DALTON

Controlled hydrolysis reactions of the Group 15 element–azamacrocyclic complexes MCl_3L (M = As, Sb or Bi; L = 1,4,7-trimethyl-1,4,7-triazacyclononane). Formation and crystal structures of $[AsCl_2L][As_2OCl_5]$, $[H_2L]_2[Sb_2OCl_6]Cl_2$, [HL]I and $[H_2L]_2[Sb_2Cl_9]Cl\cdot MeCN\cdot H_2O$†

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Reactions of MCl_3 (M = As, Sb or Bi) and 1,4,7-trimethyl-1,4,7-triazacyclononane ($Me_3[9]aneN_3$ = L) gave the respective 1 : 1 adducts as white-yellow microcrystalline solids which were characterised by microanalytical and spectroscopic (IR and ^1H NMR) data. Addition of water to $AsCl_3L$ under controlled stoichiometry in acetonitrile solution led to the formation of the white crystalline salt $[AsCl_2L][As_2OCl_5]$ **1**. A crystal structure determination revealed the cation as five-co-ordinate with ψ-octahedral metal geometry featuring a *cis*-$AsCl_2^+$ unit co-ordinated to the three donor nitrogen atoms of the ligand (*fac*) and a stereochemically active lone pair occupying the sixth site [As–Cl 2.462(7), 2.520(7) and As–N 2.18(2), 2.12(2), 2.10(2) Å with the latter directly opposite to the lone pair]. The anion is made up of a dinuclear (μ-oxo) $Cl_2As–O–AsCl_2$ unit with a single Cl^- anion linked symmetrically to the two separate arsenic atoms [mean $As–Cl_{terminal}$ 2.216(8), $As–Cl_{bridge}$ 2.795(8) Å]. Controlled hydrolysis of $SbCl_3L$ in acetonitrile solution provided colourless needle crystals of $[H_2L]_2[Sb_2OCl_6]Cl_2$ **2** as identified by X-ray diffraction studies. The structure of the dication shows protonation of two of the three nitrogen atoms with strong intramolecular hydrogen bonding N–H ··· N 2.70–2.85 Å involving the third amine centre. This is the first structural characterisation of the diprotonated form of L. The structure of the accompanying chlorooxoantimony(III) anion can be described as a single (μ-oxo) $Cl_2Sb–O–SbCl_2$ unit linked to two chloride ions *via* secondary Sb ··· Cl bonding involving the two metal centres [mean $Sb–Cl_{terminal}$ 2.435(3), $Sb–Cl_{bridge}$ 2.863(3) Å]. Each of the antimony(III) centres is further associated with a unique chloride anion, Sb ··· Cl^- 3.550(7) Å, which, in turn, forms close contacts with the two protonated nitrogen atoms of the triazamacrocycle Cl ··· H–N 3.07, 3.02 Å. Treatment of L and $SiMe_3I$ in acetonitrile solution provided yellow needle crystals of [HL]I **3**. X-Ray (diffraction) crystallographic characterisation revealed a monoprotonated ring (L) in which the single proton is bonded directly to one nitrogen atom and to the remaining two *via* intramolecular hydrogen bonding N–H ··· N 2.71 Å. The product isolated from the reaction of L and $SiCl_4$ in the presence of antimony(V) chloride as halide abstractor in acetonitrile was identified by a crystal structure determination as $[H_2L]_2[Sb_2Cl_9]Cl\cdot MeCN\cdot H_2O$ **4**. The structure reveals two $[H_2L]$ ··· Cl moieties which have dimensions similar to those found for **2**. Conformational analyses have been carried out on free L and its mono-, di- and tri-protonated forms and the results are consistent with the experimental conformations observed in this work and elsewhere.

As part of our investigations of Group 15–azamacrocycle chemistry we have recently reported $BiCl_3L$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane, $Me_3[9]aneN_3$) as having a half-sandwich structure with a six-co-ordinate (*fac*)-octahedral metal geometry and no apparent stereochemical lone-pair involvement.[1] Herein we now provide the analytical and spectroscopic characterisation data of the analogues MCl_3L where M = As or Sb. These have proved impossible to recrystallise in terms of X-ray-quality materials but there is no reason to suspect anything other than the half-sandwich arrangement which is commonplace for the general series MCl_3L' where L′ = a macrocycle such as a crown ether[2] or crown thioether.[3] The main interest in the hydrolysis reactions of these species lies in the identification and possible isolation of μ-oxo(chloro) intermediates of the type $[M_n(OH)_pCl_q(H_2O)_r]$ prior to formation of oxide with release of HCl [equation (1)].

$$2MCl_3L + 3H_2O \longrightarrow M_2O_3 + 6HCl + 2L \qquad (1)$$

Intermediates with high metal nuclearity would be of special interest. Utilisation of the incipient thermodynamic and kinetic stability of the M(macrocycle) fragment to impose some steric control of the incoming nucleophilic water molecule(s), *viz.* 'top-hat' protection, must, in turn, affect the solvolytic reactions of the M–Cl bonds. Some indication of the success of this approach can be seen in our previous study of the corresponding MCl_3(tmc)‡-water systems where tetranuclear (M = As) and dinuclear (M = Sb) μ-oxo(chloro) species were obtained.[4] In the same vein and in an earlier study Wieghardt *et al.*[5] have elegantly described the hydrolysis reactions of $InCl_3L$ leading to the formation of the tetrameric cation $[In_4(\mu\text{-}OH)_6L_4]^{6+}$ in aqueous alkaline solution and the neutral dimeric species $[In_2(O_2CMe)_4(\mu\text{-}O)L_2]\cdot 2NaClO_4$ in sodium acetate solution. Doubtless the main driving force in all these reactions is that L with its preferred endodentate conformation is an ideal blocking group for three metal co-ordination sites (*fac*-octahedral), *cf.*, the well established cyclopentadienyl ligand $C_5H_5^-$ and the related tris(pyrazolyl)borate ligands.

In this paper we describe the controlled solvolysis reactions

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† *Non-SI unit employed:* cal = 4.184 J.

‡ tmc = (tetramethylcyclam) = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

of these azamacrocyclic complexes MCl_3L (M = As, Sb or Bi) and highlight the structural features of the cationic and anionic oxochloro metal species isolated. In a separate study the inadvertent protonation of the parent ligand L was observed to provide both the mono- and di-protonated species; the structures of these novel azamacrocyclic cations involving intramolecular N–H $\cdots$ N hydrogen-bonding interactions are presented here for direct comparison(s).

Experimental

All reactions and manipulations were carried out using standard Schlenk techniques under an argon atmosphere and/or a dinitrogen atmosphere glove-box. Acetonitrile was purified as described by Walter and Ramaley,[6] stored over CaH_2 and P_4O_{10} and distilled under dinitrogen prior to use. The anhydrous chlorides MCl_3 (M = As, Sb or Bi) were used as supplied commercially (Aldrich) and the compound L was synthesized following the literature procedures.[7] Infrared spectra were recorded (Nujol mulls/CsI plates) on a Perkin-Elmer 580B instrument and ^1H (220 MHz) NMR spectra (in CD_3CN, $SiMe_4$ as internal reference) on a Perkin-Elmer R34 spectrometer. Microanalytical data were obtained using a Leemans Lab Inc. PS 1000 sequential inductively coupled plasma (ICP) spectrometer and a CE440 elemental (CHN) analyser.

