Group 15–Azamacrocyclic Chemistry. Reactions of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) with MCl_3 (M = As or Sb): Crystal and Molecular Structures of $[H_2L][As_4O_2Cl_{10}]$ and $[H_2L][Sb_2OCl_6]$†

Gerald R. Willey,* Abdul Asab, Miles T. Lakin and Nathaniel W. Alcock
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

The reactions of MCl_3 (M = As or Sb) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam, L) have been studied under controlled hydrolysis conditions as a route to anionic bridging chlorooxo arsenic- or antimony-(III) species. With M = As, the ionic complex $[H_2L][As_4O_2Cl_{10}]$ **1** has been isolated and characterised by an X-ray crystal-structure determination. The diprotonated tetraazamacrocyclic dications adopt an endodentate geometry with all four $N-CH_3$ groups positioned on the same side of the ring in an *R,S,R,S* [*trans*-(I)] configuration. The two protons are bonded to alternate nitrogen atoms and are involved in hydrogen bonding within the ring cavity. Each arsenic(III) centre of the tetranuclear μ_4-chloro-μ-oxo complex anion $[As_4O_2Cl_{10}]^{2-}$ shows ψ-octahedral co-ordination geometry with an associated stereochemically active lone pair. With M = Sb, the ionic complex $[H_2L][Sb_2OCl_6]$ **2** has been isolated and its structure determined. The macrocyclic dications are again in an endodentate conformation with intramolecular hydrogen bonding across the ring cavity but in this case the $N-CH_3$ groups are directed in pairs to opposite sides of the ring in an *R,R,S,S* [*trans*-(III)] configuration. The antimony atoms of the binuclear μ-chloro-μ-oxo complex anion $[Sb_2OCl_6]^{2-}$ have ψ-octahedral geometry with a stereochemically active lone pair. Both anions contain similar Cl_2MOMCl_2 primary units (mean As–Cl 2.21, Sb–Cl 2.43, As–O 1.77, Sb–O 1.94 Å) with Cl^- ions forming secondary M···Cl interactions (mean As···Cl 3.08, Sb···Cl 2.89 Å).

1,4,8,11-Tetraazacyclotetradecane (cyclam) and its *N*-tetramethyl derivative 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) form a kaleidoscope of transition-metal complexes and in this respect are perhaps the most widely recognised scions of the large family of azamacrocyclic ligands currently enjoying research attention.[1] In parallel with our structural studies of the tervalent halide adducts $MCl_3{\cdot}L'$ (M = As, Sb or Bi) formed with L′ = oxygen (crown ether)[2] or sulfur (crown thioether)[3] macrocycles we have examined the complexation of these p-block halides with L, the first investigation of Group 15–azamacrocyclic chemistry. Some initial results are presented herein.

Experimental

All reactions and manipulations were carried out using standard Schlenk techniques and/or a dinitrogen atmosphere glove-box. Acetonitrile was purified following the recommended procedure,[4] stored over P_4O_{10}, and distilled under dinitrogen prior to use; all other solvents were stored over calcium hydride and freshly distilled under dinitrogen prior to use. Ligand L was prepared following the literature procedures.[1a,5] The tervalent halides MCl_3 (M = As or Sb), were used as supplied commercially (Aldrich). Infrared spectra were recorded on a Perkin Elmer 580B instrument with samples as Nujol mulls placed between CsI plates. Microanalyses were performed by Medac Ltd., Uxbridge, Middlesex.

Preparation of the Complexes.—$[H_2L][As_4O_2Cl_{10}]$ **1**. A solution of $AsCl_3$ (0.57 g, 3.13 mmol) in toluene (20 cm^3) was placed in a Schlenk vessel under a dinitrogen atmosphere. A layer of MeCN (25 cm^3) was added followed by careful addition of a solution of L (0.20 g, 0.78 mmol) in acetonitrile (20 cm^3). With the reaction system maintained under a closed atmosphere of dinitrogen, addition of water (0.03 g, 1.70 mmol) was effected by syringe injection into the dinitrogen supply line. Over a period of several days the product **1** slowly deposited as a white semicrystalline solid which was collected, washed with hexane (3 × 20 cm^3) and pumped *in vacuo*. A number of crystals of suitable quality for X-ray diffraction studies were isolated directly from the bulk product (0.192 g, 26%) (Found: C, 18.10; H, 3.90; N, 6.10. $C_{14}H_{34}As_4Cl_{10}N_4O_2$ requires C, 17.80; H, 3.65; N, 5.95%); ν_{max}(Nujol) 1401, 1310, 1154, 958 (ligand), 755 (As–O–As) and 348 cm^{-1} (AsCl).

