Preparation and Characterization of Some Salts of the Difluoro-oxobromine(v) Cation

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Bromosyl fluoride $BrOF_3$ is shown to form 1 : 1 adducts by direct reaction with BF_3 and AsF_5, and the preparation of the compound $BrOF_3{\cdot}SbF_5$ by an indirect method is described. The Raman and ^{19}F n.m.r. spectra of these adducts are interpreted in terms of the ionic structures $[BrF_2O][BF_4]$, $[BrF_2O][AsF_6]$, and $[BrF_2O][SbF_6]$, although, in the solid phase, the $[AsF_6]^-$ and $[SbF_6]^-$ anions probably bridge strongly to the cation. The $[BF_4]^-$ and $[AsF_6]^-$ salts decompose thermally to the $[Br_2]^+$ cation, while the $[SbF_6]^-$ salt appears to give $[BrF_2]^+$.

We have recently reported[1,2] the preparation and characterization of $BrOF_3$ by the reaction of $K[BrF_4O]$ with the weak Lewis acids $[O_2][AsF_6]$ and HF. In this paper we report the reaction of $BrOF_3$ with the Lewis acids BF_3 and AsF_5 to give the $[BrF_2O]^+$ cation. The $[BF_4]^-$ and $[AsF_6]^-$ salts of this cation have been studied by ^{19}F n.m.r. and vibrational spectroscopy, and *X*-ray powder diffraction data have been obtained for $[BrF_2O][AsF_6]$. The hexafluoroantimonate(v) salt of the $[BrF_2O]^+$ cation has been obtained by an indirect method and has been studied by Raman spectroscopy. Very recently the preparation of $[BrF_2O][PtF_6]$ has been reported.[3,†]

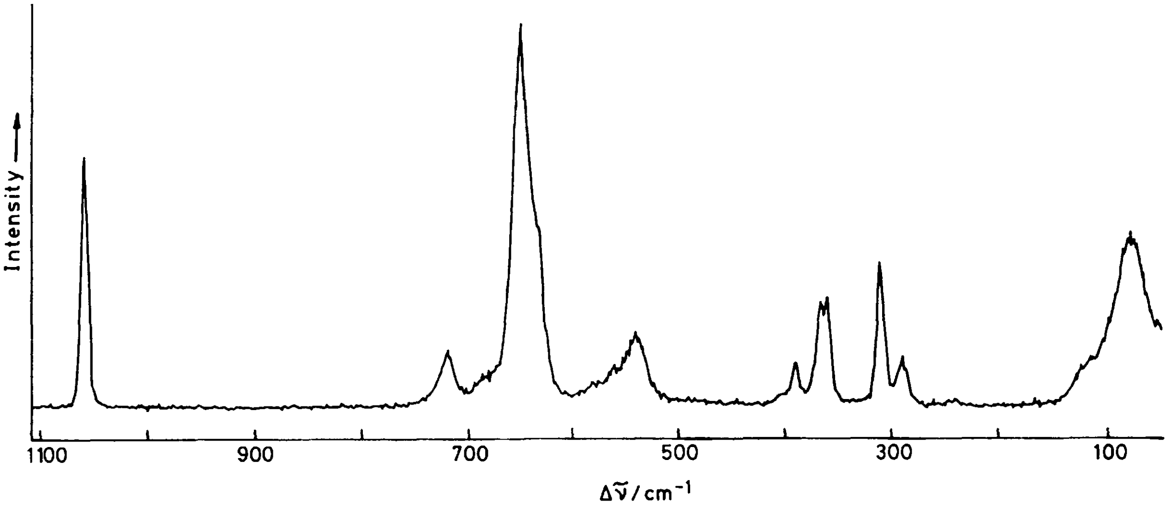

FIGURE 1 Raman spectrum of solid $[BrF_2O][AsF_6]$ recorded at room temperature in a Kel-F tube

RESULTS AND DISCUSSION

Preparation of $[BrF_2O][AsF_6]$, $[BrF_2O][BF_4]$, *and* $[BrF_2O][SbF_6]$.—The reaction of equimolar amounts of $BrOF_3$ and AsF_5 in HF gave the white crystalline adduct $AsF_5{\cdot}BrOF_3$ after removal of the solvent *in vacuo*. A product with an identical Raman spectrum was also obtained using BrF_5 as a solvent. Another preparative route for this compound is the reaction of $AsF_5{\cdot}IO_2F_3$ (ref. 4) with excess of BrF_5 at room temperature which gave a white crystalline solid. After removal of excess of BrF_5 and other volatiles *in vacuo*, the solid obtained had the same Raman spectrum as the products of the other preparations. The ^{19}F n.m.r. spectrum of the supernatant solution at the end of the reaction showed that IOF_5 was present and that there was no unchanged $AsF_5{\cdot}IO_2F_3$. It was, therefore, concluded that the reaction proceeds according to equation (1). Solid

$$AsF_5{\cdot}IO_2F_3 + BrF_5 \longrightarrow IOF_5 + AsF_5{\cdot}BrOF_3 \qquad (1)$$

$AsF_5{\cdot}BrOF_3$ does not have a measurable vapour pressure at room temperature. It turns pink on standing due to slow decomposition.

