Syntheses of $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$, $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$ and F_5TeNF_2 and Characterization by Multi-NMR and Raman Spectroscopy and by Electronic Structure Calculations; the X-ray Crystal Structures of α - and β - F_5TeNH_2 , $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$, and $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$

Schrobilgen^{†*}

S1

Calculated Geometric Parameters. (i) F_5TeNH_2 . The lowest energy conformation found is a staggered conformation having C_s point symmetry. As expected, the nitrogen coordination is essentially tetrahedral, and the Te-N bond is longer than the Te-F bonds which are lengthened with respect to those of TeF_6 (Table 2), in agreement with experimental trends.

(ii) $\text{F}_5\text{TeNH}_3^+$. Addition of a proton to F_5TeNH_2 preserves the C_s point symmetry, with one N-H/Te-F eclipsing interaction and two N-H bonds staggered, leading to shortening of the Te-F bonds and lengthening of the Te-N bond, in agreement with experiment (Table 2). Substitution of the TeF_5 group for an H atom in NH_3 significantly lowers the proton affinity of NH_3 from 204 kcal mol⁻¹ (202.6 kcal mol⁻¹ at the LDFT level [*J. Phys. Chem. Ref. Data* **1998**, 27, 413]) to 173.1 kcal/mol (298 K, LDFT with zero point energy corrections) for F_5TeNH_2 .

(iii) $\text{F}_5\text{TeN(H)Xe}^+$. Calculations were originally carried out at the HF and DFT levels using a DZVP2 basis set for comparison with F_5TeNH_2 and $\text{F}_5\text{TeNH}_3^+$ systems (Table 2). Formal substitution of Xe^+ for a H atom in F_5TeNH_2 to give $\text{F}_5\text{TeN(H)Xe}^+$ (C_1 point symmetry) leads to a structure with a pyramidal nitrogen and a bond angle sum of 330.4° compared with 360° for a planar structure and 328.5° for a tetrahedral arrangement of the lone pair and three bond pairs. The Te-N and Xe-N bond lengths are calculated to be essentially the same, 2.002 Å and 1.986 Å, respectively, consistent with the formation of a strong bond to the Xe at the LDFT level, whereas at the HF level, these two bond lengths differ by 0.03 Å (Table 2). The Te-N bond length is predicted to lengthen significantly when compared with that of F_5TeNH_2 , but is shorter than that of $\text{F}_5\text{TeNH}_3^+$ at both levels.

Attempts were made to calculate the geometry of the $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$ ion pair, but the geometry at the bridge proved to be unsatisfactory (Table S2). In order to better understand this behavior, the geometries of $\text{F}_5\text{TeN(H)Xe}^+$ and $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$ were also calculated at the HF, MP2, LDA, and B3LYP levels with the larger aug-cc-pVDZ and aug-cc-PVDZ-PP basis sets (Table S2). , the Xe-N and Te-N bond lengths are overestimated for both the cation and the ion pair, with the Te-N bond length being more overestimated than the Xe-N bond length. As observed experimentally, the Xe-N bond length is calculated to be longer than the Te-N bond, except at the MP2 level where the two bond lengths are found to be equal. Overall, the use of the augmented basis sets gave poorer agreement for both the Xe-N and Te-N bond lengths. The description of the bridge in the ion pair also was not improved when compared with the DZVP2 results. The As---F_b distance is significantly lengthened, while the Xe---F_b distance is predicted to be too short. The sums of the As---F_b and Xe---F_b bond distances, however, are very similar, 4.22, 4.27, and 4.32 Å for MP2, B3LYP, and experiment, respectively. Thus, the computational results for the ion pair predict an interaction that is too strong. As a consequence, the calculated Xe-N bond distance is elongated in the gas-phase ion pair when compared with experiment because the Xe---F fluorine bridge interaction with the AsF_6^- counterion is too short. Consequently, the As-F bridge bond and the Te-N bond distances are longer in the gas-phase ion pair when compared with experiment (Table S2). It is not surprising that the isolated ion-pair interaction is overestimated when compared with that in the crystal, because the calculated parameters correspond to an isolated gas-phase ion pair whereas the experimental parameters are derived from the crystalline compound, where other interionic contacts also occur (see X-ray Crystal Structure $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$).

