

6,6-Diphenyl-6,7-dihydro-5*H*-1,3,4,8-tetrathia-6-stannazulene-2-thione and 6,6'-spirobi[6,7-dihydro-5*H*-1,3,4,8-tetrathia-6-stannazulene]-2,2'-dithione

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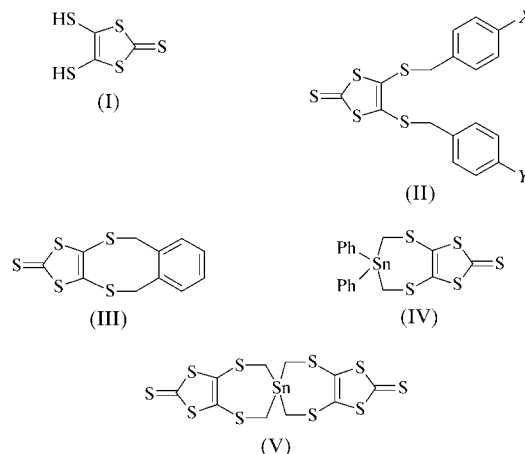
The title compounds, $[\text{Sn}(\text{C}_6\text{H}_5)_2(\text{C}_5\text{H}_4\text{S}_5)]$ and $[\text{Sn}(\text{C}_5\text{H}_4\text{S}_5)_2]$, respectively, are of interest because they can be regarded as intermediate in nature between chelates and heterocyclic compounds containing the C_3S_5 fragment. In contrast with the essentially normal bond lengths and angles within the molecules, the molecular conformations are somewhat unexpected, as are the intermolecular contacts found in the case of the latter compound.

Comment

A search of the Cambridge Structural Database (CSD, Version 5.22; Allen & Kennard, 1993) readily demonstrates that the dianion $\text{C}_3\text{S}_5^{2-}$, often designated dmit, resulting from deprotonation of the parent 1,3-dithiole-2-thione-4,5-dithiol, (I), is well known as a bidentate ligand which bonds through the exocyclic thiol S atom to form, usually anionic, chelate complexes with transition metals and main group elements. In the particular case of Sn, used as an example, other ligating species may be present along with dmit, yielding either charged, $[\text{R}_2\text{SnX}(\text{dmit})]^-$ (*R* is Me, Et, Ph, etc. and *X* is a halide), or neutral species, e.g. $[\text{R}_2\text{Sn}(\text{dmit})]$ (CSD reference Nos. 154944–154947; Allan *et al.*, 2001, and references therein). The dmit moiety is also found as a fragment in heterocyclic compounds such as the benzyl derivatives (II) (*X* and *Y* are MeO and NO_2 ; Chohan *et al.*, 1999) and 5*H*,10*H*-dithiolo[2,3-*b*]-2,5-benzodithiocine-2-thione, (III) (Chohan *et al.*, 2000).

Interest in 6,6-diphenyl-6,7-dihydro-5*H*-1,3,4,8-tetrathia-6-stannazulene-2-thione, (IV) (Fig. 1), and 6,6'-spirobi[6,7-dihydro-5*H*-1,3,4,8-tetrathia-6-stannazulene]-2,2'-dithione, (V) (Fig. 2), is primarily in their chemical and structural situation,

which falls somewhere between the true chelates, such as the $[\text{Sn}(\text{dmit})_3]^{2-}$ dianion (de Assis *et al.*, 1999), and heterocyclic compounds, such as (III).



