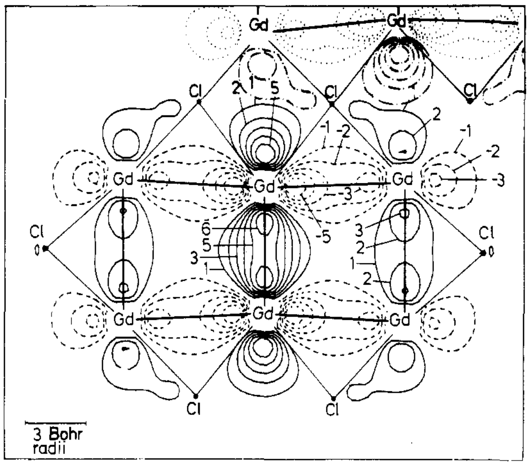

Figure 5. Lowest unoccupied molecular orbital (LUMO) of the $Gd_{10}C_4Cl_{18}$ cluster plotted in the basal plane of the double octahedron. Notice that this metal-metal bond is especially strong between the two atoms on the shared edge. The contour values are in units of 0.02(Bohr radius)$^{-3/2}$. The dash-dotted and the dotted contours indicate the LUMO on the neighboring cluster of the compound $Gd_{10}C_4Cl_{17}$.

is seen to be roughly 2ddσ and, as seen from Figure 2, this is approximately 0.2 Ry. Second, the *inter*cluster hopping integral is seen to be roughly ddσ'/3, where the ratio between the inter and the intra hopping integrals, ddσ' and ddσ, approximately equals the ratio between the intra- and the intercluster Gd–Gd distances to the fifth power. As a result, the LUMO bandwidth 2ddσ'/3 is roughly 20 mRy. This is so small that the LUMO band presumably preserves its identity and does not overlap the rest of the Gd d band. However, due to the exchange coupling with Gd 4f magnetic moments, the LUMO band will be spin split and the one extra electron will thus fill the lower subband.

The compound $Gd_{12}C_6I_{17}$, where the clusters are condensed into infinite zigzag chains,[4] also has one extra electron per double octahedron, and the LUMOs on neighboring double octahedra can be seen to interact only weakly. We believe that also in this compound the extra electron occupies a magnetic subband formed from the LUMO or similar two-center bonds concentrated on (all) the shared edges. This view is supported by the experimental fact that the edge shared in the double octahedron of this compound has the length 0.836 in units of the average Gd–Gd distance. This is very similar to the case $Gd_{10}C_4Cl_{17}$, where the LUMO is also occupied and where the corresponding number is 0.841. In $Gd_{10}C_4Cl_{18}$, where the LUMO is empty, this relative distance is 0.859, that is, considerably larger than the previous two cases. The need for using relative—rather than absolute—distances for this comparison between Cl and I compounds stems from the fact that it is the X–C_2 matrix that mostly determines the size of the metal octahedron.

Summary

In summary, by means of LMTO–ASA calculations we have studied the electronic structure of the cluster $Gd_{10}C_4Cl_{18}$. A principal conclusion was that in the compound $Gd_{10}C_4Cl_{18}$ there are no strong metal–metal bonds. The transfer of metal d electrons into the carbon atoms causes the antibonding π^* states of the C_2 molecules to be occupied, in consistence with the experimentally observed single C–C bond distance. Furthermore, our calculations and the observed differences in the shortest metal–metal distances indicate that whereas $Gd_{10}C_4Cl_{18}$ is an ionic compound with no strong bonds between the metal atoms, the compounds $Gd_{10}C_4Cl_{17}$ and $Gd_{12}C_6I_{17}$ have in contrast one occupied metal–metal bonding molecular orbital split off below the bulk of the metal states.

Acknowledgment. We thank Professor A. Simon and Dr. E. Warkentin for stimulating this research.

Registry No. $Gd_{10}C_4Cl_{18}$, 84989-58-2; $Gd_{10}C_4Cl_{17}$, 85248-21-1; $Gd_{12}C_6I_{17}$, 96826-77-6.

Contribution from the Department of Chemistry,
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Study of the $OTeF_5$ Donor Properties of $Te(OTeF_5)_4$ by ^{75}As and ^{125}Te NMR Spectroscopy. Preparation and Characterization of the $[TeFe_x(OTeF_5)_{3-x}]^+$ Cations, $TeF_x(OTeF_5)_{4-x}$, $As(OTeF_5)_5$, and $[As(OTeF_5)_6]^-$[1]

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The $OTeF_5^-$ ion donor properties have been studied for $Te(OTeF_5)_4$ in the presence of the acceptor species AsF_5 and $As(OTeF_5)_5$. The synthesis of the latter compound from $B(OTeF_5)_3$ and AsF_5 is described. The mixed cations $[TeF_x(OTeF_5)_{3-x}]^+$ (x = 0–3) and the neutral species $TeF_x(OTeF_5)_{4-x}$ (x = 0–2) have been characterized in solution by ^{125}Te NMR spectroscopy. The novel anion $As(OTeF_5)_6^-$ has also been identified. Owing to the local octahedral symmetry about the quadrupolar ^{75}As atom in $As(OTeF_5)_6^-$, the ^{75}As NMR line is sufficiently narrow to permit ready observation of the signal as well as the two-bond natural-abundance ^{125}Te–^{75}As coupling (430 Hz). The activation energy barrier to intramolecular exchange in the trigonal-bipyramidal $Te(OTeF_5)_4$ molecule also has been derived from low-temperature ^{19}F and ^{125}Te NMR studies in SO_2ClF solvent (E_a = 31.0 ± 0.4 kJ mol^{-1}). No activation energy for $As(OTeF_5)_5$ was determinable above the freezing point of SO_2ClF (−124 °C). Reduced (K) and relativistically corrected reduced (K_{RC}) coupling constants have been calculated for observed one-bond ^{19}F–^{77}Se and ^{19}F–^{125}Te and two-bond ^{75}As–^{125}Te and ^{125}Te–^{125}Te scalar couplings.

Introduction

A considerable portion of the main-group chemistry of simple binary fluorides is based upon the fluoride ion donor/acceptor properties of the parent compounds. In the present work we have extended the analogy to the $OTeF_5^-$ anion and have studied its donor/acceptor properties in a series of mixed F/$OTeF_5$ compounds of Te(IV), leading to the novel mixed-cation series $[TeF_x(OTeF_5)_{3-x}]^+$ and their counterions $[AsF_y(OTeF_5)_{6-y}]^-$. Examples of $OTeF_5$/F ligand redistributions have been reported for $O_2XeF_x(OTeF_5)_{2-x}$, $XeF_x(OTeF_5)_{4-x}$, and $OXeF_x(OTeF_5)_{4-x}$[2]

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[1] Presented, in part, at the 10th International Symposium on Fluorine Chemistry, Vancouver, Canada, 1982.

[2] Schumacher, G. A.; Schrobilgen, G. J. *Inorg. Chem.* **1984**, *23*, 2923.

