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Cesium Bis(perchlorato)bromate(I), $Cs^+[Br(OClO_3)_2]^-$

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The synthesis and some properties of the novel bis(perchlorato)bromate(I) anion are reported. Vibrational spectra were recorded and are consistent with a model containing two covalent, monodentate perchlorato groups and an approximately linear O–Br–O arrangement.

Introduction

Except for fluorine perchlorate,[1] no halogen perchlorates had been reported until 1970. With the recent discovery of chlorine perchlorate ($ClOClO_3$) by Schack[2] a versatile synthetic reagent became available for the preparation of other perchlorates. This led to the syntheses of the novel halogen perchlorates $BrOClO_3$,[3] $I(OClO_3)_3$, and $Cs^+[I(OClO_3)_4]^-$.[4] The covalent monodentate nature of the perchlorato ligand in these compounds was established by vibrational spectroscopy.[2-5] In this paper we wish to report on the synthesis and characterization of the first known example of a perchloratobromate ion.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 IF4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Anhydrous CsBr (ROC/RIC, 99.9% minimum) was used without further purification. Chlorine perchlorate was prepared and purified by the method of Schack and Pilipovich.[2] The purity of volatile materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer 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. Dry powders were recorded as pressed disks between AgCl windows. The pressing operation was carried out using a Wilks minipellet press.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[6] for the elimination of plasma lines. Glass melting point capillaries were used as sample containers in the transverse-viewing–transverse-excitation technique.

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.). For elemental analyses, the solid samples were hydrolyzed in aqueous NaOH. Perchlorate was determined with a specific ion electrode (Orion Model 92-17) and Cs and Br by X-ray fluorescence employing a GE XRD-6VS X-ray fluorescence spectrometer.

Preparation of $CsBr(ClO_4)_2$. A 30-ml prepassivated 316 stainless steel cylinder was loaded with powdered CsBr (1.03 mmol) followed by $ClOClO_3$ (6.76 mmol) at −196°. The reactor was warmed to −45° and stored at that temperature for 2 years. On recooling to −196° a few cubic centimeters of noncondensable gas was noted. Volatile products were pumped from the reactor for several hours while and after it had warmed to ambient temperature. Separation of these materials were effected by fractional condensation. They consisted of Cl_2 (1.41 mmol), a small amount of Cl_2O_6,[7] and unreacted $ClOClO_3$ (4.01 mmol). The solid product was faint yellow and weighed 416 mg, corresponding to a 96% conversion of the CsBr to $CsBr(ClO_4)_2$. *Anal.* Calcd for $CsBr(ClO_4)_2$: Cs, 32.3; Br, 19.4; ClO_4^-, 48.3. Found: Cs, 32.6; Br, 19.0; ClO_4^-, 47.2. X-Ray powder diffraction patterns of the solid showed no lines due to CsBr, $CsBrO_3$, or $CsClO_4$. The product was found to be completely stable at ambient temperature as shown by visual and spectroscopic examination after several months.

A reaction of CsBr (1.42 mmol) and $ClOClO_3$ (4.46 mmol), carried out under similar conditions, was examined after 6 days at −45°. The volatile products consisted of Cl_2 (1.43 mmol), $BrOClO_3$ (1.38 mmol),[3] and unreacted $ClOClO_3$ (1.52 mmol). The white solid residue weighed 332 mg, in excellent agreement with the weight (331 mg) calculated for a complete conversion to $CsClO_4$. The infrared spectrum of the solid showed only bands[8] attributable to the ClO_4^- ion. *Anal.* Calcd for $CsClO_4$: ClO_4^-, 42.8. Found: ClO_4^-, 42.4.

When another of these reactions was examined after 2 months at −45°, the solid product consisted of 32 mol % $CsBr(ClO_4)_2$ and 68 mol % $CsClO_4$ as shown by the observed material balance, vibrational spectroscopy, and analysis.

