complex fluoro anion in the form of a stable salt. Its potential as an oxidizer and an ingredient for a solid propellant NF_3–F_2 gas generator[2,29,30] for chemical HF–DF lasers becomes evident from the following comparison. On thermal decomposition, 1 cm^3 of solid $(NF_4)_2NiF_6$ is capable of producing 12% more useful fluorine values, i.e., in the form of F_2 and NF_3, than liquid F_2 at −187 °C. Furthermore, $(NF_4)_2NiF_6$ is a stable solid at ambient temperature which can be safely stored without requiring cryogenic cooling. The physical and spectroscopic properties of $(NF_4)_4NiF_6$ are in excellent agreement with those predicted for a solid containing NF_4^+ and NiF_6^{2-} ions. The only unexpected property was the observation of significant amounts of OF_2 during hydrolysis.

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Registry No. $(NF_4)_2NiF_6$, 63105-40-8; Cs_2NiF_6, 17218-49-4; NF_4SbF_6, 16871-76-4; NiF_2, 10028-18-9.

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Hydrogen Bonding. 10. Polyhedral Water–Fluoride Cluster Anions in Tetraethylammonium Fluoride Hydrates[1,2]

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We have prepared the previously unreported penta-, tri-, di-, and monohydrates of tetraethylammonium fluoride and have studied the water–anion complex species in these hydrates by deuterium labeling and infrared spectroscopy at 300 and 10 K. The pentahydrate contains normal clathrate water; however, the spectral properties of the trihydrate, dihydrate, and monohydrate suggest that they contain discrete polyhedral water–fluoride cluster anions. Deposition of well-formed needles of trihydrate from liquid pentahydrate affords the first macrocrystalline material containing such a cluster anion. Attempted preparation of the mixed hydroxide–fluoride $H_4O_3F^{3-}$ cluster fails via disproportionation to separate hydroxide and fluoride hydrates. Attendant decomposition of tetraethylammonium fluoride by Hofmann or S_N2 reactions competes with the formation of the lower hydrates.

Introduction

We have recently reported preparative and spectroscopic studies of the lower hydrates of tetrapropylammonium fluoride and tetramethylammonium fluoride and hydroxide. Tetrapropylammonium fluoride forms[4] hexa-, tri-, and dihydrates of the framework clathrate[5] type, in which there is an extended water–anion network; these materials have low crystallinity and melt in the vicinity of 30 °C. There is no monohydrate; further dehydration of the dihydrate results in rapid, exothermic Hofmann-type decomposition to tripropylamine, propene, and tetrapropylammonium hydrogen difluoride.[4] The tetrapropylammonium fluoride hydrates show an increase in energy for the broad librational band[6] of the structural water with decreasing hydration number, since increased framework charge density leads to tighter binding of water as the H_2O:F^- ratio is reduced.

Tetramethylammonium fluoride and hydroxide show quite different behavior. The fluoride forms a crystalline framework tetrahydrate[7] and the hydroxide a similar pentahydrate,[8] and we have found[9] that both salts form very stable, high-melting trihydrates containing strongly hydrogen-bonded water–anion networks. Unlike tetrapropylammonium fluoride, both tetramethylammonium fluoride and hydroxide form monohydrates. The water in these monohydrates is extraordinarily tightly bound, and the infrared spectra of the water–anion moieties, which show the characteristic sharp and intense rocking bands[6] of strongly coordinated trivalent oxygens, are completely different from those of compounds containing water bound in framework clathrate structures.

We have demonstrated that tetramethylammonium fluoride and hydroxide monohydrates contain discrete water–anion clusters rather than extended networks and have postulated on the basis of infrared spectra, deuterium labeling, steric limitations on anion size, internal coordinate analysis of predicted spectra, topological equivalent-orbital considerations, and spectral–crystal structure correlations that these clusters are dinegative anions based on a tetrahedral arrangement of electronegative atoms.[9,10] The hydroxide monohydrate would

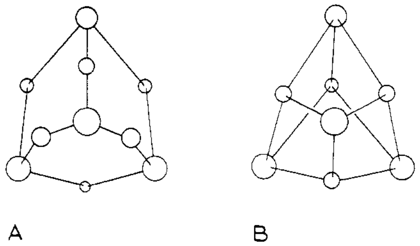

Figure 1. Idealized structures of T_d point group for (A) $H_6X_4^{n-}$ and (B) $H_4X_4^{n-}$ cluster anions. The four largest circles in each structure represent electronegative atoms and the smaller circles hydrogens.

then contain an $H_6O_4^{2-}$ ion, and the fluoride monohydrate an $H_4O_2F_2^{2-}$ species. We attribute the formation of stable cluster anions in these two salts to the fact that the symmetrical, nearly spherical, tetramethylammonium cations form cavities of convenient size and additionally stabilize the clusters by secondary hydrogen bonding from cation methyl groups to the electronegative atoms in the clusters. Such C—H···X hydrogen bonding is well established for tetramethylammonium ion salts[11] and is definitely present in these hydrates.[9]

Since there is a significant difference in the hydrate behavior of tetrapropyl- and tetramethylammonium fluorides, we were particularly interested in examining the fluoride hydrates of the intermediate tetraethylammonium cation.[12] The tetraethylammonium cation, which has been reported to have the shape of an oblate spheroid[13] in which the α hydrogens are conveniently positioned for external hydrogen bonding, more nearly resembles the tetramethylammonium ion than it does the tetrapropylammonium ion, whose preferred conformation is that of a flattened cross;[14] for this reason we believed that tetraethylammonium fluoride might also form a monohydrate containing the $H_4O_2F_2^{2-}$ cluster. Additionally, since the tetraethylammonium ion is significantly larger than the tetramethylammonium ion, we anticipated that the combined water and anion in a tetraethylammonium fluoride trihydrate, if formed, would be insufficient in extent to span the larger cations with a network structure as in the tetramethylammonium ion case, but instead might form discrete $H_6O_3F^-$ cluster anions (Figure 1) isostructural and isoelectronic with the $H_6O_4^{2-}$ cluster in tetramethylammonium hydroxide monohydrate.

Consequently, we have prepared the penta-, tri-, di-, and monohydrates of tetraethylammonium fluoride and investigated the structures of the water–fluoride species contained in these hydrates by deuterium labeling and infrared spectroscopy at 300 and 10 K. There are no previous reports on the preparation or study of tetraethylammonium fluoride hydrates in the literature. In addition, we have carried out experiments directed toward the synthesis of an $H_4O_3F^{3-}$ cluster isostructural and isoelectronic with the $H_4O_2F_2^{2-}$ ion in tetramethylammonium fluoride monohydrate.

