Investigation into Diphosphine Oxides as Ligands in Diorganotin(IV) Adducts. Part 3.[1] Synthesis and Crystal Structure[†] of Two Adducts of Dinitratodiphenyltin(IV) with *cis*- and *trans*-1,2-Bis(diphenylphosphoryl)ethylene

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The co-ordinating properties of *cis*- and *trans*-1,2-bis(diphenylphosphoryl)ethylene (cdppoet and tdppoet respectively) have been examined in two new organotin(IV) complexes, $SnPh_2(NO_3)_2(cdppoet)\cdot CHCl_3$ (**1**) and $[SnPh_2(NO_3)_2]_2(tdppoet)\cdot 2H_2O$ (**2**), on both of which an *X*-ray diffraction analysis was carried out. Crystals of (**1**) are orthorhombic, space group *Pbca*, with $a = 17.684(4)$, $b = 38.773(9)$, $c = 12.092(3)$ Å, and $Z = 8$. Crystals of (**2**) are triclinic, space group $P\bar{1}$, with $a = 12.247(10)$, $b = 12.263(11)$, $c = 11.914(11)$ Å, $\alpha = 99.13(7)$, $\beta = 110.37(7)$, $\gamma = 118.36(7)°$, and $Z = 1$. Both structures were solved by the heavy-atom technique from diffractometer data and refined by least-squares methods to a conventional *R* factor of 0.0767 for (**1**) and 0.0344 for (**2**) on the basis of 2 053 and 3 655 observed reflections. The structure of both compounds closely approximates a pentagonal bipyramid about the tin atom with five O atoms in the basal plane and with two C atoms in the apical positions. The main differences between the two structures lie in the ligand behaviour of the dppoet molecule, namely bidentate chelating in (**1**) and bidentate bridging in (**2**).

Seven-co-ordinate tin(IV) has been found to adopt generally a D_{5h} pentagonal bipyramidal geometry,[2–4] with mono-, bi-, tri-, or quinque-dentate ligands in the co-ordination sphere. Most examples involve mono- and di-organotin derivatives. With regard to these latter, the pentagonal bipyramid is always achieved with the two alkyl or aryl groups located at the apices, whereas in the structures so far determined the girdle is occupied by (*i*) two bidentate ligands and one monodentate ligand as in $[SnPh_2(NO_3)(Pr^n{}_2SO)]_2(C_2O_4)$,[5] $[SnPh_2(NO_3)(AsPh_3O)]_2(C_2O_4)$,[6] $SnPh_2(NO_3)_2(PPh_3O)$,[7] $SnPh_2(NO_3)_2(AsPh_3O)$,[3] and $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$;[8] (*ii*) one bidentate ligand and three monodentate ligands as in $[SnPh_2(NO_3)(Me_2SO)_3]NO_3$;[9] (*iii*) one tridentate ligand and two monodentate ligands as in $SnMe_2(NCS)_2$(terpy) (terpy = 2,2′:6′,2″-terpyridyl),[10] $SnBu^n{}_2Cl_2(L)$ [L = 4-oxo-2-(2′-pyridyl)-3-(*N*-2′-pyridylmethylimino)-1,2,3,4-tetrahydroquinazoline],[11] and $SnEt_2Cl_2(L')$ [L′ = 2-(5′-methyl-1′,2′,4′-oxadiazol-3′-yl)-1,10-phenanthroline];[12] and (*iv*) one quinquedentate ligand as in $SnPr^n{}_2$(daps) [H_2daps = 2,6-diacetylpyridine bis(salicyloylhydrazone)][13] and $SnPh_2$(dapa) [H_2dapa = 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone)].[14] Obviously, the base of the bipyramid can accommodate tri- and quinque-dentate ligands only if they are almost planar, while the bidentate ligands should have small bite angles.

As part of our continuing investigation into the structural chemistry of organotin(IV) and in order to obtain further information on the co-ordinating properties of diphosphine oxides, which have been recognised as versatile ligands in metal complexes, we now report the synthesis and the crystal and molecular structure of two new compounds, $SnPh_2(NO_3)_2(cdppoet)\cdot CHCl_3$ (1) and $[SnPh_2(NO_3)_2]_2(tdppoet)\cdot 2H_2O$ (2) [cdppoet and tdppoet = *cis*- and *trans*-1,2-bis(diphenylphosphoryl)ethylene respectively], in both of which tin once again enjoys pentagonal bipyramidal geometry.

