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Hydrogen bonding. Part 63. IR study of hydration of dimethonium and pentamethonium halides and NMR study of conformation of pentamethonium ion in solution

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Abstract

We have investigated hydrate formation by dimethonium and pentamethonium — $(CH_3)_3N^+ - (CH_2)_n^{-+}N(CH_3)_3$ where n = 2 and 5 — bromide, chloride, and fluoride. Dimethonium bromide forms a dihydrate which contains a $C_{2h}(H_2O\cdot Br^-)_2$ planar cluster. Dimethonium chloride forms a hypobarogenic dihydrate which is crystalline at reduced pressure but disproportionates to anhydrous material and liquid hexahydrate. Dimethonium fluoride forms three hydrates, a hexahydrate, tetrahydrate, and dihydrate. These hydrates, which represent fluoride ion trihydrate, dihydrate, and monohydrate respectively, have water-fluoride structures similar to those observed for a variety of other quaternary ammonium fluoride hydrates of corresponding stoichiometry; the dihydrate contains $C_{2h}(H_2O\cdot F^-)_2$ clusters. Pentamethonium bromide and chloride form crystalline dihydrates (halide ion monohydrates) which do not contain planar $(H_2O\cdot X^-)_2$ clusters. Pentamethonium fluoride form a fluoride ion monohydrate with $(H_2O\cdot F^-)_2$ clusters. The fact that the odd-numbered pentamethonium ion (C_{2v}) fails to form halide dihydrates with planar $(H_2O\cdot X^-)_2$ clusters while the even-numbered dimethonium, hexamethonium, and decamethonium ions (C_{2h}) all do may be a function of ion symmetry; however, further studies are required to clarify this point. FT-NMR study of the pentamethonium ion in aqueous solution and molecular modeling shows that rotation about the C1-C2 and C4-C5 σ -bonds is not possible, while rotation about the C2-C3 or C3-C4 bonds does take place.

1. Introduction

Methonium salts have a long history of use as ganglionic blocking agents [1,2], and information on their hydration and conformation is of interest in understanding interaction with receptor sites. We have recently reported studies on the stoichiometry,

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structure, and thermodynamics of the halide and hydroxide hydrates of the hexamethonium and decamethonium ions, $(CH_3)_3N^+ - (CH_2)_n ^+N(CH_3)_3$ where n = 6 and 10 [3-8]. In general the hydration behaviors of the halides of these two ions are similar, particularly in their propensity to form dihydrates which contain planar $(H_2O \cdot X^-)_2$ clusters; however, there are some differences. To investigate further the effect of ion size

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and structure on halide hydration we have undertaken a study of the remaining members of the methonium ion family. This paper reports studies on dimethonium (n = 2) and pentamethonium (n = 5).

The dimethonium ion is the smallest and most intensely charged of the methonium ions, and represents a bridge between the study of the extended methonium dications and previously studied quaternary ammonium ions such as tetramethyl- and tetraethyl-ammonium or N, N, N', N'tetramethylpiperazinium. The pentamethonium ion is the first odd-numbered methonium ion that we have studied, and presents two interesting questions. In the first place, it has been reported [9] that the odd-membered methonium halides do not form hydrates; if so, these would be the first quaternary ammonium halides we have observed to fail to form hydrates. Secondly, it is of interest to determine if the symmetry difference between the evennumbered methonium ions (C_{2h}) and the oddmembered members of the series (C_{2v}) will affect the ability to form planar $(H_2 O \cdot X^-)_2$ clusters. Formation of such clusters requires the cluster to lie at an inversion center in the crystal [10], and this structural feature may be not be favored by the symmetry of the odd-membered methonium ions.

2. Symbols

It is convenient to use shortened symbols for ions in our work, with the understanding that they have no official use outside of our manuscripts. In the past we referred to hexamethonium and decamethonium as HMO^{++} and DMO^{++} . However, if we are to study the whole series of methonium compounds from n = 2 to n = 10, this system will lead to duplicate symbols. Therefore we will adopt the shorthand symbols as nMO^{++} ; i.e., $2MO^{++}$ (dimethonium), $5MO^{++}$ (pentamethonium), $10MO^{++}$ (decamethonium) etc.

