

Long-range Ordering in Water–Halide Ion Interactions: A Database Study¹

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(Received September 30, 2004; CL-041154)

A detailed analysis of water–halide ion interactions using the Cambridge Structural Database reveals predominant cyclic hydrogen-bonded $(\text{H}_2\text{O}\cdot\text{X}^-)_2$ clusters and isostructural tapes of 4,5,6-membered rings leading to channel hydrates.

Self-assembling supramolecular structures formed by solid state organic molecules as well as network coordination polymers have greatly emerged in recent years due to the significant efforts and understanding followed by the concept of crystal engineering.² A variety of supramolecular assemblies, particularly, of organic solids have been explicated by using the strategies of ‘supramolecular synthons’ and ‘intermolecular interactions.’ For the several decades a lot of studies has been focused on inclusion compounds, a rapidly growing field of supramolecular chemistry.³ A large number of hydrate inclusion compounds in which either hydrogen-bonded water molecules or to combine with ions constitute a wide variety of structures have been hitherto reported.⁴ As the reasons for the presence of water along with other molecules are widely varied, systematic analyses of water hydrogen bonding have never been attempted until recently.^{5–7} Infantes and co-workers have analyzed the Cambridge Structural Database (CSD)⁸ to explore hydrogen-bonded water motifs and extended patterns of hydrogen bonding involving water and different chemical functional groups. These studies uncovered a wide range of water motifs in the form of 4,5,6-membered rings, chains, tapes, and layers as well as extended patterns of water molecules along with other chemical groups.

Water–halide ion clusters are of fundamental importance in chemical and biological systems. Several experimental and theoretical studies have described a number of cluster models for ion–water interactions to explain the phenomena of ionic solvation. Studies on water–halide clusters using spectroscopic methods and ab initio calculations provided useful structural and energetic information.⁹ Particularly, $\text{X}^-\cdot(\text{H}_2\text{O})_{1-6}$ ($\text{X} = \text{Cl}, \text{Br}$, etc.) clusters have been enumerated with different hydrogen-bonded networks with energies in order to characterize possible optimal configurations of water molecules around an ion,^{10,11} however, it is not clear whether such clusters really represent the ion–water structures in nature. The existence of water–halide ion interactions in the form of $(\text{X}^-\cdot\text{H}_2\text{O})_2$ clusters¹² and infinite tapes as duplexes¹³ from isomorphous halide hydrate structures were already reported. We also reinvestigated intriguing hydrogen bond patterns of water molecules with azide ion forming layer of different sized hydrogen-bonded rings.¹⁴ In the present study, we have analyzed the hydrogen bond patterns of water–halide ion $(\text{X}^-\cdot\text{H}_2\text{O})_n$ interactions using the CSD. Here we find that more than one-third interactions of the types $\text{Ow}\cdots\text{X}^-\cdots\text{Ow}$ and $\text{X}^-\cdots\text{Ow}\cdots\text{X}^-$ ($\text{X} = \text{Cl}$ and Br) to have cyclic hydrogen-bonded $(\text{H}_2\text{O}\cdot\text{X}^-)_2$ dimers¹⁵ in the form of quadrilaterals with strong and directional hydrogen bonds. Further, we identify hydrogen-bonded water and halide ions which exist as infinite mo-

lecular chains or tapes, consisting of hydrogen-bonded quadrilaterals, pentagons, and alternate quadrilaterals–hexagons. These water–halide hydrogen bonding patterns mimic those of water motifs and water with other chemical moieties such as carbonyl, hydroxy, and amino groups.⁶ The study suggests models for water–ion networks in ionic shells and membrane channels as well as challenges for designed approaches to employ water molecules and halide ions to build functional supramolecular architectures.¹⁶

The polar nature of water and its potential to form hydrogen bonds play key roles in determining the water interactions and dynamics with ions. So, the knowledge of specific hydrogen bonding information on solvated structures from a reliable source is very essential. CSD is the unique database of more than 290000 molecular structures with atomic level details and has plentiful hydrated crystal structures of about 5–10%. We used the CSD search interface ConQuest to retrieve the data for analysis using CSD update version 5.25 (November 2003). We considered all hydrate structures that have hydrogen bonded water–halide fragments $\text{HO}_w\text{H}\cdots\text{X}^-\cdots\text{HO}_w\text{H}$ (1046 and 203 hits respectively for $\text{X}^- = \text{Cl}$ and Br , **1**) and $\text{X}^-\cdots\text{HO}_w\text{H}\cdots\text{X}^-$ (1173, 213 hits respectively for $\text{X}^- = \text{Cl}$ and Br , **2**) by selecting no disorder, no errors and *R*-factor <10% with the default van der Waals radii criterion (Figure 1). The ConQuest program was again used to search for cyclic hydrogen-bonded dimeric motifs $(\text{X}^-\cdot\text{H}_2\text{O})_2$ from the retrieved water–halide fragments which yielded 390

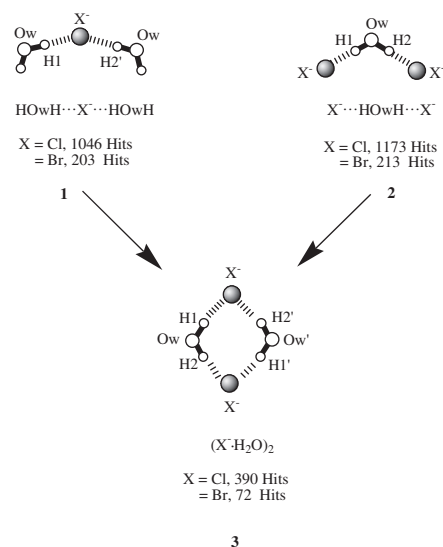


Figure 1. Schematic diagram representing hydrogen-bonded water–halide clusters and their occurrences in the Cambridge Structural Database (CSD version 5.25; November 2003 release). Note that one-third of $\text{HO}_w\text{H}\cdots\text{X}^-\cdots\text{HO}_w\text{H}$ and $\text{X}^-\cdots\text{HO}_w\text{H}\cdots\text{X}^-$ ($\text{X} = \text{Cl}$ and Br) interactions have quadrilateral hydrogen-bonded $(\text{X}^-\cdot\text{H}_2\text{O})_2$ clusters.

