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### Hydrogen Bonding Part 65. IR study of hydration of trimethonium and tetramethonium halides and comparison of halide hydration for six methonium cations

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### Abstract

The infrared spectra of bound water in trimethonium bromide monohydrate, chloride dihydrate, and fluoride dihydrate support the presence of planar  $(H_2O\cdot X^-)_2$  clusters. Trimethonium fluoride also forms a hexahydrate which apparently contains several types of bound  $H_2O$ , and a trihydrate which contains both  $F^- \cdots HOH \cdots F^-$  and  $H_2O \cdots HOH \cdots OH_2$  bridging  $H_2O$ . Tetramethonium bromide dihydrate (Br<sup>-</sup> ion monohydrate) forms a known structure with Br<sup>-</sup>  $\cdots HOH \cdots OH_2$  bridging  $H_2O$  in a ladder-like arrangement; this is different from those of other quaternary ammonium bromides we have studied previously. The bromide also forms an inexplicably stable monohydrate with an  $(H_2O\cdot Br^-)_2$  cluster. The IR spectrum of tetramethonium chloride dihydrate (Cl<sup>-</sup> ion monohydrate) differs from other chloride monohydrates studied previously, and suggests the structure may be similar to that of the bromide dihydrate. Tetramethonium fluoride forms a trihydrate quite similar to trimethonium fluoride trihydrate, and also a dihydrate. This dihydrate (F<sup>-</sup> monohydrate) is the first quaternary ammonium fluoride monohydrate among the many we have studied that does not contain a  $C_{2h}$  ( $H_2O\cdot F^-$ )<sub>2</sub> cluster. The IR spectrum supports the presence of a ladder-like fluoride—water structure similar to the arrangement known for tetramethonium bromide dihydrate. FT-NMR spectra and modeling demonstrate that in aqueous solution the trimethonium ion is locked into  $C_{2v}$  symmetry, while the tetramethonium ion, which crystallizes with  $C_{2h}$  symmetry, is free to rotate about the  $C_2-C_3$  bond. Structures for the halide hydrates of six methonium ions are compared.

Keywords: Infrared spectroscopy; Metronium cations; Halide hydration; Hydrogen bonding

#### 1. Introduction

We have previously reported studies of the halide hydrates of the methonium dications,  $(CH_3)_3N^+$  $-(CH_2)_n^- N(CH_3)_3$ , where n = 2,5,6, and 10 [1-5]. The halides of the even numbered cations (n = 2, 6, 10) showed very similar hydration behavior, while that of the odd numbered species (n = 5) was quite different. We proposed that there might be two common patterns of hydration throughout the series, one for n = even and one for n = odd, which were mediated by the common symmetries assumed in crystalline salts by the even  $(C_{2h})$  and the odd  $(C_{2v})$  sets of dications. To test this hypothesis further, we have continued our studies with the hydrates of the trimethonium and tetramethonium halides (n = 3,4).

We will continue to refer in this work to the methonium ions as  $nMO^{++}$ ; i.e., tetramethonium

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ion,  $4MO^+$ <sup>+</sup>, decamethonium ion,  $10MO^+$ <sup>+</sup>, etc. [5].

### 2. Experimental

Infrared (IR) spectra were recorded on a Perkin– Elmer Model 283 spectrophotometer as Nujol mulls on CsI plates. The H<sub>2</sub>O content of samples was determined by the NMR method [6]; values so determined are given in parentheses. Pressure of the pump system used for dehydrations were not measured exactly but was less than 1 Torr; pressure at sample site is mediated by H<sub>2</sub>O vapor [6] and was not monitored. Molecular modeling and preparation (Figs 4, and 6) was done with Chem3D<sup>(3)</sup> (Cambridge Scientific Computing, Inc. Cambridge, MA) using MM2 parameters.

