leads to a black nitride in which the rhenium is tetravalent[1] whereas heating the molybdenum and tungsten compounds above their preparation temperatures gives white products—most likely containing Mo(6) and W(6).

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

The Tetrafluorobromate(III) Anion, BrF_4^-

BY KARL O. CHRISTE AND CARL J. SCHACK

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The NO^+, NO_2^+, K^+, and Cs^+ salts of BrF_4^- have been prepared and characterized. It is shown by vibrational spectroscopy that the BrF_4^- anion is planar and not tetrahedral. The structure and bonding of BrF_4^- is similar to that of the ClF_4^- anion.

Introduction

Bromine trifluoride possesses amphoteric character and forms adducts with strong Lewis bases.[1] Thus, the existence of the salts $K^+BrF_4^-$,[2] $Rb^+BrF_4^-$,[3a] and $NO^+BrF_4^-$ [3b] has previously been reported. Only one attempt was made to establish the structure of the BrF_4^- anion. Siegel reported[4] the X-ray powder pattern of $K^+BrF_4^-$ and concluded on the basis of intensity calculations that BrF_4^- is tetrahedral. Later, Sly and Marsh pointed out[5] that Siegel's data might equally well be interpreted in terms of a square-planar configuration. No further data on the structure of BrF_4^- have been reported, thus leaving the problem unresolved.[6] In the course of a systematic investigation of adducts derived from bromine fluorides, we have also studied a number of BrF_4^--containing salts. In this paper we wish to report the data obtained for $NO^+BrF_4^-$, $K^+BrF_4^-$, $Cs^+BrF_4^-$, and $NO_2^+BrF_4^-$. The preparation of $Cs^+BrF_4^-$ has previously not been reported. Aynsley and coworkers[7] believed they had prepared material containing $NO_2^+BrF_4^-$; however, they did not successfully isolate or characterize the adduct.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise, Bourdon tube-type gauge (0–1500 mm ± 0.1%). Bromine trifluoride (from the Matheson Co.) was purified by fractional condensation, the material retained at −23° being used. It was nearly white as a solid and pale yellow as a liquid. Nitryl fluoride and nitrosyl fluoride (prepared from F_2 and N_2O_4 and NO, respectively) were purified by fractional condensation. The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

For the dissociation pressure measurements the $NO_2F \cdot BrF_3$ complex was prepared in a Teflon FEP U trap directly connected to a Heise gauge. Pressures were read to the nearest millimeter and the temperature of the cooling bath was determined with a copper–constantan thermocouple. Equilibrium pressures were approached from above and below a given temperature. Equilibrium was assumed when the pressure was constant at a given temperature for at least 30 min. The following temperature (°K)–vapor pressure (mm) data were observed: increasing temperature: 259.5, 12; 266.8, 20; 273.2, 35; 278.3, 51; 282.8, 71; 289.8, 121; 294.8, 176; decreasing temperature: 292.9, 163; 283.0, 75; 273.2, 36. The best fit of log P *vs.* T^{-1} was obtained by the method of least squares.

Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper $K\alpha$ radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (~0.3- and ~0.5-mm o.d.).

The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectra were taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP

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[1] L. Stein in "Halogen Chemistry," Vol. 1, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

[2] A. G. Sharpe and H. J. Emeléus, *J. Chem. Soc.*, 2135 (1948).

[3] (a) P. Bouy, *Ann. Chim.* (*Paris*), **4**, 853 (1959); (b) A. Chretien and P. Bouy, *C. R. Acad. Sci.*, **17**, 159 (1958).

[4] S. Siegel, *Acta Crystallogr.*, **9**, 493 (1956).

[5] W. G. Sly and R. E. Marsh, *ibid.*, **10**, 378 (1957).

[6] After completion of this study we have learned about a powder neutron diffraction study on $K^+BrF_4^-$ (A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1936 (1969)) which supports the planar structure suggested in ref 5.

[7] E. E. Aynsley, G. Hetherington, and P. L. Robinson, *J. Chem. Soc.*, 1119 (1954).

gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or clear Kel-F capillaries were used as sample containers. For the Kel-F capillaries the transverse viewing–transverse excitation technique and for the glass tube the axial viewing–transverse excitation technique was used.

Preparation of the Adducts. $K^+BrF_4^-$.—Dry KF (56.54 mmol) was placed into a 95-ml prepassivated Monel cylinder and purified BrF_3 (78.54 mmol) was added. The contents of the cylinder were shaken at 80° for 12 days. Unreacted BrF_3 (21.71 mmol) was removed *in vacuo* at 50°. The cylinder was opened in the glove box and contained a white, crystalline solid. Therefore, KF (56.54 mmol) had reacted with BrF_3 (56.83 mmol) in a mole ratio of 1:1.005 producing the complex $K^+BrF_4^-$.

$Cs^+BrF_4^-$.—CsF (35.56 mmol), when combined with excess of BrF_3 (92.60 mmol) under similar conditions, reacted with BrF_3 (35.98 mmol) in a mole ratio of 1:1.01 producing the complex $Cs^+BrF_4^-$.

