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Synthesis, Spectroscopic Properties and X-ray Structural Analysis of a Dinuclear Tin Adduct: μ-bis(diphenylphosphinyl)ethanebis(nitratotriphenyltin)

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From the reaction of nitratotriphenyltin with bis(diphenylphosphine)ethane, a dinuclear adduct of formula $[\{SnPh_3(NO_3)\}_2\{OPPh_2(CH_2)_2Ph_2PO\}]$ *has been obtained, in which the organic ligand is present in oxidised form. Crystals are triclinic (*$P\bar{1}$*), with unit-cell dimensions:* $a = 12.519(15)$, $b = 11.798(12)$, $c = 10.399(10)$ Å, $\alpha = 98.2(1)$, $\beta = 89.2(1)$, $\gamma = 111.2(1)^\circ$, $Z = 1$. *The structure has been determined from diffractometer data by conventional Patterson and Fourier techniques and refined by full-matrix least-squares to an* R *value of 3.68% for 4291 independent reflections. The adduct has a trigonal bipyramidal coordination geometry with the three phenyl rings occupying equatorial coordination sites, while the unidentate nitrate group and the bis(diphenylphosphinyl)ethane molecule are* trans *to each other and occupy the apical positions.*

Introduction

The versatility of the nitrate group as a ligand in metal complexes is well known [1] and it has been recently experienced in our laboratory in connection with some organotin compounds in which the presence of nitrate groups contributes to produce an unusual stereochemistry for tin [2] as well as an interesting molecular packing [3]. Moreover, the covalent nitrate group exhibits strong oxidising powers, which can transform, for example, aliphatic hydrocarbons into carboxylic acids [1]. Such a property has been experimented by us towards alcohols and phosphines in two adducts of $Ph_2Sn(NO_3)_2$ and Ph_3SnNO_3 with n-propylsulphoxide [4] and triphenylphosphine [5], respectively.

From the reaction of nitratotriphenyltin and bis(diphenylphosphine)ethane, a dinuclear tin adduct has been now obtained containing the parent diphosphine in its oxidised form: $[\{SnPh_3(NO_3)\}_2\{OPPh_2(CH_2)_2Ph_2PO\}]$.

This paper deals with the synthesis, the IR spectroscopic properties and the X-ray crystal analysis of this compound.

TABLE I. Crystallographic Data.

$C_{62}H_{54}N_2O_8P_2Sn_2$ $M = 1254.5$, triclinic*
$a = 12.519(15)$, $b = 11.798(12)$, $c = 10.399(10)$ Å;
$\alpha = 98.2(1)$, $\beta = 89.2(1)$, $\gamma = 111.2(1)^\circ$;
$V = 1416$ Å^3; $Z = 1$; $D_o = 1.45$, $D_c = 1.47$ g cm^{-3};
$F(000) = 634$; $\mu(MoK\alpha) = 8.99$ cm^{-1}
Space group: $P\bar{1}$.

*The present cell does not meet the requirement of the conventional triclinic cell to have $a < b < c$ and all the angles either acute or obtuse, but this can be easily obtained by applying the transformation matrix: 0 0 1/0 $\bar{1}$ 0/1 0 0 (a = 10.399, b = 11.798, c = 12.519 Å; α = 81.8, β = 89.2, γ = 68.8°). The usual reductions indicated the absence of higher symmetry.

Experimental

Nitratotriphenyltin and bis(diphenylphosphine)ethane dissolved in anhydrous acetone were reacted in equimolar amounts at room temperature under dry nitrogen atmosphere. From the solution after several hours by slow evaporation under reduced pressure, colourless air stable crystals were obtained.

Space group information and preliminary unit-cell dimensions were obtained from Weissenberg photographs. A tabular crystal of approximate dimensions 0.06 × 0.25 × 0.33 mm was mounted on a Siemens AED single-crystal diffractometer and aligned with its c axis coincident with the ϕ axis of the instrument. The orientation matrix and the final unit-cell dimensions were obtained from a least-squares fit of θ, χ and ϕ values from 24 reflections. Table I lists the most significant crystallographic data. Intensity data were collected by use of Zr-filtered MoKα radiation using the ω–2θ scanning technique. A total of 6176 independent reflections were measured in the range $5.0^\circ < 2\theta < 54.0^\circ$, and of these 4291 were considered "observed" having $I \geqslant 2\sigma(I)$. A standard reflection (2 2 2) was remeasured every twenty reflections to detect long-term drift in

