

## The Crystal and Molecular Structures of Hydroxotriphenyltin(IV) and Hydroxotriphenyllead(IV)

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Crystals of hydroxotriphenyltin(IV),  $\text{Ph}_3\text{SnOH}$ , are orthorhombic, space group  $P2_12_12_1$ , having  $a = 18.053$  (8),  $b = 10.382$  (5),  $c = 8.303$  (1) Å; hydroxotriphenyllead(IV),  $\text{Ph}_3\text{PbOH}$ , is isomorphous with  $a = 17.635$  (9),  $b = 10.247$  (6),  $c = 8.728$  (4) Å. The structures were solved by Patterson methods with diffractometer data and refined by full-matrix least squares to  $R = 0.0362$  for  $\text{Ph}_3\text{SnOH}$ , and  $R = 0.0429$  for  $\text{Ph}_3\text{PbOH}$ . The compounds are isostructural: the structures consist of zigzag chains parallel to  $\mathbf{c}$  in which planar  $\text{Ph}_3M$  ( $M = \text{Sn}, \text{Pb}$ ) fragments are joined by OH groups: in each structure the two  $M\text{—O}$  distances are unequal, being 2.197 (5) and 2.255 (5) Å in  $\text{Ph}_3\text{SnOH}$ , and 2.37 (2) and 2.44 (2) Å in  $\text{Ph}_3\text{PbOH}$ . Mean  $\text{Sn—C}$  and  $\text{Pb—C}$  distances are 2.137 (10) and 2.18 (2) Å respectively.

### Introduction

As part of a general structural study of organometallic oxo and hydroxo compounds (Glidewell & Liles, 1978*a,b*), we have determined the crystal and molecular structures of hydroxotriphenyltin(IV),  $\text{Ph}_3\text{SnOH}$ , and hydroxotriphenyllead(IV),  $\text{Ph}_3\text{PbOH}$ .

### Experimental

Hydroxotriphenyltin(IV) was prepared by treating a solution of chlorotriphenyltin(IV) in ethanol with aqueous ammonium hydroxide (Schmitz-Dumont, 1941). Recrystallization from acetonitrile yielded colourless crystals: a crystal of dimensions  $0.16 \times 0.15 \times 0.09$  mm was used for data collection.

Hydroxotriphenyllead(IV) was prepared by shaking a solution of chlorotriphenyllead(IV) in chloroform with an aqueous solution of sodium hydroxide (Bock & Deister, 1967). Recrystallization from chloroform yielded a colourless solid containing some hexagonal tabular crystals: a parallelogram-shaped tabular fragment of dimensions  $0.272 \times 0.240 \times 0.128$  mm, cleaved from a larger crystal, was used for data collection.

### Data collection

The following description refers to the collection of data for hydroxotriphenyltin(IV). Parameter values for the hydroxotriphenyllead(IV) data collection are given in parentheses where these differ.

Unit-cell parameters were determined by least-squares fits to the reflecting positions of 25 reflections each measured a total of 15 (12) times during data collection with a Philips PW1100 automatic four-circle diffractometer with graphite-monochromatized  $\text{Mo } K\alpha$

radiation. The intensities of 1767 (1055) reflections with  $3 \leq \theta \leq 35^\circ$  ( $3 \leq \theta \leq 25^\circ$ ) were measured by the  $\omega/2\theta$  scan technique, with a scan width of  $[0.90 + 0.1 \tan \theta]^\circ$  ( $[1.3 + 0.1 \tan \theta]^\circ$ ) in  $\omega$ , a scan speed of  $0.05^\circ \text{ s}^{-1}$  in  $\omega$  and a maximum of three scans per reflection [a second or third scan was made if the total count obtained in the first or first two scans, respectively, was less than 500 (4000) – the high minimum count for the hydroxotriphenyllead(IV) data collection was used because of the high background levels obtained with this crystal]. Backgrounds were measured at both ends of the scan range for a time equal to  $(\text{scan time}/2) (I_{\text{BK}}/I_{\text{INT}})^{1/2}$  or a minimum of 10 s, where  $I_{\text{BK}}$  = the background intensity scaled from an initial 10 s measurement;  $I_{\text{INT}}$  = integrated peak intensity. Three standard reflections were measured every 6 (4) h during data collection. For hydroxotriphenyltin(IV) these showed only random deviations from their mean intensities, but for hydroxotriphenyllead(IV) the standard reflections showed an approximately linear reduction in intensity *versus* the number of reflections measured, amounting to approximately a 10% reduction in intensity over the whole data collection. Lorentz and polarization corrections were applied to both data sets. The data for hydroxotriphenyllead(IV) were, in addition, corrected for the linear reduction in intensity *versus* the number of reflections measured and also corrected for absorption. The crystal was found to be centrosymmetric in shape and bounded by the following faces: (100), ( $\bar{1}00$ ), (010), ( $0\bar{1}0$ ), ( $10\bar{1}$ ) and ( $\bar{1}01$ ). No absorption corrections were applied to the data for hydroxotriphenyltin(IV).

