only small quantities of a viscous oil, which could not be identified as a discrete compound.

Treatment of Ni(cyclam)$^{2+}$ with *m*-Chloroperbenzoic Acid. A suspension of Ni(cyclam)(ClO$_4$)$_2$ (0.05 mmol) in 30 mL of dichloromethane was cooled to −78 °C, and a solution of MCPBA (0.05 mmol) in 5 mL of dichloromethane was added slowly. The mixture was stirred at −78 °C for 1 h, during which the original orange-yellow color turned pink. When a solution of phenyldimethylphosphine (0.2 mmol) in dichloromethane was added, the pink color was discharged within 5 min. GC–MS analysis confirmed the formation of the phosphine oxide in >80% yield. When this experiment was repeated with cyclohexene, no change occurred at −78 °C. When the mixture was warmed to room temperature, it turned black and no oxidation product of cyclohexene was observed.

A yellow solution of Ni(cyclam)(OTf)$_2$ (0.02 mmol) in 4 mL of dichloromethane was cooled to −78 °C and the electronic spectrum recorded. A solution of MCPBA (0.02 mmol) in dichloromethane was added slowly and the spectrum of the pink solution recorded again (Figure 1). Upon the addition of PMe$_2$Ph, the absorption band at 550 nm disappeared, and the solution returned to its yellow color. When the experiment was repeated with cyclohexene, the band at 550 nm did not disappear.

An intensely green solution of Ni^{III}(cyclam)$^{3+}$ perchlorate[20] in acetonitrile reacted completely with excess iodosylbenzene within 2 min to lead to a yellow solution that contained a quantitative yield of iodobenzene. It is possible that iodosylbenzene is acting as a reducing agent under these conditions.

Isotopic Oxygen-18 Studies. Ni(cyclam)(ClO$_4$)$_2$ (0.01 mmol) and norbornene (1 mmol) were dissolved in 1 mL of MeCN, and H$_2{}^{18}$O (1.85 mmol) was added together with 0.02 mmol of iodosylbenzene. After the mixture was stirred for 30 min, the norbornene oxide was analyzed by GC–MS for its isotopic composition. A control experiment was carried out in which norbornene oxide-^{16}O (1.0 mmol) was treated with H$_2{}^{18}$O (1.85 mmol) in the presence of Ni(cyclam)(ClO$_4$)$_2$ (0.01 mmol) and iodosylbenzene (0.02 mmol) in 1 mL of MeCN. The recovered epoxide showed no isotopic incorporation. Moreover, the treatment of iodosylbenzene (0.05 mmol) with H$_2{}^{18}$O (2 mmol) in the presence of Ni(cyclam)(ClO$_4$)$_2$ (0.01 mmol) was carried out until half of it was in solution. The remainder of the iodosylbenzene was recovered. Analysis by a procedure developed previously[3,7] showed that it contained no isotopic label.

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New, One-Step Syntheses of BrF$_3$O and BrF$_4$O$^-$ Salts and the Preparation and Characterization of RbBrF$_4$O and NaBrF$_4$O

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The reactions of an excess of BrF$_5$ with the alkali-metal nitrates NaNO$_3$, KNO$_3$, RbNO$_3$, and CsNO$_3$ provide new, simple, high-yield syntheses of the corresponding BrF$_4$O$^-$ salts and FNO$_2$. The NaBrF$_4$O and RbBrF$_4$O salts have been prepared for the first time and were characterized by vibrational spectroscopy, DSC, and their X-ray powder diffraction patterns. The reaction of LiNO$_3$ with an excess of BrF$_5$ does not result in the formation of a stable LiBrF$_4$O salt but produces free BrF$_3$O in high yield. This provides a simple, one-step synthesis of BrF$_3$O from commercially available starting materials.

Introduction

The existence of KBrF$_4$O was discovered in 1976 both by Bougon and co-workers[1] and by Gillespie and Spekkens.[2] It was prepared either by the reaction[1] of KBrO$_3$ with a large excess of BrF$_5$ at 80 °C in the presence of F$_2$ or by the reaction[2] of KBrF$_6$ with KBrO$_3$ in CH$_3$CN solution. Both methods have drawbacks. Although Bougon's method[1] can yield a pure product, the course of the reaction is difficult to control and frequently KBrF$_4$ is obtained as the only product,[3] Gillespie's method[2] produces a mixture of KBrF$_2$O$_2$ and KBrF$_4$O, which must be separated by numerous extractions with CH$_3$CN.

