

COORDINATION BEHAVIOUR OF DIPHOSPHINE AND DIARSINE OXIDES IN FOUR ORGANOTIN(IV) ADDUCTS

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Summary

Four new molecular adducts of diphenyl- and triphenyl-tin(IV) nitrates with 1,2-bis(diphenylarsoryl)ethane (dpaoe), bis(diphenylphosphoryl)methane (dppom) and *trans*-1,2-bis(diphenylphosphoryl)ethylene (tdppoet) have been synthesised and characterized by infrared spectroscopy, and an X-ray diffraction study has been carried out on two of them, $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$ (**1**) and $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$ (**2**). Both **1** and **2** crystallize in the triclinic space group $P\bar{1}$, with unit-cell dimensions. **1**: a 12.810(8), b 11.938(6), c 10.394(4) Å, α 97.92(4), β 90.00(5), γ 111.13(4)°, $Z = 1$, $R = 0.0454$; **2**: a 13.845(6), b 13.119(4), c 10.444(6) Å, α 106.50(4), β 101.24(4), γ 91.33(4)°, $Z = 2$, $R = 0.0504$. The structure of **1** consists of binuclear monomeric units in which each tin atom is bound in a trigonal bipyramidal configuration to three phenyl rings in the equatorial plane and to the diarsine ligand and the nitrate group in the axial positions. In compound **2** the tin atom exhibits a pentagonal-bipyramidal coordination geometry with five oxygen atoms, two from the chelating dppom ligand and three from the two nitrate groups, around the pentagonal girdle, and the two phenyl groups at the apices of the bipyramid. The vibrational frequencies of the nitrate groups and of the diarsine and diphosphine ligands are discussed in the light of the X-ray results.

Introduction

Our continuing interest in the synthesis and structural characterization of organotin(IV) derivatives containing phosphorus or arsenic ligands led us to investigate the coordination behaviour of diphosphine and diarsine oxides of formula $\text{Ph}_2\text{E}(\text{O})\text{-R-(O)EPh}_2$ ($\text{E} = \text{P, As}$; $\text{R} = \text{CH}_2, \text{CH}_2\text{CH}_2, \text{CH}=\text{CH}$) with the aim of studying the factors which determine the stereochemical influence of both the nature and the size of the ligands on the molecular structure of the resulting complexes and on the tin–ligand interactions.

Our interest in this research field stems from our awareness of the limited amount of X-ray structural information about mixed organotin-organophosphorus or organoarsenic derivatives (as revealed by a bibliographic search carried out using the Cambridge Crystallographic Data Files) and of the versatility shown by diphosphine and diarsine oxides in coordination to metals [1-5].

With the hopes of gaining more information on this subject we have synthesised four new organotin adducts, with the formulae $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$, $\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{dpaoe}$ (dpaoe = 1,2-bis(diphenylarsoryl)ethane), $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$ (dppom = bis(diphenylphosphoryl)methane) and $\{\text{SnPh}_3\text{NO}_3\}_2\text{tdppoet}$ (tdppoet = *trans*-1,2-bis(diphenylphosphoryl)ethylene). This paper deals with the preparation of these four compounds and with the crystal and molecular structure of two of them, namely $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$ (**1**), and $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$ (**2**). In addition, we report and discuss the IR data of these compounds together with those of other two tin adducts, $\text{SnPh}_2(\text{NO}_3)_2\text{cdppoet} \cdot \text{CHCl}_3$ (cdppoet = *cis*-1,2-bis(diphenylphosphoryl)ethylene) and $\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{tdppoet} \cdot 2\text{H}_2\text{O}$, whose synthesis and crystal structure were recently reported [5].

Experimental

Preparations. Solvents were dried and distilled before use. Bis(diphenylphosphino)methane, *trans*-1,2-bis(diphenylphosphino)ethylene, 1,2-bis(diphenylarsino)ethane, dichlorodiphenyltin and chlorotriphenyltin were purchased from Strem Chemical Co. and used without further purification. Bis(diphenylphosphoryl)methane (dppom), *trans*-1,2-bis(diphenylphosphoryl)ethylene (tdppoet), and 1,2-bis(diphenylarsoryl)ethane (dpaoe) were obtained by refluxing a toluene solution of the parent diphosphine or diarsine for 1 h with H_2O_2 (31.5%) in excess [6]. Dinitratodiphenyltin and nitratotriphenyltin were obtained as previously described [7] by using rigorously checked stoichiometric amounts of the reagents to avoid contamination by silver salts.

