

# Diorganotin 1,3-dithiole-2-thione-4,5-dithiolate compounds, $R_2Sn(dmit)$ : the crystal structure of $MePhSn(dmit)$

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## Abstract

Neutral diorganotin dmit compounds,  $R_2Sn(dmit)$ , have been synthesised from  $R_2SnX_2$  ( $R = Me, Et, Bu, octyl, Ph$  or  $o-MeOC_6H_4$ ;  $R_2 = Ph, Me$ ;  $X = Cl$  or  $Br$ ) and  $[NEt_4]_2[Zn(dmit)_2]$  ( $H_2-dmit = 4,5$ -dimercapto-1,3-dithiole-2-thione,  $H_2C_3S_5$ ). Solution and solid state NMR spectra have been obtained for selected  $R_2Sn(dmit)$  species as has the crystal structure of  $MePhSn(dmit)$  **10**. Molecules of **10** in the solid state are linked into zig-zag chains via  $Sn \cdots$  thione S intermolecular associations ( $Sn-S(5^1) = 3.139(1) \text{ \AA}$ ;  $Sn-S(5^1)-C(3^1) = 111.2(2)^\circ$ ). The links between the monomers within the chains are further strengthened by weak  $S \cdots S$  intermonomer interactions,  $S(5^1) \cdots S(2) = 3.315(2)$  and  $S(3^1) \cdots S(2) = 3.446(2) \text{ \AA}$ . Furthermore, weaker  $S \cdots S$  interactions ( $S(5^1) \cdots S(1^{11}) = 3.635(2) \text{ \AA}$ ) link the chains. The geometry at tin is distorted trigonal bipyramidal; with the equatorial sites occupied by the organic groups ( $Sn-C = 2.111(5)$  and  $2.134(2) \text{ \AA}$ ) and by a dithiolato sulphur atom ( $Sn-S(2) = 2.437(1) \text{ \AA}$ ). The axial sites are occupied by the other dithiolato sulphur atom ( $Sn-S(1) = 2.487(1) \text{ \AA}$ ) and the bridging thione sulphur ( $S(5^1)$ ): the valency angle,  $S(5^1)-Sn-S(1)$ , is  $161.63(3)^\circ$  with the dithiolate bite angle of  $89.92(4)^\circ$ . The  $R_2Sn(dmit)$  compounds react with onium halides,  $[Q]X$  to give  $[Q][R_2Sn(dmit)X]$ , form complexes,  $[R_2Sn(dmit)L]$ , with donors, (e.g.  $L = bipy, py$  or  $DMF$ ), and undergo exchange reactions with  $R'_2SnCl_2$ .

**Keywords:** Tin; Thione; Thiolato; Crystal structure

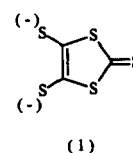
## 1. Introduction

Several complexes of the dmit ligand (**1**) have been studied; by far the majority of these have been complexes of transition metals [1,2]. Among the main group metal dmit complexes, which have been studied, are inorganic bis-dmit complexes of zinc, cadmium and mercury [3],  $[NR_4]_2[M(dmit)_2]$ , and of antimony [4],  $[NR_4][Sb(dmit)_2]$ , and tris-dmit complexes of indium and thallium [5],  $[NR_4]_3[M(dmit)_3]$ . In addition, we have reported the syntheses and crystal structures of lead [6] and tin dmit compounds [7–10]; both inorganic tin dmit [7],  $[NBu_4]_2[Sn(dmit)_2I_2]$ , and organotin dmit complexes,  $[NBu_4][Me_2Sn(dmit)Cl]$ , **2** [8],  $(RO_2CCH_2-CH_2)_2Sn(dmit)$ , **3** [9], and  $[NR_4][R_2Sn(dmit)_2]$  (**4**,  $R^1 = Bu$ ;  $R = Bu$  or  $Ph$ ;  $R^1 = Et$ ,  $R = MeO_2CCH_2CH_2$ ) [9,10] have been studied.

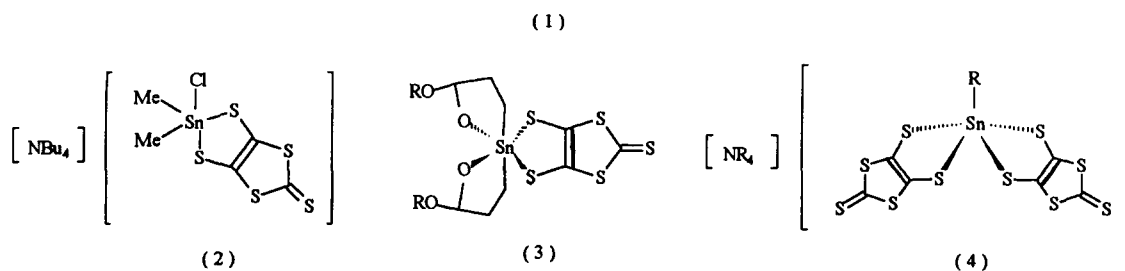
In continuation of this work, we now wish to report the syntheses and properties of other neutral diorganotin dmit species,  $R_2Sn(dmit)$ , **5–10**, as well as the crystal structure of  $MePhSn(dmit)$ , **10**.

## 2. Experimental

Solution NMR were obtained on a Bruker 250 MHz instrument and IR spectra on Philips Analytical PU 9800 FTIR and Nicolet 205 FTIR instruments. Solid state NMR spectra were recorded by the EPSRC service, based at the University of Durham and the X-ray



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diffraction data were collected by the EPSRC service, based at the the University of Wales, Cardiff.

