ON THE SYNTHESES AND PROPERTIES OF SOME HEXAFLUOROBISMUTHATE (V) SALTS AND THEIR USE IN THE METATHETICAL SYNTHESIS OF NF_4^+ SALTS

KARL O. CHRISTE, WILLIAM W. WILSON, and CARL J. SCHACK

Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304

SUMMARY

The salts $LiBiF_6$, $NaBiF_6$, $KBiF_6$, $CsBiF_6$ and NF_4BiF_6 were prepared and characterized. Differences in the observed numbers and relative intensities of some of the Raman bands of these salts are explained by crystal effects. Solubilities of these salts in anhydrous HF at -78° were determined and compared to those of the corresponding SbF_6^- salts. It was shown that, contrary to a previous report, $CsBiF_6$ does not exhibit any unusual properties such as forming a mushy volatile HF adduct. The potential of NF_4BiF_6 based metathetical processes for the production of other NF_4^+ salts was evaluated. The novel $H_3O^+BiF_6^-$ salt was prepared and characterized. The usefulness of BiF_5 for water removal from HF is briefly discussed.

INTRODUCTION

In the course of our work on oxonium salts [1] and metathetical NF_4^+ salt processes [2-6], we became interested in pentavalent bismuth compounds as possible replacements for the corresponding antimony compounds. For example, the use of the less volatile BiF_5 has been proposed [1], but has never been tested, as an alternative to SbF_5

for removal of small amounts of water from HF. Because NF_4BiF_6 has become readily accessible by direct thermal synthesis from NF_3, F_2, and BiF_5 [7], it holds potential as a starting material in metathetical processes for the production of other less accessible NF_4^+ salts. However, its usefulness in such a process depends on the relative solubilities of its salts in a suitable solvent, such as anhydrous HF. Although BiF_6^- salts have been known [8] since 1950, only a small number of papers [7, 9-18] dealing with BiF_6^- salts have been reported since then, and some of the reported data are very much open to question. For example, Surles and coworkers reported [13] that HF formed a stable adduct with $CsBiF_6$ and that this adduct readily sublimed on heating. Consequently, a more systematic study of BiF_6^- salts was necessary in order to be able to properly evaluate the potential of BiF_6^- salts in the above applications

EXPERIMENTAL

Materials and Apparatus

The apparatus, handling procedures, and the method used for the HF drying have previously been described [1,6]. Bismuth pentafluoride (Ozark Mahoning Co.) did not contain any detectable impurities and was used as received. Antimony pentafluoride (Ozark Mahoning Co.) was distilled prior to use. Lithium fluoride (Baker, A. R.) and NaF (MCB, Reagent grade) were used as received. Potassium fluoride (Allied, Reagent grade) and CsF (KBI) were dried by fusion in a platinum crucible and powdered in the drybox. The syntheses of NF_4BiF_6 [7] and NF_4SbF_6 [4] have previously been described. Except for $NaBF_4$ which was obtained from H_3BO_3 and Na_2CO_3 in concentrated aqueous HF solution, all the alkali metal tetrafluoroborates were prepared by introducing a slight excess of gaseous BF_3 into stirred solutions of the corresponding alkali metal fluorides in anhydrous HF at 20°, followed by removal of the volatile products.

Syntheses of BiF_6^- and SbF_6^- Salts

For the syntheses of the alkali metal hexafluorobismuthates, equimolar amounts of finely powdered alkali metal fluoride and BiF_5 were heated in a Monel cylinder for several days to 280° under 2 atm

of F_2. The vibrational spectra of the resulting products showed no
evidence for the presence of either unreacted BiF_5 [19] or polybismuthate
salts [7]. When these reactions were carried out at 150°, however, the
products contained some polybismuthate salts. The alkali metal hexa-
fluoroantimonates were prepared in a similar manner by heating equimolar
mixtures of SbF_5 and the corresponding alkali metal fluoride in a F_2
atmosphere to 280°. Again, vibrational spectra of the solid products
showed no evidence for the presence of polyantimonates.