All the tin adducts were prepared by adding an acetonitrile solution of $\text{SnPh}_2(\text{NO}_3)_2$ (1.1 mmol) or SnPh_3NO_3 (1.9 mmol) to a solution of stoichiometric amount of the phosphorus or arsenic ligand in chloroform (dppom and dpaoe) or dichloromethane (tdppoet). The tin ligand molar ratio was 1/1 for the diorgano- and 2/1 for the triorgano-tin derivatives. In each case the solution was stirred at room temperature for 1 h and then set aside for some hours. Slow evaporation of the solvent then gave a white crystalline product. Anal. Found: C, 54.4; H, 3.9; N, 3.6; Sn, 13.3. $\text{C}_{37}\text{H}_{32}\text{N}_2\text{O}_8\text{Sn}$ calcd.: C, 54.6; H, 4.0; N, 3.4; Sn, 14.6%. Anal. Found: C, 59.0; H, 4.1; N, 2.3; Sn, 20.0. $\text{C}_{62}\text{H}_{52}\text{N}_2\text{O}_8\text{P}_2\text{Sn}_2$ calcd.: C, 59.5; H, 4.2; N, 2.2; Sn, 19.0%. Anal. Found: C, 45.3; H, 3.3; N, 4.5; Sn, 17.2. $\text{C}_{50}\text{H}_{44}\text{As}_2\text{N}_4\text{O}_{14}\text{Sn}_2$ calcd.: C, 45.8; H, 3.4; N, 4.3; Sn, 18.1%. Anal. Found: C, 55.4; H, 4.0; N, 2.4; Sn, 17.1. $\text{C}_{62}\text{H}_{54}\text{As}_2\text{N}_2\text{O}_8\text{Sn}_2$ calcd.: C, 55.5; H, 4.1; N, 2.1; Sn, 17.7%.

Collection and reduction of X-ray data. Details of the lattice parameters, the data collection, and the structure refinement for both compounds are summarized in Table 1. In each case the unit-cell dimensions and e.s.d.'s were determined by least-squares fitting to the θ angles of 25 intense reflections chosen from diverse regions of reciprocal space.

Data for compound **1** were recorded on a computer-controlled Philips PW 1100 diffractometer, and those for compound **2** on a Siemens AED diffractometer

TABLE 1

SUMMARY OF CRYSTAL DATA, INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT FOR $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoc}$ (1) AND $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$ (2)

	1	2
Molecular formula	$\text{C}_{62}\text{H}_{54}\text{As}_2\text{N}_2\text{O}_8\text{Sn}_2$	$\text{C}_{37}\text{H}_{32}\text{N}_2\text{O}_8\text{P}_2\text{Sn}$
Molecular weight	1342.34	813.31
Space group	$P\bar{1}$	$P\bar{1}$
a , Å	12.810(8)	13.845(6)
b , Å	11.938(6)	13.119(4)
c , Å	10.394(4)	10.444(6)
α , deg	97.92(4)	106.50(4)
β , deg	90.00(5)	101.24(4)
γ , deg	111.13(4)	91.33(4)
V , Å ³	1466(1)	1778(1)
Z	1	2
ρ (calcd), g cm ⁻³	1.520	1.519
$F(000)$	670	824
radiation	graphite-monochromated Mo- K_α	Nb-filtered Mo- K_α
μ , cm ⁻¹	20.24	8.61
2θ range, deg	6.0–54.0	5.0–52.0
No. of data collected	6337	6680
No. of observed data	3252	3798
Criterion for observation	3σ	2σ
No. of parameters refined	451	579
Data/parameter, ratio	7.2	6.6
$R = \Sigma \Delta F / \Sigma F_0 $	0.0454	0.0504
$R_w = [\Sigma w(\Delta F)^2 / \Sigma wF_0^2]^{\frac{1}{2}}$	0.0486	0.0689

controlled by a G.A. 220 computer. In both cases the X-ray measurements were made at room temperature using the θ - 2θ scan mode with Mo- K_α radiation, and the intensities were measured over 50% of the reciprocal lattice ($\pm h$, $\pm k$, l). The diffraction symmetry was found by standard procedures for both crystals to be triclinic, and the assumed space group $P\bar{1}$ was later confirmed by successful refinement.

The intensities for compound 2 were evaluated from a modified version of the profile analysis method [8], while for compound 1 the three-point technique was used.

For compound 1 a reference reflection was measured at every 90 min of X-ray exposure and showed good stability. For compound 2 a reference reflection checked every 75 reflections showed small fluctuations in intensity and data were adjusted accordingly. Background, Lorentz, and polarization corrections were made for both compounds, and the data were then reduced to structure factor amplitudes. The entire data set for 1 was corrected for absorption by a semi-empirical method based on ψ scans of reflections having χ values near 90° [9]. No absorption correction was applied in the case of 2.

