Structural Characterization of a Binuclear Tin Adduct: μ-[1,2-bis(diphenylarsoryl)ethane-*O*:*O'*]-bis(chlorotriphenyltin) †

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The crystal structure of the title compound $(SnPh_3Cl)_2[Ph_2As(O)CH_2CH_2(O)AsPh_2]$ has been determined by *X*-ray diffraction. About tin, the geometry is essentially trigonal bipyramidal, the chloride ion and the diarsine ligand occupying the axial positions, with the aromatic rings in the equatorial plane.

Although the co-ordination chemistry of tin has been very widely explored by crystallographers, as recent surveys show,[1-3] bibliographic searches carried out using the Cambridge Data Files indicated that only very limited *X*-ray data have been reported for mixed tin and arsenic compounds.

As part of our wider programme to investigate the chemical and structural properties of organotin(IV) adducts with P- and As-containing ligands, we report here the structure of $(SnPh_3Cl)_2$(dpaoe) [dpaoe = $Ph_2As(O)CH_2CH_2(O)AsPh_2$], which was prepared by the addition of triphenyltin chloride to 1,2-bis(diphenylarsoryl)ethane in dry acetone–toluene (1 : 1 v/v).

Experimental

Crystal Data.—$C_{62}H_{54}As_2Cl_2O_2Sn_2$, M = 1 289.24, Monoclinic, space group $P2_1/n$ (non-standard setting of C^5_{2h}, no. 14), a = 16.534(5), b = 12.011(5), c = 13.973(4) Å, β = 90.84(3)°, D_m = 1.54, Z = 2, D_c = 1.543 g cm^{-3}, λ(Mo-K_α) = 0.710 69 Å, $F(000)$ = 1 284; specimen: tabular, 0.22 × 0.37 × 0.42 mm.

Measurements were made at room temperature with a Siemens AED three-circle diffractometer in conjunction with a Jumbo 220 computer, using Mo-K_α radiation and employing a θ—2θ scan technique. Automatic centring, indexing, and least-squares routines were carried out. 4 347 Independent reflections were recorded in the range $5.0 < 2\theta < 48.0°$. Of these 2 423 were considered observed having $I > 2\sigma(I)$ and were used in the refinement. A check reflection (352) was remeasured after every 50 reflections and showed no significant decay during the time of exposure to *X*-rays. Corrections were applied for Lorentz and polarization effects, but not for absorption.

The structure was solved by the heavy-atom method. The tin atom was found from a Patterson map, and all remaining non-hydrogen atoms were located by subsequent Fourier maps. It was also possible to recognize in these maps a disordered distribution involving the ethane group, which was found to assume two orientations, each weighted by an occupancy factor of 0.5. Full-matrix least-squares refinement with individual isotropic thermal parameters converged at a conventional R index of 0.1180. The introduction of anisotropic thermal parameters lowered R to 0.0405. Finally, all hydrogen atoms, except those of the ethane group, were located in a difference-Fourier map, included in the refinement along with the non-hydrogen atoms, and their positional parameters were refined together with isotropic thermal parameters. The final R value was 0.0325 and R' = 0.0341. The weighting function minimized was $\Sigma w(F_o - F_c)^2$, in which weights were initially unity and in the final stage of refinement were set according to $w = 0.291/[\sigma^2(F_o) + 0.0044F_o^2]$. A final difference-Fourier synthesis was featureless, the largest peak having 0.59 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 4. All computations were carried out on the Cyber 76 computer of CINECA, with the SHELX system of programs.[5]

Table 1 lists final atomic co-ordinates for non-hydrogen atoms. Selected bond distances and angles are given in Table 2.

Results and Discussion

A perspective view of the molecule showing the atom-numbering scheme is presented in the Figure. The compound exhibits a binuclear structure with the diarsine ligand bridging through the oxygen atoms two tin atoms related by a crystallographic centre of symmetry situated on the centre of gravity of the H_2C-CH_2 bond. The tin atom is co-ordinated to three phenyl rings, a chloride ion, and one oxygen atom of the arsenic ligand in a trigonal-bipyramidal co-ordination geometry, the phenyl rings occupying the equatorial positions.