$[H_2L][Sb_2OCl_6]$ **2**. Compound **2** was obtained from the reaction of $SbCl_3$ (0.36 g, 1.56 mmol) and L (0.20 g, 0.78 mmol) and water (0.02 g, 1.1 mmol) following the procedure detailed above. Again crystals of suitable quality for an X-ray structure determination were successfully isolated directly from the white semicrystalline bulk product (0.07 g, 12%) (Found: C, 24.00; H, 5.20; N, 8.15. $C_{14}H_{34}Cl_6N_4OSb_2$ requires C, 23.00; H, 4.70; N, 7.65%); ν_{max}(Nujol) 2667 (NH^+), 1403, 1311, 1154, 964 (ligand), 692 (Sb–O–Sb), 315 and 291 cm^{-1} (SbCl).

Both complexes are air- and moisture-sensitive and must be handled under a dinitrogen atmosphere. In each case exposure to air results in the formation of a white intractable solid.

X-Ray Structural Analysis.—Crystals of both **1** and **2** were mounted in Lindemann capillaries to avoid hydrolysis. Crystal data and collection information are given in Table 1. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode; a scan range of ±0.7° (ω) around the $K\alpha_1,K\alpha_2$ angles with scan speed 2.5–15° (ω) min^{-1}, depending on the intensity of a 2 s

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Crystal and data collection information

Compound	**1**	**2**
Formula	$C_{14}H_{34}As_4Cl_{10}N_4O_2$	$C_{14}H_{34}Cl_6N_4OSb_2$
M	944.6	722.1
Crystal system	Orthorhombic	Triclinic
Space group	*Ibca*	$P\bar{1}$
Absences	*hkl*, $h + k + l = 2n$; 0*kl*, $k = 2n$; *h*0*l*, $l = 2n$; *hk*0, $h = 2n$	None
a/Å	15.781(8)	9.603(11)
b/Å	17.898(9)	12.091(11)
c/Å	22.929(13)	12.562(18)
α/°	90	78.35(10)
β/°	90	72.09(8)
γ/°	90	71.35(5)
U/Å^3	6476	1311
D_c/g cm^{-3}	1.94	1.94
Z	8	2
T/K	290	290
Reflections for cell (2θ)	26–28	20–22
Angular range (2θ)/°	3–50	3–45
Index ranges	0–18, 0–20, 0–27	0–13, −14 to 14, −19 to 19
μ(Mo-Kα)/cm^{-1}	4.94	1.38
Crystal size/mm	0.28 × 0.09 × 0.38	0.35 × 0.25 × 0.12
Transmission factor range	0.30–0.37	0.76–0.90
Total no. reflections	2872	3527
Unique no. reflections	2872	3452
No. reflections with [$I/\sigma(I) \geqslant 2.0$]	1746	2782
R_{int}	—	0.022
Parameters refined	165	244
Weight parameter (g)	0.000 56	0.000 52
Shift/σ (in last cycle)	0.1	0.1
δF peaks/e Å^{-3}	±0.5	1.0–0.7
Final R	0.043	0.043
Final R'	0.051	0.045
S (goodness of fit)	1.31	1.73
R (all reflections)	0.077	0.056

Table 2 Atom coordinates (× 10^4) for complex **1**

Atom	x	y	z
As(1)	4082.2(4)	1445.1(4)	1268.1(4)
As(2)	6043.1(4)	1505.9(4)	1221.7(4)
Cl(11)	3516.4(13)	774.6(11)	1981.0(9)
Cl(12)	3620.3(14)	698.9(12)	570.9(9)
Cl(21)	6739.4(13)	792.2(13)	1852.3(10)
Cl(22)	6481.0(14)	894.0(12)	448.8(9)
Cl(5)	5000.0	2500.0	2098.6(14)
Cl(6)	5000.0	2500.0	449.8(13)
O	5088(3)	1005(3)	1310(2)
N(1)	6274(4)	−2424(3)	1254(3)
N(2)	5017(4)	−1253(4)	1422(3)
C(1)	6767(6)	−2367(5)	1783(4)
C(2)	6607(5)	−1936(5)	800(4)
C(3)	6409(6)	−1103(4)	940(4)
C(4)	5456(5)	−932(4)	914(3)
C(5)	5240(6)	−847(5)	1981(4)
C(6)	4061(5)	−1226(5)	1358(5)
C(7)	3700(6)	−1820(5)	999(4)

