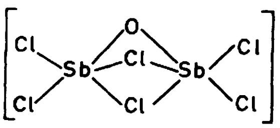
Halogeno-oxydiantimon(III)ates

Michael Hall, Michael Nunn, and D. Bryan Sowerby *
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Compounds in the halogeno-oxydiantimonate series, $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ [n = 0—6, Hpy = pyridinium(1+)], have been synthesised by partial hydrolysis from related $[Hpy]_3[Sb_2Br_nCl_{9-n}]$ species and characterised by vibrational spectroscopy and mass spectrometry. The hexachloride $[Hpy]_2[Sb_2OCl_6]$ also results from the action of adventitious water on solutions of antimony(III) chloride and pyridine.

We have previously reported the preparation of a series of nonahalogenodiantimon(III)ates, $Y_3[Sb_2Br_nCl_{9-n}]$ {Y = Hpy [pyridinium(1+)], NMe_4^+, or Cs^+}, which contain six terminal and three bridging halogen atoms.[1] The nonachloride, $[Hpy]_3[Sb_2Cl_9]$, for example, has a polymeric structure, as the three chlorines bridge to different antimony atoms, while in both $[NMe_4]_3[Sb_2Br_9]$ and $[NMe_4]_3[Sb_2Br_3Cl_6]$ there are three bromine bridges between a given pair of antimony atoms generating discrete, confacial bioctahedral structures. Differences between the chlorine and bromine structures can be related to differences in both halogen sizes and the residual charges carried by the bridging atoms. In a preliminary communication,[2] we have also shown that $[Hpy]_3[Sb_2Cl_9]$ can be partially hydrolysed on recrystallisation from moist ethanol to give unexpectedly the pyridinium salt of a discrete chloro-oxydiantimonate, $[Sb_2OCl_6]^{2-}$ (1), where the two antimony atoms are bridged by one oxygen and two chlorine atoms. This paper describes an extension of this preparative work. Details of the *X*-ray structure determinations on three compounds of this type, $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ (n = 0, 2, and 4), will be reported later.[3]



(1)

Experimental

Preparation of $[Hpy]_2[Sb_2OCl_6]$.—(*a*) *From* Sb_2O_3. A suspension of antimony(III) oxide in water was treated with concentrated hydrochloric acid until the oxide just dissolved. A solution of pyridine in water was then added and a white precipitate formed immediately. On warming, the precipitate redissolved and cooling gave crystals of $[Hpy]_2[Sb_2OCl_6]$ in high yield, m.p. 181 °C (decomp.) (Found: C, 19.1; H, 2.0; Cl, 33.8; N, 4.4. Calc. for $C_{10}H_{12}Cl_6N_2OSb_2$: C, 19.0; H, 1.9; Cl, 33.7; N, 4.4%).

(*b*) *From pyridine and antimony*(III) *chloride*. Equimolar quantities of reagent-grade pyridine and resublimed antimony(III) chloride were dissolved separately in dichloromethane. Mixing the solutions gave an immediate precipitate of the compound in an almost quantitative yield. Suitable recrystallisation solvents were absolute ethanol or glacial acetic acid.

(*c*) *From* $[Hpy]_3[Sb_2Cl_9]$. Recrystallisation of this compound from ethanol containing *ca.* 1% water gave $[Hpy]_2[Sb_2OCl_6]$ in good yield.

Preparation of $[Hpy]_2[Sb_2OBr_6]$.—Recrystallisation of $[Hpy]_3[Sb_2Br_9]$ from moist ethanol as described above gave the corresponding oxybromide. The compound could be recrystallised from anhydrous ethanol but from glacial acetic acid the product was $[Hpy][SbBr_4]$ (Found: C, 12.9; H, 1.5; N, 3.1. Calc. for $C_{10}H_{12}Br_6N_2OSb_2$: C, 13.3; H, 1.3; N, 3.1%. Found: C, 11.5; H, 1.1; Br, 59.9; N, 2.8. Calc. for $C_5H_6Br_4NSb$: C, 11.5; H, 1.2; Br, 61.3; N, 2.7%).