Preparation of the compounds

(*a*) **$AsCl_3(Me_3[9]aneN_3)$.** A solution of $Me_3[9]aneN_3$ (0.20 g, 1.17 mmol) in acetonitrile (30 cm^3) was added dropwise to a stirred, chilled (solid CO_2–acetone, −78 °C) solution of $AsCl_3$ (0.21 g, 1.17 mmol) in acetonitrile (30 cm^3) under an argon atmosphere. On warming to room temperature the resulting yellow-tinged solution was stirred for 6 h at 50 °C. Removal of solvent gave a white solid which was washed with hexane (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3). An attempted recrystallisation from acetonitrile–dichloromethane gave the required compound as a white microcrystalline solid (0.37 g, 89.2%), m.p. 232–235 °C (decomp.) (Found: C, 31.25; H, 5.25; Cl, 30.0, N, 12.05; $C_9H_{21}AsCl_3N_3$ requires C, 30.65; H, 6.00; Cl, 30.15; N, 11.90%). IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 1340s, 1291s, 1261s, 1148m, 1123m, 1058vs, 997vs, 979vs, 964vs, 895w, 779s, 739vs (ligand), 349vs and 300s [ν(AsCl)]. δ_H 2.70 (9 H, s, CH_3), 3.13 and 3.32 (12 H, midpoints of AA′BB′ multiplets, CH_2).

(*b*) **$SbCl_3(Me_3[9]aneN_3)$.** Following the procedure as in (*a*) with $Me_3[9]aneN_3$ (0.20 g, 1.17 mmol) and $SbCl_3$ (0.27 g, 1.17 mmol), the required compound was obtained as a white semicrystalline solid (0.43 g, 91.3%) m.p. 239–241 °C (decomp.) (Found: C, 26.9; H, 5.20; Cl, 26.45; N, 10.3. $C_9H_{21}Cl_3N_3Sb$ requires C, 27.05; H, 5.30; Cl, 26.65; N, 10.5%). IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 1310s, 1262s, 1245m, 1153m, 1143m, 1118s, 1058vs, 1003s, 979s, 900w, 805m, 784m, 744m, 582w, 508s (ligand), 282vs and 250s [ν(SbCl)]. δ_H 2.72 (9 H, s, CH_3), 3.18 and 3.29 (12 H, midpoints of AA′BB′ multiplets, CH_2).

(*c*) **$BiCl_3(Me_3[9]aneN_3)$.** Following the procedure as in (*a*), with $Me_3[9]aneN_3$ (0.20 g, 1.17 mmol) and $BiCl_3$ (0.536 g, 1.17 mmol), the required compound was obtained as yellow needle crystals (0.53 g, 93.1%) m.p. 246–248 °C (decomp.) (Found: C, 22.4; H, 4.30; Cl, 21.65; N, 8.75. $C_9H_{21}BiCl_3N_3$ requires C, 22.2; H, 4.35; Cl, 21.85; N, 8.65%). IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 1301s, 1263m, 1204m, 1154m, 1124vs, 1107m, 1002vs, 982s, 763vs, 740vs, 573m, 427m, (ligand) and 220vs (br) [ν(BiCl)]. δ_H 3.01 (9 H, s, CH_3) and 3.49 (12 H, s, CH_2).

(*d*) **$[AsCl_2(Me_3[9]aneN_3)][As_2OCl_5]$ 1.** A solution of $Me_3[9]aneN_3$ (0.15 g, 0.88 mmol) in tetrahydrofuran (30 cm^3) was added dropwise to a stirred, chilled (0 °C) solution of $AsCl_3$ (0.16 g, 0.87 mmol) in tetrahydrofuran (20 cm^3) under an argon atmosphere. On warming to room temperature the faint yellow solution was stirred for 2 h before being added dropwise to a solution containing water (5.5 μl, 0.29 mmol) in tetrahydrofuran (10 cm^3). After stirring for 6 h the resulting solution was concentrated (*ca.* 15 cm^3) and placed in a refrigerator to provide the required compound as a mass of colourless block crystals (0.13 g, 69.2%), m.p. 233–234 °C (decomp.) (Found: C, 16.5; H, 3.65; N, 5.70. $C_9H_{21}As_3Cl_7N_3O$ requires C, 16.35; H, 3.20; N, 6.35%). IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 1058s, 997s, 979s, 964s, 895w, 800s (br), 779s, 738s, 520m (ligand), 348vs and 300s [ν(AsCl)]. δ_H 2.71 (9 H, s, CH_3), 3.10 and 3.40 (12 H, midpoints of AA′BB′ multiplets, CH_2).

(*e*) **$[Me_3[9]aneN_3H_2]_2[Sb_2OCl_6]Cl_2$ 2.** Following the procedure as in (*d*), with $Me_3[9]aneN_3$ (0.20 g, 1.17 mmol), $SbCl_3$ (0.27 g, 1.17 mmol), and water (7.4 μl, 0.39 mmol), the required compound was obtained as colourless needle crystals (0.22 g, 63.4%), m.p. 239–241 °C (decomp.) (Found: C, 25.1; H, 5.85; N, 8.70. Calc. for $C_{18}H_{46}Cl_8N_6OSb_2$: C, 24.3; H, 5.20; N, 9.45%). IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 1058s, 1003s, 979s, 949m, 900w, 805m (br), 784s, 744w, 508m (br) (ligand), 354vs and 282s [ν(SbCl)]. δ_H 2.71 (9 H, s, CH_3) and 3.17–3.38 (12 H, m, CH_2).

(*f*) **$[Me_3[9]aneN_3H]I$ 3.** Dropwise addition of $SiMe_3I$ (0.12 g, 0.60 mmol) in acetonitrile (30 cm^3) to a solution of $Me_3[9]aneN_3$ (0.10 g, 0.58 mmol) in acetonitrile (25 cm^3) provided a pale yellow solution which was stirred at room temperature for 6 h. Gradual removal of solvent resulted in the onset of deposition of yellow block crystals. Further concentration and cooling of the solution provided a second crop of yellow crystals from which a suitable one was selected and sealed in a Lindemann tube for X-ray diffraction studies. Yield 0.06 g. IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 1337m, 1286m, 1241s, 1187m, 1133s, 1067s, 1031s, 999s, 968m, 849m, 777s, 737w, 558w and 512m (br) (ligand). δ_H 2.65 (9 H, s, CH_3), 3.04 (12 H, m, CH_2) and 5.07 (1 H, br s, NH) (Found: C, 36.05; H, 7.25; N, 13.95. Calc. for $C_9H_{22}IN_3$: C, 36.15; H, 7.40; N, 14.05). Complete removal of solvent *in vacuo* from the mother-liquor yielded a pale brown powder which was not investigated further.

