The Crystal Structures[†] of $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ where $n = 0, 2,$ and 4 and Hpy = pyridinium; Stabilisation by Very Strong N–H ··· O Hydrogen Bonds

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Crystal structures have been determined from *X*-ray diffraction data for $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ where $n = 0$ (**1**), 2 (**2**), and 4 (**3**) and Hpy = pyridinium. The compounds are isostructural, crystallising in the monoclinic space group $P2_1/c$, with the following cell dimensions: $a = 8.816(3)$, $b = 8.615(3)$, $c = 28.116(8)$ Å, $\beta = 112.73(5)°$ for (**1**); $a = 8.919(3)$, $b = 8.813(3)$, $c = 28.218(8)$ Å, $\beta = 113.57(4)°$ for (**2**); and $a = 8.982(3)$, $b = 8.884(3)$, $c = 28.343(8)$ Å, $\beta = 113.80(4)°$ for (**3**). The structures have been solved by Patterson and Fourier methods and refined by full-matrix least squares to *R* 0.074 (2 652 observed reflections) for (**1**), 0.075 (2 887) for (**2**), and 0.066 (2 706) for (**3**). The compounds all contain a discrete $[Sb_2OX_6]^{2-}$ anion in which the antimony atoms are triply bridged by one oxygen and two halogen atoms. Both (**2**) and (**3**) show halogen disorder. In the former, all six halogen positions are involved but the two bridging positions have *ca.* 53% occupancy by bromine; in (**3**) the disorder is between the two sets of terminal positions and the bridging positions are uniquely occupied by bromine. A major feature of the structures and probably a great contributor to the overall stability is a very strong hydrogen bond [2.68(1) Å in (**1**) and 2.72(1) Å in (**2**) and (**3**)] between the bridging oxygen and one of the pyridinium cations.

The preparation of a series of stable pyridinium salts containing the anions $[Sb_2OBr_nCl_{6-n}]^{2-}$ where $n = 0$—6 by partial hydrolysis of appropriately substituted $[Hpy]_3[Sb_2Br_nCl_{9-n}]$ compounds (Hpy = pyridinium) has been described previously.[1] In addition the completely chlorinated anion results from the action of adventitious moisture on mixtures of antimony(III) chloride and pyridine in chlorinated hydrocarbon solvents. This paper describes the crystal structures of three members of the $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ series, *i.e.* those where $n = 0$, 2, and 4. These were carried out to proɒe their unexpected high stability and, as in the case of the related $[Sb_2Br_nCl_{9-n}]^{3-}$ compounds,[2] to determine if there was preferential occupancy of the bridging and terminal positions by specific halogen atoms. The structure of $[Hpy]_2[Sb_2Br_nCl_{6-n}]$ based on an alternative monoclinic cell has been described in a preliminary communication.[3]

Experimental

Crystals suitable for *X*-ray analysis were obtained from samples obtained previously[1] after recrystallisation from anhydrous ethanol. Crystal data for the three compounds are summarised in Table 1.

Structure Determinations.—*For* $[Hpy]_2[Sb_2OCl_6]$ (**1**). Intensities were measured using a Hilger and Watts four-circle diffractometer for 3 733 reflections in the range $0 < \theta < 25°$ of which 2 652 with $I > 3\sigma(I)$ were considered observed. Corrections were made for Lorentz and polarisation effects. Data reduction and subsequent calculations used the CRYSTALS programs,[4] and neutral atom scattering factors.[5] The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to *R* 0.120 with isotropic and *R* 0.076 with anisotropic thermal parameters. A Fourier difference synthesis then showed possible positions for some of the hydrogen atoms, but as the set was incomplete the hydrogens were placed at the calculated positions. Further cycles of refinement with the hydrogen atoms at these fixed positions and with unit weights gave final convergence of *R* 0.074. The fractional co-ordinates of the non-hydrogen atoms are collected in Table 2.

