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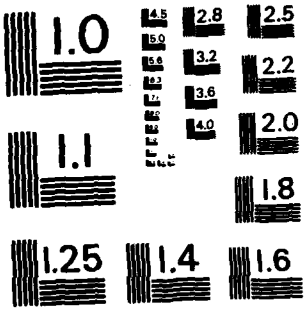

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Synthesis and Characterization of TeF_5OF

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A new method for the synthesis of hypofluorites was discovered utilizing fluorine fluorosulfate as the fluorinating agent. The method was successfully applied to the high-yield synthesis of the new hypofluorite TeF_5OF. The compound was also prepared in lower yield by the fluorination of TeF_5OH with a concentrated NF_4HF_2 solution. The physical properties and infrared, Raman, ^{19}F NMR and mass spectra of TeF_5OF are reported. The vibrational spectra of TeF_5OCl were redetermined, and complete vibrational assignments are given for TeF_5OF and TeF_5OCl.

Introduction

The number of elements known to form hypofluorites is small and until recently was limited to the following nonmetal main-group elements: H, C, N, O, S, Se, F, and Cl.[1] The synthetic method used for the syntheses of these hypofluorites involved the fluorination of the corresponding hydroxyl compounds of their metal salts with elemental fluorine. An unsuccessful attempt[2] was made to apply this method to the synthesis of the hitherto unknown TeF_5OF. This failure to prepare TeF_5OF, but the success in the synthesis of TeF_5OCl by an analogous method,[2] led to the conclusion[3] that TeF_5OF is unstable or actually nonexistent.

Our recent success[4] in preparing a stable iodine hypofluorite and the observation that hypofluorites are generally more stable than the other hypohalites suggested that TeF_5OF should not only exist but should also be stable. In this paper we present data that show that TeF_5OF indeed exists and is stable.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U-Traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. Telluric acid was prepared by a literature method[5] and also purchased from Cerac, Inc., and from Pfaltz and Bauer. Fluorosulfuric acid (Allied) was used both as it was received (light brown color) and after it was distilled to obtain the clear colorless material. Fluorine fluorosulfate was synthesized as described.[6] The reaction of TeF_5OH with either $ClOSO_2F$ or ClF was used to prepare TeF_4OCl.[7] Cesium and potassium chloride were oven-dried and then cooled and powdered under the dry N_2 atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points,[8,9] and the reported frequencies are believed to be accurate to ± 2 cm^{-1}. The spectra of gases were obtained with use of either a Teflon cell of 5-cm path length equipped with AgCl windows or a 10-cm stainless steel cell equipped with polyethylene windows that were seasoned with ClF_3. The spectra of matrix-isolated TeF_5OF and TeF_5OCl were obtained at 6 K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ne (Matheson) was used as a matrix material in a mole ratio of 400:1.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer with use of the 488-nm exciting line of an Ar ion laser and a Claassen filter[10] for the elimination of plasma lines. Quartz tubes (3 mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described[11] device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.[10]

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer. Chemical shifts were determined relative to the $CFCl_3$ solvent with positive shifts being downfield from $CFCl_3$.[12] Second-order spectra were analyzed by using the programs NMRIT and NMREN by Swalen.[13]

The mass spectra were recorded with an EAI Quad 300 quadrupole spectrometer at an ionization potential of 40 eV.

Synthesis of TeF_5OH. Telluric acid, $H_2TeO_4 \cdot 2H_2O$ or $Te(OH)_6$, was fluorinated to give TeF_5OH by the method of Seppelt and Nothe[2] with use of HSO_3F as the fluorinating agent. This technique calls for the use of distilled HSO_3F, and initially we encountered difficulty in producing TeF_5OH. Subsequently, it was discovered that adding a few milliliters of H_2O to the reaction mixture and heating the reaction mixture at 160–170 °C for 5–6 h resulted in continuous evolution of TeF_5OH at a slow to moderate rate. Finally, undistilled HSO_3F was employed which furnished TeF_5OH in 70% purified yield; 93.9 mmol of TeF_5OH from 135 mmol of $Te(OH)_6$ and 1.75 mol of HSO_3F. Fractional condensation was used for the final product purification.

