lock; ^{15}N and ^{129}Xe spectra were obtained on instruments equipped with superconducting magnets and were run unlocked. Fluorine-19 spectra were obtained on a Bruker WH-90 spectrometer at 84.66 MHz in 100–600 scans with a spectral width of 25 kHz (3.0 Hz/data point, pulse acquisition time 0.327 s) and a pulse width of 2 μs. Xenon-129 spectra were obtained at 69.20 MHz on a Bruker WM-250 in 10000–20000 scans at spectral widths of 100 kHz (6.1 Hz/data point, pulse acquisition time 0.164 s and pulse width 20 μs). Nitrogen-15 spectra were obtained at 40.55 MHz on a Bruker WH-400 spectrometer in 200–400 scans. The spectral width was 20 kHz (2.4 Hz/data point, pulse acquisition time 0.410 s) with a pulse width of 30 μs. The pulse widths cited correspond to tip angles, θ, of ~90° for ^{19}F and ^{129}Xe and ~30° for ^{15}N. A relaxation delay time of 15 s was used in the accumulation of ^{15}N data; a zero relaxation delay was applied to ^{19}F and ^{129}Xe spectral accumulations. Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to their respective data point resolutions. All spectra were obtained with precision thin-walled glass NMR tubes (Wilmad) of 5 mm o.d. (^{19}F) and 10 mm o.d. (^{15}N and ^{129}Xe).

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

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Tellurium–Nitrogen Compounds

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With $H_2N{-}TeF_5$ and $(CH_3)_3SiNHTeF_5$ as the starting materials numerous new tellurium–nitrogen compounds have been synthesized. Almost all of them contain the $>N{-}TeF_5$ group, which stabilizes many double-bonded systems such as $O{=}C{=}NTeF_5$ and $Cl_4W{=}NTeF_5$. $Cl_2Se{=}NTeF_5$ is a rare example of a compound containing a discrete selenium–nitrogen double bond.

Introduction

The chemistry of sulfur–nitrogen compounds is a vast and still expanding field. Quite in contrast very little is known about selenium–nitrogen systems. Even less is known about the system tellurium–nitrogen: not even a well-defined binary compound is known. But it was shown that TeF_6 can act as a source of tellurium–nitrogen compounds, and derivatives such as $(CH_3)_2NTeF_5$,[1,2] $(CH_3)_3SiNHTeF_5$,[3] and H_2NTeF_5[3] were prepared.

By comparison with H_2NSF_5,[4] H_2NTeF_5 turned out to be more stable against HF elimination and to be less basic, and the TeF_5 group to be probably more electron withdrawing than the SF_5 group. In this paper we describe a large number of new compounds that have been obtained by reaction with H_2NTeF_5 and/or $(CH_3)_3SiNHTeF_5$.

Experimental Section

General Considerations. Fluorine NMR spectra were taken on a Varian 360 instrument with standard 5 mm o.d. glass tubes and with $CFCl_3$ as internal or external reference.

Infrared spectra were recorded on a Beckman 11 spectrometer; the window material most commonly used was KCl.

Raman spectra were taken on a Coderg PH 1 instrument using a He–Ne laser for excitation (190 mW).

Mass spectra were taken on a Varian MAT 5 instrument with 70 eV excitation energy.

Reagents. SF_4, PF_5, MoF_6, and $(CH_3)_3SiBr$ were commercially available. ClF,[5] SOF_4,[6] COF_2,[7] SeF_4,[8] $SeCl_4$,[9] and WCl_6[10] were prepared according to literature methods.

Preparation of ((Trimethylsilyl)amino)tellurium Pentafluoride and *cis*-Bis((trimethylsilyl)amino)tellurium Tetrafluoride. *Caution*: *cis*-$[(CH_3)_3SiNH]_2TeF_4$ is explosive! The reaction of TeF_6 (0.1 mol) and $[(CH_3)_3Si]_2NH$ (0.1 mol) in a stainless steel cylinder affords over 90% yields of $(CH_3)_3SiNHTeF_5$,[3] if the cylinder has been cleaned thoroughly prior to use with concentrated nitric acid and if the reaction is run with magnetic stirring for 1 week at room temperature. The volatile contents of the cylinder are trapped at −196 °C and fractionally distilled under vacuum through a −30 °C trap. Under these conditions almost no *cis*-$[(CH_3)_3SiNH]_2TeF_4$ is formed. For the physical data of $(CH_3)_3SiNHTeF_5$, see ref 3.

The formation of *cis*-$[(CH_3)_3SiNH]_2TeF_4$ occurs if the same starting materials are reacted at elevated temperature, especially above 60 °C, or if the stainless steel cylinder has not been cleaned between two runs. Our observations point in the direction that the formation of *cis*-$[(CH_3)_3SiNH]_2TeF_4$ is autocatalytic.

Pure $(CH_3)_3SiNHTeF_5$ was distilled several times at 58 °C (19 mbar), but once it decomposed spontaneously into TeF_6 and *cis*-$[(CH_3)_3SiNH]_2TeF_4$.

