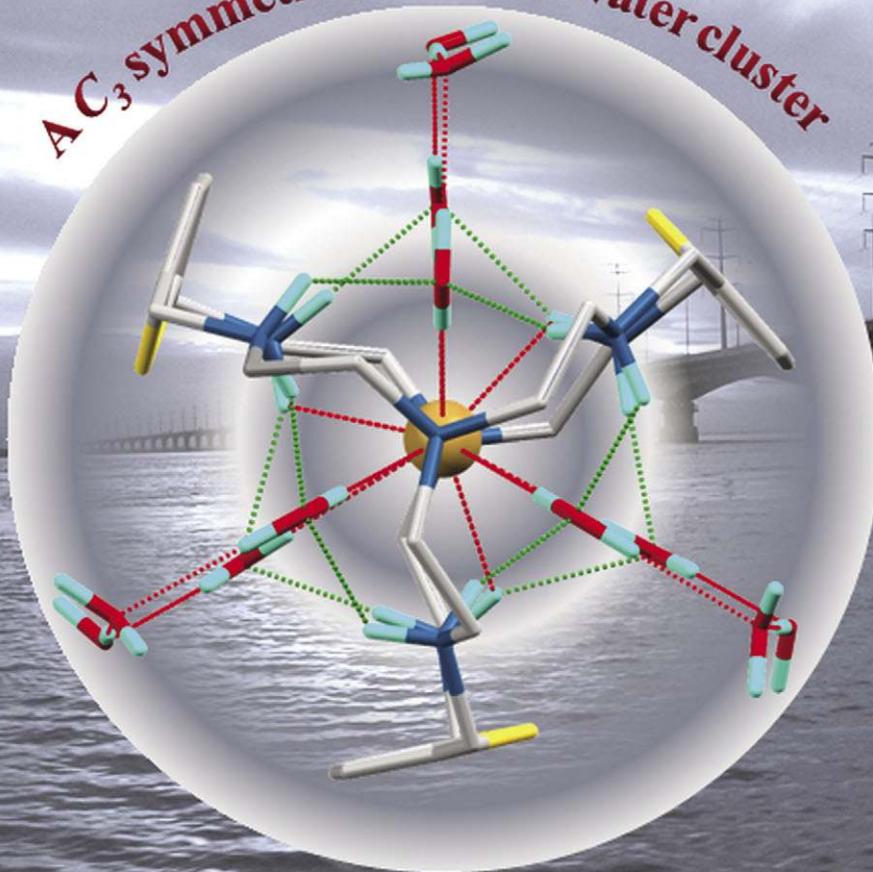


A C_3 symmetric bromide-water cluster

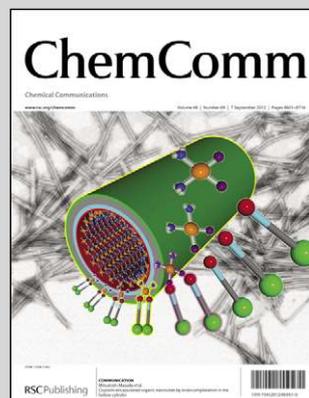


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Self-assembly of ordered water tetramers in an encapsulated $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ complex

One bromide and three highly-ordered “water tetramers” are assembled within the cavity of a cryptand to provide a C_3 symmetric bromide-water cluster. This finding represents a new type of anion-water hybrid cluster and a step towards the understanding of complex aqueous phase environments of an anion.

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Self-assembly of ordered water tetramers in an encapsulated $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ complex†Musabbir A. Saeed,^a Avijit Pramanik,^a Bryan M. Wong,^b Syed Ataul Haque,^a Douglas R. Powell,^c Dillip Kumar Chand^d and Md. Alamgir Hossain^{*a}

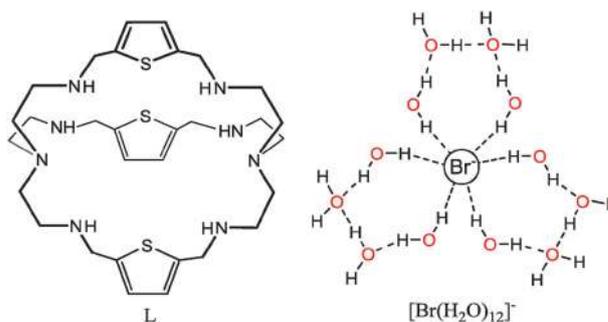
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An unanticipated anion–water cluster is assembled by one bromide and three highly-ordered “water tetramers” within the cavity of a receptor, providing a perfect C_3 symmetric propeller-shaped bromide–water cluster of $[\text{Br}(\text{H}_2\text{O})_{12}]^-$.