Preparations and Properties of the Hydrates

The first crystalline phase to separate when solutions of tetraethylammonium fluoride in water are concentrated is the trihydrate; however, there is evidence for the existence of a stoichiometric pentahydrate which is a liquid at room temperature. Removal of water from such solutions is rapid until a ratio of 5 mol of water for each mole of salt is reached and then proceeds at a greatly diminished rate. Furthermore, if the water content is reduced to a value anywhere between 5 and 3 mol of water/mol of salt, the resulting syrup will always separate into pure crystalline trihydrate and pure liquid pentahydrate. There is no tetrahydrate; material containing exactly 4 mol of water undergoes this disproportionation to the higher and lower hydrates. The pentahydrate is a water-white, viscous liquid; it loses water fairly readily in vacuo or over phosphorus pentoxide to give the lower hydrates. The infrared spectrum of the pentahydrate is characteristic of a normal clathrate hydrate[6] with a broad O–H stretching band at 3400 cm^{-1}, a bending band at 1665 cm^{-1}, and a very broad, intense librational band covering the entire 1000–400-cm^{-1} region.

Dehydration of the pentahydrate in vacuo at 55 °C yields tetraethylammonium fluoride trihydrate as a solid cake which can be ground to a white, free-flowing microcrystalline powder. The formation of the trihydrate is complete when the last traces of liquid disappear, and care must be exercised to avoid the removal of too much water. When water is removed slowly from the pentahydrate by exposure to glovebox atmosphere or storage over phosphorus pentoxide, well-formed transparent needles of the trihydrate up to 0.75 in. in length are deposited. Removal of the supernatant liquid with a dropper followed by brief drying in vacuo gives highly crystalline material. Such crystals are fogged on their surface from evaporation of the final film of pentahydrate; however, we believe that crystals suitable for diffraction studies could be obtained by this method. Alternatively, it should be possible to prepare crystalline trihydrate in an x-ray capillary via slow evaporation of water from the liquid pentahydrate.

Tetraethylammonium fluoride trihydrate will keep indefinitely in a sealed vial but loses water with relative ease by either continued heating under vacuum, extended exposure to glovebox atmosphere, or storage in a vacuum desiccator to give tetraethylammonium fluoride dihydrate. Since the dihydrate is made by dehydration of the solid trihydrate, it has not been obtained in macrocrystalline form but rather as a white, microcrystalline powder. It is extremely stable and keeps indefinitely in a dry atmosphere. Since elevated temperatures lead to decomposition of the dihydrate (see below) further dehydration to the monohydrate is effected by use of apparatus with a very short, wide path leading to a liquid nitrogen trap.

Two decomposition reactions compete with further dehydration of the dihydrate. At 35 °C loss of water is very slow and is slower than the total loss of weight from the sample; triethylamine is isolated from the cold trap in the vacuum line. Formation of trialkylamine from a tetraalkylammonium fluoride by Hofmann-type abstraction of a β proton by fluoride ion gives nonvolatile tetraalkylammonium hydrogen difluoride as a coproduct.[4] Since no hydrogen difluoride salt is formed in the decomposition of tetraethylammonium fluoride dihydrate at 35 °C, we assume—but have not confirmed—that triethylamine is formed via S_N2 attack of fluoride ion on the α carbon of the cation and that this reaction, while very slow, competes favorably with dehydration at this temperature. On the other hand, the predominant reaction at 55 °C is β elimination accompanied by formation of triethylamine, tetraethylammonium hydrogen difluoride, and, by analogy,[4] ethylene. Infrared examination of samples partially decomposed at 55 °C shows a mixture of dihydrate and hydrogen difluoride, which suggests that it is the monohydrate that is unstable at this temperature. Dehydration of tetraethylammonium fluoride dihydrate at 47 °C affords the monohydrate as a white, microcrystalline powder; only traces of triethylamine and tetraethylammonium fluoride are formed at this temperature. The monohydrate is stable in a dry atmosphere.

Attempted Preparation of $H_4O_3F^{3-}$

From topological equivalent-orbital considerations[15] one can predict several other cluster species isostructural and isoelectronic with our proposed tetrahedral ions. One such species is the face-protonated $H_4O_3F^{3-}$ ion, which is formally a mixed fluoride–hydroxide hydrate containing the primary units $F^- + 2OH^- + H_2O$.

Removal of water in vacuo at 25 °C from a solution of tetramethylammonium hydroxide which has been one-third neutralized with hydrofluoric acid affords a white crystalline mass containing an amount of water which varies from 3 to 5 mol/mol of cation. Continued dehydration at 50 °C gives a stable, stoichiometric substance with 1 mol of water for each mole of cation. This material is a 2:1 mixture of tetramethylammonium hydroxide monohydrate and fluoride monohydrate; the infrared spectrum is superimposable on that of a 2:1 mixture prepared by grinding together authentic samples of the separate monohydrates. Further dehydration of the mixture at 70 °C in vacuo gives a second stoichiometric substance containing 2 mol of water for each 3 mol of cation; the infrared spectrum of this substance demonstrates that it is a mixture of tetramethylammonium hydroxide hemihydrate[9] and tetramethylammonium fluoride monohydrate.

When water was evaporated slowly from a similar one-third neutralized solution, a crystalline phase consisting of fine, long needles separated. When the amount of solid and supernatant liquid was judged to be equal, they were separated from each other and subsequently dehydrated. The solid material afforded tetramethylammonium hydroxide monohydrate, slightly contaminated with the fluoride monohydrate, and the liquid afforded tetramethylammonium fluoride monohydrate, slightly contaminated with the hydroxide monohydrate. Thus the preparation fails as a result of disproportionation of the mixture at higher hydrate levels, with a hydroxide hydrate, presumably the pentahydrate, crystallizing first from the concentrating solution. This disproportionation cannot be avoided by eliminating the early crystallization. Rapid dehydration of a one-third neutralized solution at a temperature above the melting points of the higher hydrates still afforded a 2:1 mixture of the separate monohydrates.

This study is interesting, even though it did not achieve its intended objective. The clear-cut separation into the two monohydrate species, even under extreme conditions, demonstrates the discrete ionic nature and intrinsic stability of the cluster anions, and the formation of hydroxide hemihydrate and fluoride monohydrate, rather than hydroxide monohydrate and anhydrous fluoride, when the water to cation ratio is reduced from 3:3 to 2:3 demonstrates that the $H_6O_4^{2-}$ cluster is less stable than the $H_4O_2F_2^{2-}$ species.