Experimental

Preparations.—Solvents were dried and distilled before use. *cis*- and *trans*-1,2-Bis(diphenylphosphino)ethylene and dichlorodiphenyltin were purchased from Strem Chemical Co. and used without further purification. *cis*- and *trans*-1,2-Bis(diphenylphosphoryl)ethylene were obtained by refluxing for 1 h a toluene solution of the parent diphosphine with H_2O_2 (31.5%) in excess.[15] Dinitratodiphenyltin was obtained as previously described[16] by using rigorously checked stoicheiometric amounts of the reagents to avoid contamination by silver salts.

Compound (1) was prepared by adding an acetonitrile solution of $SnPh_2(NO_3)_2$ (0.2 g) to an equimolar amount of cdppoet dissolved in dichloromethane–chloroform (70:30 v/v). Compound (2) was obtained by adding a dichloromethane solution of $SnPh_2(NO_3)_2$ (0.2 g) to tdppoet, dissolved in the same solvent (2:1 molar ratio). In both cases, the solution was stirred at room temperature for 1 h and then allowed to stand. After slow evaporation of the solvents, a white crystalline product was isolated [Found for (1): C, 49.80; H, 3.55; N, 3.15. $C_{39}H_{33}Cl_3N_2O_8P_2Sn$ requires C, 49.60; H, 3.50; N, 2.95%. Found for (2): C, 47.15; H, 3.40; N, 4.50. $C_{50}H_{46}N_4O_{16}P_2Sn_2$ requires C, 47.75; H, 3.70; N, 4.45%].

Collection and Processing of X-Ray Data.—Diffraction measurements were made at room temperature on a Philips PW 1100 diffractometer for compound (1) and on a Siemens AED diffractometer for compound (2); Mo-K_α radiation and the θ–2θ scan mode being used in each case. The setting angles of 25 — 30 well centred reflections were used for the least-squares adjustment of the unit-cell parameters which are reported in Table 1 together with other pertinent crystal data and details for intensity data collection. For compound (1) the systematic absences for $0kl$ (k odd), for $h0l$ (l odd), and for $hk0$ (h odd) are indicative of the space group *Pbca*, while for compound (2) the space group $P\bar{1}$ was assumed and confirmed by the successful refinement of the structure. For both compounds a standard reflection was periodically monitored to check crystal and instrument stability and no systematic change in its intensity was observed during the course of the experiment. Data were converted to unscaled F_o values by application of the standard

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[†] *Supplementary data available* (No. SUP 56106, 11 pp.): thermal parameters, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Lorentz and polarization factors. Absorption was not taken into account; a ψ-scan study carried out for compound (**1**) on the Philips diffractometer showed that crystal absorption effects could be neglected.

Structure Analysis and Refinement.—Using all the measured reflections a Patterson function was calculated for both compounds, from which the positional parameters of the tin atom were readily obtained. Repeated structure factor calculations and difference-Fourier maps phased on an increasing number of atoms located the remaining non-hydrogen atoms, including a solvent molecule of chloroform in (**1**) and two of water in (**2**). The full-matrix least-squares refinement for each structure was carried out in stages, by using first isotropic and later anisotropic thermal parameters [except for the chloroform in (**1**), whose atoms were refined isotropically]. Because of the large number of independent non-hydrogen atoms to be refined, the phenyl rings in (**1**) were treated as rigid bodies with a C–C bond length of 1.395 Å. All hydrogen atoms in (**2**) were located in a ΔF map and included in the last cycle of refinement with individual isotropic thermal parameters. Final convergence was reached at an R value of 0.0344 (R' = 0.0362). For (**1**), with lower accuracy because of the large thermal motion in the structure, satisfactory hydrogen positions were not obtainable from difference-Fourier maps and therefore the hydrogens were neglected. The atomic parameters had to be divided into two blocks in (**1**) and three blocks in (**2**) due to limitations on computer memory. In both compounds the quantity minimized was $\Sigma w(F_o - F_c)^2$. The final difference map showed no features higher than 0.60 and 0.53 e Å^{-3} for (**1**) and (**2**), respectively.