It is interesting to compare the present compound with the two previously reported tin(IV) complexes with triphenylarsine oxide (tpao). As a whole, the stereochemistry is almost the same as in $SnPh_3(NO_3)$(tpao),[6] in which the five atoms bonded to tin adopt a trigonal-bipyramidal arrangement with the oxygenated ligands in the axial sites, while it is in contrast with that observed in $SnPh_2(NO_3)_2$(tpao),[7] where the geometry at tin is that of a pentagonal bipyramid in which the equatorial positions are occupied by the tpao molecule and the bidentate nitrate groups, the phenyl rings being at the apices. As regards the structural parameters involving the Sn–O–As moiety, the values found in the three compounds are as shown below.

	Bond length/Å		Angle/°
	Sn–O	O–As	Sn–O–As
$SnPh_3(NO_3)$(tpao)	2.181(5)	1.681(5)	136.0(3)
$SnPh_2(NO_3)_2$(tpao)	2.026(4)	1.677(4)	137.9(6)
$(SnPh_3Cl)_2$(dpaoe)	2.239(4)	1.665(4)	134.5(2)

The structure of the title compound has strong similarities to that of $(SnPh_3Cl)_2$(dppoe)[8] [dppoe = $Ph_2P(O)CH_2CH_2(O)PPh_2$], which is also binuclear but with a bridging diphosphine ligand. The most drastic changes caused by replacement of P by As may be found in the Sn–O–X angle which is narrowed from 161.8(2) to 134.5(2)°, and in the appearance of the disorder in the ethane group.

The Sn–Cl distance is 2.532(2) Å and is slightly longer than that [2.475(2) Å] observed in $(SnPh_3Cl)_2$(dppoe) and also than that [2.489(3) Å] observed in $SnPh_3Cl$[*cis*-$Ph_2P(O)CH=CH(O)PPh_2$].[9]

In the phenyl rings the maximum deviation of a ring atom from the corresponding least-squares plane is 0.018 Å. The planes of the phenyl rings bonded to tin are inclined by 43.8

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† *Supplementary data available* (No. SUP 23498, 20 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

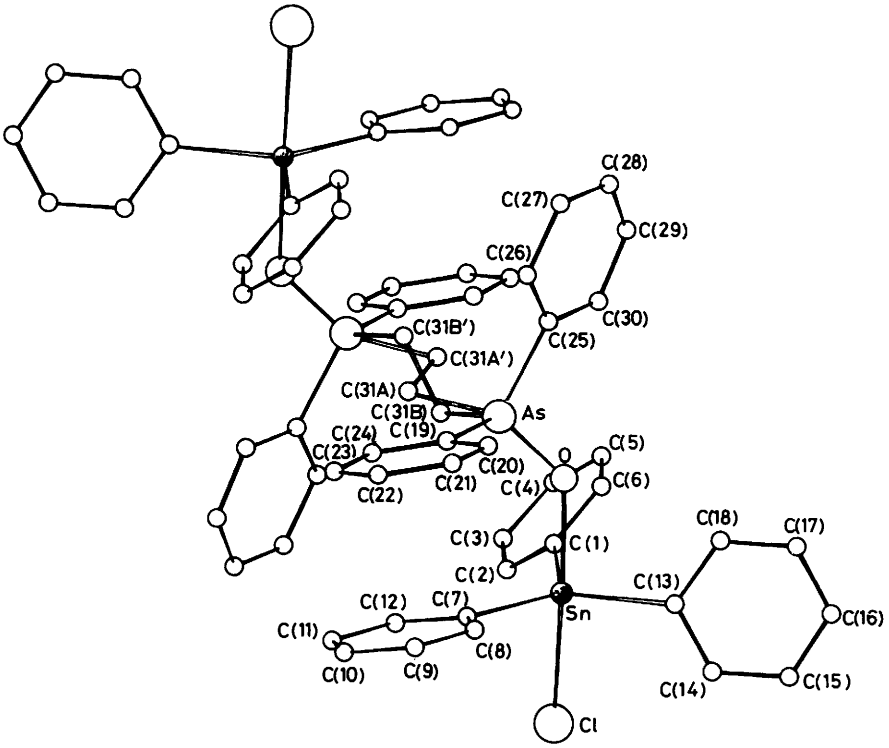

Figure. A perspective view of the molecule

Table 1. Fractional atomic co-ordinates (× 10^5 for Sn and As; × 10^4 for Cl, O, and C) for non-hydrogen atoms