Table 3 Atom coordinates (× 10^4) for complex **2**

Atom	x	y	z
Sb(1)	11 100.1(7)	−3 524.2(6)	−1 219.0(6)
Sb(2)	10 739.0(7)	−1 376.8(6)	−3 313.7(5)
Cl(1)	10 059(3)	521(3)	−2 655(3)
Cl(2)	8 254(3)	−1 990(3)	−1 642(3)
Cl(3)	10 547(3)	−2 760(3)	552(2)
Cl(4)	11 603(3)	−3 829(3)	−3 563(3)
Cl(5)	13 167(3)	−1 107(3)	−4 445(2)
Cl(6)	13 705(3)	−4 452(3)	−1 108(3)
O	11 626(7)	−2 116(6)	−2 050(5)
N(11)	4 907(9)	1 368(8)	−1 405(7)
N(12)	3 798(9)	−697(8)	−765(7)
C(11)	3 568(13)	2 363(11)	−1 397(11)
C(12)	5 465(12)	923(10)	−2 495(9)
C(13)	4 441(14)	315(11)	−2 731(9)
C(14)	4 397(12)	−825(11)	−1 999(9)
C(15)	2 126(11)	−123(11)	−482(11)
C(16)	4 209(12)	−1 827(9)	−64(9)
C(17)	3 897(12)	−1 721(10)	1 149(9)
N(21)	8 214(8)	4 760(7)	−3 523(7)
N(22)	8 288(8)	6 593(7)	−5 255(6)
C(21)	8 042(13)	5 233(10)	−2 475(9)
C(22)	6 699(10)	4 861(9)	−3 686(9)
C(23)	5 908(11)	6 109(9)	−4 108(9)
C(24)	6 772(11)	6 528(9)	−5 247(9)
C(25)	8 110(13)	7 610(10)	−4 738(10)
C(26)	9 214(11)	6 662(9)	−6 422(8)
C(27)	9 140(10)	3 514(9)	−3 491(9)

pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed a slight decrease (3%) during data collection for **1**, but were constant for **2**. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Reflections collected were processed using profile analysis and were corrected for Lorentz, polarization and absorption effects (by the Gaussian method).

For **1**, the systematic reflection conditions indicated space group *Ibca*; for **2** $P\bar{1}$ was chosen and shown to be correct by successful refinement. The structures were solved by direct methods using SHELXTL (TREF) to locate two heavy-atom positions. The remaining atoms were then found by successive Fourier syntheses. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms apart from those protonating the cation were given fixed isotropic thermal

Table 4 Bond lengths (Å) and selected bond angles (°) for complex **1***

As(1)–Cl(11)	2.216(3)	As(1)–Cl(12)	2.207(3)
As(1)–O	1.774(4)	As(1)–Cl(5)	3.048(3)
As(1)–Cl(6)	3.030(3)	As(2)–Cl(21)	2.220(3)
As(2)–Cl(22)	2.195(3)	As(2)–Cl(5)	3.149(3)
As(2)–Cl(6)	3.001(3)	As(2)–O	1.766(4)
N(1)–C(1)	1.444(11)	N(1)–C(2)	1.457(10)
N(1)–C(7a)	1.474(10)	N(2)–C(4)	1.473(11)
N(2)–C(5)	1.516(11)	N(2)–C(6)	1.517(10)
C(2)–C(3)	1.556(11)	C(3)–C(4)	1.535(12)
C(6)–C(7)	1.460(13)	C(7)–N(1a)	1.474(10)
Cl(11)–As(1)–Cl(12)	94.2(1)	Cl(11)–As(1)–Cl(6)	170.7(1)
Cl(12)–As(1)–Cl(5)	169.9(1)	Cl(11)–As(1)–O	94.6(2)
Cl(12)–As(1)–O	93.8(2)	Cl(21)–As(2)–Cl(22)	94.8(1)
Cl(21)–As(2)–Cl(6)	175.2(1)	Cl(22)–As(2)–Cl(5)	164.1(1)
Cl(21)–As(2)–O	93.2(3)	Cl(22)–As(2)–O	96.2(2)
As(1)–O–As(2)	122.2(3)		

* Position a: $1 - x, -\frac{1}{2} - y, z$.