Since the bis compound turned out to be explosive, no further attempts for its preparation were made. Crude material has been purified by sublimation at 40 °C (10^{-3} mbar). When it is heated to 100 °C, it decomposes with mild explosions. It is a colorless, crystalline solid, and its structure was resolved by NMR spectroscopy.

^{19}F NMR (in CH_2Cl_2): a_2b_2 spectrum, δ_a 26.9, δ_b 19.5; J_{a-b} = 133 Hz. ^{1}H NMR: δ_{CH_3} 0.55, δ_{NH} 4.4.

A 50-g amount of *cis*-$[(CH_3)_3SiNH]_2TeF_4$ was kept for $^1/_2$ yr in a glass cylinder. The material had definitely changed composition,

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probably by slow hydrolysis. The resulting yellow solid was extremely *explosive*; the nature of this latter material is still unknown.

Preparation of $O{=}C{=}NTeF_5$. A 10-mmol quantity of $(CH_3)_3Si{-}NH{-}TeF_5$ is filled into a 100-mL stainless steel cylinder, and 30 mmol of COF_2 is added by vacuum distillation into the cooled cylinder. The reaction mixture is then stirred for 15 h at 60 °C. The products are distilled under dynamic vacuum through −78 and −196 °C traps. The −78 °C trap contains all of the $H_2N{-}TeF_5$ and a trace of $O{=}C{=}NTeF_5$. The contents of the −196 °C trap are once again pumped through −78, −100, and −196 °C traps. The −100 °C trap contains mostly $O{=}C{=}NTeF_5$ with some $(CH_3)_3SiF$, which can be separated by another trap-to-trap distillation. The yield of pure product is low (25%) because of incomplete separation. $O{=}C{=}NTeF_5$ is a colorless, moisture-sensitive liquid: mp −95 °C; bp 39 °C. Anal. Calcd for $OCNTeF_5$: C, 4.5; N, 5.3; Te, 48.2; F, 35.9. Found: C, 4.7; N, 5.3; te, 48.5; F, 35.8.

IR spectrum (gas): 2260 (vs), 1390 (vw), 1358 (vw), 734 (s) cm^{-1}. Raman spectrum (liquid): 2253 (w, p), 1359 (w, p), 1360 (w, p), 713 (w, p), 690 (m, p), 662 (vs, p), 515 (s, p), 326 (m, p), 307 (m, dp), 204 (w, dp), 175 (w, p), 107 (w, dp) cm^{-1}. ^{19}F NMR spectrum: ab_4 type of TeF_5, δ_a 46.4, δ_b 36.1; $J_{a-b} = 177$ Hz, $J_{^{125}Te-a} = 3520$ Hz, $J_{^{125}Te-b} = 3528$ Hz.

Preparation of $CH_3OC(O)NHTeF_5$. A 3.4-mmol quantity of CH_3OH and 4.1 mmol of $O{=}C{=}N{-}TeF_5$ are condensed into a 100-mL stainless steel cylinder, and the mixture is stirred overnight at room temperature. The cylinder is then evacuated until it reaches a constant weight. The solid remainder is sublimed at 30 °C (10^{-1} mbar) onto a −30 °C cold finger. Pure $CH_3{-}O{-}CO{-}NH{-}TeF_5$ as colorless crystalline material is obtained: yield 25%; mp 77 °C. Anal. Calcd for $C_2H_4NO_2TeF_5$: C, 8.1; H, 1.35; N, 4.7; Te, 43.0; F, 32.0. Found: C, 8.1; H, 1.35; N, 4.8; Te, 43.0; F, 31.1.

Raman spectrum (solid): 3038 (m), 2963 (s), 1722 (m), 1453 (m), 1082 (m), 946 (s), 827 (m), 783 (m), 713 (m), 692 (vs), 646 (vs), 437 (m), 385 (s), 335 (m), 304 (s) cm^{-1}. ^1H NMR spectrum: δ_{NH} 8.75, δ_{CH_3} 4.53. ^{19}F NMR spectrum: ab_4 type, δ_a 39.9, δ_b 43.5; $J_{a-b} = 189$ Hz.

Preparation of Cl_2NTeF_5. A 20-mmol amount of $(CH_3)_3SiNHTeF_5$ is dissolved in 15 mL of dry $CFCl_3$ in a 50-mL two-necked glass bulb. While this solution is maintained at −78 °C, 40 mmol of gaseous ClF is bubbled through, with the outlet being protected against moisture by a −78 °C trap. The solution soon turns yellow, and after some time two phases appear. An excess of ClF was avoided because formation of NCl_3 (*explosive*!) might occur, although this has never really been observed. The reaction mixture is pumped through −78 and −196 °C traps. Cl_2NTeF_5 is retained in the −78 °C trap, along with some H_2NTeF_5. By trap-to-trap condensation from a −40 °C trap into a −78 °C trap pure Cl_2NTeF_5 is obtained in the −78 °C trap: yield 72%; mp −79 °C. Cl_2NTeF_5 is an orange-yellow liquid and should be regarded as potentially explosive. Instead of an elemental analysis the mass spectrum was obtained. It gave evidence for the positive ions $Cl_2NTeF_5^+$, $ClNTeF_5^+$, $ClTeF_4^+$, TeF_5^+, TeF_4^+, TeF_3^+, TeF_2^+, TeF^+, Te^+, NCl_2^+, NCl^+, and Cl^+. All fragments showed the expected isotopic distributions.