Hydrated anions exhibit a diverse range of complex interactions due to the strong stability of hydrogen bonds that are spontaneously formed throughout the aqueous network. Since the solvation process usually results in a random orientation of molecules in the bulk, the formation of ordered anion–water clusters in chemical receptors allows a detailed characterization of molecular interactions in these confined environments.^{1,2} In particular, there has been significant attention on understanding the ordered water clusters in hydrophobic environments³ due to their importance in chemical and biological interfaces.⁴ Hydrogen-bonded water networks can naturally grow at the hydrophobic surface, often giving rise to a stable hydrate.⁵

Upon solvation, a halide anion disperses its charge distribution spherically, making it an effective paradigm for anion hydration. Although hydrated halides $\text{X}(\text{H}_2\text{O})_n^-$ have been the subject of numerous theoretical studies over the last several years,⁶ examples of encapsulated anion–water clusters by synthetic receptors are rare^{7,8} and are mostly limited to anions coordinated with a single water as $\text{X}(\text{H}_2\text{O})^-$.⁷ Other hydrated anions have been characterized within lattices formed by a host matrix, a metal organic framework or between hosts.^{9,10} The structural characterization and energetic formation of anion–water clusters are essential for understanding mechanistic details of solvation processes, ion translocation in water-membrane interfaces, ion mobilities in the bulk, and electrical phenomena within aqueous–salt interfaces.^{11,12} Herein we report an unanticipated anion–water cluster assembled by one bromide and

Scheme 1 Bicyclic receptor L and $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ guest.

three highly-ordered “water tetramers” within the cavity of a bicyclic host L, providing a perfect C_3 symmetric propeller-shaped bromide–water cluster as $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ (Scheme 1). Such a highly symmetric, ordered assembly of a discrete anion–water cluster has not been reported previously or predicted theoretically. The rigid geometry of the host with its strategically-placed protonated nitrogens allows a stable, ordered assembly of three tetramer rings with the encapsulated bromide—a stabilized geometry that is not possible in a bulk water system.

The bromide complex crystallizes as the hydrated bromide salt, $[\text{H}_6\text{L}(\text{Br}(\text{H}_2\text{O})_{12})]\text{Br}_5$, with four water molecules per asymmetric unit. The cationic unit is found to sit on a crystallographic 3-fold rotation axis, with the two tertiary nitrogen atoms unprotonated. One bromide is located inside the cavity lying on the bridgehead N1–N14 axis. As shown in Fig. 1, the internal bromide is hexacoordinated with three “water tetramers,” forming a propeller-shaped hydrate as $[\text{Br}(\text{H}_2\text{O})_{12}]^-$. The encapsulated bromide is directly linked to three pairs of water molecules bound between the cryptand arms ($\text{O}2\text{H}\cdots\text{Br}2 = 3.656(16) \text{ \AA}$, $\text{O}2\text{H}\cdots\text{Br}2 = 179.5^\circ$; $\text{O}3\text{H}\cdots\text{Br}2 = 3.281(14) \text{ \AA}$, $\text{O}3\text{H}\cdots\text{Br}2 = 179.8^\circ$). Each pair of water molecules is further connected to a water dimer (O4 and O1) with two strong hydrogen bonds, completing the bromide–water pentameric cycle. The water molecules are held with strong hydrogen bonds ranging from 2.66(3) to 2.77(2) \AA , which are comparable to $\text{O}\cdots\text{O}$ bond distances of 2.745(6) \AA reported by Atwood and co-workers for the ice-like $(\text{H}_2\text{O})_8$,^{3f} and 2.72–2.93 \AA reported by Fujita and co-workers for the molecular ice $(\text{H}_2\text{O})_{10}$.^{3l}

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† Electronic supplementary information (ESI) available: Synthesis, NMR studies, and optimized geometries. CCDC 864063. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc30767g