Solution and refinement of the structures. Both structures were solved by conventional Patterson and Fourier techniques. The tin atom in each compound was located from the analysis of a Patterson function. Using this position as input, a Fourier synthesis was computed to provide the coordinates for the As atom in 1 and

for the two P atoms in **2**. Subsequent least-squares refinement followed by analysis of difference Fourier maps led to the location of all other non-hydrogen atoms in each structure. After three cycles of refinement in which the positional and anisotropic thermal parameters for these atoms were freely refined by blocked full-matrix least-squares, all the hydrogen atoms were located in difference maps, and were included in the least-squares treatments to yield the final residual indices R 0.0454 and 0.0504 for **1** and **2**, respectively. It should be noted that after the refinement of **2** had been completed, some degree of disorder was noticed in the unidentate nitrate; while N(1) and O(3) appeared well-defined, the two terminal oxygens, O(4) and O(5), were found in two orientations corresponding to rotation about the O(3)–N(1) bond. The occupancies for the two pairs of the partial atoms were refined to about 0.7 and 0.3, but the atoms corresponding to the smaller population were not considered in the calculations of bond distances and angles given in Table 5.

The quantity minimized in both refinements was $\Sigma w(\Delta F)^2$, the weighting scheme was based initially on unit weights, while in the final stages of refinement weights were chosen as $w = k/[\sigma^2(F_0) + g|F_0|^2]$. In the final difference map there were no peaks greater than 1.00 in **1** and 1.18 e Å⁻³ in **2**, and no holes less than 0.63 in **1** and 0.90 e Å⁻³ in **2**; the largest peak for each crystal was in close proximity (within ca. 1.05 Å) to the tin atom.

Analytical expressions for atomic scattering factors were employed, and both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [10]. The SHELX-76 [11], PLUTO [12], and PARST [13] systems of programs were employed for the calculations which were carried out on CDC 76 Cyber and GOULD-SEL 32/77 computers, with financial support from the University of Parma.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ for Sn and As, $\times 10^4$ for O, N and C) OF $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$

Atom	x	y	z	Atom	x	y	z
Sn	30317(4)	23846(5)	27470(5)	C(13)	1514(6)	2438(7)	3524(7)
As	31813(6)	45610(6)	5685(7)	C(14)	715(7)	1400(8)	3859(8)
O(1)	3300(4)	4076(4)	1970(5)	C(15)	-309(8)	1398(12)	4291(9)
O(2)	2840(5)	697(5)	3638(6)	C(16)	-567(8)	2418(12)	4393(9)
O(3)	3189(6)	1817(7)	5526(6)	C(17)	207(9)	3453(11)	4057(11)
O(4)	3272(7)	18(7)	5300(7)	C(18)	1239(8)	3459(9)	3629(10)
N	3115(6)	857(8)	4876(8)	C(19)	3230(6)	6185(7)	1022(9)
C(1)	2762(6)	1307(6)	881(7)	C(20)	3150(7)	6820(8)	-3(11)
C(2)	1710(7)	485(8)	406(9)	C(21)	3213(9)	8016(10)	347(16)
C(3)	1553(8)	-142(9)	-851(9)	C(22)	3365(9)	8528(11)	1629(19)
C(4)	2415(8)	25(8)	-1634(9)	C(23)	3447(10)	7913(10)	2591(17)
C(5)	3476(8)	816(8)	-1206(9)	C(24)	3385(8)	6718(8)	2298(10)
C(6)	3637(7)	1433(7)	55(9)	C(25)	1836(6)	3623(7)	-473(7)
C(7)	4774(6)	3095(7)	3321(7)	C(26)	1874(8)	2925(9)	-1621(9)
C(8)	5371(7)	4350(8)	3621(7)	C(27)	889(10)	2263(10)	-2380(11)
C(9)	6528(8)	4787(10)	3913(9)	C(28)	-98(10)	2337(11)	-1995(13)
C(10)	7074(9)	3982(12)	3896(11)	C(29)	-128(9)	3018(14)	-847(15)
C(11)	6504(10)	2742(13)	3626(11)	C(30)	845(8)	3698(12)	-91(12)
C(12)	5356(8)	2323(9)	3346(9)	C(31)	4467(6)	4643(8)	-427(8)

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ for Sn, $\times 10^4$ for P, O, N and C) OF $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$

