Nonahalogenodiantimon(III)ates; Their Preparation and the Crystal Structures of $[Hpy]_3[Sb_2Cl_9]$, $[NMe_4]_3[Sb_2Br_9]$, and $[NMe_4]_3[Sb_2Br_3Cl_6]$ †

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Compounds of the type $Y_3[Sb_2Br_nCl_{9-n}]$ {Y = Hpy [pyridinium(1+)], n = 0—9; Y = NMe_4^+, n = 0, 3, 6, and 9; and Y = Cs^+, n = 0, 3, 6, and 9} have been prepared by a variety of methods and investigated by i.r. and Raman spectroscopy, mass spectrometry, and X-ray single crystal and powder diffraction. Two further mixed halides $[Hpy][SbCl_2X_2]$ (X = Br or I) have also been isolated. Crystals of $[Hpy]_3[Sb_2Cl_9]$ are monoclinic, space group $C2/c$, with a = 29.168(8), b = 10.178(5), c = 9.425(5), β = 106.70(1)°, and Z = 4. Crystals of $[NMe_4]_3[Sb_2Br_9]$ and $[NMe_4]_3[Sb_2Br_3Cl_6]$ are hexagonal, space group $P6_3/mmc$, Z = 2, with a = 9.499(4), c = 22.225(8) Å, and a = 9.341(4), c = 22.038(9) Å respectively. The structure of $[Hpy]_3[Sb_2Cl_9]$ has been refined to R = 0.037 for 1 975 observed reflections and shows a polymeric structure with three terminal and three bridging chlorine atoms similar to that of β-$Cs_3[Sb_2Cl_9]$. Refinement for the two tetramethylammonium salts (R = 0.140 for 385 and R = 0.115 for 408 observed reflections for the nona- and tri-bromides respectively) was very poor, probably as a consequence of disorder in the necessarily high symmetry of the space group but both show clearly confacial bioctahedral structures. In the mixed halide, the bridging positions are occupied by the bromine atoms.

Although it is possible to rationalise the structures of the monomeric halogenoantimonates $[SbX_4]^-$ and $[SbX_5]^{2-}$ for X = Cl, Br, or I on the basis of stereochemical activity of the $5s^2$ lone pair of electrons, problems arise with the $[SbX_6]^{3-}$ ion. The previously active lone pair must now be considered inactive to account for the observed regular octahedral geometry about antimony. An alternative view of such anions is to consider the successive addition of three halide ions, *trans* to the halogen atoms of the pyramidal SbX_3 molecule (see Figure 1). Since the bond angles in the SbX_3 molecule are close to 90°, Sb–X bonding can be represented by almost pure p orbitals on antimony. After addition of a halide ion, the electron density in both the Sb–X and $Sb \cdots X^-$ bonds may rearrange up to a point when these bonds become equal in length and the charge is equally shared. This is equivalent to treating each $(Cl \cdots Sb \cdots Cl)^-$ system by a three-centre four-electron approach. Using this method, pseudo-trigonal bipyramidal (*ca.* C_{2v} symmetry) and square pyramidal structures can be predicted for $[SbX_4]^-$ and $[SbX_5]^{2-}$ respectively, but this approach necessarily leads to octahedral geometry for $[SbX_6]^{3-}$ ions.

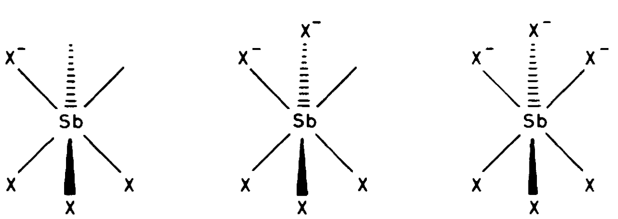

Figure 1. Formation of the $[SbX_4]^-$, $[SbX_5]^{2-}$, and $[SbX_6]^{3-}$ ions by successive addition of halide ions *trans* to halogens in SbX_3

More complex antimony halide anions are known containing bridging halogen atoms. Perhaps the best known are the $[Sb_2X_9]^{3-}$ species, where again there is an octahedral arrangement of halogen atoms about antimony and no real evidence for a stereochemically active lone pair. Of the six halogen atoms about a given antimony, three will necessarily be bridging and three terminal, and different structures are possible, depending on how bridging occurs. At one extreme, when bridging involves three different antimony atoms, there are the polymeric structures found in α-$Cs_3[Sb_2Cl_9]$[1] and β-$Cs_3[Sb_2Cl_9]$[2] while the other extreme is represented by the confacial bioctahedral structure observed for $[NMe_4]_3[Sb_2Br_9]\cdot Br_2$.[3] If bridging is based on both single and double halogen bridges it is possible to generate either discrete $[Sb_4X_{18}]^{6-}$ ions or polymers. An example of the latter occurs in the complex $Rb_3[Sb_2Cl_3F_6]\cdot Rb_3[SbCl_6]$[4] but the only example of a discrete tetrameric anion is found in the bismuth salt $[Hpy]_6[Bi_4Cl_{18}]$ [Hpy = pyridinium(1+)].[5] It is noteworthy that the only fluoride derivative of this stoicheiometry, *i.e.* $[Co(NH_3)_6][Sb_2F_9]$,[6] has a completely different structure with only one bridging fluorine atom, leaving the antimony atoms in five-fold co-ordination with strong evidence for a sterically active lone pair.

This work describes the preparation and characterisation of a series of $[Sb_2X_9]^{3-}$ compounds, where X can be chloride or bromide or a mixture of the two halogens. There are two interesting aspects of the structures of such compounds: first, when there are two different halogens present, which one will occupy the bridging positions, and secondly, at which stage in the $[Sb_2Br_nCl_{9-n}]$ series of anions would there be a change from the polymeric $[Sb_2Cl_9]^{3-}$ structure to the confacial bioctahedral structure of the nonabromide.

Experimental

Preparation of Pyridinium Nonahalogenodiantimonates.—$[Hpy]_3[Sb_2Cl_9]$ and $[Hpy]_3[Sb_2Br_9]$ were prepared by adding a solution of the pyridinium halide (3 mol) in the minimum volume of anhydrous ethanol to a solution of the appropriate, resublimed, antimony(III) halide (2 mol) in the same solvent. The product formed immediately and was recrystallised from

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† Tris(pyridinium) *catena*-tri-μ-chloro-hexachlorodiantimonate(3−), tris(tetramethylammonium) tri-μ-bromo-hexabromodiantimonate(3−), and tris(tetramethylammonium) tri-μ-bromo-hexachloro-antimonate(3−) respectively.

