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Diaquanonaphenyltristiboxane diperchlorate[†]

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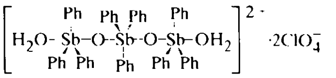
Abstract

In the title triantimony(V) compound, $[Sb_3O_2(C_6H_5)_9(H_2O)_2](ClO_4)_2$, the terminal Sb atoms adopt a mutually *cis* disposition about the O–O vector, unlike analogous molecules in which a *trans* arrangement is adopted. The cation occupies a crystallographic twofold axis.

Comment

Most of the known stiboxane compounds which have been structurally characterized are bent, with the Sb—O—Sb angle in the range 135–140°, but several are close to linear (Glidewell, 1988). We have previously reported structures of the iodide $(Ph_3SbI)_2O$, in which both linear and bent forms were obtained, with Sb—O—Sb angles of 180 and 144.6°, respectively (Taylor *et al.*, 1995). The iodine adduct of $(Ph_3SbI)_2O$ in the linear form has also been reported (Almond *et al.*, 1996). The structure of the perchlorate salt is also of interest for comparison with the compounds $[Me_3Sb(ClO_4)_2]_2O$ (Ferguson *et al.*, 1975) and $[Ph_3Bi(ClO_4)_2]_2O$ (March & Ferguson, 1975), which contain weakly coordinated perchlorate groups. Attempts to prepare the analogous perchlorate derived from $(Ph_3SbI)_2O$ yielded $[H_2O–SbPh_3–O–SbPh_3–O–SbPh_3–OH_2][ClO_4]_2$, (I), and we report here the structure of this compound.



$$\left[\mathrm{H_2O{-}\underset{Ph\ \ Ph}{\overset{Ph}{Sb}}{-}O{-}\underset{Ph}{\overset{Ph\ \ Ph}{Sb}}{-}O{-}\underset{Ph\ \ Ph}{\overset{Ph}{Sb}}{-}OH_2}\right]^{2-}\cdot 2ClO_4^-$$

(I)

The structure of (I) (Fig. 1) reveals a chain of three $SbPh_3$ units linked by oxygen bridges, with water molecules completing the fivefold coordination sphere of the terminal Sb atoms. The cation possesses crystallographically imposed C_2 symmetry, the twofold rotation axis passing through Sb1, C11 and C14. There is a trigonal-bipyramidal arrangement about each of the Sb atoms, with the phenyl groups occupying the equatorial positions. The structure is bent, with an Sb1—O1—Sb2 angle of 144.3 (2)°. The O—Sb distances are significantly different, at 2.030 (3) Å to the central Sb1 atom, and 1.927 (3) Å to the terminal Sb2 atom. The bond to the water molecule (Sb2—O2) is 2.400 (4) Å. The differences in the distances to the bridging O atom presumably reflect the weaker *trans* influence of the water molecule. The O1—Sb1—$O1(-x, y, \frac{1}{2}-z)$ angle is 172.5 (2)° and the O1—Sb2—O2 angle is 147.47 (13)°, comparable to the values found in the analogous sulfonate complex (Rüther *et al.*, 1987), where the water molecules are replaced by sulfonate groups. Comparable parameters for the Sb—O—Sb—O—Sb chain are Sb—O—Sb 140.8 (3)°, with Sb—O distances of 2.035 (5) and 1.921 (4) Å to the central and terminal Sb atoms, respectively.

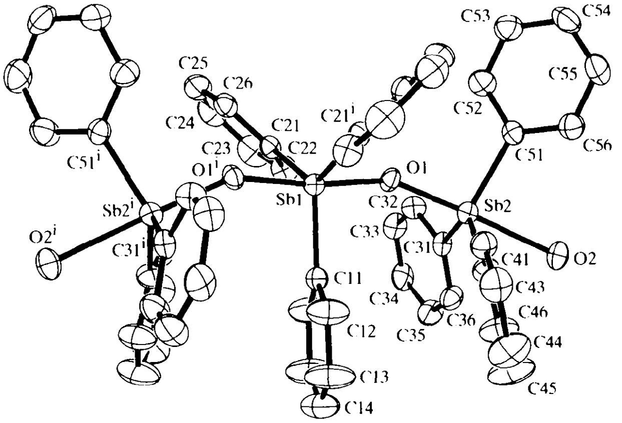


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids. The H atoms and perchlorate anions have been omitted for clarity. The symmetry code is as given in Table 2.

