predated and aided in the synthesis of the corresponding $[Fe(SR)_4]^-$ analogues. The structures of $[Ga_2S_2(SR)_4]^{2-}$ and its iron analogue have been analyzed in the context of a general discussion of the geometric parameters of edge-sharing tetrahedral dimers. Many of the structural effects found in iron(III) chalcogenide compounds are also found in the gallium(III) chalcogenide systems. There are some important differences in the observed trends in the lengths of Ga(III)–S and Fe(III)–S bonds. The $Ga{-}S_{av}$ bond lengths in $[GaS_4]$ centers are not greatly affected by the nature of the sulfur ligands; $Ga{-}S_{av}$ distances are approximately the same in $[Ga(SR)_4]^-$, $[(S_b)_2Ga(SR)_2]$, and $[Ga(S_b)_4]$ units. In the case of Fe(III)–S bonds, there is a definite trend such that the $Fe{-}S_{av}$ bond length decreases in the series $[Fe^{III}(SR)_4]$ (2.267–2.30 Å) > $[(S_b)_2Fe(SR)_2]$ (2.25–2.26 Å) > $[Fe^{III}(S_b)_4]$ (2.23 Å). A major feature in the structure of $Fe(III){-}S^{2-}{-}RS^-$ compounds is the strong tendency of Fe(III) to form short bonds to S^{2-}.[69] This tendency is displayed in several ways. The Fe–S bond distances in $[Fe(S_b)_4]$ centers are considerably shorter than Fe–S distances in $[Fe(SR)_4]^-$ compounds. The very short $Fe{-}S_b$ distance in $[Fe_2S_2(SR)_4]^{2-}$ complexes causes a reversal in normal behavior for edge-shared tetrahedra where $M{-}X_b$ is usually longer than $M{-}X_t$. In $[FeS_2Fe]^{2+}$ dimers the Fe–Fe distance is controlled by the $Fe{-}S_b$ bond distance, and the $Fe{-}S_b$ distance can affect (or be affected by) the $Fe{-}X_t$ bonds. Changes in the length of individual Fe–S bonds in an $[Fe^{III}S_4]$ unit in a cluster are counterbalanced by an opposite change in the length of another Fe–S bond in that unit. Detailed molecular orbital calculations of the $[Fe^{III}(SR)_4]^-$ and $[Fe_2S_2(SR)_4]^{2-}$ centers (performed by using the crystallographic values of Fe–S bond distances) have indicated that bridge S–Fe bonding is stronger than terminal S–Fe bonding.[70–72] Quantum mechanical calculations of gallium chalcogenide compounds would be valuable.

Although our analysis has been limited to Fe(III) centers, some of these structural observations will also be found in the structures of mixed-valence Fe–S clusters. For example, our analysis of M–S bond distances gives us a possible explanation of an anomaly that has been found in the structure of iron–sulfur model compounds. The $M{-}S_t$ bonds in $[Fe_2S_2(SR)_4]^{2-}$ (2.312 Å, R = *p*-tol)[21] are longer than the $M{-}S_t$ bonds in $[Fe_4S_4(SR)_4]^{2-}$ (2.263 Å, R = Ph) clusters[73] in spite of the fact that the average oxidation state of the iron atoms in the latter compound is +2.5 while in the former it is +3. This anomaly is removed if one considers all the ligands about each $[FeS_4]$ unit in these complexes. In $[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$ the average of the terminal and bridging Fe–S bonds is 2.257 Å while in $[Fe_4S_4(SPh)_4]^{2-}$ the average Fe–S bond distance is 2.281 Å. In a similar manner, the difference in the Fe–O bonds in $[Fe_4S_4(OPh)_4]^{2-}$ [1.865 (8) Å][74] and $[Fe_2S_2(o,o'\text{-biphenolate})_2]^{2-}$ [1.893 (3) Å][36] and the difference in the Fe–Cl bonds in $[Fe_4S_4Cl_4]^{2-}$ (2.216 Å), and $[Fe_2S_2Cl_4]^{2-}$ (2.252 Å) can be explained.[24]

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Registry No. **1**, 101165-29-1; **2**, 101165-31-5; **3**, 101165-33-7; $(Et_4N)[Ga(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$, 101165-35-9; $(Et_4N)[Ga(SMe)_4]$, 101198-38-3; $(Ph_4P)[Ga(S\text{-}i\text{-}Pr)_4]$, 101165-37-1; $((n\text{-}Pr)_4N)[Ga(S\text{-}i\text{-}Pr)_4]$, 101165-38-2; $(Ph_4P)[Ga(S\text{-}2,4,6\text{-}i\text{-}PrC_6H_2)_4]$, 101165-40-6; $((n\text{-}Pr)_4N)GaCl_4$, 18430-55-2; NH_4GaCl_4, 15636-60-9.

