Hydrogen bonding
Part 44. 1-Methyl-1,3,5,7-tetra-aza-adamantan-1-ium (N-methylhexamethylenetetramine cation) halide hydrates: IR and thermodynamic study of planar $C_{2h}$ ($H_2O\cdot Br^{-})_2$ and ($H_2O\cdot Cl^{-})_2$ clusters, a possible $C_{2h}$ ($H_2O\cdot I^{-})_2$ cluster, and two higher $Cl^{-}$ hydrates*

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Abstract

The IR spectrum of the $C_{2h}$($H_2O\cdot Br^{-})_2$ cluster in the bromide monohydrate of the N-methylhexamethylenetetramine cation (MHMTA') correlates well with that of the $C_{2h}$ ($H_2O\cdot Cl^{-})_2$ cluster in tetraethylammonium chloride monohydrate. MHMTA' $Cl^{-}$ forms a monohydrate which contains a similar cluster, as well as a dihydrate and trihydrate. Equilibrium dissociation vapor pressure measurements show that the minimum value for $H-O-H\cdot\cdot\cdot X^{-}$ hydrogen bonds is about 6.5 kcal mol$^{-1}$ in the bromide monohydrate and about 7.5 kcal mol$^{-1}$ in the chloride monohydrate. MHMTA' $I^{-}$ forms an ephemeral monohydrate; dissociation measurements over a limited range suggest a minimum value of about 8 kcal mol$^{-1}$ for $H-O-H\cdot\cdot\cdot I^{-}$ hydrogen bonds. The IR spectrum of the iodide monohydrate does not distinguish clearly between a planar cyclic and an extended spiral structure for the water–iodide structure.

INTRODUCTION

There has been considerable interest in the planar ($H_2O\cdot X^{-})_2$ clusters found in a number of tetra-alkylammonium halide monohydrates [1] (and refs. cited therein). We carried out a detailed IR analysis of the known [2] $C_{2h}$ ($H_2O\cdot Cl^{-})_2$ cluster in tetraethylammonium chloride monohydrate [3], and have demonstrated through IR spectral correlations that a similar cluster exists in tetrapropylammonium chloride monohydrate [4], and that

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*Dedicated to Professor N.D. Sokolov on the occasion of his 80th birthday.

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$C_{2h}(H_2O \cdot F^-)_2$ clusters occur in tetramethylammonium, tetaethylammonium and $N,N,N$-dimethylpyrrolidinium fluoride monohydrates [5]. No IR information on an analogous bromide cluster has been determined and, to the best of our knowledge, a tetra-alkylammonium iodide monohydrate has not been prepared [1] (and refs. cited therein).

We investigated the hydration of the halides of the $N,N,N$-trimethyl-1-adamantylammonium ion with the idea that a large cation might stabilize bromide and/or iodide monohydrate clusters. However, while the halides of this cation form an interesting variety of hydrates, none of them forms a $C_{2h}$ monohydrate cluster or, for that matter, any sort of monohydrate at all [6,7]. In all compounds containing planar $C_{2h}(H_2O \cdot X^-)_2$ clusters whose structures are known, the cluster occupies an inversion center [1 (and refs. cited therein), 2,8]. It is possible that this structural feature is required for the existence of such a cluster and cannot be achieved in the $N,N,N$-trimethyl-1-adamantylammonium halide hydrates.

Mak [8] has prepared the bromide monohydrate of the 1-methyl-1,3,5,7-tetra-aza-adaman-tan-1-ium ion ($N$-methylhexamethylenetetramine cation, hereafter called MHMTA$^+$) and shown by diffraction studies that it contains a $C_{2h}(H_2O \cdot Br^-)_2$ cluster which occupies an inversion center in the crystal. Since this cluster is isostructural with that of the $C_{2h}(H_2O \cdot Cl^-)_2$ cluster that we have already studied, we wished to compare its IR spectral properties with those of the chloride cluster. Also, if an iodide monohydrate of MHMTA$^+$ should prove to be isomorphous with the bromide monohydrate, there would be the possibility of creating a $C_{2h}(H_2O \cdot I^-)_2$ cluster at an inversion center. Since simple tetra-alkylammonium iodides are too insoluble to form hydrates [9] and $N,N,N$-trimethyl-1-adamantylammonium iodide failed to form a monohydrate, MHMTA$^+ I^-$ might offer the best possibility available to prepare a planar iodide monohydrate cluster.

