

Structure of a Dinuclear Tin Adduct: μ -[Ethylenebis(diphenylphosphine oxide)]-bis[bromobis(*p*-chlorophenyl)(*p*-tolyl)tin(IV)]

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Abstract. $[\text{Sn}_2\text{Br}_2(\text{C}_7\text{H}_7)_2(\text{C}_6\text{H}_4\text{Cl})_4(\text{C}_{26}\text{H}_{24}\text{O}_2\text{P}_2)]$, $M_r = 1456.1$, $P2_1/c$, $a = 12.304(3)$, $b = 12.850(3)$, $c = 20.363(7)$ Å, $\beta = 109.08(3)^\circ$, $V = 3043(3)$ Å³, $Z = 2$, $D_m = 1.53$, $D_x = 1.59$ g cm⁻³, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), $\mu = 23.96$ cm⁻¹, $F(000) = 1444$, $T = 297$ K, $R_{\text{av}} = 0.033$ for 3392 observed reflections ($I > 4\sigma_I$). The coordination geometry about the Sn atom is trigonal bipyramidal and the dinuclear compound is centrosymmetric with respect to the mid-point of the CH₂—CH₂ bond of the diphosphine oxide ligand. The three substituted phenyl groups are indistinguishable owing to disorder of the two chloro and one methyl groups.

Introduction. Crystal structure studies on di- and triorganotin(IV) complexes of diphosphine oxides have revealed a strong preference for bidentate coordination (Nardelli, Pelizzi & Pelizzi, 1979; Pelizzi & Pelizzi, 1980a; Harrison, Sharpe, Pelizzi, Pellizi & Tarasconi, 1983a,b; Dondi, Nardelli, Pelizzi, Pelizzi & Predieri, 1985, 1986) over monodentate bonding (Harrison, Sharpe, Pelizzi, Pelizzi & Tarasconi, 1983b; Pelizzi & Pelizzi, 1980b) of the ligands; the bidentate interaction involves both bridging and chelation for the diorganotins, but to date only the bridging mode has been encountered with the triorganotins. In order to elucidate the effect of the nature and size of the organic groups on the molecular structure of the diphosphine oxide complexes and on the tin–oxygen interactions, we have undertaken a crystal structure study of the 2:1 complex of $[(p\text{-ClC}_6\text{H}_4)_2(p\text{-MeC}_6\text{H}_4)_2\text{SnBr}]$ with $\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\}_2$, the results of which are presented in this paper.

Experimental. Solutions of $[(p\text{-ClC}_6\text{H}_4)_2(p\text{-MeC}_6\text{H}_4)_2\text{SnBr}]$ (1.0 g, 1.95 mmol) and $\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\}_2$ (0.41 g, 0.98 mmol) in ethanol were mixed and the solution allowed to evaporate slowly at room temperature. This yielded crystals of the title compound suitable for X-ray analysis, m.p. 491–493 K. Elemental analysis: Found (calc.): C, 52.89 (52.79); H, 3.72 (3.75) for formula $(\text{SnC}_{32}\text{H}_{27}\text{POCl}_2\text{Br})_2$. Tin 119m Mössbauer data (mm s⁻¹, 80 K): isomer shift, 1.25, quadrupole splitting, 3.29, τ_1 0.91, τ_2 0.92. Density measured by flotation in KI/H₂O mixture; crystal used is a colorless rectangular block (0.21 × 0.34 × 0.35 mm) mounted on a Picker FACS-I diffractometer; 15 reflections in $30 < 2\theta < 35^\circ$ used to obtain lattice parameters; 3 standard reflections measured in every 100 reflections showed no significant crystal decay throughout data collection; Lorentz, polarization and empirical absorption corrections applied, max./min. values 99.91/89.66; 6826 measured reflections with $[(\sin\theta)/\lambda]_{\text{max}} = 0.5958$ Å⁻¹, 4993 unique reflections after averaging $[R_F(\text{av.}) = 0.056]$; $h, k, l = -14$ to 13, 0 to 15, 0 to 24, respectively; 3392 reflections were retained with $F_o^2 > 4\sigma(F_o^2)$; structure was solved by direct methods using MULTAN80. The three substituted phenyl groups are indistinguishable owing to disorder of the two Cl atoms and one methyl group; the Cl atoms were refined to total occupancy of 2.262. Full-matrix least-squares refinement of 346 parameters gives $R_F = 0.060$, $wR_F = 0.095$, $w = 4(F_o^2)/[\sigma(F_o^2)]^2$, where $[\sigma(F_o^2)]^2 = \{s^2(C + R^2B) + [p(F_o^2)]^2\}/(\text{Lp})^2$, s = scan rate, C = total integrated peak count, R = ratio scan time to background time, B = total background count, $p = 0.060$, Lp = Lorentz and polarization factors, and goodness of fit $S = 2.376$. The H atoms were calculated, not refined, and each was given an isotropic temperature factor of 1.2 times that of its