$NO^+BrF_4^-$.—Liquid BrF_3 (25.4 mmol) was exposed to excess gaseous NOF (69.8 mmol) in a Teflon FEP U trap at ambient temperature. An exothermic reaction occurred and a white, crystalline solid formed. After completion of the reaction unreacted NOF (43.9 mmol) was removed at 10° *in vacuo*. Therefore, BrF_3 (25.4 mmol) had reacted with NOF (25.9 mmol) in a mole ratio of 1:1.02 producing the complex $NO^+BrF_4^-$.

$NO_2^+BrF_4^-$.—Liquid BrF_3 (5.01 mmol) was exposed to gaseous NO_2F (9.33 mmol) in a Teflon FEP U trap at ambient temperature. The liquid BrF_3 started to react with NO_2F; it became viscous, and, as it was agitated, a white solid began to form. When the NO_2F addition at room temperature became slow, the temperature of the system was lowered gradually over a 1–2-hr period to approximately −45°. An external electric vibrator was used throughout this period to agitate the trap and its contents. This caused large particles to break up and gave continual exposure of new surface to the FNO_2 vapor, finally resulting in the formation of a powdery, white solid. The complex was then cooled to −65° and pumped for 2 hr to remove unreacted NO_2F which was condensed at −196°. The recovered NO_2F (4.29 mmol) indicated that the mole ratio of NO_2F to BrF_3 in the solid formed was 1.006:1.00. The U trap containing the $NO_2^+BrF_4^-$ was warmed to room temperature and weighed. The observed weight of complex was 1.06 g, compared to 1.02 g calculated on the basis of reacted starting materials. Nitryl tetrafluorobromate melts at 27° under autogenous pressure.

SiF_4-Displacement Reaction.—A weighed sample of $NO_2^+BrF_4^-$ (6.14 mmol) was combined with SiF_4 (5.85 mmol) in a Teflon FEP U trap at −196°. The mixture was allowed to warm up to room temperature under agitation. After 18 hr the contents of the trap were cooled to −78° and unreacted SiF_4 (2.88 mmol) was removed *in vacuo* and identified by infrared spectroscopy. The observed SiF_4 consumption was 96.7% of theoretical. Complete separation of the BrF_3 and $(NO_2^+)_2SiF_6^{2-}$ could not be achieved as some of the latter was always pumped away with the BrF_3. The solid left after the displacement reaction was identified as $(NO_2^+)_2SiF_6^{2-}$ by comparison of its infrared spectrum with that of a known sample of $(NO_2^+)_2SiF_6^{2-}$.

Results and Discussion

Syntheses and Properties.—Bromine trifluoride and KF, CsF, NOF, or NO_2F, when combined, produce the 1:1 adducts $K^+BrF_4^-$, $Cs^+BrF_4^-$, $NO^+BrF_4^-$, and $NO_2^+BrF_4^-$, respectively. The syntheses of the two known adducts, $NO^+BrF_4^-$ and $K^+BrF_4^-$, were similar to those reported[3a,8] previously. The $NO^+BrF_4^-$ complex was found to have a dissociation pressure of 2 mm at 24.8° which agrees with the qualitative observation made by Chretien and Bouy[3b] that $NO^+BrF_4^-$ can be sublimed at about 100° in a nitrogen current. Single crystals of $NO^+BrF_4^-$ can be easily grown by sublimation at ambient temperature. The results of a single-crystal X-ray study on $NO^+BrF_4^-$ will be published elsewhere.[9] For the stable, white, crystalline $K^+BrF_4^-$ adduct, an X-ray powder pattern was obtained which was identical with that reported previously.[4] The $Cs^+BrF_4^-$ complex is a white, crystalline solid, completely stable at ambient temperature as expected by comparison with the stabilities reported for the known BrF_4^- salts. The Debye–Scherrer powder pattern shows no similarity to that of $K^+BrF_4^-$ but contains many more lines indicating a crystal symmetry lower than that of tetragonal $K^+BrF_4^-$,[4] $Rb^+BrF_4^-$,[3a] and $NO^+BrF_4^-$.[3] This change in the crystal symmetry is most likely due to the increased size of the cation. The $NO_2^+BrF_4^-$ adduct had previously been neither isolated nor characterized but was believed to have been prepared in a BrF_3 suspension.[7] In the present study a well-characterized 1:1 adduct was isolated and its thermal stability was measured. The interpretation of the measured dissociation pressure–temperature relation is complicated by the fact that in addition to highly volatile NO_2F, solid or liquid BrF_3 is formed. Consequently, the following data must be considered as an approximation neglecting the solubility of NO_2F in BrF_3 and the enthalpy of sublimation or vaporization of BrF_3. The calculated data are based on the process: $NO_2^+BrF_4^-(s) = NO_2F(g) + BrF_3(g)$.

The observed vapor pressures were corrected for the known[10] vapor pressures of pure BrF_3 and then doubled in order to obtain the thermodynamic data for the above given *hypothetical*[11] process. The plot of log P_{mm} *vs.* T^{-1} (in °K) for this process was a straight line following the equation $\log P_{mm} = 11.0208 - (2508.9/T)$. The standard error of the estimate of log P was 0.019 which corresponds to 4.6% deviation in pressure. The index of correlation (ζ) is 0.9986. The fact that the points measured with decreasing temperature fitted well on the plot indicates that equilibrium was very nearly achieved. From the van't Hoff equation, $\Delta H_d°$[12] = 22.96 kcal mol^{-1} was found. From $\Delta F°_T = -RT \ln Kp$ (atm), a free energy change, $\Delta F°_{298} = 1.594$ kcal mol^{-1}, and from $\Delta S°_T = (\Delta H° - \Delta F°_T)T^{-1}$,

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(8) I. Sheft, A. F. Martin, and J. J. Katz, *J. Amer. Chem. Soc.*, **78**, 1557 (1956).

