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Counteranion-Controlled Water Cluster Recognition in a Protonated Octaamino Cryptand

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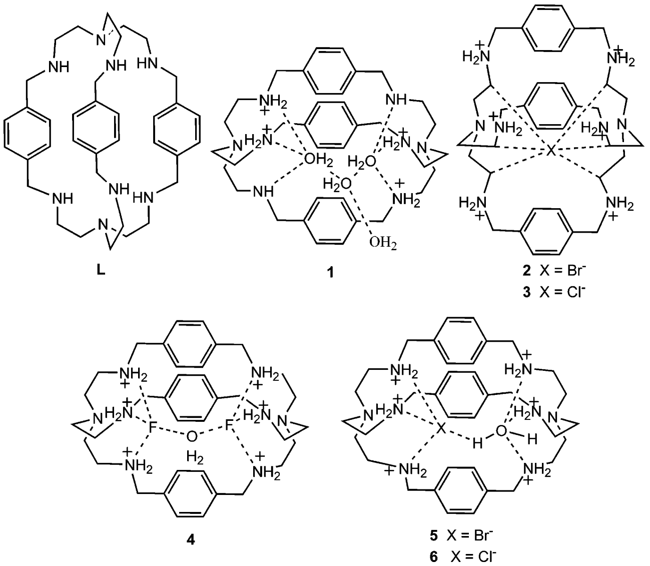
Structural aspects of binding of water cluster and halides in the octaamino cryptand **L** (1,4,11,14,17,24,29,36-octaazapentacyclo[12.12.12.2.^{6,9}2.^{19,22}2^{31,34}]tetratetraconta-6(43),7,9(44),19(41),20,22(42),31(39),32,34(40)-nonaene, $N(CH_2CH_2NHCH_2$-*p*-xylyl-$CH_2NHCH_2CH_2)_3N$) in a protonated state were examined. Crystallographic results show binding of the acyclic quasiplanar water tetramer $[H_4\mathbf{L}(H_2O)_4](I)_4\cdot 2.57H_2O$ (**1**) in a tetraprotonated cryptand **L** having an iodide counteranion, where two water molecules reside inside the two tren-based cavity, bridged by a third water molecule, and a fourth external water molecule is hydrogen bonded to the bridged water molecule. In the case of complexes $[H_6\mathbf{L}(Br)][(Br)_6H]\cdot 4H_2O\cdot 2HBr$ (**2**) and $[H_6\mathbf{L}(Cl)][(Cl)_6H]\cdot 10.86H_2O$ (**3**), a single bromide and chloride occupied, respectively, the inside of the cryptand cavity, where **L** is in a hexaprotonated state. Monotopic recognition of bromide/chloride was observed at the center of the cryptand cavity where halides show C–H···halide interactions instead of the N–H···halide interactions reported in the ditopic complexes of halides with the same cryptand, **5** and **6.** Thermal analyses on **1**–**3** were carried out, and the data obtained distinctly differentiate water cluster complex **1** from the anion-encapsulated cryptates **2** and **3**. This study represents the first example of anion-controlled cluster formation inside the cavity of a cryptand.

Introduction

Azamacropolycycles upon protonation can become good hosts for anions.[1] It has been established that these receptors bind more strongly to the anions, even monoanions, compared to monocycles, often by 2 or more order of magnitude. In recent years Bowman-James et al. have shown some unusual binding properties of these receptors. These include the first ditopic binding of nitrates,[2] binding of one fluoride and a molecule of water,[3] and the first example of an anion-based cascade complex **4** (Chart 1), where cryptand **L**, upon hexaprotonation with HF, showed two fluoride ions bridged by a water molecule,[4] whereas protonation with HCl or HBr encapsulated a halide and a water molecule inside the cavities of the cryptands **5** and **6**, respectively.[5] In all these cases,

Chart 1. Octaamino cryptand **L**, Tetraprotonated **L** Containing Water Tetramer Cluster **1**, Monotopic **2** and **3,** Tritopic **4**, and Ditopic **5** and **6** Complexes of Halides with Hexaprotonated **L**



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anions get preference for encapsulation inside the cavity over several water molecules or a water cluster. Both electrostatic interactions and hydrogen bonds between protonated amines and the anion guests govern the binding in the systems. Though inclusion of a water/dimer water inside the cavity of a macrobicyclic cryptand has been known for quite sometime, there is no report available to date of a cluster containing more than two water molecules inside the cavity of a macrobicyclic host,[6−9] except the structure of the *m*-xylyl analogue of **L** with three internal disordered water molecules.[2b,10] Any study on water clusters in a restricted environment is of considerable current interest as they have been implicated in several contemporary problems.[11−14] Herein we report the structure of a cryptand and water cluster supramolecular complex, confirming a unique binding of an acyclic quasiplanar water tetramer in a tetraprotonated cryptand **L** having an iodide counterion, **1**.[15] Interestingly, when bromide/chloride anions were examined, anion encapsulation was preferred inside the cryptand cavity, yielding **2** and **3** instead of the water cluster. To the best of our knowledge, this is the first example of water cluster formation inside the cryptand host controlled by the counteranion.