### Crystal data

Hydroxotriphenyltin(IV),  $\text{C}_{18}\text{H}_{16}\text{OSn}$ ,  $M_r = 367.01$ . Orthorhombic, space group  $P2_12_12_1$  ( $D_2^4$ , No. 19).  $a =$

18.053 (8),  $b = 10.382$  (5),  $c = 8.303$  (1) Å;  $U = 1556.2$  Å<sup>3</sup>;  $Z = 4$ ;  $D_m = 1.556$ ,  $D_c = 1.566$  g cm<sup>-3</sup>;  $F(000) = 708$ . Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 14.9$  cm<sup>-1</sup>.

Hydroxotriphenyllead(IV),  $\text{C}_{18}\text{H}_{16}\text{OPb}$ ,  $M_r = 455.51$ . Orthorhombic, space group  $P2_12_12_1$  ( $D_2^4$ , No. 19);  $a = 17.635$  (9),  $b = 10.247$  (6),  $c = 8.728$  (4) Å;  $U = 1577.2$  Å<sup>3</sup>;  $Z = 4$ ;  $D_m = 1.910$ ,  $D_c = 1.918$  g cm<sup>-3</sup>;  $F(000) = 836$ . Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 102.7$  cm<sup>-1</sup>.

The two structures are isomorphous; all atoms occupy fourfold general positions; the asymmetric unit consists of one formula unit.

### Structure solution and refinement

These were carried out with the *SHELX* program system (Sheldrick, 1976).

#### Hydroxotriphenyltin(IV)

The position of the Sn atom was found from a Patterson synthesis, and a difference synthesis was calculated. As the Sn position was close to the  $2_1$  axis parallel to  $\mathbf{c}$ , the difference synthesis displayed pseudo twofold symmetry about that axis causing the appearance of double images of the phenyl rings. Two further difference syntheses were calculated each with one or the other of the two partial sets of phenyl C positions obtained from the first difference map. One synthesis gave a confused map showing partial images of the second set of phenyl-ring positions; the second synthesis, however, gave a clearer map from which the positions of the O and all C atoms not found on the original difference map, were obtained. As this map showed no images of the alternative phenyl-ring positions, the atom positions used to calculate, and those obtained from, this map were assumed correct. Three cycles of full-matrix least-squares refinement with 1738 reflections having  $F_o \geq 6\sigma(F_o)$ , with isotropic temperature parameters for all non-hydrogen atoms (81 variables) and a weighting scheme  $w = |\sigma(F)|^{-2}$  yielded a conventional  $R$  index  $[\Sigma \Delta / \Sigma F_o]$ , ( $\Delta = |F_o - F_c|$ ) of 0.0999, a weighted index  $R_w$   $[\Sigma w^{1/2} \Delta / \Sigma w^{1/2} F_o]$  of 0.1126 and a generalized index  $R_G$   $[(\Sigma w \Delta^2 / \Sigma w F_o^2)^{1/2}]$  of 0.1304. The introduction of anisotropic temperature parameters for Sn in three cycles of refinement (86 variables) reduced  $R_G$  to 0.0573. Three further cycles of refinement with anisotropic temperature parameters for O (91 variables) yielded an  $R_G$  of 0.0559. At this stage, the contributions of the phenyl H atoms were included in the refinement with their positions constrained along the bisectors of the external C—C—C angles and  $r(\text{C—H})$  fixed at 0.96 Å. Three cycles of refinement with a common isotropic temperature parameter for the H atoms (92 variables) yielded final indices of  $R =$

0.0362,  $R_w = 0.0425$  and  $R_G = 0.0518$ . The decreases in  $R_G$  at each stage of the refinement were all significant at the 0.5% level (Hamilton, 1965). In the final refinement 92 parameters were varied, comprising 60 positional coordinates, 12 anisotropic temperature factor components, 18 individual isotropic temperature factors, one common hydrogen temperature factor and one overall scale factor: all parameter shifts were less than  $0.13\sigma$ : a difference synthesis revealed no significant residual electron density.