(9) D. Lind and K. O. Christe, to be submitted for publication.

(10) G. D. Oliver and J. W. Grisard, *J. Amer. Chem. Soc.*, **74**, 2705 (1952).

(11) The authors are indebted to an unknown referee for suggesting the above given treatment of the thermodynamic data. The actually observed vapor pressure–temperature relation is described by the equation: $\log P_{mm} = 10.9018 - (2553.8/T)$.

(12) It is not strictly correct to infer that the calculated heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, $\Delta H_d°$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.

an entropy change, $\Delta S°_{298}$ = 71.67 cal deg^{-1} mol^{-1}, were found for the hypothetical dissociation process at 25°. A heat of formation of $NO_2{}^+BrF_4{}^-(s)$, $\Delta H_f°_{298}$ = −103.1 kcal mol^{-1}, was calculated based upon $\Delta H_f°_{298}[NO_2F(g)]^{13}$ = −19 ± 2 kcal mol^{-1} and $\Delta H_f°_{298}[BrF_3(g)]^{13}$ = −61.1 kcal mol^{-1}. The heat of dissociation,[12] 22.96 kcal mol^{-1}, obtained for $NO_2{}^+BrF_4{}^-$ is of the same order of magnitude as the values obtained for the similar adducts, $NO^+ClF_2{}^-$ (15.5 kcal mol^{-1})[14] and $NO^+ClF_4{}^-$ (15.8 kcal mol^{-1}).[15]

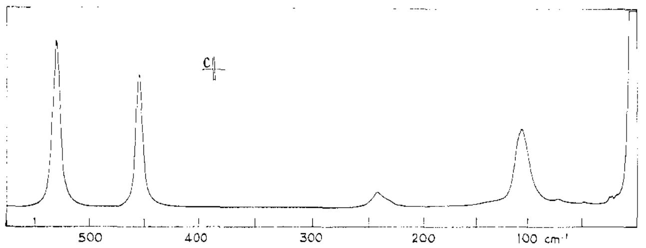

Figure 1.—Raman spectrum of solid $K^+BrF_4{}^-$. Sample container: glass tube with hollow inside glass cone. Exciting line 5145 Å; axial viewing–transverse excitation technique. C indicates spectral slit width.

The statement made by Aynsley, *et al.*,[7] that the $NO_2F–BrF_3$ interaction resulted in the formation of a yellow color due to the $NO_2{}^+$ ion, could not be confirmed. In our experiments, no appreciable change in the pale yellow color of the pure BrF_3 was noted on the addition of NO_2F, and the final product, solid $NO_2{}^+BrF_4{}^-$, was completely colorless.

Silicon tetrafluoride, being a stronger Lewis acid than amphoteric BrF_3, successfully displaced BrF_3 in $NO_2{}^+BrF_4{}^-$ according to: $2NO_2{}^+BrF_4{}^- + SiF_4 \rightarrow (NO_2{}^+)_2SiF_6{}^{2-} + 2BrF_3$.

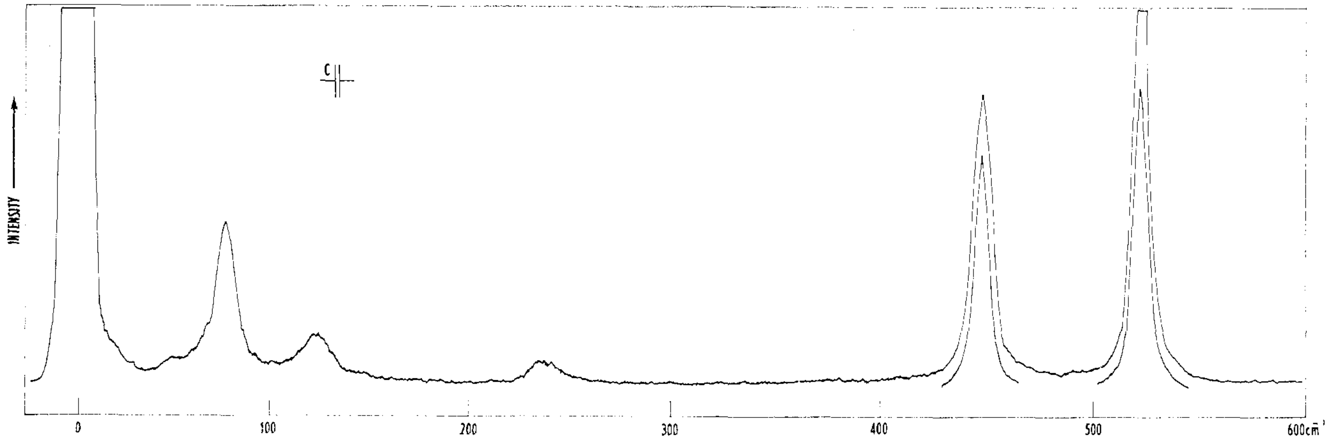

Figure 2.—Raman spectrum of solid $Cs^+BrF_4{}^-$, recorded under the same conditions as that of $K^+BrF_4{}^-$.