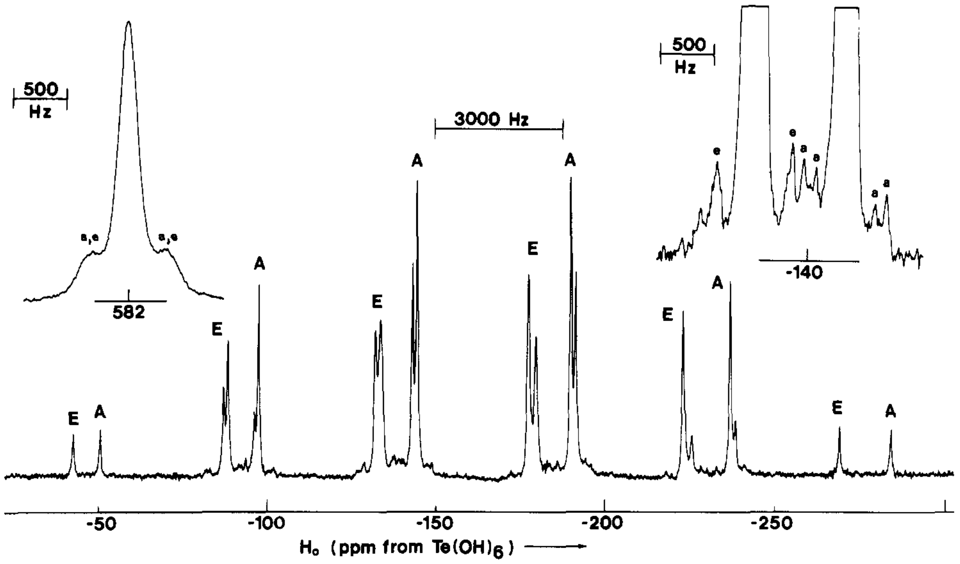

Figure 1. ^{125}Te NMR spectrum (78.97 MHz) of $Te(OTeF_5)_4$ in SO_2ClF solution at 146 K (0.18 *m*; 3500 scans; 3.0 Hz/point). A and E denote peaks for axial and equatorial $OTeF_5$ groups, respectively. The left inset shows Te(IV) (42000 scans; 6.1 Hz/point). The right inset shows $^2J_{^{125}Te(IV)-^{125}Te(VI)}$ for axial (a) and equatorial (e) $OTeF_5$ groups (42000 scans, 6.1 Hz/point).

as well as for $UF_x(OTeF_5)_{6-x}$[3], $WF_x(OTeF_5)_{6-x}$,[4] and $MoF_x(OTeF_5)_{6-x}$, and $OMoF_x(OTeF_5)_{4-x}$.[5] The only previous examples of cationic derivatives are xenon derivatives, i.e., $XeOTeF_5^+$ and $FXe{-}{-}{-}F{-}{-}{-}XeOTeF_5^+$.[6] The only other anionic derivatives of the $OTeF_5$ group reported as yet are $As(OTeF_5)_4^-$ and $As(OTeF_5)_3Cl^-$,[7] although the related $OSeF_5$ derivative, $Br(OSeF_5)_4^-$, has been prepared.[8]

The $OTeF_5$ analogue of AsF_5, $As(OTeF_5)_5$, has been prepared and employed as an acceptor species for $OTeF_5^-$ in the course of the present investigations. Its preparation has also been described recently by Lentz and Seppelt.[9]

The precursor $OTeF_5^-$ ion donor used in the present study, $Te(OTeF_5)_4$, had been prepared and studied earlier by using room-temperature ^{19}F NMR spectroscopy as the chief means of structural characterization.[10] A subsequent low-temperature ^{125}Te NMR study showed the structure of $Te(OTeF_5)_4$ to be consistent with a trigonal-bipyramidal arrangement of four bonding electron pairs and one nonbonding electron pair undergoing rapid intramolecular exchange between the axial and equatorial sites.[11] The limiting spectrum of both ligand environments was obtained at 163 K in SO_2ClF solvent, but no systematic variable-temperature study was conducted in order to determine the activation energy for the two-site intramolecular exchange process.

In order to study the complex equilibria resulting from a combination of ligand redistribution and donor/acceptor properties of the systems under study, multinuclear magnetic resonance spectroscopy of the central heavy nuclei ^{125}Te and ^{75}As has been employed. The ^{125}Te and ^{75}As resonances at natural abundances (^{125}Te, 6.99%, $I = {}^1/_2$; ^{75}As, 100%, $I = {}^3/_2$) provide a ready and definitive means of characterizing the majority of species present in these complex mixtures.

Results and Discussion

Intramolecular Exchange in $Te(OTeF_5)_4$ and $As(OTeF_5)_5$. The Te(VI) region of the ^{125}Te NMR spectrum of $Te(OTeF_5)_4$ in CH_3CN and SO_2ClF solutions at 297 K consisted of two overlapping quintets resulting from coupling of ^{125}Te to one axial and four equatorial fluorine atoms. This pattern is characteristic of an $OTeF_5$ group and indicates that only one type of $OTeF_5$ group is present. Valence-shell electron-pair repulsion (VSEPR) predictions[12] suggest that $Te(OTeF_5)_4$ should be based upon a trigonal-bipyramidal arrangement of four bond pairs and an electron lone pair with two axial and two equatorial $OTeF_5$ groups. Equivalence of these $OTeF_5$ groups with retention of a single $^{125}Te(VI)-^{125}Te(IV)$ coupling (see Table I) indicates rapid intramolecular exchange in solution. Exchange for 5-coordinate molecules (the lone pair of electrons is considered part of the coordination sphere) is generally believed to take place via a square-pyramidal transition state (Berry pseudorotation).[13] If the activation energy for exchange is sufficiently high, cooling the sample can slow the exchange sufficiently on the NMR time scale for separate axial and equatorial environments to be observed.

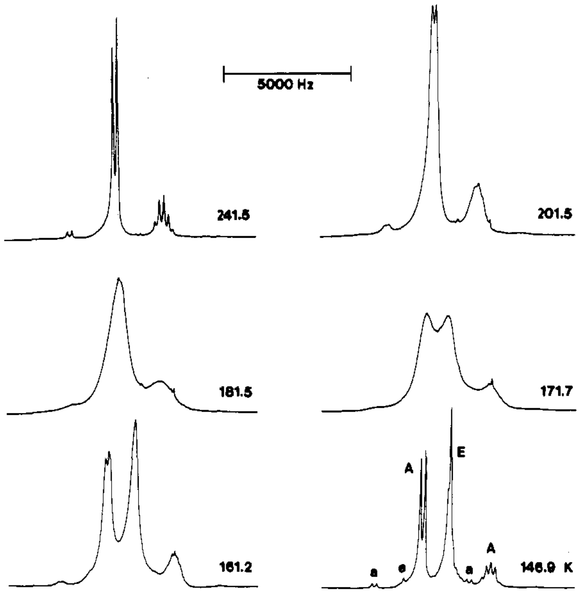

Figure 2. Variable-temperature ^{19}F NMR spectra (235.36 MHz) of $Te(OTeF_5)_4$ in SO_2ClF solution (0.18 *m*; 60 scans; 2.4 Hz/point). A and E denote peaks for axial and equatorial $OTeF_5$ groups, respectively; peaks marked a and e denote $^1J_{^{19}F-^{125}Te(VI)}$.