Experimental Section

Materials. Reagent-grade chemicals (Aldrich) were used as received. HCl, HBr, HI, and solvents were purchased from SD Fine Chemicals, Mumbai, India. All the solvents were purified prior to use.

Synthesis. The macrobicyclic cryptand **L** was synthesized according to previously published methods and isolated as the free base.[16] Complexes **1**−**3** were obtained by dissolving **L** (60 mg, 100 μmol) in MeOH (10 mL) and adding 55% HI, 49% HBr, and 37% HCl, respectively. The solid formed was redissolved by adding about 4 mL of water, and the solution was filtered. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solution at RT (room temperature).

$[H_4L(H_2O)_4][I]_4\cdot 2.57H_2O$, 1. Yield: 70−75%. ^{1}H NMR (200 MHz, D_2O): δ 2.79 (t, 12H, NCH_2), 3.35 (t, 12H, NCH$_2$CH_2), 4.28 (s, 12H, ArCH_2), 7.49 (s, 12H, ArH). ^{13}C NMR (50 MHz, D_2O): δ 44.40 (NCH$_2$), 49.55 (NCH$_2$$CH_2$), 51.49 (Ar$CH_2$), 130.87 ($C_{Ar}$), 131.71 ($CH_{Ar}$). MS (ESI): *m/z* 599.7 $[H\mathbf{L}]^+$, 727.6 $[H_2\mathbf{L}^{2+} + I^-]$, 855.5 $[H_3\mathbf{L}^{3+} + 2I^-]$. Anal. Calcd for $C_{36}H_{71.14}N_8O_{6.57}I_4$: C, 35.19; H, 5.83; N, 9.12. Found: C, 36.04; H, 6.01; N, 9.43.

$[H_6L(Br)][(Br)_6H]\cdot 4H_2O\cdot 2HBr$, 2. Yield: 80%. ^{1}H NMR (200 MHz, D_2O): δ 2.73 (t, 12H, NCH_2), 3.27 (t, 12H, NCH$_2$CH_2), 4.17 (s, 12H, ArCH_2), 7.39 (s, 12H, ArH). ^{13}C NMR (50 MHz, D_2O): δ 44.25 (NCH$_2$), 49.52 (NCH$_2$$CH_2$), 51.44 (Ar$CH_2$), 130.54 ($C_{Ar}$), 131.49 ($CH_{Ar}$). MS (ESI): *m/z* 599.6 $[H\mathbf{L}]^+$, 680.6 $[H_2\mathbf{L}^{2+} + Br^-]$, 761.5 $[H_3\mathbf{L}^{3+} + 2Br^-]$. Anal. Calcd for $C_{36}H_{71}N_8O_4Br_9$: C, 30.90; H, 5.12; N, 8.01. Found: C, 30.38; H, 5.01; N, 7.83.

$[H_6L(Cl)][(Cl)_6H]\cdot 10.86H_2O$, 3. Yield: 82%. ^{1}H NMR (200 MHz, D_2O): δ 2.82 (t, 12H, NCH_2), 3.37 (t, 12H, NCH$_2$CH_2), 4.28 (s, 12H, ArCH_2), 7.49 (s, 12H, ArH). ^{13}C NMR (50 MHz, D_2O): δ 44.76 (NCH$_2$), 49.55 (NCH$_2$$CH_2$), 51.16 (Ar$CH_2$), 129.98 ($C_{Ar}$), 131.67 ($CH_{Ar}$). MS (ESI): *m/z* 599.6 $[H\mathbf{L}]^+$, 636.0 $[H_2\mathbf{L}^{2+} + Cl^-]$, 694.5 $[H_2\mathbf{L}^{2+} + Na^+ + 2Cl^-]$, 709.5 $[H_4\mathbf{L}^{4+} + 3Cl^-]$. Anal. Calcd for $C_{36}H_{82.72}N_8Cl_7O_{10.86}$: C, 41.12; H, 7.94; N, 10.67. Found: C, 41.36; H, 7.76; N, 10.71.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 200 MHz FT-NMR spectrometers (model: Avance- DPX200). Elemental data were recorded on a Perkin-Elmer 4100 elemental analyzer. MS (ESI) measurements were carried out on Waters QTof-Micro instruments. Thermogravimetric analysis (heating rate of 10 °C/min) was performed using a Mettler Toledo Star SW 7.01.

X-ray Crystallography. The crystallographic data and details of data collection for **1**−**3** are given in Table 1. In each case, a crystal of suitable size was selected from the mother liquor and immersed in partone oil and then mounted on the tip of a glass fiber and cemented using epoxy resin.