Preparation of $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ (n = 1—5).—Compounds in this series could be produced by recrystallising the appropriate mixed nonahalogenodiantimonate from moist ethanol as described above. Preparative and analytical data are summarised in Table 1. All compounds, which were obtained in near quantitative yield, can be recrystallised from anhydrous ethanol. They melt with decomposition at *ca.* 180 °C.

Attempted Preparation of $[Hpy]_2[Sb_2OI_6]$.—Attempts to prepare this compound by the methods outlined above for $[Hpy]_2[Sb_2OCl_6]$ were unsuccessful.

Piperidinium Salts.—Equimolar solutions of piperidinium(1+) (Hpip) and either antimony(III) chloride or bromide in moist ethanol on mixing gave immediate precipitates of $[Hpip]_2[Sb_2OX_6]$ (X = Cl or Br) (Found: C, 18.6; H, 3.9; N, 4.5. Calc. for $C_{10}H_{24}Cl_6N_2OSb_2$: C, 18.6; H, 3.7; N, 4.3%. Found: C, 13.2; H, 2.8; N, 3.2. Calc. for $C_{10}H_{24}Br_6N_2OSb_2$: C, 13.2; H, 2.6; N, 3.1%).

Tetramethylammonium and Caesium Salts.—Crystallisation of either $[NMe_4]_3[Sb_2X_9]$ or $Cs_3[Sb_2X_9]$ (X = Cl or Br) from ethanol containing 1—2% water led to recovery of the unchanged starting materials. With >5% water, the caesium salts decomposed to presumably insoluble oxide halides or oxides.

Preparation of $[Hpy]_2[Sb_3OCl_9]$.—This addition compound was prepared by coprecipitation from a solution of $[Hpy]_2[Sb_2OCl_6]$ and a ten-fold excess of resublimed antimony(III) chloride in glacial acetic acid solution (Found: C, 13.8; H, 1.4; Cl, 36.8; N, 3.3. Calc. for $C_{10}H_{12}Cl_9N_2OSb_3$: C, 13.9; H, 1.4; Cl, 37.1; N, 3.3%). Similar reactions between $[Hpy]_2[Sb_2OBr_3Cl_3]$ and an excess of either $SbCl_3$ or $SbBr_3$ led to ion exchange and isolation of $[Hpy]_2[Sb_2OCl_6]$ and $[Hpy]_2[Sb_2OBr_6]$ respectively.

Results and Discussion

Compounds with the formula $[Hpy]_2[Sb_2OX_6]$, where X is either chlorine, bromine, or a mixture of the two halogens, can be readily obtained in high yields as stable crystalline solids. The most general method is *via* partial hydrolysis of a

Table 1. Preparation of halogeno-oxydiantimonates $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ (n = 0—6)

		Microanalysis (%)								
		Found				Calc.				Colour (i) Reactant (ii) Product
Reactant	Product	C	H	N	Br	C	H	N	Br	
$[Hpy]_3[Sb_2BrCl_8]$	$[Hpy]_2[Sb_2OCl_6]$	19.0	1.9	4.3	—	19.0	1.9	4.3	—	(i) White (ii) White
$[Hpy]_3[Sb_2Br_2Cl_7]$	$[Hpy]_2[Sb_2OBrCl_5]$	17.4	1.8	3.7	11.3	17.7	1.8	4.1	11.8	(i) Cream (ii) White
$[Hpy]_3[Sb_2Br_3Cl_6]$	$[Hpy]_2[Sb_2OBr_2Cl_4]$	16.5	1.7	3.8	22.4	16.6	1.7	3.9	22.2	(i) Yellow (ii) White
$[Hpy]_3[Sb_2Br_4Cl_5]$	$[Hpy]_2[Sb_2OBr_3Cl_3]$	15.8	1.6	3.8	31.6	15.7	1.6	3.6	31.3	(i) Yellow (ii) White
$[Hpy]_3[Sb_2Br_5Cl_4]$	$[Hpy]_2[Sb_2OBr_3Cl_3]$	15.9	1.6	3.7	31.7	15.7	1.6	3.6	31.3	(i) Yellow (ii) White
$[Hpy]_3[Sb_2Br_6Cl_3]$	$[Hpy]_2[Sb_2OBr_4Cl_2]$	14.8	1.5	3.4	38.5	14.8	1.5	3.4	39.4	(i) Yellow (ii) White
$[Hpy]_3[Sb_2Br_7Cl_2]$	$[Hpy]_2[Sb_2OBr_5Cl]$	14.1	1.4	3.1	45.8	14.0	1.4	3.3	46.8	(i) Yellow (ii) Pale yellow
$[Hpy]_3[Sb_2Br_8Cl]$	$[Hpy]_2[Sb_2OBr_6]$	13.1	1.3	3.2	49.3	13.3	1.3	3.1	53.3	(i) Pale orange (ii) Pale yellow