(iv) F_5TeNF_2 . When an NF_2 group is substituted for the NH_2 group in F_5TeNF_2 , the structure retains C_s symmetry with a non-planar environment at the N and the staggered configuration obtained for F_5TeNH_2 . The Te-N bond lengthens significantly when compared with that found in F_5TeNH_2 (Table 2). As expected from the predicted structure of NF_3 , the bond angles at N are all significantly less than the idealized tetrahedral value. The N-F stretches are predicted at 923 and

1037 cm⁻¹ (see Raman Spectroscopy) compared with the experimental values of 910 and 1035 cm⁻¹ in NF₃ [*Spectrochim. Acta* **1967**, 23A, 1899]. The TeF₅ stretching bands are shifted to lower frequencies relative to those in F₅TeNH₂, and are consistent with the longer Te-F bonds in F₅TeNF₂. The Te-N stretch is predicted to be strongly coupled to the NF₂ inversion mode, with this coupled motion occurring at 569 cm⁻¹. The calculated ¹⁴N/¹⁵N isotope shift for this band is -14.3 cm⁻¹. Another Te-N stretch occurs at 249 cm⁻¹, which is the lowest value calculated for a Te-N stretch in the present work (Table 2) and is consistent with a very long Te-N bond.

(v) **F₅TeN²⁻**. The electronic structure of the unknown F₅TeN²⁻ anion, which is isoelectronic with the F₅TeO⁻ anion, was also calculated for comparison. The Te-N bond is predicted to be 1.753 Å, which is much shorter than the Te-N bond length of 1.876 Å in F₅TeNH₂. The Te-F bonds in F₅TeN²⁻ are elongated when compared with the Te-F bonds in F₅TeNH₂, consistent with the high negative charge of the anion.

Supplementary Material: Benchmarking the computational methods on TeF₆.

The bond length and vibrational frequencies for TeF₆ were calculated as benchmarks. Compared with the experimental Te-F bond length of 1.815(2), (Gundersen, G.; Hedberg, K.; Strand, T. G. *J. Chem. Phys.* **1978**, 68, 3548) the calculated bond distances for TeF₆ are 1.801 Å (LDFT) and 1.784 Å (HF). The Te-F stretches occur at 721 (T_{1u}), 659 (A_{1g}), and 637 (E_g) cm⁻¹ at the LDFT level and at 714 (T_{1u}), 665 (A_{1g}), and 629 (E_g) cm⁻¹ at the HF (scaled) level. The experimental values (Bosworth, Y. M.; Clark, R. G. H.; Rippon, D. M. *J. Mol. Spectrosc.* **1973**, 46, 240) for the Te-F stretches in TeF₆ are 751 (T_{1u}), 697 (A_{1g}) and 670 (E) cm⁻¹. These trends are in accord with others observed throughout this work, i.e., LDFT values are about 30 to 40 cm⁻¹ too low for the Te-F stretches and the scaled HF values are also too low by 40 to 50 cm⁻¹. The calculated LDFT bending frequencies are at 314 (T_{1u}), 298 (T_{1g}), and 183 (T_{2u}) and the HF values are at 324 (T_{1u}), 310 (T_{1g}), and 193 (T_{2u}) with the experimental bends at 327 (T_{1u}), 314 (T_{1g}), and 197 (T_{2u}).⁷⁶ Again, both the LDFT and HF bending frequencies are slightly lower than the experimental values.

NMR data Acquisition Parameters. Xenon-129 NMR spectra at 11.7440 T were recorded using 16 - 64K data points with a spectral width of 50 - 100 kHz and with acquisition times of 0.333 - 0.164 s and data point resolutions of 3.0 - 6.1 Hz/pt (1500 - 21,000 scans). Xenon-129 NMR spectra recorded at 7.0463 T were acquired using 8 - 16K data points with a spectral width of 8000 - 10,000 Hz, acquisition times of 0.483 - 0.819 s and data point resolutions of 1.2 - 2.1 Hz/pt (4000 - 20,000 scans). Fluorine-19 NMR spectra (11.7440 T) were recorded using 1 - 64K data points with spectral width settings of 2 - 125 kHz, acquisition times of 0.256 - 0.262 s, and data point resolutions of 3.8 - 3.9 Hz/pt (4500 - 11,000 scans). Proton spectra at 11.7440 T were recorded using 16 - 32K data points, spectral widths of 10 kHz, acquisition times of 0.820 - 1.638 s and data point resolutions of 0.61 - 1.22 Hz/pt (200 - 400 scans). Proton NMR spectra at 7.0463 T were recorded using 16K data points, a spectral width of 10 kHz, an acquisition time of 0.819 s and a data point resolution of 0.610 Hz/pt (3991 scans). Nitrogen-15 NMR spectra (11.7440 T) were recorded using 32K data points, a spectral width of 25 kHz, an acquisition time of 0.655 s and a data point resolution of 1.52 Hz/pt (300 - 500 scans). Relaxation delays of 20 - 120 s were applied between scans in the accumulation of the ¹⁵N NMR spectra. Tellurium-125 NMR spectra (11.7440 T) were recorded using 32 - 64K data points, spectral width ranges of 25 - 50 kHz, acquisition times of 0.333 - 0.655 s, and data point resolutions of 1.5 - 3.0 Hz/pt (7000 - 40,850 scans).