Atom	x	y	z	Atom	x	y	z
Sn	24117(4)	25348(4)	36712(4)	C(13)	1538(5)	1111(5)	7087(7)
P(1)	1729(1)	2303(1)	6649(2)	C(14)	1419(6)	134(6)	6087(8)
P(2)	3906(1)	2337(1)	6682(2)	C(15)	1282(7)	-774(6)	6472(9)
O(1)	1635(3)	2075(4)	5138(4)	C(16)	1268(7)	-736(7)	7764(11)
O(2)	3697(3)	2362(4)	5221(4)	C(17)	1384(6)	227(7)	8739(8)
O(3)	3788(4)	2936(5)	2940(5)	C(18)	1505(6)	1145(6)	8414(7)
O(4) ^a	3309(7)	2755(10)	810(8)	C(19)	861(5)	3190(6)	7292(7)
O(5) ^a	4722(7)	2745(11)	1563(9)	C(20)	1077(7)	4261(7)	7863(10)
O(4) ^b	4651(25)	3327(25)	1759(32)	C(21)	389(8)	4933(8)	8293(11)
O(5) ^b	3412(18)	2397(17)	808(26)	C(22)	-549(9)	4517(10)	8100(12)
O(6)	1554(6)	2897(5)	1558(6)	C(23)	-787(7)	3446(10)	7559(14)
O(7)	702(4)	2479(4)	2832(6)	C(24)	-81(7)	2783(7)	7156(10)
O(8)	-31(6)	2586(6)	873(7)	C(25)	5026(5)	3140(5)	7600(7)
N(1)	3920(6)	2835(6)	1757(7)	C(26)	5608(5)	3537(6)	6859(7)
N(2)	701(7)	2648(5)	1715(7)	C(27)	6444(6)	4183(7)	7561(9)
C(1)	2435(5)	4171(5)	4730(7)	C(28)	6750(6)	4415(8)	8946(9)
C(2)	1570(7)	4662(7)	4879(10)	C(29)	6183(7)	4032(8)	9653(8)
C(3)	1587(8)	5718(8)	5624(12)	C(30)	5326(6)	3383(7)	9009(8)
C(4)	2471(9)	6303(7)	6287(11)	C(31)	3965(5)	1000(5)	6781(7)
C(5)	3327(8)	5833(7)	6173(10)	C(32)	4040(6)	770(7)	7993(8)
C(6)	3307(7)	4780(6)	5388(9)	C(33)	4085(7)	-279(9)	8005(11)
C(7)	2355(5)	907(5)	2596(6)	C(34)	4049(7)	-1061(7)	6848(15)
C(8)	1507(5)	255(5)	2362(7)	C(35)	3963(7)	-847(7)	5624(12)
C(9)	1480(7)	-823(7)	1717(8)	C(36)	3920(6)	192(6)	5597(9)
C(10)	2297(8)	-1264(7)	1299(9)	C(37)	2952(5)	2919(5)	7541(6)
C(11)	3127(7)	-637(7)	1511(10)				
C(12)	3170(6)	445(7)	2154(8)				

^a Occupancy 0.7. ^b Occupancy 0.3.

The positional parameters for the non-hydrogen atoms of **1** and **2** are shown in Tables 2 and 3. Tables of observed and calculated structure factors and thermal parameters are available from the authors.

Results and discussion

Figures 1 and 2 illustrate the molecular structure and the atom-numbering scheme used for compounds **1** and **2**, respectively. Selected bond lengths and angles are given in Tables 4 and 5.

The structural results for compound **1** show that it exists in the form of discrete monomers, which, owing to the bridging action of the dpaoe ligand, are binuclear with respect to the tin atoms which they contain. The monomer spans two asymmetric units, with each half related to the other through a crystallographic inversion centre located on the centre of gravity of the $\text{H}_2\text{C}-\text{CH}_2$ bond. The coordination about each tin atom is clearly trigonal bipyramidal, with three carbon atoms from the phenyl rings in the equatorial plane and two oxygen atoms, one from the diarsine ligand and the other from the nitrate group, at the apices. The only significant angular distortions from a regular trigonal bipyramidal configura-

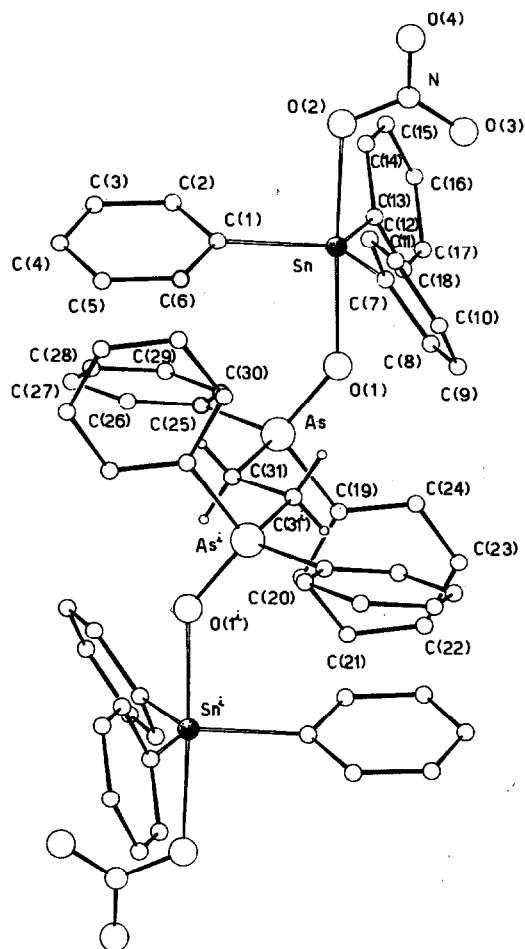


Fig. 1. Perspective view of the structure of $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoc}$.