The reaction of $IO_2F_3{\cdot}SbF_5$ (ref. 4) with excess of BrF_5 appears to proceed in a similar fashion to give the white crystalline solid $BrOF_3{\cdot}SbF_5$. The formation of IOF_5

$$IO_2F_3{\cdot}SbF_5 + BrF_5 \longrightarrow IOF_5 + BrOF_3{\cdot}SbF_5 \qquad (2)$$

and the absence of any unchanged $IO_2F_3{\cdot}SbF_5$ in the products was again confirmed by ^{19}F n.m.r. spectroscopy.

Bromosyl trifluoride forms a solid adduct at low temperature with an excess of BF_3 using HF as a solvent, but

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[†] This product was obtained in an attempt to prepare $[BrF_2O_2]^+$ by the reaction of BrO_2F and PtF_6 and was indeed first identified as $[BrF_2O_2]^+$ (M. Adelhelm and E. Jacob, *Abstr. 6th European Symp. Fluorine Chem.*, Dortmund, 28th March—1st April, 1977) but was correctly identified as $[BrF_2O][PtF_6]$ after the report of the present work at the same meeting (paper given by R. J. Gillespie and P. Spekkens) and discussion with R. Bougon (see ref. in *Angew. Chem. Internat. Edn.*, 1977, **16**, 461).

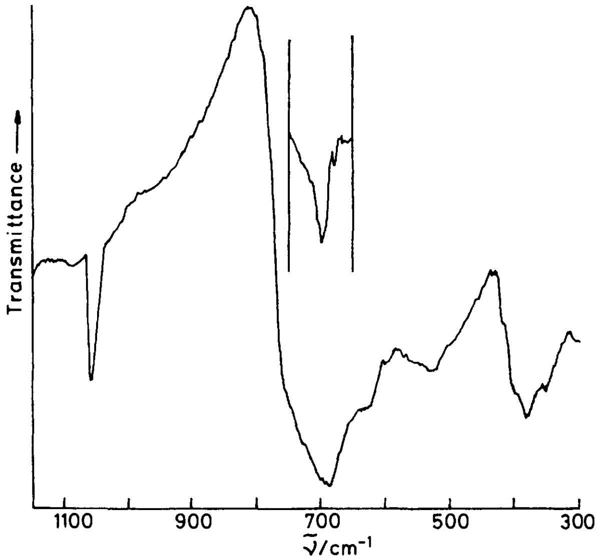
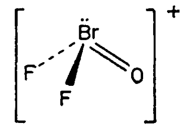


FIGURE 2 Infrared spectrum of solid $[BrF_2O][AsF_6]$ at room temperature using AgBr plates. The inset is a better resolved spectrum of the 640—750 cm⁻¹ region showing the weak peak at 660 cm⁻¹

this adduct is often yellow or orange. When the solid is allowed to warm up to room temperature under dynamic vacuum it darkens in colour and volatilizes, indicating decomposition to volatile products. Because of the marginal stability of the adducts at room temperature no analytical data could be obtained.

Characterization of $[BrF_2O]^+$ *by Vibrational Spectroscopy.*—The Raman (Figure 1) and i.r. spectra (Figure 2) of solid $AsF_5{\cdot}BrOF_3$, the Raman spectrum (Figure 3) of solid $BrOF_3{\cdot}BF_3$, and Raman spectra of solutions of $AsF_5{\cdot}BrOF_3$ (Figure 4) and $BrOF_3{\cdot}BF_3$ (Figure 5) in HF are shown, and the vibrational frequencies obtained from these spectra are listed in Table 1, together with those of the related species $SeOF_2$,[5] SOF_2,[6] and $[ClF_2O]^+$.[7,8]

The shift of the Br=O stretching frequency to higher frequency than in $BrOF_3$,[1,2] together with the occurrence of bands characteristic of the corresponding anion, suggest that the adducts should be formulated as $[BrF_2O][AsF_6]$ and $[BrF_2O][BF_4]$.



(1)

The $[BrF_2O]^+$ cation is expected to have the pyramidal geometry (1) which has C_s symmetry. The six fundamental frequencies expected ($\Gamma = 4A' + 2A''$) are all Raman and i.r. active. The three stretching frequencies can be identified by comparison of the solution spectra of $[BrF_2O][AsF_6]$ and $[BrF_2O][BF_4]$ and can be readily