Fluorination of $M^+TeF_5O^-$. The salts $CsTeF_5O$[14] and $KTeF_5O$[15] were treated with F_2 in stainless steel cylinders at low temperature. Thus $CsTeF_5O$ (1.43 mmol) and F_2 (4.46 mmol) were allowed to react for 8 days at −45 °C. The only volatile product condensable at −196 °C was TeF_6 (0.38 mmol, 26%). Similarly at −10 °C for 2 weeks a 48% yield of TeF was obtained from the cesium salt. When the potassium salt (2.92 mmol) and F_2 (4.46 mmol) were kept at −45 °C for 6 weeks, again TeF_6 (2.35 mmol, 80%) was the only volatile tellurium compound observed.

Synthesis of TeF_5OF from $CsTeF_5O$ and $FOSO_2F$. A 30-mL stainless steel Hoke cylinder was loaded with $CsTeF_5O$ (3.42 mmol) in the glovebox. After evacuation and cooling of the cylinder to −196 °C, $FOSO_2F$ (2.79 mmol) was added from the vacuum line. The closed cylinder was slowly warmed to −78 °C in a liquid-nitrogen–CO_2 slush bath and finally kept at −45 °C for 9 days. When the cylinder was recooled to −196 °C, about 4–5 cm^3 of noncondensable gas was observed to be present. This was pumped away, and the condensable products were separated by fractional condensation in a series of U-traps cooled at −78, −126, and −196 °C. The −78 °C fraction was TeF_5OH (0.19 mmol) while the −196 °C fraction was TeF_6 (0.49 mmol). A white solid was retained at −126 °C, which changed to a colorless glass and melted, over a range of a few degrees, near −80 °C to a clear, colorless liquid. This material was identified as TeF_5OF (1.91 mmol, 68% yield) on the basis of its vapor density molecular weight: found, 256.2; calculated, 257.6. Further identification was based on its spectroscopic properties (see below) and on the preparation of derivatives.[16] The observed weight loss of the solid (0.375 g) agreed

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well with that calculated (0.389 g) for the conversion of 2.79 mmol of $CsTeF_5O$ to $CsSO_3F$. The following vapor pressure–temperature data of TeF_5OF were measured (T in °C, P in mm): −79.3, 16; −64.2, 45, −57.6, 63; −46.9, 108; −32.5, 210; −23.0, 312.

Synthesis of TeF_5OF from TeF_5OH and NF_4HF_2. A sample of $NF_4HF_2{\cdot}nHF$ (10.5 mmol) was prepared and concentrated in a Teflon double-U metathesis apparatus, as previously described.[17] To this reactor was added TeF_5OH (10.5 mmol) on the vacuum line at −196 °C. The mixture was allowed to warm slowly to −23 °C and was kept at this temperature for 8 h under a dynamic vacuum. The volatile products were separated by fractional condensation through traps kept at −95, −126, −142, and −210 °C. On the basis of their infrared and ^{19}F NMR spectra the following products were collected in these traps: −210 °C, NF_3 and a trace of TeF_6; −142 °C, TeF_6 and TeF_5OF in a mole ratio of about 3:1; −126 °C, HF and some TeF_5OF; −95 °C, TeF_5OH and some HF. The white solid residue (0.57 g) decomposed during an attempt to transfer it at ambient temperature to a drybox for further characterization. The overall yield of TeF_5OF was estimated to be about 10–20% with TeF_6 and unreacted TeF_5OH being the principal products.

Results and Discussion

Synthesis of TeF_5OF. By analogy to previous attempts[2,18] to synthesize TeF_5OF from either $Hg(TeF_5O)_2$ or $CsTeF_5O$ and F_2, the fluorination of either $CsTeF_5O$ or $KTeF_5O$ with F_2 at −45 to −10 °C was unsuccessful and resulted only in TeF_6 formation. Since the decomposition of NF_4XO salts had recently been shown to provide new high-yield syntheses for hypofluorites such as $FOClO_3$,[19] $FOSO_2F$,[20] and $FOIF_4O$,[4] the synthesis of NF_4TeF_5O by metathesis of NF_4SbF_6 and $CsTeF_5O$ in anhydrous HF was attempted. This attempt, however, was preempted by the fact that $CsTeF_5O$ was found to react with anhydrous HF, undergoing a displacement reaction. Recent work[17] in our laboratory had shown that even in cases of Lewis acids that are weaker than HF their NF_4^+ salts can be prepared by treating $NF_4HF_2{\cdot}nHF$ with this acid. Therefore, this approach was studied for NF_4TeF_5O. Although the NF_4TeF_5O salt itself could not be isolated, it was found that TeF_5OH (which is equivalent to an equimolar mixture of the Lewis acid TeF_4O and HF) reacted with $NF_4HF_2{\cdot}nHF$ at −23 °C to produce TeF_5OF in moderate yield:

$$NF_4HF_2 + TeF_5OH \rightarrow NF_3 + TeF_5OF + 2HF$$

Since TeF_6 was the major product, we prefer to interpret this reaction in terms of a fluorination of TeF_5OH by nascent fluorine formed in the decomposition of NF_4HF_2, rather than in terms of a decomposition of an unstable NF_4TeF_5O intermediate. In the latter case, we would expect a near-quantitative yield of TeF_5OF.

A more facile high-yield synthesis of TeF_5OF was discovered by reacting $CsTeF_5O$ with $FOSO_2F$ at −45 °C:

$$CsTeF_5O + FOSO_2F \rightarrow CsSO_3F + TeF_5OF$$

This reaction represents a new synthetic route to hypofluorites. On the basis of the general usefulness of the analogous $ClOSO_2F$ reagent for the syntheses of hypochlorites,[21] $FOSO_2F$ may be similarly useful for the synthesis of hypofluorites.

When the synthesis of TeF_5OF from $CsTeF_5O$ and $FOSO_2F$ was carried out above −45 °C, the amount of TeF_6 byproduct sharply increased. For example, at −10 °C and with a reaction time of 7 days, the TeF_6 to TeF_5OF ratio in the product increased to 1:1. The use of an excess of $CsTeF_5O$ in this reaction was found advantageous for the product purification since it eliminates the need for separating TeF_5OF from $FOSO_2F$.

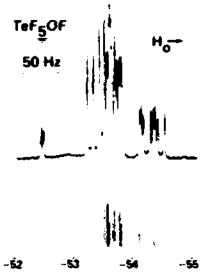

Figure 1. Observed and calculated ^{19}F NMR spectra of the AB_4 part of TeF_5OF.

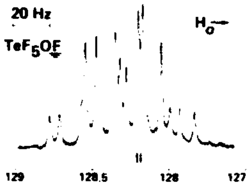

Figure 2. Observed and calculated ^{19}F NMR spectra of the X part of TeF_5OF.

Table I. Mass Spectrum of TeF_5OF Compared to Those of TeF_5OCl and TeF_5OH

TeF_5OF		TeF_5OCl		TeF_5OH	
assignt	intens	assignt	intens	assignt	intens
TeF_5OF^+	vw	TeF_5OCl^+	vvw	TeF_5OH^+	w
TeF_4OF^+	vvw	TeF_4OCl^+	vw	TeF_4OH^+	vw
TeF_5O^+					
TeF_5^+	s	TeF_5^+	s	TeF_5^+	vs
TeF_4^+	w	TeF_4^+	vw	TeF_4^+	w
TeF_3O^+	m	TeF_3O^+	ms	TeF_3O^+	s
TeF_3^+	vs	TeF_3^+	vs	TeF_3^+	vs
TeF_2^+	m	TeF_2^+	m	TeF_2^+	m
$TeFO^+$	vw	$TeFO^+$	w	$TeFO^+$	w
TeF^+	w	TeF^+	w	TeF^+	w
Te^+	w	Te^+	w	Te^+	w

Properties of TeF_5OF. This compound is colorless as a gas and liquid. Its vapor pressure–temperature relationship for the range −79 to −23 °C is given by the equation

$$\log[P\,(\mathrm{mm})] = 6.9022 - 1101.2/[T\,(\mathrm{K})]$$

The extrapolated boiling point is 0.6 °C. The derived heat of vaporization is $\Delta H_{vap} = 5039$ cal mol^{-1} and the Trouton constant is 18.4, indicating little or no association in the liquid phase. Vapor density measurements showed that in the gas phase the compound is also not associated. We were not able to observe a sharp melting point for TeF_5OF because our samples showed a tendency to form a glass near −80 °C. The compound appears to be completely stable at ambient temperature and has been stored in stainless steel cylinders for more than 4 months without any sign of decomposition.

