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4,5-Bis[(triorganotin)thiolato]-1,3-dithiole-2-thione, (R₃Sn)₂(dmit), 4,5-bis[(triorganotin)thiolato]-1,3-dithiole-2-one, (R₃Sn)₂(dmio), compounds: Crystal structures of (cyclohexyl₃Sn)₂(dmio), (Ph₃Sn)₂(dmit) and (Ph₃Sn)₂(dmio)

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Abstract

The synthesis and crystal structures of 4,5-bis[(triorganotin)thiolato]-1,3-dithiole-2-thione, (R₃Sn)₂(dmit), **1**, and 4,5-bis[(triorganotin)thiolato]-1,3-dithiole-2-one, (R₃Sn)₂(dmio), **2**, compounds are reported. Compounds, (**1** or **2**: R = Ph or cyclohexyl, Cy), have been obtained from reaction of R₃SnCl with Cs₂dmit or Na₂dmio. The presence of the two tin centres in (**2**: R = Ph) is shown in the ¹³C NMR spectrum by the couplings of both Sn atoms to the dmio olefinic carbons with J values of 29.4 and 24.7 Hz. The δ ¹¹⁹Sn values for (**1**: R = Ph) and (**2**: R = Ph) differ by about 30 ppm, values being −20.7 and −50.1 ppm, respectively, in CDCl₃ solution. X-ray structure determinations for (**1**: R = Ph) and (**2**: R = Ph or Cy) reveal the compounds to have 4-coordinate, distorted tetrahedral tin centres. The dithiolato ligands, dmit and dmio, act as bridging ligands, in contrast to their chelating roles in R₂Sn(dmit) and R₂Sn(dmio). A further difference between R₂Sn(dmit) and R₂Sn(dmio), on one hand, and **1** and **2** on the other, is that intermolecular Sn–S and Sn–O interactions are absent in **1** and **2**. However, weak intermolecular hydrogen bonding interactions are found in (**1**: R = Ph) [C–H···π] and in (**2**: R = Ph) [C–H···π and C–H···O].

1. Introduction

The 1,3-dithiole-2-thione-4,5-dithiolato ligand (dmit: $C_3S_5^{2-}$) and its chalcogen atom substituted isologs, see Fig. 1, have found use in organic and coordination chemistry [1]. Particular attention has been paid to complexes of dmit-transition metal compounds [1]. This largely arises from the conductive properties, especially of Ni(II) and Pd(II) species [2,3]. While generally less frequently studied, emphasis on main group dmit complexes has been concentrated on structure determinations, with tin compounds being in the

vanguard of these studies. Structures of various tin-dmit compounds have been reported, including those of [Q]₂[Sn-(dmit)₃] (Q = monovalent cation) [4,5], [Q]₂[X₂Sn(dmit)₂] (X = Br or I) [6], [Q][RSn(dmit)₂] [7,8], R₂Sn(dmit) [7,9,10] and [Q][R₂SnX(dmit)] [8,11] (R = alkyl or aryl). In all these tin compounds, the dmit ligand is acting as a chelating group.

Of the dmit isologs, dmio [also known as dmid] has attracted the most attention. Reported tin containing dmio compounds include [Q]₂[Sn(dmio)₃] [5,12], [NEt₄][MeO₂-CCH₂CH₂Sn(dmio)₂] [13] and [Q][R₂SnX(dmio)] and R₂Sn(dmio) [14]. Here, too, in all these compounds the dmio ligand acts as a chelating 1,2-dithiolato ligand.

What are missing from the list of organotin-dmit and -dmio compounds, so far reported, are triorganotin dmit

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X, Y, Z = O, S or Se
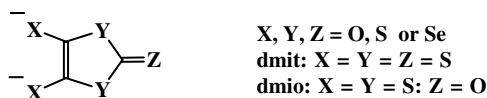dmit: X = Y = Z = S
dmio: X = Y = S: Z = O

Fig. 1. dmit and its isologs.

and dmio species and compounds in which the dmit and dmio moieties act as bridging ligands. We wish to put right this omission by reporting a study of the synthesis, structure and spectra of $(R_3Sn)_2(dmit)$, **1**, and $(R_3Sn)_2(dmio)$, **2**, species. The sole report in the literature of the structure of a related bis-metallic dmit compound concerned $(Ph_3Pb)_2(dmit)$ [15].

2. Experimental

2.1. General

^1H, ^{13}C and ^{119}Sn NMR spectra were run on Bruker 300 and 400 MHz instruments. Melting points were measured on a Melt-TempII instrument. Elemental analyses were obtained using a Perkin–Elmer 2400 apparatus. Infrared spectra were obtained in CsI pellets at room temperature on a Nicolet Magna 760 FT-IR instrument, with 4 cm^{-1} resolution.