Atomic scattering factors were taken from ref. 17 as were the real and imaginary parts of the anomalous dispersion. Most calculations were performed using the SHELX-76 system of programs[18] on the Cyber 76 computer of C.I.N.E.C.A. (Casalecchio, Bologna) with financial support from the University of Parma and the GOULD-SEL 32/77 computer of the Centro di Studio per a Strutturistica Diffrattometrica del C.N.R. (Parma). Other computer programs used in this work were PARST[19] and PLUTO.[20]

The final atomic fractional co-ordinates for the two compounds are given in Tables 2 and 3. Selected bond distances and angles are in Tables 4 and 5 for (**1**) and (**2**), respectively.

Table 1. Crystal data and summary of intensity data collection and structure refinement

Compound	(**1**)	(**2**)
Formula	$C_{39}H_{33}Cl_3N_2O_8P_2Sn$	$C_{50}H_{46}N_4O_{16}P_2Sn_2$
M	944.70	1 258.26
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a/Å	17.684(4)	12.247(10)
b/Å	38.773(9)	12.263(11)
c/Å	12.092(3)	11.914(11)
α/°	90	99.13(7)
β/°	90	110.37(7)
γ/°	90	118.36(7)
U/Å^3	8 291(3)	1 357(3)
Z	8	1
D_c/g cm^{-3}	1.514	1.539
F(000)	3 808	632
X-Radiation (λ/Å)	Mo-K_α (0.710 69)	Mo-K_α (0.710 69)
μ/cm^{-1}	9.39	10.48
2θ range/°	6—45	6—52
Standard reflection	One (006) every 90	One ($\bar{7}$33) every 75
Total data measured	5 829	4 748
Total unique data	5 223	4 748
Data with $I > 3\sigma(I)$	2 053	3 655
No. parameters varied	496	428
R	0.0767	0.0344
R'	0.0799	0.0362
k, g ($w = k/[\sigma^2(F_o) + gF_o^2]$)	1.5309, 0.001 574	1.0, 0.004 006

Table 2. Fractional atomic co-ordinates (× 10^4) for $SnPh_2(NO_3)_2$(cdppoet)·$CHCl_3$ (**1**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Sn	5 403(1)	1 382(0)	3 290(1)	C(16)	2 639(8)	2 774(3)	2 490(11)
P(1)	3 931(3)	1 771(1)	1 831(6)	C(17)	2 417(8)	2 562(3)	1 615(11)
P(2)	4 078(3)	838(1)	2 014(5)	C(18)	2 805(8)	2 255(3)	1 409(11)
O(1)	4 446(7)	1 710(3)	2 787(11)	C(19)	4 415(7)	1 834(4)	549(11)
O(2)	4 785(6)	1 042(3)	2 162(10)	C(20)	4 763(7)	2 151(4)	360(11)
O(3)	6 332(9)	946(4)	3 564(13)	C(21)	5 175(7)	2 205(4)	−610(11)
O(4)	6 916(11)	488(4)	3 091(21)	C(22)	5 239(7)	1 942(4)	−1 391(11)
O(5)	5 785(10)	484(5)	3 043(19)	C(23)	4 891(7)	1 624(4)	−1 202(11)
N(1)	6 350(10)	637(5)	3 232(18)	C(24)	4 479(7)	1 570(4)	−232(11)
O(6)	5 542(8)	1 920(4)	4 175(14)	C(25)	3 796(10)	576(4)	3 162(12)
O(7)	6 475(9)	1 583(5)	4 615(13)	C(26)	4 138(10)	257(4)	3 360(12)
O(8)	6 366(11)	2 078(5)	5 439(16)	C(27)	3 934(10)	65(4)	4 289(12)
N(2)	6 094(13)	1 866(6)	4 782(19)	C(28)	3 389(10)	191(4)	5 021(12)
C(1)	4 858(8)	1 221(4)	4 773(11)	C(29)	3 048(10)	509(4)	4 823(12)
C(2)	4 323(8)	1 434(4)	5 277(11)	C(30)	3 251(10)	702(4)	3 893(12)
C(3)	3 954(8)	1 325(4)	6 237(11)	C(31)	4 164(9)	566(4)	837(11)
C(4)	4 121(8)	1 004(4)	6 694(11)	C(32)	4 791(9)	615(4)	153(11)
C(5)	4 656(8)	791(4)	6 190(11)	C(33)	4 855(9)	431(4)	−835(11)
C(6)	5 024(8)	899(4)	5 230(11)	C(34)	4 293(9)	197(4)	−1 139(11)
C(7)	6 133(7)	1 542(4)	1 997(10)	C(35)	3 666(9)	148(4)	−456(11)
C(8)	6 350(7)	1 886(4)	1 882(10)	C(36)	3 602(9)	332(4)	532(11)
C(9)	6 850(7)	1 981(4)	1 042(10)	C(37)	3 225(11)	1 440(6)	1 595(20)
C(10)	7 133(7)	1 732(4)	318(10)	C(38)	3 250(12)	1 100(5)	1 706(19)
C(11)	6 916(7)	1 388(4)	433(10)	Cl(1)	7 757(7)	3 759(3)	1 240(11)
C(12)	6 416(7)	1 293(4)	1 272(10)	Cl(2)	6 520(7)	3 734(3)	2 544(12)
C(13)	3 414(8)	2 161(3)	2 078(11)	Cl(3)	6 982(9)	4 360(4)	1 884(13)
C(14)	3 635(8)	2 373(3)	2 953(11)	C(39)	6 899(19)	3 984(9)	1 347(28)
C(15)	3 248(8)	2 680(3)	3 159(11)				

