Insights into supramolecular design from analysis of halide coordination geometry in a protonated polyamine matrix†

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Single-crystal X-ray diffraction analysis at 100 K of nineteen hydrogen bonded structures formed from reaction of five aliphatic polyamines with hydrochloric, hydrobromic and hydriodic acid is reported. The polyamines included are diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$ **1**, *N*-(2-aminoethyl)propane-1,3-diamine, $H_2N(CH_2)_3NH(CH_2)_2NH_2$ **2**, triethylenetetramine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ **3**, *N*,*N*′-bis(3-aminopropyl)ethylenediamine, $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ **4** and 2,2′,2″-triaminotriethylamine, $N[(CH_2)_2NH_2]_3$ **5**. The anions interact *via* hydrogen bonds with the protonated amines in a variety of complexation geometries and coordination numbers. A marked deviation from the extended all-*anti* conformation is observed for some of the polyammonium cations, depending on their shape, protonation sites, the polyammonium cation : anion ratio and the size of the amines and the complexed halides. The analysis of the crystal structures showed some preference for three- and four-coordinate $N–H\cdots X^-$ hydrogen bonded geometries for the complexed halides, with additional longer interactions, including $C–H\cdots X^-$ hydrogen bonds and $N^+\cdots X^-$ electrostatic interactions. Some chelate effects were also observed. To a first approximation, however, the halides act as spherical charges and their coordination sphere is highly flexible. In general, solid-state self-assembly occurs in such a way as to maximise the number and strength of hydrogen bonds and non-directional interactions in the system as a whole.

Introduction

Anion coordination chemistry[1–3] has been, until recently, one of the least studied fields of supramolecular chemistry despite its fundamental role in many chemical and biological processes. Applications of anion coordination chemistry include binding and transport of biologically important anions,[4] catalysis of organic reactions,[5] analytical chemistry[6,7] and synthesis of receptors for the clean-up of anionic pollutants.[8,9]

For the halide anions specifically, an enormous number of receptors, some of them quite successful, have been synthesized, including a wide variety of conformations, binding sites, geometries and interaction types. However, the problem of designing strong and yet highly selective halide receptors has not yet been solved. Indeed, it is often found in analytical applications that strength and selectivity in binding are mutually antagonistic. For this goal to be achieved, the question of the existence of any preferential environment (coordination geometry, hydrogen bond distances, connectivity patterns) for the anions of interest, is of great importance. Crystal structure analysis reveals that in known complexes, hydrogen bonded halide anions adopt tetrahedral,[10–12] octahedral[13] or even a quasi-trigonal prismatic geometries.[13] This is usually the case for three-dimensional anion cryptates that possess a high degree of preorganization.[4] On the other hand, it has been found that the halides display recognisable coordination polyhedra even in some cases where the cationic hosts lack any degree of preorganization.[14,15] To make matters more complicated, many other crystal structures with preorganized monocyclic hosts are known in which no preference for a specific geometry or a coordination number is observed for the complexed halides.[16–18] However, the most effective hosts interact with halides in well defined geometries and display three-dimensional binding.[10–13,19,20] These hosts posses a greater degree of preorganisation compared to monocyclic[16–18] or acyclic compounds.[14,15,21,22] Despite this, the question of the existence of any preferred coordination environment for halide anions has still not been answered.

In the present contribution, we approach the subject by reacting the aliphatic polyamines **1**–**5** (Fig. 1) with hydrochloric, hydrobromic and hydriodic acid in ratios of 1 : 1 to 1 : 4. The logic of the experiment is to leave the halides free to interact with a highly flexible, sterically unencumbered polyammonium host and thus elucidate statistically "preferred" solid-state anion coordination environments, if any, by X-ray crystallography.

The aliphatic polyamines **1**–**5** have been chosen in particular because they can be easily protonated in solution and donate their protons to anionic species to give hydrogen bond networks. In addition, the fully protonated two- and three-dimensional cyclic analogues of those amines exhibiting similar donor patterns, have been successfully used for the encapsulation of the halides.[10,11,13,16–20]

Results

Before the discussion of the crystal structures, a clear distance criterion for hydrogen bonding has to be adopted. A simple length-based approach suggests[23] hydrogen bonding between the groups X–H and Y when the distance $H\cdots Y$ is shorter than the van der Waals approach: $d < W_H + W_Y$. The van der Waals radii for the elements of interest[23,24] are *ca.* 1.20 Å for

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† Electronic supplementary information (ESI) available: Table 1, hydrogen bonds for new complexes [Å and °]; Table 2, anion coordination environments for the complexed halides. See http://www.rsc.org/suppdata/nj/b0/b004641h/

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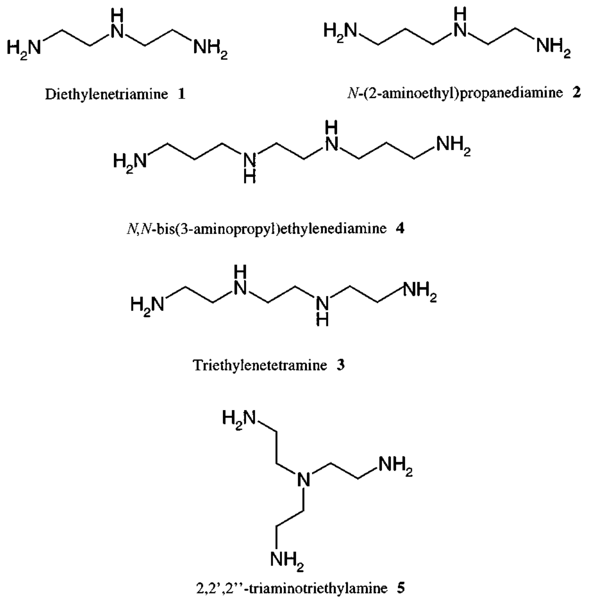

Fig. 1 The free amines **1**–**5** in all-*anti* conformations.

hydrogen, 1.40 Å for oxygen, 1.50 Å for nitrogen, 1.80 Å for chloride, 1.95 Å for bromide and 2.15 Å for iodide. Therefore, hydrogen bonded N–H···X distances are expected to be less than 2.60, 2.70, 3.00, 3.15 and 3.35 Å for X = O, N, Cl, Br and I, respectively. More recent results, especially involving neutron diffraction analysis, indicate that longer, weaker hydrogen bonds exist beyond that criterion, however, particularly those involving C–H bonds.[25] In this work we have concerned ourselves with the environment of the anions as a whole, coupling distance and angular criteria with a more wide ranging analysis of apparently "exposed" regions of the guest anions.

A full list of the compounds prepared with all the relevant crystallographic data is given in Table 1. Hydrogen bond distances and angles as well as all the relevant information on the coordination environments of the anions are given as ESI†. In each case effort has been made to locate protons involved in hydrogen bonding interactions experimentally and refine their positions.

Our original, simplistic prediction concerning the halide salts of polyammonium cations derived from **1**–**5** was that each N–H proton would take part in one hydrogen bond (although there is also a significant possibility of bifurcated interactions). Beginning with diethylene triamine **1**, therefore, for the mono-, di- and tri-protonated forms, a total of six, seven and eight hydrogen bonds would be expected, divided by a total of one, two and three anions, respectively. This results in predicted anion coordination numbers of 6, 3/4 and 3/3/2 in the absence of any other significant hydrogen bond acceptors. The occurrence of amine lone pairs in all but the triprotonated form may well reduce the number of N–H functionalities available for interaction with the anions by N–H···N interactions.

In fact, reaction of haloacids with **1** resulted in the isolation and structural characterisation of the following species: $[NH_2(CH_2)_2NH_2^+(CH_2)_2NH_2]\cdot Br^-$ **1a**, $[NH_3^+(CH_2)_2NH(CH_2)_2NH_3^+]\cdot 2Cl^-$ **1b**, $[NH_3^+(CH_2)_2NH(CH_2)_2NH_3^+]\cdot 2Br^-$ **1c**, $[NH_3^+(CH_2)_2NH(CH_2)_2NH_3^+]\cdot 2I^-$ **1d**, $[NH_3^+(CH_2)_2NH_2^+(CH_2)_2NH_3^+]\cdot 3Cl^-$ **1e**, $[NH_3^+(CH_2)_2NH_2^+(CH_2)_2NH_3^+]\cdot 3Br^-$ **1f**. The crystal structure of triprotonated diethylenetriamine trichloride **1e** has been previously analyzed at room temperature but has been redetermined to greater precision in the present work in order to locate NH protons.[26] In this species the polyammonium ion adopts an extended, all-*anti* conformation that minimises electrostatic repulsions between the three protonated nitrogen atoms. The chloride anion Cl(1), which is hydrogen bonded to the two central $-NH_2^+-$ units, is two-coordinate (in terms of N–H···Cl hydrogen bonds), while the other two anions, Cl(2) and Cl(2)′, are in symmetry-identical three-coordinate environments (Fig. 2). This arrangement saturates (in hydrogen bonding terms) all of the hydrogen bond donors, consistent with expectation. In accordance with the sterically unencumbered environment around Cl(1), the two symmetry equivalent hydrogen bonded N···Cl distances are short, 3.0627(16) Å, and N–H···Cl angles are close to 180° (Table 1 of ESI†). The N···Cl···N angle of 112.8° is far from linear, however, suggesting the need to avoid excessive empty space between the two cation strands. This allows the exposed face of the halide anion to take part in two additional, weaker C–H···Cl interactions with ethylene groups on adjacent molecules (H···Cl 2.82 Å). Similarly, the three-coordinate Cl(2) anion forms the apex of an irregular trigonal pyramid, somewhat resembling a letter 'Y' when viewed along the pseudo-trigonal axis. Longer C–H···Cl interactions are again observed on the non-hydrogen bonded face.

