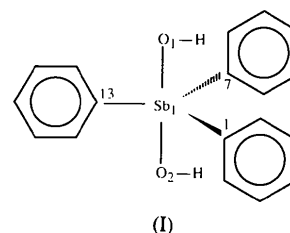


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Elemental analysis was in agreement with the formula $\text{Ph}_3\text{Sb}(\text{OH})_2$. An IR absorption at 507 cm^{-1} indicated the presence of an Sb—O (not an Sb=O) bond, and absorption at 3546 and 3432 cm^{-1} was assigned to ν_{OH} . Since no band that could be attributed to an Sb—O—Sb group was observed, the formation of a dihydroxide during the reaction was inferred. Considering the position and sharpness of the ν_{OH} band, the dihydroxide was inferred to be monomeric in the solid state. The mass spectrum showed a molecular ion peak which confirmed the molecular weight of the compound as 387. The final proof of this composition came from a single-crystal structure determination. $\text{Ph}_3\text{Sb}(\text{OH})_2$ proved to be monomeric in the solid state and in the molecule Sb is pentacoordinate, two OH groups being in the apical positions and three C(Ph) atoms in the equatorial plane of a trigonal bipyramid.

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Triphenylstibine Dihydroxide

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Abstract

Triphenylstibine dihydroxide [alternative name: dihydroxytriphenylantimony(V)], $[\text{Sb}(\text{OH})_2(\text{C}_6\text{H}_5)_3]$, was synthesized by the oxidative hydrolysis of $\text{Et}_4\text{N}^+ \cdot [\text{PhSbCl}_2\text{Br}]^-$ in methanol. The dihydroxide was characterized by IR spectroscopy, mass spectrometry and X-ray diffraction. The molecule is monomeric with very slightly distorted trigonal bipyramidal geometry around Sb with two OH groups in axial positions [Sb—O 1.963 (6) and 2.079 (7), Sb—C 2.090 (13)—2.109 (19) Å, O—Sb—O 178.5 (5)°].

Comment

Very few trialkylantimony(V) dihydroxides have been reported in the literature (Long, Doak & Freedman, 1964; Huang, Chen & Shen, 1989), and there had been no report of a triarylantimony(V) dihydroxide until recently; the first triarylantimony(V) dihydroxide, $\text{Mes}_3\text{Sb}(\text{OH})_2$ (mes = mesityl), was reported by Huber, Westhoff & Preut (1987) and characterized by X-ray crystallography (Huber *et al.*, 1987; Westhoff, Huber, Ruther & Preut, 1988). The title compound, (I), was prepared and characterized by IR, mass spectrometry and X-ray diffraction methods in order to compare its structure with that of $\text{Mes}_3\text{Sb}(\text{OH})_2$.

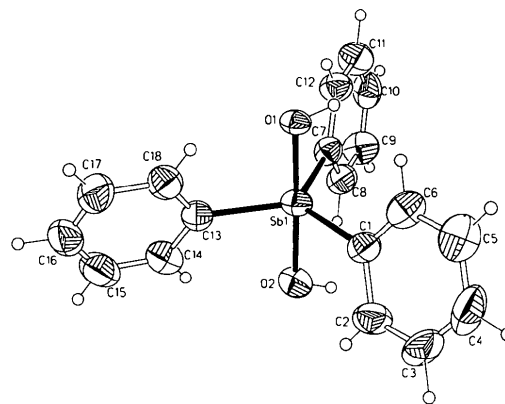


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids.

The two Sb—O distances [1.963 (6) and 2.079 (7) Å] are different from the one type of bond distance found in $\text{Mes}_3\text{Sb}(\text{OH})_2$ [2.027 (3) Å; Westhoff *et al.*, 1988]. The mean Sb—O bond distance [2.02 (6) Å] corresponds with distances in analogous compounds containing this bond, *e.g.* 2.048 (5) Å in Ph_4SbOH (Beauchamp, Bennett & Cotton, 1969) and 2.033 (8) Å in $\text{Ph}_3\text{Sb}(\text{OMe})_2$ (Keiweishen, McEwen, La Placa, Hamilton & Wolf, 1968). There is no O—H...O hydrogen bonding; the shortest O...O intermolecular contact is $\text{O1} \cdots \text{O1}(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ 4.632 (2) Å. The absence of hydrogen bonding was also inferred from the fact that there is

no IR band in the range 3000–3400 cm⁻¹. One strong sharp IR band can be safely assigned to the stretching frequency of a free OH group.