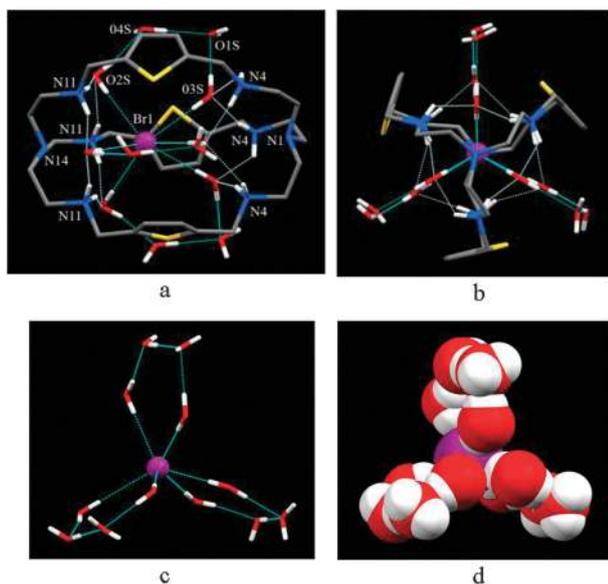


Fig. 1 Crystal structure of $[\text{H}_6\text{L}(\text{Br}(\text{H}_2\text{O})_{12})]^{5+}$ showing the interlocked $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ guest with the cryptand: (a) side view, and (b) view down the three-fold axis (external bromides and hydrogen atoms of carbons are not shown for clarity); (c) perspective and (d) space filling views showing only $[\text{Br}(\text{H}_2\text{O})_{12}]^-$. [Selected hydrogen bonding distances: $\text{O4H} \cdots \text{O1} = 2.66(3)$, $(\text{O2S} \cdots \text{O4S} = 2.77(2)$ and $\text{O3S} \cdots \text{O1S} = 2.76(2)$ Å)].

In the bromide–water complex, each coordinating water molecule (O2 or O3) is further bonded with two protonated secondary amines ($\text{NH} \cdots \text{O} = 2.75(2)$ to $2.92(2)$ Å) at both ends of L, providing an additional stability to these two water molecules as compared to other water molecules (O4S and O1S) in a given cycle, which is also reflected in the thermal analysis (discussed later). Three water molecules, which are directly coordinated with the bromide anion at each end of L, are linked alternately with three secondary amines to form a circular hydrogen bonding network (Fig. 1a and b). This specific arrangement of water molecules coupled with electrostatic interactions results in an interlocking of $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ within the cryptand to bring the anion–water cluster inside the cavity.

In order to characterize the nature of water molecules and the thermal stability of the complex, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. As shown in Fig. 2, the complex exhibited a first weight loss of 8.5% at a temperature of 200 °C, which corresponds to six water molecules. Another 8.5% weight loss occurred in the temperature range of 200 to 262 °C, corresponding to the remaining six water molecules. As seen in the solid-state structure, the complex contains twelve water molecules which are tightly held in the strong H-bonding network. The equivalent loss (8.5%) in the TGA, which corresponds to six water molecules at the two different temperature ranges, indicates that the water molecules are held with two different strengths in the cluster. The first loss could be due to the elimination of six water molecules that are not bound to the protonated amines, while the second loss could arise from the removal of tightly bonded water molecules with the cryptand as well as with the central bromide ion. This observation clearly indicates that the $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ species is highly stable due to the interlocking with the cryptand, requiring high temperatures for

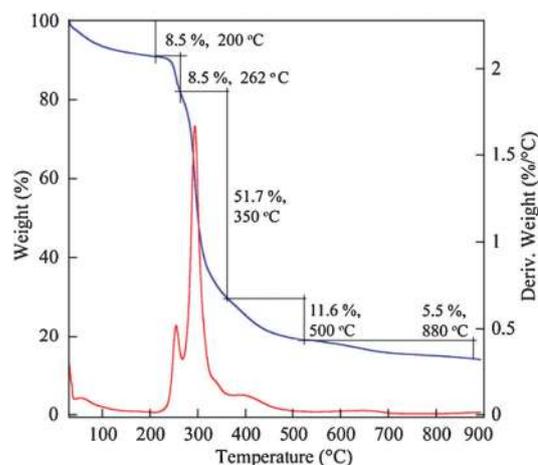


Fig. 2 Thermogravimetric analysis (TGA) curve of $[\text{H}_6\text{L}(\text{Br}(\text{H}_2\text{O})_{12})]\text{Br}_5$ at a heating rate of 10 °C min^{-1} .

the elimination of water.^{3m,10d} In the DSC, two exothermic peaks are seen at around 210 and 240 °C with 23 J g^{-1} and 43 J g^{-1} , respectively (see ESI†). Further major weight loss (51.7%) in the TGA occurred at 350 °C, followed by 11.6% and 5.5% at 500 °C and 880 °C, respectively, due to the decomposition and combustion of the complex.

