Table 5. *Selected geometric parameters (Å, °) for (II)*

Br1—Cu1	2.482 (1)	Cu1—N2	2.734 (4)
Br2—Cu1	2.419 (1)	Br1—Br2ⁱ	4.007 (2)
Br2—Cu1—Br1	90.08 (3)		

Symmetry code: (i) $x, y, z - 1$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···Br1	0.94 (7)	2.50 (7)	3.43 (1)	170 (6)
N3—H3*B*···Br2ⁱ	0.77 (7)	2.58 (7)	3.31 (1)	162 (7)

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

The structure was solved by Patterson and Fourier methods (Beurskens *et al.*, 1992). Non-H atoms were refined anisotropically by full-matrix least-squares techniques. Some of the H atoms were isotropically refined, others were geometrically calculated and refined riding with common isotropic displacement parameters in both structures. The final difference Fourier maps show several electron density peaks greater than 1 e Å^{-3}, for both structures, close to the Br and Cu atoms. A free anisotropic refinement of atom C3 in structure (II) leads to odd values for the principal axis of the thermal tensor, which are also affected by rounding off errors. Anisotropic refinement using similar parameters (*SIMU* in *SHELXL*93; Sheldrick, 1993) for all C atoms of the 2-aminopyrimidine leads to physically acceptable results. All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray group DEC/AXP computers

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CRYSDA DIRDIF*; data reduction: *REFLEX* (local program); molecular graphics: *Xtal_GX* (Hall & Boulay, 1995). Geometrical calculations made with *PARST* (Nardelli, 1983); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1316). Services for accessing these data are described at the back of the journal.

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The 1:1 Antimony Trichloride Adduct of Chlorobis(2,6-dimethylpiperidin-1-yl)phosphine Oxide

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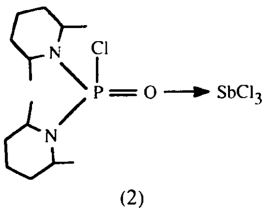
Abstract

In the structure of the title complex, $[(C_7H_{14}N)_2Cl-P(O)].SbCl_3$, the Sb atom shows a distorted trigonal bipyramidal geometry (including the lone pair). The O—Sb interaction of antimony with the phosphoryl O atom is only moderate and is weaker than that observed in the known compound $Cl_3PO \rightarrow SbCl_5$.

Comment

The phosphoryl unit in compounds of type $X_3P{=}O$ contains an electron-rich O atom that can act as a donor to metal centres (Burford, 1992). Several such complexes have been structurally characterized in which the angle at the phosphoryl O atom varies from 130 to 180° depending on the substituents and metal centres. Antimony trihalides can also act as weak acceptors (Pohl, Saak, Lotzand & Haase, 1990). In this paper, we report the synthesis and structure of the title compound $[(Me_2C_5H_8N)_2P(Cl)O] \rightarrow SbCl_3$, (2).



(2)

Compound (2) was obtained in an attempted preparation of $[(Me_2C_5H_8N)_2P][SbCl_6]$ by reacting $(Me_2C_5H_8N)_2PCl$, (1), with $SbCl_5$, presumably by hydrolysis. An *ORTEP* (Johnson, 1965) drawing of the molecule of (2) is shown in Fig. 1. The Sb—O distance of 2.396 (4) Å in (2) suggests only a moderate interaction of the Sb atom with the phosphoryl O atom; this distance is much longer than that in $Cl_3P{=}O.SbCl_5$ [2.17 (2)°; Bovin, 1976; Branden & Lindquist, 1963] reflecting the lower acidity of $SbCl_3$ compared with $SbCl_5$ and thus leading to a weaker Sb—O bond in the former. The Sb—Cl distances are in the normal range (Lipka, 1979; Rogers & Jezl, 1994). The P=O distance [1.492 (3) Å] as well as the P—O—Sb angle [133.4 (2)°] are also consistent with a mainly σ donation with a moderate or low π interaction for the Sb—O bond.

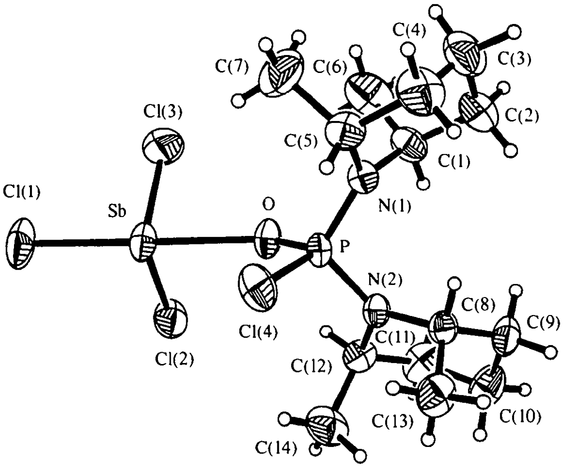


Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the molecule of compound (2) with displacement ellipsoids plotted at the 50% probability level; only non-H atoms are labelled.