(*g*) **$[Me_3[9]aneN_3H_2]_2[Sb_2Cl_9]Cl{\cdot}MeCN{\cdot}H_2O$ 4.** The compound $SiCl_4$ (0.12 g, 0.71 mmol) was added dropwise *via* a syringe to a stirred solution of $SbCl_5$ (0.20 g, 0.67 mmol) in acetonitrile (30 cm^3). The clear light yellow solution was stirred for 5 h and then added dropwise to a solution of $Me_3[9]aneN_3$ (0.12 g, 0.70 mmol) in acetonitrile (30 cm^3). The resulting solution was stirred at room temperature for 5 h. Removal of solvent *in vacuo* provided an orange-brown powder which was washed with toluene (2 × 20 cm^3) and hexane (2 × 20 cm^3) and pumped *in vacuo* for 1 h. Recrystallisation from acetonitrile–dichloromethane provided the required compound as colourless needle crystals. Yield 0.037 g. IR, $\tilde{\nu}/cm^{-1}$ (Nujol): 3220m [ν(NH)], 1299s, 1142m, 1110m, 1059s, 999s, 973w, 781m, 770w, 737m, 578m, 542m (ligand) and 345 [ν(SbCl)]. δ_H 2.77 (9 H, s, CH_3), 3.19 (12 H, m, CH_2) and 5.46 (2 H, br s, NH).

X-Ray crystallography

Crystal data for the four compounds are given in Table 7, together with refinement details. Data were collected at 293(2) K with Mo-Kα radiation (λ 0.710 73 Å) using the MARresearch image plate system. The crystals were positioned at 75 mm from the image plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[8] The structures were solved using direct methods with the SHELXS 86 program.[9] In

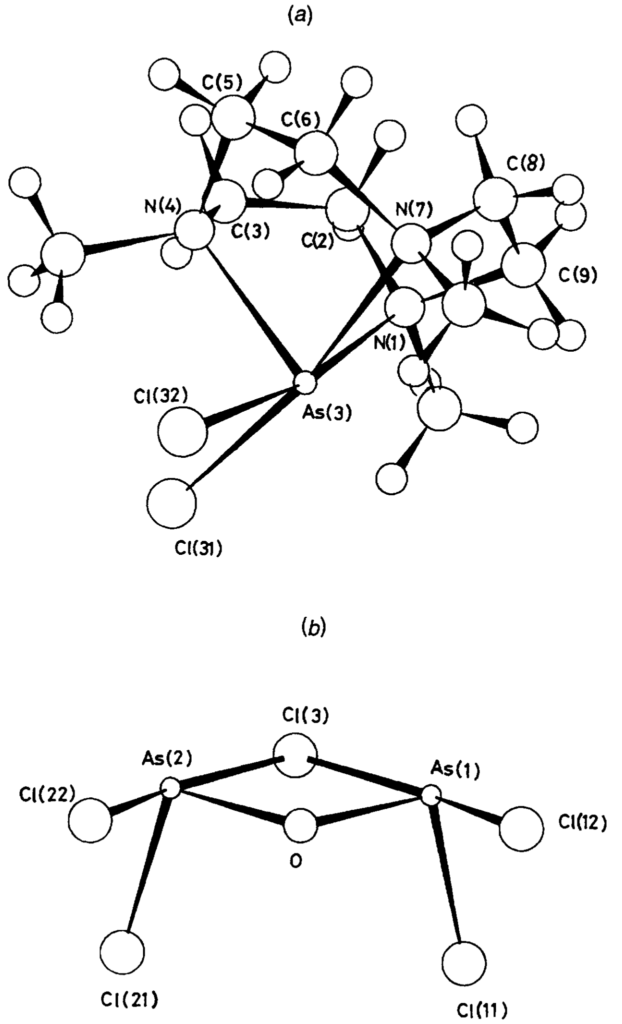

Fig. 1 Structures of (*a*) an individual $[AsCl_2L]^+$ cation and (*b*) an individual $[As_2OCl_5]^-$ anion in compound **1** complete with atom numbering

compound **2** there are two macrocycles in the asymmetric unit and one was disordered. Three of the carbon atoms were given two alternative positions each with an occupancy factor of 50%. In compound **4** there was an acetonitrile solvent molecule and two water solvent molecules which were refined with 50% occupancy. Apart from the disordered atoms, in each structure all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. For compounds **2**–**4** one or two of the nitrogen atoms in the macrocycle were protonated. In **3** and **4** these atoms were located in Fourier-difference maps and refined successfully. In **2** for one of the ligands, three hydrogens were located, one on each nitrogen, and each one was refined with an occupancy of 0.666. In all structures the thermal parameters of hydrogen atoms bound to nitrogen atoms were allowed to refine freely as a check on the successful positioning of these atoms. Empirical absorption corrections were applied[10] and the structures were then refined on F^2 using SHELXL.[11] All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Selected bond lengths (Å) and angles (°) for compounds **1**–**4** are listed in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/201.

Results and Discussion

Direct addition (equimolar) of MCl_3 (M = As, Sb or Bi) and L in acetonitrile solutions under an argon atmosphere provides the corresponding neutral 1 : 1 adducts as white semicrystalline solids. Their analytical and principal spectroscopic data are without controversy and are listed in the Experimental section. Typically the IR spectra show a series of bands in the 1200–500 cm^{-1} region characteristic of the aza ligand and one or two broad intense bands in the far IR region assigned to metal–chlorine ν(MCl) stretching modes (for strict C_{3v} symmetry two such modes are expected). The ^1H NMR spectral profile is constant with separate signals for the N–CH_3 (δ 2.70–3.01) and the ring backbone CH_2CH_2 (δ 3.13–3.49) protons. The similar profiles of the spectroscopic data for MCl_3L where M = As, Sb or Bi are a convincing argument for a common half-sandwich structure as authenticated by the crystal structure determination for M = Bi.[1]

Hydrolysis reactions

The hydrolysis reaction of $AsCl_3L$ was carried out in acetonitrile solution using the controlled stoichiometry (2). The

$$3AsCl_3L + H_2O \xrightarrow{MeCN} [AsCl_2L][As_2OCl_5] + 2L + 2HCl \quad (2)$$

identity of the white crystalline product **1** was only established by a crystal structure determination.

The structure, which is shown in Fig. 1 together with the atomic numbering scheme, consists of discrete $[LAsCl_2]^+$ cations and $[As_2OCl_5]^-$ anions. Looking at the $[LAsCl_2]^+$ cation the central five-co-ordinate arsenic atom is bonded to the three nitrogen atoms of the macrocycle [As–N 2.12(2), 2.10(2), 2.18(2) Å] and two chlorine atoms As–Cl [2.462(7), 2.520(7) Å]. Each chlorine atom sits *trans* to a ring nitrogen atom and the geometry of the co-ordination site is best described as ψ-octahedral with a lone pair occupying the sixth site in a *trans* location to the remaining ring nitrogen. There is a further contact with a chlorine atom As(3) ··· Cl(3) ($-x$, $-y$, $1 - z$) at 3.433 Å but this is rather distant to be considered realistically as a bonding interaction. The conformation of the ring is described by the torsion angles (see Table 5) which are very similar to those observed in $BiCl_3L$ as might be expected for a tridentate exodentate ligand. Clearly the ligand is not protonated and the N ··· N distances are 2.77, 2.72, 2.80 Å. Whereas macrocyclic stabilisation of $SbCl_2^+$ [with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane)[12] and with L[13]] and of $BiCl_2^+$ (with 18-crown-6[2b,h]) is known the present structure provides the first example for $AsCl_2^+$. The dimensions around the five-co-ordinate explicit ψ-octahedral metal centres of *cis*-$[MCl_2L]^+$ (M = As or Sb) are listed in Table 2.

