the color. This material was not characterized further, but its density and conditions of preparation place it at the transition region between fused, amorphous BeH_2 and phase 338-208. It may represent a transitory structure in which electrons are largely delocalized and free to migrate within the incipient lattice (similar to F centers).

Crystallization of BeH_2 Slurry. An alternative procedure to hydrostatic compaction of encapsulated dry feed utilized the slurry of BeH_2 directly as it was recovered from the solution pyrolysis reaction.[3] The same types of aluminum capsules employed with the dry-feed procedure were used, these being filled with a slurry of the amorphous Li-doped BeH_2 in the pyrolysis medium. Best results were obtained at solid concentrations of 20–70% and pressures of 5.5–9.7 kbars at 205–230 °C. Phase 338-208 predominated in all crystallized slurry products except at the most rigorous conditions—9.7 kbar and 230 °C, where phase 378-295 was produced in 55% concentration.

Other Additives. A number of additives to amorphous BeH_2 other than lithium were tested, but none proved as effective in promoting crystallization. These included various complex metal hydrides containing Be, B, and Al, AlH_3 and alkylaluminum compounds, and others. Coadditives to the Li-doped BeH_2 also were tested. The alkali and alkaline earth fluorides as well as Be powder showed some effect in lowering the crystallization pressure and time requirements. Similarly, a 1:1 mixture of crystalline and amorphous BeH_2 could be densified using 13.8-kbar pressure alone. However, this effect was not sustained through more than one or two cycles. The density of the product dropped regularly as the concentration of original seed decreased.

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Registry No. BeH_2, 7787-52-2.

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Preparation and Characterization of Some Monofluoroselenite and -tellurite Compounds

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Compounds with the related anions monofluoroselenite and tellurite, SeO_2F^- and TeO_2F^-, have been prepared and characterized. $M^I(SeO_2F)$ (M^I = Cs, Me_4N, Et_4N) compounds are readily prepared from aqueous solutions. The vibrational spectrum of the SeO_2F^- ion has been firmly established by IR and Raman spectroscopy on the solids and polarization measurements on solutions of Et_4NSeO_2F in acetonitrile. $CsSeO_2F$ has been shown to be isomorphous with $CsBrO_3$. Three monofluorotellurite compounds, $M^I(TeO_2F)$ (M^I = Na, K, Me_4N), have been prepared and characterized. Melts of TeO_2 with NaF and KF yield the monofluorotellurite compounds and not mixtures of M^IF and $M^I_2TeO_2F_2$ as found for M^I = Cs and Rb. The vibrational spectra have been reported.

Introduction

Selenium and tellurium in oxidation state IV form both difluoro[1,2] and pentafluoro[3] anions $MO_2F_2^{2-}$ and MF_5^-. Selenium forms in addition the monofluoro[2,4] and trifluoro anions[5] SeO_2F^- and $SeOF_3^-$, while tellurium gives a tetrafluoroanion[1] $TeOF_4^{2-}$. Recently, NMR evidence has been presented for the existence, in acetonitrile solution, of the TeF_6^{2-} ion,[6] a species sought by several research groups.[1,7] The monofluorotellurite anion is unknown. Milne and Moffett[1] attempted to prepare the rubidium and cesium monofluorotellurites from 1:1 melts of the alkali metal fluoride and tellurium dioxide. The product was found to be a mixture of $M^I_2TeO_2F_2$ and TeO_2. It was considered of interest to attempt to prepare M^ITeO_2F compounds using other ionic fluorides and different methods.

Although monofluoroselenites are well-known,[2,4] it is not clear whether they exist as individual or as condensed anions in the solid state. The present study of the SeO_2F^- ion was undertaken to clarify this question.

Experimental Section

Materials. Selenious acid (Merck) was used directly; selenium dioxide (Ventron) was pumped dry at ca. 70 °C for several hours; tellurium dioxide (Fisher) was used directly. Potassium (BDH) and cesium (Fluka) fluorides were dried at 650 °C under a stream of N_2/HF before use. Sodium fluoride (Ventron ultrapure) was used directly. Tetraethyl- (BDH) and tetramethylammonium (Merck) hydroxides, 25% aqueous, and 48% aqueous hydrofluoric acid (J. T. Baker) were standardized before use. Acetonitrile (Fisher) was first refluxed over P_2O_5 and then distilled and stored over molecular sieves. Dimethyl sulfoxide (Fisher) was distilled from CaO at reduced pressure and stored over molecular sieves.