Intensity data for all three crystals were collected using Mo Kα ($\lambda = 0.7107$ Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed with SAINT[17] software. An absorption correction was applied to the collected reflections with SADABS[18] using XPREP.[19] The structures were solved by direct methods using SHELXTL[20] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[21] program package. Graphics were generated using PLATON[22] and MERCURY 1.3.[23] For all three cases, non-hydrogen atoms were refined

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Table 1. Crystallographic Data for $[H_4\mathbf{L}(H_2O)_4][I]_4\cdot\mathbf{2.57H_2}O$ (**1**), $[H_6\mathbf{L}(Br)][(Br)_6H]\cdot\mathbf{4H_2}O\cdot\mathbf{2HBr}$ **(2)**, and $[H_6\mathbf{L}(Cl)][(Cl)_6H]\cdot\mathbf{10.86H_2}O$ (**3**)

param	**1**	**2**	**3**
empirical formula	$C_{36}H_{62}I_4N_8O_{6.57}$	$C_{18}H_{32}Br_{4.50}N_4O_2$	$C_6H_{10}Cl_{1.17}N_{1.33}O_{1.81}$
fw	1219.74	696.07	171.13
cryst system	monoclinic	monoclinic	hexagonal
space group	$P2_1/n$	$C2/c$	$P6_3/m$
a (Å)	14.002(3)	20.8971(14)	12.548(2)
b (Å)	20.058(4)	12.3263(8)	12.548(2)
c (Å)	17.647(4)	21.8600(15)	20.391(7)
α (deg)	90.00	90.00	90.00
β (deg)	104.511(4)	105.2050(10)	90.00
γ (deg)	90.00	90.00	120.00
V (Å^3)	4798.2(18)	5433.7(6)	2780.5(11)
Z	4	8	12
d_{calc} (g/cm^3)	1.688	1.702	1.226
cryst size (mm^3)	0.78 × 0.54 × 0.31	0.76 × 0.54 × 0.34	0.85 × 0.43 × 0.28
diffractometer	Smart CCD	Smart CCD	Smart CCD
λ (Å)	0.710 73	0.710 73	0.710 73
F(000)	2394	2732	1076
μ(Mo Kα) (mm^{-1})	2.646	6.680	0.411
abs corr	SADABS	SADABS	SADABS
T (K)	100(2)	100(2)	100(2)
θ range	1.57−25.00	1.94−28.29	1.87−22.50
reflcns collcd	22 962	15 563	5218
indep reflcns	8415	6154	1215
R(int)	0.0520	0.0240	0.0474
data/restr/param	8415/0/518	6154/0/266	1215/0/101
R_1; wR_2	0.500; 0.1234	0.0309; 0.0767	0.0826; 0.1792
GOF(F^2)	1.053	1.094	1.226

anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In all other cases, the hydrogen atoms were geometrically fixed. The disordered oxygen atoms of the water molecules were refined as follows. The SOF values of these oxygen peaks were refined keeping the positional parameters and temperature factors fixed (at 0.05). The refined SOF values of the disordered oxygen atoms were fixed, and positional and isotropic temperature parameters were refined in the subsequent cycles.

Results and Discussion

The cryptand **L** was prepared as reported earlier with high yield. Complexes **1**−**3** were obtained by titrating **L** with 55% HI, 49% HBr, and 37% HCl, respectively, in methanol. In the case of **1**, a brownish precipitate was obtained after addition of hydroiodic acid to the methanolic solution of **L** whereas the solutions turned turbid in the cases of **2** and **3**. To maintain similar conditions of crystallization for **1**−**3,** complex **1** was not isolated from the reaction mixture; instead in all three cases solids were dissolved by adding the appropriate amount of distilled water maintaining pH ∼ 2.0. Syntheses of the complexes were all straightforward, resulting in high yields.

Description of the Crystal Structures. $\mathbf{[H_4L(H_2O)_4][I]_4\cdot 2.57H_2O}$ **, (1).** The complex crystallizes in the tetraprotonated form, with the cryptand containing a water tetramer (where three water molecules O1w, O2w, and O3w are inside the cryptand cavity and one water molecule O4w is outside the cavity), a discrete water dimer (O5w···O6w), and a disordered water molecule outside the cavity through hydrogen-bonding interactions (Figure 1A). The tetraprotonated charge of the cryptand moiety is satisfied by four external iodide counterions. In the water tetramer, central O2w is hydrogen bonded with O1w, O3w, and O4w resulting an acyclic structure with an average O···O distance of 2.830 Å (Table 2) and O2w is slightly deviated from the plane comprising the periphery oxygen atoms O1w, O3w, and O4w by 0.204 Å, resulting in a quasiplanar geometry of the cluster. The water molecules O1w and O3w in the tetramer are recognized at the two ends of tren units through hydrogen-bonding interactions to one secondary amine and two protonated secondary amines in a distorted tetrahedral fashion. O1w and O3w are almost equidistant from their respective bridgehead amines, at a distance of 3.045 and 3.027 Å, respectively, which are slightly less than the sum of the van der Waals radii of nitrogen and oxygen (3.05 Å).[24]