We have carried out equilibrium vapor pressure studies on tetaethylammonium and tetrapropylammonium chloride monohydrates [4], and wished to extend these studies to MHMTA$^+ Br^- \cdot H_2O$ and, if it could be prepared, MHMTA$^+ I^- \cdot H_2O$ to determine thermodynamic parameters for the dissociations of these hydrates.

EXPERIMENTAL

The vapor pressure apparatus has been described elsewhere [10]. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as Nujol mulls on CsI plates. The $H_2O$ content of samples was determined by NMR [11]; values obtained by this method are given in parentheses below. The MHMTA$^+$ cation in the three halides was identified by $^1H$ NMR:
5.00 ppm (singlet, 6H, \( \gamma \text{CH}_3 \)), 4.60 ppm (singlet, 6H, \( \alpha \text{CH}_2 \)), and 2.60 ppm (singlet, 3H–\( \text{CH}_3 \)); no other absorptions were observed.

Hexamethylenetetramine (HMTA, Aldrich (Milwaukee, WI)) and methyl chloride, bromide and iodide were used as supplied. MHMTA+ Br− was prepared using the method of Mak [8] by addition of one mole equivalent of liquid methyl bromide to a chilled solution of HMTA in 95% ethanol, followed by slow evaporation. MHMTA+Br− · \( \text{H}_2\text{O} \) was obtained as clear plates (1.05 \( \text{H}_2\text{O} \)). MHMTA+I− was prepared in a similar manner by addition of one mole equivalent of methyl iodide to HMTA in 95% ethanol (protected from light); the iodide precipitated from this solution and was removed by filtration. A portion of the iodide was dissolved in the minimum amount of \( \text{H}_2\text{O} \) and the mixture ground in a mortar until just dry, to yield MHMTA+I− · \( \text{H}_2\text{O} \) as a white microcrystalline powder (1.04 \( \text{H}_2\text{O} \)). MHMTA+Cl− was prepared by dissolution of methyl chloride vapor in a saturated solution of HMTA in ether. The reaction is quite slow; the solution was treated with a number of portions of methyl chloride over a period of two days and allowed to stand for several hours between additions, but even then reaction was not complete. The ether solution was finally decanted and the chloride dried in vacuo. MHMTA+Cl− was dissolved in the minimum amount of \( \text{H}_2\text{O} \) and ground in a mortar until just dry, to yield MHMTA+Cl− · 3\( \text{H}_2\text{O} \) as a white powder (3.05\( \text{H}_2\text{O} \)); further grinding for a few minutes gave a new hydrate (identified by IR) believed to be MHMTA+Cl− · 2\( \text{H}_2\text{O} \) (see Discussion). A similar solution of MHMTA+Cl− in \( \text{H}_2\text{O} \) was ground in the drybox for about 10 min to yield MHMTA+Cl− · \( \text{H}_2\text{O} \) (1.05\( \text{H}_2\text{O} \)).

The above directions are simpler in description than in practice. The respective equilibrium vapor pressures of \( \text{H}_2\text{O} \) over the chloride, bromide and iodide monohydrates are 2.9, 6.7 and 15 Torr at 20°C, and 4.5, 9.8 and 24 Torr at 25°C. Thus, depending on ambient temperature and humidity, the chloride and bromide monohydrates may either deliquesce or effloresce on exposure to room atmosphere, and the iodide monohydrate can only be handled when the atmosphere is very moist. Satisfactory samples for our purposes were prepared by judicious choice of time and weather conditions. However, anyone planning on extended handling of these hydrates would be advised to work in a humidistat [12], with \( \text{H}_2\text{O} \) pressure slightly above the dissociation pressure of the hydrate at ambient temperature.

RESULTS AND DISCUSSION

*Thermodynamic measurements*

Equilibrium vapor pressure measurements for MHMTA+Cl− · \( \text{H}_2\text{O} \) and MHMTA+Br− · \( \text{H}_2\text{O} \) gave excellent straight line plots of \( \ln P = -(a/T) + b \)
Fig. 1. Plot of lnP vs. 1/T for: A, MHMTA' Br · H₂O; B, MHMTA' Cl · H₂O.