Equipment. Most of the IR spectra were taken with a Beckman IR 20A spectrometer although a Perkin-Elmer 225 was used for the spectra of $CsSeO_2F$ and Me_4NSeO_2F products. Nujol mulls between CsBr plates were used.

Raman spectra were measured with a Jobin-Yvon monochromator in conjunction with a PAR photon-counting system. The spectra were excited with a Control Laser Ar^+ laser, operating at 488 nm. The Raman spectra of $CsSeO_2F$ and Me_4NSeO_2F were taken on a Cary 82 spectrometer with Ar^+ 488-nm excitation. In all cases, 90° illumination was used and polarizations were measured with the exciting beam polarized parallel to or perpendicular to the viewing direction. All samples were contained in sealed melting point tubes.

X-ray powder photographs were measured with a Guinier-Hagg camera, using Cu $K\alpha_1$ (0.1504-nm) irradiation. The camera was calibrated using Mo powder, which was added to the powdered samples in most instances. The average deviation of the *d* spacings for five Mo photographs (15 reflexes) was 0.2%. The moisture-sensitive samples were pressure sealed into thin polyethylene envelopes. The three weak and diffuse polyethylene lines caused little interference and were readily eliminated in the photographs. In the case of the $CsSeO_2F$ photograph, the compound was sufficiently stable to moisture that it could be distributed on adhesive tape, and a Guinier photograph was taken in this way. In this case also, a Mo powder standard was included with the sample and the reflexes of $CsSeO_2F$ were in this way precisely determined.

Preparations. $CsSeO_2F$ and Me_4NSeO_2F. Both of these compounds crystallize readily upon cooling from concentrated aqueous solutions of 1:1 mole ratio selenious acid–fluoride. The products were washed with cold ethanol, followed by a small portion of cold ethyl ether. This approach was not successful in the preparation of the analogous compounds of NH_4^+, Rb^+, Et_4N^+, and pyH^+ cations. In the case of the ammonium preparations, NH_4F and NH_4HF_2 were obtained instead, while the other preparations failed to yield a product which remained crystalline at room temperature. Attempted preparation from 48% HF yielded hydrogen difluorides. The $CsSeO_2F$ compound was not very sensitive to moisture, but Me_4NSeO_2F was especially deliquescent. Anal. Calcd for $CsSeO_2F$: Se, 30.04; F, 7.23. Found: Se, 30.01; F, 7.10. Calcd for Me_4NSeO_2F: Se, 38.69; F, 9.31; N, 6.86. Found: Se, 38.50; F, 9.47; N, 6.72 (Bernhardt Analytical Laboratory).

Et_4NSeO_2F. While this product could not be crystallized from aqueous HF by cooling, a stoichiometric mixture of 1:1:1 Et_4NOH (as a 25% solution)/HF (as a 48% solution)/SeO_2 gave upon pumping to dryness in an all metal and plastic vacuum line anhydrous Et_4NSeO_2F: F(calcd), 7.31; F(found), 7.35. This compound was very deliquescent. It dissolved readily in dimethyl sulfoxide and acetonitrile. A similar procedure using an aqueous solution of KF and SeO_2 failed to yield $KSeO_2F$. Judging from the Raman spectrum, the product was a mixture of KHF_2 and $KH_3(SeO_3)_2$ (see below).

$KSeO_2F$. This substance was prepared by the method of Paetzold and Aurich.[4] A similar procedure, that of melting together the fluoride with SeO_2, was attempted for the preparation of $NaSeO_2F$. In a 1:1 NaF/SeO_2 mixture, 39% of the SeO_2 was rapidly lost from the melt at 250 °C. The melt was never completely clear. The Raman spectrum of this mixture did not resemble that of $KSeO_2F$ or SeO_2 [principal Raman peaks of the product: 904 (10), 874 (6), 663 (1), 560 (0), 477 (2), 417 (0), 333 (1), 277 (1), 100 (0) cm^{-1}]. In an attempted preparation of $RbSeO_2F$ by melting together RbF and SeO_2, the melt was found to lose SeO_2 at 250 °C and the Raman spectrum was similar to that reported for $K_2SeO_2F_2$.[2] The preparation of $KSeO_2F$, reported earlier,[2] could not be repeated. Crystallization of 1:1 KF/SeO_2 from 40% HF yielded only KHF_2 and, from water, yielded a mixture of KHF_2 and $KH_3(SeO_3)_2$ as shown by comparison of X-ray powder photographs and Raman spectra with those reported in the literature.[8,9] The reaction in water proceeds according to

