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STRUCTURAL RESEARCHES ON NITRATO COMPLEXES OF ORGANOTIN: COORDINATIVE INTERACTIONS Sn—O IN NITRATOTRIPHENYL(TRIPHENYLARSINE OXIDE)TIN(IV)

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Summary

A molecular adduct of nitratotriphenyltin with triphenylarsine oxide $[Sn(C_6H_5)_3(NO_3)\{(C_6H_5)_3AsO\}]$ has been synthesized and its IR spectroscopic properties and X-ray crystal structure are reported. Crystals are orthorhombic ($P2_12_12_1$) with unit-cell dimensions: *a* 17.35(1), *b* 19.30(2), *c* 9.56(1) Å, *Z* 4. The structure has been solved from 2070 independent diffractometer data and refined anisotropically by block-diagonal least-squares methods to the conventional *R* factor 3.6%. The coordination about tin is trigonal bipyramidal with the phenyl rings in equatorial and the oxygenated ligands in axial positions.

Introduction

Interest in triphenyltin derivatives is justified by the many uses of these compounds, which are essentially based on their high biological activity combined with the fact that the inorganic species they produce are non toxic, in contrast to those of the organolead and organomercury derivatives [1,2,3].

Continuing our researches on adducts of triphenyltin with unidentate ligands containing oxygen groups such as N—O, S—O, As—O, P—O [4,5], we have now synthesized and examined by spectroscopic techniques and X-ray diffraction methods, a molecular adduct of nitratotriphenyltin(IV) with triphenylarsine oxide, $Sn(C_6H_5)_3(NO_3)[(C_6H_5)_3AsO]$.

Experimental

Triphenylarsine oxide (3.2 g) in dry acetone was added under nitrogen to a solution of Ph_3SnNO_3 (4.1 g) in the same solvent. The crude product was pre-

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TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS (Å^2) ^{a,b}

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{12}(\sigma)$	$B_{13}(\sigma)$	$B_{23}(\sigma)$
Sn	−864(0)	−1629(0)	1060(1)	3.78(2)	3.58(2)	4.24(2)	−0.10(2)	−0.17(2)	0.01(2)
As	−2465(1)	−2603(0)	2317(1)	2.29(3)	2.21(3)	2.38(3)	−0.14(3)	−0.14(3)	0.10(3)
O(1)	28(3)	−1224(3)	−461(6)	6.4(3)	4.3(3)	5.3(3)	−1.4(3)	−0.1(3)	0.1(3)
O(2)	−259(4)	−185(3)	161(9)	6.9(4)	4.7(3)	11.1(6)	0(3)	−0.8(4)	1.5(4)
O(3)	553(4)	−350(4)	−1472(8)	11.5(6)	11.0(5)	7.1(5)	−6.4(5)	2.9(4)	1.0(4)
O(4)	−1690(3)	−2097(3)	2481(6)	3.4(2)	3.9(2)	4.8(3)	−0.7(2)	−0.1(2)	0.2(2)
N	103(4)	−564(4)	−594(8)	5.6(4)	6.1(4)	5.4(4)	−1.4(3)	−1.2(3)	0.3(3)
C(1)	−491(4)	−2604(4)	378(9)	3.8(3)	4.4(4)	4.7(4)	−0.2(3)	−0.5(3)	0.9(4)
C(2)	−409(4)	−3147(4)	1323(10)	3.8(4)	4.6(4)	7.1(6)	−0.1(3)	0(4)	0(4)
C(3)	−207(6)	−3835(4)	906(14)	6.0(5)	4.3(4)	11.9(8)	0.7(4)	0.2(6)	3.5(6)
C(4)	−81(6)	−3945(5)	−495(13)	8.5(7)	4.2(4)	10.3(8)	−0.1(5)	2.7(7)	−1.1(5)
C(5)	−153(6)	−3441(6)	−1455(11)	6.9(5)	6.7(6)	8.8(7)	−1.8(5)	3.8(5)	−2.8(6)
C(6)	−353(5)	−2766(4)	−1081(12)	5.2(4)	5.3(4)	7.2(5)	−1.0(4)	0.9(5)	0.7(5)
C(7)	−314(4)	−1225(4)	2860(9)	3.2(3)	3.2(3)	4.9(4)	0.4(3)	0.1(3)	0.1(3)
C(8)	−672(4)	−1169(4)	4122(11)	4.3(4)	4.8(4)	6.9(6)	0.1(3)	−1.3(4)	−1.3(5)
C(9)	−289(6)	−922(5)	5285(10)	6.1(5)	6.1(5)	5.5(5)	1.2(4)	1.2(4)	−2.0(4)
C(10)	461(5)	−720(5)	5210(11)	6.4(5)	4.9(5)	7.0(6)	1.4(4)	−2.4(5)	−2.6(5)
C(11)	822(5)	−788(4)	3972(11)	4.8(4)	5.7(4)	6.9(5)	0.4(4)	−1.2(5)	−1.4(5)
C(12)	441(5)	−1017(4)	2796(10)	4.8(4)	5.0(4)	4.7(4)	−0.5(3)	−0.4(4)	−0.1(4)
C(13)	−1739(5)	−1134(4)	−98(9)	4.2(4)	4.8(4)	4.2(4)	−0.5(3)	0.2(4)	0.7(4)
C(14)	−1804(5)	−1231(5)	−1515(10)	5.7(5)	7.9(6)	5.5(5)	−0.6(5)	0.1(4)	1.3(5)
C(15)	−2414(7)	−927(6)	−2250(10)	8.0(6)	10.8(7)	4.6(5)	−1.3(6)	−0.9(6)	2.5(5)