Spectra

Infrared spectra of solids were recorded as dry powders between
pressed AgCl or AgBr disks on a Perkin Elmer Model 283 spectrometer.
Raman spectra were recorded in glass melting point, quartz or Kel-F
capillaries on a Cary Model 83 spectrophotometer using the 4880Å exciting
line of an Argon ion laser. Debye-Scherrer powder patterns were taken
using a GE Model XRD-6 diffractometer with nickel filtered copper Kα
radiation and quartz capillaries as sample containers. The thermal
decomposition of salts was examined with a Perkin Elmer differential
scanning calorimeter (Model DSC-1B) using crimp-sealed aluminum pans
as sample containers and a heating rate of 2.5°/min at atmospheric
pressure.

Solubility Measurements

Solubilities of the salts in anhydrous HF at -78° were measured
in an apparatus similar to that previously described [6] for metathetical
reactions, except for eliminating trap I. Saturated solutions were
prepared at -78° and separated from excess undissolved salt by filtration
at -78°. The HF solvent was pumped off at ambient temperature, and the
amount of HF used and of the solid residues obtained after HF removal
were determined by weighing.

Metathetical Reactions

Metathetical reactions between NF_4BiF_6 or NF_4SbF_6 and different
alkali metal tetrafluoroborates in anhydrous HF solution were carried
out as previously described [4,6].

Synthesis of H_3OBiF_6

Bismuth pentafluoride (10.08 mmol) was transferred in the glove
box into a passivated (with ClF_3) Teflon FEP ampule containing a Teflon
coated magnetic stirring bar. Anhydrous HF (10.12 g) which had been
stored over BiF_5 was condensed into the ampule at -196°. The mixture
was warmed to room temperature, and the Raman spectrum of the resulting
clear solution was recorded. It showed bands similar, but not
identical, to those expected for either BiF_6^- (see below) or solid BiF_5
[16, 19]. The ampule was cooled to -196°, and distilled H_2O (10 mmol)
was syringed into the ampule. On warm up to ambient temperature, a
copius white precipitate was formed. The mixture was stirred for ten
hours at 25°. The Raman spectrum of the clear solution above the white
solid precipitate showed the bands characteristic for BiF_6^- (see below).
Removal of the HF solvent in a dynamic vacuum at -45° resulted in the
formation of a white solid (3.469g, weight calcd for 10.08 mmol of
H_3OBiF_6 = 3.447g) which was identified by Raman and infrared spectro-
scopy as $H_3O^+BiF_6^-$. This solid was stable at ambient temperature only
under an HF pressure of about 20mm. On evacuation of the ampule, the
white solid would immediately turn dark brown. When the valve of the
ampule was closed to allow the pressure to build up again, the white
color of the sample was restored. Complete decomposition of H_3OBiF_6
in a dynamic vacuum at 35°for 3 days resulted in a light cream colored
solid. Based on its weight, physical properties (nonhygroscopic,
insoluble in H_2O and aqueous HCl, sublimination at the softening point
of glass), and elemental analysis (found: Bi, 77.2; F, 23.3; O, 0.2;
calcd for BiF_3: Bi, 78.57, F, 21.43; O, 0) this solid appeared to be
mainly BiF_3. The vibrational spectra of the solid decomposition
product did not show any evidence for the presence of either H_3O^+
or BiF_6^-.

RESULTS AND DISCUSSION

Syntheses and Properties of Hexafluorobismuthates

The alkali metal hexafluorobismuthates were prepared from
equimolar amounts of BiF_5 and the corresponding alkali metal fluoride
by heating to 280° in a Monel cylinder. Fluorine was added to the

cylinder to suppress possible decomposition of BiF_5 to BiF_3 and F_2. This synthesis is similar to that [9] previously reported, except for using a significantly higher temperature. Using the previously reported [9] temperature conditions (85-150°), the product always contained some polybismuthate salt. For the syntheses of the alkali metal hexafluoroantimonates, similar reaction conditions were required to suppress the formation of polyantimonates.