3. Experimental

IR spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as Nujol mulls on CsI plates. NMR spectra were recorded variously on a Varian T-60 single wave instrument and on a Brucker 300 MHz FT-NMR spectrometer; illustrated spectra were recorded on the Brucker instrument. Water content of samples was determined by the NMR method [11].

Aldrich (Milwaukee, WI) N, N, N', N'-tetramethylethylenediamine was dissolved in ethanol, the solution cooled to 0°C, and 2.5 mol eq of liquid CH₃Br added. The mixture was allowed to stand overnight, then solvent was removed with a rotary evaporator and the material dried for 24 h in vacuo to yield 2MOBr₂, identified by its characteristic NMR spectrum, $\delta = 3.90$ ppm, singlet (4H), 3.17 ppm, singlet (18H). A portion of the bromide was covered with a quantity of H₂O insufficient to dissolve the entire sample and allowed to equilibrate. The saturated solution contained 2.5 mol H_2O per mol salt. A portion of the equilibrated solid was ground in the glove box to yield slightly dry dihydrate $(2MOBr_2 \cdot 1.80H_2O)$. Longer grinding gave a powder with the composition $2MOBr_2 \cdot 1.00H_2O$.

Aqueous solutions of 2MOCl₂ and 2MOF₂ were prepared from the bromide by the silver oxide method [12]. Concentration of the chloride solution in vacuo gave a crystalline mass which separated immediately on return to 760 Torr (dry N_2) into a white solid and a syrupy liquid; NMR analysis of the liquid portion showed $6.02 \text{ mol } H_2O$ per mol salt. The IR spectrum of the solid showed it to be anhydrous 2MOCl₂. Evaporation of the fluoride solution in vacuo gave a damp crystalline material which was ground until just dry in the glove box to yield the hexahydrate $(2MOF_2 \cdot 6.25H_2O)$. This was dried in vacuo overnight at 45°C to give the tetrahydrate $(2MOF_2 \cdot 4.00H_2O)$, and the tetrahydrate dried overnight in vacuo at 65°C to give the dihydrate $(2MOF_2 \cdot 2.00H_2O)$.

A solution of Aldrich 1,5-dibromopentane was dissolved in ethanol and the solution saturated with trimethylamine. The mixture was allowed to stand overnight and again saturated with trimethylamine; the solution remained basic and the odor of trimethylamine persisted, which indicated that reaction was complete. The solvent was removed on the rotary evaporator and the resulting solid dried in vacuo to yield 5MOBr₂, identified by its characteristic NMR spectrum, $\delta = 3.30$ ppm,

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Absorption ^d	Assignment	$10MOBr_2 \cdot 2.00H_2O^e$	$6MOBr_2 \cdot 2.00H_2O^f$	$2MOBr_2 \cdot 2.00H_2O$
$\nu_{13}(\mathbf{B}_{n})$	Unsym HOH stretch	3490 vs	3500 s	3450 sh
$\nu_{14}(\mathbf{B}_{u})$	Sym HOH stretch	3435 vs	3460 s	3360 s
$2\nu_{15}$	HOH bend overtone	3240 w	3220 w	3230 w
$\nu_{15}(\mathbf{B}_n)$	HOH bend	1630 s	1630 s	1635 s
$\nu_{10}(\mathbf{A}_{11})$	HOH torsion (z)	555 vs	510 s	605 vs
$\nu_{11}(A_n)$	HOH wag (z)	g	g	g
$\nu_{16}(\mathbf{B}_{\mathrm{u}})$	HOH rock (x, y)	420 s	480 m	470 s

Correlation of IR absorptions^a of c_{2h} (H₂O · Br)₂ clusters in deca-, hexa-, and di-methonium bromide dihydrates^{b,c}

^a Units are cm^{-1} (wavenumbers).

^b Nujol mulls on CsI plates.

^c Symbols used: strong, s; medium, m; weak, w; broad, b; very, v; shoulder, sh.

^d Cluster absorption assignments from Ref. [14].