nonahalogenodiantimonate by recrystallisation from ethanol containing a small amount of water [equation (1)]. The complete series of mixed bromide chlorides, $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$, required mixed-halide starting materials. In all these processes three halogens are lost and, depending on whether the starting material is bromine or chlorine rich, halogen loss will involve either two bromines and one chlorine or one bromine and two chlorines [equations (2) and (3)].

$$[Hpy]_3[Sb_2X_9] + H_2O \longrightarrow [Hpy]_2[Sb_2OX_6] + [Hpy]X + 2HX \quad (1)$$

X = Cl or Br

$$[Hpy]_3[Sb_2Br_nCl_{9-n}] \xrightarrow[-Br^-,\,-2Cl^-]{+H_2O} [Hpy]_2[Sb_2OBr_{n-1}Cl_{7-n}] \quad (2)$$

n = 1—3

$$[Hpy]_3[Sb_2Br_nCl_{9-n}] \xrightarrow[-2Br^-,\,-Cl^-]{+H_2O} [Hpy]_2[Sb_2OBr_{n-2}Cl_{8-n}] \quad (3)$$

n = 4—8

The corresponding iodide could not be prepared by this method; small amounts of water gave only unchanged $[Hpy]_3[Sb_2I_9]$, but complete decomposition to insoluble solids occurred with increased amounts of water. This is probably a consequence of low polarity of the Sb–I bonds which reduces hydrolytic susceptibility and the high degree of steric protection provided by large iodide ions. A similar effect occurred in the mixed bromide chloride series when larger amounts of water were necessary to hydrolyse the bromine rich reactants.

The second method is from pyridine and an antimony(III) halide. The well known Lewis acidity of the latter would suggest ready formation of pyridine addition compounds, but Brodie and Wilkins[4] obtained neither $SbCl_3{\cdot}py$ nor $SbCl_3{\cdot}2py$ even with dried reagents. Their product, which had a distinctive i.r. spectrum and *X*-ray powder diffraction pattern, is most likely $[Hpy]_2[Sb_2OCl_6]$. Our attempts to prepare discrete adducts were similarly unsuccessful, even though anhydrous materials were used, and if $SbCl_3$–py addition compounds are formed, they are exceedingly unstable to hydrolysis and rapidly convert to the observed product $[Hpy]_2[Sb_2OCl_6]$. Although there is no unambiguous evidence for the initial formation of $SbCl_3{\cdot}py$, similar compounds are known and single-crystal *X*-ray structures are available for, *inter alia*, $SbCl_3{\cdot}NH_2Ph$,[5] $SbCl_3{\cdot}2NH_2Ph$,[5] and $SbCl_3{\cdot}$bipy (bipy = 2,2′-bipyridine).[6] In addition, normal 1:1 and 1:2 addition compounds can be isolated from solutions of $[SbPhCl_2]$ and pyridine in chloroform.[7]

In spite of the ready formation of $[Sb_2OX_6]^{2-}$ species from $[Sb_2X_9]^{3-}$ starting materials, the hydrolysis reaction is strongly cation dependent and appears to proceed only with those such as pyridinium or piperidinium, which are capable of hydrogen bonding. Attempts using $Cs_3[Sb_2X_9]$ or $[NMe_4]_3[Sb_2X_9]$ gave either unchanged starting materials with small amounts of water or the products of complete hydrolysis with larger amounts. The crystal-structure determinations[2,3] show that strong hydrogen bonding between cation and anion is a major feature in these systems.