An improved synthesis of BrF$_4$O$^-$ salts was reported by Christe and co-workers[3] who reacted BrO$_4{}^-$ salts with BrF$_5$ and F$_2$. In addition to KBrF$_4$O, the latter authors also prepared and characterized CsBrF$_4$O. Although this method results in a pure product in essentially quantitative yield,[3] the required BrO$_4{}^-$ starting materials are difficult to prepare.[4] Except for NF$_4{}^+$BrF$_4$O$^-$,[5] no other BrF$_4$O$^-$ salts have been reported.

Three methods have previously been reported for the synthesis of BrF$_3$O. Bougon and Bui Huy[6] reacted KBrF$_4$O with O$_2$AsF$_6$ in BrF$_5$ solution.

$$\mathrm{KBrF_4O + O_2AsF_6 \rightarrow KAsF_6 + BrF_3O + O_2 + {}^1/_2F_2} \qquad (1)$$

Gillespie and Spekkens[2] dissolved KBrF$_4$O in anhydrous HF

$$\mathrm{KBrF_4O + HF \rightleftarrows KHF_2 + BrF_3O} \qquad (2)$$

and extracted the formed BrF$_3$O with BrF$_5$ at low temperature. Adelhelm and Jacob[7] obtained BrF$_3$O, together with FBrO$_2$, by treatment of a mixture of BrF$_2$OPtF$_6$ and BrO$_2$PtF$_6$ with FNO$_2$.

$$\mathrm{BrF_2OPtF_6 + FNO_2 \rightarrow NO_2PtF_6 + BrF_3O} \qquad (3)$$

$$\mathrm{BrO_2PtF_6 + FNO_2 \rightarrow NO_2PtF_6 + FBrO_2} \qquad (4)$$

All three methods are elaborate and involve several steps and exotic starting materials. The development of a new, simple, one-step synthesis of BrF$_3$O from commerically available starting materials was therefore highly desirable.

Experimental Section

Materials. Commercial LiNO$_3$ (J. T. Baker, 99.7%), NaNO$_3$ (J. T. Baker, 99.5%), KNO$_3$ (J. T. Baker, 99.1%), and RbNO$_3$ (K & K Labs, Inc., 99.9%) were dried in a vacuum oven at 120 °C for one day prior to their use. The CsNO$_3$ was prepared from Cs$_2$CO$_3$ and HNO$_3$ and dried in the same manner. The BrF$_5$ (Matheson) was treated with 35 atm of F$_2$ at 100 °C for 24 h and then purified by fractional condensation through traps kept at −64 and −95 °C, with the material retained at −95 °C being used. BrF$_5$ and BrF$_3$O are powerful oxidizers, and contact with organic materials or moisture must be avoided.

Apparatus. Volatile materials used in this work were handled in a well-passivated (with BrF$_5$ until it was recovered as a white solid at −196

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(1) Bougon, R.; Bui Huy, T.; Charpin, P.; Tantot, G. *C. R. Seances Acad. Sci., Ser. C* **1976**, *283*, 71.

(2) Gillespie, R. J.; Spekkens, P. *J. Chem. Soc., Dalton Trans.* **1976**, 2391.

(3) Christe, K. O.; Wilson, R. D.; Curtis, E. C.; Kuhlmann, W.; Sawodny, W. *Inorg. Chem.* **1978**, *17*, 533.

(4) Appelman, E. H. *Inorg. Chem.* **1969**, *8*, 223.

(5) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1986**, *25*, 1904.

(6) Bougon, R.; Bui Huy, T. *C. R. Seances Acad. Sci., Ser. C* **1976**, *283*, 461.

(7) Adelhelm, M.; Jacob, E. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 461.

