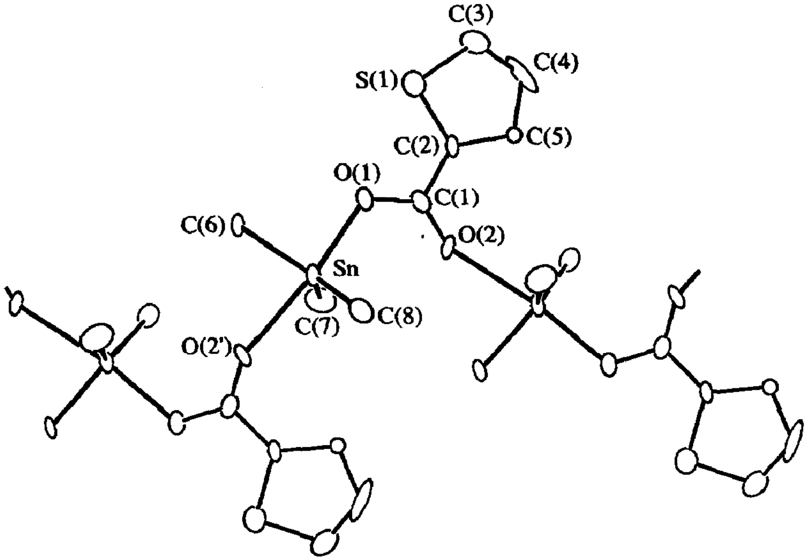


Fig. 1. Molecular structure and crystallographic numbering scheme employed for $[Me_3Sn(O_2CC_4H_3S)]_n$.

angle of 6.2° between the least-squares planes passing through the O_2C and C_4H_3S groups. Notable in the structure is the absence of a significant interaction between the Sn atom and the thiophene S atom. In many respects the structure of $[Me_3Sn(O_2CC_4H_3S)]_n$ resembles closely that found for the 2-furoic acid derivative $[Me_3Sn(O_2CC_4H_3O)]_n$ [8].

The polymeric structure found for $[Me_3Sn(O_2CC_4H_3S)]_n$ can be contrasted with the monomeric structure found for the triphenyltin analogue, $[Ph_3Sn(O_2CC_4H_3S)]$ [8]. In the latter the Sn atom exists in a distorted tetrahedral environment comprised of three phenyl groups and an O atom derived from a monodentate carboxylate group; the pendant O atom is 2.768(4) Å from the Sn atom. This distance is not indicative of a substantial interaction between these atoms, but the presence of the

Table 1

Selected interatomic parameters (Å; °) for $[Me_3Sn(O_2CC_4H_3S)]_n$

Sn–O(1)	2.149(8)	Sn–O(2)	3.227(8)
Sn–O(2′)	2.482(8)	Sn–C(6)	2.13(1)
Sn–C(7)	2.119(9)	Sn–C(8)	2.14(1)
C(1)–O(1)	1.30(1)	C(1)–O(2)	1.23(1)
C(1)–C(2)	1.49(2)	C(2)–S(1)	1.69(1)
S(1)–C(3)	1.68(2)	C(3)–C(4)	1.32(2)
C(4)–C(5)	1.41(2)	C(5)–C(2)	1.45(2)
O(1)–Sn–O(2′)	173.4(2)	O(1)–Sn–C(6)	91.5(4)
O(1)–Sn–C(7)	96.6(5)	O(1)–Sn–C(8)	95.2(4)
O(2′)–Sn–C(6)	82.5(4)	O(2′)–Sn–C(7)	83.9(4)
O(2′)–Sn–C(8)	89.9(4)	C(6)–Sn–C(7)	119.3(7)
C(6)–Sn–C(8)	113.7(5)	C(7)–Sn–C(8)	125.2(6)
Sn–O(1)–C(1)	121.5(7)	Sn–O(2′)–C(1′)	150.7(7)
O(1)–C(1)–O(2)	124(1)		

O atom may contribute to the distortion of the coordination geometry about the Sn atom.

That the two thiophene-2-carboxylate structures discussed above adopt different structural types contrasts with the behaviour of the acetate analogues $[Me_3Sn(O_2CCH_3)]_n$ [9] and $[Ph_3Sn(O_2CCH_3)]_n$ [10], both of which adopt the familiar *trans*-R_3SnO_2 type, i.e. structure **C**. However, we note that the acetate anion does not induce a **C** type structure in all the $[R_3Sn(O_2CCH_3)]$ compounds, a monomeric essentially four-coordinate form **A**, being found for the $[(cyclohexyl)_3Sn(O_2CCH_3)]$ compound [11]. Clearly, there are factors other than electronic and steric effects of the R and R′ groups [1–3], such as packing forces, that must be taken into account, when attempting to rationalize the structural types found for compounds of the general formula $[R_3Sn(O_2CR')]$.