In contrast to the chloro analogue, triprotonated diethylenetriamine tribromide **1f** adopts a chelating conformation with one terminal and the central ammonium functionality N(1) and N(2) interacting with the five-coordinate anion Br(2). Anion Br(1) is three-coordinate and adopts a nearly planar T-shape coordination geometry with N···Br(1)···N angles of 171.4, 109.3 and 78.6°. This T-shape represents an extreme distortion of the geometry seen for Cl(2) above in which the anion forms the apex of a trigonal pyramid. One interaction is significantly longer than the other two and is bifurcated. Anions Br(2) and Br(3) are respectively five- and four-coordinate. Br(2) is in the centre of a distorted square pyramid although the interaction to H(32) of N(3) is highly non-linear and may well be better described as a short [3.385(7) Å] electrostatic $N^+\cdots Br^-$ interaction rather than a hydrogen bond. Similarly, Br(3) does not display any regular coordination geometry and some interactions are again highly non-linear (Fig. 3). In general there is a total of eight hydrogen bond donors taking part in twelve interactions falling within the cut-off limits adopted, suggesting at least four bifurcated hydrogen bonds or the existence of non-hydrogen bonded short contacts and indeed N···Br distances fall over a wide range (see Table 1 of ESI†). The chelate interaction to Br(2) involves strong hydrogen bonds, however, and clearly the larger size of the bromide anion enables the N(1) and N(2) donors to approach one another without overwhelming electrostatic repulsion. This results in an overall much less regular

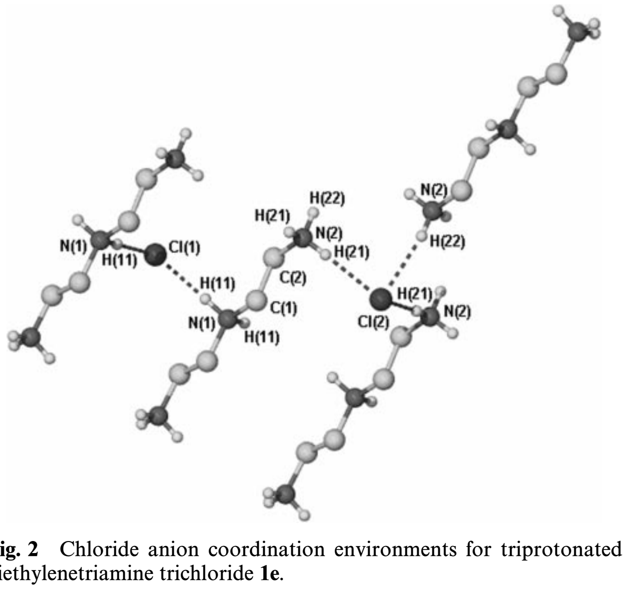

Fig. 2 Chloride anion coordination environments for triprotonated diethylenetriamine trichloride **1e**.

Table 1 Crystallographic parameters for new compounds

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**2a**	**3a**	**3b**	**3c**
Formula	$C_4H_{14}BrN_3$	$C_4H_{15}Cl_2N_3$	$C_4H_{15}Br_2N_3$	$C_4H_{15}I_2N_3$	$C_4H_{16}Cl_3N_3$	$C_4H_{16}Br_3N_3$	$C_5H_{19}Br_2N_3O$	$C_6H_{24}Cl_2N_4O_2$	$C_6H_{24}Br_2N_4O_2$	$C_6H_{24}I_2N_4O_2$
M	184.09	176.09	265.01	358.99	212.55	345.93	297.05	255.20	344.12	438.10
T/K	100	100	100	100	100	100	100	100	100	100
Crystal system	Tetragonal	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{4}2_1m$	$Pnma$	$Pbca$	$Pbca$	$Pmmm$	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
μ/mm^{-1}	5.080	0.647	8.583	5.808	0.832	10.972	7.050	0.483	5.863	4.170
a/Å	8.6698(4)	8.6597(6)	11.6664(10)	12.035(2)	5.1016(7)	6.2094(12)	4.8037(10)	4.7197(9)	4.7413(9)	4.8139(10)
b/Å	8.6698(4)	8.7948(4)	9.1552(5)	9.7006(19)	21.343(3)	19.674(4)	11.005(2)	10.658(2)	10.935(2)	11.418(2)
c/Å	5.2977(3)	11.9359(8)	17.5536(18)	18.374(4)	4.7440(5)	9.0026(4)	10.871(2)	13.046(3)	13.315(3)	13.689(3)
β						93.351(4)	95.627(7)	93.252(3)	91.770(3)	90.484(3)
V/Å^3	398.20(3)	909.04(10)	1874.9(3)	2145.1(7)	516.54(12)	1097.9(4)	571.9(2)	655.2(2)	690.0(2)	752.4(3)
Z	2	4	8	8	2	4	2	4	4	4
No. measd. reflns.	2896	6490	9938	16 401	3561	7068	4550	7597	9018	10 258
No. unique reflns.	426	950	1812	2092	662	2145	2091	1280	1348	1457
R_{int}	0.088	0.037	0.068	0.055	0.046	0.068	0.106	0.031	0.076	0.053
$R1$ [on F, $I > 2\sigma(I)$]	0.0282	0.0235	0.0410	0.0388	0.0313	0.0538	0.0711	0.0228	0.0283	0.0182
$wR2$ (on F^2, all data)	0.0651	0.0585	0.0980	0.0933	0.0672	0.1369	0.1667	0.0545	0.0760	0.0432

	3d	**3e**	**4a**	**4b**	**5a**	**5b**	**5c**	**5d**	**5e**
Formula	$C_6H_{24}Br_4N_4O$	$C_6H_{24}I_4N_4O$	$C_8H_{24}Cl_2N_4$	$C_8H_{24}Br_2N_4$	$C_6H_{19}BrN_4$	$C_6H_{21}IN_4O$	$C_6H_{21}Cl_3N_4$	$C_6H_{21}I_3N_4$	$C_6H_{24}Br_4N_4O$
M	487.92	675.89	247.22	336.14	227.16	292.17	255.62	529.97	487.94
T/K	100	100	100	100	100	100	100	100	100
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Cubic	Hexagonal	Monoclinic
Space group	$Aba2$	$Aba2$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_13$	$R3c$	$P2_1/c$
μ/mm^{-1}	9.819	6.529	0.452	5.797	3.915	2.614	0.683	6.194	10.127
a/Å	14.286(3)	15.091(3)	5.5047(11)	5.9645(12)	8.6143(17)	8.5019(17)	10.8750(13)	16.501(2)	14.889(3)
b/Å	16.187(3)	16.774(3)	11.895(2)	12.573(3)	8.7903(18)	9.6112(19)			10.685(2)
c/Å	14.162(3)	15.060(3)	10.410(2)	9.4371(19)	13.772(3)	14.840(3)		9.5919(19)	20.754(4)
β/°			90.671(6)	100.238(5)	95.505(4)	91.083(3)		120(γ)	105.922(4)
V/Å^3	3274.9(11)	3812.2(13)	681.6(2)	696.4(2)	1038.1(4)	1212.4(4)	1286.1(3)	2261.8(6)	3175.2(11)
Z	8	8	4	4	4	4	4	6	4
No measd. reflns.	13 121	30 570	5871	7580	8138	16 396	2576	9839	27 438
No unique reflns.	2999	3527	1330	1599	2983	2367	747	947	6191
R_{int}	0.048	0.086	0.040	0.074	0.097	0.064	0.025	0.052	0.095
$R1$ [on F, $I > 2\sigma(I)$]	0.0409	0.0316	0.0405	0.0319	0.0406	0.0242	0.0199	0.0325	0.0592
$wR2$ (on F^2, all data)	0.1088	0.0798	0.0940	0.0845	0.1019	0.0636	0.0477	0.0855	0.1405

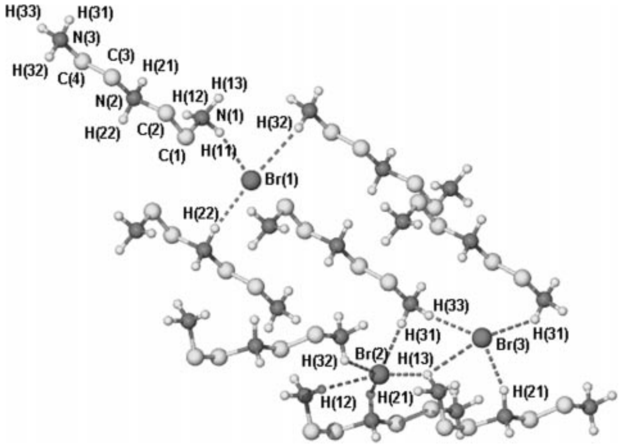

Fig. 3 Bromide anion coordination environments and ligand conformation for triprotonated diethylenetriamine tribromide **1f**.

and less predictable structure, which highlights the ability of the larger anion to take part in more hydrogen bonding interactions. It is possible that the chelating structure is adopted instead of the linear motif seen for **1e** simply because the crystal lattice is unable to tolerate the additional empty space caused by the expansion necessary in order to accommodate bridging bromides in the positions seen for Cl(1).

The crystal structure of diprotonated diethylenetriamine dichloride **1b** has also been previously analyzed at room temperature ($R1 = 0.060$)[26] and has been redetermined for the same reason as for **1e**. The availability of seven N–H protons suggests that the two chloride anions should be three and four-coordinate. Like **1f**, the ammonium cation in **1b** displays a remarkable anion chelate effect with the two terminal protonated nitrogen atoms pointing towards the chloride anion Cl(1). Another cation chelates the opposite face of the anion which is four-coordinate and constitutes the apex of a square-based pyramid interacting with two ammonium cations, each one donating two protons (Fig. 4). The other anion, Cl(2), is three-coordinate and forms the apex of a trigonal pyramid, as for Cl(2) in **1e**. Since the secondary amine nitrogen is not protonated there is presumably much less electrostatic barrier to adopting a chelate (bent) coordination mode.