Unlike the analogous sulfonate complex (Rüther *et al.*, 1987) in which the terminal Sb groups adopt a mutually *trans* arrangement about the O–O vector, the aqua complex in (I) adopts a *cis* configuration about the O–O vector. Two phenyl rings on the central Sb atom, directed away from the terminal Sb atom, are twisted 50.0 (2)° out of the equatorial plane, while the third, on the same side as the terminal Sb atom, is twisted only 21.3 (3)° out of the plane, reflecting the greater steric crowding in this region. Similarly, the two phenyl rings on the more crowded side of the terminal Sb are twisted 36.1 (2) and 35.7 (2)° out of the equatorial plane, while the remaining ring on the less crowded side is twisted 49.8 (2)°.

The water molecules form hydrogen bonds with the perchlorate groups. Thus, the O2 atom makes an approach of 2.827 (6) Å to $O3(x-1, 1-y, z-\frac{1}{2})$ and an approach of 2.745 (6) Å to $O4(\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z)$.

A spectrum of the crystal from which data was collected, using Raman microscopy, revealed a band at

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[†] Alternative name: diaqua-1κO,3κO-di-μ-oxo-1:2$\kappa^2 O$;2:3$\kappa^2 O$-nonaphenyl-1$\kappa^3 C$,2$\kappa^3 C$,3$\kappa^3 C$-triantimony(V) diperchlorate.

928 cm^{-1}, indicative of ionic perchlorate, and a band at 658 cm^{-1}, which is probably attributable to the Sb—O symmetric stretching mode. Other bands at 160, 201 and 216 cm^{-1} are likely to be phenyl-group modes.

Experimental

The title compound resulted from an attempt to prepare $[Ph_3Sb(ClO_4)]_2O$. A suspension of $(Ph_3SbI)_2O$ (0.10 g, 0.1 mmol) in acetonitrile (4 ml) was treated with $AgClO_4$ (0.04 g, 0.2 mmol) dissolved in acetonitrile (1 ml), which gave a curdy precipitate of AgI. The solution phase was withdrawn, centrifuged until clear and allowed to evaporate to dryness. Recrystallization from aqueous acetonitrile gave a glassy material which proved, on X-ray examination, to be amorphous and which is likely to be Ph_3SbO, the polymeric structure of which has been deduced from EXAFS data (Carmalt *et al.*, 1996), and a few small colourless crystals of (I). One of these crystals was selected for the investigation reported here.

Crystal data

$[Sb_3O_2(C_6H_5)_9(H_2O)_2]$-$(ClO_4)_2$
$M_r = 1326.08$
Monoclinic
$C2/c$
$a = 14.984\ (8)$ Å
$b = 14.437\ (5)$ Å
$c = 25.361\ (9)$ Å
$\beta = 107.39\ (3)°$
$V = 5235\ (4)$ Å^3
$Z = 4$
$D_x = 1.682$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$12°$
$\mu = 1.701$ mm^{-1}
$T = 193\ (2)$ K
Rectangular prism
0.30 × 0.25 × 0.22 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.629$, $T_{max} = 0.706$
4578 measured reflections
4396 independent reflections
3636 reflections with $I > 2\sigma(I)$