Table 3. Fractional atomic co-ordinates (× 10^5 for Sn, × 10^4 for P, O, N, C, and H) for $[SnPh_2(NO_3)_2]_2$(tdppoet)·$2H_2O$ (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	44 726(3)	20 148(3)	21 447(3)	C(19)	503(4)	−1 989(4)	−1 719(4)
P	1 117(1)	−973(1)	−101(1)	C(20)	1 380(6)	−1 623(6)	−2 258(5)
O(1)	2 557(3)	299(3)	397(3)	C(21)	929(7)	−2 412(7)	−3 507(6)
O(2)	5 763(4)	2 324(4)	1 020(3)	C(22)	−451(8)	−3 574(7)	−4 230(6)
O(3)	6 884(4)	3 718(3)	3 004(4)	C(23)	−1 341(6)	−3 926(5)	−3 713(6)
O(4)	7 966(5)	3 998(6)	1 846(6)	C(24)	−880(6)	−3 170(5)	−2 449(4)
O(5)	5 028(4)	3 156(4)	4 229(4)	C(25)	−167(5)	−625(4)	−186(4)
O(6)	2 849(4)	1 474(4)	2 949(4)	H(2)	4 230(56)	−661(52)	816(52)
O(7)	3 483(6)	2 709(5)	4 878(4)	H(3)	5 014(40)	−1 740(39)	1 464(37)
O(8)	−942(8)	−934(8)	3 672(7)	H(4)	6 349(74)	−1 124(69)	3 738(66)
N(1)	6 908(5)	3 375(4)	1 958(5)	H(5)	6 864(62)	381(55)	5 397(58)
N(2)	3 768(6)	2 448(4)	4 051(4)	H(6)	5 836(59)	1 805(56)	4 760(55)
C(1)	5 096(5)	789(5)	2 750(5)	H(8)	4 603(65)	4 611(59)	3 033(59)
C(2)	4 897(5)	−235(5)	1 819(5)	H(9)	4 109(93)	6 032(87)	2 573(85)
C(3)	5 366(6)	−1 017(6)	2 187(7)	H(10)	3 506(85)	5 602(80)	322(76)
C(4)	6 010(8)	−790(7)	3 483(8)	H(11)	2 948(70)	3 799(64)	−1 103(64)
C(5)	6 222(7)	191(7)	4 416(7)	H(12)	3 300(54)	2 385(51)	−296(47)
C(6)	5 758(6)	1 027(6)	4 070(5)	H(14)	1 916(57)	−2 754(52)	−19(52)
C(7)	4 037(5)	3 330(4)	1 476(4)	H(15)	2 070(87)	−3 725(78)	1 500(78)
C(8)	4 375(7)	4 487(5)	2 327(6)	H(16)	788(68)	−4 119(65)	3 042(62)
C(9)	4 111(8)	5 349(6)	1 885(7)	H(17)	407(51)	−2 481(46)	3 113(45)
C(10)	3 507(7)	5 060(7)	570(8)	H(18)	396(57)	−1 311(53)	1 840(51)
C(11)	3 177(7)	3 935(7)	−282(7)	H(20)	2 195(60)	−716(58)	−1 784(54)
C(12)	3 418(6)	3 051(5)	155(5)	H(21)	1 478(94)	−1 788(84)	−4 141(84)
C(13)	1 033(5)	−1 965(4)	852(4)	H(22)	−664(88)	−4 610(82)	−5 135(78)
C(14)	1 444(6)	−2 833(5)	672(6)	H(23)	−2 289(87)	−4 881(83)	−3 764(79)
C(15)	1 412(7)	−3 577(6)	1 460(8)	H(24)	−1 428(59)	−3 359(54)	−1 879(52)
C(16)	989(7)	−3 476(6)	2 361(7)	H(25)	−1 202(65)	−1 509(61)	−433(56)
C(17)	597(8)	−2 623(7)	2 530(7)	H(81)	37(60)	104(56)	4 401(54)
C(18)	629(6)	−1 850(6)	1 783(6)	H(82)	−1 196(45)	−1 512(38)	3 780(40)