3MOBr<sub>2</sub> and 4MOBr<sub>2</sub> were prepared by treating portions of Aldrich (Milwaukee, WI) N,N,N',N'-tetramethylpropane-1,3-diamine and N,N,N',N'-tetramethylbutane-1,4-diamine dissolved in ethanol at 0°C with a 50% mol excess of liquid CH<sub>3</sub>Br (collected at -20°C). The two reactions were allowed to stand overnight while warming to 25°C, then solvent was removed by rotary evaporator to yield crystalline anhydrous 3MOBr<sub>2</sub> and 4MOBr<sub>2</sub>·2.2OH<sub>2</sub>O respectively. Portions of these materials were covered with an amount of  $H_2O$  insufficient to dissolve all of the sample, and the mixtures allowed to stand for several days to equilibrate. The resulting solids were ground in the glove box until free-flowing powders were just attained to give  $3MOBr_2$  monohydrate (1.00  $H_2O$ ) and  $4MOBr_2$  dihydrate (1.93  $H_2O$ ). Since  $3MOBr_2 \cdot H_2O$  was an unexpected stoichiometry (all other methonium bromides examined give dihydrates) the preparation was repeated several times with identical results.

 $3MOBr_2 \cdot H_2O$  loses  $H_2O$  readily in vacuo at 25°C to yield anhydrous salt. However,  $H_2O$  was removed from  $4MOBr_2 \cdot 2H_2O$  at a much slower rate. A sample of the dihydrate was heated for several days in vacuo at 40°C to yield  $4MOBr_2 \cdot 0.68H_2O$ . Heating in vacuo for 30 min at > 100°C failed to remove a significant amount of additional  $H_2O$ .

Aqueous solutions of  $3MOCl_2$  and  $4MOCl_2$  were prepared by the Ag<sub>2</sub>O method [7]. In each case the solutions were reduced to a damp paste on the rotary evaporator and the pastes ground in the glove box until just powdery. This gave  $3MOCl_2$  dihydrate (1.95 H<sub>2</sub>O) and  $4MOCl_2$  dihydrate (2.00 H<sub>2</sub>O).

Aqueous solutions of  $3MOF_2$  and  $4MOF_2$  were prepared by the Ag<sub>2</sub>O method [7]. Concentration of the solution of  $3MOF_2$  gave the hexahydrate (5.91 H<sub>2</sub>O) as a white solid. This was dried in vacuo at 45°C for 24 h to yield slightly dry trihydrate (2.86 H<sub>2</sub>O) which

Table 1

IR absorptions<sup>a</sup> associated with bound H<sub>2</sub>O in trimethonium and tetramethonium halide hydrates<sup>b,c</sup>

Hydrate	$\nu_{\rm s}$ H <sub>2</sub> O (H <sub>2</sub> O stretch)	$\nu_{\rm b}$ H <sub>2</sub> O (H <sub>2</sub> O bend)	$\nu_{\rm r}$ H <sub>2</sub> O (H <sub>2</sub> O libration) 550 vs, 480 vs			
3MOBr <sub>2</sub> ·H <sub>2</sub> O <sup>d</sup>	3420 bs, 3380 s	1615 m				
3MOCl <sub>2</sub> ·2H <sub>2</sub> O <sup>e</sup>	3350 vbs	1640 s, 1615 m	580 vs, 515 vs			
3MOF <sub>2</sub> ·6H <sub>2</sub> O	3400 vbs	1740 bm	850 vbm <sup>g</sup> , 650 sh			
3MOF <sub>2</sub> ·3H <sub>2</sub> O	3350 bs, 2900 bvs	1690 bw	815 s, 640 m			
3MOF <sub>2</sub> ·2H <sub>2</sub> O	3300 sh, 2900 bvs	1715 sh, 1610 bm	820 s, 760 m			
4MOBr <sub>2</sub> ·2H <sub>2</sub> O	3350 vbs	1635 bm	600 bs			
4MOBr <sub>2</sub> ·H <sub>2</sub> O <sup>f</sup>	3440 s, 3390 s	1605 m	480 s			
4MOCl <sub>2</sub> ·2H <sub>2</sub> O	3450 sh, 3200 vbs	1625 m, 1620 m	630 bs			
4MOF <sub>2</sub> ·3H <sub>2</sub> O	3470 s, 3000 bvs	1710 bm, 1580 bm	820 bs, 645 s			
4MOF <sub>2</sub> ·2H <sub>2</sub> O	3250 sh, 2900 bvs	1590 bw	775 vs			
-						

