Journal of Organometallic Chemistry 693 (2008) 2424–2430

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of bis(*tert*-butyl)(2-thioxo-1,3-dithiole-4,5-dithiolato)stannane, $\mathrm{Bu}^t_2\mathrm{Sn(dmit)}$, and bis(*tert*-butyl)(2-oxo-1,3-dithiole-4,5-dithiolato)stannane, $\mathrm{Bu}^t_2\mathrm{Sn(dmio)}$: Crystal structures, at 120 K, of polymeric $\mathrm{Bu}^t_2\mathrm{Sn(dmit)}$, and two polymorphs of $\mathrm{Bu}^t_2\mathrm{Sn(dmio)}$, a polymer and a cyclic tetramer

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ARTICLE INFO

Article history:
Received 24 February 2008
Received in revised form 10 April 2008
Accepted 13 April 2008
Available online 27 May 2008

Keywords:
Dithiolate
1,2-Dithiole
Organotin
X-ray crystallography
Dimorphism
Cyclic tetramer

ABSTRACT

The syntheses of bis(*tert*-butyl)(2-thioxo-1,3-dithiole-4,5-dithiolato)stannane, $\mathrm{Bu}^t_2\mathrm{Sn(dmit)}$ **1**, and bis(*tert*-butyl)(2-oxo-1,3-dithiole-4,5-dithiolato)stannane, $\mathrm{Bu}^t_2\mathrm{Sn(dmio)}$ **2**, are reported. Compounds **1** and **2** were prepared by the exchange reactions of $\mathrm{Bu}^t_2\mathrm{SnCl}_2$ with $[\mathrm{NEt}_4]_2[\mathrm{Zn(dmit)}_2]$ and $[\mathrm{NEt}_4]_2[\mathrm{Zn(dmio)}_2]$, respectively. X-ray structure determinations reveal the existance of two polymorphs of **2**, **2m** and **2o**. In all three phases, intermolecular $\mathrm{Sn–S}_{\mathrm{thioxo}}$ or $\mathrm{Sn–O}_{\mathrm{oxo}}$, as appropriate, create five-coordinate, trigonal bipyramidal tin centres. In **1** and **2o** these intermolecular contacts link the molecules in chains, while in **2m** they create a centrosymmetric cyclic tetramer, with a 24 membered, $\mathrm{Sn_4C_8O_4S_8}$, ring. These findings of aggregated structures are in contrast to the published report that the simpler ethane-1,2-dithiolato compound, $\mathrm{Bu}^t_2\mathrm{Sn(edt)}$, is a molecular species in the solid state.

1. Introduction

We have previously reported the preparations and structures of the 1,2-dithiolato compounds, diorgano(2-thioxo-1,3-dithiole-4,5-dithiolato)stannanes, $\mathrm{R_2Sn(dmit)}$ [1–5], and diorgano(2-oxo-1,3-dithiole-4,5-dithiolato)stannanes, $\mathrm{R_2Sn(dmio)}$ compounds [6,7], while others have reported the uses of $\mathrm{R_2Sn(dmit)}$ as dmit transfer agents [8] (Fig. 1).

The $\mathrm{R_2Sn(dmit)}$ and $\mathrm{R_2Sn(dmio)}$ compounds, where $\mathrm{R_2}$ are non-functionalised groups, e.g., $\mathrm{Me_2}$, PhMe, $\mathrm{Et_2}$ and $\mathrm{Ph_2}$, are polymeric species in the solid state with intermolecular Sn–S (thione) or Sn–O interactions leading to aggregation. As shown in Table 1, the strength and number of the Sn–S intermolecular interactions vary. Single Sn–S intermolecular interactions per molecule have been found for $\mathrm{Ph_2Sn(dmit)}$ [intermolecular Sn–S = 2.8174(9) Å] [3], PhMeSn(dmit) [3.139(1) Å] [1], $\mathrm{Me_2Sn(dmit)}$ [2.960(2) Å, in Mol. A, and 3.001(2) Å, in Mol. B] [2], and *orthorhombic*-$\mathrm{Et_2Sn(dmit)}$ [3.0083(15) Å [2], with the formation of chains of molecules. In contrast, for one of the independent molecules of *monoclinic*-$\mathrm{Et_2Sn(dmit)}$ [2], two intermolecular Sn–S interactions per molecule are apparent from the bond lengths of 3.567(2) and 3.620(3) Å, both being relatively well within the van der Waals radii sum of 4.05 Å [9]. These Sn–S intermolecular interactions lead to the formation of layers of molecules. For the other independent molecule of *monoclinic*-$\mathrm{Et_2Sn(dmit)}$, only one intermolecular Sn–S separation, 3.555(2) Å, is clearly within the van der Waals sum: the next, at 3.927(2) Å, is only slightly less than this limit. At the very most, this indicates a very weak interaction. Considering just the single intermolecular Sn–S interaction, a chain arrangement of molecules is formed.

Essentially molecular structures, however, have been found, with no intermolecular Sn–S interactions, for $\mathrm{(MeO_2CCH_2CH_2)_2Sn(dmit)}$ [4], $\mathrm{(MeCOCMe_2CH_2)_2Sn(dmit)}$ [5] and $\mathrm{(MeO_2CCH_2CH_2)_2Sn(dmio)}$ [7], compounds, in which the carbonyl oxygens in both organic groups coordinate to tin intramolecularly, with the tin centre thus becoming six coordinate and coordinatively saturated.

