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Hydrogen Bonding. V. Possible Existence of Strongly Hydrogen-Bonded Water–Fluoride and Water–Hydroxide Complex Anions, $(F^-\cdot H_2O)_2{}^{2-}$ and $(OH^-\cdot H_2O)_2{}^{2-}$, in Tetramethylammonium Ion Salt Hydrates[1,2]

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Tetramethylammonium fluoride and hydroxide form stable monohydrates from which water is removed only with difficulty at high temperatures with concurrent decomposition to trimethylamine. The infrared spectra of the monohydrates are completely different from those of the higher clathrate hydrates and show, in addition to cation bands and stretching and bending bands representative of strongly hydrogen-bonded O–H, two intense bands in the region assigned to rocking or torsional modes of tightly coordinated water (tricoordinated oxygen). Cation C–H to anion hydrogen bonding is present but is not strong enough to account for the third coordinate link to water. This fact, coupled with steric limitations on anion size and the appearance of the cation infrared spectra of the hydrates, suggests that discrete, probably dinegative, water–anion species exist in these salts. This is supported by symmetry coordinate analysis of the proposed molecular ions and by topological equivalent-orbital approach comparisons.

Introduction

Tetraalkylammonium ions have a remarkable ability to order water about themselves both in solution[4] and in a wide variety of solid clathrate hydrates.[5-13] Of these latter compound types, Jeffrey[14] has written: "We may expect to find a rational and continuous series of hydrated crystal structures ranging from the pure clathrates of the gas hydrate type through intermediate framework structures, to structures where the water molecules are arranged in hydrogen bonded sheets, ribbons, and chains, and finally structures where the water molecules are isolated from each other as in many of the simpler hydrated salts." This paper reports work on compounds at the low end of Jeffrey's hydration scale for which structures have not been determined, including tetramethylammonium hydroxide trihydrate,[15] the new compounds tetramethylammonium fluoride trihydrate and hydroxide hemihydrate, and most particularly tetramethylammonium hydroxide monohydrate[15] and fluoride monohydrate.[16] These latter two hydrates, which—although known for many years—have not previously been studied by physical–chemical methods, apparently represent the final hydration type listed by Jeffrey, in which water and anion are bound tightly together in discrete molecular ions.

Preparation and Properties of the Hydrates

The higher hydrates of tetramethylammonium fluoride lose water with relative ease to give the white, crystalline monohydrate; however, the salt clings to this last mole of water with great tenacity. We find that drying at 117° and 0.1 Torr over phosphorus pentoxide for 1 week gives no change in the O–H:N–C infrared intensity ratio. The anhydrous salt can be prepared by extended heating in vacuo at 160°,[16] but this process is accompanied by some decomposition to methyl fluoride and trimethylamine. This suggests that the water is unusually tightly bound in the crystal. By comparison, hydroxytropenylium iodide monohydrate, in which the hydrogen bond between cation hydroxyl and water is in the range of 17 kcal/mol and the water is additionally hydrogen bonded to anions,[17] readily loses its water on drying in vacuo at room temperature.

The thermal decomposition of tetramethylammonium hydroxide has been studied in some detail.[18-20] This de-

composition, which takes place to some extent even in solution,[18] renders it impossible to prepare completely pure tetramethylammonium hydroxide monohydrate. By means of short-path connection to a liquid nitrogen trap we were able to keep heating to a minimum and prepare monohydrate with satisfactory analyses; however, this material still shows infrared absorptions of trace impurities which are presumed to be polymethylene.[19] Deuterium oxide is removed from tetramethylammonium hydroxide monohydrate-d_3 more easily than water from the corresponding hydrate, and it is possible to approach the stoichiometry of the monohydrate-d_3 at room temperature without apparent decomposition.

An interesting side observation was made in early attempts to prepare the monohydrate-d_3 by treatment of tetramethylammonium chloride with silver oxide in deuterium oxide followed by concentration of the solution and warming of the crystalline mass in vacuo. Even though all reagents and the reaction system were rigorously freed of water and the initial pentahydrate obtained was shown by infrared analysis to contain only deuterium oxide, the material left after drying consisted only of the ordinary monohydrate. Since the only proton source in the system is the cation and the salt was observed to decompose significantly in the drying process, this observation offers strong support for the Musker mechanism of decomposition by ylide formation through proton abstraction.[19,21]

Tetramethylammonium fluoride trihydrate and tetrahydrate and the hydroxide trihydrate were prepared by addition of the required amount of water to the respective monohydrates; the fluoride trihydrate is apparently a new compound. Tetramethylammonium hydroxide hemihydrate was prepared by extended drying of the pentahydrate with mild warming in vacuo. Since this process was accompanied by relatively little overall loss of sample through decomposition, the formation of the ylide does not become prominent until at least this stage of drying has been reached. We are investigating the preparation of the anhydrous hydroxide but are not sanguine.