Results and Discussion

Caution! Chlorine perchlorate is shock sensitive.[2] Proper safety precautions must be taken when working with this compound. Although during our experiments $CsBr(ClO_4)_2$ appeared to be stable, it should be kept in mind that we have previously observed explosive decompositions for the closely related iodine perchlorate compounds.[4]

Synthesis. The experimental data show that CsBr interacts with an excess of $ClOClO_3$ at −45° relatively fast according to

$$CsBr + 2ClOClO_3 \rightarrow CsClO_4 + BrOClO_3 + Cl_2$$

This reaction is followed by the much slower second step

$$CsClO_4 + BrOClO_3 \rightarrow CsBr(ClO_4)_2$$

Acceleration of the second step by raising of the reaction temperature was not feasible owing to the thermal instability of the halogen monoperchlorates. The use of a proper solvent is likely to increase the reaction rate. However, owing to the pronounced incompatibility of halogen perchlorates with most solvents and owing to the slowness of the reaction, studies in this direction were beyond the scope of the present investigation.

The above data demonstrate that the reactivity of CsBr toward $ClOClO_3$ is intermediate between those previously observed for CsCl and CsI.[2,4] Whereas CsCl or $CsClO_4$ do not form any stable adduct with $ClOClO_3$, CsI is readily converted to $CsI(ClO_4)_4$. The fact that iodide is oxidized by $ClOClO_3$ to the +III oxidation state whereas bromide is oxidized only to the +I state is not surprising since iodide is a stronger re-

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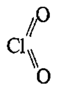
ducing agent than bromide. Our previous attempts[4] to synthesize the iodine(I) salt $CsI(ClO_4)_2$ from $CsIBr_2$ and $ClOClO_3$ resulted only in a mixture of unreacted $CsIBr_2$ and $CsI(ClO_4)_4$. This indicated instability of the iodine(I) salt may be caused by its pronounced tendency to disproportionate and to achieve a higher coordination number.

Properties. The compound $CsBr(ClO_4)_2$ is a faint yellow solid. It was stored for more than 6 months at ambient temperature in dry nitrogen without noticeable decomposition. It is hygroscopic and readily hydrolyzes in water. The solid is crystalline and its X-ray powder pattern is listed in Table I. Surprisingly, the pattern shows little resemblance to that reported[9] for the similar compound $CsBr(SO_3F)_2$.

Vibrational Spectrum. Figure 1 shows the infrared and the Raman spectrum of solid $CsBr(ClO_4)_2$. The observed frequencies and their assignments are listed in Table II.

Before discussing these assignments in more detail, the nature of the perchlorate moiety in $CsBr(ClO_4)_2$ must be established. The perchlorate could be present as a ClO_4^- anion or as a covalent perchlorato ligand. In the latter case, the perchlorato group could be either mono- or bidentate. Since bromine(I) has three free valence electron pairs, two bidentate perchlorato ligands would result in a coordination number of 7. This coordination number is not unreasonable in view of the existence[10] of the BrF_6^- anion which has one free valence electron pair on the central atom. The vibrational spectra of the ClO_4^- anion[8] and of covalent monodentate perchlorates, such as $ClOClO_3$ and $BrOClO_3$,[6] are well known and understood. Recently, we have also established the vibrational spectrum of $Ti(ClO_4)_4$, a compound containing four bidentate perchlorato ligands.[11] Since relative bandwidths of the individual bands are very important for distinguishing antisymmetric from symmetric motions, we have added to Figure 1 for comparison the vibrational spectra of the typical covalent monodentate $ClOClO_3$, of the bidentate $Ti(ClO_4)_4$, and of the ClO_4^- anion.

