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Coordinative Tin–Oxygen Interactions in Dinitratodiphenyl(triphenylarsine oxide)-tin(IV)

M. NARDELLI, C. PELIZZI, G. PELIZZI and P. TARASCONI

Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via Massimo D'Azeglio 85, 43100 Parma, Italy

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The title compound has been synthesized and its IR spectroscopic properties and X-ray structure have been studied. Crystals are triclinic, space group P$\bar{1}$, with unit-cell dimensions: a = *8.987(3),* b = *16.649(6),* c = *11.002(5) Å; α = 97.4(2), β = 113.1(1), γ = 100.0(1)° and Z = 2. The structure has been solved from X-ray diffractometric data by the heavy-atom method and refined by least-squares techniques to R 0.038 for 3823 independent reflections. Coordination around tin is pentagonal bipyramidal with the bidentate nitrate groups and the triphenylarsine oxide molecule occupying the equatorial positions and the two phenyl rings at the apices.*

Introduction

Seven-coordination is rather unusual for tin(IV) compounds, the tin atom acting as an acceptor for one or two electron pairs and increasing its coordination number from four to five or six; nevertheless we have observed that the presence of the covalent nitrate group as anion and of two phenyl rings facilitates the seven-coordination in organotin compounds [1–3].

Continuing our research program on nitrato-organotin derivatives of the type R_3SnNO_3, $R_2Sn(NO_3)_2$ (R = Ph, Pr, Bu) with P, As, O containing ligands, we have now synthesized a new seven-coordinated compound of formula $[Sn(C_6H_5)_2(NO_3)_2\{As(C_6H_5)_3O\}]$. The present paper deals with the synthesis, the IR spectroscopic properties and the X-ray crystal structure of the title compound.

Experimental

Triphenylarsine oxide (TPAO), dissolved in dry acetone, was added in equimolar quantity under a nitrogen atmosphere to a solution of dinitratodiphenyltin in the same solvent. Evaporation of the solvent *in vacuo* gave, after some days, a colourless air-stable microcrystalline product. Recrystallization occurred from chloroform–toluene. Found C, 50.3; H, 3.3; N, 4.2; Sn, 16.7. Calc. for $C_{30}H_{25}AsN_2O_7Sn$: C, 50.1; H, 3.5; N, 3.9; Sn, 16.5%.

Preliminary unit-cell dimensions and space-group information were deduced from rotation and Weissenberg photographs taken with Cu-K_α radiation ($\bar{\lambda}$ = 1.54178 Å). Accurate unit-cell parameters, with estimated standard deviations, were determined by a least-squares refinement based on 2θ values for 17 strong high-theta reflections measured on a single-crystal Siemens AED diffractometer. Crystallographic data are as follows: $[Sn(C_6H_5)_2(NO_3)_2\{As(C_6H_5)_3O\}]$, Mol. wt. 719.1. a = 8.987(3), b = 16.649(6), c = 11.002(5) Å; α = 97.4(2), β = 113.1(1), γ = 100.0(1)°; V = 1462 Å^3; Z = 2; D_{calc} = 1.64 g cm^{-3}; μ(Mo-K_α) = 21.2 cm^{-1}; $F(000)$ = 716. Space group P$\bar{1}$.

All the 5711 accessible independent reflections within the range θ 2.5–26.0° were examined by single-crystal diffractometry using the Mo-K_α radiation ($\bar{\lambda}$ = 0.71068 Å) and the ω-2θ scan technique; of these 3823 were considered as observed having $I > 2\sigma(I)$. A standard reflection ($\bar{4}$ 4 4) was recorded every twenty reflections as a check for electronic and crystal stability. Correction for Lorentz and polarization effects, but not for absorption, were applied. Data were placed on an absolute scale first by Wilson's method and then refining the scale factor for the F_0 as a variable parameter in the least-squares procedure.