$$2KF + 2SeO_2 + 2H_2O \rightarrow KHF_2 + KH_3(SeO_3)_2$$

$KTeO_2F$ and $NaTeO_2F$. These compounds were prepared from 1:1 melts of the alkali metal fluoride and TeO_2. A platinum crucible was used in a crucible furnace. Clear melts were formed for $KTeO_2F$ at 400 °C and for $NaTeO_2F$ at 530 °C. No precautions were taken against ingress of water and the products appeared to be nonhygroscopic, although they were cooled, stored, and handled in a drybox. The weight change upon melting the reactants was negligible. Fluoride analyses on $KTeO_2F$ confirmed that no hydrolysis had occurred: F(calcd), 8.73; F(found), 8.67. The analysis was complicated by the insolubility of the product. For this reason the compound was first dissolved in a 1:1 Na_2CO_3/K_2CO_3 melt, digested in water and neutralized, and then treated with H_2S to ensure complete removal of tellurium. After filtration and removal of H_2S by boiling, the solution was titrated with thorium nitrate using a fluoride-sensitive electrode.

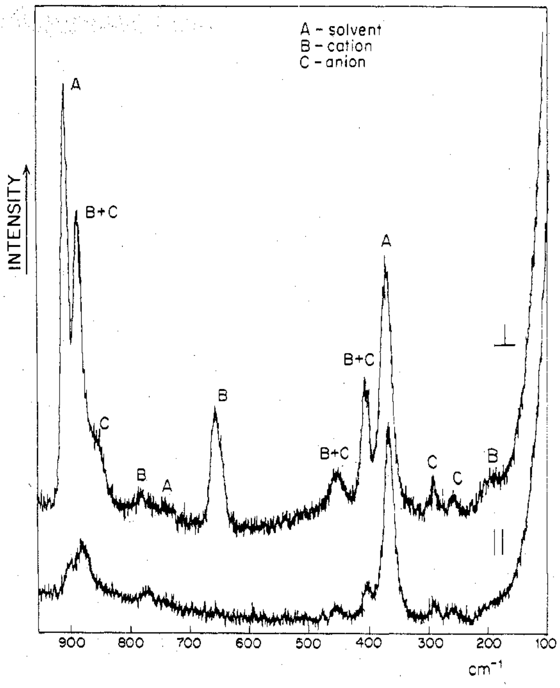

Figure 1. Raman spectra of Et_4NSeO_2F (saturated solution in MeCN): $\perp$, polarization vector perpendicular to viewing direction; $\parallel$, polarization vector parallel to viewing direction. Where peaks are marked B + C, the relative contribution of the cation is small (see Table I).

Me_4NTeO_2F. This was prepared by triturating a 1:1:1 mixture of $Me_4NOH/HF/TeO_2$ while evaporating to dryness on a hot plate at 120 °C and finally drying in a desiccator over P_2O_5. The TeO_2 is sparingly soluble in the Me_4NF solution but reaction proceeds as the mixture becomes a paste as indicated by the color change of solid from the original pale yellow color of TeO_2 to white. Anal. Calcd: F, 7.52. Found: 7.52. The preparation of $CsTeO_2F$ was tried by this method but the Raman spectrum showed a very complex pattern unlike that of the TeO_2F^- ion. A similar attempt to make Et_4NTeO_2F led to decomposition of the cation giving a strong amine odor.

All fluoride analyses were carried out by titration with thorium nitrate using a fluoride-sensitive electrode after prior removal of selenium or tellurium with H_2S.

