Structural Characterization of a Binuclear Tin Adduct: μ-Oxalato-bis[nitratodiphenyl(triphenylarsine oxide)tin(IV)] †

Corrado Pelizzi,* Giancarlo Pelizzi, and Pieralberto Tarasconi
Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

The crystal structure of the title compound $[SnPh_2(NO_3)(AsPh_3O)]_2(C_2O_4)$ has been determined by *X*-ray diffraction. The co-ordination geometry of the tin atom is a slightly distorted pentagonal bipyramid, the two phenyl rings occupying the axial positions, with the nitrate and oxalate ions and the triphenylarsine oxide in the equatorial plane. The compound exhibits a binuclear structure with the oxalate ion acting as centrosymmetric bridge between two co-ordination polyhedra.

Whereas considerable structural work has been recently devoted to the co-ordination chemistry of tin,[1-3] relatively few mixed tin and arsenic compounds have been reported and crystallographic information is available on only three of them.[4-6]

As part of our continuing investigation of the structural chemistry of organotin(IV) adducts with arsine oxides [7-9] and to contribute to the knowledge of seven-co-ordinate tin, we now report the crystal and molecular structure of the title compound, which was obtained in very poor yield by reaction of dinitratodiphenyltin(IV) with triphenylarsine. In order to ascertain the correct formula for this compound, which could not be unambiguously established on the basis of the analytical and spectroscopic data, an *X*-ray analysis was undertaken, from which the compound could be formulated as $[SnPh_2(NO_3)(AsPh_3O)]_2(C_2O_4)$. The appearance of the oxalate group is attributed to the strong oxidising properties of the covalently bound nitrate group, as explained later.

Experimental

Preparation.—$[SnPh_2(NO_3)(AsPh_3O)]_2(C_2O_4)$ was obtained as a by-product (yield *ca.* 2%) from the reaction of equimolar amounts of dinitratodiphenyltin(IV) with triphenylarsine in dry acetonitrile under an N_2 atmosphere, the main reaction product being the adduct $SnPh_2(NO_3)_2(AsPh_3O)$. The appearance of the oxalate anion, as shown by the *X*-ray analysis, prompted us to carry out a reaction between $SnPh_2(NO_3)_2$, $AsPh_3O$, and $H_2C_2O_4$ (2 : 2 : 1 mol ratio). A microcrystalline compound was isolated which showed analytical and spectroscopic data identical to those of the title compound, so confirming unequivocally the presence of the oxalate anion.

Crystal Data.—$C_{62}H_{50}As_2N_2O_{12}Sn_2$, M = 1 402.31, Monoclinic, a = 15.165(1), b = 14.782(1), c = 13.298(1) Å, β = 92.01(1)°, U = 2 979.2(4) Å^3, D_m = 1.58 g cm^{-3}, Z = 2, D_c = 1.563 g cm^{-3}, $F(000)$ = 1 396, Cu-K_α radiation, λ = 1.541 78 Å, μ(Cu-K_α) = 85.8 cm^{-1}, space group $P2_1/n$ (a non-standard setting of C_{2h}^5, no. 14), from systematic absences.

Cell dimensions and intensity data were measured on a Siemens AED three-circle diffractometer, using Cu-K_α radiation. Intensities of 5 186 reflections were collected at room temperature with the θ—2θ scan technique up to θ = 62.5°. After data collection, intensities were corrected for Lorentz and polarization effects as well as for some slight decay of the sample during the time of exposure to *X*-rays. No absorption

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

Atom	*X/a*	*Y/b*	*Z/c*
Sn	7 386(2)	14 855(2)	38 016(2)
As	21 428(3)	25 175(3)	56 789(4)
O(1)	1 601(2)	2 403(2)	4 568(2)
O(2)	1 238(2)	2 375(2)	2 499(3)
O(3)	320(3)	1 363(2)	1 959(3)
O(4)	945(3)	2 245(3)	898(3)
O(5)	674(2)	908(2)	5 359(2)
O(6)	257(2)	−283(2)	6 247(2)
N	825(3)	1 995(3)	1 758(3)
C(1)	1 751(3)	567(3)	3 438(4)
C(2)	1 629(5)	−362(4)	3 348(5)
C(3)	2 359(6)	−937(4)	3 171(5)
C(4)	3 165(5)	−585(5)	3 064(6)
C(5)	3 286(4)	323(5)	3 129(7)
C(6)	2 588(4)	892(4)	3 328(6)
C(7)	−338(3)	2 388(4)	3 990(4)
C(8)	−244(5)	3 292(5)	3 728(6)
C(9)	−860(7)	3 931(7)	3 962(7)
C(10)	−1 599(7)	3 676(8)	4 438(8)
C(11)	−1 703(5)	2 801(9)	4 719(7)
C(12)	−1 093(4)	2 131(6)	4 482(5)
C(13)	1 324(3)	2 597(3)	6 739(4)
C(14)	1 569(5)	2 365(4)	7 701(4)
C(15)	960(8)	2 411(5)	8 451(6)
C(16)	132(8)	2 653(6)	8 233(8)
C(17)	−129(6)	2 873(6)	2 723(8)
C(18)	478(4)	2 864(5)	6 510(5)
C(19)	2 962(3)	1 554(3)	5 950(4)
C(20)	3 855(3)	1 701(4)	5 784(4)
C(21)	4 441(4)	988(5)	5 902(6)
C(22)	4 148(5)	163(5)	6 177(6)
C(23)	3 269(5)	14(4)	6 334(6)
C(24)	2 664(4)	705(4)	6 235(5)
C(25)	2 805(3)	3 613(3)	5 562(4)
C(26)	2 926(4)	3 956(4)	4 620(4)
C(27)	3 463(5)	4 708(4)	4 507(5)
C(28)	3 840(4)	5 129(4)	5 331(5)
C(29)	3 708(4)	4 796(4)	6 268(5)
C(30)	3 198(4)	4 028(4)	6 387(4)
C(31)	268(3)	175(3)	5 469(4)