C(16)	−2955(5)	−521(6)	−1489(15)	3.7(4)	8.8(7)	14.9(11)	−0.4(5)	−2.1(6)	5.7(8)
C(17)	−2869(6)	−430(5)	−138(12)	6.9(6)	7.4(6)	7.6(6)	2.8(5)	−1.4(5)	2.0(5)
C(18)	−2262(5)	−726(5)	552(10)	6.1(5)	5.1(4)	5.7(5)	0.5(4)	−0.9(4)	0.3(4)
C(19)	−2780(4)	−2752(4)	339(7)	2.9(3)	4.0(3)	2.5(3)	−1.0(3)	−0.8(3)	−0.3(3)
C(20)	−2286(4)	−3192(4)	−388(8)	4.3(4)	4.5(4)	4.0(4)	−0.2(3)	−0.1(3)	−1.1(3)
C(21)	−2421(6)	−3255(5)	−1829(7)	7.4(5)	7.4(5)	1.9(3)	−2.4(5)	0.6(4)	−1.3(4)
C(22)	−3011(6)	−2858(5)	−2393(9)	6.6(5)	8.4(6)	3.7(4)	−0.9(5)	−1.5(4)	−0.3(4)
C(23)	−3447(5)	−2432(6)	−1588(9)	5.0(4)	8.7(6)	5.0(5)	0.2(5)	−1.5(4)	1.5(5)
C(24)	−3316(5)	−2375(5)	−179(9)	3.9(4)	7.2(6)	4.3(4)	−0.6(4)	0.2(3)	0.1(4)
C(25)	−2259(4)	−3490(4)	3144(8)	3.6(3)	4.1(4)	4.2(4)	0.6(3)	0.4(3)	0.6(3)
C(26)	−1712(5)	−3544(4)	4190(9)	4.8(4)	5.8(5)	4.1(4)	0.2(3)	−0.8(4)	0.8(4)
C(27)	−1558(5)	−4192(5)	4765(10)	6.1(5)	6.2(5)	5.3(5)	1.9(4)	0.3(4)	3.1(4)
C(28)	−1968(6)	−4753(5)	4332(10)	8.6(6)	4.5(4)	6.1(6)	2.5(4)	1.3(5)	1.8(4)
C(29)	−2581(6)	−4703(4)	3330(10)	8.6(6)	3.2(3)	7.1(6)	−0.2(5)	0.1(6)	0.3(4)
C(30)	−2674(5)	−4061(4)	2722(10)	6.4(5)	3.9(4)	6.0(5)	−0.2(4)	0.4(5)	−1.1(4)
C(31)	−3265(4)	−2181(4)	3348(9)	3.2(3)	4.4(4)	4.1(4)	0.2(3)	0.1(3)	0.4(3)
C(32)	−3869(4)	−2547(4)	3824(9)	3.9(3)	4.8(4)	5.5(4)	0.9(3)	1.6(3)	2.4(4)
C(33)	−4415(5)	−2242(5)	4699(10)	5.0(4)	6.9(5)	5.5(5)	−0.1(4)	2.5(4)	1.3(4)
C(34)	−4835(5)	−1575(5)	5043(10)	5.3(5)	7.8(6)	5.1(5)	2.8(5)	0.1(4)	0(5)
C(35)	−3738(5)	−1185(5)	4596(11)	6.0(5)	5.4(5)	6.4(6)	1.6(4)	−1.0(5)	−2.0(4)
C(36)	−3183(4)	−1484(4)	3775(10)	4.7(4)	4.7(4)	6.1(5)	0.7(3)	0(4)	−0.8(4)

[a] Anisotropic thermal parameters are in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Standard deviations occurring in the last significant figure are given in parentheses.

cipitated by slow evaporation under reduced pressure of the solvent and recrystallized from chloroform/benzene or chloroform/toluene to yield colourless crystals. Found: C, 59.2; H, 4.1; N, 2.2; Sn, 16.4. $C_{36}H_{30}AsNO_4Sn$ calcd.: C, 58.9; H, 4.1; N, 1.9; Sn, 16.2%.