However, O2w is almost equidistant from bridgehead nitrogen atoms at distances of 5.605 and 5.670 Å, respectively, suggesting that the quasiplanar water tetramer is residing at the center of the host molecule. Within the receptor cavity, the water molecule O3w is exactly sitting on the axis passing through two bridgehead amines N1 and N2 (Figure 1b), whereas O1w is 0.149 Å displaced from the mean plane that comprises the N1, O3w, N2 atoms. The partially encapsulated water oxygen O2w is displaced 1.683 Å from the plane whereas the external water of the tetramer cluster O4w is 3.784 Å away from the plane passing through central axis. The hydrogen-bonding motif of the water tetramer in the cryptand is very different from those observed experimentally or predicted theoretically in the gas phase.[25,26] In this tetramer cluster, two water molecules (O1w and O3w) are involved in the formation of four hydrogen bonds and one water molecule (O2w) is involved in the formation of three hydrogen bonds, whereas O4w, which is outside the cryptand cavity, is only involved in the formation of one hydrogen bond. The unique hydrogen-bonding motif of the water tetramer is due to the influence of the surrounding organic moieties and spatial geometry of the binding sites of the cryptand. It is important to note that the water dimer (O5w···O6w) with a distance 2.899 Å is also formed outside the cryptand, which is hydrogen-bonded with N6 of the cryptand unit. The coexistence of the outside water dimer indicates the influence of the constrained media and binding site arrangements for recognition of the acyclic quasiplanar water tetramer in a cryptand environment.

Figure 2a,b show space-filling models of the cryptand moiety with and without the water tetramer, respectively, which show the bowl shape of the host cryptand. It is observed that the tetraprotonated cryptand has an elongated ellipsoidal shape with a distance between the bridgehead nitrogen atoms (N1 and N2) of 10.758 Å and an ∼6.5 Å

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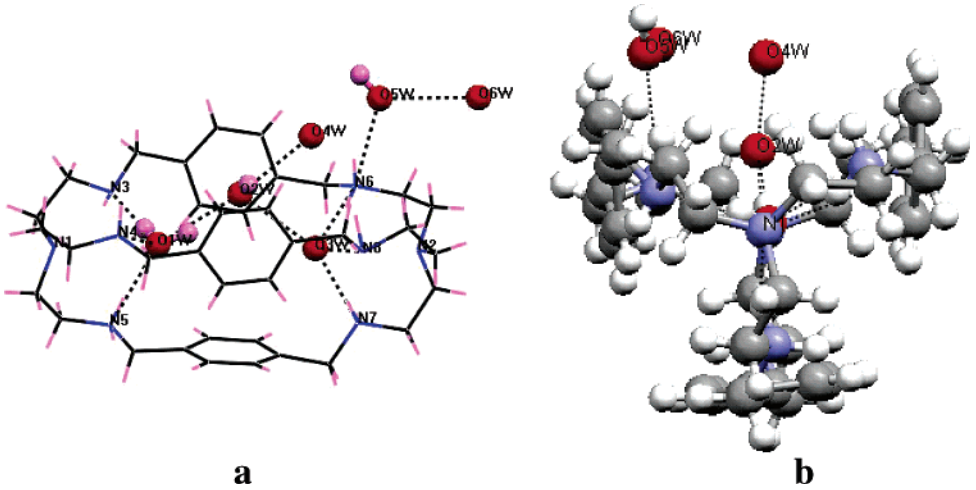

Figure 1. (a) View of $[H_4L(H_2O)_4][I]_4\cdot 2.57H_2O$, **1**, showing the water tetramer and dimer H-bonding interactions with cryptand (red color indicates the oxygen atom of water). (b) View down the pseudo-3-fold axis passing through bridgehead nitrogen atoms of (a) (ball-and-stick model).

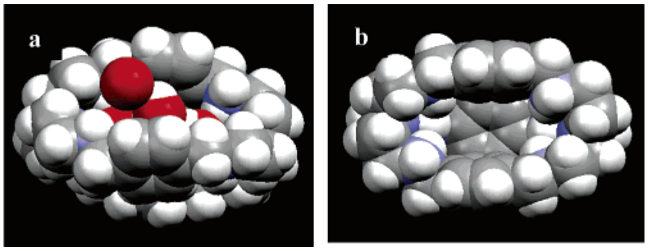

Figure 2. (a) Space-filling model of water tetramer (red color) in a cryptate bowl of complex **1**. (b) Space-filling model of empty cryptand bowl.

Table 2. Interatomic Distances (Å) for Hydrogen-Bonding Interactions of the Water Molecules of **1**

atoms	dist	atoms	dist
O2w•••O1w	2.833(8)	O3w•••N6	2.815(7)
O2w•••O3w	2.864(8)	O3w•••N7	2.806(7)
O2w•••O4w	2.793(8)	O3w•••N8	2.703(8)
O5w•••O6w	2.899(10)	O5w•••N6	2.773(9)
O1w•••N3	2.696(8)	O1w•••N3	2.696(8)
O1w•••N5	2.856(7)		

wide-open bowl, where the acyclic quasiplanar higher energy water tetramer is recognized (Figure 2a). In Figure 2b it is clear that the bottom of the cryptand bowl is covered by a flat phenyl ring of one cryptand arm whereas the perpendicular orientation of other two phenyl rings with respect to the rest of the cryptand arms constitutes the two sides of the bowl. Viewing from different angles the space filling model of **1** confirms the one-sided open cryptand bowl.[27]

The structural features between the coordination of three water molecules (O1w, O2w, and O3w) in **1** and the anion cascade complex **4** of two fluorides and one water molecule reported by Bowman-James et al.[4] are quite similar. The span between the bridgehead nitrogens in **4** is 10.717 Å, which is close to the span in **1**. Quite similar spans in **1** and **4** might be anticipated for the same type (tritopic) of recognition of $H_2O-H_2O-H_2O$ and $F-H_2O-F$ guests, respectively. Further, the O1w•••O3W and F•••F separation is 4.690 and 4.736 Å respectively, with each water oxygen and fluoride almost equidistant from the bridgehead amines and each exhibiting pseudotetrahedral coordination via hydrogen-bonding interactions with the free/protonated amine hydrogens and bridging water molecules.