^e From Ref. [7].

Table 1

^f From Ref. [3].

^g Cannot resolve ν_{10} and ν_{11} at 300 K.

multiplet (4H), 3.06 ppm, singlet (18H), 1.83 ppm, multiplet (4H), 1.39 ppm, quintet (2H). Solid 5MOBr₂ was equilibrated with H₂O as above, and the solid portion ground in the glove box to powdered dihydrate (5MOBr₂ \cdot 2.01H₂O).

Aqueous solutions of $5MOCl_2$ and $5MOF_2$ were prepared by the silver oxide method [12]. Evaporation of the chloride solution gave a white crystalline material which was equilibrated with H₂O. The liquid portion contained 3.90 mol H₂O per mol salt, and the solid was ground to a powdered dihydrate ($5MOCl_2 \cdot 2.05 H_2O$). The fluoride solution was concentrated in vacuo to a pasty solid, and this was dried overnight at $45^{\circ}C$ to yield the trihydrate ($5MOF_2 \cdot 3.00H_2O$). Extended further drying in vacuo at $60^{\circ}C$ reduced the H₂O content to ($5MOF_2 \cdot 2.40 H_2O$); however, there was no change in the infrared spectrum of the water-fluoride species present.

4. Results and discussion

4.1. 2MO⁺⁺ halide hydrates: stoichiometry, structure, and IR spectra

The stoichiometry and cluster structure of the hydrate of $2MOBr_2$ is essentially the same as that of the corresponding hydrates of $6MOBr_2$ and $10MOBr_2$. Both of these latter bromides form

dihydrates at 25°C, and our analysis [3,7] of previously published X-ray diffraction data [9,13] has shown that $10MOBr_2 \cdot 2H_2O$ contains a planar $C_{2h}(H_2O \cdot Br^-)_2$ cluster. The infrared spectrum of bound H_2O in all three methonium bromide dihydrates is essentially identical (Table 1); the spectrum of $2MOBr_2 \cdot 2H_2O$ (Fig. 1(A)) is the characteristic spectrum of the planar cluster [3,7,14]. The "monohydrate" of $2MOBr_2$ has an identical IR spectrum to that of the dihydrate, with diminished intensity of cluster peaks relative to cation peaks; this material is assumed to be a mixture of dihydrate and anhydrous bromide, as is the "monohydrate" of $6MOBr_2$ [5].

2MOF₂ forms a hexahydrate, tetrahydrate, and dihydrate, which are a fluoride ion trihydrate, dihydrate, and monohydrate respectively. This behavior parallels that of other quaternary ammonium fluorides such as 6MOF₂, and tetraethylammonium and N, N, N', N'-tetramethylpiperazinium fluorides. The IR spectra of the 2MOF₂ hydrates (Fig. 2) and those of the fluoride hydrates of other cations are extremely similar at each hydration level (Table 2), which suggests that the basic fluoride ion-water structures are mediated by F⁻ and relatively independent of cation. The structures of the trihydrate species and a proposed structure for the dihydrate species have been discussed in detail elsewhere [15]. Correlation of the IR spectrum [14] with the crystal structure [16] of



Fig. 1. Infrared spectra (Nujol mulls on CsI plates) of dimethonium bromide salts: A, dihydrate; B, anhydrous. Units are cm⁻¹ (wavenumbers); %T. Peaks marked N are from Nujol.

tetramethylammonium fluoride monohydrate has defined the characteristic spectrum of the planar $C_{2h}(H_2O \cdot F^-)_2$ cluster. The spectrum of 2MOF₂ · 2H₂O (Fig. 2(C)) shows the normal spectrum of this cluster.

The compound 2MOCl₂ acts like a typical hypobarogenic clathrate [17], i.e., it forms a monohydrate which is stable in vacuo, but which disproportionates to liquid hydrate $2MOCl_2 \cdot 6H_2O$ and anhydrous $2MOCl_2$ when the pressure is raised. We have proposed [7] that formation of hypobarogenic monohydrates is favored by halides of small, densely charged cations with correspondingly high lattice energy for the anhydrous salt and, thus hypobarogenic behavior for $2MOCl_2$ is not surprising.