The complex,  $[\text{NEt}_4]_2[\text{Zn}(\text{dmit})_2]$ , was prepared by an analogous procedure to that published [11] for  $[\text{NBu}_4]_2[\text{Zn}(\text{dmit})_2]$ . Published procedures were used to prepare di-*o*-anisyltin dibromide [12], from (*o*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn and SnBr<sub>4</sub>, and MePhSnBr<sub>2</sub> [13], from Ph<sub>3</sub>Sn-Me and Br<sub>2</sub>. Trimethyl(trimethylstannylmethyl)ammonium iodide [14] was obtained from Me<sub>3</sub>SnCH<sub>2</sub>NMe<sub>2</sub> and MeI. It had a melting point (m.p.) of 202–205°C;  $\delta^{119}\text{Sn}$  (CDCl<sub>3</sub>, 93.3 MHz) –12.8 ppm.

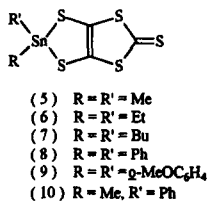
Diocetyl tin dichloride was a gift from the International Tin Research Institute, Uxbridge. All other diorganotin dichlorides and the onium halides were commercial samples.

### 3. Preparation of R<sub>2</sub>Sn(dmit)

#### 3.1. Method 1

A solution of the diorganotin dihalide (2 mmol) and  $[\text{NEt}_4]_2[\text{Zn}(\text{dmit})_2]$  (1 mmol) in acetone was agitated in an ultrasonic bath for 10 min. Water (35 ml) was added with vigorous shaking. Addition of petroleum ether (b.p. 40–60°C, 10 ml) and vigorous scraping of the sides of the flask resulted in the formation of an orange-brown coloured precipitate of R<sub>2</sub>Sn(dmit). This solid was collected and refluxed for 1 h in a 2:1 water:methanol mixture, filtered and dried under vacuum.

Recrystallisation was from either petroleum ether (60–80°C)–acetone or petroleum ether (60–80°C)–methanol. Yields were typically 60–80%.



#### 3.1.1. Me<sub>2</sub>Sn(dmit), 5

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 250 MHz):  $\delta$  1.19 (s,  $J(^{119}\text{Sn}-\text{H}) = 75.3$  Hz, Me).

<sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 62.9 MHz):  $\delta$  9.3 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 515$  Hz, Me), 130.1 (C=C), 209.3 (C=S).

#### 3.1.2. Et<sub>2</sub>Sn(dmit), 6

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 250 MHz):  $\delta$  1.43 (t, 6H,  $J(\text{H}-\text{H}) = 8.0$  Hz,  $J(^{119}\text{Sn}-\text{H}) = 127.9$  Hz, Me), 1.79 (q, 4H,  $J(^1\text{H}-^1\text{H}) = 8.0$  Hz,  $J(^{119}\text{Sn}-\text{H}) = 59.3$  Hz, SnCH<sub>2</sub>).

<sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 62.9 MHz):  $\delta$  10.5 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 40.4$  Hz, CH<sub>3</sub>CH<sub>2</sub>Sn), 20.6 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 535.1$  Hz, SnCH<sub>2</sub>), 130.4 (C=C), 209.5 (C=S).

#### 3.1.3. Bu<sub>2</sub>Sn(dmit), 7

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 250 MHz):  $\delta$  0.89 (t, 4H,  $J(\text{H}-\text{H}) = 7.3$  Hz,  $J(^{119}\text{Sn}-\text{H}) = 125.4$  Hz, SnCH<sub>2</sub>), 1.4 (sextuplet, 4H,  $J(\text{H}-\text{H}) = 7.2$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Sn), 1.8–2.1 (m, 10H, Me and SnCH<sub>2</sub>CH<sub>2</sub>).

<sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 62.9 MHz):  $\delta$  13.7 (Me), 26.7 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 92.7$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Sn), 27.4 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 444.3$  Hz, SnCH<sub>2</sub>), 28.2 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 35.7$  Hz, CH<sub>2</sub>CH<sub>2</sub>Sn), 130.2 (C=C), 211.4 (C=S).

#### 3.1.4. Ph<sub>2</sub>Sn(dmit), 8

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 250 MHz):  $\delta$  7.53 (m, 6H, *m*- + *p*-H), 7.94 (m, 4H,  $J(^{119}\text{Sn}-\text{H}) = 76.6$  Hz, *o*-H).

<sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 62.9 MHz):  $\delta$  129.6 (C=C), 129.8 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 80.7$  Hz, *m*-C), 131.3 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 17.0$  Hz, *p*-C), 136.4 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 61.2$  Hz, *o*-C), 142.9 (*i*-C), 210.5 (C=S).

#### 3.1.5. MePhSn(dmit), 10

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 250 MHz):  $\delta$  1.48 (s, 3H,  $J(^{119}\text{Sn}-\text{H}) = 77.3$  Hz, Me), 7.47 (m, 3H, *m*- + *p*-H), 7.79 (m, 2H,  $J(^{119}\text{Sn}-\text{H}) = 80.4$  Hz, *o*-H).

<sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 62.9 MHz):  $\delta$  7.1 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 545.3$  Hz, Me), 129.4 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 77.2$  Hz, *m*-C), 130.7 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 16.5$  Hz, *p*-C), 135.8 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 59.0$  Hz, *o*-C), 145.0 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 716.6$  Hz, *i*-C), 210.8 (C=S). (The peak for C=C was obscured by the aromatic peaks).

Melting points,  $\delta^{119}\text{Sn}$  values and analytical data are shown in Table 1.

### 3.2. Method 2

Compound **9**. Solutions of  $(o\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2$  (0.924 g, 2 mmol) in acetone (20 ml) and  $[\text{NEt}_4]_2[\text{Zn}(\text{dmit})_2]$  (0.717 g, 1 mmol) in acetone (20 ml) were mixed and stirred for 1 h. The reaction mixture was filtered and the filtrate was evaporated. The residue, compound **9**, was very poorly soluble in most organic solvents; it was purified only by washing with acetone. It was obtained as an amorphous red powder.