The IR spectra were recorded on a Perkin—Elmer model 457 spectrophotometer using KBr disks.

From the systematic absences, as indicated from Weissenberg photographs (h 0 0, h odd; 0 k 0, k odd; 0 0 l, l odd), the space group was unambiguously determined as $P2_12_12_1$. Crystal data for $[Sn(C_6H_5)_3(NO_3)\{(C_6H_5)_3AsO\}]$: M.w.734.2. a 17.53(1); b 19.30(2); c 9.56(1) Å; V 3234.4 $Å^3$; Z 4, D_{obs} 1.50 g cm^{-3}, D_{calc} 1.51 g cm^{-3}; $\mu(Mo\text{-}k_\alpha)$ 19.1 cm^{-1}; $F(000)$ 1472. Accurate measurements of the unit-cell dimensions and collection of intensity data were made on a Siemens AED diffractometer with Mo-K_α radiation ($\bar{\lambda}$ 0.7107 Å). The sample was roughly a prism with a mean radius of 0.10 mm. One quarter of the reciprocal sphere was recorded in the range $4.0° \leqslant 2\theta \leqslant 52.0°$. Of the 3565 independent reflections recorded, 2070 were considered as observed having $I > 2\sigma(I)$. A standard reflection was periodically measured during the course of data collection to check crystal alignment and/or decomposition. The intensity of this reflection did not vary to any appreciable extent, although it was necessary to realign the crystal from time to time when a drift in the reference reflection was observed. Data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

From a three-dimensional Patterson map the coordinates of the tin atom were obtained by assuming the strongest peaks to be due to tin—tin vectors. The positions of the remaining non-hydrogen atoms were obtained by application of the heavy-atom method. Refinement was by block-diagonal least-squares where the function minimized was $\Sigma w|\Delta F|^2$. Four cycles of isotropic refinement gave a conventional R of 7.0% for all observed reflections. Another five cycles using anisotropic thermal parameters reduced the R value to 4.4%. At this stage the hydrogen atoms were included in their calculated positions (C—H 1.08 Å) as fixed contributions to F_c assuming isotropic thermal parameters (B 6.0 $Å^2$). The final R's were 3.6% for the observed reflections and 7.1% for the total number of reflections. As a final check of the correctness of the structure, a ΔF map was calculated, and found to be featureless.

Final atomic coordinates and thermal parameters are listed in Table 1. A list of observed and calculated structure factors can be obtained from the authors. Scattering factors were from Cromer and Mann [6]. Table 2 lists the main IR absorption bands.

All the calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale.

Results and discussion

As pointed out by Muetterties and Schunn [7], for pentacoordinated XML_3L' species, there are four possible isomers for a trigonal bipyramid and four for a tetragonal pyramid and of the eight isomers, only one, the C_{3v} trigonal bipyramidal model, can be uniquely defined from symmetry arguments. In all other cases the more important factor governing the choice of the pentacoordinate

TABLE 2

SELECTED INFRARED ABSORPTION BANDS (cm^{-1})

1575w 1480(sh) 1468vs 1438s	ν(CC)
1430s	$\nu(NO)_{as}$
1382ms	ν(CC)
1295vs	$\nu(NO)_s$
1260m 1185w 1160w	β(CH)
1087ms (1093) [a]	ν(AsC)
1080(sh) 1025m	β(CH)
1012m	ν(NO)
1000m	ring
925w 915w	γ(CH)
855vs (880)	ν(AsO)
810m	$\delta(NO_2)$
742s 732(sh) 725(sh)	γ(CH)
695s (685) 690(sh)	ν(AsC) + φ(CC)
475m (470) 455ms (450)	ν(AsC) + ring
380m	ν(SnO)
355m (355) — (340)	ν(AsC)
270m	ν(SnC)

[a] The bands of uncoordinated triphenylarsine oxide are reported in parentheses.

geometry is the non-bonding repulsion between ligands, particularly when bulky ligands are present.