The bond distances and angles involving Sn in (IV) and (V) are given in Tables 1 and 2, respectively. In (IV), the Sn atom is in a comparatively regular tetrahedral environment unperturbed by intermolecular interactions. In (V), however, with the inclusion of the intermolecular $\text{Sn1} \cdots \text{S5}^i$ contact of 3.7788 (9) Å, the Sn atom is five-coordinate in a highly distorted trigonal-bipyramidal environment, with atoms S5^i and C6 axial and atoms C1, C2 and C7 equatorial [symmetry code: (i) $-x, 1 - y, 2 - z$]. This contact is only *ca* 0.27 Å less than the sum of the van der Waals radii for Sn and S [4.05 Å (Huheey *et al.*, 1993) or 4.06 Å (PLATON; Spek, 1990)], has comparatively little effect on the C–Sn–C angles [105.46 (18)–114.51 (16)°, still closely grouped around the ideal tetrahedral value] and, although given some credibility by the C6–Sn1– S5^i *trans* axial angle of 174.96 (13)°, which is close to the ideal for a trigonal-bipyramidal arrangement, is perceived as an extremely weak interaction. If, however, it is regarded as significant, it represents, to our knowledge, the first case of a tetraorganotin compound with a coordination number greater than four as a consequence of an intermolecular interaction with a soft, S, donor. In contrast, while some five- (e.g. Tzschach & Jurkschat, 1986; Das, Mun, Wei, Blunden & Mak, 1987; Jousseau *et al.*, 1988; Jastrzebski *et al.*, 1991; Doidge-Harrison *et al.*, 1993; Willem *et al.*, 1994; Kayser *et al.*, 1994) and even six-coordinate (Das, Mun, Wei & Mak, 1987) tetraorganotin compounds have been reported, invariably these are intramolecular and involve, almost exclusively, O- or N-donor groups suitably sited in fairly rigid molecules. It seems that the α -dmit groups in (V) effectively reduce the electron density at the Sn centre, at the same time enhancing the thione $\text{S10} \cdots \text{S10}^{ii}$ intermolecular interaction noted below.

The remaining bond lengths and angles in (IV) and (V) (Table 3) show few unusual features. In particular, the geometry of the dmit (C_3S_5) fragment within these compounds is much the same as it is in related chelate and heterocyclic compounds, such as those noted above. One feature, however, is the similarity between the Sn1–C1–S1–C3 and Sn1–

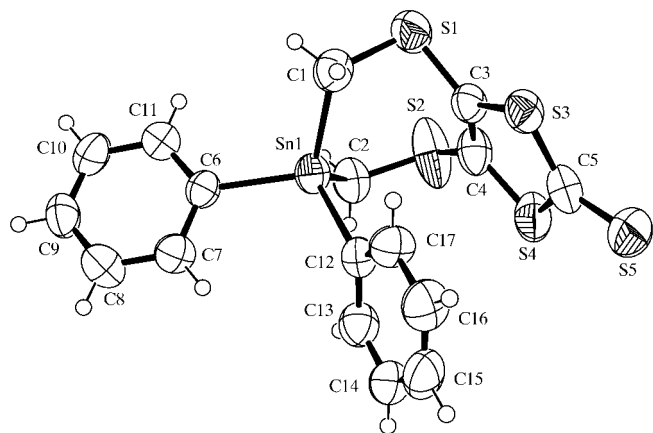


Figure 1
The molecule of (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

C2–S2–C4 torsion angles in (IV) and the corresponding angles of one stannazulene of (V) but not the other, *i.e.* with (Vb) but not with (Va) [(Va) is the moiety C1/S1/C3/S3/C5/S5/S4/C4/S2/C2, and (Vb) is the moiety C6/S6/C8/S8/C10/S10/S9/C9/S7/C7].

There is also a degree of interest in the conformation of the molecules. In both compounds, the stannazulene rings are boat-shaped relative to the basal fragment comprising atoms C1, C2, S1 and S2 [or the equivalent in the second stannazulene ring of (V)], and thus are perceived as U-shaped when seen side on. This is exactly the same as the situation in the α and β forms of (III), whose molecular conformations were investigated and confirmed as optimum by molecular mechanics calculations (Chohan *et al.*, 2000). For (IV), this results in the overlap of the C12–C17 phenyl ring with the dithiole ring of the dmit fragment, such that the angle between the least-squares planes is 22.8 (4)°, and for (V), it renders the molecule U-shaped overall.