Table 1. *Atom coordinates and isotropic temperature parameters*

#### (a) Hydroxotriphenyltin(IV)

The common isotropic temperature factor for the hydrogen atoms refined to 0.12 (1) Å<sup>2</sup>.

	$x$	$y$	$z$	$U$ (Å <sup>2</sup> )
Sn	0.24688 (2)	-0.00129 (7)	0.18862 (5)	—
O	0.2156 (4)	0.0489 (6)	0.4365 (6)	—
C(11)	0.2604 (4)	0.1980 (8)	0.135 (1)	0.039 (2)
C(12)	0.3213 (5)	0.2373 (9)	0.046 (1)	0.050 (2)
C(13)	0.3288 (7)	0.369 (1)	0.005 (1)	0.072 (3)
C(14)	0.2799 (8)	0.453 (1)	0.055 (1)	0.083 (4)
C(15)	0.2181 (8)	0.423 (1)	0.138 (2)	0.085 (4)
C(16)	0.2081 (6)	0.291 (1)	0.180 (1)	0.068 (3)
C(21)	0.3412 (4)	-0.1095 (7)	0.262 (1)	0.035 (2)
C(22)	0.3370 (5)	-0.241 (1)	0.267 (1)	0.056 (2)
C(23)	0.4007 (6)	-0.314 (1)	0.315 (1)	0.079 (3)
C(24)	0.4641 (7)	-0.250 (1)	0.352 (1)	0.081 (4)
C(25)	0.4691 (6)	-0.120 (1)	0.343 (1)	0.072 (3)
C(26)	0.4072 (5)	-0.052 (1)	0.295 (1)	0.055 (2)
C(31)	0.1446 (4)	-0.1033 (8)	0.150 (1)	0.043 (2)
C(32)	0.0797 (6)	-0.060 (1)	0.220 (1)	0.073 (3)
C(33)	0.0116 (7)	-0.125 (1)	0.190 (2)	0.090 (4)
C(34)	0.0138 (8)	-0.231 (1)	0.092 (2)	0.092 (4)
C(35)	0.0770 (7)	-0.278 (1)	0.026 (2)	0.088 (4)
C(36)	0.1436 (5)	-0.213 (1)	0.052 (1)	0.054 (2)

#### (b) Hydroxotriphenyllead(IV)

The common isotropic temperature factor for the hydrogen atoms refined to 0.07 (2) Å<sup>2</sup>.

	$x$	$y$	$z$	$U$ (Å <sup>2</sup> )
Pb	0.24624 (3)	-0.0006 (1)	0.17012 (7)	—
O	0.207 (1)	0.066 (2)	0.418 (2)	—
C(11)	0.264 (1)	0.202 (2)	0.113 (3)	0.051 (6)
C(12)	0.325 (1)	0.236 (3)	0.014 (3)	0.059 (7)
C(13)	0.338 (2)	0.363 (3)	-0.029 (4)	0.09 (1)
C(14)	0.294 (2)	0.454 (3)	0.022 (4)	0.10 (1)
C(15)	0.235 (2)	0.433 (3)	0.120 (4)	0.09 (1)
C(16)	0.221 (2)	0.303 (3)	0.155 (4)	0.084 (8)
C(21)	0.344 (1)	-0.111 (2)	0.256 (2)	0.034 (4)
C(22)	0.339 (1)	-0.246 (2)	0.264 (3)	0.065 (7)
C(23)	0.401 (2)	-0.322 (3)	0.313 (4)	0.10 (1)
C(24)	0.463 (2)	-0.255 (3)	0.358 (4)	0.09 (1)
C(25)	0.469 (2)	-0.125 (3)	0.349 (4)	0.081 (9)
C(26)	0.408 (1)	-0.052 (3)	0.294 (3)	0.068 (7)
C(31)	0.139 (1)	-0.103 (2)	0.131 (3)	0.051 (6)
C(32)	0.073 (1)	-0.070 (3)	0.198 (3)	0.076 (8)
C(33)	0.004 (2)	-0.133 (3)	0.176 (3)	0.086 (9)
C(34)	0.008 (2)	-0.243 (3)	0.077 (4)	0.10 (1)
C(35)	0.072 (2)	-0.276 (4)	0.015 (4)	0.09 (1)
C(36)	0.140 (2)	-0.210 (3)	0.039 (3)	0.074 (9)

