based on 2-butyne appears to be reliable since the thermochemical data for $C_4H_7^+$ are based upon a consistent set of measurements.[7-9] Using 198 ± 2 kcal/mol for the proton affinity of 2-butyne, we can establish limits on the proton affinity of borazine or PA(borazine) = 203 ± 7 kcal/mol. Thus borazine should be considered as a relatively strong base. It is a stronger base than benzene ($PA(C_6H_6) = 183 \pm 3$ kcal/mol).[2] It seems probable that under selected conditions the cation $B_3N_3H_7^+$ may be stabilized for further investigations.

Acknowledgment.—We are grateful for support by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency through the Materials Science Center, Cornell University.

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A Raman Study of the Hydrolysis of the Hexafluoroantimonate(1−) Ion

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Effects of ionic solutes on water structure were examined in a recent Raman spectral investigation.[1] In that work it was necessary to establish the nature of the prominent anionic species present. In the case of sodium hexafluoroantimonate, it was not certain that SbF_6^- ions were present at all. Rate of hydrolysis studies[2] suggested that $SbF_5(OH)^-$ and $SbF_4(OH)_2^-$ ions would predominate in aqueous solution. Further, the behavior of the OH and OD stretching band contours in $NaSbF_6$ solutions[1] was significantly different from that expected if SbF_6^- were the predominant anionic species. In order to clarify the nature of the anionic species in aqueous solutions of $NaSbF_6$, Raman spectra of solid $NaSbF_6$, of $NaSbF_6$ in H_2O, and of $NaSbF_6$ in aqueous HF were obtained and are reported here.

Experimental Section

Samples of $NaSbF_6$ (98%) were obtained in polyethylene bottles from Alpha Inorganics, Inc., Beverly, Mass. Analyses of ultrafiltered aqueous solutions yielded Na:Sb:F = 1.0:1.0:(6.0 ± 0.1). Analyses for sodium and antimony were accomplished by atomic absorption spectrometry. Fluorine was determined as CaF_2 after rigorous alkaline hydrolysis.

Raman cells made of Pyrex and silica were found to be totally unsuitable for use with aqueous solutions and with solutions containing excess HF because of severe etching. Polished Raman cells fabricated from ingots of aluminum metaphosphate were used, and they were found to be ideal for the present work. Aluminum metaphosphate is colorless and it strongly resists attack even from 48% HF.[3]

Samples of solid polycrystalline $NaSbF_6$ were sealed in dry melting point tubes made of glass. No attack of the glass was noted, and Raman lines ascribable to $NaSbF_6$ only (and not to glass) were observed. In addition, the infrared spectrum from solid $NaSbF_6$ was recorded, because conflicting infrared data involving the ν_4 fundamental of SbF_6^- had been reported previously.[4-6]

Finely ground crystalline $NaSbF_6$ was examined in pellets of CsI and of KBr. Nujol mulls as well as a dispersion in a thin polyethylene film were also examined. The Christiansen effect was serious for the CsI and KBr pellets, but it was virtually eliminated by carefully grinding the $NaSbF_6$ with the other dispersants. The infrared spectra were then recorded with Beckman IR-11 and -12 instruments. The frequency error limits, 1.5 cm^{-1}, were determined mainly by absorption bandwidths.

The Raman spectra were obtained by use of a Carson Laboratories argon ion laser,[7] a Jarrell-Ash Model 25-100 double monochromator, and a noise-squaring photodetection system.[8] Polarization measurements were accomplished by use of a Polaroid sheet analyzer (HN 38), with a quartz wedge scrambler in front of the entrance slit. The optically filtered and focused beam (4880 Å, 400 mW) was passed once through the Raman cell. Scanning rates of 20 cm^{-1} min^{-1} were employed with spectral slit widths of 3.0 cm^{-1} or less and time constants of 1.5 or 2.0 sec. The dark count rate of the EMI 6256 photomultiplier tube employed was 15 sec^{-1} at −20°. The Raman displacements are accurate to ±2 cm^{-1} for sharp lines and to ±5 cm^{-1} for broad lines.

Results and Discussion

Raman and infrared spectra from dry polycrystalline $NaSbF_6$ are shown in Figure 1. Frequencies (and intensities) corresponding to Raman intensity maxima and to the infrared absorption maximum, shown in the inset, are listed and compared with corresponding values reported for $LiSbF_6$[4] and $KSbF_6$[5,6,9] in Table I. The principal frequency discrepancies evident from Table I involve the $\nu_4(F_{1u})$ fundamental. Hence, the other active fundamental is not included in Figure 1.