The analogous diprotonated diethylenetriamine dibromide (Fig. 5) and diiodide (**1c** and **1d**) are isostructural with one another and display some similarities with **1b**, which adopts a different packing arrangement. The anions Br(1) and I(1) are chelated in a similar fashion to Cl(1) in **1b** by only one ammonium cation (Fig. 4), with the two terminal nitrogen atoms from each one of two different amines interacting with the opposite face of the four-coordinate anions. The second anions, Br(2) and I(2), which would be predicted to be three-coordinate, are ostensibly five-coordinate (Fig. 5) and adopt a square pyramidal geometry, implying two bifurcated interactions. In fact, both Br(2) and I(2) are based upon a two-coordinate geometry analogous to Cl(1) in **1e**, with three much longer interactions to the opposite face of the anion, two of which are bifurcated and the other is to the proton on the non-protonated secondary amine N(2). Interestingly the amine lone pair does not take part in any significant hydrogen bonds. The unit cell dimensions as well as the hydrogen bond distances are slightly longer for **1d** than for **1c** in all directions. These differences, of course, must be attributed to the greater ionic radius of iodide compared to bromide. The ammonium ion N(1)–N(3) axis for both compounds is almost parallel to the crystallographic *c* axis and the N(1)–N(3) distance is 4.477 and 4.520 Å for **1c** and **1d** respectively, reflecting the expansion of the host to accommodate the larger I^-. The chelate bite angle of the cationic host in **1b–d** is 79.7, 76.7 and 73.9°, respectively, consistent with the increasing length of the hydrogen bonds. Diethylenetriamine fragments have also been incorporated in efficient halide receptors like the macrocycle $[24]N_6O_2 \cdot 6HCl$ $\{[24]N_6O_2 = $ 1,13-dioxa-4,7,10,16,19,22-hexaazacyclotetracosane$\}$[17] and the macrobicycle bis(tren) $\{N[(CH_2)_2NH(CH_2)_2O(CH_2)_2NH(CH_2)_2]_3N$ $(BT\text{-}6H^+ \cdot 6Cl^-)\}$[19] in 1 : 1 host : guest ratio for both cases. Similar chelate effects are also noted in these instances.

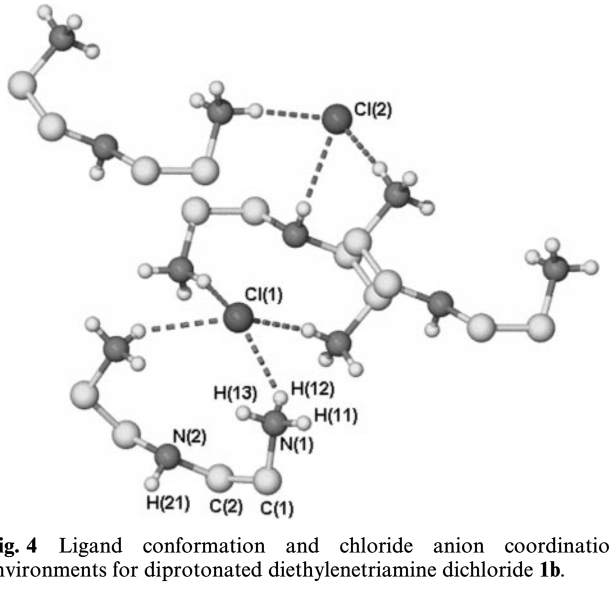

Fig. 4 Ligand conformation and chloride anion coordination environments for diprotonated diethylenetriamine dichloride **1b**.

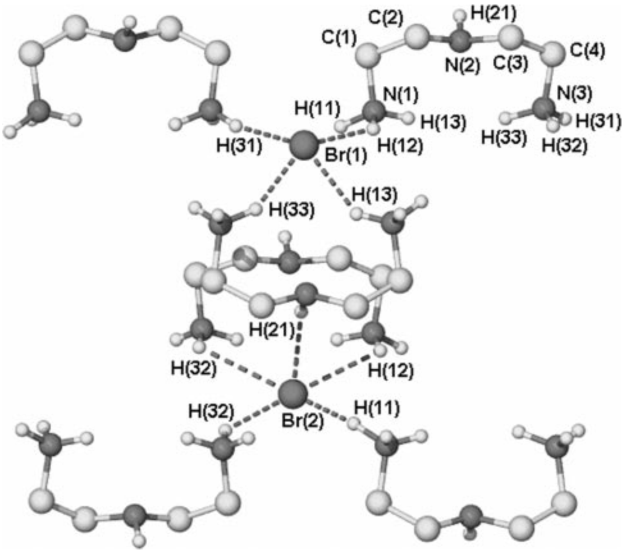

Fig. 5 Bromide anion coordination environments and ligand conformation for diprotonated diethylenetriamine dibromide **1c**.

Moving to the structure of monoprotonated diethylenetriamine bromide, compound **1a** reveals an extended all-*anti* conformation (*cf.* **1e**) with the secondary nitrogen atom being protonated (Fig. 6). This nitrogen donates both of its protons for two short, near-linear charge assisted hydrogen bonds with the primary nitrogen atoms of the neighbouring amines, N(1)· · ·N(2) 2.793(6) Å. This leaves four N–H protons from protonated nitrogen atoms to interact with the single bromide anion, which is indeed four-coordinate, forming hydrogen bonds with four terminal nitrogens each from different ammonium cations in a distorted tetrahedral arrangement N(1)· · ·Br(1)· · ·N(1) angles 127.9 and 101.1° (two symmetry equivalent pairs).

Given the ability of amine **1** to alternate between chelating and linear coordination modes according to the dictates of the anion radii and degree of protonation, it is instructive to move to a longer chain triamine, **2**, which might be anticipated to be

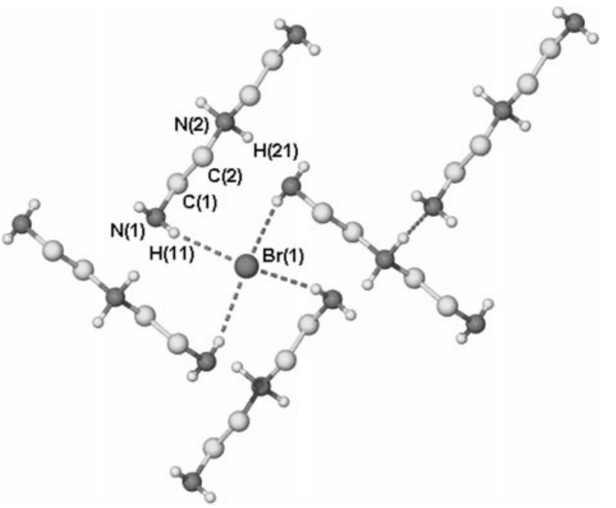

Fig. 6 Bromide anion coordination environment and N(2)–H(21)···N(1)′ hydrogen bond in monoprotonated diethylenetriamine bromide **1a**.

more flexible as a result of the propylene spacer and hence more able to separate adjacent positive charges. Indeed replacing C_2 with C_3 spacers in cyclic analogues results in marked changes in protonation constants.[19] Amine **2** crystallized only with hydrobromic acid, forming the diprotonated, salt $[NH_3{}^+(CH_2)_3NH(CH_2)_2NH_3{}^+]\cdot 2Br^-\cdot H_2O$ **2a**. A water molecule is also incorporated in the asymmetric unit to give a total of 9 hydrogen bond donors, which form 9 unique interactions. Anion Br(1) is four-coordinate in an array that is quite similar to the complexation geometry of Cl(1) in **1b**, Br(1) in **1c** and I(1) in **1d** with the anion forming the apex of a square pyramid (Fig. 7). However, unlike these complexes, the ammonium cation does not show any deviation from the all-*anti* conformation and there is no chelation. Instead, one hydrogen bond comes from the water molecule. The other water proton interacts with an amine lone pair. Anion Br(2) is three-coordinate forming the apex of a trigonal pyramid as observed for Cl(2) in **1b** and **1e** which exhibit essentially mutually perpendicular hydrogen bonds. Bromide anions are arranged along with water molecules in hydrophilic channels that run parallel to hydrophobic regions formed by the hydrocarbon background of the ammonium cations. We have found that this phenomenon becomes even more pronounced in complexes of polyammonium cations with the much more hydrophilic phosphates and sulfates, which will be reported separately.

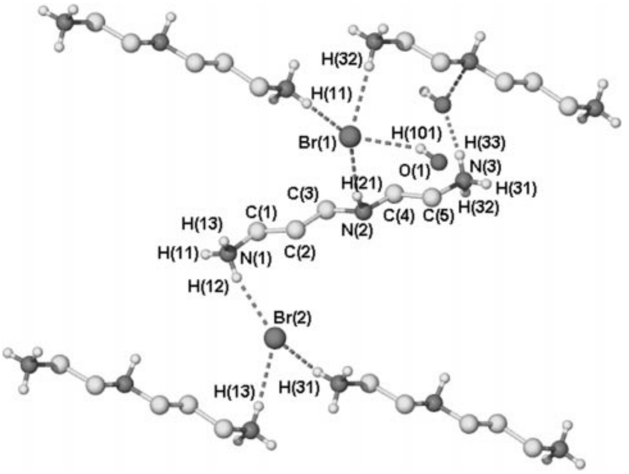

Fig. 7 Bromide anion environments and participation of water molecules in the hydrogen bond network in the crystal structure of diprotonated *N*-(2-aminoethyl)propane-1,3-diamine dibromide **2a**.