$^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 250 MHz):  $\delta$  3.73 (s, 3H, MeO), 7.13 (m, 4H), 7.48 (m, 2H) and 7.59 (m, 2H) (aryl-H). Other data for **9** are in Table 1.

### 3.3. Addition of halide ions to **8**

The compound,  $[\text{NEt}_4][\text{Ph}_2\text{Sn}(\text{dmit})\text{Br}]$ , was prepared from a solution of **8** (0.21 g, 0.45 mmol) and  $[\text{NEt}_4]\text{Br}$  (0.40 g, 1.9 mmol) in MeOH (20 ml) on agitation in an ultrasonic bath for 2 h. The yellow solid, which formed, was collected and recrystallised from MeOH as orange crystals. The yield of  $[\text{NEt}_4][\text{Ph}_2\text{Sn}(\text{dmit})\text{Br}]$  was 0.13 g, 40%; m.p. 74–77°C. Anal. Found: C, 40.47; H, 4.29; N, 1.84.  $\text{C}_{23}\text{H}_{30}\text{BrNS}_5\text{Sn}$ . Calc.: C, 40.66; H, 4.45; N, 2.06%.

$^1\text{H}$  NMR (acetone- $d_6$ , 250 MHz):  $\delta$  1.36 (tt, 12H,  $J(\text{H}-\text{H}) = 7.3$  Hz, Me), 3.43 (q, 8H,  $J(\text{H}-\text{H}) = 7.3$  Hz,  $\text{NCH}_2$ ), 7.38 (m, 6H,  $m$ - +  $p$ -H), 8.10 (m, 4H,  $J(^{119}\text{Sn}-\text{H}) = 81.8$  Hz,  $o$ -H).

$^{119}\text{Sn}$  NMR (acetone- $d_6$ , 93.3 MHz):  $\delta$  -149.9.

The compound,  $[\text{NBu}_4][\text{Ph}_2\text{Sn}(\text{dmit})\text{Br}]$ , was prepared similarly from **8** and  $[\text{NBu}_4]\text{Br}$ ; m.p. 119–122°C. IR (KBr,  $\text{cm}^{-1}$ ): 3044, 2959–2872, 1480, 1455, 1429, 1057, 1036, 737, 696.

$^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 250 MHz):  $\delta$  0.93 (t, 12H,  $J(\text{H}-\text{H}) = 7.2$  Hz, Me), 1.31 (m, 8H,  $\text{NCH}_2\text{CH}_2$ ), 1.56

(m, 8H,  $\text{NCH}_2\text{CH}_2\text{CH}_2$ ), 3.16 (t, 8H,  $\text{NCH}_2$ ), 7.42 (m, 6H,  $m$ - +  $p$ -H), 7.92 (d, 4H,  $o$ -H).

$^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 62.9 MHz):  $\delta$  13.5, 19.2, 23.1, 57.5 (cation peaks), 128.4 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 82.6$  Hz,  $m$ -C), 129.4 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 22.9$  Hz,  $p$ -C), 131.5 (C=C), 135.2 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 60.1$  Hz,  $o$ -C), 146.4 ( $i$ -C), 206.2 (C=S).

$[1,4\text{-Me}_2\text{-pyridinium}][\text{Ph}_2\text{Sn}(\text{dmit})\text{I}]$  was prepared from **8** (1.0 g, 2.13 mmol) and  $[1,4\text{-Me}_2\text{-pyridinium}]\text{I}$  (1.4 g, 5.96 mmol) in MeOH (40 ml). The compound was obtained as orange crystals, 1.06 g, 71%; m.p. 134–136°C. Anal. Found: C, 37.52; H, 2.86; N, 1.99.  $\text{C}_{22}\text{H}_{20}\text{INS}_5\text{Sn}$ . Calc.: C, 38.06; H, 2.77; N, 2.02%.

$^1\text{H}$  NMR (acetone- $d_6$ , 250 MHz):  $\delta$  2.69 (s, 3H, Me), 4.49 (s, 3H, MeN), 7.41 (m, 6H,  $m$ - +  $p$ -H), 7.98 (d, 2H,  $J(\text{H}-\text{H}) = 6.3$  Hz), 8.07 (m, 4H,  $J(^{119}\text{Sn}-\text{H}) = 89.3$  Hz,  $o$ -H), 8.84 (d, 2H,  $J(\text{H}-\text{H}) = 6.3$  Hz).

$^{13}\text{C}$  NMR (acetone- $d_6$ , 62.9 MHz):  $\delta$  21.9 (Me), 48.3 ( $\text{NCH}_2$ ), 128.8 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 82.4$  Hz,  $m$ -C), 129.3 (cation), 129.8 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 17.0$  Hz,  $p$ -C), 131.2 (C=C), 136.2 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 61.7$  Hz,  $o$ -C), 145.3 (cation), 148.2 ( $J(^{119}\text{Sn}-^{13}\text{C}) = 791.0$  Hz,  $i$ -C), 160.2 (cation), 207.8 (C=S).

$^{119}\text{Sn}$  NMR (acetone- $d_6$ , 93.3 MHz):  $\delta$  -160.3.

Other additions of halides to  $\text{R}_2\text{Sn}(\text{dmit})$  were investigated using solution  $^{119}\text{Sn}$  NMR spectroscopy. A solution of  $\text{R}_2\text{Sn}(\text{dmit})$  (ca. 40 mg) in acetone- $d_6$  (1 ml) was added to an excess of the appropriate onium halide. The solution was allowed to stand for 2 h before the NMR spectrum was recorded. The results are shown in Table 2.