2.2. Synthesis

All synthetic procedures were carried out under argon using standard Schlenk techniques. The compounds, $(PhCO)_2dmit$ [16], $(PhCO)_2dmio$ [17] and the Cs_2dmit [18], were prepared according to published procedures.

2.2.1. Preparation of $(Ph_3Sn)_2dmit$ (**1**: R = Ph)

To a dark red solution of Cs_2dmit (0.217 g, 0.47 mmol) in methanol (10 ml) was added, under argon, Ph_3SnCl (0.418 g, 1.08 mmol). There was an immediate colour change and a yellow solid (**1**: R = Ph) precipitated. The reaction mixture was concentrated under vacuum and the precipitate of (**1**: R = Ph) was collected and recrystallized from methanol/dichloromethane. Yield 52% (0.221 g), m.p. 150–151 °C.

^1H NMR: (300 MHz, CDCl$_3$)δ: 7.4–7.8 (m).
^{13}C NMR: (75.4 MHz, CDCl$_3$)δ: 129.2 [$J(^{119,\,117}Sn–^{13}C)$ = 60.0 Hz, m-C], 130.5 [$J(^{119,\,117}Sn–^{13}C)$ = 12.8 Hz, p-C], 136.4 [$J(^{119,\,117}Sn–^{13}C)$ = ca. 25 Hz, C=C], 136.8 [$J(^{119}Sn–^{13}C)$ = 564.6 Hz, $J(^{117}Sn–^{13}C)$ = 539.4 Hz, i-C], 136.9 [$J(^{119,117}Sn–^{13}C)$ = 44.7 Hz, o-C], 211.8 (C=S).
^{119}Sn NMR: (93.3 MHz, CDCl$_3$)δ: −20.7.
IR: (CsI) 3064, 3044, 3023, 2990, 1578, 1479, 1458, 1066 (C=S), 884, 660, 517, 466, 303 (Sn–S), 271 cm^{-1}.
Anal. Calc. for $C_{39}H_{30}S_5Sn_2$: C, 52.25; H, 3.37. Found: C, 52.42; H, 3.56%.

2.2.2. Preparation of $(Ph_3Sn)_2dmio$ (**2**: R = Ph)

To a stirred suspension of 4,5-bis(benzoylthio)-1,3-dithiole-2-one (0.390 g, 1.0 mmol) in methanol (10 ml), under argon, was added a sodium methoxide solution prepared by dissolving sodium (0.050 g, 2.1 mmol) in methanol (10 ml). To the resulting purple solution of Na$_2$dmio was added with stirring Ph$_3$SnCl (0.780 g, 2.0 mmol). There was an immediate colour change and a yellow solid (**2**: R = Ph) precipitated. The reaction mixture was concentrated under vacuum and the precipitated of (**2**: R = Ph) was collected and recrystallized from methanol/dichloromethane. Yield 25% (0.221 g), m.p. 141–145 °C.

^1H NMR: (300 MHz, CDCl$_3$)δ: 7.44–7.52 (m, 9H, m- + p-H), 7.70–7.73 (m, o-H).
^{13}C NMR: (75.4 MHz, CDCl$_3$)δ: 127.0 [$J(^{119,\,117}Sn–^{13}C)$ = 29.4, 24.7 Hz, C=C], 129.0 [$J(^{119,117}Sn–^{13}C)$ = 59.1 Hz, m-C], 130.2 [$J(^{119,117}Sn–^{13}C)$ = 12 Hz, p-C], 136.7 [$J(^{119,117}Sn–^{13}C)$ = 44.1 Hz, o-C], 136.9 [$J(^{119}Sn–^{13}C)$ = 562.9 Hz, $J(^{117}Sn–^{13}C)$ = 538.1 Hz, i-C], 189.9 (C=O).
^{119}Sn NMR: (93.3 MHz, CDCl$_3$)δ: −50.1.
IR: (CsI) 3066, 3044, 3019, 1655 (C=O), 1614, 1576, 1460, 880, 660, 557, 463, 367, 291 (Sn–S), 272 cm^{-1}.
Anal. Calc. for $C_{39}H_{30}OS_4Sn_2$: C, 53.21; H, 3.43. Found: C, 52.98; H, 3.70%.

2.2.3. Preparation of $(Cy_3Sn)_2dmio$ (**2**: R = Cy)

This was prepared analogously to (**2**: R = Ph) using 4,5-bis(benzoylthio)-1,3-dithiole-2-one (0.390 g, 1.0 mmol), sodium (0.050 g, 2.1 mmol), methanol (10 ml) and a solution of Cy$_3$SnCl (0.780 g, 2.0 mmol) in chloroform (10 ml). Product (**2**: R = Cy) was recrystallized from methanol/dichloromethane. Yield 30% (0.267 g), m.p. 170–172 °C.