TABLE II. Fractional Atomic Coordinates ($\times 10^5$ for Sn and $\times 10^4$ for P, O, N and C) for non-Hydrogen Atoms.

	x	*y*	*z*		*x*	*y*	*z*
Sn	19643(3)	27048(3)	22883(3)	C(18)	1363(7)	3689(7)	4987(8)
P	1767(1)	486(1)	4405(1)	C(19)	1730(4)	−1040(4)	3941(5)
C(1)	202(7)	1902(7)	1734(7)	C(20)	1856(4)	−1707(5)	4890(7)
C(2)	−383(7)	653(8)	1419(7)	C(21)	1804(5)	−2894(6)	4520(10)
C(3)	−1532(8)	184(10)	1135(9)	C(22)	1649(6)	−3396(6)	3249(10)
C(4)	−2136(9)	959(11)	1175(11)	C(23)	1512(7)	−2749(6)	2311(9)
C(5)	−1577(9)	2186(12)	1483(11)	C(24)	1534(5)	−1579(5)	2651(7)
C(6)	−435(9)	2650(10)	1766(10)	C(25)	3026(4)	1311(4)	5422(5)
C(7)	3478(6)	2556(7)	1476(7)	C(26)	4038(5)	1203(7)	5049(8)
C(8)	3729(8)	1516(9)	1418(9)	C(27)	5034(6)	1846(8)	5794(9)
C(9)	4754(9)	1476(11)	961(11)	C(28)	5010(6)	2575(7)	6917(8)
C(10)	5536(8)	2474(12)	543(10)	C(29)	4021(5)	2703(6)	7299(6)
C(11)	5314(8)	3517(13)	612(11)	C(30)	3027(5)	2072(5)	6554(6)
C(12)	4290(7)	3575(9)	1081(9)	C(31)	555(4)	364(4)	5396(5)
C(13)	2253(6)	3823(6)	4134(7)	O(1)	1698(3)	1025(3)	3209(3)
C(14)	3331(7)	4641(7)	4575(8)	O(2)	2150(3)	4341(3)	1353(3)
C(15)	3500(9)	5278(9)	5822(9)	O(3)	1755(5)	3177(5)	−525(4)
C(16)	2618(9)	5115(9)	6641(9)	O(4)	1683(5)	4981(5)	−304(5)
C(17)	1552(9)	4325(8)	6234(8)	N	1851(4)	4156(5)	130(5)

TABLE III. Fractional Atomic Coordinates ($\times 10^3$) and Thermal Parameters ($Å^2 \times 10^2$) for Hydrogen Atoms.

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
H(2)	−5(4)	12(4)	140(5)	5(1)	H(18)	64(5)	321(5)	473(5)	6(2)
H(3)	−189(5)	−52(5)	107(6)	8(2)	H(20)	199(6)	−142(7)	574(8)	9(3)
H(4)	−291(5)	57(5)	108(6)	9(2)	H(21)	194(6)	−333(7)	513(7)	12(2)
H(5)	−188(5)	264(5)	155(5)	7(2)	H(22)	153(7)	−420(8)	305(8)	14(3)
H(6)	−12(4)	335(5)	199(5)	5(1)	H(23)	134(7)	−308(7)	157(8)	12(3)
H(8)	323(5)	94(5)	176(6)	9(2)	H(24)	134(5)	−121(6)	210(6)	5(2)
H(9)	493(5)	77(6)	88(6)	9(2)	H(26)	402(7)	70(7)	431(8)	9(3)
H(10)	632(5)	247(5)	22(5)	8(2)	H(27)	578(6)	180(6)	545(7)	12(2)
H(11)	581(5)	416(6)	33(6)	9(2)	H(28)	566(6)	310(7)	738(7)	11(2)
H(12)	418(4)	437(4)	109(4)	5(1)	H(29)	390(5)	312(6)	795(7)	10(2)
H(14)	391(4)	485(5)	389(5)	6(1)	H(30)	237(6)	217(6)	684(6)	7(2)
H(15)	417(4)	579(5)	610(5)	7(2)	H(31)	59(4)	114(5)	569(5)	4(1)
H(16)	266(4)	547(4)	744(5)	6(1)	H′(31)	67(4)	1(5)	619(5)	5(1)
H(17)	96(5)	420(5)	676(6)	7(2)					

the equipment or changes in the crystal. The intensity of this reflection as a function of X-ray exposure showed only small random fluctuations. The data were corrected for Lorentz and polarization factors, while no correction for absorption effects was made.