All of the hydrates are white, crystalline materials which are extremely hygroscopic; tetramethylammonium fluoride monohydrate readily deliquesces in the presence of slightly filmed phosphorus pentoxide, although it is stable in the

presence of the dry powder, and the others are of similar hygroscopicity. With the exception of the hydroxide pentahydrate they are stable enough to be stored and handled in a good drybox without significant loss of water.

Experimental Section

The samples were handled at all times in an inert-atmosphere glove box with dynamic scrubbing over a molecular sieve column. Drying operations were carried out in all-glass vacuum apparatus with liquid nitrogen trapping; a short, large-diameter connection to the trap is necessary for the hydroxide hydrates to minimize heating. Infrared spectra were determined on a Beckman IR-12 instrument using predried[17] Nujol or Fluorolube mulls on sodium chloride or potassium bromide plates. NMR spectra were recorded on a Varian T-60 instrument in 99.7% deuterium oxide solvent. Tetramethylammonium ion was estimated by precipitation of the tetraphenylborate salt and fluoride by precipitation as lead chlorofluoride.

Tetramethylammonium Hydroxide Hydrates. A. Pentahydrate. Eastman Kodak White Label tetramethylammonium hydroxide pentahydrate was used as supplied. Anal. Calcd for $(CH_3)_4NOH \cdot 5H_2O$: neut equiv, 181.23. Found: neut equiv, 179.23.

B. Trihydrate. Exactly 2 molar equiv of water was added by microsyringe to a weighed portion of tetramethylammonium hydroxide monohydrate in a flask sealed with a rubber septum. The initial clear liquid that formed crystallized to a mass of hard white prisms with no loss or gain of weight.

C. Monohydrate. A portion of Eastman Kodak White Label tetramethylammonium hydroxide solution (10% in H_2O) was evaporated in a plastic flask on the rotatory evaporator to a crystalline slush, and this was then heated in vacuo at 60° for 48 hr; the composition of the white solid present at this point was approximately that of the trihydrate. The solid was transferred to a glass vial and heated in an Abderhalden over phosphorus pentoxide at 78° for 24 hr to yield a white, microcrystalline powder. Anal. Calcd for $(CH_3)_4NOH \cdot H_2O$: $(CH_3)_4N^+$, 67.92; neut equiv, 109.17. Found: $(CH_3)_4N^+$, 67.18; neut equiv, 109.12.

D. Hemihydrate. A portion of tetramethylammonium hydroxide pentahydrate was dried in vacuo in the short-path drying apparatus at room temperature for 40 hr and then 45° for 6 hr. The white, microcrystalline powder that resulted was analyzed by NMR. Anal. Calcd for $(CH_3)_4NOH \cdot 1/2 H_2O$: C–H:O–H proton ratio, 6:1. Found: C–H:O–H proton ratio, 6:1.[22]

E. Pentahydrate-d_{11}. A portion of tetramethylammonium hydroxide pentahydrate was dissolved three times in excess deuterium oxide, and the solvent was removed in vacuo. The resulting crystalline slush was dried in the short-path apparatus for 48 hr at room temperature to give a white powder. Anal. Calcd for $(CH_3)_4NOD \cdot 5D_2O$: neut equiv, 192.23. Found: neut equiv, 191.2. The infrared spectrum showed no water proton bands.

F. Monohydrate-d_3. A portion of tetramethylammonium hydroxide pentahydrate-d_{11} prepared as above was dried further in the short-path apparatus at room temperature for 4 days. An infrared spectrum of the resulting white, microcrystalline powder did not show any bands of decomposition products, and no trimethylamine could be detected in the trap. The material contained excess deuterium oxide. Anal. Calcd for $(CH_3)_4NOD \cdot 1.57D_2O$: neut equiv, 123.58; $(CH_3)_4N^+$, 60.00. Found: neut equiv, 123.5; $(CH_3)_4N^+$, 60.0.

Further removal of water from this material always resulted in some decomposition, with the concurrent replacement of deuterium by hydrogen. Since the infrared spectrum of the compound containing 1.57 D_2O was essentially identical with that of the ordinary monohydrate with the expected isotope shifts, we believed that the strong absorptions of the monohydrate-d_3 moiety in the substance (which we presume to be a 65:35 mixture of monohydrate-d_3 and trihydrate-d_7) mask the broader, less intense bands of the trihydrate-d_7.