<sup>a</sup> Units are cm<sup>-1</sup> (wavenumbers).

<sup>b</sup> Nujol mulls on CsI plates

<sup>c</sup> Symbols used: strong, s; medium, m; weak, w; broad, b; very, v; shoulder, sh.

<sup>d</sup> Additonal combination band at 2080 cm<sup>-1</sup>.

<sup>e</sup> Additonal combination band at 2100 cm<sup>-1</sup>.

<sup>f</sup> Tentative stoichiometry, see text.

<sup>8</sup> Center of broad absorption from 1100 to 400 cm<sup>-1</sup>.



Fig. 1. IR spectra (Nujol mulls on CsI plates) of trimethonium halide salts: A, chloride dihydrate; B, Bromide monohydrate; C, anhydrous bromide. Units are  $cm^{-1}$  (wavenumbers); W. Peaks marked N are from Nujol.



Fig. 2. IR spectra (Nujol mulls on CsI plates) of trimethonium fluoride hydrates: A, hexahydrate; B, trihydrate; C, dihydrate. Units are  $cm^{-1}$  (wavenumbers); %T. Peaks marked N are from Nujol.

in turn was dried in vacuo at  $65^{\circ}$ C to give  $3MOF_2$ dihydrate (1.99 H<sub>2</sub>O).  $4MOF_2$  retains H<sub>2</sub>O more tenaciously than  $3MOF_2$ ; The first solid obtained by drying in vacuo at  $45^{\circ}$ C for 48 h was a trihydrate (3.03 H<sub>2</sub>O). This material was further dried in vacuo at  $70^{\circ}$ C for 48 h to yield  $4MOF_2$  dihydrate (2.08 H<sub>2</sub>O).

### 3. Results and discussion

# 3.1. IR spectra and structure: trimethonium halide hydrates

The IR spectra of bound water in 3MOCl<sub>2</sub>·2H<sub>2</sub>O and 3MOBr<sub>2</sub>·H<sub>2</sub>O (Fig. 1 (A,B), Table 1) closely resemble the characteristic spectra of planar  $(H_2O \cdot X^-)_2$  clusters [3]. One significant difference is the doublet character of the bending band for the chloride monohydrate. This, coupled with the somewhat broader than usual HOH stretching band suggests that the two water molecules in 3MOCl<sub>2</sub>·H<sub>2</sub>O may have slightly different environments in the crystal, and the that the cluster is not of pure  $C_{2h}$  symmetry. In addition, both 3MOCl<sub>2</sub>·2H<sub>2</sub>O and 3MOBr<sub>2</sub>·H<sub>2</sub>O show combination (of bending and librational modes) bands near 2100 which are more intense than is usually observed. These discrepancies are insufficient, however, to obviate an assignment of planar ( $H_2O\cdot X^ )_2$  type clusters to these hydrates.

The stoichiometry of  $3MOBr_2 H_2O$  (bromide ion hemihydrate) is unusual, as other methonium chlorides, bromides, and iodides all yield dihydrates as the highest stable crystalline hydrate. Since the IR spectrum clearly shows the presence of the dimeric planar cluster, this hydrate must also contain unhydrated bromide ions.