Turning to the $[As_2OCl_5]^-$ anion, each arsenic atom is strongly bonded to three atoms in a *fac* arrangement, namely a bridging oxygen atom [As–O 1.75(2), 1.80(2) Å] and two terminal chlorine atoms [As–Cl 2.193(8), 2.236(6), 2.202(8), 2.233(7) Å]. In addition both of the arsenic atoms are weakly bonded to a bridging chlorine atom [As–Cl 2.802(7), 2.787(8) Å]. There are some intramolecular close contacts with other chlorine atoms but we have not designated these as bonding interactions, *e.g.* As(1) ··· Cl(32) ($\frac{1}{2} - x$, $y - \frac{1}{2}$, $1 - z$) 3.486 and As(2) ··· Cl(32) ($\frac{1}{2} - x$, $y - \frac{1}{2}$, $1 - z$) 3.175 Å.

Interestingly the hydrolysis reaction of $AsCl_3$·cyclam provided diprotonated cyclam ligand cations and $[As_4O_2Cl_{10}]^{2-}$ anions.[4] The structure of the latter, **A**, comprises a square-planar array of As atoms with two central chlorine atoms located one above and one below this plane such that each chlorine is linked to all four metal centres. A similar tetranuclear arsenic(III) anion previously described by Churchill

Table 1 Selected dimensions (distances in Å, angles in °) in structures **1**, **2** and **4**

Compound **1**			
As(1)–O	1.75(2)	As(2)–Cl(21)	2.202(8)
As(1)–Cl(11)	2.193(8)	As(2)–Cl(22)	2.233(7)
As(1)–Cl(12)	2.236(6)	As(1)–Cl(3)	2.802(7)
As(2)–O	1.80(2)	As(2)–Cl(3)	2.787(8)
As(3)–N(4)	2.10(2)	As(3)–Cl(31)	2.462(7)
As(3)–N(1)	2.12(2)	As(3)–Cl(32)	2.520(7)
As(3)–N(7)	2.18(2)		
O–As(1)–Cl(11)	99.4(6)	O–As(1)–Cl(3)	83.5(3)
O–As(1)–Cl(12)	89.7(5)	Cl(11)–As(1)–Cl(3)	88.3(3)
Cl(11)–As(1)–Cl(12)	92.9(3)	Cl(12)–As(1)–Cl(3)	173.2(3)
O–As(2)–Cl(21)	99.0(6)	Cl(21)–As(2)–Cl(3)	88.8(3)
O–As(2)–Cl(22)	89.8(5)	Cl(22)–As(2)–Cl(3)	172.9(3)
Cl(21)–As(2)–Cl(22)	93.5(3)	As(1)–O–As(2)	123.4(8)
O–As(2)–Cl(3)	83.2(5)	As(1)–Cl(3)–As(2)	68.1(4)
N(4)–As(3)–N(1)	80.3(8)	N(7)–As(3)–Cl(31)	168.6(5)
N(4)–As(3)–N(7)	81.6(8)	N(4)–As(3)–Cl(32)	91.7(7)
N(1)–As(3)–N(7)	80.0(7)	N(1)–As(3)–Cl(32)	169.5(5)
N(4)–As(3)–Cl(31)	87.9(6)	N(7)–As(3)–Cl(32)	92.3(5)
N(1)–As(3)–Cl(31)	93.8(6)	Cl(31)–As(3)–Cl(32)	92.6(3)
Compound **2**			
Sb(1)–O	1.921(4)	Sb(2)–O	1.923(4)
Sb(1)–Cl(11)	2.432(3)	Sb(2)–Cl(22)	2.410(3)
Sb(1)–Cl(12)	2.456(2)	Sb(2)–Cl(21)	2.441(3)
Sb(1)–Cl(31)	2.817(3)	Sb(2)–Cl(32)	2.838(3)
Sb(1)–Cl(32)	2.859(3)	Sb(2)–Cl(31)	2.939(3)
O–Sb(1)–Cl(11)	90.5(2)	O–Sb(2)–Cl(21)	88.4(2)
O–Sb(1)–Cl(12)	88.9(2)	Cl(22)–Sb(2)–Cl(21)	90.65(9)
Cl(11)–Sb(1)–Cl(12)	93.35(8)	O–Sb(2)–Cl(32)	76.7(2)
O–Sb(1)–Cl(31)	79.8(2)	Cl(22)–Sb(2)–Cl(32)	96.85(9)
Cl(11)–Sb(1)–Cl(31)	86.93(8)	Cl(21)–Sb(2)–Cl(32)	163.53(8)
Cl(12)–Sb(1)–Cl(31)	168.63(7)	Cl(31)–Sb(2)–Cl(21)	89.4(1)
O–Sb(1)–Cl(32)	76.2(2)	Cl(31)–Sb(2)–Cl(22)	168.9(1)
Cl(11)–Sb(1)–Cl(32)	164.10(8)	Cl(31)–Sb(2)–Cl(32)	80.5(1)
Cl(12)–Sb(1)–Cl(32)	95.01(9)	Cl(31)–Sb(2)–O	76.5(2)
Cl(31)–Sb(1)–Cl(32)	82.23(8)	Sb(2)–Cl(32)–Sb(1)	69.93(5)
O–Sb(2)–Cl(22)	92.4(2)	Sb(1)–O–Sb(2)	116.3(2)
Compound **4**			
Sb(1)–Cl(13)	2.401(5)	Sb(2)–Cl(22)	2.373(4)
Sb(1)–Cl(11)	2.425(4)	Sb(2)–Cl(24)	2.441(5)
Sb(1)–Cl(12)	2.468(4)	Sb(2)–Cl(23)	2.509(4)
Sb(1)–Cl(30)	2.902(4)	Sb(2)–Cl(21)	2.688(5)
Sb(1)–Cl(32)	2.976(4)	Sb(2)–Cl(30)	2.923(5)
Sb(1)–Cl(21)	3.139(6)	Sb(2) ··· Cl(11)	3.532(5)
Cl(13)–Sb(1)–Cl(11)	90.7(2)	Cl(22)–Sb(2)–Cl(24)	93.8(2)
Cl(13)–Sb(1)–Cl(12)	94.1(2)	Cl(22)–Sb(2)–Cl(23)	89.3(2)
Cl(11)–Sb(1)–Cl(12)	87.9(2)	Cl(24)–Sb(2)–Cl(23)	90.9(2)
Cl(30)–Sb(1)–Cl(13)	91.3(2)	Cl(22)–Sb(2)–Cl(21)	86.1(2)
Cl(30)–Sb(1)–Cl(11)	87.2(2)	Cl(24)–Sb(2)–Cl(21)	89.1(2)
Cl(30)–Sb(1)–Cl(12)	172.8(1)	Cl(23)–Sb(2)–Cl(21)	175.4(2)
Cl(32)–Sb(1)–Cl(13)	86.9(1)	Cl(30)–Sb(2)–Cl(22)	87.6(2)
Cl(32)–Sb(1)–Cl(11)	173.7(1)	Cl(30)–Sb(2)–Cl(24)	108.5(2)
Cl(32)–Sb(1)–Cl(12)	86.4(1)	Cl(30)–Sb(2)–Cl(23)	112.3(2)
Cl(32)–Sb(1)–Cl(30)	98.7(1)	Cl(30)–Sb(2)–Cl(21)	87.7(2)
Cl(21)–Sb(1)–Cl(13)	169.5(1)	Cl(11)–Sb(2)–Cl(22)	148.1(2)
Cl(21)–Sb(1)–Cl(11)	82.9(1)	Cl(11)–Sb(2)–Cl(24)	108.5(2)
Cl(21)–Sb(1)–Cl(12)	94.0(1)	Cl(11)–Sb(2)–Cl(23)	112.3(2)
Cl(21)–Sb(1)–Cl(30)	80.1(1)	Cl(11)–Sb(2)–Cl(21)	72.1(2)
Cl(21)–Sb(1)–Cl(32)	100.3(1)	Cl(11)–Sb(2)–Cl(30)	69.1(2)