Table S1. Experimental Geometries for the AsF_6^- Anion in $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$, $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$ and F_5TeNH_2 ,

$[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$

Bond Lengths (Å)

As(1)-F(9)	1.707(2)	As(2)-F(13)	1.734(2)
As(1)-F(10)	1.732(2)	As(2)-F(14)	1.729(2)
As(1)-F(11)	1.724(2)	As(2)-F(15)	1.709(2)
As(2)-F(12)	1.716(2)	As(3)-F(16)	1.721(2)
As(3)-F(17)	1.722(2)	As(3)-F(18)	1.721(2)
As(3)-F(19)	1.727(2)		

Bond Angles (deg.)

F(9)-As(1)-F(9A)	180.0	F(12)-As(2)-F(13)	89.61(8)
F(16)-As(3)-F(17)	90.74(8)	F(9)-As(1)-F(10)	89.43(9)
F(12)-As(2)-F(13A)	89.61(8)	F(16)-As(3)-F(17A)	90.74(8)
F(9)-As(1)-F(10A)	90.57(9)	F(12)-As(2)-F(14)	90.19(8)
F(16)-As(3)-F(18)	89.43(8)	F(9)-As(1)-F(11)	90.31(9)
F(12)-As(2)-F(14A)	90.19(8)	F(16)-As(3)-F(18A)	89.43(8)
F(9)-As(1)-F(11A)	89.69(9)	F(12)-As(2)-F(14A)	90.19(8)
F(16)-As(3)-F(19)	179.03(10)	F(9A)-As(1)-F(10A)	89.43(9)
F(12)-As(2)-F(15)	179.57(11)	F(17)-As(3)-F(17A)	90.30(11)
F(9A)-As(1)-F(11A)	90.32(9)	F(13)-As(2)-F(13A)	90.24(11)
F(17)-As(3)-F(18)	89.19(9)	F(10)-As(1)-F(9A)	90.57(9)
F(13)-As(2)-F(14)	89.82(8)	F(17)-As(3)-F(18A)	179.46(7)
F(10)-As(1)-F(10A)	180.0	F(13)-As(2)-F(14A)	179.79(9)
F(17)-As(3)-F(19)	89.95(8)	F(10)-As(1)-F(11)	89.87(8)
F(13A)-As(2)-F(14A)	89.82(8)	F(17A)-As(3)-F(18A)	89.19(9)
F(10)-As(1)-F(11A)	90.13(8)	F(14)-As(2)-F(13A)	179.79(9)
F(18)-As(3)-F(17A)	179.46(7)	F(10A)-As(1)-F(11A)	89.87(8)
F(14)-As(2)-F(14A)	90.11(12)	F(18)-As(3)-F(18A)	91.33(11)
F(11)-As(1)-F(9A)	89.69(9)	F(14)-As(2)-F(15)	90.11(8)
F(18)-As(3)-F(19)	89.89(8)	F(11)-As(1)-F(10A)	90.13(8)
F(15)-As(2)-F(13A)	90.09(8)	F(19)-As(3)-F(17A)	89.95(8)
F(11)-As(1)-F(11A)	180.0	F(15)-As(2)-F(14A)	90.11(8)
F(19)-As(3)-F(18A)	89.89(8)		

Table S1. (continued...)

[F₅TeN(H)Xe][AsF₆]

Bond Lengths (Å)

F(11)-As(1)	1.740(4)	As(1)-F(8)	1.686(4)
As(1)-F(6)	1.697(4)	As(1)-F(9)	1.684(4)
As(1)-F(7)	1.701(3)	As(1)-F(10)	1.712(3)

Bond Angles (deg.)