The structure was solved by the heavy atom technique, assuming the centrosymmetric space group $P\bar{1}$. The intensity statistics did not permit to distinguish clearly between the centric or acentric space group. The coordinates of the tin atom have been derived from a three-dimensional Patterson map. A Fourier synthesis phased on tin yielded a clear picture of the whole molecule with the exclusion of the hydrogen atoms. Two cycles of isotropic full-matrix least-squares refinement followed by three cycles of anisotropic refinement yielded a conventional R index of 0.046. The shifts of the atomic parameters were negligible, all being well below the corresponding σ. A difference Fourier map performed at this point gave sufficient evidence for a sure location of all hydrogen atoms. Two further cycles were computed including the H atoms with isotropic thermal parameters. The final R was 0.0368 (observed reflections only). The quantity minimized was $\Sigma w\ (F_o - F_c)^2$ with $w = \sigma^{-2}(F_o)$. Scattering factors were taken from Cromer and Mann [6] for non-hydrogen atoms and from Stewart, Davidson and Simpson [7] for hydrogen atoms. As a final check of the correctness of the structure, a difference Fourier synthesis was calculated and found to contain no

TABLE IV. Anisotropic Thermal Parameters ($Å^2 \times 10^4$ for Sn, P; $Å^2 \times 10^3$ for O, N, and C) for non-Hydrogen Atoms.*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	442(2)	358(2)	399(2)	56(1)	31(1)	174(1)
P	324(5)	334(5)	472(6)	75(4)	38(4)	138(4)
C(1)	50(4)	52(4)	42(4)	7(3)	1(3)	24(3)
C(2)	61(5)	55(5)	40(4)	3(3)	−3(3)	25(4)
C(3)	57(5)	65(6)	61(5)	−1(4)	−11(4)	7(5)
C(4)	47(6)	106(8)	89(7)	−11(6)	−12(5)	31(6)
C(5)	67(6)	98(8)	104(8)	−13(6)	−20(5)	57(6)
C(6)	72(6)	62(6)	77(6)	−8(5)	−17(5)	39(5)
C(7)	42(4)	51(4)	40(4)	1(3)	1(3)	16(3)
C(8)	54(5)	55(5)	78(6)	1(5)	14(4)	21(4)
C(9)	68(6)	78(7)	93(7)	−7(6)	10(5)	38(6)
C(10)	43(5)	123(9)	65(6)	9(6)	7(4)	32(6)
C(11)	38(5)	120(9)	91(7)	50(7)	8(4)	12(6)
C(12)	45(5)	67(6)	68(5)	33(4)	0(4)	12(4)
C(13)	50(4)	37(3)	46(4)	6(3)	1(3)	21(3)
C(14)	48(5)	52(4)	56(5)	1(4)	−2(4)	16(4)
C(15)	53(6)	64(5)	72(6)	−13(4)	−20(5)	19(5)
C(16)	84(8)	67(5)	47(5)	−9(4)	−8(5)	42(5)
C(17)	75(6)	63(5)	53(5)	7(4)	18(4)	34(5)
C(18)	47(5)	45(4)	55(4)	6(3)	7(4)	12(4)
C(19)	32(2)	37(2)	76(3)	13(2)	9(2)	16(2)
C(20)	50(3)	49(3)	95(5)	26(3)	0(3)	20(2)
C(21)	60(4)	49(3)	160(7)	38(4)	3(4)	28(3)
C(22)	72(4)	38(3)	183(9)	8(5)	29(5)	27(3)
C(23)	92(5)	56(3)	118(6)	−11(4)	21(4)	28(3)
C(24)	69(3)	44(3)	80(4)	3(3)	10(3)	25(3)
C(25)	39(2)	42(2)	52(3)	10(2)	−5(2)	10(2)
C(26)	36(3)	96(4)	90(5)	−13(4)	0(3)	17(3)
C(27)	36(3)	117(6)	126(6)	2(5)	−2(4)	18(3)
C(28)	58(4)	86(5)	95(5)	5(4)	−24(4)	8(3)
C(29)	67(4)	84(4)	72(3)	−12(3)	−18(3)	20(3)
C(30)	55(3)	59(3)	66(3)	−5(2)	−11(3)	19(2)
C(31)	36(2)	44(2)	49(3)	5(2)	5(2)	15(2)
O(1)	50(2)	38(2)	55(2)	12(1)	5(1)	17(1)
O(2)	79(3)	52(2)	55(2)	16(2)	4(2)	31(2)
O(3)	118(4)	97(3)	56(2)	9(2)	3(2)	56(3)
O(4)	146(5)	107(4)	88(3)	55(3)	25(3)	81(4)
N	76(3)	73(3)	61(3)	30(2)	20(2)	39(3)