^{19}F NMR Spectrum. The ^{19}F NMR spectrum of TeF_5OF in $CFCl_3$ solution at 28 °C is shown in Figures 1 and 2 and is characteristic for a second-order AB_4X spin system. A computer-aided analysis of the spectrum resulted in the following parameters: $\phi^*(A) = -52.5$, $\phi^*(B_4) = -54.0$, $\phi^*(X) = 128.3$, $J_{AB} = 180$ Hz, $J_{AX} = 4.9$ Hz, $J_{BX} = 19.0$ Hz, $R = 1.20$, $J_{^{125}Te^{19}F} = 3800$ Hz. These values are in excellent agreement with those found for numerous other covalent TeF_5O-type compounds.[22]

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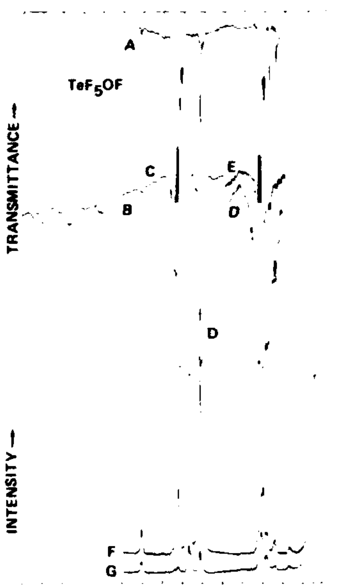

Figure 3. Vibrational spectra of TeF_5OF: trace A, infrared spectrum of TeF_5OF isolated in a neon matrix (mole ratio 400:1) and recorded at 6 K; traces B and C, infrared spectra of the gas, recorded at pressures of 74 and 3 mm, respectively, in a 5-cm path length cell equipped with AgCl windows (the very weak bands at 1272, 1105, 640, and 548 cm^{-1} in spectrum B are due to a trace of $FClO_2$ resulting from the ClF_3 used for passivation); traces D and E, infrared spectra of the gas, recorded at pressures of 86 and 8 mm, respectively, in a 10-cm path length cell equipped with polyethylene windows and with polyethylene windows in the reference beam; traces F and G, Raman spectra of the liquid, recorded in 3 mm o.d. quartz tubes at −55 °C with the incident polarization parallel and perpendicular, respectively.

Table II. Vibrational Spectra of TeF_5OF

obsd freq, cm^{-1} (rel intens[a])				
IR		Raman		
gas	Ne matrix	liquid, −55 °C	solid, −110 °C	assignt[b]
1800 vw				$2\nu_{11}$
1449 vw				$2\nu_1$
1403 w				$\nu_2 + \nu_8$
908 vw		905 (0.4) p	904 (0.8)	ν_{11}
738 vs {	738[c] vs	738 sh, dp	735 sh	ν_8
	727 vs	721 (1.1) p	721 (1.3)	ν_1
	718 vw			} impurity?
	709 vw			
	668 vw	669 (10) p	670 (10)	ν_2
		660 (0.3) dp	662 sh	ν_5
616 m	618 m	613 (3.8) p	613 (4)	ν_3
324 vs {	327 vs	325 sh, dp	325 sh	ν_9
	318 vs		319 sh	ν_{10}
	308 vw	309 (1.0) dp	309 (1.6)	ν_7
300 sh	302 m	301 (0.5) p	301 sh	ν_4
280 mw	278 m	279 (0.2) dp	279 (0.2)	ν_{11}
241 mw	239 mw	240 (0.2) p	240 (0.2)	ν_{13}
		166 (0.1) dp	167 (0.1)	ν_{14}

[a] Uncorrected Raman intensities (peak heights). [b] For mode description see Table IV. [c] Band shows tellurium isotope fine structure with splittings of about 1.30 cm^{-1}.

Mass Spectrum. The mass spectrum of TeF_5OF is listed in Table I together with the spectra of TeF_5OCl and TeF_5OH, which were measured for comparison. All of the listed fragments showed the characteristic tellurium isotope pattern, and therefore the individual *m/e* listings were omitted for simplicity. The spectra of all three compounds show weak parent ions and TeF_3^+ as the base peak.