Results and Discussion

X-ray Powder Data. X-ray powder diffraction data for all pure products have been deposited with the American Society for Testing and Materials. Although Paetzold and Aurich[4] showed that $KSeO_2F$ and $KBrO_3$ were not isomorphous, and we have confirmed this, the analogous cesium compounds are both rhombohedral, space group *R3M*. The hexagonal unit cell of $CsSeO_2F$ has $a = 6.585$ Å and $c = 8.087$ Å ($Z = 3$) while that of $CsBrO_3$ has $a = 6.507$ Å and $c = 8.232$ (ASTM, File No. 8-285). This indicates that the fluorine atoms in $CsSeO_2F$ must be statistically located on one of the three possible sites in each anion throughout the structure.

X-ray powder photographs of $KTeO_2F$ and Me_4NTeO_2F showed them to be crystalline and unique with no indication of the presence of starting materials. The powder pattern of $KTeO_2F$ bore no resemblance to those of $KSeO_2F$ or KIO_3. The $NaTeO_2F$ product gave a diffuse powder photograph indicating that this material was amorphous. Tellurium dioxide itself is known to readily form an amorphous glass.

Vibrational Spectra. M^ISeO_2F Compounds. The vibrational spectra of the M^ISeO_2F compounds and the solutions of

Table I. SeO_2F^- Vibrational Spectra (cm^{-1})[a]

$KSeO_2F$		$CsSeO_2F$		Me_4NSeO_2F[c]		Et_4NSeO_2F[d]		Et_4NSeO_2F[e] in MeCN	Et_4NSeO_2F[e] in Me_2SO
IR	Raman	IR	Raman	IR	Raman	IR	Raman	Raman	Raman
	240[b]		232[b]		239[b]				
280 sh	286 (1)	273 m	279 (2)	271 s	276 (1)	272 w	266 (1)	268 (1, dp)	273 (1)
320 ms	320 (1)	312 m	316 (2)	302 s	306 (1)		297 (1)	295 (1, p)	*f*
		360 m, sh					331 (0)		
403 vs	424 (2, br)	401 s, br	402 (2)	396 s	395 (1)	390 m	389 (2)[g]	*g*	*f, g*
440 s		434 m, br	430 (2)	460 s, br	469 (2)	460 s	452 (1)	463 (2, p)	468 (1)
		775 m, sh	830 (0)						
	859 (1)	852 s, br	863 (6)	860 m	866 (1)	870 m, sh	864 (1)	870 (2, sh)	*f*
884 vs	886 sh		882 (10)						
912 vs	902 (10)	890 m, sh	890 sh	890 m	902 (10)	898 vs, br	910 (10)[g]	893 (10, p)	890 (10)

[a] The Raman spectra are given up to 1000 cm^{-1} and the IR spectra are given in the range 250–1000 cm^{-1}. [b] Se^0 peak.[10] [c] Cation bands: Raman 375 (0), 458 (1), 755 (3), 951 (3) cm^{-1}; IR 460 w, 918 w, 946 m cm^{-1}. [d] Cation bands: Raman 200 (0), 390 (1), 465 (0.5), 590 (0), 662 (2), 791 (0.5), 896 (1) cm^{-1}; IR 600 m, 801 s, 1007 m cm^{-1}. [e] In addition to the cation bands listed for the solids, which were of the same relative intensity in the solution spectra, there were solvent peaks present as follows: MeCN 376 (6, dp), 752 (1, p), 917 (10, p) cm^{-1}. Me_2SO: 301 (3), 333 (4), 373 (1), 663 (10), 694 (8), 896 (1), 951 (1) cm^{-1}. [f] Coincident with solvent peak. [g] Coincident with cation peak.