(Fig. 1); thermodynamic parameters derived from this data are listed in Table 1. Similar measurements for MHMTA' I' · H₂O were taken over a very narrow range, which was limited by the high $P_{H₂O}$ values of this hydrate. This data is plotted in Fig. 2. Since $P_{H₂O}$ values for the iodide monohydrate appeared to be close to that of H₂O itself, values for pure H₂O were also plotted in Fig. 2. The two lines have a crossover point at 24.45°C, but the lines diverge below this point which shows that H₂O is bound to the iodide at lower temperatures. Thermodynamic parameters for MHMTA' I' · H₂O are also listed in Table 1; due to the narrow range of the data they should be taken as less definitive than the values for the other halide monohydrates.

A plot of vapor pressure of H₂O vs. H₂O content for MHMTA' I' (Fig. 3) shows a normal pressure plateau in the region between 1 and 0 H₂O; coupled with the equilibrium vapor pressure data (above) this demonstrates

<table>
<thead>
<tr>
<th>Hydrate</th>
<th>a</th>
<th>b</th>
<th>$R^2$</th>
<th>Std. error</th>
<th>$\Delta G^0$ (kcal mol⁻¹)</th>
<th>$\Delta H^0$ (kcal mol⁻¹)</th>
<th>$\Delta S^0$ (eu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻ · H₂O</td>
<td>-7549</td>
<td>20.20</td>
<td>0.997</td>
<td>0.021</td>
<td>3.03</td>
<td>15.00</td>
<td>40.14</td>
</tr>
<tr>
<td>Br⁻ · H₂O</td>
<td>-6604</td>
<td>17.80</td>
<td>0.998</td>
<td>0.016</td>
<td>2.57</td>
<td>13.12</td>
<td>35.37</td>
</tr>
<tr>
<td>I⁻ · H₂O</td>
<td>-8187</td>
<td>24.01</td>
<td>0.963</td>
<td>0.026</td>
<td>2.04</td>
<td>16.27</td>
<td>47.71</td>
</tr>
</tbody>
</table>
that MHMTA$^+$I$^-$ does form a discrete monohydrate, albeit a relatively unstable one. A similar plot for MHMTA$^+$Cl$^-$ suggests the formation of a dihydrate (Fig. 4), which is supported by IR spectra (see below). Vapor pressures of the chloride trihydrate are not included in Fig. 4, as evacuation of the cell removed H$_2$O from this hydrate.

Since two H–O-H × X hydrogen bonds are broken in the dissociation of a halide monohydrate, the minimum value [4,10] for each hydrogen bond is
half of $\Delta H_{\text{diss}}^0$ for that hydrate. The minimum value for each H–O–H ⋅⋅⋅Cl– hydrogen bond in MHMTA$^+$Cl$^–$ $\cdot$ H$_2$O is 7.50 kcal mol$^{-1}$, which is intermediate between the values found for the $C_{2h}$ clusters in tetrapropylammonium chloride monohydrate (6.48 kcal mol$^{-1}$) and tetraethylammonium chloride monohydrate (8.03 kcal mol$^{-1}$) [4]. The corresponding value for MHMTA$^+$Br$^–$ $\cdot$ H$_2$O is 6.56 kcal mol$^{-1}$, which is surprisingly close to the value for the chloride monohydrate, when the lower acceptor strength of the bromide ion is considered. For MHMTA$^+$I$^–$ $\cdot$ H$_2$O, the limited data suggests a minimum value of about 8.1 kcal mol$^{-1}$ for each H–O–H ⋅⋅⋅I– hydrogen bond broken. Enthalpic binding of H$_2$O is apparently greater in the iodide monohydrate than in the chloride or bromide monohydrates. The marked instability of the iodide monohydrate is due to the larger positive value of $\Delta S_{\text{diss}}^0$.

For a discussion of possible relationships between thermodynamic values and monohydrate structures, see below.

**Infrared spectra**

The IR spectra of the three anhydrous MHMTA$^+$ halides (Figs. 5B, 6D and 7B) are quite similar, although that of the iodide is more sharply resolved than those of the bromide and chloride. Correspondence of all of the peaks is observed between the three spectra, and there are no major differences that would suggest that the halides are not isomorphous. The greatest difference lies in the group of absorptions between 1100 and 900 cm$^{-1}$, which we assign to $C_3\equiv N$ stretching motions.
Fig. 5. IR spectra (Nujol mulls on CsI plates) of: A, MHMTA$^+$ Br$^- \cdot$ H$_2$O; B, anhydrous MHMTA$^+$ Br$^-$. Units are: cm$^{-1}$ (wavenumbers); % T. Peaks marked N are from Nujol.