Table 2 Mean dimensions of *cis*-$[MCl_2L]^+$

	M = As This work	M = Sb Ref. 13
M–N/Å	2.13(2)	2.359(8)
M–Cl/Å	2.491(7)	2.466(3)
Cl–M–Cl/°	92.6(3)	95.45(14)
N–M–N/°	80.6(7)	74.2(3)
cis N–M–Cl/°	91.4(6)	88.5(2)

Table 3 Mean dimensions of $(As_2OCl_5)_n{}^{n-}$

	n = 2 Structure **A** Ref. 4	*n* = 2 Structure **B** Ref. 14	*n* = 1 This work
As–$Cl_{terminal}$/Å	2.21	2.24	2.216(8)
As–O/Å	1.77	1.77	1.78(2)
As–Cl_{bridge}/Å	3.00–3.15	2.89–3.35	2.802(2)–2.787(8)
Cl–As–Cl/°	94.6(1)	93.5(1)	93.2(3)

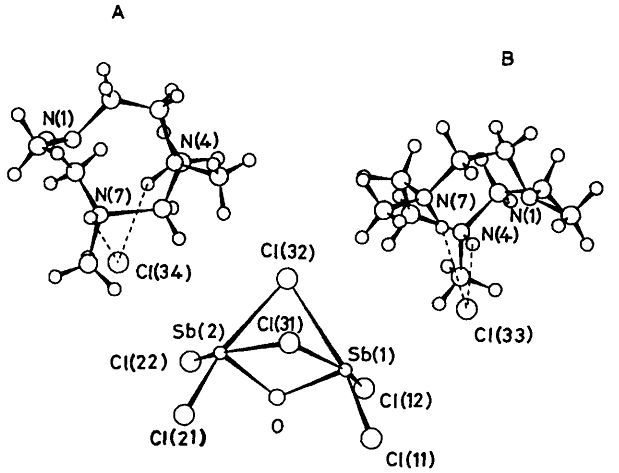

Fig. 2 Structure of $[H_2L]_2[Sb_2OCl_6]Cl_2$ **2** showing the atomic numbering scheme. Hydrogen bonds are shown as dashed lines. For macrocycle **B** only one of the two orientations is shown. For clarity the postulated intramolecular ring NH ··· N hydrogen bonds are not shown. The weak interactions Sb(2) ··· Cl(34) 3.551 and Sb(1) ··· Cl(33) 3.550 Å are not shown as discrete bonds

et al.[14] features two $Cl_2As–O–AsCl_2$ groups linked by two chlorine atoms each of which is linked (μ_3-Cl) to three of the arsenic atoms, structure **B**. As we pointed out at the time perhaps the most appropriate description of these tetranuclear anions is that of two $Cl_2As–O–AsCl_2$ units and two chloride anions held as an aggregate by As ··· Cl^- secondary bonds.[4] Evidently what we have in the present instance is the basic unit with a single Cl^- anion linked symmetrically to the two arsenic atoms of a single dinuclear (μ-oxo) $Cl_2As–O–AsCl_2$ group. The structure can be viewed as two fused ψ-trigonal-bipyramidal $AsCl_3O$(lone pair) units involving a bridging oxygen atom and a bridging chlorine (axial) atom as the common ClO edge. The mean dimensions of these three anions are listed for comparison in Table 3.

Controlled solvolysis of $SbCl_3L$ with water–acetonitrile using the stoichiometry (3) provided colourless crystals of the

$$3SbCl_3L + 2H_2O \xrightarrow{MeCN} \underset{\mathbf{2}}{2[H_2L]^{2+}[Sb_2OCl_6]^{2-}2Cl^-} + L + [Sb(O)Cl]_{residues} \quad (3)$$

ionic antimony(III) compound **2**. The structure of **2** consists of two independent $[H_2L]^{2+}$ cations, one of which is disordered, two chloride ions and an $[Sb_2OCl_6]^{2-}$ anion. A perspective view of the arrangement of these constituent ions is shown in Fig. 2 together with the atom numbering scheme. Each antimony(III) is strongly bound to two terminal chlorine atoms and a bridging oxygen atom in a *fac* arrangement [Sb–Cl 2.432(3), 2.456(2), 2.441(3), 2.410(3); Sb–O 1.921(4), 1.923(4) Å]. In addition each metal atom is weakly bound to two further chlorine atoms which occupy bridging positions [Sb–Cl 2.817(3), 2.859(3), 2.939(3), 2.838(3) Å] and are located *trans* to the terminal chlorine atoms.

Table 4 Mean dimensions of $[Sb_2OCl_6]^{2-}$

	Structure **C** Ref. 15	Structure **D** Ref. 4	This work
Sb–$Cl_{terminal}$/Å	2.44	2.43	2.435(3)
Sb–Cl_{bridge}/Å	2.89	2.89	2.863(3)
Sb–O/Å	1.95	1.94	1.922(4)
Sb–Cl–Sb/°	71.3	70.1	69.93(5)
Cl–Sb–$Cl_{terminal}$/°	89.9	90.3	92.00(8)
Sb–O–Sb/°	119.5	117.1	116.3(2)

The $[Sb_2OCl_6]^{2-}$ anion has been identified previously by Hall and Sowerby[15] (structure **C**) and, interestingly, was the particular μ-oxo-μ-chloro antimony(III) anion isolated in the hydrolysis reaction of $SbCl_3$·cyclam, structure **D**.[4] The structure can be described as two face-to-face fused ψ-octahedral $SbCl_4O$ (lone pair) units in which the bridging oxygen atom of the common OCl_2 face is *trans* to the lone pair associated with each of the antimony(III) centres. Again perhaps a more generalised view of this anion as a single Cl_2Sb–O–$SbCl_2$ unit linked to two chloride ions *via* secondary Sb ··· Cl^- bonding interactions involving the two metal centres is the more appropriate. {In passing we note several related antimony(III) cluster anions, *viz.* $[Sb_2OCl_7]^{3-}$ which can be viewed as a basic Cl_2Sb–O–$SbCl_2$ unit linked to three chloride anions[16] and $[Sb_4OCl_{12}]^{2-}$ which can be regarded as a loose aggregate of a Cl_2Sb–O–$SbCl_2$ unit, two molecules of $SbCl_3$ and two bridging chloride anions (μ- and μ_4-Cl).[17]} The mean bond dimensions of these several $[Sb_2OCl_6]^{2-}$ anions are listed in Table 4.