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Table I. Reaction Conditions and Yields for the Synthesis of $MBrF_4O$ Salts

M	run no.	reacn temp, °C	reacn time, h	mole ratio BrF_5:MNO_3	conversion of MNO_3 to $MBrF_4O$, %
Cs	1^a	−31	1	4.9	99.8
Rb	2^a	−31	1	5.0	73.2
	3^b	25	1	5.1	98.7
	4^b	25	96	5.1	99.5
K	5^a	−31	1	5.0	34.3
			4		37.1
			5		63.3^c
	6^a	−31	1	15.1	33.5
	7^a	25	1	5.2	37.5
			4		55.6
			5		68.8^c
			6		77.7^d
	8^b	25	20	15.2	99.7^e
	9^b	70	4	15.1	72.1
	10^b	100	20	15.1	99.9
	11^b	100	88	2.9	99.9
Na	12^a	−31	1	5.0	0
	13^b	0	624	15.1	72^f
	14^a	25	67	5.0	53^g

[a] Reactor: 0.75-in-o.d. Teflon–FEP ampule. [b] Reactor: 30-mL stainless-steel cylinder. [c] Sample was reground after 4 h reaction time. [d] Sample was reground after 5 h reaction time. [e] Reactants were subjected to ball-milling during reaction. [f] Volatile products contained 14% free BrF_3O, and solid residue showed the presence of a trace of $NaBrO_2F_2$. [g] Volatile products contained BrF_3O and BrF_3 and solid residue $BrO_2F_2^-$ and BrF_4^- as byproducts.

°C) stainless-steel Teflon–FEP vacuum line.[8] Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed glass tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Phillips camera. DSC measurements were carried out with a Perkin-Elmer Model DSC-1B instrument using crimp-sealed aluminum pans and a heating rate of 10 °C/min.

Preparation of $M^+BrF_4O^-$ (M = Cs, Rb, K, Na). Inside the drybox, a weighed amount (typically about 3 mmol) of MNO_3 was loaded into a prepassivated reactor (either a 30-mL stainless-steel cylinder or a 0.75-in-o.d. Teflon–FEP ampule), which was closed by a valve. The reactor was connected to the vacuum line, and a fivefold excess of BrF_5 was added at −196 °C. The reactor was warmed to a given temperature for a specified period of time with occasional agitation, followed by fractional condensation of the volatile products through a series of two U-traps kept at −142 (BrF_5) and −196 °C (FNO_2). The material balances were determined from the weight gain of the solid residue in the reactor and the amounts of volatiles collected in the cold traps. All materials were identified by vibrational spectroscopy. The reaction conditions and product yields for the various BrF_4O^- salts are summarized in Table I.

Preparation of BrF_3O. Inside the drybox, $LiNO_3$ (2.12 mmol) was loaded into a passivated 30-mL stainless-steel cylinder. On the vacuum line, BrF_5 (31.93 mmol) was added at −196 °C, and the cylinder was stored at 0 °C for 20 days with occasional agitation. The cylinder was reconnected to the vacuum line and cooled to −196 °C and did not contain any material volatile at this temperature. While the cylinder was allowed to slowly warm toward ambient temperature, the volatile material was separated in a dynamic vacuum by fractional condensation through a series of traps kept at −64, −142, and −196 °C. The −64 °C trap contained BrF_3O (2.01 mmol, 95% yield based on $LiNO_3$), the −142 °C trap collected the excess of BrF_5 and a small amount of BrF_3O, and the −196 °C trap retained the FNO_2 (2.05 mmol, 97% yield based on $LiNO_3$). The white, solid residue (about 0.06 g, weight calculated for 2.12 mmol of LiF = 0.055 g) was identified by its X-ray powder pattern as LiF. Its powder pattern and vibrational spectra did not exhibit any lines attributable to either $LiNO_3$ or a BrF_4O^- salt. When the duration of this reaction was shortened to 4 h, the conversion of $LiNO_3$ and the concomitant yield of BrF_3O decreased to 70%.

Results and Discussion

Syntheses of BrF_4O^- Salts and BrF_3O. The reaction of an excess of BrF_5 with the alkali-metal nitrates $CsNO_3$, $RbNO_3$, KNO_3, and $NaNO_3$ proceeds in high yield according to (5). The reactivity of MNO_3 decreases from Cs to Na. Thus, the reaction