To test this we prepared a sample of ordinary monohydrate of similar composition. A portion of the pentahydrate was dried and the loss of water tracked by repeated weighings until a composition of $(CH_3)_4NOH \cdot 1.6H_2O$ was indicated. The composition was checked by NMR. Anal. Calcd for $(CH_3)_4NOH \cdot 1.6H_2O$: C–H:O–H proton ratio, 2.86:1. Found:[22] C–H:O–H proton ratio, 2.8:1. The infrared spectrum of the material containing 1.6 H_2O is identical with that of the monohydrate, with the exception that the ν_s band shows a greater bulge on the high-energy side and the ν_r bands are diminished in intensity relative to the N–C breathing mode; the shape and maxima of the absorptions are unchanged. Thus, we conclude that the infrared

spectrum of the material containing 1.57 D_2O can be taken to represent accurately the spectrum of tetramethylammonium hydroxide monohydrate-d_3.[23]

Tetramethylammonium Fluoride and Its Hydrates. A. Tetrahydrate. A weighed sample of tetramethylammonium fluoride monohydrate contained in a flask sealed with a rubber septum was treated with exactly 3 molar equiv of water. The resulting liquid crystallized on standing overnight to very hard white prisms with no loss or gain in weight.

B. Trihydrate. A reaction was carried out as in part A using exactly 2 molar equiv of water. The initial liquid did not crystallize on standing at room temperature; however, it crystallized to extremely hard white prisms when exposed for a few minutes to a pressure of 1 Torr. The pumping did not result in a detectable loss of weight.

C. Monohydrate. A solution of tetramethylammonium hydroxide (10% in H_2O) was neutralized with hydrofluoric acid to the inflection point of the titration curve, the solvent was removed in vacuo, and the resultant slush was dried at 70° and 0.1 Torr for several days to give a solid cake. This was powdered and dried further in an Abderhalden over phosphorus pentoxide at 56° and 0.1 Torr for 1 week to give the monohydrate as a free-flowing white powder. Anal. Calcd for $(CH_3)_4NF \cdot H_2O$: F, 17.11. Found: F, 17.34. Further drying at 117° under the above conditions for 1 week did not affect any change in this material.

D. Monohydrate-d_2. Tetramethylammonium fluoride monohydrate-d_2 was prepared by solution of the anhydrous fluoride in excess deuterium oxide (99.7% D_2O) and subsequent drying in a manner identical with that used for the monohydrate.

E. Anhydrous Fluoride. The anhydrous fluoride was prepared by the method of Tunder and Siegel.[24] Infrared analysis showed no trace of water.

Results and Discussion

Infrared Spectra and Structure of the Hydrates. In a forthcoming paper,[25] we summarize the infrared spectral characteristics of types of coordinated water. In brief, in order for the rocking and wagging modes of coordinated water to be observed the water molecule must act as a donor in two hydrogen bonds and as an acceptor in a third strong coordinate link to the water oxygen; the energy and intensity of these bands can be correlated with the strength of this coordinate linkage. The infrared spectra of the tetramethylammonium ion salt hydrates (Table I) indicate significant increases in the strength of both hydrogen-bond formation by water and hydrogen-bond coordination to water as the water content is decreased, with the effects particularly marked in the monohydrates.

The detailed crystal structures of tetramethylammonium hydroxide pentahydrate[12] and fluoride tetrahydrate[13] are known; both of these hydrates belong to the intermediate framework type in which the water and anions are hydrogen bonded into a lattice with void spaces in which cations are found. In the hydroxide pentahydrate some of the oxygens in the water–anion structure are tetracoordinate and some are tricoordinate; the oxygens of water and hydroxide cannot be differentiated. This is confirmed by the infrared spectrum (Table I); unlike the alkali metal hydroxide hydrates,[25-28] in which a sharp, intense stretching band shows the presence of the non-hydrogen-bonded hydroxyl groups, the hydroxide pentahydrate shows a single broad O–H stretching absorption. Thus, all of the hydrogens are involved in hydrogen bonding. In tetramethylammonium fluoride tetrahydrate the oxygens are all tricoordinate in the water–anion framework, and the hydrogens are not disordered.

The infrared spectrum of the water–anion moiety in tetramethylammonium hydroxide pentahydrate is essentially that of hydrogen-bonded water; there are two absorptions, the broad hydrogen-bonded O–H stretching band, ν_s, centered at 3410 cm^{-1} and the bending mode, ν_b, at 1660 cm^{-1}, that show characteristic shifts on deuterium substitution, and no bending or wagging bands are observed. Similarly, the fluoride tetrahydrate shows only ν_s and ν_b (Table I and Figure 1). Thus

Table I. Infrared Spectral Bands Associated with Water–Anion Complex Species in Tetramethylammonium Hydroxide and Fluoride Hydrates and Their Deuterated Analogs[a-c]