At hydration levels below which framework clathrate hydrates cannot form, quaternary ammonium fluorides usually show a common pattern of hydration which is mediated by fluoride ion. This involves dehydration through similarly structured  $F^- \cdot 3H_2O$ ,  $F^- \cdot 2H_2O$ , and  $F^- \cdot H_2O$  hydrates [8]. The highest hydrate of  $3MOF_2$  is a hexahydrate ( $F^- \cdot 3H_2O$ ); however, the IR spectrum (Fig. 2 (A), Table 1) is dissimilar to those of other fluoride hydrates at the  $F^- \cdot 3H_2O$ stoichiometry. Little can be concluded from the diffuse spectrum of  $3MOF_2 \cdot 6H_2O$  except that it most likely contains  $F^- \cdots HOH \cdots F^-$  (absorptions above 800 cm<sup>-1</sup>) and  $H_2O\cdots HOH\cdots OH_2$  (shoulder at 650 cm<sup>-1</sup>) bridging  $H_2O$  molecules [8].

3MOF<sub>2</sub> does not form a tetrahydrate ( $F^-$  ·2H<sub>2</sub>O) as expected (above) but rather a trihydrate ( $F^-$  ·1.5H<sub>2</sub>O). The IR spectrum of this fluoride ion sesquihydrate (Fig. 2 (B), Table 1) clearly shows absorptions assigned [8] to  $F^-$  ···HOH···F<sup>-</sup> (815 cm<sup>-1</sup>) and H<sub>2</sub>O···HOH···OH<sub>2</sub> (640 cm<sup>-1</sup>) bridging H<sub>2</sub>O. Dehydration of the trihydrate gives a dihydrate ( $F^-$  ·H<sub>2</sub>O) with the characteristic [3] spectrum (Fig. 2 (C), Table 1) of the known [9] planar (H<sub>2</sub>O·F<sup>-</sup>)<sub>2</sub> clusters.

### 3.2. IR spectra and structure: tetramethonium halide hydrates

4MOBr<sub>2</sub> forms a dihydrate with an IR spectrum (Fig. 3 (A)) that is not the same as that of any previous bromide ion monohydrate we have recorded. This is expected, as the known structure of this hydrate [10] is neither that of the planar  $(H_2O \cdot Br^-)_2$  cluster [11,12] or the linear HOH···Br<sup>-</sup> ···HOH···Br<sup>-</sup> hydrogen bond arrangement [13] which are found in other bromide ion monohydrates we have studied [3].

Barrans [10] has carried out an X-ray diffraction study of  $4MOBr_2 \cdot 2H_2O$ . Although the precise location of  $H_2O$  molecules was not possible due to disorder, examination of the structure shows that they occur in pairs staggered between rows of  $Br^-$  ions, and the author concludes that  $H_2O$  and anions form chains parallel to the z axis with  $Br^- \cdots HOH \cdots (H)OH \cdots Br^$ hydrogen bonding. The hydrogen in parentheses forms a hydrogen bond to another  $H_2O$  molecule. We conclude that a reasonable interpretation of this structure is that shown in Fig. 4. We will refer to this structure as the "ladder" type hydrate.

The IR spectrum of bound H<sub>2</sub>O in 4MOBr<sub>2</sub>·2H<sub>2</sub>O (Fig. 3 (A), Table 1) is markedly different from that shown by (H<sub>2</sub>O·Br<sup>-</sup>)<sub>2</sub> clusters. While it more similar to the spectra shown by the linear type of hydrogen bonding [1], it is clearly different to visual comparison. In particular, the HOH stretching, bending, and librational bands are broader, and significantly less symmetric. The IR spectrum of  $4MOCl_2·2H_2O$  (Fig. 5 (A), Table 1) is quite similar, and we conclude that this hydrate also has the ladder-type water-anion structure. The previously unexplained spectra of  $5MOCl_2·2H_2O$  [5] are quite



Fig. 3. IR spectra (Nujol mulls on CsI plates) of tetramethonium bromide hydrates: A, dihydrate; B, monohydrate. Units are cm<sup>-1</sup> (wavenumbers); %T. Peaks marked N are from Nujol.

similar to that of  $4MOCl_2 \cdot 2H_2O$ , and we assume that the water-anion structures of these two dihydrates are of the ladder-type.