^{119}Sn NMR: (93.3 MHz, CDCl$_3$)δ: +32.2.
IR: (CsI) 2919, 2845, 1657 (C=O), 1612, 1466, 1444, 658 (Sn–C), 557, 464, 371, 361, 304 (Sn–S), 271 cm^{-1}.
Anal. Calc. for $C_{39}H_{66}OS_4Sn_2$: C, 51.10; H, 7.26. Found: C, 50.81; H, 7.52%.

2.3. X-ray crystallography

2.3.1. Data collection

Data for (**1**: R = Ph) and (**2**: R = Ph and Cy) 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, UK. Data collection was carried out under the control of the program COLLECT [19] and data reduction and unit cell refinement were achieved with the COLLECT and DENZO [20] programs. Correction for absorption, by comparison of the intensities of equivalent reflections, was applied using the program SADABS [21]. The program ORTEP-3 for Windows [22] has been used in the preparation of the Figures and SHELXL-97 [23] and PLATON [24] in the calculation of molecular geometry.

2.3.2. Structure solution and refinement

All structures were solved by direct methods using, in the case of (**2**: R = Cy), SHELXS-86 [25] and SHELXS-97 [26] otherwise and in every case the initial solution was expanded and fully refined by means of the program

Table 1
Crystal data and structure refinement

Compound	(**1**: R = Ph)	(**2**: R = Ph)	(**2**: R = Cy)
Empirical formula	$C_{39}H_{30}S_5Sn_2$	$C_{39}H_{30}OS_4Sn_2$	$C_{39}H_{66}OS_4Sn_2$
Formula weight	896.31	880.25	916.54
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$
Unit cell dimensions			
a (Å)	19.1857(3)	20.9766(4)	10.0991(2)
b (Å)	9.1004(2)	10.0826(2)	19.5723(4)
c (Å)	23.1223(6)	16.8233(2)	33.0361(6)
α (°)	90	90	70.2668(6)
β (°)	113.8869(13)	90.8413(13)	82.3519(6)
γ (°)	90	90	83.7394(2)
Volume (Å^3)	3691.30(14)	3557.72(11)	6077.4(2)
Z, calculated density (Mg/m^3)	4, 1.613	4, 1.643	6, 1.503
Absorption coefficient (mm^{-1})	1.663	1.669	1.468
$F(000)$	1776	1744	2832
Crystal size (mm)	$0.20 \times 0.18 \times 0.05$	$0.20 \times 0.16 \times 0.12$	$0.48 \times 0.29 \times 0.10$
Θ range for data collection (°)	3.09–27.51	3.29–27.49	2.83–30.77
Index ranges	$-24 \leqslant h \leqslant 23$,	$-26 \leqslant h \leqslant 25$,	$-13 \leqslant h \leqslant 13$,
	$-11 \leqslant k \leqslant 11$,	$-12 \leqslant k \leqslant 13$,	$-25 \leqslant k \leqslant 25$,
	$-29 \leqslant l \leqslant 30$	$-18 \leqslant l \leqslant 21$	$-42 \leqslant l \leqslant 42$
Reflections collected/unique	46 809/8452	19 396/4058	119 174/28 932
	[$R(\text{int}) = 0.0645$]	[$R(\text{int}) = 0.0242$]	[$R(\text{int}) = 0.0414$]
Completeness to θ_{max} (%)	27.51–99.5	27.49–99.3	26.50–99.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7383	1.0000 and 0.7927	1.0000 and 0.6655
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8452/0/409	4058/0/210	28 932/0/1243
Goodness-of-fit on F^2	1.025	1.218	1.039
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0469$	$R_1 = 0.0259$,	$R_1 = 0.0341$,
	$wR_2 = 0.0963$	$wR_2 = 0.0730$	$wR_2 = 0.0846$
R indices (all data)	$R_1 = 0.0828$,	$R_1 = 0.0289$,	$R_1 = 0.0527$,
	$wR_2 = 0.1097$	$wR_2 = 0.0748$	$wR_2 = 0.0926$
Extinction coefficient		0.00299(15)	
Largest diff. peak and hole (e/Å^3)	1.125 and −0.979	1.327 and −0.775	1.092 and −1.459

