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CRYSTAL AND MOLECULAR STRUCTURES OF SPIRO-BIS(TRITHIASTANNOCANE), $Sn(SCH_2CH_2SCH_2CH_2S)_2$, AND SPIRO-BIS(OXADITHIASTANNOCANE), $Sn(SCH_2CH_2OCH_2CH_2S)_2$. DISTORTION OF THE SnS_4 TETRAHEDRAL COORDINATION PRODUCED BY TRANSANNULAR $Sn\cdots X$ ($X = S, O$) INTERACTIONS

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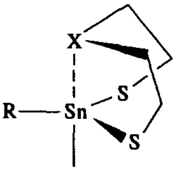
Abstract—The title compounds, prepared from $X(CH_2CH_2SNa)_2$ ($X = S, O$) and $SnCl_4$ were investigated by X-ray diffraction. In both compounds transannular $Sn\cdots X$ interactions in the eight-membered rings produce a distortion of the SnS_4 tetrahedron. This consists of an enlargement of S—Sn—S angle [to 126.1° when X = S and 118.9° (118.4°) when X = O] with simultaneous decrease of the opposite tetrahedral angle [to 93.2° when X = S and 94.4° (93.2°) when X = O]. The coordination geometry in both compounds can be described as based upon a bicapped tetrahedron.

Eight-membered rings of type **1** (1,3-dithia-6-elementa-2-stannocanes, with X = S, O and NR) are known to contain transannular $Sn\cdots X$ secondary interactions, leading to coordination geometries which represent the transition between four-coordinate (tetrahedral) and five-coordinate (trigonal bipyramidal) tin(IV).[1]



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Depending upon the nature of X and also influenced by the nature of R and R′, the coordination geometries of these compounds cover the whole range between the capped tetrahedron (when X = S, R = R′ = Ph)[1a] and trigonal bipyramid (when X = S, R = R′ = Cl).[1b] The compounds with X = O[1c] and NMe,[1e,f] are situated between these two extremes.

Given that transannular $X\cdots Sn$ secondary interactions distort the coordination geometry at tin and formally increase the coordination number of the metal, several questions arise: (1) How would the coordination geometry be influenced in a spiro-bicyclic system containing a heteroatom X in each ring (**2a**, X = S; **2b**, X = O)? (2) Would both heteroatoms participate in a secondary interaction? (3) If they do, will the tin atom achieve an octahedral geometry or how will the natural tetrahedral arrangement of the four primary Sn—S bonds be distorted in the presence of two additional secondary $Sn\cdots S$ interactions?

Two geometries can be anticipated: (a) a *trans*-octahedral geometry (**3**) with four sulphur atoms in the equatorial plane and the two heteroatoms on

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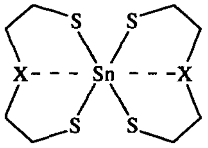
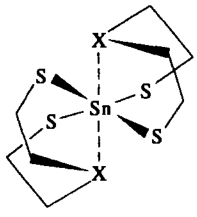


2a X = S
2b X = O

the axis perpendicular to this plane; and (b) a *cis*-octahedral (distorted) geometry (**4**) with four primary Sn—S bonds in a close to tetrahedral arrangement and two additional Sn···X interactions completing the geometry of a distorted octahedron.



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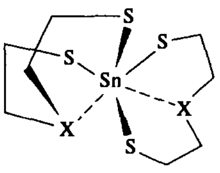

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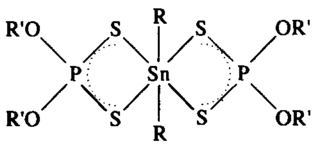
Both types have precedents in the structures of organotin derivatives of 1,1-dithiolato ligands.[2] Thus, an octahedral geometry was found in **5** (R = Ph, R′ = Pr^i)[3] and **6** (R = Me, R′ = Ph),[4] both based upon a regular octahedron, whilst a *cis* arrangement was found in **7**, i.e. $Ph_2Sn[S_2P(OEt)_2]_2$,[5a] $Me_2Sn(S_2PMe_2)_2$,[5b] $Me_2Sn(S_2PEt_2)_2$[5c] or $Me_2Sn(S_2AsMe_2)_2$,[5d] and in other 1,1-dithiolates (dithiocarbamates, xanthates).[2]