tion are in the equatorial plane, where the three in-plane trigonal angles depart significantly from the theoretical 120° value, the $\text{C}(7)\text{--Sn--C}(13)$ angle, $137.9(3)^\circ$, is remarkably wide and the other two are correspondingly compressed to $109.9(3)$ and $112.2(3)^\circ$. The trigonal axis is very close to the linearity with $\text{O}(1)\text{--Sn--O}(2)$ $176.6(2)^\circ$, and the equatorial-to-axial angles are, as expected, near 90° , ranging from $87.6(3)$ to $94.2(2)^\circ$. The tin atom lies in the $\text{C}(1)\text{C}(7)\text{C}(13)$ plane, and is $0.13\text{--}0.14 \text{ \AA}$ above the plane formed by each of the three coordinated phenyl rings. The dihedral angles between the C_3Sn equatorial plane and the planes of the aromatic rings are $18.5(3)$, $56.7(3)$, and $69.3(3)^\circ$.

Clearly relevant to the present structure is that of the other recently reported tin-dpaoc complex $\{\text{SnPh}_3\text{Cl}\}_2\text{dpaoc}$ [4], which also shows a binuclear nature and is also pentacoordinate with trigonal bipyramidal coordination at tin. A comparison of the X-ray structural results for these two adducts demonstrates that the introduction of a nitrate group in place of a chlorine atom does not significantly alter the

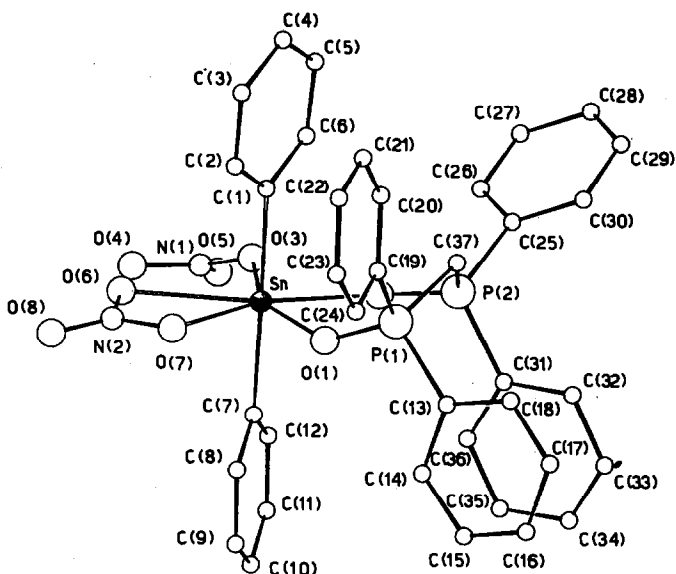


Fig. 2. Perspective view of the structure of $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$.

immediate environment of the metal atom; the main differences between the title compound and the chloro analogue are a small, but significant, shortening (ca. 0.05 Å) in the Sn–O bond distance, and more marked degree of distortion in the trigonal plane as indicated by the larger spread (28° vs. 13°) in the equatorial angles. A more direct comparison of the present structure can be made with the analogous phosphorus derivative $\{\text{SnPh}_3\text{NO}_3\}_2\text{dppoe}$ [14]. This comparison reveals that the two

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR $\{\text{SnPh}_3\text{NO}_3\}_2\text{dppoe}$

Bonds					
Sn–O(1)	2.190(6)	As–O(1)	1.666(6)	C(31)–C(31 ⁱ) ^a	1.526(10)
Sn–O(2)	2.266(6)	As–C(19)	1.909(8)	N–O(2)	1.304(10)
Sn–C(1)	2.128(7)	As–C(25)	1.916(7)	N–O(3)	1.219(12)
Sn–C(7)	2.134(7)	As–C(31)	1.925(8)	N–O(4)	1.227(14)
Sn–C(13)	2.124(8)				
Angles					
O(1)–Sn–O(2)	176.6(2)	O(1)–As–C(19)	105.9(3)		
C(1)–Sn–C(7)	109.9(3)	O(1)–As–C(25)	115.0(3)		
C(7)–Sn–C(13)	137.9(3)	O(1)–As–C(31)	109.6(3)		
C(1)–Sn–C(13)	112.2(3)	C(19)–As–C(25)	109.1(4)		
O(1)–Sn–C(1)	94.2(3)	C(19)–As–C(31)	107.1(4)		
O(1)–Sn–C(7)	87.6(3)	C(25)–As–C(31)	109.8(4)		
O(1)–Sn–C(13)	90.0(3)	Sn–O(2)–N	116.6(5)		
O(2)–Sn–C(1)	88.3(3)	O(2)–N–O(3)	118.1(8)		
O(2)–Sn–C(7)	89.4(3)	O(2)–N–O(4)	116.9(8)		
O(2)–Sn–C(13)	91.1(3)	O(3)–N–O(4)	124.9(9)		
Sn–O(1)–As	140.2(3)				

^a $i = 1 - x, 1 - y, \bar{z}$.