Hydrate	ν_s(O-H)		ν_b(O-H)		ν_r(O-H)	
OH⁻·5H₂O		3410 b, s	1660 b, m			
OD⁻·5D₂O		2570 b, s	1225 b, s			
OH⁻·3H₂O		3350 b, s	1650 b, w		780 b, s[d]	
OH⁻·H₂O		3020 b, s[e]	1570 b, w		890 s	730 s
OD⁻·D₂O		2220 b, s	1160 b, w		650 s	530 s
OH⁻·½H₂O		2900 b, s	1590 w		850 w	
F⁻·4H₂O		3410 b, s	1660 b, m			
F⁻·3H₂O	3400 b, s	3150 b, s	1700 b, m		660 b, s[d]	
F⁻·H₂O	3440 sh	2950 b, s[e,f]	1750 b, w	1560 b, m	895 s	822 s
F⁻·D₂O	2460 sh	2300 b, s[g]	1295 b, w	1170 b, m	655 s	578 s
ν_H/ν_D (OH)[h]		1.36	1.35		1.38	1.38
ν_H/ν_D (F)[i]	1.32	1.32	1.35	1.33	1.37	1.42

[a] Values in cm⁻¹. [b] Nujol mulls on NaCl or KBr unless noted. [c] Symbols used: broad strong, b, s; strong, s; broad medium, b, m; broad weak, b, w; shoulder, sh. [d] Very broad intense band, 600 cm⁻¹ (OH) or 900 cm⁻¹ (F) wide. [e] Fluorolube mull. [f] Structured peak at 3100 (sh), 3010, 2900 cm⁻¹. [g] Structured peak at 2360 (sh), 2315, 2250 cm⁻¹. [h] Ratio of ν_H to ν_D for tetramethylammonium hydroxide monohydrate and its deuterated analog. [i] Ratio of ν_H to ν_D for tetramethylammonium fluoride and its deuterated analog.
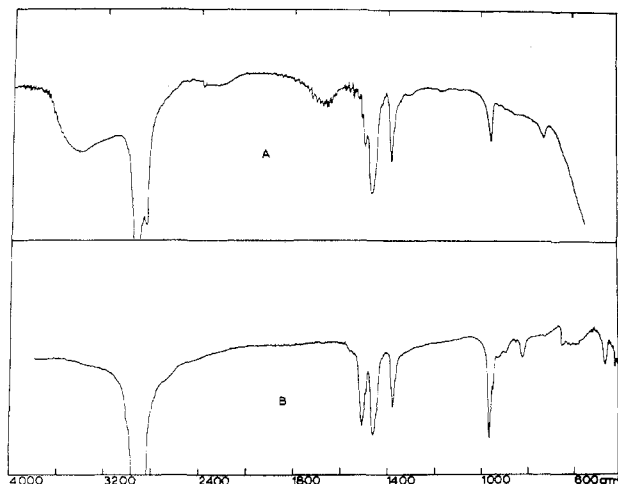

Figure 1. Infrared spectra (Nujol mulls) of (A) tetramethylammonium fluoride tetrahydrate (NaCl plate) and (B) tetramethylammonium fluoride (KBr plate).

Figure 2. Infrared spectra (Nujol mulls on KBr plates) of (top) tetramethylammonium hydroxide monohydrate and (bottom) tetramethylammonium hydroxide monohydrate-d_3.

Figure 3. Infrared spectra (Nujol mulls on KBr plates) of (A) tetramethylammonium fluoride monohydrate and (B) tetramethylammonium fluoride monohydrate-d_2.

tricoordination resulting from inclusion in the hydrogen-bonded lattices of these compounds does not provide strong enough coordination to oxygen to give rise to bands in the lower energy region of the spectrum.

In tetramethylammonium hydroxide and fluoride trihydrates the ν_s stretching band of the complexed water is moved to lower energy by about 100 cm⁻¹ relative to the higher hydrates described above; thus hydrogen bonding in these species is somewhat stronger. In addition, both trihydrates show an extremely broad low-energy absorption (Table I) arising from librational modes of the coordinated water. The width and position of these bands indicate that coordination to oxygen in these hydrates is greater than in the higher hydrates but less than in the alkali metal hydroxide monohydrates[25] where the water is presumably coordinated with metal ion. We believe that these trihydrates probably contain framework or sheet type water–anion structures in which hydrogen bonding both by and to water is stronger as a result of the increased charge density of the structural lattice.