As(1)-F(11)-Xe(1)	128.1(2)	F(7)-As(1)-F(10)	176.4(2)
F(6)-As(1)-F(7)	90.1(2)	F(7)-As(1)-F(11)	89.0(2)
F(6)-As(1)-F(8)	176.8(2)	F(8)-As(1)-F(9)	90.5(2)
F(6)-As(1)-F(9)	91.9(2)	F(8)-As(1)-F(10)	88.8(2)
F(6)-As(1)-F(10)	89.1(2)	F(8)-As(1)-F(11)	88.6(2)
F(6)-As(1)-F(11)	88.9(2)	F(9)-As(1)-F(10)	90.8(2)
F(7)-As(1)-F(8)	91.9(2)	F(9)-As(1)-F(11)	178.1(2)
F(7)-As(1)-F(9)	92.8(2)	F(10)-As(1)-F(11)	87.4(2)

Table S2. Experimental and Calculated Bond Lengths for F₅TeN(H)Xe⁺ and [F₅TeN(H)Xe][AsF₆]

	aug-cc-pVDZ(-PP)						DZVP2				exptl
	cation				ion pair		cation		ion pair		
	HF	DFT	MP2	B3LY P	MP2	B3LYP	HF	DFT	HF	DFT	
Te(1)-F(2)	1.830	1.893	1.886	1.897	1.895	1.908	1.765	1.873	1.801	1.919	1.791
Te(1)-F(3)	1.826	1.887	1.879	1.892	1.886	1.899	1.794	1.811	1.796	1.907	1.805
Te(1)-F(4)	1.824	1.887	1.873	1.891	1.887	1.904	1.786	1.803	1.797	1.915	1.819
Te(1)-F(5)	1.803	1.856	1.847	1.862	1.864	1.879	1.789	1.811	1.781	1.891	1.820
Te(1)-F(6)	1.816	1.871	1.862	1.878	1.876	1.892	1.778	1.791	1.790	1.898	1.801
Te(1)-N(7)	2.074	2.117	2.101	2.152	2.042	2.071	2.036	2.002	1.949	2.025	1.982
Xe(8)-N(7)	2.136	2.136	2.101	2.189	2.154	2.188	2.067	1.986	2.015	2.149	2.044
N(7)-H(16)	1.017	1.055	1.041	1.039	1.040	1.034	1.011	1.045	1.004	1.044	0.930
Xe(8)-F(13)					3.092	3.186					
Xe(8)---F(14)					2.293	2.321			2.308	2.244	2.580
As(9)---F(14)					1.926	1.953			1.852	1.978	1.740
As(9)-F(11)					1.767	1.771			1.712	1.763	1.712
As(9)-F(12)					1.733	1.741			1.684	1.731	1.697
As(9)-F(13)					1.766	1.771			1.713	1.759	1.701
As(9)-F(10)					1.733	1.741			1.684	1.730	1.684
As(9)-F(15)					1.725	1.730			1.675	1.717	1.686

Table S3. Vibrational Frequencies (cm^{-1}) for $\text{F}_5\text{TeN}^{2-}$ ^a

907 (97)	ν_1 (A_1), $\nu(\text{TeN})$
525 (126)	ν_2 (A_1), $\nu_s(\text{TeF}_a + \text{TeF}_e)$
461 (557)	ν_8 (E), $\nu_s(\text{TeF}_e)$
425 (9)	ν_3 (A_1), $\nu_{as}(\text{TeF}_a - \text{TeF}_e)$
408 (0)	ν_5 (B_1), $\nu(\text{TeF}_2 + \text{TeF}_6) - \nu(\text{TeF}_3 + \text{TeF}_4)$
364 (45)	ν_9 (E), $\delta(\text{F}_a\text{TeF}_e)$
329 (39)	ν_4 (A_1), F_e inversion
302 (48)	ν_{10} (E), $\delta(\text{N}\text{TeF}_e)$
225 (0)	ν_6 (B_1), $\text{F1TeF}_3 - \text{F2TeF}_4$ i.p.
225 (0)	ν_7 (B_2), $\text{F2TeF}_3 + \text{F1TeF}_4$ scissor
154 (2)	ν_{11} (E), F_eTeF_e o.o.p. bend (plane = $\text{F}_e\text{TeNF}_a\text{F}_e$)

^a Infrared intensities, in km mol^{-1} , are given in parentheses.