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Table I. ^{125}Te NMR Parameters for $\mathrm{TeF_x(OTeF_5)_{4-x}}$ and $\mathrm{[TeF_x(OTeF_5)_{3-x}]^+}$

		J, Hz				
solute	$\delta_{^{125}\mathrm{Te}}{}^a$	^{19}F–^{125}Te	^{125}Te(IV)–^{125}Te(VI)	solvent	temp, K	concn, *m*
$\mathrm{Te(OTe'F_5)_4}^b$	Te 394.0	F (E) 3639^d	544	$\mathrm{CH_3CN}$	297	1.00
	Te′ − 157.6	F (A) 3403				
$\mathrm{Te(OTe'F_5)_4}^b$	Te 633.3	31.8^c		$\mathrm{SO_2ClF}$	297	0.18
	Te′ −160.8	F (E) 3665^d				
		F (A) 3555				
$\mathrm{Te(OTe'F_5)_4}$	Te 581.6			$\mathrm{SO_2ClF}$	143	0.18
	Te′(E) −156.0	F (E) 3620^d	840			
		F (A) 3440				
	Te′ (A) −167.7	F (E) 3714	670			
		F (A) 3602				
$\mathrm{Te(OTe'F_5)_4}$	Te 602.4			$\mathrm{SO_2ClF}$	200	0.18
	Te′ −159.4					
$\mathrm{Te(OTe'F_5)_4}$	Te 566.8			$\mathrm{SO_2}$	200	0.03
	Te′ −160.7					
$\mathrm{TeF(OTe'F_5)_3}$	Te 563.0	2810	1730	$\mathrm{SO_2ClF}$	200	0.45
$\mathrm{TeF(OTe'F_5)_3}$	Te 535.3	2814		$\mathrm{SO_2}$	200	0.03
$\mathrm{TeF_2(OTe'F_5)_2}$	Te 540.7	40^c	2440	$\mathrm{SO_2ClF}$	200	0.17
		2850				
$\mathrm{TeF_4}$	606.6			$\mathrm{SO_2}$	200	*e*
$\mathrm{Te(OTe'F_5)_3^+}$	Te 646.0		311	$\mathrm{SO_2}$	200	0.12
	Te′ −162.5	F (E) 3736^d				
		F (A) 3706				
$\mathrm{TeF(OTe'F_5)_2^+}$	Te 637.2	15^c		$\mathrm{SO_2}$	200	0.12
		2630				
	Te′ −159.2	F (E) 3724^d				
		F (A) 3681				
$\mathrm{TeF_2(OTe'F_5)^+}$	Te 644.5	21^c		$\mathrm{SO_2}$	200	0.17
		2736				
	Te′ −151.3	F (E) 3724^d				
		F (A) 3656				
$\mathrm{TeF_3^+}$	671.2	2905		$\mathrm{SO_2}$	200	0.17

^{a}Referenced with respect to saturated aqueous $\mathrm{Te(OH)_6}$ at 295 K. ^{b}Taken from ref 11. $^c\,{}^3J_{^{19}\mathrm{F}-^{125}\mathrm{Te}}$. ^{d}A and E denote axial and equatorial, respectively. ^{e}Saturated.

The ^{19}F and ^{125}Te NMR spectra of $\mathrm{Te(OTeF_5)_4}$ down to ca. 180 K show only one set of $\mathrm{OTeF_5}$ resonances in $\mathrm{CH_3CN}$, $\mathrm{SO_2}$ and $\mathrm{SO_2ClF}$ solvents (Table I).[14] Two distinct Te(VI) environments were observed, however, upon cooling to 146 K in $\mathrm{SO_2ClF}$ solvent (Figure 1). The axial bonds in a trigonal bipyramid are generally somewhat longer than the equatorial bonds[12] so that the magnitude of the coupling from the central Te(IV) to Te(VI) in $\mathrm{OTeF_5}$ should be smaller for the axial groups. A weaker (longer) Te–$\mathrm{OTeF_5}$ bond should be complemented by stronger Te(VI)–F bonds and larger directly bonded ^{125}Te(VI)–^{19}F couplings. The axial and equatorial $\mathrm{OTeF_5}$ groups are assigned in Figure 1 by using these assumptions (the observed couplings are listed in Table I).

The ^{19}F NMR spectrum of the same sample at 297 K (Figure 2) was an $\mathrm{AB_4}$ spectrum as expected for a single $\mathrm{OTeF_5}$ ligand environment. When the solution was cooled, however, the signals broadened and eventually resonances for two separate environments emerged. The ^{19}F–^{125}Te(VI) satellite peaks were of sufficient intensity to assign the two different $\mathrm{OTeF_5}$ resonances by comparing these couplings with those observed in the ^{125}Te NMR spectrum. For the equatorial $\mathrm{OTeF_5}$ groups, only a few of the lines of the second order $\mathrm{AB_4}$ spectrum could be resolved ($J_{\mathrm{FF}}/\delta\nu_{\mathrm{AB}} \sim 1$). An $\mathrm{AB_4}$ pattern was also observed for the axial $\mathrm{OTeF_5}$ groups but the $J_{\mathrm{FF}}/\delta\nu$ ratio was clearly much smaller ($J_{\mathrm{FF}}/\delta\nu_{\mathrm{AB}} = 0.066$), and this spectrum more closely approximated a first-order spectrum.

Rate data were extracted for an equal-population two-site exchange process from the temperature dependence of the chemical shift differences of the axial and equatorial environments in the intermediate exchange region and from line width measurements in the slow and intermediate exchange regions (Table II). An activation energy of 30.7 ± 0.3 kJ mol^{-1} was determined by using previously established equations[15] (correlation coefficient $R^2 = 0.994$). The low entropy of activation (3.48 J K^{-1} mol^{-1} at 295 K) is consistent with an intramolecular exchange process.

Table II. Exchange Rate Data Extracted from Variable-Temperature ^{19}F NMR Spectra of $\mathrm{Te(OTeF_5)_4}$ in $\mathrm{SO_2ClF}$

T, K	T^{-1}, K^{-1} × 10^{-3}	$\delta\nu$,^{a} Hz	$\delta\nu_{1/2}$,^{b} Hz	τ^{-1}	log (τ^{-1})
146.9	6.81		86	95^c	1.98^c
151.0	6.62		113	180^c	2.25^c
156.1	6.41	1121^d	157	319^c	2.50^c
161.2	6.20	1101	308	793^c, 937^e	2.90^c, 2.97^e
166.6	6.00	1032		1945^e	3.29^e
171.7	5.82	830		3348^e	3.52^e
294.5			56^f		

^{a}Separation of axial B resonance and largest resonance of equatorial $\mathrm{AB_4}$ multiplet. ^{b}Width at half-height of the high-field component of the axial B doublet. ^{c}Obtained from $\delta\nu_{1/2}$. $^d\,\delta\nu_0$. ^{e}Obtained from $\delta\nu$. $^f\,\delta\nu^0{}_{1/2}$.