The geometry around antimony, including the lone pair, is distorted trigonal bipyramidal (tbp) [valence-shell electron-pair repulsion (VSEPR) theory] with the O and Cl(1) atoms *trans* to one another; the deviation from tbp to a square-pyramidal structure based on the angles between the planes containing Cl(1), Cl(2), Cl(3) and Cl(2), Cl(3), Cl(4) is *ca* 15%. The Sb—Cl distance [2.460 (3)°] *trans* to the Sb—O bond is more than the other two Sb—Cl distances [mean: 2.347 Å], as expected in a tbp geometry.

Although an attempt was made to prepare the analogous 1:1 adduct of $[(OCH_2CMe_2CH_2O)P(O)Cl]$ with $SbCl_3$, the resulting solid (3) analysed as the 2:1 adduct; the crystals obtained were not good enough to study the nature of the Sb—O interaction.

Experimental

For the preparation of $[C_5H_8(Me)_2N]_2PCl$, (1), a mixture of *cis*-2,6-dimethylpiperidine (8.2 g, 72 mmol) and triethylamine (7.3 g, 72 mmol) in hexane (50 ml) was added dropwise to a solution of phosphorus trichloride (4.98 g, 36 mmol) in hexane (100 ml) with continuous stirring at 298 K. The reaction mixture was heated under reflux for 48 h and filtered. Evaporation of the solvent followed by vacuum distillation afforded (1) as a liquid (b.p. 383 K/3 mm). Yield: 6.86 g (65%). ^1H NMR ($CDCl_3$): 1.22 (*s*, 6H, CH_3), 1.24 (*s*, 6H, CH_3), 1.25–1.80 (*m*, 12H, CH_2), 3.70–3.90 (*br*, 4H, NCH). ^{31}P NMR: 156.5. For the preparation of $[(C_7H_{14}N)_2P(Cl)O].SbCl_3$, (2), a solution of antimony pentachloride (prepared by reacting the trichloride with chlorine) (0.52 g, 1.75 mmol) in dichloromethane (10 ml) was added dropwise with continuous stirring to a solution of (1) (0.5 g, 1.75 mmol) in dichloromethane (10 ml) maintained at 195 K. After stirring for a further 2 h, the solvent was completely removed to give an oil. Attempted crystallization from acetonitrile–hexane (1:10) afforded a small quantity of (2) (0.1 g) as a crystalline material (m.p. 419–421 K). ^1H NMR: 1.31 (*s*, 6H, CH_3), 1.42 (*s*, 6H, CH_3), 1.45–2.10 (*m*, 12H, CH_2), 3.85–4.10 (*m*, 4H, CHNH). ^{31}P NMR: 23.3. Analysis calculated for $C_{14}H_{28}Cl_4N_2OPSb$: C 31.40, H 5.20, N 5.2%; found: C 31.08, H 5.30, N, 4.9%. For the preparation of $[(OCH_2CMe_2CH_2O)P(O)Cl]_2.SbCl_3$, (3), $[(OCH_2CMe_2CH_2O)P(O)Cl]$ (0.46 g, 2.02 mmol) was reacted with antimony trichloride (0.46 g, 2.02 mmol) in ether (10 + 10 ml) for 24 h. Slow removal of solvent afforded a crystalline solid (m.p. 333 K). ^1H NMR: 0.95 (*s*, 3H, CH_3), 1.35 (*s*, 3H, CH_3), 3.90–4.30 (*m*, 4H, CH_2). ^{31}P NMR: −3.36. Analysis calculated for $C_{10}H_{20}Cl_5O_7P_2Sb$: C 19.50, H 3.28%; found: C 19.70, H 3.25%.

