The Crystal Structure of the Tetrameric Adduct of Antimony Trichloride and Phosphoryl Isothiocyanate, $[SbCl_3 \cdot OP(NCS)_3]_4$

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The crystal and molecular structure of the tetrameric complex of the composition $[SbCl_3 \cdot OP(NCS)_3]_4$ synthesized from $SbCl_3$ and $OP(NCS)_3$ in CCl_4 was determined by X-ray crystallography [$I\bar{4}3m$ space group, cubic system with $a = 13.927(4)$ Å]. The complex exhibits a tetranuclear "cage" structure with a $[Sb_4O_4]$ core which consists of μ_3-bridging oxygen and six coordinate antimony(III) atoms; the Sb–O distance, 3.060 Å, is exceptionally long.

Introduction

The preparation of a range of adducts of Lewis acids with $OP(NCS)_3$ was reported earlier [1–6]. The two molecules, antimony trichloride and phosphoryl isothiocyanate were shown to combine in the ratio 1 : 1, but the nature of the bonding between the components in the adduct remained unknown. The structure of the $SbCl_3 \cdot OP(NCS)_3$ complex is now reported and some indications as to the bonding involved are suggested.

Experimental

Preparation of $[SbCl_3 \cdot OP(NCS)_3]_4$

$OP(NCS)_3$ was prepared according to [7] and purified two times by distillation *in vacuo* (b.p. 106–107 °C, at 0.5 mm Hg). CCl_4 was purified according to the conventional method [8] and distilled in an atmosphere of dry argon. Antimony trichloride was prepared in accord with [9]. Because of the extremely hygroscopic nature of the starting materials and the adduct, the crystals of $[SbCl_3 \cdot OP(NCS)_3]_4$ were obtained in an atmosphere of dry argon by the following method: to the cool (0 °C) suspension of $SbCl_3$ (4.6 g, 20 mmol) in CCl_4 (30 cm^3) upon stirring in a Schlenk flask a solution of $OP(NCS)_3$ (4.42 g, 20 mmol) in CCl_4 (20 cm^3) was added dropwise (20 min) from an addition funnel with a pressure-equalization arm and a Teflon stopcock; colorless, almost cubic crystals were obtained after several hours.

Analytical data for $C_{12}N_{12}O_4Cl_{12}P_4S_{12}Sb_4$

	C	N	S	P	Sb	Cl
Calcd	8.0	9.4	21.4	6.9	27.1	23.7%,
Found	7.9	9.5	21.2	6.7	26.8	23.7%.

The complex is readily soluble in methanol, ethanol, acetone, acetonitrile, dimethylsulfoxide and benzene, and sparingly soluble in CCl_4 and hexane.

A cryoscopic measurement in benzene established that it is almost totally dissociated in this solvent.

Crystallography

Because of their extremely hygroscopic nature the crystals were sealed into thin walled Lindemann glass capillary tubes for X-ray crystal structure analysis.

Crystallographic measurements were made on an Enraf-Nonius CAD-4 diffractometer (graphite monochromator) operating in the $\omega/2\theta$ scan mode, the ratio of the scanning rates being $\omega/\theta = 1:2$. The accurate unit cell parameters and the orientation matrix for data collection were obtained from a least squares refinement, using the setting angles of 24 reflections in the range $13 < \theta < 15°$. Corrections for Lorentz and polarization effects were applied; absorption was not taken into account. The crystallographic data are summarized in Table I. The structure was solved by direct methods (MULTAN) and refined by full matrix least squares techniques with anisotropic displacement parameters. Convergence was reached at the agreement factors listed in Table I.

All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [10].

The atomic fractional coordinates and the equivalent isotropic thermal parameters are listed in Table II.

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Table I. Crystallographic data for $[SbCl_3 \cdot OP(NCS)_3]_4$.

Empirical formula	$C_{12}N_{12}O_4Cl_{12}P_4S_{12}Sb_4$
Formula weight	1797.2
Crystal system	cubic
Space group	$I\bar{4}3m$
Unit cell dimensions	$a = 13.927(4)$ Å
Volume	2701(1) Å^3
Z	2
Density (calc)	2.21 g cm^{-3}
Absorption coefficient	31.9 cm^{-1}
F(000)	1696
Color; habit	colorless; cubic
Crystal size (mm)	$0.20 \times 0.20 \times 0.20$
Diffractometer used	Enraf-Nonius CAD-4
Radiation	MoKα ($\lambda = 0.71073$ Å)
Temperature	293 K
$(\sin\theta)/\lambda$ limits	$(\sin\theta)/\lambda \leq 0.57$ Å^{-1}
Reflections collected	372
Reflections used	338 $[I > 3\sigma(I)]$
Weighting scheme	$\omega^{-1} = \sigma^2(F) + 0.0016\,F^2$
R indices	$R = 0.034$, $\omega R = 0.033$

Table II. The atomic fractional coordinates and the equivalent isotropic thermal parameters (Å^2).