4.2. 5MO⁺⁺ halide hydrates: stoichiometry and IR spectra

The compounds $5MOCl_2$ and $5MOBr_2$ each form a dihydrate, and no other hydrates. $5MOF_2$ also forms only a single hydrate, $5MOF_2 \cdot 3H_2O$, which is a F⁻ ion sesquihydrate. Attempts to remove further H₂O by extended heating in vacuo resulted in a composition of $5MOF_2 \cdot 2.4H_2O$; however, the IR spectrum of the waterfluoride species was unchanged, which suggests that this latter material is a mixture of trihydrate and anhydrous material. Considerable trimethylamine was liberated during this attempted dehydration, which would be expected from Hofmann-type



Fig. 2. Infrared spectra (Nujol mulls on CsI plates) of dimethonium fluoride salt hydrates: A, hexahydrate; B, tetrahydrate; C, dihydrate. Units are cm⁻¹ (wavenumbers); %T. Peaks marked N are from Nujol.

elimination reaction of the anhydrous fluoride. The failure of $5MOF_2$ to form a fluoride ion monohydrate is unexpected; all other quaternary ammonium fluorides we have examined form monohydrates with planar $C_{2h}(H_2O \cdot F^-)_2$ clusters [7], with the exception of trimethyl-1-adamantylammonium fluoride [18], which forms a hemihydrate and no monohydrate.

The IR spectra of the three $5MO^{++}$ halide hydrates (Fig. 3, Table 3) are quite undefined,

Table 2

Correlation of IR	absorptions ^a	of dimethonium	fluoride	hydrates	with	those	of	tetraethylammonium	and	tetramethylammonium
fluoride ^{b, c}										

Absorption	Assignment	TEAF · 2.75H ₂ O ^{d, €}	2MOF ₂ • 6.00H ₂ O	TEAF · 2.00H ₂ O ^d	2MOF ₂ •4.00H ₂ O	TMAF •1.00H ₂ O ^f	2MOF ₂ • 2.00H ₂ O
2 <i>и</i> ь НОН	Bend overtone		3300 sh	3400 sh	3200 sh	3300 sh	3200 sh
ν, HOH	HOH stretch ^e	3200 bvs	3000 bs	2950 bvs	2900 bvs	2950 bvs	2900 bvs
$\nu_{\rm b}$ HOH	HOH bend	1715 bm	1660 bm	1690 bm,	1695 bm	1750 bw	1675 sh
-				1645 m	1575 bm	1560 bm	1580 m
$\nu_{\rm t}$ HOH	$F^- \cdots HOH \cdots F^-$ torsion	790 bvs	800 bs	850 vs	840 s	895 vs	845 vs
$\nu_{\rm r}$ HOH	$F^- \cdots HOH \cdots F^-$ rock	g	g	710 s	760 s	830 s	770 s
и HOH	$H_2O \cdots HOH \cdots F^- lib^h$			635 vs	635 s		
ν _l HOH	$H_2O\cdots HOH\cdots OH_2 \ lib^h$	590 m	615 s				

^a Units are cm⁻¹ (wavenumbers)

^b Nujol mulls on CsI plates.

^c Symbols used: strong, s; medium, m; weak, w; broad, b; very, v; shoulder, sh.

^d From Ref. [15].

^e (TEAF)₄ (H₂O)₁₁; cation bulk prevents inclusion of one bridging H₂O in idealized trihydrate structure of (TEAF)₄ (H₂O)₁₂. ^f From Ref. [14].

^g Cannot distinguish between ν_1 and ν_r at 300 K. ^h Precise motion of these librational bands not assigned.

and do not vield useful information on the wateranion structures. It is significant, however, that dihydrates of 5MOCl₂ and 5MOBr₂ do not show the characteristic spectra of planar $(H_2 O \cdot X^-)_2$ clusters, since they lack the structure of the HOH stretching band, the extremely narrow and intense HOH bonding band, and the two strong librational bands associated with such clusters (compare Fig. 3(A), (B) with Fig. 1(A) and Fig. 1 of Ref. [7]) [3,7]. The hydration behavior of the halides of the odd-numbered C_{2v} 5MO⁺⁺ ion is not the same as the common hydration behavior of the evennumbered C_{2h} methonium ions with n = 2, 6, and 10.

