Co-ordinative Tin–Oxygen Interactions in Dinitratodiphenyl(triphenylphosphine oxide)tin(IV)

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The crystal and molecular structure of the title compound has been determined by the heavy-atom method and refined by least-squares techniques on 1 639 independent *X*-ray diffractometer data to *R* 0.059. Crystals are orthorhombic, space group *Pbca*, with $a = 29.76(4)$, $b = 9.80(1)$, $c = 19.95(3)$ Å, and $Z = 8$. The structure consists of discrete monomeric units containing seven-co-ordinate tin in a pentagonal-bipyramidal geometry, the two nitrate groups and the triphenylphosphine oxide molecule being equatorial, with the two phenyl rings at the apices. One of the two rings is disordered between two crystal orientations.

As part of a chemical and structural investigation of organotin compounds involving the nitrate group and P-, As-, or O-containing ligands, we recently investigated adducts of nitratotriphenyltin(IV) with oxygen-containing ligands such as PPh_3O, $AsPh_3O$, and C_5H_5NO.[1-4] Continuing this program, we have now considered adducts of dinitratodiphenyltin(IV) with the same ligands with the aim of determining what influence replacement of a phenyl ring by a nitrate group has on the stereochemistry and on the co-ordinative interactions of the tin atom. The present paper deals with the synthesis and the *X*-ray diffraction analysis of a new adduct between triphenylphosphine oxide and $SnPh_2(NO_3)_2$.

EXPERIMENTAL

Preparation.—Triphenylphosphine oxide dissolved in dry acetone was added in a nitrogen atmosphere to a solution containing an equimolar amount of dinitratodiphenyltin in the same solvent. Evaporation of the solvent *in vacuo* gave, after some days, colourless *crystals* (Found: C, 53.5; H, 3.9; N, 4.0; Sn, 17.2. Calc. for $C_{30}H_{25}N_2O_7PSn$: C, 53.4; H, 3.7; N, 4.2; Sn, 17.6%).

Crystal Data and Data Collection.—Preliminary cell dimensions and space-group information were deduced from rotation and Weissenberg photographs. The crystals showed an orthorhombic cell with systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) uniquely defining the space group *Pbca*. Accurate cell parameters were obtained by least-squares calculations based on 2θ values for 15 strong reflections measured on an automated single-crystal Siemens diffractometer. Crystal data are as follows: $M = 675.2$, $a = 29.76(4)$, $b = 9.80(1)$, $c = 19.95(3)$ Å, $U = 5\,820(4)$ Å^3, $D_m = 1.51$, $Z = 8$, $D_c = 1.54$ g cm^{-3}, $F(000) = 2\,720$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ (Mo-K_α) = 8.9 cm^{-1}.

All the 5 120 accessible independent reflections within the range θ 2.5—25.0° were examined by single-crystal diffractometry using Mo-K_α radiation and the ω—2θ scan technique; of these, only 1 639 having a net intensity greater than $2\sigma(I)$ † were used in the analysis. The intensity of a standard reflection monitored at regular intervals showed only statistical variations in spite of the progressive yellowing of the sample during the exposure to *X*-rays. The intensities were corrected for Lorentz and polarization effects, but no correction for absorption was applied. The absolute scale was determined first by correlating observed and calculated values, then refining the scale factor for the F_o as a variable parameter in the least-squares procedure.

Structure Analysis.—The structure was solved by the heavy-atom method. Co-ordinates for tin were obtained from a three-dimensional Patterson synthesis. Successive cycles of block-diagonal least-squares refinement and electron-density calculations revealed the positions of the phosphorus, oxygen, and nitrogen atoms as well as those of seven carbon atoms, six of which clearly defined a phenyl ring.

With tin and phosphorus refined anisotropically and all the other atoms isotropically, the conventional *R* index converged to 0.101. A difference-Fourier synthesis calculated at this stage revealed a disordered distribution involving the second phenyl ring present in the structure, and for which the carbon atom bound to tin had previously been located. From an accurate inspection of this region and from the arrangement of the atoms, it was inferred that this ring was distributed in two positions, related by rotation about the C–Sn bond. Three further cycles of refinement, assuming this disorder and fixing the occupancies at 0.50, improved *R* to 0.059.