The activation energy, E_a, can also be determined[16] from the coalescence temperature, T_c (the temperature at which the exchanging peaks just merge), and the separation of the two exchanging peaks at the slow-exchange limit, $\delta\nu_0$. In the ^{19}F NMR spectra, $T_c = 177 \pm 2$ K and $\delta\nu_0 = 1121 \pm 3$ Hz. The activation energy is 31.0 ± 0.4 kJ mol^{-1}. In the ^{125}Te NMR spectra, coalescence of the two lowest frequency lines of the $\mathrm{OTeF_5}$ resonances ($\delta\nu_0 = 1206 \pm 4$ Hz) was observed at 179 ± 2 K. The activation energy then is 31.3 ± 0.4 kJ mol^{-1}. The mean activation energy from these three determinations is 31.0 ± 0.4 kJ mol^{-1}. This value

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(14) In the case of the more strongly basic solvent, $\mathrm{CH_3CN}$, it appears that there is a significant interaction between the solvent and $\mathrm{Te(OTeF_5)_4}$. The Te(IV) chemical shift in $\mathrm{CH_3CN}$ solvent is considerably more shielded (by ca. 200 ppm) than in the less basic solvents $\mathrm{SO_2}$ and $\mathrm{SO_2ClF}$. This chemical shift change may be attributed to Lewis base behavior on the part of $\mathrm{CH_3CN}$ according to the equilibrium $\mathrm{:Te(OTeF_5)_4 + CH_3CN: \rightarrow CH_3CN\text{–}\overset{\cdot\cdot}{Te}(OTeF_5)_4}$. Thus, it appears that Te(IV) may actually be 6-coordinate in $\mathrm{CH_3CN}$ solvent. The related adduct $\mathrm{As(OTeF_5)_3{\cdot}CH_3CN}$ has been recently reported.[7]

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Table III. NMR Parameters for $As(OTeF_5)_5$ and $As(OTeF_5)_6^{-}$ [a]

		$As(OTeF_5)_5$			$As(OTeF_5)_6^-$	
					Cs^+	$Te(OTeF_5)_3^+$
solvent		SO_2ClF	SO_2ClF	SO_2	CH_3CN	SO_2
temp, K		295	190	295	295	295
concn, *m*		0.31	0.24	0.05	0.15	0.12
$\delta(^{19}F)$	A[b]	−49.3		−46.4		
	E	−39.6		−37.2		
$\delta(^{75}As)$					−28.9	−28.2
$\delta(^{125}Te)$			−165.8	−165.8	−171.1	−170.3
$^2J_{^{19}F-^{19}F}$		178				
$^1J_{^{19}F-^{123}Te}$	A	3030[c]				
	E	3080		3082[c]		
$^1J_{^{19}F-^{125}Te}$	A	3650[c]	3650[d]	3714[c]	3408[d]	3396[d]
	E	3714	3722	3724	3598	3616
$^2J_{^{75}As-^{125}Te}$					420[e]	432[e]

[a] ^{19}F, ^{75}As, and ^{125}Te NMR spectra are referenced with respect to external neat $CFCl_3$, a saturated CH_3CN solution of $NaAsF_6$, and saturated aqueous $Te(OH)_6$, respectively, at 295 K. Coupling constants, *J*, are given in Hz. [b] A and E denote axial and equatorial F atoms. [c] Obtained from the ^{19}F NMR spectrum. [d] Obtained from the ^{125}Te NMR spectrum. [e] Obtained from the ^{75}As NMR spectrum.

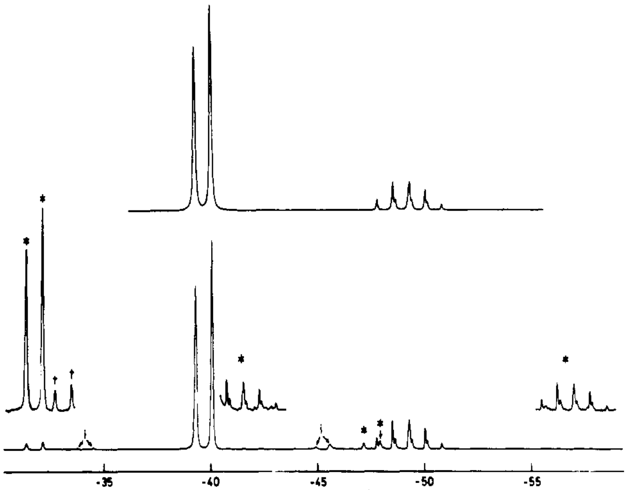

Figure 3. ^{19}F NMR spectrum (235.36 MHz) of $As(OTeF_5)_5$ in SO_2ClF at 297 K (0.1 *m*; 1100 scans; 1.7 Hz/point). Asterisks and daggers denote ^{125}Te and ^{123}Te satellites, respectively; (i) impurity lines. The upper trace is a computer-simulated plot of the AB_4 spin system ignoring coupling to ^{125}Te and ^{123}Te.

is comparable to the value of 30 ± 2 kJ mol^{-1} obtained for intramolecular exchange in both PF_3Cl_2 and PF_3Br_2 as determined by ^{19}F NMR.[17]

A single $OTeF_5$ environment was observed in both the ^{19}F (Figure 3) and ^{125}Te NMR spectra of $As(OTeF_5)_5$ in SO_2ClF solution (Table III), indicating that this five-coordinate molecule also undergoes rapid exchange. Unlike $Te(OTeF_5)_4$, however, the exchange could not be slowed sufficiently on the NMR time scale to observe separate axial and equatorial $OTeF_5$ ligand environments. It would appear that either the lone electron pair in $Te(OTeF_5)_4$ is more effective in obstructing pseudorotation than is the fifth $OTeF_5$ group in $As(OTeF_5)_5$ (giving a lower exchange barrier in the latter compound) or the chemical shift difference between the axial and equatorial $OTeF_5$ groups in $As(OTeF_5)_5$ is considerably smaller than in $Te(OTeF_5)_4$. If the latter were the case, coalescence could then occur at a substantially lower temperature in $As(OTeF_5)_5$ than in $Te(OTeF_5)_4$ even if the exchange barriers in the two compounds are similar.[16]

$TeF_x(OTeF_5)_{4-x}$. The individual compounds $TeF_x(OTeF_5)_{4-x}$ (x = 0, 1, or 2) were identified from the ^{125}Te NMR spectrum of a $TeF_4/B(OTeF_5)_3$ mixture in SO_2ClF solution (Figure 4). As previously reported,[11] a $Te(OTeF_5)_4$ signal is observed at 602.4 ppm in the Te(IV) region of the spectrum. The monofluoro derivative, $TeF(OTeF_5)_3$, is identified by the doublet pattern resulting from a directly bonded ^{19}F–^{125}Te(IV) coupling and shows a further coupling to the equatorial fluorine atoms on Te(VI) of 40 Hz. This long-range coupling was not resolved for the other two $TeF_x(OTeF_5)_{4-x}$ compounds here but has been reported[11] to be 31.8 Hz for $Te(OTeF_5)_4$ in SO_2ClF. Long-range coupling of Te(IV) to the axial fluorine atom was not resolved for any of the compounds. The ^{129}Xe NMR spectra of $XeOTeF_5^+$, $XeF_y(OTeF_5)_{2-y}$, $OXeF_x(OTeF_5)_{4-x}$, $XeF_x(OTeF_5)_{4-x}$ and $O_2XeF_y(OTeF_5)_{2-y}$ (x = 0–4 and y = 0–2) similarly display fine structure resulting from ^{129}Xe coupling to the equatorial fluorine atoms of the $OTeF_5$ groups only.[2] All of the peaks are broadened due to residual coupling to the axial fluorines on Te(VI) and/or possibly some residual ligand exchange.