### 3.4. Reaction of **5** and pyridine

Pyridine (0.36 g) was added to a suspension of  $\text{Me}_2\text{Sn}(\text{dmit})$  (0.80 g) in acetone (50 ml). Reaction occurred as shown by the dissolution of the  $\text{Me}_2\text{Sn}(\text{dmit})$ . The volume of the solution was reduced to one

Table 1  
Analytical and other data for  $\text{R}_2\text{Sn}(\text{dmit})$

| $\text{R}_2\text{Sn}(\text{dmit})$ | M.p. (°C)        | NMR (acetone) (ppm)     |                                          |                                          | IR (nujol) ( $\text{cm}^{-1}$ ) |                          | Analysis found, (calc) (%) |                |
|------------------------------------|------------------|-------------------------|------------------------------------------|------------------------------------------|---------------------------------|--------------------------|----------------------------|----------------|
|                                    |                  | $\delta^{119}\text{Sn}$ | $\delta^{13}\text{C}(\text{C}=\text{C})$ | $\delta^{13}\text{C}(\text{C}=\text{S})$ | $\nu(\text{C}=\text{C})$        | $\nu(\text{C}=\text{S})$ | 3C                         | H              |
| $\text{Me}_2$                      | 200(dec)         | 135.2                   | 130.2                                    | 209.2                                    | 1439                            | 1060, 1029               | 17.59<br>(17.40)           | 1.57<br>(1.75) |
| $\text{Et}_2$                      | 202–205<br>(dec) | 165.6                   | 130.3                                    | 209.4                                    | 1442                            | 1062, 1020               | 22.87<br>(22.53)           | 2.51<br>(2.70) |
| $\text{Bu}_2$                      | 163–165          | 161.5                   | 130.1                                    | 211.4                                    | 1439                            | 1069, 1011               | 30.55<br>(30.78)           | 3.78<br>(4.23) |
| $\text{Ph}_2$                      | 205–207          | -24.8                   | 129.5                                    | 210.4                                    | 1433                            | 1063, 1015               | 38.81<br>(38.39)           | 2.21<br>(2.14) |
| $(o\text{-MeOC}_6\text{H}_4)_2^a$  | > 210            | -                       | -                                        | -                                        | -                               | -                        | 38.54<br>(38.57)           | 2.67<br>(2.88) |
| MePh                               | 176–178          | 75.2                    | obscured                                 | 210.7                                    | 1456                            | 1054, 1025               | 29.42<br>(29.50)           | 1.80<br>(1.98) |
| $\text{Oct}_2$                     | 82–85            | 159.8                   | 130.3                                    | 211.3                                    | -                               | -                        | -                          | -              |

<sup>a</sup> Very poorly soluble in organic solvents.

half and petroleum ether (40–60°C) was added and a brown crystalline product was precipitated, and was washed with petroleum ether. The titled compound had a m.p. of 195–200°C.

$^1\text{H}$  NMR (pyridine- $d_5$ , 250 MHz):  $\delta$  1.36 (s, 6H,  $J(^{119}\text{Sn}-\text{H}) = 74.1$  Hz, Me), 7.20 (m, 2H), 7.59 (m, 1H), 8.72 (m, 2H).

$^1\text{H}$  NMR (acetone- $d_6$ , 250 MHz):  $\delta$  1.22 (s, 6H,  $J(^{119}\text{Sn}-\text{H}) = 74.6$  Hz, Me), 7.46 (m, 2H), 7.87 (m, 2H), 8.63 (m, 2H).

$^{119}\text{Sn}$  NMR (acetone- $d_6$ , 93.3 MHz):  $\delta$  118.1; (pyridine- $d_5$ , 93.3 MHz) 19.3.

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3677, 1701, 1449, 1441, 1036, 1028, 770.

### 3.5. Preparation of $[\text{Ph}_2\text{Sn}(\text{dmit})\text{bipy}]$

A solution of 2,2'-bipyridine (0.234 g, 1.5 mmol) in acetone (10 ml) was added to a solution of **8** (0.470 g, 1 mmol) in acetone (10 ml) with stirring, and the solution allowed to stand at room temperature for 2 h. A dark coloured solid formed and was filtered off. Concentration of the filtrate gave further solid material. Recrystallisation from MeOH gave a dark brown crystalline solid; yield 0.2 g, 32%; m.p. 182–185°C. Anal. Found: C, 47.61; H, 2.86; N, 4.29.  $\text{C}_{25}\text{H}_{18}\text{N}_2\text{S}_5\text{Sn}$ . Calc.: C, 48.01; H, 2.90; N, 4.48%.

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3045, 1595, 1474, 1447, 1439, 1424, 1314, 1057, 1036, 1017, 766, 731, 698.

### 3.6. X-ray crystallography of **10**

Red crystals of  $\text{MePhSn}(\text{dmit})$  were obtained from petroleum ether–methanol. Data were collected on a Delft Instruments FAST diffractometer with monochromatised  $\text{Mo K}\alpha$  radiation. Corrections were made solely for Lorentz and polarisation effects. Crystal data and structure refinement details are given in Table 3. All atomic positions were located by a direct methods pro-