Supplementary data available (No. SUP 56478, 6 pp.): thermal parameters, calculated H-atom co-ordinates. 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. Preparation and analysis of $[Hpy]_3[Sb_2Br_nCl_{9-n}]$ (n = 0—9)

					Found (%)				Calc. (%)				
Compound	[Hpy]Cl g (mol)	[Hpy]Br g (mol)	$SbCl_3$ g (mol)	$SbBr_3$ g (mol)	C	H	N	Br	C	H	N	Br	Colour
$[Hpy]_3[Sb_2Cl_9]$	3.80 (0.032)		5.00 (0.022)		22.3	2.3	5.3		22.4	2.2	5.2		White
$[Hpy]_3[Sb_2BrCl_8]$	2.53 (0.022)	1.75 (0.011)	5.00 (0.022)		21.2	2.1	5.1	9.1	21.2	2.1	5.0	9.5	White
$[Hpy]_3[Sb_2Br_2Cl_7]$	1.26 (0.011)	3.50 (0.022)	5.00 (0.022)		20.4	2.0	4.8	17.2	20.2	2.0	4.7	17.9	Cream
$[Hpy]_3[Sb_2Br_3Cl_6]$		5.20 (0.033)	5.00 (0.022)		19.3	1.9	4.4	25.6	19.2	1.9	4.4	25.6	Yellow
$[Hpy]_3[Sb_2Br_4Cl_5]$	5.06 (0.044)	3.50 (0.022)	5.00 (0.22)	7.90 (0.022)	18.4	1.9	4.4	33.1	18.4	1.8	4.3	32.6	Pale yellow
$[Hpy]_3[Sb_2Br_5Cl_4]$	1.26 (0.011)	3.50 (0.022)	2.50 (0.011)	3.90 (0.011)	17.7	1.8	4.2	40.0	17.5	1.8	4.1	39.0	Yellow
$[Hpy]_3[Sb_2Br_6Cl_3]$	2.40 (0.021)			5.00 (0.014)	16.8	1.7	4.1	45.2	16.8	1.7	3.9	44.8	Yellow
$[Hpy]_3[Sb_2Br_7Cl_2]$	2.24 (0.019)	1.55 (0.010)		7.00 (0.019)	16.2	1.7	3.8	50.0	16.2	1.6	3.8	50.2	Yellow
$[Hpy]_3[Sb_2Br_8Cl]$	0.79 (0.007)	2.20 (0.014)		5.00 (0.014)	15.3	1.6	3.5	55.3	15.5	1.6	3.6	55.2	Pale orange
$[Hpy]_3[Sb_2Br_9]$		3.30 (0.021)		5.00 (0.014)	15.0	1.5	3.8	58.9	15.0	1.5	3.5	59.8	Orange

anhydrous ethanol. Members of the series $[Hpy]_3[Sb_2Br_nCl_{9-n}]$, where n = 1—8, were obtained similarly using mixtures of pyridinium halides and antimony(III) halides appropriate to the stoicheiometry of the required product. Preparative and analytical details are summarised in Table 1.

Attempts to prepare $[Hpy]_3[Sb_2I_9]$ from [Hpy]I and SbI_3 in anhydrous ethanol invariably led to $[Hpy][SbI_4]$, but the nonaiodide was obtained from a solution of pyridine (0.49 g, 0.006 mol) in 66% aqueous AnalaR hydroiodic acid added to a solution of antimony(III) iodide (2.0 g, 0.004 mol) in the same solvent. The precipitate, which formed immediately, was redissolved by heating and on cooling gave dark red crystals of $[Hpy]_3[Sb_2I_9]$ (Found: C, 11.0; H, 1.1; I, 71.2; N, 2.6. Calc. for $C_{15}H_{18}I_9N_3Sb_2$: C, 11.1; H, 1.1; I, 70.3; N, 2.6%).

$[Hpy]_3[Sb_2Cl_9]$ and $[Hpy]_3[Sb_2Br_9]$ were prepared similarly from solutions of pyridine and the antimony(III) halide in a 3:2 molar ratio with the appropriate concentrated acid HX as solvent.

Attempts to recrystallise $[Hpy]_3[Sb_2X_9]$ (X = Br or I) from hot concentrated hydrochloric acid gave $[Hpy][SbX_2Cl_2]$ (Found: C, 13.8; H, 1.4; Br, 36.9; N, 3.3. Calc. for $C_5H_6Br_2Cl_2NSb_2$: C, 13.9; H, 1.4; Br, 36.9; N, 3.2%. Found: C, 11.2; H, 1.2; I, 48.2; N, 2.7. Calc. for $C_5H_6Cl_2I_2NSb_2$: C, 11.4, H, 1.1; I, 48.2; N, 2.7%).

Preparation of Tetramethylammonium Nonahalogenodiantimonates.—$[NMe_4]_3[Sb_2Cl_9]$. Antimony(III) chloride (7.7 g, 0.034 mol) was dissolved in the minimum of anhydrous ethanol and to this was added to an ethanol solution of tetramethylammonium chloride (5.5 g, 0.05 mol). The white precipitate, which formed immediately, was redissolved by heating and on cooling gave white crystals, m.p. 320 °C (decomp.) (Found: C, 18.3; H, 4.6; N, 5.3. Calc. for $C_{12}H_{36}Cl_9N_3Sb_2$: C, 18.4; H, 4.6; N, 5.3%). This compound can also be prepared as described below for $[NMe_4]_3[Sb_2Br_9]$.

$[NMe_4]_3[Sb_2Br_9]$. To a solution of antimony(III) bromide (7.0 g, 0.019 mol) in 47% aqueous AnalaR hydrobromic acid was added an aqueous solution of tetramethylammonium hydroxide (1.3 g, 0.015 mol). The resulting dark orange precipitate was redissolved by warming and on cooling gave dark orange crystals, m.p. 340 °C (decomp.) (Found: C, 11.9; H, 3.1; N, 3.6. Calc. for $C_{12}H_{36}Br_9N_3Sb_2$: C, 12.1; H, 3.0; N, 3.5%).

$[NMe_4]_3[Sb_2Br_6Cl_3]$. Recrystallisation of $[NMe_4]_3[Sb_2Cl_9]$ from the minimum volume of hot 47% aqueous AnalaR hydrobromic acid gave $[NMe_4]_3[Sb_2Br_6Cl_3]$ as pale orange hexagonal plates (Found: C, 13.6; H, 3.4; Br, 46.2; N, 4.1. Calc. for $C_{12}H_{36}Br_6Cl_3N_3Sb_2$: C, 13.7; H, 3.4; Br, 45.7; N, 4.0%).

$[NMe_4]_3[Sb_2Br_3Cl_6]$. Recrystallisation of $[NMe_4]_3[Sb_2Br_9]$ from the minimum volume of hot concentrated hydrochloric acid gave the corresponding tribromide as pale yellow hexagonal plates (Found: C, 15.6; H, 3.9; Br, 27.0; N, 4.6. Calc. for $C_{12}H_{36}Br_3Cl_6N_3Sb_2$: C, 15.7; H, 3.9; Br, 26.2; N, 4.6%).