The presence of water in the complex was also identified by FT-IR spectra (ESI†). The complex showed a broad band at around 3480 cm^{-1} that is assigned to the O–H stretching vibration of water in the sample.^{3m,3n} Another IR spectrum taken after heating at 200 °C overnight gave an almost identical spectrum, indicating a tight bonding of water molecules—an observation which is consistent with the TGA and X-ray data (*vide supra*).

The formation of discrete, ordered $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ with the cryptand was indeed a surprise since the negatively-charged bromide was expected to interact directly with the hexaprotonated host. To further understand the energetics of this unusual situation, density functional theory (DFT) calculations were performed on both the cryptand– $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ complex and the isolated $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ species using the M06-2X hybrid functional which has been shown to accurately predict the binding energies of ions and other noncovalent bonding interactions in large molecular systems.¹³ Molecular geometries (including the empty ligand) were completely optimized without constraints at the M06-2X/6-31G(d,p) level of theory, and single-point energies with a very large 6-311+G(d,p) basis set were carried out *in vacuo*. Optimized geometries, vibrational frequencies, and enthalpies of formation are tabulated in the ESI.† Our calculations show that the cryptand– $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ complex has a complexation enthalpy of 627.4 kcal mol^{-1} and further indicate that the isolated $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ complex without the cryptand undergoes significant re-arrangement upon geometry optimization. In contrast, the C_3 symmetry of the cryptand with its unique positions of protonated nitrogens at each of the C_3 -symmetric positions keeps each of the $(\text{H}_2\text{O})_4$ tetramer units between the ligand arms (Fig. 3a). The symmetric geometry of $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ with the cryptand is undoubtedly due to both the hydrogen bonding and positive charge of the cryptand as can be seen by the electrostatic potential (Fig. 3b).‡

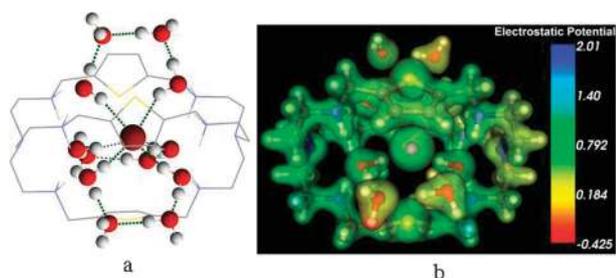


Fig. 3 (a) Optimized DFT geometry of $[\text{H}_6\text{L}(\text{Br}(\text{H}_2\text{O})_{12})]^{5+}$ showing stabilization of the $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ guest with the cryptand at the M06-2X/6-31G(d,p) level of theory. (b) Electrostatic DFT potential of $[\text{H}_6\text{L}(\text{Br}(\text{H}_2\text{O})_{12})]^{5+}$ in PCM water solvent.

In conclusion, we have presented a very unusual, highly-ordered anion–water cluster assembled by one central bromide anion and three “water tetramers” forming a discrete $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ species interlocked with a bicyclic receptor. Each “water tetramer” is involved in coordinating the encapsulated bromide at both ends, resulting in a perfect C_3 symmetric propeller-shaped bromide–water cluster. The specific orientation of the cryptand provides both directional H-bonds and an accurate spacing for water molecules to be coordinated with the central anion, resulting in a complementary host for the large hydrated bromide. Our results from both experimental studies and theoretical calculations clearly demonstrate that the formation of the stable $[\text{Br}(\text{H}_2\text{O})_{12}]^-$ species is assisted by the hydrophobic environment of the host and efficient molecular recognition within the cavity *via* water...amine^{3m} and water...anion⁷ interactions. This finding represents a prototype for new types of highly-ordered, anion–water hybrid clusters and a step towards the understanding of complex aqueous phase environments of an anion, particularly with large hydrophobic surroundings in biological systems.¹⁴

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Notes and references

† Crystal data for $\text{C}_{30}\text{H}_{54}\text{N}_8\text{S}_3\cdot 6\text{Br}\cdot 12(\text{H}_2\text{O})$, $M = 1318.64$, cubic, $a = 17.7890(9)$ Å, $b = 17.7890(9)$ Å, $c = 17.7890(9)$ Å, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 5629.3(5)$ Å³, $T = 100(2)$ K, space group $P2_13$, $Z = 4$, $\mu(\text{MoK}\alpha) = 4.444$ mm⁻¹, 73 811 reflections measured, 3105 independent reflections ($R_{\text{int}} = 0.1045$). The final $R_1 = 0.1191$ ($I > 2\sigma(I)$). CCDC 864063.

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