SHELXL-97 [23]. In the final stages of the refinements hydrogen atoms, as appropriate, were introduced in calculated positions with C–H = 0.95, 0.99 and 1.00 Å for aryl, methylene and hydrogen on tertiary carbon, respectively, and refined with a riding model with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameter of the carbon atom to which they are attached. Correction for extinction, in the standard SHELXL-97 manner, was applied only in the case of (**2**: R = Ph). The asymmetric unit of (**2**: R = Cy) comprises three crystallographically distinct molecules, which have been labelled identically and are distinguished by suffix as A, B and C. In the molecule of (**2**: R = Ph), the oxo oxygen atom and its attached carbon atom, lie on a crystallographic twofold axis and the asymmetric unit is completed by a further carbon atom and two sulphur atoms, of a dmio ligand, and a triphenyltin group all in the general (eightfold) positions of the space group $C2/c$. In the molecule of (**1**: R = Ph), the phenyl group defined by C(31)–C(36) is disordered over two sites of equal occupancy, which correspond to two orientations related to one another by a rotation about the join of C(31) and C(34)

of roughly 90°. The atoms disordered in this way are present in the structural model in pairs as, for example, C(31A)/C(31B). Several of the other phenyl groups of (**1**: R = Ph) are also disordered but to a much lesser degree and in a different manner and their disorder has not been modelled in detail but manifests itself in comparatively severe anisotropy in the displacement parameters of the atoms concerned.

Crystal data and structure refinement details are listed in Table 1.

3. Results and discussion

3.1. General

The compounds, **1** and **2**, were readily available from reactions of R_3SnCl and Cs_2dmit or Na_2dmio at 2:1 mol ratios, equation 1. NMR spectra indicate that the compounds contain four coordinate tin and are stable in solution. The presence of two tin centres in (**2**: R = Ph) is shown by the presence in the ^{13}C NMR spectrum of couplings of both Sn atoms to the dmio olefinic carbons with

J values of 29.4 and 24.7 Hz: at this stage we have not distinguished the $^2J(^{119,117}Sn–^{13}C)$ and $^3J(^{119,117}Sn–^{13}C)$ couplings. The resolution of the ^{13}C NMR spectrum of (**1**: R = Ph) was insufficient to separate these two couplings.
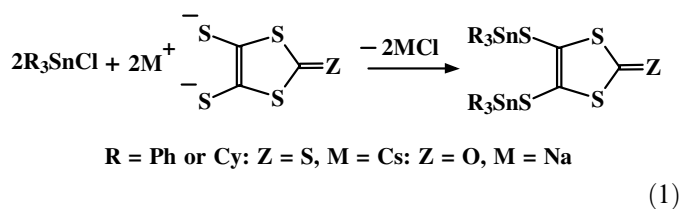
R = Ph or Cy: Z = S, M = Cs: Z = O, M = Na

(1)

The δ ^{119}Sn values for (**1**: R = Ph) and (**2**: R = Ph) differ by about 30 ppm, values being −20.7 and −50.1 ppm, respectively, in CDCl₃ solution. Considering the overall δ ^{119}Sn range of about 2000 ppm for tin compounds, these values can be considered as being in the region found for triphenyltin monomercaptides, Ph₃SnSR, e.g., δ ^{119}Sn =

−47 ± 1, −54.5 and −65.2 ppm for R = Me, PhCH₂ and Ph, respectively [27]. The lower field δ ^{119}Sn value, +31.2 ppm for (**2**: R = Cy) compared to (**2**: R = Ph) is as expected for a change from a triphenyl to a trialkyl derivative.

The 30 ppm low field shift between (**2**: R = Ph) to (**1**: R = Ph) matches other low field changes in going from tin-dmio to tin-dmit compounds, for example, δ ^{119}Sn values = ca. −280/−250 ppm for [Q]₂[Sn(dmio)₃]/[Q]₂[Sn (dmit)₃] [5], −175 ± 5/−145 ± 1 ppm for [Q][Ph₂SnCl(dmio)]/ [Q][Ph₂SnCl(dmit)] [11,14], 48/88 for [MeO₂CCH₂-CH₂]₂Sn(dmio)]/[MeO₂CCH₂CH₂]₂Sn(dmit)] [7,13] and −50/6 ppm [Q][MeO₂CCH₂CH₂Sn(dmio)₂]/[Q][MeO₂C-CH₂CH₂Sn(dmit)₂] [7,13]. In contrast to **1** and **2**, all the above compounds contain chelating dmio/dmit moieties, but similarly to **1** and **2**, they do not contain strong intra-molecular or interanion Sn–O or Sn–S interactions. When such strong intermolecular Sn–O and Sn–S interactions occur, the δ ^{119}Sn differences are considerably greater, e.g., δ ^{119}Sn values for polymeric Ph₂Sn(dmio)/Ph₂Sn-(dmit) the differences are ca. −237/−25 ppm, a difference of over 200 ppm [10,14]. This larger difference reflects the additional bonding to tin of the different carbonyl and thione chalcogen atoms.