For $[Hpy]_2[Sb_2OBr_2Cl_4]$ (**2**). Data were collected as described above for 3 840 reflections of which 2 887 were considered observed. In addition to corrections for Lorentz and polarisation effects, the data were corrected for absorption using the ABSORB program,[6] and the scattering factors included the anomalous dispersion contributions for all non-hydrogen atoms.[4] The structure was solved and refined as above to *R* 0.151 with isotropic and *R* 0.089 with anisotropic thermal parameters. From the thermal parameters of the bridging bromine and terminal chlorine atoms, it was obvious that there was halogen disorder and a correction for this was applied in subsequent cycles of refinement by allowing the halogen occupation factors to refine. After two cycles it was clear that within the estimated standard deviations the occupation factors were equal in pairs, *i.e.* Cl(1) and Cl(2), Cl(3) and Cl(4), Br(5) and Br(6), and subsequently the atoms in a given pair were constrained to have the same occupation factor. The hydrogen atoms were placed at the calculated positions and after application of a four-coefficient Chebyshev weighting scheme, there was final convergence at *R* 0.075. Refined co-ordinates for non-hydrogen atoms are in Table 3. Refined values for the occupation factors are: Cl(1), Cl(2), 1.07(2); Cl(3), Cl(4), 1.44(2); and Br(5), Br(6), 0.76(2).

For $[Hpy]_2[Sb_2OBr_4Cl_2]$ (**3**). Data were collected and treated as described for compound (**2**) for 4 182 reflections of which 2 706 were observed. The refinement converged at *R* 0.161 with isotropic and *R* 0.101 with anisotropic thermal parameters. This structure also showed halogen disorder and although the bridging positions are occupied by bromine atoms (when allowed to refine, the occupation factors remained at unity), there was statistical occupancy of the terminal positions by bromine and chlorine atoms. In subsequent cycles of refinement,

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[†] *Supplementary data available* (No. SUP 56548, 8 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Crystal data *

	$[Hpy]_2[Sb_2OCl_6]$ $C_{10}H_{12}Cl_6N_2OSb_2$	$[Hpy]_2[Sb_2OBr_2Cl_4]$ $C_{10}H_{12}Br_2Cl_4N_2OSb_2$	$[Hpy]_2[Sb_2OBr_4Cl_2]$ $C_{10}H_{12}Br_4Cl_2N_2OSb_2$
M	632.4	721.4	810.2
a/Å	8.816(3)	8.919(3)	8.982(3)
b/Å	8.615(3)	8.813(3)	8.884(3)
c/Å	28.116(8)	28.218(8)	28.343(8)
β/°	112.73(5)	113.57(4)	113.80(4)
U/Å^3	1 969.6	2 033.0	2 069.4
D_c/g cm^{-3}	2.13	2.36	2.60
F(000)	1 192	1 336	1 480
μ/cm^{-1}	35.7	76.0	113.0
Crystal size/mm	0.2 × 0.4 × 0.4	0.2 × 0.5 × 0.5	0.4 × 0.4 × 0.2

* Details common to all three compounds: $Z = 4$; crystal habit, monoclinic; space group, $P2_1/c$; $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å.

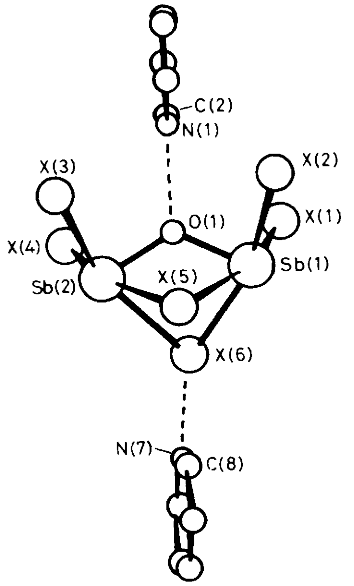

Figure 1. The structure of $[Hpy]_2[Sb_2OCl_6]$ (1; X = Cl). For (2), X(1)—X(4) = Cl, X(5) and X(6) = Br; for (3), X(1) and X(2) = Cl, X(3)—X(6) = Br. See text for discussion of halogen disorder

the occupation factors of the four terminal atoms were allowed to vary in pairs as described for (2). The hydrogen atoms were placed at their calculated positions but not refined, and after application of a four-coefficient Chebyshev weighting scheme there was final convergence at R 0.066. Refined fractional atomic co-ordinates are in Table 4. Final values for the halogen occupation factors are: Cl(1), Cl(2), 1.40(2); and Br(3), Br(4), 0.81(1).