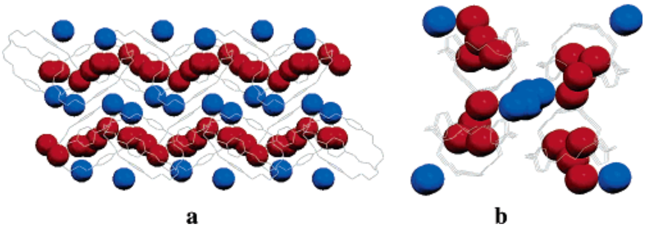

Figure 3. (a) Packing of water clusters and the cryptand moiety of **1** viewed along the crystallographic *c* axis: cryptand moiety, wire frame; tetramer water oxygen, red ball; dimer water oxygen, blue ball. (b) Packing of water clusters and the cryptand moiety of **1** viewing along *a* axis.

Figure 3a represents the packing of water clusters and the cryptand moiety in **1** along the *c* axis. It shows that water tetramer clusters are packed in a zigzag fashion along with the cryptand layers whereas water dimers are forming a distinct layer between two cryptand layers. The orientation of the cryptand in a particular plane is shown in Figure 3b. The bottom side of a cryptand moiety almost covers the open side of the other bowl whereas the adjacent layer shows that bowls are oriented in the reverse direction.

$[H_6L(Br)][(Br)_6H]\cdot 4H_2O\cdot 2HBr$ (2). Complex **2** crystallizes in a noncentric space group as a monobromide-encapsulated hexaprotonated **L** without any internal water molecule (Figure 4a). The asymmetric unit comprises of half a molecule of cryptand, two water molecules, and five bromides, where the internal bromide sits in a special position with occupancy of 0.5 accounting for one internal bromide, eight bromides including two molecules of free hydrobromic acid, and four external water molecules per **L** moiety. Within the receptor cavity, the bromide is located almost on the central axis joining the two bridgehead amines (Figure 4c). The hexaprotonated charge of the cryptand is satisfied by six external bromide counterions where protonated nitrogens are in short contact with these bromide anions through N−H•••Br interactions. The distance between the bridgehead nitrogen atoms in **2** of 6.486 Å is much less than the distance observed (10.758 Å) in the cluster complex **1**. Due to flexibility of the cryptand structure, the cavity bulged in other

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(27) See Supporting Information.