Table 5 Bond lengths (Å) and selected bond angles (°) for complex **2***

Sb(1)–Cl(2)	2.900(5)	Sb(1)–Cl(3)	2.431(5)
Sb(1)–Cl(4)	2.920(5)	Sb(1)–Cl(6)	2.425(5)
Sb(1)–O	1.941(7)	Sb(2)–Cl(1)	2.423(5)
Sb(2)–Cl(2)	2.865(5)	Sb(2)–Cl(4)	2.868(5)
Sb(2)–Cl(5)	2.432(5)	Sb(2)–O	1.944(7)
N(11)–C(11)	1.452(13)	N(11)–C(12)	1.461(15)
N(11)–C(17a)	1.479(18)	N(12)–C(14)	1.508(14)
N(12)–C(15)	1.496(12)	N(12)–C(16)	1.473(13)
C(12)–C(13)	1.521(22)	C(13)–C(14)	1.500(16)
C(16)–C(17)	1.488(16)	C(17)–N(11a)	1.479(18)
N(21)–C(21)	1.485(16)	N(21)–C(22)	1.492(15)
N(21)–C(27)	1.485(11)	N(22)–C(24)	1.480(14)
N(22)–C(25)	1.445(16)	N(22)–C(26)	1.475(11)
C(22)–C(23)	1.522(13)	C(23)–C(24)	1.507(13)
C(26)–C(27b)	1.499(15)	C(27)–C(26b)	1.499(15)
Cl(2)–Sb(1)–Cl(3)	90.9(1)	Cl(2)–Sb(1)–Cl(4)	80.5(1)
Cl(3)–Sb(1)–Cl(4)	165.8(1)	Cl(2)–Sb(1)–Cl(6)	167.2(1)
Cl(3)–Sb(1)–Cl(6)	89.9(1)	Cl(4)–Sb(1)–Cl(6)	96.1(1)
Cl(2)–Sb(1)–O	76.3(2)	Cl(3)–Sb(1)–O	91.1(2)
Cl(4)–Sb(1)–O	76.0(2)	Cl(6)–Sb(1)–O	90.9(2)
Cl(1)–Sb(2)–Cl(2)	91.1(1)	Cl(1)–Sb(2)–Cl(4)	166.5(1)
Cl(2)–Sb(2)–Cl(4)	82.0(1)	Cl(1)–Sb(2)–Cl(5)	90.7(1)
Cl(2)–Sb(2)–Cl(5)	167.6(1)	Cl(4)–Sb(2)–Cl(5)	93.6(1)
Cl(1)–Sb(2)–O	89.9(2)	Cl(2)–Sb(2)–O	77.2(2)
Cl(4)–Sb(2)–O	77.3(2)	Cl(5)–Sb(2)–O	90.6(2)
Sb(1)–Cl(2)–Sb(2)	70.2(1)	Sb(1)–Cl(4)–Sb(2)	69.9(1)
Sb(1)–O–Sb(2)	117.1(4)		

* Position a: $1 - x, -y, -z$; position b: $2 - x, 1 - y, 1 - z$.

parameters, $U = 0.08$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, with their initial orientation based on staggered conformations. Final refinement was on F by least-squares methods. Weighting schemes of the form $w = 1/[\sigma^2(F) + gF^2]$ were used and shown to be satisfactory by a weight analysis. All the calculations were carried out on a DEC Microvax-II computer using SHELXTL PLUS.[6]

Scattering factors in the analytical form and anomalous dispersion factors are taken from ref. 7. Final atomic coordinates are given in Tables 2 and 3, and selected bond lengths and angles in Tables 4 and 5.

In complex **1**, the cation lies on a two-fold axis and the anion on a two-fold axis passing through Cl(5) and Cl(6). The unique proton on the cation was identifiable on Fourier difference syntheses and its position and isotropic thermal parameter were refined. In **2** the asymmetric unit contains two independent centrosymmetric half-cations and one anion. The unique proton of one cation was identified on a Fourier difference synthesis and its coordinates refined. The proton of the second cation was not located, possibly because it is disordered between the two alternative nitrogen atoms.

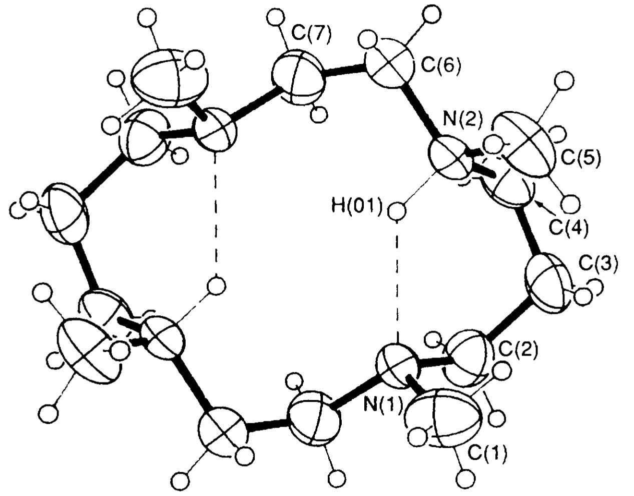


Fig. 1 View of the $[H_2L]^{2+}$ cation [*trans*-(I)] in complex **1** with atomic numbering

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond angles.

