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Triphenyltin(IV) Isobutoxide Isobutanol Solvate

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Abstract

The structure consists of monomeric Ph$_3$SnO^{i}Bu.-^{i}BuOH molecules, which are linked together by hydrogen bridges to give one-dimensional chains. Each molecule has a nearly trigonal-bipyramidal structure with a distorted trigonal-planar triphenyltin moiety and an isobutoxide group and an isobutanol molecule in axial positions. The corresponding tin–oxygen distances are 2.065 (5) and 2.550 (6) Å, respectively.

Comment

In the literature only the crystal structure of the trimethyltin methoxide is described (Domingos & Sheldrick, 1974). This structure consists of trigonal-planar Me$_3$Sn moieties bridged by μ_2-OMe groups which form one-dimensional zigzag chains. The title compound represents the first example of a structurally characterized solvated triorganotin alkoxide and therefore may be a good model for the structure of triorganotin alkoxides (R_3SnOR') in solutions of Lewis acid donor solvents. This crystal structure contains one-dimensional chains of single molecules (Ph$_3$SnO^{i}Bu.^{i}BuOH) which are connected with two neighbouring molecules by hydrogen bridges. Each bridge leads from the H atom [$\angle$(O—H···O) = 177.3 (2)°] of the hydroxyl group of a coordinated isobutanol molecule to the O atom [d(O···O) =

2.687 (7) Å] of the isobutoxide group of the second molecule. Between the individual chains only van der Waals forces exist.

The trigonal-bipyramidal structure of the molecules is somewhat distorted since the alkoxide ligand is much more strongly bonded than the solvent molecule as can be seen from the tin–oxygen bond distance, which is very long [2.550 (6) Å] in the case of the isobutanol molecule and short [2.065 (5) Å] for the isobutoxide group. However, the latter bond length is still longer than the Sn—O distance in molecules with tetrahedrally coordinated tin where a value of around 2 Å has been observed (Puff & Reuter, 1989). Nevertheless, a trace of an unsolvated tetrahedral Ph$_3$SnO^{i}Bu molecule is still present in the complex since all of the corresponding O—Sn—C angles are greater [93.3 (2)–99.7 (2)°] than in an undistorted trigonal bipyramid [90°] and, moreover, the Sn atom is displaced by 0.208 (3) Å from the plane of the three coordinating phenyl-C atoms.
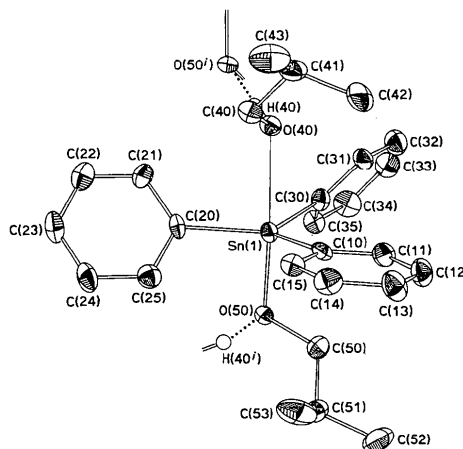

Fig. 1. Perspective view of the Ph$_3$SnO^{i}Bu.^{i}BuOH molecule showing the atomic numbering scheme used and the hydrogen-bonding system. Non-H atoms are drawn as thermal ellipsoids representing the 50% probability level. H atoms are drawn as spheres of arbitrary size.

Experimental

Crystal data

[Sn(C$_6$H$_5$)$_3$][C$_4$H$_9$O].C$_4$H$_{10}$O	Mo Kα radiation
M_r = 497.22	λ = 0.71069 Å
Monoclinic	Cell parameters from 25
Cc	reflections
a = 14.863 (3) Å	θ = 8.13–13.54°
b = 15.751 (3) Å	μ = 1.102 mm^{-1}
c = 11.940 (3) Å	T = 213 (1) K
β = 122.51 (1)°	Transparent
V = 2357.9 (4) Å^3	0.34 × 0.27 × 0.23 mm
Z = 4	Colourless
D_x = 1.401 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$h = 0 \rightarrow 17$
ω–2θ scans	$k = 0 \rightarrow 18$
Absorption correction: none	$l = -14 \rightarrow 11$
2152 measured reflections	2 (intensity) standard reflections
2152 independent reflections	frequency: 60 min
2101 observed reflections $[F_o \geq 4\sigma(F_o)]$	intensity variation: none
$\theta_{max} = 24.96°$	2 (orientation) standard reflections
	monitored every 200 reflections