Experimental Section

The rate of water loss from a solid hydrate is a function of temperature, sample size, sample–glass contact area, degree of crystallinity, and cold-trap temperature. Consequently, it is difficult to duplicate specific experimental conditions, and the primary requisite of a dehydration apparatus is that the cell containing the sample be demountable from the vacuum system so that the course of the dehydration can be followed by repeated weighings. We employ three types of cells. The short-path cell is a Pyrex test tube equipped with a septum seal for solvent injection or grease-free removal of sample and a high-vacuum, large-bore stopcock side arm connected by a ball joint directly to a cold trap. The cell is heated with an external heating tape. The septum flask is a small three-necked flask fitted with a septum, a stopper, and a stopcock pumping head attached to the cold trap with a short length of vacuum hose. This flask is heated by an external bath. The normal apparatus is a modified Abderhalden chamber connected through a high-vacuum stopcock to an all-glass vacuum system; this chamber can be detached from the system and taken into the glovebox. The sample is contained in a weighed vial within the chamber and is heated by an external heating tape wound around the chamber. The traps in the vacuum line are cooled by either liquid nitrogen (N_2 trap) or a dry ice–acetone slush (CO_2 trap).

Hydrates containing normal water were analyzed by NMR; a sample of the hydrate was dissolved in D_2O and the water protons were integrated against cation methylene protons. In each analysis the background water signal of the D_2O was determined and subtracted from the total water signal. Hydrates containing heavy water were tracked to calculated sample weight. Samples containing hydroxide were also analyzed by titration with standard hydrochloric acid. Dehydration temperatures were controlled with an I^2R L6-1000 Thermowatch apparatus. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer using KBr or CsI plates; predried Nujol was used for mulls. Low-temperature infrared spectra were obtained with the use of an Air Products and Chemicals, Inc., Displex CSW-202 two-stage helium refrigerator unit equipped with KBr windows. NMR spectra were taken on a Varian T-60 instrument.

All operations, including preparation of analytical and spectral samples, were carried out in an efficient glovebox under dry nitrogen. All of the hydrates deliquese rapidly in air.

Tetraethylammonium Fluoride Hydrates. A. General Information. The starting material for these preparations was a stock solution of standardized (0.7127 N) Eastman Kodak White Label tetraethylammonium hydroxide. For each reaction aliquots of this solution were carefully neutrallized with hydrofluoric acid in a polyethylene vessel and then transferred to appropriate glass apparatus for dehydration.

B. Pentahydrate. Water was removed rapidly (~5 min) from a solution of tetraethylammonium fluoride by rotary evaporation at 25 °C (water bath) to afford a water-white syrup with a composition of $(C_2H_5)_4N^+F^-\cdot 4.95H_2O$; subsequent loss of water was extremely slow.

In a similar preparation the water to cation ratio was reduced to 4.05:1 by continued evaporation with mild heating, and the resulting syrup was allowed to stand in a sealed flask for 2 days. After this time large, transparent needles had separated from a water-white supernatant liquid. The liquid was removed by fine dropper and shown to have the composition $(C_2H_5)_4N^+F^-\cdot 5.02H_2O$; the crystals, when dried in vacuo overnight, gave an infrared spectrum identical with that of authentic trihydrate.

C. Trihydrate. A weighed portion of tetraethylammonium fluoride dihydrate (below) was placed in a septum flask and sufficient water added by syringe to effect dissolution. Water was removed in vacuo at 30 °C (24 h) to give a slush which was dried further at 55 °C (~5 h, CO_2 trap) with continuous monitoring of sample weight. The resulting solid cake was ground to a white, microcrystalline powder with a composition of $(C_2H_5)_4N^+F^-\cdot 3.05H_2O$.

D. Dihydrate. An aqueous solution of tetraethylammonium fluoride was concentrated to a slush; this was dried at 25 °C (24 h) and then at 65 °C (2 h) to give a white solid containing 2.57 mol water/mol cation. This solid was ground and transferred to the short-path cell where it was dehydrated at 45 °C (24 h, N_2 trap) to give a white, free-flowing powder with a composition of $(C_2H_5)_4N^+F^-\cdot 2.00H_2O$.

E. Monohydrate. A portion of tetraethylammonium fluoride dihydrate was placed in the short-path cell and heated at 47 °C (11 h, N_2 trap) to afford a white powder with a composition of $(C_2H_5)_4N^+F^-\cdot 0.98H_2O$. The infrared spectrum of this material showed a trace of the hydrogen difluoride.

F. Trihydrate-d_6. A portion of tetraethylammonium fluoride dihydrate was placed in a septum flask and 5 mL of 99.7% deuterium oxide injected by syringe. The material was dried in vacuo at 25 °C (24 h, CO_2 trap) to give a white solid. This succession of dissolution and evaporation was repeated twice more. The sample was then dried at 55 °C (~4 h, CO_2 trap) to a composition of $(C_2H_5)_4N^+F^-\cdot 3.09D_2O$.

G. Dihydrate-d_4. A portion of tetraethylammonium fluoride trihydrate-d_6 was placed in a vial in the normal apparatus and heated at 50 °C (12 h, N_2 trap) to give a white powder with a composition of $(C_2H_5)_4N^+F^-\cdot 2.02D_2O$.

H. Monohydrate-d_2. A portion of tetraethylammonium dihydrate-d_4 was placed in the short-path cell and heated at 48 °C (12 h, N_2 trap) until the composition reached $(C_2H_5)_4N^+F^-\cdot 1.15D_2O$.

Thermal Decomposition of Tetraethylammonium Fluoride Dihydrate. A sample of tetraethylammonium fluoride dihydrate was heated in the short-path cell at 75 °C (6.5 h, N_2 trap). The sample weight indicated a water to cation ratio of 1.39:1; however, the infrared spectrum did not show a mixture of dihydrate and monohydrate but rather a mixture of dihydrate and hydrogen difluoride (ν_3 1900 cm^{-1} (b, m); ν_2 1300 cm^{-1} (b, s)). Further heating at 90 °C (3 h, N_2 trap) gave spectroscopically pure tetraethylammonium hydrogen difluoride in 53% yield (theory 50.0%).

In an attempted preparation of the monohydrate-d_2 a sample of the dihydrate-d_4 was heated in a vial in the normal apparatus at 56 °C (48 h, N_2 trap) to give a 55% yield of a water-free mixture of tetraethylammonium hydrogen difluoride and hydrogen-d_1 difluoride.