The rather low proportion of significant reflections led to an observations : parameters ratio of 8.4 : 1, 6.0 : 1 being the usually accepted absolute lower limit for structure analysis. Anisotropic refinement of all the atoms was discouraged as the ratio would have had to decrease even further to 3.9 : 1. The quantity minimized was $\Sigma w(\Delta F)^2$, where the weight for each reflection was unity. Atomic-scattering

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† The estimated standard deviations of the intensities were calculated from the following formula taken from ref. 5: $\sigma_I = \sigma_{PK}^2 + C^2N_{PK}^2$, where $C = 0.005$.

[1] M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Organometallic Chem.*, 1976, **112**, 263, and refs. therein.

[2] M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Organometallic Chem.*, 1977, **125**, 161.

[3] C. Pelizzi, G. Pelizzi, and P. Tarasconi, *J. Organometallic Chem.*, 1977, **124**, 151.

[4] G. Pelizzi, *Inorg. Chim. Acta*, 1977, **24**, L31.

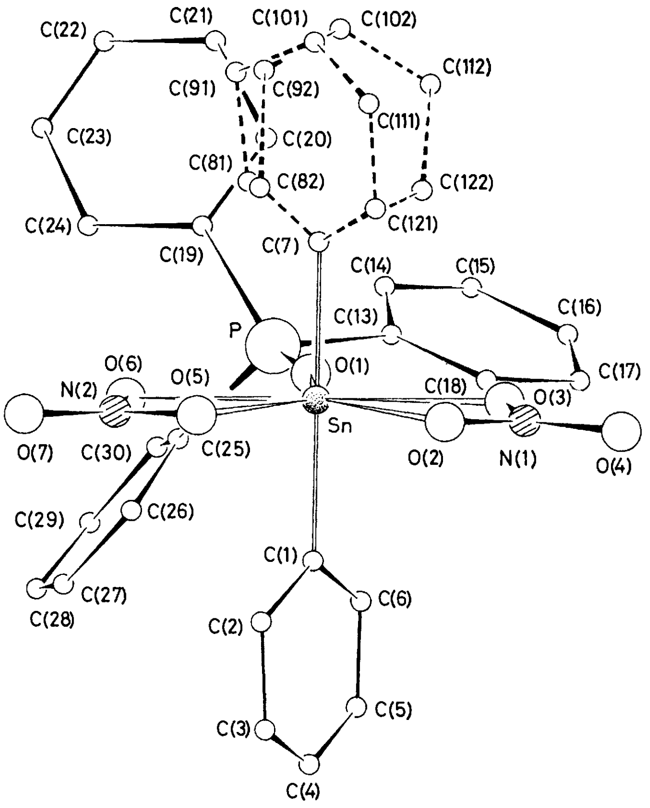
[5] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination, A Practical Guide,' McMillan, London, 1968, p. 456.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x	*y*	*z*
Sn	3 799(0)	7 572(1)	5 649(0)
P	3 728(1)	6 960(2)	3 876(1)
O(1)	3 718(2)	6 968(6)	4 621(3)
O(2)	3 842(3)	6 601(7)	6 710(3)
O(3)	3 739(2)	5 260(6)	5 889(3)
O(4)	3 753(2)	4 386(9)	6 853(5)
O(5)	3 901(3)	9 575(7)	6 297(3)
O(6)	3 810(2)	9 816(7)	5 223(3)
O(7)	3 900(2)	11 586(8)	5 878(4)
N(1)	3 777(3)	5 423(9)	6 515(4)
N(2)	3 867(3)	10 336(9)	5 794(4)
C(1)	3 092(2)	7 722(8)	5 773(4)
C(2)	2 906(4)	8 670(11)	6 223(5)
C(3)	2 421(5)	8 661(14)	6 270(6)
C(4)	2 156(4)	7 835(11)	5 900(5)
C(5)	2 322(4)	6 914(12)	5 473(6)
C(6)	2 821(4)	6 826(12)	5 423(6)
C(7)	4 490(3)	7 423(14)	5 564(5)
C(81)	4 721(8)	8 173(23)	5 145(10)
C(91)	5 233(8)	8 259(23)	5 122(12)
C(101)	5 429(7)	7 594(28)	5 630(17)
C(111)	5 219(10)	7 198(38)	6 159(15)
C(121)	4 740(9)	7 152(30)	6 178(12)
C(82)	4 774(7)	8 269(23)	5 569(14)
C(92)	5 276(10)	8 096(28)	5 403(14)
C(102)	5 388(8)	6 918(25)	5 163(12)
C(112)	5 097(7)	5 729(20)	5 139(12)
C(122)	4 632(7)	5 934(22)	5 270(11)
C(13)	3 671(3)	5 220(9)	3 590(4)
C(14)	3 767(4)	4 902(9)	2 925(4)
C(15)	3 678(3)	3 545(10)	2 702(5)
C(16)	3 521(3)	2 607(15)	3 174(6)
C(17)	3 432(4)	2 900(11)	3 830(6)
C(18)	3 514(3)	4 274(10)	4 059(5)
C(19)	4 232(3)	7 619(12)	3 540(4)
C(20)	4 619(4)	6 820(12)	3 548(6)
C(21)	5 047(4)	7 290(14)	3 346(5)
C(22)	5 062(4)	8 649(14)	3 128(7)
C(23)	4 687(4)	9 472(14)	3 076(7)
C(24)	4 250(4)	8 959(13)	3 301(6)
C(25)	3 265(3)	7 976(9)	3 552(5)
C(26)	3 050(4)	8 871(12)	3 991(6)
C(27)	2 705(4)	9 697(12)	3 743(6)
C(28)	2 562(4)	9 565(11)	3 076(5)
C(29)	2 756(4)	8 611(12)	2 677(6)
C(30)	3 120(3)	7 842(11)	2 892(5)