4.3. FT-NMR study of the conformation of $5MO^{++}$

The ¹H NMR spectra of 1,2-disubstituted ethanes with fixed conformations, such as compounds related to acetylcholine, has been studied extensively [19]. The splitting patterns of such immobilized methylene groups are easily recognizable, and either trans or gauche conformations can be identified from the magnitude of the vicinal coupling constants. We have recently used comparison of FT-NMR spectra of acetylcholine

and tetrapropylammonium ion combined with molecular modeling to demonstrate that the α - and β -methylene groups of tetrapropylammonium ion are fixed in a semi-trans conformation [20]. Since the conformations of methonium ions in solution may well play a role in interaction with receptors, it is of interest to determine if similar conformational evidence can be obtained for these compounds.

If the $-(CH_2)_5$ -chain of the 5MO⁺⁺ ion were free to rotate about the four $CH_2-CH_2 \sigma$ -bonds, the NMR signal of the α -hydrogens (on C₁ and C₅) would be a 1:2:1 triplet. Instead, the absorption of the α -hydrogens shows a five-peak pattern (Fig. 4(A), Table 4) essentially identical to the coupling pattern found for acetylcholine, tetrapropylammonium ion, and other compounds with fixed, nonrotating methylene groups [19,20]. The vicinal coupling constants of 12.93 and 4.91 Hz derived from L and N [21] are in accord with a fixed trans arrangement of the $(CH_3)_3N^+$ groups and the γ -CH₂ (C₃) about the C₁-C₂ and C₄-C₅ bonds [19-21].

Similarly, free rotation of the chain would predict a 1:4:6:4:1 quintet for the NMR signal of the β -hydrogens (on C₂ and C₄). Instead there is a



Fig. 3. Infrared spectra (Nujol mulls on CsI plates) of pentamethonium halide salts: A, chloride dihydrate; B, bromide dihydrate; C, fluoride trihydrate. Units are cm⁻¹ (wavenumbers); %T. Peaks marked N are from Nujol.

complex pattern with seven major peaks (Fig. 4(B), Table 4); this arises from coupling with the α -hydrogens on C₁ and C₅ in a fixed arrangement, and with the γ -hydrogens on C₃. The γ -hydrogens, however, show a normal 1:4:6:4:1 quintent (Fig. 4 (C), Table 4) expected for hydrogens flanked by two freely rotating CH_2 groups. Therefore, the $5MO^{++}$ ion has two rigid $(CH_3)_3N^+-CH_2CH_2-$ units hinged through the central $-CH_2-$, and rotation about the C_2-C_3 and C_3-C_4 bonds is allowed.

Hydrate	$\nu_{\rm s}$ H ₂ O (H ₂ O stretch)	$\nu_{\rm b}$ H ₂ O (H ₂ O bend)	ν_1 H ₂ O (H ₂ O libration)	
5MOBr ₂ · 2.00H ₂ O	3300 bs	1620 bm	560 bm, 450 sh	
5MOCl ₂ · 2.00H ₂ O	3330 vbs	1665 m, 1645 m	625 bs	
5MOF ₂ • 3.00H ₂ O	3000 vbs	1700 bw	865 bm, 805 bm	

Table 3 IR absorptions^a associated with bound H_2O in various pentamethonium halide hydrates^{b, c}

^a Units are cm⁻¹ (wavenumbers).

^b Nujol mulls on CsI plates.

^c Symbols used: strong, s; medium, m; weak, w; broad, b; very, v; shoulder, sh.

The above conclusion is supported by molecular models. The structure of $5MO^{++}$ in the iodide salt has been determined by a diffraction study [22]. The ion assumes the fully staggered conformation of C_{2v} symmetry shown in Fig. 5(B). The ion can rotate freely about the C_2-C_3 or C_3-C_4 bonds, with no steric inhibition other than eclipsed hydrogens. However, rotation about the C_1-C_2 or C_4-C_5 bonds leads to prohibitive steric interference between methyl groups on nitrogen and the hydrogens on C_3 (Fig. 6).