$$MNO_3 + BrF_5 \rightarrow MBrF_4O + FNO_2 \qquad (5)$$

of $CsNO_3$ is complete within 1 h at −31 °C (see Table I, run 1). For KNO_3, a 31% conversion to $KBrF_4O$ was obtained under the same conditions (run 5), but thereafter the reaction progressed only very slowly. Because tripling the amount of BrF_5 did not significantly increase the conversion of KNO_3 (run 6) and since the solubility of $KBrF_4O$ in BrF_5 is quite low, coating of the solid KNO_3 phase by product was suspected as the principal cause for the observed falloff in the reaction rates. This suspicion was confirmed. Fine grinding of the product, followed by a second treatment with BrF_5, almost doubled the yield of $KBrF_4O$ (run 5). Complete conversion of KNO_3 to $KBrF_4O$ was achieved at ambient temperature by ball-milling the reagents during the reaction (run 8). Alternatively, complete conversion of KNO_3 to $KBrF_4O$ could be achieved by heating to 100 °C (run 10). Run 11 shows that these reactions do not require a fivefold excess of BrF_5 but also go to completion with lower BrF_5 to metal nitrate ratios.

The reactions of $NaNO_3$ with BrF_5 differed somewhat from those of $CsNO_3$, $RbNO_3$, and KNO_3, which produced exclusively the corresponding BrF_4O^- salts. At a reaction temperature of 0 °C, some free BrF_3O was always isolated in addition to $NaBrF_4O$ (run 13). When the reaction temperature was increased to 25 °C, the solid products contained significant amounts of BrF_4^- and $BrO_2F_2^-$ salts (run 14). The formation of BrF_4^- and $BrO_2F_2^-$ at 25 °C is not surprising. BrF_3O is known[5,6,9] to decompose above 0 °C to $BrF_3 + O_2$, and reaction of BrF_3O with a second mole of $NaNO_3$ can generate BrO_2F. Both BrF_3 and BrO_2F can then react with NaF to give the corresponding anions, as shown in (6)–(10). A rationale for the formation of free BrF_3O in the $NaNO_3$–BrF_5 system will be given below.

$$NaNO_3 + BrF_5 \rightarrow NaF + BrF_3O + FNO_2 \qquad (6)$$

$$NaNO_3 + BrF_3O \rightarrow NaF + BrO_2F + FNO_2 \qquad (7)$$

$$NaF + BrO_2F \rightarrow NaBrO_2F_2 \qquad (8)$$

$$2BrF_3O \rightarrow 2BrF_3 + O_2 \qquad (9)$$

$$NaF + BrF_3 \rightarrow NaBrF_4 \qquad (10)$$

The isolation of some free BrF_3O from the $NaNO_3$–BrF_5 reaction suggested the possibility of preparing BrF_3O in a simple, one-step synthesis from a metal nitrate whose metal fluoride does not form a stable BrF_4O^- salt at 0 °C or below. This concept was verified for $LiNO_3$. When $LiNO_3$ is reacted with an excess of BrF_5 at 0 °C, BrF_3O is formed in essentially quantitative yield according to (11). Ball-milling of the solid reagents during the reaction, as in run 8, might also be advantageous for this system if shorter reaction times are desired.

$$LiNO_3 + BrF_5 \rightarrow LiF + BrF_3O + FNO_2 \qquad (11)$$

When BrF_5 was reacted for 1 h at either −31 or +25 °C with an excess of $CsNO_3$, a quantitative conversion of BrF_5 to $CsBrF_4O$ and FNO_2 was observed. The solid product consisted exclusively of $CsBrF_4O$ and unreacted $CsNO_3$. With an excess of $LiNO_3$, however, the course of the reaction was very different and will be reported in a separate paper.

The above described syntheses of $MBrF_4O$ and BrF_3O offer numerous advantages over the previously used methods. Among

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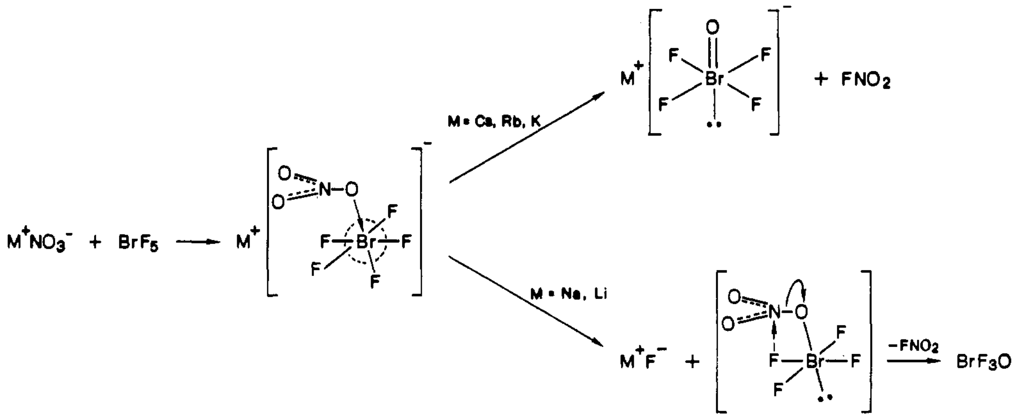
(8) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(9) Gillespie, R. J.; Spekkens, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1539; *Isr. J. Chem.* **1978**, *17*, 11.