Results and Discussion

These determinations show that all three compounds are isostructural and contain discrete $[Sb_2OX_6]^{2-}$ anions, hydrogen bonded to two pyridinium cations. For each compound the anion consists of two antimony atoms bridged by an oxygen and two halogen atoms; each antimony also carries two terminal halogen atoms which are *trans* to the bridging halogens.

Bond distances and angles for the three anions are summarised in Table 5; the distances (*ca.* 1.34°) and angles (*ca.* 120°) in the cations are not unusual allowing for the rather high thermal motion. Figure 1 shows a diagram of the $[Hpy]_2[Sb_2OCl_6]$ structure and gives the atom numbering scheme for the three compounds; a projection of the unit-cell contents down the b axis is given in Figure 2.

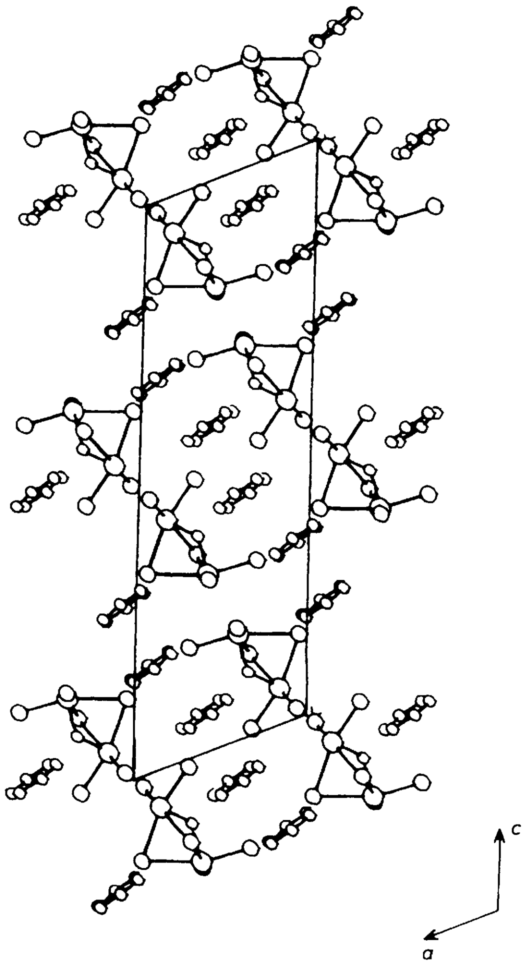

Figure 2. Diagram of the unit-cell contents of $[Hpy]_2[Sb_2OCl_6]$ projected down the b axis

The similarity in anion structure, irrespective of the chlorine content, is in marked contrast to that for members of the related $[Sb_2Br_nCl_{9-n}]^{3-}$ series of compounds[2] where halogen atoms also occupy both terminal and bridging positions. In $[Sb_2Cl_9]^{3-}$, for example, three chlorine atoms bridge to three different antimony atoms giving a polymeric structure, while in $[Sb_2Br_3Cl_6]^{3-}$ and $[Sb_2Br_9]^{3-}$ three bromine atoms occupy

Table 2. Fractional atomic co-ordinates for $[Hpy]_2[Sb_2OCl_6]$ (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	0.407 55(9)	0.141 54(9)	0.187 99(3)	C(3)	0.727(2)	0.447(2)	0.058 8(6)
Sb(2)	0.158 12(9)	0.063 44(9)	0.065 27(3)	C(4)	0.682(2)	0.600(2)	0.054 6(6)
Cl(1)	0.693 0(4)	0.146 5(4)	0.196 2(1)	C(5)	0.552(2)	0.646(2)	0.064 4(7)
Cl(2)	0.413 7(4)	0.428 0(4)	0.198 2(2)	C(6)	0.468(2)	0.533(2)	0.080 0(6)
Cl(3)	0.056 4(4)	0.302 4(5)	0.018 6(2)	N(7)	0.018(2)	−0.265(3)	0.172 3(6)
Cl(4)	0.317 2(4)	0.013 9(5)	0.012 8(2)	C(8)	−0.102(3)	−0.193(2)	0.182 3(7)
Cl(5)	0.053 9(4)	0.144 6(4)	0.147 5(2)	C(9)	−0.201(2)	−0.274(2)	0.197 9(8)
Cl(6)	0.341 6(4)	−0.161 8(4)	0.146 2(2)	C(10)	−0.187(2)	−0.431(2)	0.202 1(6)
O(1)	0.344 6(9)	0.176 2(9)	0.114 4(3)	C(11)	−0.068(2)	−0.504(2)	0.191 7(7)
N(1)	0.512(1)	0.387(1)	0.083 6(4)	C(12)	0.033(2)	−0.420(3)	0.177 5(8)
C(2)	0.642(2)	0.341(2)	0.073 6(6)				