Inspection of Figure 1 immediately rules out for $CsBr(ClO_4)_2$ a structure containing ClO_4^- anions. The spectrum of a typical bidentate perchlorate should show two pairs of strong infrared bands at about 1310 and 1170 and at 880 and 660 cm^{-1}, respectively. These pairs are due to the antisymmetric and symmetric stretching vibrations of the



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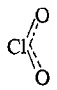
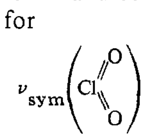


groups, respectively. The absence of a strong infrared band in the region 800-1000 cm^{-1} and of a strong sharp Raman band above 1100 cm^{-1} for



clearly rules out for $CsBr(ClO_4)_2$ a bidentate perchlorate structure.

Table I. X-Ray Powder Data for $CsBr(ClO_4)_2$

d, A	Intens	d, A	Intens	d, A	Intens
5.13	w	2.445	m	1.536	w
3.47	m	2.188	s	1.512	vw
3.40	vs	2.018	ms	1.490	w
2.77	m	1.973	w	1.467	vw
2.579	vw	1.834	w	1.411	m
2.518	m	1.709	ms	1.397	mw

Table II. Infrared and Raman Spectrum of Solid $CsBr(ClO_4)_2$

Obsd freq, cm^{-1}, and intens[a]		Approx description of mode in point group C_2
Ir	Raman	
2930 vw		1115 + 1078 + 720 = 2913
2360 w		1289 + 1078 = 2367
2040 w		1105 + 947 = 2052
1663 vw		947 + 720 = 1667
1300 vs, br	1289 (0.6)	$\nu_{as}(ClO_3)$ in phase (2 A)
1115 vs, br	1105 (0.3) br	$\nu_{as}(ClO_3)$ out of phase (2 B)
1076 vw	1078 (10)	$\nu_{sym}(ClO_3)$ in phase (A)
947 vw	947 (6.2)	$\nu_{sym}(ClO_3)$ out of phase (B)
	933 (1.4)	
	904 (0.1)	
720 vs, br	719 (1.1)	$\nu_{as}(BrOCl)$ out of phase (B)
633 m	633 (1.4)	$\nu_{sym}(BrOCl)$ out of phase (B)
622 mw	625 (0.5)	
581 ms	584 (1.8)	$\delta_{sciss}(ClO_2)$ (A, B)
572 ms	578 (1.8)	$\delta_{as}(ClO_3)$ (A, B)
558 mw	558 (2.1)	$\delta_{umbrella}(ClO_3)$ (A, B)
	466 (1.2)	$\nu_{as}(BrOCl)$ in phase (A)
	450 (1.5)	$\nu_{sym}(BrOCl)$ in phase (A)
	407 (2.7)	$\delta_{rock}(ClO_3)$ (A)
	396 (2.5)	$\delta_{rock}(ClO_3)$ (B)

[a] Uncorrected Raman intensities.

A superficial comparison between the spectra of $CsBr(ClO_4)_2$ and $ClOClO_3$ also reveals pronounced differences. However, these differences can be easily reconciled by taking into account that $Br(ClO_4)_2^-$ contains two perchlorato groups. Their motions should strongly couple owing to the approximately linear configuration of the O-Br-O group expected by comparison with pseudoisoelectronic ClF_2^-,[12] KrF_2, and XeF_2.[13] This coupling results in a splitting of each mode into an in-phase and an out-of-phase motion of the two perchlorato groups. The observed bandwidths make it easy to assign the bands to antisymmetric (broad) and symmetric (narrow) vibrations. The agreement between the vibrational spectra of $ClOClO_3$ and $Br(OClO_3)_2^-$ is excellent if one takes the average frequency of each band pair and keeps in mind the expected frequency decrease when going from neutral $XOClO_3$ to the $Br(OClO_3)_2^-$ anion. This frequency trend in the order cation > neutral molecule > anion has been established for numerous halogen compounds[14] and can be explained by the increasing polarity of the bonds.