As illustrated in Fig. 1, which shows a clinographic projection of the title compound (M = Sn, X = NO_3, L = C_6H_5, L' = $(C_6H_5)_3AsO$), the coordination geometry at tin is trigonal bipyramidal. The equatorial positions are occupied by the phenyl rings, and the axial sites are taken up by the nitrate group and the triphenylarsine oxide (TPAO) molecule, so that the arrangement of the ligand atoms corresponds well to a C_{3v} model. Thus this compound has a structure similar to that of nitratotriphenyl(triphenylphosphine oxide)tin(IV) $SnPh_3(NO_3)TPPO$ [4] and nitratotriphenyl(pyridine *N*-oxide)tin(IV) $SnPh_3(NO_3)pyO$ [5]. In Table 3 bond distances and angles in the coordination polyhedron for these three compounds are compared. From the bond angles it can be seen that the trigonal bipyramidal arrangement is only slightly distorted from the ideal geometry. Thus the axial to axial

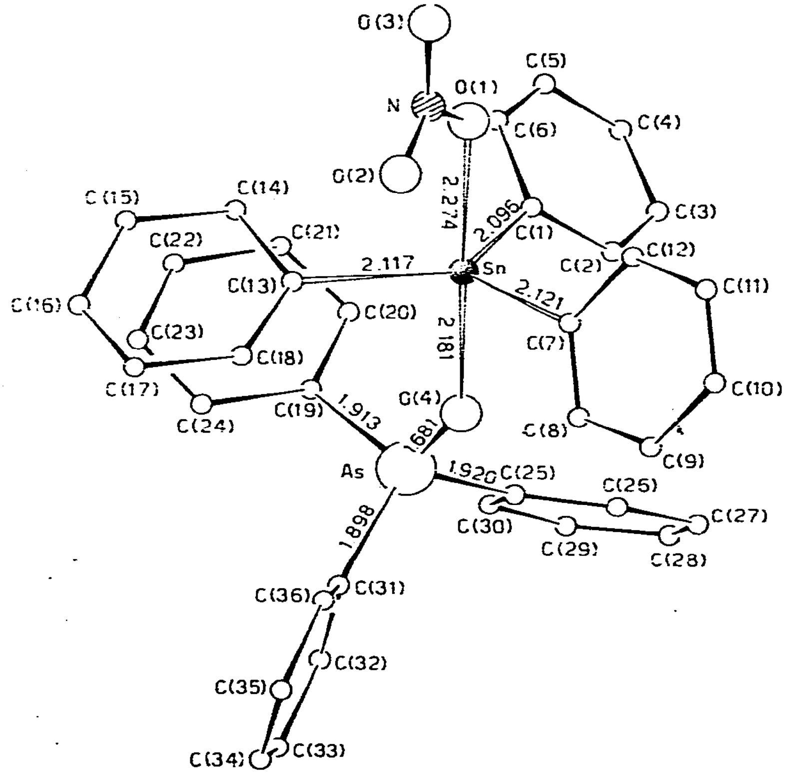

Fig. 1. Clinographic projection of $[Sn(C_6H_5)_3(NO_3)\{(C_6H_5)_3AsO\}]$ with bond distances (Å) at tin and arsenic.

angle is 174.1 (TPPO), 171.4 (pyO) and 175.6° (TPAO). Similar small deviations from the theoretical values are observed for the equatorial angles [113.4—126.0 (TPPO); 118.0—120.9 (pyO); 116.1—125.9° (TPAO)]. The Sn—O bonds in the three compounds are noteworthy. The $Sn—O(NO_3)$ distance increases in the order TPPO < pyO < TPAO, while the opposite is true for the Sn—O(org. lig.) distance, the two distances being linearly related (Fig. 2). In the present compound the Sn—O(org. lig.) stretching vibration, which falls in the range found for other TPAO—tin complexes [8—11], shows a frequency value higher (380 cm^{-1}) than those observed in $SnPh_3(NO_3)TPPO$ (295 cm^{-1}) and in $SnPh_3(NO_3)pyO$ (325 cm^{-1}) complexes, indicating a stronger bonding in the TPAO complex. In addition, as expected, along with an increase in ν(Sn—O(org. lig.)) in the order TPPO < pyO < TPAO there is a regular decrease of the relevant Sn—O bond distance, as shown in Fig. 3. In order to elucidate this behaviour a systematic structural study of the $SnPh_3(NO_3)X$ species (X = oxygenated ligand) is in progress in our laboratory.