Preparation of Caesium Nonahalogenodiantimonates.—Compounds containing a single type of halogen, *i.e.* $Cs_3[Sb_2X_9]$ (X = Cl, Br, or I), were prepared from 3:2 mixtures of CsX and SbX_3 using concentrated HX as solvent. The product precipitated immediately and was recrystallised from concentrated HX. The chloride is white, the bromide orange, and the iodide dark red (Found: Cs, 42.1. Calc. for $Cl_9Cs_3Sb_2$: Cs, 41.5%. Found: Br, 51.7; Cs, 30.0. Calc. for $Br_9Cs_3Sb_2$: Br, 52.8; Cs, 29.3%. Found: Cs, 21.9; I, 63.0. Calc. for $Cs_3I_9Sb_2$: Cs, 22.3; I, 64.0%).

$Cs_3[Sb_2Br_3Cl_6]$ was prepared using a 3:2 mixture of CsBr and $SbCl_3$ in anhydrous methanol solution and recrystallised from methanol (Found: Br, 21.4; Cs, 36.0. Calc. for $Br_3Cl_6Cs_3Sb_2$: Br, 21.8; Cs, 36.4%). $Cs_3[Sb_2Br_6Cl_3]$ was similarly obtained from CsCl and $SbBr_3$ (3:2) (Found: Br, 38.9; Cs, 33.1. Calc. for $Br_6Cl_3Cs_3Sb_2$: Br, 39.0; Cs, 32.5%).

Crystal Structure of $[Hpy]_3[Sb_2Cl_9]$.—*Crystal data.* $C_{15}H_{18}Cl_9N_3Sb_2$, M = 802.9, monoclinic, a = 29.168(8), b = 10.178(5), c = 9.425(5) Å, β = 106.70(1)°, U = 2 680.0 Å^3, Z = 4, D_c = 1.98 g cm^{-3}, $F(000)$ = 1 536, space group $C2/c$ from systematic absences and subsequent refinement, Mo-K_α radiation, λ = 0.7107 Å, μ = 29.3 cm^{-1}, crystal radius μR = *ca.* 0.3 mm.

Structure determination. Crystals suitable for X-ray diffraction were obtained by slow recrystallisation from a solution of anhydrous HCl in ethanol. Data for 1 975 reflections with

Table 2. Atomic co-ordinates for $[Hpy]_3[Sb_2Cl_9]$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.102 29(1)	0.175 31(3)	0.398 58(4)
Cl(1)	0.0000	0.175 1(3)	0.2500
Cl(2)	0.111 06(9)	−0.026 5(2)	0.191 4(2)
Cl(3)	0.107 65(7)	0.328 8(2)	0.211 5(2)
Cl(4)	0.190 73(6)	0.179 0(2)	0.498 4(2)
Cl(5)	0.093 46(8)	0.361 8(2)	0.551 0(2)
N(1)	0.337 2(2)	0.242 8(8)	0.085 0(8)
C(2)	0.331 1(3)	0.116 0(9)	0.098 8(10)
C(3)	0.299 8(4)	0.050 8(8)	−0.009 2(13)
C(4)	0.273 6(3)	0.115 7(10)	−0.134 5(10)
C(5)	0.281 9(4)	0.245 6(11)	−0.147 9(9)
C(6)	0.313 6(4)	0.309 3(8)	−0.036 1(13)
N(7)	0.5000	0.344 9(11)	0.2500
C(8)	0.520 4(4)	0.280 2(12)	0.375 9(11)
C(9)	0.520 5(4)	0.148 5(10)	0.375 7(10)
C(10)	0.5000	0.082 0(13)	0.2500

$I > 3\sigma(I)$ were collected for a crystal sealed in a thin-walled Lindemann tube using a Hilger and Watts four-circle diffractometer. Corrections were made for Lorentz and polarisation effects but no absorption correction was necessary. Data reduction and subsequent calculations used the CRYSTALS[7] programs; scattering factors were for neutral atoms.[8] The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. As the asymmetric unit contains one half of the formula unit, one chlorine atom and the nitrogen and one carbon atom of a pyridinium cation lie on a two-fold axis at $\frac{1}{2}$, *y*, $\frac{1}{4}$. The refinement converged at $R = 0.094$ with isotropic and at $R = 0.042$ with anisotropic thermal parameters. Hydrogen-atom positions were obtained from a difference-Fourier synthesis and further refinement with these positions fixed gave final convergence at $R = 0.037$. Refined co-ordinates of the non-hydrogen atoms are listed in Table 2.

Attempts at refinement in the non-centric space group *Cc* gave non-convergence with unreasonable bond distances and angles for the pyridinium cations; the position of Cl(1), which lies on the two-fold axis in *C*2/*c*, refined back to this position in *Cc* and as the thermal parameters of this atom do not differ markedly from the others the position is not considered to be disordered.

Crystal structure of $[NMe_4]_3[Sb_2Br_9]$.—*Crystal data.* $C_{12}H_{36}Br_9N_3Sb_2$, $M = 1\,184.7$, hexagonal, $a = 9.499(4)$, $c = 22.225(8)$ Å, $U = 1\,736.7$ Å^3, $Z = 2$, $D_c = 2.26$ g cm^{-3}, $F(000) = 1\,092$, space group $P6_3/mmc$ from systematic absences and subsequent refinement, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 125.5$ cm^{-1}, crystal size 0.15 × 0.25 × 0.25 mm.

Structure determination. Data were collected and treated as described above for 1 136 reflections of which 385 were independent with $I > 3\sigma(I)$. These data were corrected for absorption using the ABSORB program;[9] scattering factors included the anomalous dispersion contributions for all non-hydrogen atoms. The solution employed closely followed that used for $[NMe_4]_3[Sb_2Br_9]\cdot Br_2$ by Hubbard and Jacobson.[3] The asymmetric unit consists of $\frac{1}{12}$ of the formula unit, *i.e.* $(NMe_4)_{\frac{1}{6}}(NMe_4)_{\frac{1}{12}}Sb_{\frac{1}{6}}Br_{\frac{3}{4}}$. Possible positions for the antimony and two independent bromine atoms were obtained from Patterson and Fourier syntheses at $\frac{1}{3}$, $\frac{2}{3}$, *z* (3*m* position, occupancy $\frac{1}{6}$) for antimony, at *x*, 2*x*, $\frac{1}{4}$ (*mm* position, occupancy $\frac{1}{4}$) for the bridging bromine, and at *x*, 2*x*, *z* (*m* position, occupancy $\frac{1}{2}$) for the terminal bromine atom. Refinement of the heavy-atom co-ordinates converged at $R = 0.211$ with isotropic and $R = 0.175$ with anisotropic thermal parameters.