Supplementary Material Available: Tables of hydrogen coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (24 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Notes

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Synthesis and Characterization of $NF_4^+BrF_4^-$ and $NF_4^+BrF_4O^-$

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Received November 13, 1985

Although the NF_4^+ cation is known to form salts with a large variety of anions, such as XF_2^- (X = H), XF_4^- (X = B, Al), XF_5^- (X = Ge, Sn, Ti), XF_6^- (X = P, As, Sb, Bi, Pt, Cr), $X_2F_{11}^-$ (X = Sb, Bi, Pt), XF_6^{2-} (X = Si, Ge, Sn, Ti, Mn, Ni), XF_7^- (X = W, U, Xe), XF_8^{2-} (X = Xe), XF_5O^- (X = W, U), XO_3F^- (X = S), and XO_4^- (X = Cl),[1] no salts are presently known in which the anion is derived from a halogen fluoride or oxyfluoride. Previous attempts[2] have been unsuccessful to prepare and isolate, for example, $NF_4^+XF_4O^-$ (X = Br, Cl), by metathesis according to

$$NF_4SbF_6 + CsXF_4O \xrightarrow{HF}\!\!\!\!\!\!\!/\;\; CsSbF_6\downarrow + NF_4XF_4O \qquad (1)$$

When HF was used as a solvent, solvolysis of $CsXF_4O$ occurred according to

$$CsXF_4O + HF \rightarrow CsHF_2 + XF_3O \qquad (2)$$

For $CsClF_4O$, substitution of HF by BrF_5 also resulted in a displacement reaction:

$$CsClF_4O + BrF_5 \rightarrow CsBrF_6 + ClF_3O \qquad (3)$$

For $CsBrF_4O$ the analogous displacement by BrF_5 was not observed, and the observation of the correct amounts of $CsSbF_6$, NF_3, F_2, and BrF_3O for reaction 1 indicated the possible formation of $NF_4^+BrF_4O^-$ as an unstable intermediate. These results encouraged us to attempt the isolation and characterization of $NF_4^+BrF_4O^-$ and possibly $NF_4^+BrF_4^-$.

Experimental Section

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[1] $CsBrF_4O$,[3] and $CsBrF_4$.[4] The BrF_5 (Matheson) was treated with

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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. These materials 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 ClF_3 and/or BrF_5) stainless-steel Teflon FEP vacuum line.[5] Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. For the transfer of unstable solids, the cold materials were taken into the drybox and handled under a layer of either liquid Ar or liquid N_2 in an aluminum dish placed inside a Styrofoam-brand dish. Metathetical reactions were carried out in BrF_5 solution by using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.[1]

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer by placing the chilled powder between two cold, thin AgCl disks. The resulting AgCl sandwich was held in a liquid-N_2-cooled sample holder of an evacuated low-temperature infrared cell with external CsI windows.[6] The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488-nm exciting line of an Ar ion laser and a Claassen filter[7] for the elimination of plasma lines. Sealed 3-mm-o.d. quartz tubes were used as sample containers in a previously described[8] low-temperature device.