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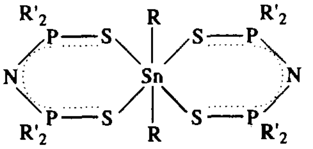

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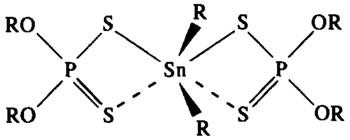

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In order to answer the questions (1)–(3) mentioned above, we prepared the spiro-bicyclic compounds **2a** and **2b** and established their crystal and molecular structures by X-ray diffraction. These two compounds have been mentioned earlier in the literature, as by-products of the reaction of $Sn(OBu)_2$ with $X(CH_2CH_2SH)_2$ (X = O, S)[6a] or of the reaction between $X(CH_2CH_2S)_2Sn$ and dithiols.[6b]

RESULTS AND DISCUSSION

Preparation of compounds **2a** *and* **2b**

Spiro-bis(trithiastannocane) (**2a**)* was obtained in a 40%·yield by reacting tin(IV) chloride with the sodium salt of bis(2-mercaptoethyl)sulphide in benzene:

$$SnCl_4 + 2S(CH_2CH_2SNa)_2 \longrightarrow Sn(SCH_2CH_2SCH_2CH_2S)_2 + 4NaCl. \quad (1)$$
$$\mathbf{2a}$$

In a similar manner, bis(2-mercaptoethyl)ether reacted with tin(IV) chloride to give spiro-bis(oxadithiastannocane) (**2b**):†

$$SnCl_4 + 2O(CH_2CH_2SNa)_2 \longrightarrow Sn(SCH_2CH_2OCH_2CH_2S)_2 + 4NaCl. \quad (2)$$
$$\mathbf{2b}$$

The two compounds are colourless crystalline solids, stable in air and soluble in common organic solvents. The compounds have melting points close to those reported in the literature,[6] and were routinely characterized by ^1H, ^{13}C and ^{119}Sn NMR, mass spectra and IR spectra. The spectra do not exhibit any unusual features and are in agreement with the proposed composition; therefore, they will not be discussed further here.

Molecular structure of **2a**

Spiro-bis(trithiastannocane), $Sn(SCH_2CH_2SCH_2CH_2S)_2$ (**2a**), consists of isolated molecules (Fig. 1) packed in the crystal lattice without significant intermolecular interactions. Important interatomic distances and bond angles are given in Table 1.

In the molecule of **2a**, the tin atom forms four primary Sn—S bonds to S(1), S(3), S(4) and S(6) (average 2.418 Å). Additionally, the two sulphur heteroatoms of the rings, S(2) and S(5), approach

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* *Chemical Abstracts* nomenclature: 1,4,7,9,12,15-hexathia-8-stannaspiro[7.7]pentadecane.

† *Chemical Abstracts* nomenclature: 4,12-dioxa-1,7,9,15-tetrathia-8-stannaspiro[7.7]pentadecane.

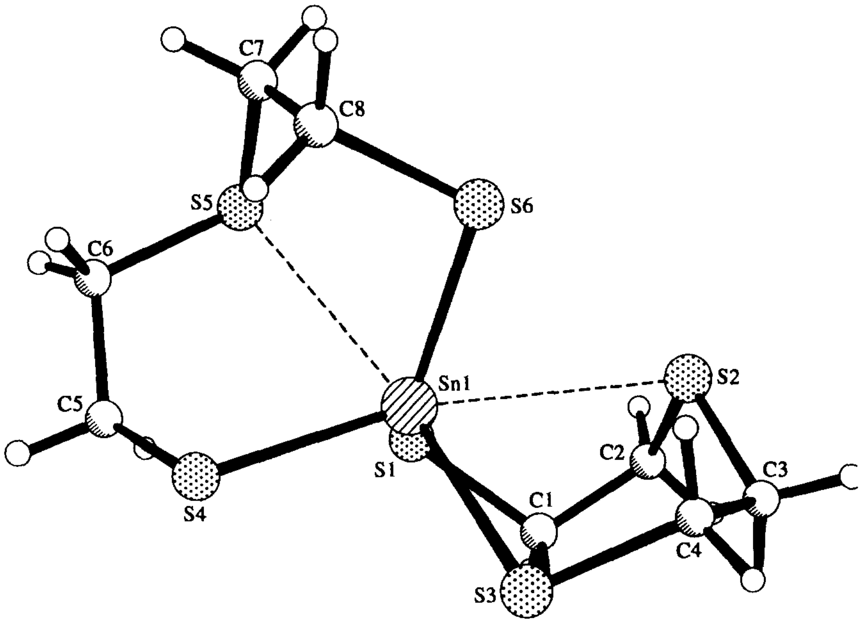


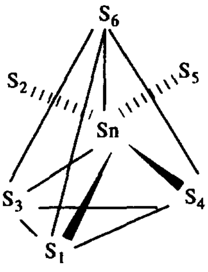
Fig. 1. Molecular structure of compound **2a**.