Table 4. Bond distances (Å) and angles (°) in $SnPh_2(NO_3)_2$(cdppoet)·$CHCl_3$ (**1**)

Sn–O(1)	2.203(12)	P(2)–O(2)	1.49(1)
Sn–O(2)	2.189(12)	P(2)–C(25)	1.79(2)
Sn–O(3)	2.380(16)	P(2)–C(31)	1.78(1)
Sn–O(6)	2.357(16)	P(2)–C(38)	1.82(2)
Sn–O(7)	2.602(16)	C(37)–C(38)	1.33(3)
Sn–C(1)	2.130(14)	N(1)–O(3)	1.26(2)
Sn–C(7)	2.120(13)	N(1)–O(4)	1.17(3)
Sn · · · O(5)*	3.555(20)	N(1)–O(5)	1.18(3)
P(1)–O(1)	1.49(1)	N(2)–O(6)	1.24(3)
P(1)–C(13)	1.79(1)	N(2)–O(7)	1.30(3)
P(1)–C(19)	1.79(1)	N(2)–O(8)	1.24(3)
P(1)–C(37)	1.81(2)		

O(1)–Sn–O(2)	78.0(4)	C(19)–P(1)–C(37)	106.8(9)
O(2)–Sn–O(3)	90.2(5)	O(2)–P(2)–C(25)	116.2(7)
O(3)–Sn–O(7)	67.9(5)	O(2)–P(2)–C(31)	109.8(7)
O(7)–Sn–O(6)	51.6(5)	O(2)–P(2)–C(38)	113.8(8)
O(6)–Sn–O(1)	72.2(5)	C(25)–P(2)–C(31)	107.9(7)
C(1)–Sn–C(7)	169.2(5)	C(25)–P(2)–C(38)	104.5(9)
Sn–O(1)–P(1)	140.8(8)	C(31)–P(2)–C(38)	103.6(8)
Sn–O(2)–P(2)	144.4(8)	O(3)–N(1)–O(4)	122(2)
Sn–O(3)–N(1)	130.3(13)	O(4)–N(1)–O(5)	117(2)
Sn–O(6)–N(2)	101.6(14)	O(3)–N(1)–O(5)	121(2)
O(1)–P(1)–C(13)	108.4(7)	O(6)–N(2)–O(7)	117(2)
O(1)–P(1)–C(19)	113.7(7)	O(7)–N(2)–O(8)	117(2)
O(1)–P(1)–C(37)	115.5(9)	O(6)–N(2)–O(8)	125(2)
C(13)–P(1)–C(19)	105.9(7)	Sn–O(7)–N(2)	88.3(13)
C(13)–P(1)–C(37)	105.8(8)		

*This non-bonded distance has been included for comparison, following the suggestion of a refereee.