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Table 1. *Positional and thermal parameters and their e.s.d.'s*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B(Å ²)
Sn	0.29207 (6)	0.24224 (5)	0.01293 (3)	2.70 (1)
Br	0.4609 (1)	0.3023 (2)	-0.02625 (8)	6.88 (4)
Cl(1)	-0.0154 (7)	0.0926 (7)	-0.3038 (3)	6.9 (2)
Cl(2)	0.2448 (4)	0.6999 (3)	0.1543 (2)	5.9 (1)
Cl(3)	0.5502 (4)	-0.1405 (4)	0.2233 (2)	8.0 (1)
P	0.0831 (2)	0.1116 (2)	0.0837 (1)	2.32 (5)
O	0.1310 (5)	0.1884 (5)	0.0451 (3)	2.7 (1)
C(1)	0.0439 (8)	-0.0098 (8)	0.0367 (5)	2.8 (2)
C(11)	0.1910 (8)	0.1975 (8)	-0.0879 (5)	2.8 (2)
C(12)	0.2379 (9)	0.1334 (9)	-0.1290 (6)	3.9 (3)
C(13)	0.174 (1)	0.1027 (9)	-0.1939 (5)	3.9 (2)
C(14)	0.0621 (9)	0.134 (1)	-0.2245 (5)	3.8 (3)
C(15)	0.0153 (9)	0.198 (1)	-0.1868 (6)	4.2 (3)
C(16)	0.0757 (9)	0.2281 (9)	-0.1204 (5)	3.4 (2)
C(21)	0.2737 (8)	0.3901 (8)	0.0573 (5)	2.8 (2)
C(22)	0.3640 (8)	0.4603 (9)	0.0767 (5)	3.6 (2)
C(23)	0.3570 (9)	0.5533 (9)	0.1053 (6)	4.0 (3)
C(24)	0.256 (1)	0.5796 (9)	0.1166 (6)	4.0 (3)
C(31)	0.3835 (8)	0.1228 (8)	0.0769 (5)	3.2 (2)
C(32)	0.451 (1)	0.141 (1)	0.1472 (6)	4.2 (3)
C(33)	0.504 (1)	0.058 (1)	0.1915 (6)	5.1 (3)
C(34)	0.4903 (9)	-0.039 (1)	0.1675 (6)	4.2 (3)
C(35)	0.424 (1)	-0.063 (1)	0.0987 (6)	5.2 (3)
C(36)	0.374 (1)	0.0186 (9)	0.0561 (6)	4.5 (3)
C(41)	-0.0492 (8)	0.1629 (8)	0.0921 (5)	2.8 (2)
C(42)	-0.111 (1)	0.234 (1)	0.0441 (6)	4.3 (3)
C(43)	-0.217 (1)	0.265 (1)	0.0469 (6)	5.4 (3)
C(44)	-0.257 (1)	0.227 (1)	0.0972 (7)	5.0 (3)
C(45)	-0.196 (1)	0.161 (1)	0.1434 (6)	4.8 (3)
C(46)	-0.090 (1)	0.127 (1)	0.1417 (6)	4.3 (3)
C(51)	0.1745 (7)	0.0775 (8)	0.1680 (4)	2.4 (2)
C(52)	0.2110 (9)	0.1569 (9)	0.2175 (6)	3.8 (3)
C(53)	0.278 (1)	0.133 (1)	0.2864 (6)	4.6 (3)
C(54)	0.310 (1)	0.031 (1)	0.3045 (5)	4.2 (3)
C(55)	0.276 (1)	-0.045 (1)	0.2535 (6)	4.6 (3)
C(56)	0.2115 (9)	-0.0224 (8)	0.1871 (5)	3.5 (2)
C(26)	0.1738 (9)	0.4197 (9)	0.0680 (7)	4.9 (3)
C(25)	0.163 (1)	0.515 (1)	0.0992 (7)	5.0 (3)
C(17)	-0.006	0.101	-0.294	6.0*
C(27)	0.246	0.681	0.151	5.0*
C(37)	0.460	-0.137	0.196	6.8*

*Starred atoms were refined isotropically. See text for occupancy factors at Cl atoms and disorder in one methyl group.