the tin atom at 3.241 and 3.074 Å, respectively. These interatomic distances are at the middle of the range between the sum of covalent radii (d_{cov} Sn—S = 2.42 Å)[7] and the sum of van der Waals radii (d_{vdW} Sn—S = 4.0 Å),[8] thus indicating significant secondary bonding[9] ("semibonding") interaction.

The coordination geometry around tin can be best described as a bicapped tetrahedron (**8**). The tetrahedron determined by the four primary bonds [Sn—S(1), Sn—S(3), Sn—S(4) and Sn—S(6)] is distorted through the capping of the S(1)—S(6)—S(3) and S(1)—S(6)—S(4) faces by the atoms S(2) and S(5) respectively, as shown in **8**. As

Table 1. Interatomic distances (Å) and bond angles (°) in compound **2a**

Sn—S distances			
Sn(1)—S(1)	2.408(2)	Sn(1)···S(2)	3.241(3)
Sn(1)—S(3)	2.434(2)	Sn(1)···S(5)	3.074(2)
Sn(1)—S(4)	2.424(2)		
Sn(1)—S(6)	2.407(2)		
Tetrahedron edges (non-bonded distances)			
S(1)···S(3)	3.939	S(1)···S(4)	3.898
S(1)···S(6)	4.292	S(3)···S(4)	3.530
S(3)···S(6)	3.856	S(4)···S(6)	3.970
Bond angles			
S(1)—Sn(1)···S(2)	73.00(8)	S(1)—Sn(1)—S(3)	108.90(8)
S(1)—Sn(1)—S(4)	107.54(9)	S(1)—Sn(1)···S(5)	76.47(7)
S(1)—Sn(1)—S(6)	126.08(9)		
S(2)···Sn(1)—S(3)	75.36(8)	S(2)···Sn(1)—S(4)	167.78(11)
S(2)···Sn(1)···S(5)	113.76(7)	S(2)···Sn(1)—S(6)	77.32(8)
S(3)—Sn(1)—S(4)	93.21(9)	S(3)—Sn(1)···S(5)	170.73(10)
S(3)—Sn(1)—S(6)	105.60(9)		
S(4)—Sn(1)···S(5)	77.82(8)	S(4)—Sn(1)—S(6)	110.52(9)
S(5)···Sn(1)—S(6)	75.87(7)		
Sn(1)—S(1)—C(1)	100.5(3)	Sn(1)—S(3)—C(4)	101.9(4)
Sn(1)—S(4)—C(5)	101.7(3)	Sn(1)—C(6)—C(8)	99.6(3)



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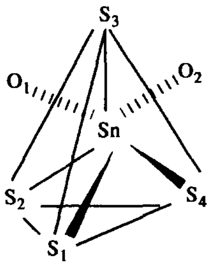
a result the S(1)—S(6) edge, shared by the two capped faces, is subtended by a much enlarged S—Sn—S angle [S(1)—Sn—S(6) = 126.1°] at the expense of the S(3)—Sn—S(4) angle on the opposite side of the tetrahedron. The magnitude of this angle is much diminished compared to the ideal tetrahedral value of 109.5°. Other S—Sn—S bond angles do not deviate more that 4° from the tetrahedral value, and even the endocyclic bond angles are well accommodated by the ligand bite. Consequently, in the tetrahedron, the S(1)—S(6) edge is the largest (4.292 Å) and the S(3)—S(4) edge is the shortest (3.530 Å).

Molecular structure of **2b**

Spiro-bis(oxadithiastannocane), $Sn(SCH_2CH_2OCH_2CH_2S)$ (**2b**), contains two independent molecules in the crystal lattice. These are shown in Fig. 2. Interatomic distances and bond angles are collected in Table 2. The two molecules are very similar and only the one containing Sn(1) will be discussed in more detail here.

