Journal of Fluorine Chemistry, *27* (1985) 249–256

Received July 2, 1984, accepted July 20, 1984

COMPLEXES OF CESIUM AND RUBIDIUM FLUORIDES WITH BROMINE TRIFLUORIDE

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SUMMARY

Vibrational spectra are reported for the new complexes $CsF{\cdot}3BrF_3$, $RbF{\cdot}3BrF_3$, and $RbF{\cdot}2BrF_3$ and the previously known complex $CsF{\cdot}2BrF_3$. The spectra suggest that these compounds are salts having general formulas $M^+Br_3F_{10}^-$ and $M^+Br_2F_7^-$.

INTRODUCTION

Emeléus and co-workers [1-3] have shown that lithium fluoride forms no adduct with bromine trifluoride and that sodium and potassium fluorides form the adducts $NaBrF_4$ and $KBrF_4$. Other workers [4-6] have shown that rubidium and cesium fluorides form the corresponding adducts $RbBrF_4$ and $CsBrF_4$. Recently, we have found that rubidium and cesium fluorides also form the higher complexes $RbF{\cdot}3BrF_3$ and $CsF{\cdot}3BrF_3$, from which $RbF{\cdot}2BrF_3$ (in mixtures with other phases) and $CsF{\cdot}2BrF_3$ can be derived. Thus it is apparent that the size of the alkali metal atom plays an important role in determining the maximum degree of complexation by bromine trifluoride. In this article, we report methods of preparation and vibrational spectra of the 1:3 and 1:2 adducts. The 1:3 adducts are analogous to $RbF{\cdot}3IF_5$ and $CsF{\cdot}3IF_5$, which have been prepared by Christe [7]. One of the bromine trifluoride adducts, $CsF{\cdot}2BrF_3$, has been observed previously by Sukhoverkhov *et al.* [8] in the BrF_3-CsF-HF system.

0022-1139/85/$3.30

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EXPERIMENTAL

$CsBrF_4$, prepared by the method of Christe and Schack [6], was used as the starting material for the preparation of $CsF{\cdot}3BrF_3$, since it reacts more smoothly with bromine trifluoride than CsF. A weighed amount of the 1:1 complex was added in a drybox to a sapphire spectral cell [9] containing excess bromine trifluoride. The cell was closed with a Teflon PFA valve, and the mixture was heated and shaken until solution was complete. $CsF{\cdot}3BrF_3$ appeared as the solid phase in contact with saturated solution as the system cooled to 23°C. The excess bromine trifluoride was pumped off in stages at 23° until the solid was dry and the weight corresponded to that of the 1:3 complex. At each stage, a Raman spectrum was obtained. These spectra allowed mixtures of products to be readily distinguished and showed that at the 1:3 composition, a single phase was obtained. In a typical experiment, 0.659 g of $CsBrF_4$ (2.28 mmol) and 0.626 g of BrF_3 (4.57 mmol) yielded 1.285 g of $CsF{\cdot}3BrF_3$ (2.28 mmol) as a fused mass of yellow crystals (incongruent M.P. approximately 41°C).

$CsF{\cdot}2BrF_3$ was prepared by pumping on molten $CsF{\cdot}3BrF_3$ at 115-130°C until the composition was that of the 1:2 complex, then cooling the melt. It was also prepared by heating and cooling equimolar mixtures of $CsBrF_4$ and BrF_3. When the latter method was used, 0.541 g of $CsBrF_4$ (1.87 mmol) and 0.259 g of BrF_3 (1.89 mmol) yielded 0.800 g of pale yellow $CsF{\cdot}2BrF_3$ (1.88 mmol) (M.P. 110°C).

$RbF{\cdot}3BrF_3$ was prepared from $RbBrF_4$ and BrF_3 by a procedure analogous to that which was used to prepare $CsF{\cdot}3BrF_3$. Like the latter compound, it was found to be the stable solid phase coexisting with saturated solution at 23°C. In a typical experiment, 0.356 g of $RbBrF_4$ (1.47 mmol) and 0.408 g of BrF_3 (2.98 mmol) yielded 0.764 g of yellow, crystalline $RbF{\cdot}3BrF_3$ (1.48 mmol) (incongruent M.P. approximately 59°C).

$RbF{\cdot}2BrF_3$ was not obtained as a pure solid phase by melting and cooling an equimolar mixture of $RbBrF_4$ and BrF_3 or pumping on molten $RbF{\cdot}3BrF_3$; instead, a mixture of phases was obtained. However, $RbF{\cdot}2BrF_3$ was shown to be present by its Raman spectrum, which is similar to that of $CsF{\cdot}2BrF_3$.