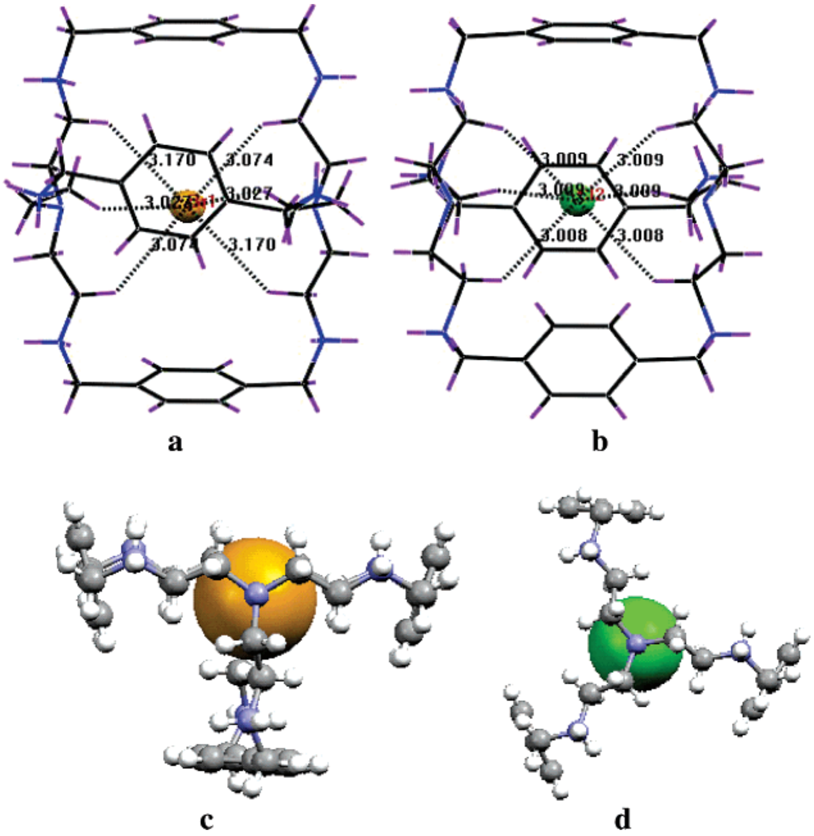

Figure 4. (a) View of $[\mathrm{H_6}\mathbf{L}(\mathrm{Br})][(\mathrm{Br})_6\mathrm{H}]\cdot 4\mathrm{H_2O}\cdot 2\mathrm{HBr}$, **2**, showing the bromide encapsulation (orange color). (b) View of $[\mathrm{H_6}\mathbf{L}(\mathrm{Cl})][(\mathrm{Cl})_6\mathrm{H}]\cdot 10.86\mathrm{H_2O}$, **3**, showing the chloride encapsulation (green color). Dotted lines show $\mathrm{C{-}H\cdots X^-}$ ($\mathrm{X = Br/Cl}$) interactions. (c) View down the pseudo-3-fold axis of (a). (d) View down the 3-fold axis of (b). Cryptand: ball-and-stick model. Halide: space filling model in (c) and (d).

direction from ~6.5 to ~9.95 Å in **2**, where the anion is involved in weak $\mathrm{C{-}H\cdots Br^-}$ interactions in the range 3.027−3.170 Å. The electrostatic interactions and six $\mathrm{C{-}H\cdots Br^-}$ interactions (six C−H hydrogens next to the ammonium nitrogens of two tren units) hold the internal bromide in a pseudooctahedral fashion at the center of the cavity.[28]

The hydrogen-bonding geometry of the internal bromide in **2** is completely different from the geometry of guests in the ditopic (two cavity occupants) complex of hexaprotonated **L** with one bromide and a water, **5**, reported very recently.[5] In **5** the bromide and internal water molecule are located at two tren units of **L** where the distance between the bridgehead nitrogens is 10.377 Å, which is 3.891 Å longer than that of monotopic complex **2** and ~0.35 Å shorter than the tritopic complexes **1** and **4** (three cavity occupants). The small difference in the bridgehead distance for ditopic (two cavity occupants) **5** and tritopic **1** and **4** is because in all three cases two individual tren cavities are occupied by a distinct guest and their pseudotetrahedral coordination sphere is completed in similar fashion. The large difference in the conformation of the cryptand in monotopic complex **2** is attributed to only one occupant at the center of cavity where the pseudooctahedral coordination sphere is completed by six $\mathrm{C{-}H\cdots Br^-}$ interactions.

Figure 5 shows the hydrogen-bonding interaction of the ammonium nitrogen of **L**, water molecules, and counterions in the lattice of **2**. It shows all ammonium nitrogen centers as well as four water molecules are in strong interaction with external bromides. No free water molecule is observed in the lattice. Interestingly, four bromide ions (Br3, Br4) and four water oxygens (O1, O2) are forming a cluster of two fused pentagonal rings with an average $\mathrm{halide\cdots O_{water}}$ distance 3.20 Å and a short $\mathrm{O_{water}\cdots O_{water}}$ distance of 2.40 Å. Furthermore, two bromide ions (Br2) form a tetracycle which includes two ammonium nitrogen centers of two cryptand units. The interaction observed in the remaining two external bromide ions Br4 is the short contact with ammonium nitrogen centers, whereas there is no such interaction observed with internal bromide Br1.

$[\mathrm{H_6}\mathbf{L}(\mathrm{Cl})][(\mathrm{Cl})_6\mathrm{H}]\cdot 10.86\mathrm{H_2O}$ (3). Complex **3** crystallizes as a chloride-encapsulated hexaprotonated **L** similar to **2**, where anion encapsulation is preferred over water cluster formation inside the cavity. In the asymmetric unit the chloride ion (Cl1) sits in a general position and the other chloride ion sits in a special position with one-sixth of the cryptand molecule and disordered water molecules accounting for seven chlorides/cryptand molecules. The cryptand moiety possess a perfect 3-fold symmetry, and Cl1 is exactly located on the 3-fold axis at a distance 3.120 Å from the bridgehead nitrogen atoms (Figure 4b,d), 0.123 Å shorter than that observed for **2,** which is due to the smaller size of the chloride. Hydrogen-bonding interactions of chloride are

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(28) (a) Moorthy, J. N.; Natarajan, R.; Mal, P.; Venugopalan, P. *J. Am. Chem. Soc.* **2002**, *124*, 6530. (b) Thallapally, P. K.; Nangia, A. *CrystEngComm.* **2001**, *27*, 1.