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$

<i>Bonds</i>					
Sn–O(1)	2.237(5)	P(1)–O(1)	1.499(5)	P(2)–O(2)	1.506(5)
Sn–O(2)	2.223(4)	P(1)–C(13)	1.776(8)	P(2)–C(25)	1.790(6)
Sn–O(3)	2.289(6)	P(1)–C(19)	1.784(7)	P(2)–C(31)	1.788(8)
Sn–O(6)	2.472(7)	P(1)–C(37)	1.812(6)	P(2)–C(37)	1.803(7)
Sn–O(7)	2.350(6)	N(1)–O(3)	1.255(10)	N(2)–O(6)	1.272(12)
Sn–C(1)	2.113(6)	N(1)–O(4)	1.147(11)	N(2)–O(7)	1.248(11)
Sn–C(7)	2.103(6)	N(1)–O(5)	1.170(13)	N(2)–O(8)	1.189(11)
<i>Angles</i>					
O(1)–Sn–O(2)	79.5(2)	O(1)–P(1)–C(13)	111.1(3)		
O(2)–Sn–O(3)	74.1(2)	O(1)–P(1)–C(19)	112.6(3)		
O(3)–Sn–O(6)	82.5(2)	O(1)–P(1)–C(37)	110.0(3)		
O(6)–Sn–O(7)	51.9(2)	C(13)–P(1)–C(19)	107.3(3)		
O(7)–Sn–O(1)	72.1(2)	C(13)–P(1)–C(37)	108.3(3)		
C(1)–Sn–C(7)	178.7(3)	C(19)–P(1)–C(37)	107.2(3)		
Sn–O(3)–N(1)	130.5(5)	O(2)–P(2)–C(25)	109.7(3)		
Sn–O(6)–N(2)	93.5(5)	O(2)–P(2)–C(31)	111.4(3)		
Sn–O(7)–N(2)	100.1(6)	O(2)–P(2)–C(37)	111.1(3)		
O(3)–N(1)–O(4)	125.6(9)	C(25)–P(2)–C(31)	111.2(4)		
O(3)–N(1)–O(5)	118.4(8)	C(25)–P(2)–C(37)	105.8(3)		
O(4)–N(1)–O(5)	115.8(9)	C(31)–P(2)–C(37)	107.6(4)		
O(6)–N(2)–O(7)	113.9(8)	Sn–O(1)–P(1)	139.2(3)		
O(6)–N(2)–O(8)	122.8(8)	Sn–O(2)–P(2)	138.0(3)		
O(7)–N(2)–O(8)	123.2(8)	P(1)–C(37)–P(2)	112.5(4)		

compounds are isostructural and that, except for the obvious difference in the ligand, most of the corresponding structural parameters are remarkably similar in the two structures. The only possibly significant dimensional difference between the two compounds is in the two Sn–O bonds. In the title compound the two distances are distinctly different, the values for the dpaoe and the nitrate oxygen atoms being 2.190(6) and 2.266(6) Å respectively, whereas in the case of the phosphorus adduct the two bonds are quite similar in length, the difference being only 0.02 Å, with the shorter distance involving the nitrate group.

As shown in Fig. 2, the structure of compound **2** consists of discrete monomers in which the tin atom is in a distorted pentagonal bipyramidal environment. Two phenyl rings are positioned at the axial sites of the bipyramid with a linear arrangement of the two coordinated carbon atoms (C(1)–Sn–C(7) 178.7(3)°), five oxygen atoms, two from the chelating dppom ligand and three provided by the two nitrate groups are bonded to tin in the pentagonal region. The five donor oxygens are approximately coplanar, deviating by only up to 0.01 Å from the mean least-squares plane through them; the tin atom is displaced by only 0.005 Å from this plane. The bonds from the tin atom to the axial carbons are almost perpendicular to the pentagonal plane, the corresponding angles being 88.5(1) and 88.3(1)°. There are appreciable distortions from the ideal pentagonal bipyramidal geometry as a result of the small bite of the bidentate NO₃ group, which subtends an angle of only 51.9(2)° at tin.

The structure of this compound is qualitatively similar to that of $\text{SnPh}_2(\text{NO}_3)_2$

cdppoet · CHCl₃ [5], except for the different P-ligand and the absence of crystallization in the present compound. Another difference concerns the apical C–Sn–C angle, which in the present case is less distorted from linearity (178.7(3) vs. 169.2(5)°). Features common to the two compounds are: the nature of the ligand donor atoms, the geometry of the coordination polyhedron, the monomeric nature of the complex, the bidentate chelating behaviour of the P-ligand, the unidentate coordination of one of the two nitrates, and the bidentate coordination of the other.