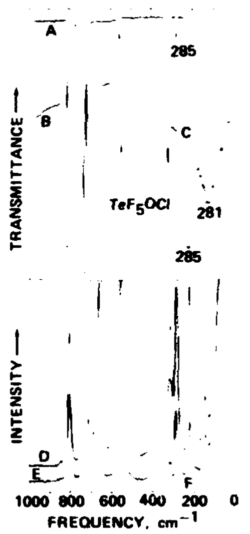

Figure 4. Vibrational spectra of TeF_5OCl: traces A and C, infrared spectra of TeF_5OCl isolated in a neon matrix (mole ratio 400:1) at 6 K; trace B, infrared spectrum of the gas, recorded at a pressure of 27 mm in a 5-cm path length cell equipped with AgCl windows; traces D and E, Raman spectra of the liquid, recorded in 3 mm o.d. quartz tubes at −80 °C with the incident polarization parallel and perpendicular, respectively; trace F, spectrum recorded under the same conditions as for trace D, except for a narrower slit width.

Table III. Vibrational Spectra of TeF_5OCl

obsd freq, cm^{-1} (rel intens[a])			
IR		Raman liquid, −80 °C	assignt[b]
gas	Ne matrix		
1365 vw			$\nu_3 + \nu_{12}$
812 s	814 s	809 (0.9) p	ν_{12}
	811 s		
732 vs	732 vs[c]	730 sh, dp	ν_8
	718 s	713 (1.6) p	ν_1
		663 (10) p	ν_2
		655 sh, dp	ν_5
551 m	558 m	554 (6.5) p	ν_3
	327 vs	328 sh, dp	ν_9
	322 vs	316 (0.8) dp	ν_{10}
		308 (0.8) dp	ν_7
	285 m		ν_{11}
	281 m	281 (2.8) p	ν_4
		218 (1.1) p	ν_{13}
		141 (0.3) dp	ν_{14}

[a] Uncorrected Raman intensities. [b] For mode description see Table IV. [c] Band shows fine structure with splittings of about 1.30 cm^{-1} due to tellurium isotopes.

Vibrational Spectra of TeF_5OF and TeF_5OCl. The infrared spectra of gaseous and of neon-matrix-isolated TeF_5OF and the Raman spectra of liquid and solid TeF_5OF were recorded (see Figure 3), and the observed frequencies are summarized in Table II. Since the assignments previously reported[23] for TeF_5OCl could not be reconciled with our results for TeF_5OF, the vibrational spectra of TeF_5OCl were also recorded (see Figure 4 and Table III). The following deviations from the

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(23) Seppelt, K. *Z. Anorg. Allg. Chem.* **1973**, *399*, 87.

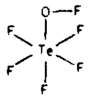
Table IV. Vibrational Spectra of TeF_5OF and TeF_5OCl and Their Assignment Compared to Those of TeF_5Cl

assignt	approx descripn of mode	obsd freq, cm^{-1} (rel intens^a)					
		TeF_5Cl^b		TeF_5OCl		TeF_5OF	
		IR (gas)	Raman (liquid)	IR (gas, matrix)	Raman (liquid)	IR (gas, matrix)	Raman (liquid)
C_{4v} A_1 ν_1	$\nu(TeF)$	711 sh, m	708 (3.1) p	718 s	713 (1.6) p	727 vs	721 (1.1) p
ν_2	$\nu_s(TeF_4)$	662 vw	659 (10) p		663 (10) p		669 (10) p
ν_3	$\nu(TeX)$	411 ms	413 (7.7) p	551 m	554 (6.5) p	616 m	613 (3.8) p
ν_4	$\delta_s(TeF_4)$	317 s	312 (0.8) p	281 m	281 (2.8) p	301 m	301 (0.5) p
B_1 ν_5	$\nu_s(TeF_4)$		651 (0.8) dp		655 sh, dp		660 (0.3) dp
ν_6	$\delta(TeF_4)$						
B_2 ν_7	$\delta_{sciss}(TeF_4)$		302 (0.5) dp		308 (0.8) dp	308 vw	309 (1.0) dp
E ν_8	$\nu_{as}(TeF_4)$	726 vvs	726 (0.6) dp	732 vs	730 sh, dp	738 vs	738 sh, dp
ν_9	$\delta(FTeF_4)$	325 ms	327 (0.9) dp	327 vs	328 sh, dp	327 vs	325 sh, dp
ν_{10}	$\delta(XTeF_4)$		167 (1.8) dp	322 vs	316 (0.8) dp	318 vs	(309–325)
ν_{11}	$\delta_{as}(TeF_4)$	259 m	259 (1.7) dp	285 m		280 mw	279 (0.2) dp
C_s A′ ν_{12}	$\nu(XY)$			812 s	809 (0.9) p	908 vw	905 (0.4) p
A″ ν_{13}	$\delta(TeXY)$				218 (1.1) p	240 mw	240 (0.2) p
ν_{14}	$\tau(TeXY)$				141 (0.3) dp		166 (0.1) dp