Extending the chain length even further, triethylenetetramine **3** was crystallized with all the haloacids studied yielding compounds $[NH_3{}^+(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_3{}^+]\cdot 2X^-\cdot 2H_2O$ (X = Cl, **3a**; Br, **3b**; I, **3c**) and $[NH_3{}^+(CH_2)_2NH_2{}^+(CH_2)_2NH_2{}^+(CH_2)_2NH_3{}^+]\cdot 4X^-\cdot H_2O$, (X = Br, **3d**; I, **3e**). Diprotonated triethylenetetramine dichloride **3a**, dibromide **3b** and diiodide **3c** are isostructural and contain a 1 : 2 polyammonium cation : anion ratio. The unit cell contains two water molecules to give a total of twelve acidic protons. Consistent with this, 12 hydrogen bonds are observed per formula unit (six unique). The protonated polyamines are linear and no chelation is observed. The chloride (Fig. 8) and bromide anions are four-coordinate and form the apex of a square pyramid as seen for the four-coordinate halides in **1b**, **1c**, **1d** and **2a**. The iodide anion in **3c** (Fig. 9) is large enough to form an additional long, non-linear bifurcated hydrogen bond [N(2)–H(22)···I(1′) 3.21(3) Å, N(2)···I(1′) 3.619 (3) Å, N(2)–H(22)···I(1′) 112(2)°] while still conforming to the

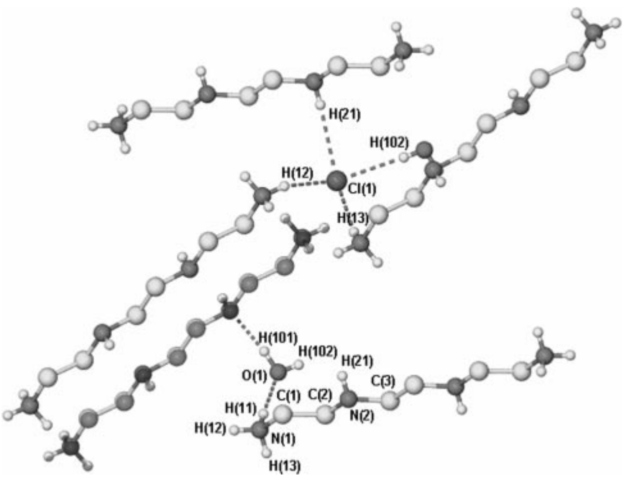

Fig. 8 Chloride anion coordination environment and participation of water molecules in the hydrogen bond network in the crystal structure of diprotonated triethylenetetramine dichloride **3a**.

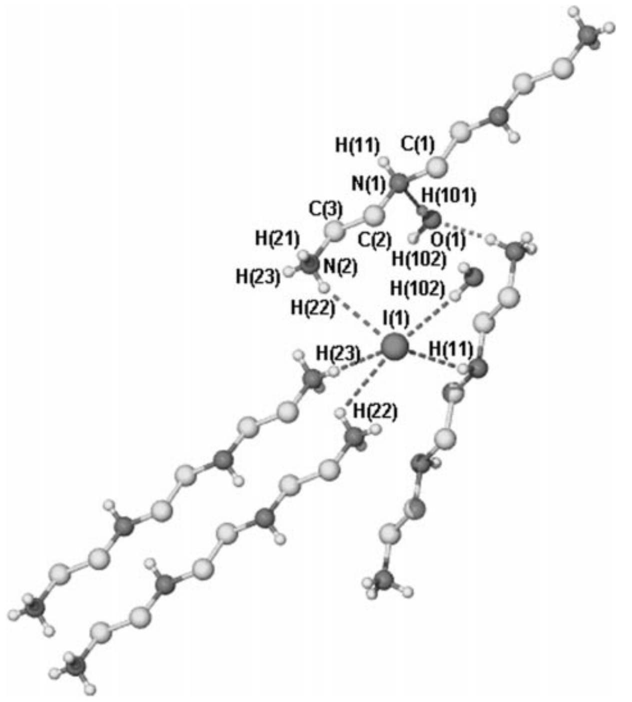

Fig. 9 Iodide anion coordination environment and participation of water molecules in the hydrogen bond network in the crystal structure of diprotonated triethylenetetramine diiodide **3c**.

same basic geometry. As noted for **1c**, hydrogen bonds to non-protonated amines are significantly longer than the charge-assisted interactions to the $-NH_3^+$ moieties, reinforcing the recent observations of Braga *et al.* on the validity of the strength–length analogy in charged systems.[27] The overall structure involves the formation of alternating hydrophilic and hydrophobic channels with water molecules coexisting with halide anions in the hydrophilic regions as in **2a**. Also as in **2a** water molecules do not act as hydrogen bond acids to two anions simultaneously and instead donate their protons to one anion and one amine lone pair.

Tetraprotonated triethylenetetramine tetrabromide **3d** and tetraiodide **3e** are also mutually isostructural. There are twelve acidic protons but sixteen unique short contacts clearly indicating the presence of bifurcated hydrogen bonds or $N^+\cdots Br^-$ interactions. As in previous cases with bifurcated interactions the amine adopts a remarkable chelating geometry in which each tetracation binds as a bis(bidentate) ligand to two anions (Fig. 10). Chelate bite angles are 58.1 and 55.1° for Br(1) and I(1), respectively, and 58.7 and 55.5° for Br(2) and I(2). The coordination numbers for the complexed halides vary from two to five and there are 5 crystallographically unique anions. The chelated anion Br(1) [and I(2)] is five-coordinate and strongly resembles the chelated Br(2) in **1f**. The other chelated anion, Br(2) is of the more common four-coordinate type, forming the apex of a square pyramid [*cf.* Br(3) in **1f**]. Anion Br(3) is also four-coordinate and placed in the apex of a square pyramid. Anions Br(4) and Br(5) exhibit low coordination numbers (two and three) which clearly represents the general tendency for compounds with lower ammonium cation : anion ratios, as the competition for hydrogen bonding between the anions is greater. A similar situation is encountered in the salts **1b** and **1e**. No overall preferred binding geometries are observed. Finally, the water molecule participates in the formation of hydrophilic channels as part of the extensive hydrogen bonding network.

As for the triamines, longer chain C_3 spacer analogues were also investigated to give diprotonated *N*,*N'*-bis(3-aminopropyl)ethylenediamine dichloride and dibromide, $[NH_3^+(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_3^+]\cdot 2X^-$, (X = Cl, **4a**, Br, **4b**). These two species are very approximately isostructural but there is a significant difference between the ligand conformations. Compound **4a** (Fig. 11) is distorted in Z-shaped fashion with the twist occurring at C(3) at the end of the three-carbon chain. In **4b** (Fig. 12) there is a bend that occurs at C(2) in the middle of the C_3 spacer, resulting in a much more extended cation. There is no chelate effect however, and this is possibly because of the entropically unfavorable folding of the long ammonium chain that such a process would require to bring the two cationic ammonium moieties into close proximity with one particular anion. This contrasts with compounds such as **1b**, **1c** and **1d** in which the fully protonated groups are close together, and display a marked chelate effect. Consistent

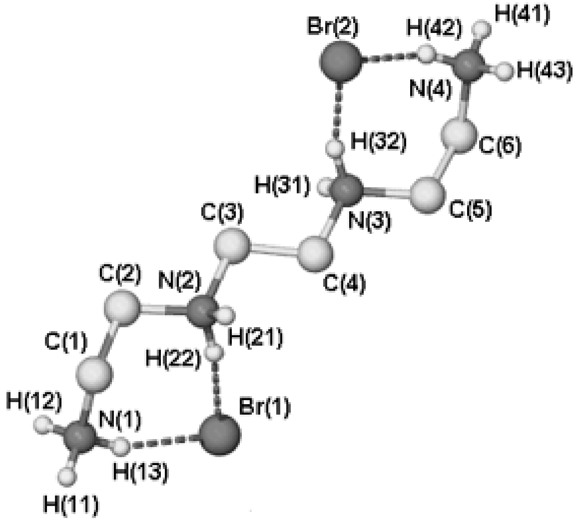

Fig. 10 Part of the unit cell for tetraprotonated triethylenetetramine tetrabromide **3d**. Only the four hydrogen bonds between the bromide anions and the neighbouring terminal nitrogens are shown. Note that N(1) and N(2) as well as N(3) and N(4) nitrogen atoms point towards the bromide anions Br(1) and Br(2), respectively.

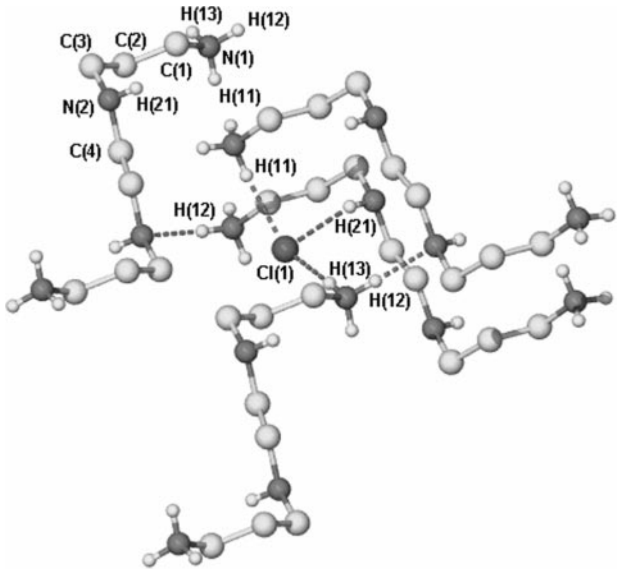

Fig. 11 Ligand conformation, chloride anion coordination environment and the N(1)–H(12)···N(2) hydrogen bond for diprotonated *N*,*N'*-bis(3-aminopropyl)ethylenediamine dichloride **4a**.