The Sn–O intermolecular bond length in the only $\mathrm{R_2Sn(dmio)}$ structure to have been previously reported, that for $\mathrm{Me_2Sn(dmio)}$, is 2.654(6) Å [6], compared to the van der Waals radii sum of Sn and O of 3.78 [9].

Weaker S···S and S···O interactions just within the sum of van der Waals radii may also feature in the solid state structures of $\mathrm{R_2Sndmit}$ and $\mathrm{R_2Sndmio}$.

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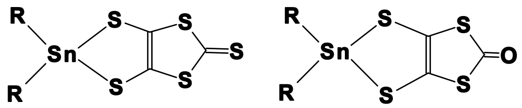
doi:10.1016/j.jorganchem.2008.04.019



$R_2Sn(dmit)$ **$R_2Sn(dmio)$**

Fig. 1. Molecular structures.

Other diorganotin 1,2-dithiolato complexes have been found to have higher coordinate tin centres in the solid state: these include diorganotin di(cyanoethylene-1,2-dithiolates) (organic group = Me, Bu or Ph), which posses intermolecular tin–nitrogen interactions, [10] and some R_2Sn(edt) complexes (edt = 1,2-ethanedithiolato) [11–13]. Published reports indicated, in contrast to polymeric R_2Sn(edt), (R = Me [11], R = Bu [12], R = Ph [13], Bu^t_2Sn(edt) [14]) was a monomeric compound. The intermolecular interactions in R_2Sn(edt), which clearly have to involve the thiolato S atoms, also varied in strength and number, e.g., for R = Me, one short Sn–S contact of 3.182(1) Å [11], for R = Bu, two longer Sn–S contacts of 3.688 Å [12] and for R = Ph, one relatively long Sn–S contact of 3.885 Å, [13]. The intermolecular interactions in R_2Sn(edt) appear not to persist in solution [12].

We turned our attention to di-*tert*-butyltin-dmit and -dmio compounds to investigate the influence of the bulk of the organic groups on the solid state structures, with the anticipation that Bu^t_2Sn(dmit) (**1**) and Bu^t_2Sn(dmio) (**2**) would be monomeric in the solid state. However these were found to have aggregated structures too. Our interest was heightened when a cyclic tetrameric polymorph of Bu^t_2Sn(dmio) (**2m**) was found, along with that of the more usually found chain structure, (**2o**). The related Bu^t_2Sn(dmit) compound, **1,** exists in a chain form. Attempts to obtain other forms of **1** were unsuccessful, and only the chain form has been detected.

2. Experimental

2.1. General

$[NEt_4]_2[Zn(dmit)_2]$ [15] and$[NEt_4]_2[Zn(dmio)_2]$ [6] were prepared according to published procedures. Di-*tert*-butyltin dichloride was a commercial sample and was used as received. Melting points were measured on a Melt-TempII. Elemental analyses were

Table 1
Summary of selected geometric parameters for diorganotin-dmit and -dmio compounds

R_2	Tin geometry molecular aggregation	Temperature (K)	Selected intramolecular geometric parameters, (Å, °)		Selected intermolecular geometric parameters, (Å, °)		Ref.
			Sn–S	C–Sn–C	Sn···S	Sn···S–C	
(A) R_2Sn(dmit)							
Ph_2Sn	Dist. trig. bipy. Zig-zag chains	150(2)	2.5327(9), 2.4547(10)	120.47(11)	2.8174(9)	106.11(12)	[3]
PhMe	Dist. trig. bipy. Zig-zag chains	293(2)	2.487(1), 2.437(1)	115.8(1)	3.139(1)	113.1(1)	[1]
Me_2		150(2)					[2]
Mol. A	Dist. trig. bipy		2.440(3), 2.518(2)	124.9(4)	3.001(2)	116.4(3)	
Mol. B	Zig-zag chains		2.457(3), 2.521(2)	126.0(4)	2.960(2)	114.1(3)	
Et_2							[2]
orthorhombic monoclinic	Dist. trig. bipy	150(2)	2.513(4), 2.436(4)	130.8(2)	3.0083(15),	111.1(2)	
	Zig-zag chains	298(2)	2.513(5), 2.436(4)	128.7(8)	3.037(4)	112.1(5)	
Mol. A	Dist.octahedron Sheets of molecules	298(2)	2.449(2), 2.460(2)	126.3(3)	3.567(2), 3.620(3)	109.4(3), 104.0(3)	[2]
Mol. B	Dist. trig. bipy.[a] Zig-zag chains		2.447(3), 2.458(3)	119.5(5)	3.555(2)	109.4(3)	
Bu^t_2							This study
Mol. A	Dist. trig. bipy.		2.4629(6), 2.5339(6)	120.95(9)	2.9790(6)	118.44(9)	
Mol. B	Zig-zag chains		2.4450(6), 2.5334(6)	121.44(9)	3.03839(6)	115.17(8)	
$(MeO_2CCH_2CH_2)_2$[b]	Dist. octahedron monomeric	298(2)	2 × 2.471(2)	121.0(4)			[4]
$(MeOCCH_2CMe_2)_2$[c]	Dist. octahedron monomeric	150(2)	2.4921(6), 2.5018(6)	131.15(9)			[5]