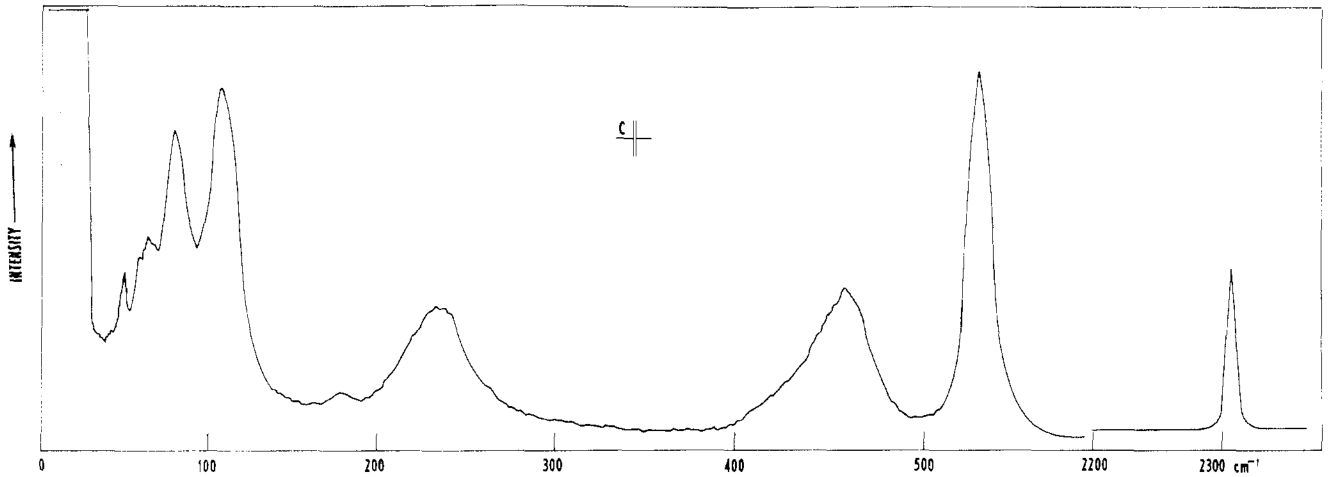

Figure 3.—Raman spectrum of solid $NO^+BrF_4{}^-$. Sample tube: Kel F capillary. Exciting line 5145 Å; transverse viewing–transverse excitation technique.

Vibrational Spectra.—Figures 1–3 show the Raman spectra of solid $K^+BrF_4{}^-$, $Cs^+BrF_4{}^-$, and $NO^+BrF_4{}^-$, respectively. Figures 4–6 show the corresponding infrared spectra. The observed frequencies are listed in Table I. Whereas the Raman spectra are of very good quality, the infrared spectra of the dry powders showed only one broad absorption in the range 400–

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(13) "JANAF Interim Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1961.

(14) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 905 (1965).

(15) E. D. Whitney, R. O. MacLaren, T. J. Hurley, and C. E. Fogle, *J. Amer. Chem. Soc.*, **86**, 4340 (1964).

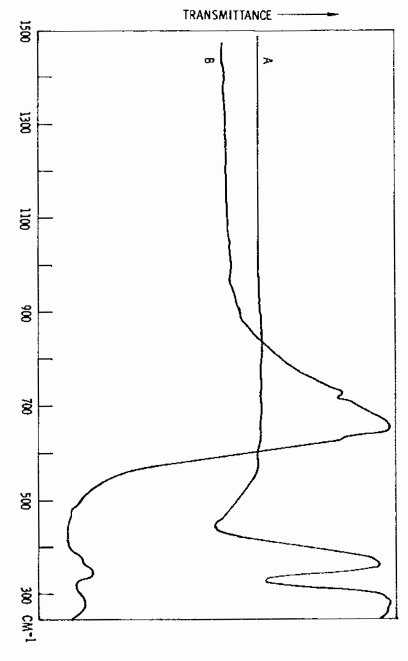

Figure 4.—Infrared spectrum of solid $K^+BrF_4^-$ (trace A as AgBr disk; trace B as dry powder between AgBr plates).

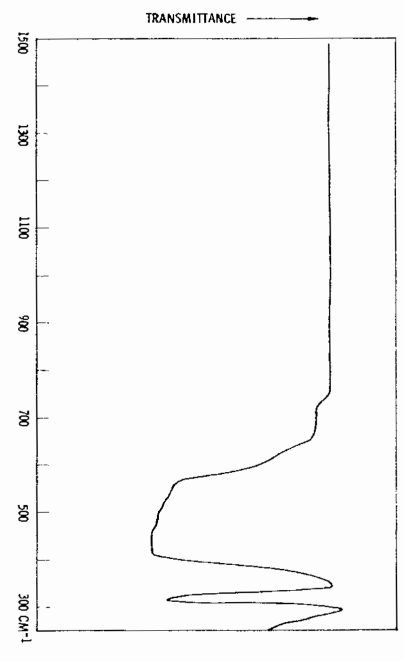

Figure 5.—Infrared spectrum of solid $Cs^+BrF_4^-$ as dry powder in a AgBr disk.