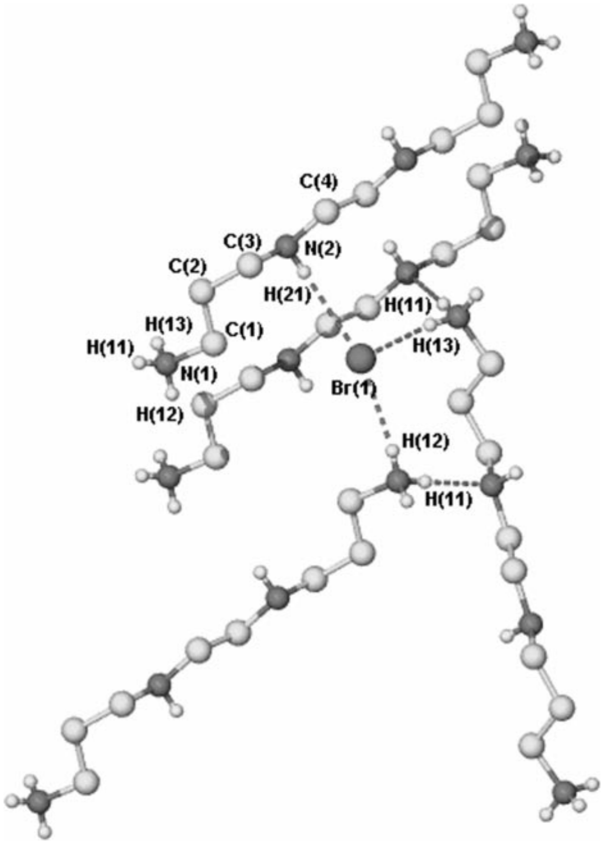

Fig. 12 Ligand conformation, bromide anion coordination environment and the N(1)–H(11)···N(2) hydrogen bond for diprotonated *N*,*N*-bis(3-aminopropyl)ethylenediamine dibromide **4b**.

with previous results observed in a non-chelate geometry, there are an equal number of donors and hydrogen bonding interactions (eight in each case, four of which are crystallographically unique). The halide anions are all three-coordinate, forming the apex of a trigonal pyramid as for Cl(2) in compound **1e**. The hydrogen bond to the secondary amine is significantly longer than the two charge assisted interactions. The fourth hydrogen bond is from $-NH_3^+$ moiety N(1) to secondary amine N(2) and here neither chloride or the larger bromide anions have expanded their coordination sphere. The origin of the different conformations of the amines in these two species seems to be entirely due to the larger size of the bromide anion which requires a more extended amine conformation in order to match the longer N–H···Br distances.

Given the interesting behaviour observed in linear amines **1**–**4** in which chelating geometries occur in cases where it is sterically feasible to wrap two cationic ammonium moieties around the same anion, we moved finally to the branched tetramine **5** which has the possibility of adopting a perching geometry and tris-chelating individual anions. Indeed, **5** has been extensively used as a building block for the synthesis of many three-dimensional organic receptors which display encapsulation of halide anions within the receptor cavity in a 1 : 1 host : guest ratio, as in the bis(tren) macrobicycle prepared by Lehn and coworkers.[13,19,20] Amine **5** was crystallized with all of the acids studied in host : anion ratios of 1 : 1, 3 and 4, to give $[\{NH_2(CH_2)_2\}_2N(CH_2)_2NH_3^+]\cdot Br^-$ **5a**, $[\{NH_2(CH_2)_2\}_2N(CH_2)_2NH_3^+]\cdot I^-\cdot H_2O$ **5b**, $N[(CH_2)_2NH_3^+]_3\cdot 3X^-$ (X = Cl, **5c**; I, **5d**) and $NH^+[(CH_2)_2NH_3^+]_3\cdot 4Br^-\cdot H_2O$ **5e**.

Most interestingly, the bromo and iodo complexes **5a** and **5b** are *not* isostructural. The monoprotonated 2,2′,2″-triaminotriethylamine bromide **5a** displays a remarkable tris-chelate effect in which the ligand binds the anion with all of its three terminal nitrogen atoms [Fig. 13, N···Br distances 3.409(18) (protonated), 3.5627(17) and 3.5900(16) Å; ligand torsion angles N(1)–C(1)–C(2)–N(2) 56.8(2)°; N(1)–C(3)–C(4)–N(3) 61.2(2)°; N(1)–C(5)–C(6)–N(4) 57.1(2)°]. Anion Br(1) is also hydrogen bonded to two other amine groups from two different ligands to give a five-coordinate geometry. The protonated amine functionality, N(2) is also connected to primary amines N(3) and N(4) *via* two strong *intermolecular* hydrogen bonds [distances 2.864(2) and 2.777(2) Å] to give a total of seven interactions for seven H-bond donors. The five-coordinate geometry of the bromide anion is a necessary consequence of the large excess of donors present and it is noteworthy that a six-coordinate geometry is not adopted, nor is the basic tertiary amine protonated or involved in hydrogen bonding. Clearly structural, as opposed to electronic, constraints determine the proton distribution.

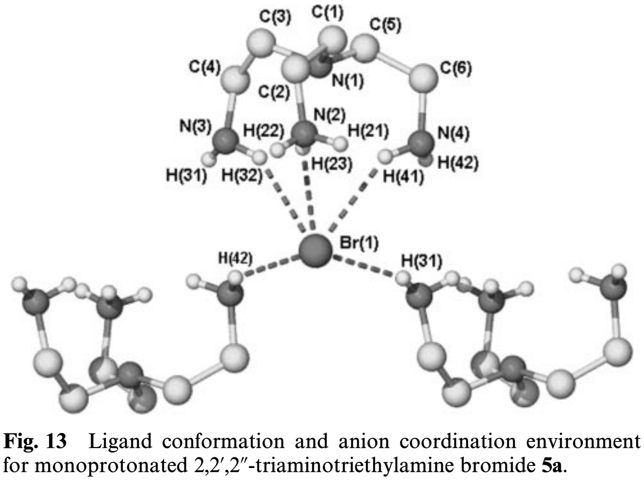

Fig. 13 Ligand conformation and anion coordination environment for monoprotonated 2,2′,2″-triaminotriethylamine bromide **5a**.

The monoiodide analogue **5b** is also chelated [torsion angles N(1)–C(1)–C(2)–N(2) −62.4(2)°; N(1)–C(3)–C(4)–N(3) −67.9(2)°, N(1)–C(5)–C(6)–N(4) −63.5(3)°] but the five-coordinated anion I(1) (Fig. 14) is bonded only to two of the three terminal amine groups [N···I distances 3.697(2), 3.849(2) Å]. The coordination 'bite' angle N(2)···I(1)···N(4) is 68.5°. Anion I(1) is also hydrogen bonded to three other amine groups from three different ligands. This strongly suggests that iodide is too large to form hydrogen bonds with all three terminal amine groups. This is consistent with the fact that iodide is too large to be incorporated in the cavity of the macrobicyclic octaazacryptand obtained by the multiple condensation of the amine **5**.[19] Interestingly, however, given the total of nine acidic protons within the structure, there are only eight hydrogen bonds falling within our criteria. The unbonded proton is primary amine proton H(32). Closer examination reveals that this proton forms an extremely long interaction with I(1), [N···I 4.131(3) Å] making the iodide anion pseudo-six-coordinate. The extreme length of this 'bond' is again consistent with the poor fit of the large iodide within the ligand as a tris-chelate. The displacement of the iodide anion to one side of the ammonium ion disrupts the N···N hydrogen bonding seen for **5a** and results in the incorporation of a water molecule which interacts solely with the primary amine lone pairs, (Fig. 15).

A comparison between the triprotonated 2,2′,2″-triaminotriethylamine trichloride **5c** and triiodide **5d** illustrates more clearly some of the focal points relevant to anion coordination environment that have been discussed so far. The trichloride compound **5c** has been previously analyzed at room temperature, however the redetermination in the present work represents a significantly more reliable structure ($R1 = 0.142$ *cf.* 0.0199).[28] Compound **5c** possesses nine donors, leading to a prediction of three hydrogen bonds per anion, which is entirely borne out by the structure. Anion Cl(1) is tris-chelated with three short N–H···Cl bonds in an entirely regular geometry forming the apex of an undistorted trigonal pyramid [Fig. 16, *cf.* Cl(1) in **1e**]. The other two chloride anions Cl(2) and Cl(3) (Fig. 17 and 18) are connected *via* hydrogen bonds to three nitrogen atoms which belong to three different ligands and adopt slightly more flattened, although threefold-symmetric trigonal pyramid-type geometries [angle N···Cl(1)···N 84.0°, *cf.* 77.3 and 76.7° for Cl(2) and Cl(3)]. In contrast, the iodo analogue, **5d**, is very different. There is one crystallographically unique iodide anion that, on a simple proton counting basis, should be three-coordinate and indeed,

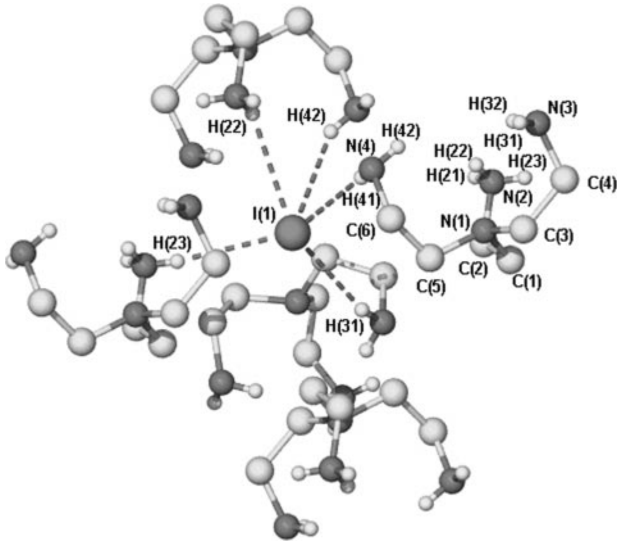

Fig. 14 Ligand conformation and iodide anion coordination environment for monoprotonated 2,2′,2″-triaminotriethylamine iodide **5b**.