Dehydration of a 2:1 Tetramethylammonium Hydroxide to Tetramethylammonium Fluoride Solution. A 3.00-mL portion of tetramethylammonium hydroxide solution was carefully neutralized with

Table I. Infrared Spectral Absorptions of the Water-Anion Cluster Species in Tetraethylammonium Fluoride Trihydrate and Fluoride Trihydrate-d_6[a]

Band[b]	Description[c]	3 H_2O (300 K)	3 D_2O (300 K)	3 D_2O (10 K)	ν_H/ν_D[d]
$\nu_7(t_2)$	Unsym XH str	3400 sh	2530 sh	2510 m	1.34
			2400 sh	2420 s	
		3100 b, s	2330 b, s	2300 s	1.35
$\nu_8(t_2)$	Unsym XH bend	1715 b, m	1240 m	1260 m	1.38
$\nu_9(t_2)$	Torsional XH rock	790 b, s	590 s	608 s	1.34
			535 sh	545 m	
$\nu_{10}(t_2)$	X_4 def	590 b, m	445 m	455 m	1.33

[a] Values reported in wavenumbers (cm^{-1}). Abbreviations used: weak, w; medium, m; strong, s; broad, b; very, v; shoulder, sh. [b] Band assignments and descriptions for symmetrical edge-protonated H_6X_4 (T_d point group) from ref 10. [c] X stands for O or F interchangeably; XH refers to hydrogen motions, recognizing that more than one electronegative atom is involved with each hydrogen. [d] At 10 K.

hydrofluoric acid, and exactly 6.00 additional mL of the hydroxide solution was added. The solution was quantitatively transferred to a septum flask and dried at 25 °C (24 h, N_2 trap) to give a white solid with a water to cation of 3.51:1. The material was further dehydrated at 50 °C (24 h, N_2 trap) to a white solid with a composition (NMR) of $((CH_3)_4N^+)_3(OH^-)_2F^-\cdot 2.98H_2O$. Equivalent weight: calcd for $((CH_3)_4N^+)_3(OH^-)_2F^-\cdot 3H_2O$, 164.85; found, 165.0. The infrared spectrum of this material was identical with that of a 2:1 mixture of authentic[9] tetramethylammonium hydroxide and fluoride monohydrates.

A portion of the monohydrate mixture described above was placed in the short-path cell and dried at 70 °C (15 h, N_2 trap) to give a white powder with a composition (NMR) of $((CH_3)_4N^+)_3(OH^-)_2F^-\cdot 2.00H_2O$. Equivalent weight: calcd for $((CH_3)_3N^+)_3(OH^-)_2F^-\cdot 2H_2O$, 155.74; found, 155.6. The infrared spectrum of this material was interpreted as a combination of those of tetramethylammonium hydroxide hemihydrate[9] and tetramethylammonium fluoride monohydrate.

The close agreement between the titrametric and NMR analyses for these two compounds validates the use of NMR analyses for the fluoride hydrates.

Discussion

In previous papers[9,10] we have interpreted the infrared spectra at 300 and 10–20 K of the water–anion clusters in tetramethylammonium hydroxide and fluoride monohydrates as consonant with the presence of dinegative polyhedral anions in these salts. The idealized geometries proposed for such cluster ions are shown in Figure 1; the symmetrical $H_6X_4^{n-}$ type cluster of T_d point group would have six nonlinear hydrogen bonds along the edges of a tetrahedron of four electronegative atoms, while the T_d $H_4X_4^{n-}$ cluster type is visualized as having the hydrogens involved in bifurcated hydrogen bonds above the four faces of the tetrahedron. The infrared spectra of the actual cluster species in tetramethylammonium hydroxide and fluoride monohydrates are more complex, particularly at low temperature, than theory predicts for ions of pure T_d symmetry. We have demonstrated[10] that the observed spectra can be accounted for as arising from distortion of the idealized $H_6O_4^{2-}$ and $H_4O_2F_2^{2-}$ geometries to S_4 and C_{2v} respectively by intra- and interionic forces in the crystal lattices of the hydroxide and fluoride monohydrates.

The success of these spectral–structural correlations for our proposed models does not, of course, prove that the models are correct; definitive delineation of the structures of these cluster ions awaits diffraction studies, and we are currently working on the preparation of suitable crystalline materials. At this time we will continue, in the discussion that follows, to discuss the spectra of these hydrates in terms of the tetrahedral model, since our accumulated information on these compounds to date remains in accord with this proposed formulation for the cluster anions.

Infrared Spectra and Structure of the Hydrates. A. Tetraethylammonium Fluoride Trihydrate. At 300 K the infrared spectrum of tetraethylammonium fluoride trihydrate shows four bands which give the expected shifts on deuterium substitution and are thus associated with the water–anion moiety. These consist of a broad, strong X–H stretching band centered at 3100 cm^{-1}, a bending band at 1715 cm^{-1}, and two additional absorptions at 790 and 590 cm^{-1} (Figure 2 and Table I). The spectrum is not that of an extended framework clathrate; in particular the presence of two relatively sharp and intense bands above 500 cm^{-1} asserts the presence of strongly tricoordinated water[6] of the type we have observed previously in water–anion cluster species.[9,10]

The spectrum of the water–fluoride species in the fluoride trihydrate closely resembles that of the cluster ion in tetramethylammonium hyroxide monohydrate;[9,10] from this we conclude that the fluoride trihydrate contains an $H_6O_3F^-$ ion structurally similar to the proposed $H_6O_4^{2-}$ ion in the hydroxide monohydrate. An $H_6X_4^{n-}$ cluster of T_d symmetry should possess four infrared-active bands, an unsymmetrical X–H stretch, $\nu_7(t_2)$, an unsymmetrical X–H bend, $\nu_8(t_2)$, a torsional rocking motion of the hydrogens against the X_4 skeleton, $\nu_9(t_2)$, and a deformation of the X_4 skeleton, $\nu_{10}(t_2)$.[10] We assign these four vibrations to the trihydrate bands at 3100, 1715, 790, and 590 cm^{-1}, respectively. The corresponding stretching band of the $H_6O_4^{2-}$ cluster lies at slightly lower energy (2920 cm^{-1}) and the rocking and deformation bands at somewhat higher energies (890 and 730 cm^{-1}) presumably as a result of stronger hydrogen bonding due to increased charge density in the dinegative $H_6O_4^{2-}$ compared to that in the singly charged $H_6O_3F^-$ cluster. The weaker hydrogen bonds in the fluoride trihydrate cluster are also reflected in the ease of dehydration of tetraethylammonium fluoride trihydrate compared to the case of tetramethylammonium hydroxide monohydrate.

The infrared spectrum of tetraethylammonium fluoride trihydrate-d_6 at 10 K (Figure 2) demonstrates departure of the cluster from pure T_d symmetry by incipient splitting of the stretching mode through partial lifting of the degeneracy of the T_2 vibration and by separation of the rocking mode into two bands. In addition to significant splitting of fundamental bands, the $H_6O_4^{2-}$ cluster in tetramethylammonium hydroxide monohydrate shows a second, strong cage deformation band, $\nu_4(e)$, which is infrared active under S_4 and appears at 425 cm^{-1}. We do not believe that the presence of three peaks in the 600–400-cm^{-1} region of the low-temperature spectrum of tetraethylammonium fluoride trihydrate-d_6 indicates that $\nu_4(e)$ is active in this species. The frequency ratio of the two cage deformation peaks of the spectrum of $D_6O_4^{2-}$ is 1.7, while the ratio of the two lowest energy peaks of the $D_6O_3F^-$ cluster is only 1.1. We conclude, therefore, that $\nu_4(e)$ is inactive in this species and that the pair of peaks at 608 and 545 cm^{-1} in the 10-K spectrum of the fluoride trihydrate-d_6 arise from splitting of the torsional rocking band which appears at 590 cm^{-1} in the 300-K spectrum.