$R_{int} = 0.051$
$\theta_{max} = 25.97°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 16$
$l = -31 \rightarrow 29$
3 standard reflections every 100 reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.098$
$S = 1.052$
4396 reflections
328 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 22.2597P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.57$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sb1	0	0.12296 (3)	1/4	0.02169 (13)
Sb2	−0.14393 (2)	0.16785 (2)	0.346330 (12)	0.02349 (12)
O1	−0.0992 (2)	0.1137 (2)	0.28951 (14)	0.0271 (7)
O2	−0.2132 (2)	0.2389 (3)	0.41019 (15)	0.0337 (8)
C11	0	0.2682 (5)	1/4	0.0261 (15)
C12	0.0772 (4)	0.3178 (4)	0.2810 (3)	0.0493 (16)
C13	0.0763 (5)	0.4127 (5)	0.2812 (4)	0.066 (2)
C14	0	0.4615 (6)	1/4	0.054 (2)
C21	−0.0971 (3)	0.0567 (3)	0.18220 (18)	0.0252 (10)
C22	−0.1904 (4)	0.0868 (4)	0.1658 (2)	0.0366 (12)
C23	−0.2520 (4)	0.0504 (5)	0.1182 (3)	0.0490 (16)
C24	−0.2233 (4)	−0.0153 (5)	0.0880 (2)	0.0470 (16)
C25	−0.1319 (4)	−0.0468 (4)	0.1047 (2)	0.0438 (14)
C26	−0.0683 (4)	−0.0091 (4)	0.1516 (2)	0.0311 (11)
C31	−0.2704 (3)	0.2150 (4)	0.29103 (19)	0.0271 (11)
C32	−0.3200 (3)	0.1510 (4)	0.2519 (2)	0.0314 (11)
C33	−0.4008 (4)	0.1793 (4)	0.2115 (2)	0.0362 (13)
C34	−0.4299 (4)	0.2692 (4)	0.2100 (2)	0.0399 (14)
C35	−0.3814 (4)	0.3320 (4)	0.2491 (2)	0.0424 (14)
C36	−0.3013 (4)	0.3056 (4)	0.2901 (2)	0.0356 (12)
C41	−0.0360 (4)	0.2600 (4)	0.3869 (2)	0.0314 (11)
C42	0.0535 (3)	0.2234 (4)	0.4075 (2)	0.0330 (12)
C43	0.1267 (4)	0.2816 (5)	0.4339 (2)	0.0443 (14)
C44	0.1107 (5)	0.3745 (5)	0.4392 (3)	0.0593 (19)
C45	0.0221 (5)	0.4097 (5)	0.4196 (4)	0.064 (2)
C46	−0.0527 (4)	0.3519 (4)	0.3929 (3)	0.0501 (16)
C51	−0.1477 (3)	0.0430 (4)	0.3882 (2)	0.0270 (10)
C52	−0.1677 (4)	−0.0386 (4)	0.3574 (2)	0.0370 (12)
C53	−0.1627 (4)	−0.1229 (4)	0.3837 (3)	0.0425 (14)
C54	−0.1363 (4)	−0.1273 (4)	0.4410 (3)	0.0437 (14)
C55	−0.1179 (5)	−0.0474 (5)	0.4709 (3)	0.0510 (16)
C56	−0.1231 (4)	0.0383 (4)	0.4456 (2)	0.0422 (14)
Cl1	0.57527 (9)	0.81821 (9)	0.94677 (5)	0.0332 (3)
O3	0.5949 (4)	0.7366 (3)	0.9796 (2)	0.0737 (16)
O4	0.6034 (3)	0.8045 (5)	0.89809 (17)	0.0715 (16)
O5	0.4789 (3)	0.8400 (4)	0.9305 (2)	0.0601 (13)
O6	0.6278 (4)	0.8921 (4)	0.9779 (2)	0.0888 (19)

Table 2. *Selected geometric parameters (Å, °)*

Sb1—O1	2.030 (3)	Sb2—C51	2.102 (5)
Sb1—C11	2.097 (7)	Sb2—C31	2.105 (5)
Sb1—C21	2.119 (5)	Sb2—C41	2.110 (5)
Sb2—O1	1.927 (3)	Sb2—O2	2.400 (4)
O1^{i}—Sb1—O1	172.5 (2)	Sb2—O1—Sb1	144.29 (19)
O1—Sb2—O2	174.47 (13)		

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O3^{ii}	0.80 (2)	2.05 (3)	2.827 (6)	163 (6)
O2—H2A···O4^{iii}	0.81 (2)	1.94 (2)	2.745 (6)	172 (6)

Symmetry codes: (ii) $x - 1, 1 - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

The molecule lies on a twofold axis passing through the central Sb atom. The H atoms of the water molecules were located from difference maps and their coordinates allowed to refine with distance restraints. All other H atoms were located geometrically and allowed to ride on their carrier atom. All H atoms had their isotropic displacement parameters fixed at 20% greater than U_{eq} of the carrier atom. The largest ΔF residuals all lie within 1 Å of an Sb centre.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL*

(Siemens, 1994). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1295). Services for accessing these data are described at the back of the journal.