TABLE 1

Vibrational bands (cm⁻¹)[a] for $[BrF_2O][AsF_6]$ and $[BrF_2O][BF_4]$

$[BrF_2O][AsF_6]$			$[BrF_2O][BF_4]$				$[ClF_2O]^+$ ion[d] ($[BF_4]^-$ salt in HF solution)	Assignments			
Solid[e] (i.r.)	Solid	Solution in HF	Solid	Solution in HF	$SeOF_2$[b] Gas	SOF_2[c] Liquid		OXF_2 (C_s)	$[AsF_6]^-$ (O_h)[f]	$[BF_4]^-$ (T_d)	Other
1 055m[g]	1 059(59)[h]	1 056(76)	1 051(40)	1 052(95)p	1 049vs	1 308(100)	1 333(35) 1 323(sh) } p	$\nu_1(A')$ $\nu(X{=}O)$			
			1 005(1) 991(1) } br							ν_3 (T_2)	
			768(25)	776(15)p						ν_1 (A_1)	
		729(sh)									AsF_5, ν_1
730(sh)	720(15)								ν_3 (T_{1u})		
688s	688(sh)										
660w		683(40)							ν_1 (A_{1g})		
	647(100)	654(100)	666(25) 656(100)	654(100)p	667vs	804(60)	741(100)	$\nu_2(A')$ $\nu_{sym}(XF_2)$			
630(sh)	632(sh)	637(sh)	640(sh) 627(50)	633(sh)[i]	637m	716(60)	710(sh)	$\nu_5(A'')$ $\nu_{asym}(XF_2)$			
535m	560(sh) 540(19)	542br(9)							ν_2 (E_g)		
			532(2)							ν_4 (T_2)	
405(sh)	402(sh)								ν_4 (T_{1u})		
385ms	390(11)										
355(sh)	366 360 } (27)	367(22) 386(sh)	373(25)	369(25)	362m	528(80)	512(25)	$\nu_3(A')$ $\delta_{sym}(OXF)$			
									ν_5 (T_{2g})		
			360(10) 353(sh)	360(sh)						ν_2 (E)	
	311(37)	311(18)	322(15)	314(17)	282m,br	399(70)	402(19)	$\nu_6(A'')$ $\delta_{asym}(OXF)$			
	290(12)	290(sh)	296(6)	296(sh)	253vw	380(50)	383(10)	$\nu_4(A')$ $\delta_{sym}(XF_2)$			
	242(1)								ν_6 (T_{2u})		
	117(sh) 78br(32)										Lattice vibrations

[a] From Raman spectra except where indicated. [b] Ref. 5. [c] Ref. 6. [d] Ref. 7. [e] Lower-frequency range limited by absorption of the AgBr plates. [f] The actual symmetry in the solid is much lower than O_h since the selection rules for O_h are not respected. [g] m = Medium, s = strong, w = weak, sh = shoulder, br = broad, and p = polarized. [h] Numbers in parentheses give relative intensities. [i] State of polarization is uncertain for this line and those of lower frequency.

assigned. They are very similar to the corresponding frequencies in $SeOF_2$, and lower than those in $[ClF_2O]^+$ which is consistent with the greater electronegativity and smaller mass of chlorine compared to bromine. The bending modes cannot be assigned with equal certainty since the polarization data obtained for these lines were inconclusive. For all the related molecules, ν_3 is the highest-frequency bending mode and ν_3 of $[BrF_2O]^+$ was, therefore, assigned to the peak at *ca.* 369 cm^{-1} in the solution spectra. Since a bending motion involving the Br=O double bond would be expected to occur at a higher frequency than one involving only the Br–F single bonds, ν_6 would be expected to occur at higher frequency than ν_4. This is in agreement with the previous assignments for $SeOF_2$,[5] SOF_2,[6] and $[ClF_2O]^+$.[7] The assignments of ν_6 and ν_4 in Table 1 were made on this basis. However, they could be reversed since Bougon *et al.*[8] have concluded from a statistical analysis of polarization ratios for $[ClF_2O]^+$ that the peak at 402 cm^{-1} shows a significantly lower polarization ratio than that at 383 cm^{-1}, and that therefore the assignments of ν_6 and ν_4 of $[ClF_2O]^+$ should be the reverse of those given in Table 1. The assignments of these two modes in $[BrF_2O]^+$ are, therefore, tentative.