Table 3. Fractional atomic co-ordinates for $[Hpy]_2[Sb_2OBr_2Cl_4]$ (**2**) with e.s.d:s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	0.407 88(9)	0.153 83(9)	0.188 72(4)	C(3)	0.721(2)	0.450(2)	0.059 9(7)
Sb(2)	0.156 35(9)	0.067 54(9)	0.065 33(3)	C(4)	0.673(2)	0.596(2)	0.054 4(6)
Cl(1)	0.694 5(3)	0.157 9(4)	0.196 7(1)	C(5)	0.540(2)	0.640(2)	0.064 1(7)
Cl(2)	0.408 7(4)	0.435 6(3)	0.197 0(1)	C(6)	0.459(2)	0.531(2)	0.078 6(6)
Cl(3)	0.043 4(3)	0.305 9(3)	0.013 7(1)	N(7)	−0.002(2)	−0.245(3)	0.172 6(7)
Cl(4)	0.317 8(3)	0.015 3(3)	0.010 8(1)	C(8)	−0.110(3)	−0.188(2)	0.182 2(9)
Br(5)	0.041 7(2)	0.152 4(2)	0.148 06(9)	C(9)	−0.207(3)	−0.264(3)	0.196 8(9)
Br(6)	0.344 6(2)	−0.162 2(2)	0.148 9(1)	C(10)	−0.188(3)	−0.420(3)	0.202 6(8)
O(1)	0.340 7(9)	0.182 1(9)	0.114 1(3)	C(11)	−0.070(3)	−0.486(2)	0.192 2(7)
N(1)	0.508(1)	0.390(1)	0.083 3(4)	C(12)	0.033(2)	−0.392(2)	0.176 8(8)
C(2)	0.634(2)	0.345(2)	0.074 3(6)				

the bridging positions and discrete confacial, bioctahedral structures result.

The Structure of $[Hpy]_2[Sb_2OCl_6]$ (**1**).—It is most convenient to discuss this structure first and then consider the effects of bromine substitution. The $[Sb_2OCl_6]^{2-}$ anion can be considered as arising by adding two chloride ions (in bridging positions) to the unknown basic antimony(III) chloride, $Cl_2SbOSbCl_2$. This is in agreement with the presence of three short (primary) bonds to two terminal chlorines (2.420—2.483, mean 2.44 Å) and to oxygen (1.948 Å). The angles between these bonds range between 87.4 and 90.0°, and are, as expected, close to 90°. The Sb–Cl (bridging) distances, 2.832—2.952 Å (mean 2.89 Å), can then be considered as secondary bonds.

The Sb–O–Sb and Sb–Cl(5)–Sb bridging systems are symmetrical, but the third bridge with Cl(6) is involved in cation hydrogen bonding and is distinctly asymmetric, Sb(1)–Cl(6) 2.832(2), Sb(2)–Cl(6) 2.952(4) Å. The angle at the bridging oxygen is close to 120° and this necessarily enforces close contact (3.366, *cf.* 4.4 Å for the van der Waals separation) between the antimony atoms. A consequence is that to maintain reasonable Sb–Cl (bridging) distances the angles at the bridging chlorines are reduced to *ca.* 71°. This is unusually low; in a number of chloroantimonate structures[7] the angles are in the range 90—100°, although linear Sb–Cl–Sb systems are also known.[2] Minimisation of non-bonded interactions in the $Cl_2SbOSbCl_2$ system requires that the Sb_2O plane and the two $SbCl_2$ (terminal) planes are orthogonal giving the system almost C_{2v} symmetry.