*The temperature factor is in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots + 2U_{12}hka^*b^*)]$.

TABLE V. Selected Bond Lengths (Å) and Angles (°).

Sn–C(1)	2.113(8)	C(17)–C(18)	1.38(1)
Sn–C(7)	2.119(8)	C(18)–C(13)	1.39(1)
Sn–C(13)	2.124(7)	N–O(2)	1.297(6)
Sn–O(1)	2.238(5)	N–O(3)	1.221(8)
Sn–O(2)	2.220(5)	N–O(4)	1.213(9)
C(1)–C(2)	1.38(1)	P–O(1)	1.492(4)
C(2)–C(3)	1.36(1)	P–C(19)	1.780(5)
C(3)–C(4)	1.38(2)	P–C(25)	1.788(5)
C(4)–C(5)	1.35(2)	P–C(31)	1.795(6)
C(5)–C(6)	1.35(2)	C(19)–C(20)	1.39(1)
C(6)–C(1)	1.38(2)	C(20)–C(21)	1.38(1)
C(7)–C(8)	1.37(1)	C(21)–C(22)	1.36(1)
C(8)–C(9)	1.38(2)	C(22)–C(23)	1.37(1)

TABLE V. *(continued)*

C(9)–C(10)	1.35(2)	C(23)–C(24)	1.37(1)
C(10)–C(11)	1.35(2)	C(24)–C(19)	1.38(1)
C(11)–C(12)	1.39(1)	C(25)–C(26)	1.36(1)
C(12)–C(7)	1.38(1)	C(26)–C(27)	1.38(1)
C(13)–C(14)	1.38(1)	C(27)–C(28)	1.36(1)
C(14)–C(15)	1.38(1)	C(28)–C(29)	1.35(1)
C(15)–C(16)	1.36(1)	C(30)–C(25)	1.37(1)
C(16)–C(17)	1.35(1)	C(31)–C(31^{i})	1.52(1)
C(1)–Sn–C(7)	134.5(7)	O(1)–P–C(19)	108.9(5)
C(1)–Sn–C(13)	111.9(7)	O(1)–P–C(25)	114.8(6)
C(7)–Sn–C(13)	113.5(7)	O(1)–P–C(31)	111.7(6)

(continued overleaf)

TABLE V. *(continued)*

O(1)–Sn–O(2)	177.6(5)	C(19)–P–C(25)	107.7(5)
C(1)–Sn–O(1)	86.3(5)	C(19)–P–C(31)	106.3(6)
C(1)–Sn–O(2)	91.3(4)	C(25)–P–C(31)	107.1(5)
C(7)–Sn–O(1)	89.2(4)	P–O(1)–Sn	148.3(8)
C(7)–Sn–O(2)	92.6(5)	P–C(31)–C(31^{i})	110(1)
C(13)–Sn–O(1)	91.4(4)	P–C(25)–C(26)	119(1)
C(13)–Sn–O(2)	89.3(4)	P–C(25)–C(30)	123(1)
C(2)–C(1)–Sn	124(1)	P–C(19)–C(20)	119(1)
C(6)–C(1)–Sn	119(1)	P–C(19)–C(24)	120(1)
C(8)–C(7)–Sn	123(1)	N–O(2)–Sn	117.5(6)
C(12)–C(7)–Sn	119(1)	O(2)–N–O(3)	119(1)
C(14)–C(13)–Sn	122(1)	O(2)–N–O(4)	117(1)
C(18)–C(13)–Sn	120(1)	O(3)–N–O(4)	123(1)

i = $\bar{x}$, $\bar{y}$, 1 – z

features of chemical significance. The maximum residual electron density was 0.85 e Å^{-3}, mainly in the region near the tin atom.

