

## Bis(tetra-*n*-butylammonium) and bis(tetraphenylphosphonium) salts of tris(2-oxo-1,3-dithiole-4,5-dithiolato)-stannate(IV), both at 120 K

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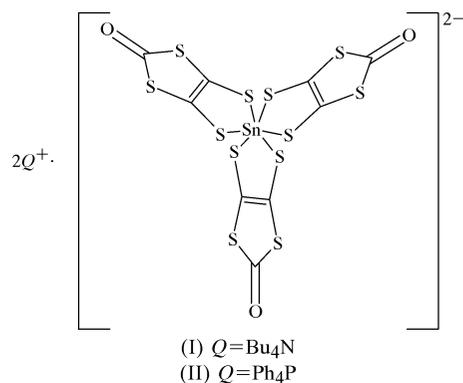
The title compounds,  $(C_{16}H_{36}N)_2[Sn(C_3OS_4)_3]$ , (I), and  $(C_{24}H_{20}P)_2[Sn(C_3OS_4)_3]$ , (II), are examples of complex salts of the general form  $[Q]_2[Sn(dmio)_3]$ , where  $Q$  is  ${}^nBu_4N^+$  or  $Ph_4P^+$  and dmio is the 2-oxo-1,3-dithiole-4,5-dithiolate dianion. Features of both structures are the slightly distorted octahedral coordination of tin in the propeller-shaped dianions and the absence of any significant inter-anion contacts. The structure of (I) is particularly notable because all of the dianions in the sample crystal have the same propeller configuration, which is very unusual in this type of structure.

### Comment

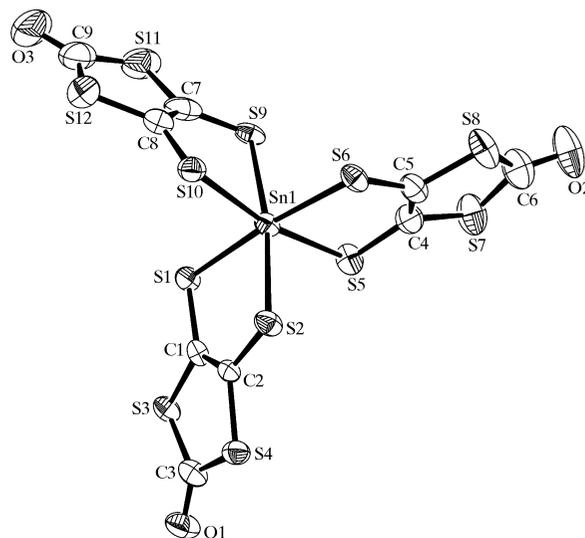
Compounds of the general form  $[Q]_2[Sn(dmit)_3]$ , where  $Q$  is an onium counter-cation and dmit represents the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion, have already received considerable attention (de Assis *et al.*, 1999; Comerlato *et al.*, 2004). The compounds discussed here, namely (I) with  $Q = {}^nBu_4N^+$  and (II) with  $Q = Ph_4P^+$ , are entirely analogous, but with dmit replaced by the equivalent 2-oxo dianion, here designated dmio, although the acronym dmio, referring to the same 2-oxo species, occurs elsewhere in the literature. The dmio complexes (I) and (II) were obtained in order to investigate further the influence of cation variation on the overall shapes of  $[Sn(dmio)_3]^{2-}$  dianions and to compare such influences with those found in the analogous  $[Sn(dmit)_3]^{2-}$  complexes described by de Assis *et al.* (1999). The counter-cations are not, in themselves, remarkable and thus their bond lengths and angles are not discussed in detail. The anions of (I) and (II) are shown in Figs. 1 and 2, respectively.

Details of the coordination of the Sn atoms in both compounds in terms of bond lengths and angles are given in Table 1. The Sn atoms are in octahedral environments,

somewhat distorted by the chelate bite angles and by slightly asymmetric chelation by the ligands. This situation is consistent with what has been found in previously studied  $[Sn(dmit)_3]$  and  $[Sn(dmio)_3]$  compounds. Geometric data for the ligands are given in Table 2; in this table and in the discussion below, the individual ligands in both structures are designated  $L1$  for that comprising atoms S1–S4, C1–C3 and O1,  $L2$  for that comprising atoms S5–S8, C4–C6 and O2, and  $L3$  for that comprising atoms S9–S12, C7–C9 and O3.