The rather unusual properties previously reported [13] for $CsBiF_6$ could not be confirmed. Thus, $CsBiF_6$ was quantitatively recovered from HF solutions by pumping at ambient temperature, without any evidence for the formation of a stable $CsBiF_6 \cdot xHF$ adduct. Furthermore, no evidence was found for sublimation without decomposition for either HF treated or untreated $CsBiF_6$. DSC data obtained for $CsBiF_6$ showed a small reversible endotherm at 190°, attributed to a phase change, and the onset of a large endotherm at 308°, attributed to decomposition. Thermal decomposition of $CsBiF_6$ around 300° was confirmed by visual observation of samples sealed in melting point capillaries. At this temperature, sublimation of BiF_5 to the colder parts of the capillary occurred. For comparison, DSC data were also recorded for $CsSbF_6$. They showed a small reversible endotherm (phase change) at 187° and the onset of endothermic decomposition at 296°. These data show that the thermal stabilities of $CsSbF_6$ and $CsBiF_6$ are similar, with the bismuth salt being slightly more stable.

The vibrational spectra of the alkali metal hexafluorobismuthates were also recorded and showed some remarkable differences (see Figure 1). Particularly, the Raman active deformation mode exhibited different numbers of bands and intensity ratios. In order to determine whether the observed splittings were caused by the simultaneous presence of more than one crystal modification, the Debye-Scherrer powder patterns of these compounds were recorded. In excellent agreement with a previous report [10], it was found that $LiBiF_6$ and $NaBiF_6$ were rhombohedral ($LiSbF_6$ type), $KBiF_6$ was cubic (low-temperature α-modification), and $CsBiF_6$ was rhombohedral ($KOsF_6$ type). No evidence was found for the presence of other modifications in either the thermally prepared (280°) or the HF recrystallized (-78°) samples. The observed splittings can be readily explained, however, by solid state effects. In the rhombohedral compounds (space group $R\bar{3}-C_{3i}^2$, Nr. 148, 1 molecule per Bravais cell [10]), the site symmetry of BiF_6^- is C_{3i}.
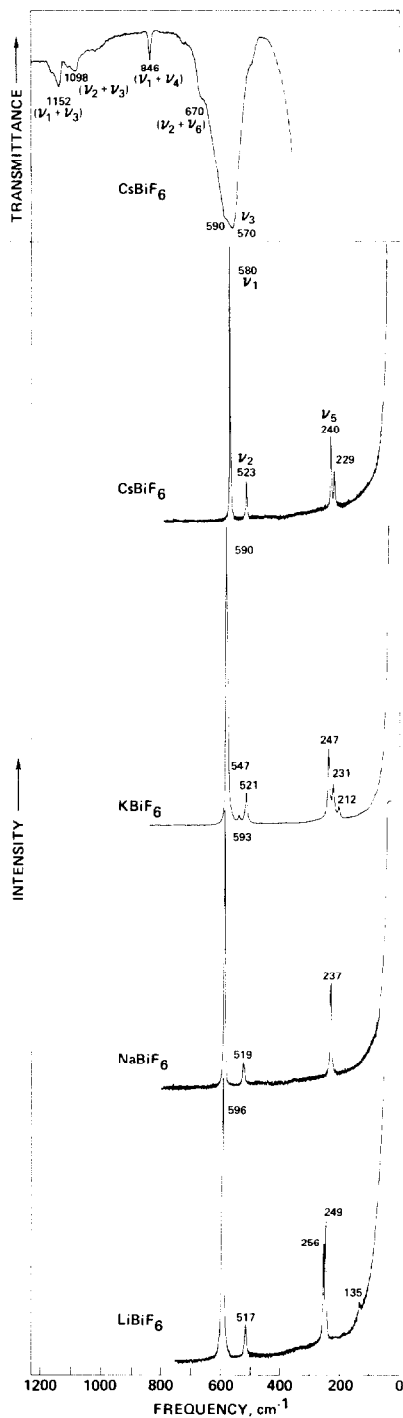
<u>Figure 1.</u>

Infrared spectrum of $CsBiF_6$ and Raman spectra of $CsBiF_6$, $KBiF_6$, $NaBiF_6$, and $LiBiF_6$. The infrared spectrum was recorded as a dry powder between pressed AgCl disks. The broken line is due to absorption by the window material.

TABLE I.