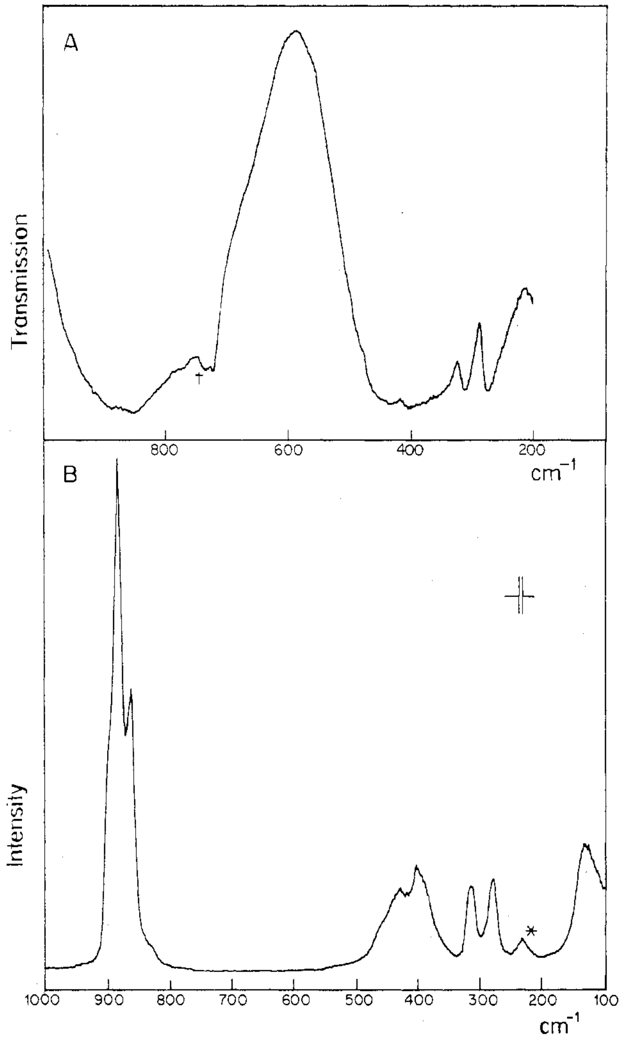

Figure 2. IR (A) and Raman (B) spectra of $CsSeO_2F$: †, Nujol peak; ∗, elemental Se.

Et_4NSeO_2F in MeCN and Me_2SO are given in Table I. The Raman spectrum of a saturated solution of Et_4NSeO_2F in MeCN is given in Figure 1. In the case of the spectra of the quaternary ammonium compounds and solutions, the cation and solvent bands have been identified and eliminated on the basis of spectra of the corresponding quaternary ammonium chloride and its solution. The cation and solvent bands are also listed in the tables. The intensities of the cation bands are those in the spectrum of the fluoroselinite. Where there was band overlap, they were normalized by means of the relative intensities in the corresponding chlorides. The Raman and IR spectra of $CsSeO_2F$ are given in Figure 2. The spectra agree well with those reported earlier,[2,4] but the assignment of the modes, which is supported by polarization measurements, differs from the earlier work. Bands observed in the Raman spectra below 200 cm^{-1}, which are unlikely to be fundamentals but are lattice modes, have not been considered here. The weak peak near 235 cm^{-1} observed in the Raman spectra of $KSeO_2F$, $CsSeO_2F$, and Me_4NSeO_2F and also reported earlier for $KSeO_2F$[2,4] is due to elemental selenium and is not a fundamental as assigned earlier. This peak grows in intensity with exposure of the sample to the 488-nm Ar^+ laser beam and after long exposure to the laser, the sample shows a red coloration characteristic of elemental selenium. Moreover, chain-type amorphous selenium exhibits a Raman peak at 235 cm^{-1}.[10] This band in the spectrum of SeO_2F^- has been, however, previously assigned to a deformation mode of SeO_2F^-.

Table II. Assignment of the Vibrational Spectrum of the SeO_2F^- Ion and Comparison with Spectra of Related Species

SeO_2F^-	BrO_2F[a]	SO_2F^- [b]	SeO_2-$(OH)^-$ [c]	XeO_2-F^+ [d]	assignt (XO_2F)
893	908	1102	855	863	$\nu_1(A')$, $\nu_{sym}(XO_2)$
463	506	593	615	580	$\nu_2(A')$, $\nu(XF)$
389	394	498	410	334	$\nu_3(A')$, $\delta_{sym}(XO_2)$
295	305	350	345		$\nu_4(A')$, $\delta_{sym}(XO_2F)$
870	953	1180	790	923	$\nu_5(A'')$, $\nu_{asym}(XO_2)$
268	271	265	320		$\nu_6(A'')$, $\delta_{asym}(XO_2F)$

[a] R. J. Gillespie and P. Spekkens, *J. Chem. Soc., Chem. Commun.*, 314 (1975). [b] E. A. Robinson, D. S. Lavery, and S. Weller, *Spectrochim. Acta, Part A*, **25a**, 151 (1969). [c] G. E. Walrafen, *J. Chem. Phys.*, 37, 1468 (1962). [d] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Inorg. Chem.*, **15**, 1256 (1976).