The bond-length and angle data show little variation from one ligand to another, both within and between the compounds. However, in the distances and angles referenced to the ligand planes, clear distinctions between the compounds and the ligands within them are evident. It is convenient, in this context, to define the plane of each ligand in terms of the C=C bond and the four S atoms directly associated with it, *e.g.* for  $L1$ , atoms C1, C2 and S1–S4. Of some significance are the displacements from such a plane of the oxo O atoms and the C atoms to which they are connected. These are indicative of slight variations in the ligand shape and, specifically, small departures from planarity of the five-membered ring of which the oxo O atom is a substituent. It is the displacement of the



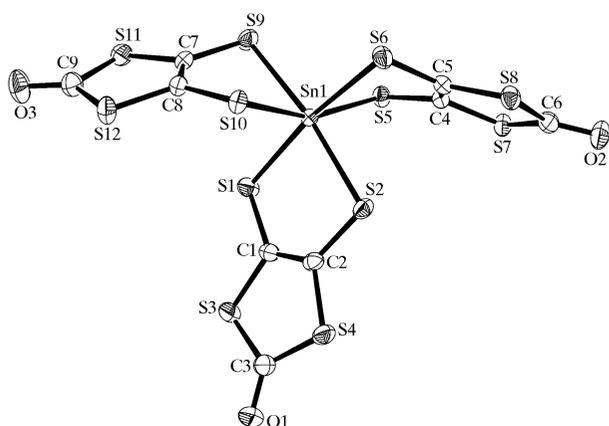
**Figure 1**  
The dianion of (I). Displacement ellipsoids are drawn at the 50% probability level.

Sn atom from such ligand planes which relates to the overall shape of the dianion. These displacements correlate closely with the dihedral angles, ligand by ligand, between the ligand plane as defined above and the plane defined by the Sn atom and the two chelating S atoms of the same ligand, *e.g.* Sn1 and, for *L1*, atoms S1 and S2. Both of these are a measure of the tilt of the ligand about the vector joining the chelating S atoms. The values in Table 2 are compatible with the overall ligand shape (Figs. 1 and 2) and are crudely measured by the O··Sn··O angles (Table 2). These angles demonstrate the T shape of the dianion in (II), as distinct from the comparatively regular three-pointed star shape of the dianion in (I). Despite the difference in overall shape, both dianions have a propeller-like configuration in terms of the tilt of the ligands relative to the plane defined by the three oxo O atoms [the Sn-atom displacements are  $-0.900$  (3) and  $-0.2241$  (12) Å in (I) and (II), respectively]. The tilt is seen in the orientation of the C=C bonds in Figs. 1 and 2.

The structure of (I) is unusual in that all of the dianions have the same configuration in terms of the pitch of the propellers, because there is no crystallographic symmetry plane or centre of symmetry to bring about inversion. This is in contrast with (II), and with all literature examples of  $[\text{Sn}(\text{dmit})_3]^{2-}$  dianions and the single  $[\text{Q}]_2[\text{Sn}(\text{dmio})_3]$  compound ( $\text{Q} = \text{Et}_4\text{N}^+$ ) for which structural data are available (de Assis *et al.*, 1999). The resolution of the enantiomeric dianions in (I) occurred spontaneously during crystal growth, rendering the bulk sample as a racemic conglomerate.

In both structures, the completeness of the coordination of the Sn atoms (coordinative saturation) precludes the existence of Sn··X inter-anion ( $X = \text{S}$  or  $\text{O}$ ) interactions. The distribution of dianions and counter-cations, as shown in Figs. 3 and 4 for (I) and in Fig. 5 for (II), is such that the separation between the dianions is too great to permit S··S or S··O inter-anion interactions, such as those which have been found when less bulky *Q* moieties are present.