Stucture Determination and Refinement

Coordinates for tin and arsenic were obtained from a three-dimensional Patterson map. A structure factor calculation including these two atoms and using an overall temperature factor, B, of 3.5 Å^2, gave a residual R of 28%. Three successive Fourier syntheses yielded the positions for all the non-hydrogen atoms. Refinement by block-diagonal isotropic least-squares gave R = 10.7% and this value improved to 4.8% after a few anisotropic cycles. At this stage a difference electron density map was computed to attempt to locate the hydrogen atoms. Accordingly, all these atoms were found readily with the exception of the hydrogen attached to C(28), which was not clearly resolved. Finally, two further cycles of refine-

TABLE I. Final Atomic Coordinates ($\times 10^4$) and Anisotropic Temperature Factors ($Å^2$)[a], for Non-Hydrogen Atoms with Their Standard Deviations.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	−994(1)	7453(0)	−1065(0)	3.25(1)	3.34(1)	3.03(1)	0.55(1)	1.27(1)	0.44(1)
As	520(1)	7842(0)	2424(1)	2.12(2)	1.72(2)	1.89(2)	−0.16(2)	0.85(2)	0.13(2)
O(1)	606(4)	7808(2)	923(3)	3.4(1)	4.8(2)	2.7(1)	−0.1(1)	1.0(1)	0.3(1)
O(2)	710(4)	8611(2)	−1068(4)	4.1(2)	4.7(2)	4.1(2)	0.4(2)	2.0(1)	1.4(1)
O(3)	−1154(5)	8148(3)	−3120(4)	6.3(2)	6.2(2)	4.6(2)	2.2(2)	2.1(2)	1.0(2)
O(4)	775(6)	9285(3)	−2580(5)	8.1(3)	9.8(3)	9.2(3)	2.0(3)	5.3(3)	6.0(3)
O(5)	−2049(5)	6390(2)	−342(4)	4.7(2)	4.6(2)	4.0(2)	0.0(1)	1.7(1)	0.8(1)
O(6)	−3521(5)	6094(2)	−2493(4)	5.5(2)	5.0(2)	4.4(2)	1.4(2)	0.7(2)	−0.2(1)
O(7)	−3950(7)	5230(3)	−1291(6)	9.6(3)	4.0(2)	13.4(4)	−1.3(2)	5.0(3)	1.7(2)
N(1)	97(6)	8691(3)	−2300(5)	5.1(2)	6.0(3)	6.1(3)	2.3(2)	3.6(2)	3.4(2)
N(2)	−3219(6)	5875(3)	−1404(5)	4.5(2)	3.7(2)	6.6(3)	0.5(2)	2.5(2)	0.5(2)
C(1)	214(6)	6683(3)	−1829(5)	3.6(2)	3.0(2)	4.5(3)	0.6(2)	1.7(2)	0.0(2)
C(2)	−64(8)	6539(3)	−3186(6)	6.2(3)	4.1(3)	4.8(3)	0.9(2)	2.8(3)	0.1(2)
C(3)	807(9)	6046(4)	−3626(7)	8.0(4)	4.9(3)	5.8(3)	1.3(3)	4.0(3)	0.0(3)