Table 2. *Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Sn—Br	2.574 (1)	Sn—O	2.384 (4)
Sn—C(11)	2.103 (7)	Sn—C(21)	2.147 (7)
Sn—C(31)	2.089 (7)	Cl(1)—C(14)	1.676 (8)
Cl(2)—C(24)	1.750 (7)	Cl(3)—C(34)	1.731 (8)
P—O	1.499 (4)	P—C(1)	1.811 (6)
P—C(41)	1.815 (7)	P—C(51)	1.774 (6)
C(1)—C(1')	1.556 (5)	(C—C) _{phenyl}	1.37 (1)
Br—Sn—O	177.9 (1)	Br—Sn—C(11)	93.3 (2)
Br—Sn—C(21)	94.1 (2)	Br—Sn—C(31)	95.3 (2)
O—Sn—C(11)	84.9 (2)	O—Sn—C(21)	86.0 (2)
O—Sn—C(31)	86.5 (2)	C(11)—Sn—C(21)	123.0 (3)
C(11)—Sn—C(31)	115.7 (3)	C(21)—Sn—C(31)	119.8 (3)
O—P—C(1)	112.0 (3)	O—P—C(41)	109.2 (3)
O—P—C(51)	115.9 (3)	C(1)—P—C(41)	105.7 (3)
C(1)—P—C(51)	105.8 (3)	C(41)—P—C(51)	107.8 (3)
Sn—O—P	147.2 (3)	Sn—C(11)—C(12)	120.6 (5)
Sn—C(11)—C(16)	124.3 (5)	Cl(1)—C(14)—C(13)	120.8 (7)
Cl(1)—C(14)—C(15)	121.2 (7)	Sn—C(21)—C(22)	120.8 (5)
Sn—C(21)—C(26)	122.2 (5)	Cl(2)—C(24)—C(23)	119.4 (6)
Cl(2)—C(24)—C(25)	118.9 (6)	Sn—C(31)—C(32)	121.9 (5)
Sn—C(31)—C(36)	122.8 (6)	Cl(3)—C(34)—C(33)	119.3 (7)
Cl(3)—C(34)—C(35)	118.1 (7)	P—C(41)—C(42)	118.9 (5)
P—C(41)—C(46)	120.9 (6)	P—C(51)—C(52)	118.0 (5)
P—C(51)—C(56)	123.4 (5)	(C—C) _{phenyl}	120.0 (7)
P—C(1)—C(1')	110.4 (3)		

(i) Symmetry transformation $\bar{x}, \bar{y}, \bar{z}$.

respective parent C atom. Final difference Fourier map showed maximum density of $1.46 \text{ e } \text{Å}^{-3}$ near the Sn atom, minimum $-2.24 \text{ e } \text{Å}^{-3}$ near the Br atom; maximum least-squares shift/e.s.d. = 0.07 in the last cycle; atomic scattering factors were obtained from Cromer & Waber (1974); anomalous dispersion for non-H atoms included in F_c (Cromer, 1974); computer programs used: *TEXRAY* package (Molecular Structure Corporation, 1985) on a PDP11/73 minicomputer and *SDP* (Enraf-Nonius, 1979) on a PDP11/44 computer. Atomic coordinates and thermal parameters are listed in Table 1, and bond distances and angles in Table 2.*

Discussion. As shown in Fig. 1, the title compound has essentially trigonal bipyramidal coordination at tin, with the *ipso* C atoms of the *p*-tolyl and the two *p*-chlorophenyl rings in the equatorial plane and one O atom of $\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\}_2$ and the bromide ligand

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52987 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