Like in **2a**, the tin atom forms a distorted octahedron (**9**) determined by the primary bonds Sn(1)—S(1), Sn(1)—S(2), Sn(1)—S(3) and Sn(1)—S(4). Two faces of the tetrahedron, i.e. S(1)—S(3)—S(2) and S(1)—S(3)—S(4) are capped by two oxygen heteroatoms, O(1) and O(2), situated at a distance from tin of 2.90 and 2.758 Å, respectively. These values are in the middle of the range between the sum of covalent radii (d_{cov} Sn—O = 2.13 Å)[7] and the sum of van der Waals radii (d_{vdW} Sn—O = 3.70 Å),[8] again indicating significant secondary bonding[9] interactions. As a result of oxygen capping, the S(1)—S(3) edge, shared by the two capped faces of the octahedron, is subtended by a broadened S(1)—Sn(1)—S(3) bond angle (118.9°), while the opposite bond angle S(2)—Sn(1)—S(4) is diminished to 94.4°. These are the major deviations from the ideal tetrahedral bond angle, since the other S—Sn—S bond angles suffer only minor changes (*ca* 4° below the tetrahedral value). Consequently, in the tetrahedron, the S(1)—S(3) edge is the longest (4.138 Å) and the S(2)—S(4) edge is the shortest (3.535 Å).



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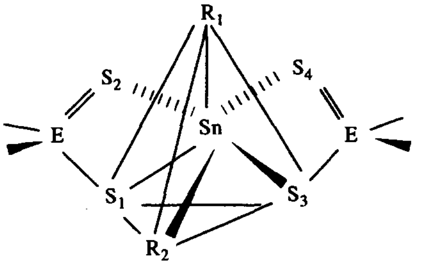
Comparisons with other structures

The molecular geometry in **2a** and **2b** bears certain similarities with the structures of diorganotin derivatives of ansiobidentate 1,1-dithiolates, like dithiocarbamates, xanthates, dithiophosph(in)ates and dithioarsinates (for a review see Ref. 2). We choose to illustrate this relationship by comparing our compounds with the dithiophosph(in)ates and arsinates. The distorted coordination geometry in these compounds (**10**) can best be described as intermediate between tetrahedral (considering only the primary bonds to tin) and octahedral (including the secondary interactions as well).



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The analogy between the coordination geometries under discussion becomes obvious if the R(1)—R(2) edge of the tetrahedron **10** is replaced by the shared edge S(1)—S(6) in **2a** (see **7**) and the S(1)—S(3) in **2b** (see **8**). All three are subtended by the largest bond angle at tin. A smaller S—Sn—S bond angle is then observed on the opposite side of the tetrahedron [S(1)—Sn—S(3) in dithiophosph(in)ates, S(3)—Sn—S(4) in **2a** and S(2)—Sn—S(4) in **2b**]. The secondary bonds, in all three cases, also form large bond angles [S(2)—Sn—S(4) in dithiophosph(in)ates, S(2)—Sn—S(5) in **2a** and O(1)—Sn—O(2) in **2b**]. Numerical values, compared in Table 3, illustrate this similarity; surprisingly, the distortions of the