Atom	x/a	y/b	z/c	B_{eq}*
Sb	0.10619(4)	0.10619(4)	0.10619(4)	3.14(1)
Cl	0.0992(1)	0.0992(1)	0.2740(2)	5.52(9)
O	0.1133(4)	−0.1133(4)	0.1133(4)	4.20(2)
P	0.1733(2)	−0.1733(2)	0.1733(2)	3.65(8)
S	0.1307(2)	−0.1307(2)	0.4704(2)	7.70(1)
C	0.1472(5)	−0.1472(5)	0.3660(7)	5.30(4)
N	0.1608(4)	−0.1608(4)	0.2829(7)	10.90(6)

* Equivalent isotropic thermal parameter B_{eq} devined as one third of the trace of the orthogonalized B_{ij} tensor, $B_{eq} = 1/3(B_{11} + B_{22} + B_{33})$.

Additional X-ray material is available from the Cambridge Crystallographic Data Centre*.

Results and Discussion

The molecular structure of the complex $[SbCl_3 \cdot OP(NCS)_3]_4$ with the atomic labeling scheme of the asymmetric unit and a perspective view of the packing in the unit cell of the molecular type crystal lattice are shown in Fig. 1 and 2, while selected bond lengths and angles are contained in Table III.

All atoms are found on crystallographic mirror planes while Sb, O and P atoms occupy positions on threefold axes, too. The cubic molecule belongs to the $\bar{4}3m$ point group.

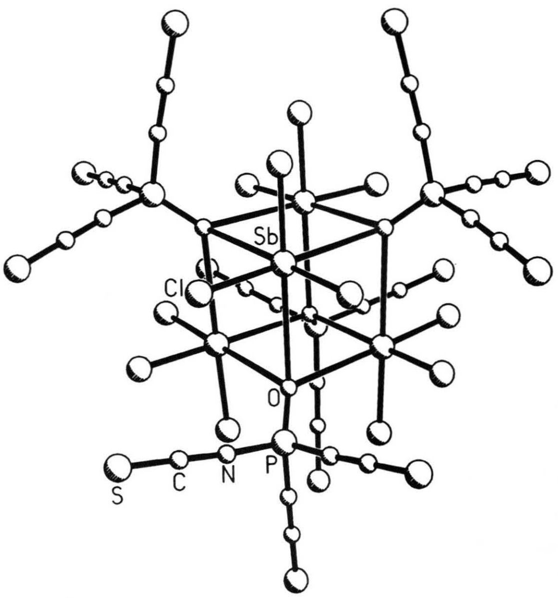

Fig. 1. The molecular structure of $[SbCl_3 \cdot OP(NCS)_3]_4$.

The coordination environment of the antimony(III) atom is far from regular and consists of chlorine and oxygen atoms: there are three chlorines at a normal distance, 2.341(2) Å, and three μ_3-bridging oxygen atoms at the significantly longer distance of 3.060(5) Å. Hence, the nearest coordination environment of the antimony atom has trigonal pyramidal geometry, $[SbCl_3]$, whilst the oxygen atoms supplement it to a grossly distorted octahedral environment, *i.e.* $[SbCl_3O_3]$; the planes of chlorine and oxygen atoms are parallel (the chlorine atoms form an equilateral triangle with the edge of 3.443(3) Å, which is less than the calculated van der Waals' distance of 3.6 Å [11]).

Supporting evidence for the Sb–O bond formation comes from the IR spectrum of the complex (Perkin-Elmer 325; Nujol): the customary stretching frequency of the P–O vibration is shifted to 1200 cm^{-1} in comparison with ν(P–O) in $OP(NCS)_3$ (1305 cm^{-1}). Changes of such magnitude have previously been related to complex formation [1–6].

The trigonal pyramidal geometry of the $SbCl_3$ molecule {d(Sb–Cl) *ca.* 2.340–2.368 Å; Cl–Sb–Cl *ca.* 91–95.7° [12]} is almost retained in the crystal structure of the adduct under consideration (Table III, Fig. 1); the value of the Cl–Sb–Cl angle indicates the influence of the stereoactive lone pair

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Table III. Selected bond lengths (Å) and angles (°).