In compound (I), the two counter-cations, namely cation *A*, comprising atom N1 and the butyl groups C10–C25, and cation *B*, comprising atoms N2 and C26–C41, contribute in very



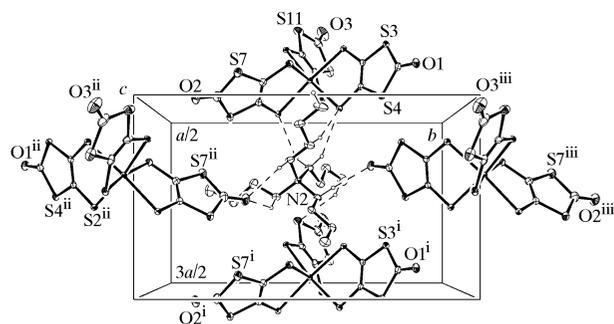
**Figure 2**

The dianion of (II). Displacement ellipsoids are drawn at the 50% probability level.

different ways to the dispersal of the dianions. The dianions and cation *B* in (I) can be considered as being in pseudo-*C*-centred layers parallel to (001) (Fig. 3), in which can be found all but the last two hydrogen bonds listed in Table 3. One other hydrogen bond, involving cation *B* [ $\text{C37}-\text{H37A}\cdots\text{O3}^{\text{iv}}$ ; symmetry code: (iv)  $\frac{1}{2} - x, 1 - y, z + \frac{1}{2}$ ], interconnects the layers in the *c* direction. Cation *A*, flatter than cation *B* and seen edge-on in Fig. 4, lies between the layers, providing the  $\text{C10}-\text{H10B}\cdots\text{S6}^{\text{v}}$  hydrogen bond and the first three C—H··π contacts in Table 4 [symmetry code: (v)  $1 - x, y + \frac{1}{2}, \frac{3}{2} - z$ ]. The remaining contact in this table is provided by cation *A*.

For compound (II), all of the inter-ion interactions given in Tables 5 and 6, with the exception of hydrogen bonds  $\text{C26}-\text{H26}\cdots\text{O3}^{\text{iii}}$  and  $\text{C36}-\text{H36}\cdots\text{S10}^{\text{iv}}$  [symmetry codes: (iii)  $x - 1, y, z$ ; (iv)  $x, y, z - 1$ ], are represented in the chain of interconnected ions shown in Fig. 5. Also present within the chain is the π–π interaction between the five-membered ring of *L1*, defined by atoms C1–C3/S3/S4, and the C40–C45 phenyl group at symmetry position  $(2 - x, 2 - y, 1 - z)$ , for which the distance between the ring centroids, the average perpendicular distance of the centroid of one ring from the least-squares plane of the other, and the lateral displacement or slippage of the rings are 3.824, 3.560 and 1.396 Å, respectively. The hydrogen bonds missing from Fig. 5 connect the chains, themselves propagated in the *a* direction, in the *c* direction, to form layers parallel to (010) in which adjacent chains are related by the operation of crystallographic centres of symmetry. The interaction between the layers involves only van der Waals contacts between ligands *L2* and *L3* of the dianion on the surface of one layer and between the phenyl groups of the counter-cations on the surface of the other.

The arrangement in (II) is surprisingly different from that found by Comerlato *et al.* (2004) in the formally analogous, but solvated, compound  $[\text{Ph}_4\text{As}]_2[\text{Sn}(\text{dmit})_3]\cdot\text{Me}_2\text{CO}$ , (III). The structure of (II) contains voids of  $69.6 \text{ \AA}^3$ , but there is no evidence of even partial occupancy of these by solvent. Both structures contain chains in which T-shaped dianions are



**Figure 3**

A layer of ions in (I). Displacement ellipsoids are drawn at the 20% probability level. H atoms which participate in the formation of hydrogen bonds (dashed lines) are shown as small circles of arbitrary radii. For the purposes of this figure, the origin of the unit cell has been shifted to  $(\frac{1}{2}, 0, 0)$ . [Symmetry codes: (i)  $1 + x, y, z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$ ; (iii)  $\frac{1}{2} + x, \frac{3}{2} - y, 2 - z$ .]