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	52 475(2)	23 674(3)	75 785(3)	C(15)	5 753(5)	2 022(10)	4 511(8)
As	60 413(4)	46 901(5)	89 322(5)	C(16)	5 871(5)	3 064(11)	4 207(7)
Cl	4 654(1)	459(1)	7 252(1)	C(17)	5 875(5)	3 913(9)	4 851(7)
O	5 764(2)	4 045(3)	7 925(3)	C(18)	5 749(4)	3 713(6)	5 805(5)
C(1)	4 090(3)	3 054(5)	7 825(4)	C(19)	7 025(4)	4 141(4)	9 475(4)
C(2)	3 496(5)	2 507(6)	8 336(5)	C(20)	7 706(5)	4 215(7)	8 962(6)
C(3)	2 760(6)	2 927(9)	8 467(7)	C(21)	8 434(5)	3 841(9)	9 345(9)
C(4)	2 560(4)	3 942(10)	8 052(7)	C(22)	8 447(7)	3 378(10)	10 211(10)
C(5)	3 117(5)	4 509(6)	7 538(5)	C(23)	7 786(9)	3 274(8)	10 753(7)
C(6)	3 876(4)	4 068(6)	7 450(5)	C(24)	7 055(6)	3 679(6)	10 366(6)
C(7)	5 987(4)	1 668(5)	8 663(5)	C(25)	6 176(4)	6 233(5)	8 638(4)
C(8)	6 802(5)	1 522(5)	8 258(5)	C(26)	6 786(5)	6 835(6)	9 045(5)
C(9)	7 308(5)	1 047(7)	9 203(8)	C(27)	6 799(6)	7 985(6)	8 877(6)
C(10)	6 968(8)	713(7)	10 050(9)	C(28)	6 215(7)	8 460(6)	8 338(7)
C(11)	6 165(8)	834(8)	10 218(7)	C(29)	5 626(7)	7 859(7)	7 959(7)
C(12)	5 680(5)	1 326(6)	9 507(6)	C(30)	5 607(5)	6 728(6)	8 093(6)
C(13)	5 616(3)	2 633(5)	6 146(5)	C(31A)	5 392(8)	4 703(15)	10 131(13)
C(14)	5 633(4)	1 804(6)	5 467(7)	C(31B)	5 020(12)	4 529(13)	9 649(10)

Table 2. Selected bond distances (Å) and angles (°)

Sn–Cl	2.532(2)	As–C(19)	1.903(6)
Sn–O	2.239(4)	As–C(25)	1.912(6)
Sn–C(1)	2.118(5)	As–C(31A)	2.00(2)
Sn–C(7)	2.108(7)	As–C(31B)	1.99(2)
Sn–C(13)	2.124(7)	C(31A)–C(31A$^{\mathrm{I}}$)	1.52(2)
As–O	1.665(4)	C(31B)–C(31B$^{\mathrm{I}}$)	1.50(2)
Cl–Sn–O	177.8(1)	C(1)–Sn–C(7)	123.6(2)
Cl–Sn–C(1)	91.9(1)	C(1)–Sn–C(13)	111.5(2)
Cl–Sn–C(7)	89.3(2)	C(7)–Sn–C(13)	124.5(2)
Cl–Sn–C(13)	94.7(2)	Sn–O–As	134.5(2)
O–Sn–C(1)	87.5(2)	O–As–C(19)	113.5(2)
O–Sn–C(7)	89.3(2)	O–As–C(25)	107.5(2)
O–Sn–C(13)	87.4(2)	C(19)–As–C(25)	108.6(2)

Symmetry equivalent position: I 1 − *x*, 1 − *y*, 2 − *z*.

[ring C(1)—C(6)], 15.6 [ring C(7)—C(12)], and 71.3° [ring C(13)—C(18)] to that of the SnC_3 grouping. The tin atom is within 0.10 Å of the first two aromatic planes, departing by a significant amount (0.30 Å) from the plane of the third ring. In the $OAsPh_2$ moiety the dihedral angle between the two phenyl planes is 69.3°, and the deviation of the As atom is 0.01 [ring C(19)—C(24)] and 0.20 Å [ring C(25)—C(30)].

The molecular packing is dominated by van der Waals interactions, the shortest contacts being Cl $\cdots$ C(29) (x, $y-1$, z) 3.642(9), C(3) $\cdots$ C(16) ($x-\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) 3.51(1), and C(14) $\cdots$ C(22) ($x-\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) 3.63(1) Å.

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