Correlation Table for Isolated BiF_6^- of Point Group O_h and for Site Symmetry C_{3i}

O_h	C_{3i}
A_{1g}	A_g
E_g	E_g
F_{2g}	$A_g + E_g$
F_{1u}	$A_u + E_u$
F_{2u}	$A_u + E_u$

Therefore, from Table I only the F_{2g} mode in the Raman and the F_{1u} modes in the infrared are expected to be split into two components. For cubic $KBiF_6$ (space group Ia3, Nr. 206) the site symmetry of BiF_6^- is again C_{3i}, but since the Bravais cell contains four molecules, factor group splitting can further cause the doubly degenerate E_g modes to split into two components. These predictions are in good agreement with our observations (see Figure 1), except for $NaBiF_6$ which exhibits only one Raman band in the BiF_6^- deformation region. This lack of splitting for $NaBiF_6$ is attributed to a coincidence of the frequencies of the A_g and the E_g components of ν_5. This is plausible since the weaker (probably the E_g) component has a higher frequency in $LiBiF_6$ and a lower frequency in $CsBiF_6$ than the more intense (probably the A_g) component. The frequency separation of the two components in $NaBiF_6$ must be rather small since, even at a spectral slit width of 1 cm^{-1}, we could not resolve the band into two components.

The infrared spectrum of $CsBiF_6$ (see Figure 1) shows a very intense and broad band for the antisymmetric BiF_6^- stretching mode ν_3 (F_{1u}) at 570 cm^{-1}. It exhibits a pronounced shoulder at 590 cm^{-1} which probably represents the second component of ν_3 predicted for C_{3i} symmetry (see Table 1). In addition, several infrared allowed combination bands were observed (see Figure 1). From these, the frequencies of the two remaining deformation modes can be derived as: $\nu_4(F_{1u})$ = 277 and $\nu_6(F_{2u})$ = 147 cm^{-1}. It should be noted that the combination bands involving ν_3 show splittings of about 20 cm^{-1}, analogous to that exhibited by ν_3 itself. This lends further support to the above assignments.

The previously reported [16] Raman spectrum of $NOBiF_6$ exhibits the same splittings and intensity pattern as α-$KBiF_6$, indicating that the two compounds are probably isotypic. Of the six frequency values reported by Bougon and coworkers [14] for BiF_6^-, ν_4 and ν_5 appear too low and should be revised. In agreement with a previous report [7], it was found that infrared spectroscopy is well suited for the detection of polybismuthate impurities in BiF_6^- salts. The polyanions result in an intense infrared band at around 440 cm^{-1}.

Solubility Measurements

The metathetical production of NF_4^+ salts is based on the following principle. A readily available and highly soluble NF_4^+ salt, such as NF_4SbF_6, is reacted in a suitable solvent, such as anhydrous HF, with an alkali metal salt containing the desired anion. If the alkali metal is chosen in such a manner that the starting materials and the desired NF_4^+ salt product are highly soluble and the resulting alkali metal SbF_6^- salt, for example, is of very low solubility, the following general equilibrium, where X=Sb, can be shifted far to the right hand side:

$$MY + NF_4XF_6 \xrightarrow{\ \ HF\ \ } MXF_6\downarrow + NF_4Y$$
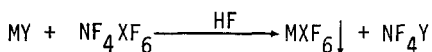
The principle has been demonstrated for salts where Y = BF_4^- [2-4], SnF_6^{2-} [6], TiF_6^{2-} [5], and NiF_6^{2-} [20]. Prior to now, X had always been Sb; but the case where X could be Bi had not been tested. Since NF_4BiF_6 has recently become readily available by direct synthesis [7], and since an extrapolation of crude solubility data, previously measured [2] for alkali metal XF_6^- salts (X=As, Sb) in HF at room temperature, indicated that $LiBiF_6$ might possess the lowest solubility of any MXF_6 salt, quantitative solubility data for MXF_6 salts in anhydrous HF were desired. These data should allow to determine whether a BiF_6^- based process would offer any significant advantages over one based on SbF_6^-.