C(4)	1935(9)	5705(4)	−2747(8)	6.6(4)	5.4(3)	8.6(4)	1.3(3)	4.7(3)	−0.2(3)
C(5)	2219(8)	5838(4)	−1424(8)	5.0(3)	5.4(3)	8.2(4)	2.2(3)	2.3(3)	1.3(3)
C(6)	1345(8)	6332(4)	−968(6)	5.1(3)	5.1(3)	5.2(3)	1.5(2)	1.6(2)	0.4(2)
C(7)	−2847(6)	8100(3)	−1184(5)	3.7(2)	3.3(2)	3.4(2)	0.9(2)	1.6(2)	0.5(2)
C(8)	−4531(7)	7724(3)	−1682(6)	3.8(2)	4.2(3)	5.8(3)	0.5(2)	2.2(2)	−0.8(2)
C(9)	−5661(7)	8187(4)	−1713(7)	4.0(3)	6.2(3)	7.2(4)	1.1(2)	2.4(3)	−0.8(3)
C(10)	−5166(8)	9040(4)	−1250(7)	5.7(3)	5.6(3)	7.6(4)	2.9(3)	3.9(3)	1.2(3)
C(11)	−3511(8)	9418(3)	−713(6)	7.4(4)	3.6(3)	6.6(3)	1.8(2)	4.8(3)	0.9(2)
C(12)	−2349(7)	8973(3)	−679(6)	4.9(3)	3.6(2)	5.1(3)	0.6(2)	2.9(2)	0.5(2)
C(13)	1616(6)	8945(3)	3469(5)	3.6(2)	3.1(2)	3.1(2)	0.3(2)	1.4(2)	0.4(2)
C(14)	1500(7)	9196(3)	4635(5)	5.7(3)	3.6(2)	3.9(2)	0.2(2)	2.5(2)	0.3(2)
C(15)	2276(8)	10005(4)	5389(6)	6.3(3)	4.4(3)	3.9(3)	0.4(2)	2.4(2)	−0.6(2)
C(16)	3121(7)	10559(3)	4924(6)	5.4(3)	3.2(2)	5.1(3)	0.4(2)	1.8(2)	−0.1(2)
C(17)	3247(8)	10312(3)	3763(6)	5.9(3)	3.3(2)	4.9(3)	−0.4(2)	2.3(2)	0.7(2)
C(18)	2480(7)	9498(3)	2990(5)	4.6(2)	3.5(2)	3.7(2)	0.2(2)	1.9(2)	0.6(2)
C(19)	1707(7)	7070(3)	3230(5)	5.0(3)	3.1(2)	3.9(2)	0.9(2)	2.1(2)	1.1(2)
C(20)	1171(7)	6226(3)	2593(6)	5.7(3)	3.8(2)	4.8(3)	0.6(2)	2.6(2)	0.5(2)
C(21)	2070(9)	5680(4)	3145(7)	8.0(4)	3.9(3)	7.1(4)	1.8(3)	4.1(3)	1.3(3)
C(22)	3506(10)	5953(4)	4274(7)	9.4(5)	6.3(4)	6.7(4)	4.1(3)	3.9(4)	3.5(3)
C(23)	4088(10)	6794(5)	4914(7)	8.2(4)	7.7(4)	4.6(3)	3.2(3)	1.3(3)	1.7(3)
C(24)	3151(8)	7348(4)	4387(6)	5.5(3)	5.0(3)	3.6(2)	1.3(2)	1.2(2)	0.7(2)
C(25)	−1680(7)	7613(4)	2294(6)	3.6(2)	5.2(3)	4.3(3)	−0.5(2)	2.1(2)	−0.8(2)
C(26)	−2575(8)	8210(5)	1976(6)	4.2(3)	10.5(5)	4.0(3)	2.0(3)	1.9(2)	0.4(3)
C(27)	−4170(9)	8104(6)	1841(7)	5.8(4)	14.3(7)	5.3(4)	1.5(4)	2.5(3)	−1.7(4)
C(28)	−4853(10)	7405(6)	1987(9)	6.2(4)	13.4(7)	8.8(5)	−0.6(4)	2.6(4)	−5.2(5)
C(29)	−4090(12)	6780(6)	2369(10)	12.0(6)	8.3(5)	12.8(6)	−6.8(5)	8.7(5)	−3.5(4)
C(30)	−2378(11)	6888(5)	2527(9)	9.2(5)	6.1(4)	11.9(6)	−1.2(4)	7.7(5)	−0.3(4)