Raman spectrum (liquid): 746 (m), 702 (s), 629 (vs), 619 (sh), 412 (s), 347 (m), 315 (w), 261 (m), 240 (w), 200 (m) cm^{-1}. ^{19}F NMR spectrum: ab_4 type, δ_a 50.0, δ_b 59.1; $J_{a-b} = 163.6$, $J_{^{125}Te-a} = 4136$ Hz, $J_{^{125}Te-b} = 4399$ Hz.

Preparation of $(CH_3)_3SiNClTeF_5$. A 16.7-mmol amount of Cl_2NTeF_5 is dissolved in 10 mL of $CFCl_3$, and 18 mmol of $(CH_3)_3SiBr$ is slowly added by a dropping funnel. Again the outlet of the glass vessel is protected against moisture. During the addition the liquid turns brown and a reaction time of 2 h with stirring at room temperature is required. Several trap-to-trap distillations under vacuum through −30, −78, and −136 °C traps afford pure $(CH_3)_3SiNClTeF_5$ in 55% yield. The compound is a yellow liquid; bp −30 °C (10^{-2} mbar). Instead of an analysis the mass spectrum of this rather unstable compound was obtained. It gave evidence of the ions $(CH_3)_3SiNClTeF_5^+$, $HClNTeF_5^+$, $H_2NTeF_4^+$, TeF_5^+, and smaller fragments.

^{19}F NMR spectrum: ab_4 type, δ_a 35.6, δ_b 40.9; $J_{a-b} = 172$ Hz, $J_{^{125}Te-a} = 3292$ Hz, $J_{^{125}Te-b} = 3750$ Hz. ^1H NMR spectrum: singlet at δ 0.98.

Because of slow decomposition at room temperature into $(CH_3)_3SiF$ no IR gas spectrum could be obtained.

Attempted Preparation of $ClHNTeF_5$. A 5.2-mmol amount of $(CH_3)_3SiNClTeF_5$ is filled into a poly(perfluoroethylene-*co*-perfluoropropene) vessel, and 5.2 mmol of anhydrous HF is condensed onto it with the help of a metal vacuum line. The mixture is magnetically stirred for $1^1/_2$ days and then distilled through −60 and −196 °C traps. $(CH_3)_3SiF$ and a little TeF_6 are trapped at −196 °C and yellow $ClHNTeF_5$ and H_2NTeF_5 at −60 °C. The latter mixture is distilled again, being held at −45 °C and trapped at −78 °C, as H_2NTeF_5 has little volatility at −45 °C. The resulting material, a yellow liquid at room temperature that attacks glass, is still contaminated with $(CH_3)_3SiF$ and H_2NTeF_5.

IR spectrum (gas): 3308 (m), 740 (m, sh), 715 (vs), 642 (w), 475 (m) cm^{-1}. ^{19}F NMR spectrum: ab_4 type, δ_a 44.3, δ_b 52.2; $J_{a-b} = 181$ Hz. ^1H NMR spectrum: broad line at δ 6.7.

Preparation of $F_2S{=}NTeF_5$. A 50-mmol quantity of SF_4 is added by vacuum distillation into a cooled 100-mL stainless steel cylinder containing 95 mmol of $(CH_3)_3SiNHTeF_5$. The mixture is allowed to react at room temperature overnight with magnetic stirring. The contents are then separated by slow vacuum distillation through −20, −65, and −196 °C traps. The −20 °C trap contains the bulk of the $H_2N{-}TeF_5$, the −65 °C trap the $F_2S{=}NTeF_5$, and the −196 °C trap the $(CH_3)_3SiF$ and excess SF_4. In order to achieve a pure product, the contents of the −65 °C trap have to be vacuum distilled at least twice again under similar conditions. The absence of $(CH_3)_3SiF$ is finally confirmed by IR and ^{19}F NMR spectroscopy. Pure $F_2S{=}NTeF_5$ is obtained in 40% yield as a colorless liquid, which is sensitive towards moisture; mp −78 °C. Anal. Calcd for $NSTeF_7$: N, 4.6; S, 10.4; Te, 41.6; F, 43.4. Found: N, 4.7; S, 11.0; Te, 39.4; F, 44.9.

IR spectrum (gas): 1287 (s), 790 (m), 728 (s) cm^{-1}. Raman spectrum (liquid): 795 (m, p), 696 (s, p), 646 (vs, p), 567 (s, p), 480 (s, p), 397 (w, dp), 329 (m, dp), 302 (m, dp), 249 (s, p), 167 (s, p), 104 (m, p) cm^{-1}. ^{19}F NMR: ab_4x_2 type spectrum, δ_a 42.5, δ_b 32.2, δ_x −66.2; $J_{a-b} = 177$ Hz, $J_{b-x} = 14$ Hz, $J_{^{125}Te-xF} = 329$ Hz, $J_{^{125}Te-a} = 3438$ Hz, $J_{^{125}Te-b} = 3684$ Hz.