There are no significant intermolecular interactions in the structure of (IV). The situation in (V) is very different. Here, both thione (S5 and S10) and thiol (S1, S2 and S7) S atoms

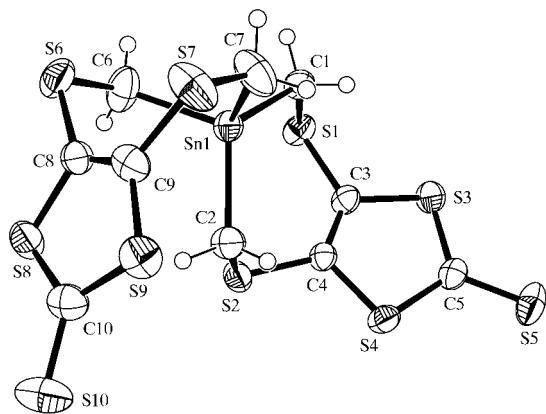


Figure 2
The molecule and labelling scheme for (V). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

participate in intermolecular Sn \cdots S or S \cdots S interactions, with interatomic distances less than the corresponding sums of the van der Waals radii. The Sn1 \cdots S5ⁱ contacts alluded to above interconnect the molecules to form centrosymmetric dimers, and then S10 \cdots S10ⁱⁱ contacts of 3.328 (2) Å interconnect the dimers to form zigzag chains parallel to [10 $\bar{1}$] (Fig. 3) [symmetry code: (ii) 1 – x, 1 – y, 1 – z]. This last (S10 \cdots S10ⁱⁱ)

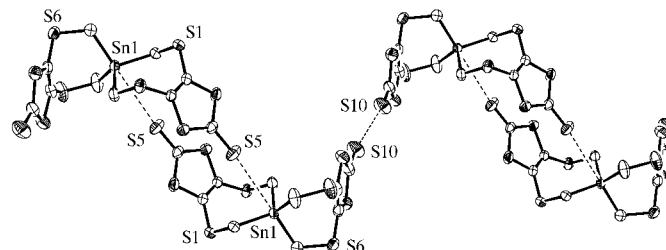


Figure 3
A portion of a zigzag chain of molecules of (V). Selected atoms are labelled in a generic manner and dashed lines represent intermolecular contacts. H atoms have been omitted for clarity.

is, to our knowledge, the shortest, and presumably strongest, interaction of this specific type so far identified. Additional weaker S \cdots S contacts, such as S2 \cdots S7ⁱⁱⁱ [3.4724 (12) Å] and S5 \cdots S1^{iv} [3.4122 (13) Å], interconnect the chains and complete the three-dimensional connectivity of the structure [symmetry codes: (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $-x - \frac{1}{2}, y + \frac{1}{2}, \frac{3}{2} - z$].

Experimental

Ph₂Sn(CH₂I)₂ and Sn(CH₂I)₄ (Burnett *et al.*, 1998), and [NEt₄]₂[Zn(dmit)₂], where dmit is the (C₅S₅)²⁻ anion (Doidge-Harrison *et al.*, 1996), were prepared according to published procedures. The title compounds were obtained from reactions of [NEt₄]₂[Zn(dmit)₂] (0.286 g, 0.4 mmol) with either Ph₂Sn(CH₂I)₂ (0.445 g, 0.8 mmol), for (IV), or Sn(CH₂I)₄ (0.274 g, 0.4 mmol), for (V), in refluxing Me₂CO (20 ml). After refluxing for 1 h, the reaction mixtures were cooled and rotary evaporated. The products were isolated from the residues after several recrystallizations from ethanol, as dark-red-brown crystalline solids. Analysis for (IV), m.p. 393–398 K (decomposition); ¹H NMR (250 MHz, CDCl₃, δ , p.p.m.): 2.89 [s, 4H, $J(^{119,117}\text{Sn}-^1\text{H}) = 33$ Hz, CH₂], 7.40–7.46 (*m*, 10H, aryl); ¹³C NMR (63 MHz, CDCl₃, δ , p.p.m.): 15.3 [$J(^{119,117}\text{Sn}-^{13}\text{C}) = 345$ and 329 Hz, CH₂], 128.8, 129.2, 130.0, 136.1, 142.9 (aryl and C=C); ¹¹⁹Sn NMR (93 MHz, CDCl₃, δ , p.p.m.): –94.8. Analysis for (V), decomposition on heating above 373 K; ¹H NMR (250 MHz, CDCl₃, δ , p.p.m.): 2.84; no Sn coupling detected; ¹¹⁹Sn NMR (93 MHz, C₆D₆, δ , p.p.m.): –30.