Scheme I



(12)

(13)

these are the following: (i) the starting materials, BrF_5 and MNO_3, are commerically available and relatively inexpensive; (ii) the yields are essentially quantitative; (iii) the reactions can be carried out at convenient temperatures and at autogenous pressures; (iv) these syntheses are one-step reactions requiring only simple equipment. In addition to being useful methods for the preparation of $MBrF_4O$ and BrF_3O, these reactions also can be used as a convenient new laboratory method for the preparation of FNO_2 under mild conditions. The yields of FNO_2 are quantitative, and product separation is very easy. The FNO_2 is much more volatile than the other products and can readily be isolated in high purity by either fractional condensation or removal in vacuo at low temperature (BrF_5 stops at −95 °C, whereas FNO_2 still passes through a −142 °C trap but stops at −196 °C).

Some interesting questions concerning the mechanism of the MNO_3–BrF_5 reactions are raised by the following facts. For the $NaNO_3$–BrF_5 system at 0 °C some BrF_3O was obtained as a byproduct besides $NaBrF_4O$, and at 25 °C the formed BrF_3O underwent either fast decomposition to $BrF_3 + O_2$ or further reaction with $NaNO_3$ to BrO_2F, followed by complexing with NaF to form the corresponding sodium salts. In marked contrast to these observations, the heavier alkali-metal salts (K, Rb, and Cs) form, even at reaction temperatures as high as 100 °C, the corresponding $MBrF_4O$ salts in quantitative yield. As shown below, $NaBrF_4O$ is stable up to about 160 °C. Therefore the free BrF_3O could not have formed by decomposition of $NaBrF_4O$, but must have been generated from a less stable intermediate that is capable of generating either $BrF_3O + MF + FNO_2$ or $MBrF_4O + FNO_2$.

A logical candidate for this intermediate is the $[NO_3{\cdot}BrF_5]^-$ polyanion. BrF_5 is well-known to exhibit some Lewis acidity and forms, for example with F^-, an octahedral BrF_6^- anion in which the free valence electron pair on bromine occupies a sterically inactive s orbital.[10] Therefore, the formation of an analogous $[NO_3{\cdot}BrF_5]^-$ anion is quite plausible. Decomposition of the resulting $M^+[NO_3{\cdot}BrF_5]^-$ salt could involve either FNO_2 elimination from the anion resulting in the direct formation of $M^+BrF_4O^-$ (12) or F^- abstraction from the $[NO_3{\cdot}BrF_5]^-$ anion by M^+ followed by FNO_2 elimination from an unstable BrF_4ONO_2 molecule thus producing free BrF_3O (13). Whether (12) or (13) dominates should depend on the F^- ion affinity of M^+ and the thermal stability of $M^+[NO_3{\cdot}BrF_5]^-$. Sodium is expected to form the least stable $M^+[NO_3{\cdot}BrF_5]^-$ salt and therefore should be most prone to decomposition to MF and BrF_4ONO_2. On the basis of these arguments, the mechanism shown in Scheme I is proposed to explain the observed reaction chemistry. For M = Na, dissociation of the intermediate $M^+[NO_3{\cdot}BrF_5]^-$ salt to MF and BrF_4ONO_2 would be faster than intramolecular FNO_2 elimination, while the reverse could be said for M = Cs, Rb, or K.

Attempts were unsuccessful to isolate the proposed $[NO_3{\cdot}BrF_5]^-$ intermediate anion by condensation of BrF_5 onto an excess of $CsNO_3$ at −196 °C, brief warming of the mixture to the melting point of BrF_5 (−60.5 °C), and recooling it to −196 °C. Low-temperature Raman spectra of the resulting product showed only $CsBrF_4O$, FNO_2, and unreacted BrF_5.