	Geometry at tin molecular aggregation	Temperature K	Selected intramolecular parameters, (Å < °)		Selected intermolecular parameters, (Å < °)			
			Sn–S	C–Sn–C	Sn···O	Sn···S	Sn···O–C	
(B) R_2Sn(dmit)								
Me_2	6-coord. tin Very dist. octahedron Layers of molecules	298(2)	2.440(2), 2.487(2)	124.2(4)	2.654(6)	3.649(3)		[6]
Bu^t		120(2)						This study
Orthorhombic	5-coord. Tin							
Mol. A	Dist. trig. bipy		2.442(2), 2.490(2)	125.5(3)	2.784(5)		166.8(6)	
Mol. B	Chains of molecules.		2.448(2), 2.4891(19)	126.4(3)	2.780(6)		167.5(5)	
Mol. C			2.451(2), 2.496(2)	126.8(4)	2.697(5)		162.3(6)	
Mol. D			2.442(2), 2.483(2)	127.3(4)	2.702(6)		164.3(6)	
Monoclinic	5-coord. tin	120(2)						
Mol. A	Dist.trig. bipy.		2.435(2), 2.492(3)	122.0(3)	2.730(6)		151.2(8)	This study
Mol. B	Cyclic tetramers		2.4323(19), 2.478(3)	122.1(3)	2.734(7)		141.7(6)	
Mol. C			2.435(11), 2.505(13)	122.2(4)	2.65(2)		148(2)	
Mol. D			2.449(11), 2.449(12)	124.8(2)	2.74(2)		155(2)	

[a] There is an additional intermolecular Sn···S contact at 3.927(2) Å, only 0.12 Å less than the sum of the van der Waals radii for Sn and S.

[b] There are also 2 intramolecular Sn–O bonds, lengths = 2.629(7) Å.

[c] There are also intramolecular Sn–O bonds, lengths = 2.6933(16) & 2.5386(16) Å.

obtained using a Perkin Elmer 2400 apparatus. Infrared spectra were obtained in CsI pellets on a Nicolet Magna 760 FT-IR instrument between 4000 and 200 cm^{-1}. UV–Vis spectra were obtained in acetonitrile solutions using a Varian-Cary 1E spectrometer.

*2.1.1. Preparation of $Bu^t_2Sn(dmit)$ (**1**)*

Solutions of $Bu^t_2SnCl_2$ (0.607 g, 2 mmol) in acetone (20 mL) and $[NEt_4]_2[Zn(dmit)_2]$ (0.717 g, 1 mmol) (20 mL) were mixed and stirred for 1 h. Water (60 mL) was added with vigorous shaking, followed by petroleum ether (b.p. 40–60 °C, 10 mL). The red coloured precipitate was collected and refluxed for 1 h in a 2:1 water/methanol mixture, filtered and dried under vacuum. Yield 90% (0.858 g). The compound was recrystallised from $Et_2O/CHCl_3$, m.p. (with decomposition) 95 °C.

Anal. Calc. for $C_{11}H_{18}S_5Sn$: C, 30.7; H, 4.22. Found: C, 30.26; H, 4.27%. IR: (cm^{-1}) 2959–2868 (C–H), 1447 (C=C), 1026 (C=S), 895 (C–S), 463 (C–S), 327 (Sn–S). UV–Vis: (CH_3CN, max. nm) 438, 321, 290, 202.

*2.1.2. Preparation of $Bu^t_2Sn(dmio)$ (**2**)*

This was prepared analogously to (**1**) using $Bu^t_2SnCl_2$ (0.607 g, 2 mmol) and $[NEt_4]_2[Zn(dmio)_2]$ (0.689 g, 1 mmol). A yellow solid was obtained, yield 84% (0.826 g), m.p. 140 °C (decomposition). Recrystallisation from $Et_2O/CHCl_3$ gave the orthorhombic-**2** (**2o**),

Table 2
Crystal data and structure refinement[a]