To learn whether potassium fluoride would form a higher complex with bromine trifluoride, $KBrF_4$ was prepared by the method of Sharpe and Emeléus [1] and was heated with excess BrF_3. When the resulting solution cooled, $KBrF_4$ recrystallized. This 1:1 complex is therefore the stable solid phase in contact with saturated bromine trifluoride solution at 23°.

Raman spectra of products in the sapphire cell were obtained at room temperature with a Spex Model 1403 spectrometer, which was operated in the photon-counting mode and controlled by a SCAMP computer (Norland Corp.) The 514.5 nm line of a Spectra-Physics Model 165 argon ion laser was used for excitation. Extraneous plasma lines were eliminated with a Spex Lasermate grating monochromator. Laser power at the sample ranged from 100 to 500 mW, and the entrance and exit slits were set for a spectral bandwidth of 2.5 cm^{-1}.

Solid products were removed from the cell in a drybox, lightly ground, and pressed between silver chloride windows. Infrared spectra were then obtained with a Beckman IR-12 spectrophotometer. Attempts to obtain infrared spectra at long wavelengths with polyethylene windows were unsuccessful, due to reaction of the products with the windows.

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of liquid bromine trifluoride and the solid adducts $CsF{\cdot}3BrF_3$, $CsF{\cdot}2BrF_3$ and $CsBrF_4$. One notable feature of these spectra is the downward shift in the frequencies of bromine-fluorine stretching vibrations with the decreasing proportions of bromine trifluoride in the compounds. Thus, the strongest bands occur at 673 and 531 cm^{-1} in liquid BrF_3 (vibrations ν_1 and ν_2, respectively, of the T-shaped monomer) [10] but at 647, 620 and 518 cm^{-1} in $CsF{\cdot}3BrF_3$ (Table 1), 608 and 503 cm^{-1} in $CsF{\cdot}2BrF_3$, and 523 and 449 cm^{-1} in $CsBrF_4$ (vibrations ν_1 and ν_4, respectively, of the square-planar BrF_4^- anion) [6]. This suggests that the 1:3 and 1:2 adducts are salts as well as the 1:1 adduct, since, for the formulations $Cs^+Br_3F_{10}^-$, $Cs^+Br_2F_7^-$, and $Cs^+BrF_4^-$, the negative charge of the anion, distributed over three, two and one bromine atom, respectively, lowers the bromine-fluorine bond strength in the order that is observed.