*Hydroxotriphenyllead(IV)*

The refined positional parameters for hydroxotriphenyltin(IV) were used as starting values in this refinement. Three cycles of full-matrix least-squares refinement with 963 reflections having  $F_o \geq 6\sigma(F_o)$ , with isotropic temperature parameters for all non-hydrogen atoms (81 variables) and a weighting scheme  $w = [\sigma(F)]^{-2}$  yielded  $R = 0.0637$ ,  $R_w = 0.0669$  and  $R_G = 0.0750$ . Following the same course of refinement as for

Table 2. *Geometry at the metal atoms*

Superscripts refer to the following symmetry positions:

(i)  $\frac{1}{2} - x, -y, -\frac{1}{2} + z$ ; (ii)  $\frac{1}{2} - x, -y, \frac{1}{2} + z$ .

Hydroxotriphenyltin(IV)		Hydroxotriphenyllead(IV)	
(a) Bond distances (Å)			
Sn—O	2.197 (5)	Pb—O	2.37 (2)
Sn—O <sup>i</sup>	2.255 (5)	Pb—O <sup>i</sup>	2.44 (2)
Sn—C(11)	2.131 (8)	Pb—C(11)	2.16 (2)
Sn—C(21)	2.128 (8)	Pb—C(21)	2.19 (2)
Sn—C(31)	2.153 (8)	Pb—C(31)	2.19 (2)
(b) Bond angles (°)			
Sn—O—Sn <sup>ii</sup>	137.8 (3)	Pb—O—Pb <sup>ii</sup>	130.0 (8)
O—Sn—O <sup>i</sup>	177.6 (3)	O—Pb—O <sup>i</sup>	176.3 (8)
O—Sn—C(11)	89.8 (3)	O—Pb—C(11)	88.6 (8)
O—Sn—C(21)	93.6 (3)	O—Pb—C(21)	93.7 (7)
O—Sn—C(31)	92.1 (3)	O—Pb—C(31)	91.6 (8)
O <sup>i</sup> —Sn—C(11)	89.1 (3)	O <sup>i</sup> —Pb—C(11)	90.5 (8)
O <sup>i</sup> —Sn—C(21)	84.8 (3)	O <sup>i</sup> —Pb—C(21)	84.3 (7)
O <sup>i</sup> —Sn—C(31)	90.6 (3)	O <sup>i</sup> —Pb—C(31)	91.2 (8)
C(11)—Sn—C(21)	118.7 (3)	C(11)—Pb—C(21)	117.7 (7)
C(11)—Sn—C(31)	123.0 (3)	C(11)—Pb—C(31)	123.2 (8)
C(21)—Sn—C(31)	118.0 (3)	C(21)—Pb—C(31)	118.9 (8)

Table 3. *Geometry within phenyl rings*

Hydroxotriphenyltin(IV)				Hydroxotriphenyllead(IV)		
Ring, <i>i</i>	1	2	3	1	2	3
(a) Bond distances (Å) C( <i>ij</i> )—C( <i>ik</i> )						
<i>j—k</i>						
1—2	1.39 (1)	1.37 (1)	1.38 (1)	1.42 (3)	1.39 (3)	1.34 (3)
2—3	1.42 (1)	1.43 (1)	1.42 (2)	1.38 (3)	1.41 (3)	1.39 (3)
3—4	1.31 (2)	1.36 (2)	1.36 (2)	1.29 (4)	1.34 (3)	1.43 (4)
4—5	1.35 (2)	1.35 (2)	1.36 (2)	1.37 (4)	1.34 (4)	1.30 (4)
5—6	1.42 (2)	1.38 (1)	1.40 (2)	1.39 (4)	1.39 (3)	1.39 (4)
6—1	1.40 (1)	1.36 (1)	1.40 (1)	1.33 (3)	1.33 (3)	1.36 (3)
(b) Bond angles (°) C( <i>ij</i> )—C( <i>ik</i> )—C( <i>il</i> ) or C( <i>ij</i> )—C( <i>ik</i> )—M (M = Sn, Pb)						
<i>j—k—l (M)</i>						
6—1—2	118.4 (8)	118.6 (8)	119.7 (9)	114 (3)	119 (2)	118 (2)
1—2—3	119 (1)	119 (1)	120 (1)	122 (3)	121 (3)	126 (3)
2—3—4	120 (1)	119 (1)	117 (1)	119 (3)	116 (3)	114 (3)
3—4—5	124 (1)	122 (1)	124 (1)	124 (4)	124 (3)	120 (4)
4—5—6	117 (1)	118 (1)	119 (1)	115 (3)	119 (3)	124 (4)
5—6—1	121 (1)	123 (1)	120 (1)	125 (3)	120 (3)	118 (3)
2—1—M	119.2 (6)	119.4 (7)	120.4 (7)	119 (2)	119 (2)	124 (2)
6—1—M	122.3 (7)	121.9 (6)	119.9 (6)	127 (2)	121 (2)	118 (2)