Characteristic vibrational frequencies in the IR spectra for the dmit and dmio ligands in **1** and **2** are those for C=C (1463 ± 3 cm⁻¹), C=S (1064 ± 2 cm⁻¹) or C=O (1656 ± 1 cm⁻¹) and ring breathing modes (557/515 cm⁻¹). These frequencies are generally observed in the IR spectra of tin and organotin complexes containing dmit or dmio ligands.

As pointed out in Section 1, an analogous lead complex, (Ph₃Pb)₂(dmit), to (**1**: R = Ph) has been reported [15]. Complexes **1** and **2** are the first reported monomeric tin compounds to contain bridging dmit and dmio ligands.
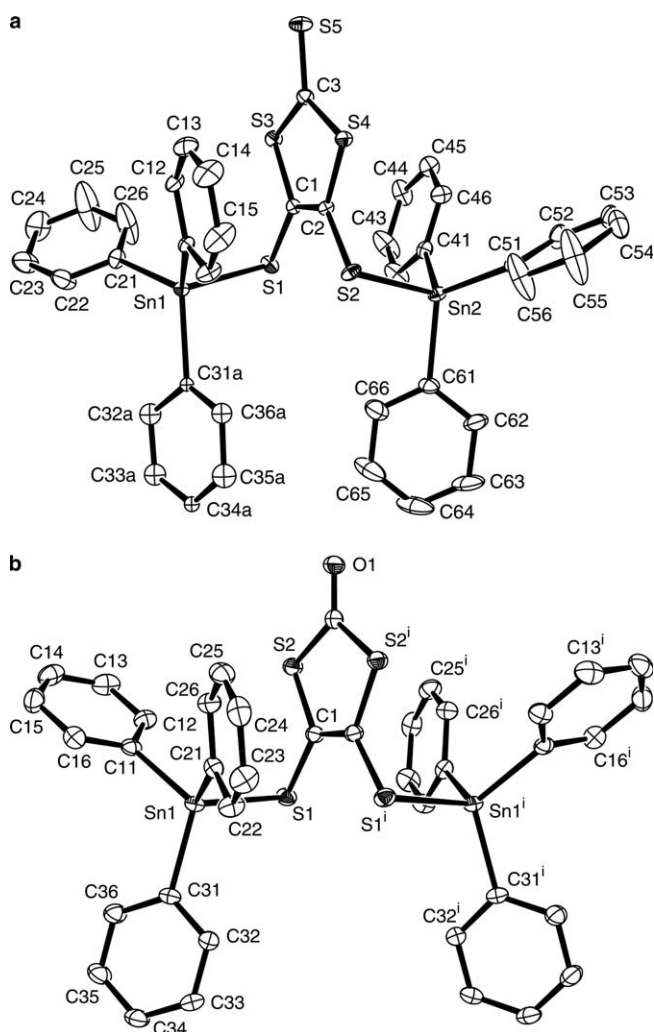
Fig. 2. Atom arrangements and numbering schemes for (a) (**1**: R = Ph) and (b) (**2**: R = Ph). Probability ellipsoids are drawn at the 20% level in (a) and the 50% level in (b) and hydrogen atoms have been omitted in both cases. Symmetry code in (b) (i) 1 − x, y, 1/2 − z.
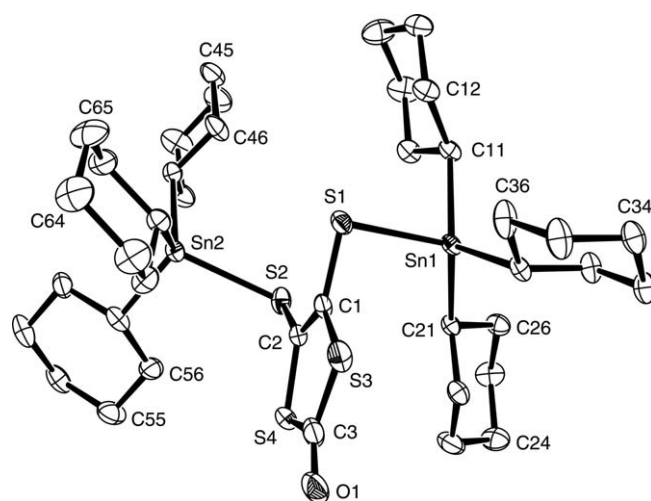
Fig. 3. Atom arrangement and numbering scheme for one of the three independent molecules of (**2**: R = Cy). Probability ellipsoids are drawn at the 50% level and hydrogen atoms have been omitted for clarity. The example shown is molecule A.