In the compound, the mean Sb—C distance [2.103(9) Å] is comparable with the average Sb—C bond distances in compounds such as Ph₄Sb(OH)I [2.120(3) Å; Ferguson, Harris & Khan, 1987] and Mes₃Sb(OH)₂ [2.142(3) Å; Westhoff *et al.*, 1988]. Considering the axial angle [O1—Sb1—O2 178.5(5)°] and the equatorial and equatorial/axial bond angles (Table 2) with maximum deviations of 2.6 and 0.8°, respectively, from the values 120 and 90°, respectively, found in a regular trigonal bipyramid, it can be inferred that there is very slight distortion of the coordination polyhedron. The conformation of the phenyl rings in the molecule is described by the torsion angles C1—Sb1—C7—C8 85.6(13), C7—Sb1—C13—C14 77.0(11) and C13—Sb1—C1—C2 70.2(18)°.

Experimental

To a solution of Et₄N⁺[PhSbCl₂Br]⁻ (2.39 g, 5 mmol) [which was prepared by the method of Jha, Jalil & Pankaj (1993)] in methanol (20 ml), a solution of hydrogen peroxide (30% in water) in aqueous methanol was added slowly with external cooling in an ice bath; the H₂O₂ was used in slight excess. The mixture was stirred for 2 h at room temperature and kept in a refrigerator for crystallization. After 1 d, white crystals were obtained, which were filtered and washed with ethanol and ether. Yield 65%; m.p. 268 K. Analysis of Sb: found (calculated) 31.69% (31.34%). IR (cm⁻¹): 3546 (*m*), 3432 (*m, br*), 3090 (*w*), 2990 (*s*), 2950 (*sh*), 2763 (*vw*), 1975 (*w*), 1499 (*m*), 1482 (*m*), 1435 (*s*), 1399 (*m*), 1308 (*w, br*), 1176 (*m*), 1079 (*s, br*), 1035 (*s*), 803 (*m*), 741.8 (*s*), 695 (*m*), 539 (*w*), 522 (*sh*), 507 (*s*), 457 (*s*), 360 (*vw*), 307 (*s*). Mass spectra [FAB]⁺ of Ph₃Sb(OH)₂: 387 [M]⁺, 384 [M-2H]⁺, 275 [SbPh₂]⁺, 215 [PhSbO]⁺, 198 [PhSb]⁺, 121 [Sb]⁺. IR spectra in the range 400–4000 cm⁻¹ were recorded in KBr on a Nicolet Magna 750 spectrometer. The mass spectra were obtained using a Jeol JMS-SX102A mass spectrometer. Antimony was analysed by a reported method (Ouchi, Nakatani & Takahashi, 1975).

Crystal data

[Sb(OH) ₂ (C ₆ H ₅) ₃]	Mo Kα radiation
<i>M_r</i> = 387.1	λ = 0.71073 Å
Monoclinic	Cell parameters from 40 reflections
<i>C</i> 2/ <i>c</i>	θ = 5.23–12.40°
<i>a</i> = 25.497(2) Å	μ = 1.699 mm ⁻¹
<i>b</i> = 9.208(2) Å	<i>T</i> = 293 K
<i>c</i> = 18.012(2) Å	Prism
β = 129.78(2)°	0.40 × 0.24 × 0.14 mm
<i>V</i> = 3249.7(8) Å ³	Colourless
<i>Z</i> = 8	
<i>D_x</i> = 1.582 Mg m ⁻³	

Data collection

Siemens P4 diffractometer	<i>R</i> _{int} = 0.0366
ψ scans	θ _{max} = 27.5°

Absorption correction: *h* = 0 → 33
ψ scans (XEMP; Siemens, 1990) *k* = 0 → 11
*T*_{min} = 0.494, *T*_{max} = 1.000 *l* = -23 → 17
 3 standard reflections monitored every 300 reflections
 3807 measured reflections
 3729 independent reflections
 1810 observed reflections
 [F > 4σ(*F*)]
 intensity decay: 5.17%

Refinement

Refinement on *F*²
R = 0.0591 Δρ_{max} = 0.95 e Å⁻³
wR = 0.0673 Δρ_{min} = -0.57 e Å⁻³
S = 1.240 Extinction correction: none
 1810 reflections Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 190 parameters
 H atoms riding; *U* = 0.08 Å²
w = 1/[σ²(*F*) + 0.0008*F*²]
 (Δ/σ)_{max} < 0.001