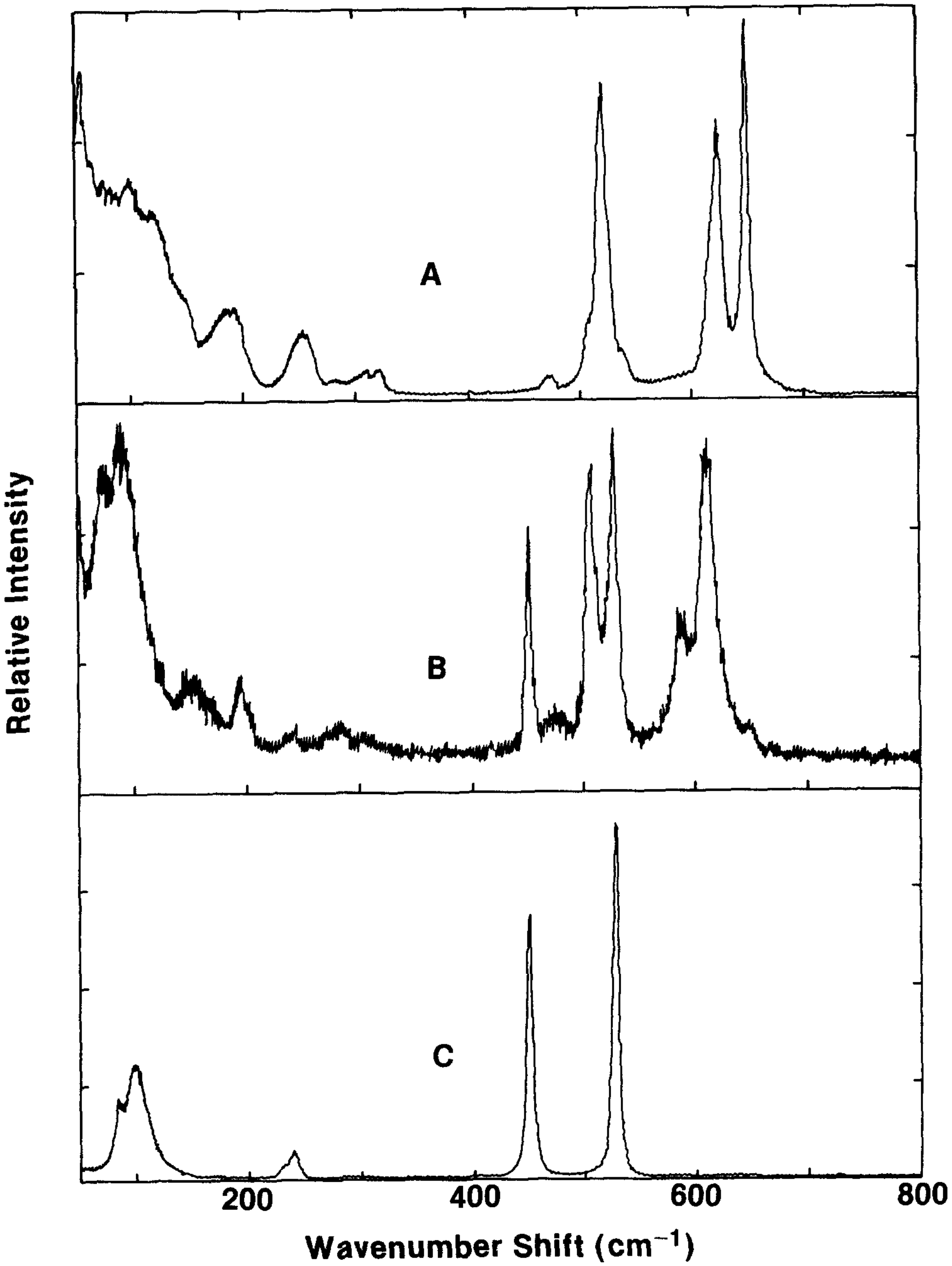


Fig. 2. Raman spectra of (A) solid $RbF\cdot 3BrF_3$, (B) a mixture of solid $RbF\cdot 2BrF_3$ and $RbBrF_4$, and (C) solid $RbBrF_4$.

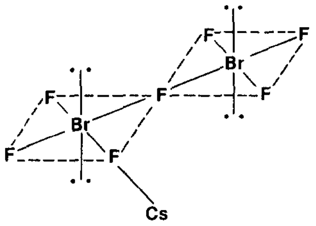
TABLE 1

Vibrational spectra of the solid compounds $CsF \cdot 3BrF_3$, $CsF \cdot 2BrF_3$, $RbF \cdot 3BrF_3$, and $RbF \cdot 2BrF_3$ (frequencies in cm^{-1})

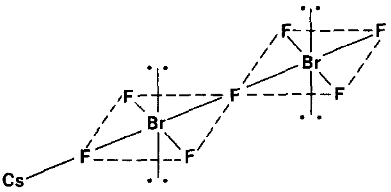
$CsF \cdot 3BrF_3$		$CsF \cdot 2BrF_3$		$RbF \cdot 3BrF_3$		$RbF \cdot 2BrF_3$ (in Mixtures)
Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman
647 VS	615 W	608 VS	848 M	648 VS	615 M	611 VS
620 S	535 Sh	584 M	615 Sh	622 S	535 M	586 M
570 VW	475 Sh	517 Sh	520 Sh	570 VVW	475 Sh	520 Sh
535 Sh	415 VS	503 VS	415 VS	538 Sh	412 S	506 VS
518 VS	340 M	473 W	340 W	519 VS	335 S	474 W
506 Sh		303 VW		506 Sh		305 VW
472 W		287 VVW		472 W		282 VW
380 VVW		274 VW		320 W		191 W
317 W		188 W		307 VW		150 W
304 VW		147 W		250 M		86 S
252 M		78 Sh		188 M		73 Sh
188 M		68 VS		145 Sh		
142 Sh				122 W		
120 W				98 W		
94 Sh				80 VW		
80 M						

S = strong; M = medium; W = weak; V = very; Sh = shoulder

The Raman spectrum of the 1:2 adduct (Fig. 1C) shows a remarkable resemblance to that of $CsBrF_4$ (Fig. 1D). Thus, it seems probable that the $Br_2F_7^-$ anion is comprised of two BrF_4 groups joined by a common fluorine atom. The Cs^+ cation may be in either a <u>cis</u> position (I) or a <u>trans</u> position (II) relative to the second BrF_4 group.



I



II

With this structure, the band at 608 cm^{-1} can be ascribed to an in-phase stretching mode and the band at 503 cm^{-1} to an out-of-phase stretching mode of four planar fluorine atoms. In ions such as $Sb_2F_{11}^-$ [11], $As_2F_{11}^-$ [12], $Ta_2F_{11}^-$ [13], and $Xe_2F_{11}^+$ [14], which have fluorine-bridged structures, the bridge stretching modes occur at 360-525 cm^{-1}. We observe a band at 415 cm^{-1} in the infrared spectrum of $CsF{\cdot}2BrF_3$ which can readily be assigned to the Br-F-Br bridge in $Br_2F_7^-$.