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A degraded glycol-substituted *iso-closo* ten-vertex ruthenaborane: $[(PPh_3)HClRuB_9H_5(OCH_2CH_2OH)_2(PPh_3)_2]\cdot 1.2CHCl_3$

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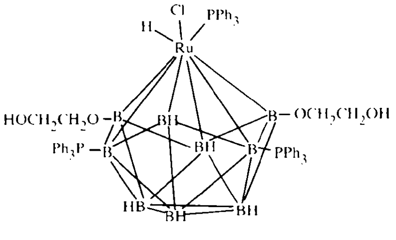
Abstract

1-Chloro-1-hydrido-2,6-bis(2-hydroxyethoxy)-1,3,5-tris(triphenylphosphine)-*iso-closo*-1-ruthenadecaborane–chloroform (1/1.2), $[RuHCl(C_{40}H_{45}B_9O_4P_2)(C_{18}H_{15}P)]\cdot 1.2CHCl_3$, is a ruthenaborane based on an *iso-closo* C_{3v} stack, with the nine-coordinate metal occupying the six-connected apical position. The $\{RuB_9\}$ cage has two B-terminal $-OCH_2CH_2OH$ groups and two PPh_3 substituents.

Comment

$RuCl_2(PPh_3)_3$ is a versatile metalloborane synthon. A series of ruthenaboranes have been synthesized by the reaction of $RuCl_2(PPh_3)_3$ with the *closo* ten-vertex borane anion $B_{10}H_{10}^{2-}$ under various conditions (Crook *et al.*, 1984, 1985; Fontaine *et al.*, 1987; Yao *et al.*, 1995). We now report the crystal structure of a degraded glycol-substituted *iso-closo* ten-vertex ruthenaborane, $[(PPh_3)HClRuB_9H_5(OCH_2CH_2OH)_2(PPh_3)_2]$, (I), synthesized in glycol at about 373 K.



(I)

A drawing of the molecular structure of (I) is shown in Fig. 1. The ten-vertex *iso-closo* structure adopts the closed 1:3:3:3 $RuB_3B_3B_3$ cluster structure, which is similar to that in $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$, (II) (Crook *et al.*, 1985). The Ru atom is bound to three *exo*-polyhedral ligands (H, Cl and PPh_3) and six B atoms. The distances of Ru to H1, P1 and Cl1 [1.69 (8), 2.363 (2) and 2.482 (2) Å, respectively] are somewhat longer than the corresponding distances in compound (II) [1.53 (3), 2.354 (4) and 2.456 (4) Å, respectively]. Thus, the corresponding *trans*-Ru—B distances [Ru1—B3 2.482 (9), Ru1—B5 2.392 (10) and Ru1—B7 2.341 (9) Å] are shorter than those in compound (II) [2.517 (9), 2.402 (10) and 2.353 (9) Å, respectively]. The upper belt of three Ru-bound B atoms (B2, B4 and B6) is closer to the metal atom [2.057 (9)–2.205 (9) Å] than is the middle belt (B3, B5 and B7), and the Ru1—B3 distance (*trans* to Ru1—H1) is significantly longer than the distances to B5 and B7, which are *trans* to Ru1—P1 and Ru1—Cl1, respectively. Each B atom in the upper belt has a cluster connectivity of four, whereas each in the middle belt has a cluster connectivity of five.

In addition to the two PPh_3 substituents on the middle belt of B atoms, there are two $-OCH_2CH_2OH$ substituents on the upper belt at B2 and B6; these groups distinguish the present compound from compound (II). The effects of the two $-OCH_2CH_2OH$ ligands are the