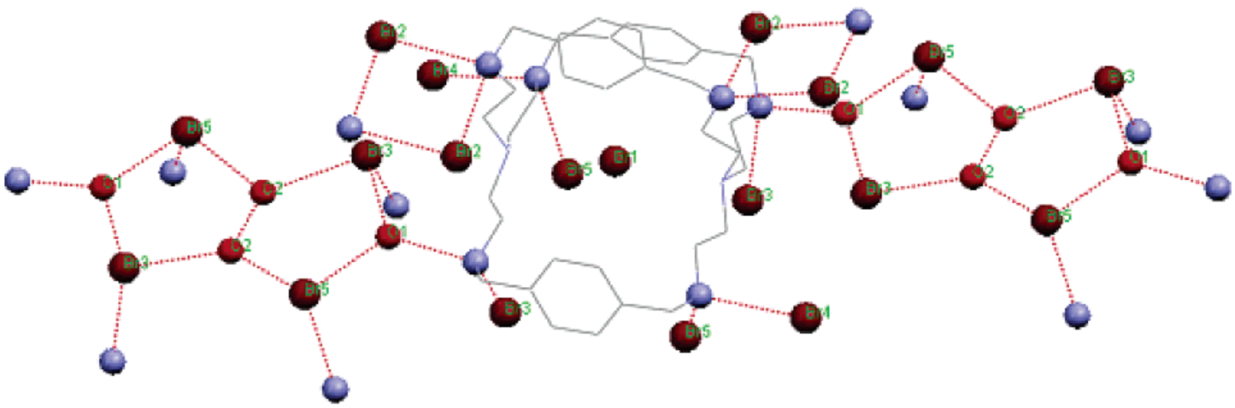

Figure 5. Interactions of water molecules, bromide, and ammonium nitrogens of **L** in the lattice of **2**: water, red color; bromide, brown color; ammonium nitrogen, blue color; cryptand, wire frame. Shown are all water molecules in strong interactions with bromide forming fused pentamer rings.

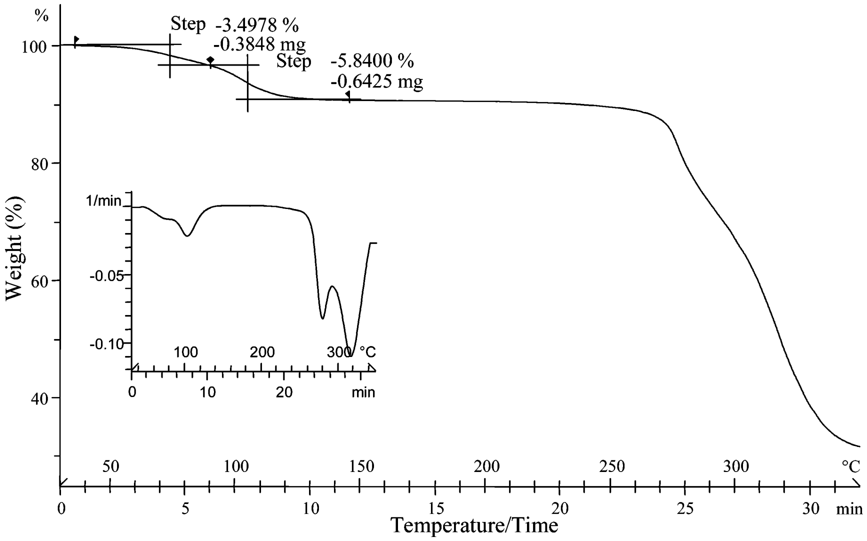

Figure 6. Thermogravimetric curve of $[H_4\mathbf{L}(H_2O)_4][I]_4\cdot2.57H_2O$, **1**, at a heating rate of 10 °C. The inset shows the first derivative of the TGA curve.

quite similar to those of the bromide complex, where weak C−H$\cdots$Cl$^-$ interactions are observed at a distance of 3.009 Å.[28] The protonated nitrogen atoms are in short contact with the surrounding chloride anion and the disordered water molecules (N$\cdots$Cl = 3.005 Å, shortest N$\cdots$O$_{water}$ distance = 2.701 Å). The structural geometry of the monotopic chloride complex **3** is similar to the structure of **2** but different from the structure of reported ditopic chloride complex **6.** Centrally located monotopic complexes of chloride and bromide with different cryptands are also known in the literature, but in theses cases the halide is tightly held by a hydrogen-bond network with the amine nitrogens.[29]

Thermal Analysis. Thermal analysis of **1** shows that onset of water loss starts at about 50 °C and complete loss of water takes place within 125 °C. Total weight loss in this temperature range is 9.338%, corresponding to 6.38 molecules water (Figure 6). The facile removal of all tetramer, dimmer, and disorder water molecules from **1** indicates weak interaction of water molecules with the cryptand. The first derivative curve of TGA clearly shows two types of water loss in the temperature range 50−125 °C (Figure 5). The first loss of water that takes place between 50 and 90 °C is 3.5% corresponding to 2.38 molecules of water that might be the external water dimer and disorder water. The second loss of water about 5.8% corresponding to 3.95 molecules of water at relatively higher temperature range (90−125 °C) might be the guest water tetramer cluster in the cryptand.

Figure 7a shows a TGA curve for **2**. There is no loss up to 100 °C, which reconfirms there are no free water molecules in the lattice. The X-ray structural analysis showed that all the water molecules in the lattice are strongly hydrogen bonded with the external halides. The first loss that takes place at the temperature range 100−170 °C is 12.18%, corresponding to the loss of two molecules of hydrobromic acid.