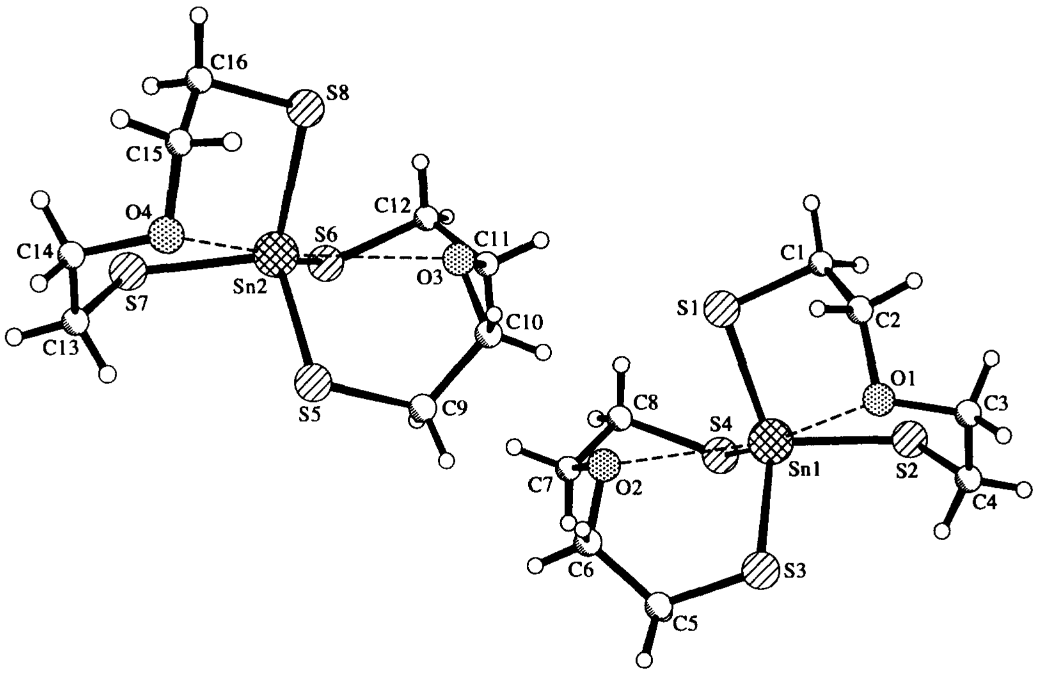

Fig. 2. Molecular structure of compound **2b** (two independent molecules).

tetrahedra are less dramatic in **2a** and **2b**, thus making a possible relationship with an octahedral geometry less obvious.

The primary bond Sn—S interatomic distances in **2a** and **2b** are comparable to those observed in other Sn—S heterocycles, including dithiastannolanes,[10a–d] oxathiastannolanes,[10d,11] trithiastannocanes,[1a,b] oxadithiastannocanes,[1c,d] azadithiastannocanes,[1e,f] numerous 1,1-dithiolato complexes,[2] other organotin thiolates[12] and cyclic stannathianes (diorganotin sulphides).[13–15] In all these cases the Sn—S bond lengths observed are close to the sum of covalent radii of tin and sulphur (2.42 Å).[7] In the six-coordinate tin–sulphur compound the Sn—S bonds are longer. Thus, in the six-coordinate $Sn(C_6H_5)_4 \cdot bipy$, the Sn—S lengths are only slightly (but significantly) longer (2.497–2.502 Å),[16] but in regular octahedral, symmetrical complexes with isobidentate dithio ligands, e.g. $Ph_2Sn[S_2P(OPr^i)_2]_2$ (**6**) (Sn—S 2.669 and 2.670 Å)[3] or $Me_2Sn[(SPPh_2)_2N]_2$ (**7**) (Sn—S 2.733 and 2.737 Å)[4] the tin–sulphur covalent bonds are significantly elongated.

The interatomic distances corresponding to secondary Sn···S interactions cover a broader spectrum of values between the sum of covalent radii and the sum of van der Waals radii for the tin–sulphur pair. The values observed for the latter, in **2a** (3.074 and 3.242 Å) are larger than the intramolecular Sn···S distances observed in $Cl_2Sn(SCH_2CH_2)_2S$ (2.760 Å)[1b] or $BrMe_2SnCH_2CH_2P(S)Ph_2$ (2.872 Å)[17a] or $Cl_2Sn(CH_2CH_2CH_2)S$[17b] and compare well with some intermolecular Sn···S distances, e.g. 3.18 Å in associated $Me_2\overline{SnSCH_2CH_2S}$[10a,b] or $Me_2Sn(SOPPh_2)_2$ (2.93 Å),[18] but are shorter (indicating stronger interaction) than those observed in $Sn(\overline{SCH_2CH_2S})_2$ (3.75 Å)[19] and $Bu_2\overline{SnSCH_2CH_2S}$ (3.688 Å).[10c]

The interatomic distances due to secondary Sn···O interactions observed in numerous functional organotin derivatives[12] cover a broad range. The values measured in **2b** (2.900 and 2.758 Å) indicate a moderately strong secondary interaction. These values are larger than the intramolecular Sn···O (transannular) distances found in related monocyclic diorganostannocanes, e.g. 2.66 Å in $Ph_2Sn(SCH_2CH_2)_2O$,[1c] or in some dioxostannolanes (2.253 Å).[10d] It should be mentioned that the transannular Sn···O and Sn···S interatomic distances observed in our compounds are close to the values calculated from "intramolecular non-bonded radii" suggested by Glidewell,[20] i.e. 3.27 Å for Sn—S and 2.94 Å for Sn—O. These measure the lower limit of E···E distances in EXE′ angular systems and although not directly relevant to our case, may give an indication as to how close two non-bonded atoms can get in a molecule.