Compound/structure	**1**	**2m**	**2o**	**2t**[b]
Empirical formula	$C_{11}H_{18}S_5Sn$	$C_{11}H_{18}OS_4Sn$	$C_{11}H_{18}OS_4Sn$	$C_{11}H_{18}OS_4Sn$
Formula weight	429.24	413.18	413.18	413.18
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $I2/a$	Orthorhombic, $P2_12_12_1$	Tetragonal, $P4_12_12$
Unit cell dimensions				
a (Å)	14.2795(2)	16.1460(3)	15.6980(2)	15.7305(2)
b (Å)	17.2546(3)	23.4829(5)	15.7631(2)	15.7305(2)
c (Å)	13.4716(2)	17.1871(3)	26.3065(3)	26.3065(3)
β (°)	98.3394(8)	92.5936(8)	90	90
Volume (Å^3)	3284.13(9)	6509.9(2)	6509.52(14)	6509.51(14)
Z, calculated density (Mg/m^3)	8, 1.736	16, 1.686	16, 1.686	16, 1.686
Absorption coefficient (mm^{-1})	2.170	2.067	2.067	2.067
$F(000)$	1712	3296	3296	3296
Crystal size (mm)	0.44 × 0.40 × 0.16	0.50 × 0.16 × 0.14	0.20 × 0.20 × 0.06	0.20 × 0.20 × 0.06
θ Range for data collection (°)	3.06–27.48	2.94–27.50	1.29–27.55	1.29–27.55
Index ranges	$-18 \leqslant h \leqslant 18$, $-22 \leqslant k \leqslant 22$, $-16 \leqslant l \leqslant 17$	$-20 \leqslant h \leqslant 20$, $-29 \leqslant k \leqslant 30$, $-22 \leqslant l \leqslant 22$	$-20 \leqslant h \leqslant 17$, $-20 \leqslant k \leqslant 20$, $-30 \leqslant l \leqslant 34$	$-20 \leqslant h \leqslant 17$, $-20 \leqslant k \leqslant 20$, $-30 \leqslant l \leqslant 34$
Reflections collected/unique (R_{int})	39872/7526 (0.0278)	47588/7472 (0.0544)	68218/14961 (0.0547)	68214/7514 (0.1473)
Reflections observed [$I > 2\sigma(I)$]	6875	5650	12652	6745
Maximum and minimum transmission	0.7228 and 0.5918	0.7607 and 0.4910	0.8860 and 0.6562	0.8860 and 0.6562
Data/restraints/parameters	7526/0/320	7472/60/381	14961/0/634	7514/0/309
Goodness-of-fit on F^2	1.359	1.185	1.099	1.254
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.030$ $wR_2 = 0.079$	$R_1 = 0.067$ $wR_2 = 0.157$	$R_1 = 0.043$ $wR_2 = 0.098$	$R_1 = 0.096$ $wR_2 = 0.218$
R indices (all data)	$R_1 = 0.034$ $wR_2 = 0.081$	$R_1 = 0.093$ $wR_2 = 0.168$	$R_1 = 0.056$ $wR_2 = 0.105$	$R_1 = 0.103$ $wR_2 = 0.221$
Absolute structure parameter	n/a	n/a	0.05(3)	0.00(14)
Extinction coefficient[c]	0.0069(2)	0.00148(9)	0.00262(9)	0.00157(13)
Largest peak and hole (e/ Å^3)	1.828 and −1.411	1.316 and −0.969	2.124 and −2.249	2.194 and −2.301

[a] In all cases data taken at 120(2) K with radiation wavelength 0.71073 Å, absorption correction was semi-empirical from equivalents and refinement by full-matrix least-squares on F^2.

[b] Rerefinement of the same data as **2o**.

[c] x in $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$.

Table 3
Selected geometric parameters, (Å, °) for **1** and **2**

	Sn(1)–S(1)	Sn(1)–S(2)	Sn(1)–S[a]	S(1)–Sn(1)–S(2)	S(2)–Sn(1)–S[a]
*Compound **1***					
Molecule A	2.4629(6)	2.5339(6)	2.9790(6)	87.654(19)	162.938(19)
Molecule B	2.4450(6)	2.5334(6)	3.0839(6)	88.38(2)	162.915(19)
	Sn(1)–S(1)	Sn(1)–S(2)	Sn(1)–O[a]	S(1)–Sn(1)–S(2)	S(2)–Sn(1)–O[a]
*Compound **2m***					
Molecule A	2.435(2)	2.492(3)	2.730(6)	88.82(8)	160.38(15)
Molecule B	2.4323(19)	2.478(3)	2.734(7)	89.78(8)	160.30(16)
Molecule C	2.435(11)	2.505(13)	2.65(2)	89.2(3)	162.8(7)
Molecule D	2.449(11)	2.499(12)	2.74(2)	88.9(3)	161.2(7)
*Compound **2o***					
Molecule A	2.442(2)	2.490(2)	2.784(5)	89.92(7)	159.58(13)
Molecule B	2.448(2)	2.4891(19)	2.780(6)	89.57(7)	159.70(14)
Molecule C	2.451(2)	2.496(2)	2.697(5)	89.32(7)	160.77(14)
Molecule D	2.442(2)	2.483(2)	2.702(6)	89.48(7)	161.14(14)

[a] O(1) or S(5) of a neighbouring molecule.

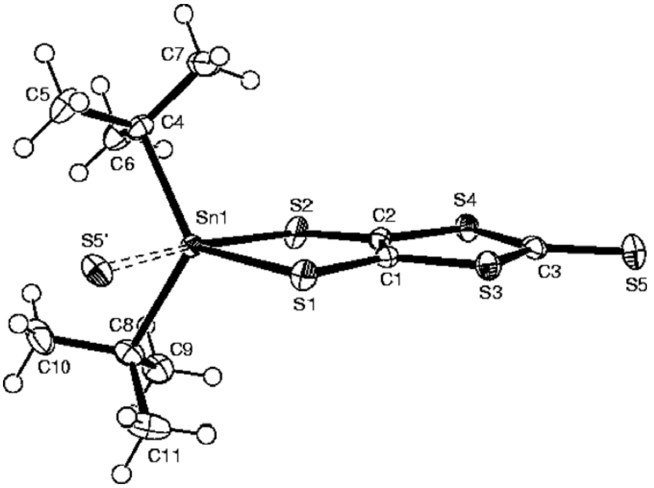


Fig. 2. Example atom labelling scheme. The example shown is molecule A of **1**. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as spheres of arbitrary radii. The dashed bond is to the thione atom of a neighbouring molecule.

while recrystallisation from MeOH/CHCl$_3$, gave the monoclinic form (**2m**).