linked by cations through a variety of inter-ionic contacts. In both cases, the ligand forming the stem of the T, *L1* in the case of (II), lies between two cations, making a  $\pi$ - $\pi$  contact with one and a C-H... $\pi$  contact with the other (Fig. 5). In both structures, the ligands forming the top of the T, *L2* and *L3* in the case of (II), are involved in rather fewer inter-ionic contacts than *L1* and its equivalent in (III). It is in the constitution and arrangement of the chains that significant differences between the structures of (II) and (III) are observed. Along the chain length in (II), two cations, one of each type present in the asymmetric unit, lie between adjacent dianions, which are then separated enough to allow the top of the T to be aligned with the direction of propagation of the chain. In the chains of (III), only one cation, always of the same type, separates the dianions, and the top of the T is now

roughly at right angles to the chain. In (II), as noted earlier, the chains are located side by side, forming layers. In the structure of (III), they are located in centrosymmetrically related pairs creating a tube-like arrangement, with the cation associated with chain formation at the centre of the tube and the tops of the T-shaped dianions at the tube surface. The remaining cations in (III) are found in separate columns.

## Experimental

The syntheses of (I) and (II),  $[Q]_2[Sn(dmio)_3]$ , were based on the procedure described by Akasaka *et al.* (2002). 4,5-Bis(benzoylthio)-1,3-dithiol-2-one (0.819 mg, 2.1 mmol) and  $[Q]Br$  (4.2 mmol) were successively added to a solution of NaOMe, obtained from Na (0.100 g) and MeOH (10 ml), with agitation and under an argon atmosphere. The resulting orange solid was collected under argon and washed with dry ether (100 ml). The dried solid,  $[Q]_2[dmio]$ , was added to MeOH (10 ml), followed by  $SnCl_4 \cdot 5H_2O$  (0.245 mg, 0.7 mmol). The reaction mixture was stirred for 24 h at room temperature and the precipitate collected, washed successively with  $H_2O$  and  $Et_2O$ , and dried *in vacuo*. The compounds were crystallized from acetone-methanol (1:1 v/v). For  $[Bu_4N]_2[Sn(dmio)_3]$ , (I): yield 0.44 g (56%), m.p. 430–431 K; elemental analysis for  $C_{41}H_{72}N_2O_3 \cdot S_{12}Sn$  calculated (found): C 42.8 (43.0), H 6.2 (6.3), N 2.2% (2.4%); IR (CsI,  $cm^{-1}$ ): 2962, 1671, 1618, 1461, 896, 463. For  $[Ph_4P]_2[Sn(dmio)_3]$ , (II): yield 0.57 g (61%), m.p. 424–425 K; IR (CsI,  $cm^{-1}$ ): 3055, 1660, 1609, 1432, 1108, 997, 894, 724, 527, 465.

## Compound (I)

### Crystal data

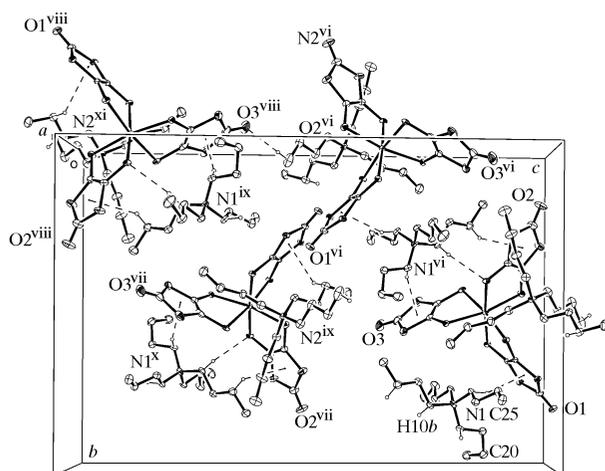
$(C_{16}H_{36}N)_2[Sn(C_3OS_4)_3]$   
 $M_r = 1144.42$   
 Orthorhombic,  $P2_1/n$   
 $a = 10.7732$  (4) Å  
 $b = 18.3479$  (7) Å  
 $c = 27.5862$  (9) Å  
 $V = 5452.8$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.394$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 26 026 reflections  
 $\theta = 2.9$ – $27.5^\circ$   
 $\mu = 0.96$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Plate, dark red  
 $0.55 \times 0.26 \times 0.08$  mm