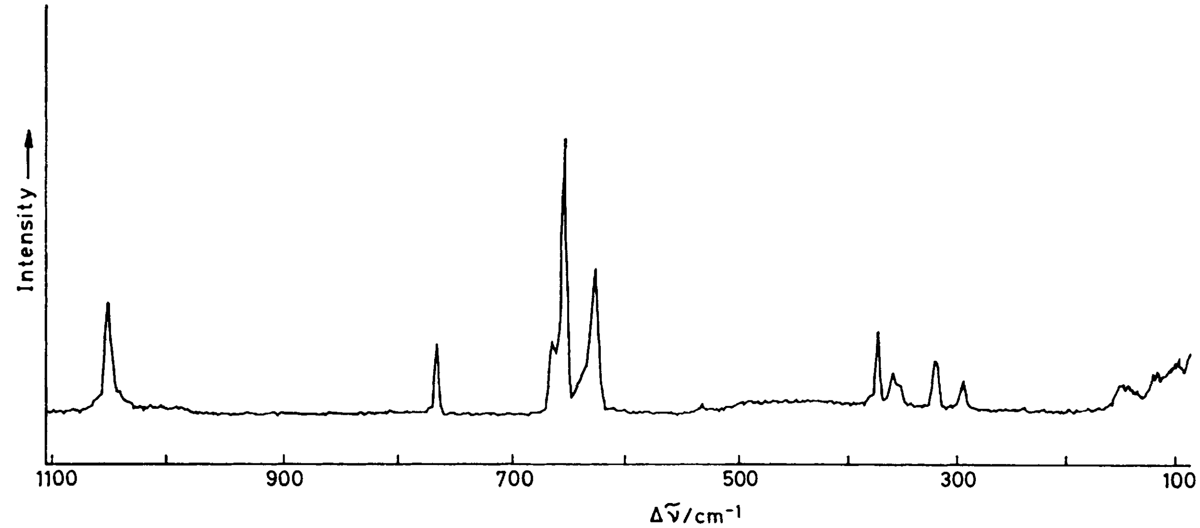


FIGURE 3 Raman spectrum of solid $[BrF_2O][BF_4]$ at −196 °C in a quartz tube

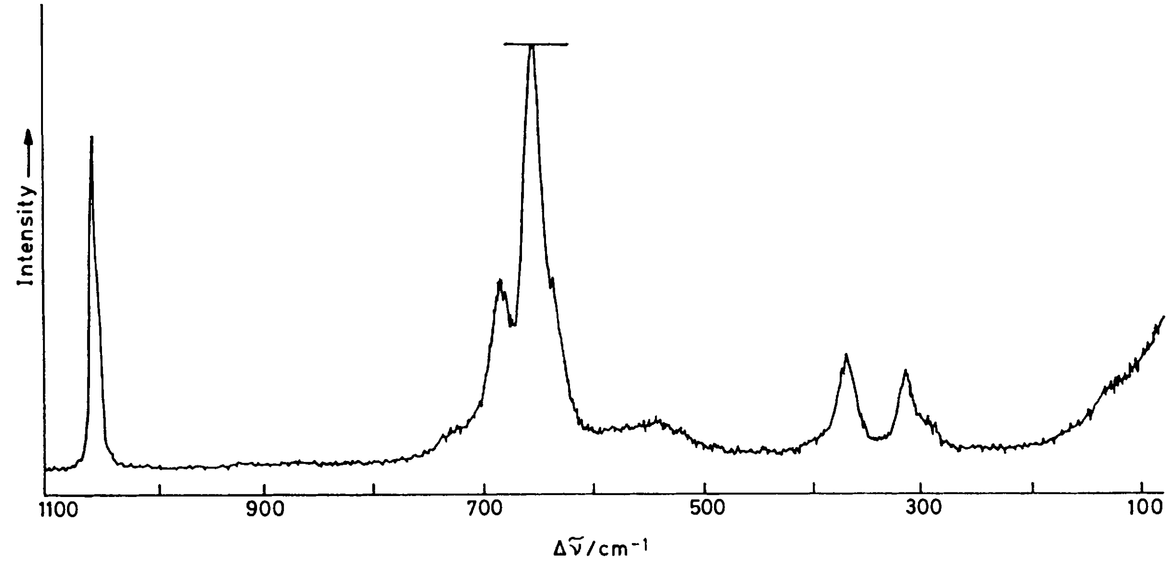


FIGURE 4 Raman spectrum of a solution of $[BrF_2O][AsF_6]$ in HF at room temperature in a Kel-F tube

The anion lines in the Raman spectrum of $[BrF_2O][BF_4]$ can be readily assigned and are very similar to the $[BF_4]^-$ lines in $[ClF_2O][BF_4]$.[7] The $[BF_4]^-$ ion is expected to have tetrahedral symmetry and the four fundamentals ($\Gamma = A_1 + E + 2T_2$) are all Raman active. In solution, only $\nu_1(A_1)$ of $[BF_4]^-$ can be clearly observed and $\nu_3(T_2)$ and $\nu_4(T_2)$ are too weak to be seen at all. The shoulder at 360 cm^{-1} has been assigned to $\nu_2(E)$ of $[BF_4]^-$, but since the strongest peak of the decomposition product (see below) also occurs at 360 cm^{-1} this assignment is uncertain. The decomposition product is also responsible for the weak broad line at *ca.* 716 cm^{-1}. The two lines at 872 and 937 cm^{-1} are due to a small amount of $[BrO_2]^+$,[9] probably produced by attack on the quartz reaction vessel.