Table 3  
Crystal data and structure refinement

|                                        |                                                                |
|----------------------------------------|----------------------------------------------------------------|
| Empirical formula                      | $\text{C}_{10}\text{H}_8\text{S}_5\text{Sn}$                   |
| Formula weight                         | 406.5                                                          |
| Temperature                            | 293(2) K                                                       |
| Wavelength                             | 0.71069 Å                                                      |
| Crystal system                         | Orthorhombic                                                   |
| Space group                            | $P_{cab}$                                                      |
| Unit cell dimensions                   | $a = 12.405(5)$<br>$b = 14.120(3)$<br>$c = 15.608(8)$          |
| Volume                                 | $2784 \text{ Å}^3$                                             |
| Z                                      | 8                                                              |
| Density (calculated)                   | $1.98 \text{ g cm}^{-3}$                                       |
| Absorption coefficient                 | 2.58                                                           |
| $F(000)$                               | 1584                                                           |
| $\theta$ Range for data collection     |                                                                |
| Index ranges                           | $0 \leq h \leq 13$<br>$0 \leq k \leq 15$<br>$0 \leq l \leq 16$ |
| Reflections collected                  | 10683                                                          |
| Independent reflections                | 2144 ( $R_{\text{int}}$ 0.09)                                  |
| Observed reflections                   | 1476 (cut off $\theta = 25^\circ$ )                            |
| Refinement method                      | Full-matrix least squares on $F$                               |
| Number of parameters                   | 133                                                            |
| Goodness-of-fit on $F$                 | 1.1574                                                         |
| Final $R$ -values [ $I > 3\sigma(I)$ ] | $R = 0.044$ , $R_w = 0.037$                                    |
| Weighting scheme                       | Chebyshev polynomial <sup>a</sup>                              |

<sup>a</sup> J.R. Carruthers and D.J. Watkin *Acta Crystallogr. Sect. A*, 35 (1979) 698.

cedure using SIR88 [15]. Hydrogen atom positions were calculated from geometric considerations using a C–H bond length of 1.00 Å and an isotropic thermal vibration parameter ( $U_{\text{iso}}$ ) of  $0.05 \text{ Å}^2$ . Hydrogen atom positions and thermal parameters were not refined. Full-matrix least squares calculations with anisotropic thermal vibration parameters for all non-hydrogen atoms were performed using the program CRYSTALS [16]. During the refinement, the phenyl group was refined as a rigid body. Molecular diagrams were obtained using the program CAMERON [17]. A complete list of bond lengths and angles, and tables of thermal parameters and H-atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre.

## 4. Results and discussion

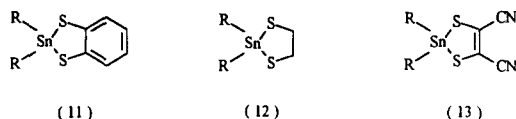
### 4.1. Synthesis

The reaction of  $\text{R}_2\text{SnX}_2$  with  $[\text{NEt}_4]_2[\text{Zn}(\text{dmit})_2]$  in a 2:1 mol ratio in acetone ( $\text{R} = o\text{-MeOC}_6\text{H}_4$ ,  $\text{X} = \text{Br}$ ) or acetone–water ( $\text{R} = \text{Me}$ ,  $\text{Et}$  or  $\text{Ph}$ ;  $\text{X} = \text{Cl}$ :  $\text{R}_2 = \text{Ph, Me}$ ;  $\text{X} = \text{Br}$ ) produced  $\text{R}_2\text{Sn}(\text{dmit})$ . We have previously reported [8] the syntheses of  $[\text{NBu}_4][\text{Me}_2\text{Sn}(\text{dmit})\text{Cl}]$  from  $\text{Me}_2\text{SnCl}_2$  and  $[\text{NBu}_4]_2[\text{Zn}(\text{dmit})_2]$  in a 2:1 mol ratio in dry methanol. However, as shown in this study, the use of mixed aqueous/organic solvent

Table 2  
Values of  $\delta^{119}\text{Sn}$  (ppm) for products of reactions of onium halides with  $\text{R}_2\text{Sn}(\text{dmit})$  in  $\text{CD}_3\text{COCD}_3$

| $\text{R}_2\text{Sn}(\text{dmit})$<br>( $\delta^{119}\text{Sn}$ ) | Onium<br>halide                                               | $\delta^{119}\text{Sn}$ of<br>product |
|-------------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------|
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | $\text{NEt}_4\text{Br}$                                       | –149.9                                |
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | $\text{NBu}_4\text{Br}$                                       | –150.4                                |
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | $[1,4\text{-Me}_2\text{pyridinium}]\text{I}$                  | –160.3                                |
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | $\text{NEt}_4\text{Br}-\text{NaSCN}$                          | –163.7                                |
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | mvd <sup>a</sup>                                              | –144.2                                |
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | $[\text{Me}_3\text{SO}]\text{I}$                              | –125.9                                |
| $\text{Ph}_2\text{Sn}(\text{dmit})$ (–24.8)                       | crystal violet <sup>b</sup>                                   | –24.8                                 |
| $\text{Bu}_2\text{Sn}(\text{dmit})$ (161.5)                       | $\text{NEt}_4\text{Br}$                                       | –36.1                                 |
| $\text{Me}_2\text{Sn}(\text{dmit})$ (135.2)                       | $[\text{Me}_3\text{NCH}_2\text{SnMe}_3]\text{I}$ <sup>c</sup> | 4.5 and<br>–12.1                      |

<sup>a</sup> mvd, methyl viologen dichloride. <sup>b</sup> crystal violet, ( $p\text{-Me}_2\text{NC}_6\text{H}_4$ ) $_3\text{C}^+\text{Cl}^-$ . <sup>c</sup>  $\delta^{119}\text{Sn} = -12.8$  ppm.



systems for reactions of  $[\text{NR}_4][\text{Zn}(\text{dmit})_2]$  and  $\text{R}_2\text{SnX}_2$  results in the isolation of neutral  $\text{R}_2\text{Sn}(\text{dmit})$  species. Furthermore, the addition of water to an acetone solution of  $[\text{NEt}_4][\text{Ph}_2\text{Sn}(\text{dmit})\text{Cl}]$ , prepared according to the method of Doidge-Harrison et al. [8], precipitated the neutral compound,  $\text{Ph}_2\text{Sn}(\text{dmit})$ , **8**. Of interest, compounds containing internal donor groups, such as **9** and the previously reported [9] six-coordinate **3**, were directly isolated from dry acetone solutions of the appropriate  $\text{R}_2\text{SnCl}_2$  and  $[\text{NEt}_4][\text{Zn}(\text{dmit})_2]$  without the addition of water.