An alternative view of the anion structure is in terms of face sharing between two $SbCl_4O$ square pyramids or, if the antimony lone pair is sterically active, between two pseudo-octahedral $:SbCl_4O$ units so that the shared chlorines are *trans* to terminal chlorines and the oxygen atom is *trans* to either a vacant co-ordination site or the antimony lone pair.

The square-pyramidal geometry about each antimony atom is necessarily distorted as two of the halogens in the basal plane are involved in bridging. The four chlorine atoms are, however, closely planar (the maximum deviation of any atom from the best plane is 0.02 Å) with the antimony lying *ca.* 0.35 Å below this plane. This geometry, which also follows from the antimony bond angles, can be a result of either the stereochemical activity of the antimony lone pair of electrons or, more likely, a consequence of constraints resulting from the participation of two of the halogens in bridging.

A major feature of the structure is the formation of a very short, strong hydrogen bond [2.68(1) Å] between the oxygen atom and the nitrogen [N(1)] of one of the pyridinium cations. The *X*-ray data were not of sufficient quality to locate the hydrogen atom. Although many compounds are known containing N–H $\cdots$ O=C hydrogen bonds where the N $\cdots$ O separations are *ca.* 2.9 Å,[8] there are few where the oxygen is attached to a non-carbon atom. In $[NH_4][H_2PO_4]$, for example, the N–H $\cdots$ O distance is 2.91 Å;[9] on the other hand, the O–H $\cdots$ N hydrogen bonds in, for example, $N_2H_4 \cdot 4MeOH$ (2.68 Å)[10] and $N_2H_4 \cdot H_2O$ (2.79 Å)[11] are substantially shorter.

The second pyridinium cation forms a much weaker hydrogen bond to the bridging atom Cl(6) [N $\cdots$ Cl 3.32(2) Å]; this is significantly longer than that in $N_2H_4 \cdot HCl$ (3.13 Å) but comparable with those in $[Hpy]_3[Sb_2Cl_9]$.[2]

There are a number of weaker interactions (Table 6) which affect the solid-state packing (see Figure 2). The Sb(1) $\cdots$ Cl(2′) interaction at 3.49 Å is *trans* to the Sb–O bond, both linking the anions into chains and completing distorted octahedral geometry about Sb(1). There is similarly a longer contact (3.81 Å) between Sb(2) and the centrosymmetrically related atom, again completing distorted octahedral co-ordination.

The Structures of $[Hpy]_2[Sb_2OBr_2Cl_4]$ (**2**) *and* $[Hpy]_2[Sb_2OBr_4Cl_2]$ (**3**).—These structures show that no marked changes occur in either the basic anion structures or in the hydrogen-bonding systems on replacing the chlorine atoms by bromine. The Sb–O distance increases slightly but the Sb–O–Sb angle remains effectively constant. The major cation hydrogen-bonding interaction with the bridging oxygen atoms increases

Table 4. Fractional atomic co-ordinates for $[Hpy]_2[Sb_2OBr_4Cl_2]$ **(3)** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	0.407 3(1)	0.155 4(1)	0.188 31(4)
Sb(2)	0.155 3(1)	0.067 9(1)	0.065 03(4)
Cl(1)	0.697 5(3)	0.158 8(4)	0.196 5(1)
Cl(2)	0.407 9(3)	0.438 7(3)	0.196 7(1)
Br(3)	0.039 5(3)	0.306 0(3)	0.012 6(1)
Br(4)	0.318 1(3)	0.016 1(3)	0.010 24(9)
Br(5)	0.040 4(2)	0.153 4(2)	0.148 16(8)
Br(6)	0.344 2(3)	−0.160 1(2)	0.148 53(9)
O(1)	0.339(1)	0.184(1)	0.113 8(4)
N(1)	0.503(2)	0.390(2)	0.082 4(5)
C(2)	0.632(2)	0.345(3)	0.074 3(7)
C(3)	0.718(2)	0.443(2)	0.061 0(6)
C(4)	0.672(2)	0.593(2)	0.055 7(6)
C(5)	0.542(2)	0.635(2)	0.064 9(7)
C(6)	0.458(2)	0.529(2)	0.078 4(6)
N(7)	−0.006(3)	−0.243(3)	0.171 0(8)
C(8)	−0.119(4)	−0.190(3)	0.181(1)
C(9)	−0.210(3)	−0.275(4)	0.197(1)
C(10)	−0.188(3)	−0.420(3)	0.201 6(9)
C(11)	−0.067(4)	−0.482(2)	0.191 0(9)
C(12)	0.028(2)	−0.392(4)	0.176 7(8)