4.4. Conformation of $2MO^{++}$

The most stable conformation of th $2MO^{++}$ ion is shown in Fig. 5(A); like the conformations of $6MO^{++}$ and $10MO^{++}$ in their halide salts [9,13] this structure is of C_{2h} symmetry. Modeling demonstrates that rotation about the CH_2-CH_2 bond is impossible, as the methyl groups on nitrogen would be forced to occupy the same volume of space; therefore, the ion is locked into the C_{2h} conformation. Since the two methylene groups



Fig. 4. Partial ¹H NMR spectra of pentamethonium ion: A, α -CH₂ (C1, C5); B, β -CH₂ (C2,C4); C, γ -CH₂ (C3).

are chemically equivalent they have the same chemical shift, and no coupling is observed in the NMR spectrum; the methylene hydrogens show a singlet at $\delta = 3.90$ ppm.

At normal sweep width the absorption for the 18 hydrogens of the two $(CH_3)_3N^+$ groups appear as a singlet at ≈ 3.17 ppm. At high resolution this is seen to consist of two absorptions at 3.17299 ppm (6H) and 3.17077 ppm (12H). This suggests that the $(CH_3)_3N^+$ groups are not rotating about the $N-CH_2$ bonds, which leads to two chemically different types of methyl groups (Fig. 5(A)). Similar lack of rotation of $(CH_3)_3N^+$ groups has been observed in X-ray structural studies of other methonium ion salts [9,13,22].

5. Conclusion

The ions $10MO^{++}$, $6MO^{++}$, and $2MO^{++}$ all crystallize in extended, fully staggered conformations of C_{2h} symmetry. $2MO^{++}$ forms bromide, chloride, and fluoride dihydrates (halide ion monohydrates) with $C_{2h}(H_2O \cdot X^-)_2$ water-anion clusters. In addition, $2MOF_2$ forms a hexahydrate (F⁻ trihydrate) and a tetrahydrate (F⁻ dihydrate). This



Fig. 5. Models of methonium ions in most stable all-trans conformations: A, dimethonium; B, pentamethonium.

Table 4

Chemical shifts $(\delta, \text{ ppm})$ for methylene groups of pentamethonium ion and values derived therefrom^{a,b}

Quantity	α-CH ₂ (C1, C5)	β-CH ₂ (C2, C4)	γ-CH ₂ (C3)
δ (ppm)	3.32496	1.88320	1.43911
	3.30817	1.85740	1.41338
	3.29595	1.84356	1.38798
	3.28287	1.82889	1.36197
	3.26781	1.81547	1.33630
		1.80265	
		1.77477	
L, N (Hz)	17.145, 7.332		
$J (\beta CH_2 - \gamma CH_2)$,	7.74	7.71

^a In D_2O solvent.

^b Values are relative to DDS (sodium dimethyl-2-silapentane-5-sulfonate) as internal standard.

hydration behavior is identical to that of the 6MO⁺⁺ halides, and similar to that of the 10MO⁺⁺ halides; the only exception is that 10MOF₂ forms a 4.5H₂O hydrate rather than a hexa- and tetra-hydrate. 5MO⁺⁺ assumes an extended, fully staggered conformation of C_{2v} symmetry in the crystal. In sharp contrast to the evennumbered methonium ions noted above, the halides of the odd-numbered $5MO^{++}$ ion fail to form $(H_2O \cdot X^-)_2$ clusters; the chloride and bromide form dihydrates that do not contain such planar clusters, and the fluoride only forms a trihydrate. Whether the difference between the hydration behavior of $5MO^{++}$ and that of the even-membered methonium ions is a general property of the oddmembered ions is a question to be answered when we have completed our studies of the remaining methonium ions where n = 3, 4, 7, 8, and 9.



Fig. 6. Models of pentamethonium ion in (A) gauche and (B) syn conformations about the C1–C2 σ -bond.

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