hydroxotriphenyltin(IV), the introduction of anisotropic temperature parameters for Pb, and subsequently also for O reduced  $R_G$  to 0.0536 and 0.0524 respectively. Three further cycles of refinement with the phenyl H atoms in constrained positions as before and with a common temperature parameter for the H atoms yielded final indices of  $R = 0.0429$ ,  $R_w = 0.0446$  and  $R_G = 0.0515$ . At each stage of the refinement the reductions in  $R_G$  were all significant at the 0.5% level. In the final refinement 92 parameters were varied as for hydroxotriphenyltin(IV); all parameter shifts were less than  $0.0430\sigma$ : a difference synthesis revealed no significant residual electron density.

For both structures complex neutral-atom scattering factors (Cromer & Mann, 1968; Doyle & Turner, 1968) were employed for all atoms.

Analysis of variance showed no significant dependence on the parity group,  $\sin \theta$ , or the magnitude of  $F_o$  for either structure.\* For both structures there are relatively few reflections in the parity groups having  $l$  odd. This is because of the proximity of the metal atoms to the  $2_1$  axis parallel to  $c$  which results in a 'pseudo-halving' of the  $c$ -axis dimension. Hence layers of reflections with  $l$  odd are weak and contain relatively few observed reflections.

The results from the final least-squares cycles for both structures are given in Table 1 (positional and isotropic temperature parameters):\* these, together with the full-covariance matrix, were used to calculate the bond lengths and angles, which are given with e.s.d.'s in Tables 2 and 3. No correction for thermal motion has been applied to the bond lengths. Least-

\* Lists of structure factors, anisotropic thermal parameters and the table of analyses of variance have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32982 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

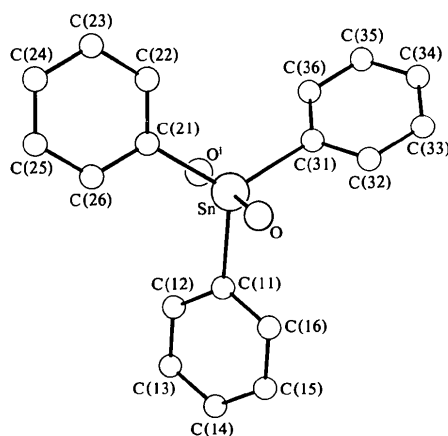


Fig. 1. An O—SnPh<sub>3</sub>—O fragment of the Ph<sub>3</sub>SnOH oligomer, showing the atom-numbering scheme.

squares planes were calculated for the  $C_3M$  'cores' ( $M = \text{Sn, Pb}$ ) and for each of the phenyl rings: these and the deviations of the atoms from them, and the dihedral angles between the 'core' plane and the phenyl-ring

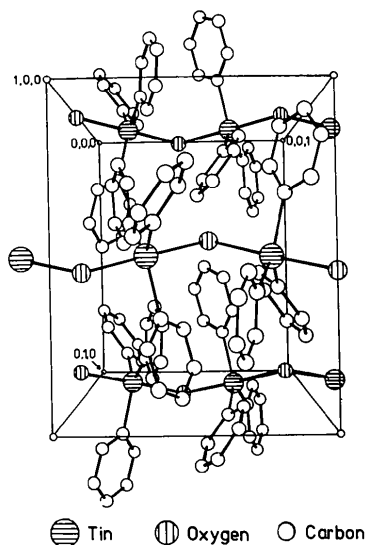


Fig. 2. Perspective view of the unit cell of  $\text{Ph}_3\text{SnOH}$ .

planes are given in Table 4. Some non-bonded distances are listed in Table 5. Fig. 1 shows an  $\text{O}-\text{Ph}_3\text{Sn}-\text{O}$  fragment of the hydroxotriphenyltin(IV) oligomer, together with the atom-numbering scheme employed for both structures. Fig. 2 shows a perspective view of the unit cell for hydroxotriphenyltin(IV). The equivalent views for hydroxotriphenyllead(IV) are similar and are not shown. In the tables, H atoms are given the numbers of the C atoms to which they are bonded.