Table 5. Important bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ where n = 0 **(1)**, 2 **(2)**, and 4 **(3)**

	(1)	**(2)**	**(3)**
Sb(1)–X(1)*	2.437(3)	2.475(3)	2.521(3)
Sb(1)–X(2)	2.483(3)	2.494(3)	2.527(3)
Sb(1)–X(5)	2.877(4)	2.998(2)	3.022(2)
Sb(1)–X(6)	2.832(2)	2.972(2)	2.989(2)
Sb(1)–O(1)	1.947(8)	1.961(8)	1.964(9)
Sb(2)–X(3)	2.420(4)	2.525(2)	2.553(3)
Sb(2)–X(4)	2.434(4)	2.535(2)	2.569(2)
Sb(2)–X(5)	2.884(4)	2.994(2)	3.026(2)
Sb(2)–X(6)	2.952(4)	3.052(2)	3.055(2)
Sb(2)–O(1)	1.949(8)	1.950(8)	1.965(9)
O(1)–N(1)	2.68(1)	2.72(1)	2.72(1)
X(6)–N(7)	3.32(2)	3.49(2)	3.53(2)
X(1)–Sb(1)–X(2)	89.8(1)	90.7(1)	90.9(3)
X(1)–Sb(1)–X(5)	163.5(1)	164.2(1)	164.7(1)
X(1)–Sb(1)–X(6)	95.4(1)	94.7(1)	94.5(1)
X(1)–Sb(1)–O(1)	87.6(2)	87.6(2)	87.7(3)
X(2)–Sb(1)–X(5)	90.5(1)	90.1(1)	90.1(1)
X(2)–Sb(1)–X(6)	163.1(1)	164.0(1)	164.1(1)
X(2)–Sb(1)–O(1)	87.4(2)	87.8(2)	88.0(2)
X(5)–Sb(1)–X(6)	80.0(1)	80.68(6)	80.8(1)
X(5)–Sb(1)–O(1)	76.0(2)	76.7(3)	77.1(3)
X(6)–Sb(1)–O(1)	76.8(2)	77.4(2)	77.4(3)
X(3)–Sb(2)–X(4)	90.0(1)	89.6(1)	89.7(1)
X(3)–Sb(2)–X(5)	93.6(1)	93.5(1)	93.4(1)
X(3)–Sb(2)–X(6)	162.8(1)	165.3(1)	165.6(1)
X(3)–Sb(2)–O(1)	89.7(2)	89.6(1)	90.5(1)
X(4)–Sb(2)–X(5)	164.8(1)	166.6(1)	166.5(2)
X(4)–Sb(2)–X(6)	94.6(1)	94.5(1)	94.4(1)
X(4)–Sb(2)–O(1)	89.5(2)	89.9(3)	89.7(1)
X(5)–Sb(2)–X(6)	77.9(1)	79.47(6)	79.7(1)
X(5)–Sb(2)–O(1)	75.7(2)	77.0(2)	77.1(3)
X(6)–Sb(2)–O(1)	73.8(2)	75.5(2)	75.8(3)
Sb(1)–X(5)–Sb(2)	71.5(1)	68.9(1)	68.4(1)
Sb(1)–X(6)–Sb(2)	71.1(1)	68.5(1)	68.5(1)
Sb(1)–O(1)–Sb(2)	119.5(4)	120.1(4)	120.0(5)
Sb(1)–O(1)–N(1)	118.7(5)	117.2(4)	118.6(2)
Sb(2)–O(1)–N(1)	121.8(5)	122.7(4)	118.0(2)
Sb(1)–X(6)–N(7)	102.0(5)	99.2(4)	100.1(4)
Sb(2)–X(6)–N(7)	94.8(4)	91.8(4)	91.2(4)

* X(1)—X(6) = Cl for compound **(1)**, X(1)—X(4) = Cl, X(5) and X(6) = Br for **(2)**, and X(1) and X(2) = Cl, X(3)—X(6) = Br for **(3)** (see text for discussion of halogen disorder).