$[Hpy]_2[Sb_2OCl_6]$ is soluble only in polar solvents such as ethanol and glacial acetic acid and with acetic anhydride is converted to $[Hpy]_2[SbCl_5]$ and presumably $[Sb(O_2CMe)_3]$. With thioacetic acid it yields the corresponding thioacetate, $[Sb(SOCMe)_3]$.[8] Attempted halogen-exchange reactions using either KBr or KI in ethanol gave the tetrahalogenoantimonates, $[Hpy][SbX_4]$ (X = Br or I), but there was no reaction between $[Hpy]_2[Sb_2OCl_6]$ and potassium acetate in glacial acetic acid at 80 °C.

A 1:1 addition compound, $[Hpy]_2[Sb_3OCl_9]$, was isolated from the hexachloride and a ten-fold excess of antimony(III) chloride in glacial acetic acid, but in reactions of $[Hpy]_2[Sb_2OBr_3Cl_3]$ with either $SbCl_3$ or $SbBr_3$ halogen exchange takes place preferentially to give $[Hpy]_2[Sb_2OCl_6]$ and $[Hpy]_2[Sb_2OBr_6]$ respectively.

$[Hpy]_2[Sb_2OCl_6]$ sublimes at *ca.* 140 °C with slight decomposition in a dynamic vacuum while on heating at atmospheric pressure, pyridine, and presumably water, are lost to leave a residue of the addition compound $[Hpy]_2[Sb_3OCl_9]$.

Vibrational Spectra.—Details of the i.r. and Raman spectra of solid samples in the range below 520 cm^{-1} are collected in Table 2; the region above 520 cm^{-1} shows bands associated with the pyridinium cations and is almost identical for each compound. A major feature of each spectrum is the strong i.r. and Raman band at *ca.* 500 cm^{-1}, which is absent from the spectra of the

Table 2. Vibrational spectra of $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ (n = 0—6)

$[Hpy]_2$-$[Sb_2OBr_6]$		$[Hpy]_2$-$[Sb_2OBr_5Cl]$		$[Hpy]_2$-$[Sb_2OBr_4Cl_2]$		$[Hpy]_2$-$[Sb_2OBr_3Cl_3]$		$[Hpy]_2$-$[Sb_2OBr_2Cl_4]$		$[Hpy]_2$-$[Sb_2OBrCl_5]$		$[Hpy]_2$-$[Sb_2OCl_6]$		
I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	Assignment
515(sh)	512(sh)	508(sh)	513(sh)											
498s	492s	497s	495s	497vs	495s	498s	496m	500s	499m	499vs	507m	515vs	511s	ν(SbO)
394w		398vw		398vw		396vw		398vw		397vw		396vw		Hpy deformation
													326w	
		308(sh)		300(sh)		291(sh)		292(sh)		300(sh)		300(sh)		
			281m	282w	284s	280w	284s	284(sh)	284s	280s	286s	290s	296vs	ν(SbCl)
													282vs	
			260w	260w	259(sh)		257(sh)	256(sh)	258(sh)	267(sh)	255(sh)	270(sh)	250(sh)	
258m	252w	243(sh)		247(sh)		240(sh)								
248(sh)														
212(sh)		203w	203(sh)	213(sh)	204w	217(sh)	201(sh)		200(sh)	208w			191w	ν(SbBr)
205vs	205s		181s		181s		182s		183s		187m			
	175s													
	128m		125w		125m		125w		128w		135w		157w	
													132w	
											106w		105w	