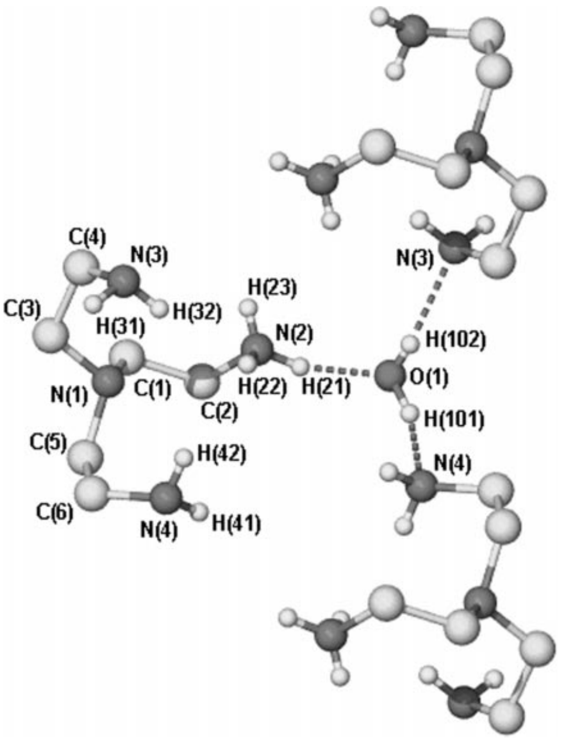

Fig. 15 The participation of water molecules in the hydrogen bond network for monoprotonated 2,2′,2″-triaminotriethylamine iodide **5b**.

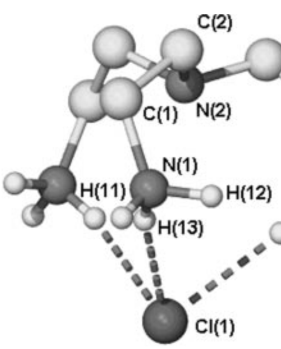

Fig. 16 Ligand conformation and Cl(1) coordination environment for triprotonated 2,2′,2″-triaminotriethylamine trichloride **5c**.

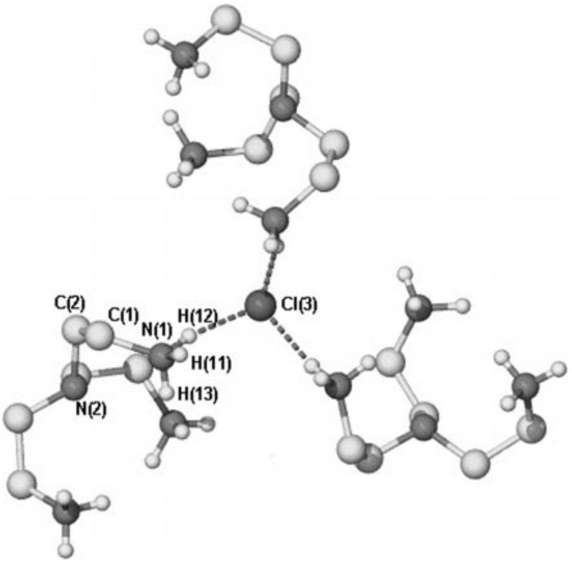

Fig. 18 Ligand conformation and Cl(3) coordination environment for triprotonated 2,2′,2″-triaminotriethylamine trichloride **5c**.

it is (Fig. 19). However, it is hydrogen bonded to three nitrogen atoms which belong to three different ligands, forming the apex of a distorted trigonal pyramid. The ligands are not chelated in any way and adopt an extended 'starfish-like' conformation. This is again consistent with the large size of the iodide anions.

Finally, tetraprotonated 2,2′,2″-triaminotriethylamine tetrabromide **5e** was crystallized with two water molecules incorporated within the crystal structure (Fig. 20). Ligand conformations are quite similar to that of **5d**. The two crystallographically unique ligands are severely distorted from the all-*anti* conformation but they are not chelated. This is probably because of the steric hindrance caused by the large number of anions per cationic host. There are eight crystallographically unique bromide anions. Two are three-coordinate, five are four-coordinate and one is five-coordinate but without displaying any particular coordination geometry. The structure is considerably supported by non-hydrogen bond electrostatic $N^{+}\cdots Br^{-}$ interactions in the region of 3.4–3.5 Å, which are an alternative to weak C–H···X hydrogen bonds to the uncoordinated surfaces of the halides. The overall complexity of the structure apparently arises as a consequence of the

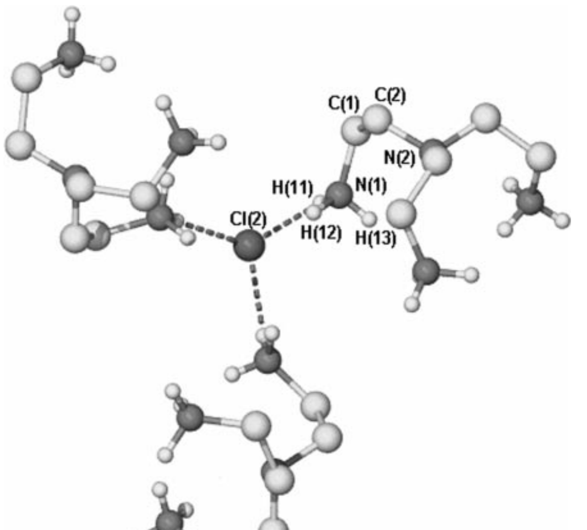

Fig. 17 Ligand conformation and Cl(2) coordination environment for triprotonated 2,2′,2″-triaminotriethylamine trichloride **5c**.

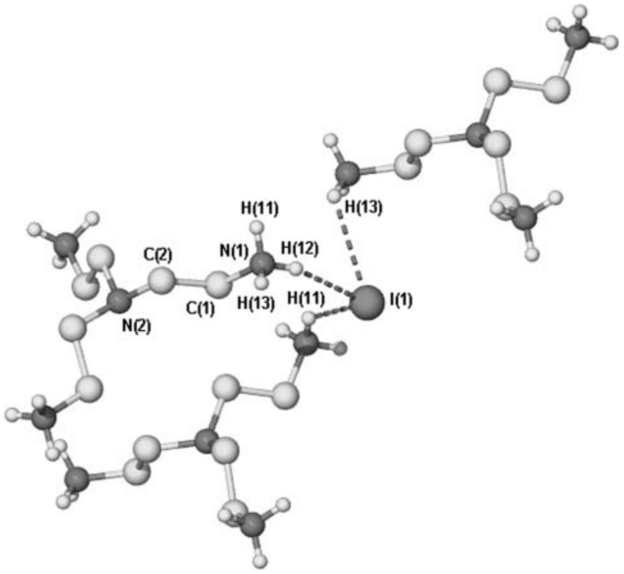

Fig. 19 Ligand conformation and iodide coordination environment for triprotonated 2,2′,2″-triaminotriethylamine triiodide **5d**.

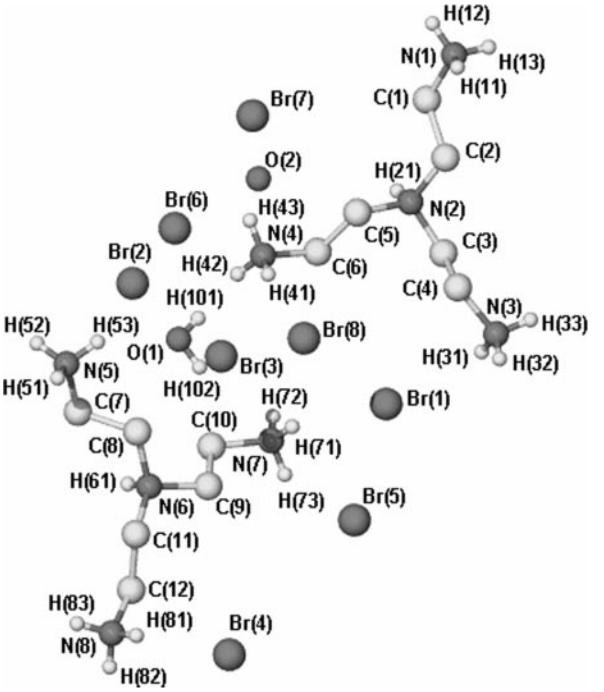

Fig. 20 Unit cell of tetraprotonated 2,2′,2″-triaminotriethylamine tetraiodide **5e**.

hydrogen bonding of the protonated tertiary amine moieties to the halide anions. The water molecules are arranged within hydrophilic channels and participate fully in the hydrogen bond network.