The solubilities of NF_4^+ and of several alkali metal BiF_6^- and SbF_6^- salts were measured in anhydrous HF at -78°. The low temperature was chosen based on our past experience [4]. The results of our measurements are summarized in Table II. As can be seen, the measured solubilities clearly favor a process based on a cesium rather than a

lithium salt. Furthermore, the solubility of CsBiF$_6$ is only slightly lower than that of CsSbF$_6$, thus not compensating for the significantly lower solubility of the NF$_4$BiF$_6$ starting material in HF and its less favorable formation rate [7], compared to those of NF$_4$SbF$_6$ [4]. Consequently, based on all the presently available experimental data, a CsSbF$_6$ based process appears to be the most attractive method for the metathetical preparation of other NF$_4^+$ salts.

TABLE II

Solubilities of Various BiF$_6^-$ and SbF$_6^-$ Salts in Anhydrous HF at -78°

Anion Cation	SbF$_6^-$		BiF$_6^-$	
	a	b	a	b
NF$_4^+$	259.0	0.7951	173.1	0.4191
Li$^+$	9.21	0.0379	11.9	0.0361
Na$^+$	7.48	0.0289	25.6	0.0740
K$^+$	c	c	20.2	0.0558
Cs$^+$	1.80	0.00488	1.71	0.00373

a) in mg of solute per g of HF
b) in mole of solute per 1000g of HF
c) not measured

Metathetical NF$_4$BF$_4$ Production

Since in the metathetical production of NF$_4$BF$_4$ highly concentrated HF solutions are used, the activity coefficients of the ions are expected to differ significantly from those of the more dilute solutions of the solubility measurements. Consequently, the knowledge of solubility data is insufficient to predict accurately the product composition obtainable from metathetical experiments.

Metathetical NF_4BF_4 production runs using different MBF_4 and NF_4XF_6 salts in HF were carried out. Typical results from such experi-ments are shown in Table III. As can be seen, the data of Tables II and III are only in qualitative, but not quantitative, agreement. As

TABLE III.

Comparison of the Composition of the Crude Products Obtained by the Metatheses of NF_4^+ Salts with Different Alkali Metal Tetra-fluoroborates in HF at -78°

System[a]	Composition of Product (weight %)		
	NF_4BF_4	NF_4XF_6	MXF_6
$LiBF_4 - NF_4SbF_6$	81.7	8.4	9.9
$LiBF_4 - NF_4BiF_6$	86.7	5.9	7.4
$NaBF_4 - NF_4SbF_6$	68.3	12.6	19.1
$KBF_4 - NF_4SbF_6$	15.3	79.6	5.1
$CsBF_4 - NF_4SbF_6$	85.4	13.3	1.3

(a) A 5 mole % excess of the NF_4^+ salt was used in all runs, except for the $LiBF_4 - NF_4BiF_6$ system, where approximately stoichiometric amounts of starting materials were used.

expected, the solubilities of the alkali metal hexafluoro-antimonates and bismuthates are much higher in the concentrated solutions of the metathetical runs. Furthermore, Table III shows that a cesium salt-based process results in the best product purity. The extremely low yield of NF_4BF_4 for the $KBF_4 - NF_4SbF_6$ system is caused by KBF_4 being less soluble in HF than $KSbF_6$. Keeping the difference in the stoichiometry of the used starting materials in mind, (see footnote of Table III) the results obtained for the $LiBF_4 - NF_4SbF_6$ and the $LiBF_4 - NF_4BiF_6$ system are roughly comparable.

Oxonium Hexafluorobismuthate

Our interest in the possible existence of $H_3O^+BiF_6^-$ was twofold. The salt has previously been proposed [1] as a potential candidate for the removal of traces of water from HF. Furthermore, its possible formation in wet HF solutions of BiF_5 might interfere with metathetical experiments, or result in undesired by-products, particularly when BiF_6^- salts are prepared from BiF_5 and alkali metal fluorides in HF solution [13].

It was found that, contrary to a previous literature report [13], BiF_5 is quite soluble in anhydrous HF and has a solubility in excess of 300 mg of BiF_5 per g of HF at 22°. The Raman spectrum of this solution (Figure 2, trace A) significantly differs in the deformation region from those of the BiF_6^- anion in HF solution (Figure 2, trace B) and of solid BiF_5 [16, 19], but is not unreasonable for an associated hexacoordinated bismuth fluoride.

