catena-Poly[[triphenyltin(IV)]-μ-hydroxo-κ²O:O] at 120 K

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The structure of the title compound, $[Sn(C_6H_5)_3(OH)]_n$, has been re-investigated at 120 (2) K. The hydroxyl H atom was readily located and the threefold coordination about the O atom is planar. There are no hydrogen bonds involving the hydroxyl group, either as donor or as acceptor.

Comment

The structure of the title compound, (I), was reported many years ago (Glidewell & Liles, 1978), but the data set employed (293 K, 1767 reflections uncorrected for absorption) did not permit either the anisotropic refinement of the C atoms or the location of the H atoms, although H atoms bonded to C atoms were included in the final refinement in calculated positions. Crucially, however, it was not possible at the time to identify the H atom of the hydroxyl group, and hence it was not possible either to assess whether the coordination about the O atom was planar or pyramidal, or to analyse whether there are significant hydrogen bonds within the structure.


(I)
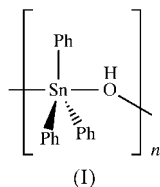
By use of a larger low-temperature data set collected using a CCD diffractometer (120 K, 3376 reflections corrected for absorption, of which 3120 are labelled observed), it has been possible not only to refine all non-H atoms anisotropically, but to locate all of the H atoms from difference maps, including that bonded to the O atom. The cell dimensions and space group, and the general structural features, with planar Ph_3Sn groups and OH units alternating in chains generated by a 2_1

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axis in $P2_12_12_1$, show there is no change of phase between 293 and 120 K.

In the original structure analysis, the overall precision was rather modest [$\sigma(Sn-O)$ 0.005 Å, $\sigma(Sn-C)$ 0.008 Å and $\sigma(C-C)$ 0.01–0.02 Å]. The present refinement has reduced these σ values to 0.0017, 0.003 and 0.004–0.005 Å, respectively. Although the bond angles in the SnC_3O_2 core unit indicate almost ideal trigonal–bipyramidal geometry, with axial O and equatorial C atoms, as expected, the two independent Sn—O distances nonetheless differ by ca 0.07 Å (Table 1). Similarly, although the three independent Sn—C distances are almost identical, the conformation of the Ph_3Sn fragment is very far from the idealized C_3 local symmetry, as demonstrated by the O—Sn—C—C torsion angles. The unique Sn—O—Sn angle is very large, and the hydroxyl H atom is located very close to the plane defined by the Sn—O—Sn^i fragment [symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$], with the sum of the bond angles at O being almost 360°.

It is striking that the hydroxyl group in (I) does not participate in any hydrogen bonds, either with the O atom as hydrogen-bond donor to another O atom or to an aryl group, or with the O atom as acceptor from either O or C atoms. The disposition of the zigzag chains is, in fact, such that the only C or O atoms within 3.50 Å of O1 at (x, y, z) are those within the same chain, and all are ipso- or ortho-C atoms in the two Ph_3Sn units bonded to O1. Table 2 lists the shortest intra-chain non-bonding contacts involving the O atom as a potential hydrogen-bond donor and as an acceptor, and the contacts with both the shortest H···O and the shortest C···O distances are shown. These data, particularly the D—H···A angles, demonstrate that, even within a given chain, the hydroxyl group acts neither as a donor nor as an acceptor of hydrogen bonds.
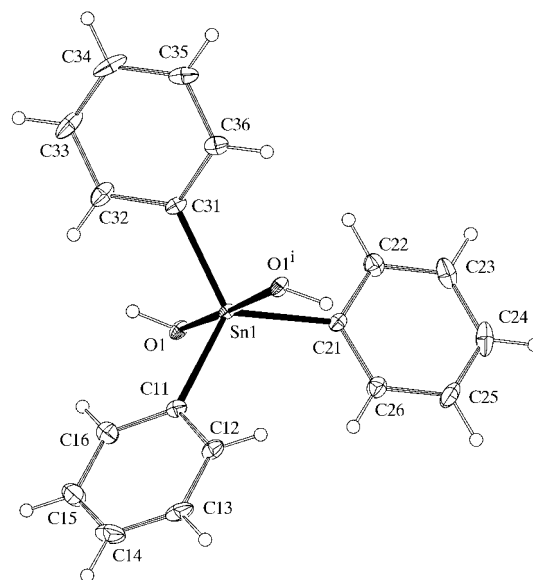
Figure 1
A view of the molecular structure of (I), showing the coordination around Sn and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$].