Preparation of $NF_4^+BrF_4O^-$. Inside the drybox, $CsBrF_4O$ (3.06 mmol) and NF_4SbF_6 (3.06 mmol) were loaded into a passivated Teflon FEP double-U-tube metathesis apparatus. On the vacuum line BrF_5 (81.11 mmol) was added at −196 °C. The mixture was allowed to warm to −55 °C and stored in a freezer at this temperature for 8 days with periodic agitation. The cold apparatus was reconnected to the vacuum line, pressurized with 2 atm of dry N_2, and inverted, and the pressure-assisted filtration was carried out at −55 °C. Although the reaction mixture had the appearance of a clear colorless gel with few solid particles in it, a copious white precipitate was collected on the filter. The receiver U-tube was kept at −55 °C, and all volatile material was pumped off through two traps kept at −126 °C (methylcyclohexane slush) and −210 °C (nitrogen slush) for the collection of BrF_5 and NF_3, respectively. After 3 h of pumping, BrF_5 (72.64 mmol) and NF_3 (0.08 mmol) were collected. Pumping was continued for an additional 95 h with periodic measurement of the collected BrF_5 and NF_3 until no more BrF_5 was collected and essentially all of the BrF_5 solvent (81 mmol) had been recovered. The filter was separated from the apparatus, and the filter cake consisted of 1.146 g (weight calculated for 3.06 mmol of $CsSbF_6$ 1.128 g) of a white solid, which based on its Raman spectrum was $CsSbF_6$ containing a trace of $NF_4^+SbF_6^-$. The filtrate residue was identified by low-temperature infrared and Raman spectroscopy as $NF_4^+BrF_4O^-$ contaminated by a trace of SbF_6^- and some BrF_3O.

Preparation of $NF_4^+BrF_4^-$. This preparation was analogous to that of NF_4BrF_4O except for the following modifications. The reaction mixture (NF_4SbF_6 and $CsBrF_4$, 3.02 mmol each in 5 mL of BrF_5) was stored at −55 °C for 4 months before the filtration was carried out at −31 °C. The volatile material was pumped off at −31 °C for 6 h and then at −22 °C for 1 h until no more volatile material was trapped. The filter cake consisted of 1.108 g (weight calculated for 3.02 mmol of $CsSbF_6$ 1.114 g) of a white solid, which based on its Raman spectrum was $CsSbF_6$. The white residue remaining after evaporation of the solvent was identified as $NF_4^+BrF_4^-$ by its low-temperature infrared and Raman spectra and thermal decomposition at 25 °C, which yielded the correct amount of an equimolar mixture of NF_3 and BrF_5.

Results and Discussion

The first examples of NF_4^+ salts with halogen fluoride and halogen oxyfluoride anions were prepared by the following low-temperature metathetical reactions in BrF_5 solution:

$$NF_4SbF_6 + CsBrF_4O \xrightarrow[-55\ °C]{BrF_5} CsSbF_6\downarrow + NF_4BrF_4O \quad (4)$$

$$NF_4SbF_6 + CsBrF_4 \xrightarrow[-31\ °C]{BrF_5} CsSbF_6\downarrow + NF_4BrF_4 \quad (5)$$

Both NF_4^+ salts are white solids that are unstable at room temperature. The NF_4BrF_4O salt is less stable than NF_4BrF_4, as evidenced by the fact that even at −55 °C a very small, but constant and measurable, amount of NF_3 was evolved during removal of the BrF_5 solvent in a dynamic vacuum. This renders the synthesis of NF_4BrF_4O time-consuming (about 90-h pumping time) and requires close temperature control. The NF_4BrF_4 salt is stable at −22 °C, thus permitting a more rapid BrF_5 removal.

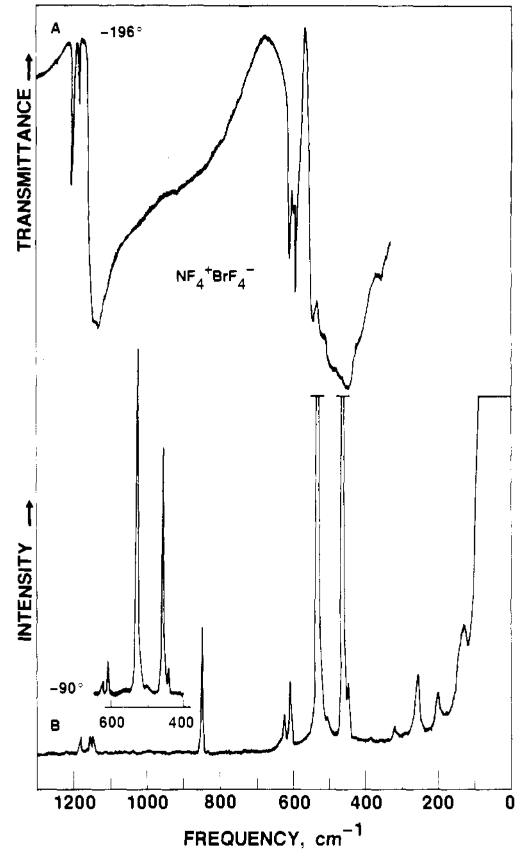

Figure 1. Vibrational spectra of solid NF_4BrF_4: trace A, infrared spectrum; trace B, Raman spectrum recorded at two different sensitivities.