Tin complexes of other 1,2-dithiolato bridging ligands have however been reported. For example, $[NEt_4]_2[(edt-S,S')-Me(Cl)SnSCH_2CH_2SSn(Cl)Me(edt-S,S')]$ [28], $[NEt_3H]_2-[(edt-S,S')_2SnSCH_2CH_2SSn(edt-S,S')_2]$ (edt = $-SCH_2CH_2S-$) and $[(bdt-S,S')MeSnSC_6H_4SSn(bdt-S,S')]$ (bdt = $-o-SC_6H_4S-$) [29]. All of these compounds contain both bridging and chelating 1,2-dithiolato groups. Attempts to prepare similar complexes with dmit or dmio ligands have all failed.

3.2. Crystal structures

The atom arrangements and numbering schemes for (**1**: R = Ph), (**2**: R = Ph) and (**2**: R = Cy) are shown in Figs. 2, 3. The asymmetric unit of (**2**: R = Cy) comprises three crystallographically distinct molecules, that of (**2**: R = Ph), which has a crystallographic twofold axis, consists of the carbonyl atoms, a carbon atom and two sulphur atoms of a dmio ligand, and a triphenyltin group and that of (**1**: R = Ph), a
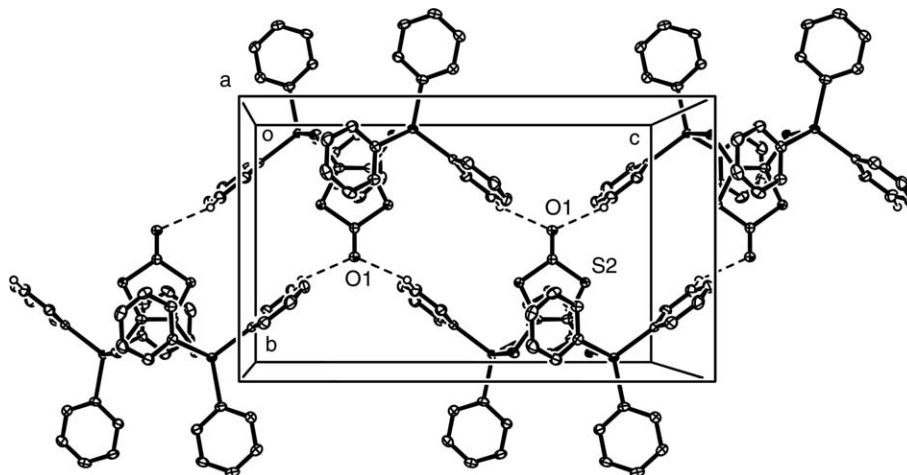

Fig. 4. Molecules of (**2**: R = Ph) linked by C–H···O hydrogen bonds: C–H···π interactions, also present, are not indicated.

Table 2
Selected geometric parameters, (Å, °), for (**1**: R = Ph)

Sn1–S1	2.4605(13)		Sn2–S2		2.4603(13)
Sn1–C11	2.122(5)		Sn2–C61		2.123(5)
Sn1–C21	2.130(5)		Sn2–C51		2.123(5)
Sn1–C31[a]	2.221(12), 2.066(12)		Sn2–C41		2.129(5)
C11–Sn1–C21	114.55(19)		C61–Sn2–C51		113.2(2)
C11–Sn1–C31[a]	112.7(4), 120.4(4)		C61–Sn2–C41		116.6(2)
C21–Sn1–C31[a]	115.2(4), 106.9(4)		C51–Sn2–C41		113.5(2)
C11–Sn1–S1	105.25(13)		C61–Sn2–S2		98.68(15)
C21–Sn1–S1	104.46(15)		C51–Sn2–S2		105.59(14)
C31[a]–Sn1–S4	103.0(3), 103.6(3)		C41–Sn2–S2		107.28(13)
C1–S1–Sn1	99.09(16)		C2–S2–Sn2		100.70(15)

CgI, CgJ	Cg–Cg (Å)	α (°)	β (°)	γ (°)	CgI$_{perp}$ (Å)	CgJ$_{perp}$ (Å)
Intramolecular π–π interaction[b]						
Cg3, Cg4	3.820	13.86	20.27	27.55	3.386	3.583

C–H···π	H···Cg (Å)	H$_{perp}$(Å)	γ (°)	C–H···Cg (Å)	C···Cg (Å)
Intermolecular C–H···π interactions[c]					
C12–H12···Cg7[i]	3.068	3.058	4.78	137.45	3.823
C24–H24···Cg8[ii]	3.172	2.963	20.89	128.56	3.837
C32A–H32A···Cg8[iii]	3.352	3.168	19.07	129.17	4.019
C64–H64···Cg5[iv]	3.217	3.197	6.33	134.97	3.947

[a] Data values in pairs due to disorder affecting C31.