TABLE I
FUNDAMENTAL FREQUENCIES (CM^{-1}) OF THE SbF_6^- ION[a]

No.	Species	$NaSbF_6$[c]	$LiSbF_6$[d]	$KSbF_6$[e]
1	a_{1g}	669 (10)	668 (10)	661 (vs)
2	e_g	579 (2)	570[b] (2)	575 (s)
3	f_{1u}	672 (vs)	669 (s)	655 (vs)
4	f_{1u}	289 (s)	350 (m) (?)	284 (s)[c]
5	f_{2g}	278 (5)		278 (m)
			294 (4)	294 (m)

[a] All spectra refer to the crystalline solid. Integrated intensities in this work are listed on a scale of 10 (±20%) for Raman spectra, and qualitative infrared intensities are listed in the usual way. [b] A misprint seems to be present in the data of Table I in ref 4. Figure 2 in ref 4 suggests that 570 cm^{-1} would be a more appropriate frequency value for ν_2 in $LiSbF_6$. [c] This work. [d] Reference 4. [e] References 5 and 6.

Raman spectra from aqueous solutions of $NaSbF_6$ and from aqueous solutions of $NaSbF_6$ containing excess HF are shown in Figure 2 and the data are listed in Table II.

Spectra from Solid $NaSbF_6$.—The Raman spectrum from solid $NaSbF_6$ (Figure 1) shows the three sharp lines expected for the SbF_6^- ion (O_h point group). Site symmetry splittings are absent in contrast to the case of $KSbF_6$ where ν_5 is split into two bands.[4-6] (The spectrum was obtained with a spectral slit width of 2 cm^{-1}.)

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(7) A Carson Laboratories argon ion laser tube of BeO and a magnet from a Model 100 system were adapted for use with nonstandard electronic components. A Brewster-angle wavelength-selector prism was used instead of the usual Littrow prism.

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TABLE II

RAMAN SPECTRA OF AQUEOUS AND ACID SOLUTIONS OF $NaSbF_6$

$NaSbF_6$ in H_2O (3.5 and 4.6 *M*)				$NaSbF_6$ (20% HF soln) (2.7 *M*)				$NaSbF_6$ (48% HF soln) (0.4 *M*)				$NaSbF_6$(s)	
$\Delta\nu$[a]	I_p	$\nu_{1/2}$	Polarization	$\Delta\nu$	I_p	$\nu_{1/2}$	Polarization	$\Delta\nu$	I_p	$\nu_{1/2}$	Polarization	$\Delta\nu$	I_p
692	17	37	p	691	6	33	p						
649	90	12	p	649	100	12	p	649	100	12	p	669	100
638	100	14	p	638	34	14	p						
573	17	50	p	574	9	42		577	11	40	dp	579	20
557	16		p	558	7								
278	33	37	dp	277	25	28	dp	278	32	28	dp	278	50

[a] $\Delta\nu$ is in cm^{-1}; I_p is the peak intensity on a scale of 100 (±20%); $\nu_{1/2}$ is the bandwidth in cm^{-1} at half-height (±10–15%); p means polarized and dp means depolarized.

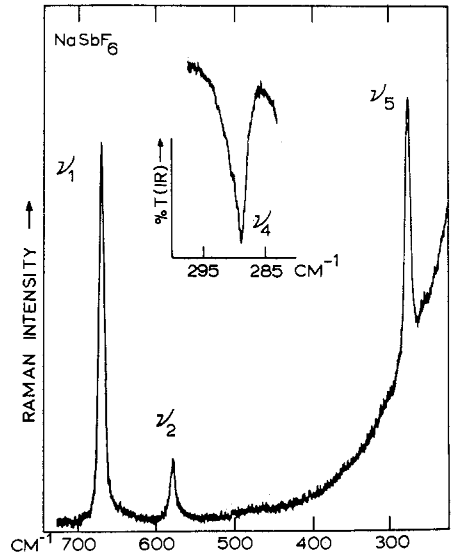

Figure 1.—Raman spectrum from dry polycrystalline $NaSbF_6$. The inset shows the infrared spectrum in the region of the ν_4 fundamental.

The infrared spectrum shown in the inset of Figure 1 was obtained with a spectral slit width of ~1.4 cm^{-1}. Site symmetry splittings are apparently absent in this case as well, in agreement with the Raman result. In Table I the absorption maximum at 289 cm^{-1} has been assigned to the degenerate fundamental ν_4 (F_{1u}). The corresponding fundamental ν_4 in $KSbF_6$ was investigated and observed to be at 284 cm^{-1} and not at 270 cm^{-1} as previously claimed.[5,6] The five observed fundamentals and their relative shapes and intensities confirm our expectations that the SbF_6^- ion in solid $NaSbF_6$ has a regular octahedral structure unperturbed by site symmetry effects.