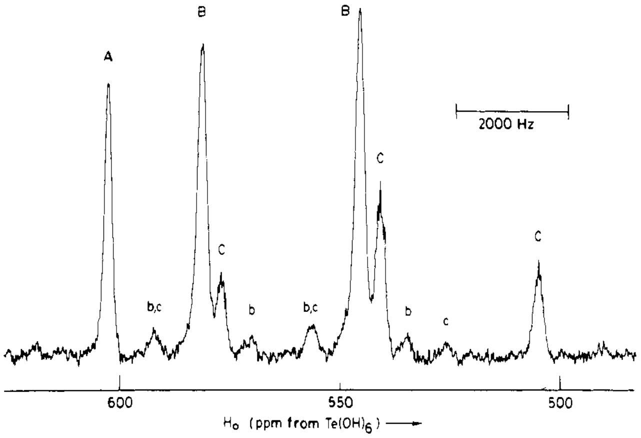

Figure 4. ^{125}Te NMR spectrum (78.97 MHz) of a 3:2 mixture of TeF_4 and $B(OTeF_5)_3$ in SO_2ClF at 200 K, Te(IV) region (0.77 *m* Te(IV); 48 000 scans; 6.1 Hz/point): (A) $Te(OTeF_5)_4$; (B) $TeF(OTeF_5)_3$; (C) $TeF_2(OTeF_5)_2$. Peaks marked b and c denote $^2J_{^{125}Te(IV)-^{125}Te(VI)}$; $^3J_{^{19}F-^{125}Te(IV)}$ is resolved for $TeF_2(OTeF_5)_2$.

Satellite peaks resulting from ^{125}Te(IV)–^{125}Te(VI) couplings are observed for $TeF(OTeF_5)_3$ and $TeF_2(OTeF_5)_2$ (Table I).[18] Analogous two-bond ^{129}Xe–^{125}Te couplings have been observed in the case of $OTeF_5$ derivatives of Xe(II), Xe(IV), and Xe(VI) and are similar in magnitude to those of the Te(IV) derivatives,[2] in accord with the similar magnetogyric ratios of ^{129}Xe and ^{125}Te. The ^{125}Te(IV)–^{125}Te(VI) coupling constant increases with increasing x in the compounds $TeF_x(OTeF_5)_{4-x}$ (x = 0–2), consistent with an increase in the covalency of the Te–$OTeF_5$ bond. Since F is more electronegative than $OTeF_5$ and a Te–F bond is more ionic than a Te–$OTeF_5$ bond,[11] an increase in the number of Te(IV)–F bonds causes an increase in the covalency of the remaining Te–$OTeF_5$ bonds. As covalency increases, so does the

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(17) Mahler, W.; Meutterties, E. L. *Inorg. Chem.* **1965**, *4*, 1520.

(18) The tetrakis derivative, $Te(OTeF_5)_4$, is the only member of the Te(IV) series for which individual axial and equatorial $OTeF_5$ groups have been distinguished. Intramolecular exchange cannot be slowed sufficiently for the other species above the freezing point of the solvent, SO_2ClF.

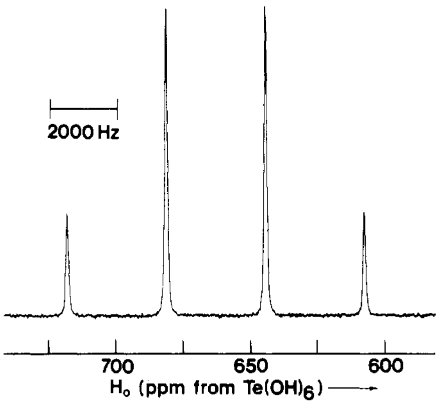

Figure 5. ^{125}Te NMR spectrum (78.97 MHz) of the TeF_3^+ cation in SO_2 at 200 K (0.47 *m*, 5800 scans, 6.1 Hz/point).

Table IV. Comparison of Fluorine–Selenium and Fluorine–Tellurium $^1J_{MF}$,[a] $^1K_{MF}$,[b] and $(^1K_{MF})_{RC}$[c] Coupling Constants[d]

species	J_{MF}, Hz	$^1K_{MF}$, N A^{-2} m^{-3} × 10^{21}	$(^1K_{MF})_{RC}$, N A^{-2} m^3 × 10^{-43}	ref
SeF_3^+	1202[e]	5.579	5.885	*f*
TeF_3^+	2905[g]	8.136	5.660	*f*
SeF_6	1421	6.596	6.958	38
TeF_6	3736	10.463	7.279	11
$HOSeF_5$	1300[h]	6.034	6.365	39
$HOTeF_5$	3577[h]	10.018	6.970	6
$Xe(OSeF_5)_2$	1338[h]	6.210	6.550	40
$Xe(OTeF_5)_2$	3600[h]	10.082	7.014	40
$F_5SeOOSeF_5$	1431[h]	6.641	7.005	40
$F_5TeOOTeF_5$	3830[h]	10.727	7.463	40

[a] Observed scalar coupling constant. [b] Reduced coupling constant: $^nK_{AB} = (4\pi^2/h\gamma_A\gamma_B)^nJ_{AB}$, where *h* is Planck's constant, γ_A and γ_B are the magnetogyric ratios of the spin-coupled nuclei A and B and $^nJ_{AB}$ is the measured scalar coupling constant. [c] Relativistically corrected reduced coupling constant: $(^nK_{AB})_{RC} = (^nK_{AB}/S^2(0)_AS^2(0)_B)$ where $S^2(0)_A$ and $S^2(0)_B$ are the s-electron densities at nuclei A and B, respectively, and $^nK_{AB}$ is the reduced coupling constant. The s-electron densities used in these calculations have been corrected for relativistic effects.[21] [d] All couplings are absolute values. [e] Mean of 1201 and 1203 Hz observed in the ^{19}F and ^{77}Se spectra, respectively, of a 0.20 *m* solution of $SeF_3^+AsF_6^-$ in SO_2 at 200 K. [f] This work. [g] See Table I. [h] Coupling to equatorial fluorine atoms.

magnitude of the coupling. This same effect is observed in the long-range ^{19}F–^{125}Te(IV) couplings noted above and in the homologous series of Xe(II), Xe(IV), and Xe(VI) mixed F/$OTeF_5$ compounds.[2] A decrease in the directly bonded ^{19}F–^{125}Te(IV) coupling from $TeF_2(OTeF_5)_2$ to $TeF(OTeF_5)_3$ (Table I) is also consistent with the above description; i.e., as more relatively electro-positive $OTeF_5$ groups are added, the remaining Te(IV)–F bonds become more ionic and $^1J_{^{19}F-^{125}Te(IV)}$ is reduced.

SeF_3^+ and TeF_3^+ Cations. The ^{19}F, ^{77}Se, and ^{125}Te NMR spectra of the SeF_3^+ and TeF_3^+ cations were recorded in SO_2 solution. An excess of Lewis acid (AsF_5) was used in the case of TeF_3^+ in order to help reduce line broadening by suppression of fluoride exchange (Figure 5). The ^{77}Se–^{19}F and ^{125}Te–^{19}F coupling constants are compared with those of other selenium and tellurium fluorides in Table IV. The SeF_3^+ coupling constant of 1202 Hz compares well with the value of 1213 Hz reported for the ^{19}F NMR spectrum of SeF_4·BF_3 in HF.[19] Observed coupling constants involving different nuclei cannot be compared directly, but useful comparisons can be made by using reduced coupling constants, K_{AB},[20] which take into account the different magnetogyric ratios of the nuclides being compared. A relativistically corrected reduced coupling constant, $(K_{AB})_{RC}$, can be defined to further correct for relativistic effects, which become important for heavy nuclei.[21-23] It is assumed that the Fermi contact mechanism is dominant for spin–spin coupling in these cases.[24] This mechanism is dependent upon the electron densities in the valence s orbitals at each of the respective coupled nuclei. The relativistically corrected reduced coupling constants for a given pair of Se(VI) and Te(VI) compounds in Table IV should be approximately equal since the environments and geometries and bonding of the species are expected to be nearly identical (i.e. octahedral, or pseudooctahedral for the OMF_5 species). These couplings are in fact very close in value, although $^1(K_{Te-F})_{RC}$ is generally somewhat larger than $^1(K_{Se-F})_{RC}$. The relativistically corrected reduced coupling constant for SeF_3^+, however, is somewhat larger than the same coupling for TeF_3^+. This indicates that the F–M bonds have more s character in SeF_3^+ than in TeF_3^+ or, in other words, that the F–Se–F bond angle is somewhat larger than the F–Te–F bond angle, which is consistent with X-ray crystallographic findings.[25] This NMR result may be fortuitous, however, since other terms may also contribute to spin–spin coupling.