Results and Discussion

Direct treatment of MCl_3 (M = As or Sb) and L in acetonitrile under a dinitrogen atmosphere produces white solids suggesting adduct formation. Purification of these extremely air- and moisture-sensitive complexes proved impossible and their analytical data indicate rapid formation of oxo species resulting from M–Cl hydrolysis reactions despite the strict anhydrous controls imposed. However with careful introduction of stoichiometric amounts of water we have established that these hydrolysis reactions can be exploited as a route to anionic polynuclear bridging chlorooxo species of As^{III} and Sb^{III}.

M = As.—The tetraazamacrocyclic salt $[H_2L][As_4O_2Cl_{10}]$ **1** was isolated as a white semicrystalline solid from the reaction of $AsCl_3$ and L in acetonitrile in the presence of water under the stoichiometry required in equation (1).

$$4AsCl_3 + L \xrightarrow{MeCN} 4AsCl_3{\cdot}L \xrightarrow{2H_2O} \underset{\mathbf{1}}{[H_2L][As_4O_2Cl_{10}]} + 2HCl \quad (1)$$

The X-ray crystal structure of **1** reveals independent doubly-charged $[H_2L]^{2+}$ cations and $[As_4O_2Cl_{10}]^{2-}$ anions and shows several interesting features. The parent macrocyclic ligand has not been characterised by X-ray analysis and the present work provides the first structure determination of it in a protonated form. The $[H_2L]^{2+}$ cation in this complex (Fig. 1) lies on a two-fold axis with all four nitrogen atoms coplanar and has adopted a *R,S,R,S* [*trans*-(I)] conformation, *i.e.* all N–CH_3 groups are oriented towards the same side of the ring.[8] The two protons are located within the ring cavity and are linked to alternate nitrogen atoms [N(2), N(2a)] with N(2)–H(01) 1.038 Å. Further contacts N(2)–H(01) ··· N(1) 2.121 Å provide a hydrogen-bonding network which must be instrumental in the adoption of an endodentate geometry by the macrocyclic ring. The *trans*-separation distances N(2) ··· N(2a) 4.463, N(1) ··· N(1a) 4.031 Å provide a measure of the ring cavity size. The N–CH_3 bond distances form two sets, those associated with the protonated amine centres being appreciably longer than those

Table 6 Mean dimensions of $[As_4O_2Cl_{10}]^{2-}$ *

	This work	Ref. 9
$As-Cl_{terminal}/Å$	2.21	2.24
As–O/Å	1.77	1.77
$As-Cl_{bridge}/Å$	3.00–3.15	2.89–3.35
Cl–As–Cl/°	94.6(1)	93.5(1)

* $AsCl_3$ has As–Cl (mean) 2.17 Å and Cl–As–Cl (mean) 97.7°.

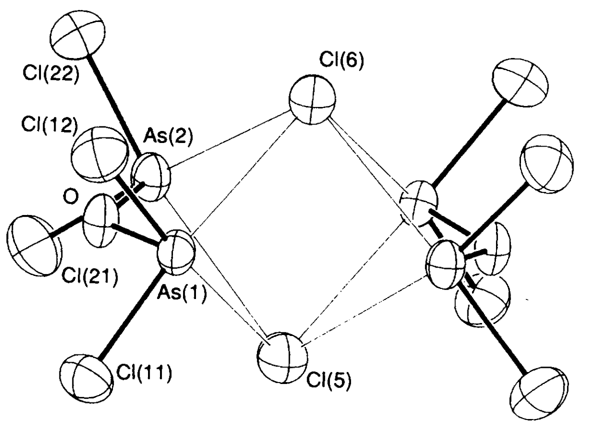


Fig. 2 View of the $[As_4O_2Cl_{10}]^{2-}$ anion in complex **1** with atomic numbering

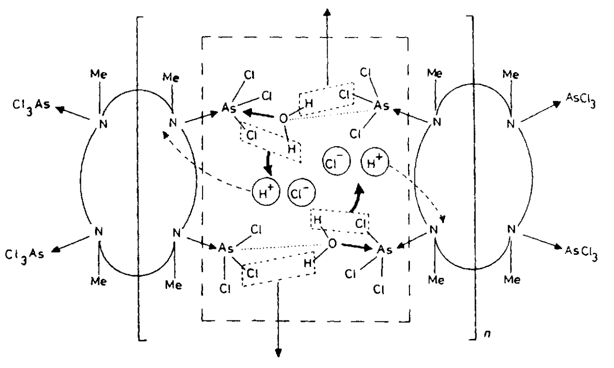
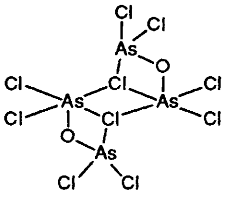


Fig. 3 Schematic representation of the hydrolysis reaction leading to the formation of complex **1**

belonging to the 'free' amine sites [N(2)–C(5) 1.516(11) Å and N(1)–C(1) 1.444(11) Å respectively]. A similar trend is observed in the C–N bond distances whereby those involving a protonated amine centre are marginally longer than those incorporating a 'free' amine centre *viz.*, mean distances of 1.495 and 1.466 Å respectively. Whether these differences between protonated (four-co-ordinate) and basic (three-co-ordinate) nitrogen centres are significant in any bonding sense is open to question.