Tables II and III list the final fractional coordinates and the corresponding estimated standard deviations for the non-hydrogen and for the hydrogen atoms respectively. Table IV reports the anisotropic thermal parameters of the non-hydrogen atoms. A list of calculated and observed structure factors has been deposited with the Editor.

All calculations were carried out at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.

Results and Discussion

From a chemical point of view the most interesting feature of the present compound is given by the oxidation, caused by the action of the covalent nitrate group, of bis(diphenylphosphine)ethane to bis(diphenylphosphinyl)ethane. This latter molecule coordinates to tin through its oxygen atoms and is responsible for the dinuclear nature of the compound; the centre of gravity of the C(sp^3)–C(sp^3) bond is located on a crystallographic symmetry centre. As can be seen from Fig. 1, three carbon atoms from the phenyl rings and an oxygen atom from the nitrate ion complete the coordination to tin which so results to be trigonal bipyramidal with the aromatic rings occupying the equatorial coordination sites and the two oxygen containing ligands at the apices of the bipyramid. Tin is nearly coplanar with the three attached carbon atoms, being only 0.04 Å out of the C(1) C(7) C(13) plane; the phenyl rings are tilted differently with respect to the equatorial plane, the angles they make with this plane being 52.4° (C(1)...C(6)), 69.2° (C(7)...C(12)) and 19.2° (C(13)...C(18)).

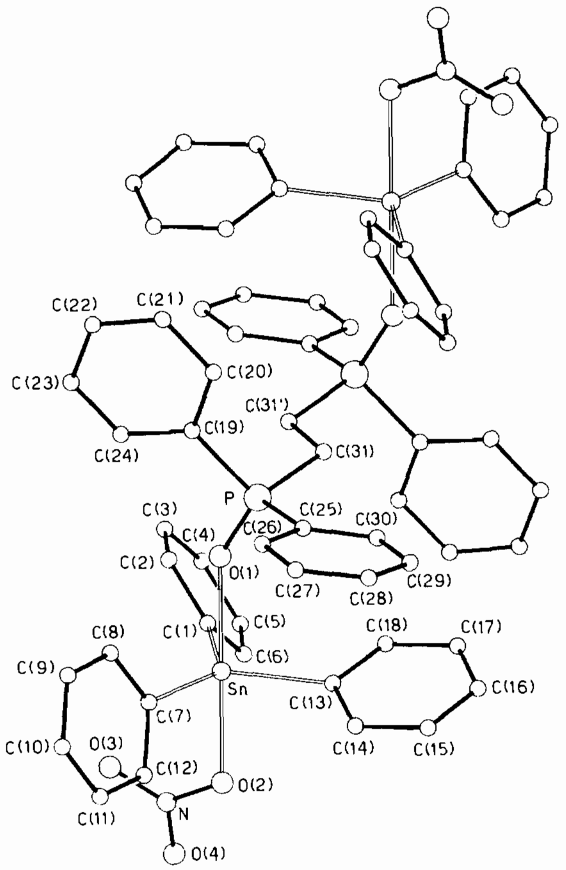

Figure 1. Projection of the structure. For clarity hydrogen atoms are omitted.

Table V lists bond distances and angles; individual angles within the phenyl rings have not been listed as they are of no consequence and are not used in the subsequent discussion. The values of the bond angles at tin indicate that the distortion from the ideal trigonal bipyramidal geometry is small but significant, and is reflected particularly in the equatorial angles which are 111.9(7), 113.5(7) and 134.5(7)°. The angles between axial and equatorial sites range from 86.3 to 92.6°, while the two bonds Sn–O(1) and Sn–O(2) are approximately collinear (O–Sn–O = 177.6°).

In Table VI all the five coordinated triphenyltin derivatives of known crystal structure are reported for a comparison; the data tabulated refer to the coordination polyhedron which in all compounds is a trigonal bipyramid. In comparing these data it is noteworthy that in seven out of the nine compounds all the three phenyl rings occupy the equatorial positions; only in $SnPh_3(PhCO \cdot PhNO)$ [8] and in $SnPh_3(PhC(O)CHC(O)Ph)$ [9], where the oxygen containing ligand acts as bidentate, one of the phenyl rings is constrained to occupy an apical position. This situation is responsible for some interesting differences found between the two aforementioned and the

TABLE VI. Structural Parameters (Distances in Å, angles in °) in the Coordination Polyhedron of Fivecoordinated Triphenyltin Derivatives.