The pyramidal SeO_2F^- ion has C_s symmetry and six normal modes ($\Gamma = 4\,A' + 2\,A''$), active in the IR and Raman spectra, are expected. Of these, the four A′ modes will be polarized. The IR and Raman spectra of the four solid compounds studied permit the identification of these six modes. In the Raman spectrum of Et_4NSeO_2F in MeCN, five anion modes are identified, of which three are polarized (893, 463, 295 cm^{-1}) and one is apparently depolarized (268 cm^{-1}). The

Table III. IR and Raman Spectra of $M^{I}TeO_2F$ (cm^{-1})[a]

$NaTeO_2F$		$KTeO_2F$		Me_4NTeO_2F		
Raman	IR	Raman	IR	Raman[b]	IR[b]	approx descrip of mode
		97 (0)				
				118 (10)		
		150 (0)		146 (10)		defs
				190 (1)		
	310 m, sh	279 (2)	300 m, sh	284 (2)	318 m	
288 (1, br)						
	360 s, br	324 (1)	330 s	391 (2)	388 m	
461 (3)	456 m, sh	456 (5)	470 m, sh	461 (1)	442 m	ν_{TeF}
				589 (1)		
661 (10)	640 s, br	668 (8)	660 s, br	648 (10)	650 s	ν_{TeO}
763 (8)	750 vs, br	789 (10)	778 vs, br	808 (4)	789 s	
	965 w		972 w		992 w	overtones, combinations
	1075 vw, br				1070 w	
	1152 w		1152 w		1175 w	

[a] IR spectra listed for 250–1200 cm^{-1}; Raman spectra listed to 1000 cm^{-1}. [b] Cation bands: Raman 375 (0), 458 (0), 755 (2), 951 (2) cm^{-1}; IR 460 w, 918 sh, 946 s cm^{-1}.

assignment of the spectrum is given in Table II along with those for related species for comparison. The polarization measurements on the SeO stretching bands (893 and 870 cm^{-1}) confirm the assignment of the higher frequency band to the symmetric mode, $\nu_1(A')$, as proposed earlier.[2] The other band at 870 cm^{-1} belongs to $\nu_5(A'')$, the antisymmetric SeO_2 stretch. The next highest frequency band at 463 cm^{-1} is assigned to $\nu_2(A')$, the SeF stretch. This band is polarized as expected. Besides the antisymmetric SeO_2 stretch, $\nu_5(A'')$, the antisymmetric $\delta(SeO_2F)$, $\nu_6(A'')$, is the other depolarized mode and this is assigned to 268 cm^{-1}. Of the two remaining modes unassigned, the symmetric SeO_2 deformation, $\nu_3(A')$, is expected to lie higher than $\delta_{sym}(SeO_2F)$, $\nu_4(A')$, because of the greater mean bond strength in the SeO_2 skeleton and thus, these are assigned respectively at 389 and 295 cm^{-1}. The $\nu_3(A')$ mode is, in fact, obscured by solvent peaks in both MeCN and Me_2SO solutions and its degree of polarization could not be measured. The value in Table II has been taken from the Raman spectrum of solid Et_4NSeO_2F. This assignment differs from those given earlier[2,4] for which polarization measurements were not available.

The low frequency of the SeF stretching mode in the SeO_2F^- anion and the breadth and complexity of some of the bands in the Raman spectrum of $KSeO_2F$ suggested that there may be bridging in these compounds.[2] However, the absence of any major changes in the spectrum of the anion with increasing cation size, which should affect any bridging present, and the minimal differences between the spectrum of Et_4NSeO_2F in solid and solution show that the SeO_2F^- ion does not form strong bridges. Moreover, the isomorphous crystal structures of $CsSeO_2F$ and $CsBrO_3$, where the latter compound shows no anion bridging,[11] and the statistical occupation of the oxygen sites in the $CsBrO_3$ structure by F and O lead to the same conclusion. The breadth and structure of the bands in the spectra are expected in view of the variety of crystal fields in which the anions are located as a result of the statistical distribution of O and F. The low frequency of the SeF stretch therefore indicates that this bond is relatively weak as has been discussed earlier.[2,4]