### Discussion

The structures of both  $\text{Ph}_3\text{SnOH}$  and  $\text{Ph}_3\text{PbOH}$  consist of zigzag chains parallel to  $c$  in which  $\text{Ph}_3M$  groups ( $M = \text{Sn, Pb}$ ) planar at  $M$  are joined by OH groups, giving trigonal bipyramidal geometry at  $M$ ; similar chains are observed in many  $R_3\text{SnX}$  species, for example  $\text{Me}_3\text{SnF}$  (Clark, O'Brien & Trotter, 1964),  $\text{Me}_3\text{SnOH}$  (Kasai, Yasuda & Okawara, 1965),  $\text{Me}_3\text{SnCN}$  (Schlemper & Britton, 1966),  $\text{Me}_3\text{SnOMe}$  (Domingos & Sheldrick, 1974) and  $\text{Me}_3\text{SnO}_2\text{SMe}$  (Sheldrick & Taylor, 1977): however, no oligomeric  $R_3\text{PbX}$  compound appears to have been characterized previously, although  $\text{Ph}_2\text{PbCl}_2$  forms chains in which octahedral Pb atoms are linked by Cl bridges (Mammi, Busetti & Del Pra, 1967).

Table 4. *Least-squares planes*

Planes are defined in terms of orthogonal Cartesian coordinates by the equation:  $AX + BY + CZ + 1 = 0$ .  $X$ ,  $Y$  and  $Z$  are related to the cell (ångström) coordinates by:  $X = x + y \cos \gamma + z \cos \beta$ ,  $Y = y \sin \gamma - z \sin \beta \cos \alpha^*$ ,  $Z = z \sin \beta \sin \alpha^*$ .

Plane	$i$	$A$	$B$	$C$	Atom distances from the plane ( $\text{\AA} \times 10^3$ )						
Hydroxotriphenyltin(IV)											
		(i) Plane through			Sn	C(11)	C(21)	C(31)			
I		0.6298	-0.5321	-2.516	-48	20	6	32			
		(ii) Planes through phenyl rings†			C( $i$ 1)	C( $i$ 2)	C( $i$ 3)	C( $i$ 4)	C( $i$ 5)	C( $i$ 6)	Sn
II	1	-0.1399	-0.0408	-0.2337	-10	-1	16	-20	7	8	40
III	2	1.027	-0.2398	-3.520	-13	13	4	-14	-3	13	19
IV	3	-0.0795	0.2811	-0.3919	7	-11	2	11	-14	5	57
Hydroxotriphenyllead(IV)											
		(i) Plane through			Pb	C(11)	C(21)	C(31)			
I		1.436	-1.291	-4.996	-32	15	1	28			
		(ii) Planes through phenyl rings†			C( $i$ 1)	C( $i$ 2)	C( $i$ 3)	C( $i$ 4)	C( $i$ 5)	C( $i$ 6)	Pb
II	1	-0.1575	-0.0299	-0.2116	-13	-2	4	7	-22	27	8
III	2	-1.278	0.2590	3.225	49	34	-24	-7	-22	-16	68
IV	3	-0.0995	0.2909	-0.3868	14	-13	5	2	-1	-7	-16
Dihedral angles between planes ( $^\circ$ )											
Planes					I and II	I and III	I and IV				
Hydroxotriphenyltin(IV) angle					44.3	8.2	52.6				
Hydroxotriphenyllead(IV) angle					52.3	11.1	57.7				

† Planes through phenyl rings are calculated from carbon positions only.

In  $\text{Ph}_3\text{SnOH}$  the two Sn—O distances, 2.197 (5) and 2.255 (5) Å, are closely similar to those reported for  $\text{Me}_3\text{SnOMe}$ , 2.20 (3) and 2.26 (3) Å (Domingos & Sheldrick, 1974), but significantly longer than the 1.94 (1) Å reported for monomeric  $(\text{Me}_3\text{Sn})_2\text{O}$  (Vilkov & Tarasenko, 1969). Despite the planarity found for the  $\text{C}_3\text{Sn}$  fragment [ $\Sigma \angle \text{C—Sn—C} = 359.7(5)^\circ$ ], the Sn—O distances are not equal: this residual non-equivalence may perhaps be ascribed to the presence of the hydroxyl proton, whose position, however, could not be identified. The Sn—O—Sn angle is  $137.8(3)^\circ$ , and the Sn...Sn distance along the chain is 4.15 Å.