factors for all the atoms were taken from ref. 6. Final co-ordinates are given in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22136 (23 pp.).* All the calculations were made on the Cyber 76 computer of the



Clinographic projection of the structure

TABLE 2

Selected bond distances (Å) and angles (°)

(*a*) In the tin environment			
Sn–O(1)	2.148(6)	Sn–O(5)	2.370(7)
Sn–O(2)	2.324(7)	Sn–O(6)	2.358(7)
Sn–O(3)	2.323(7)	Sn–C(1)	2.124(7)
Sn–C(7)	2.07(2)		
O(1)–Sn–O(3)	85.4(2)	O(2)–Sn–C(7)	89.5(7)
O(3)–Sn–O(2)	54.4(2)	O(3)–Sn–C(1)	88.1(3)
O(2)–Sn–O(5)	80.5(2)	O(3)–Sn–C(7)	91.4(8)
O(5)–Sn–O(6)	54.7(2)	O(5)–Sn–C(1)	90.4(3)
O(6)–Sn–O(1)	85.1(2)	O(5)–Sn–C(7)	88.6(8)
O(1)–Sn–C(1)	91.1(3)	O(6)–Sn–C(1)	89.5(3)
O(1)–Sn–C(7)	90.8(6)	O(6)–Sn–C(7)	91.3(8)
O(2)–Sn–C(1)	88.7(3)	C(1)–Sn–C(7)	178.0(6)
(*b*) In the triphenylphosphine oxide molecule			
P–O(1)	1.487(7)	P–C(19)	1.765(9)
P–C(13)	1.806(9)	P–C(25)	1.819(9)
C–C (av.)	1.40(2)		
O(1)–P–C(13)	108.6(4)	C(13)–P–C(19)	107.8(5)
O(1)–P–C(19)	113.3(4)	C(13)–P–C(25)	109.5(4)
O(1)–P–C(25)	109.7(4)	C(19)–P–C(25)	108.0(4)
Sn–O(1)–P	162.5(4)	P–C–C (av.)	119.2(7)
C–C–C (av.)	120(1)		
(*c*) In the nitrate groups			
N(1)–O(2)	1.23(1)	N(2)–O(5)	1.25(1)
N(1)–O(3)	1.26(1)	N(2)–O(6)	1.26(1)
N(1)–O(4)	1.22(1)	N(2)–O(7)	1.24(1)
O(2)–N(1)–O(3)	116.3(8)	O(5)–N(2)–O(6)	119.6(8)
O(2)–N(1)–O(4)	127.9(9)	O(5)–N(2)–O(7)	118.2(8)
O(3)–N(1)–O(4)	115.8(9)	O(6)–N(2)–O(7)	122.2(8)
Sn–O(2)–N(1)	95.0(5)	Sn–O(5)–N(2)	92.6(5)
Sn–O(3)–N(1)	94.2(5)	Sn–O(6)–N(2)	93.1(5)
(*d*) In the phenyl rings			
C–C (av.)	1.40(3)		
Sn–C–C (av.)	120(1)	C–C–C (av.)	120(3)
(*e*) Some significant van der Waals contacts			
O(4) · · · C(15^{I})	3.34(1)	O(5) · · · C(14^{II})	3.31(1)
O(4) · · · C(16^{I})	3.35(1)	O(7) · · · C(4^{III})	3.37(1)
O(2) · · · C(24^{II})	3.44(1)	O(7) · · · O(4^{IV})	3.39(1)
O(2) · · · C(30^{II})	3.24(1)		