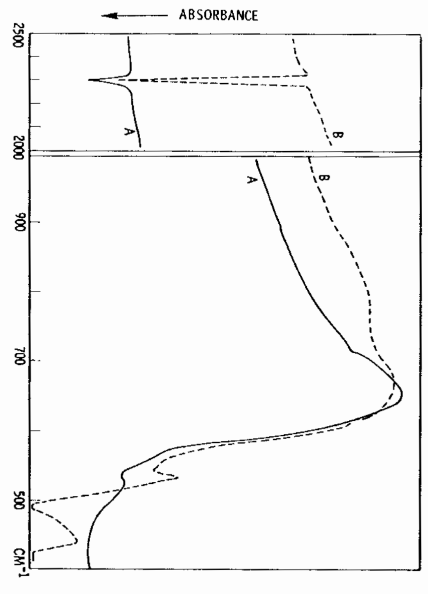

Figure 6.—Infrared spectrum of solid $NO^+BrF_4^-$ (trace A dry powder between AgCl plates; trace B low-temperature film on AgCl).

580 cm^{-1}. This is consistent with our general experience with complex fluorides of the type XF_4^-, XF_5^-, and XF_4O^- containing an approximately square-planar XF_4 group. The broad infrared absorption occurs at different frequencies for different adducts and, hence, is most likely due to the samples and not due to the sampling or recording technique. Consequently, more weight will be given to the Raman than to the infrared spectra.

The following conclusions can be drawn from the vibrational spectra. (i) The 1:1 adducts $NO_2F \cdot BrF_3$ and $NOF \cdot BrF_3$ have the ionic structures NO_2^+-

TABLE I

VIBRATIONAL SPECTRA OF $K^+BrF_4^-$, $Cs^+BrF_4^-$, AND $NO^+BrF_4^-$ AND THEIR ASSIGNMENT COMPARED TO THOSE OF ISOELECTRONIC ClF_4^- AND THOSE OF THE APPROXIMATELY SQUARE-PLANAR PART OF BrF_5 AND SeF_5^-

Obsd freq, cm^{-1}															
$K^+BrF_4^-$		$Cs^+BrF_4^-$		$NO^+BrF_4^-$			SeF_5^- [a]		BrF_5 [b]		$Cs^+ClF_4^-$ [c]		Assignment in point group D_{4h}	Approx description of vibration
				Ir										
Ir	Raman	Ir	Raman	Low temp film	Amb temp powder	Raman	Ir	Raman	Ir	Raman	Ir	Raman		
				2303 s	2300 s	2309 (3.1)								$\nu(NO^+)$
722 vw		720 vw											$\nu_1 + \nu_7$ (E_u)	Combination
640 vw		640 vw											$\nu_4 + \nu_7$ (E_u)	Combination
410–580 vs, br		410–580 vs, br		542 s 488 vs	420–570 vs, br		475 vs, br	480 sh	644 vs	. . .	500–680 vs, br		ν_6 (E_u)	$\nu_{as}(XF_4)$
	531 (10)		523 (10)			527 (10)	520 sh	515 (7.5)	587 m	570 (10)		505 (10)	ν_1 (A_{1g})	$\nu_s(XF_4)$ in phase
	454 (7.9)		449 (7.9)			461 (4)		460 (7.0)		535 (10)		417 (9)	ν_4 (B_{2g})	$\nu_s(XF_4)$ out of phase
325 s		317 s					335 s	332 (3.2)	369 s	365 (2)	425 m		ν_2 (A_{2u})	$\delta_s(XF_4)$ out of plane
	242 (0.9)		246 (0.7)			235 (3)		282 (2.6)		312 (1)		288 (0+)	ν_3 (B_{1g})	$\delta_s(XF_4)$ in plane
[188] [d]		[194] [d]				183 (0.4)		202 (0.7)		237 (0+)			ν_7 (E_u)	$\delta_{as}(XF_4)$ in plane

[a] K. O. Christe, C. J. Schack, and E. C. Curtis, to be submitted for publication. [b] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965). [c] K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **357**, 125 (1968); *ibid.*, in press. [d] Estimated from combination bands.