EXPERIMENTAL

Reagent grade tin (IV) chloride, bis(2-mercaptoethyl)sulphide and bis(2-mercaptoethyl)ether

Table 2. Interatomic distances (Å) and bond angles (°) in compound **2b**[a]

Molecule A		Molecule B	
Sn—S and Sn···O distances			
Sn(1)—S(1)	2.389(2)	Sn(2)—S(5)	2.403(1)
Sn(1)—S(2)	2.416(2)	Sn(2)—S(6)	2.412(2)
Sn(1)—S(3)	2.409(1)	Sn(2)—S(7)	2.412(2)
Sn(1)—S(4)	2.403(2)	Sn(2)—S(8)	2.397(2)
Sn(1)···O(1)	2.900(4)	Sn(2)···O(3)	2.837(4)
Sn(1)···O(2)	2.758(4)	Sn(2)···O(4)	2.776(4)
Tetrahedron edges (non-bonded distances)			
S(1)···S(2)	4.023	S(5)···S(6)	4.045
S(1)···S(3)	4.138	S(5)···S(7)	3.867
S(1)···S(4)	3.889	S(5)···S(8)	4.122
S(2)···S(3)	2.827	S(6)···S(7)	3.505
S(2)···S(4)	3.535	S(6)···S(8)	3.886
S(3)···S(4)	4.041	S(7)···S(8)	4.024
Bond angles			
S(1)—Sn(1)S(2)	113.46(6)	S(5)—Sn(2)—S(6)	114.31(6)
S(1)—Sn(1)—S(3)	118.89(6)	S(5)—Sn(2)—S(7)	106.88(5)
S(1)—Sn(1)—S(4)	108.27(6)	S(5)—Sn(2)—S(8)	118.36(6)
S(2)—Sn(1)—S(3)	104.97(5)	S(6)—Sn(2)—S(7)	93.19(6)
S(2)—Sn(1)—S(4)	94.38(6)	S(6)—Sn(2)—S(8)	107.81(7)
S(3)—Sn(1)—S(4)	114.23(5)	S(7)—Sn(2)—S(8)	113.59(7)
S(1)—Sn(1)···O(1)	72.41(8)	S(5)—Sn(2)···O(3)	74.16(8)
S(1)—Sn(1)···O(2)	76.90(9)	S(5)—Sn(2)···O(4)	74.83(9)
O(1)···Sn(1)—S(2)	71.52(9)	O(3)···Sn(2)—S(6)	72.08(10)
O(1)···Sn(1)—S(3)	77.42(8)	O(3)···Sn(2)—S(7)	163.62(13)
O(1)···Sn(1)···O(2)	121.16(13)	O(3)···Sn(2)···O(4)	122.37(14)
O(1)···Sn(1)—S(4)	164.14(12)	O(3)···Sn(2)—S(8)	78.66(10)
S(2)—Sn(1)···O(2)	166.51(12)	S(6)—Sn(2)···O(4)	165.36(14)
S(3)—Sn(1)···O(2)	75.46(8)	S(7)—Sn(2)···O(4)	77.77(11)
O(2)···Sn(1)···S(4)	73.59(9)	O(4)···Sn(2)···S(8)	75.23(11)
Sn(1)—S(1)—C(1)	99.9(2)	Sn(2)—S(5)—C(9)	102.3(2)
Sn(1)—S(2)—C(4)	99.5(2)	Sn(2)—S(6)—C(12)	102.8(2)
Sn(1)—S(3)—C(5)	101.1(2)	Sn(2)—S(7)—C(13)	100.2(2)
Sn(1)—S(4)—C(8)	100.4(2)	Sn(2)—S(8)—C(16)	99.3(2)

[a] Two independent molecules in the unit cell.

(Aldrich) were used as received. The reactions were performed under nitrogen and the solvents were dried and distilled before use. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded in $CDCl_3$ solutions on a Varian VXR-300S instrument, mass spectra on a Hewlett–Packard 5985 GC/MS instrument and IR spectra with a Perkin–Elmer 283-B spectrophotometer on KBr plates. The crystal structures were determined as described below.