The $[As_4O_2Cl_{10}]^{2-}$ anion (Fig. 2) lies on a crystallographic two-fold axis with the four arsenic atoms and two oxygen atoms essentially coplanar (maximum deviations ±0.10 Å from the least-squares plane). Each arsenic atom shows ψ-octahedral local geometry with four chlorine atoms in non-equivalent equatorial positions and a stereochemically active lone pair inferred *trans* to the axial bridging oxygen atom.

A similar tetranuclear arsenic(III) anion has been isolated previously *via* aerobic oxidation of benzene solutions containing ferrocene and arsenic trichloride; the structure of $[Fe(\eta-C_5H_5)_2]_2[As_4O_2Cl_{10}]$[9] contains discrete ferrocenium cations and arsenic(III) cluster anions. For the latter Rheingold and co-workers[9] found a different halogen bridging structure to that in **1** in which two $Cl_2As-O-AsCl_2$ groups are linked by two chloride ions each of which is linked to three arsenic atoms in a μ_3-bridging mode as shown by **A**.



A

In our structure the two central chlorine atoms, which lie above and below the square-planar array of arsenic atoms, are linked to all four metal centres to provide, in effect, quadruply-bonded chlorine bridges. For comparison the relevant As–Cl dimensions of the two structures are listed in Table 6. The complex anion is probably best described as a loose aggregation of two $Cl_2As-O-AsCl_2$ units and two Cl^- ions held together by $As\cdots Cl^-$ secondary bonds.[10] The bridging As–O–As linkages in **1** are symmetrical; the dimensions are comparable with those in the relatively few similar As–O–As units that have been reported, including arsenic(III) oxide itself [As–O(mean) 1.789 Å, As–O–As(mean) 125.2°],[11] $o-C_6H_4[(AsCl)O]$ [As–O 1.787(3) Å, As–O–As 121.8(3)°][12] and μ-oxo[tetrakis(pentafluorophenyl)]diarsenic(III) [As–O 1.792(3) Å, As–O–As 116.2(3)°].[13]

The formation of complex **1** can be viewed as the result of a controlled hydrolysis sequence in which the preferred formation of a diprotonated cation of L is seen as a sensitising factor (Fig. 3). Initial adduct formation, represented as $4AsCl_3{\cdot}L$ involves all the tertiary amine centres in weak $N\!:\!\rightarrow As$ linkages with the azamacrocycle adopting an exodentate geometry similar to that observed in the aluminium(III) adduct $4AlMe_3{\cdot}L$.[14] As individual molecules draw together (perhaps assisted by weak intermolecular chlorine bridging) limited hydrolysis of As–Cl bonds allows the formation of discrete $Cl_2As-O-AsCl_2$ units with accompanying release of HCl and rupture of the As–N bonds. Proton abstraction by the azamacrocycle [the pK_a profile of L (pK_a 9.34, 8.99, 2.58, 2.25)[15] clearly favours diprotonation] results in the formation of the observed cation. Individual $Cl_2As-O-AsCl_2$ units are subsequently paired and stabilised by chloride ion interactions with the two bridging Cl atoms.

M = Sb.—The reaction of $SbCl_3$ and L in acetonitrile in the presence of water provided the chlorooxo antimony(III) salt **2** [equation (2)].

$$2SbCl_3 + L \xrightarrow{MeCN} 2SbCl_3{\cdot}L \xrightarrow{H_2O} \underset{\mathbf{2}}{[H_2L][Sb_2OCl_6]} \quad (2)$$