However there is one significant and crucial difference with the present structure; each of the individual antimony(III) centres is further associated, *i.e.* 'long-distance' with a separated and unique chloride anion lying along the direction of the presumed lone pair which is *trans* to the bridging oxygen atom. These chloride anions are, it is true, far distant [Sb ··· Cl 3.550(3), 3.551(3) Å] but their precise and equivalent separation distance means that they are crucially located for involvement in hydrogen-bonding interactions with the cations. In fact each chloride anion forms quite close contacts to two of the three nitrogen atoms of the triaza ring, *viz.* the ones that are protonated. For example Cl(33) is situated at 3.07, 3.02 Å from the protonated nitrogen centres N(4B) and N(7B) respectively and 3.48 Å from the unprotonated N(1B) of macrocycle B. As discussed in the Experimental section, the two protons associated with macrocycle A were disordered over three positions which means that the separation distances here are less clear-cut than those in macrocycle B. However the most likely scenario is that N(4A) and N(7A) are protonated with the chloride anion Cl(34) located 3.13 Å from N(7A), 3.08 Å from N(4A) and 3.35 Å from (unprotonated) N(1A). The N ··· N distances of the individual macrocycles (A and B) also point to the fact that in each case the two associated protons form bifurcated hydrogen bonds involving a chloride anion and the unprotonated nitrogen atom, *e.g.* in macrocycle A N(4) ··· N(7) 2.95, N(4) ··· N(1) 2.85, N(7) ··· N(1) 2.70 Å and in macrocycle B N(4) ··· N(7) 3.02, N(4) ··· N(1) 2.71, N(7) ··· N(1) 2.80 Å.

Two main points emerge from these controlled hydrolysis studies involving MCl_3·cyclam and MCl_3·Me_3[9]aneN_3: (*i*) there is formation of a common set of anions based on the fundamental μ-oxo dinuclear unit Cl_2M–O–MCl_2 where M = As or Sb; (*ii*) most conspicuously, hydrolytic decomposition with formation of μ-oxo species is not observed with the corresponding bismuth(III) systems.

Formation of the basic Cl_2M–O–MCl_2 unit which represents the first identifiable fragment in the hydrolysis sequence toward oxide formation [equation (1)] can be viewed as the result of initial nucleophilic attack by water molecule(s) followed by condensation reactions involving $LMCl_2(OH)$ fragments. The presence of HCl facilitates the breakdown of metallo-ring bonds with release of the azamacrocycle ligands as protonated (cationic) species. For the arsenic(III) systems, aggregation of the basic dinuclear unit with a single chloride ion gives rise to $(As_2OCl_5)_n^{n-}$ where $n = 2$ for the cyclam system and $n = 1$ for the present Me_3[9]aneN_3 system. With Sb^{III} there are two chloride anions involved in the aggregation leading to the formation of $[Sb_2OCl_6]^{2-}$ in both systems. Specifically the $[Sb_2OCl_6]^{2-}$ anion arising from the present Sb^{III}–Me_3[9]aneN_3 system is associated with two more chloride anions which, as detailed above, play an important part in the resulting fabric of hydrogen-bonding interactions incorporating the NH^+ sites of the diprotonated L cation. Why the fully protonated form of L is not formed is an interesting question. For the parent non-methylated triaza macrocycle [9]aneN_3 (L^0) the protonation constants (log K_1 10.42, log K_2 6.82, log K_3 very small)[18] indicate that stepwise formation of $[HL^0]^+$, $[H_2L^0]^{2+}$ and $[H_3L^0]^{3+}$ is possible but that the fully protonated species only exists in highly acidic conditions due to the very strong repulsions engendered by three protonated NH centres when restricted to a relatively small ring cavity. A similar picture is projected for the present methyl-substituted L based on ^1H NMR/pH-dependence studies where three inflections at pH 11.7, 5.1, and 0.4 (±0.2) correspond to stepwise protonation at the amine centres with the sequence only completed under highly acidic conditions.[19] Double protonation with a Cl^- anion positioned directly above and equidistant from the two protonated amine centres to maximise hydrogen-bonding interactions [(intramolecular) N–H ··· N and N–H ··· Cl^-] evidently represents the most favourable (stable) arrangement in the present situation.

With regard to the protonated series $[HL]^+$, $[H_2L]^{2+}$ and $[H_3L]^{3+}$ this is the first description of the structure of the diprotonated form of L. The monoprotonated cation has been isolated (following direct reaction of L and perchloric acid) and structurally characterised by Wieghardt *et al.*[20] In that structure the acidic proton is bonded to one ring nitrogen atom and forms strong intramolecular hydrogen bonds (N–H ··· N 2.71, 2.71 Å) within the cavity. The other N ··· N distance is 2.90 Å. We have isolated the same cation but by an entirely circuitous route. An investigation of the reaction system $SiMe_3I$–L–MeCN, carried out as a separate but related study for possible silicon(IV) adduct formation, provided colourless needle crystals of [HL]I **3** as confirmed by a crystal structure determination. The proton source is presumed as HI resulting from inadvertent hydrolysis of Si–I bond(s) *via* water contamination; no effort was made to identify the silicon-containing residues. The structure of **3** consists of independent $[HL]^+$ cations and iodine anions and is shown in Fig. 3 together with the atom labelling used. The proton was located on N(1) and is involved in intramolecular hydrogen bonding with both N(4) and N(7). The separation distances from N(1) to N(4) and N(7) are equal at 2.71 Å whereas that between N(4) and N(7) is significantly larger at 2.90 Å exactly the same as in the Wieghardt structure. The iodide anion has no contacts with any of the ring nitrogen atoms less than 4.3 Å. Surprisingly the torsion angles around the aza ring are different from those observed in $[HL]^+[ClO_4]^-$, as shown in Table 5, despite the fact that both structures have very similar N ··· N distances. These two conformations of $[HL]^+$ are, however, related to the mean values of the two clusters from the crystal structures containing L (see later discussion and Table 5).

In a further study of the related reaction system $SiCl_4$–L–$SbCl_5$–MeCN the product isolated as colourless crystals, compound **4**, was identified by X-ray crystallography as another example of the diprotonated $[H_2L]^{2+}$ cation. Again the fate of the silicon-containing component(s) was not pursued

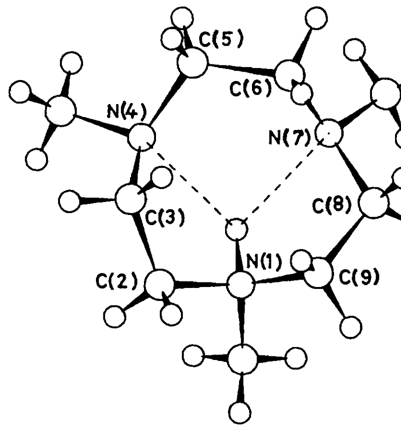

Fig. 3 Structure of an individual $[HL]^+$ cation in compound **3** complete with atom labelling. Hydrogen bonds are shown as dashed lines