Preparation of spiro-bis(trithiastannocane) (**2a**)

Sodium metal (0.575 g, 25.1 mmol) was dissolved in 10 cm^3 of anhydrous methanol (excess) to form sodium methoxide. This was treated with bis(2-mercaptoethyl)sulphide (2.075 g, 13.4 mmol) and a solution of $SnCl_4$ (1.3 g, 4.99 mmol) in 30 cm^3 anhydrous benzene was then added. The volume was made up to *ca* 60 cm^3 by adding more benzene. The mixture was refluxed for 8 h. A colourless solid (NaCl) was formed, and was filtered off. The solution was evaporated to dryness and the product was recrystallized from dichloromethane. Yield: 0.854 g (44.5%), m.p. 206–208°C (lit. 210°).[6a] ^{1}H NMR (δ, ppm rel. to TMS): 2.9 (Sn—S—CH_2), 3.15 (CH_2—S).[6a] ^{13}C NMR (δ, ppm rel. to TMS): 28.32 (Sn—S—CH_2), 41.17 (CH_2—S). ^{119}Sn NMR (δ, ppm rel. to $SnMe_4$): −350.75. Mass spectrum (*m*/*z*, % relative intensity): 423 (8), M^+; 392 (11), $(CH_2)_8S_5Sn$; 364 (20), $(CH_2)_6S_5Sn$; 272 (15),

Table 3. Comparison of structural parameters of diorganotin dithiophosph(in)ates and spiro-bis(dithiaheterostannocanes)

	Interatomic distances (Å)		Bond angles (°)			
Compound	Primary bonds Sn—S	Secondary bonds Sn···S	Between primary bonds		Between secondary bonds	Ref.
Dithiophosph(in)ates			C(1)—Sn—C(2)	S(1)—Sn—S(3)	S(2)···Sn···S(4)	
$Ph_2Sn[S_2P(OEt)_2]_2$	2.490	3.23	135	84.5	136.9	5a
$Me_2Sn(S_2PMe_2)_2$	2.482	3.334	122.6	79.9	142.3	5b
$Me_2Sn(S_2PEt_2)_2$	2.476	3.33	123.7	80.6	143.4	5c
$Me_2Sn(S_2AsMe_2)_2$	2.471	3.515	121.8	80.3	139.2	5d
Spiro-bis(dithiaheterostannocanes)						
Compound **2a**			S(1)—Sn—S(6)	S(3)—Sn—S(4)	S(2)···Sn···S(5)	
	2.424	3.074	126.08	93.21	113.76	this work
	2.434	3.241				
	2.407	av. 3.157				
	2.408					
	av. 2.418					
Compound **2b**		Sn(1)···O	S(1)—Sn(1)—S(3)	S(2)—Sn(1)—S(4)	O(1)···Sn(1)···O(2)	
Molecule A						
	2.416	2.900	118.89	94.38	121.16	this work
	2.403	2.758				
	2.409	av. 2.829				
	2.396					
	av. 2.40					
Molecule B		Sn(2)···O	S(5)—Sn(2)—S(8)	S(6)—Sn(2)—S(7)	O(3)···Sn(2)···O(4)	
	2.403	2.837	118.36	93.19	122.37	this work
	2.412	2.776				
	2.412	av. 2.806				
	2.397					
	av. 2.406					

$(CH_2)_4S_3Sn$; 211 (35), $(CH_2)_2S_2Sn$; 152 (26), $(CH_2)_4S_3$; 120 (10), Sn; 92 (50), $(CH_2)_2S_2$; 60 (35), $(CH_2)_2S$. IR (KBr pellets, cm^{-1}): CH_2, 890 s, 1490 s, 1399 m, 1280 s, 1260 s; C—C, 1245 w, 1171 w, 1079 s, 980 m; C—S, 655 m, 615 w.