Table S4. Natural Bond Orbital Analyses for $\text{F}_5\text{TeNH}_3^+$, $\text{F}_5\text{TeN(H)Xe}^+$, F_5TeNF_2 , F_5TeNH_2 and $\text{F}_5\text{TeN}^{2-}$ ^a **$\text{F}_5\text{TeNH}_3^+$**

Orbital	Orb. Pop.	Atom%	%s(Te)	%p(Te)	%d(Te)	%s(F)	%p(F)	%s(N)	%p(N)	%s(H)
$\sigma(\text{Te-F}_a)$	1.89	Te [15.0] F _a [85.0]	17.7	54.9	27.4	16.3	83.4			
$\sigma(\text{Te-F}_e)$	1.88	Te [13.7] F _e [86.3]	17.2	50.1	32.7	15.7	84.0			
$\sigma(\text{Te-F}_e)$	1.88	Te [13.7] F _e [86.3]	17.2	50.1	32.7	15.8	84.0			
$\sigma(\text{Te-F}_e)$	1.88	Te [13.7] F _e [86.3]	17.2	50.0	32.7	15.7	84.0			
$\sigma(\text{Te-F}_e)$	1.89	Te [13.7] F _e [86.3]	17.2	50.1	32.7	15.7	84.0			
$\sigma(\text{Te-N})$	1.87	Te [14.5] N [85.5]	13.9	44.4	41.7			18.4	81.6	
$\sigma(\text{N-H})$ each	2.00	N [76.4] H [23.6]						27.0	72.9	99.9
$\sigma(\text{Te-F}_a)^*$	0.18									
$\sigma(\text{Te-F}_e)^*$	0.18									
$\sigma(\text{Te-F}_e)^*$	0.18									
$\sigma(\text{Te-F}_e)^*$	0.18									
$\sigma(\text{Te-F}_e)^*$	0.18									

Table S4. (continued...)

F₅TeN(H)Xe⁺ ^b

Orbital	Orb. Pop.	Atom%	%s(Te)	%p(Te)	%d(Te)	%s(F)	%p(F)	%s(N)	%p(N)	%s(Xe)	%p(Xe)	%d(Xe)	%s(H)
σ(Te-F _a)	1.88	Te [14.5] F _a [85.5]	17.1	54.5	28.4	16.6	83.1						
σ(Te-F _e)	1.88	Te [13.0] F _e [87.0]	16.7	49.3	34.1	15.9	83.8						
σ(Te-F _e)	1.88	Te [13.3] F _e [85.9]	16.8	50.2	32.9	16.0	83.7						
σ(Te-F _e)	1.89	Te [12.9] F _e [87.1]	16.3	49.9	33.8	16.6	83.2						
σ(Te-F _e)	1.89	Te [14.1] F _e [85.9]	17.9	50.8	31.3	15.9	83.9						
σ(Te-N)	1.85	Te [16.4] N [83.6]	15.7	45.7	38.7			21.1	78.8				
σ(N-Xe)	1.99	Xe [46.7] N [53.3]						11.2	88.6	9.5	89.8	0.7	
σ(N-H)	1.99	N [74.6] H [25.4]						32.8	67.1				99.9
N lp	1.97	N [100]						34.8	65.0				
σ(Te-F _a)*	0.18												
σ(Te-F _e)*	0.18												
σ(Te-F _e)*	0.18												
σ(Te-F _e)*	0.18												
σ(Te-F _e)*	0.18												
σ(Te-F _e)*	0.18												
σ(Te-N)*	0.17												
σ(N-Xe)*	0.05												

Table S4. (continued...)

TeF₅NF₂

Orbital	Orb. Pop.	Atom%	%s(Te)	%p(Te)	%d(Te)	%s(F)	%p(F)	%s(N)	%p(N)
$\sigma(\text{Te-F}_a)$	1.90	Te [14.3]	15.6	58.7	25.7	16.6	83.1		
		F _a [85.7]							
$\sigma(\text{Te-F}_e)$	1.89	Te [12.9]	16.4	49.4	34.2	15.5	84.3		
		F _e [87.1]							
$\sigma(\text{Te-F}_e)$	1.89	Te [13.0]	16.6	50.0	33.4	15.8	84.0		
		F _e [87.0]							
$\sigma(\text{Te-F}_e)$	1.89	Te [13.0]	16.6	50.0	33.4	15.8	84.0		
		F _e [87.0]							
$\sigma(\text{Te-F}_e)$	1.89	Te [13.0]	15.8	50.6	32.6	16.2	83.6		
		F _e [87.0]							
$\sigma(\text{Te-N})$	1.78	Te [22.3]	18.3	41.0	40.7			8.8	91.1
		N [77.7]							
$\sigma(\text{N-F})$	1.99	N [35.6]				15.5	84.4	13.2	86.5
		F [64.4]							
N (lp)								65.5	34.4
$\sigma(\text{Te-F}_a)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-N})^*$	0.20								
$\sigma(\text{N-F})^*$	0.08								

Table S4. (continued...)