The Sn—C bond lengths do not differ significantly from each other in the three derivatives. They fall at the lower limit of the range of lengths observed in five-coordinated monomer organotin compounds (2.10—2.20 Å) [4] and within the wide range (1.93—2.27 Å) observed for triphenyltin derivatives, without

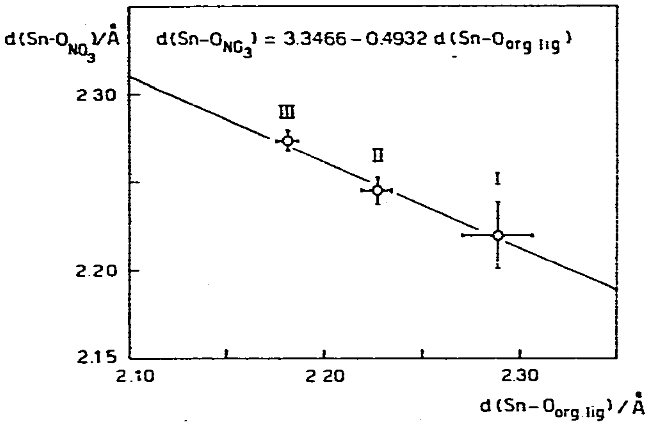

Fig. 2. Plot of Sn—O(NO_3) against Sn—O(org. lig.) for $SnPh_3(NO_3)$TPPO (I), $SnPh_3(NO_3)$pyO (II) and $SnPh_3(NO_3)$TPAO (III). The e.s.d. intervals are also shown.

regard for the metal coordination (see Table 4). In this connexion it can be observed that out of about 60 triorganotin species for which the structures are known, only one third involves phenyl derivatives. In most of them, coordination to metal is tetrahedral, while in the methyl compounds the less bulky nature of CH_3 compared with C_6H_5 seems to favour pentacoordination. In the compounds listed in Table 4 the phenyl rings occupy equatorial positions with only two exceptions, in which one phenyl ring is axial. Comparing the Sn—C stretching vibrations in the TPPO, pyO and TPAO tin-complexes, it can be observed that the frequency value is insensitive to the nature of the oxygenated ligand.

Table 5 lists bond distances and angles in the title compound, except for those relating to the coordination polyhedron, which are given in Table 3.

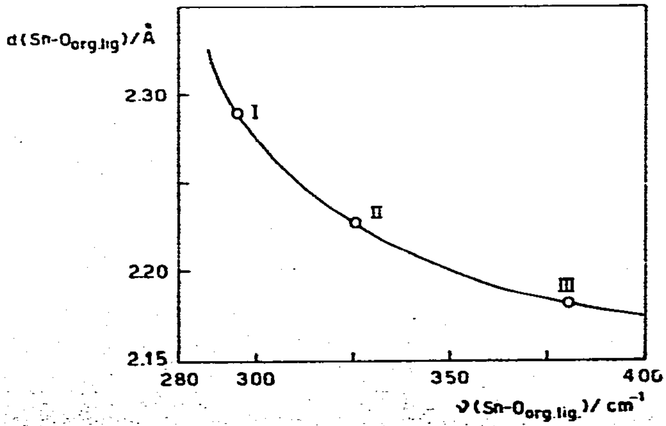

Fig. 3. Plot of Sn—O(org. lig.) bond distance against ν(Sn—O(org. lig.)) frequency for $SnPh_3(NO_3)$TPPO (I), $SnPh_3(NO_3)$pyO (II), $SnPh_3(NO_3)$TPAO (III).

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) IN THE COORDINATION POLYHEDRON FOR $SnPh_3(NO_3)X$ COMPOUNDS (X = UNIDENTATE OXYGENATED LIGAND BONDED TO Sn THROUGH O)

	I (X = TPPO) [4]	II (X = pyO) [5]	III (X = TPAO)
Sn—O(NO_3)	2.22(2)	2.245(8)	2.274(6)
Sn—O(X)	2.29(2)	2.227(8)	2.181(5)
Sn—C	2.10(2), 2.13(2), 2.14(2)	2.096(9), 2.112(9), 2.126(9)	2.096(8), 2.117(8), 2.121(8)
O(NO_3)—Sn—O(X)	174.1(7)	171.4(2)	175.6(2)
O(NO_3)—Sn—C	84.9(8), 94.7(8), 97.3(8)	82.6(3), 94.6(3), 97.3(3)	84.0(3), 90.6(3), 94.6(3)
O(X)—Sn—C	86.1(8), 87.1(7), 89.4(7)	86.5(3), 89.4(3), 89.6(3)	87.1(3), 91.7(3), 91.7(3)
C—Sn—C	113.4(9), 120.0(9), 126.0(9)	118.0(3), 120.8(3), 120.9(3)	116.1(3), 118.0(3), 125.9(3)