Preparation of $Cl_2S{=}NTeF_5$. An 8-mmol amount of $F_2S{=}NTeF_5$, 10 mL of CF_2Cl_2, and 18 mmol of BCl_3 are condensed into a 100-mL stainless steel cylinder. The mixture is then magnetically stirred for 2 days at room temperature. Slow vacuum distillation through −78 and −196 °C cooled traps gives an 85% yield of pure $Cl_2S{=}NTeF_5$ in the −78 °C trap. CF_2Cl_2, BF_3, and BCl_3 are found in the −196 °C trap. $Cl_2S{=}NTeF_5$ is a colorless, sometimes slightly yellow liquid, mp 16 °C; sublimation point −30 °C (10^{-2} mbar). Anal. Calcd for $NSTeCl_2F_5$: N, 4.1; S, 9.4; Te, 37.6; Cl, 20.9; F, 28.0. Found: N, 4.2; S, 9.6; Te, 37.6; Cl, 20.8; F, 28.3.

Raman spectrum (liquid): 1162 (4, p), 721 (sh), 699 (s, p), 643 (vs, p) 546 (s, p), 523 (sh), 451 (sh), 425 (vs, p), 407 (s, p), 376 (s, p), 329 (m, dp), 305 (m, dp), 248 (s, p), 243 (s, p), 215 (s, p), 207 (s, p), 153 (vs, p), 100 (m, p), 77 (m, dp) cm^{-1}. ^{19}F NMR spectrum: ab_4 type, δ_a 38.1, δ_b 34.5; $J_{a-b} = 182$ Hz, $J_{^{125}Te-a} = 3412$ Hz, $J_{^{125}Te-b} = 3857$ Hz.

Preparation of $O{=}S{=}NTeF_5$. A 10-mmol amount of $Cl_2S{=}NTeF_5$ is condensed into a glass vessel filled with 16 mmol of silver trifluoroacetate. After it is warmed to room temperature, the mixture is magnetically stirred. Further cautious warming to 45 °C starts the reaction, which is finished within 1 h. The mixture of products ($O{=}S{=}NTeF_5$ and $(CF_3CO)_2O$) is condensed into a −196 °C trap under vacuum. The separation is achieved by trap-to-trap distillation through −45 and −78 °C cooled traps. $O{=}S{=}NTeF_5$, a colorless, foul smelling, moisture-sensitive liquid, is stopped in the −45 °C trap. It turns yellow either on warming or on standing in the presence of light: yield 68%; mp −24.6 °C. Anal. Calcd for $NOSTeF_5$: N, 4.9; F, 33.4; S, 11.3; Te, 44.8. Found: N, 4.9; F, 34.1; S, 10.4; Te, 44.5.

^{19}F NMR spectrum: ab_4 type, δ_a 41.2, δ_b 33.4; $J_{a-b} = 171.7$ Hz, $J_{^{125}Te-a} = 3459$ Hz, $J_{^{125}Te-b} = 3854$ Hz. IR spectrum (gas): 1291 (vs), 1250 (vw), 1210 (vw), 1138 (s), 1090 (vw), 1070 (vw), 890 (m), 740 (vs), 654 (m) cm^{-1}. Raman spectrum (liquid): 1261 (w, p), 1118 (m, dp), 703 (w, p), 643 (s, p), 590 (m, p), 442 (vs, p), 409 (sh), 372 (vw, p), 324 (w, p), 303 (s, p), 250 (s, p), 224 (m, p), 173 (s, p), 143 (s, p), 110 (m, p). Mass spectrum: $OTeF_5^+$, TeF_5^+, TeF_4^+, TeF_3^+, TeF_2^+, TeF^+, Te^+, SO_2^+, SO^+.

Preparation of $O{=}SF_2{=}NTeF_5$. A 32-mmol quantity of $(CH_3)_3SiNHTeF_5$ is filled into a 100-mL stainless steel autoclave prior to the addition at −196 °C of 48 mmol of sulfur oxide tetrafluoride. This mixture is slowly warmed to 65 °C and stirred at this temperature for 40 h to complete the reaction. All volatile materials are then pumped into a −196 °C cooled trap. Vacuum distillation through −25, −78, and −196 °C cooled traps affords 3.5 g of H_2NTeF_5 in the −25 °C trap, 4.3 g (83% yield) of $O{=}SF_2{=}NTeF_5$ in the −78 °C trap, and $(CH_3)_3SiF$ and excess SOF_4 in the −196 °C trap. O=S-

$F_2{=}NTeF_5$ is a colorless, foul smelling, moisture-sensitive liquid; mp <-78 °C. Anal. Calcd for $NOSTeF_7$: N, 4.3; F, 41.2; S, 9.9; Te, 39.5. Found: N, 4.3; F, 41.5; S, 10.1; Te, 39.6.