Crystal data

$C_{14}H_{28}ClN_2OP.SbCl_3$
$M_r = 534.9$
Triclinic
$P\bar{1}$
$a = 10.092\,(11)$ Å
$b = 10.514\,(11)$ Å
$c = 12.415\,(14)$ Å
$\alpha = 70.53\,(8)^\circ$
$\beta = 71.81\,(8)^\circ$
$\gamma = 61.85\,(7)^\circ$
$V = 1076\,(2)$ Å^3
$Z = 2$
$D_x = 1.651$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 10$–12°
$\mu = 1.857$ mm^{-1}
$T = 293$ K
Block
0.3 × 0.2 × 0.2 mm
White

Data collection

Siemens–Stoe AED-2 diffractometer
ω–θ scans
Absorption correction: none
2820 measured reflections
2820 independent reflections
2820 reflections with $F > 4\sigma(F)$

$\theta_{max} = 22.5^\circ$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R = 0.0322$
$wR = 0.0853$
$S = 1.147$ (on F^2)

$(\Delta/\sigma)_{max} = 0.105$
$\Delta\rho_{max} = 0.966$ e Å^{-3}
$\Delta\rho_{min} = -1.289$ e Å^{-3}
Extinction correction: none

2820 reflections
208 parameters
H atoms: see below
$w = 1/[\sigma(F_o^2) + (0.0501P)^2 + 1.4214P]$
where $P = (F_o^2 + 2F_c^2)/3)$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Sb—Cl(1)	2.460 (3)	P—O	1.492 (3)
Sb—Cl(2)	2.345 (3)	P—N(1)	1.621 (4)
Sb—Cl(3)	2.348 (3)	P—N(2)	1.613 (4)
Sb—O	2.396 (4)	P—Cl(4)	2.037 (3)
Cl(2)—Sb—Cl(3)	95.85 (10)	O—P—N(1)	117.4 (2)
Cl(2)—Sb—O	83.78 (12)	O—P—Cl(4)	106.3 (2)
Cl(3)—Sb—O	83.89 (13)	N(2)—P—Cl(4)	108.9 (2)
Cl(2)—Sb—Cl(1)	92.42 (11)	N(2)—P—N(1)	108.8 (2)
Cl(3)—Sb—Cl(1)	92.10 (12)	N(1)—P—Cl(4)	104.6 (2)
Cl(1)—Sb—O	174.15 (7)	P—O—Sb	133.4 (2)
O—P—N(2)	110.4 (2)		

X-ray data for (2) were collected after inserting the crystal into a Lindemann capillary. The structure was solved by conventional methods (*SHELX*86; Sheldrick, 1990) and refined by full-matrix least-squares methods (*SHELXL*93; Sheldrick, 1993). H atoms bonded to C atoms were placed in calculated positions using a riding model. They were assigned isotropic displacement parameters of 1.2 times that of the parent C atom; all non-H atoms were refined anisotropically.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Molecular graphics: *ORTEP* (Johnson, 1965).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1057). Services for accessing these data are described at the back of the journal.

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Piperidinium Diazidotriphenylstannate and Quinuclidinium Diazidotriphenylstannate

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Abstract

Two triphenyltin–azide adducts with cyclic aliphatic amines are shown by X-ray diffraction to be $[LH][(C_6H_5)_3Sn(N_3)_2]$, where for (I), L = piperidine ($C_5H_{11}N$), and for (II), L = quinuclidine ($C_7H_{13}N$). The anions have quasi-trigonal-bipyramidal symmetry, with the azide groups occupying axial positions. In each case, the azide groups are non-equivalent due to one of them hydrogen bonding with the cation. In (I), the NH_2 of the cation hydrogen bonds with azides of adjacent anions forming chains through the lattice. For (II), the asymmetric unit has two cations and anions. One cation singly hydrogen bonds to an azide group of one anion, while the other cation forms a bifurcated hydrogen bond linked to azide groups on the two different anions. The cations have their usual geometries, the piperidinium ion having the expected chair conformation.

Comment

Following our earlier reports on adducts (1/1) of triphenyltin pseudo-halides with various O- and N-donor ligands, with particular reference to their Raman and far-IR spectra (Wharf, Piehler, Sailofsky, Onyszchuk & Simard, 1987, and references therein), we have recently completed a similar study on triphenyltin azide and its adducts (1/1) with a range of O- and N-donor ligands (Wharf, Wojtowski, Lebuis, Bowes & Onyszchuk, 1997). While many amines did form 1/1 adducts, some aliphatic amines [L = morpholine, triethylamine, 1,2-bis(dimethylamino)ethane, piperidine, quinuclidine] gave products that appeared from elemental analysis to contain two azide groups which, together with IR data [$\sim$2050 cm^{-1}, $\nu_{as}(N_3)$; $\sim$3400 cm^{-1}, ν(N—H)], suggested these compounds were perhaps $[LH^+][Ph_3Sn(N_3)_2^-]$, analogues of the $(CH_3)_4N^+$ and $(C_6H_5)_4As^+$ salts with the same anion [IR (cm^{-1}); $\nu_{as}(N_3)$, 2050*s*, 2070*sh* and 2040*s*, 2055*s*, respectively] reported by Barbieri, Bertazzi & Tomarchio (1975). In the same way, the compound having