[b] Cg3 is the centroid of 5-membered ring comprising S(3), C(1), C(2), S(4) and C(3) and Cg4 is the centroid of 6-membered ring comprising C11–C16; α = dihedral angle between the least squares planes of the rings; β = angle at Cg(I) between Cg–Cg and CgIperp; γ = angle at Cg(J) between Cg–Cg and CgJperp; CgIperp is the perpendicular distance of Cg(I) from ring J; CgJperp is the perpendicular distance of Cg(J) from ring I. The distances correspond to a slippage or lateral displacement of the rings, in a direction parallel to a plane equally inclined to both of them, of 1.565 Å.

[c] Ring 5 defined by C21–C26; ring 7 defined by C51–C56; ring 8 defined by C61–C66; Symmetry codes: (i) x, 1/2 − y, 1/2 + z; (ii) x, −1/2 − y, 1/2 + z;

Table 3
Selected geometric parameters, (Å, °), for (**2**: R = Ph)

Sn1–S1	2.4458(6)		Sn1–C31	2.124(2)
Sn1–C21	2.1321(19)		Sn1–C11	2.138(2)
C31–Sn1–C21	113.18(8)		C31–Sn1–C11	114.36(8)
C21–Sn1–C11	107.50(8)		C31–Sn1–S1	106.81(6)
C21–Sn1–S1	106.17(5)		C11–Sn1–S1	108.44(6)
C1–S1–Sn1	95.62(7)		C1–S2–C2	97.22(11)

	d(C–H) (Å)	d(H$\cdots$O) (Å)	d(C$\cdots$O) (Å)	$\angle$C–H$\cdots$O (°)
Hydrogen bond parameters				
C13–H13$\cdots$O1^v	0.95	2.55	3.315(2)	139

C–H$\cdots\pi$ (Å)	H$\cdots$Cg (Å)	H^{perp} (Å)	γ (°)	C–H$\cdots$Cg (Å)	C$\cdots$Cg (Å)
C–H$\cdots\pi$ interactions[a]					
C12–H12$\cdots$Cg4^i	3.294	2.938	26.87	131.40	3.987
C13–H13$\cdots$Cg4^i	3.370	2.924	29.82	127.60	4.020
C15–H15$\cdots$Cg3^{ii}	3.238	2.937	24.89	150.60	4.092
C24–H24$\cdots$Cg4^{iii}	2.987	2.946	9.56	135.75	3.728
C26–H26$\cdots$Cg1	3.280	3.191	13.35	93.56	3.471
C34–H34$\cdots$Cg2^{iv}	2.933	2.921	5.17	144.30	3.746

Symmetry code: (v) $1 - x$, $2 - y$, $-z$.
Symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $1/2 - x$, $3/2 - y$, $-z$; (iii) $1/2 - x$, $1/2 + y$, $1/2 - z$; (iv) x, $-1 + y$, z.

single disordered molecule. As indicated in Section 2, the disorder within (**1**: R = Ph) involves some of the phenyl rings and does not effect the situations about the tin centres.

The dmit and dmio ligands in **1** and **2** act as bridging ligands. Intramolecular Sn$\cdots$S separations, Sn1$\cdots$S2 and Sn2$\cdots$S1, in (**1**: R = Ph) [4.2177(14) and 4.2347(14) Å],

Table 4
Selected geometric parameters (Å, °) for (**2**: R = Cy)

	Molecule A	Molecule B	Molecule C
S1–Sn1	2.4174(8)	2.4220(7)	2.4310(7)
S2–Sn2	2.4969(8)	2.5092(8)	2.4862(8)
Sn1–C11	2.127(3)	2.126(3)	2.116(3)
Sn1–C31	2.174(3)	2.171(3)	2.175(3)
Sn1–C21	2.226(3)	2.226(3)	2.220(3)
Sn2–C51	2.036(3)	2.017(3)	2.105(3)
Sn2–C41	2.129(3)	2.127(3)	2.127(3)
Sn2–C61	2.188(3)	2.183(3)	2.142(3)
C1–S1–Sn1	90.14(10)	90.63(10)	91.96(10)
C2–S2–Sn2	102.63(10)	102.95(10)	105.39(10)
C11–Sn1–C31	120.41(11)	121.49(10)	120.43(11)
C11–Sn1–C21	116.25(11)	114.57(11)	115.15(11)
C31–Sn1–C21	109.38(11)	109.86(11)	109.98(11)
C11–Sn1–S1	88.54(8)	87.58(8)	88.23(8)
C31–Sn1–S1	107.09(8)	107.00(8)	108.35(8)
C21–Sn1–S1	113.02(7)	114.21(7)	112.55(7)
C51–Sn2–C41	109.94(11)	110.44(12)	105.88(11)
C51–Sn2–C61	116.44(11)	115.70(11)	120.39(11)
C41–Sn2–C61	110.58(11)	110.03(11)	114.51(12)
C51–Sn2–S2	101.70(9)	102.80(10)	103.19(8)
C41–Sn2–S2	107.86(8)	108.44(8)	108.80(8)
C61–Sn2–S2	109.71(8)	108.99(8)	103.02(8)