Within the dpaoe ligand in **1**, the structural parameters are very closely comparable to those previously observed for the same ligand in the afore-mentioned {SnPh₃Cl}₂dpaoe complex, which was the only dpaoe complex previously characterized by X-ray diffraction. In both structures the diarsine ligand lies across a centre of symmetry.

In **2** the dppom ligand chelates the metal atom almost symmetrically with Sn–O bonds of 2.237(5) and 2.223(4) Å, and this symmetry is reflected in the equality of the associated O–P distances and Sn–O–P angles. As a result of a coordination, a puckered six-membered chelate ring is formed, the total puckering amplitude being 0.746(6) Å [15]. There are only two other dppom complexes whose structures are known [16,17], and in both of them the ligands chelate a sodium ion in a trigonal prismatic arrangement of six oxygens. The structural information for the diphosphine oxides herein studied points to a versatility in the behaviour of the P-ligand toward metal ions. Indeed, these ligands have been found to function as chelating bidentate or as bridging bidentate, to form binuclear or polymeric systems; an example of unidentate behaviour is also known [1].

As indicated by the values given in Table 4 and 5, the N–O distances and the O–N–O angles in the nitrate groups of both compounds span a rather wide range; the spread seems to be real and can be correlated to bonding effects. In **1** the nitrate group is functioning as unidentate ligand towards the tin atom, with a normal Sn–O length of 2.266(6) Å. The coordinated oxygen atom O(2) has a longer N–O bond distance, 1.304(10) Å, than the other two, which are practically indistinguishable at 1.219(12) and 1.227(14) Å. The difference in the N–O distances is mirrored in the O–N–O angles; that opposite the coordinated oxygen is considerably larger (124.9(9)°) than 120° and larger than the other two (118.1(8) and 116.9(8)°). The value of 116.6(5)° for the Sn–O(2)–N angle agrees well with the observation that the angle at the coordinated oxygen is greater than 110° when the nitrate is unidentate and smaller when bidentate. There is a relatively close approach of a second oxygen atom, O(3), to tin (Sn–O 3.079(7) Å), and this behaviour seems to characterize the nitrate groups located in apical positions. In **2** one nitrate group is unidentate and the other is asymmetrically bidentate. The Sn–O bond distance involving the former, 2.289(6) Å, is shorter than those involving the latter, 2.350(6) and 2.472(7) Å, as might have been expected. A detailed discussion of the dimensions of the unidentate ligand is not practicable owing to the disorder involving the two terminal oxygen atoms. The Sn–O–N angle of 130.5(5)° is indicative of a fully unidentate bonding, without additional bonding by a second oxygen. Within the bidentate nitrate the terminal oxygen O(8) has a N–O bond distance significantly shorter, 1.189(11) Å, than those involving the two coordinated oxygens (1.272(12), 1.248(11) Å). Related to this shortening is the contraction of the O–N–O angle involving the coordinated oxygens, which is reduced to 113.9(8)°; this narrowing occurs at the expense of the other two angles which are correspondingly increased to

TABLE 6
SELECTED VIBRATIONAL BANDS (cm^{-1}) RECORDED WITH NUJOL MULLS

	$\nu_1 + \nu_4$	$\nu(\text{NO}_3)_{\text{as}}$	$\nu(\text{NO}_3)$	$\nu(\text{NO}_3)_s$	$\nu(\text{E}=\text{O})^a$	$\delta(\text{NO}_3)$	$\nu(\text{Sn}-\text{C})$
$\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$	1768w	1495s	1340m	1300s	1150s	810m	295ms
	1745vw	1480s		1282sh	1130ms		
	1720vw						
$\text{SnPh}_2(\text{NO}_3)_2\text{cdppoet} \cdot \text{CHCl}_3$	1770w	1490s	1345m	1298s	1150s	815m	295m
	1730w	1480s	1340mw	1285sh	1120s	810m	
	1710w						
$\{\text{SnPh}_2(\text{NO}_3)_2\}_2 \cdot \text{tdppoet} \cdot 2\text{H}_2\text{O}$		1535sh	1360sh	1275ms	1135ms	802mw	300m
		1510s	1350s	1255ms	1125ms		
			1340sh				
$\{\text{SnPh}_3\text{NO}_3\}_2\text{tdppoet}$	1770vw	1485s	1345m	1300ms	1150s	808mw	305w
				1280ms	1125s		295w
				1260m			280m
$\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$		1485s	1340m	1285s	878s	810mw	280m
				1260m			
$\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{dpaoe}$	1740w	1530ms	1360s	1305sh	850s	802mw	295m
	1705w	1505s	1350s	1275s			
			1340s	1255ms			

^a E = P, As.