The structure of **2** consists of independent $[H_2L]^{2+}$ cations and $[Sb_2OCl_6]^{2-}$ anions. In this instance, however, the diprotonated cation (Fig. 4) has assumed a different conformation containing *R,R,S,S*-[*trans*-(III)] configurations. Again the four nitrogen atoms are coplanar and hydrogen bonding is present within the ring cavity in conjunction with the endodentate ring geometry, N(12)–H(11) 0.921, N(12)–H(11)$\cdots$N(11) 2.221 Å; *trans*-separation distances are N(12)$\cdots$N(12a) 4.275 and N(11)$\cdots$N(11a) 4.326 Å. The chlorooxo antimony(III) anion in this complex $[Sb_2OCl_6]^{2-}$ (Fig. 5) has been isolated previously by Hall and Sowerby[16] following partial hydrolysis of $[Hpy]_3[Sb_2Cl_9]$ (py = pyridine) in ethanol. The structure of this, and the related anions in $[Hpy]_2[Sb_2OBr_2Cl_4]$ and $[Hpy]_2[Sb_2OBr_4Cl_2]$[17] comprise two face-to-face fused ψ-octahedral $[SbCl_4O$ (lone pair)] units such that the bridging oxygen atom of the common OCl_2 triangular face is *trans* to the stereochemically active lone pair of electrons on each metal centre. A preferable description, which highlights the difference between the bridging and terminal Sb–Cl bonds and the similarity to the anion of **1**, picks out a single $Cl_2Sb-O-SbCl_2$

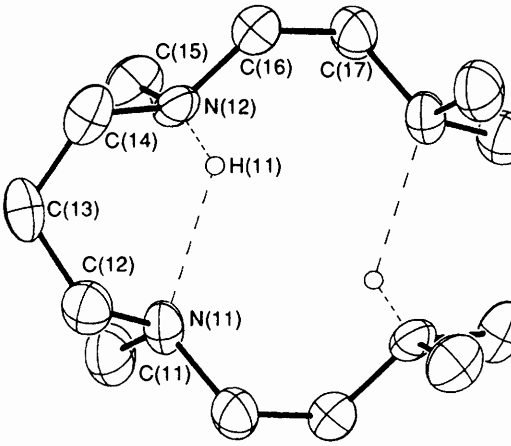


Fig. 4 View of the $[H_2L]^{2+}$ cation [*trans*-(III)] in complex **2** with atomic numbering

Table 7 Mean dimensions of $[Sb_2OCl_6]^{2-}$ *

	This work	Ref. 16
$Sb-Cl_{terminal}$/Å	2.43	2.44
$Sb-Cl_{bridge}$/Å	2.89	2.89
Sb–O/Å	1.94	1.95
Sb–Cl–Sb/°	70.1	71.3
$Cl-Sb-Cl_{terminal}$/°	90.3	89.9
Sb–O–Sb/°	117.1	119.5

* $SbCl_3$ has Sb–Cl (mean) 2.36 Å and Cl–Sb–Cl (mean) 94.1°.

unit forming secondary bonds to two chloride ions both bound to both antimony(III) centres. It is notable that the secondary bonds formed to Sb are shorter than those to As in contrast to the primary M–Cl bonds. Bond distances and angles for the two $[Sb_2OCl_6]^{2-}$ structures are listed in Table 7.

A comparison of the two structures shows: (*a*) whereas the bridging chlorine atoms occupy symmetrical positions in our structure, those in the previous determination do not, one being weakly hydrogen bonded to a pyridinium cation.

(*b*) In the previous structure the bridging oxygen atom forms a strong hydrogen bond with the second pyridinium cation which, together with the weaker interaction (*a*) above, is regarded as an important factor in the resulting overall stability. No such interactions are possible in our case. Interestingly the bridging Sb–O–Sb dimensions are invariant between the two structures. The arsenic(III) counterpart $[Hpy]_2[As_2OCl_6]$[18] is isostructural [$As-Cl_{bridge}$ 2.836(1), 2.965(1), 2.855(1), 2.925(1) Å, As–O–As 119.3(1)°, As–O 1.765(1), 1.777(1) Å] but also appears to show asymmetry in the bridging As–Cl–As linkages presumably the result of hydrogen-bonding interactions with the pyridinium cations.

Formation of the $[Sb_2OCl_6]^{2-}$ anion can be viewed in terms of a sensitised hydrolysis sequence along the lines outlined above for the arsenic(III) complex **1**. In this instance however individual $Cl_2Sb-O-SbCl_2$ units are stabilised by secondary bonding involving $Sb\cdots Cl^-$ interactions with two chlorine atoms in bridging positions but there are no further interactions with other $Cl_2Sb-O-SbCl_2$ units to give larger aggregates. Attempts to isolate a tetranuclear antimony(III) anion *cf.* **1** proved unsuccessful no matter what the molar ratio of $SbCl_3$ to water used. However a related antimony(III) cluster anion *viz.*, in $[Fe(\eta-C_5H_5)_2]_4[Sb_4OCl_{12}]_2\cdot 2C_6H_6$ is obtained[19] from photolysis of benzene solutions of ferrocene and antimony trichloride in the presence of oxygen. The structure, shown by **B**, involves multiple halogen-bridging environments, μ-Cl (3.00 Å) and μ_4-Cl (3.012, 3.031, 3.149, 3.192 Å), and can be regarded as a loose aggregate of a $Cl_2Sb-O-SbCl_2$ unit, two molecules of $SbCl_3$ and two chloride ions. Interestingly controlled hydrolysis of this anion would provide the direct antimony(III) analogue of **1** [equation (3)].