Table II. X-ray Powder Data for $RbBrF_4O$[a]

d_{obsd}, Å	d_{calcd}, Å	intens	*hkl*	d_{obsd}, Å	d_{calcd}, Å	intens	*hkl*
7.22	7.214	m	200	2.583	2.582	vw	334
5.34	5.336	m	202	2.427	2.428	w	442
4.61	4.602	w	301	2.351	2.350	m	415
4.38	4.385	w	311		2.346		226
3.95	3.964	vs	004	2.285	2.281	s	620
	3.954		312		2.287		316
3.61	3.607	s	400	2.236	2.231	s	541
3.45	3.454	w	313	2.099	2.099	ms	534
3.276	3.283	w	402	2.050	2.049	ms	307
3.124	3.125	vs	332	1.984	1.982	mw	720
	3.130		224	1.934	1.931	m	516
2.914	2.918	ms	413	1.836	1.837	ms	545
2.860	2.860	ms	333		1.835		651
2.650	2.647	vw	305	1.804	1.804	m	800

[a] Cu Kα radiation and Ni filter; tetragonal; $a = 14.43$ Å, $c = 15.86$ Å, $Z = 32$, $V = 3302$ Å^3, $D_{calcd} = 4.14$ g cm^{-3}.

Table III. X-ray Powder Data for $NaBrF_4O$ and $CsBrF_4O$[a]

$NaBrF_4O$

d_{obsd}, Å	intens	d_{obsd}, Å	intens
5.43	s	2.390	w
5.02	vs	2.302	m
4.40	m	2.255	m
4.01	vs	2.189	m
3.84	vw	2.036	s
3.69	s	1.986	m
3.46	vs	1.945	m
3.312	s	1.868	mw
2.919	vs	1.829	m
2.661	vw	1.797	ms
2.489	w	1.717	ms

$CsBrF_4O$

d_{obsd}, Å	intens	d_{obsd}, Å	intens
4.02	s	2.330	vs, br
3.70	m	2.174	w
3.206	s	2.102	mw
2.976	m	2.004	w
2.516	w	1.981	mw
2.427	mw		

[a] Cu Kα radiation and Ni filter.

Properties of the MBrF₄O Salts. The only previously known BrF_4O^- salts were $KBrF_4O$,[1,2] $CsBrF_4O$,[3] and NF_4BrF_4O.[5] It was therefore of interest to characterize the two new salts, $NaBrF_4O$ and $RbBrF_4O$. All these alkali-metal BrF_4O^- salts are white, stable crystallinic solids. On the basis of DSC data, the onset of thermal decomposition occurs at the following temperatures (°C): $NaBrF_4O$, 161; $KBrF_4O$, 221; $RbBrF_4O$, 226; $CsBrF_4O$, 189. The X-ray powder diffraction patterns were also recorded

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(10) Tantot, G.; Bougon, R. *C. R. Seances Acad. Sci., Ser. C* **1975**, *281*, 271.

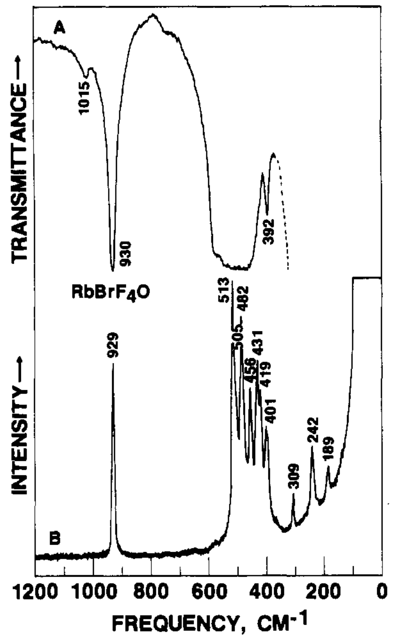

Figure 1. Vibrational spectra of solid $RbBrF_4O$: trace A, infrared spectrum of a sample in an AgCl disk; trace B, Raman spectrum.