Raman Spectra from Solutions.—A comparison between the spectra obtained from solid $NaSbF_6$ (Figure 1) and a 0.4 *M* solution of $NaSbF_6$ in 48% HF (Figure 2, bottom) shows some similarities. The intensity distribution, the number of Raman lines, the polarization of these lines, and the frequencies suggest that in this solution the principal anionic species is the octahedral SbF_6^- ion, and that hydrolysis is negligible. The strongly polarized ν_1 fundamental frequency is slightly lower (649 cm^{-1}) in the solution than in the solid (669 cm^{-1}). This is a common observation for a number of hexafluoride ions (SiF_6^{2-}, solid, 663 cm^{-1},[4] solution, 649 cm^{-1},[10] 655 cm^{-1};[11] PF_6^-, solid 751 cm^{-1},[4] solution 741 cm^{-1} [12]). Such a frequency change is most likely related to anionic hydration, but this conclusion, in the absence of supporting quantitative evidence, can only be considered tentative.

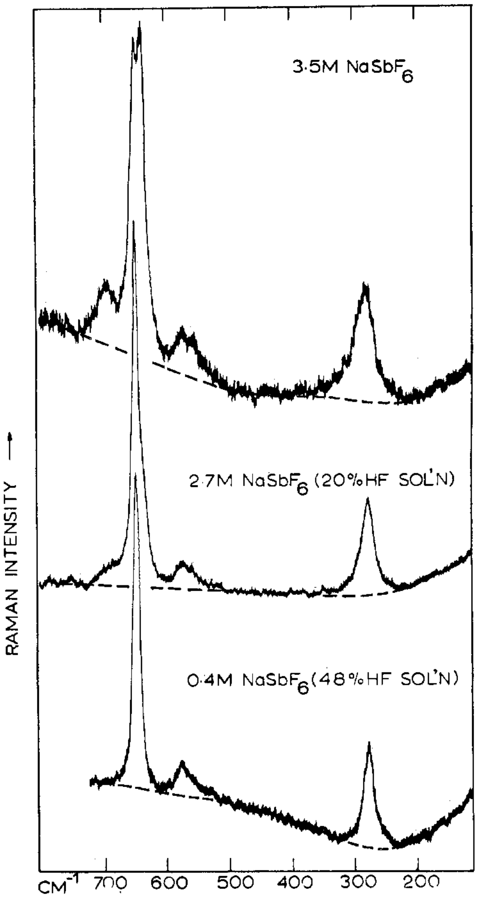

Figure 2.—Raman spectra from $NaSbF_6$ in water (top), from $NaSbF_6$ in 20 wt % HF (middle), and from $NaSbF_6$ in 48 wt % HF (bottom). Concentrations are in moles of Sb per liter.

When the HF concentration is lowered and the stoichiometric $NaSbF_6$ concentration is raised, conditions are more favorable for the hydrolysis of SbF_6^- to occur. The rate of hydrolysis of $KSbF_6$ in water has been studied[2] and the first step

$$SbF_6^- + 2H_2O \longrightarrow SbF_5(OH)^- + H_3O^+ + F^- \qquad (1)$$

is virtually instantaneous, whereas further hydrolysis steps to form $SbF_n(OH)_{6-n}^-$ (n = 0–6) are considerably

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[10] Y. K. Syrkin and M. V. Wolkenstein, *Acta Physiochem. URSS*, **2**, 308 (1935).

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slower. The present work focuses attention on the primary step.[13]

A number of changes in the Raman spectrum of the SbF_6^- species should be observed when the first hydrolysis step occurs to form $SbF_5(OH)^-$. New fundamentals should be evident, notably one associated with the Sb–O stretching mode. Because the study involves aqueous solutions, the O–H fundamentals of the $SbF_5(OH)^-$ species are expected to be masked by those of the solvent. New Sb–F stretching and deformation vibrations are also to be expected and are observed.

The Sb–O stretching fundamental occurs at 692 cm^{-1} (Figure 2, top) and decreases in intensity as the HF concentration is increased (Figure 2, middle and bottom). The frequency agrees with work on a series of antimonate salts by Siebert[14] and the intensity pattern, with respect to the lower frequency Sb–F stretching fundamentals, is similar to that observed by Burger for the structurally related neutral TeF_5OH species.[15]

The two Raman-active Sb–F stretching fundamentals in $NaSbF_6$ change to four in aqueous solution at 649, 638, 573, and 557 cm^{-1}. As HF is added and the hydrolysis is suppressed, the Raman lines at 638 and 557 cm^{-1} decrease substantially in intensity as expected. The low-frequency ν_5 deformation fundamental in $NaSbF_6$ has a substantially larger bandwidth in aqueous solution which supports the view that the overall band corresponds to more than one fundamental. Increased HF concentration narrows the line width as expected if hydrolysis were being suppressed (Figure 2 top to bottom).