The infrared spectra of tetramethylammonium hydroxide and fluoride monohydrates are completely different. In addition to ν_s stretching bands characteristic of very strong hydrogen bonding (Table I) these compounds both show two sharp and intense bands in the low-energy region; these bands appear at 890 and 730 cm⁻¹ for the hydroxide monohydrate and 895 and 822 cm⁻¹ for the fluoride monohydrate and show characteristic shifts on deuterium substitution (Figures 2 and 3 and Table I). This isotope shift, coupled with the observation that these bands do not appear in the spectra of the trihydrates
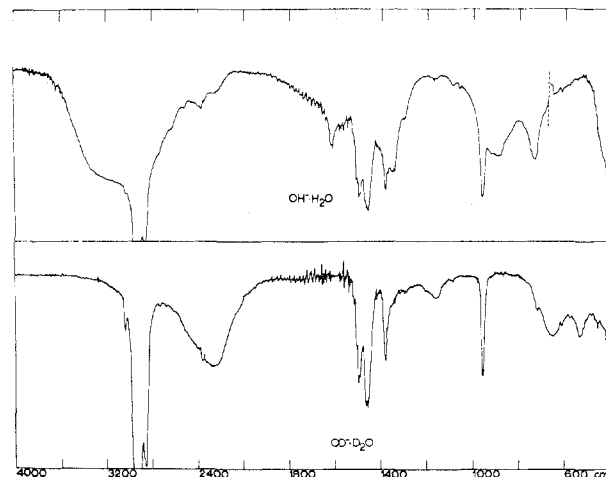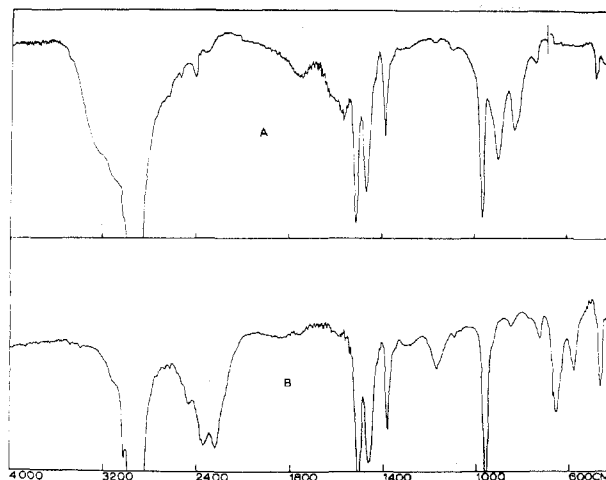
and are also lacking in the anhydrous fluoride (Figure 1), show that these absorptions are uniquely connected with the water–anion complex species in the monohydrates. In sharpness, intensity, and energy these bands do not resemble those of water bound into an extended lattice structure; rather they are extremely similar to those observed in lithium hydroxide monohydrate, where spectral and structural analysis[25] has shown the presence of a [(OH⁻)₂(H₂O)₂] subunit. It is
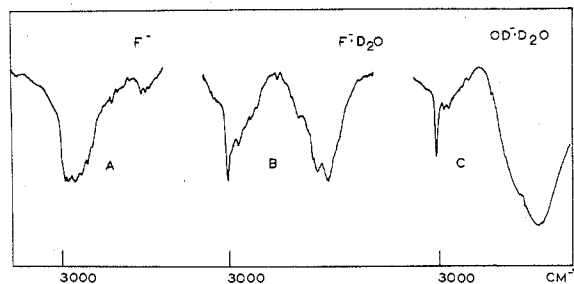
Figure 4. Infrared spectra (Fluorolube mulls) of the C–H stretching region of (A) anhydrous tetramethylammonium fluoride, (B) tetramethylammonium fluoride monohydrate-d_2, and (C) tetramethylammonium hydroxide monohydrate-d_3. The large peak to lower energy in parts B and C is the O–D stretching band.

our belief, as discussed in the sections below, that the tetramethylammonium ion salt monohydrates also contain discrete complex anions.

Hydrogen Bonding by Cation C–H. The intensities and relatively high energies of the ν_r bands in the hydroxide and fluoride monohydrates show that in addition to the two strong hydrogen bonds formed by the water hydrogens there is a third extremely strong coordinate link to water oxygen. In lithium hydroxide monohydrate the water and hydroxide oxygen atoms are strongly coordinated by lithium.[25,29] Since we have previously demonstrated that the methyl groups of the tetramethylammonium cation are capable of hydrogen bonding to a wide variety of anions,[30,31] it is reasonable to ask if C–H···O hydrogen bonding provides the additional coordination to water oxygen in the tetramethylammonium ion salt monohydrates. Figure 4 shows the C–H stretching region of tetramethylammonium hydroxide-d_3 and fluoride-d_2 monohydrates. The increased absorption to the low-energy side of the C–H antisymmetric stretching band—which appears as a sharp singlet in salts of anucleophilic anions—shows that C–H···X hydrogen bonding is present in these compounds; however, it is very much weaker than in the anhydrous fluoride (Figure 4). In the hydroxide monohydrate the degree of C–H···X hydrogen bonding is similar to that seen in salts with weak acceptor anions such as the perchlorate or chloride[30,31] and would thus be much too weak to account for the third coordinate link to oxygen. Also, the significant difference in the spectra of the hydroxide monohydrate and the fluoride monohydrate C–H stretching regions suggests that the C–H hydrogen bonding is to oxygen in the former case and to fluoride in the latter. We conclude, therefore, that the third coordinate link to oxygen in the water–anion complexes in these monohydrates is not provided by the cation and that the coordination of oxygen in the complex species must be accounted for by the elements of water and anion alone.