Table 3. Monoisotopic mass spectra of $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ as % total ion current

m/z	$n = 6$[a]	$n = 5$	$n = 4$	$n = 3$	$n = 2$	$n = 1$	$n = 0$[b]	Ion
363	—	—	—	—	—	—	0.3	$[Sb_2OCl_3]^+$
358	40.1	15.8	12.1	5.3	4.3	2.4	—	$[SbBr_3]^+$
314	—	6.8	15.3	11.1	11.7	5.8	—	$[SbBr_2Cl]^+$
279	39.5	14.4	19.6	11.4	8.8	10.8	—	$[SbBr_2]^+$
270	—	2.1	5.9	8.7	10.3	14.0	—	$[SbCl_2Br]^+$
235	—	14.6	26.3	29.3	27.2	16.1	—	$[SbBrCl]^+$
226	—	2.7	1.5	4.7	5.2	11.8	36.7	$[SbCl_3]^+$
200	11.6	9.5	4.7	4.7	2.2	7.3	—	$[SbBr]^+$
191	—	4.9	10.8	21.6	25.9	8.0	41.2	$[SbCl_2]^+$
156	—	3.2	1.7	3.4	1.6	12.9	11.0	$[SbCl]^+$
121	8.1	4.6	2.8	4.5	10.7	10.7	9.4	Sb^+

[a] In addition $[SbBr]^{2+}$ (0.5), $[Sb_2Br]^+$ (trace). [b] In addition $[SbCl_2]^{2+}$ (0.5) and traces of $[Sb_2Cl_2]^+$ and $[SbCl]^{2+}$.

parent nonahalogenodiantimonates, and is assigned to Sb–O stretching. On the basis of the structure of $[Hpy]_2[Sb_2OCl_6]$,[2,3] the isolated anion will have *ca.* C_{2v} symmetry with two Sb–O stretching modes (A_1 and B_2), active in both the i.r. and Raman; the bromine analogue will be similar and two Sb–O modes are also expected for the mixed halides which with the exception of $[Hpy]_2[Sb_2OBr_2Cl_4]$ will be of lower symmetry (C_i or C_s). In all cases, the observed 500 cm^{-1} band is broad and only for the two bromine rich members of the series is there evidence for two components, separated by *ca.* 15 cm^{-1}. For other members, the two modes must be almost degenerate.

A range of values has been reported for Sb–O stretching frequencies, which appear to be sensitive to both oxidation state and compound type. Matrix isolated $K[SbO_2]$, for example, shows bands[9] at 745 and 765 cm^{-1} and a band at 700 cm^{-1} has been assigned to Sb–O–Sb stretching in $[(SbMe_2)_2O]$.[10] Compounds of the type $[(SbR_3X)_2O]$ absorb between 720 and 790 cm^{-1} while related compounds containing an Sb–OH bond absorb at 560—610 cm^{-1}.[11] Bands between 500 and 600 cm^{-1} occur in the spectra of polymeric alkoxides such as $[Sb(OEt)_3]$ and $[SbCl(OEt)_2]$[12] while antimony(V) species containing four-membered $\overline{Sb(OH)SbO}$ rings show two bands in the 445—475 and 480—545 cm^{-1} regions.[13] The dimer $[(SbPh_2BrO)_2]$, which contains a simple Sb_2O_2 ring, also has Sb–O stretching bands at 495 and 650 cm^{-1}.[14]

The halogen stretching region should contain four modes in each of the regions associated with the terminal and bridge bonds based on Group Theory and the structure of $[Hpy]_2[Sb_2OCl_6]$. The observed spectra, as found previously for the $[Sb_2Br_nCl_{9-n}]^{3-}$ series of compounds,[1] are poorly resolved and apart from noting the expected high intensity of bands in the 200 and 290 cm^{-1} regions for, respectively, the bromine and chlorine rich members, detailed assignments are difficult. The intense Raman band at 284 cm^{-1} for $[Sb_2OBr_nCl_{6-n}]^{2-}$, where n = 2—4, however, does imply that chlorine atoms preferentially occupy terminal positions, as is confirmed by the crystal-structure determinations for $[Hpy]_2[Sb_2OBr_2Cl_4]$ and $[Hpy]_2[Sb_2OBr_4Cl_2]$.[3]

The i.r. region below 500 cm^{-1} contains one weak pyridinium band at *ca.* 395 cm^{-1} not observed in the Raman, which is assigned to a deformation mode.[15] Although the *X*-ray structures point to strong hydrogen bonding between cation and anion, at normal mull concentrations there are no obvious associated i.r. absorptions.