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

ment were carried out assuming isotropic thermal parameters for the H atoms (H(28) was included at its calculated position). This refinement of 470 variables over 3823 data converged to R of 3.8%. The quantity minimized was $\Sigma\, w(\Delta F^2)$, where the weight for each reflection was unity. Atomic scattering factors used were from Cromer and Mann [4] for non-hydrogen atoms and from Stewart, Davidson and Simpson [5] for hydrogen atoms.

Final coordinates and thermal parameters are given in Table I and II. Observed and calculated structure factors can be obtained from the Editor upon request.

All calculations were carried out on the Cyber 76 computer of *Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.*

The IR spectrum was registered on a Perkin-Elmer mod. 457 spectrophotometer using KBr disks.

Table III lists the main vibrational absorption bands with relative assignments; Table IV gives selected bond distances and angles.

TABLE II. Final Atomic Coordinates ($\times 10^3$) and Isotropic Temperature Factors (Å^2) for Hydrogen Atoms.

	x	*y*	*z*	*B*
H(2)	−96(11)	680(5)	−396(9)	8(2)
H(3)	65(11)	590(5)	−461(9)	8(2)
H(4)	265(10)	537(5)	−311(8)	6(2)
H(5)	301(11)	553(5)	−70(9)	8(2)
H(6)	154(11)	644(5)	−1(9)	7(2)
H(8)	−472(10)	713(5)	−206(8)	7(2)
H(9)	−681(11)	792(5)	−216(8)	7(2)
H(10)	−605(10)	937(5)	−140(8)	6(2)
H(11)	−333(11)	1000(5)	−37(9)	7(2)
H(12)	−116(10)	921(5)	−33(8)	6(2)
H(14)	83(10)	879(5)	496(8)	6(2)
H(15)	219(10)	1014(5)	627(8)	6(2)
H(16)	379(10)	1118(5)	555(8)	7(2)
H(17)	394(10)	1071(5)	339(8)	7(2)
H(18)	253(10)	929(5)	210(8)	6(2)
H(20)	12(10)	606(5)	169(8)	6(2)
H(21)	170(11)	510(5)	267(9)	7(2)
H(22)	432(11)	556(5)	466(9)	8(2)
H(23)	528(12)	698(6)	581(9)	9(3)
H(24)	360(10)	800(5)	497(8)	6(2)
H(26)	−200(11)	866(6)	195(9)	9(2)
H(27)	−481(12)	865(6)	166(9)	9(3)
H(28)	−619	730	161	9
H(29)	−457(12)	633(6)	250(10)	9(3)
H(30)	−166(11)	656(5)	287(9)	8(2)

TABLE III. Selected Infrared Absorption Bands (cm^{-1}).

Frequency	Assignment	Frequency	Assignment
1762 w	$\nu_1 + \nu_4$	930 sh	γ(CH)
1710 vw		925 w	
1485 vs, br	$\nu(NO)_{as} + \nu(CC)$	860 s	ν(AsO)
1440 s	ν(CC)	805 s	ν(AsO)
1390 vs	ν(CC)	740 s	γ(CH)
1280 s	$\nu(NO)_s$	705 sh	$\nu(AsC) + \phi(CC)$
1087 s	ν(AsC)	690 s	
1075 sh		480 m	ν(AsC)
1022 sh	$\beta(CH) + \nu(NO)$	460 m	
1012 sh		410 m	ν(SnO)
1010 m		370 s	ν(AsC)
1000 sh		345 m	ν(AsC)
		295 m	ν(SnC)

TABLE IV. Selected Bond Distances (Å) and Angles (°) with Their Estimated Standard Deviations.

a) In the Tin Environment

Sn–O(1)	2.026(4)	Sn–O(5)	2.244(5)
Sn–O(2)	2.245(4)	Sn–O(6)	2.692(7)
Sn–O(3)	2.636(6)	Sn–C(1)	2.110(7)
Sn–C(7)	2.107(6)		
O(1)–Sn–O(2)	79.3(3)	O(2)–Sn–C(7)	91.1(3)
O(2)–Sn–O(3)	51.6(2)	O(3)–Sn–C(1)	83.0(3)
O(3)–Sn–O(6)	97.0(3)	O(3)–Sn–C(7)	79.7(3)
O(6)–Sn–O(5)	50.6(2)	O(5)–Sn–C(1)	90.2(4)
O(5)–Sn–O(1)	81.5(3)	O(5)–Sn–C(7)	95.3(4)
O(1)–Sn–C(1)	101.6(5)	O(6)–Sn–C(1)	78.9(3)
O(1)–Sn–C(7)	102.6(4)	O(6)–Sn–C(7)	86.4(3)
O(2)–Sn–C(1)	91.4(3)	C(1)–Sn–C(7)	156(1)

b) In the Triphenylarsine Oxide Molecule

As–O(1)	1.677(4)	As–C(19)	1.898(6)
As–C(13)	1.898(6)	As–C(25)	1.891(6)
C–C(av.)	1.37(1)		
O(1)–As–C(13)	107.1(6)	C(13)–As–C(19)	110.4(5)
O(1)–As–C(19)	106.1(5)	C(13)–As–C(25)	107.5(6)
O(1)–As–C(25)	113.6(6)	C(19)–As–C(25)	112.1(6)
Sn–O(1)–As	137.9(6)	As–C–C(av.)	119.9(9)
C–C–C(av.)	120(1)		