Compound (IV)

Crystal data

[Sn(C₆H₅)₂(C₅H₄S₅)]
M_r = 497.27
 Monoclinic, *P*2₁
a = 8.6706 (5) Å
b = 8.5319 (6) Å
c = 13.3143 (9) Å
 β = 103.8400 (10)°
V = 956.35 (11) Å³
Z = 2

D_x = 1.727 Mg m^{–3}
 Mo *K* α radiation
 Cell parameters from 3614 reflections
 θ = 2.8–25.0°
 μ = 1.88 mm^{–1}
T = 303 (2) K
 Block, dark red-brown
 0.38 × 0.28 × 0.22 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.295$, $T_{\max} = 0.662$
 6046 measured reflections

3107 independent reflections
 2767 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 25.8^\circ$
 $h = -9 \rightarrow 10$
 $k = -10 \rightarrow 9$
 $l = -16 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.118$
 $S = 1.04$
 3107 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 1.2361P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.12 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.58 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983),
 1133 Friedel pairs
 Flack parameter = -0.03 (5)

Table 1

Selected geometric parameters (\AA , $^\circ$) for (IV).

Sn1—C12	2.149 (8)	Sn1—C1	2.152 (10)
Sn1—C6	2.151 (7)	Sn1—C2	2.165 (8)
C12—Sn1—C6	109.0 (3)	C12—Sn1—C2	108.2 (4)
C12—Sn1—C1	112.8 (3)	C6—Sn1—C2	107.8 (3)
C6—Sn1—C1	109.2 (3)	C1—Sn1—C2	109.8 (4)

Compound (V)

Crystal data

$[\text{Sn}(\text{C}_5\text{H}_4\text{S}_5)_2]$
 $M_r = 567.45$
 Monoclinic, $P2_1/n$
 $a = 11.3973$ (4) \AA
 $b = 14.2749$ (5) \AA
 $c = 12.5609$ (5) \AA
 $\beta = 114.6250$ (10) $^\circ$
 $V = 1857.74$ (12) \AA^3
 $Z = 4$

$D_x = 2.029 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 7784 reflections
 $\theta = 2.3\text{--}30.6^\circ$
 $\mu = 2.49 \text{ mm}^{-1}$
 $T = 297$ (2) K
 Rod, dark red—brown
 $0.60 \times 0.25 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.347$, $T_{\max} = 0.780$
 15 205 measured reflections

5312 independent reflections
 4279 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 30.8^\circ$
 $h = -16 \rightarrow 16$
 $k = -10 \rightarrow 19$
 $l = -18 \rightarrow 17$

Table 2

Selected geometric parameters (\AA , $^\circ$) for (V).