Table IV. Vibrational Spectra[a] of $NaBrF_4O$ and $RbBrF_4O$

obsd freq, cm^{-1} (rel intens[b])				
$RbBrF_4O$		$NaBrF_4O$		assignts in point group C_{4v}
IR[c]	Ra	IR[d]	Ra	
1015 vw				$\nu_2 + \nu_7(E)$
930 s	929 (7.0)	943 s	941 (7.0)	$\nu_1(A_1)$, $\nu(BrO)$
	505 sh			
570-450 vs, br	482 (8.7)	590–450 vs, br		$\nu_7(E)$, $\nu_{as}(BrF_4)$
	456 (6)			
	513 (10)		528 (10)	$\nu_2(A_1)$, $\nu_s(BrF_4)$ in phase
	431 (7)		421 (6.7)	$\nu_4(B_1)$, $\nu_s(BrF_4)$ out of phase
420 sh	419 (6)	410 sh		
	401 (4)		405 sh	$\nu_8(E)$, $\delta(OBrF_4)$
392 mw	393 sh			
	309 (1.2)	320 m	303 (0.4)	$\nu_3(A_1)$, $\delta_s(BrF_4)$ out of plane
	242 (2.2)		262 (1.9)	$\nu_6(B_2)$, $\delta_s(BrF_4)$ in plane
	189 (0.9)		172 (1.2)	$\nu_9(E)$, $\delta_{as}(BrF_4)$ in plane

[a] All spectra recorded at ambient temperature. [b] Uncorrected Raman intensities (peak heights). [c] AgCl disk. [d] AgBr disk.

for these salts. It was found that $RbBrF_4O$ is isotypic with $KBrF_4O$, and its diffraction pattern (see Table II) was indexed for a tetragonal cell by analogy to that previously published for $KBrF_4O$.[1] Many of the lines in the powder patterns of $CsBrF_4O$ and $NaBrF_4O$ (see Table III) can be indexed for similar tetragonal cells; however, the correspondence is not as good, and in view of the large unit cells involved, our confidence in such an indexing is low.

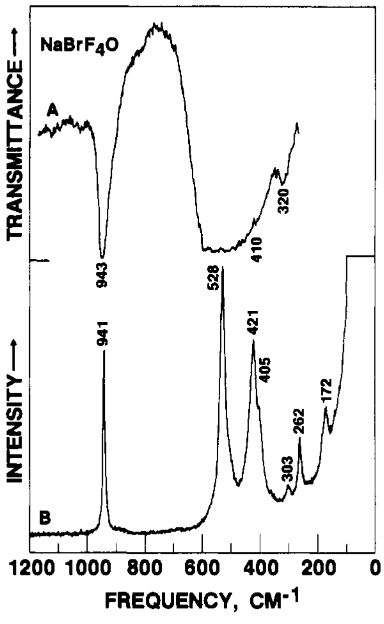

Figure 2. Vibrational spectra of solid $NaBrF_4O$: trace A, infrared spectrum of a sample in an AgBr disk; trace B, Raman spectrum.

The vibrational spectra of BrF_4O^- salts are interesting. For $KBrF_4O$[1] and $CsBrF_4O$[3] numerous splittings of degenerate modes into their components were observed that made assignments[3] difficult. The vibrational spectra of $RbBrF_4O$ (see Figure 1) are similar to those of $CsBrF_4O$ and also exhibit these pronounced splittings. However, the spectra of $NaBrF_4O$ (see Figure 2) are much simpler and therefore can be used to examine the correctness of the previous assignments.[3] As can be seen from Table IV, the Raman spectrum of $NaBrF_4O$ allows unambiguous assignments for ν_1, ν_2, ν_3, ν_4, ν_6, and ν_9. The extra Raman bands in the spectra of $KBrF_4O$,[1] $CsBrF_4O$,[3] and $RbBrF_4O$ are due to splittings of the degenerate E modes into their components, accompanied by significant gains in intensity, and have previously been assigned[3] correctly. The minor frequency differences between $RbBrF_4O$ and $NaBrF_4O$ are normal for salts with different cations and are as expected.

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Registry No. $Cs^+BrF_4O^-$, 65391-03-9; $Rb^+BrF_4O^-$, 106781-97-9; $K^+BrF_4O^-$, 60995-34-8; $Na^+BrF_4O^-$, 106781-98-0; BrF_3O, 61519-37-7; $CsNO_3$, 7789-18-6; $RbNO_3$, 13126-12-0; KNO_3, 7757-79-1; $NaNO_3$, 7631-99-4; BrF_5, 7789-30-2; FNO_2, 10022-50-1; $LiNO_3$, 7790-69-4.