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} \leq 0.001$
Final $R = 0.023$	$\Delta\rho_{max} \leq 0.778$ e Å^{-3}
$wR = 0.062$	$\Delta\rho_{min} = -1.276$ e Å^{-3}
$S = 1.029$	Atomic scattering factors
2152 reflections	from *International Tables*
261 parameters	*for X-ray Crystallography*
Only H-atom U's refined, common U with restraints	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn(1)	0.5	0.08087 (12)	0.5	0.0209 (1)
C(10)	0.5009 (6)	0.2157 (2)	0.4828 (6)	0.023 (2)
C(11)	0.5938 (5)	0.2616 (4)	0.5415 (6)	0.028 (3)
C(12)	0.5945 (5)	0.3501 (4)	0.5378 (6)	0.034 (3)
C(13)	0.4984 (6)	0.3930 (3)	0.4703 (6)	0.038 (3)
C(14)	0.4032 (5)	0.3482 (4)	0.4080 (6)	0.035 (3)
C(15)	0.4032 (5)	0.2610 (4)	0.4144 (6)	0.026 (3)
C(20)	0.3459 (5)	0.0253 (4)	0.3923 (6)	0.023 (3)
C(21)	0.3093 (5)	−0.0314 (4)	0.2855 (6)	0.030 (3)
C(22)	0.2074 (6)	−0.0632 (4)	0.2215 (8)	0.039 (3)
C(23)	0.1391 (5)	−0.0387 (4)	0.2610 (6)	0.039 (3)
C(24)	0.1718 (5)	0.0182 (5)	0.3629 (6)	0.038 (3)
C(25)	0.2755 (5)	0.0497 (5)	0.4281 (6)	0.030 (3)
C(30)	0.6546 (5)	0.0267 (4)	0.5733 (5)	0.025 (3)
C(31)	0.7179 (5)	0.0531 (5)	0.5258 (6)	0.027 (3)
C(32)	0.8187 (5)	0.0194 (4)	0.5788 (6)	0.039 (3)
C(33)	0.8594 (5)	−0.0401 (4)	0.6794 (7)	0.039 (3)
C(34)	0.7987 (6)	−0.0661 (4)	0.7286 (8)	0.038 (4)
C(35)	0.6948 (5)	−0.0325 (4)	0.6745 (6)	0.031 (3)
O(40)	0.4894 (4)	0.0740 (3)	0.2799 (5)	0.023 (2)
C(40)	0.4046 (5)	0.1217 (4)	0.1719 (5)	0.026 (3)
C(41)	0.4419 (6)	0.1785 (4)	0.1030 (6)	0.031 (3)
C(42)	0.5329 (8)	0.2360 (6)	0.1981 (8)	0.049 (5)
C(43)	0.3468 (8)	0.2280 (5)	−0.0053 (8)	0.056 (6)
O(50)	0.5109 (5)	0.0717 (3)	0.6795 (5)	0.023 (2)
C(50)	0.5921 (5)	0.1218 (4)	0.7849 (5)	0.024 (3)
C(51)	0.5527 (6)	0.1769 (4)	0.8524 (6)	0.037 (4)
C(52)	0.6443 (9)	0.2311 (6)	0.9585 (8)	0.060 (6)
C(53)	0.4608 (9)	0.2331 (6)	0.7555 (10)	0.053 (5)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	n = 1	n = 2	n = 3
C(n0)—C(n1)	1.371 (10)	1.404 (9)	1.398 (9)
C(n1)—C(n2)	1.394 (8)	1.373 (10)	1.381 (9)
C(n2)—C(n3)	1.381 (10)	1.385 (10)	1.381 (10)
C(n3)—C(n4)	1.387 (10)	1.373 (10)	1.379 (11)
C(n4)—C(n5)	1.376 (9)	1.392 (9)	1.418 (10)
C(n5)—C(n0)	1.417 (10)	1.382 (9)	1.383 (9)