Compound	Equatorial Bonds			Axial Bonds		Equatorial Angles			Axial Angle	Equatorial to Axial Angles	Reference
$SnPh_3(SC_5H_4N)$	Sn–C 2.14(2)	2.17(2)	2.17(2)	Sn–N 2.62(2)		116.3(9)	121.0(8)	120.7(7)	172.1(5)	82.1–98.1	10
				Sn–S 2.576(7)							
$SnPh_3(PhCO{\cdot}PhNO)$	Sn–C 2.142(9)	2.131(7)		Sn–C 2.176(9)		110.9(2)	116.9(3)	125.5(2)	157.2(2)	71.3–105.7	8
	Sn–O 2.091(5)			Sn–O 2.308(4)							
$SnPh_3(PhC(O)CHC(O)Ph)$	Sn–C 2.149(7)	2.181(6)		Sn–C 2.180(6)		110.3(3)	120.1(3)	124.1(2)	163.7(2)	78.1–105.5	9
	Sn–O 2.094(7)			Sn–O 2.276(7)							
$SnPh_3(NO_3)(C_5H_5NO)$ (monoclinic form)	Sn–C 2.096(9)	2.126(9)	2.112(9)	Sn–O 2.245(8)	2.227(8)	118.0(3)	120.8(3)	120.9(3)	171.4(2)	82.6–97.3	11
$SnPh_3(NO_3)(C_5H_5NO)$ (triclinic form; two independent molecules)	Sn–C 2.116(10)	2.087(11)	2.084(8)	Sn–O 2.227(8)	2.299(7)	112.7(10)	126.3(10)	120.9(10)	171.2(4)	82.8–98.5	12
	2.075(9)	2.104(7)	2.142(11)	2.253(7)	2.238(6)	112.6(9)	128.9(10)	118.4(9)	174.2(4)	84.7–96.4	
$SnPh_3(NO_3)(Ph_3PO)$	Sn–C 2.10(2)	2.13(2)	2.14(2)	Sn–O 2.22(2)	2.29(2)	113.4(9)	120.0(9)	126.0(9)	174.1(7)	84.9–97.3	5
$SnPh_3(NO_3)(Ph_3AsO)$	Sn–C 2.096(8)	2.117(8)	2.121(8)	Sn–O 2.274(6)	2.181(5)	116.1(3)	118.0(3)	125.9(3)	175.6(2)	84.0–94.6	13
$SnPh_3OH$	Sn–C 2.131(8)	2.128(8)	2.153(8)	Sn–O 2.197(5)	2.255(5)	118.0(3)	118.7(3)	123.0(3)	177.6(3)	84.8–93.6	14
$\{SnPh_3(NO_3)\}_2\{OPPh_2(CH_2)_2Ph_2PO\}$	Sn–C 2.113(8)	2.119(8)	2.124(7)	Sn–O 2.238(5)	2.220(5)	111.9(7)	113.5(7)	134.5(7)	177.6(5)	86.3–92.6	This work

other seven compounds: for instance the axial to axial angle is far removed from linearity in the first case (157.2, 163.7°), while it is close to the expected 180° in the second one (171.2–177.6°). Moreover there is a small but significant lengthening of the Sn–C distance when going from equatorial bonds (weighted mean 2.124(5) Å) to apical bonds (weighted mean 2.179(5) Å). Finally, even though the angular distortion in the equatorial plane is rather considerable in all compounds, nevertheless the planarity is maintained when the phenyl rings are all equatorial (the sum of the three valence angles ranging from 358.0 to 360.0°), while the coordination plane is significantly distorted when one ring is axial (the sum of the valence angles being 353.3 and 354.5°).