Discussion

Anion–host interactions observed in this work generally fall into three categories, namely $\mathrm{X{-}H\cdots A^-}$ hydrogen bonds (X = N or O), $\mathrm{C{-}H\cdots A^-}$ hydrogen bonds and $\mathrm{N^+\cdots A^-}$ electrostatic interactions. The former type of hydrogen bond is significantly shorter (and perhaps stronger) when charge assisted. Together, these interactions result in coverage of most of the halide charge sphere at varying distances according to the strength of the interaction and the geometric constraints of the system. In terms of strong hydrogen bonds, which are the most directional of these interactions, a clear increase in coordination (hydrogen bond) number is observed with increasing halide size. Coordination numbers of 2–4 are observed for chloride with three-coordinate geometries in which the anion forms the apex of an (often distorted) trigonal pyramid being by far the most common. Bromide anions adopt 3–5 coordinate geometries and iodide generally 5–6. Four-coordinate anions are also often pyramidal. The reason for this pyramidalization appears to be a response to the optimum van der Waals distance between the host aliphatic chains and the need to separate the charged ammonium functionalities. This results in the exposure of one hemisphere of the anion to further stabilising interactions as detailed above. In general, coordination spheres are highly flexible in response to the geometry of the crystal as a whole and clearly a rigidly preorganised host may readily impart other environments to the anion. In addition, some of the five-coordinate halides appear to be located in the middle of the base of a square pyramid, again exposing one face of the anion.

Perhaps the most interesting feature of the present work is the observation of two very different kinds of coordination modes; one which involves a kind of anion chelate effect with the incorporation of a large number of bifurcated hydrogen bonds and the other a linear host with linear hydrogen bond motif. Chelating hosts apparently arise most commonly with two-carbon spacers between protonated primary and secondary amines, although compounds **1b–d** are an exception because the protonated amines are not adjacent. More generally, chelate effects are observed in cases where two positively charged nitrogen moieties may approach an anion without causing unfavourable steric or entropic effects. This particularly favours chelation of the larger anions. Of particular relevance is the structure of **5d** which clearly demonstrates that there is a size-based limit on the flexibility of anion coordination spheres (or host expansion), which is of key importance in future supramolecular design of solution anion binding hosts.

A comparison between the hydrogen bond networks of the halides in the structures discussed so far and the hydrogen bond networks of the halides in other polyprotonated organic frameworks and specially designed hosts is very helpful for the understanding of the malleability of the coordination geometry adopted by the halides. Many compounds with identical host and host : guest ratio are isostructural (*e.g.* **3a**, **3b** and **3c** as well as **3d** and **3e**) or almost isostructural to each other (*e.g.* **1b**, **1c** and **1d**, as well as **4a** and **4b**). This shows that the crystal system is robust enough to tolerate the necessary expansion arising from the increased anion radii. This is also observed in the crystal structures of specifically designed hosts for the encapsulation of halides. In most cases, the hydrogen bond patterns are repeated for almost all of the halides, which are bonded by the same host in the same host : anion ratio. This is strong evidence that the coordination geometries of the complexed halides are largely determined by the conformation of the host molecules.

The geometries found for the chloride anions are quite different from those previously reported for chloride anions encapsulated in cryptates like the macrotricyclic azacrown ether known as "soccer ball"[10,11] in which the chloride anion is coordinated in a tetrahedral array, the bis(tren) macrobicycle ($\mathrm{BT\text{-}6H^+ \cdot 6Cl^-}$)[13] where the chloride anion is complexed in an octahedral fashion and the macrobicycle $\mathrm{N[(CH_2)_2NH(CH_2)_3NH(CH_2)_2]_3N}$[19] where the chloride anion is hexa-coordinate in a quasi-perfect ternary geometry. Coordination numbers of five and four are reported for the two chlorides that are positioned close to the cavity in $\mathrm{[22]N_6H_6{}^+ \cdot 6Cl^-}$[17] {$\mathrm{[22]N_6}$ = 1,4,7,12,15,18-hexaazacyclodocosane} and a coordination number of five is observed for the centrally bound $\mathrm{Cl^-}$ in the $\mathrm{[24]N_6O_2 \cdot 6HCl}$ macrocycle[17] without any particular geometry for both of the latter two systems. The crystal structure of $\mathrm{[27]N_5O_2}$bipy[18] reveals six crystallographically unique chloride anions with coordination numbers varying from one to five. Lower coordination numbers for the complexed chloride anions are displayed in expanded porphyrin systems. A coordination number of four has been reported for the chloride anion in the structure of the diprotonated anthraphyrin[29] whereas three-coordinate and four-coordinate chloride anions have been revealed for the tri- and tetra-protonated forms of rosarin and turcasarin.[30,31] A tetrahedral environment for the chloride anion has also been found in ammonium halides in the solid state.[22] The chloride anions are three-coordinate in the crystal structures of monoprotonated sapphyrin[29] and rubyrin bishydrochloride.[32] The crystal structure of ethylenediammonium chloride[14] reveals a two-dimensional network with three-coordinated chloride anions. A coordination number of three is also observed in the structure of $\mathrm{H_4L(NO_3)_2 \cdot Cl_2 \cdot H_2O}$ (L = hexacyclen).[16]

A variety of coordination numbers and complexation geometries have also been reported for the bromide anion. An octahedral binding fashion has been observed for the bromide anion in the complex $\mathrm{BT \cdot 6HBr}$[13] which is identical to the coordination geometry of the chloride anion included in the same macrobicycle. A more perplexing situation is encountered in the compound $\mathrm{[21]N_5O_2 \cdot 5HBr \cdot MeOH}$[18] {$\mathrm{[21]N_5O_2}$ = 1,13-dioxa-4,7,10,16,19-pentaazacycloheneicosane} in which the five crystallographically unique bromide anions display coordination numbers of two, four and five. Inclusion of the bromide anion within the "soccer ball" ligand is also observed by ^{13}C NMR studies,[11] suggesting a tetrahedral complexation geometry. Besides, the crystal structure of ethylenediammonium dibromide[15] shows $N^+\cdots Br^-\cdots N^+$ angles close to 90°.

The versatile bis(tren) macrobicyclic ligand forms a stable complex in its hexaprotonated form with I^-, suggesting an hexacoordinated binding fashion.[20] However, a tetrahedral complexation geometry is observed for the iodide anion in the salt $[I^- \ L^{4+}]^{3+} \cdot 3I^- \cdot 3MeCN \cdot H_2O$ $[L = N_4Me_4(C_6H_{12})_6]$.[12]

Conclusions

The crystal structure analysis of the salts **1a**–**5e** reveals a lack of overwhelming preference of the complexed halides for specific coordination geometries. The coordination environment of the hydrogen bonded halides is largely imposed by the conformation and the protonation sites of the host, the host : guest ratio, the existence of any hydrogen bonds between the protonated hosts, the size and the electronegativity of the complexed halide. Therefore, the halides should be considered as species that are able to participate in hydrogen bond networks in a variety of geometries, depending on the features of the polyprotonated environment that are to be bonded. These principles can also be applied to solutions, bearing in mind of course the interactions between the host or the guest and the solvent molecules, and suggest that preorganisation[33] in terms of a specific hydrogen bonded geometry, might be less important than an overall encapsulation of the halide negative charge. We envisage as future work the preparation of solid-state and solution hosts for halides (particularly Cl^-) capable of mimicking the three-coordinate trigonal pyramid-type environment commonly observed in this study. Such hosts will enable us to begin to assess the relative importance of directional interactions in the form of hydrogen bonds to one face of the anion as opposed to less specific (electrostatic) interactions to the other (exposed) hemisphere.

Experimental

Electronic supplementary data

Hydrogen bond distances and angles as well as all the relevant information on the coordination environments of the anions are given in the electronic supplementary data section.†

Materials

The amines **1**–**4** as well as hydrobromic and hydriodic acid were purchased from Aldrich Chemical Co. Amine **5** was purchased from Lancaster. Hydrochloric acid and ethanol were purchased from BDH.

Preparations

In all cases the compounds were crystallized from water or ethanol by slow evaporation for a period of time varying from 1–2 days to several weeks. Conditions were chosen for preparation of X-ray quality crystals and are unoptimized.

$[NH_2(CH_2)_2NH_2(CH_2)_2NH_2]\cdot Br$, 1a. The amine **1** (1.00 mL, 9.16 M) was mixed with hydrobromic acid (1.04 mL, 8.78 M) in ethanol (1.00 mL) to give pale yellow crystals. Yield 0.82 g, 4.32 mmol, 47%. Anal. Calc. for $C_4H_{14}BrN_3$: C, 26.10; H, 7.67; N, 22.83. Found: C, 25.89; H, 7.77; N, 22.44%.

$[NH_3(CH_2)_2NH(CH_2)_2NH_3]\cdot 2Cl$, 1b. The amine **1** (0.50 mL, 9.16 M) was mixed with hydrochloric acid (0.38 mL, 11.98 M) in ethanol (3.84 mL) to give colourless crystals. Yield 0.10 g, 0.55 mmol, 12%. Anal. Calc. for $C_4H_{15}Cl_2N_3$: C, 27.28; H, 8.95; N, 23.86. Found: C, 27.05; H, 8.54; N, 23.37%.

$[NH_3(CH_2)_2NH(CH_2)_2NH_3]\cdot 2Br$, 1c. The amine **1** (0.50 mL, 9.16 M) was mixed with hydrobromic acid (1.04 mL, 8.78 M) in ethanol (1.00 mL) to give yellow crystals. Yield 0.67 g, 2.54 mmol, 55%. Anal. Calc. for $C_4H_{15}Br_2N_3$: C, 18.13; H, 5.71; N, 15.85. Found: C, 18.53; H, 6.06; N, 15.88%.