Preparation of spiro-bis(oxadithiastannocane) (**2b**)

The sodium salt was prepared by dissolving sodium metal (1.15 g, 50.2 mmol) in 17.5 cm^3 of absolute ethanol (excess) and adding bis(2-mercaptoethyl)ether (4.15 g, 30 mmol). This was treated with a solution of $SnCl_4$ (2.6 g, 9.9 mmol) dissolved in 50 cm^3 of anhydrous benzene. The volume was made up to *ca* 150 cm^3 by adding more benzene. The reaction mixture was refluxed for 7 h and, after cooling, the solid deposited (NaCl) was filtered. Evaporation of the solvents left a colourless solid, which was recrystallized from benzene. Yield: 2.03 g (52%), m.p. 122°C (lit. m.p. 124°C).[6a] ^1H NMR (δ, ppm rel. to TMS): 3.15 (Sn—S—CH_2), 3.88 (CH_2—O). ^{13}C NMR (δ, ppm rel. to TMS): 28.5 (Sn—S—CH_2), 72.2 (CH_2—O). ^{119}Sn NMR (δ, ppm rel. to $SnMe_4$): −359.87. Mass spectrum (*m/z*, % relative intensity): 392 (20), M^+; 359 (20), $(CH_2)_8O_2S_3SN$; 331 (100), $(CH_2)_6O_2S_3Sn$; 254 (35), $(CH_2)_4OS_2Sn$; 196 (35), $(CH_2)_2OSSn$; 136 (40), $(CH_2)_4OSn$; 120 (38) Sn. IR (KBr pellets, cm^{-1}): C—H, 2930 w, 2910 m, 2855 m, 1460 m, 1440 w, 1410 m; C—C, 1235 w, 1282 s; C—O, 1180 w, 1170 cm, 1080 s, 1020 s, 980 m, 925 m.

X-ray crystallography

A structure determination summary for the two compounds, **2a** and **2b**, is given in Table 4. Crystals of dimensions 0.34 × 0.24 × 0.18 mm for **2a** and 0.32 × 0.22 × 0.18 mm for **2b** were used for data collection on a Siemens P4/PC diffractometer, using graphite monochromatized Mo-K_α radiation

Table 4. Structure determination summary

	2a	**2b**
Crystal data		
Empirical formula	$C_8H_{16}S_6Sn$	$C_8H_{16}O_2S_4Sn$
Formula weight	423.3	391.1
Crystal system	orthorhombic	monoclinic
Space group	$Pca2_1$	$P2_1/c$
Unit cell dimensions (Å)	$a = 12.309(4)$	$a = 16.132(3)$
	$b = 11.779(1)$	$b = 7.516(1)$ $\beta = 95.50°$
	$c = 10.400(1)$	$c = 23.627(4)$
Volume (Å^3)	1507.8	2851.6(8)
Z	4	8
D_{calc} (g cm^{-3})	1.865	1.822
Absorption coefficient (cm^{-1})	24.95	23.58
$F(000)$	840	1522
Data collection		
Scan range (omega)	$0 \leqslant h \leqslant 14$	$0 \leqslant h \leqslant 19$
	$-14 \leqslant k \leqslant 0$	$0 \leqslant k \leqslant 8$
	$0 \leqslant l \leqslant 12$	$-28 \leqslant l \leqslant 27$
Reflections collected	1559	5639
Independent reflections	1415 ($R_{int} = 0.00\%$)	5008 ($R_{int} = 1.91\%$)
Observed reflections	1253 [$F > 3.0\sigma(F)$]	3324 [$F > 4.0\sigma(F)$]
Absorption correction	semi-empirical	semi-empirical
Data refinement		
System used	Siemens SHELXTL PLUS (PC Version)	
Solution	Patterson	Direct methods
Refinement method	Full matrix least squares	
Weighting scheme	$w^{-1} = s(F)^2 + 0.0002F^2$	$w = s(F)^2 + 0.0003F^2$
Final R indices (obs. data) (%)	$R = 2.94$; $R_w = 3.40$	$R = 3.47$; $R_w = 3.83$
R indices (all data) (%)	$R = 3.57$; $R_w = 4.03$	$R = 6.18$; $R_w = 4.48$

($\lambda = 0.71073$ Å) at 298 K. Lattice parameters were refined using 25 reflections in the range $3 \leqslant 2\theta \leqslant 50$. Three standard reflections were measured every 97 reflections. Other data are given in Table 4 and further details are available as supplementary material (atomic coordinates and equivalent displacement coefficients, bond lengths and angles, anisotropic displacement coefficients are hydrogen atom coordinates) deposited with the Editor at the Cambridge Crystallographic Data Centre.

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