After establishing the covalent monodentate nature of the perchlorato ligands in $Br(OClO_3)_2^-$, assignments of the observed bands to individual modes can be discussed. Since the highly electronegative perchlorato ligand might be considered as a pseudohalide, the structure of $Br(OClO_3)_2^-$ should be analogous to those found for the pseudoisoelectronic fluorides ClF_2^-,[12] KrF_2, or XeF_2.[13] The central atoms of these species possess three free valence electron pairs and, hence, have a coordination number of 5. This results in a trigonal bipyramid in which the three free valence electron pairs occupy the equatorial positions and the two electronegative ligands the two axial positions. If this analogy is

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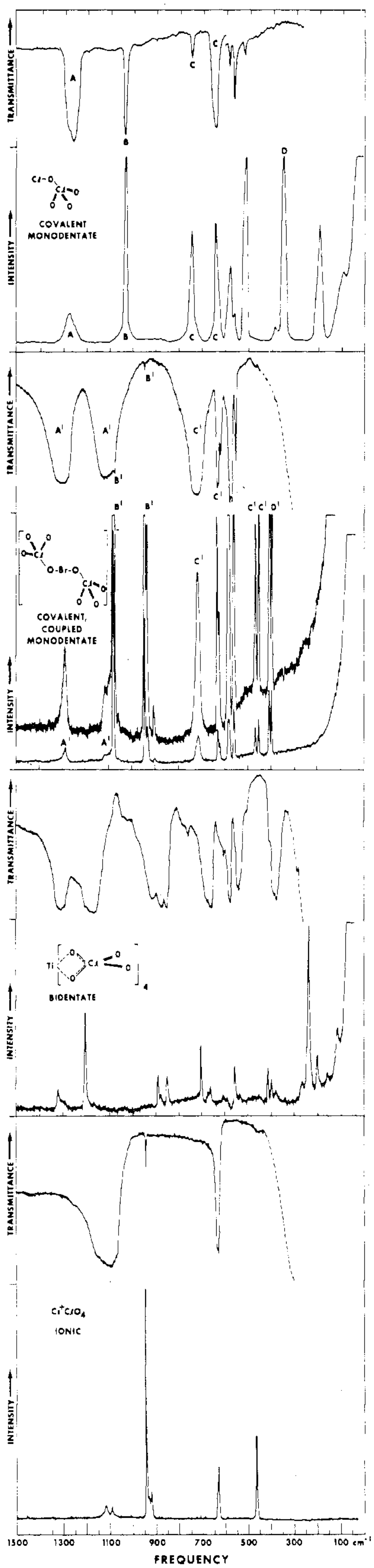
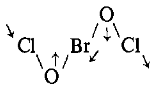
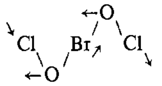


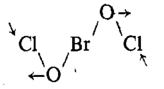
Figure 1. Vibrational spectra of solid $CsBr(ClO_4)_2$, $Ti(ClO_4)_4$, and $CsClO_4$ (infrared spectra recorded as AgCl disks). Raman spectrum of liquid $ClOClO_3$ and infrared spectrum of solid $ClOClO_3$ as a film on a CsI window cooled to 4°K. Spectral slit width used for the recording of the Raman spectra of the solids was 4 cm^{-1}. The bands of $CsBr(ClO_4)_2$ marked by A', B', C', and D' represent the in-phase and out-of-phase motion components of the A, B, C, and D bands, respectively, of $ClOClO_3$.

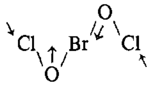
Table III. Summary of 27 Fundamentals Expected for $Br(OClO_3)_2^-$ in Point Group C_2

ClOBrOCl Skeletal Modes


ν_{sym}(BrOCl) out of phase (B)


ν_{asym}(BrOCl) out of phase (B)


ν_{asym}(BrOCl) in phase (A)


ν_{sym}(BrOCl) in phase (A)

δ(BrOCl) in plane $\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$

δ(BrOCl) out of plane = τ(BrO) $\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$

δ(OBrO) in plane (B)