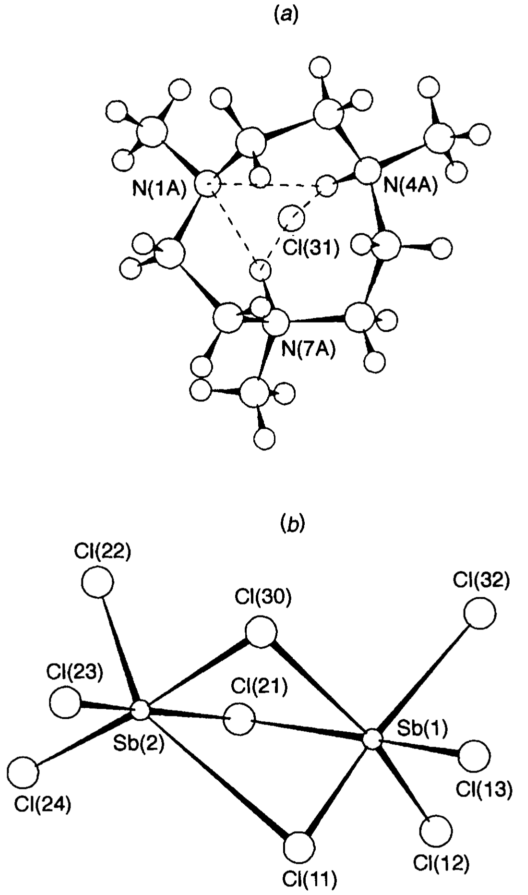

Fig. 4 Structure of (*a*) an individual $[H_2L]\cdots Cl$ moiety and (*b*) the structure of an individual $[Sb_2Cl_9]^{3-}$ anion in compound **4** including the atom numbering

and hydrolysis of Si–Cl bonds from water contamination with release of HCl is the most obvious source of protons. The asymmetric unit of **4** consists of two $[H_2L]^{2+}$ cations, an $[Sb_2Cl_9]^{3-}$ anion, a chloride anion, one solvate MeCN molecule and two solvate H_2O molecules each with 50% occupancy. Characterisation of the anion as $[Sb_2Cl_9]^{3-}$ and based on Sb^{III} is made from a study of bond dimensions which are listed in Table 1. Atom Sb(1) is strongly bound to three chlorine atoms in a *fac* arrangement [Cl(13) at 2.401(5), Cl(11) at 2.425(4), Cl(12) at 2.468(4) Å] and weakly bound to three other chlorine atoms [Cl(30) at 2.902(4), Cl(32) at 2.976(4) and Cl(21) at 3.139(6) Å] representing an approximate octahedral environment. The other metal centre Sb(2) is also strongly bound to three chlorine atoms in a *fac* arrangement [Cl(22) at 2.373(4), Cl(24) at 2.441(5) and Cl(23) at 2.509(4) Å] with an additional relatively strong bond to Cl(21) at 2.688(5) Å and a somewhat weaker linkage to Cl(30) at 2.923(5) Å. Both these latter chlorine atoms form bridges to Sb(1). Thus the immediate environment of Sb(2) is made up of five chlorine atoms in a distorted square-pyramidal arrangement. Atom Sb(2) is also relatively close to Cl(11) at 3.532(5) Å which constitutes a third chlorine atom bridging the two antimony centres. However it is not clear that this is definitely a bonding interaction as the position of Cl(11) is far removed from the final octahedral position. We have thus designated the anion as $[Sb_2Cl_9]^{3-}$; the structure of this anion with the atom labelling used is shown in Fig. 4. With the additional chloride anion Cl(31) in the lattice the two cations can therefore be designated as the diprotonated species $[H_2L]^{2+}$. Interestingly the positioning of this additional chloride ion relative to one of the cations provides an associated $[H_2L]\cdots Cl$ moiety which has dimensions similar to those found in structure **2**, see Fig. 4. Thus Cl(31) is located above the cation at separation distances of 3.49, 3.16 and 3.08 Å from N(1A), N(4A) and N(7A) respectively. This is in accord with our selection of N(4A) and N(7A) as the protonated sites. However the two hydrogen atoms on N(4A) and N(7A) also form strong intracavity hydrogen bonding to N(1A). An identical arrangement is found for Cl(32) which is positioned above the other cation, *i.e.* Cl(32) lies 3.10, 3.11 and 3.55 Å from N(4B), N(7B) and N(1B) respectively and the separation distances of the ring nitrogen atoms are N(1B) ⋯ N(4B) 2.75, N(1B) ⋯ N(7B) 2.72 and N(4B) ⋯ N(7B) 3.03 Å.

In summary the structure of the triaza macrocycle L has been determined in several different situations, *viz.* when co-ordinated to an $AsCl_2^+$ cation in compound **1**, and then in its monoprotonated form in **3** and diprotonated form in **2** and **4**. Set against the massive list of metal complexes of L[21] there is only one reported crystal structure involving an ionic form of L namely $[HL][ClO_4]$.[20] As noted above the conformation of the ligand in the two $[HL]^+$ structures is surprisingly different despite the fact that the intramolecular hydrogen-bonding pattern is common to both and there is no anion involvement in hydrogen bonding in either. Table 5 lists the torsion angles around the triaza ring as observed in compounds **1**–**4** and Table 6 includes N ⋯ N and N ⋯ Cl intramolecular distances indicative of the extent of hydrogen bonding in the four structures.

All our attempts to protonate the third amino group and isolate the $[H_3L]^{3+}$ cation ended in failure. Wieghardt *et al.*[20] have reported the fully methylated cation in the compound 1,1,4,4,7,7-hexamethyl-1,4,7-triazoniacyclononane tris(tetrafluoroborate) but no structural details are available.

There are 214 examples of L bonded to metal ions in the Cambridge Crystallographic Database.[22] We carried out an assessment of the conformations of these structures based on the nine torsion angles around the ring. The conformations were then clustered using the root-mean-square (r.m.s.) deviation of torsion angles. Our program takes into account all six equivalent permutations of the atoms in the ring (*e.g.* nitrogen atoms 1,2,3; 2,3,1; 3,1,2; 1,3,2; 2,1,3; 3,2,1) as well as sign changes. Conformations with r.m.s. deviations of less than 20° were included in the same cluster. All 214 examples could be classified in two clusters with 99 and 115 members each. We then calculated the mean torsion angles in these two clusters and these are presented in Table 5. Note that these two are very similar with differences of *ca.* 30° in the torsion angles. The conformations of the ligand in compound **1** and in $BiCl_3L$ are somewhat closer to the A conformation than the B. We then carried out detailed conformational analyses using molecular dynamics and molecular mechanics methods on L and its protonated forms. For this we used the quanta/CHARMm software.[23] The input structure files were created from the