Steric Limitations on Anion Size. The limited amount of water present in the tetramethylammonium ion places severe restrictions on the possible size of extended water–anion structures. In the case of the hydroxide monohydrate, where stoichiometry requires that each hydroxide ion act as a donor in a single hydrogen bond to a water molecule and each water molecule act as a donor in hydrogen bonds to two different hydroxide ions, the extended structure with the greatest possible area would be a planar, hexagonal, or graphite-like array of oxygen atoms held together by hydrogen bonds. If we assume that the two species retain their identity in the lattice, a convenient unit cell of this planar lattice has an area of 35.13 Å^2 if we assume the hydrogen bond distance to be 2.6 Å. This unit contains two water and two hydroxide oxygens and has a charge of −2. Conversely, the most compact arrangement of tetramethylammonium cations that could be packed with this extended water–anion structure would be a close-packed layer. A unit cell of such a layer has an area of 78.68 Å^2 if we use 3.37 Å as the radius of the cation[31] and for convenience

choose a cell containing two cations. Thus it does not seem possible, even in the most favorable arrangement possible, that there is enough water–anion material to construct an extended water–anion network in this salt.[32] Ribbon or linear type structures are possible but would not fit with the infrared data.

In the case of tetramethylammonium fluoride monohydrate it is not possible to construct three-dimensional or sheet-like arrays of water and anion; there are not enough hydrogens present to provide the required hydrogen bonding. Linear or ladder-like arrays can be formulated, but again these would not appear to fit with the spectral data.

The above discussion again suggests that the most likely structural arrangement in the two tetramethylammonium ion monohydrates would have water and anion grouped into small, discrete units in which the strong coordination to electronegative atoms is provided by internal hydrogen bonding.

Symmetry Coordinate Analysis of Possible Water–Anion Complex Species. The crystallinity and high melting points of the tetramethylammonium ion salt monohydrates coupled with the infrared spectral characteristics of the cation in these salts (see below) suggests that they contain small anions which pack well to give strong coulombic interactions. For some time we have been intrigued[1,25,30,33,34] by scattered information in the literature and our own observations which suggest the possible existence of hydrogen-bonded cluster anions based on a tetrad of electronegative atoms. The infrared spectra of the water–anion complex species in tetramethylammonium hydroxide and fluoride monohydrates are consonant with the formulation of the anion species as $H_6O_4^{2-}$ and $H_4O_2F_2^{2-}$ ions, respectively.

The model we have chosen for the postulated $H_6O_4^{2-}$ complex ion in tetramethylammonium hydroxide monohydrate consists of a tetrahedron of oxygen atoms with O···H···O hydrogen bonds along each of its six edges.[35] This ten-atom species of T_d symmetry will have 30 degrees of motional freedom which may be described by the displayed reducible representation based on the cartesian coordinates of the individual atoms.[36,37] This representation may be reduced to

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{cart}	30	0	−2	0	4

$2 A_1 + 2 E + 3 T_1 + 5 T_2$; in T_d the translations and rotations belong to T_2 and T_1, respectively, so the vibrational modes will be given by $2 A_1 + 2 E + 2 T_1 + 4 T_2$. Of these only the T_2 vibrations will be infrared active.

If we choose as three sets of internal coordinates the twelve O–H bond lengths, the twelve H–O–H angles, and the six O···O distances, we may write three reducible representations as displayed. Γ_{O-H} and Γ_{H-O-H} each reduce to $A_1 + E +$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{O-H}	12	0	0	0	2
Γ_{H-O-H}	12	0	0	0	2
$\Gamma_{O\cdots O}$	6	0	2	0	2

$T_1 + 2 T_2$, and $\Gamma_{O\cdots O}$ reduces to $A_1 + E + T_2$; thus the combination of the three would give $3 A_1 + 3 E + 2 T_1 + 5 T_2$. Three of these bands, an A_1, an E, and a T_2, are redundant; this redundancy is expected since an excessive number of internal coordinates were chosen.