C–H$\cdots\pi$ (Å)	H$\cdots$Cg (Å)	H$_{perp}$ (Å)	γ (°)	C–H$\cdots$Cg (Å)	C$\cdots$Cg (Å)
Intramolecular C–H$\cdots\pi$ interactions[a]					
C22A–H22A$\cdots$Cg1	2.566	2.552	5.92	150.11	3.4259
C22C–H22E$\cdots$Cg3	2.609	2.601	4.66	149.24	3.496
C26B–H26D$\cdots$Cg2	2.657	2.643	5.89	148.34	3.538
C56B–H56D$\cdots$Cg2	2.906	2.757	18.43	165.08	3.872
C61C–H61C$\cdots$Cg3	3.207	2.900	25.27	140.98	4.034
C62A–H62A$\cdots$Cg1	2.816	2.705	16.11	165.20	3.781

[a] Ring 1 defined by S3A, C2A, C1A, S4A and C3A; ring 2 defined by S3B, C1B, C2B, S4B and C3B; ring 3 defined by S3C, C1C, C2C, S4C and C3C.

(**2**: R = Ph) [4.3850(5) Å] and in (**2**: R = Cy) [4.1558(7) and 4.2381(8) (Mol A), 4.1617(7) and 4.2941(7) (Mol B) and 4.1790(7) and 4.5806(8) Å (Mol C)] are all outside the sum of the van der Waals radii for Sn and S [4.05 Å] and thus indicate the absence of Sn1···S2 and Sn2···S1 interactions.

In all three compounds, the geometries about the tin centres are clearly distorted tetrahedral, with the C–Sn–C and C–Sn–S bond angles in (**1**: R = Ph) ranging from 106.9(4)–120.4(4)° and 98.68(15)–107.28(13)°, respectively. Those in (**2**: R = Ph) are 107.50(8)–114.36(8)° and 106.17(5)–108.44(6)°, respectively, while in (**2**: R = Cy) the ranges over the three independent molecules are much wider, being 105.88(11)–121.49(10)° and 87.58(8)–114.21(7)°, respectively. The greatest distortion from tetrahedral geometry thus is found in (**2**: R = Cy). Distortions from ideal tetrahedral geometries are not a direct consequence of having two tin centres in relatively close proximities in the molecules, since distortions from tetrahedral arrays are also found for simpler triorganotin mercaptides, such as $Ph_3SnSC_6H_4Bu^t$-p, in which C–Sn–C and C–Sn–S bond angle ranges are 108.6(4)–112.0(4)° and 98.5(3)–114.0(3)°, respectively [30]. The Sn–C and Sn–S bond lengths, 2.066(12)–2.221(12) and 2.4603(13)–2.4605(13) Å in (**1**: R = Ph), 2.124(2)–2.138(2) and 2.4458(6) Å in (**2**: R = Ph), and 2.017(3)–2.226(3) and 2.4174(8)–2.5092(8) Å in (**2**: R = Cy) can be compared with values determined for $Ph_3SnSC_6H_4Bu^t$-p, which are Sn–C 2.122(10)–2.132(9) and Sn–S 2.413(3) Å [30].

The cyclohexyl rings in (**2**: R = Cy) have the expected chair conformations, with the organotin group in the equatorial position.

The bond lengths and angles associated with the dmit ligand are all in the ranges found for other tin-dmit compounds. All three compounds, (**1**: R = Ph) and (**2**: R = Ph and Cy), are essentially molecular species, with no strong intermolecular interactions. Generally absent are S···S and S···O intermolecular interactions, which have been detected in other tin-dmit compounds. However, weak intermolecular C–H···π interactions in (**1**: R = Ph), and both C–H···O, see Fig. 4, and C–H···π interactions in (**2**: R = Ph) are present. For (**2**: R = Cy), C–H···O interactions are absent but C–H···π interactions are present: the latter occur within the three molecule asymmetric unit. An intramolecular π···π interaction completes the series of weak interactions found in (**1**: R = Ph).

Selected bond lengths and angles for (**1**: R = Ph), (**2**: R = Ph) and (**2**: R = Cy) are listed in Tables 2–4.

4. Supplementary material

Full details of the structure determinations have been deposited with the Cambridge Crystallographic Data Base, deposition numbers: 281540 (**1**: R = Ph), 281541 (**2**: R = Ph) and 281542 (**2**: R = Cy). Copies can be obtained free of charge on written application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: = +44 1223 336

033); on request by e-mail to deposit@ccdc.cam.ac.uk or by access to http//www.ccdc.cam.ac.uk.

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