**Table 1**

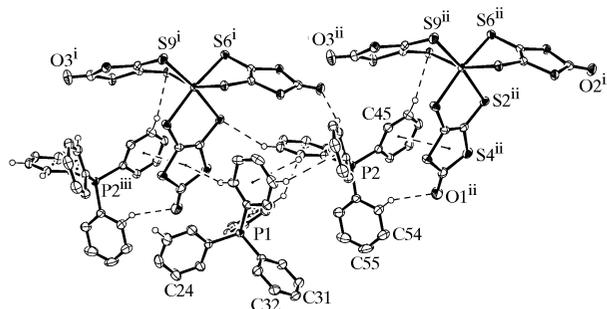
Bond lengths and angles (Å, °) involving the Sn atom in (I) and (II).

	(I)	(II)
Sn1—S1	2.5386 (12)	2.5354 (6)
Sn1—S2	2.5284 (13)	2.5435 (5)
Sn1—S5	2.5282 (14)	2.5649 (6)
Sn1—S6	2.5394 (12)	2.5536 (6)
Sn1—S9	2.5457 (12)	2.5549 (6)
Sn1—S10	2.5626 (14)	2.5639 (6)
S1—Sn1—S2	85.24 (4)	85.117 (18)
S5—Sn1—S6	85.96 (4)	82.271 (18)
S9—Sn1—S10	85.45 (4)	82.013 (19)
S1—Sn1—S6	174.24 (4)	170.76 (2)
S2—Sn1—S9	171.52 (4)	171.61 (2)
S5—Sn1—S10	169.37 (5)	160.47 (2)
S1—Sn1—S5	92.46 (4)	99.667 (19)
S2—Sn1—S5	94.97 (5)	94.268 (18)
S2—Sn1—S6	89.37 (4)	85.728 (19)
S1—Sn1—S9	87.64 (4)	86.53 (2)
S5—Sn1—S9	89.93 (5)	87.899 (19)
S6—Sn1—S9	97.88 (4)	102.61 (2)
S1—Sn1—S10	96.90 (4)	96.384 (19)
S2—Sn1—S10	90.83 (4)	98.136 (19)
S6—Sn1—S10	85.20 (4)	83.666 (18)



**Figure 4**

The unit cell of (I). Displacement ellipsoids are drawn at the 20% probability level. H atoms participating in the formation of hydrogen bonds and C-H... $\pi$  contacts (dashed lines) are depicted as for Fig. 3. The labels N1 and N2 designate counter-cations rather than specific atoms. [Symmetry codes: (vi)  $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (vii)  $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$ ; (viii)  $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ ; (ix)  $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$ ; (x)  $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$ ; (xi)  $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$ .]



**Figure 5**

Inter-ionic contacts in (II), propagating a chain in the *a* direction (left to right across the page). Displacement ellipsoids are drawn at the 50% probability level. H atoms participating in the formation of hydrogen bonds and C-H... $\pi$  contacts (dashed lines) are shown as small circles of arbitrary radii. Dashed lines also indicate  $\pi$ - $\pi$  contacts. [Symmetry codes: (i)  $1 - x, 2 - y, 1 - z$ ; (ii)  $2 - x, 2 - y, 1 - z$ ; (iii)  $x - 1, y, z$ .]

**Table 2**

Bond lengths and angles (Å, °) and other geometric parameters associated with the dmio ligands† in (I) and (II).

