Diphenyl(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S')plumbane at 295 K and diphenyl(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S')stannane at 150 K

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Molecules of diphenyl(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S')plumbane, $[Pb(C_3S_5)(C_6H_5)_2]$, are linked into sheets *via* two intermolecular $Pb\cdots S_{thione}$ interactions of 3.322 (4) and 3.827 (4) Å; the Pb centre has a distorted octahedral geometry. In contrast, molecules of diphenyl(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S')stannane, $[Sn(C_3S_5)(C_6H_5)_2]$, are linked into chains *via* a single intermolecular $Sn—S_{thione}$ interaction of 2.8174 (9) Å; the Sn centre has a distorted trigonal-bipyramidal geometry.

Comment

While structures of various neutral diorganotin 1,2-dithiolates, (I), are listed in the Cambridge Structural Database (Allen & Kennard, 1993) at the chemical database service of the EPSRC (Fletcher *et al.*, 1996), there are no entries for diorganolead derivatives, (II). In order to compare related diorganolead– and diorganotin–1,2-dithiolate complexes, the structures of diphenyl(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S')lead, $Ph_2Pb(dmit)$, (III), and of diphenyl(2-thioxo-1,3-dithiole-4,5-dithiolato-S,S')tin, $Ph_2Sn(dmit)$, (IV), have been determined.
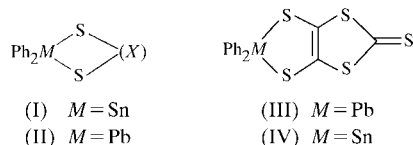
The two compounds are isostructural in the sense that they crystallize in the same space group and the atomic coordinates and cell dimensions are similar. However, the two molecules exhibit differences in the geometries at the metal-atom centre and in the intermolecular interactions. The atom-labelling

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schemes for (III) and (IV) are shown in Figs. 1 and 2, respectively, and selected geometric parameters are listed in Table 2.

Molecules of (III) are linked into sheets *via* secondary $Pb\cdots S_{thione}$ intermolecular interactions $[Pb\cdots S5^i$ 3.322 (4) Å and $Pb\cdots S5^{ii}$ 3.827 (4) Å; symmetry codes: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $z - \frac{1}{2}$; (ii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, z; Fig. 3(*a*)]. Thus, the Pb centre is six-coordinate, with a distorted octahedral geometry, as shown by the bond angles at Pb (Table 2). The chelate bite angle is 87.33 (11)°. The secondary $Pb\cdots S$ bonds are considerably longer than the primary and intramolecular $Pb\cdots S$ bonds [2.561 (4) and 2.591 (4) Å], but are both within the van der

Figure 1
The asymmetric unit of (III), with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii [symmetry codes: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $z - \frac{1}{2}$; (ii) $x - \frac{1}{2}$, $y - \frac{1}{2}$, z].
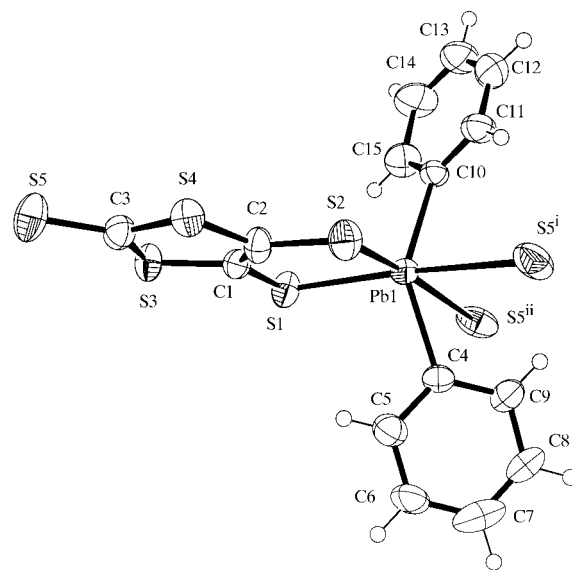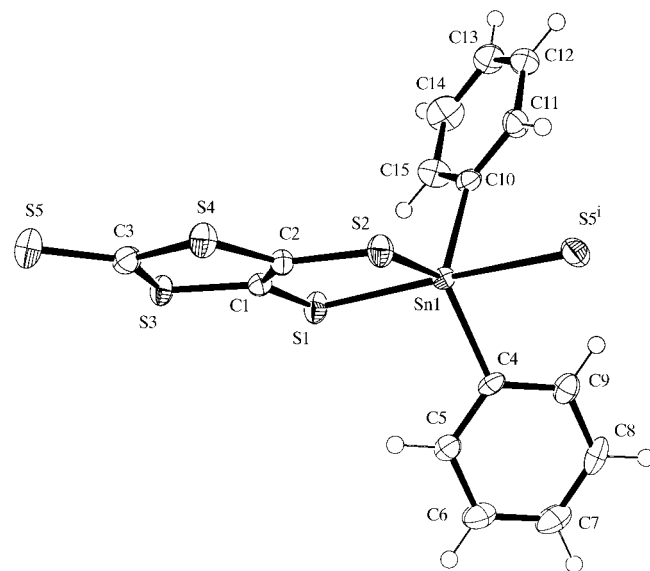