The three independent Sn—C distances are almost identical with a mean of 2.137 (10) Å, and are very close to those reported in  $\text{Ph}_4\text{Sn}$ , 2.144 (14) Å (Chieh & Trotter, 1970),  $\text{Ph}_3\text{SnCl}$ , 2.12 (2) Å (Bokii, Zakharova & Struchkov, 1970), and  $\text{Ph}_3\text{SnSC}_6\text{H}_4\text{CMe}_3$ , 2.128 (6) Å (Clarke, Cradwick & Wardell, 1973).

Within the phenyl rings, the C(*i*3)—C(*i*4) and C(*i*4)—C(*i*5) (*i* = 1, 2, 3) distances are apparently shorter than the remainder: this phenomenon has been

ascribed to thermal motion (Goldstein, Seff & Trueblood, 1968). The internal angles at C(*i*1) have a mean value of  $118.9(10)^\circ$ , which may be compared with the values in  $\text{Ph}_4\text{Sn}$ ,  $121(2)^\circ$  (Chieh & Trotter, 1970), and  $\text{Ph}_3\text{SnSC}_6\text{H}_4\text{CMe}_3$ ,  $119.1(12)^\circ$  (Clarke, Cradwick & Wardell, 1973); however, in  $(\text{C}_6\text{F}_5)_4\text{Sn}$  this angle is smaller,  $116.1(8)^\circ$  (Karipides, Forman, Thomas & Reed, 1974). Approximately linear relations between the magnitude of the internal angle at C(1) in a compound  $\text{Ph}_x\text{M}$  and the electronegativity of *M* have been demonstrated (Domenicano, Vaciego & Coulson, 1975) when *M* is an element of the second (Al—Cl) or third (Zn—Br) rows of the periodic table. The plots have similar slopes, but the intercept (*i.e.* the internal angle at zero electronegativity of *M*) is greater for the third-row elements: the data for the  $\text{Ph}_x\text{Sn}$  compounds cited above, and for  $(\text{Ph}_2\text{Sb})_2\text{O}$  (Bordner, Andrews & Long, 1974) suggest that this trend may continue into the deeper rows of the periodic table.

The phenyl rings in  $\text{Ph}_3\text{SnOH}$  are planar within experimental error, but the dihedral angles between the rings and the  $\text{SnC}_3$  plane show no discernible pattern: they are presumably determined primarily by inter- and intramolecular H...H interactions, although there appear to be few, if any, H...H distances which are unusually short (Table 5).

$\text{Ph}_3\text{PbOH}$  is isostructural with the Sn analogue. Again the two metal—oxygen distances are unequal: they are however much longer than the Pb—O distance reported in  $\text{Ph}_3\text{PbOSiPh}_3$ , 2.01 (3) Å (Harrison, King, Richards & Phillips, 1976). The mean Pb—C distance found here is 2.18 (2) Å: in  $\text{Ph}_4\text{Pb}$  and  $\text{Ph}_2\text{PbCl}_2$  the corresponding distances are 2.19 (3) Å (Busetti, Mammi, Signor & Del Pra, 1967) and 2.12 (2) Å (Mammi, Busetti & Del Pra, 1967). For  $\text{Ph}_3\text{PbOSiPh}_3$  (Harrison, King, Richards & Phillips, 1976) the Pb—C distances are reported as 2.06 (4), 2.12 (4) and 2.27 (4) Å, with a mean of 2.15 (10) Å, the large range possibly being ascribed to the partial disorder of the Si and Pb atoms. The dimensions of the phenyl rings in  $\text{Ph}_3\text{PbOH}$  could not be determined with high precision: equivalent C—C distances span ranges up to a maximum of 0.14 Å, and equivalent C—C—C angles span ranges up to  $9^\circ$ .

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Table 5. Selected non-bonded distances (Å)

Superscripts refer to the following symmetry positions: (i)  $\frac{1}{2} - x, -y, -\frac{1}{2} + z$ ; (ii)  $\frac{1}{2} - x, -y, \frac{1}{2} + z$ ; (iii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iv)  $x, 1 + y, z$ ; (v)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (vi)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .  $M \cdots X < 3.5$  Å,  $X \cdots X \leq 3.0$  Å (*M* = Sn, Pb; *X* = O, C, H) excluding intra-phenyl-ring distances.