^{19}F NMR spectrum: ab_4x_2 type, δ_a 42.8, δ_b 35.5, δ_x −52.5; J_{a-b} = 146.3, J_{b-x} = 5.5 Hz, $J_{^{129}Te-b}$ = 3553 Hz. IR spectrum (gas): 1450 (vs), 1427 (w), 1347 (w), 1255 (vs), 1165 (w), 876 (w), 876 (vs), 740 (vs), 655 (w), 630 (w), 560 (w), 518 (w), 488 (w) cm^{-1}. Raman spectrum (liquid): 1439 (s, p), 1422 (m, p), 1254 (w, p), 1240 (w, p), 868 (s, p), 730 (sh), 706 (s, p), 659 (vs, p), 646 (vs, p), 619 (vs, p), 554 (m, p), 510 (vw, dp), 442 (m, p), 427 (m, p), 327 (m, p), 298 (s, p), 278 (sh), 263 (s, p), 180 (m, p), 102 (vw, dp) cm^{-1}. Mass spectrum: $OSF_2NTeF_5^+$, $OSF_2NTeF_4^+$, TeF_5^+, TeF_3^+, TeF_2^+, TeF^+, Te^+, OSF_2N^+, SO_2^+, SO^+.

Preparation of $F_2Se{=}NTeF_5$. An 8.9-mmol amount of SeF_4 and 18.0 mmol of $(CH_3)_3SiNHTeF_5$ are condensed under dynamic vacuum into a 100-mL trap. After it is slowly warmed to room temperature, the mixture is cooled to −78 °C and all of the volatile materials are pumped off. This warming–cooling–pumping cycle is repeated twice. The resulting mixture is shown by ^{19}F NMR spectroscopy to contain H_2NTeF_5 and $F_2Se{=}NTeF_5$, which could not be separated. Leaving this material at room temperature results in slow precipitation of elemental selenium.

^{19}F NMR: ab_4 spectrum for TeF_5 and a broad single line for SeF_2, δ_a 36.5, δ_b 29.0; J_{a-b} = 180 Hz, $J_{^{125}Te-a}$ = 3366 Hz, $J_{^{125}Te-b}$ = 3683 Hz; δ_{SeF_2} −38.0; $^1J_{^{77}Se-F}$ = 808.4 Hz, $^3J_{^{125}Te-F}$ = 206 Hz.

Preparation of $Cl_2Se{=}NTeF_5$. A 21.3-mmol quantity of $SeCl_4$ is placed into a 50-mL glass vessel under anhydrous conditions. A solution of 21.8 mmol of H_2NTeF_5 in 30 mL of CH_2Cl_2 is then added slowly. With magnetic stirring, the mixture is refluxed for 48 h, by which time the undissolved $SeCl_4$ has disappeared completely. The mixture is then distilled through −30 and −196 °C traps under dynamic vacuum. The −30 °C trap contains colorless, crystalline $Cl_2Se{=}NTeF_5$: mp 16 °C; yield 82%. Anal. Calcd for $NSeTeCl_2F_5$: N, 3.6; Se, 20.4; Te, 33.0; Cl, 18.4; F, 24.6. Found: N, 3.5; Se, 20.4; Te, 33.9; Cl, 19.7; F, 22.8.

IR spectrum (liquid): 965 (m), 697 (s) cm^{-1}. Raman spectrum (liquid): 952 (m, p), 691 (m, p), 625 (m, p), 507 (m, p), 385 (vs, p), 355 (vs, p), 322 (s, p), 270 (s, p), 251 (s, p), 225 (m, dp), 173 (s, p), 161 (s, p), 135 (s, p), 90 (sh) cm^{-1}. ^{19}F NMR spectrum: degenerate ab_4 spectrum, δ_a 30.0, δ_b 30.4.

Preparation of $F_3P{=}NTeF_5$. A 10-mmol amount of $(CH_3)_3SiNHTeF_5$ is filled into a 100-mL stainless steel cylinder, and 20 mmol of PF_5 is added by vacuum distillation into the cooled cylinder. The mixture is magnetically stirred for 14 h at room temperature, and the products are then distilled under dynamic vacuum through −30, −78, and −196 °C traps. The −30 °C trap contains almost all of the H_2NTeF_5 and the −78 °C trap $F_3P{=}NTeF_5$, and $(CH_3)_3SiF$ and excess PF_5 are found in the −196 °C trap. If this distillation is done slowly enough, the product is analytically pure. $F_3P{=}NTeF_5$ is a moisture-sensitive, colorless liquid: yield 75%; bp 54 °C; mp −60 °C. Anal. Calcd for $NPTeF_8$: N, 4.3; P, 9.6; Te, 39.3; F, 46.8. Found: N, 4.4; P, 9.7; Te, 39.3; F, 46.5.

IR spectrum (gas): 1430 (w), 1365 (s), 1005 (s), 937 (m), 722 (s) cm^{-1}. Raman spectrum (liquid): 1018 (w, dp), 941 (m, p), 720 (sh), 700 (s, p), 650 (vs, p), 616 (vs, p), 502 (w, p), 336 (m, dp), 307 (m, dp), 272 (s, p), 185 (m, p) cm^{-1}. ^{19}F NMR: doublet of P–F and ab_4 spectrum of TeF_5, δ_{PF} 80.9, δ_a 39.1, δ_b 35.5; J_{a-b} = 172 Hz, $^4J_{(P)F-b}$ = 3.6 Hz, $^3J_{P-b}$ = 2 Hz, $^3J_{P-a}$ = 10 Hz, $^1J_{P-F}$ = 1077 Hz, $J_{^{125}Te-(P)F}$ = 55 Hz, $J_{^{125}Te-a}$ = 3372 Hz, $J_{^{125}Te-b}$ = 3358 Hz. ^{31}P NMR (50% H_3PO_4 external standard): quartet at −34.8 ppm; $^1J_{P-F}$ = 1063 Hz, $^3J_{P-F_a}$ = 12 Hz.