Figure 2
The asymmetric unit of (IV), with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii [symmetry code: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $z - \frac{1}{2}$].

Waals radii sum of 4.14 Å for Pb and S. The shorter Pb···S5[i] bond links molecules into zigzag chains, while the longer Pb···S5[ii] bond links the chains into sheets. S···S separations [S2···S5[i] 3.515 (6) Å], at just less than the van der Waals radii sum of 3.60 Å, further augment the chain formation.

The six-coordinate structure of (III) has similiarities with that of molecule *B* in monoclinic Et$_2$Sn(dmit) (Allan *et al.*, 2001), in which the Sn centre forms one secondary bond [Sn···S 3.555 (2) Å] and a much longer second Sn···S contact at 3.927 (2) Å, the latter being just within the van der Waals radii sum of 4.05 Å.

In contrast with (III), molecules of (IV) are solely linked into chains *via* a single secondary Sn···S$_{thione}$ intermolecular interaction [Sn···S5[i] 2.8174 (9) Å; Fig. 3(*b*)]. The next shortest Sn···S[ii] separation is at a distance of 4.7683 (10) Å, which is much longer than the sum of the van der Waals radii of 4.05 Å for Sn and S. Thus, the Sn centre in (IV) is five-coordinate, with a distorted trigonal-bipyramidal geometry (Fig. 2). The degree of distortion along the pathway from trigonal bipyramidal toward square planar is calculated to be 33%, using the τ parameter of Addison *et al.* (1984), or 23%, using the Berry pseudorotational coordinate of Holmes (1984). The axial sites are occupied by the intermolecular thione S and S1 atoms [Sn—S1 2.5327 (9) Å]. The equatorial Sn—S2 bond length is shorter, as expected, at 2.4547 (10) Å. *PLATON* (Spek, 1994) recognized the two hydrogen bonds in (IV) (Table 1).

Compound (IV) has a similar chain structure to those reported for orthorhombic Et$_2$Sn(dmit), Me$_2$Sn(dmit) and PhMeSn(dmit) (Allan *et al.*, 2001; Doidge-Harrison, Irvine, Khan *et al.*, 1996), although both Et$_2$Sn(dmit) and Me$_2$Sn(dmit) also possess interchain S···S interactions of less than 3.60 Å (Allan *et al.*, 2001), while neither PhMeSn(dmit) (Doidge-Harrison, Irvine, Khan *et al.*, 1996) nor (IV) exhibit these interactions. Comparisons of selected geometric parameters of the four compounds are shown in Table 3. The variations in the intermolecular Sn—S$_{thione}$ bond lengths follow from no obvious steric or electronic property of the organic groups. There are also significant differences in the molecular C—Sn—C and the intermolecular C=S···Sn angles in the four compounds.