c) In the Nitrate Groups

N(1)–O(2)	1.282(7)	N(2)–O(5)	1.293(6)
N(1)–O(3)	1.239(6)	N(2)–O(6)	1.238(7)
N(1)–O(4)	1.209(8)	N(2)–O(7)	1.206(8)
O(2)–N(1)–O(3)	117.2(9)	O(5)–N(2)–O(6)	116.0(8)
O(2)–N(1)–O(4)	118.1(11)	O(5)–N(2)–O(7)	119.8(10)
O(3)–N(1)–O(4)	124.7(12)	O(6)–N(2)–O(7)	124.1(13)
Sn–O(2)–N(1)	104.4(5)	Sn–O(5)–N(2)	106.7(5)
Sn–O(3)–N(1)	86.8(4)	Sn–O(6)–N(2)	86.5(4)

d) In the Phenyl Rings

C–C(av.)	1.38(1)		
Sn–C–C(av.)	121.1(8)	C–C–C(av.)	120(1)

e) Some Significant van der Waals Contacts

C(29)–O(7^{i})	3.32(1)	C(14)–O(4^{v})	3.36(1)
C(21)–O(7^{ii})	3.48(1)	C(15)–O(4^{v})	3.28(1)
C(16)–O(3^{iii})	3.37(1)	C(10)–O(4^{vi})	3.48(1)
C(23)–O(6^{iv})	3.32(1)		

i $\bar{x} - 1,\ 1 - y,\ \bar{z}$
ii $\bar{x},\ 1 - y,\ \bar{z}$
iii $\bar{x},\ 2 - y,\ \bar{z}$
iv $1 + x,\ y,\ 1 + z$
v $x,\ y,\ 1 + z$
vi $x - 1,\ y,\ z$

Results and Discussion

The crystal structure of the title compound consists of discrete monomeric molecules having a pentagonal bipyramidal arrangement of coordinated ligands about tin, with two apical phenyl rings and an equatorial plane consisting of two bidentate nitrate groups and a triphenylarsine oxide molecule. A similar pentagonal bipyramidal arrangement around tin with triphenylarsine oxide replaced by triphenylphosphine oxide (TPPO) has been recently observed in dinitratodiphenyl(triphenylphosphine oxide)tin(IV) [3]. Some interesting differences between the two compounds concern: (i) the bidentate nitrate group which is symmetrical in the TPPO- and unsymmetrical in the TPAO-complex, in agreement with the

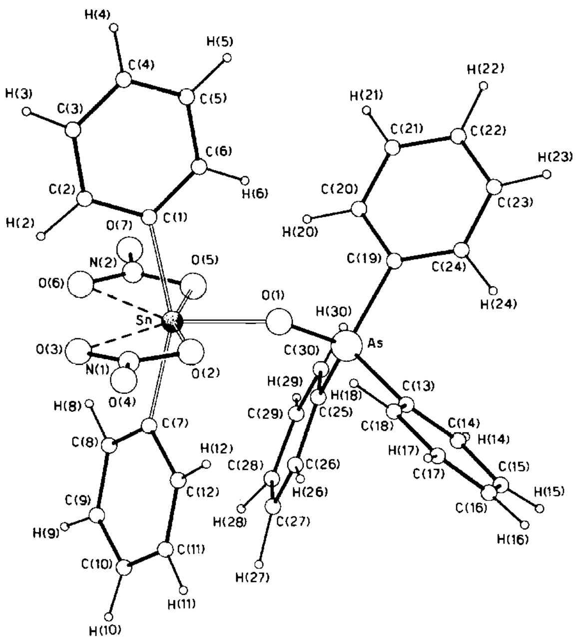

Figure 1. Clinographic projection of the structure.

IR absorptions which show a higher $\nu(NO)_{as}$-$\nu(NO)_s$ frequency value for the first ($\Delta\nu = 250$ cm^{-1}) than for the second ($\Delta\nu = 205$ cm^{-1}) compound. (ii) The Sn–O_{org} bond length which is shorter in the TPAO (2.026 Å) than in the TPPO (2.15 Å) complex; this difference causes a lower ν(Sn–O_{org}) value in the latter (300 cm^{-1}) than in the former (410 cm^{-1}). (iii) The C–Sn–C angle which in the TPPO-complex is nearly linear (178°), while in the present compound is only 156°.