#### 4.2. Properties

The  $\text{R}_2\text{Sn}(\text{dmit})$  compounds, **5–10**, are orange or red coloured solids. Solutions of  $\text{R}_2\text{Sn}(\text{dmit})$ , in acetone, chloroform or methanol, are yellow in colour with values of  $\lambda_{\text{max}}$  between 430 and 455 nm and with extinction coefficients in the range  $(1.1\text{--}1.4) \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ . The colour arises from the high degree of electron delocalisation over the dmit moiety, including the  $\text{C}=\text{S}$  group. Other delocalised  $\text{C}=\text{S}$ -containing compounds are also coloured [18]. The diorganotin dithiolate derivatives, **11–13**, have been reported to be either colourless or pale yellow in colour [19–21].

The solubility of each of the  $\text{R}_2\text{Sn}(\text{dmit})$  compounds was greater in co-ordinating solvents such as acetone and DMSO, than in non-co-ordinating ones such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ .

#### 4.3. Crystal structure of *MePhSn(dmit)*, **10**

Crystals of **10** were grown from a methanol–petroleum ether solution. The atom arrangement and number-

Table 4  
Fractional atom coordinates for **10**

| Atom  | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>iso</sub> |
|-------|------------|------------|------------|-------------------------|
| Sn    | 0.75050(2) | 0.30757(2) | 0.07108(2) | 0.0210                  |
| S(1)  | 0.68554(8) | 0.46534(8) | 0.11963(7) | 0.0284                  |
| S(2)  | 0.86312(9) | 0.29574(7) | 0.19857(7) | 0.0248                  |
| S(3)  | 0.75161(8) | 0.57439(7) | 0.27368(7) | 0.0245                  |
| S(4)  | 0.89797(8) | 0.43458(7) | 0.33956(6) | 0.0237                  |
| S(5)  | 0.87486(9) | 0.61421(7) | 0.43580(6) | 0.0264                  |
| C(1)  | 0.7622(3)  | 0.4704(3)  | 0.2133(3)  | 0.0234                  |
| C(2)  | 0.8309(3)  | 0.4047(3)  | 0.2449(3)  | 0.0209                  |
| C(3)  | 0.8414(3)  | 0.5447(3)  | 0.3536(2)  | 0.0225                  |
| C(4)  | 0.6129(3)  | 0.2208(3)  | 0.0550(3)  | 0.0339                  |
| C(5)  | 0.8422(2)  | 0.3344(2)  | −0.0420(1) | 0.0225                  |
| C(6)  | 0.8955(2)  | 0.4203(2)  | −0.0522(1) | 0.0287                  |
| C(7)  | 0.9554(2)  | 0.4373(1)  | −0.1259(2) | 0.0340                  |
| C(8)  | 0.9620(2)  | 0.3684(2)  | −0.1894(1) | 0.0300                  |
| C(9)  | 0.9087(2)  | 0.2826(2)  | −0.1791(1) | 0.0317                  |
| C(10) | 0.8488(2)  | 0.2656(1)  | −0.1055(1) | 0.0264                  |

ing system are shown in Fig. 1. The fractional atom co-ordinates are given in Table 4 with selected bond angles and lengths in Table 5. The structure of **10** consists of zig-zag chains of molecules held together mainly by inter-monomer Sn–thione–S ( $\text{Sn}(\text{S}(5^1)) = 3.139(1) \text{ \AA}$ ) bonding but also by weak intermolecular  $\text{S} \cdots \text{S}$  interactions within the chains, at separations less than the sum of the van der Waals radii (Fig. 2). These  $\text{S} \cdots \text{S}$  interactions involve  $\text{S}(5^1) \cdots \text{S}(2) = 3.315(2)$  and  $\text{S}(3^1) \cdots \text{S}(2) = 3.446(2) \text{ \AA}$ . The  $\text{Sn}(\text{S}(5^1))$  bond length is appreciably longer than that of a normal Sn–S single bond (ca.  $2.4 \text{ \AA}$ ), but is well within the sum of the van der Waals radii. The appropriate van der Waals radii are taken to be 2.20 and  $1.85 \text{ \AA}$  for Sn and S respectively. Further and weaker  $\text{S} \cdots \text{S}$  interactions ( $\text{S}(5^1) \cdots \text{S}(1^1) = 3.635 \text{ \AA}$ ) link the chains into a three-dimensional framework. The tin centre has a distorted trigonal bipyramidal geometry, with the equatorial sites occupied by the organic groups and one of the dithiolate sulphur atoms, S(2) ( $\text{Sn}(\text{C}) = 2.111(5)$  and  $2.134(2) \text{ \AA}$ ;  $\text{Sn}(\text{S}(2)) = 2.437(1) \text{ \AA}$ ). The other dithiolate

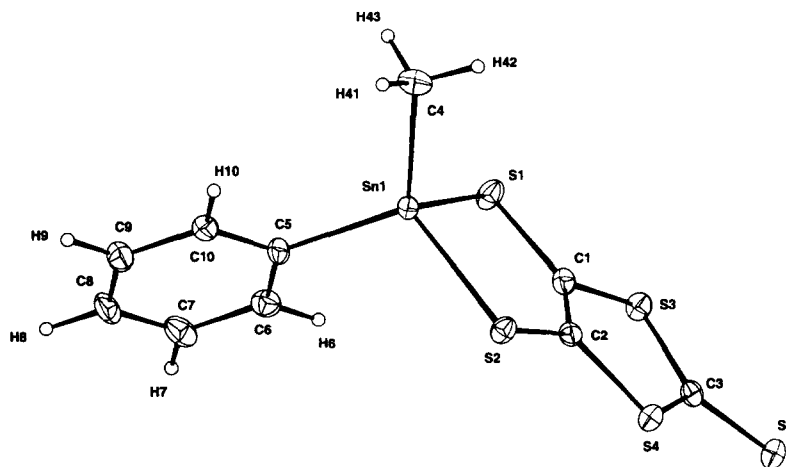


Fig. 1. Atom arrangement and numbering system for **10**.