	n = 1	n = 2	n = 3
Sn(1)—C(n0)—C(n5)	119.9 (5)	116.6 (5)	119.2 (5)
Sn(1)—C(n0)—C(n1)	122.1 (5)	125.3 (4)	121.5 (4)
C(n1)—C(n0)—C(n5)	117.9 (4)	118.0 (6)	119.2 (6)
C(n0)—C(n1)—C(n2)	122.2 (6)	120.7 (6)	120.1 (6)
C(n1)—C(n2)—C(n3)	119.0 (6)	120.1 (6)	121.4 (6)
C(n2)—C(n3)—C(n4)	120.1 (4)	120.5 (6)	119.4 (6)
C(n3)—C(n4)—C(n5)	120.5 (6)	119.2 (6)	119.9 (7)
C(n0)—C(n5)—C(n4)	120.3 (6)	121.5 (6)	120.2 (6)

O(40)—C(40)	1.439 (7)		O(50)—C(50)	1.424 (8)
C(40)—C(41)	1.508 (8)		C(50)—C(51)	1.502 (8)
C(41)—C(42)	1.513 (11)		C(51)—C(52)	1.528 (11)
C(41)—C(43)	1.521 (10)		C(51)—C(53)	1.513 (12)

Sn(1)—O(40)—C(40)	116.1 (4)		Sn(1)—O(50)—C(50)	115.8 (3)
O(40)—C(40)—C(41)	113.4 (5)		O(50)—C(50)—C(51)	113.9 (5)
C(40)—C(41)—C(43)	108.8 (6)		C(50)—C(51)—C(53)	112.4 (5)
C(40)—C(41)—C(42)	112.8 (5)		C(50)—C(51)—C(52)	109.7 (6)
C(42)—C(41)—C(43)	112.2 (7)		C(52)—C(51)—C(53)	110.1 (7)

Sn(1)—C(10)	2.134 (4)		Sn(1)—O(40)	2.550 (6)
Sn(1)—C(20)	2.122 (6)		Sn(1)—O(50)	2.065 (5)
Sn(1)—C(30)	2.149 (7)			

C(10)—Sn(1)—O(40)	86.7 (2)		C(30)—Sn(1)—O(50)	94.6 (2)
C(20)—Sn(1)—O(40)	84.8 (2)		O(40)—Sn(1)—O(50)	173.5 (1)
C(30)—Sn(1)—O(40)	82.1 (2)		C(10)—Sn(1)—C(20)	114.4 (3)
C(10)—Sn(1)—O(50)	99.7 (2)		C(20)—Sn(1)—C(30)	130.8 (2)
C(20)—Sn(1)—O(50)	93.3 (2)		C(30)—Sn(1)—C(10)	111.9 (3)

Triphenyltin(IV) isobutoxide isobutanolate was formed as an unexpected main product during an attempt to prepare diphenyltin(IV) diisobutoxide by the reaction of diphenyltin dichloride with two equivalents of sodium isobutoxide. Suitable single crystals of the moisture-sensitive compound were obtained by slow evaporation of the organic solvent. The crystal specimen investigated was fixed in a glass fibre with epoxy resin to protect it from moisture.

Lattice constants and systematic absences (hkl observed only for $h+k = 2n$, $h0l$ observed only for $h,k = 2n$ and $0k0$ observed only for $k = 2n$) referred to the space groups Cc (No. 9) and $C2/c$ (No. 15). The correct choice of the non-centrosymmetric group was inferred by the symmetry of the trigonal-bipyramidal molecule found in its asymmetric unit which turned out to be incompatible with the higher multiplicity and symmetry elements of the centrosymmetric space group $C2/m$. In addition, an attempt to refine the structure in the latter space group [with a twofold axis along C(13)—C(10)—Sn(1)] resulted in a very poor R value and unreasonably high anisotropic displacement factors, especially for all atoms of the two axial ligands. The origin of the non-centrosymmetric cell was defined by the x and z coordinates of Sn(1) which were fixed to 0.5. The correctness of the absolute structure was established by the Flack x parameter (Flack, 1983) which was found to be 0.18(3).