Sn1—C7	2.146 (4)	Sn1—C2	2.168 (3)
Sn1—C1	2.151 (3)	Sn1—S5 ⁱ	3.7788 (9)
Sn1—C6	2.157 (3)		
C7—Sn1—C1	106.37 (13)	C6—Sn1—C2	108.73 (16)
C7—Sn1—C6	105.46 (18)	C7—Sn1—S5 ⁱ	70.88 (13)
C1—Sn1—C6	108.40 (13)	C1—Sn1—S5 ⁱ	70.01 (9)
C7—Sn1—C2	114.51 (16)	C6—Sn1—S5 ⁱ	174.96 (13)
C1—Sn1—C2	112.98 (12)	C2—Sn1—S5 ⁱ	76.17 (9)

Symmetry code: (i) $-x, 1 - y, 2 - z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.091$
 $S = 1.01$
 5312 reflections
 190 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 1.0773P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.75 \text{ e } \text{\AA}^{-3}$

Table 3

Comparison of selected bond lengths and angles (\AA , $^\circ$) for (IV) and (V).

	(IV)	(Va)	(Vb) [†]
C1—S1	1.818 (9)	1.822 (3)	1.791 (4)
C2—S2	1.768 (9)	1.813 (3)	1.784 (4)
S1—C3	1.776 (13)	1.754 (3)	1.758 (3)
S2—C4	1.742 (9)	1.759 (3)	1.755 (3)
C3—C4	1.336 (15)	1.342 (4)	1.345 (5)
C3—S3	1.744 (7)	1.744 (3)	1.749 (3)
C4—S4	1.751 (12)	1.741 (3)	1.744 (4)
S3—C5	1.716 (12)	1.717 (3)	1.726 (4)
S4—C5	1.728 (10)	1.726 (3)	1.735 (4)
S5—C5	1.657 (11)	1.650 (3)	1.643 (4)
Sn1—C1—S1	114.4 (5)	115.34 (16)	114.44 (19)
Sn1—C2—S2	118.1 (4)	113.67 (16)	119.35 (19)
C1—S1—C3	100.2 (4)	97.83 (14)	101.69 (17)
C2—S2—C4	105.5 (4)	100.33 (14)	104.44 (16)
S1—C3—S3	116.1 (6)	117.47 (17)	117.5 (2)
S1—C3—C4	126.4 (7)	126.9 (2)	126.4 (3)
S3—C3—C4	117.5 (9)	115.6 (2)	116.1 (3)
S2—C4—S4	119.2 (6)	117.28 (17)	116.9 (2)
S2—C4—C3	126.3 (9)	126.6 (2)	127.1 (3)
S4—C4—C3	114.5 (7)	116.1 (2)	116.0 (3)
C3—S3—C5	97.1 (5)	98.02 (15)	97.74 (17)
C4—S4—C5	98.0 (5)	97.74 (14)	97.75 (17)
S3—C5—S4	112.8 (6)	112.45 (16)	112.5 (2)
S3—C5—S5	123.9 (6)	123.7 (2)	123.8 (2)
S4—C5—S5	123.3 (7)	123.8 (2)	123.8 (2)
Sn1—C1—S1—C3	-43.1 (5)	-75.49 (17)	-39.5 (3)
Sn1—C2—S2—C4	19.8 (8)	71.67 (19)	10.6 (3)

[†] The numerical elements of the atom designations which are directly applicable to (IV) and (Va) are incremented by 5 for application to (Vb).

In the final stages of refinement, H atoms were placed in calculated positions, with C—H = 0.93 and 0.97 \AA for phenyl and methylene H, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{H})$ of the parent atom. Specifically, in (IV), one reflection, *viz.* 001, showing particularly poor agreement, was omitted and comparatively large displacement parameters were associated with atom S2. Refinement with this atom split over two sites was attempted but proved unsuccessful, and it is therefore presumed that the libration is genuine and the bond lengths and angles associated with S2 correspondingly dubious. The maximum residual electron density for (IV) was 0.84 \AA from atom Sn1, while that for (V) was 0.8 \AA from atom Sn1.

For both compounds, data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990) for (IV) and SHELXS97 (Sheldrick 1997) for (V). For both compounds, program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1026). Services for accessing these data are described at the back of the journal.

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