122.8(8) and 123.2(8) $^\circ$. The values of the two Sn–O–N angles of 93.5(5) and 100.1(6) $^\circ$ are consistent with a bidentate coordination.

In both compounds there is no intermolecular contact shorter than the sums of commonly accepted Van der Waals radii.

Infrared spectra. The main vibrational bands of the four organotin adducts are listed in Table 6 together with those of the two derivatives, $\text{SnPh}_2(\text{NO}_3)_2\text{cdppoet} \cdot \text{CHCl}_3$ and $\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{tdppoet} \cdot 2\text{H}_2\text{O}$ previously described.

In the case of the nitrate groups, two absorption regions may be considered as being indicative of their ligand behaviour: bands attributable to the symmetric and asymmetric stretching modes appear at 1600–1200 cm^{-1} , while bands arising from deformation modes mainly appear around 800 cm^{-1} [18–21]. A third region of the spectrum, that around 1000 cm^{-1} , is less useful in assignment, because the presence in it of co-ligand bands.

In the spectrum of $\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{tdppoet} \cdot 2\text{H}_2\text{O}$, which contains bidentate nitrate groups, two pairs of medium intense bands at 1535–1510 and 1275–1255 cm^{-1} are present. There is also a third strong broad band around 1350 cm^{-1} , but it is less informative because it lies very close to an absorption frequency of Nujol. In $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$, where only unidentate nitrate coordination occurs, there is a less intense band at 1340 cm^{-1} which appears as a shoulder of the Nujol peak, while the afore-mentioned groups of bands at frequency values above and below 1300 cm^{-1} tend to approach each other, the former gradually decreasing to 1490 cm^{-1} , and the latter rising smoothly to ca. 1285 cm^{-1} .

The presence of both bidentate and unidentate groups in the same compound, as in $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$ and $\text{SnPh}_2(\text{NO}_3)_2\text{cdppoet} \cdot \text{CHCl}_3$, makes the assignment very difficult. Moreover, the degree of asymmetry shown by the bidentate nitrate complicates the structural diagnosis, since the band at 1350 cm^{-1} , which is strong when the nitrate group is in a symmetric bidentate situation, becomes less intense as

the asymmetric character increases, and so tends towards the value found for the unidentate nitrate.

On the basis of the arguments presented above, we can assign a bidentate behaviour to the NO_3 group in $\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{dpaoe}$ and a unidentate behaviour in $\{\text{SnPh}_3\text{NO}_3\}_2\text{tdppoet}$.

Concerning the region of the spectrum around 800 cm^{-1} , there are two absorption frequencies characterizing the nitrate group, one in the range $830\text{--}800\text{ cm}^{-1}$ (out-of-plane deformation) and the other in the range $740\text{--}700\text{ cm}^{-1}$ (doubly degenerate in-plane bending). There is a sharp band at 810 cm^{-1} in the spectrum of $\{\text{SnPh}_3\text{NO}_3\}_2\text{dpaoe}$ and one at 802 cm^{-1} in that of $\{\text{SnPh}_2(\text{NO}_3)_2\}_2\text{tdppoet} \cdot 2\text{H}_2\text{O}$. In $\text{SnPh}_2(\text{NO}_3)_2\text{cdppoet} \cdot \text{CHCl}_3$ and $\text{SnPh}_2(\text{NO}_3)_2\text{dppom}$, where both uni- and bi-dentate nitrate groups are present, two bands would be expected. In fact, whereas there are two peaks, at 815 and 810 cm^{-1} , for the dppoet complex, only one, at 810 cm^{-1} , is evident for the dppom derivative, a second absorption being probably overlapped by the strong absorption due to the P-ligand, which lies at 795 cm^{-1} .

Only weak absorptions, assigned to $\nu_1 + \nu_4$ combination modes, appear in the $1800\text{--}1700\text{ cm}^{-1}$, and we have not succeeded in correlating them with the structural behaviour of the nitrate groups [22].

The vibrational absorptions attributable to the $\text{P}=\text{O}$ groups in the diphosphine ligands are indicative of the participation of the oxygen atom (negative shift of ca. 50 cm^{-1}) in the coordination as well as distinguishing between uni- and bi-dentate behaviour. In fact, when the diphosphine acts as bidentate ligand, either chelating or bridging, a series of bands is present in the $1200\text{--}1080\text{ cm}^{-1}$ region, with a maximum at 1150 cm^{-1} , but the spectroscopic pattern is different, with the maximum at 1170 cm^{-1} , when the ligand is unidentate, as we previously found in the case of $\text{SnPh}_3\text{Clcdppoet}$ [1].

Unlike $\nu(\text{P}=\text{O})$ the $\nu(\text{As}=\text{O})$ band shows no significant changes upon coordination; the band usually appears at 870 cm^{-1} in the free ligand spectrum and has the same value or is slightly shifted to 850 cm^{-1} on complex formation.

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