ClO_3 Modes

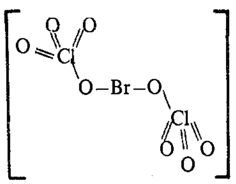
$\nu_{asym}(ClO_3)\left\{\begin{matrix}\text{in phase (2 A)}\\ \text{out of phase (2 B)}\end{matrix}\right.$ $\tau(ClO_2)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$

$\nu_{sym}(ClO_3)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$ $\delta_{umbrella}(ClO_3)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$

$\delta_{asym}(ClO_3)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$ $\delta_{rock}(ClO_3)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$

$\delta_{sciss}(ClO_2)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$ $\tau(OCl)\left\{\begin{matrix}\text{in phase (A)}\\ \text{out of phase (B)}\end{matrix}\right.$

extended to $Br(OClO_3)_2^-$ and if a bond angle of about 100° is assumed for BrOCl with the two ClO_3 groups being in a trans position to minimize their mutual repulsion, the following structure of symmetry C_2 is obtained



The twofold symmetry axis is perpendicular to the ClOBrOCl plane and passes through the Br central atom.

For an 11-atom species of symmetry C_2 one would expect a total of 27 fundamentals. Of these, 13 belong to species A representing the in-phase motions of the two ligands and 14 belong to species B representing the out-of-phase motions and the OBrO in-plane deformation. These 27 modes may be broken down further into nine ClOBrOCl skeletal modes by treating the ClO_3 group as one point of mass. A summary of the 27 fundamentals is given in Table III.

Assignments to the modes involving internal motions of the ClO_3 group can be readily made by comparison with those previously given[5] for $ClOClO_3$ and $BrOClO_3$. As expected, the two antisymmetric ClO_3 stretching modes are nearly degenerate (for $ClOClO_3$ and $BrOClO_3$ splitting into the components was observed only for the matrix-isolated species)[5] and, therefore, result for $Br(OClO_3)_2^-$ in a single broad band. However, the frequency difference of ~10 cm^{-1} observed between the band centers of the infrared and the Raman bands suggests that these modes are not completely degenerate and are of different relative intensities in the infrared and Raman spectra. The assignments are given in Table II and are supported by the observed bandwidths and intensities. For example, the symmetric ClO_3 stretching modes should give rise to very intense, sharp Raman bands with weak infrared counterparts, with the strongest Raman band representing the in-phase motion. The slight splitting observed for the 947-cm^{-1} Raman band does not show the right (3:1) intensity ratio for the ^{35}Cl-^{37}Cl isotopes and, hence, is ascribed to crystal effects.

After assigning the ClO_3 modes, four bands in the region 450-750 cm^{-1} remain unassigned. Based on their frequencies, these bands must represent the four skeletal stretching modes. Of the four bands the two lower frequency ones do not show a counterpart in the infrared spectrum and, therefore, must be assigned to the two A modes which do not involve a change of the dipole moment (see Table III). Based on its higher Raman intensity and lower frequency the 450-cm^{-1} band is assigned to ν_{sym}(BrOCl) in phase which involves more of a Br-O stretch than a Cl-O stretch. For the two higher frequencies we prefer to assign the 720-cm^{-1} band to the antisymmetric BrOCl motion based on its strong infrared intensity and large bandwidth. The two components of the 633-cm^{-1} band show the correct intensity ratio of 3:1 for ^{35}Cl and ^{37}Cl isotopes and, hence, this splitting is ascribed to isotope effects.

In summary, the observed spectrum is in excellent agreement with our predictions for a covalent, monodentate perchlorato structure containing a strongly coupled and, therefore, approximately linear OBrO configuration.[15] Except for the torsional modes and the BrO_2 and BrOCl in plane deformations (which are expected to be of relatively low frequency and intensity) all of the predicted fundamentals were observed. For the stretching vibrations, the strong coupling causes pronounced frequency splittings owing to in-phase and out-of-phase motions of the two ligands. For the ClO_3 deformation modes, such a splitting was not observed except for an 11-cm^{-1} separation of the two rocking modes.