Attempts to dry 4MOBr<sub>2</sub>·2H<sub>2</sub>O in vacuo failed, which is remarkable since most quaternary ammonium bromide hydrates lose H<sub>2</sub>O easily; indeed, vapor pressure studies often need to be carried out below room temperature to keep P H<sub>2</sub>O in a reasonable range. However, heating 4MOBr<sub>2</sub>·2H<sub>2</sub>O in vacuo at 40° for several days afforded material just below the monohydrate level, and further drying at 65°C did not remove additional H<sub>2</sub>O. The monohydrate was then essentially roasted in vacuo with a heated air gun for ca. 30 m; an IR spectrum showed insignificant further removal of H<sub>2</sub>O. The remarkable stability of 4MOBr<sub>2</sub> hydrates will be investigated in the future by equilibrium vapor pressure studies.

The IR spectrum of  $4MOBr_2 \cdot H_2O$  (Fig. 3 (B), Table 1) shows the presence of a planar  $(H_2O \cdot Br^-)_2$ cluster; thus this bromide ion hemihydrate, like  $3MOBr_2 \cdot H_2O$  (above) must contain unhydrated bromide ions.

4MOF<sub>2</sub> does not form a hexahydrate. The IR spectrum of bound H<sub>2</sub>O in 4MOF<sub>2</sub>·3H<sub>2</sub>O (Fig. 5 (B), Table 1) is very similar to that of 3MOF<sub>2</sub>·3H<sub>2</sub>O (Fig. 2 (B)) and again demonstrates the presence of  $F^-$ ···HOH···F<sup>-</sup> (820 cm<sup>-1</sup>) and H<sub>2</sub>O···HOH···OH<sub>2</sub> (645 cm<sup>-1</sup>) bridging H<sub>2</sub>O [8]. Since the trihydrate (F<sup>-</sup> sesquihydrate) is the first hydrate of 4MOF<sub>2</sub> to separate from solution, it may be possible to prepare crystals suitable for



Fig. 4. Ladder-type hydration structure for tetramethonium bromide dihydrate.

diffraction study of this apparently new and unknown hydrate structure.

 $4MOF_2 \cdot 2H_2O$  is a fluoride ion monohydrate. To date, all quaternary ammonium fluoride monohydrates we have examined have contained the known [9] planar  $C_{2h}$  (H<sub>2</sub>O·F<sup>-</sup>)<sub>2</sub> cluster, with its characteristic IR spectrum [3]. The spectrum of bound  $H_2O$  in  $4MOF_2 \cdot 2H_2O$  differs from that of the planar cluster. In particular, there is only a single strong, sharp librational band, in contrast to the two bands shown by other fluoride monohydrates. Also, this absorption is at 775  $\text{cm}^{-1}$ ; all other fluoride monohydrates have one librational band  $(v_{10}(a_u))$  above 800 cm<sup>-1</sup>. The absorption at 775 cm<sup>-1</sup> is at a value associated with  $F^-$  ... HOH... OH<sub>2</sub> bridging H<sub>2</sub>O [8]. From the narrow stretching band and the sharp librational band, we assume that all H<sub>2</sub>O in  $4MOF_2 \cdot 2H_2O$  are similar, and from the frequency of absorption deduce that they bridge between F and H<sub>2</sub>O. The most likely structure for this unique fluoride ion monohydrate is an arrangement similar to the ladder-type structure shown by  $4MOBr_2 \cdot 2H_2O$  [10].