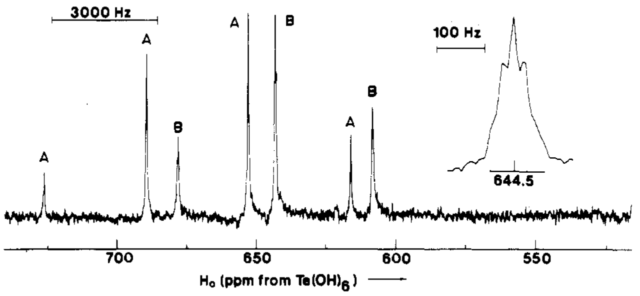

Figure 6. ^{125}Te NMR spectrum (78.97 MHz) for the reaction of $Te(OTeF_5)_4$ with excess AsF_5 in SO_2, Te(IV) region at 200 K (0.34 *m* $Te(OTeF_5)_4$; 35 000 scans; 6.1 Hz/point): (A) TeF_3^+; (B) $TeF_2(OTeF_5)^+$. The inset shows the quintet resulting from coupling of Te(IV) to the equatorial fluorine atoms of the $OTeF_5$ group in $TeF_2(OTeF_5)^+$. Coupling to the axial fluorine atom is not resolved.

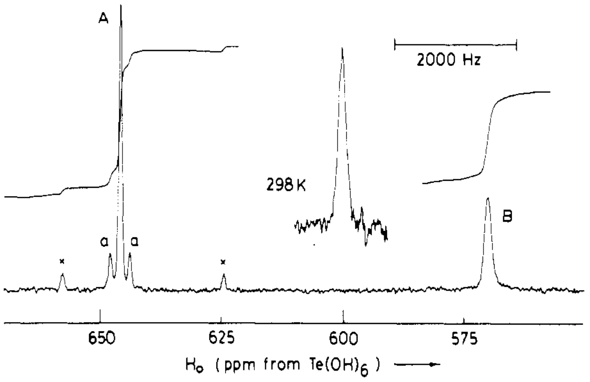

Figure 7. ^{125}Te NMR spectrum (78.97 MHz) of an SO_2 solution of a 1:1 $Te(OTeF_5)_4/As(OTeF_5)_5$ mixture at 200 K, Te(IV) region (initial concentration 0.24 *m* in $Te(OTeF_5)_4$; 30 000 scans; 6.1 Hz/point): (A) $Te(OTeF_5)_3^+$ with (a) satellites from ^{125}Te(IV)–^{125}Te(VI) coupling; (B) $Te(OTeF_5)_4$; (x) $TeF(OTeF_5)_2^+$ impurity. The inset shows the exchange-averaged resonance at 298 K.

$[TeF_x(OTeF_5)_{3-x}]^+$ Cations. Figure 6 depicts the Te(IV) region of the ^{125}Te NMR spectrum resulting from the reaction of $Te(OTeF_5)_4$ with AsF_5. Two distinct species were observed in the Te(IV) region. The TeF_3^+ quartet appeared and was approximately equal in intensity to a triplet assigned to $TeF_2(OTeF_5)^+$.

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Clearly, AsF_5 behaves as a fluorinating agent as well as an $OTeF_5$ acceptor in this reaction. The directly bonded $^{19}F-^{125}Te(IV)$ coupling in $TeF_2(OTeF_5)^+$ is somewhat less than that observed for TeF_3^+ (Table I). Each of the peaks of the $TeF_2(OTeF_5)^+$ triplet was further split into a quintet arising from the coupling of Te(IV) to the equatorial fluorine atoms of the $OTeF_5$ group (Figure 6). When less AsF_5 was allowed to react with $Te(OTeF_5)_4$, the $TeF(OTeF_5)_2^+$ cation was observed. The $^{19}F-^{125}Te(IV)$ coupling constants follow the same trends described above for the $TeF_x(OTeF_5)_{4-x}$ species (Table I). In addition, couplings of Te(VI) to both axial and equatorial fluorine atoms decrease steadily in the series $Te(OTeF_5)_3^+$, $TeF(OTeF_5)_2^+$, and $TeF_2(OTeF_5)^+$ (Table I), consistent with stronger (more covalent) $Te-OTeF_5$ bonds being offset by weaker Te(VI)–F bonds.

A significant concentration of $Te(OTeF_5)_3^+$ was not observed in reactions of $Te(OTeF_5)_4$ with AsF_5 but was produced when $As(OTeF_5)_5$ was used as the $OTeF_5$ acceptor (Figure 7). The Raman spectrum of the solidified 1:1 melt $Te(OTeF_5)_4 \cdot As(OTeF_5)_5$ only revealed the original starting materials (see the Experimental Section and ref 10). When this melt was dissolved in SO_2, however, it was clear from the NMR spectra that reaction did take place in solution. The room-temperature ^{125}Te NMR spectrum of this solution consisted of a single broad resonance at 601 ppm in the Te(IV) region. When the spectrum was recorded at 200 K, two distinct resonances were visible. The resonance at 570 ppm corresponded to that observed for $Te(OTeF_5)_4$ in SO_2 at this temperature (Table I). The remaining resonance, at 646 ppm, was in the same region as Te(IV) in the $TeF_2(OTeF_5)^+$ and $TeF(OTeF_5)_2^+$ cations, and the satellite peaks observed about the main resonance were consistent in intensity with coupling to three natural abundance Te atoms.[26] These observations indicate that this second resonance results from the $Te(OTeF_5)_3^+$ cation.

Three groups of resonances (doublets of quintets, characteristic of the $OTeF_5$ group) were observed in the Te(VI) region of the 295 K spectrum. One of these, at −158 ppm, split into two sets of resonances at 200 K. The component at −160 ppm corresponds to $Te(OTeF_5)_4$, while the other component, at −162 ppm, was assigned to $Te(OTeF_5)_3^+$ on the basis of the similar exchange behavior observed in the Te(IV) region of the spectrum. The $Te(OTeF_5)_4$ lines, in the Te(VI) region, are very broad at 200 K, owing to the slow intramolecular exchange at this temperature. Of the two other groups of resonances in the Te(VI) region at 295 K, the group centered at −165 ppm corresponds to $As(OTeF_5)_5$, while the other, at −171 ppm, was assigned to $As(OTeF_5)_6^-$ (Table III). This anion was observed, along with $^{75}As-^{125}Te$ coupling, in the ^{75}As NMR spectrum of the same solution at 295 K (see below). Clearly, the $OTeF_5$ exchange is not between Te(IV) and As, which would result in equivalence of all of the $OTeF_5$ groups and a single set of resonances in the Te(VI) region.