TeF₅NH₂

Orbital	Orb. Pop.	Atom%	%s(Te)	%p(Te)	%d(Te)	%s(F)	%p(F)	%s(N)	%p(N)	%(H)
$\sigma(\text{Te-F}_a)$	1.87	Te [12.6]	14.6	52.2	33.2	16.8	83.0			
		F _a [87.4]								
$\sigma(\text{Te-F}_e)$	1.89	Te [12.4]	16.1	49.5	34.4	16.6	83.2			
		F _e [87.6]								
$\sigma(\text{Te-F}_e)$	1.89	Te [12.5]	15.9	50.0	34.1	17.4	82.3			
		F _e [87.5]								
$\sigma(\text{Te-F}_e)$	1.89	Te [12.5]	15.9	50.0	34.2	17.5	82.3			
		F _e [87.5]								
$\sigma(\text{Te-F}_e)$	1.89	Te [13.1]	16.8	50.9	32.2	17.1	82.7			
		F _e [86.9]								
$\sigma(\text{Te-N})$	1.86	Te [22.7]	21.1	47.7	31.2			21.4	78.4	
		N [77.3]								
$\sigma(\text{N-H})$	1.99	N [73.3]						31.0	68.9	99.9
		H [26.7]								
N lp	1.93							16.6	83.3	
$\sigma(\text{Te-F}_a)^*$	0.18									
$\sigma(\text{Te-F}_e)^*$	0.20									
$\sigma(\text{Te-F}_e)^*$	0.20									
$\sigma(\text{Te-F}_e)^*$	0.20									
$\sigma(\text{Te-F}_e)^*$	0.20									
$\sigma(\text{Te-N})^*$	0.14									

Table S4. (continued...)

TeF₅N²⁻

Orbital	Orb. Pop.	Atom%	%s(Te)	%p(Te)	%d(Te)	%s(F)	%p(F)	%s(N)	%p(N)
$\sigma(\text{Te-F}_a)$	1.87	Te [9] F _a [91]	11	47	42	15	84		
$\sigma(\text{Te-F}_e)$	1.87	Te [7] F _e [93]	14	38	48	16	84		
$\sigma(\text{Te-N})$	1.81	Te [34] N [66]	37	47	16			13	87
$\sigma(\text{Te-N})$	1.88	Te [12] N [88]	0	64	36			0	100
$\sigma(\text{Te-N})$	1.88	Te [12] N [88]	0	64	36			0	100
N lp	1.92							87	13
$\sigma(\text{Te-F}_a)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-F}_e)^*$	0.20								
$\sigma(\text{Te-N})^*$	0.10								
$\sigma(\text{Te-F})^*$	0.15								
$\sigma(\text{Te-F})^*$	0.15								

^a The labels correspond to those used in Structures I (F₅TeNH₂), II (F₅TeNH₃⁺), III (F₅TeN(H)Xe⁺), and IV (F₅TeNF₂).

Raman Spectra of Unreacted $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$ and $[\text{Xe}_2\text{F}_3][\text{AsF}_6]$ in $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$. The presence of $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$ and $[\text{Xe}_2\text{F}_3][\text{AsF}_6]$ in the solid product mixture prevents a rigorous assignment of the anion bands for $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$. The amount of $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$ in the natural abundance sample was less than in the ^{15}N -enriched sample, as a less intense band was observed at 682 cm^{-1} [$\nu_{\text{sym}}(\text{TeF}_4)$] (Figure 11), which is the most intense band in the Raman spectrum of $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$. This band is also coincident with $\nu_1(\text{A}_{1g})$ of the AsF_6^- anions of all three species. Overlap of the $\nu_2(\text{E}_g)$ and $\nu_5(\text{T}_{2g})$ AsF_6^- bands for $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$ and $[\text{Xe}_2\text{F}_3][\text{AsF}_6]$ is also expected. Bands at 687 and 691 cm^{-1} and at 397 and 402 cm^{-1} are assigned to the split $\nu_3(\text{T}_{1u})$ and $\nu_4(\text{T}_{1u})$ AsF_6^- modes. These bands are not observed in the Raman spectrum of $[\text{Xe}_2\text{F}_3][\text{AsF}_6]$ (see Table S1, footnote c), and must arise from $[\text{F}_5\text{TeN(H)Xe}][\text{AsF}_6]$. Their observation in the Raman spectrum is consistent with the observed distortion of the AsF_6^- anion in the crystal structure as a result of fluorine bridging with the cation.