The spectra of $[Hpy]_2[Sb_3OCl_9]$ show a decrease in the energy of the Sb–O stretch (485 and 480 cm^{-1} in the i.r. and Raman respectively), but the band remains broad and of high intensity. The major Sb–Cl bands at 286s, 300vs, and 335s cm^{-1} in the i.r. and 304s, 321(sh), and 328vs cm^{-1} in the Raman, on the other hand, move to higher energies than the comparable bands in the uncomplexed $[Hpy]_2[Sb_2OCl_6]$.

Mass Spectra.—Electron-impact spectra have been recorded for all the compounds and the intensities of the (monoisotopic) peaks at m/z values above 120 are given in Table 3 as a percentage of the total ion current. In no case is a 'parent' ion observed and only trace quantities of Sb_2O based fragments occur suggesting that cleavage of the oxygen bridges occurs early in the fragmentation process. The data in general yield little structural information. As with the mass spectra of the $[Sb_2Br_nCl_{9-n}]^{3-}$ series of compounds, the major peaks here contain only single antimony atoms and with the obvious exceptions of $[Sb_2OCl_6]^{2-}$ and $[Sb_2OBr_6]^{2-}$, the compounds show complete series of $[SbBr_nCl_{3-n}]^+$ ($n = 0$—3) and $[SbBr_nCl_{2-n}]^+$ ($n = 0$—2) ions, together with $[SbBr]^+$ and $[SbCl]^+$, implying extensive halogen redistribution in the ion source.

The mass spectrum of $[Hpy]_2[Sb_3OCl_9]$ is similar to that of the uncomplexed hexachloride but in addition there is a weak signal at *m/z* 484, assigned on the basis of the isotopic peaks to $[Sb_3OCl_3]^+$.

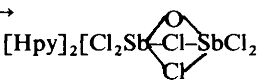
As discussed above, the formation of a pyridinium salt of a discrete oxygen bridged halogenodiantimonate from a reaction between antimony(III) chloride and pyridine implies that if an $SbCl_3$–py adduct is formed, it reacts rapidly with traces of moisture from either the atmosphere or the solvent. As an alternative first step a 1:1 adduct of $SbCl_3$ with water could be formed. A possible mechanism for the formation of $[Hpy]_2[Sb_2OCl_6]$ is given in equations (4)—(7).

$$SbCl_3{\cdot}py + H_2O \longrightarrow [Hpy][SbCl_3(OH)] \quad (4)$$

$$[Hpy][SbCl_3(OH)] + SbCl_3 \longrightarrow [Hpy][Cl_3Sb(OH)SbCl_3] \quad (5)$$

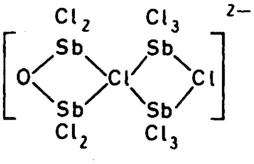
$$[Hpy][Cl_3Sb(OH)SbCl_3] + py \longrightarrow [Hpy]_2[Cl_3Sb(O)SbCl_3] \quad (6)$$