Preparation of $Cl_3P{=}NTeF_5$. Under anhydrous conditions 20.6 mmol of PCl_5 is placed into a 50-mL glass vessel. A solution of 19.9 mmol of H_2NTeF_5 in 30 mL of CH_2Cl_2 is then added slowly. The resulting mixture is magnetically stirred under reflux for 4 days, by which time the PCl_5 has disappeared completely. The mixture is then distilled under dynamic vacuum through −30 and −196 °C traps. The −30 °C trap contains colorless, crystalline $Cl_3P{=}NTeF_5$: yield 77%; mp 23.4 °C; bp 84 °C (22 mbar). Anal. Calcd for $NPTeCl_3F_5$: N, 3.7; P, 8.3; Te, 34.1; Cl, 28.4; F, 25.4. Found: N, 3.8; P. 8.4; Te, 33.9; Cl, 27.8; F, 25.6.

Raman spectrum (liquid): 1304 (s, p), 699 (s, p), 640 (sh, p), 623 (s, p), 517 (m, p), 491 (s, p), 471 (vs, p), 404 (w, p), 384 (w, dp), 345 (s, p), 311 (m, p), 301 (w, dp), 272 (m, p), 253 (s, dp), 225 (m, dp), 211 (w, dp), 197 (m, dp), 170 (s, p), 152 (s, dp) cm^{-1}. ^{19}F NMR spectrum: ab_4 spectrum, δ_a 33.3, δ_b 34.3; $J_{^{125}Te-F}$ = 3606 Hz. ^{31}P NMR spectrum (50% H_3PO_4 external standard): 17.3 ppm; J_{P-F_a} = 3.2 Hz, J_{P-F_b} = 13.6 Hz.

$Cl_4W{=}NTeF_5$. In a drybox 7.5 mmol of WCl_6 is filled into a 50-mL glass vessel; 15 mL of CH_2Cl_2 and 16.0 mmol of $(CH_3)_3SiNHTeF_5$ are then added. The mixture is magnetically stirred at room temperature for 2 days. By this time the black color of WCl_6 has disappeared and the orange crystalline $Cl_4W{=}NTeF_5$ has precipitated. The solution is also orange. All volatile materials are then distilled under vacuum at room temperature. A 3.7-g amount of the solid remainder is sublimed under vacuum, where at 75 °C some dark orange $WOCl_4$ is observed and at 100 °C light orange $Cl_4W{=}NTeF_5$: yield 65%; mp 136–145 °C. Anal. Calcd for $NTeWCl_4F_5$: N, 2.5; Te, 22.7; W, 32.7; Cl, 25.2; F, 16.9. Found: N, 2.4; Te, 22.0; W, 32.3; Cl, 25.2; F, 17.0.

Raman spectrum (solid): 1147 (m), 728 (w), 718 (m), 663 (s), 401 (vs), 360 (s), 237 (m), 212 (s), 181 (m), 150 (m) 131 (s), 118 (m), 93 (w), 53 (s), 33 (s), 19 (s) cm^{-1}. ^{19}F NMR spectrum (in CH_2Cl_2): degenerate ab_4 spectrum, $\delta_a \simeq \delta_b$, 45.2.

Crystal Data for $Cl_4W{=}NTeF_5$. Crystals were grown by very slow cooling of a saturated solution of $Cl_4W{=}NTeF_5$ in $C_4F_9SO_2F$. A platelike crystal of approximate size 0.48 × 0.36 × 0.06 mm is sealed under dry argon into a quartz capillary. Crystal data: triclinic, $P\bar{1}$; $a = 6.053$ (6), $b = 6.090$ (6), $c = 13.797$ (15) Å; $\alpha = 84.53$ (5), $\beta = 87.48$ (5), $\gamma = 81.56$ (5)°; $V = 500.0$ Å^3; $d_{calcd} = 3.73$ g cm^{-3} for $Z = 2$; Mo Kα radiation, $\lambda = 0.71069$ Å; μ(Mo Kα) = 160.26 cm^{-1}; $F(000) = 492.0$.

Data collection was carried out on a Siemens AED automated diffractometer (Mo Kα radiation, Zr filter, $\theta/2\theta$ scan). Unit cell parameters were based on a least-squares refinement of the setting angles of the unresolved Mo Kα peaks of 20 reflections ($25 < 2\theta < 35°$). The intensities of 2 standard reflections were measured every 40 reflections to monitor crystal decay and alignment. Crystal decay was severe but approximately linear. At the end of data collection the standards had diminished to nearly 40% of their original intensities. The data were adjusted accordingly.

A total of 1764 reflections were collected in two steps ($5.5 \le 2\theta \le 40°$ and $40 \le 2\theta \le 52.5°$) in the hemisphere with $-7 \le h \le 4$, $-7 \le k \le 4$, $-17 \le l \le 17$. A total of 1396 of these reflections were considered as observed ($I \ge 2\sigma(I)$). Absorption corrections calculated by an analytical integration[11] with the crystal shape described by seven faces showed transmission coefficients from 0.382 to 0.015.