Table 3. Atomic co-ordinates for $[NMe_4]_3[Sb_2Br_9]$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.3333	0.6667	0.160 9(3)
Br(1)	0.474 1(6)	0.949(1)	0.2500
Br(2)	0.200 3(5)	0.402(1)	0.096 4(3)
N(1)	0.0000	0.0000	0.2500
C(1)	0.1070	0.0535	0.1965
C(2)	−0.1038	0.0755	0.2500
N(2)	0.6667	0.3333	0.0995
C(3)	0.6667	0.3333	0.1665
C(4)	0.6824	0.1932	0.0788

Table 4. Atomic co-ordinates for $[NMe_4]_3[Sb_2Br_3Cl_6]$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.3333	0.6667	0.161 9(2)
Br(1)	0.476 9(5)	0.954(1)	0.2500
Cl(1)	0.205 0(6)	0.408(1)	0.097 4(4)
N(1)	0.0000	0.0000	0.2500
C(1)	0.1070	0.0535	0.1965
C(2)	−0.1038	0.0755	0.2500
N(2)	0.6667	0.3333	0.0995
C(3)	0.6667	0.3333	0.1665
C(4)	0.6824	0.1932	0.0788

A difference-Fourier synthesis then showed approximate positions for the cations. The two highest peaks were associated with the nitrogen atoms of the two independent cations at 0, 0, $\frac{1}{4}$ ($\bar{6}m2$ position, occupancy $\frac{1}{12}$) for N(1) and $\frac{2}{3}$, $\frac{1}{3}$, *z* (3*m* position, occupancy $\frac{1}{6}$) for N(2). Carbon atoms C(1) and C(2) attached to N(1), which exhibit three-fold site disorder, occur at 2*x*, *x*, *z* (*m* position, occupancy $\frac{1}{6}$) and *x*, *y*, $\frac{1}{4}$ (*m* position, occupancy $\frac{1}{6}$) respectively. C(3) at $\frac{2}{3}$, $\frac{1}{3}$, *z* (3*m* position, occupancy $\frac{1}{6}$) is not disordered, while C(4) in a general position is two-fold site disordered (occupancy $\frac{1}{2}$). Because of this disorder, least-squares refinement of the cation positions was not successful and the values in Table 3, although based on peaks from the difference Fourier synthesis, were constrained to represent NC_4 tetrahedra with C–N distances of *ca.* 1.48 Å. These positions contrast with those found by Hubbard and Jacobson.[3] The final *R* value was 0.140. As expected at this level of refinement, a difference map showed a large number of peaks with intensities up to 1.6 e Å^{-3}. The final atomic co-ordinates are listed in Table 3.

Crystal Structure of $[NMe_4]_3[Sb_2Br_3Cl_6]$.—*Crystal Data.* $C_{12}H_{36}Br_3Cl_6N_3Sb_2$, $M = 918.6$, hexagonal, $a = 9.341(4)$, $c = 22.038(9)$ Å, $U = 1\,665.3$ Å^3, $Z = 2$, $D_c = 1.83$ g cm^{-3}, $F(000) = 876$, space group $P6_3/mmc$ from systematic absences and subsequent refinement, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 59.5$ cm^{-1}, crystal size 0.15 × 0.35 × 0.40 mm.

Structure determination. Crystals for the determination were obtained by reaction of $[NMe_4]_3[Sb_2Br_9]$ with hot AnalaR hydrochloric acid followed by slow cooling of the solution. Data were collected for 712 observed reflections of which 408 were independent and treated as described previously. This compound is isostructural with $[NMe_4]_3[Sb_2Br_9]$ and the asymmetric unit again consists of $\frac{1}{12}$ of the formula unit, *i.e.* $(NMe_4)_{\frac{1}{6}}(NMe_4)_{\frac{1}{12}}Sb_{\frac{1}{6}}Br_{\frac{1}{4}}Cl_{\frac{1}{2}}$. Positions of the three heavy atoms were obtained from a Patterson synthesis followed by a difference-Fourier synthesis. The halogen atoms were initially all input as bromine atoms but after three cycles of refinement it was clear from the values of the isotropic thermal parameters that the terminal halogen atoms were, in fact, chlorines. Further refinement gave convergence with isotropic thermal parameters at $R = 0.157$. The absence of halogen disorder was confirmed by allowing the occupation factors of the two halogen atoms as well as the co-ordinates and thermal parameters to refine in two subsequent cycles. The problem of disorder in the cation positions was identical to that discussed for $[NMe_4]_3[Sb_2Br_9]$ and was treated similarly. The final stages of refinement with anisotropic thermal parameters for Sb, Br, and Cl converged at $R = 0.115$ and as for the nonabromide, a difference synthesis showed a number of peaks with electron density up to 1.6 e Å^{-3}. The final atomic co-ordinates are listed in Table 4.

Results and Discussion

Preparation of Compounds.—All the pyridinium salts in the series $[Hpy]_3[Sb_2Br_nCl_{9-n}]$ (n = 0—9) are readily obtained by recrystallising mixtures of $SbCl_3$, $SbBr_3$, [Hpy]Cl, and [Hpy]Br in the ratios required by the stoicheiometry [equation (1), where

$$x\mathrm{SbCl_3} + y\mathrm{SbBr_3} + a\mathrm{[Hpy]Cl} + b\mathrm{[Hpy]Br} \longrightarrow \mathrm{[Hpy]_3[Sb_2Br_nCl_{9-n}]} \quad (1)$$

$x + y = 2$ and $a + b = 3$] from anhydrous ethanol. Exclusion of oxygen is not necessary but the antimony halides must be resublimed before use and moisture excluded during the preparation otherwise hydrolysis occurs to give oxygen bridged compounds.[10] The compounds have no fixed melting points and sublime at temperatures above 250 °C. There is, as expected, a gradual increase in colour from white to pale orange as the bromine content increases. The two end members of the series can also be obtained from the pyridinium halide and antimony(III) halide in the appropriate concentrated acid but attempts to prepare mixed-halide species, for example, by recrystallising $[Hpy]_3[Sb_2Cl_9]$ from concentrated hydrobromic acid led to the mononuclear $[Hpy][SbBr_2Cl_2]$. This approach to mixed-halide salts was however successful with tetramethylammonium salts and recrystallisation of $[NMe_4]_3[Sb_2Cl_9]$ from concentrated hydrobromic acid and $[NMe_4]_3[Sb_2Br_9]$ from concentrated hydrochloric acid led to, respectively, $[NMe_4]_3[Sb_2Br_6Cl_3]$ and $[NMe_4]_3[Sb_2Br_3Cl_6]$. The nonachloride and nonabromide themselves could be obtained readily using either anhydrous ethanol or the concentrated acid as solvent.