(*a*)

(*b*)
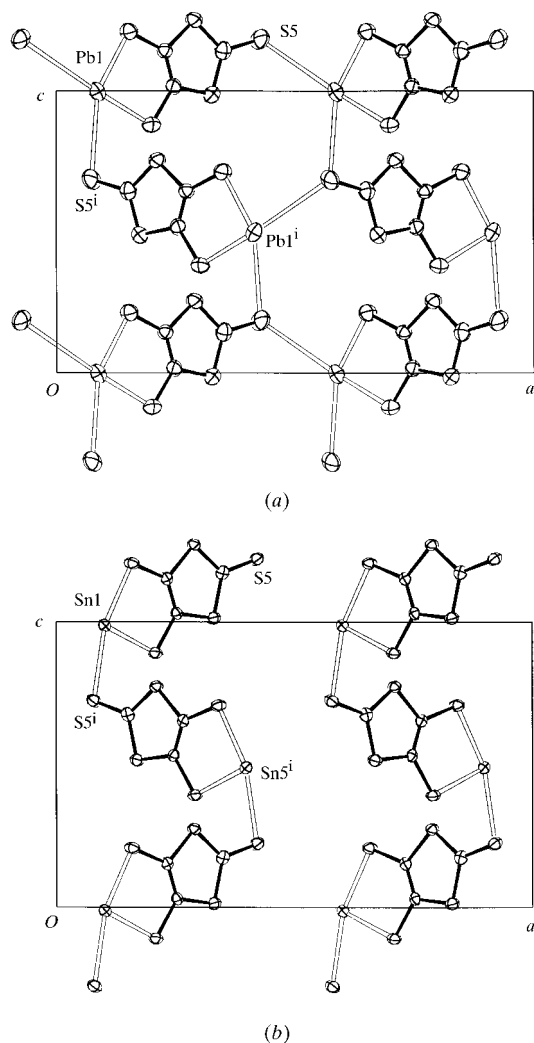
Figure 3
Projection of the structures of (III) and (IV) down [010], showing the formation of (*a*) a two-dimensional sheet and (*b*) a one-dimensional chain [symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$]. Phenyl groups have been omitted for clarity.

Experimental

Compounds (III) (Doidge-Harrison, Irvine, Spencer *et al.*, 1996) and (IV) (Doidge-Harrison, Irvine, Khan *et al.*, 1996) were prepared by published routes and recrystallized from EtOH. Crystals of (III) formed as very thin plates and data were collected at room temperature; consequently, the data for (III) were of poorer quality than those for (IV), which were collected at 150 K on larger crystals.

Compound (III)

Crystal data

[Pb(C$_3$S$_5$)(C$_6$H$_5$)$_2$]	Mo $K\alpha$ radiation
$M_r = 557.73$	Cell parameters from 4683
Orthorhombic, $Pna2_1$	reflections
$a = 17.5109$ (9) Å	$\theta = 2.3$–30.1°
$b = 9.5222$ (5) Å	$\mu = 10.40$ mm^{-1}
$c = 10.3232$ (5) Å	$T = 295$ (2) K
$V = 1721.31$ (15) Å^3	Plate, dark red
$Z = 4$	$0.25 \times 0.18 \times 0.02$ mm
$D_x = 2.152$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	5088 independent reflections
	3310 reflections with $I > 2\sigma(I)$
φ/ω scans	$R_{int} = 0.10$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$\theta_{max} = 32.5°$
	$h = -26 \rightarrow 26$
$T_{min} = 0.181$, $T_{max} = 0.819$	$k = -14 \rightarrow 12$
16 869 measured reflections	$l = -12 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 8.9418P]$
$wR(F^2) = 0.140$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
5088 reflections	$\Delta\rho_{max} = 1.89$ e Å^{-3}
190 parameters	$\Delta\rho_{min} = -2.04$ e Å^{-3}
H-atom parameters constrained	Absolute structure: (Flack, 1983)
	Flack parameter = 0.015 (14)

Compound (IV)