Anal. Calc. for $C_{11}H_{18}OS_4Sn$: C, 31.97; H, 4.39. Found: C, 31.38; H, 4.15%. IR: (cm^{-1}) 2959-2868 (C–H), 1600(C=O), 1465(νC=C), 886 (C–S), 466 (C–S), 329 (Sn–S). UV–Vis: (CH$_3$CN, max nm) 437, 374, 295, 274, 203.

2.2. X-ray crystallography

2.2.1. Data collection

All of the intensity data were obtained at 120 K with Mo Kα radiation by means of the Enraf Nonius KappaCCD area detector diffractometer of the EPSRC National crystallographic service at the University of Southampton. Data collection was carried out under the control of the program COLLECT [16] and data reduction and unit cell refinement were achieved with the COLLECT and DENZO [17] programs. Correction for absorption, by comparison of the intensities of equivalent reflections, was applied using the program SADABS [18]. The program ORTEP-3 for Windows [19] has been used in the preparation of the figures and SHELXL-97 [20] and PLATON [21] in the calculation of molecular geometry.

2.2.2. Structure solution and refinement

The structure determinations of the three phases with which this paper is concerned are denoted by the codes **1**, **2m** and **2o**. A fourth code, **2t**, refers to a further structure determination investigating the pseudo-tetragonal symmetry found for **2m**. In all four cases the initial partial solution obtained by direct methods as implemented in the program SHELXS-97 [22] was expanded and refined by means of the program SHELXL-97 [20]. In the later stages of the refinements the methyl hydrogen atoms were placed in calculated positions at C–H distances of 0.98 Å and were, in all cases, refined with a riding model with $U_{iso}(H) = 1.5U_{eq}(C)$. Except in the case of **2t**, and for some Me in **2m**, the torsion angles of the methyl groups were also refined. In all four cases the SHELXL-97 [20] extinction coefficient was also refined.

In refinement **2m** major [molecules A and B, 84.28(13)%] and minor [molecules C and D, 15.72(13)%] structural components were found to be present such that the cyclic connectivity of the tetramer was reversed between them. The minor component of the disorder is represented by Sn atoms and dmio ligands of low occupancy but the Bu^t groups, determined for the major component, were treated as ordered species. Hence the methyl groups of the minor component are absent from the structural model. Twinning was encountered in refinements **2o** and **2t** requiring interchange of cell edges *a* and *b* in **2o** and reversal of the direction of *c* in **2t** with minor twin components to the extent of 25.74(9)% and 17(9)%, respectively. Crystal data and structure refinement details are given in Table 2 and selected geometric parameters in Table 3 and Supplementary Tables 1 and 2.

3. Results and discussion

3.1. General

The syntheses of **1** and **2** were carried out using the procedure previously used for related compounds [2], that is by reaction of $Bu^t_2SnCl_2$ with $[NEt_4]_2[Zn(dmit)_2]$ or $[NEt_4]_2[Zn(dmio)_2]$ followed by treatment with water. The finding of the two polymorphs for **2** came about serendipitously. The first set of crystals, obtained from MeOH/CHCl$_3$, gave only a poor refinement of the monoclinic, tetrameric (**2m**), and so other solvent systems were tried. Crystals grown

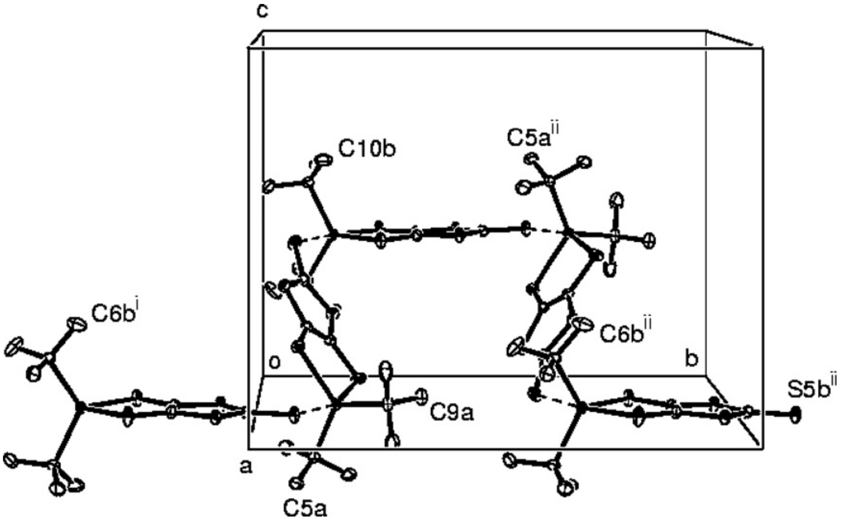


Fig. 3. A chain of molecules in **1**. Ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity. Intermolecular Sn(1)–S(5) bonds are represented by dashed lines. [Symmetry codes: (i) 1 – *x*, *y* – 1/2, 1/2 – *z*; (ii) 1 – x, *y* + 1/2, 1/2 – *z*.].

from $Et_2O/CHCl_3$ were subsequently found to be suitable for X-ray crystallography: the finding that these were the orthorhombic, chain form (**2o**), led to further and successful attempts to obtain suitable crystals of the monoclinic form. Only the monoclinic form of **1** was found despite the use of different solvent systems as recrystallisation media.

The densities of the two polymorphs of Bu^t_2Sn(dmio) are the same, and hence densities could not be used to indicate their relative thermodynamic stabilities. Furthermore decomposition, prior to melting or another phase change, also prevented the identification of the more stable polymorph. ESMS experiments failed to distinguish between the two polymorphs.