TABLE 4

LENGTHS OF Sn—C BONDS (Å) IN TRIPHENYLTIN DERIVATIVES

Compound	Coordination [a]	Sn—C		
$Mn(CO)_4(PPh_3)(SnPh_3)$ [12]	T	2.16(4)	2.17(4)	2.17(4)
$Mn(CO)_5(SnPh_3)$ [13]	T	2.08—2.22		
$Mn(CO)_3[C_5Ph_4(OSnPh_3)]$ [14]	T	2.09(1)	2.13(1)	2.17(1)
$Fe(CO)_2(C_5H_5)(SnPh_3)$ [15]	T	2.10—2.17		
$Fe(CO)(C_2Ph_2)(C_5H_5)SnPh_3)$ [16]	T	(2.21)		
$SnPh_3Cl$ [17]	T	2.12		
$SnPh_3CHT$ [b] [18]	T	2.16(1)	2.16(1)	2.16(1)
$SnPh_3(SC_5H_4N)$ [19]	TBP	2.14(2)	2.17(2)	2.17(2)
$SnPh_3(SC_6H_2Me_3)$ [20]	T	2.09(1)	2.13(1)	2.17(1)
$SnPh_3(SC_6H_2FBr_2)$ [21]	T	2.11	2.11	2.12
$SnPh_3(SC_6H_4Me)$ [21]	T	2.15(3)	2.16(3)	2.18(3)
$SnPh_3(ONPhCOPh)$ [22]	TBP	2.131(7)	2.142(9)	2.176(9) [d]
$SnPh_3(SC_6H_4\text{-t-Bu-}p)$ [23]	T	2.122(10)	2.124(9)	2.132(9)
$SnPh_3(NCS)$ [24]	Int	2.01—2.15		
$SnPh_3DPD$ [c] [25]	TBP	2.149(7)	2.181(6)	2.180(6) [d]
Sn_2Ph_6 [26]	T	2.14—2.27		
$Sn(NO_3)(SnPh_3)$ [27]	T	1.93(1)	1.93(1)	1.98(1)
$Sn(NO_3)(SnPh_3)_3$ [27]	T	1.93—1.99		
$SnPh_3(NO_3)TPPO$ [4]	TBP	2.10(2)	2.13(2)	2.14(2)
$SnPh_3(NO_3)pyO$ [5]	TBP	2.096(9)	2.112(9)	2.126(9)
$SnPh_3(NO_3)TPAO$	TBP	2.096(9)	2.117(8)	2.121(8)

[a] T = tetrahedral, TBP = trigonal bipyramidal, Int = intermediate. [b] CHT = 7-cyclohepta-1,3,5-trienyl; [c] DPD = 1,3-diphenylpropane-1,3-dionato. [d] Axial bonds.

The triphenylarsine oxide is covalently bonded to tin through its oxygen atom, with a consequent small lengthening of the O—As bond (1.681 Å) compared with that in the free ligand (1.644 Å) [28]. The geometry at the arsenic atom is essentially tetrahedral, with $(O—As—C)_{aver}$ 109.5° and $(C—As—C)_{aver}$ 109.4°; but the C_{3v} trigonal symmetry is not present because of the different inclination of the three aromatic rings with respect to the plane defined by oxygen, arsenic and carbon bonded to As (i.e. 76.6° for C(19) ... C(24); 23.9° for C(25) ... C(30); 19.7° for C(31) ... C(36)). The arsenic atom departs by a small amount from the C(19) ... C(24) (0.20 Å) and the C(31) ... C(36) (0.15 Å) phenyl planes, while is practically coplanar (0.01 Å) with the third phenyl ring C(25) ... C(30). An inspection of Table 6, which gives the structural parameters for TPAO in the free ligand and in its metal complexes, as determined by X-ray methods, suggests that, with the sole exception of a small weakening of the O—As bond, the geometry and dimensions of the uncomplexed molecule are preserved during the coordination to the metal.