The cesium salts $Cs_3[Sb_2X_9]$ (X = Cl, Br, or I) could be prepared using concentrated HX as the reaction medium while the mixed species, $Cs_3[Sb_2Br_3Cl_6]$ and $Cs_3[Sb_2Br_6Cl_3]$, were obtained from 3:2 mixtures of, respectively, CsBr and $SbCl_3$ and CsCl and $SbBr_3$.

Mass Spectra.—Mass spectra were obtained for all the pyridinium salts but they show only traces of species containing two antimony atoms, *e.g.* $[Sb_2Cl_7]^+$ was detected in the $[Hpy]_3[Sb_2Cl_9]$ spectrum, $[Sb_2Br_2]^+$ for both $[Hpy]_3[Sb_2Br_3Cl_6]$ and $[Hpy]_3[Sb_2Br_6Cl_3]$, and $[Sb_2Br_3]^+$ for the latter and $[Hpy]_3[Sb_2Br_9]$. This provides some evidence that bromines preferentially occupy the bridging positions when both chlorine and bromine atoms are present. The spectra, as shown for $[Hpy]_3[Sb_2Br_6Cl_3]$ and $[Hpy]_3[Sb_2Br_3Cl_6]$ in Table 5, contain all possible members of the $[SbCl_3]^+$, $[SbBr_3]^+$, and mixed-halide series. The $[SbBr_n]^+$ series of ions however, carry far more of the ion current (67.2%) in $[Hpy]_3[Sb_2Br_6Cl_3]$ than the $[SbCl_n]^+$ ions in the chlorine rich $[Hpy]_3[Sb_2Br_3Cl_6]$ (35.6%).

Table 5. Monoisotopic mass spectra, as % total ion current, for $[Hpy]_3[Sb_2Br_6Cl_3]$ and $[Hpy]_3[Sb_2Br_3Cl_6]$

	$[Hpy]_3[Sb_2Br_6Cl_3]$	$[Hpy]_3[Sb_2Br_3Cl_6]$
$[SbBr_3]^+$	24.7	3.4
$[SbBr_2]^+$	35.7	14.2
$[SbBr]^+$	6.8	1.9
$[SbCl_3]^+$	4.4	14.3
$[SbCl_2]^+$	0.1	13.4
$[SbCl]^+$		7.9
$[SbBr_2Cl]^+$	6.3	14.8
$[SbBrCl_2]^+$	2.4	9.9
$[SbBrCl]^+$	14.6	15.1

Vibrational Spectra.—It should be possible to obtain structural information from the i.r. and Raman spectra of the $[Sb_2X_9]^{3-}$ compounds and indeed the literature already contains a number of such studies, *e.g.* X = Cl,[11-14] Br,[14-17] and I.[14,18] Absorptions due to terminal and bridging Sb–Cl stretching modes occur in the reasonably well defined spectral regions of 340—270 and 240—200 cm^{-1} respectively; the corresponding Sb–Br modes occur at 250—170 and 170—120 cm^{-1} respectively. Group Theory will also give the number and activity of the terminal and bridging stretching modes for the confacial, bioctahedral (D_{3h} symmetry) and the polymeric $[Sb_2X_9]^{3-}$ structures (C_{3v} symmetry).

For this approach to be successful, it is necessary that the symmetry about antimony should correspond to one of the two above and that the spectra should be sufficiently well resolved to show discrete bands. It is most doubtful if either of these criteria is satisfied in the present investigation.

Spectra have been obtained using solid samples and where compounds have been investigated previously, there is general agreement. However, it has not been possible to make any definitive structural assignments mainly because the bands are very broad. Under these circumstances, it is not possible to separate out for example, the antisymmetric and symmetric SbX_n stretching modes; in the gas-phase spectra of $SbCl_3$ and $SbBr_3$ these differ by 22 and 7 cm^{-1} respectively.[19]

Solution spectra should give greater resolution but here there is high probability of anion dissociation.

X-Ray Powder Diffraction.—Powder diffraction data have been collected for all the compounds in this study. In the pyridinium series of salts there is a distinct difference between the powder patterns of the nonachloride and those of the bromine containing compounds $[Hpy]_3[Sb_2Br_nCl_{9-n}]$ (n = 3, 6, and 9). The nonaiodide pattern is of a third type. As described later $[Hpy]_3[Sb_2Cl_9]$ is isostructural with β-$Cs_3[Sb_2Cl_9]$ which has a polymeric structure,[2] and it is most likely that $[Hpy]_3[Sb_2I_9]$ will be confacial bioctahedral. The three bromine complexes appear to be isostructural, but with neither of these types and a full *X*-ray determination will it be necessary to solve the problem. Currently it has not been possible to obtain single crystals of any of the compounds.

There is a similar difference in powder patterns between $[NMe_4]_3[Sb_2Cl_9]$ and the related tri-, hexa-, and nonabromides, the latter appearing to be isostructural. Full *X*-ray structure determinations of two of these compounds, $[NMe_4]_3[Sb_2Br_3Cl_6]$ and $[NMe_4]_3[Sb_2Br_9]$, have been determined as confacial bioctahedral and are described in detail below. The third bromide, $[NMe_4]_3[Sb_2Br_6Cl_3]$, then has the same structure. A polymeric structure is suggested by the powder diffraction data for $[NMe_4]_3[Sb_2Cl_9]$.

Powder patterns for the caesium series of compounds are different in the sense that here the nonachloride, nonabromide,

Table 6. Unit-cell parameters for $Cs_3[Sb_2Br_nCl_{9-n}]$ (n = 0, 3, 6, or 9)

	β-$Cs_3[Sb_2Cl_9]$*	$Cs_3[Sb_2Br_3Cl_6]$	$Cs_3[Sb_2Br_6Cl_3]$	$Cs_3[Sb_2Br_9]$
a/Å	7.63 (7.630)	7.69	7.76	7.86
b/Å	13.17 (13.079)	13.92	14.17	14.07
c/Å	18.70 (18.633)	18.86	19.05	19.11
U/Å^3	1 879 (1 862.4)	2 019	2 095	2 113
D_c/g cm^{-3}	3.39	3.59	3.88	4.27

* Values in parentheses are taken from ref. 2.