$[NH_3(CH_2)_2NH(CH_2)_2NH_3]\cdot 2I$, 1d. The amine **1** (1.00 mL, 9.16 M) was mixed with hydriodic acid (1.15 mL, 7.95 M) to give colourless crystals. Yield 1.26 g, 3.51 mmol, 77%. Anal. Calc. for $C_4H_{15}I_2N_3$: C, 13.38; H, 4.21; N, 11.71. Found: C, 14.35; H, 4.31; N, 12.30%.

$[NH_3(CH_2)_2NH(CH_2)_2NH_3]\cdot 3Cl$, 1e. The amine **1** (0.50 mL, 9.16 M) was mixed with hydrochloric acid (0.76 mL, 11.98 M) in ethanol (1.29 mL) to give white crystals. Yield 0.15 g, 0.70 mmol, 15%. Anal. Calc. for $C_4H_{16}Cl_3N_3$: C, 22.60; H, 7.59; N, 19.76. Found: C, 21.90; H, 7.42; N, 18.96%.

$[NH_3(CH_2)_2NH(CH_2)_2NH_3]\cdot 3Br$, 1f. The amine **1** (0.5 mL, 9.16 M) was mixed with hydrobromic acid (1.56 mL, 8.78 M) in ethanol (1.50 mL) to give white crystals. Yield 0.43 g, 1.23 mmol, 27%, Anal. Calc. for $C_4H_{16}Br_3N_3$: C, 13.89; H, 4.66; N, 12.15. Found: C, 13.85; H, 4.63; N, 11.61%.

$[NH_3(CH_2)_3NH(CH_2)_2NH_3]\cdot 2Br\cdot H_2O$, 2a. The amine **2** (1.00 mL, 7.68 M) was mixed with hydrobromic acid (0.87 mL, 8.78 M) in ethanol (0.6 mL) to give white–yellow crystals. Yield 2.17 g, 7.32 mmol, 95%. Anal. Calc. For $C_5H_{18}Br_2N_3O$: C, 20.22; H, 6.45; N, 14.15. Found: C, 20.37; H, 6.38; N, 14.01%.

$[NH_3(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_3]\cdot 2Cl\cdot 2H_2O$, 3a. The amine **3** (1.47 g, 10.1 mmol) was mixed with hydrochloric acid (0.84 mL, 11.98 M) in ethanol (1.00 mL) to give pale yellow crystals. Yield 0.27 g, 1.05 mmol, 10%. Anal. Calc. for $C_6H_{24}Cl_2N_4O_2$: C, 28.24; H, 9.48; N, 21.95. Found: C, 28.65; H, 9.49; N, 21.75%.

$[NH_3(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_3]\cdot 2Br\cdot 2H_2O$, 3b. The amine **3** (0.59 g, 4.03 mmol) was mixed with hydrobromic acid (0.46 mL, 8.78 M) in ethanol (0.90 mL) to give colourless crystals. Yield 0.73 g, 2.13 mmol, 53%. Anal. Calc. for $C_6H_{24}Br_2N_4O_2$: C, 20.94; H, 7.03; N, 16.28. Found: C, 22.36; H, 6.86; N, 17.12%. Visual observation of the sample suggests dehydration. Analytical data indicate the presence of one molecule of water per formula unit. Anal. Calc. for $C_6H_{22}Br_2N_4O$: C, 22. 10; H, 6.80; N, 17.18%.

$[NH_3(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_3]\cdot 2I\cdot 2H_2O$, 3c. The amine **3** (0.30 g, 2.05 mmol) was mixed with hydriodic acid (0.26 mL, 7.95 M) in ethanol (0.42 mL) to give white crystals. Yield 0.41 g, 0.92 mmol, 45%. Anal. Calc. for $C_6H_{24}I_2N_4O_2$: C, 16.45; H, 5.52; N, 12.79. Found: C, 17.40; H, 5.72; N, 13.22%.

$[NH_3(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2NH_3]\cdot 4Br\cdot H_2O$, 3d. The amine **3** (0.30 g, 2.05 mmol) was mixed with hydrobromic acid (0.70 mL, 8.78 M) in ethanol (1.50 mL) to give white crystals. Yield 0.66 g, 1.36 mmol, 66%. Anal. Calc. for $C_6H_{23}Br_4N_4O$: C, 14.77; H, 4.96; N, 11.48. Found: C, 14.40; H, 4.99; N, 11.08%.

$[NH_3(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2NH_3]\cdot 4I\cdot H_2O$, 3e. The amine **3** (0.30 g, 2.05 mmol) was mixed with hydriodic acid (1.04 mL, 7.95 M) in ethanol (1.69 mL) to give white crystals. Yield 0.40 g, 0.59 mmol, 29%. Anal. Calc. for $C_6H_{24}I_4N_4O$: C, 10.66; H, 3.65; N, 8.29. Found: C, 10.69; H, 3.25; N, 8.12%.

$[NH_3(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_3]\cdot 2Cl$, 4a. The amine **4** (0.80 mL, 5.13 M) was mixed with hydrochloric acid (0.34 mL, 11.98 M) in ethanol (3.40 mL) to give white crystals. Yield 0.33 g, 1.33 mmol, 32%. Anal. Calc. for $C_8H_{24}Cl_2N_4$: C, 38.87; H, 9.79; N, 22.66. Found: C, 37.63; H, 10.18; N, 21.49%. Visual observation of the sample suggests it to be somewhat hygroscopic. Analytical data indicate the presence of 0.5 molecules of water per formula unit. Anal. Calc. for $C_8H_{25}Cl_2N_4O_{0.5}$: C, 37.50; H, 9.84; N, 21.87%.

$[NH_3(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_3]\cdot 2Br$, 4b. The amine **4** (1.00 mL, 5.13 M) was mixed with hydrobromic acid (1.16 mL, 8.78 M) in ethanol (1.26 mL) to give white crystals. Yield 1.59 g, 4.72 mmol, 92%. Anal. Calc. for $C_8H_{24}Br_2N_4$: C, 28.59; H, 7.20; N, 16.67. Found: C, 29.50; H, 7.50; N, 16.64%.

$[NH_2(CH_2)_2]_2N(CH_2)_2NH_3]\cdot Br$, 5a. The amine **5** (0.25 mL, 6.63 M) was mixed with hydrobromic acid (0.19 mL, 8.78 M) in ethanol (0.11 mL) to give yellow crystals. Yield 0.32 g, 1.40 mmol, 85%. Anal. Calc. for $C_6H_{19}BrN_4$: C, 31.72; H, 8.43; N, 24.66. Found: C, 31.37; H, 8.49; N, 24.33%.

$[NH_2(CH_2)_2]_2N(CH_2)_2NH_3]\cdot I\cdot H_2O$, 5b. The amine **5** (0.25 mL, 6.63 M) was mixed with hydriodic acid (0.20 mL, 7.95 M) in water (0.10 mL) to give yellow crystals. Yield 0.38 g, 1.32 mmol, 79%. Anal. Calc. for $C_6H_{21}IN_4O$: C, 24.67; H, 7.25; N, 19.18. Found: C, 25.61; H, 7.46; N, 19.27%.

$N[(CH_2)_2NH_3]_3\cdot 3Cl$, 5c. The amine **5** (0.13 mL, 6.63 M) was mixed with hydrochloric acid (0.14 mL, 11.98 M) in water (1.57 mL) to give yellow crystals. Yield 0.14 g, 0.56 mmol, 67%. Anal. Calc. for $C_6H_{21}Cl_3N_4$: C, 28.19; H, 8.28; N, 21.92. Found: C, 29.22; H, 8.34; N, 21.43%.

$N[(CH_2)_2NH_3]_3\cdot 3I$, 5d. The amine **5** (0.06 mL, 6.63 M) was mixed with hydriodic acid (0.20 mL, 7.95 M) in water (0.29 mL) to give yellow crystals. Yield 0.47 g, 0.22 mmol, 54%. Anal. Calc. for $C_6H_{21}I_3N_4$: C, 13.60; H, 3.99; N, 10.57. Found: C, 12.17; H, 3.71; N, 9.29%. Visual observation of the sample suggests it to be somewhat hygroscopic. Analytical data indicate the presence of 3.5 molecules of water per formula unit. Anal. Calc. for $C_6H_{28}I_3N_4O_{3.5}$: C, 12.15; H, 3.57; N, 9.44%.

$NH[(CH_2)_2NH_3]_3\cdot 4Br\cdot H_2O$, 5e. The amine **5** (0.08 mL, 6.63 M) was mixed with hydrobromic acid (0.19 mL, 8.78 M) in ethanol (0.28 mL) to give brown crystals. Yield 0.24 g, 0.50 mmol, 73%. Anal. Calc. for $C_6H_{23}Br_4N_4O_2$: C, 14.80; H, 4.76; N, 11.51. Found: C, 14.72; H, 4.84; N, 11.22%.

Crystallography

Crystal data and data collection parameters are summarized in Table 1. Crystals were mounted using silicon grease on a thin glass fibre. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite-monochromated Mo-Kα radiation using wide ϕ- and ω-scans. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption (scalepack) and crystal decay using an overall volume and scaling approach based on the average intensity of each frame. Structures were solved using the direct methods option of SHELXS-86[34] and developed using conventional alternating cycles of least-squares refinement (SHELXL-97[35]) and difference Fourier synthesis with the aid of the program XSeed.[36] In all cases non-hydrogen atoms were refined anisotropically except for some which were disordered, while C–H hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. Acidic hydrogen atoms were located experimentally and their positional and displacement parameters were refined whenever possible. Otherwise a riding model was adopted. All calculations were carried out on an IBM-PC compatible personal computer.

CCDC reference number 440/195. See http://www.rsc.org/suppdata/nj/b0/b004641h/ for crystallographic files in .cif format.

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