The Raman spectrum of the 1:3 adduct (Fig. 1B) is more complex than that of the 1:2 adduct but can be ascribed to a $Br_3F_{10}^-$ anion containing three BrF_4 groups joined by two fluorine bridges. The $Br_3F_{10}^-$ anion can be regarded as an analog of $Sb_3F_{16}^-$, which has a <u>trans</u>-bridged structure in $Br_2^+Sb_3F_{16}^-$ [15].

Figure 2 shows the Raman spectra of solid $RbF{\cdot}3BrF_3$, a mixture of solid $RbF{\cdot}2BrF_3$ and $RbBrF_4$, and solid $RbBrF_4$. Although $RbF{\cdot}2BrF_3$ was not obtained as a pure phase in the present study, we believe that a further study of the solid-liquid equilibria in the RbF-BrF_3 system will reveal conditions under which the 1:2 adduct can be isolated as a pure compound. The spectrum of each of the adducts is almost identical to that of the corresponding cesium compound, as shown by the data in Table 1. Hence, we conclude that the 1:3 and 1:2 adducts of rubidium fluoride and bromine trifluoride can also be formulated as the salts $Rb^+Br_3F_{10}^-$ and $Rb^+Br_2F_7^-$.

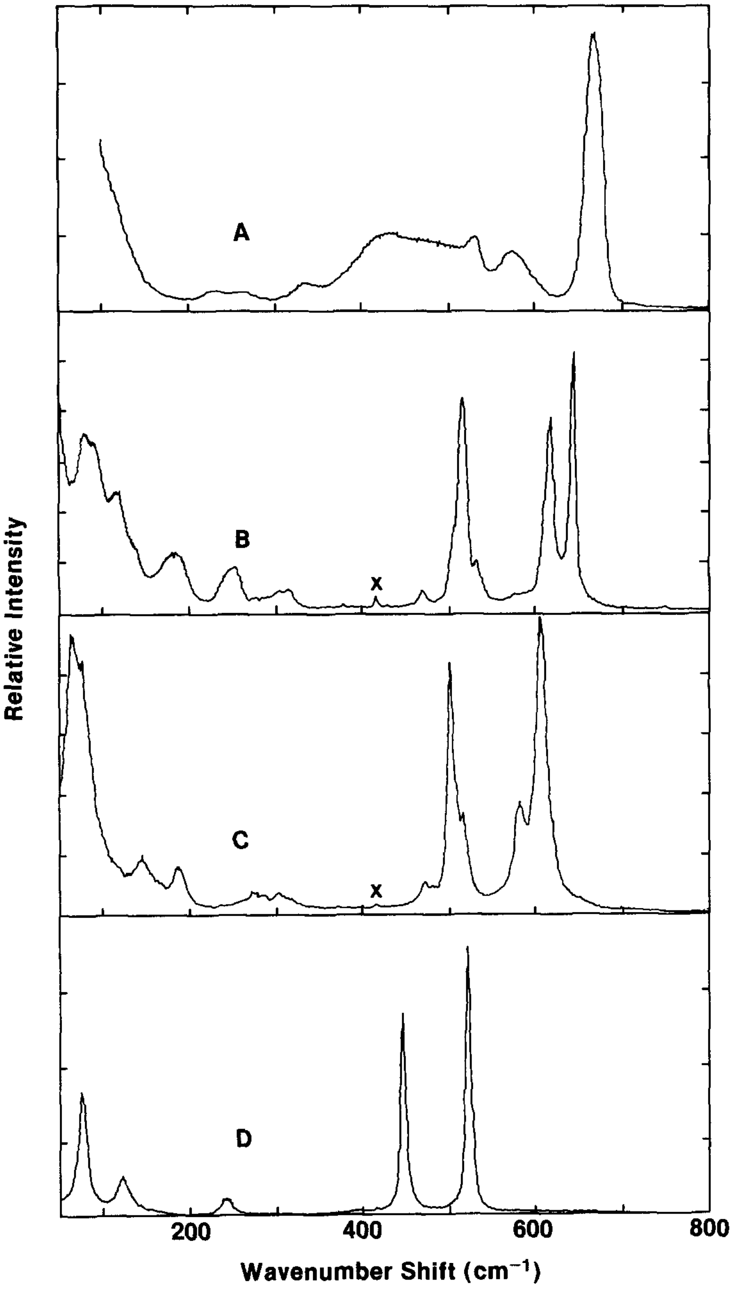


Fig. 1. Raman spectra of (A) liquid BrF_3, (B) solid $CsF \cdot 3BrF_3$, (C) solid $CsF \cdot 2BrF_3$, and (D) solid $CsBrF_4$. (X=sapphire band)

ACKNOWLEDGMENT

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract W-31-109-ENG-38.

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