Table 7. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[Hpy]_3[Sb_2Cl_9]$*

Sb(1)–Ci(1)	2.909	Sb(1)–Cl(4)	2.479(2)
Sb(1)–Cl(2)	2.896(2)	Sb(1)–Cl(5)	2.438(2)
Sb(1)–Cl(2′)	3.093(3)	N(1)–Cl(2)	3.225(7)
Sb(1)–Cl(3)	2.394(2)	N(7)–Cl(1)	3.36(1)
Cl(1)–Sb(1)–Cl(2)	87.24(7)	Cl(1)–Sb(1)–Cl(4)	173.80(5)
Cl(1)–Sb(1)–Cl(2′)	103.86(6)	Cl(1)–Sb(1)–Cs(5)	90.97(7)
Cl(1)–Sb(1)–Cl(3)	85.47(6)		
Cl(2)–Sb(1)–Cl(2′)	104.69(2)	Cl(2)–Sb(1)–Cl(4)	89.01(7)
Cl(2)–Sb(1)–Cl(3)	85.95(7)	Cl(2)–Sb(1)–Cl(5)	173.86(7)
Cl(2′)–Sb(1)–Cl(3)	165.98(7)	Cl(2′)–Sb(1)–Cl(5)	81.44(6)
Cl(2′)–Sb(1)–Cl(4)	81.87(6)		
Cl(3)–Sb(1)–Cl(4)	89.34(6)	Cl(4)–Sb(1)–Cl(5)	92.24(7)
Cl(3)–Sb(1)–Cl(5)	88.05(7)		
Sb(1)–Cl(1)–Sb(1″)	179.9(1)	Sb(1″)–Cl(1)–N(7)	90.0(1)
Sb(1)–Cl(2)–Sb(1′)	161.5(1)	Sb(1)–Cl(2)–N(1)	100.9(1)
Sb(1)–Cl(1)–N(7)	90.0(1)	Sb(1′)–Cl(2)–N(1)	97.6(1)

* Atoms carrying a prime are related to the unprimed atoms by the transformation $x, y, z \longrightarrow x, -y, z - \frac{1}{2}$; atoms carrying a double prime are related to the unprimed atoms by the transformation $x, y, z \longrightarrow -x, y, \frac{1}{2} - z$.

and the two mixed bromide chlorides appear to be isostructural while the pattern for $Cs_3[Sb_2I_9]$ is markedly different. $Cs_3[Sb_2I_9]$ is known to have the triply-bridged bioctahedral structure[20] while there are two modifications of $Cs_3[Sb_2Cl_9]$, both of which have polymeric structures.[1,2] Our data for $Cs_3[Sb_2Cl_9]$ can be indexed as the orthorhombic β modification (space group *Pmcn*); the alternative α form is trigonal (space group *P*321). The other three caesium salts could also be indexed on the basis of a similar orthorhombic cell leading to the cell parameters, volumes, and calculated densities listed in Table 6.

Structure of $[Hpy]_3[Sb_2Cl_9]$.—Bond distances and angles associated with the heavier atoms are collected in Table 7; the mean C–C and C–N distances in the pyridinium cations are 1.35 and 1.33 Å respectively and the mean bond angle is 120°. The independent antimony atom is bonded to six chlorine atoms whose distances fall into two groups, *i.e.* those which are terminal atoms at distances of 2.394(2), 2.438(2), and 2.479(2) Å (mean 2.44 Å), and the bridging atoms which lie at 2.896(2), 2.909, and 3.093(3) Å (mean 2.97 Å) from the central atom. These can be compared with mean terminal and bridging distances of 2.43 and 3.08 Å respectively in the polymeric $[NHMe_3]_3[Sb_2Cl_9]$.[11] The angles between the terminal, primary bonded, atoms are close to 90°, *i.e.* 88.1, 89.3 and 92.2°, while those between the bridging, secondary bonded, atoms, *i.e.* 87.2, 103.9, and 104.7°, are more variable with two substantially greater than 90°. The arrangement is clearly distorted octahedral; this is further shown by *trans* angles of 166.0, 173.8, and 173.9°. There is no apparent site for a stereochemically active lone pair.

Of the bridging chlorine atoms, Cl(1) lies on a two-fold axis, necessarily leading to a symmetrical bridge but the Sb(1)–Cl(1)–Sb(1″) bond angle at 179.9(1)° is very large. Such angles generally fall in the range 120—160°. Although there is the possibility of disorder across the two-fold axis, as found for the bridging atom in $[Co(NH_3)_6][Sb_2F_9]$,[6] refinement showed that this was not the case and, indeed, there is no crystallographic constraint on the Cl(1) bond angle. The second bridging system is less symmetrical (Sb–Cl 2.90, 3.09 Å) with a reduced (161.5°) bond angle.

The bridging system develops a polymeric structure (see Figure 2), very similar to that in β-$Cs_3[Sb_2Cl_9]$. Although the latter was described in terms of a close-packed arrangement of caesium and chlorine atoms with the antimony atoms occupying two thirds of the chlorine octahedral sites, the present interpretation stresses the covalent nature of the antimony–chlorine interactions which fall well within the sum of the van der Waals radii. Figure 2 shows separately the orientations of the double chain anions ('pleated ribbon' structure) and the pyridinium cations. In the β modification of the caesium salt, which crystallises in the space group *Pmcn*, a non-standard setting of *Pnma*, the double chain packing is different. This is perhaps a consequence of the different steric requirements of the two cations and the hydrogen-bonding capabilities of the pyridinium cation.

The pyridinium cations are hydrogen bonded to the three bridging chlorine atoms Cl(1), Cl(2), and Cl(2′) giving Cl ··· N distances of 3.36, 3.23, and 3.23 Å respectively. Using hydrogen positions from a difference map, the N(1)–H(1) and Cl(2) ··· H(1) distances are 0.96 and 2.31 Å respectively with a value of 160.3° for the N(1)–H(1)–Cl(2) angle; the corresponding N(7)–H(7) and Cl(1) ··· H(7) distances are 1.01 and 2.36 Å and the angle is necessarily 180°.

Structures of $[NMe_4]_3[Sb_2Br_9]$ *and* $[NMe_4]_3[Sb_2Br_3Cl_6]$.—Although there are problems with the poor state of refinement for both these compounds, there is no doubt that both anions adopt the triply-bridged octahedral structure shown for the tribromide in Figure 3. One of the problems leading to the poor state of refinement is undoubtedly the disorder forced on the cations by the space group symmetry, but even allowing for this the final *R* values are extremely high for a modern *X*-ray study. It is worth noting in passing that poor refinements have been obtained previously[3] for this type of compound and although the cause is uncertain it is probably a function of disorder forced by the high symmetry.

Because of this high symmetry the anions are defined by only two antimony–halogen distances, associated with the bridging and terminal atoms respectively; these are listed together with the five angles in Table 8. The terminal distances are normal for single bonds but there is a decrease of *ca.* 0.02 Å in the Sb–Br(bridging) distance in the $[Sb_2Br_3Cl_6]^{3-}$ anion, probably a consequence of the increased Lewis acidity of the antimony atom. The Sb ··· Sb separation in this anion is also decreased slightly (*ca.* 0.08 Å) compared with that in $[Sb_2Br_9]^{3-}$ following a small decrease in angle at the bridging bromine atom and a slight increase in the angle at antimony between the bridging bromine atoms.