$M^{I}TeO_2F$ Compounds. The Raman and IR spectra of the $NaTeO_2F$, $KTeO_2F$, and Me_4NTeO_2F are given in Table III and the spectra for $KTeO_2F$ are given in Figure 3. In the case of the spectra of Me_4NTeO_2F, the peaks due to the Me_4N^+ cation have been eliminated on the basis of the Raman and IR spectra of Me_4NCl with the spectra of Me_4NTeO_2F and Me_4NCl normalized with respect to cation band intensities. The spectra are unlike those of TeO_2[13] or the $TeO_2F_2^{2-}$ ion,[1] indicating that a different species is formed. The presence of a tellurium–fluorine bond is indicated by the Raman band near 460 cm^{-1} in all compounds. The mean TeF stretching frequencies in $Te(OH)F_4^-$ [12] and TeF_5^-,[3] which are uninegative like the TeO_2F^-, are 455 and 480 cm^{-1}.

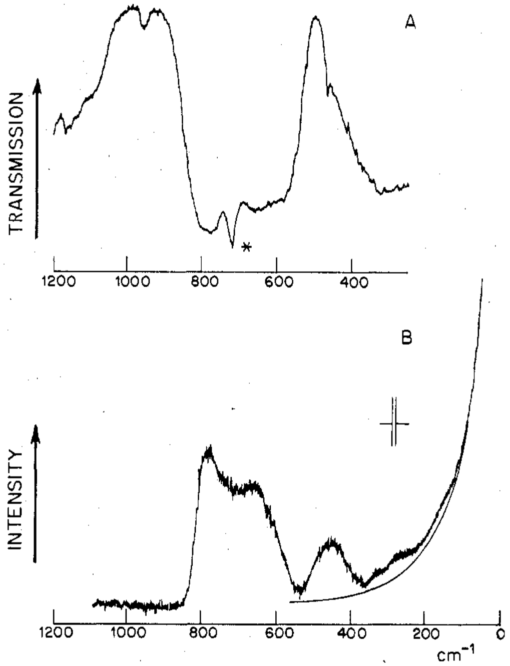

Figure 3. IR (A) and Raman (B) spectra of $KTeO_2F$: *, Nujol peak.

In general, tellurium exhibits higher coordination numbers in its compounds compared to those in compounds of sulfur and selenium. This appears also to be the case for the dioxofluoroanions of group 6. The SO_2F^- and SeO_2F^- anions are essentially monomeric in their compounds but the spectra of the TeO_2F^- anion suggests that this anion is polymeric. In particular the large separation between the strong TeO stretching peaks (648 and 808 cm^{-1}) and the breadth suggest the bands in the spectra support this supposition. Tellurium dioxide, which has an oxygen-bridged structure, has Raman-active TeO_2 stretching bands at 648, 667, 717, and 766 cm^{-1}.[13] The low solubility of Me_4NTeO_2F in water and the amorphous character of $NaTeO_2F$ are further indications of structures with significant anion bridging. Moreover, the Raman spectrum of the related $TeO_2F_2^{2-}$ anion shows pronounced splitting of the TeO stretching bands, indicating bridging.[1] The Raman spectrum of IO_2F, which is isoelectronic with the TeO_2F^- ion, shows a broad splitting of the IO stretches also (705–866 cm^{-1}).[14] These species differ, however, from the isoelectronic TeO_3^{2-},[15] IO_3^-,[11] and XeO_2F^+ [16] ions, which are monomeric in their compounds. Apparently the electron-withdrawing character of the fluoro ligand and the relatively greater electropositive character of Te(IV) and I(V) compared to Xe(VI) favor the formation of bridges between anions.

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Registry No. $KSeO_2F$, 15190-23-5; $CsSeO_2F$, 16004-28-7; Me_4NSeO_2F, 67891-59-2; Et_4NSeO_2F, 67891-60-5; $NaTeO_2F$, 67904-80-7; $KTeO_2F$, 67904-81-8; Me_4NTeO_2F, 67904-83-0.