B. Tetraethylammonium Fluoride Dihydrate. The infrared spectrum of tetraethylammonium fluoride dihydrate contains the general features of the spectra of the three tetrahedral cluster ions but differs markedly in several ways. The X–H stretching region appears to contain two different types of stretching vibrations; this is most clearly seen in the spectrum

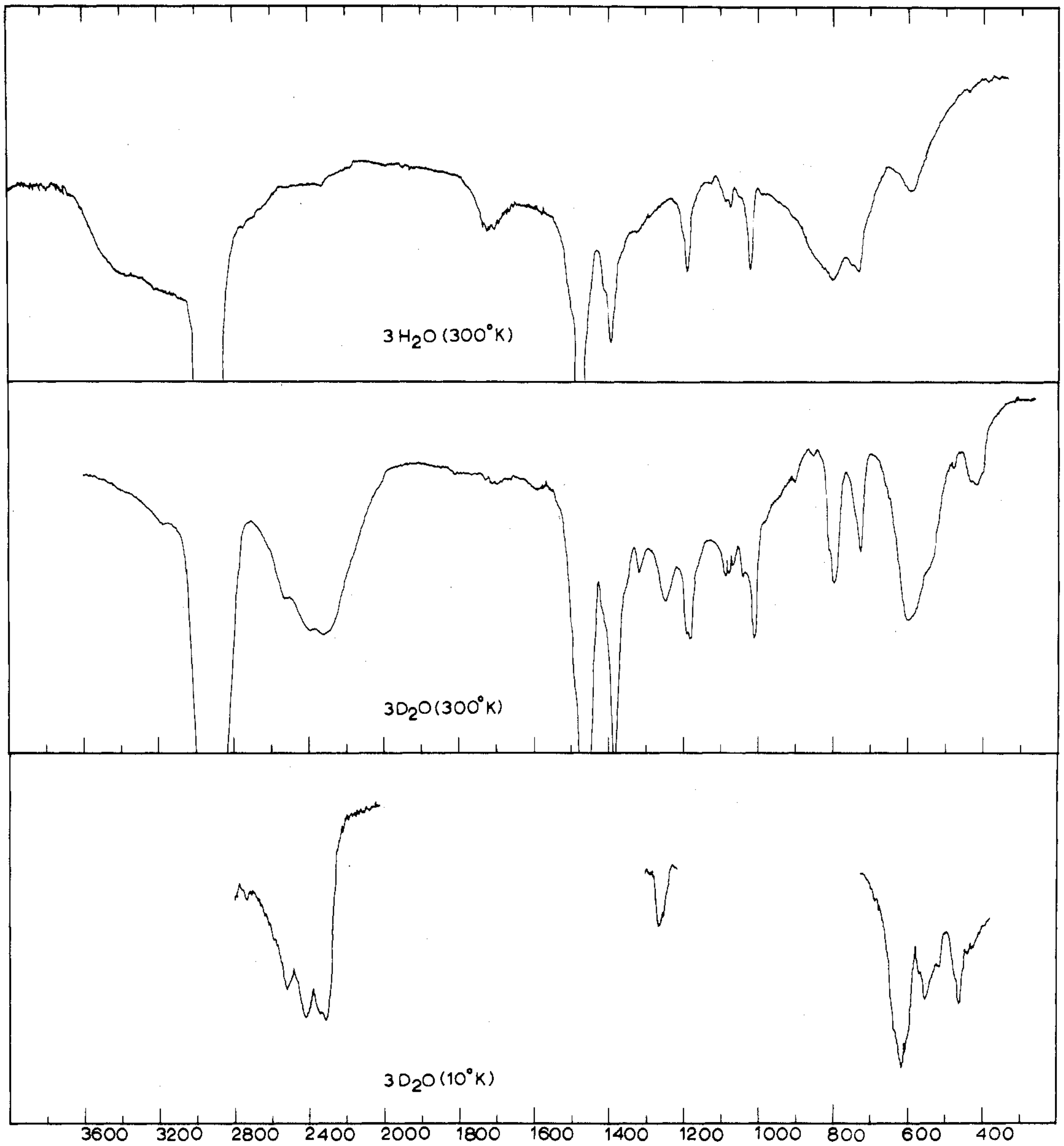

Figure 2. Infrared spectra (Nujol mulls on CsI) of tetraethylammonium fluoride trihydrate and fluoride trihydrate-d_6. Ordinate scale in % *T*.

Table II. Infrared Spectral Absorptions of the Water–Anion Cluster Species in Tetraethylammonium Fluoride Dihydrate and Fluoride Dihydrate-d_4[a]

Region[b]	2 H_2O (300 K)	2 H_2O (10 K)	2 D_2O (300 K)	2 D_2O (10 K)	ν_H/ν_D[c]
XH str	3410 sh	3385 vs[d]	2540 b, m	2515 s	1.35
				2400 m	
	3100 b, s	3190 s[d]	2300 b, s	2320 vs	1.38
		3160 sh[d]		2280 vs	1.38
XH bend		1750 sh	1260 sh	1270 sh	1.38
	1690 b, w	1710 m	1230 w	1240 m	1.39
XH rock[e]	850 b, s	860 vs	625 b, s	637 vs	1.35
		820 s		595 s	1.38
	f	780 m	570 m	570 m	1.37
X_n def[e]	*g*	720 vs	515 w	525 s	1.37
		675 s		495 m	1.36
	645 s	662 vs	463 s	480 s	1.38

[a] Footnote *a*, Table I. [b] Footnote *c*, Table I. [c] At 10 K. [d] Low-temperature XH stretch values for dihydrate from isotope-diluted sample. [e] Assignments to torsional rock and cage deformation not definitive. [f] Peak near 780 cm^{-1} masked by cation; seen at 10 K. [g] Peak near 720 cm^{-1} masked by Nujol; seen at 10 K.

of the dihydrate-d_4 (Figure 3). The bending region also has doublet character, and in the 850–600-cm^{-1} region there are four absorptions, presumably associated with the rocking and deformation motions of strongly tricoordinated water (Table II). In the 10-K spectrum of the dihydrate-d_4 six very narrow and intense bands are observed in this rocking region.