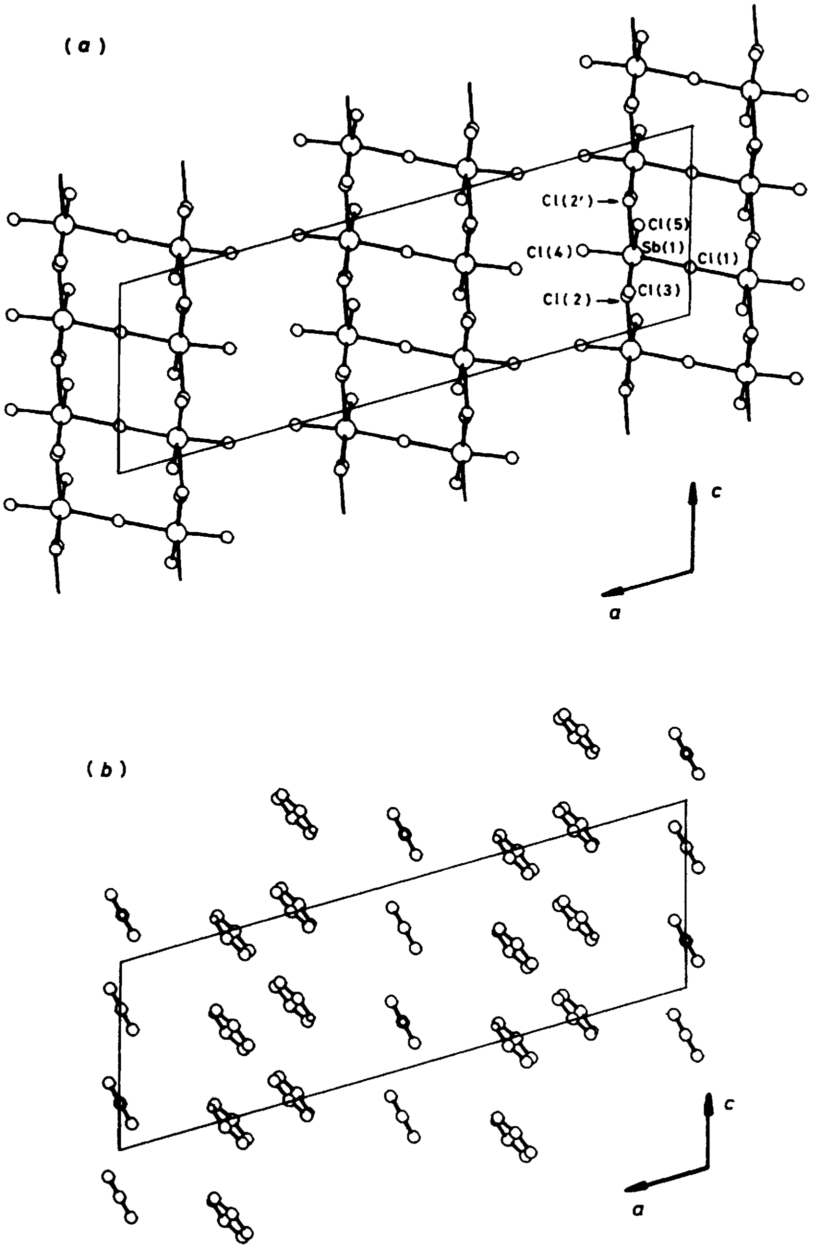

Figure 2. Projection of the unit-cell contents on to the *ac* plane for $[Hpy]_3[Sb_2Cl_9]$ showing (*a*) the double chain ('ribbon') structure of the polymeric anion and (*b*) the orientation of the pyridinium cations

The geometry about antimony is basically octahedral with no stereochemical position for the lone pair of electrons, but the expected deviations from 90°-angles are observed in the closing of the angles between bridging bromines and corresponding increases in those between terminal atoms.

Compounds previously investigated containing the $[Sb_2Br_9]^{3-}$ anion have included either two additional bromide ions[21] or a molecule of bromine.[3] The latter was disordered and bridged between terminal bromines of neighbouring $[Sb_2Br_9]^{3-}$ anions; the stability of the red product was attributed partially to this bromine bridge. In the present investigation the orange, uncomplexed $[NMe_4]_3[Sb_2Br_9]$ was used and showed no evidence of instability.

The discrete dimeric structure for $[Sb_2Br_9]^{3-}$ is not unexpected but the same structure for $[Sb_2Br_3Cl_6]^{3-}$ is probably a direct consequence of three bromine atoms which

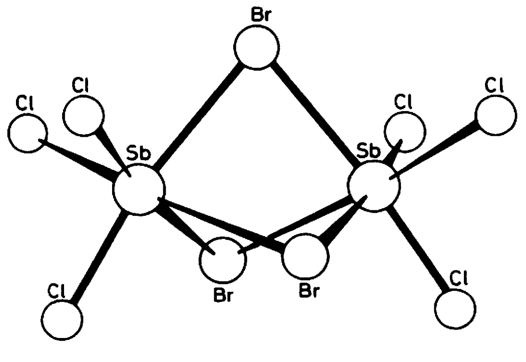

Figure 3. Structure of the anion in $[NMe_4]_3[Sb_2Br_3Cl_6]$

Table 8. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[NMe_4]_3[Sb_2Br_9]$ and $[NMe_4]_3[Sb_2Br_3Cl_6]$[a]

$[NMe_4]_3[Sb_2Br_9]$		$[NMe_4]_3[Sb_2Br_3Cl_6]$	
Sb(1)–Br(1)[b]	3.051(4)	Sb(1)–Br(1)[b]	3.027(2)
Sb(1)–Br(2)[c]	2.610(4)	Sb(1)–Cl(1)[c]	2.525(2)
Sb(1) ··· Sb(1′)	3.959(5)	Sb(1) ··· Sb(1′)	3.881(3)
Br(1)–Sb(1)–Br(2)	172.9(2)	Br(1)–Sb(1)–Cl(1)	174.3(2)
Br(1)–Sb(1)–Br(1″)	82.4(2)	Br(1)–Sb(1)–Br(1″)	83.3(2)
Br(1)–Sb(1)–Br(2″)	92.2(2)	Br(1)–Sb(1)–Cl(1″)	92.4(2)
Br(2)–Sb(1)–Br(2″)	92.7(2)	Cl(1)–Sb(1)–Cl(1″)	91.6(2)
Sb(1)–Br(1)–Sb(1′)	80.9(2)	Sb(1)–Br(1)–Sb(1′)	79.8(2)