Table 5. Bond distances (Å) and angles (°) in $[SnPh_2(NO_3)_2]_2$(tdppoet)·$2H_2O$ (**2**)

Sn–O(1)	2.188(5)	P–C(19)	1.781(6)
Sn–O(2)	2.346(6)	P–C(25)	1.790(7)
Sn–O(3)	2.343(5)	C(25)–C(25^i)	1.333(8)
Sn–O(5)	2.325(5)	N(1)–O(2)	1.270(5)
Sn–O(6)	2.364(5)	N(1)–O(3)	1.266(8)
Sn–C(1)	2.101(7)	N(1)–O(4)	1.222(9)
Sn–C(7)	2.109(6)	N(2)–O(5)	1.274(8)
P–O(1)	1.503(4)	N(2)–O(6)	1.270(5)
P–C(13)	1.784(6)	N(2)–O(7)	1.200(9)

O(1)–Sn–O(2)	89.8(2)	C(13)–P–C(19)	108.5(4)
O(2)–Sn–O(3)	54.6(2)	C(13)–P–C(25)	105.2(4)
O(3)–Sn–O(5)	79.5(2)	C(19)–P–C(25)	106.4(3)
O(5)–Sn–O(6)	54.7(2)	O(2)–N(1)–O(3)	116.0(7)
O(6)–Sn–O(1)	81.3(2)	O(3)–N(1)–O(4)	122.8(7)
C(1)–Sn–C(7)	173.3(4)	O(2)–N(1)–O(4)	121.2(6)
Sn–O(2)–N(1)	94.5(4)	O(5)–N(2)–O(6)	115.7(6)
Sn–O(3)–N(1)	94.7(4)	O(6)–N(2)–O(7)	123.0(7)
Sn–O(1)–P	144.5(3)	O(5)–N(2)–O(7)	121.2(6)
O(1)–P–C(13)	115.5(3)	Sn–O(5)–N(2)	95.6(4)
O(1)–P–C(19)	109.1(4)	Sn–O(6)–N(2)	93.9(5)
O(1)–P–C(25)	111.6(4)		

i = $\bar{x}, \bar{y}, \bar{z}$.

Results and Discussion

The molecular structures of the two title compounds are shown in Figures 1 and 2 with the atom-numbering scheme. In each case the co-ordination geometry about the tin atom is distorted pentagonal bipyramidal, with five equatorial oxygen atoms and two carbon atoms in the axial sites. Despite the resemblance in the co-ordination polyhedron, the two molecular structures show large and noteworthy differences, which are mainly associated with their different stoicheiometries, the metal: principal ligand ratio being 1:1 in (**1**) and 2:1 in (**2**) and with the different nature of the dppoet molecule. Summarizing therefore: (*i*) in (**1**) cdppoet acts as a chelating ligand forming a puckered

Table 6. Comparison of structural data for tin complexes containing dppoet or dppoe

Compound	Co-ordinating behaviour of the P ligand	Structure	Sn–O (Å)	O–P (Å)	Sn–O–P (°)	Ref.
$[SnPh_3(NO_3)]_2$(dppoe)	Bidentate bridging	Dinuclear	2.238(5)	1.492(4)	148.3(8)	*a*
$SnPh_3Cl$(cdppoet)	Monodentate	Monomeric	2.346(6)	1.496(7)	141.2(4)	*b*
$(SnPh_3Cl)_2$(dppoe)	Bidentate bridging	Dinuclear	2.357(3)	1.487(3)	161.8(3)	*c*
$SnBu^n{}_2Cl_2$(dppoe)	Bidentate bridging	Polymeric	2.386(7) 2.640(7)	1.491(7) 1.483(6)	163.9(4) 167.8(4)	*d*
$SnPr^n{}_2Cl_2$(cdppoet)	Bidentate chelating	Monomeric	2.24(1) 2.58(1)	1.48(1) 1.50(1)	155.7(6) 143.1(6)	1
$SnBu^n{}_2Cl_2$(cdppoet)	Bidentate chelating	Monomeric	2.29(1) 2.27(1)	1.48(1) 1.50(1)	150.1(7) 148.7(7)	1
$SnPh_2(NO_3)_2$(cdppoet)	Bidentate chelating	Monomeric	2.203(12) 2.189(12)	1.49(1) 1.49(1)	140.8(8) 144.4(8)	This work
$[SnPh_2(NO_3)_2]_2$(tdppoet)	Bidentate bridging	Dinuclear	2.188(5)	1.503(4)	144.5(3)	This work

[a] M. Nardelli, C. Pelizzi, and G. Pelizzi, *Inorg. Chim. Acta*, 1979, **33**, 181. [b] C. Pelizzi and G. Pelizzi, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 451. [c] C. Pelizzi and G. Pelizzi, *J. Organomet. Chem.*, 1980, **202**, 411. [d] P. G. Harrison, N. W. Sharpe, C. Pelizzi, G. Pelizzi, and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1983, 921.