On addition of water to this solution a copious white precipitate formed. The formation of this less soluble solid in the presence of small amounts of water could explain the previous report [13] on the low solubility of BiF_5 in supposedly anhydrous HF. The Raman spectrum (Figure 2, trace B) of the HF solution above the white solid showed one polarized (591 cm^{-1}) and two depolarized bands (520 and 220 cm^{-1}), in agreement with our expectations for octahedral BiF_6^-. These frequency values are similar to those observed for the alkali metal BiF_6^- salts in the solid state (see above). The Raman spectrum of the precipitate was also recorded and was similar to that of the liquid phase. These observations show that water addition converts HF dissolved BiF_5 into a BiF_6^- salt.

Further identification of the formed precipitate was achieved by pumping off the HF solvent at -45°. Based on the observed material balance and vibrational spectra, the following reaction occurred

$$H_2O + HF + BiF_5 \longrightarrow H_3O^+BiF_6^-$$
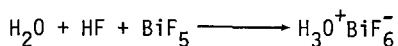
The Raman spectra of the solid product (Figure 2, traces C) showed the presence of the bands characteristic for BiF_6^- (see above) and H_3O^+ [1]. The presence of these ions was further confirmed by infrared spectroscopy at -196° which showed a strong band at 3240 cm^{-1} with a shoulder at 3000 cm^{-1} due to H_3O^+ stretching and a very intense
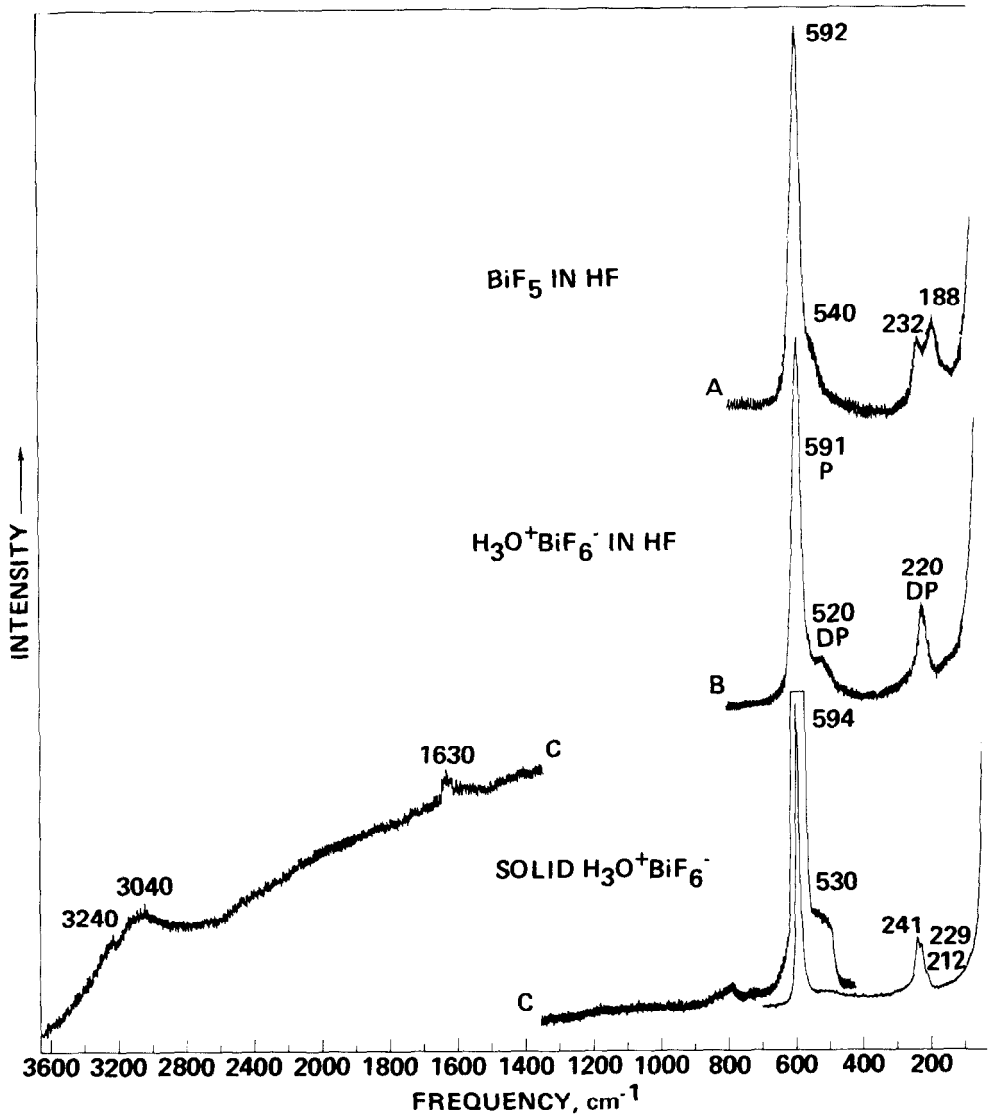
Figure 2. Raman spectra of a 1 molar solution of BiF_5 in HF (trace A), a saturated solution of H_3OBiF_6 in HF (trace B), and of solid H_3OBiF_6 (trace C). All spectra were recorded at room temperature. P and DP indicates polarized and depolarized lines, respectively.

