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Bis(tetraphenylarsonium) tris(2-thioxo-1,3-dithiole-4,5-dithiolato)stannate(IV) acetone solvate at 120 K

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The title compound, $(C_{24}H_{20}As)_2[Sn(C_3S_5)_3]\cdot C_3H_6O$, is a further example of a salt of the general form $Q_2[Sn(dmit)_3]$ (dimit is 1,3-dithiole-2-thione-4,5-dithiolate), where Q, the onium counter-cation, is in this case $[AsPh_4]^+$. As in all such compounds, the coordination of the Sn atom is in the form of a distorted octahedron, with Sn—S distances in the range 2.5310 (10)–2.5585 (12) Å provided by three chelating dmit ligands with bite angles in the range 81.59 (3)–87.42 (3)°.

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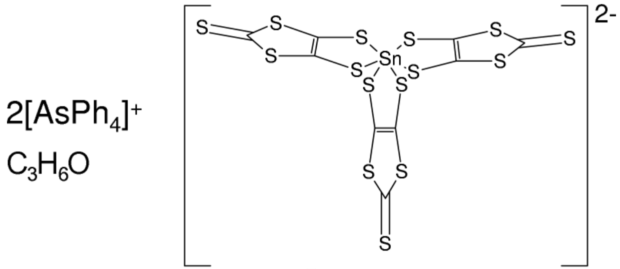
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.006 Å
R factor = 0.045
wR factor = 0.079
Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), is a solvated complex salt which can be formulated as $[AsPh_4]_2[Sn(dmit)_3]\cdot Me_2CO$ and is isostructural with similarly solvated $[PPh_4]_2[Sn(dmit)_3]\cdot Me_2CO$, (II) (de Assis *et al.*, 1999), but with better refinement of the solvent molecule. Indeed, the acetone molecule was eliminated from the refinement of the structure of (II) by means of the *SQUEEZE* subroutine of *PLATON* (Spek, 2003).



(I)

The asymmetric unit of (I) consists of two $[AsPh_4]^+$ cations, the complete dianion and an acetone molecule. The anion is shown in Fig. 1 and selected bond lengths and angles within it are given in Table 1. The two cations, each with near tetrahedral As, show very small differences. Bond lengths and angles in the cations, and within the dmit ligands, are as expected. The three chelating dmit ligands are bound to the Sn atom with differing degrees of asymmetry, with Sn—S bond lengths falling in the range 2.5310 (10)–2.5585 (12) Å and chelate bite angles of 81.59 (3)–87.42 (3)°, providing distorted octahedral coordination. This situation is entirely comparable with that found in other $[Q]_2[Sn(dmit)_3]$ complexes, where Q is an onium counter-cation, such as those described by de Assis *et al.* (1999). With the dmit plane defined as that containing the C═C bond and the attached S atoms and the individual ligands defined as $L1$ (S1–S5/C1–C3), $L2$ (S6–S10/C4–C6) and $L3$ (S11–S15/C7–C9), the displacements of the Sn atom from the mean planes of the ligands are 1.1470 (16), 1.5966 (13) and −0.0362 (14) Å, respectively. These displace-

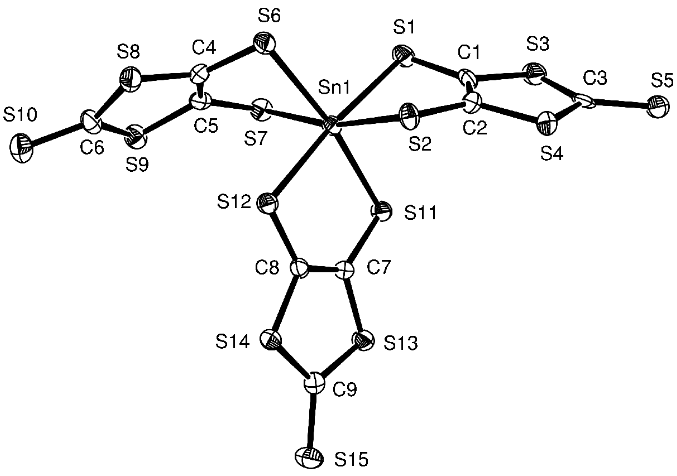


Figure 1
The anion of (I). Displacement ellipsoids are drawn at the 50% probability level.