A comparison between pentagonal bipyramidal tin(IV) compounds is reported in Table V: even though a full discussion does not seem to be possible in view of the different nature of the ligands, nevertheless it can be observed that:

(a) The stoichiometry seems to be a factor of no importance in fixing this bonding geometry. Surprisingly, none of the tabulated compounds shows the MX_5Y_2 stoichiometry for which the D_{5h} configuration would be favoured by energy minimization [10].

(b) The atoms forming the pentagonal girdle are all equal, *i.e* oxygens or nitrogens.

(c) Most compounds contain ligands such as tropolonato, acetato, nitrato, which are well adapted to achieve high co-ordination numbers, as a consequence of their relatively small bite.

(d) The interligand contacts in the pentagonal girdle are close to the sum of the van der Waals radii (2.8 Å for O...O; 3.0 Å for N...N) with the exception of those belonging to bidentate ligands which are much shorter; 2.15, 2.16 and 2.54 Å are the average bites for nitrato, acetato and tropolonato respectively.

(e) The angles subtended at tin in the pentagonal girdle range from 50.6 to 97.0° but only the acetato and nitrato derivatives show a great deal of scatter about the average value which is 72.2°. The sum of the five angles in each girdle ranges from 360.0° to 362.9°.

(f) In most compounds the axis of the bipyramid is close to straight, the angle L_{ap}–Sn–L_{ap} being less 172° only in three compounds, including the present one.

It can be added that these observations are not limited to tin compounds or to the ligands in question, but are equally true in most cases and in most of the details for the heptacoordinated mononitrosylmolibdenumtris(NN-di-n-butyldithiocarbamate) [11].

In the present compound the five coordinated oxygen atoms lie at the vertices of an irregular pentagon; they are nearly coplanar, with none of them displaced more than 0.06 Å out of the mean least-squares plane. The irregularity of the pentagon can be seen considering the values of the five O...O contacts in the pentagonal girdle, which are 2.147, 2.152, 2.732, 2.792, 3.991 Å. The first two values refer to the oxygen atoms within the bidentate NO_3 groups and correspond fairly well to the normal bite for this group, the third and the fourth values are as expected and very close to the sum of van der Waals radii (2.80 Å); the fifth value is surprisingly long and involves the two oxygen atoms weakly bonded to metal.

Another interesting comparison can be made between the present compound and $[Sn(C_6H_5)_3NO_3(TPAO)]$ in which the coordination around tin is trigonal bipyramidal, with the unique nitrate ion acting as unidentate ligand [12]. The different environment of the tin atom in the two compounds seems to be related to the different number of phenyl rings involved in coordination, as already observed in the corresponding triphenylphosphine oxide derivatives [3, 13]: when two phenyl rings are present, they prefer the apical positions of a pentagonal bipyramid allowing a bidentate behaviour of the nitrate groups, while three phenyl rings occupy the equatorial plane of a trigonal bipyramid, the apices of which are occupied by TPAO and NO_3. This different situation affects especially the vibrational absorptions of the nitrate group and the stretching modes of the Sn–$O_{org.}$ bond. In particular the bidentate nature of the NO_3 ion is well shown by $\nu(NO)_{as}$-$\nu(NO)_s$ = 205 cm^{-1}, a value higher than that observed in the triphenylderivative ($\Delta\nu$ = 135 cm^{-1}). As already observed in the two corresponding TPPO compounds, the more the Sn–$O_{org.}$ bond length is short (2.026 in the diphenyl, 2.18 Å in the triphenyl compound), the more the frequency value of ν(Sn–$O_{org.}$) is high (410 in the diphenyl, 380 cm^{-1} in the triphenyl compound).

TABLE V. Comparison between Pentagonal Bipyramidal Tin(IV) Compounds (distances in Å, angles in °)[a].