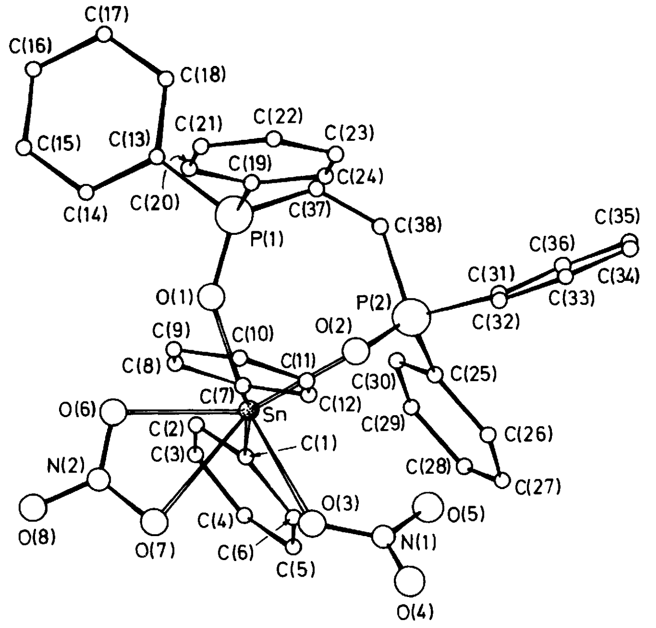

Figure 1. Perspective diagram of $SnPh_2(NO_3)_2(cdppoet){\cdot}CHCl_3$ (**1**)

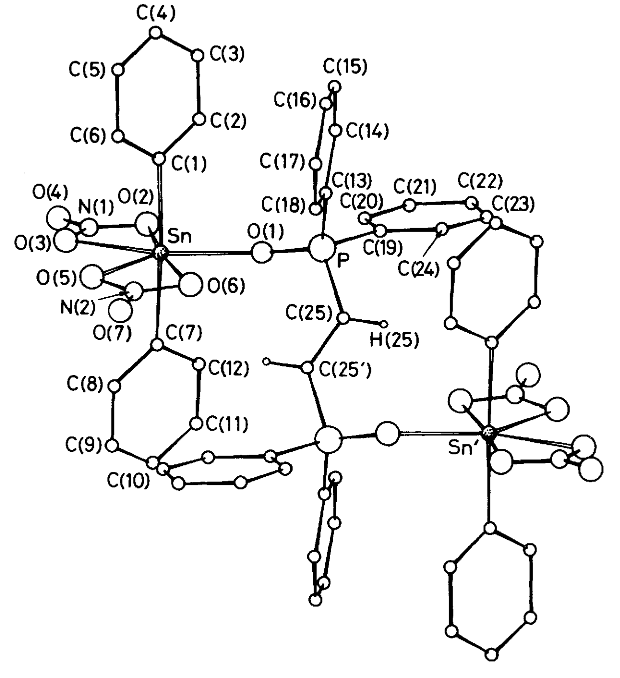

Figure 2. Perspective diagram of $[SnPh_2(NO_3)_2]_2(tdppoet){\cdot}2H_2O$ (**2**)

seven-membered chelate ring $(\overline{\text{O–P–C–C–P–O–Sn}})$, while in (**2**) tdppoet bridges two symmetry related tin atoms. The different bonding behaviour results in the presence of mononuclear units in (**1**) and dinuclear units in (**2**). (*ii*) In (**1**) the basal plane is made up of two atoms from cdppoet, one from a monodentate nitrate, and two from a bidentate nitrate, while in (**2**) the basal positions are occupied by one atom from tdppoet and four from the two bidentate nitrate groups. (*iii*) The different co-ordinating behaviour of the two P ligands is also reflected in the co-ordinating properties of the nitrate groups. In fact, in (**2**) the bridging conformation of the tdppoet molecule allows the accommodation in the pentagonal girdle of both nitrate groups in a symmetrical bidentate manner, while in (**1**) the *cis*-chelate attachment of cdppoet converts one of the two nitrate groups to a monodentate mode and forces the other to an asymmetrical bidentate behaviour. (*iv*) Lastly, as mentioned earlier, (**1**) crystallizes with one molecule of chloroform and (**2**) with two molecules of water.