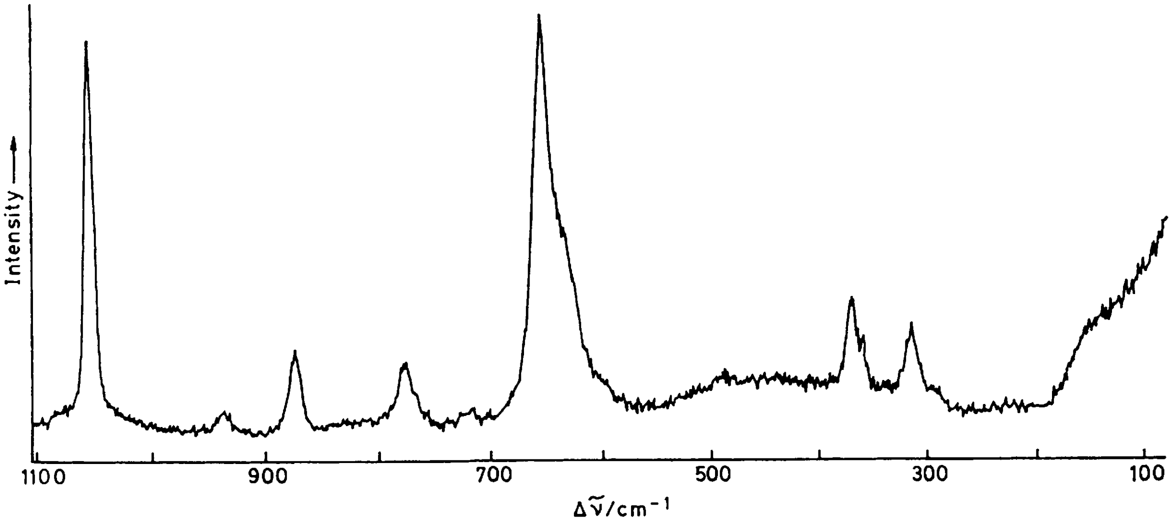


FIGURE 5 Raman spectrum of a solution of $[BrF_2O][BF_4]$ in HF at −72 °C in a quartz tube. The peaks at 872 and 937 cm^{-1} are due to $[BrO_2]^+$, and the broad fluorescence line between 450 and 550 cm^{-1} is due to attack on the quartz vessel

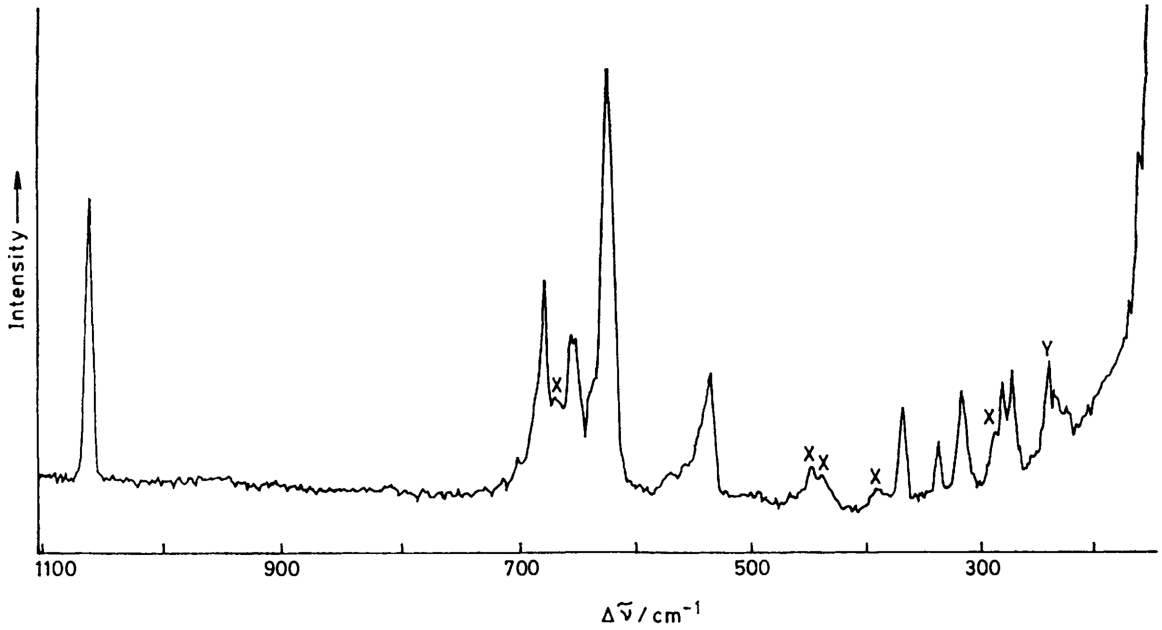


FIGURE 6 Raman spectrum of solid $[BrF_2O][SbF_6]$ at −95 °C in a Kel-F tube. Peaks marked X are due to the Kel-F container and Y is due to the glass of the Dewar which surrounded the sample