[a] Uncorrected Raman intensities (peak heights). [b] Data from ref 24.

previous literature data[23] were observed. (i) The infrared spectrum of the gas does not exhibit a very strong band at 708 cm^{-1}. Although our Ne-matrix spectra show the presence of two intense bands at 732 and 718 cm^{-1}, respectively, their frequencies are too close to result in two separate bands in the gas-phase spectrum. (ii) In the Raman spectrum of the liquid the 141-cm^{-1} band is depolarized and the 809-cm^{-1} band is polarized. (iii) The infrared spectrum of the neon-matrix sample shows the presence of two fundamental vibrations in the 280-cm^{-1} region (see trace C of Figure 4).

Using the well-established[24] assignments of TeF_5Cl and the revised experimental data of TeF_5OCl for comparison, we can readily assign the vibrational spectra of TeF_5OF (see Table IV), assuming a model with C_{4v} symmetry for the TeF_5O part and C_s symmetry for the TeOF part of the molecule:



Except for the symmetric out of phase, out of plane TeF_4 deformation mode in species B_1, which is usually not observed for pseudooctahedral molecules and is inactive under O_h symmetry, all fundamentals expected for the above C_{4v}–C_s model were observed. The assignments (see Table IV) are straightforward and show for the three molecules almost identical frequencies for the TeF_5 part of the molecules. The modes involving the XY group of this TeF_5XY molecule show the expected mass effects for different X and Y groups. Since the Te–O stretching mode is expected to couple strongly with the O–Hal stretch and to couple moderately with $\delta_s(TeF_4)$ (A_1),[25] these modes also exhibit a mass effect.

Comparison of the assignments of Table IV with those previously given[23] for TeF_5OCl shows that with the exception of ν_7 (B_2) and ν_{13} all the previously given assignments for the deformation modes should be revised. Since a thorough normal-coordinate analysis has previously been carried out[24] for TeF_5Cl and since the TeF_5Cl and TeF_5XY spectra are similar, a normal-coordinate analysis of the latter molecules appears unwarranted.

Conclusion. The results of this study show that $FOSO_2F$ is a useful reagent for the synthesis of hypofluorites.[26] Furthermore, it is shown that TeF_5OF, as expected from comparison with TeF_5OCl, TeF_5OBr, and $FOIF_4O$, indeed exists and is a stable molecule. The TeF_5OF molecule was characterized, and the vibrational assignments were made for TeF_5OF and TeF_5OCl.

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Registry No. TeF_5OH, 57458-27-2; $CsTeF_5O$, 19610-48-1; $KTeF_5O$, 19610-51-6; TeF_5OF, 83314-21-0; $FOSO_2F$, 13536-85-1; NF_4HF_2, 71485-49-9; TeF_5OCl, 41524-13-4.

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(24) Brooks, W. V. F.; Eshaque, M.; Lau, C.; Passmore, J. *Can. J. Chem.* 1976, *54*, 817.

(25) Christe, K. O.; Curtis, E. C. *Inorg. Chem.* 1982, *21*, 2938.

(26) After completion of this work, D. D. DesMarteau has informed us in a private communication that he has also used $FOSO_2F$ for the preparation of $CF_3C(O)OF$ from the corresponding alkali-metal salt

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A new method for the synthesis of hypofluorites was discovered utilizing fluorine fluorosulfate as the fluorinating agent. The method was successfully applied to the high-yield synthesis of the new hypofluorite TeF_5OF. The compound was also prepared in lower yield by the fluorination of TeF_5OH with a concentrated NF_4HF_2 solution. The physical properties and infrared, Raman, ^{19}F NMR and mass spectra of TeF_5OF are reported. The vibrational spectra of TeF_5OCl were redetermined, and complete vibrational assignments are given for TeF_5OF and TeF_5OCl.

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