Table 6. Closest intermolecular contacts (Å)

	(1)	**(2)**	**(3)**
Sb(1)···X(2′)[a]	3.49	3.55	3.57
Sb(2)···Sb(2″)[b]	3.81	3.82	3.81
Sb(2)···X(3″)	3.95	3.98	3.98
Sb(2)···X(4″)	3.96	3.97	3.98

[a] X(2)—X(4) = Cl for compounds **(1)** and **(2)**; X(2) = Cl, X(3) and X(4) = Br for **(3)**; but see text for discussion of halogen disorder. X(2′) is related to X(2) by the symmetry operation $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$. [b] Atoms carrying a double prime are related to unprimed atoms by the symmetry operation $-x, -y, -z$.

from 2.68(1) Å for compound **(1)** to 2.72(1) Å for **(2)** and **(3)** but still can be considered as being very strong. The second hydrogen-bonding system is, however, much longer, a consequence mainly of the progressive occupation of the bridging positions by bromine atoms.

A major problem in both these structures is disorder among the halogen positions, which for **(2)** involves all six positions. From the refined occupation factors, the halogen contents at these positions are: X(1), X(2) 93% Cl, 7% Br; X(3), X(4) 58% Cl, 42% Br; and X(5), X(6) 47% Cl, 53% Br. In the tetrabromide **(3)**, the situation is more straightforward as the bridging positions are occupied exclusively by bromine. The halogen contents at the terminal positions are: X(1), X(2) 62% Cl, 38% Br; and X(3), X(4) 37% Cl, 63% Br.

In agreement with the high chlorine content at the X(1) and X(2) positions in compound **(2)**, there is only a small increase (*ca.* 0.02 Å) in the distances from antimony, and in general the increases in the lengths of the terminal distances reflect the increase in bromine content. In spite of differences in the halogen content at the Sb(1) and Sb(2) terminal positions in **(2)** and **(3)**, the bridging systems at X(5) and X(6) remain symmetrical and asymmetrical respectively as found for $[Sb_2OCl_6]^{2-}$ **(1)**. The asymmetry at X(6), however, becomes less marked.

With increasing occupancy of the bridging positions by bromine, there is a decrease in the angles at the bridging halogen atoms from *ca.* 71° in **(1)** to *ca.* 68° in **(2)** and **(3)**. For comparison, the bridging angles in the $[Sb_2Br_9]^{3-}$ and $[Sb_2Br_3Cl_6]^{3-}$ confacial bioctahedral structures are *ca.* 80°.[2] The reduction of the bridging halogen angle is then added confirmation that the $[Sb_2OBr_nCl_{6-n}]^{2-}$ geometry is determined mainly by the Sb–O–Sb angle achieving the optimum 120° value.

There are two remaining points arising from the specific disordering of the halogen atoms in compounds **(2)** and **(3)**, which are difficult to rationalise. Although the bridging positions in **(3)** are exclusively occupied by bromine as might be predicted from the structure of $[Sb_2Br_3Cl_6]^{3-}$, there is a much lower tendency for bromine to be the bridging atom in **(2)**. The second point concerns the disorder between the two pairs of terminal positions which differs markedly for both **(2)** and **(3)**.

With respect to the latter point, it is useful to consider the hexachloride **(1)** where, perhaps contrary to simple expectations, there are clearly different intermolecular interactions involving Sb(1) and Sb(2) (see Table 6). The strongest interaction occurs at Sb(1), where there is a contact to chlorine *trans* to the oxygen atom. This type of interaction is presumably not possible at Sb(2) due to packing problems and the closest contact to this atom is a symmetry-related antimony atom. The secondary bonding of chlorine to Sb(1) is important and probably determines the direction of the asymmetry in the Cl(6) bridging system.

Extension of this argument to structures (**2**) and (**3**) would rationalise the observation that the disorder is such that there is a greater chlorine content at the halogens attached to Sb(1). This would increase the Lewis acidity of Sb(1) and in turn strengthen the interaction with a neighbouring halogen atom. It is significant that this neighbouring atom is also that having the greater chlorine content.

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