Although a 1:1 stoichiometry of $Te(OTeF_5)_4$ and $As(OTeF_5)_5$ was used in the preparation, it was clear that a significant quantity of $Te(OTeF_5)_4$ remained unreacted and that the observed facile exchange of $OTeF_5$ groups in solution was between $Te(OTeF_5)_4$ and $Te(OTeF_5)_3^+$. That is, the $Te(OTeF_5)_3^+$ initially formed in the reaction appears to compete as a ligand acceptor toward unreacted $Te(OTeF_5)_4$, thus preventing complete reaction of $Te(OTeF_5)_4$ with $As(OTeF_5)_5$. Since $^{125}Te(IV)-^{125}Te(VI)$ and $^{125}Te(IV)-^{19}F$ couplings are retained for samples of $Te(OTeF_5)_4$ alone in solution at 297 K, it would appear that $Te(OTeF_5)_4$ does not dissociate to $Te(OTeF_5)_3^+$ and $OTeF_5^-$ ions at this temperature. The observed facile exchange of $OTeF_5$ groups between $Te(OTeF_5)_3^+$ and $Te(OTeF_5)_4$ in the present sample then implies that $OTeF_5$-bridged species may act as intermediates for this exchange. Such proposed bridged intermediates would be of considerable interest since there are at present no known compounds with $OTeF_5$ bridges. The presumed lack of bridging in $OTeF_5$ compounds may be cited as a key difference between the donor–acceptor chemistry of $OTeF_5$ and that of fluorine.

Excess $As(OTeF_5)_5$ was also observed in the Te(VI) region of the ^{125}Te NMR spectrum but was not observed in the ^{75}As spectrum, presumably because the resonance was severely quadrupole relaxed and therefore severely broadened and collapsed into the spectral baseline. A sample of pure $As(OTeF_5)_5$ in SO_2 similarly did not produce an observable ^{75}As signal. The line widths of ^{75}As resonances are discussed in more detail elsewhere.[27,28]

^{75}As NMR Spectroscopy of the $As(OTeF_5)_6^-$ Anion. Arsenic-75 has a spin of $^3/_2$, 100% natural abundance, and a sensitivity of 2.51×10^{-2} relative to ^1H, which is similar to that of ^{125}Te. Despite a favorable natural abundance and sensitivity, arsenic NMR spectra are difficult to obtain as a result of the large quadrupole moment of the spin-$^3/_2$ ^{75}As nucleus ($Q = 0.3 \times 10^{-24}$ cm^2), which tends to produce very broad lines owing to quadrupole relaxation. The ^{75}As NMR spectrum of the $As(OTeF_5)_6^-$ anion in CH_3CN solution has been discussed elsewhere.[26] The ^{75}As line width at 298 K is surprisingly narrow (165 Hz). It is clear that the local symmetry about the arsenic atom in this anion must be nearly octahedral for a signal to be observed at all. Balimann and Pregosin[27] have reported a value of 94 Hz for 0.1 M aqueous $KAsF_6$ at 303 K. An additional feature of the spectrum is the observation of long-range $^{75}As-^{125}Te$ coupling, which appears as shoulders about the central resonance. The magnitude of $^2J_{^{75}As-^{125}Te}$, as measured from the simulated spectrum, is 420 ± 40 Hz. In SO_2 solution, $\delta\nu_{1/2}$ was 240 Hz and $^2J_{^{75}As-^{125}Te}$ was 430 ± 40 Hz.[28]

The narrow ^{75}As resonances in both solvent media are consistent with an octahedral arrangement of $OTeF_5$ ligands, and the observed $^{75}As-^{125}Te$ coupling is consistent with the six tellurium atoms maintaining an octahedral disposition about the central arsenic atom. The central uranium and tellurium atoms in $U(OTeF_5)_6$[29] and the two crystallographic forms of $Te(OTeF_5)_6$[10] are octahedrally coordinated to the oxygen atoms of six $OTeF_5$ ligands, and all three central atoms lie on inversion centers in their respective structures so that the tellurium atoms of the $OTeF_5$ groups are octahedrally arranged about the central atoms as well. It therefore seems reasonable to suppose that the same arrangement is found in $As(OTeF_5)_6^-$.

The relativistically corrected reduced coupling constant, $(^1K_{As-F})_{RC}$, of AsF_6^- calculated from the observed scalar coupling constant of 930 Hz[27] is 6.38×10^{-43} N A^{-2} m^3, in good agreement with the relativistically corrected reduced coupling constants of the isoelectronic SeF_6 and TeF_6 molecules (see Table IV). The two-bond $^{75}As-^{125}Te$ and $^{125}Te-^{125}Te$ scalar couplings of 430 and 1302 Hz in $As(OTeF_5)_6^-$ and $Te(OTeF_5)_6$, respectively, (see Table III and ref 11) give comparable corrected reduced coupling constants (3.69×10^{-43} and 3.16×10^{-43} N A^{-2} m^3, respectively). The $Sb(OTeF_5)_6^-$ anion should have a scalar coupling constant, $^2J_{^{121}Sb-^{125}Te}$, of roughly 960 Hz if the relativistically corrected reduced coupling constant is considered to be approximately equal to $(^2K_{As-Te})_{RC}$ of $As(OTeF_5)_6^-$.

Experimental Section

Apparatus and Materials. Manipulations were carried out under anhydrous conditions on vacuum lines constructed of 316 stainless steel, nickel, Teflon, and FEP. All preparative work was carried out in 7 or 9 mm o.d. lengths of FEP tubing heat sealed at one end and connected through 45° SAE flares to Kel-F valves.

Tellurium tetrafluoride was prepared from TeO_2 (British Drug House) and SF_4 (Matheson) according to the method described previously.[10] The ligand-transfer reagent, $B(OTeF_5)_3$, and $HOTeF_5$ were prepared as previously described by Sladky et al.[30] and Engelbrecht and Sladky.[31]

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[26] Tellurium-125 has a natural abundance of 6.99%. The satellite doublet produced by coupling of Te(IV) in $Te(OTeF_5)_3^+$ to three natural abundance Te(VI) nuclei consequently has 22.4% of the intensity of the central line.

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Sulfurylchlorofluoride (Columbia Organic Chemicals) was purified as described previously.[32] Sulfur dioxide (Canadian Liquid Air) and CH_3CN (Caledon Laboratories) were dried over P_2O_5 followed by vacuum distillation.

$TeF_x(OTeF_5)_{4-x}$. Tellurium tetrakis(pentafluoroorthotellurate) was prepared by the stoichiometric reaction of TeF_4 with $B(OTeF_5)_3$ as reported previously.[10] Mixed fluoride/pentafluoroorthotellurates were prepared by using half the stoichiometric amount of $B(OTeF_5)_3$ required for complete reaction to $Te(OTeF_5)_4$. In a typical reaction, TeF_4 (0.5906 g, 2.901 mmol) was weighed into a glass vessel equipped with a Rotaflo valve, $B(OTeF_5)_3$ (1.405 g, 1.934 mmol) distilled onto the TeF_4, the valve closed, and the mixture fused at ca. 120 °C. Boron trifluoride was slowly liberated. When no further gas evolution was observed, the mixture was cooled to room temperature and the BF_3 removed by pumping under vacuum for several minutes, leaving a colorless crystalline solid.