Roman numeral superscripts refer to the following equivalent positions:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $x, \frac{3}{2} - y, \frac{1}{2} + z$
III $\frac{1}{2} - x, \frac{1}{2} + y, z$
IV $x, y + 1, z$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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

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RESULTS AND DISCUSSION

The structure consists of discrete monomeric molecules each composed of a central tin atom bonded to two phenyl rings, two bidentate nitrate groups, and a triphenylphosphine oxide molecule (Figure). Table 2 lists selected bond distances and angles. The donor atoms of the ligands are arranged in a pentagonal-bipyramidal configuration around tin with five oxygen atoms spanning the equatorial positions and two phenyl carbon atoms at the apices of the bipyramid. The five oxygen atoms are coplanar with tin within the experimental errors.

It is interesting to compare the present compound with $SnPh_3(NO_3)(PPh_3O)$,[1] in which the co-ordination around tin is trigonal bipyramidal. The number of phenyl rings involved in co-ordination to metal is probably the most important factor in fixing the geometry of the co-ordination polyhedron: when three phenyl rings are present, they prefer an equatorial arrangement in a trigonal bipyramid, the apices of which are occupied by PPh_3O and NO_3, while the presence of two phenyl rings, with the apparent necessity of maintaining two short Sn–C bonds in apical positions, favours a pentagonal arrangement of the other ligands, allowing bidentate behaviour of the $[NO_3]^-$ ions. Unlike the Sn–C bond distances, the Sn–O bond distances experience the effects of this different situation even if in an opposite sense. The Sn–O(nitrate) bond distances are longer in $SnPh_2(NO_3)_2(PPh_3O)$, where the NO_3 groups are bidentate (2.32—2.37 Å), than in $SnPh_3(NO_3)(PPh_3O)$ where NO_3 is unidentate (2.22 Å); on the other hand, $Sn–O(PPh_3O)$ is much shorter in the present compound (2.15 Å) than in the triphenyl derivative (2.29 Å). As a consequence, in the present compound there is a slight lengthening of the O–P bond distance (1.49 as against 1.47 Å). None of the structural parameters of PPh_3O differs significantly from the corresponding values observed in its complexes.[1] Moreover, as usually observed, the M–O–P angle is not linear (162.5°), indicating bent co-ordination of PPh_3O. Two i.r. bands, at 1 152(sh) and 1 138s cm^{-1}, are observed in the region of P–O stretching frequencies, as previously found for other tin–phosphine oxide compounds.[7]

The packing is determined by normal van der Waals interactions. Selected non-bonded distances involving the oxygen atoms of the two nitrate groups and the carbon atoms of the aromatic ring are listed in Table 2.

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[7] V. G. Kumar Das and W. Kitching, *J. Organometallic Chem.*, 1968, **13**, 523.