$$[Hpy]_2[Cl_3Sb(O)SbCl_3] \longrightarrow$$

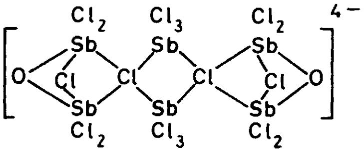


$$[Hpy]_2[Cl_2Sb\overset{O}{\underset{Cl}{-Cl-}}SbCl_2] \quad (7)$$

The oxygen bridged product can be formulated in a number of ways, *e.g.* as a pyridinium salt of the unknown neutral $Cl_2Sb(O)SbCl_2$ and two chloride ions or as $[(SbCl_3)_2O]^{2-}$, the latter pointing to abstraction by pyridine of the two protons from a mol of water associated with two mol of antimony(III) chloride. A related antimonate, $[Fe(\eta\text{-}C_5H_5)_2]_2[Sb_4OCl_{12}]$, obtained by photolysis of a mixture of antimony(III) chloride with ferrocene in the presence of oxygen, has a solid-state structure based on dimerisation of two $[Sb_4OCl_{12}]^{2-}$ (2) units.[16] This can be formulated as either $[(SbCl_3)_4O]^{2-}$ or a 2:1 adduct of $SbCl_3$ with $[Sb_2OCl_6]^{2-}$; the $[Sb_3OCl_9]^{2-}$ species isolated in this work then fits into the same series as either $[(SbCl_3)_3O]^{2-}$ or a 1:1 adduct between $SbCl_3$ and $[Sb_2OCl_6]^{2-}$. Although its structure is not known, vibrational and mass spectrometric data point to a close relationship with that of $[Sb_2OCl_6]^{2-}$; a dimer such as (3) is considered a reasonable possibility.



(2)



(3)

These basic antimony(III) halide anions represent a new class of compound and although related bismuth species have not been reported, $[Hpy]_2[As_2OCl_6]$ has recently been isolated.[17] The previously known ferrocenium salt, $[Fe(\eta\text{-}C_5H_5)_2]_2$-$[As_4O_2Cl_{10}]$,[18] can be considered a member of a parallel series containing one chloride ion per neutral $Cl_2As(O)AsCl_2$ unit.

References

1 M. Hall, M. Nunn, M. J. Begley, and D. B. Sowerby, preceding paper.
2 M. Hall and D. B. Sowerby, *J. Chem. Soc., Chem. Commun.*, 1979, 1134.
3 M. Hall, M. Nunn, M. J. Begley, and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, in the press.
4 A. M. Brodie and C. J. Wilkins, *Inorg. Chim. Acta*, 1974, **13**, 8.
5 R. Hulme and D. Mullen, *Acta Crystallogr., Sect. A*, 1969, **25**, S171.
6 A. Lipka and H. Wunderlich, *Z. Naturforsch., Teil B*, 1980, **35**, 1548.
7 M. Nunn and D. B. Sowerby, unpublished work.
8 M. Hall and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1980, 1292.
9 J. S. Ogden and S. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1982, 825.
10 H. J. Breunig and H. Jarrad, *Z. Naturforsch., Teil B*, 1982, **37**, 1104.
11 Y. Kawasaki, Y. Yamamoto, and M. Wada, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 145.
12 G. E. Binder, U. Ensinger, W. Dorsch, and A. Schmidt, *Z. Anorg. Allg. Chem.*, 1983, **507**, 163.
13 S. Blösl, W. Schwarz, and A. Schmidt, *Z. Anorg. Allg. Chem.*, 1982, **495**, 165, 177; C. H. Belin, M. Chaabouni, J. L. Pascal, and J. Potier, *Inorg. Chem.*, 1982, **21**, 3557.
14 D. M. Wesolek, D. B. Sowerby, and M. J. Begley, *J. Organomet. Chem.*, 1985, **293**, C5.
15 C. H. Kline, jun. and J. Turkevich, *J. Chem. Phys.*, 1944, **12**, 300.
16 A. L. Rheingold, A. G. Landers, P. Dahlstrom, and J. Zubietta, *J. Chem. Soc., Chem. Commun.*, 1979, 143.
17 J. Kaub and W. S. Sheldrick, *Z. Naturforsch., Teil B*, 1984, **39**, 1252, 1257.
18 M. R. Churchill, A. G. Landers, and A. L. Rheingold, *Inorg. Chem.*, 1981, **20**, 849.

Received 29*th July* 1985; *Paper* 5/1307