$[TeF_x(OTeF_5)_{3-x}]^+[AsF_y(OTeF_5)_{6-y}]^-$. Mixed $F/OTeF_5$ derivatives of $TeF_3^+AsF_6^-$ were prepared directly in 10-mm NMR tubes by the addition of AsF_5 to $Te(OTeF_5)_4$ or $TeF_x(OTeF_5)_{4-x}$ in SO_2 solution. In a typical reaction AsF_5 (0.0692 g, 0.408 mmol) was distilled onto SO_2 (2 mL) and $Te(OTeF_5)_4$ (0.4433 g, 0.4097 mmol) in a 10-mm NMR tube, and the end of the tube was flame sealed. When the reaction mixture was thawed, a colorless solution was produced with no residue.

$As(OTeF_5)_5$.[33] The synthetic route employed here is analogous to that used for $Te(OTeF_5)_4$. In a typical reaction $B(OTeF_5)_3$ (5.7893 g, 7.968 mmol) was weighed into one bulb of a double-bulb reaction vessel equipped with a magnetic stirring bar and a glass frit separating the two bulbs. Arsenic pentafluoride (0.8217 g, 4.836 mmol) was added to a thin-walled glass weighing bulb prior to being condensed, along with SO_2 (30 mL), into the reaction vessel containing $B(OTeF_5)_3$. The vessel was then flame sealed, the resulting colorless solution was stirred for 48 h, and, upon removal of the solvent by static distillation into the other bulb of the reaction vessel, colorless crystals of $As(OTeF_5)_5$ were deposited. The low-melting crystals were washed several times with cold (ca. −20 °C) SO_2. Residual SO_2 was removed by freezing the other bulb of the vessel in liquid N_2 for 1 h before flame sealing the bulb containing $As(OTeF_5)_5$. Mp: 36 °C. Raman spectrum (cm^{-1}, values in parentheses denote intensities) at −196 °C: 760 (6), 722 (77), 690 (85), 679 (31), 670 (100), 658 (13), 554 (31), 535 (17), 519 (56), 486 (10), 331 (16), 318 (38), 283 (6), 250 (15), 215 (5), 144 (46), 134 (13).

$Cs^+[As(OTeF_5)_6]^-$. Cesium pentafluoroorthotellurate was prepared from CsCl and $HOTeF_5$ as previously described.[34] Cesium chloride was dried at 160 °C for 96 h and under vacuum at 180 °C overnight. Stoichiometric portions of $Cs^+[OTeF_5]^-$ (0.1542 g, 0.4151 mmol) and $As(OTeF_5)_5$ (0.5247 g, 0.4138 mmol) were combined in an FEP tube fitted with a valve and melted and thoroughly mixed at ca. 80 °C.

$SeF_3^+AsF_6^-$ and $TeF_3^+AsF_6^-$. A sample of $SeF_3^+AsF_6^-$ was prepared by oxidizing $Se_4^{2+}(AsF_6^-)_2$[35] with $O_2^+AsF_6^-$[36] in HF solvent at room temperature according to eq 1. An excess of $Se_4^{2+}(AsF_6^-)_2$ (0.1319 g, 0.1901 mmol) was allowed to react with $O_2^+AsF_6^-$ (0.3762 g, 1.703 mmol) in an FEP reaction vessel. Although $Se_4^{2+}(AsF_6^-)_2$ is only sparingly soluble in HF at room temperature, $O_2^+AsF_6^-$ is very soluble and reacts rapidly with the evolution of O_2 gas, possibly according to eq 1. The resulting supernatant solution containing $SeF_3^+AsF_6^-$ and a small amount of $Se_4^{2+}(AsF_6^-)_2$ was cooled at −80 °C whereupon the $Se_4^{2+}(AsF_6^-)_2$ remaining in solution precipitated. The cold supernatant was then decanted from the solid unreacted $Se_4^{2+}(AsF_6^-)_2$ into an FEP sidearm and evaporated and dried under vacuum. The resulting colorless sample of $SeF_3^+AsF_6^-$ was transferred to a dry glass NMR tube and dissolved in 3.0 g of SO_2.

$$Se_4^{2+}(AsF_6^-)_2 + 14O_2^+AsF_6^- \rightarrow 4SeF_3^+AsF_6^- + 14O_2 + 12AsF_5 \quad (1)$$

An NMR sample containing $TeF_3^+AsF_6^-$ (colorless) was prepared by condensing 3.0 g of SO_2 as solvent and excess AsF_5 (1.28 g, 7.51 mmol) onto TeF_4 (0.3862 g, 1.897 mmol) in a thick-walled glass NMR tube.

Nuclear Magnetic Resonance Spectroscopy. All spectra were recorded unlocked (field drift <0.1 Hz/h) on a Bruker WM-250 superconducting spectrometer using a 10-mm probe (broad-banded over the frequency range 23–103 MHz) tuned to 78.972 and 42.817 MHz to observe ^{125}Te and ^{75}As, respectively. Fluorine-19 spectra were obtained on the same probe by using the ^1H decoupler coils retuned to 235.361 MHz as the observation coils or with a 5-mm combination $^1H/^{19}F$ probe. Free-induction decays were typically accumulated in a 32K memory. Spectral width settings of 50 and 100 kHz were employed, yielding data point resolutions of 3.0 and 6.1 Hz and acquisition times of 0.328 and 0.164 s, respectively. No relaxation delays were applied. The number of free-induction decays accumulated varied with concentration and sensitivity of the nucleus under consideration with 60 scans being typical for ^{19}F, 3000–30 000 scans being typical for ^{125}Te, and 60 000 scans being typical for ^{75}As. Pulse widths corresponding to bulk magnetization tip angles, θ, of approximately 90° were 0.5 (^{19}F), 20 (^{125}Te), and 40 μs (^{75}As). Line broadening parameters used in exponential multiplication of the free-induction decays were equal to the data point resolutions.

The respective nuclei were referenced to neat $CFCl_3$ (^{19}F), saturated aqueous $Te(OH)_6$ (^{125}Te),[37] and a saturated solution of $NaAsF_6$ in CH_3CN (^{75}As) at 22 °C. The chemical shift convention used is that a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.

Variable-temperature studies were carried out by using a Bruker temperature controller. Temperatures were measured with a copper-constantan thermocouple inserted directly into the sample region of the probe and were considered accurate to ±1 °C.

Laser Raman Spectroscopy. Raman spectra were recorded on the instrument described previously.[6]

Acknowledgments. We thank Dr. U. R. K. Rao for simulating the ^{75}As NMR spectra and the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $Te(OTeF_5)_4$, 63599-48-4; $TeF(OTeF_5)_3$, 97011-95-5; $TeF_2(OTeF_5)_2$, 95641-51-3; TeF_4, 15192-26-4; $Te(OTeF_5)_3^+$, 97011-96-6; $TeF(OTeF_5)_2^+$, 97011-97-7; $TeF_2(OTeF_5)^+$, 97011-98-8; $TeF_3^+AsF_6^-$, 97011-99-9; $As(OTeF_5)_5$, 87197-53-3; $Cs^+As(OTeF_5)_6^-$, 95179-20-7; $Te(OTeF_5)_3^+As(OTeF_5)_6^-$, 97012-01-6; $SeF_3^+AsF_6^-$, 25930-45-4; AsF_5, 7784-36-3; $B(OTeF_5)_3$, 40934-88-1; $Cs^+[OTeF_5]^-$, 19610-48-1; $Se_4^{2+}(AsF_6^-)_2$, 53513-64-7; $O_2^+AsF_6^-$, 12370-43-3; $CH_3CN-Te(OTeF_5)_4$, 97011-94-4; As, 7440-38-2; ^{125}Te, 14390-73-9.

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