3.2. Crystal structures

Two crystallographically independent molecules, distinguished from one another by suffices A and B, are present in the asymmetric units of **1** and **2t**. In **2m** and **2o** the suffices are extended by the addition of C and D to distinguish between the crystallographically independent molecules, now four in number, in their asymmetric units. Apart from the suffices and the replacement, where appropriate, of S(5) of dmit by O(1) of dmio all of the molecules are labelled in precisely the same manner as shown in the example seen in Fig. 2. In all cases weak intermolecular Sn(1)–X bonds [X = S(5) for dmit and X = O(1) for dmio] create five-coordinate, trigonal bipyramidal tin centres with X and S2, of the ligand directly bonded to tin, in the apical sites, see Table 3 and Supplementary Table 1. The Sn(1)–X bonds create a variety of polymers as later described. The intermolecular bonds also induce anisobidentate bonding of the dmit and dmio ligands where the Sn(1)–S(2) bonds are always longer than the Sn(1)–S(1) bonds.

In **1** intermolecular Sn(1)–S(5) bonds of length 2.9790(6) and 3.0839(6) Å in the two independent molecules connect the molecules to form zig-zag chains propagated in the direction of **b** by the operation of a crystallographic twofold screw axis as shown in Fig. 3. The intermolecular Sn(1)–S(5) bond lengths in each of the independent molecules of **1** can be compared with values for other R_2Sn(dmit) compounds: Ph_2Sn(dmit) [2.8174(9) Å] [5], PhMeSn(dmit) [3.139(1) Å] [1], Me_2Sn(dmit) [2.960(2) Å, in Mol. A, and 3.001(2) Å, in Mol. B] [2]. These values clearly indicated the lack of any significant steric effect by the organic groups at the tin centres.

Formation of these intermolecular Sn–S bonds creates angles S(5)–Sn(1)–S(2) of 162.938(19) and 162.915(19)° and C(3)–S(5)–Sn(1) of 118.44(9) and 115.17(8)°. The chains take the form of ribbons whose width, parallel to (1 0 1), is created by the dmit of molecule A while the dmit of molecule B lies entirely along the length of the ribbon. The Bu^t groups are directed to either side of the ribbon at its edges and their bulk allows only van der Waals interactions between adjacent ribbons which are related to one another by the operation of crystallographic centres of symmetry.

Discussion here of disordered **2m** (see Section 2.2.2) is confined to molecules A and B of the major component. Now Sn(1)–O(1) intermolecular bonds of length 2.730(6) and 2.734(7) Å connect the molecules to form centrosymmetric cyclic tetramers (Fig. 4), creating angles O(1)–Sn(1)–S(2) of 160.38(15) and 160.30(16)° and angles C(3)–O(1)–Sn(1) of 151.2(8)° and 141.7(6)°. The Sn atoms and dmio ligands of the tetramer form an essentially planar unit parallel to (1 0 1) with the methyl groups on either side and directed towards the centres of neighbouring tetramers. Once again the bulk of the Bu^t groups allows only van der Waals interactions between adjacent tetramers.

In polymorph **2o**, the molecules are found in well defined layers parallel to (0 0 1) which are stacked in the direction of *c* at intervals of *c*/4. The layers are of two types. One type, centred on *z* = 0 and 1/2, involves only molecules C and D and is designated, therefore, a CD layer and is shown in Fig. 5. The primary connectivity within the layer is in the form of intermolecular Sn(1)–O(1) bonds which connect the molecules to form zig-zag chains propagated in the direction of *a*. In this case the Sn(1)–O(1) distances are 2.697(5) and 2.702(6) Å, the O(1)–Sn(1)–S(2) angles 160.77(14)° and 161.14(14)° and the C(3)–O(1)–Sn(1) angles 162.3(6)° and 164.3(6)°.

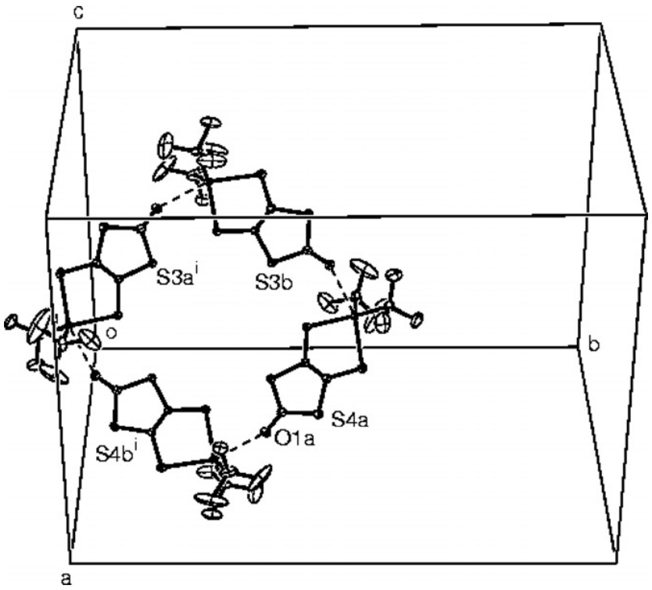


Fig. 4. The tetramer of **2m**. Ellipsoids are drawn at the 20% probability level and hydrogen atoms have been omitted for clarity. Intermolecular Sn(1)–O(1) bonds are represented by dashed lines. [Symmetry code: (i) 1/2 − *x*, 1/2 − *y*, 1/2 − *z*.].