	Compound (I)			Compound (II)		
	Ligand 1	Ligand 2	Ligand 3	Ligand 1	Ligand 2	Ligand 3
S1—C1	1.746 (5)	1.732 (6)	1.713 (7)	1.750 (2)	1.747 (2)	1.749 (2)
S2—C2	1.738 (5)	1.731 (6)	1.783 (6)	1.745 (2)	1.746 (2)	1.740 (2)
S3—C1	1.747 (5)	1.763 (6)	1.751 (6)	1.753 (2)	1.754 (2)	1.760 (2)
S3—C3	1.766 (6)	1.758 (7)	1.734 (9)	1.773 (3)	1.772 (2)	1.766 (3)
S4—C2	1.764 (5)	1.749 (5)	1.752 (6)	1.757 (2)	1.756 (2)	1.751 (2)
S4—C3	1.770 (6)	1.750 (7)	1.787 (8)	1.766 (3)	1.769 (2)	1.760 (2)
C1—C2	1.350 (7)	1.356 (7)	1.354 (8)	1.346 (3)	1.352 (3)	1.352 (3)
C3—O1	1.214 (6)	1.225 (7)	1.238 (8)	1.214 (3)	1.218 (3)	1.229 (3)
C1—S1—Sn1	98.84 (16)	98.47 (19)	97.9 (2)	99.78 (7)	93.81 (7)	94.68 (7)
C2—S2—Sn1	98.91 (16)	99.05 (18)	95.5 (2)	99.49 (7)	93.80 (7)	94.88 (8)
C1—S3—C3	97.5 (2)	97.1 (3)	96.7 (4)	97.18 (12)	97.13 (11)	97.37 (11)
C2—S4—C3	97.0 (2)	97.3 (3)	95.4 (4)	97.03 (12)	97.10 (10)	97.06 (11)
C2—C1—S1	126.1 (4)	128.0 (4)	127.0 (4)	126.65 (17)	125.45 (17)	125.46 (17)
C2—C1—S3	117.0 (4)	116.0 (4)	116.8 (5)	116.66 (17)	116.83 (16)	115.80 (16)
S1—C1—S3	116.9 (3)	116.0 (3)	116.2 (4)	116.67 (12)	117.63 (13)	118.58 (13)
C1—C2—S2	127.3 (4)	126.5 (4)	127.3 (5)	126.71 (17)	125.00 (17)	124.74 (17)
C1—C2—S4	116.5 (4)	116.9 (4)	117.3 (5)	117.09 (17)	116.80 (16)	117.45 (16)
S2—C2—S4	116.1 (3)	116.4 (3)	115.4 (4)	116.20 (13)	118.11 (12)	117.63 (13)
O1—C3—S3	124.3 (5)	123.5 (6)	124.3 (7)	123.6 (2)	124.14 (18)	123.45 (19)
O1—C3—S4	123.8 (5)	123.8 (6)	122.0 (7)	124.4 (2)	123.84 (18)	124.4 (2)
S3—C3—S4	111.9 (3)	112.7 (4)	113.7 (4)	111.94 (14)	112.02 (12)	112.16 (13)
Sn1 <sub>oop</sub> ‡	0.6438 (19)	−0.505 (2)	0.861 (2)	0.4930 (9)	1.3871 (8)	1.3721 (8)
C3 <sub>oop</sub>	0.035 (6)	−0.046 (8)	0.070 (7)	0.064 (3)	−0.012 (2)	−0.015 (3)
O1 <sub>oop</sub>	0.042 (5)	−0.094 (7)	0.130 (6)	0.115 (2)	−0.047 (2)	−0.082 (2)
IP§	19.89 (6)	15.36 (6)	27.01 (7)	15.15 (3)	45.38 (2)	44.34 (3)
O1...Sn1...O2	117.68 (6)			97.58 (2)		
O1...Sn1...O3	112.41 (6)			84.83 (2)		
O2...Sn1...O3	124.86 (7)			175.42 (2)		

† Atom designations apply to all three ligands if, for a ligand *n*, where *n* = 1 to 3, S*x* becomes S[*x* + 4(*n*−1)], C*x* becomes C[*x* + 3(*n*−1)] and O*x* becomes O*n*. ‡ oop denotes displacements of the atoms so designated from the ligand planes as defined in the text. § IP is the dihedral angle, ligand by ligand, between the ligand plane and the plane defined by the Sn atom and the chelating S atoms.