The ν(As—O) frequency agrees well with the values observed for other tin or organotin complexes which usually exhibit a negative shift with respect to the free ligand absorption (880 cm^{-1}) [8,36,37]. The sequence $\Delta\nu$(P—O) > $\Delta\nu$(N—O) > $\Delta\nu$(As—O), with values −40, −37 and −25 cm^{-1} respectively for the TPPO, pyO and TPAO tin-complexes, is noteworthy; such negative shifts are consistent with a lowering of the respective bond orders upon coordination [36]. The vibrational modes involving As—C stretching show only very small shifts on coordination.

TABLE 5

BOND DISTANCES (Å) AND ANGLES (°) [a, b]

(i) in the triphenylarsine oxide molecule					
As—O(4)	1.681(5)				
As—C(19)	1.913(7)	As—C(25)	1.920(8)	As—C(31)	1.898(
C(19)—C(20)	1.38(1)	C(25)—C(26)	1.39(1)	C(31)—C(32)	1.35(1
C(20)—C(21)	1.40(1)	C(26)—C(27)	1.39(1)	C(32)—C(33)	1.40(1
C(21)—C(22)	1.40(1)	C(27)—C(28)	1.36(1)	C(33)—C(34)	1.34(1
C(22)—C(23)	1.36(1)	C(28)—C(29)	1.38(1)	C(34)—C(35)	1.36(1
C(23)—C(24)	1.37(1)	C(29)—C(30)	1.39(1)	C(35)—C(36)	1.38(1
C(24)—C(19)	1.37(1)	C(30)—C(25)	1.38(1)	C(36)—C(31)	1.41(1
As—O(4)—Sn	136.0(3)				
O(4)—As—C(19)	111.9(3)	O(4)—As—C(25)	109.1(3)	O(4)—As—C(31)	107.4(
C(19)—As—C(25)	107.8(3)	C(19)—As—C(31)	112.5(3)	C(25)—As—C(31)	107.9(
As—C(19)—C(20)	118.7(5)	As—C(25)—C(26)	119.5(6)	As—C(31)—C(32)	122.0(
As—C(19)—C(24)	119.2(6)	As—C(25)—C(30)	119.5(6)	As—C(31)—C(36)	118.9(
C(20)—C(19)—C(24)	122.0(7)	C(26)—C(25)—C(30)	120.9(8)	C(32)—C(31)—C(36)	118.7(
C(19)—C(20)—C(21)	119.7(7)	C(25)—C(26)—C(27)	119.0(8)	C(31)—C(32)—C(33)	121.1(
C(22)—C(21)—C(20)	117.2(8)	C(26)—C(27)—C(28)	119.4(9)	C(32)—C(33)—C(34)	118.7(
C(23)—C(22)—C(21)	122.0(8)	C(27)—C(28)—C(29)	122.2(8)	C(33)—C(34)—C(35)	122.5(
C(24)—C(23)—C(22)	120.7(9)	C(28)—C(29)—C(30)	118.8(8)	C(34)—C(35)—C(36)	119.5(
C(23)—C(24)—C(19)	118.5(8)	C(29)—C(30)—C(25)	119.6(9)	C(35)—C(36)—C(31)	119.5(
(ii) in the nitrate group					
N—O(1)	1.29(1)	N—O(2)	1.21(1)	N—O(3)	1.22(1
O(1)—N—O(2)	119.1(7)	O(2)—N—O(3)	123.0(8)	O(1)—N—O(3)	117.9(
N—O(1)—Sn	118.3(5)				
(iii) in the phenyl rings					
C(1)—C(2)	1.39(1)	C(7)—C(8)	1.36(1)	C(13)—C(14)	1.38(1
C(2)—C(3)	1.43(1)	C(8)—C(9)	1.38(1)	C(14)—C(15)	1.41(1
C(3)—C(4)	1.37(2)	C(9)—C(10)	1.37(1)	C(15)—C(16)	1.43(1
C(4)—C(5)	1.34(2)	C(10)—C(11)	1.35(1)	C(16)—C(17)	1.31(2
C(5)—C(6)	1.41(1)	C(11)—C(12)	1.38(1)	C(17)—C(18)	1.38(1
C(6)—C(1)	1.40(1)	C(12)—C(7)	1.38(1)	C(18)—C(13)	1.36(1
Sn—C(1)—C(2)	120.4(6)	Sn—C(7)—C(8)	122.5(6)	Sn—C(13)—C(14)	120.8(
Sn—C(1)—C(6)	123.5(6)	Sn—C(7)—C(12)	120.4(6)	Sn—C(13)—C(18)	121.0(
C(2)—C(1)—C(6)	116.0(8)	C(8)—C(7)—C(12)	117.1(8)	C(14)—C(13)—C(18)	118.1(
C(1)—C(2)—C(3)	122.9(9)	C(7)—C(8)—C(9)	121.0(8)	C(13)—C(14)—C(15)	119.9(
C(2)—C(3)—C(4)	117.1(9)	C(8)—C(9)—C(10)	121.4(9)	C(14)—C(15)—C(16)	118.6(
C(3)—C(4)—C(5)	122.6(9)	C(9)—C(10)—C(11)	117.9(9)	C(15)—C(16)—C(17)	119.9(
C(4)—C(5)—C(6)	119.8(10)	C(10)—C(11)—C(12)	121.3(9)	C(16)—C(17)—C(18)	120.3(
C(5)—C(6)—C(1)	121.7(9)	C(11)—C(12)—C(7)	121.3(8)	C(17)—C(18)—C(13)	123.1(