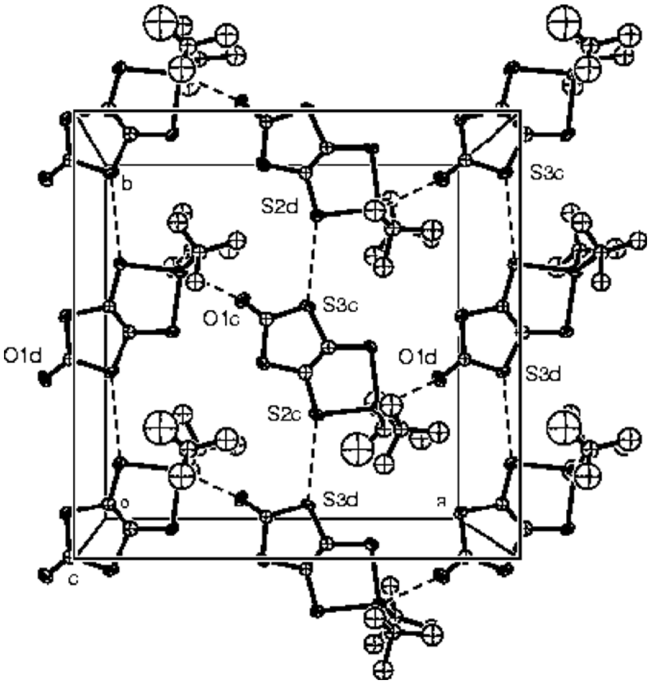
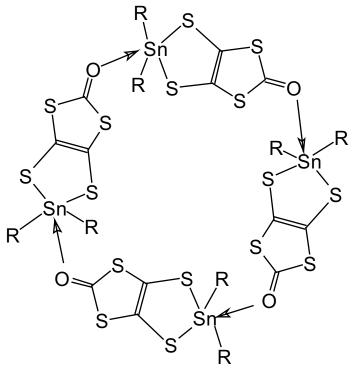


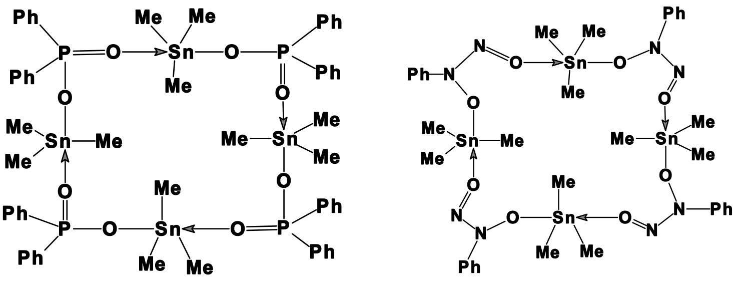
Fig. 5. Sn(1)–O(1) and S(2)–S(3) intermolecular interactions (dashed lines) within a CD layer in the structure of **2o**. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. No attempt has been to indicate symmetry codes but the outline of the unit cell is shown.

The chains lie side by side and the shortest interactions between adjacent chains takes the form of S(2C)–S3(D^{ii}) and S(3C)–S(2D^{iii}) contacts of 3.616(3) and 3.610(3) Å, respectively [symmetry codes: (ii) $x + 1/2$, $-y + 1/2$, $-z + 1$; (iii) $x + 1/2$, $-y + 3/2$, $-z + 1$], which provide very weak connectivity in the direction of b. Both layer surfaces are occupied by methyl groups. Similar AB layers involving only molecules A and B occur at $Z = 1/4$ and 3/4 with precisely the same forms of intermolecular contact except that the Sn–O bonded chains and the S–S contacts are now in the directions of *b* and *a*, respectively. Now the Sn(1)–O(1) distances are 2.784(5) and 2.780(6) Å, the O(1)–Sn(1)–S(2) angles 159.58(13)° and 159.70(14)°, the C(3)–O(1)–Sn(1) angles 166.8(6)° and 167.5(5)° and the S(2)–S(3) distances 3.570(3) and 3.587(3) Å. Because of the similarity of the orthorhombic unit cell edges *a* and *b*, the orientational relationship between the AB and CD layers already mentioned and the indication of possible alternative tetragonal symmetry provided by the ADDSYM component of PLATON [21] the structure was re-determined, on the basis of the same intensity data, in the tetragonal space group $P4_12_12$ and is reported, briefly, under the designation **2t**. In the tetragonal, **2t**, structural model the distinct AB and CD layers of the orthorhombic, **2o**, model are related by the operation of the crystallographic fourfold screw axis of the tetragonal space group and the number of crystallographically independent molecules in the asymmetric unit is reduced from four to two. However, the **2t** refinement, with higher *R*-factors, very extreme displacement parameters and poor estimates of bond lengths and bond angles, is inferior to the **2o** refinement and is, therefore, perhaps an idealised representation of the structure which is not wholly compatible with the intensity data presently available.