The tin atom and the five O atoms forming the base of the bipyramid are nearly coplanar in each compound; they do not deviate from the best-weighted least-squares plane passing through them by more than 0.03 Å. The average equatorial angle at tin is 72.0° in each compound, exactly the same as that in an idealized pentagonal bipyramid. The molecular axis of the bipyramid is significantly far from linear in both compounds, the C–Sn–C angle being 169.2(5)° in (**1**) and 173.3(4)° in (**2**). The planes of the phenyl rings are nearly perpendicular to the equatorial plane in each of the two structures, the dihedral angles being 95.3(3) and 82.8(3)° in (**1**) and 96.6(2) and 86.3(2)° in (**2**).

The Sn–O(dppoet) bond lengths are practically equivalent in (**1**) and (**2**) and are close to normal single bonds. These distances are the shortest so far observed for the structurally determined dppoet and 1,2-bis(diphenylphosphoryl)ethane (dppoe) tin adducts (see Table 6). In each of the present compounds there are distortions from exact tetrahedral geometry around the P atom with the O–P–C angles being larger than the normal tetrahedral angle and the C–P–C angles slightly smaller.

There is very little difference between the four Sn–O(NO_3) bond distances in (**2**), which are nearly equal ranging from 2.325(5) to 2.364(5) Å, and two of the three Sn–O(NO_3) distances in (**1**), namely that involving the monodentate nitrate [2.380(16) Å] and the short one from the bidentate nitrate [2.357(16) Å]. The two nitrate groups are planar in both compounds. The tilt angles of the bidentate nitrates from the corresponding equatorial plane are 6.4(5)° in (**1**) and 4.7(2) and 5.1(2)° in (**2**), while the monodentate group makes an angle of 30.9(9)° with that plane. As usually observed in symmetrically bidentate nitrates, the two co-ordinated O atoms for each group in (**2**) exhibit O–N bond distances longer than that involving the terminal O atom. Related to this lengthening is the contraction of the O–N–O angle involving the two co-ordinated O atoms which is reduced to *ca.* 116°, whereas the other two are correspondingly increased to *ca.* 122°. The four Sn–O–N angles range from 93.9(5) to 95.6(4)°, in good agreement with the statement that the angle at the co-ordinated oxygens is less than 110° when the nitrate is bidentate and larger when monodentate. Due to the lower accuracy in the structure determination, less significance can be attached to the differences in the molecular parameters of the NO_3 groups in (**1**). However, with regard to the monodentate nitrate the lengthening of the O–N bond distance involving the co-ordinated O atom as compared to the other two and the value of the Sn–O–N angle [130.3(13)°] are both in agreement with this mode of co-ordination for NO_3^-.

In both structures the molecules are linked by van der Waals interactions, the most significant contacts being O(4) ··· C(38^i) ($\frac{1}{2} + x$, y, $\frac{1}{2} - z$) 3.36(3) and O(7) ··· C(39^i) (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$) 3.13(4) Å for (**1**); O(4) ··· C(16^i) ($1 + x$, $1 + y$, z) 3.26(1), O(3) ··· C(22^i) ($1 + x$, $1 + y$, $1 + z$) 3.36(1), and O(2) ··· C(3^i) ($1 - x$, $\bar{y}$, $\bar{z}$) 3.37(1) Å for (**2**). Unlike chloroform in (**1**), the water molecules in (**2**) do not participate in crystal packing with the complex, the only interaction of interest being O(8) ··· O(8^i) ($\bar{x}$, $\bar{y}$, $1 - z$) 2.86(1) Å.

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Received 16*th April* 1984; *Paper* 4/630