Since this is the first bis(diphenylphosphinyl) ethane–tin adduct, no comparison with strictly analogous compounds is possible. The Sn–O(1) bond distance, 2.238(5) Å, is intermediate between those observed in two triphenylphosphine oxide tin adducts, 2.148(6) Å, $SnPh_2(NO_3)_2(Ph_3PO)$ [2] and 2.29(2) Å, $SnPh_3(NO_3)(Ph_3PO)$ [5]. The structural parameters of the organic molecule found in the present compound agree fairly well with the corresponding ones observed in *catena*-μ-bis(1,2-diphenylphosphinyl)ethanedichlorocopper(II) [15] and in trichloro{[2-(diphenylphosphinyl)ethyl]-dimethylammonium}copper(II) [16]. A survey of the main data given in Table VII shows that for all compounds coordination around phosphorus cannot be considered as quite regular tetrahedral, particularly because of the values of the O–P–C angles which are significantly larger than those of the C–P–C angles, in agreement with the increased electron density associated with the P–O double bond. The value of this last bond, which is nearly identical in the three compounds (weighted mean 1.496(2) Å) is slightly longer than that observed in triphenylphosphine oxide (1.46(1) Å in the orthorhombic form [17], 1.483(2) Å in the monoclinic form [18]). The $P–C(sp^2)$ (mean 1.794(4) Å) and $P–C(sp^3)$ (mean 1.805(5) Å) bond lengths are comparable to or even smaller than those usually assigned to the $P–C(sp^2)$ and $P–C(sp^3)$ covalent single bonds. In all three compounds the M–O–P moiety is significantly bent. In the present compound the ν(P–O) vibration, listed together with other infrared data in Table VIII, appears at 1145 cm^{-1}, a value which is in agreement with those previously observed in the two aforementioned triphenylphosphine oxide tin complexes.

The nitrate group acts as unidentate ligand through O(2). The Sn–O(2) bond distance, 2.220(5) Å, compares with the corresponding bonds observed in tin compounds containing unidentate nitrate groups, *e.g.*: 2.22(3) Å in $Sn(OH_2)Me_3(NO_3)$ [19]; 2.30(3) Å in $[Sn(OH)Me_2(NO_3)]_2$ [20]; 2.22(2) Å in $SnPh_3(NO_3)(Ph_3PO)$ [5]; 2.274(6) Å in $SnPh_3$-

TABLE VII. Comparison of Some Structural Parameters (Distances in Å, Angles in °) in Complexes Containing the Diphenylphosphinylethane Moiety.

	I	II	III
P–O	1.497(2)	1.51(2) 1.49(2)	1.492(4)
P–C(sp^2)	1.793(3) 1.801(3)	1.76(2) 1.85(2) 1.85(3) 1.78(1)	1.780(5) 1.788(5)
P–C(sp^3)	1.809(3)	1.76(2) 1.82(3)	1.795(6)
C(sp^3)–C(sp^3)	1.522(8)	1.55(4) 1.59(4)	1.52(1)
O–P–C (sp^2)	108.8(1) 112.6(1)	118(1) 106(1) 109(1) 111(1)	108.9(5) 114.8(6)
O–P–C(sp^3)	112.3(1)	109(1) 116(1)	111.7(6)
C(sp^2)–P–C(sp^3)	107.6(1) 104.6(1)	102(1) 111(1) 105(1) 112(1)	106.3(6) 107.1(5)
C(sp^2)–P–C(sp^2)	110.8(1)	107(1) 106(1)	107.7(5)
P–C(sp^3)–C(sp^3)	112.4(2)	116(2) 112(2)	110(1)
P–O–M	148.9(1)	143(1) 148(1)	148.3(8)

I catena-μ-bis(1,2-diphenylphosphinyl)ethanedichlorocopper(II) [15]; II trichloro{[2-(diphenylphosphinyl)ethyl]dimethylammonium}copper(II) [16] (two independent molecules in the unit cell); III μ-bis(diphenylphosphinyl)ethanebis(nitratotriphenyltin) (present work).

TABLE VIII. Main Vibrational Bands (cm^{-1}) and Relative Assignments.