BrF_4^- and $NO^+BrF_4^-$, respectively. Their spectra show in addition to the bands in the Br–F region the characteristic NO^+ [16,17] and NO_2^+ [18,19] stretching vibrations at 2300 and 2384 cm^{-1}, respectively. Comparison with the low-temperature spectra of solid NOF[17] and BrF_3[20] shows the absence of any unreacted starting materials in the low-temperature infrared spectrum of $NO^+BrF_4^-$. Furthermore, the low-temperature infrared spectrum of $NO^+BrF_4^-$ strongly resembles that of $NO^+ClF_4^-$ [17] disregarding the expected frequency shifts. Additional proof for the ionic formulation, $NO^+BrF_4^-$, can be derived from the similar crystal structures found for $NOF \cdot BrF_3$ and ionic $K^+BrF_4^-$.[4] (ii) The BrF_4^- anion in $K^+BrF_4^-$ and $Cs^+BrF_4^-$ is planar. It has previously been shown[4] that $K^+BrF_4^-$ is ionic; however, no distinction between the tetrahedral[4] and the square-planar[5] configuration could be made for BrF_4^- based upon the available X-ray data. Since our Debye–Scherrer pattern of $K^+BrF_4^-$ is identical with that reported previously[4] and since our Raman spectrum is of good quality, distinction between the tetrahedral and a planar configuration should be possible. Table II lists the total number of fundamentals and their activity in the infrared and Raman spectra for the various symmetries possible for an XF_4^- anion. Since in the Raman spectra of $Cs^+BrF_4^-$ and $K^+BrF_4^-$ only three bands were observed in the region of the fundamental vibrations (the bands occurring below 120 cm^{-1} are assigned to lattice vibrations), BrF_4^- should belong to either point group D_{4h} or D_{2h}. In both cases BrF_4^- is planar and has a symmetry center. For D_{4h} the four fluorine atoms form a square; for D_{2h}, a rectangle. However, even if the actually observed symmetry is D_{2h}, the isolated BrF_4^- anion could have symmetry D_{4h} but the site symmetry in the crystal might be only D_{2h} as indicated by the symmetry mmm suggested by Sly and Marsh[5] for the bromine atoms in $K^+BrF_4^-$. (iii) The Raman spectrum of $NO^+BrF_4^-$ resembles those of $Cs^+BrF_4^-$ and $K^+BrF_4^-$; however, the relative intensities of the bands have changed somewhat, the band at 461 cm^{-1} has broadened and has possibly a shoulder at about 425 cm^{-1}. Furthermore, the spectrum shows an additional band of very low intensity at 183 cm^{-1}. These changes might be due to the fact that the NO^+ cation is not spherical which may cause slight distortion of the BrF_4^- anion. However, the changes should be minor since $NO^+BrF_4^-$ and $K^+BrF_4^-$ have very similar unit cell dimensions.[3b] It is noteworthy that $K^+BrF_4^-$ and $Cs^+BrF_4^-$ have nearly identical vibrational spectra but different crystal structures, whereas $K^+BrF_4^-$ and $NO^+BrF_4^-$ have tetragonal unit cells of very similar dimensions but show differences in the vibrational spectra.

TABLE II

NUMBER OF FUNDAMENTALS EXPECTED FOR BrF_4^- IN VARIOUS POINT GROUPS AND THEIR INFRARED AND RAMAN ACTIVITY

Point group	Total no. of fundamentals	Raman active	Ir active	No. of coincidences
T_d	4	4	2	2
D_{4h}	7	3	3	0
C_{4v}	7	7	4	4
D_{2h}	9	3	6	0
C_{2v}	9	9	8	8
C_1	9	9	9	9

Assignments for BrF_4^- in point group D_{4h} are shown in Table I and are based on the following considerations. The presence of only three Raman bands above 120 cm^{-1} and the fact that the sharp, intense ir band at about 320 cm^{-1} in $K^+BrF_4^-$ and $Cs^+BrF_4^-$ is Raman inactive indicate symmetry D_{4h} or D_{2h}. For symmetry D_{4h} the seven normal modes of vibration are classified as $A_{1g} + A_{2u} + B_{1g} + B_{2g} + 2\,E_u$. Of these, only the three A_{1g}, B_{1g}, and B_{2g} modes will be Raman active, whereas the A_{2u} and the two E_u modes will be infrared active. The B_{1u} mode is inactive in both the infrared and Raman spectra. If the symmetry of BrF_4^- is lowered from D_{4h} to D_{2h}, the two doubly degenerate E_u modes will split into their components and the B_{1u} mode should become infrared active. Hence only the infrared spectra could distinguish between D_{4h} and D_{2h}. Unfortunately, for $K^+BrF_4^-$ and $Cs^+BrF_4^-$ this distinction is not possible. The B_{1u} mode is expected to be of very low intensity, the E_u stretching mode is in the range of the broad unresolved band between 410 and 580 cm^{-1}, and the E_u deformation mode occurs below 250 cm^{-1}. We have preferred D_{4h} over D_{2h} since it simplifies the force constant calculations and since the possible lowering of the symmetry from D_{4h} to D_{2h} might be due exclusively to a lower site symmetry and not due to distortion of the square plane. The assignment of the three Raman-active bands to the A_{1g}, B_{1g}, and B_{2g} modes presents no difficulty. Of the infrared bands the strong band at about 320 cm^{-1} should belong to the A_{2u} mode; whereas the strong broad absorption between 410 and 580 cm^{-1} should contain the E_u stretching mode. By comparison with the spectra of BrF_5[21] and SeF_5^- [22] (see Table I), both of which contain an approximately square-planar XF_4 group, the E_u deformation mode should occur between 150 and 200 cm^{-1}. It was not directly observed; however, there are two weak combination bands in the infrared spectra at about 720 and 640 cm^{-1} which can be assigned to $\nu_1 + \nu_7$ (E_u) and $\nu_4 + \nu_7$ (E_u), respectively. The frequency value thus obtained for ν_7 (E_u) coincides with the very weak band at 183 cm^{-1} observed in the Raman spectrum of $NO^+BrF_4^-$ and hence is tentatively assigned to ν_7 (E_u). In the low-temperature infrared spectrum of $NO^+BrF_4^-$ two bands were observed in the range of ν_6 (E_u) at 542 and 488 cm^{-1} in agreement with the splitting expected for this doubly degenerate mode upon lowering of the symmetry from D_{4h} to D_{2h}. A more detailed discussion of the ν_6 (E_u) fre-

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(16) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

(17) K. O. Christe and J. P. Guertin, *ibid.*, **5**, 473 (1966).