The thermal decomposition of the two solids follows a different path:

$$NF_4BrF_4 \xrightarrow{25\ °C} NF_3 + BrF_5 \quad (6)$$

$$NF_4BrF_4O \xrightarrow{25\ °C} NF_3 + F_2 + BrF_3O \quad (7)$$

Whereas NF_4^+ is a strong enough oxidizer to oxidatively fluorinate BrF_4^- to BrF_5, it is not capable of fluorinating BrF_4O^- to either BrF_5O or BrF_4OF.

The composition of the NF_4BrF_4O and NF_4BrF_4 salts was established by the material balances observed for both the syntheses and decomposition reactions and by low-temperature Raman and infrared spectroscopy. The observed spectra are shown in Figures 1 and 2 and the frequencies and their assignments are summarized in Table I. Since the vibrational spectra of the NF_4^+ cation,[9] the BrF_4O^- anion,[3] and the BrF_4^- anion[4] are well established, the discussion of the above results can be kept brief. In both salts, the degeneracy of the ideally triply degenerate F_2 modes (ν_3 and ν_4) of NF_4^+ is removed and these bands are split into their components. The number of fundamental vibrations and the frequencies observed for the BrF_4^- bands in NF_4BrF_4 agree well with those previously reported for its K^+, Cs^+, and NO^+ salts.[4] However, the BrF_4^- bands in $NF_4^+BrF_4^-$ do not obey the selection rules for a square-planar XY_4 species of point group D_{4h} [A_{1g}(RA) + B_{1g}(RA) + A_{2u}(IR) + B_{2g}(RA) + B_{2u}(inactive) + $2E_u$(IR)], but follow those of point group C_{4v} [$2A_1$(IR,RA) + $2B_1$(RA) + B_2(RA) + 2E(IR,RA)].[4] This strongly suggests that the BrF_4^- anion in NF_4BrF_4 is not square planar but slightly distorted from D_{4h} to C_{4v} symmetry by the influence of the nonspherical NF_4^+ counterions. The bands of BrF_4O^- in NF_4BrF_4O are in good

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Table I. Vibrational Spectra of NF_4BrF_4 and NF_4BrF_4O

obsd freq, cm^{-1}, and rel intens[a]				assignments (point group)		
NF_4BrF_4		NF_4BrF_4O				
IR	RA	IR	RA	NF_4^+ (T_d)	BrF_4^- (C_{4v})	BrF_4O^- (C_{4v})
1220 mw		1220 sh		$2\nu_4$ (A_1 + E + F_2)		
1202 w		1216 mw				
	1182 (0.2)					
1156 sh	1158 (0.2)	1165 s	1165 (0.4)	ν_3 (F_2), ν_{as}		
1147 vs	1149 (0.2)	1149 vs	1152 sh			
		949 s	953 (1.7)			ν_1 (A_1), ν(BrO)
	851 (2.0)		853 (2.7)	ν_1 (A_1), ν_s		
618 mw	622 (0.5)	614 w	614 (2.0)			
608 w	608 (1.0)	608 ms	605 sh	ν_4 (F_2), δ_{as}		
600 m		600 sh				
(550 vw)					?	
530 sh	535 (10)		506 (10)		ν_1 (A_1), ν_s	ν_2 (A_1), ν_s(BrF_4)
500 sh	505 sh	520 sh, br	520 sh		ν_6 (E), ν_{as}	ν_7 (E), ν_{as}(BrF_4)
452 vs		470 vs	470 (0.4)			
430 sh		449 sh	451 (1.4)			
	466 (7.2)	420 vw	427 (7.5)		ν_3 (B_1), ν_s	ν_4 (B_1), ν_s(BrF_4)
	448 (0.8)		451 (3)	ν_2 (E), δ_s		
			402 (0+)			ν_8 (E), δ($OBrF_4$)
		388 w	389 (0.8)			
(363 vw)			352 (0+)		?	?
325 vw	320 (0.2)		304 (0.2)		ν_2 (A_1), δ_s out of plane	ν_3 (A_1), δ_s out of plane
	258 (1.0)		251 (0.7)		ν_5 (B_2), δ_s in plane	ν_6 (B_2), δ_s in plane
			225 (0+)			ν_5 (B_1), δ_{as} out of plane
	202 (0.5)		184 (0.5)		ν_7 (E), δ_{as} in plane	ν_9 (E), δ_{as} in plane
	129 (1.0)			lattice mode		

[a] Uncorrected Raman intensities (peak heights).