[a] Bond distances and angles in the coordination polyhedron are given in Table 3. [b] Standard deviations occurring in the last significant figure are given in parentheses.

The values of the M—O—As angles (Table 6), which range from 122 to 159°, indicate that only bent coordination by TPAO occurs, in contrast with the case with TPPO, for which both linear and bent coordination have been observed [4].

The nitrate group is bonded as unidentate ligand to tin and its orientation is defined by the dihedral angle of 4.7° its plane makes with NO(1)Sn plane. Its structural parameters and its vibrational bands are consistent with the unidentate ligand behaviour [4,38,39].

The average of the 36 C—C distances and the 36 C—C—C angles within the six phenyl rings are 1.38 Å and 120.0° respectively, and none of the individual values

TABLE 6

BOND DISTANCES (Å) AND ANGLES (°) IN TRIPHENYLARSINE OXIDE AND ITS METAL COMPLEXES [a]

	I	II		III		IV	V	VI	VII	VIII	IX
M—O	—	2.32(3)	2.37(3)	2.46(2)	2.48(2)	2.36(3)	2.30(2)	2.25(3)	2.20—2.30	1.92(1)	2.181(5)
As—O	1.644(7)	1.69(3)	1.69(3)	1.66(2)		1.65(4)	1.64(2)	1.70	1.66—1.69	1.67(1)	1.681(5)
As—C (mean)	1.907(9)	1.92(4)		1.92(5)		1.87(5)	1.89(5)		1.91(2)	1.89(1)	1.910(8)
M—O—As	—	137(2)	134(2)	122(1)	129(1)	153(1)	159(1)	157	142—153	149.8(7)	136.0(3)
O—As—C(mean)	110.9(4)	111(2)		110(2)		111(2)	111(2)		110(1)	109.9(6)	109.5(3)
C—As—C(mean)	108.0(4)	108(2)		109(2)		108(2)	107(2)		109(1)	109.1(7)	109.4(3)
As—C—C(mean)	119.1(8)			117(4)		118(4)	120(3)		120(2)		119.6(6)

[a] I = TPAO · H_2O [28]; II = $HgCl_2(TPAO)_2$ [29]; III = $[HgCl_2TPAO]_2$ [30]; IV = $UO_2(NO_3)_2(TPAO)_2$ [31]; V = $UO_2[(C_2H_5)_2NCS_2]_2TPAO$ [32]; VI = $UO_2[(C_2H_5)_2NCSe_2]_2TPAO$ [33]; VII = $Bi_2I_6(TPAO)_3$ [34]; VIII = $CoCl_2(TPAO)_2$ [35]; IX = $Sn(C_6H_5)_3(NO_3)TPAO$ (present work).

TABLE 7

INTERMOLECULAR CONTACTS (Å) LESS THAN 3.60 Å [a]

O(4) ... C(27^{i})	3.28	O(3) ... C(35^{ii})	3.22
O(4) ... C(28^{i})	3.42	O(4) ... C(10^{iii})	3.26
C(10) ... C(4^{i})	3.50	C(12) ... C(22^{iv})	3.50
O(3) ... C(34^{ii})	3.47	O(4) ... C(30^{iv})	3.52

[a] σ are 0.01 Å; ^{i} $\bar{x}$, $1/2 + y$, $1/2 - z$; ^{ii} $-1/2 - x$, $\bar{y}$, $z - 1/2$; ^{iii} x, y, $z - 1$; ^{iv} $1/2 + x$, $-1/2 - y$, $\bar{z}$.

differs significantly from these mean values, which agree fairly well with those accepted for aromatic rings.

Packing is due to weak Van der Waals interactions (Table 7), as steric factors due to the bulky phenyl rings tend to maximise the intra- and inter-atomic distances.

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