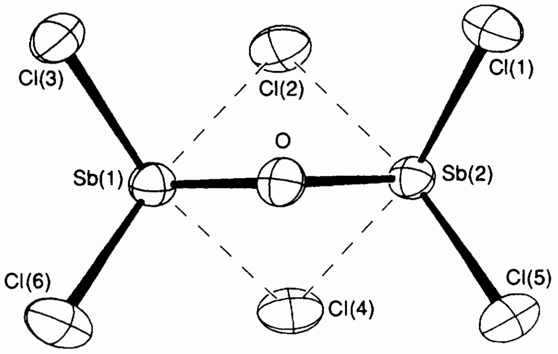
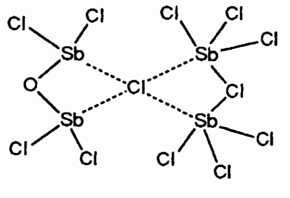


Fig. 5 View of the $[Sb_2OCl_6]^{2-}$ anion in complex **2** with atomic numbering



B

$$[Sb_4OCl_{12}]^{2-} \xrightarrow[-2HCl]{H_2O} [Sb_4O_2Cl_{10}]^{2-} \qquad (3)$$

Acknowledgements

We thank the SERC and the Cookson Group plc, Central Research for financial support.

References

1 See, for example, (*a*) E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435; (*b*) N. W. Alcock, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1978, 1282; (*c*) P. Moore, J. Sachinidis and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1323; (*d*) E. Iwamoto, T. Yokoyama, S. Yamasaki, T. Yabe, T. Kumamaru and T. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 1988, 1935; (*e*) A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1988, 1561; (*f*) T. A. Tyson, K. O. Hodgson, B. Hedman and G. R. Clark, *Acta Crystallogr., Sect. C*, 1990, **46**, 1638; (*g*) H. N. Po, E. Brinkman and R. J. Doedens, *Acta Crystallogr., Sect. C*, 1991, **47**, 2310; (*h*) P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297 and refs. therein.

2 N. W. Alcock, M. Ravindran and G. R. Willey, *J. Chem. Soc., Chem. Commun.*, 1989, 1063; N. W. Alcock, M. Ravindran, S. M. Roe and G. R. Willey, *Inorg. Chim. Acta*, 1990, **167**, 115; N. W. Alcock, M. Ravindran and G. R. Willey, *Acta Crystallogr., Sect. A*, 1990, **46**, C237; *Acta Crystallogr., Sect. B*, in the press.

3 G. R. Willey, M. T. Lakin, M. Ravindran and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 271; G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 591, 1339.

4 M. Walter and L. Ramaley, *Anal. Chem.*, 1973, **45**, 165.

5 E. K. Barefield, F. Wagner, A. W. Herlinger and A. R. Dahl, *Inorg. Synth.*, 1976, **16**, 220.

6 G. M. Sheldrick, SHELXTL PLUS, User's Manual, Nicolet Instrument Co., Madison, WI, 1986.

7 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, vol. 4 (present distributor Kluwer Academic Publishers, Dordrecht).

8 B. Bosnick, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102; A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1986, **108**, 713.

9 M. R. Churchill, A. G. Landers and A. L. Rheingold, *Inorg. Chem.*, 1981, **20**, 849.

10 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

11 F. Pertlik, *Monatsch. Chem.*, 1975, **106**, 755.
12 J. C. Dewan, K. Henrick, A. H. White and S. B. Wild, *Aust. J. Chem.*, 1975, **28**, 15.
13 A. L. Rheingold, D. L. Staley and M. E. Fountain, *J. Organomet. Chem.*, 1989, **365**, 123.
14 G. H. Robinson, H. Zhang and J. L. Atwood, *J. Organomet. Chem.*, 1987, **331**, 153.
15 B. S. Nakani, J. J. B. Welsh and R. D. Hancock, *Inorg. Chem.*, 1983, **22**, 2956.
16 M. Hall and D. B. Sowerby, *J. Chem. Soc., Chem. Commun.*, 1979, 1134.
17 M. Hall, M. Nunn, M. J. Begley and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1986, 1231.
18 J. Kaub and W. S. Sheldrick, *Z. Naturforsch., Teil B*, 1984, **39**, 1252.
19 A. L. Rheingold, A. G. Landers, P. Dahlstrom and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1979, 143.

Received 21*st August* 1992; *Paper* 2/04529J