In the infrared spectrum we are concerned with the nature of the redundant T_2 mode. Examination of the possible vibrations of the proposed $H_6O_4^{2-}$ model shows that two of the vibrational modes in Γ_{O-H} are identical with two in $\Gamma_{O\cdots O}$. One of these, of type A_1, involves the simultaneous lengthening of all six O···O distances, which is equivalent to the simultaneous lengthening of all twelve O–H distances. The other, of type T_2, involves the lengthening of one O···O distance and the concurrent shortening of the distance between the other orthogonal pair of oxygen atoms. This triply degenerate infrared-active vibration of the oxygen tetrahedron is equivalent

to the single T_2 infrared-active deformation mode of P_4,[38] which in turn can be related to the ν_4 vibration of a tetrahedral MX_4 species such as methane.[38] It appears in Γ_{O-H} as a triply degenerate T_2 mode involving simultaneous shortening and lengthening of the pairs of O–H bonds in two orthogonal edges of the tetrahedron.

From the above analysis we would expect an $H_6O_4^{2-}$ anion composed of a tetrahedron of oxygen atoms hydrogen bonded along the six edges with symmetrical hydrogen bonds to show four infrared-active T_2 modes: one O–H stretching band, two H–O–H deformation bands, a bend and a rock, and one deformation band of the O_4 skeleton which is equivalent to an O–H–O symmetric stretching mode. This model agrees well with the observed spectrum of the water–anion complex species in tetramethylammonium hydroxide monohydrate (Figure 2 and Table I). The spectrum shows a strong O–H stretching absorption at 3020 cm^{-1}, an H–O–H bending absorption at 1570 cm^{-1}, and two strong absorptions at 890 and 730 cm^{-1}, which would correspond to the rocking mode of the tricoordinated water and the deformation mode of the O_4 skeleton.

As a model for the proposed $H_4O_2F_2^{2-}$ species in tetramethylammonium fluoride we have chosen a tetrahedron composed of two oxygen and two fluorine atoms, with four bifurcated[39] hydrogen bonds, one in each face of the tetrahedron. Although this species is formally of C_{2v} symmetry, we would not expect the actual ion to be greatly perturbed from T_d symmetry; thus the general features of its spectrum could be predicted by comparison to that expected for the analogous T_d ion, $H_4O_4^{4-}$, in which all four electronegative atoms are oxygens. The 24 degrees of freedom of this eight-atom species are described by the reducible representation displayed. This

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_v$
Γ_{cart}	24	0	0	0	4

representation reduces to $2\,A_1 + 2\,E + 2\,T_1 + 4\,T_2$; when the rotations and translations are removed, the vibrations of the species are given by $2\,A_1 + 2\,E + T_1 + 3\,T_2$. The tetrahedral $H_4O_4^{4-}$ ion should thus show three infrared-active T_2 bands. One of these bands will again be a deformation mode of the O_4 tetrahedron similar to that found in $\Gamma_{O\cdots O}$ for $H_6O_4^{2-}$, and it is reasonable to assume that the other two would be associated with O–H stretching and bending modes.[40]

The water–anion species in tetramethylammonium fluoride monohydrate shows absorption in these three regions of the infrared spectrum (Figure 3 and Table I). There is a structured peak in the O–H stretching region centered at 2950 cm^{-1}, two bands in the O–H bending region at 1750 and 1560 cm^{-1}, and two closely spaced peaks in the region associated with the skeletal deformation at 895 and 822 cm^{-1}. The apparent doubling of the bands might be expected in light of the fact that there would actually be two slightly different kinds of hydrogens, those in OOF faces and those in FFO faces.

Infrared Spectrum of the Cation. We have previously shown[30,31] that the infrared spectrum of the cation in tetramethylammonium ion salts can be correlated with the type of crystal environment in which it is found. The spectrum of the cation in tetramethylammonium hydroxide monohydrate (ν_sC–H, 3035(s) 2950(bm); δ_{as}C–H, 1495(vs); ν_{rot}C–H, 1457(m); δ_{sym}C–H, 1430(w); ν_BC–N, 957(vs) cm^{-1}) is essentially identical with that in the hexafluorosilicate salt.[41] Since the crystal type, and thus the infrared spectrum, is a function of both anion type and size, we would expect the hydroxide monohydrate to contain anions which are dinegative and of about the same diameter as the hexafluorosilicate anion.[42] If we assume a normal O$\cdots$H$\cdots$O hydrogen-bond distance of 2.6 Å for the bonds of the proposed tetrahedral $H_6O_4^{2-}$ ion, the calculated spherical radius of the ion would be 3.00 Å. The radius of the hexafluorosilicate ion is 3.04 Å.[31]

Molecular Orbital Model of the Proposed Ions. Our discussion of the proposed $H_6O_4^{2-}$ and $H_4F_2O_2^{2-}$ ions has been based on a pattern of conventional valence-type hydrogen bonds. An alternative picture is given by the topological equivalent-orbital approach to bonding in tetrahedral molecules developed by Kettle.[43] By this method tetrahedral molecules are pictured as having six equivalent bonding molecular orbitals along the edges (type A orbitals) which form a basis for the reducible representations A_1, E, and T_2 of the T_d group, four equivalent three-centered orbitals in the faces (type B orbitals) which form a basis for A_1 and T_2, and six antibonding orbitals corresponding to the type A orbitals (type C orbitals) which from a basis for T_1 and T_2. Thirty-two electrons are required to fill this set of orbitals completely. In many of the compounds discussed by Kettle[43] electron pairs are contributed by ligand atoms involved in three-center interactions with the edges or four-center interactions with the faces of the tetrahedral cluster.