(18) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *ibid.*, **3**, 857 (1964).

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quency value will be given in the force constants section. Comparison of the observed frequencies with those of the approximately square-planar XF_4 part of BrF_5[21] and SeF_5^-[22] shows excellent agreement thus lending additional support to our assignment. The frequencies of the deformation modes show a slight increase from BrF_4^- to SeF_5^- to BrF_5. This order is expected since the size of the central atom should decrease with increasing oxidation state (BrF_4^- (+III), SeF_5^- (+IV), and BrF_5 (+V). Similarly, comparison between isoelectronic BrF_4^- and ClF_4^-[23,24] (see Table I) shows that the Raman-active stretching modes in BrF_4^- have a slightly higher frequency and the deformation mode has a slightly lower frequency than those in ClF_4^-. This can be expected by comparison with the trends observed for the series ClF_5, BrF_5, and IF_5.[21] This trend is due to the fact that the central atom does not move in these modes, and, hence, the mass effect of the central atom does not influence these frequencies. The increasing size of the central atom, however, will make deformations of the ion easier and thus lower the frequencies of the deformation modes.

Force Constants.—Table III shows the force constants obtained for BrF_4^-. The computation of force constants for BrF_4^- presented no difficulties, since there is only one normal mode in each species except for E_u. In species E_u there are only two modes. Their frequencies are sufficiently different and the mass of the central atom is large enough that the stretch–bend interaction constant, F_{67}, can be neglected.

TABLE III
SYMMETRY FORCE CONSTANTS (MYDYN/Å) OF BrF_4^-

Symmetry species	Obsd freq, cm^{-1}	Symmetry force constants
A_{1g}	ν_1 523	$F_{11} = f_r + 2f_{rr} + f_{rr'} = 3.06$
A_{2u}	ν_2 317	$F_{22} = f_\gamma = 0.577$
B_{1g}	ν_3 246	$F_{33} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'} = 0.169$
B_{2g}	ν_4 449	$F_{44} = f_r - 2f_{rr} + f_{rr'} = 2.258$
E_u	ν_6 542	$F_{66} = f_r - f_{rr'} = 2.198$
	ν_7 183	$F_{67} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'}) \equiv 0$
		$F_{77} = f_\alpha = f_{\alpha\alpha'} = 0.143$

TABLE IV
FORCE CONSTANTS (MYDYN/Å) OF SPECIES E_u OF BrF_4^-

ν_6, cm^{-1}	ν_7, cm^{-1}	F_{66}	F_{77}	f_r	f_{rr}	$f_{rr'}$
542	183	2.198	0.143	2.43	0.20	0.23
515	183	1.980	0.144	2.32	0.20	0.34
488	183	1.772	0.145	2.22	0.20	0.44
488	100	1.798	0.0426			
488	150	1.785	0.0964			
488	200	1.763	0.174			
488	250	1.730	0.277			
488	300	1.660	0.415			

TABLE V
INTERNAL FORCE CONSTANTS (MDYN/Å) OF
BrF_4^-, BrF_5, ClF_4^-, AND ClF_5

	BrF_5[a]	ClF_5[a]	BrF_4^-	ClF_4^-[b]
f_r	3.19	2.57	2.38	2.11
f_{rr}	0.11	0.17	0.20	0.23
$f_{rr'}$	0.23	0.33	0.28	0.29
f_γ	...	...	0.58	0.63
$f_\alpha - f_{\alpha\alpha'}$	0.25	0.38	0.14	0.15–0.24
$f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$	0.25	0.38	0.17	0.23

[a] See ref 21. [b] See ref 24.

Since the force constant of greatest interest is the stretching force constant and since the assignment of ν_7 is only tentative, we have computed F_{66} varying ν_7 between 100 and 300 cm^{-1} at 50-cm^{-1} intervals. As can be seen from Table IV a change of ν_7 by ±50 cm^{-1} would hardly influence the value of F_{66}. Since it is difficult precisely to locate the frequency of ν_6 from the broad infrared band, we have also computed the E_u block assuming ν_6 equal to 488, 515, and 542 cm^{-1} corresponding to the lower, the average, and the higher frequency value, respectively, of the two bands observed in the low-temperature infrared spectrum of $NO^+BrF_4^-$. The value of the interaction constant $f_{rr'}$ is very sensitive to changes in ν_6 (see Table IV) and, hence, might be useful in narrowing down the choice for the frequency value of ν_6. By comparison with the known force constants of BrF_5,[21] ClF_5,[21,23] and ClF_4^-[23,24] (see Table V) a value of 0.23 mdyn/Å appears preferable and a value of 0.34 mdyn/Å acceptable for BrF_4^-. Due to this uncertainty in ν_6 we suggest a value of 2.38 ± 0.06 for f_r and of 0.28 ± 0.05 for $f_{rr'}$ of BrF_4^-. If the symmetry of BrF_4^- should actually be D_{2h} instead of the assumed D_{4h}, the geometry of BrF_4^- should approximate that of a square plane and the force constants should be similar to those given above.