The structure of the water–fluoride species in the dihydrate is presently unknown. The simplest cluster based on the stoichiometric unit $F^- \cdot 2H_2O$ would be a planar unit of C_s symmetry (if the difference between fluorine and oxygen is

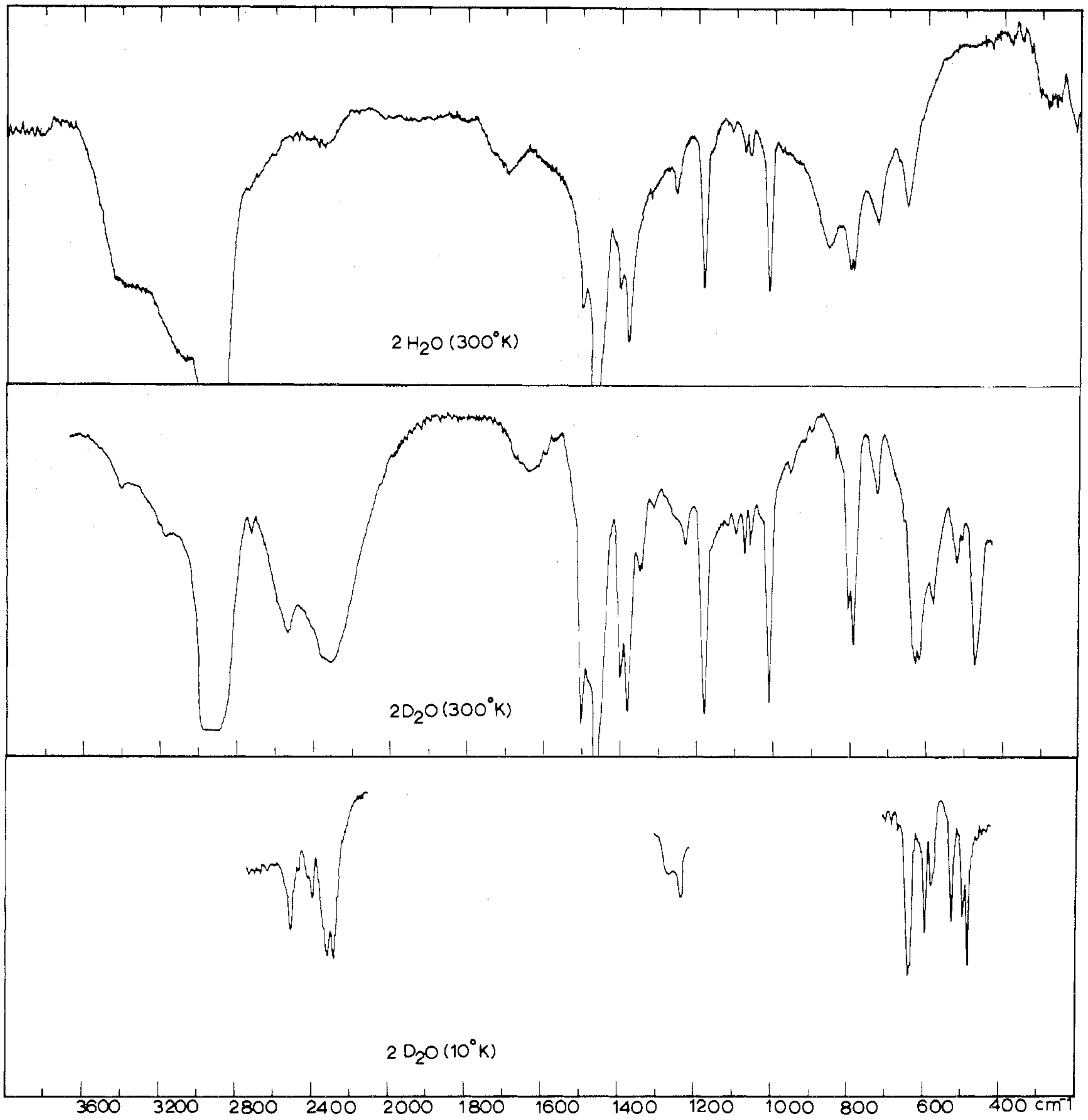

Figure 3. Infrared spectra (Nujol mulls on CsI) of tetraethylammonium fluoride dihydrate and fluoride dihydrate-d_4. Ordinate scale is in % *T*.

Table III. Infrared Spectral Absorptions of the Water-Anion Cluster Species in Tetraethylammonium Fluoride Monohydrate and Monohydrate-d^a

Band^b	Description^c	1 H_2O (300 K)	1 D_2O (300 K)	1 D_2O (10 K)	$\nu_H/\nu_D{}^d$
$\nu_6(t_2)$	Unsym XH str		2460 sh	2460 m	
		2930 b, s	2290 b, s	2295 vs	1.28
			2200 sh	2210 m	
$\nu_7(t_2)$	Unsym XH bend	1650 b, w	*e*	*e*	
$\nu_8(t_2)$	X_4 def	800 b, s	575 s	595 vs	1.39
				575 vs	

^{a} Footnote *a*, Table I. ^{b} Band assignments and descriptions for symmetrical face-protonated H_4X_4 (T_d point group) from ref 10. ^{c} Footnote *c*, Table I. ^{d} At 10 K. ^{e} Masked by cation absorption.

neglected) isostructural with the planar form of $OH^-\cdot 2H_2O$ which is calculated by Newton and Ehrenson[16] to be the most stable geometry for this cluster. Such a species, however, would not be expected to show the bands in the rocking region exhibited by tetraethylammonium fluoride dihydrate. The simplest polyhedral structure based on two stoichiometric units, $(F^-\cdot 2H_2O)_2$, is a face-protonated H_8X_6 octahedron; however, such a species should only show three infrared-active T_{1u} fundamental vibrations.

One thing is clear: the water–fluoride species in the dihydrate is not a random collection of fragments but is a distinct species of molecular ion; it has a complex and specific infrared spectrum which is duplicated precisely in repeated preparations of this stable hydrate. The elucidation of this structure is of considerable interest. Not only does it represent a new type of cluster anion which from its stoichiometry is almost surely not tetrahedral, it also represents a definite chemical intermediate in the solid-state transformation of two $H_6O_3F^-$ clusters into one $H_4O_2F_2{}^{2-}$ cluster, and knowledge of its structure would shed significant light on the dynamics of such hydrates in the solid state. Further work on this and related dihydrates is in progress.