Table 5  
Selected bond lengths (Å) and angles (deg) for **10**<sup>a</sup>

|                                          |           |                            |          |
|------------------------------------------|-----------|----------------------------|----------|
| Sn–S(1)                                  | 2.487(1)  | Sn–S(2)                    | 2.437(1) |
| Sn–C(4)                                  | 2.115(4)  | Sn–C(5)                    | 2.134(2) |
| S(1)–C(1)                                | 1.745(4)  | S(2)–C(2)                  | 1.747(4) |
| S(3)–C(1)                                | 1.749(4)  | S(3)–C(3)                  | 1.724(4) |
| S(4)–C(2)                                | 1.747(4)  | S(4)–C(3)                  | 1.720(4) |
| S(5)–C(3)                                | 1.668(4)  | C(1)–C(2)                  | 1.353(5) |
| Sn–S(5 <sup>1</sup> )                    | 3.139(1)  |                            |          |
| S(1)–Sn–S(2)                             | 89.91(3)  | S(1)–C(1)–C(2)             | 128.3(3) |
| S(1)–Sn–C(4)                             | 107.1(1)  | S(3)–C(1)–C(2)             | 115.2(3) |
| S(2)–Sn–C(4)                             | 121.3(1)  | S(2)–C(2)–S(4)             | 117.0(2) |
| S(1)–Sn–C(5)                             | 105.41(7) | S(2)–C(2)–C(1)             | 126.7(3) |
| S(2)–Sn–C(5)                             | 112.45(8) | S(4)–C(2)–C(1)             | 116.3(3) |
| C(4)–Sn–C(5)                             | 115.8(1)  | S(3)–C(3)–S(5)             | 125.1(2) |
| Sn–S(1)–C(1)                             | 96.6(1)   | S(4)–C(3)–S(5)             | 121.9(2) |
| Sn–S(2)–C(2)                             | 98.4(1)   | Sn–C(5)–C(6)               | 120.2(1) |
| C(1)–S(3)–C(3)                           | 97.9(2)   | Sn–C(5)–C(10)              | 119.8(1) |
| C(2)–S(4)–C(3)                           | 97.6(2)   |                            |          |
| S(1)–C(1)–S(3)                           | 116.4(2)  | S(3)–C(3)–S(4)             | 113.0(2) |
| S(1)–Sn–S(5 <sup>1</sup> )               | 161.53(3) | S(2)–Sn–S(5 <sup>1</sup> ) | 71.73(3) |
| S(5 <sup>1</sup> )–Sn–C(4)               | 83.6(1)   | S(5 <sup>1</sup> )–Sn–C(5) | 82.19(7) |
| Sn–S(5 <sup>1</sup> )–C(3 <sup>1</sup> ) | 113.1(1)  |                            |          |

<sup>a</sup> Symmetry:  $\frac{1}{2}x, -\frac{1}{2}y, \frac{1}{2}z$ .

sulphur atom, S(1), and the thione sulphur atom are in the axial sites (Sn–S(1) = 2.487(1) Å, S(1)–Sn–S(5<sup>1</sup>) = 161.63(3)°]. The bite angle of the dmit ligand in **10** is 89.92(4)°. As expected, the axial Sn–S(dithiolate) bond is longer than the equatorial Sn–S bond; the corresponding values [8] in **2** are 2.622(3) and 2.451(3) Å while the Sn–S bond length [9] in six-coordinate **3** is 2.471(2) Å.

Organotin co-ordination to the S atoms of C=S-containing ligands has been reported in aggregated Ph<sub>3</sub>Sn–NCS (Sn–S = 2.904(4) Å) [22], in [Me<sub>2</sub>SnCl<sub>2</sub>(2(H)-pyridinethione)<sub>2</sub>] (Sn–S = 2.729(2) Å) [23] and in *trans*–[(H<sub>2</sub>C=CH)<sub>2</sub>SnCl<sub>2</sub>(S=CNHCH=CHNH)<sub>2</sub>] (Sn–

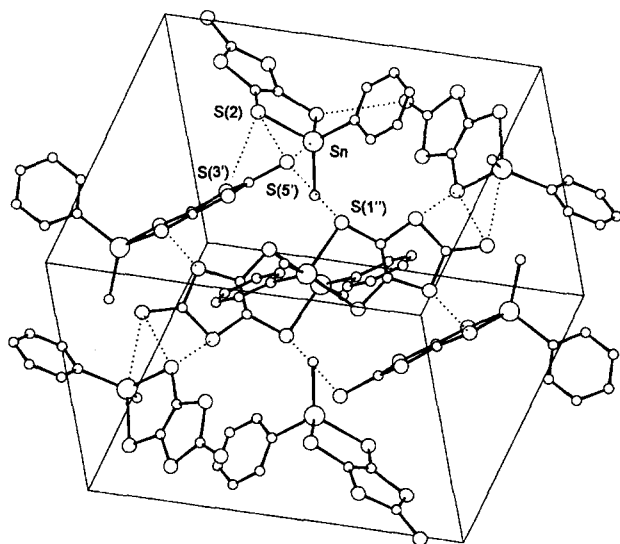


Fig. 2. Intermolecular interactions and packing arrangement in **10**.