The force constants of BrF_4^- compare favorably with those of ClF_4^-,[24] BrF_5,[21] and ClF_5[21,23] (see Table V). The good agreement between the force constants of BrF_4^- and ClF_4^- indicates that the bonding in these two ions is similar. Consequently, a semiempirical molecular orbital model is most likely for BrF_4^- (for reasons analogous to those previously discussed for ClF_4^-[23]) involving mainly two delocalized p-electron pairs of the bromine central atom for the formation of two semiionic three-center four-electron p–σ bond pairs. Comparison of the stretching force constants, f_r, and bond distances, r, in BrF_4^- and BrF_2^+[20,25] demonstrates the different nature of bonding in these two ions. The value of f_r in BrF_2^+ (4.60 mdyn/Å)[20] is about twice that found for BrF_4^- (2.38 mdyn/Å). This marked difference in the values of f_r can be used to distinguish between semiionic 3c–4e and mainly covalent bonds[26] and agrees well with the observed bond distances ($r_{BrF_2^+}$ = 1.69 Å,[25] $r_{BrF_4^-}$ = 1.89 Å[5,6]) which generally show a close correlation with the f_r values. The fact that the value of f_r in BrF_4^- has decreased somewhat when compared to that of BrF_5 is due to the formal negative charge and the lower oxidation state of the central atom in BrF_4^-.

The planar structure of BrF_4^- as evidenced by the above given data is not unexpected. The BrF_4^- anion possesses two free-electron pairs which almost certainly are sterically active, thus eliminating the possi-

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bility of a tetrahedral structure. Furthermore, structural investigations on the isoelectronic species ICl_4^-,[27] ClF_4^-,[23,24] and XeF_4[28] have shown that all of them are planar and not tetrahedral.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

Redetermination of the Crystal Structure of Tris(ethylenediamine)copper(II) Sulfate, $Cu(NH_2CH_2CH_2NH_2)_3SO_4$

BY DAVID L. CULLEN AND E. C. LINGAFELTER

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The structure of tris(ethylenediamine)copper(II) sulfate, $Cu(NH_2CH_2CH_2NH_2)_3SO_4$, has been redetermined using full three-dimensional X-ray diffraction data and anisotropic thermal parameters. The compound crystallizes in the trigonal space group $P\bar{3}1c$ with hexagonal cell dimensions $a_0 = b_0 = 8.966$ (1) Å and $c_0 = 9.597$ (1) Å. The observed density is 1.69 (1) g/cm³, while the calculated density is 1.688 g/cm³ for two molecules in the unit cell. Intensities of 513 independent reflections were measured on a Picker automated four-circle diffractometer. Of these, 29 were considered as unobserved. The structure was refined by full-matrix least squares to a final conventional R factor of 0.034. The complex is isostructural with $Ni(en)_3SO_4$. The copper and sulfur atoms are located at positions of 32 (D_3) symmetry. This site symmetry for the copper atom is in apparent violation of the Jahn–Teller theorem. There is some evidence for the existence of a dynamic Jahn–Teller effect, since the thermal parameters are larger than those in $Ni(en)_3SO_4$ but this difference is small, making it difficult to draw any definite conclusion about the existence of such an effect. The Cu–N, N–C, and C–C bond lengths are 2.150 (2), 1.472 (5), and 1.507 (5) Å, respectively. The oxygen atoms of the sulfate ion are disordered and the apparent SO_4^{2-} tetrahedron is somewhat distorted. The O–S–O angles range from 100 to 119°, while the S–O bond distances range from 1.46 to 1.50 Å.

Introduction

In virtually all six-coordinate copper(II) complexes, the coordination octahedron is distorted, generally having two apical bonds much longer than the four equatorial bonds. This distortion is generally explained by the Jahn–Teller theorem.[1] However several esr studies have shown examples of octahedral (or presumably octahedral) complexes which have isotropic spectra.[2-4] In addition three X-ray structure determinations of copper(II) compounds have been reported, in which the symmetry of the copper coordination polyhedron is higher than allowed by the Jahn–Teller theorem. Two of these, potassium lead hexanitrocuprate(II)[5,6] and tris(ethylenediamine)copper(II) sulfate, $Cu(en)_3SO_4$[7] (en = $NH_2CH_2CH_2NH_2$) were carried out using two-dimensional methods and assuming overall isotropic temperature factors. Three-dimensional methods and anisotropic thermal parameters were used in the structure determination of the third example, tris(octamethylpyrophosphoramide)-copper(II) perchlorate, $Cu(OMPA)_3(ClO_4)_2$, which has only recently been reported.[8] A neutron diffraction study has also been recently completed on $K_2PbCu(NO_2)_6$.[9]

The two most general proposals that have been advanced to explain these apparent violations of the Jahn–Teller theorem follow. (1) The complex is oscillating among three equivalent (*e.g.*, tetragonal) distortions so that on a time average the structure appears regular. This is called the dynamic Jahn–Teller effect.[10] (2) Each molecule is trapped in one of several such distortions. Molecules in each of these distortions are distributed at random throughout the crystal, so that on a space average, the structure appears regular.

In most modern X-ray structure determinations, the average of the thermal motion of an atom is approximated by an ellipsoid. If either of the effects postulated above is present, the apparent thermal motion of the atom should be increased. In addition it might be

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