The anion lines for $[BrF_2O][AsF_6]$ are more difficult to assign. An octahedral anion has six normal modes of vibration ($\Gamma = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$). Of these, the A_{1g}, E_g, and T_{2g} modes are only Raman active, the two T_{1u} modes are only i.r. active, while the T_{2u} mode is inactive. In the Raman spectrum of the HF solution only the three allowed fundamentals, ν_1, ν_2, and ν_5 are observed, indicating the presence of free $[AsF_6]^-$ of O_h symmetry. In the solid, however, the symmetry of the anion must be lower than O_h since the selection rules are not obeyed. All the six fundamentals are observed in the Raman spectrum and three 'forbidden' modes (A_{1g}, T_{2g}, and E_g) are observed in the i.r. Moreover, some of the lines attributed to degenerate modes are split in the solid. Thus, $\nu_3(T_{1u})$ is observed as two weak lines at 688 and 720 cm^{-1} in the Raman and as a strong line at 688 cm^{-1} (with a shoulder at 730 cm^{-1}) in the i.r. spectrum. Similarly, $\nu_4(T_{1u})$ is weak in the Raman spectrum (390 cm^{-1} with a shoulder at 402 cm^{-1}) but more intense in the i.r. (385 cm^{-1} with a shoulder at 405 cm^{-1}). The normal mode $\nu_6(T_{2u})$ is observed as a weak line at 242 cm^{-1} in the Raman spectrum, but could not be seen in the i.r. spectrum due to the limited range of the AgBr windows. The normal modes $\nu_5(T_{2g})$ and $\nu_2(E_g)$ were observed at 360 and 540 cm^{-1} in the Raman spectrum. The $\nu_1(A_{1g})$ mode, which in the free ion (in solution) occurs at 683 cm^{-1}, must be coincident with ν_1 of $[BrF_2O]^+$ in the Raman spectrum, and was observed as a weak peak at 660 cm^{-1} in the i.r. spectrum. The large shift in frequency of ν_1 of $[AsF_6]^-$ from the free-ion value to the value found in the solid adduct indicates strong interaction between the anion and the cation, and the observation of all the fundamentals of $[AsF_6]^-$ in the Raman spectrum of the solid indicates a lowering of the symmetry of the anion. Similar changes in the spectra have been found for several $[ClF_2O][MF_6]$ salts.[7,8] Moreover, in the crystal structure of $[SeF_3][NbF_6]$,[10] where the cation is isoelectronic with $[BrF_2O]^+$, there is strong fluorine bridging between the anion and the cation and the $[NbF_6]^-$ octahedra are very distorted. There is undoubtedly similar fluorine bridging in $[BrF_2O][AsF_6]$. It is noteworthy, however, that the cation frequencies are very similar in the solid $[AsF_6]^-$ and $[BF_4]^-$ salts, and in solution.

The weak shoulder at 729 cm^{-1} in the solution spectrum of $[BrF_2O][AsF_6]$ is due to ν_1 of AsF_5 (ref. 11) which was present in slight excess. When solutions with a larger excess of AsF_5 were prepared (such as those used for ^{19}F n.m.r. spectroscopy, see later), the peak at 729 cm^{-1} grew in intensity. In addition, two peaks at 760 and 703 cm^{-1} appeared which are assigned to the $[As_2F_{11}]^-$ anion which has been shown [12,13] to be present in solutions of AsF_5 in HF.

The Raman spectrum of solid $BrOF_3{\cdot}SbF_5$ is shown in Figure 6, and Table 2 lists the frequencies obtained from this spectrum. The line at 1 061 cm^{-1} is the characteristic Br=O stretching frequency of the $[BrF_2O]^+$ cation. The remainder of the spectrum is rather complex, however, and must consist of the remaining $[BrF_2O]^+$ lines and the lines due to the anion. An approximate assignment of the observed lines is given in Table 2. This assignment cannot be made with as much certainty as for the other two salts because of the complexity of the spectrum. Comparison of the spectrum with those of $[XeF][Sb_2F_{11}]$,[14] $Cs[Sb_2F_{11}]$,[14] and $[BrF_4][Sb_2F_{11}]$,[15] however, clearly indicates that $[Sb_2F_{11}]^-$ is not present in any appreciable amount and indeed this would not have been expected from the stoicheiometry of the reaction. Moreover, since all the $IO_2F_3{\cdot}SbF_5$ was consumed in the reaction, the $[Sb_2F_{11}]^-$ ion could only reasonably be formed by the disproportionation (3). No $BrOF_3$ nor its

$$2[BrF_2O][SbF_6] \longrightarrow BrOF_3 + [BrOF_2][Sb_2F_{11}] \quad (3)$$

decomposition products such as Br_2 or $[BrF_2]^+$ were observed in the Raman spectrum of the products. Thus, it seems clear that the product does not contain any appreciable amount of the $[Sb_2F_{11}]^-$ salt and that it must, therefore, be an essentially pure $[SbF_6]^-$ salt. The complexity of the spectrum is presumably due to a lowering of the symmetry of the $[SbF_6]^-$ anion which probably arises from both fluorine-bridging and site-symmetry effects. It may be noted that the anion lines are similar to those observed for β-$[XeF_3][SbF_6]$,[16] for which an X-ray crystallographic study has shown the existence of strong fluorine bridges.[17]

TABLE 2

Raman bands (cm^{-1}) of $[BrF_2O][SbF_6]$

Distorted $[SbF_6]^-$ in β-$[XeF_3]^+$ salt [a]	$[BrF_2O]^+$ cation [b]	$[BrF_2O][SbF_6]$ solid	Approximate assignment
	1 059 (59)	1 061 (66)	$\nu(Br{=}O)$
689 (9)		686 (sh)	$[SbF_6]^-$
		678 (50)	
659 (52)			
	647 (100)	656 (37)	$\nu_{sym}(BrF_2)$
629 (68)	632 (sh)	636 (sh)	$\nu_{asym}(BrF_2)$
624 (100)		624 (100)	$[SbF_6]$
		560 (sh)	
514 (38)		538 (29)	
360 (17)	366 (27)	367 (20)	$\delta_{sym}(OBrF)$, $[SbF_6]^-$
		336 (10)	
296 (12)	311 (37)	312 (21)	$\delta_{asym}(OBrF)$
287 (3)			
271 (8)	290 (12)	278 (22)	$\delta_{sym}(BrF_2)$
257 (1)		268 (23)	$[SbF_6]^-$
		228 (10)	
		224 (5)	

[a] Ref. 16. Only the anion lines are listed and the intensities (shown in parentheses) have been normalized with respect to the strongest anion line. [b] Solid $[AsF_6]^-$ salt.