broad band with maxima at 598, 566 and 538 cm^{-1} due to BiF_6^- stretching. The splittings for the BiF_6^- stretching mode is not surprising since at the low temperature rotational motions of the ions in the crystal lattice are frozen out [1] causing symmetry lowering due to strong anion-cation interactions. The same temperature effect was observed for the Raman spectra. At -100°, the 594 cm^{-1} band was observed to split into the following bands: 595 vs, 586 s, 574 mw, 562 w, 555 sh.

An interesting behavior was observed for solid H_3OBiF_6. At ambient temperature, H_3OBiF_6 appears to be stable only under an HF pressure of about 20 torr. When the HF is pumped off, the compound turns instantly dark brown indicating hydrolysis of BiF_5 [9]. When the HF pressure is restored, the solid turns white again. The nature of the decomposition product was established by allowing a sample of H_3OBiF_6 to completely decompose in a dynamic vacuum for 3 days at 35°. The solid residue was found to be mainly BiF_3, as expected from the known [9] hydrolysis of BiF_5. Based on these observations, it appears that H_3OBiF_6 first undergoes a reversible dissociation according to

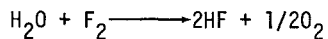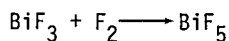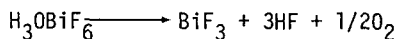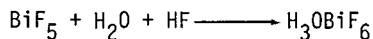$$H_3OBiF_6 \rightleftharpoons H_2O + HF + BiF_5$$
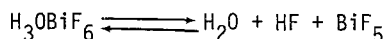
followed by the irreversible hydrolysis

$$BiF_5 + H_2O \longrightarrow BiF_3 + 2HF + 1/2O_2$$
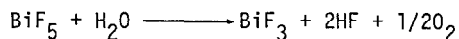
with the first step being strongly suppressed by HF.

Although the thermal stability of H_3OBiF_6 appears to be lower than that [1] of H_3OSbF_6, the following reaction cycle might offer a convenient method for drying HF:

$$BiF_5 + H_2O + HF \longrightarrow H_3OBiF_6$$

$$H_3OBiF_6 \longrightarrow BiF_3 + 3HF + 1/2O_2$$

$$\underline{BiF_3 + F_2 \longrightarrow BiF_5}$$

$$H_2O + F_2 \longrightarrow 2HF + 1/2O_2$$

The advantage of this cycle over one using SbF_5 would be that BiF_5 is a nonvolatile solid which is easier to handle. As shown by the above equations, the proposed cycle amounts to a fluorination of water to yield HF and oxygen. Although this objective can also be achieved by a direct treatment of wet HF with high pressure fluorine with agitation [1], the proposed cycle could offer practical advantages. For example, in the proposed cycle the fluorination step could be limited to a relatively small amount of BiF_3 instead of treating the bulk of the HF with a large excess of high pressure fluorine which has to be recovered.

Acknowledgement

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