Frequency	Assignment	Frequency	Assignment
3070 w	$\nu(CH)_{aryl}$	1145 s	ν(PO)
3050 w		1120 m	ν(PC)
2960 w	$\nu(CH)_{alkyl}$	1025 mw	ν(NO)
2920w		1000 sh	ring
1590 m	ν(CC)	990 s	
1580 sh		810 w	$\delta(NO_2)$
1495 vs	ν_{as}(NO)	730 s	ν(PC)
1480 s		530 m	δ(PC)
1435 m	ring	455 ms	ν(PC)
1430 m		280 m	ν(SnO)
1410 w			
1285 vs	ν_s(NO)	265 m	ν(SnC)
1260 sh			

(NO_3)(Ph_3AsO) [13]; 2.245(8) Å in $SnPh_3(NO_3)(C_5H_5NO)$, monoclinic form [11]; 2.227(8), 2.253(7) Å in $SnPh_3(NO_3)(C_5H_5NO)$, triclinic form [12]. A second oxygen atom, O(3), is at 3.087(6) Å from tin. Within the nitrate group the differences in bond distances and angles seem to be due to bonding effects, since the N–O(2) bond, which involves the coordinated oxygen atom, is significantly longer (1.297(6) Å) than the others two, with N–O(3) (1.221(8) Å) and N–O(4) (1.213(9) Å) practically indistinguishable. As a consequence of this fact, the O(3)–N–O(4) angle (123(1)°) is larger than the other two (119(1), 117(1)°) and greater than 120° as usually observed in this mode of coordination. The NO_3 group is perfectly planar and its plane makes an angle of 73.6° with the equatorial C(1)C(7)C(13)Sn plane. The structural situation of this ion is not well clear from the infrared spectra (Table VIII): unfortunately the combination bands in the 1800–1700 cm^{-1} region, which are indicative of the nitrate behaviour, are not easily assignable owing to their too weak intensity; moreover the frequency values of the asymmetric and symmetric stretching modes ($\nu_{as} - \nu_s = 210$ cm^{-1}) can be considered as intermediate between those characterizing unidentate and bidentate nitrates.

TABLE IX. Significant Packing Interactions (Å).

C(2)...C(2^{i})	3.42(1)	O(2)...C(22^{iii})	3.33(1)
C(3)...C(8^{i})	3.65(1)	O(4)...C(11^{iv})	3.56(1)
O(4)...C(16^{ii})	3.37(1)	C(11)...C(16^{v})	3.65(1)
C(11)...C(29^{ii})	3.67(1)		

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

The molecular packing is determined by normal van der Waals interactions. As can be seen from Table IX, which lists some significant packing contacts, the C...C intermolecular distances are all longer than 3.6 Å, with the only exception of the C(2)...C(2^{i}) interaction which is 3.42 Å; the closest C...O approaches are 3.33 Å.

References

1 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Quart. Rev., 25,* 289 (1971).

2 M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Chem. Soc. Dalton,* 131 (1978).

3 C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Chem. Soc. Dalton,* 1935 (1977).

4 A. Mangia, C. Pelizzi and G. Pelizzi, *J. Chem. Soc. Dalton,* 2557 (1973).

5 M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Organomet. Chem., 112,* 263 (1976).

6 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).

7 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).

8 P. G. Harrison and T. J. King, *J. Chem. Soc. Dalton,* 2298 (1974).

9 G. M. Bancroft, B. W. Davies, N. C. Payne and T. K. Sham, *J. Chem. Soc. Dalton,* 973 (1975).

10 N. G. Bokii, Yu. T. Struchkov, D. N. Kravtsov and E. M. Rokhlina, *Zh. Strukt. Khim., 14,* 502 (1973).

11 C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Organometal. Chem., 124,* 151 (1977).

12 G. Pelizzi, *Inorg. Chim. Acta, 24,* L31 (1977).

13 M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Organometal. Chem., 125,* 161 (1977).

14 C. Glidewell and D. C. Liles, *Acta Cryst., B34,* 129 (1978).

15 M. Mathew and G. J. Palenik, *Inorg. Chim. Acta, 5,* 573 (1971).

16 M. G. Newton, H. D. Caughman and R. C. Taylor, *J. Chem. Soc. Dalton,* 1031 (1974).

17 G. Bandoli, G. Bortolozzio, D. A. Clemente, U. Croatto and C. Panattoni, *J. Chem.Soc. A,* 2778 (1970).

18 G. Ruban and V. Zabel, *Cryst. Struct. Comm., 5,* 671 (1976).

19 R. E. Drew and F. W. B. Einstein, *Acta Cryst., B28,* 345 (1972).

20 A. M. Domingos and G. M. Sheldrick, *J. Chem. Soc. Dalton,* 475 (1974).