Characterization of $[BrF_2O]^+$ *by* ^{19}F *N.M.R. Spectroscopy*.—Both $[BrF_2O][AsF_6]$ and $[BrF_2O][BF_4]$ are soluble in HF, with the $[BF_4]^-$ salt being the more soluble of the two. The ^{19}F n.m.r. spectrum of a solution of $[BrF_2O][AsF_6]$ in HF did not show a separate signal in the F-on-Br^V region and this indicates that the cation undergoes rapid exchange with the HF solvent, probably by reaction (4). Addition of excess of Lewis

$$[BrF_2O]^+ + [HF_2]^- \rightleftharpoons BrOF_3 + HF \quad (4)$$

acid resulted in the observation of a separate signal for $[BrF_2O]^+$ in HF, presumably because the exchange reaction is slowed down by removal of $[HF_2]^-$ from solution by reaction (5). A solution of $[BrF_2O][AsF_6]$

$$AsF_5 + [HF_2]^- \longrightarrow [AsF_6]^- + HF \quad (5)$$

in HF containing excess of AsF_5 at 10 °C showed a singlet (width *ca.* 35 Hz) at -202 p.p.m. attributed to $[BrF_2O]^+$ and a second peak at 112 p.p.m. attributed to HF exchanging with $[AsF_6]^-$ and AsF_5. Decreasing the temperature caused the signals to shift upfield (-199 and 117 p.p.m., respectively, at -60 °C). Similarly, the ^{19}F n.m.r. spectrum of a solution of $[BrF_2O][BF_4]$ in HF containing excess of BF_3 at -78 °C showed a sharp singlet at -192 p.p.m. assigned to $[BrF_2O]^+$ and a strong singlet at 190 p.p.m. assigned to HF exchanging with BF_3 and $[BF_4]^-$. The $[BrF_2O]^+$ singlet has a chemical shift in the F-on-Br^V region, close to that reported for the isoelectronic BrO_2F (-210 p.p.m.) [18] and downfield from the parent molecule (*ca.* -160 p.p.m.).[1,2] That the signal is a singlet is in agreement with the equivalence of the fluorine atoms in the proposed structure (1).

Characterization of $[BrF_2O][AsF_6]$ *by* X*-Ray Powder Diffraction*.—The X-ray diffraction pattern of $[BrF_2O]$-

$[AsF_6]$ was indexed in a simple cubic cell with $a = 8.726 \pm 0.004$ Å, which corresponds to a volume of 664.4 Å^3. The assignment of the lines is shown in Table 3. The observed volume would give a reasonable[19] value of 18.4 Å^3 for the average volume per F or O atom (neglecting contributions from the Br or As) if there are four molecules in the unit cell. This would be consistent with the structure of $[SeF_3][NbF_6]$,[10] but different from that of $[ClF_2O][AsF_6]$ where six molecules per unit cell have been postulated.[20]

Decomposition of $[BrF_2O]^+$ *Salts*.—When $[BrF_2O][AsF_6]$ is allowed to stand at room temperature it slowly turns pale pink indicating decomposition. The Raman spectrum of a partially decomposed sample of $[BrF_2O][AsF_6]$ shows an increase in intensity of the lines at 360 and 720 cm^{-1} and the appearance of a line at 1 080 cm^{-1}. These three lines increase in intensity together, with that at 360 cm^{-1} being the more intense and that at 1 080 cm^{-1} the least intense. In the Raman spectrum of decomposed samples of $[BrF_2O][BF_4]$ lines at 360 and 716 cm^{-1} are again observed. These results are consistent with the formation of $[Br_2][AsF_6]$ and $[Br_2][BF_4]$ as decomposition products since the lines at 360, 720, and 1 080 cm^{-1} are the characteristic, intense, resonance-Raman spectrum of the $[Br_2]^+$ ion,[21] which is obtained when 514.5-nm exciting radiation of an argon-ion laser is used.

TABLE 3

X-Ray powder data for $[BrF_2O][AsF_6]$

		d/Å		
n	*hkl*	Obs.	Calc.	Intensity
2	110	6.14	6.17	23
3	111	5.00	5.04	30
4	200	4.35	4.36	42
5	210	3.88	3.90	100
6	211	3.56	3.56	54
8	220	3.076	3.085	11
9	300, 221	2.906	2.908	17
10	310	2.753	2.759	9
11	311	2.619	2.630	20
12	222	2.510	2.519	3
14	321	2.325	2.332	6
16	400	2.177	2.181	4
17	410, 322	2.111	2.116	8
18	411, 330	2.052	2.057	21
19	331	1.996	2.002	3
20	420	1.947	1.951	2
21	421	1.904	1.901	13
22	332	1.856	1.860	4
24	422	1.779	1.781	4
25	500, 430	1.741	1.745	1