Table 5 Torsion angles (°) in the macrocycle

								Experimental structures[b]		Theoretical structures (lowest-energy conformations[c])				
								L		L				
	1	$BiCl_3L$	**3**	$[HL][ClO_4]$	**2A**[a]	**4A**	**4B**	A	B	A	B	$[HL]^+$	$[H_2L]^{2+}$	$[H_3L]^{3+}$
N(1)–C(2)–C(3)–N(4)	34(5)	38(3)	27(2)	7	43(1)	42(2)	30(2)	46	14	49	−135	42	42	−122
C(2)–C(3)–N(4)–C(5)	76(4)	70(3)	80(2)	91	64(1)	60(2)	70(2)	69	91	65	81	69	62	84
C(3)–N(4)–C(5)–C(6)	−123(4)	−125(3)	−121(1)	−103	−121(2)	−130(2)	−123(2)	−132	−111	−130	−65	−131	−126	−70
N(4)–C(5)–C(6)–N(7)	38(5)	38(3)	36(2)	11	48(1)	59(2)	46(2)	46	16	49	115	49	59	115
C(5)–C(6)–N(7)–C(8)	75(4)	69(3)	74(2)	91	68(1)	59(2)	69(2)	69	90	65	−65	66	54	−63
C(6)–N(7)–C(8)–C(9)	−131(3)	−132(2)	−122(2)	−108	−122(1)	−126(2)	−108(2)	−132	−106	−130	−74	−128	−118	−64
N(7)–C(8)–C(9)–N(1)	50(3)	45(3)	37(2)	17	36(1)	50(2)	23(2)	46	10	49	117	45	49	113
C(8)–C(9)–N(1)–C(2)	68(3)	69(3)	83(2)	95	77(1)	75(2)	95(2)	69	94	65	−60	77	76	−68
C(9)–N(1)–C(2)–C(3)	−120(3)	−126(3)	−128(2)	−113	−134(1)	−138(2)	−125(2)	−132	−111	−130	88	−137	−136	82

[a] Compound **2B** is disordered. [b] Two clusters A and B (see text). [c] Two low-energy conformations A and B are given for L (see text).

crystal structures. They were then subjected to 100 ps of molecular dynamics at 3000 K. The step size was 1 fs and the structures were saved every 100 steps so that 1000 structures were obtained. These were all minimised by molecular mechanics and subsequently analysed. In all structures there was a distinct energy-minimum conformation (described in Table 5) although all had many other low-energy conformations within a few kcal mol^{-1}.

The minimum-energy conformation (18.46 kcal mol^{-1}) for free L is very similar to that found for cluster type A in the experimental structures and indeed in **1** and $BiCl_3L$. The second lowest-energy conformation (18.77 kcal mol^{-1}) does not have C_3 symmetry as shown by the torsion angles in Table 5. The minimum-energy conformation for the monoprotonated form $[HL]^+$ is similar to that of free L but it is slightly distorted so that two intramolecular hydrogen bonds are formed at 2.74 Å. The third N · · · N distance is 2.92 Å. The conformation is very similar to that observed in **3** and therefore different from the more planar arrangement observed in $[HL][ClO_4]$ which is much closer to that of the cluster type B found in the experimental structures. Similar good agreement with experiment is found for $[H_2L]^{2+}$ where the lowest-energy conformation also has two intramolecular hydrogen bonds (N–H · · · N 2.86, 2.88) with the third N · · · N distance of 3.22 Å. The torsion angles are very similar to those observed in **2A**, **4A** and **4B**. This would suggest that the intermolecular bonding to the chloride anion which is a fundamental feature of these structures is the 'icing on the cake' rather than a conformation-determining interaction. All these three theoretical structures maintain approximate C_3 symmetry though with slight variations because of the intramolecular hydrogen bonds. However the minimised structure of $[H_3L]^{3+}$ has an irregular conformation, which is however similar to that found for the second lowest-energy conformation of L (Table 5), but because of the protonation the ligand is expanded in size such that the three N · · · N distances are 3.75, 3.75, 3.67 Å compared to 2.99, 3.04, 3.22 Å in the similar conformation for free L. It seems likely then that the triprotonated conformation would not have C_3 symmetry and that it is likely to be stabilised in the crystal by intermolecular hydrogen bonds to the anion, particularly as there can be no intermolecular hydrogen bonds.

It is remarkable then that experimental and theoretical studies show that free L and the mono- and di-protonated cations have similar conformations with minor adjustments occurring to facilitate the formation of intermolecular hydrogen bonds.

Table 6 Possible hydrogen bonding (distances in Å) in the structures

(*a*) N · · · N intramolecular distances

	1	**2A**	**2B**	**3**	**4A**	**4B**
N(1) · · · N(4)	2.72	2.85*	2.71*	2.71*	2.79*	2.75*
N(1) · · · N(7)	2.77	2.70*	2.80*	2.71*	2.73*	2.72*
N(4) · · · N(7)	2.80	2.95	3.02	2.90	3.06	3.03

(*b*) Cl · · · N intramolecular distances

Compound **2**			
Cl(33) · · · N(1B)	3.48	Cl(34) · · · N(1A)	3.35
Cl(33) · · · N(4B)	3.07*	Cl(34) · · · N(4A)	3.08*
Cl(33) · · · N(7B)	3.02*	Cl(34) · · · N(7A)	3.13*
Compound **4**			
Cl(31) · · · N(1A)	3.49	Cl(32) · · · N(1B)	3.55
Cl(31) · · · N(4A)	3.16*	Cl(32) · · · N(4B)	3.10*
Cl(31) · · · N(7A)	3.08*	Cl(32) · · · N(7B)	3.11*

* Postulated hydrogen bond.

Acknowledgements

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Note added at proof. Since this paper was submitted for publication molecular-orbital *ab initio* calculations have been reported on some tri- and tetra-aza cyclic amines, including L, aimed at the determination of minimum-energy geometries and relative conformational energies in different protonation states.[24]

Table 7 Crystal data and structure refinement for compounds **1**–**4***

	1	**2**	**3**	**4**
Empirical formula	$C_9H_{21}As_3Cl_7N_3O$	$C_{18}H_{46}Cl_8N_6OSb_2$	$C_9H_{22}IN_3$	$C_{20}H_{51}Cl_{10}N_7Sb_2O$
M	660.20	887.7	299.2	1002.6
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a/Å	11.744(9)	10.408(9)	8.727(7)	14.072(7)
b/Å	12.513(9)	17.003(12)	11.372(12)	10.843(12)
c/Å	14.242(12)	19.31(2)	13.018(12)	27.23(2)
β/°	92.310(10)	102.64(1)		91.30(1)
U/Å^3	2091	3335	1292	4154
D_c/Mg m^{-3}	2.097	1.768	1.535	1.603
μ/mm^{-1}	5.664	2.285	2.448	1.968
F(000)	1288	1768	600	1980
Crystal size/mm	0.20 × 0.15 × 0.20	0.15 × 0.10 × 0.20	0.30 × 0.25 × 0.20	0.15 × 0.17 × 0.25
θ Range/° for data collection	2.74–25.07	2.87–24.88	3.91–24.97	2.82–24.83
hkl Ranges	0–13, −14 to 14, −16 to 16	−12 to 0, −19 to 19, −22 to 22	0–9, −13 to 13, −15 to 15	−16 to 16, 0–11, 0–32
Reflections collected	4901	9594	2071	11 636
Independent reflections (R_{int})	3131 (0.0687)	5634 (0.0411)	1378 (0.0359)	6304 (0.0576)
a, *b* in weighting scheme	0.051, 118.29	0.07, 18.10	0.05, 2.09	0.109, 168.2
Data, restraints, parameters	3131, 0, 210	5634, 0, 323	1378, 0, 123	6304, 0, 368
Goodness of fit on F^2	1.145	1.126	1.066	1.024
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.1034, 0.2314	0.0520, 0.0952	0.0398, 0.0990	0.0980, 0.2005
(all data)	0.1657, 0.2915	0.0727, 0.1023	0.0581, 0.1088	0.1157, 0.2086
Largest difference peak and hole/e Å^{-3}	1.709, −1.228	0.638, −0.650	0.595, −0.805	1.286, −1.038

* $Z = 4$; weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

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