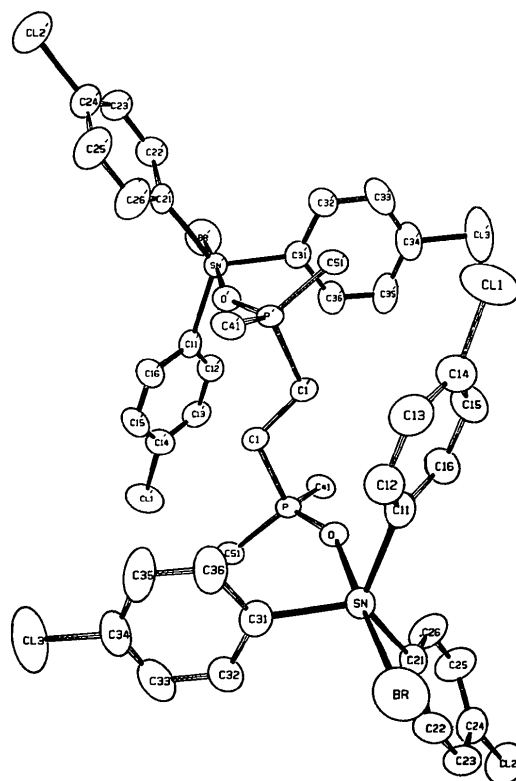


Fig. 1. A perspective view of the dinuclear molecule. The phenyl groups at P, except for the connecting C atoms, were omitted for clarity; Cl(1), Cl(2) and Cl(3) are averaged for two Cl and one methyl groups.

occupying the axial sites. The geometry is similar to that reported for the complexes of the ligand with triphenyltin chloride and nitrate (Nardelli *et al.*, 1979; Pelizzi & Pelizzi, 1980a). All three complexes are dinuclear with respect to the Sn atoms they contain: the {Ph₂P(O)CH₂}₂ ligand bridges the Sn atoms through the O atoms and the molecule has a crystallographic centre of symmetry lying in the middle of the CH₂—CH₂ bond. The Sn—O—P angle in the title compound [147.2 (3)°] is close to that in the nitrate analogue [148.3 (8)°] (Nardelli *et al.*, 1979), but significantly less than the value of 161.8 (2)° observed in the chloro complex (Pelizzi & Pelizzi, 1980a). The odd result for the latter complex has been ascribed to steric effects of the phenyl rings which although located in the equatorial plane are bent towards the O—P vector (Sn is 0.18 Å from the equatorial plane towards the Cl atom). In the title compound, the metal atom is only 0.001 Å from the equatorial plane towards the Br atom, and the longer Sn—O and P=O bonds together with larger O—P—CH₂ bond angle minimize the steric hindrance. The dihedral angles that the phenyl rings make with the equatorial plane are 40.6 (5)° for ring C(11)—C(16), 70.1 (4)° for ring C(21)—C(26) and 11.5 (9)° for ring C(31)—C(36), respectively. The coordination around P is not regularly tetrahedral with O=P—C angles significantly larger than the

C—P—C angles, in agreement with the increased electron density associated with the P=O double bond.

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Structure of Tris(diethyldithiophosphato-*S,S'*)- μ -(diethylthiophosphate-*O,S*)-(oxazole)- μ_3 -sulfido-tri- μ_2 -sulfido-cyclo-trimolybdenum(3 *Mo-Mo*)

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Abstract. [Mo₃(C₄H₁₀O₃PS)(C₄H₁₀O₂PS₂)₃(S)₄(C₃H₃NO)], *M_r* = 1209.694, triclinic, *P* $\bar{1}$, *a* = 11.931 (3), *b* = 13.203 (4), *c* = 15.014 (3) Å, α = 78.17 (2), β = 91.34 (2), γ = 109.63 (2)°, *V* = 2178 (2) Å³, *Z* = 2, *D_x* = 1.845 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 15.038 cm⁻¹, *F*(000) = 1212, *T* = 296 K. The final *R* = 0.048 for 6548 reflections. The crystal structure consists of discrete neutral molecules [Mo₃S₄{ μ -SOP(OEt)₂}{S₂P(OEt)₂}(C₃H₃ON)] which contain three Mo—Mo bonds. One of these is bridged

by an unsymmetrical bidentate ligand obtained by the oxidation of μ -{S₂P(OEt)₂}. The three Mo—Mo bond lengths are 2.7328 (7), 2.7605 (7) and 2.7687 (7) Å. A comparison of the structure with those of [Mo₃S₄{S₂P(OEt)₂}(C₃H₃ON)] and [Mo₃OS₃{S₂P(OEt)₂}(C₃H₃ON)] is given.

Introduction. As part of a systematic study of the reactivity of the molybdenum cluster [Mo₃S₄{S₂P(OEt)₂}(H₂O)] (1) (Huang *et al.*, 1987), we treated Fe(ClO₄)₃ with (1) in CH₃CN solution containing 0.3% oxazole as impurity. The reaction led unexpectedly to the title compound.

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