Table S5. $\text{F}_5\text{TeNH}_3^+$ and Xe_2F_3^+ Cation Frequencies Observed in $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$ Resulting from the Reaction of $[\text{F}_5\text{TeNH}_3][\text{AsF}_6]$ with XeF_2 ^a

^{14}N	^{15}N	
682(68)	683(178)	} $\text{F}_5\text{TeNH}_3^+$ (see Table 6)
589(203)	589(348)	
543(9)	548(16)	
355(2)	355(3)	
310(18)	310(42)	
599(198)	600(317)	} Xe_2F_3^+ ^c
589(203)	589(348)	
366(21) ^b	368(37) ^b	
164(61)	165(92)	

^a All intensities are given relative to the most intense mode of the $\text{F}_5\text{TeN(H)Xe}^+$ cation ($\nu(\text{TeN-TeXe})$) which is assigned an intensity of 100. ^b Overlaps with the FTeF and FTeN bending modes of $\text{F}_5\text{TeN(H)Xe}^+$ (see Table 6). ^c *J. Fluorine Chem.*, **2000**, 105, 159.

Table S6. Correlation Diagram for the Vibrational Modes of $F_5TeNH_2^a$

		free molecule symmetry C_s	site symmetry C_1	crystal symmetry C_2	
2R,4T	$2(\nu_1 - \nu_{13})$	A'	A	A (Ra, IR)	$(\nu_1 - \nu_{21})$ 2R,2T (-R,-T)
4R,2T	$2(\nu_{14} - \nu_{21})$	A''		B (Ra, IR)	$(\nu_1 - \nu_{21})$ R,T (-2R,-2T)

^aThe irreducible representation of the free molecule is $\Gamma = 13A' + 8A'' (C_s)$ for F_5TeNH_2 ; $Z = 2$.

Table S7. Correlation Diagrams for the Vibrational Modes of $[F_5TeNH_3][AsF_6]^a$

$F_5TeNH_3^+$					
	free cation symmetry C_s	site symmetry #1 C_1	crystal symmetry C_{2h}		
4R,8T	$4(\nu_1 - \nu_{15})$	A'	A	A_g (Ra) $(\nu_1 - \nu_{24})$	2R,3T (-R)
				B_g (Ra) $(\nu_1 - \nu_{24})$	R,3T (-2R)
				A_u (IR) $(\nu_1 - \nu_{24})$	3R,2T (-T)
				B_u (IR) $(\nu_1 - \nu_{24})$	3R,T (-2T)
8R,4T	$4(\nu_{16} - \nu_{24})$	A''			
	free cation symmetry C_s	site symmetry #2 C_s	crystal symmetry C_{2h}		
2R,4T	$2(\nu_1 - \nu_{15})$	A'	A'	A_g (Ra) $(\nu_1 - \nu_{15})$	2T (-R)
				B_g (Ra) $(\nu_{16} - \nu_{24})$	T (-2R)
				A_u (IR) $(\nu_{16} - \nu_{24})$	2R (-T)
				B_u (IR) $(\nu_1 - \nu_{15})$	R (-2T)
4R,2T	$2(\nu_{16} - \nu_{24})$	A''	A''		

Table S7. (continued...)

AsF₆⁻					
	free anions symmetry <i>O_h</i>	site symmetry #1 <i>C_i</i>	crystal symmetry <i>C_{2h}</i>		
6R	2v ₁	A _{1g}	A _g	A _g (Ra) (v ₁ , 2v ₂ , 3v ₅)	2R (-R)
		A _{2g}			
	2v ₂	E _g			
		T _{1g}			
		T _{2g}			
	2v ₅			B _g (Ra) (v ₁ , 2v ₂ , 3v ₅)	R (-2R)
6T		A _{1u}	A _u	A _u (IR) (3v ₃ , 3v ₄ , 3v ₆)	2T (-T)
		A _{2u}			
		E _u			
	2v ₃ , 2v ₄	T _{1u}			
		T _{2u}			
	2v ₆			B _u (IR) (3v ₃ , 3v ₄ , 3v ₆)	T (-2T)
	free anions symmetry <i>O_h</i>	site symmetry #2 <i>C_s</i>	crystal symmetry <i>C_{2h}</i>		
12R	4v ₁	A _{1g}	A'	A _g (Ra) (2v ₁ , 2v ₂ , 4v ₃ , 4v ₄ , 4v ₅ , 2v ₆)	R,4T (-R)
		A _{2g}			
	4v ₂	E _g			
		T _{1g}			
		T _{2g}			
	4v ₅			B _g (Ra) (2v ₃ , 2v ₄ , 2v ₅ , 4v ₆)	2R,2T (-2R)
12T		A _{1u}	A''	A _u (IR) (2v ₃ , 2v ₄ , 2v ₅ , 4v ₆)	4R,T (-T)
		A _{2u}			
		E _u			
	4v ₃ , 4v ₄	T _{1u}			
		T _{2u}			
	4v ₆			B _u (IR) (2v ₁ , 2v ₂ , 4v ₃ , 4v ₄ , 4v ₅ , 2v ₆)	2R,2T (-2T)