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined by full-matrix least squares with *SHELXL92* (Sheldrick, 1992) minimizing $\Sigma w(F_o)^2$ with $w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 2.04P]$ where $P = [(F_o^2)_{max} + 2(F_c)^2]/3$. All H atoms, including those of the hydroxyl group, were localized unambiguously on difference Fourier maps. They were included in the refinement procedure using geometrically meaningful positions with fixed C—H (0.93 Å, phenyl; 0.98 Å, alkyl) and O—H (0.86 Å) distances and a common isotropic displacement factor. All other atoms were refined with anisotropic displacement factors. Apart from four peaks less than 1.08 Å from Sn(1), the final difference electron density map only showed insignificant features. Neutral atom scattering factors were corrected for the real part of the anomalous dispersion. The fractional coordinates and equivalent isotropic displacement factors are listed in Table 1. Selected bond lengths and angles are listed in Table 2. Fig. 1 shows a perspective view of the molecule and

the atomic numbering scheme used. The figure was designed by *KPLOT* (Hundt, 1979) and executed with *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55771 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1008]

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Bis(5-bromocytosinium) Tetrachloropalladate(II)

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Abstract

The structure consists of discrete $C_4H_5BrN_3O^+$ and $PdCl_4^{2-}$ ions in a network of N—H···Cl hydrogen bonds with the crystal packing being different from that of the analogous compound bis(cytosinium) tetrachloropalladate(II). The largest deviations from bond lengths and angles of 5-bromocytosine [4-amino-5-bromo-2(1*H*)-pyrimidinone] observed upon protonation are analogous to those found for cytosine.

Comment

This report extends work on halogenated nitrogen bases (Valle & Ettorre, 1992; Casellato, Graziani & Sánchez González, 1992).

The structure consists of discrete $C_4H_5BrN_3O^+$ and $PdCl_4^{2-}$ ions in a network of N—H···Cl hydrogen bonds. The $PdCl_4^{2-}$ anion is planar with the metal atom located at the origin of the centrosymmetric triclinic cell. Coordination bond lengths and angles are normal. The largest deviations from bond lengths and angles of 5-bromocytosine (Kato, Takenaka & Sasada, 1979) observed upon protonation are the decrease of C(4)—N(4) (*ca* 0.04 Å, 4σ), C(2)—O(2) (*ca* 0.05 Å, 4σ), N(3)—C(4)—C(5) (*ca* 4°, 5σ) and N(1)—C(2)—N(3) (*ca* 5°, 6σ), and the increase of C(2)—N(3)—C(4) (*ca* 6°, 8σ) [$\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$]. Analogous effects have been observed for cytosine (Bagieu-Beucher, 1990).

The crystal packing is different from that of bis-(cytosinium) tetrachloropalladate(II) (Kindberg & Amma, 1975) where, for example, the planes of the anions have two orientations.

The O(2)···Br (x, $y - 1$, z) contact of 2.972 (4) Å is remarkably close in relation to reported van der Waals radii for O (1.54 Å) and Br atoms (1.54–1.84 Å) (Nyburg & Faerman, 1985).

As shown in Table 2, each coordinated Cl(1) atom forms hydrogen bonds with the H—N(1) groups of two different cations, and Cl(2) is involved in bifurcated hydrogen bonds with the H—N(3) and H—N(4)H groups of a third cation, so that each centrosymmetric $PdCl_4^{2-}$ anion is hydrogen bonded to six cations, which gives compactness and stability to the crystal packing.
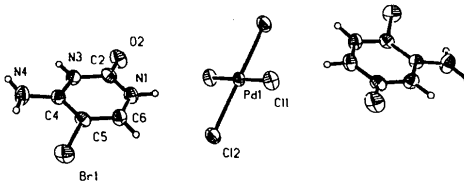

Fig. 1. Plot of the anion and two cations of the title compound showing the atomic numbering scheme.

Experimental

Crystal data

[C₄H₅BrN₃O]₂[PdCl₄]	Mo $K\alpha$ radiation
$M_r = 630.2$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 30
$P\bar{1}$	reflections
$a = 9.146$ (4) Å	$\theta = 6$–12°
$b = 8.650$ (4) Å	$\mu = 5.987$ mm^{-1}
$c = 6.622$ (3) Å	Room temperature
$\alpha = 109.05$ (4)°	Plates
$\beta = 71.05$ (4)°	0.2 × 0.2 × 0.2 mm
$\gamma = 109.03$ (5)°	Brick red