Hydroxotriphenyltin(IV)		Hydroxotriphenyllead(IV)	
(a) Intramolecular distances			
Sn...Sn <sup>ii</sup>	4.15	Pb...Pb <sup>ii</sup>	4.37
O...O <sup>i</sup>	4.45	O...O <sup>i</sup>	4.82
Sn...C(12)	3.06	Pb...C(12)	3.11
Sn...C(16)	3.09	Pb...C(16)	3.14
Sn...C(22)	3.04	Pb...C(22)	3.11
Sn...C(26)	3.07	Pb...C(26)	3.10
Sn...C(32)	3.09	Pb...C(32)	3.14
Sn...C(36)	3.10	Pb...C(36)	3.07
Sn...H(12)	3.09	Pb...H(12)	3.11
Sn...H(16)	3.17	Pb...H(16)	3.19
Sn...H(22)	3.07	Pb...H(22)	3.12
Sn...H(26)	3.10	Pb...H(26)	3.13
Sn...H(32)	3.12	Pb...H(32)	3.16
Sn...H(36)	3.12	Pb...H(36)	3.08
O...C(21) <sup>ii</sup>	2.96		
O...H(16)	2.93	O...H(16)	2.90
O...H(32)	2.76	O...H(32)	2.77
O...H(12) <sup>ii</sup>	2.75	O...H(12) <sup>ii</sup>	2.70
O...H(36) <sup>ii</sup>	2.70	O...H(36) <sup>ii</sup>	2.67
C(32)—H(12) <sup>ii</sup>	2.92	C(32)...H(12) <sup>ii</sup>	2.90
C(36)...H(26) <sup>i</sup>	3.00	C(36)...H(26) <sup>i</sup>	2.97
(b) Intermolecular distances			
H(12)...H(24) <sup>iii</sup>	2.62	C(13)...H(25) <sup>ii</sup>	2.93
H(13)...H(25) <sup>iii</sup>	2.60	H(13)...H(25) <sup>iii</sup>	2.66
H(14)...H(22) <sup>iv</sup>	2.53		
H(24)...H(26) <sup>v</sup>	2.66		
H(32)...H(34) <sup>vi</sup>	2.64		

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## The Crystal and Molecular Structure of *o*-Phthalatocopper(II) Dihydrate

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Crystals of the title compound are monoclinic, space group  $P2_1$ , with  $Z = 2$  in a unit cell of dimensions:  $a = 10.263$  (7),  $b = 6.540$  (9),  $c = 6.795$  (8) Å,  $\beta = 94.8$  (1)°. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to  $R = 0.031$  for 1279 observed reflections. The Cu coordination polyhedron is a square pyramid whose base is formed by two water molecules [Cu–O<sub>w</sub> = 1.980 (5), 2.007 (5) Å] and by two O atoms [Cu–O = 1.950 (5), 1.965 (5) Å] from two *o*-phthalate groups. The *o*-phthalate anion bridges adjacent Cu atoms through two O atoms of both carboxylate groups in linear polymeric chains running along [001]. The apex of the pyramid is occupied by an O atom from an *o*-phthalate group of an adjacent chain [Cu–O = 2.154 (5) Å] so the anion behaves as a tridentate ligand bridging the chains along [010]. A sixth Cu–O = 2.861 (6) Å contact involving an O atom of a phthalate group makes coordination severely distorted octahedral. O<sub>w</sub>–H···O hydrogen bonding completes the linkage of the polymeric chains in layers parallel to (100).

### Introduction

Investigations on the behaviour of the *o*-phthalate (pht) anion as a ligand have been carried out in our laboratory [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>2</sub>pht (Cingi, Guastini, Musatti & Nardelli, 1970); Li<sub>2</sub>Cu<sup>II</sup>pht<sub>2</sub>·4H<sub>2</sub>O, Rb<sub>2</sub>Cu<sup>II</sup>pht<sub>2</sub>·2H<sub>2</sub>O (Cingi, Lanfredi, Tiripicchio & Camellini, 1977); Na<sub>2</sub>Cu<sup>II</sup>pht<sub>2</sub>·2H<sub>2</sub>O, K<sub>2</sub>Cu<sup>II</sup>pht<sub>2</sub>·2H<sub>2</sub>O (Cingi, Lanfredi, Tiripicchio & Camellini, 1978)] and others are in progress. In the above compounds the

ligand always acts as a bridge when coordinating to Cu atoms giving rise to different kinds of polymeric chains. The compound described in the present paper was obtained from the mother liquid of the preparation of the Sr derivative, while the monohydrate form was prepared from a neutral aqueous solution containing only Cu<sup>II</sup> and *o*-phthalate ions. The structure of this last compound was determined and the results agreed well with those found independently by Prout, Carruthers & Rossotti (1971).