Crystal data

$[Sn(C_3S_5)(C_6H_5)_2]$
$M_r = 469.23$
Orthorhombic, $Pna2_1$
$a = 17.3574 (5)$ Å
$b = 9.2270 (2)$ Å
$c = 10.3775 (2)$ Å
$V = 1662.03 (7)$ Å^3
$Z = 4$
$D_x = 1.875$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6500
  reflections
$\theta = 2.9$–$27.5°$
$\mu = 2.15$ mm^{-1}
$T = 150 (2)$ K
Needle, orange–red
$0.48 \times 0.10 \times 0.06$ mm

Data collection

Nonius KappaCCD area-detector
  diffractometer
φ/ω scans
Absorption correction: empirical
  (*SORTAV*; Blessing, 1995, 1997)
  $T_{min} = 0.425$, $T_{max} = 0.882$
11 483 measured reflections

3622 independent reflections
3405 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.5°$
$h = -22 \rightarrow 19$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.061$
$S = 1.08$
3622 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -1.25$ e Å^{-3}
Absolute structure: (Flack, 1983)
Flack parameter = $-0.004 (19)$

Table 1
Hydrogen-bonding geometry (Å, °) for (IV).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5$\cdots$S1	0.95	2.84	3.434 (4)	122
C11—H11$\cdots$S5^i	0.95	2.70	3.401 (4)	131

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$.

Table 2
Selected geometric parameters for (III) and (IV) (Å, °).

	(III) (M = Pb) at 295 K	(IV) (M = Sn) at 150 K
$M-$C4	2.185 (10)	2.138 (3)
$M-$C10	2.210 (10)	2.135 (3)
$M-$S1	2.591 (4)	2.5327 (9)
$M-$S2	2.561 (4)	2.4547 (10)
$M-$S5^i	3.322 (4)	2.8174 (9)
$M-$S5^{ii}	3.827 (4)	
S1—M1—S2	87.33 (11)	88.06 (3)
C4—M1—S1	98.5 (5)	94.72 (5)
C10—M1—S1	103.3 (3)	100.38 (10)
C4—M1—S2	110.2 (4)	124.49 (8)
C10—M1—S2	104.5 (3)	113.34 (9)
C4—M1—C10	139.6 (4)	120.47 (11)
C4—M1—S5^i	80.5 (5)	88.74 (9)
C10—M1—S5^i	91.3 (4)	90.77 (11)
S1—M1—S5^i	157.32 (11)	164.51 (3)
S2—M1—S5^i	72.07 (12)	77.59 (3)
C4—M1—S5^{ii}	67.7 (4)	
C10—M1—S5^{ii}	78.5 (3)	
S2—M1—S5^{ii}	176.61 (11)	
S1—M1—S5^{ii}	90.44 (11)	
S5^i—M1—S5^{ii}	109.68 (6)	
C3^i—S5^i—M1	108.4 (5)	106.11 (12)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Table 3
Comparison of selected parameters in five-coordinate $R_2Sn(dmit)$ compounds (Å,°).

Compound	Intermolecular Sn—S	C=S—Sn	C—Sn—C	T (K)
Me$_2$Sn(dmit)^a	3.001 (2)	116.4 (3)	126.3 (3)	150
	2.960 (2)	114.1 (3)	119.5 (5)	
Et$_2$Sn(dmit)^a	3.037(4)	112.1(5)	128.7(8)	295
orthorhombic^a	3.0083(15)	111.1(2)	130.8(2)	150
MePhSn(dmit)^b	3.139 (1)	113.1 (1)	115.8 (1)	295
Ph$_2$Sn(dmit)^c	2.8174 (9)	106.11 (12)	120.47 (11)	150

Notes: (a) Allan *et al.* (2001); (b) Doidge-Harrison, Irvine, Khan *et al.* (1996); (c) this work.

All H atoms were placed in geometrical positions and refined using a riding model, with C—H = 0.93–0.95 Å. The number of Friedel-related reflections for each compound was 1825 for (III) and 1623 for (IV).

For compound (III), data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*. For compound (IV), data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For both compounds, program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL* (McArdle, 1994, 2000) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1047). Services for accessing these data are described at the back of the journal.

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