S = 2.733(1) Å) [24]. All these Sn–S(=C) bonds appear to be stronger than that found in **10**.

Crystal structures have been determined [20,21,25] for some R<sub>2</sub>Sn(edt) compounds (**12**, R = Me, Bu or <sup>t</sup>Bu). Intermolecular associations result for (**12**), (R = Me or Bu), but not for (**12**) (R = <sup>t</sup>Bu), where the bulky <sup>t</sup>Bu groups prevent associations. The intermolecular Sn–S bond length in (**12**) (R = Me), which contains a penta-co-ordinated tin centre, is 3.18 Å, while in (**12**), (R = Bu), which contains a hexa-co-ordinate tin centre, it is 3.69 Å. These intermolecular Sn ⋯ S interactions in (**12**), (R = Me or Bu) are weaker than in **10**.

#### 4.4. Spectroscopic studies

The ν(C=S) absorptions in the IR spectra of R<sub>2</sub>Sn(dmit), in KBr discs or nujol mulls, occur within the regions 1011 to 1034 and 1054 to 1069 cm<sup>−1</sup>. The values of δ<sup>13</sup>C(C=S) in the solution <sup>13</sup>C NMR spectra of R<sub>2</sub>Sn(dmit) are found in the region 209.2 to 211.4 ppm. Acetone was generally used as the solvent for the NMR work as its use allowed reasonably concentrated solutions to be obtained. However, it is an effective co-ordinating solvent and can complex with the R<sub>2</sub>Sn(dmit), e.g. as found with the donors, DMF and pyridine, (see later). Solution <sup>119</sup>Sn NMR spectra of **7** and **8** were also obtained in the non-co-ordinating solvent, CD<sub>2</sub>Cl<sub>2</sub>, see Table 6. The similarity of the solution δ<sup>119</sup>Sn values for **8** in acetone and CD<sub>2</sub>Cl<sub>2</sub> suggests similar co-ordination environments at tin in the two solvents. The difference in the δ<sup>119</sup>Sn values for **7** in the two solvents, however, indicates differences in the tin co-ordination.

Solid state <sup>119</sup>Sn NMR spectra have also been obtained for compounds **6**, **7**, **8** and **10**; details are displayed in Table 6. Several δ<sup>119</sup>Sn values were recorded in the solid state spectrum of a sample of pure **6**, in contrast to the single value indicated for the same sample in acetone solution. Further investigation of the solid state structure(s) of **6** is currently underway.

The magnitude of the difference between the δ<sup>119</sup>Sn values in CD<sub>2</sub>Cl<sub>2</sub> solution and in the solid state (Δδ<sup>119</sup>Sn = 41.2 ppm) for **6** suggests differences in the structures in the two phases. The δ<sup>119</sup>Sn values indicate the structure of **8** changes little on dissolution in CD<sub>2</sub>Cl<sub>2</sub> or (D<sub>3</sub>C)<sub>2</sub>CO.

Table 6  
Values of δ<sup>119</sup>Sn for RR<sup>1</sup>Sn (dmit)

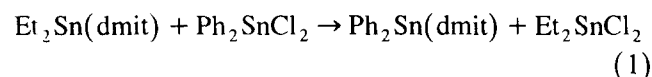
| Compound  | Solution<br>(Me <sub>2</sub> CO – d <sub>6</sub> ) | Solution<br>(CD <sub>2</sub> Cl <sub>2</sub> ) | Solid state           |
|-----------|----------------------------------------------------|------------------------------------------------|-----------------------|
| <b>6</b>  | 165.6                                              |                                                | 153.6; 127.4<br>121.3 |
| <b>7</b>  | 161.5                                              | 128.1                                          | 86.9                  |
| <b>8</b>  | −24.8                                              | −24.4                                          | −51.6                 |
| <b>10</b> | 75.2                                               |                                                | 94.9                  |

#### 4.5. Reactions of $R_2Sn(dmit)$

Ligands L (e.g. L = py, DMF or 2,2'-bipy) and halide ions,  $X^-$  can add to  $R_2Sn(dmit)$  to form  $[R_2Sn(dmit)L]$  and  $[R_2Sn(dmit)X]^-$  ions respectively. Representative  $[R_2Sn(dmit)L]$  compounds isolated from interaction of  $[R_2Sn(dmit)]$  with L are  $[Me_2Sn(dmit)py]$ ,  $[Ph_2Sn(dmit)DMF]$  and  $[Ph_2Sn(dmit)bipy]$ . Complexation of other diorganotin dithiolates, **11–13**, by N-donors (e.g. py or phen) have been previously reported [19]; 1:1 adducts were formed, in these cases too. Onium halides,  $[Q]X$ , e.g. 1,4- $Me_2$ -pyridinium iodide and  $[NEt_4]Br$ , react with  $Ph_2Sn(dmit)$  to give isolable salts,  $[Q][Ph_2Sn(dmit)X]$ , see Table 2. Similar reactions have been reported for other diorganotin dithiolates [26], e.g. (**12**) ( $R = Ph$ ) with  $[NEt_4]Cl$ .

Such interactions between  $QX$  and  $R_2Sn(dmit)$  could also be detected directly in solution by  $^{119}Sn$  NMR spectroscopy, Table 2. The  $\delta$   $^{119}Sn$  values recorded for the  $QX-R_2Sn(dmit)$  systems may not be values for complete formation of  $[R_2Sn(dmit)X]^-$ , but rather reflect the average values for rapidly equilibrating  $R_2Sn(dmit)$  and  $[R_2Sn(dmit)X]^-$  species.

Exchange reactions occur between  $R_2Sn(dmit)$  and  $R_2SnCl_2$  in solution, e.g. Eq. 1.



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