† *Supplementary data available* (No. SUP 23727, 24 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

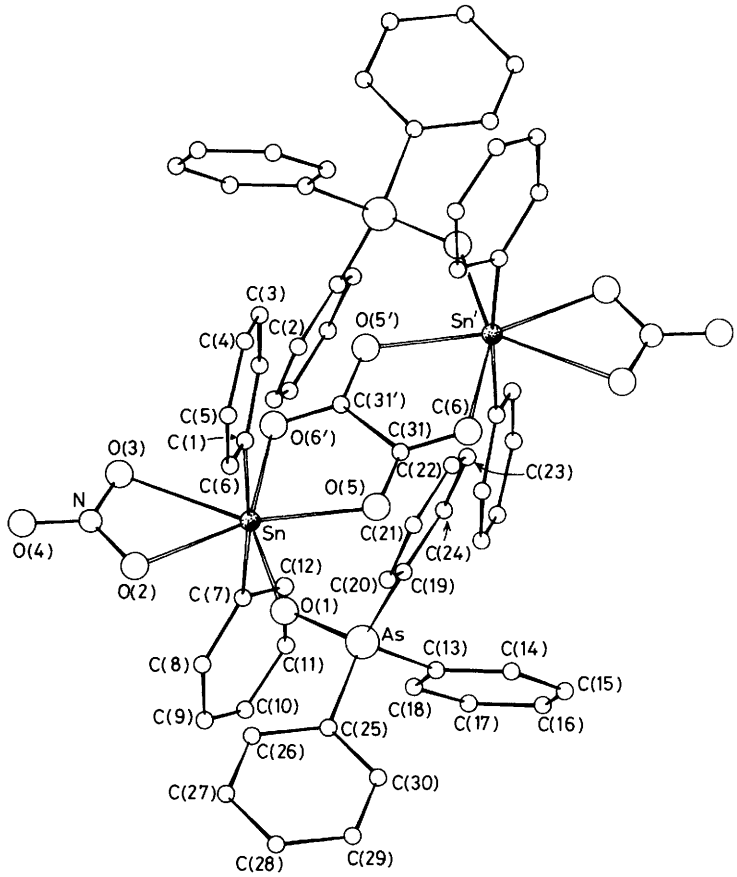

Figure. A perspective view of the molecule $[SnPh_2(NO_3)(AsPh_3O)]_2(C_2O_4)$

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

Sn–O(1)	2.119(3)	As–C(19)	1.915(4)
Sn–O(2)	2.322(4)	As–C(25)	1.915(4)
Sn–O(3)	2.517(4)	N–O(2)	1.279(5)
Sn–O(5)	2.245(3)	N–O(3)	1.243(6)
Sn–O(6')	2.333(3)	N–O(4)	1.221(6)
Sn–C(1)	2.118(5)	O(5)–C(31)	1.257(5)
Sn–C(7)	2.130(5)	O(6)–C(31)	1.237(6)
As–O(1)	1.674(3)	C(31)–C(31')	1.553(7)
As–C(13)	1.915(5)		
C(1)–Sn–C(7)	173.2(2)	C(13)–As–C(19)	109.9(2)
O(1)–Sn–O(2)	77.6(1)	C(13)–As–C(25)	111.3(2)
O(2)–Sn–O(3)	52.6(1)	C(19–As–C(25)	107.8(2)
O(3)–Sn–O(6)	77.1(1)	Sn–O(2)–N	99.4(3)
O(6')–Sn–O(5)	71.7(1)	Sn–O(3)–N	91.1(3)
O(5)–Sn–O(1)	81.2(1)	Sn–O(5)–C(31)	118.2(3)
Sn–O(1)–As	139.8(2)	Sn–O(6')–C(31')	114.9(3)
O(1)–As–C(13)	110.2(2)	O(5)–C(31)–O(6)	126.2(4)
O(1)–As–C(19)	112.7(2)	O(5)–C(31)–C(31')	116.0(4)
O(1)–As–C(25)	104.8(2)	O(6)–C(31)–C(31')	117.9(4)

Primed atoms indicate the symmetry equivalent position: $\bar{x}$, $\bar{y}$, 1-z.

correction was made because the crystal was approximately symmetrical (0.20 × 0.21 × 0.27 mm).