It seemed possible that the distortion of the C$_3$N stretching regions of the anhydrous chloride and bromide salts might arise from perturbations of these motions as a result of C–H⋯X$^-$ hydrogen bonding. Such hydrogen bonding would be expected to involve hydrogen atoms attached to carbon atoms which are bonded to three nitrogen atoms [13], particularly since the unusual upfield absorption of the CH$_3$N$^+$ protons in the NMR spectrum (2.6 ppm) shows that a significant portion of the charge of the quaternary nitrogen is transferred to the atoms of the cage by transannular interactions. The C–H stretching region of the anhydrous bromide shows the increase in absorption at a lower frequency than expected [13 (and refs. cited therein), 14] for C–H hydrogen bonding (Fig. 8). However, this effect is minimal in the iodide and absent in the chloride (Fig. 8). Similar results were observed in the high temperature forms of the choline halides, which have similar cubic crystal structures. Only β-choline bromide showed evidence of C–H hydrogen bonding [15] and this was ascribed to a balance between ion acceptor strength and ion size. In the case of the MHMTA$^+$ halides, a definitive answer to the question of the existence or extent of C–H⋯X$^-$ hydrogen bonding must await diffraction studies.
Fig. 6. IR spectra (Nujol mulls on CsI plates) of: A, MHMTA\(^+\)Cl\(^-\)·3H\(_2\)O; B, MHMTA\(^+\)Cl\(^-\)·2H\(_2\)O; C, MHMTA\(^+\)Cl\(^-\)·H\(_2\)O; D, anhydrous MHMTA\(^+\)Cl\(^-\). Units are: cm\(^{-1}\) (wavenumbers); %T. Peaks marked N are from Nujol.
Fig. 7. IR spectra (Nujol mulls on CsI plates) of: A, MHMTA⁻⁻ I⁻ · H₂O; B, anhydrous MHMTA⁻⁻ I⁻. Units are: cm⁻¹ (wavenumbers); %T. Peaks marked N are from Nujol.

Fig. 8. IR spectra (Fluorolube mulls on CsI plates) of the C–H stretching region of anhydrous MHMTA⁺ halides. Units are: cm⁻¹ (wavenumbers); %T. Peaks marked N are from Nujol.
TABLE 2

IR absorptions associated with bound H₂O in tetraethylammonium and tetrapropylammonium chloride monohydrates and in hydrates of halides of the N-methylhexamethylenetetramine cation\textsuperscript{a,b,c}

<table>
<thead>
<tr>
<th>Hydrate</th>
<th>(v_\nu) (H₂O stretch)</th>
<th>(2v_\nu) (overtone)</th>
<th>(v_\delta) (H₂O bend)</th>
<th>(v_\gamma) (H₂O rock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA(^+) Cl(^-) \cdot H₂O(^d)</td>
<td>3430 sh, 3373 s</td>
<td>3256 m</td>
<td>1637 m</td>
<td>615 vs, 536 vs</td>
</tr>
<tr>
<td>TPA(^+) Cl(^-) \cdot H₂O(^d)</td>
<td>3480 sh, 3400 s</td>
<td>3258 m</td>
<td>1625 m</td>
<td>590 s, 530 bs</td>
</tr>
<tr>
<td>MHMTA \cdot Br(^-) \cdot H₂O</td>
<td>3450 s, 3390 s</td>
<td>3256 m</td>
<td>1630 m</td>
<td>560 bm, 510 m</td>
</tr>
<tr>
<td>MHMTA \cdot I(^-) \cdot H₂O</td>
<td>3450 bs</td>
<td></td>
<td>1640 bm</td>
<td>580 bm, 450 bm(^g)</td>
</tr>
<tr>
<td>MHMTA \cdot Cl(^+) \cdot H₂O</td>
<td>3330 bs</td>
<td></td>
<td>1620 m</td>
<td>630 bs(^f), 570 s</td>
</tr>
<tr>
<td>MHMTA \cdot Cl(^-) \cdot 2H₂O</td>
<td>3350 bs, 3000 sh</td>
<td></td>
<td>1635 bm</td>
<td>580 vbs(^h)</td>
</tr>
<tr>
<td>MHMTA \cdot Cl(^-) \cdot 3H₂O</td>
<td>3420 bvs</td>
<td></td>
<td>1640 bs</td>
<td>600 vbs(^i)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Units are cm\(^{-1}\) (wavenumbers). \textsuperscript{b}Nujol mulls on CsI plates. \textsuperscript{c}Symbols used: strong, s; medium, m; weak, w; broad, b; very, v; shoulder, sh. \textsuperscript{d}From ref. 3. \textsuperscript{e}From ref. 4. \textsuperscript{f}Not observed. \textsuperscript{g}Partially masked by cation peak. \textsuperscript{h}Center of broad absorption between 800 and 250 cm\(^{-1}\). \textsuperscript{i}Center of broad absorption between 1000 and 250 cm\(^{-1}\).