No attempts were made to compute a force field for $Br(OClO_3)_2^-$ owing to the size (11 atoms) of the ion, the inavailability of the skeletal deformation frequencies, and an expected[5] strong mixing of the symmetry coordinates of the skeletal stretching modes.

Acknowledgment. We are indebted to Dr. L. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

Registry No. CsBr, 7787-69-1; $ClOClO_3$, 27218-16-2; $CsBr(ClO_4)_2$, 51108-46-4.

(15) Quantitative computations have been carried out for M-O-M linkages containing a light central atom: I. R. Beattie and M. J. Gall, *J. Chem. Soc. A*, 3569 (1971). Qualitatively, their arguments should also be valid for our case with Br as a central atom, where the observed frequency separation of the average of the BrOCl stretches of species B from that of the corresponding A modes is 216 cm^{-1}.

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Fluorine-19 Nuclear Magnetic Resonance Studies of Some Xenon(II) Compounds

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The ^{19}F nmr spectra of solutions of XeF_2, $FXeSO_3F$, and $Xe(SO_3F)_2$ in HF and HSO_3F and of solutions of the adducts $XeF_2 \cdot AsF_5$, $XeF_2 \cdot SbF_5$, and $XeF_2 \cdot 2SbF_5$ in HSO_3F have been studied. Spectra were also obtained for solutions of XeF_2 in SbF_5 and SbF_5-HSO_3F and for the adduct $2XeF_2 \cdot AsF_5$ in BrF_5. Fluorine-19 chemical shifts and ^{129}Xe-^{19}F coupling constants for the species $FXeSO_3F$, $Xe(SO_3F)_2$, $Xe_2F_3^+$, and XeF^+ have been obtained from the results.

Introduction

Although ^{19}F nmr spectroscopy is in principle capable of providing useful information concerning the structure and bonding of fluorine compounds as well as an easy and convenient method for the identification of species in solution, there has been very little work published on the ^{19}F nmr spectra of xenon-fluorine compounds in solution.

The purpose of the present work was to make an extensive study of the ^{19}F nmr spectra of xenon-fluorine compounds with a view to obtaining further information on the nature of the species present in solution and on their nmr parameters.

The present paper is concerned with xenon(II) compounds. Apart from an early study of XeF_2 in HF[1] the only other published work on xenon(II) compounds is a report by Cohen and Peacock[2] of the ^{19}F nmr spectrum of a solution of $XeF_2 \cdot 2SbF_5$ in SbF_5. These authors observed a single line due to fluorine on xenon accompanied by satellites arising from ^{129}Xe-^{19}F coupling. The result was tentatively interpreted as indicating that the compound $XeF_2 \cdot 2SbF_5$ had the structure $F_5SbFXeFSbF_5$. Since that time the compound has been shown by X-ray crystallography to have the structure $FXeFSb_2F_{10}$.[3] The structure consists essentially of XeF^+ and $Sb_2F_{11}^-$ ions which have a rather short anion-cation contact, indicating a rather strong fluorine bridge F-Xe- - -F-Sb with presumably considerable covalent character.

We report here the results of our studies of XeF_2, $FXeSO_3F$, $Xe(SO_3F)_2$, $2XeF_2 \cdot AsF_5$, $XeF_2 \cdot AsF_5$, $XeF_2 \cdot 2SbF_5$, and $XeF_2 \cdot SbF_5$ in the solvents HSO_3F, HF, SbF_5, and BrF_5.

Results and Discussion

Xenon(II) Fluorosulfates. Bartlett, *et al.*,[4] showed that when xenon difluoride is allowed to react with stoichiometric amounts of HSO_3F at −75°, the compounds $FXeSO_3F$ and $Xe(SO_3F)_2$ are obtained. The crystal structure of $FXeSO_3F$ has been determined and was found to consist of covalent

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