**Table 3**

Hydrogen-bond geometry for (I) (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C26—H26 <i>A</i> ...S6	0.99	2.72	3.606 (6)	149
C26—H26 <i>B</i> ...S2	0.99	2.77	3.621 (6)	144
C29—H29 <i>B</i> ...S11 <sup>i</sup>	0.98	2.81	3.711 (8)	153
C30—H30 <i>B</i> ...O2 <sup>ii</sup>	0.99	2.53	3.280 (8)	133
C34—H34 <i>B</i> ...O2 <sup>ii</sup>	0.99	2.56	3.459 (8)	152
C35—H35 <i>A</i> ...S2	0.99	2.85	3.819 (6)	165
C38—H38 <i>B</i> ...O1 <sup>iii</sup>	0.99	2.44	3.418 (7)	168
C37—H37 <i>A</i> ...O3 <sup>iv</sup>	0.98	2.51	3.466 (9)	165
C10—H10 <i>B</i> ...S6 <sup>v</sup>	0.99	2.80	3.772 (5)	166

Symmetry codes: (i) *x* + 1, *y*, *z*; (ii) *x* + ½, ½ − *y*, 2 − *z*; (iii) *x* + ½, ¾ − *y*, 2 − *z*; (iv) ½ − *x*, 1 − *y*, *z* + ½; (v) 1 − *x*, *y* + ½, ¾ − *z*.

**Table 4**

Geometry of C—H...π contacts in (I) (Å, °).

C—H...Cg†	C—H	H...Cg	H <sub>perp</sub> ‡	γ§	C—H...Cg	C...Cg
C12—H12 <i>A</i> ...Cg2 <sup>v</sup>	0.99	2.87	2.78	15	145	3.729
C18—H18 <i>B</i> ...Cg3 <sup>v</sup>	0.99	3.09	2.88	21	158	4.029
C22—H22 <i>B</i> ...Cg1	0.99	3.16	2.75	29	154	4.073
C40—H40 <i>B</i> ...Cg1 <sup>i</sup>	0.99	3.27	3.05	21	144	4.114

† Cg*n* is the centroid of the C<sub>3</sub>S<sub>2</sub> ring of ligand *n*. ‡ H<sub>perp</sub> is the perpendicular distance of the H atom from the mean plane of the ring. § γ is the angle at H between H...Cg and H<sub>perp</sub>. Symmetry codes: (i) 1 + *x*, *y*, *z*; (v) 1 − *x*, *y* + ½, ¾ − *z*.

**Data collection**

Nonius KappaCCD area-detector diffractometer  
 12 433 independent reflections  
 9169 reflections with *I* > 2σ(*I*)  
 φ and ω scans  
 R<sub>int</sub> = 0.081  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)  
 θ<sub>max</sub> = 27.5°  
 T<sub>min</sub> = 0.619, T<sub>max</sub> = 0.923  
 43 550 measured reflections  
*h* = −13 → 13  
*k* = −23 → 23  
*l* = −34 → 35

**Refinement**

Refinement on *F*<sup>2</sup>  
 R[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.050  
 wR(*F*<sup>2</sup>) = 0.110  
*S* = 1.02  
 12 433 reflections  
 532 parameters  
 H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0476*P*)<sup>2</sup> + 1.7266*P*]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.002  
 Δρ<sub>max</sub> = 0.94 e Å<sup>−3</sup>  
 Δρ<sub>min</sub> = −0.62 e Å<sup>−3</sup>  
 Absolute structure: Flack (1983),  
 with 5583 Friedel pairs  
 Flack parameter: −0.007 (19)

**Compound (II)**

**Crystal data**

(C<sub>24</sub>H<sub>20</sub>P)<sub>2</sub>[Sn(C<sub>3</sub>OS<sub>4</sub>)<sub>3</sub>]  
*M*<sub>r</sub> = 1338.24  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 14.2844 (2) Å  
*b* = 26.4828 (4) Å  
*c* = 15.4538 (2) Å  
 β = 90.4168 (6)°  
*V* = 5845.88 (14) Å<sup>3</sup>  
*Z* = 4

*D*<sub>x</sub> = 1.521 Mg m<sup>−3</sup>  
 Mo Kα radiation  
 Cell parameters from 13 144 reflections  
 θ = 2.9–27.5°  
 μ = 0.96 mm<sup>−1</sup>  
*T* = 120 (2) K  
 Block, dark red  
 0.20 × 0.18 × 0.16 mm