The first material to crystallize when an aqueous solution of MHMTA\(^+\) Cl\(^-\) is concentrated is a trihydrate. The IR spectrum of bound H₂O in this hydrate is the typical ice-like spectrum of a framework clathrate hydrate (Fig. 6A, Table 2). When the trihydrate is further dehydrated, crystals of a new spectral type are formed (Fig. 6B, Table 2); this substance is neither the trihydrate nor the monohydrate. Since the new substance contains less H₂O than the trihydrate and more H₂O than the monohydrate it is assumed to be a dihydrate; however, further characterization was not attempted. The existence of a dihydrate is further supported by vapor pressure studies (Fig. 4).

IR spectral characteristics of the monohydrates are discussed in the section below.

The monohydrates: cluster spectra, structures and stabilities

The IR spectra of the absorptions of the MHMTA\(^+\) cation in the three monohydrates, like those of the three anhydrous halides, are similar in all general characteristics. In this case, however, it is the bromide, rather than the iodide, that has the most clearly resolved spectrum (Figs. 5A, 6C and 7A). Either the three monohydrates are isomorphous or differences in crystal structure between them are not reflected in gross spectral changes.

Our initial object in this work was to obtain the IR spectrum of the \(C_{2h}(\text{H}_2\text{O} \cdot \text{Br}^-)_2\) cluster in the bromide monohydrate. The spectrum of bound H₂O in this cluster (Fig. 5B, Table 2) is remarkably similar in appearance to that of bound H₂O in the \(C_{2h}(\text{H}_2\text{O} \cdot \text{Cl}^-)_2\) cluster in tetraethylammonium chloride monohydrate (compare Fig. 5B with Fig. 1C of ref. 4).
Spectral values for the chloride cluster are listed in Table 2 for comparison. Each cluster shows two H$_2$O stretching bands, a characteristically sharp and narrow H$_2$O bending band, two H$_2$O rocking bands and a bending overtone band. Detailed analysis of the spectrum of the chloride monohydrate cluster at 300 and 12K with specific band assignments has been previously reported [3,5]. The only significant difference between the spectra of the two C$_{2h}$ clusters is that rocking bands are more intense in the chloride case. The frequency values for absorptions of bound H$_2$O in MHMTA$^+$Br$^-$·H$_2$O are very similar to those of tetraethylammonium chloride monohydrate and even closer to those of tetrapropylammonium chloride monohydrate (Table 2), where the minimum value of the strength of each H-O-H⋯Cl hydrogen bond (6.48 kcal mol$^{-1}$ [5]) is essentially the same as for each H-O-H⋯Br$-$ hydrogen bond in MHMTA$^+$Br$^-$·H$_2$O (6.56 kcal mol$^{-1}$).

It is surprising that hydrogen bonds in the C$_{2h}$ bromide and chloride monohydrate clusters are so similar in strength. This is not an effect of the MHMTA$^+$ cation, as the hydrogen bonds in MHMTA$^+$Cl$^-$·H$_2$O do not differ appreciably from those in the tetra alkylammonium chloride monohydrates. It should be noted that the O⋯Cl$^-$ distances in tetraethylammonium chloride monohydrate are not significantly different from the sum of the van der Waals radii of oxygen and the chloride ion [2], while the O⋯Br$^-$ distances in MHMTA$^+$Br$^-$·H$_2$O are about 6.0 Å shorter than the sum of the van der Waals radii [8]. The O⋯X⋯O angles in the two clusters (Cl, 76.2° and Br, 74.3°) are not optimal for interaction with the sp$^3$ lone pair orbitals of the halide ion. It is possible that the involvement of d orbitals in the bromide ion allows partial rehybridization, and leads to a stronger interaction than would be expected from the normal hydrogen-bond acceptor strength of the bromide ion.