ments correlate closely with the dihedral angles between each of the ligand planes as defined above and the plane defined, ligand by ligand, by Sn1 and the two chelating S atoms which, in the same order of the ligands as before, are 36.67 (5), 53.32 (5) and 1.15 (5)°, respectively. Thus the variation in these displacements and the corresponding dihedral angles can be ascribed to variation in tilt of the ligands about the line joining the chelating S atoms. This form of ligand tilt is clearly implicated in the wide variation in the overall shape of the $[Sn(dmit)_3]^{2-}$ dianion, ranging from T-shaped as in (I) and (II) to Y-shaped when other *Q* counter-cations are present in the structure (see *e.g.* de Assis *et al.*, 1999). The ligands also differ in the displacements from the ligand plane of their terminal thione S atoms and the C atoms to which these are attached, which fall in the ranges −0.53 (2)–0.329 (2) and −0.025 (4)–0.122 (4) Å, respectively. The completeness of the coordination (coordinative saturation) of the Sn atom precludes interanion metal–sulfur interactions, which are therefore entirely absent. The size of the counter-cations keeps the anions apart, with the result that interanion S···S contacts of any significance are also entirely absent. As would be expected, however, π–π and C—H···π interactions between the cations do occur, but these interactions are not discussed here.

Experimental

Compound (I) was obtained from a mixture of solutions of $[AsPh_4]_2[Zn(dmit)_2]$ (1.00 mmol) (Wardell *et al.*, 1997, 2000) in acetone (25 ml) and anhydrous $SnCl_4$ (0.1 ml, 0.223 g, 0.85 mmol) in MeOH (20 ml). After stirring for 1 h, the reaction mixture was filtered and the red precipitate of $[AsPh_4]_2[Sn(dmit)_3]$ was collected. Further product was isolated from the filtrate left overnight at 273 K after addition of methanol. Recrystallization of the total product, yield 80%, from Me_2CO gave the solvate, $[AsPh_4]_2[Sn(dmit)_3]\cdot Me_2CO$, m.p. 451–452 K. Analysis found: C 46.98, H 3.00%; calculated for $C_{60}H_{46}As_2OS_{15}Sn$: C 47.02, H 3.03%. IR (CsI, cm^{-1}): ν 3057, 1710, 1438, 1482, 1438, 1413, 1082, 1054, 1033, 737, 687, 477, 464, 351, 318, 280, 254, 173, 161. Raman (cm^{-1}): ν 3504, 1576, 1432, 1414, 1038, 1053, 1021, 1000, 522, 467, 348, 320, 238, 188, 173, 163.

Crystal data

$(C_{24}H_{20}As)_2[Sn(C_3S_5)_3]\cdot C_3H_6O$
$M_r = 1532.40$
Triclinic, $P\bar{1}$
$a = 11.2238$ (3) Å
$b = 14.7826$ (5) Å
$c = 19.9333$ (7) Å
$\alpha = 99.0800$ (12)°
$\beta = 99.966$ (2)°
$\gamma = 101.187$ (2)°
$V = 3132.15$ (17) Å^3
$Z = 2$
$D_x = 1.625$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 626 reflections
$\theta = 2.9$–27.5°
$\mu = 2.00$ mm^{-1}
$T = 120$ (2) K
Rod, red
0.36 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.891$, $T_{max} = 0.943$
43 056 measured reflections
14 151 independent reflections
8442 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -19 \rightarrow 19$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.079$
$S = 0.93$
14151 reflections
714 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.90$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—S12	2.5310 (10)	Sn1—S7	2.5517 (10)
Sn1—S11	2.5320 (11)	Sn1—S2	2.5553 (10)
Sn1—S1	2.5503 (10)	Sn1—S6	2.5585 (12)
S12—Sn1—S11	87.42 (3)	S1—Sn1—S2	82.97 (3)
S12—Sn1—S1	173.46 (3)	S7—Sn1—S2	167.34 (4)
S11—Sn1—S1	89.51 (3)	S12—Sn1—S6	86.64 (3)
S12—Sn1—S7	96.99 (3)	S11—Sn1—S6	171.55 (3)
S11—Sn1—S7	93.20 (4)	S1—Sn1—S6	97.00 (4)
S1—Sn1—S7	88.95 (3)	S7—Sn1—S6	81.59 (3)
S12—Sn1—S2	91.63 (3)	S2—Sn1—S6	89.70 (3)
S11—Sn1—S2	96.46 (3)		

In the final stages of refinement H atoms were placed in calculated positions, with C—H = 0.95 and 0.98 Å for aryl and methyl H atoms, respectively, and refined with a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ for aryl H atoms and $1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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