Bond lengths			
Sb–Cl	2.341(1)	P–N	1.546(10)
Sb–O	3.060(5)	N–C	1.188(10)
O–P	1.447(3)	C–S	1.490(10)
Angles			
Cl–Sb–Cl	94.67(6)	Sb–O–P	127.9(2)
O–Sb–Cl	85.84(7)	O–P–N	116.1(3)
O–Sb–Cl*	179.25(7)	N–P–N***	102.2(4)
O–Sb–O**	93.65(8)	P–N–C	176.2(6)
Sb–O–Sb**	86.35(7)	N–C–S	179.6(7)

*, ** and *** denote the following equivalent positions $\langle y, z, x\rangle$, $\langle -x, -y, z\rangle$ and $\langle z, -x, -y\rangle$.

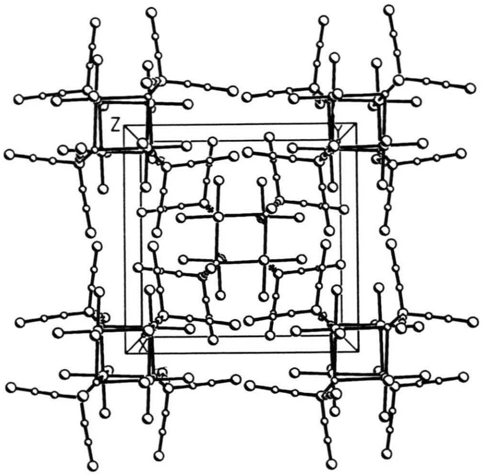

Fig. 2. A fragment of the unit cell packing of $[SbCl_3 \cdot OP(NCS)_3]_4$.

of the antimony atom [13, 14]. The orientation of the lone pair on antimony is considered to be in the direction through the center of the triangle formed by the oxygen atoms, thus accounting for the expansion of that triangle when compared to the chlorine atoms. Thus all four lone pairs of the four Sb atoms are located in the tetranuclear closed "cage" structure of the $[Sb_4O_4]$ core. The antimony atoms form a distorted tetrahedron with an Sb–Sb edge of 4.186(1) Å, which is less than the calculated van der Waals' distance of 4.40 Å and allows to postulate a weak specific interaction of these atoms (the close interatomic distances in the rhombohedral crystal lattice of antimony are 2.908 and 3.355 Å [12]).

In a formal sense in the complex every antimony atom has a total of seven pairs of electrons. The lone pair then has to occupy a capping position over a triangular face formed by the oxygen atoms in the severely distorted octahedral environment of the antimony atom, $[SbCl_3O_3]$.

Every sulphur atom has a normal van der Waals' contact [3.733(1) Å] with two sulphur atoms [S–S $\langle -x, y, -z\rangle$ and S–S $\langle x, -y, -z\rangle$] and a shorter contact [3.613(1) Å] with a chlorine atom [S–Cl $\langle x, -y, 1-z\rangle$] [11, 15].

The most interesting feature of the structure is the length of the Sb–O bond, 3.060 Å (the calculated van der Waals' distance for the above mentioned atoms is about 3.7 Å [11]). Other quite long Sb–O bond distances had been previously observed in cubic antimony oxide Sb_2O_3 (2.918 Å) and in antimony oxoiodide Sb_5O_7I (2.988 Å) [13]; but had not been detected in a adducts {a rather long Sb–O bond distance of 2.455 Å is reported for $SbCl_3 \cdot 2\,OP(C_6H_5)_3$ [16]}. The sum of the single bond covalent radii [11, 15] of oxygen and six coordinate antimony(III) atoms is *ca.* 2.16 Å, but this distance should be lengthened a little to allow for ionic contributions in order to correspond to the de Bolster theory of bonding in phosphoryl complexes [16]. Further lengthening may arise from the interaction of the lone pair of every antimony atom with a neighbouring group of three oxygen atoms. It is reasonable to assume that the energy gained by the formation of the Sb–O bond, supplemented by the extra lattice energy arising from $OP(NCS)_3$ occurring in the solid state, is sufficient to offset the promotion energy required to involve d orbitals in the hybridization scheme of the antimony atom.

This hybridization together with weak Sb–Sb, S–S and S–Cl interactions and lower steric restrictions favours the "cage" formation over an alternative mononuclear structure of a complex with the same stoichiometry.

In accord with general theoretical predictions [16] the geometry of the coordinated molecule of $OP(NCS)_3$ is normal.

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