C. Tetraethylammonium Fluoride Monohydrate. A symmetrical face-protonated H_4X_4 cluster ion should show three

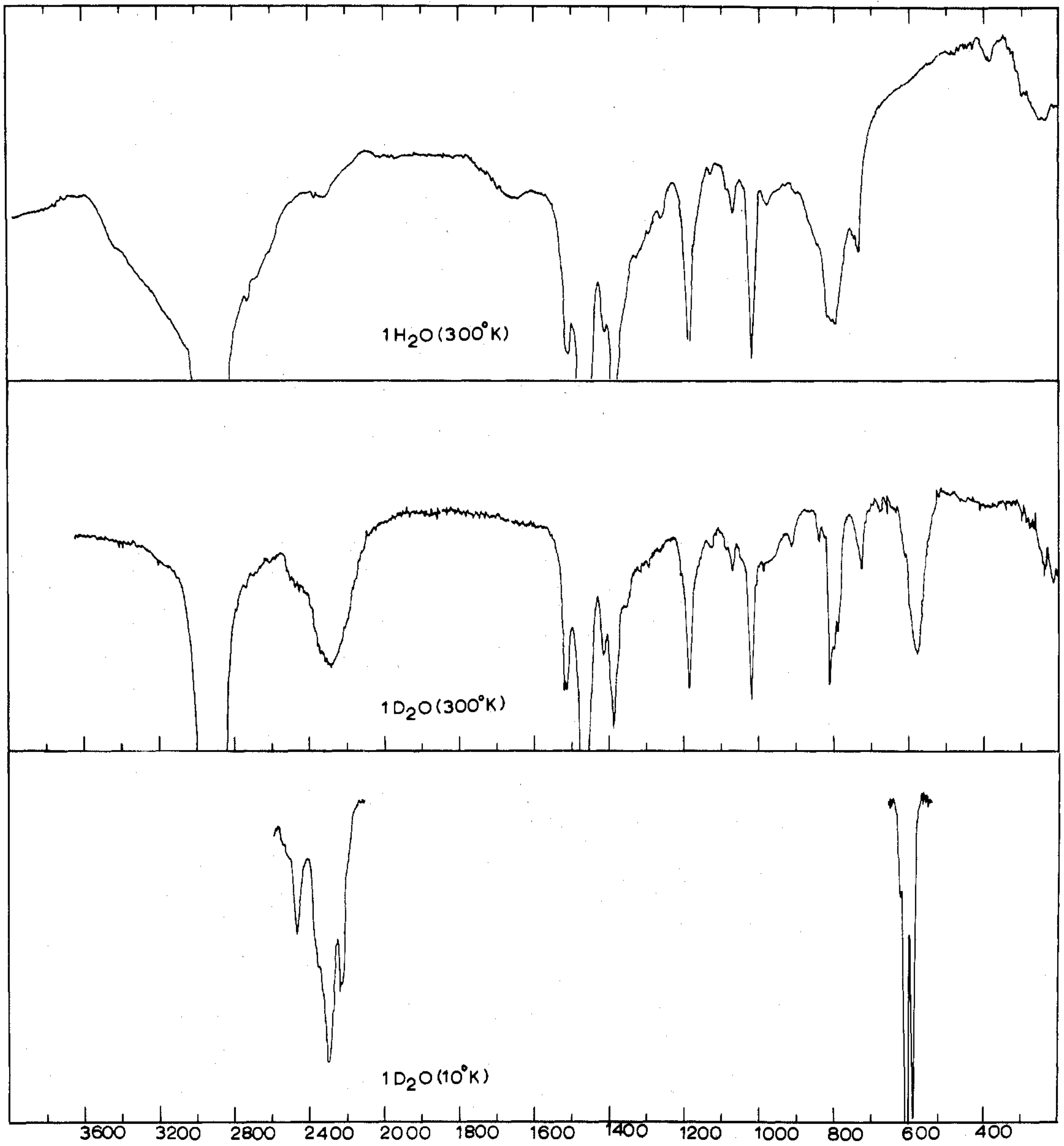

Figure 4. Infrared spectra (Nujol mulls on CsI) of tetraethylammonium fluoride monohydrate and fluoride monohydrate-d_2. Ordinate scale is in % *T*.

infrared-active fundamental vibrations: an unsymmetrical X–H stretch, $\nu_6(t_2)$, an unsymmetrical X–H bend, $\nu_7(t_2)$, and an X_4 cage deformation, $\nu_8(t_2)$.[10] In the infrared spectrum of the $H_4O_2F_2^{2-}$ ion in tetramethylammonium fluoride monohydrate the degeneracies of these fundamental bands are significantly lifted via distortion from T_d toward C_{2v} symmetry in the ionic lattice of the solid salt.[9,10]

In contrast, the water–fluoride cluster in tetraethylammonium fluoride monohydrate shows only three bands which shift on deuterium substitution (Figure 4 and Table III). In the normal monohydrate these consist of a stretching band at 2930 cm^{-1}, a bending band at 1650 cm^{-1}, and a cage deformation at 800 cm^{-1}, which are assigned to $\nu_6(t_2)$, $\nu_7(t_2)$, and $\nu_8(t_2)$ respectively. In the 300-K infrared spectrum of the monohydrate-d_2 the cage deformation band remains a singlet, and a shoulder can be seen on the stretching mode. At 10 K both of these bands are split (Figure 4 and Table III) in the same manner but to a very much lesser extent than the corresponding bands split in the low-temperature spectrum of tetramethylammonium fluoride monohydrate-d_2.[10] We therefore conclude that the structure of the $H_4O_2F_2^{2-}$ ion in tetraethylammonium fluoride monohydrate is essentially that of a regular tetrahedron and that distortion of this ion from T_d toward C_{2v} symmetry in the presence of the larger tetraethylammonium ion is significantly less than under the influence of the greater charge density in the lattice of the tetramethylammonium ion salt.

Registry No. $(C_2H_5)_4N^+F^-{\cdot}5H_2O$, 63123-09-1; $(C_2H_5)_4N^+F^-{\cdot}3H_2O$, 63123-00-2; $(C_2H_5)_4N^+F^-{\cdot}2H_2O$, 63123-01-3; $(C_2H_5)_4N^+F^-{\cdot}H_2O$, 63123-02-4; $(C_2H_5)_4N^+F^-{\cdot}3D_2O$, 63123-03-5; $(C_2H_5)_4N^+F^-{\cdot}2D_2O$, 63123-04-6; $(C_2H_5)_4N^+F^-{\cdot}D_2O$, 63123-05-7; $((CH_3)_4N^+)_3(OH^-)_2F^-{\cdot}3H_2O$, 63123-07-9; $((CH_3)_4N^+)_3(OH^-)_2F^-{\cdot}2H_2O$, 63123-08-0.

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(3) (a) PRF–ACS, NSF–URP, Research Corp., and Oakland University Alumni Fund Fellow. (b) PRF–ACS Fellow.