Among the various oligomeric and polymeric organotin compounds reported in the literature are some cyclic tetrameric organotin compounds [23]. These include compounds **3** [$(Me_3SnO_2PPh)_4$] [24], **4** [$(Me_3SnONPhNO)_4$] [25], **5** [(1-IPh_2SnCH_2-1,2,4-triazole)$_4$] [26], **6** [$(Bu_3SnO_2CAr)_4$: Ar = 2,6-$F_2C_6H_3$] [27], shown in Fig. 6, and [(*Z*)-$Bu_3SnO_2CCPh{=}CHC_6H_4NO_2$-*p*]$_4$ [28]. As in R_2Sn(dmio) com-

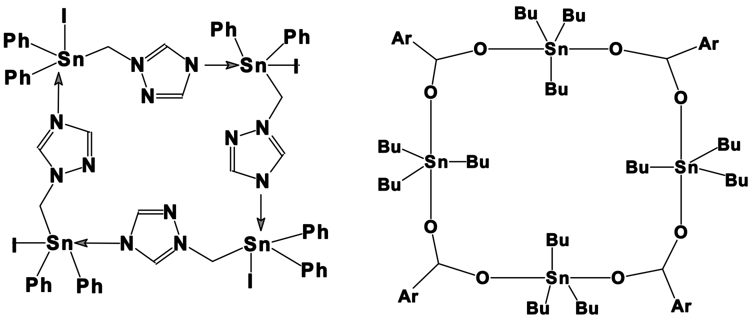


2m: R = Bu^t : 24 membered , $Sn_4C_8O_4S_8$ ring
[this study]



3: 16 membered , $Sn_4O_8P_4$ ring [24]

4: 20 membered $Sn_4N_8O_8$ ring [25]



5: 20 membered $Sn_4C_8N_8$ ring [26]

6: (Ar = 2,6-$F_2C_6H_3$) 16 membered $Sn_4C_4O_8$ ring [27]

Fig. 6. Selected cyclo-tetrameric organotin compounds.

pounds, variations of substituents can lead to different degrees and types of aggregation. Thus $Ph_3SnO_2PR_2$ is hexameric [29,30], R_3SnO_2CR' are, in general, polymeric [31,32] and 1-$BrPh_2SnCH_2$-1,2,4-triazole is dimeric [26] in the solid state. The ring size found for **2m** with 24 atoms is the largest so far reported. Of further interest of the compounds exhibited in Fig. 6 only **2** has been found in an alternative form.

3.3. Structural comparisons

The different situations of potential donor atoms in Bu^t_2Sn(dmit) and Bu^t_2Sn(dmio), on one hand, and Bu^t_2Sn(edt), on the other, must be considered when comparing the structures of the series of R_2Sn(dmit), R_2Sn(dmio) and R_2Sn(edt) compounds. The intermolecular interactions in the dmit and dmio compounds invariably involve the thione S in the dmit molecules or the carbonyl O in the dmio compounds and never the thiolato S atoms. In the case of the edt complexes, the only S atoms are, of course, the thiolato atoms. These thiolato atoms, adjacent to tin, will experience much greater steric resistance in trying to complex with the tin centres of other molecules. Clearly Me, Bu and Ph substituents in R_2Sn(edt) are not sufficiently bulky to prevent intermolecular Sn–S(thiolato) interactions, as shown by the intermolecular Sn–S distances of 3.182(1) Å in Me_2Sn(edt) [11], 3.688Å in Bu_2Sn(edt) [12] and 3.885 Å in Ph_2Sn(edt) [13], although, in the case of the phenyl derivative, only a very weak Sn–S intermolecular interaction appears present.

The Sn–S intermolecular bond lengths in R_2Sn(dmit) compounds, having a single Sn–S intermolecular interaction per molecule, are 2.8174(9) Å, in Ph_2Sn(dmit) [3], 3.139(1) Å, in PhMeSn(dmit) [1], 2.960(2) Å, in Mol. A, and 3.001(2) Å, in Mol. B, in Me_2Sn(dmit) [2], 3.0083(15) Å, in *orthorhombic*-Et_2Sn(dmit) [2], and 2.9790(6) and 3.0839(6) Å in the two independent molecules of Bu^t_2Sn(dmit) [this study], see Table 1. No correlation is apparent between the strength of the intermolecular Sn–S interactions, as measured by Sn–S distances, and the bulk of the organic groups, R, in each of the R_2Sn(dmit) and R_2Sn(edt) series. Based on bond lengths, the Sn–S interactions in R_2Sn(dmit) appear stronger than those in the corresponding R_2Sn(edt) compounds.

The intermolecular Sn–O bond lengths, 2.654(6) Å in Me_2Sn(dmio) [6] and the values found, in this study, for **2m** [2.65(2)–2.734(7) Å] and for **2o** [2.697(5) –2.780(6) Å] indicate little influence here of the bulk of the R group. However, the additional intermolecular Sn···S(thiolato) interaction found in Me_2Sn(dmio) is missing in the two Bu^t_2Sn(dmio) polymorphs and thus there is some indication that the steric bulk of the *tert*-butyl groups is influencing the structures.

Acknowledgements

The use of the EPSRC X-ray crystallographic service at the University of Southampton, England and the valuable assistance of the staff there is gratefully acknowledged. J.L.W. acknowledges support from FAPEMIG.

Appendix A. Supplementary material

CCDC 678394, 678395, 678396 and 678397 contain the supplementary crystallographic data for refinement **1**, refinement **2m**, refinement **2o** and alternative refinement **2t**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary Tables S1 and S2 are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.019.

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