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sb1	0.1665 (1)	0.2386 (1)	0.1173 (1)	0.065 (1)
C1	0.1227 (6)	0.0388 (15)	0.0502 (9)	0.071 (8)
C2	0.0540 (7)	0.029 (2)	-0.0353 (11)	0.097 (11)
C3	0.0303 (9)	-0.107 (3)	-0.0742 (14)	0.123 (14)
C4	0.0689 (12)	-0.227 (3)	-0.0399 (16)	0.131 (19)
C5	0.1347 (10)	-0.2195 (17)	0.0436 (14)	0.110 (15)
C6	0.1599 (8)	-0.0848 (16)	0.0858 (10)	0.087 (10)
C7	0.2416 (6)	0.3309 (13)	0.1160 (8)	0.067 (7)
C8	0.2243 (7)	0.4136 (15)	0.0407 (10)	0.084 (9)
C9	0.2735 (9)	0.4695 (19)	0.0401 (12)	0.100 (12)
C10	0.3400 (9)	0.4478 (18)	0.1135 (12)	0.098 (14)
C11	0.3582 (7)	0.3638 (17)	0.1891 (12)	0.098 (11)
C12	0.3100 (7)	0.3037 (15)	0.1919 (10)	0.083 (8)
C13	0.1331 (6)	0.3397 (14)	0.1857 (9)	0.072 (8)
C14	0.0887 (7)	0.4552 (15)	0.1431 (11)	0.089 (11)
C15	0.0634 (9)	0.514 (2)	0.1853 (16)	0.123 (15)
C16	0.0847 (9)	0.461 (2)	0.2702 (17)	0.126 (16)
C17	0.1285 (9)	0.343 (2)	0.3149 (12)	0.115 (13)
C18	0.1530 (7)	0.2811 (16)	0.2716 (10)	0.086 (9)
O1	0.2371 (3)	0.1368 (7)	0.2385 (5)	0.057 (4)
O2	0.0906 (4)	0.3480 (9)	-0.0095 (6)	0.079 (6)

Table 2. Selected geometric parameters (Å, °)

Sb1—O1	1.963 (6)	Sb1—C7	2.109 (17)
Sb1—O2	2.079 (7)	Sb1—C13	2.109 (19)
Sb1—C1	2.090 (13)		
O1—Sb1—O2	178.5 (5)	O1—Sb1—C13	89.2 (4)
O1—Sb1—C7	90.7 (4)	O2—Sb1—C13	89.3 (5)
O2—Sb1—C7	90.3 (4)	C7—Sb1—C1	120.1 (7)
O1—Sb1—C1	89.6 (4)	C7—Sb1—C13	122.5 (5)
O2—Sb1—C1	90.8 (4)	C1—Sb1—C13	117.4 (7)
C13—Sb1—C1—C2	70.2 (18)	C7—Sb1—C13—C14	77.0 (11)
C1—Sb1—C7—C8	85.6 (13)		

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXTL/PC. Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a packing diagram, have been deposited with the IUCr (Reference: FG1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Low-Temperature Structure of Two Copper-Based Precursors for MOCVD: Aquabis(*tert*-butyl acetoacetato)copper(II) and Bis(dipivaloylmethanido)copper(II)

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Abstract

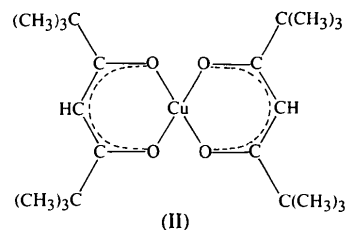
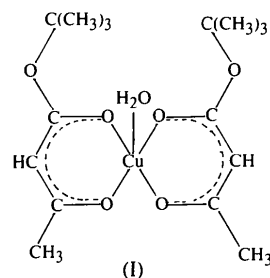
The Cu atoms in aquabis(*tert*-butyl acetoacetato)-copper(II), [Cu(C₈H₁₃O₃)₂(H₂O)], and bis(dipivaloyl-

methanido)copper(II), [Cu(C₁₁H₁₉O₂)₂], adopt square-pyramidal and planar conformations, respectively, with average Cu—O distances of 1.933 Å in the former (not including the water ligand) and 1.892 Å in the latter. It is interesting to note that the lability of the *tert*-butyl and methyl groups in both structures, which renders even the location of the terminal C atoms difficult, is reduced at *T* = 130 K, enabling location of all the protons in the difference Fourier map.

Comment

The structure determinations of aquabis(*tert*-butyl acetoacetato)copper(II), (I), and bis(dipivaloylmethanido)-copper(II), (II), which are used as copper-containing precursors for the metal-organic chemical vapour deposition (MOCVD) of thin film of YBa₂Cu₃O_(7-δ) (Harima, Ohnishi, Hanaoka, Tachibana & Goto, 1990), were undertaken to study their structural stability and the coordination geometry around their respective Cu atoms.

Compound (I) is hydrated and is different from bis(ethyl acetoacetato)copper(II) (Barclay & Cooper, 1965). Compound (II) is isostructural with bis(dipivaloylmethanido)nickel(II) (Cotton & Wise, 1966) and there are no significant differences in the bond parameters in the comparable portion of the two structures. An earlier report on the structure of compound (II) at room temperature (Watson & Holley, 1984) has an *R* factor of 0.107 and there are large displacement ellipsoids on the terminal groups, obscuring the location of H atoms. It was also reported that the compound is X-ray sensitive; however, there was no deterioration of the crystal in the present study.



Least-squares calculations involving Cu and its neighbouring O atoms showed that the Cu—O groups are