Experimental

The compound, $[Me_3Sn(O_2CC_4H_3S)]$, was prepared as described previously [7], and crystals suitable for X-ray studies were obtained by slow evaporation of an ethanol solution. Intensity data were measured at 205 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 used to measure 1593 reflections up to a maximum Bragg angle of 25°. The data were corrected for Lorentz and polarization effects and for absorption by use of an analytical procedure [12]. Relevant crystal data are listed in Table 2.

The structure was solved by direct methods [13] and refined by a full-matrix least-squares procedure based on F [12]. Except for the C(5) atom all non-hydrogen atoms were refined with anisotropic thermal parameters. The C(5) atom was

Table 2

Crystal data and refinement details for $[Me_3Sn(O_2CC_4H_3S)]_n$

Formula	$C_8H_{12}O_2SSn$
Mol. wt.	291.5
Crystal system	hexagonal
Space group	$P6_3$
a, Å	13.698(3)
c, Å	10.010(3)
V, Å^3	1626.6
Z	6
D_c, g cm^{-3}	1.786
$F(000)$	852
μ, cm^{-1}	23.19
Transmission factors (max/min)	0.745, 0.635
θ limits (°)	1.5–25.0
No. of data collected	1593
No. of unique data	1387
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	1067
R	0.045
g	0.0179
R_w	0.044

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for remaining atoms) for $[Me_3Sn(O_2CC_4H_3S)]_n$

Atom	*x*	*y*	*z*
Sn	43803(4)	47550(5)	50000(-)
S(1)	1055(3)	2260(3)	2112(4)
O(1)	3099(7)	3739(7)	3573(8)
O(2)	4294(6)	4213(7)	1851(8)
C(1)	3336(9)	3723(9)	2317(11)
C(2)	2349(8)	3045(9)	1439(12)
C(3)	443(11)	1821(11)	607(18)
C(4)	1181(12)	2230(13)	−377(14)
C(5)	2321(7)	2907(6)	6(21)
C(6)	3153(10)	4360(13)	6525(12)
C(7)	5263(9)	3853(9)	4915(24)
C(8)	4879(10)	6319(10)	4014(14)

disordered over several sites however, these were could not be resolved into the separate components; this atom was therefore refined isotropically. Hydrogen atoms were included in the model at their calculated positions. After the inclusion of a weighting scheme of the form, $w = [\sigma^2(F) + g|F|^2]^{-1}$, the refinement was continued until convergence. The absolute configuration of the compound was determined on the basis of differences in Friedel pairs included in the data set. Final refinement details are listed in Table 2. The analysis of variance showed no special features. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed is shown in Fig. 1 drawn with ORTEP [14] at 50% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program and refinement was performed on a SUN4/280 computer. Lists of thermal parameters, hydrogen atom parameters, all bond distances and angles, and observed and calculated structure factors are available from E.R.T.T.

Acknowledgements

The Australian Research Council is thanked for support of the crystallographic facility.

References

1 M.M. Amini, S.W. Ng, K.A. Fidelis, M.J. Heeg, C.R. Muchmore, D. van der Helm and J.J. Zuckerman, J. Organomet. Chem., 365 (1989) 103.
2 S.W. Ng, C. Wei and V.G. Kumar Das, J. Organomet. Chem., 345 (1988) 59.
3 K.C. Molloy, S.J. Blunden and R. Hill, J. Chem. Soc., Dalton Trans., (1988) 1259.
4 S.W. Ng, V.G. Kumar Das, F. van Meurs, J.D. Schagen and L.H. Shavers, Acta Crystallogr. C, 45 (1989) 568.
5 C.S. Parelukar, V.K. Jain, T.K. Das, A.R. Gupta, B.F. Hoskins and E.R.T. Tiekink, J. Organomet. Chem., 372 (1989) 193.
6 C.S. Parelukar, V.K. Jain, T. Kesavadas and E.R.T. Tiekink, J. Organomet. Chem., 387 (1990) 163.
7 G.K. Sandhu and S.P. Verma, Polyhedron, 6 (1987) 587.
8 E.R.T. Tiekink, G.K. Sandhu and S.P. Verma, Acta Crystallogr. C, 45 (1989) 1810.
9 H. Chih and B.R. Penfold, J. Cryst. Mol. Struct., 3 (1973) 285.
10 K.C. Molloy, T.G. Purcell, K. Quill and I.W. Nowell, J. Organomet. Chem., 267 (1984) 237.

11 N.W. Alcock and R.E. Timms, J. Chem. Soc., (A), (1968) 1876.

12 G.M. Sheldrick, SHELX76, Program for crystal structure determination, Cambridge University, U.K., 1976.

13 G.M. Sheldrick, SHELXS86, A program for the automatic solution of crystal structures, University of Göttingen, F.R.G., 1986.

14 C.K. Johnson, ORTEP-II Report ORNL-2794, Oak Ridge National Laboratory, Tennessee, U.S.A., 1971.