^aThe irreducible representation is $\Gamma = 15A' + 9A''$ (*C_s*) for the F₅TenH₃⁺ cation and $\Gamma = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$ (*O_h*) for the AsF₆⁻ anion; Z = 6.

Table S8. Correlation Diagrams for the Vibrational Modes of $[\text{F}_5\text{TeN}(\text{H})\text{Xe}][\text{AsF}_6]^\text{a}$

$\text{F}_5\text{TeN}(\text{H})\text{Xe}^+$				
	free cation symmetry C_1		site symmetry C_1	crystal symmetry C_i
6R,6T $2(\nu_1 - \nu_{21})$	A	—————	A	$\swarrow$ $A_g (\text{Ra}) (\nu_1 - \nu_{21})$ 3T (-3R) $\searrow$ $A_u (\text{IR}) (\nu_1 - \nu_{21})$ 3R (-3T)
AsF_6^-				
	free anion symmetry C_1		site symmetry C_1	crystal symmetry C_i
6R,6T $2(\nu_1 - \nu_{15})$	A	—————	A	$\swarrow$ $A_g (\text{Ra}) (\nu_1 - \nu_{15})$ 3T (-3R) $\searrow$ $A_u (\text{IR}) (\nu_1 - \nu_{15})$ 3R (-3T)

^aThe irreducible representation is $\Gamma = 21A (C_1)$ for the $\text{F}_5\text{TeN}(\text{H})\text{Xe}^+$ cation and $\Gamma = 15A (C_1)$ for the AsF_6^- anion; $Z = 2$.

a

b

Figure S1. ^1H NMR spectra (500.138 MHz) of (a) natural abundance $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ ($-53\text{ }^\circ\text{C}$; BrF_5 solvent) and (b) 99.5 atom % ^{15}N -enriched $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ ($-56\text{ }^\circ\text{C}$; BrF_5 solvent). Asterisks (*) denote ^{125}Te satellites.

Figure S2. ^{19}F NMR spectrum (470.599 MHz) of natural abundance $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ in BrF_5 solvent ($-44\text{ }^\circ\text{C}$); (A) resonance of equatorial fluorine atoms bonded to tellurium, (B) resonance of axial fluorine atom bonded to tellurium, (C) unidentified resonance, (D) TeF_6 , (E) AsF_6^- . Asterisks (*) denote ^{125}Te satellites.

Figure S3. ^{15}N NMR spectrum (50.698 MHz) of 99.5 atom % $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ in HF solvent ($-40\text{ }^\circ\text{C}$). Asterisks (*) denote ^{125}Te satellites.

Figure S4. ^{125}Te NMR spectrum (157.795 MHz) of 99.5 atom % ^{15}N -enriched $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ in HF solvent (-45°C); entire multiplet, dagger (†) denotes a peak of the TeF_6 multiplet (not shown in full), and (b) expansion of the central region of the multiplet attributed to $\text{F}_5\text{TeNH}_3^+$.

Figure S5. Raman spectra of solid natural abundance (lower traces) and 99.5 atom % ¹⁵N-enriched (upper traces) F₅TeNH₂ recorded at -160 °C by use of 514.5-nm excitation; (a) 1000 – 1050, 1450 – 1550 and 3250 – 3400 cm⁻¹ regions and (b) 150 – 800 cm⁻¹ region.

Figure S6. (a) Raman spectrum of natural abundance $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ and (b) (a) Raman spectra of natural abundance (lower trace) and 99.5 atom % ^{15}N -enriched (upper trace) $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ recorded at ambient temperature by use of 514.5-nm excitation.

Figure S7. Raman spectrum of natural abundance $\text{F}_5\text{TeN}(\text{H})\text{Xe}^+\text{AsF}_6^-$ recorded at $-165\text{ }^\circ\text{C}$ with use of 514.5-nm excitation. Asterisks (*) denote FEP sample tube lines, a dagger (†) denotes an artifact characteristic of the Raman instrument.