[a] Atoms carrying single and double primes are related to unprimed atoms by the relationships $x, y, z \longrightarrow x, y, \frac{1}{2} - z$ and $x, y, z \longrightarrow 1 - y, 1 + x - y, z$ respectively. [b] Bridging. [c] Terminal.

can occupy the bridging positions. The heavier halogen atoms in $Rb_3[Sb_2Cl_3F_6]$[4] also occupy bridging positions but this compound is still polymeric with a system of double and single chlorine bridges. In passing it should be noted that although only polymeric structures have been observed for $[Sb_2Cl_9]^{3-}$ species, the related $[Sb_2OCl_6]^{2-}$ anion has a discrete structure where two antimony atoms are bridged by one oxygen and two chlorine atoms.[10]

Factors influencing the type of structure adopted by $[Sb_2X_9]^{3-}$ anions include the following: the size of the cation and the possibility of specific interactions with the anion, the size of the halogen atoms and the residual charges carried by these atoms.

A large cation may inhibit formation of a polymeric anion simply by steric effects and specific cation–anion interactions, particularly hydrogen bonding, could modify the anion structure. This does occur as the $[Sb_2Cl_9]^{3-}$ ribbons are differently oriented in the unit cells of β-$Cs_3[Sb_2Cl_9]$ and $[Hpy]_3[Sb_2Cl_9]$, but it is doubtful if hydrogen bonding would be sufficiently important to determine whether a polymeric or bioctahedral structure would result.

A more major influence on structure is the size of the halogen. Electronic and steric factors in connection with mainly transition-metal M_2L_9 species have been investigated by Summerville and Hoffmann[22] and Cotton and Ucko,[23] the latter considering an ideal situation where bridging and terminal distances are equal thus giving an angle of 70.53° at the bridging atom. In real systems the two distances will be unequal, with bridging angles smaller than the ideal value in strongly metal–metal bonded compounds but greater than 70.53° when the central atoms are main group elements. In an $[Sb_2X_9]^{3-}$ species a discrete bioctahedral structure would be expected if the bridging atoms were large enough to prevent too close an approach of the antimony atoms. The bridging angle would also increase, in the present cases to *ca.* 80°, giving a greater Sb ··· Sb separation. Within the constraints of this desirable geometry, atom separations should be such as to minimise repulsions between the bridging atoms themselves but also to allow for the strongest possible Sb–X(bridge) bonding. Sb ··· Sb separations will increase in the order F < Cl < Br < I and the conditions can generally be met by bridging bromine and iodine atoms; in mixed-halide systems the larger halogens would preferentially occupy the bridging positions. With fluorine or chlorine as bridging atoms, the bioctahedral structure is not observed probably because at distances giving strong bridge bonding, both Sb ··· Sb and halogen–halogen interactions are too large.

Table 9. Statistically determined single and half bond lengths for antimony(III)- and bismuth(III)-halogen systems

System	$D(1)$/Å	$D(0.5)$/Å	k
Sb–F	1.94	2.07	0.43
Sb–Cl	2.32	2.62	1.00
Sb–Br	2.46	2.79	1.10
Sb–I	2.65	3.02	1.26
Bi–Cl	2.45	2.66	0.70
Bi–Br	2.54	2.85	1.03
Bi–I	2.62	3.08	1.53

Table 10. Bond order and residual charge calculations

	d/Å	n	δ
(*i*) $[Hpy]_3[Sb_2Cl_9]$[a]			
Sb–Cl(b)[b]	2.97	0.25	0.50
Sb–Cl(t)	2.44	0.75	0.25
(*ii*) $[NMe_4]_3[Sb_2Br_9]$			
Sb–Br(b)	3.051(4)	0.29	0.42
Sb–Br(t)	2.610(4)	0.72	0.28
(*iii*) $[NMe_4]_3[Sb_2Br_3Cl_6]$			
Sb–Br(b)	3.027(2)	0.31	0.38
Sb–Cl(t)	2.525(2)	0.63	0.37

[a] Mean bond lengths used. [b] b = Bridging, t = terminal.

The final consideration is the possibility of delocalisation of the anion charge *via* secondary bonding. One approach to this is to calculate the apparent residual charge (δ) at a specific halogen atom, which is related to the sum of the bond orders, n, of all the interactions involving that halogen atom, *i.e.* $\delta = 1 - \Sigma n$. The bond order, n, can be obtained from the Pauling relationship[24] (2), where $D(n)$ = observed bond length, $D(1)$ =

$$D(n) = D(1) - k \log n \qquad (2)$$

single bond length, and k = a constant. The significance of the constant k can be seen by rearranging equation (2) and considering a bond of order 0.5, when $k = [D(0.5) - D(1)]/0.3101$. An antimony–halogen bond of order 0.5 represents a situation where the lengths of the two Sb–X bonds *trans* to each other at an antimony(III) centre are equal.

Because of secondary bonding effects, antimony–halogen bond lengths vary over a very wide range; most data are available for Sb–Cl systems where, for example, separations range between 2.3 and 3.5 Å. Using statistical methods, Hall[25] has analysed these data to give the best values for $D(0.5)$ and $D(1)$, collected in Table 9, from which values for k can be calculated. Table 9 also includes the results of a similar analysis for bismuth systems. Because fewer structures have been determined for Sb–I, Bi–Cl, and Bi–I anions, their entries in Table 9 are less certain.

Bond orders, and thus residual charges, can now be calculated (see Table 10). Two points arise. First, the residual charge carried by a bridging bromine atom (*ca.* 0.4) is substantially less than that carried by a bridging chlorine (*ca.* 0.5), though it is doubtful if the smaller residual charge on bromine in $[Sb_2Br_3Cl_6]^{3-}$ compared with $[Sb_2Br_9]^{3-}$ can be fully justified by these simple calculations. It would, however, be in accordance with general electronegativity effects. Secondly, there is an increase in the bridge bond order from 0.25 in $[Sb_2Cl_9]^{3-}$ to *ca.* 0.3 in $[Sb_2Br_9]^{3-}$. Extension of these calculations to $[Sb_2I_9]^{3-}$ shows that the trend continues, with bridging iodine atoms showing greater charge delocalisation and higher bond order. The high residual charge carried by bridging chlorine atoms in conjunction with the size argument above thus make it very unlikely that triply-bridged bioctahedral $[Sb_2Cl_9]^{3-}$ structures would form. Because of difficulties in obtaining single crystals of salts containing the $[Sb_2Br_2Cl_7]^{3-}$ and $[Sb_2BrCl_8]^{3-}$ anions, it has not yet been possible to test whether or not three bromine atoms are required in bridging positions to stabilise the confacial bioctahedral structure.

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