Data collection

Bruker-Nonius 95mm CCD camera on $\kappa$ -goniostat diffractometer $\varphi$ and $\omega$ scans	13 360 independent reflections 10 973 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$\theta_{\text{max}} = 27.5^\circ$ $h = -18 \rightarrow 18$ $k = -34 \rightarrow 33$ $l = -20 \rightarrow 19$
$T_{\text{min}} = 0.673$ , $T_{\text{max}} = 0.857$	
64 111 measured reflections	

Refinement

Refinement on $F^2$ $R[F^2 > 2\sigma(F^2)] = 0.031$ $wR(F^2) = 0.078$ $S = 1.09$ 13 360 reflections 676 parameters H-atom parameters constrained	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 1.8314P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.002$ $\Delta\rho_{\text{max}} = 0.50 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.72 \text{ e } \text{\AA}^{-3}$
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Table 5

Hydrogen-bond geometry for (II) ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C38—H38 $\cdots$ S2 <sup>i</sup>	0.95	2.85	3.573 (2)	133
C47—H47 $\cdots$ O2 <sup>i</sup>	0.95	2.41	3.323 (3)	162
C44—H44 $\cdots$ S10 <sup>ii</sup>	0.95	2.81	3.751 (3)	172
C53—H53 $\cdots$ O1 <sup>ii</sup>	0.95	2.46	3.211 (3)	135
C26—H26 $\cdots$ O3 <sup>iii</sup>	0.95	2.46	3.188 (3)	133
C36—H36 $\cdots$ S2 <sup>iv</sup>	0.95	2.71	3.576 (2)	151

Symmetry codes: (i)  $1-x, 2-y, 1-z$ ; (ii)  $2-x, 2-y, 1-z$ ; (iii)  $x-1, y, z$ ; (iv)  $x, y, z-1$ .

Table 6

Geometry of C—H $\cdots\pi$  contacts in (II) ( $\text{\AA}$ ,  $^\circ$ ).

C—H $\cdots$ Cg <sup>†</sup>	C—H	H $\cdots$ Cg	H <sub>perp</sub> <sup>‡</sup>	$\gamma$ <sup>§</sup>	C—H $\cdots$ Cg	C $\cdots$ Cg
C12—H12 $\cdots$ Cg5	0.95	3.23	2.96	24	123	3.838
C15—H15 $\cdots$ Cg1 <sup>i</sup>	0.95	2.79	2.75	9	160	3.693
C18—H18 $\cdots$ Cg3	0.95	3.21	3.05	18	124	3.821
C39—H39 $\cdots$ Cg2	0.95	3.06	2.92	17	131	3.758

<sup>†</sup> Cg<sub>n</sub>, where  $n = 1, 2, 3$  and  $5$ , are the centroids of the rings C1—C3/S3/S4, C10—C15, C34—C39 and C46—C51, respectively. <sup>‡</sup> H<sub>perp</sub> is the perpendicular distance of the H atom from the mean plane of the ring. <sup>§</sup>  $\gamma$  is the angle at H between H $\cdots$ Cg and H<sub>perp</sub>. Symmetry code: (i)  $1-x, 2-y, 1-z$ .

In the final stages of both refinements, H atoms were introduced in calculated positions, with C—H distances of 0.95, 0.98 and 0.99  $\text{\AA}$  for phenyl, methyl and methylene H atoms, respectively, and refined with a riding model, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for all other H atoms.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998) for (I); COLLECT for (II). For both compounds, cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; structure solution: SHELXS97 (Sheldrick, 1997); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); publication software: SHELXL97 and PLATON (Spek, 2003).

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References

Akasaka, T., Nakano, M., Tamura, H. & Matsubayashi, G. (2002). *Bull. Chem. Soc. Jpn.*, **75**, 2621–2628.  
 Assis, F. de, Chohan, Z. H., Howie, R. A., Khan, A., Low, J. N., Spencer, G. M., Wardell, J. L. & Wardell, S. M. S. V. (1999). *Polyhedron*, **18**, 3533–3544.  
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–37.  
 Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.  
 Comerlato, N. M., Ferreira, G. B., Howie, R. A. & Wardell, J. L. (2004). *Acta Cryst.* **E60**, m1781–m1783.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Hooft, R. W. W. (1998). COLLECT. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.  
 Sheldrick, G. M. (2003). SADABS. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.