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Preparation, Spectroscopic Properties, and Structure of the Pentabismuth(3+) Cation, Bi_5^{3+}

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The oxidation of bismuth with PF_5, AsF_5, SbF_5, $SbCl_5$, HSO_3F, and HSO_3Cl has been studied in SO_2 as the solvent. It was found that the pentafluorides oxidize bismuth first to Bi_8^{2+} and then to Bi_5^{3+}, but no evidence for polyatomic cations of bismuth was obtained in the reactions with the other oxidants. The new compound $Bi_5(AsF_6)_3\cdot 2SO_2$ was isolated and characterized. The Raman and infrared spectra of the compounds $Bi_5(AsF_6)_3\cdot 2SO_2$ and $Bi_5(AlCl_4)_3$ have been obtained and interpreted to show that the Bi_5^{3+} cation has a trigonal-bipyramidal structure. A complete vibrational analysis was carried out which indicates that the axial–equatorial bonds are somewhat stronger than the equatorial–equatorial bonds, with force constants of ~0.73 and ~0.55 mdyn/Å, respectively.

Introduction

The chemistry of bismuth in oxidation states of 1+ and lower has been rather extensively studied in investigations of the systems $Bi–BiCl_3$ and $Bi–BiCl_3–MCl_x$, where MCl_x is a metal chloride such as $AlCl_3$. The results of emf[1] and spectroscopic[2,3] studies of solutions of bismuth in $BiCl_3$ have been interpreted as indicating the formation of the species Bi^+ and $Bi_3^+\cdot nBi^{3+}$. A compound isolated from these $Bi–BiCl_3$ melts was originally thought to be the monochloride[4] "BiCl" but was later shown to have the composition $Bi_{24}Cl_{28}$ and to have a structure consisting of Bi_9^{5+} cations accompanied by $BiCl_5^{2-}$ and $Bi_2Cl_8^{2-}$ anions.[5] The Bi_9^{5+} cation has also been found in the compound $Bi_{10}Hf_3Cl_{18}$, which has been isolated from the $Bi–BiCl_3–HfCl_4$ melt system. This was shown to be $Bi^+Bi_9^{5+}(HfCl_6^{2-})_3$ by an X-ray crystallographic study.[6] Spectroscopic studies on solutions of Bi and $BiCl_3$ in molten $NaCl–AlCl_3$ and $KCl–ZnCl_2$ eutectics have led to the identification of the cations Bi_5^{3+} and Bi_8^{2+} in addition to Bi^+.[7,8] The solid salts $Bi_5(AlCl_4)_3$ and $Bi_8(AlCl_4)_2$ were subsequently isolated by Corbett and shown to have reflectance spectra similar to the absorption spectra of Bi_5^{3+} and Bi_8^{2+} in the molten salt solutions.[9] The structures of Bi_5^{3+} and Bi_8^{2+} were not determined in this earlier work although simplified LCAO–MO calculations suggested that the former has a trigonal-bipyramidal geometry and that the latter has a square-antiprismatic structure.[9]

More recently the reactions of SbF_5 and AsF_5 with sulfur, selenium, or tellurium in SO_2 as a solvent have been used to prepare a large variety of polyatomic cations such as S_8^{2+}, Se_4^{2+}, Te_6^{4+}, $Te_2Se_8^{2+}$, $Te_3S_3^{2+}$, and $Te_2Se_4^{2+}$.[10-14] Many of these cations have also been prepared by the reactions of their respective elements with the very strong acids HSO_3F and $H_2S_2O_7$.[15,16] In every case it appears that stable solutions or stable crystalline salts of these polyatomic cations can only be obtained when the cation is accompanied by a large, very weakly basic anion such as $AlCl_4^-$, SbF_6^-, or SO_3F^-. The object of the present work was to study the oxidation of bismuth with a variety of oxidants in solution in SO_2 to investigate the formation of bismuth polyatomic cations in this medium, with the particular objective of obtaining more information on the structures of Bi_5^{3+}, Bi_8^{2+}, and any other bismuth cations that might be formed.

Experimental Section

Materials. Bismuth metal (200 mesh), as obtained from Alfa Inorganics, was indicated to be 99.999% pure and was used without further purification.

Commercial bismuth trichloride was dehydrated under vacuum at 140 °C and sublimed five times under a dynamic vacuum. The product so obtained was pure white, with no indication of carbonaceous impurity.[6]