The $H_6O_4^{2-}$ and $H_4F_2O_2^{2-}$ ions each contain 32 electrons and would thus have filled sets of molecular orbitals. The $H_6O_4^{2-}$ ion is formally analogous to P_4O_6, in which each oxygen is assumed to contribute a pair of electrons to edge bonds, and the $H_4F_2O_2^{2-}$ ion is analogous to the trialkylplatinum halides, in which each halide ligand contributes an electron pair to face bonds.[43] Of course, in the molecule ions proposed herein the 32 electrons may best be formally considered to arise from the tetrad of electronegative atoms, with protons involved in stabilizing three- and four-center interactions on the edges and faces, respectively.

Conclusions

The extreme stability and unusual infrared spectra of tetramethylammonium hydroxide and fluoride monohydrates demonstrate that unusual water–anion species are present in these salts. The infrared spectra clearly indicate that these salts do not contain an extended water–anion structure and that the oxygen atoms are tricoordinate.[25] Through consideration of steric limitations of anion size, symmetry coordinate analysis of model ions, cation infrared spectra, and molecular orbital treatment of analogous isoelectronic tetrahedral species we propose that these salts contain discrete dinegative anions based on a tetrahedron of electronegative atoms.

These studies are preliminary; extended vibrational spectra or single-crystal diffraction studies will be needed to resolve the nature of these species. No single portion of our information conclusively supports our proposed models; however, we cannot find another model that will fit with that information when taken collectively. If we take into account the restrictions on anion size and coordination requirements, we are unable to construct a model of different symmetry or bonding pattern that will account for the observed infrared spectra.[44] Further study on these interesting compounds is desirable. We invite correspondence from and cooperation with scientists interested in structural or physical chemical studies of these salts.

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Reactions of N-Trimethylborazine with Anhydrous Hydrogen Halides

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N-Trimethylborazine undergoes reversible addition reactions with hydrogen halides to form compounds of the empirical formula (CH3)3N3B3H3·3HX. At elevated temperatures, hydrogen–halogen exchange occurs to yield B-halogenated derivatives of N-trimethylborazine and hydrogen. Bromine reacts under equivalent conditions to yield the previously unreported N-trimethyl-B-dibromoborazine. Hydrogen bromide forms a 3:1 adduct with B-trichloroborazine but the analogous reaction between hydrogen chloride and B-tribromoborazine could not be effected. The infrared spectra of the hydrogen halide adducts were recorded in the 4000–650-cm⁻¹ region and partial assignments are proposed.

Introduction

The reactions of N-trimethylborazine with heavy-metal halides yield unsymmetrically B-substituted haloborazines;[1-3] secondary products arise from the liberated hydrogen halide and the starting borazine. Although the addition reactions between hydrogen halides and borazines are well-known,[4,5] the hydrogen halide adducts of N-trimethylborazine have not been characterized. Moreover the reactions between hydrogen halides and borazines under the conditions necessary to effect reaction between heavy-metal halides and N-trimethylborazine[23] have not been investigated. We report here the preparation of the hydrogen halide adducts of N-trimethylborazine, the results of pyrolyzing these adducts under varied conditions, and an investigation of the reaction between N-trimethylborazine and bromine. In addition an interpretation is given of the infrared spectra of the hydrogen halide

adducts of N-trimethylborazine and the hydrogen bromide adduct of B-trichloroborazine.

Experimental Section

Standard methods of syntheses were employed for the preparation of N-trimethylborazine,[6] B-tribromoborazine,[7] and B-trichloroborazine.[8]

Hydrogen iodide was generated by the reaction of sodium iodide with 85% phosphoric acid at 150°;[9] the resulting hydrogen iodide was swept in a stream of dry nitrogen through a trap at −23° and a phosphorus pentoxide drying tower.

Bromine (reagent grade, Mallinckrodt) was stored over pulverized potassium bromide for approximately 6 months and distilled into a trap maintained at −196° immediately prior to use.[10] Hydrogen bromide (99.8%, Matheson) and hydrogen chloride (technical grade, Matheson) were passed through phosphorus pentoxide drying towers. Benzene and hexane were distilled after refluxing for several hours over sodium.