Structure Determination and Refinement. The structure was solved with conventional heavy-atom techniques in the centrosymmetric space group $P\bar{1}$. The tungsten and tellurium atoms were located with a Patterson map. Subsequent difference Fourier maps revealed the positions of the remaining chlorine, fluorine, and nitrogen atoms. Full-matrix least-squares refinement in the space group $P\bar{1}$ converged to the final structure; the maximum parameter shift in the last cycle was less than 0.06σ. All atoms were refined with anisotropic temperature factors. Scattering factors used for the neutral tungsten, tellurium, chlorine, fluorine, and nitrogen atoms and dispersion corrections for tungsten, tellurium, and chlorine atoms were those of ref 12. In the final cycles of least-squares refinement weights were calculated with $w = x{\cdot}y$ ($x = 1$ for $\sin\theta \ge 0.2$; $x = \sin\theta$ for $\sin\theta < 0.2$; $y = 1$ for $F_o \le 35.0$; $y = 35.0/F_o$ for $F_o > 35.0$). Several cycles of full-matrix least squares with this weighting scheme converged to $R_1 = 0.10$ and $R_2 = 0.122$ ($R_1 = \sum(|F_o - F_c|)\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$).

Neither refinement in the space group $P1$ nor omission of the last measured reflections gave a better agreement with the diffraction data.

The final positional and thermal parameters are listed in Table I. A listing of observed and calculated structure factor amplitudes is given in the supplementary material. All crystallographic calculations were performed on a Cyber 170-835 computer (unless stated otherwise) with use of the program system X-RAY 76.[13]

Results

The methods of preparation of the many new tellurium–nitrogen-containing species are shown in Scheme I. In general

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Scheme I. Schematic Representation of the $>NTeF_5$ Chemistry

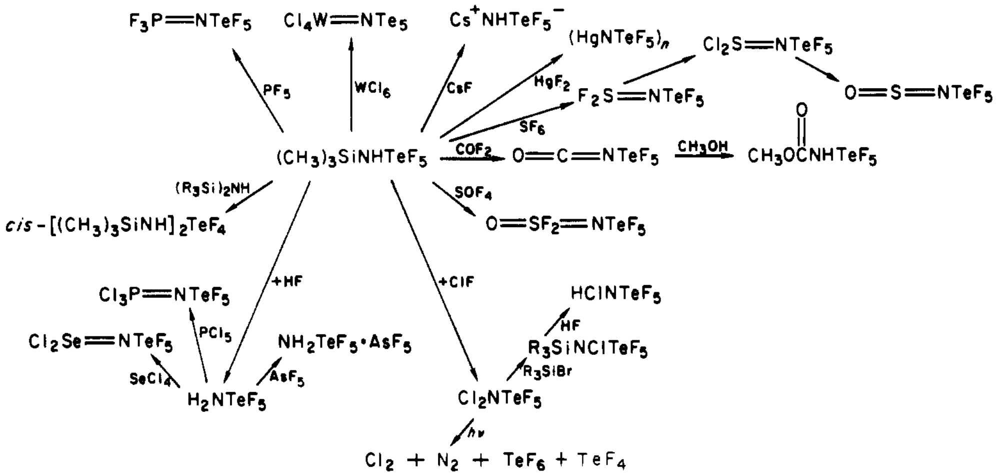

Table I. Atomic Parameters for Cl_4WNTeF_5 (Standard Deviations in Parentheses)

atom	*x*	*y*	*z*
W	0.0358 (2)	−0.0277 (3)	0.8569 (1)
Cl(1)	0.139 (2)	0.208 (2)	0.9697 (6)
Cl(2)	−0.113 (2)	−0.296 (2)	0.7973 (8)
Cl(3)	0.337 (2)	−0.279 (2)	0.9045 (7)
Cl(4)	−0.301 (2)	0.197 (2)	0 8594 (7)
N	0.150 (5)	0.093 (5)	0.785 (2)
Te	0.254 (5)	0.2036 (5)	0.6268 (2)
F(1)	0.517 (5)	0.040 (6)	0.647 (2)
F(2)	0.996 (6)	0.372 (7)	0.604 (3)
F(3)	0.347 (7)	−0.565 (6)	0.675 (3)
F(4)	0.835 (7)	0.025 (8)	0.420 (3)
F(5)	0.641 (7)	−0.302 (8)	0.491 (2)

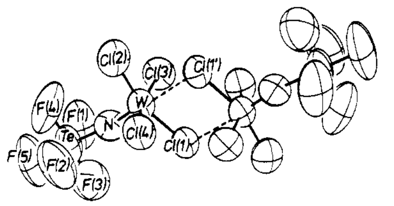

Figure 1. Molecular structure of two adjacent $Cl_4W{=}NTeF_5$ molecules. The W=NTe linkage is almost linear. The coordination sphere of tungsten is increased to 6 by a cis double bridge of chlorine atoms. The thermal ellipsoids are scaled to 50% probability.