	Stoichiometry	Sn–L$_{eq}$				Sn–L$_{ap}$			L$_{eq}$···L$_{eq}$			L$_{eq}$–Sn–L$_{eq}$			L$_{ap}$–Sn–L$_{ap}$
I[b]	MX$_7$	X = O	1.88	2.12		X = O	2.01	2.10	2.12	2.20	2.64	58.0	58.2	77.8	168.5
			2.23	2.22	2.30				2.78	2.83		79.7	86.4		
II	MX$_6$Y	X = O	2.138	2.130		X = O	2.050		2.52	2.52	2.53	71.6	71.9	72.6	175.7
			2.162	2.128	2.168	Y = Cl	2.362		2.54	2.55		73.0	73.0		
III	MX$_6$Y	X = O	2.148	2.139		X = O	2.057		2.52	2.54	2.54	71.3	72.0	72.2	174.1
			2.132	2.180	2.220	Y = O	1.974		2.57	2.61		72.9	73.4		
IV	MX$_6$Y	X = O	2.148	2.331		X = O	2.105		–			–			159
			2.130	2.298	2.240	Y = C	2.092								
V	MX$_4$Y$_2$Z	X = O	2.324	2.323		Y = C	2.124	2.07	2.12	2.17	3.03	54.4	54.7	80.5	178.0
			2.358	2.370					3.03	3.05		85.1	85.4		
		Z = O	2.148												
VI	MX$_4$Y$_2$Z	X = O	2.245	2.636		Y = C	2.107	2.110	2.147	2.152	2.732	50.6	51.6	79.3	156
			2.244	2.692					2.792	3.991		81.5	97.0		
		Z = O	2.026												
VII	MX$_3$Y$_2$Z$_2$	X = N	2.570	2.479		Z = C	2.091	2.119	2.68	2.70	2.84	64.5	65.3	76.5	173.7
			2.497						3.01	3.01		76.8	78.3		
		Y = N	2.280	2.285											
VIII	MX$_3$Y$_2$Z$_2$	X = O	2.17	2.19		Z = C	2.15	2.16	2.17	2.75	2.80	51.7	72.5	77.0	172.0
			2.24						2.84	2.92		78.4	80.5		
		Y = O	2.49	2.50											
IX	MX$_2$Y$_2$Z$_2$W	X = O	2.388	2.408		Z = C	2.115	2.116	2.14	2.69	2.79	53.0	73.0	73.2	176.8
		Y = O	2.282	2.248					2.89	2.93		79.2	81.6		
		W = O	2.178												

[a] eq = equatorial, ap = apical. Some of these values have been calculated by us on the basis of the coordinates given by the authors. For compound IV reported information is insufficient for computation. [b] Data refer to one of two independent molecules present in the structure, those of the second molecule being less accurate owing to disordered effects. I Tetramethylammonium pentacetatostannate [6]. II Tris(tropolonato)monochlorotin chloroform solvate [7]. III Tris(tropolonato)monohydroxotin hydrate methanol solvate [7]. IV Methyltintrinitrate [8]. V Dinitratodiphenyl(triphenylphosphine oxide)tin [3]. VI Dinitratodiphenyl(triphenylarsine oxide)tin, present work. VII Dimethyldiisothiocyanato(terpyridyl)tin [9]. VIII Tris(dimethylsulphoxide)nitratodiphenyltin [2]. IX μ-Oxalatobis[(di-n-propylsulphoxide)nitratodiphenyltin] [1].

As observed in all its metal complexes, the TPAO molecule is covalently bonded to metal through its oxygen atom with a consequent small lengthening of the O–As bond (1.677 Å) compared with that in the free ligand (1.644 Å) [14]. The geometry and the dimensions of this molecule compare favourably with those observed in related TPAO-complexes [12].

Each nitrate group is chelated to tin with a short (Sn–O(2) = 2.245; Sn–O(5) = 2.244 Å) and a long (Sn–O(3) = 2.636; Sn–O(6) = 2.692 Å) bond as usually observed for nitrate and nitro groups. This kind of chelation can be defined as bidentate unsymmetrical in conformity with the definition of Addison and coworkers [15] that a metal–oxygen bond distance difference of 0.2–0.7 Å for a bidentate nitrate constitutes unsymmetrical chelation. Bond distances and angles within the NO_3 groups indicate deviations from D_{3h} symmetry and this can be regarded as a consequence of bonding effects, since, as one might expect, the N–O bond involving the oxygen atom more strongly coordinated to metal is longer than the other N–O bonds, and the O–N–O angle opposite this bond is greater than the other two angles and larger than 120°.

In the phenyl rings the planarity is fairly good and there are no significant departures from the expected structural parameters.

The molecular packing is dominated by van der Waals type interactions between carbon atoms from phenyl rings and oxygen atoms from nitrate groups; the most significant of these interactions are given in Table IV.

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