and 72 hits, respectively for $X^- = \text{Cl}$ and Br (**3**). The hydrogen bond parameters for all water–halide ion interactions (**1** and **2**) and that for only $(X^- \cdot \text{H}_2\text{O})_2$ quadrilaterals (**3**) have been analyzed by using interactive analytical and statistical program VIS-TA v2.1. Strong hydrogen bonding selectivity and directionality in hydrogen-bonded $(X^- \cdot \text{H}_2\text{O})_2$ quadrilaterals (**3**) were observed and compared with that of linear hydrogen-bonded fragments (**1** and **2**). The D–H...A distances range from 1.8 to 3.0 Å for water–chloride ion and 2.0 to 3.2 Å for water–bromide ion interactions. A narrow range of angles 80° and 100° ($\pm 20^\circ$), respectively at $\text{O}_w \cdots X^- \cdots \text{O}_w$ and $X^- \cdots \text{O}_w \cdots X^-$ distinguish the $(X^- \cdot \text{H}_2\text{O})_2$ quadrilaterals from other linear fragments which span through 60–160° for such angles.

To find out other extended hydrogen-bonded motifs in water–halide interactions, we used extensively Mercury software, a part of the CSD graphical visualization tool for the exploration of crystal packing. As the Cl^- ion has a spectroscopically better characteristic shift associated with participating as a hydrogen bond acceptor and is abundant in the CSD, further analysis was restricted to chloride hydrates. Using the water–halide structural data, three major categories of hydrogen bonding patterns involving water molecules and halide ions were generated with Mercury software by applying symmetry operations of translation and inversion: infinite molecular chains of quadrilaterals (**A1**), pentagons (**B1**), and edge-sharing alternate quadrilaterals and hexagons (**C1**) as depicted in Figure 2. These novel molecu-

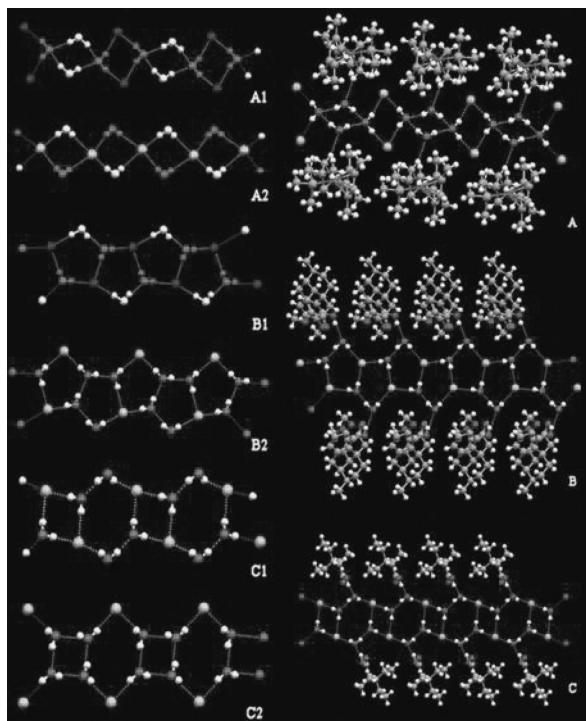


Figure 2. Water–halide structures from hydrate compounds in CSD. Left column: infinite hydrogen-bonded isostructural tapes of quadrilaterals (A1, A2), edge-sharing pentagons (B1, B2) and edge-sharing alternate quadrilaterals and hexagons (C1, C2). Right column: A, B, and C - sections of water–halide host lattices engaging other molecules through network of hydrogen bonds to form channel hydrates with supramolecular architectures (CSD refcodes A1-GENJOY, A2-ALPALC10, B1-CHEABZ, B2-CADBUE, C1-GEYMAY, C2-QQQEQG01).

lar chains are reminiscent of double helical ladder DNA polymers. Importantly, Cl^- ions and water molecules share similar stereochemistry in forming three or four-coordinated hydrogen bonds, resulting in isostructurality of the molecular chains. Therefore, the sites of Cl^- ion and water molecule are mutable between **A1** and **A2**, **B2** and **B2** as well as **C1** and **C2** (Figure 2). This isostructural effect is evidently seen at ion–water configurations in recently identified membrane protein channels.¹⁷ In conclusion, a halide ion requires 2–4 water molecules to dissolve, i.e., engaging completely by hydrogen bonds, promoting long-range contacts via only selected fundamental patterns of $2(C_2)$, $2(C_{2h})$, $3(C_{3h})$ and $4(C_{4h})$ among different gas phase cluster structures.¹⁸ Furthermore, these water–halide ion chains are found to behave as host lattices for other guest molecules interacting through an array of hydrogen bonds as illustrated in **A**, **B**, and **C** (Figure 2), leading to channel hydrates of supramolecular architectures with water–ion channels.

The findings reported here provide insights into the hydrogen bond structures of water and halide ions, implicative models for ions in the hydration shells and the water–ion interactions in membrane channels, and evidences for supramolecular nature of water and halide ions. These results suggest for newer and broader perspectives on the structured water–halide ion interactions.

We thank Prof. Akinori Sarai for computational facility.

References and Notes

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