The structure was solved from a Patterson map which allowed placement of the tin atom, while the positions of all remaining non-hydrogen atoms were determined by subsequent difference-Fourier syntheses. The structure was initially refined by full-matrix least squares using isotropic thermal parameters to a conventional R index of 0.0654. A subsequent refinement with varying anisotropic thermal parameters lowered R to 0.0349. Hydrogen atom positions could then be found from a difference-Fourier map and were included in the refinement with individual isotropic thermal parameters to give a final R of 0.0278 (R' = 0.0297) for 3 065 independent reflections having $I \geqslant 3\sigma(I)$. A final difference-Fourier map showed no peak larger than 0.16 e Å^{-3}. Complex neutral-atom scattering factors and corrections for anomalous dispersion (both real and imaginary) were from ref. 10. Major computations were carried out on a Cyber 7 600 computer using the SHELX program package.[11]

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

Results and Discussion

The most outstanding feature of this structure arises from the unexpected presence of the oxalate group which is responsible for the binuclear nature of the compound, as its centre of gravity lies on a crystallographic centre of symmetry. As the reaction was carried out in absence of both air and moisture, the formation of triphenylarsine oxide and the appearance, through an oxidation process involving the acetonitrile, of the oxalate anion have to be attributed to the well known strong oxidising power of the covalently bound nitrate group.[12] An analogous effect with formation of the oxalate anion has been observed previously by us in the closely related μ-oxalato-bis[(di-n-propyl sulphoxide)nitratodiphenyltin(IV)].[13]

As illustrated in the Figure which shows a perspective view of the molecule with hydrogen atoms omitted for clarity, the tin environment is that of a slightly distorted pentagonal bipyramid with the metal bound equatorially by five oxygen

Table 3. Comparison of bond distances (Å) and angles (°) in organotin(IV) triphenylarsine oxide complexes

Complex	Co-ordination number	Sn–O	O–As	Sn–O–As	As–C (average)	O–As–C (average)	C–As–C (average)	Ref.
$SnPh_3(NO_3)(AsPh_3O)$	5	2.181(5)	1.681(5)	136.0(3)	1.910(7)	109.5(3)	109.4(3)	7
$SnPh_2(NO_3)_2(AsPh_3O)$	7	2.026(4)	1.677(4)	137.9(6)	1.896(6)	108.9(6)	111.0(6)	8
$[SnPh_2(NO_3)(AsPh_3O)]_2(C_2O_4)$	7	2.119(3)	1.674(3)	139.8(2)	1.915(4)	109.2(2)	109.7(2)	*

* This work.

atoms, two from the nitrate ion, two from the oxalate ion, and one from the $AsPh_3O$ molecule, the two phenyl rings occupying the axial positions. The maximum deviation from the best plane of tin and the five O donor atoms is 0.09 Å. The pentagonal plane makes an angle of 4.6° with the nitrate plane and an angle of 5.4° with the oxalate plane. The axis of the bipyramid is nearly normal to the O_5 plane (88.4°). The dihedral angle between the two phenyl rings bonded to tin is 23.8° and the deviation of Sn is 0.12 Å [ring C(1)—C(6)] and 0.29 Å [ring C(7)—C(12)].

A similar pentagonal-bipyramidal arrangement around the tin atom, with $AsPh_3O$ replaced by di-n-propyl sulphoxide, has been found in the above mentioned $[SnPh_2(NO_3)(Pr^n_2SO)]_2(C_2O_4)$.[13] In this compound, however, the bidentate nitrate and oxalate groups are symmetrically bonded to tin [Sn–O(nitrate) 2.388(6) and 2.408(6) Å, Sn–O(oxalate) 2.282(5) and 2.248(5) Å], while in the present compound both the ligands have been found to bind in an unsymmetrical bidentate fashion [Sn–O(nitrate) 2.322(4) and 2.517(4) Å, Sn–O(oxalate) 2.245(3) and 2.333(3) Å]. The most directly comparable structures are those of $SnPh_3(NO_3)(AsPh_3O)$ [7] and $SnPh_2(NO_3)_2(AsPh_3O)$ [8] which we have previously characterized by *X*-ray diffraction. The principal structural parameters of these compounds are compared in Table 3 with those of the title compound: (*i*) the most significant differences occur in the Sn–O bond distances, with the longest value observed for the Sn–O axial distance in the five-co-ordinate $SnPh_3(NO_3)(AsPh_3O)$; [7] (*ii*) the Sn–O–As moiety is bent to about the same extent in each compound; (*iii*) the As–C and the As–O bond distances are quite similar in the three compounds; the co-ordination by O produces a lengthening of the As–O bond distance when compared with the free ligand [1.644(7) Å[14]]; (*iv*) the arsenic environment shows very small distortions from the ideal tetrahedral geometry.

Some short intermolecular contacts take place between the oxygen atoms of the NO_3 group and the carbon atoms of the phenyl rings, the most significant are O(2) · · · C(4) ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) 3.244(8), O(3) · · · C(29) ($x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$) 3.098(7), and O(4) · · · C(15) (x, y, $z - 1$) 3.264(9) Å.

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