The second loss at the temperature range 170−250 °C is 8.94%, corresponding to two water molecules associated with one molecule of hydrobromic acid. In the case of complex **3**, the TGA curve shows a different pattern (Figure 7b). Since complex **3** has a number of disordered free as well as protonated water molecules in the lattice, the onset of water loss occurs at about 50 °C and the first step loss completed at 125 °C is 13.52%, corresponding to 7.88 water molecules. The TGA curve shows a second step of loss in the temperature range 130−210 °C which is 7.19%. This loss

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(29) (a) Dietrich, B.; Guilhem, Lehn, J.-M.; J.; Pascard, C.; Sonveaux, E. *Helv. Chim. Acta* **1984**, *67*, 91. (b) Hossain, M. A.; Llinares, J. M.; Miller, C.; Bowman-James, K. *Chem. Commun.* **2000**, 2269.

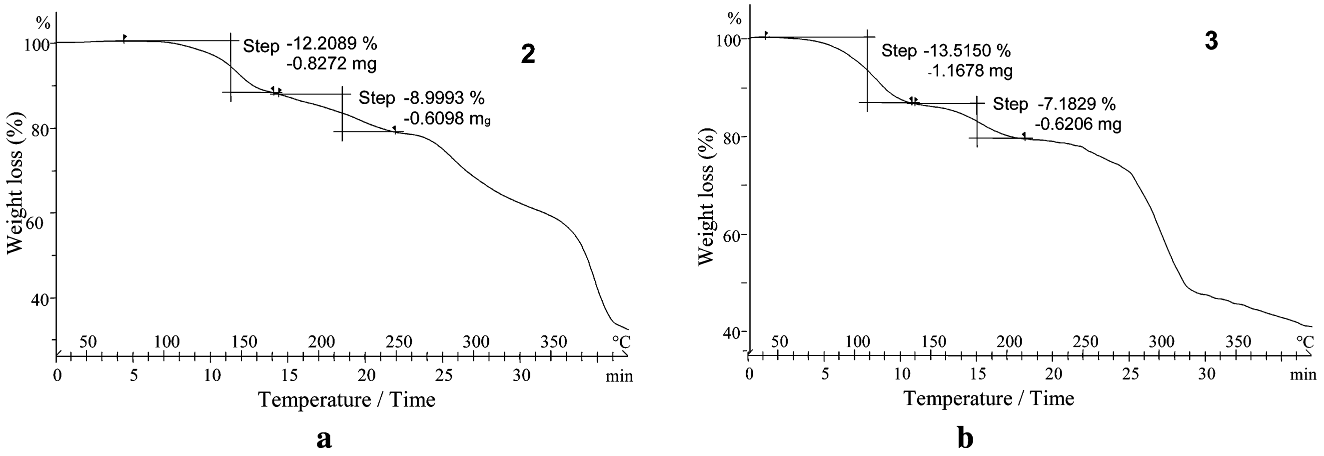

Figure 7. (a) Thermogravimetric curve of $[H_6\mathbf{L}(Br)][(Br)_6H]\cdot 4H_2O\cdot 2HBr$, **2**. (b) Thermogravimetric curve of $[H_6\mathbf{L}(Cl)][(Cl)_6H]\cdot 10.86H_2O$, **3**. In both cases, the heating rate is 10 °C/min.

may be attributed to the loss of one HCl with 2.17 water molecules. Therefore, the total loss in these two steps is one HCl (corresponds to an internal chloride which is in a weak interaction with CH) and about 10 solvated water molecules. Thermal analysis data of these three complexes distinctly differentiate water cluster complex **1** from the anion-encapsulated cryptates **2** and **3**.

Conclusions

We have succeeded in forming a supramolecular complex of a water tetramer cluster and a cryptand, **1**, when the largest radii and lowest electronegative halide, I^-, was chosen as a counteranion. The structural features between the coordination of three water molecules (O1w, O2w, and O3w) in **1** and the anion cascade (tritopic) complex of two fluorides and one water molecule, **4**, are quite similar. Monotopic anion recognition inside the cryptand cavity in complexes **2** and **3** was preferred over water cluster formation in the case of Br^-/Cl^- counterions. Structural geometry and hydrogen-bonding interactions of the internal halide in **2** and **3** are largely different from the ditopic complexes **5** and **6** reported recently. In the cases of **2** and **3**, an internal halide resides in pseudooctahedral fashion at the center of the crytand cavity with weak C−H···halide interactions whereas N−H···halide interactions encapsulate the halide tetrahedrally at one of the N_4 cavities along with an internal water molecule at the other N_4 cavity of the cryptand moiety in **5** and **6**. Stabilization of the acyclic water tetramer observed in the solid state structure of **1** is due to the restricted cryptand cavity size, the larger counteranion, and its surrounding free and protonated secondary amine, which form hydrogen-bonding interactions with the acyclic water tetramer.

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Supporting Information Available: Three crystallographic files in CIF format for complexes **1**−**3**, additional crystallographic data including a table of hydrogen-bonding parameters, ORTEPs, and packing diagrams, and a space-filling model of the cryptand bowl in complex **1** viewed from different angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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