The decomposition of $[BrF_2O][SbF_6]$ differs from that of the $[AsF_6]^-$ and $[BF_4]^-$ salts. Whereas the $[BF_4]^-$ salt decomposes completely after *ca.* 15 min at room temperature and the $[AsF_6]^-$ salt begins to change colour after 1 h at room temperature, the $[SbF_6]^-$ salt can be kept at room temperature for several hours before lines assigned to the decomposition product begin to appear in the Raman spectrum. Even after several days at room temperature the characteristic Br=O stretching frequency of the $[BrF_2O]^+$ cation is still observable in the Raman spectrum of the decomposing material. The product of the decomposition of $[BrF_2O][SbF_6]$ is also different from that of the other two salts. The Raman spectrum of a sample of $[BrF_2O][SbF_6]$ which had stood at room temperature for 10 d showed the solid to consist entirely of $[BrF_2][SbF_6]$.[22] The solid was, however, pink in colour, presumably indicating that some $[Br_2]^+$ was formed, although it could not be observed in the Raman spectrum. This $[Br_2]^+$ does not necessarily result from the decomposition of $[BrF_2O][SbF_6]$ however, since $[BrF_2][SbF_6]$ has also been reported to turn pink on prolonged storage.[23]

EXPERIMENTAL

The preparation of $BrOF_3$ has been described elsewhere.[1,2] Boron trifluoride (Matheson Co.) was purified by bubbling it through 100% sulphuric acid containing B_2O_3; $AsF_5 \cdot IO_2F_3$ and $IO_2F_3 \cdot SbF_5$ were obtained from Dr. J. P. Krasznai.[4] The purification of HF, BrF_5, and AsF_5, as well as the ^{19}F n.m.r. and Raman instrumentation and the vacuum systems used at McMaster, have been described elsewhere.[24-26] Materials and instrumentation used at Saclay have also been described.[27,28] Chemical shifts are reported with respect to $CFCl_3$ used as an external standard, and a shift to high field is considered positive.

Difluoro-oxobromine(V) *Hexafluoroarsenate*(V).—In a typical preparation, $BrOF_3$ (0.174 g, 1.14 mmol) was dissolved in HF (0.26 g, 13 mmol) in a Kel-F tube and AsF_5 (1.15 mmol) was condensed in at −196 °C. The mixture was warmed to room temperature, giving a pale yellow solution. The bottom of the tube was cooled slightly to precipitate most of the product, and the HF was then removed *in vacuo*. 0.343 g of a white crystalline solid was obtained, which corresponds to 1.06 mmol of $AsF_5 \cdot BrOF_3$. Preparations using excess of AsF_5 gave solids showing identical Raman spectra and *X*-ray powder photographs. The solid $AsF_5 \cdot BrOF_3$ was also prepared in Teflon–FEP tubes and was transferred to quartz tubes in the dry-box.

The adduct $AsF_5 \cdot IO_2F_3$ was dissolved in an excess of BrF_5 (mol ratio $\approx 1:20$) in a Teflon–FEP n.m.r. tube and warmed to room temperature. After 10 min at room temperature a white crystalline solid was deposited. The n.m.r. spectrum of the supernatant solution showed the BrF_5 solvent,[29] IOF_5,[13] and a small amount of IF_5.[29] No signals due to $AsF_5 \cdot IO_2F_3$ (ref. 4) were observed. The IF_5 is probably produced by thermal or photochemical decomposition of the $AsF_5 \cdot IO_2F_3$ adduct to $[IF_2O][AsF_6]$, followed by fluorination to IF_5 by the BrF_5 solvent. The white solid produced had a Raman spectrum characteristic of $[BrF_2O][AsF_6]$. The reaction of $IO_2F_3 \cdot SbF_5$ with BrF_5 to produce $[BrF_2O][SbF_6]$ was performed in a similar manner.

For the ^{19}F n.m.r. spectrum of $AsF_5 \cdot BrOF_3$, a mixture with a molar composition $BrOF_3 \cdot AsF_5 : AsF_5 : HF = 7:8:100$ was prepared in a Kel-F n.m.r. tube.

Difluoro-oxobromine(V) *Tetrafluoroborate*.—In a typical preparation, $BrOF_3$ (0.284 mmol) was dissolved in HF (0.4 g) in a Teflon–FEP n.m.r. tube, and BF_3 (0.63 mmol) was distilled in at −196 °C. The mixture was warmed to −72 °C and a clear yellow solution was formed. This solution was used to record the ^{19}F n.m.r. spectrum. The HF and excess of BF_3 were then removed *in vacuo* at

-72 °C to give a yellowish solid which had a Raman spectrum consistent with $BrOF_3 \cdot BF_3$. Samples were also prepared in Kel–F and quartz vessels.

The salt was also prepared by the direct reaction of $K[BrF_4O]$ with excess of BF_3 in HF, giving a mixture of $K[BF_4]$ and $[BrF_2O][BF_4]$. Potassium tetrafluoroborate is only slightly soluble in HF, however, and the more soluble $[BrF_2O][BF_4]$ could be separated by decanting the HF solution into a sidearm of the reaction vessel and then removing the HF *in vacuo*.

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