The IR spectrum of bound H$_2$O in MHMTA$^+$Cl$^-$·H$_2$O is quite similar to that in the spectra of the known C$_{2h}$ clusters (Fig. 6C, Table 2). In particular, it shows the characteristic sharp and narrow H$_2$O bending absorption and two H$_2$O rocking bands. The H$_2$O stretching region, however, does not show two distinct H$_2$O stretching absorptions, and the $2v_2$ band, if present, cannot be distinguished in the broad and undifferentiated H$_2$O stretching absorption. From the overall similarity of the IR spectra, the apparent isomorphous nature of the crystals, and the similarity of the strength of hydrogen bonds to those in the tetra alkylammonium chloride monohydrates, we assume that MHMTA$^+$Cl$^-$·H$_2$O contains a planar C$_{2h}$ cluster.

MHMTA$^+$I$^-$·H$_2$O is the most intriguing of the compounds prepared in this work, as it represents the first quaternary ammonium iodide monohydrate to be studied. The IR spectrum of bound H$_2$O in MHMTA$^+$I$^-$·H$_2$O (Fig. 7A) is extremely close to that expected for a planar C$_{2h}$ cluster, but
there are sufficient differences to prevent a definite conclusion from being reached. The H$_2$O stretching region is broad and undifferentiated as in the chloride monohydrate, and again the bending overtone cannot be distinguished. The H$_2$O bending absorption is broad and relatively weak and does not resemble the characteristic sharp absorption shown by the C$_{2h}$ clusters. There are two bending bands present. As expected from the apparently greater strength of hydrogen bonds in the iodide monohydrate, these are at higher frequency than in any of the other halide monohydrates discussed here (Table 2).

If it is surprising that hydrogen bonds in the bromide monohydrate are as strong as those in the chloride monohydrates, it is even more surprising that hydrogen bonds in the iodide monohydrate are stronger than in the bromide case. Since some effect increases the acceptor ability of the bromide ion relative to the chloride ion, it is possible that the same effect operates to an even greater extent with the larger and more polarizable iodide ion. However, the possibility that this effect occurs because of a fundamental difference in the water–halide structure cannot be ruled out.

In addition to the planar C$_{2h}$ clusters, a common structural feature for halide monohydrates consists of extended spiral chains of H$_2$O and halide ion [16]. Due to the differences in the IR spectrum of bound H$_2$O in MHMTA$^+$I$^-$·H$_2$O and the abnormal order of hydrogen-bond strength relative to expected acceptor ability of the iodide ion, we feel that it is not possible to determine at this stage whether MHMTA$^+$I$^-$·H$_2$O contains a planar, a spiral, or some other water–iodide structure.

Diffraction information on MHMTA$^+$I$^-$·H$_2$O would be of significant interest. Since equilibrium dissociation vapor pressures can be estimated from the data in Table 1, it should be possible to grow crystals in a cooled, carefully controlled humidistat. Alternatively, a crystal might be prepared in a capillary in contact with the mother liquor. We have no facilities for diffraction studies, but would be very interested in learning of any such results.

CONCLUSIONS

The N-methylhexamethylenetetramine cation forms a chloride trihydrate, dihydrate and monohydrate, a bromide monohydrate known to contain a planar C$_{2h}$(H$_2$O·Br$^-$)$_2$ cluster, and an iodide monohydrate. The chloride trihydrate and dihydrate are framework clathrate hydrates. On the basis of IR comparison with compounds of known structure, the chloride monohydrate is assumed to contain a planar C$_{2h}$(H$_2$O·Cl$^-$)$_2$ cluster. The IR spectrum of bound H$_2$O in the bromide monohydrate correlates well with that of the known isostructural cluster in tetraalkylammonium chloride monohydrates. The strengths of H–O–H···X$^-$
hydrogen bonds in the bromide monohydrate are surprisingly close to those in the chloride monohydrate, and those in the iodide monohydrate are slightly stronger than those in either the chloride or bromide monohydrates. The iodide monohydrate is the first such hydrate to be prepared and studied. It is not possible to determine from our IR and thermodynamic information whether the iodide monohydrate contains a planar $C_{2v}(H_2O \cdot I^-)_2$ cluster; diffraction studies on this hydrate would be of interest.

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