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Preparation and Properties of $H_2B_2S_5$ and Its Decomposition Products[1]

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The preparation of solid $H_2B_2S_5$ and its decomposition product $H_2S{\cdot}xBS_2$, $x = 4.84 \pm 1.75$, and observations of their properties by visual and chemical means and by x-ray, infrared, Raman, and mass spectrometry are reported. Metathioboric acid, $(HBS_2)_3$, was prepared by two methods and heated with sulfur in evacuated, sealed Vycor tubes to yield $H_2S{\cdot}xBS_2$. Diiodotrithiadiborolane, $I_2B_2S_3$, was prepared and treated with H_2S to obtain $H_2B_2S_5$ in benzene solution. Solid $H_2B_2S_5$ decomposed and polymerized spontaneously to yield $H_2S{\cdot}xBS_2$. X-ray, infrared, and Raman spectrometry revealed polymerization and extensive S–S bonding in the solid. Mass spectrometry of the vapor from the solid products gave predominantly $H_2B_2S_5^+$, H_2S^+, and their fragments at temperatures below 80 °C and then high molecular weight ions up to $B_8S_{16}^+$ at higher temperatures. Fragmentation of $H_2B_2S_5^+$ was shown to yield HBS_3^+ by identification of the corresponding metastable ion. A relationship of $H_2B_2S_5$ to $(BS_2)_n$ through polymerization and condensation is proposed.

Introduction

The only previously known solid thioboric acid was metathioboric acid, HBS_2. It can be prepared by reaction of H_2S with hot boron[2] or by reaction of H_2S with BBr_3 in solution.[3] The solid is trimeric, $(HBS_2)_3(s)$,[4-6] with monoclinic crystal structure in space group C_{2h}^2 or $P2_1/c$.[6] The decomposition and vapor over $(HBS_2)_3$ have been extensively studied.[4,7-13] This paper reports the preparation of $H_2B_2S_5$ and its decomposition product $H_2S{\cdot}xBS_2$, $x = 4.84 \pm 1.75$, and observations of their properties by visual and chemical means and by x-ray, infrared, Raman, and mass spectrometry.

When heated under vacuum below 100 °C $(HBS_2)_3(s)$ decomposes with loss of $H_2S(g)$ toward $B_2S_3(s)$, vaporizes and decomposes to produce $(HBS_2)_3(g)$ and $H_3BS_3(g)$, disproportionates toward a sulfur-rich solid, and produces in small amounts the sulfur-rich gas $H_2B_2S_5(g)$. At higher temperatures, $HBS_2(g)$ and $(HBS_2)_2(g)$ have been reported.[4] Mass spectrometry of the vapor over partially decomposed $(HBS_2)_3(s)$ at temperatures above 250 °C yields polymeric ions $B_nS_{2n}^+$ with n up to 12.[8,11-13] Prominent among the polymeric ions is $B_8S_{16}^+$. It has been proposed that the polymeric ions result from gaseous polymers $(BS_2)_n(g)$[8] and that condensation of $H_2B_2S_5$ with loss of H_2S could be the source of B_8S_{16}.[12]

The goal of this work was to prepare $H_2B_2S_5$ and other materials in the H_2S–BS_2 system, viz., $H_2S{\cdot}xBS_2$, and to determine their properties. Chemical decomposition with loss of H_2S was of particular interest because of the possibility that the proposed BS_2 polymers would be produced.

Experimental Section

Starting Materials. Sulfur (99.9999%) and boron (99.8%) from Electronics Space Products, Inc., 92% ^{10}B-enriched boron from Oak Ridge National Laboratory, CP grade hydrogen sulfide gas from Matheson Co., and boron triiodide and boron tribromide from K & K Laboratories were used as starting materials. The H_2S was bubbled through $Ba(OH)_2$ solution and dried before use. The method given by Perrin et al.[14] was utilized to purify reagent grade CS_2. Reagent grade benzene was treated in succession with concentrated sulfuric acid, sodium carbonate solution, and anhydrous calcium chloride and then was distilled over phosphorus pentoxide. All other solvents were reagent grade chemicals and were dried before use.

Preparation of $H_2S{\cdot}xBS_2$. Metathioboric acid, $(HBS_2)_3$, was prepared by the method of Moissan[2]

$$6H_2S(g) + 3B(s) \xrightarrow{600-750\ ^\circ C} (HBS_2)_3(s) + {}^9/_2H_2(g) \qquad (1)$$

and by the method of Stock and Poppenberg[3]

$$6H_2S(g) + 3BBr_3(soln) \xrightarrow[\text{benzene}]{\text{refluxing}} (HBS_2)_3(soln) + 9HBr(g) \qquad (2)$$

In reaction 1 two volumes of $H_2(g)$ were added to each volume of $H_2S(g)$ to suppress dissociation of the latter in the hot zone. Samples isotopically enriched with 92% ^{10}B were prepared by reaction 1. Products from reactions 1 and 2 will be denoted I and II, respectively.

Stoichiometric amounts of metathioboric acid I or II and sulfur were heated in an evacuated, sealed Vycor tube in a resistance furnace between 350 and 500 °C for several days.

$$(x/3)(HBS_2)_3 + (x/16)S_8 = H_2S{\cdot}xBS_2 + [(x-2)/2]\,H_2S \qquad (3)$$

Fourteen samples of 1.0–1.5 g were prepared by this method, the first 12 with natural boron, the 13th with 92% ^{10}B in $(HBS_2)_3$ from reaction 1, and the 14th with $(HBS_2)_3$ from reaction 2. In the first preparation the sealed tube was cooled to room temperature over a period of 24 h, in the fifth the tube was air quenched, and in the others the tubes were quenched in liquid nitrogen. The tubes were opened by breaking them in a dry nitrogen atmosphere in a glovebox. Samples were transferred to vials and stored in a desiccator over magnesium perchlorate.

Preparation of $H_2B_2S_5$. The method of Schmidt and Siebert[15] was used to prepare 3,5-diiodo-1,2,4,3,5-trithiadiborolane, $I_2B_2S_3$

$$2BI_3 + {}^3/_8S_8 \xrightarrow[25\ ^\circ C]{CS_2} I_2B_2S_3 + 2I_2 \qquad (4)$$

The solvent was evaporated and excess I_2 was removed from the product by vacuum pumping at 50 °C; then the $I_2B_2S_3$ was vacuum distilled from the reaction flask at 95 °C. Dry hydrogen sulfide saturated with benzene vapor was passed into a refluxing solution of $I_2B_2S_3$ in benzene

$$2H_2S(g) + I_2B_2S_3(soln) \xrightarrow[\text{benzene}]{\text{refluxing}} H_2B_2S_5(soln) + 2HI(g) \qquad (5)$$