In addition to the above observations, a very weak, broad Raman band was centered at 170 cm^{-1}. Although this may refer to fundamental(s) of the $SbF_5(OH)^-$ species, it is more likely to represent the well-known intermolecular 170-cm^{-1} band of the solvent. The presence of HF greatly reduces the intensity of this band.[3]

The evidence strongly indicates that $SbF_5(OH)^-$ is formed in aqueous solutions of $NaSbF_6$ and that HF reverses the hydrolysis. It is valid to note, however, that the 649-cm^{-1} line occurs both in aqueous and in strongly HF solutions. Thus on this basis it is difficult to say whether the aqueous solution contains $SbF_5(OH)^-$ ions alone or a mixture of $SbF_5(OH)^-$ and SbF_6^- ions. Because of structural similarities, accidental degeneracies would not be surprising. A comparison of relative intensities of the 649- and 278-cm^{-1} lines in Figure 2 (top and bottom), where the Sb concentration varies almost tenfold, suggests that in aqueous solution the SbF_6^- species, if present, is roughly lower in concentration by an order of magnitude from that of the $SbF_5(OH)^-$ species. Therefore, the ambiguity is narrowed to the case where $SbF_5(OH)^-$ only is present or where $SbF_5(OH)^-$ and a relatively small amount of SbF_6^- are present in aqueous solution.

Acknowledgment.—Chemical analyses of solutions for Na, Sb, and F as well as analytical studies dealing with the complete hydrolysis of $NaSbF_6$ were performed by Mr. L. D. Blitzer and are very greatly appreciated.

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[13] Solutions containing $NaSbF_6$ in low concentrations in water and in moderately strong HF were found to yield Raman spectra definitely more complicated than those presented in Figure 2, when the solutions were examined about 2 weeks after preparation. The spectral complications involved the region above ~550 cm^{-1} primarily, but no attempt was made to identify the species responsible by means of contour analysis. Instead emphasis was placed on studies involving high concentrations.

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Metal Complexes of *P*,*P*′-Dialkyl-*N*,*N*,*N*′,*N*′-tetramethylpyrophosphoramide

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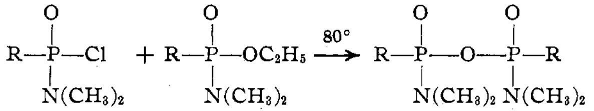
The present work is part of a continuing investigation of the influence of organic substituents on the coordinating ability of the pyrophosphate linkages.[1] Complexes of ligands with one alkyl group and one dimethylamino group attached to each phosphorus atom in a pyrophosphate linkage have been prepared and characterized. ^{31}P nmr spectroscopy has been used to detect the presence of asymmetric phosphorus atoms in the ligands.

Experimental Section

A. Preparation of Ligands.—*Caution! The organophosphorus compounds described below are toxic anticholinesterase agents and should be handled with care.* The general reaction used to prepare the ligands was



$$R-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{\|}}{P}}-Cl + R-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{\|}}{P}}-OC_2H_5 \xrightarrow{80°} R-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{\|}}{P}}-R$$

1 2 3

where R is CH_3, C_2H_5, or *i*-C_3H_7.

Compound 1 was prepared from the corresponding alkylphosphonyl dichloride by literature methods.[2,3] Compound 2 was prepared from ethylalkylphosphonic chlorides[4–6] by the method of Crofts and Fox.[2]

Compound 3 was prepared by heating 1 with an equivalent amount of 2 under nitrogen at 80° for about 6 hr. The evolved ethyl chloride was collected in a trap cooled with a Dry Ice–acetone bath. The reaction mixture was distilled under vacuum. Fractions were collected at 135–140° (3 mm) for R = CH_3, 117–119° (0.3 mm) for R = C_2H_5, and 135–140° (2 mm) for R = *i*-C_3H_7. The yields were about 20% for all ligands.

B. Preparation of Complexes.—All complexes were prepared in 50–75% yield by the same method. Excess 2,2-dimethoxypropane was added to 1.366 mmol of the hydrated perchlorate dissolved in a minimum amount of acetone. This mixture was stirred for 45 min at room temperature. Then 5.5 mmol of ligand was added directly to the mixture. If the complex did not precipitate from solution at this point, excess ether was added, In some cases oils were obtained initially which were worked up with ether. All complexes are hygroscopic.

C. Physical Measurements.—Infrared spectra were obtained as KBr pellets with a Beckman IR-10 spectrophotometer. Visible and near-infrared spectra of nitromethane solutions of the complexes were recorded with a Cary 14 spectrophotometer.

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