# 3.3. Conformations of trimethonium and tetramethonium ions in solution

We have recently used FT-NMR to analyze the conformations of acetylcholine [14], and tetrapropylammonium [14], pentamethonium [5], and tri-i-propylammonium ions [15] in aqueous solution. Since the background [16,17] and our approach have been discussed in detail, they will not be repeated here. The <sup>1</sup>H NMR spectrum of trimethonium ion in aqueous solution is essentially identical to that of acetylcholine, with the expected chemical shift of the  $\beta$ -hydrogens (C2) in the absence of ester oxygen. Thus the molecule is locked in a fixed trans arrangement about both the C-C  $\sigma$ -bonds, to give the conformation of  $C_{2v}$ symmetry shown in Fig. 6 (A). This is further confirmed by molecular modeling which demonstrates that rotation about a C-C bond is impossible, as the  $-N(CH_3)_3$  groups would have to occupy much of the same space.

The tetramethonium ion crystallizes [10] in an all trans form of  $C_{2h}$  symmetry (Fig. 6 (B)). The <sup>1</sup>H NMR spectrum of the tetramethonum ion in solution demonstrates that again the  $\alpha$ - and  $\beta$ -CH<sub>2</sub> groups (C1-C2 and C3-C4) are locked in a trans conformation, but suggests that free rotation takes place about the C3-C4  $\sigma$ -bond. This observation is supported by molecular modeling, which shows that no abnormal non-bonded interactions are generated by this rotation.

## 3.4. Types of quaternary ammonium halide monohydrate structures

Quaternary ammonium halide ion monohydrates divide into four classes. Three are based on different water-anion structures, which have been identified by diffraction studies, while the fourth is marked by its unusual behavior. Each type has distinctive IR spectral features by which it can be recognized [3]. All of the forty or so quaternary ammonium halide ion monohydrates that we have studied can be assigned by IR correlations to one of these four classes. For purposes of this paper we will designate these structural types as A, B, C, and H.

Type A is the  $C_{2h}$  planar  $(H_2O \cdot X^-)_2$  cluster in which two  $H_2O$  molecules mutually bridge two halide ions. Diffraction studies of this cluster include tetramethylammonium fluoride monohydrate [9],



Fig. 5. IR spectra (Nujol mulls on CsI plates) of tetramethonium halide salts: A, chloride dihydrate; B, fluoride trihydrate; C, fluoride dihydrate. Units are cm<sup>-1</sup> (wavenumbers); %T. Peaks marked N are from Nujol.

tetraethylammonium chloride monohydrate [18], *N*methylhexamethylene tetramine cation bromide monohydrate [11], decamethonium bromide dihydrate [12], and hexamethonium chloride dihydrate [19]. In all known examples, the cluster is found on an inversion center in the crystal, and this structural feature may be required for its formation [20]. Type B has linear  $X^- \cdots HOH \cdots X^- \cdots HOH$  hydrogen bonding in



Fig. 6. Models of: trimethonium ion; B, tetramethonium ion

which H<sub>2</sub>O molecules again bridge two halide ions, but in an extended chain rather than in a closed cluster. This structure can be seen clearly in the diffraction study of 6MOBr<sub>2</sub>·2H<sub>2</sub>O [12]. Since we have demonstrated [1] that 6MOBr<sub>2</sub>·2H<sub>2</sub>O has Type A structure below 49°C, and Type B structure above 49°C, we assume that the sample used for X-ray diffraction was raised to this temperature during data collection. Type C is the ladder-type of structure described above for 4MOBr<sub>2</sub>·2H<sub>2</sub>O, in which each H<sub>2</sub>O hydrogen bonds to one halide ion and one other H<sub>2</sub>O. The hydrates of the fourth type, Type H, are the hypobarogenic monohydrates [3,22] which are crystalline in vacuo, but which disproportionate to anhydrous material and higher liquid hydrate at 760 Torr. The IR spectra of these hypobarogenic hydrates show that the low pressure crystalline forms are of the Type B linear structure [3].