metal-organic compounds

It is interesting to note that, in all compounds of type Ph$_3M$OH, for M = C, Si, Ge, Sn or Pb, the location of the hydroxyl H atom has hitherto proved troublesome. When M = C, the molecules form tetrahedral tetramers, but the hydroxyl H atoms could not be located from ambient-temperature X-ray data (Ferguson, Gallagher, Glidewell *et al.*, 1992). These H atoms are, in fact, mobile over a number of sites at ambient temperature (Aliev *et al.*, 1998), and neutron diffraction at 100 K was required to locate these H-atom sites unambiguously (Serrano-González *et al.*, 1999). The compounds Ph$_3$SiOH (Puff *et al.*, 1991) and Ph$_3$GeOH (Ferguson, Gallagher, Murphy *et al.*, 1992) are isostructural, both forming cyclic tetramers with S_4 ($\bar{4}$) symmetry. In neither structure was the site of the hydroxyl H atom identified. Ph$_3$PbOH is isostructural with Ph$_3$SnOH (Glidewell & Liles, 1978) and, again, the hydroxyl H atom could not be located. The structure analyses for M = Si, Ge and Pb were all based on ambient-temperature data. The success of the present analysis for M = Sn indicates that re-investigation of the analogous Ph$_3M$OH structures using low-temperature CCD data should readily reveal the hydroxyl H atom when M = Si or Ge, although when M = Pb this task may be more taxing.
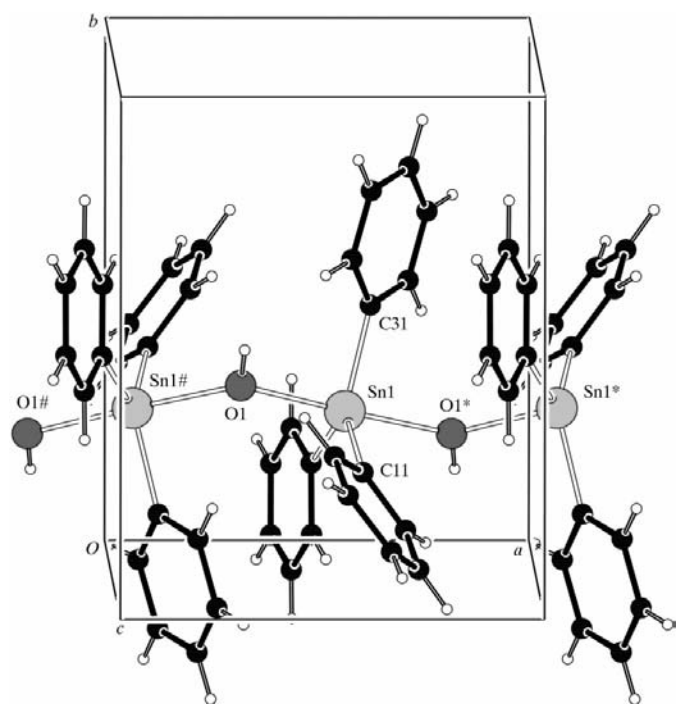
Figure 2
Part of the crystal structure of (I), showing the formation of a zigzag chain generated by the 2$_1$ axis along $(x, \frac{1}{4}, 0)$. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$ and $(x - \frac{1}{2}, \frac{1}{2} - y, -z)$, respectively.

Experimental

A sample of compound (I) was prepared by hydrolysis of triphenyltin(IV) azide in an ethanol–water mixture (97:3 v/v). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

[Sn(C$_6$H$_5$)$_3$(OH)]	Mo $K\alpha$ radiation
$M_r = 367.00$	Cell parameters from 3376
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.2573$ (2) Å	$\theta = 3.0$–27.5°
$b = 10.2229$ (2) Å	$\mu = 1.70$ mm^{-1}
$c = 17.6996$ (5) Å	$T = 120$ (2) K
$V = 1494.09$ (6) Å^3	Block, colourless
$Z = 4$	0.40 × 0.22 × 0.20 mm
$D_x = 1.632$ Mg m^{-3}	

Data collection

Nonius KappaCCD area-detector diffractometer	1968 independent reflections (plus 1408 Friedel-related reflections)
φ scans, and ω scans with κ offsets	3120 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.062$
	$\theta_{\text{max}} = 27.5°$
	$h = -9 \rightarrow 10$
$T_{\text{min}} = 0.554$, $T_{\text{max}} = 0.712$	$k = -13 \rightarrow 11$
10 366 measured reflections	$l = -18 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 1.0158P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.68$ e Å^{-3}
3376 reflections	$\Delta\rho_{\text{min}} = -1.06$ e Å^{-3}
181 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = -0.01 (3)

Table 1
Selected geometric parameters (Å, °).

Sn1—C11	2.133 (3)	Sn1—O1	2.1797 (17)
Sn1—C21	2.125 (3)	Sn1—O1$^{\text{i}}$	2.2500 (17)
Sn1—C31	2.126 (3)		
O1—Sn1—O1$^{\text{i}}$	176.842 (12)	C11—Sn1—O1	92.79 (10)
Sn1—O1—Sn1$^{\text{ii}}$	137.66 (10)	C21—Sn1—O1	93.29 (9)
Sn1—O1—H1	106	C31—Sn1—O1	90.36 (8)
Sn1$^{\text{ii}}$—O1—H1	115	C11—Sn1—O1$^{\text{i}}$	90.36 (9)
C11—Sn1—C21	116.84 (11)	C21—Sn1—O1$^{\text{i}}$	85.43 (9)
C21—Sn1—C31	120.24 (11)	C31—Sn1—O1$^{\text{i}}$	87.81 (8)
C31—Sn1—C11	122.51 (11)		
O1—Sn1—C11—C12	147.0 (2)	O1$^{\text{i}}$—Sn1—C11—C12	−33.1 (2)
O1—Sn1—C21—C22	78.8 (2)	O1$^{\text{i}}$—Sn1—C21—C22	−98.3 (2)
O1—Sn1—C31—C32	45.2 (2)	O1$^{\text{i}}$—Sn1—C31—C32	−137.3 (2)

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

Table 2
Short intra-chain non-bonded contacts (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$C32	0.90	2.75	3.289 (4)	120
C12—H12$\cdots$O1$^{\text{i}}$	0.95	2.69	3.178 (4)	113
C36—H36$\cdots$O1$^{\text{i}}$	0.95	2.71	3.134 (4)	108

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$.

Compound (I) crystallized in the orthorhombic system; space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps. H atoms bonded to C atoms were treated as riding, with C—H = 0.95 Å. The H atom attached to the hydroxyl O atom was allowed to ride at the position found in the difference map.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1536). Services for accessing these data are described at the back of the journal.

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