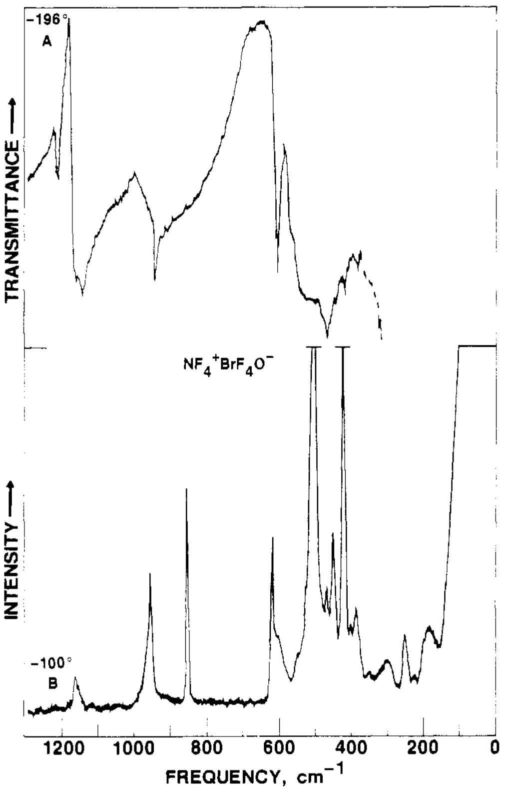

Figure 2. Vibrational spectra of solid NF_4BrF_4O: trace A, infrared spectrum; trace B, Raman spectrum.

agreement with those previously observed for $Cs^+BrF_4O^-$[3] and were assigned correspondingly.

In conclusion, the above results show that the NF_4^+ cation is capable of forming marginally stable salts with certain halogen fluoride or oxyfluoride anions. The synthesis of such salts is difficult and requires the use of a solvent that is (i) sufficiently polar to dissolve ionic salts, (ii) sufficiently volatile to allow solvent removal at low temperature, (iii) stable toward the strongly oxidizing NF_4^+ cation, and (iv) incapable of undergoing a solvolysis reaction with the starting materials. So far, the only solvent known to meet or approximate these requirements is BrF_5.

Acknowledgment. The authors are indebted to C. J. Schack, R. D. Wilson, and L. R. Grant for help and to the Army Research Office and the Office of Naval Research for financial support.

Registry No. $NF_4^+BrF_4O^-$, 101652-54-4; $NF_4^+BrF_4^-$, 101756-83-6; $CsBrF_4O$, 65391-03-9; NF_4SbF_6, 16871-76-4; $CsBrF_4$, 15705-88-1; NF_3, 7783-54-2; BrF_3O, 61519-37-7; F_2, 7782-41-4.

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Photochemical Studies of $[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-COT})]PF_6$ and $[(\eta^5\text{-}C_5R_5)M(\eta^4\text{-1,5-COT})L]PF_6$ Complexes of Iron and Ruthenium

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We have examined the photochemistry of a series of complexes of the form $[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-COT})]PF_6$ and $[(\eta^5\text{-}C_5H_5)M(\eta^4\text{-COT})L]PF_6$ (R = H, CH_3; M = Fe, Ru; COT = cyclooctatetraene; L = CO, $P(OCH_3)_3$) to determine the potential for stepwise COT release through coordinatively unsaturated η^2 and η^4 intermediates. The cyclooctatetraene complexes were chosen because of the documented ability of COT to coordinate in both η^6 and η^4 configurations.[2]

Experimental Section

General Information. The organic solvents used in this study were of spectroscopic grade and were dried over activated alumina or activated 4-Å molecular sieves prior to use. Cyclooctatetraene was purified by passage down a short alumina column. All other reagents were purchased as reagent grade and used as received. UV-vis spectra were obtained on either a Cary 17D spectrophotometer or a Hewlett Packard 8450A spectrophotometer. ^1H NMR were obtained either with a Varian CFT 20 spectrometer equipped with a 79.5-MHz proton accessory or on a Nicolet 300-MHz spectrometer.

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