3.5. Comparison of hydrate structures for a variety of methonium halides

4MO<sup>++</sup>, 6MO<sup>++</sup>, and 10MO<sup>++</sup> halides showed quite

Table 2
Classification of water-halide structures for methonium dihalides based on infrared spectral similarities <sup>a,b,c</sup>

Dication	21-	2Br <sup>-</sup>	2Cl <sup>-</sup>	2 <b>F</b> <sup>-</sup>	
Decamethonium	2.00 (A)	2.00 (A)	2.00 (A)	4.50 (X)	
				2.00 (A)	
Hexamethonium	2.00 (B)	$2.00 (A)^{e}$	2.00 (A) <sup>e</sup>	6.00 (D)	
	. ,	2.00 (B) <sup>f</sup>	$2.00 (B)^{f}$	4.00 (E)	
		1.00 (A)	1.50 (A)	2.00 (A)	
			1.00 (A)		
Pentamethonium	g	2.00 (C)	2.00 (C)	3.00 (X)	
Tetramethonium	g	2.00 (C)	2.00 (C)	3.00 (F)	
		1.00 (A)		2.00 (C)	
Trimethonium	g	1.00 (A)	2.00 (A)	6.00 (X)	
				3.00 (F)	
				2.00 (A)	
Dimethonium	g	2.00 (A)	2.00 (H)	6.00 (D)	
				4.00 (E)	
				2.00 (A)	

<sup>a</sup> Numbers represent mol H<sub>2</sub>O per mole methonium dihalide salt.

<sup>b</sup> Anion hydration stoichiometry is 1/2 that of salt: hexahydrate =  $X^{-3}H_2O$  etc.

<sup>c</sup> Symbols used:<sup>d</sup> (A), planar  $C_{2h}$  (H<sub>2</sub>O·X<sup>-</sup>)<sub>2</sub> cluster (known [9,11,12,18,19]); (B), linear X<sup>-</sup>···HOH···X<sup>-</sup> H-bonding (known [12]); (C), laddertype H-bonding, see Fig 4 (known [10]); F<sup>-</sup> 3H<sub>2</sub>O structure (known [22]); (E), F<sup>-</sup> 2H<sub>2</sub>O structure (proposed [8]); (F), unknown F<sup>-</sup> 1.5H<sub>2</sub>O structure (see text); (H); hyopbarogenic hydrate (crystalline only at low pressure) [3,21]; (X) structure unknown.

<sup>d</sup> References in c refer to known structures of hydrate types based on diffraction stuides or proposed structure based on IR and thermodynamic information.

<sup>e</sup> Low temperature form [1].

<sup>f</sup> High temperature form [1]

<sup>g</sup> Not studied.

similar hydration patterns, while the halide hydrates of 5MO<sup>+</sup> <sup>+</sup> differed significantly. We postulated that hydration type might be controlled by cation symmetry, with the even-membered ( $C_{2h}$ ) and odd-membered ( $C_{2v}$ ) series of methonium ions each showing a constant and characteristic hydration pattern. With additional information available, it is clear that this is not the case.

Table 2 sums up the information available to date on the methonium halide hydrates. Of the 22 halide ion monohydrates or halide ion hemihydrates (which appear to occur as  $X^- \cdot H_2O + X^-$ ), there are 16 Type A planar cluster monohydrates, 5 Type C ladder-type monohydrates, and one Type H hypobarogenic monohydrate. The only Type B hydrates are the high temperature forms of 6MOBr<sub>2</sub>·2H<sub>2</sub>O and 6MOCl<sub>2</sub>·2H<sub>2</sub>O. Type A monohydrate structure predominates with the smaller  $(2MO^{++} and 3MO^{++})$  and the larger  $(6MO^{++})$ and 10MO<sup>+</sup> <sup>+</sup>) cations, while Type C is limited to cations of intermediate size (4MO<sup>+</sup> <sup>+</sup> and 5MO<sup>+</sup> <sup>+</sup>). However, examples of Type A and Type C occur with both even and odd-numbered methonium cations. The only higher hydrates occur with the fluorides; with the exception of 2MOF<sub>2</sub> and 6MOF<sub>2</sub>, which show normal fluoride ion hydration, there are no established patterns of hydration among the methonium fluorides. We note, however, that 3MOF<sub>2</sub> (odd) and  $4MOF_2$  (even) appear to form the same F<sup>-</sup>·1.5H<sub>2</sub>O structure.

With data available on the hydration of the halides of six methonium ions, it is clear that the like symmetries of the even and odd series do not lead to a specific hydration pattern for each series. The closest approach to the appearance of a pattern of hydration is that small and large methonium ions tend to resemble each other, while those of intermediate size form another set. However, there are variations even within this pattern. Thus we conclude that the structures of methonium halide hydrates are controlled by a variety of factors, in which cation size and resulting charge distribution in the crystal may play a predominant role.

#### 4. Conclusion

The stoichiometry of the crystalline hydrates of trimethonium and tetramethonium bromide, chloride, and fluoride have been determined, and the wateranion structures identified, where possible, by IR spectral correlation with available crystallographic information. When this data is combined with previous data for di, penta-, hexa-, and decamethonium halide hydrates it is clear that there are not separate and unique hydration patterns for the odd and even membered sets of ions. The structures of the halide hydrates of the methonium ions appear to be mediated by a variety of factors, of which ion size and associated charge distribution appear to play an important role.

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### References

- [1] K.M. Harmon, D.M. Brooks and P.K. Keefer, J. Mol. Struct., 317 (1994) 17.
- [2] B.L. Snider and K.M. Harmon, J. Mol. Struct., 318 (1994) 79.
- [3] K.M. Harmon and D.M. Brooks, J. Mol. Struct., 323 (1994)
- 117, and references therein.[4] K.M. Harmon and J.A. Bulgarella, J. Mol. Struct., (1995) 63.
- [5] K.M. Harmon and J.A. Bulgarella, J. Mol. Struct., 354 (1995)
- 179.
  [6] K.M. Harmon, G.F. Avci, J.M. Gabriele and M.J. Jacks, J. Mol. Struct., 159 (1987) 255.
- [7] K.M. Harmon and Dawn M. Brooks, J. Mol. Struct., 299 (1993) 73.
- [8] K.M. Harmon, B.A. Southworth and J. Harmon, J. Mol. Struct., 300 (1993) 339.
- [9] D. Säben and D. Mootz, Z. Naturforsch., 48b (1993) 1057.
- [10] Y. Barrens, Acta Crystallogr., Sect. B, 28, (1972) 651.
- [11] T.C.W. Mak, Inorg. Chem., 23 (1984) 620.
- [12] K. Lonsdale, H.J. Milledge and L.M. Pant, Acta Crystallogr., 19 (1965) 827.
- [13] K.M. Harmon and B.A. Southworth, J. Mol. Struct., 298 (1993) 23.
- [14] K.M. Harmon and J.A. Bulgarella, J. Mol. Struct., 351 (1995) 181.
- [15] K.M. Harmon and J.A. Bulgarella, J. Mol. Struct., (in press, Part 64).
- [16] P. Partington, J. Feeny and A.S.V. Burgen. Mol. Pharmacol., 8 (1972) 209.

- [17] T.D. Inch, R.A. Chittenden and C. Dean, J. Pharm. Pharmacol., 22 (1970) 954.
- [18] J.H. Loehlin and A. Kvick, Acta Crystallogr., Sect. B, 34 (1978) 3488.
- [19] Y. Barrens and C. Gardia, J. R. Acad. Sc. Paris, 264 (1967) 876.
- [20] T.C.W. Mak, S.P. So, C. Chieh and K.S. Jasim, J. Mol. Struct., 127 (1985) 375.
- [21] K.M. Harmon, G.F. Avci and A.C. Thiel, J. Mol. Struct., 161 (1987) 205.
- [22] T.C.W. Mak, J. Incl. Phenom., 3 (1985) 347.