it can be said that fluorides preferably react with $(CH_3)_3SiNHTeF_5$ because of the ease of formation of $(CH_3)_3SiF$. But in these reactions half of the $(CH_3)_3SiNHTeF_5$ is always used as HF scavenger, e.g.

$$2(CH_3)_3SiNHTeF_5 + PF_3 \rightarrow 2(CH_3)_3SiF + H_2NTeF_5 + F_3P{=}NTeF_5$$

Sometimes the separation of the new product and H_2NTeF_5 was difficult; however, this problem is not encountered if chlorides are reacted with H_2NTeF_5:

$$H_2NTeF_5 + SeCl_4 \rightarrow Cl_2Se{=}NTeF_5 + 2HCl$$

The third general reaction route starts with Cl_2NTeF_5. This is a very reactive species, although as of yet, explosions have not been observed. Irradiation of it did not produce any desirable compounds such as $F_5TeN{=}NTeF_5$ or F_5TeTeF_5:

$$2Cl_2NTeF_5 \rightarrow 2Cl_2 + N_2 + TeF_4 + TeF_6$$

The chlorine atoms in $Cl_2N\text{-}TeF_5$ behave as if partially positive:

$$Cl_2NTeF_5 + (CH_3)_3SiBr \rightarrow BrCl + (CH_3)_3SiNClTeF_5$$

The final product of this series, $ClHNTeF_5$, was so unstable

Table II. Stretching Frequencies of the Nitrogen Element Double Bond (cm^{-1})

$O{=}C{=}NTeF_5$	2260, 1390	$F_2Se{=}NTeF_5$	not obtained
$F_2S{=}NTeF_5$	1287	$Cl_2Se{=}NTeF_5$	965
$Cl_2S{=}NTeF_5$	1162	$F_3P{=}NTeF_5$	1365
$O{=}S{=}NTeF_5$	1291, 1138	$Cl_3P{=}NTeF_5$	1304
$O{=}SF_2{=}NTeF_5$	1450, 1255	$Cl_4W{=}NTeF_5$	1147

Table III. Bond Distances (pm) and Angles (deg) (Standard Deviations in Parentheses)

W-N	167 (3)	Te-F(1)	176 (3)
Te-N	198 (3)	Te-F(2)	176 (4)
W-Cl(1)	237.8 (9)	Te-F(3)	179 (4)
W-Cl(2)	222.2 (12)	Te-F(4)	175 (5)
W-Cl(3)	226.8 (8)	Te-F(5)	180 (3)
W-Cl(4)	227.4 (9)		
W-Cl(1′)	277.0 (8)		

W-N-Te	169 (2.1)	N-Te-F(1)	89.6 (1.2)
Cl(1)-W-N	97.2 (1.2)	N-Te-F(2)	92.0 (1.4)
Cl(1′)-W-N	175.8 (1.1)	N-Te-F(3)	91.2 (1.5)
Cl(2)-W-N	102.2 (1.2)	N-Te-F(4)	88.5 (1.5)
Cl(3)-W-N	98.6 (0.9)	N-Te-F(5)	177.9 (1.5)
Cl(4)-W-N	98.9 (1.0)	F(1)-Te-F(2)	178.2 (1.6)
Cl(1)-W-Cl(1′)	78.6 (0.3)	F(1)-Te-F(3)	90.6 (1.7)
Cl(1)-W-Cl(2)	160.6 (0.4)	F(1)-Te-F(4)	88.8 (1.8)
Cl(1)-W-Cl(3)	87.6 (0.4)	F(1)-Te-F(5)	88.5 (1.5)
Cl(1)-W-Cl(4)	84.8 (0.4)	F(2)-Te-F(3)	88.5 (1.8)
Cl(1′)-W-Cl(2)	82.0 (0.4)	F(2)-Te-F(4)	92.0 (1.9)
Cl(1′)-W-Cl(3)	80.8 (0.3)	F(2)-Te-F(5)	89.9 (1.6)
Cl(1′)-W-Cl(4)	81.3 (0.3)	F(3)-Te-F(4)	179.3 (1.7)
Cl(2)-W-Cl(3)	90.0 (0.4)	F(3)-Te-F(5)	88.1 (1.8)
Cl(3)-W-Cl(4)	161.6 (0.4)	F(4)-Te-F(5)	92.2 (1.9)

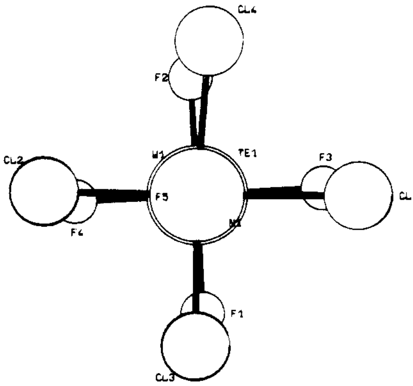

Figure 2. View of the $Cl_4W{=}NTeF_5$ molecule along the almost linear W=NTe axis. The four fluorine and four chlorine atoms, respectively, are completely eclipsed. This suggests some double-bond character through the entire system.

that it could only be identified by NMR spectroscopy.

Due to the well-known electron-withdrawing force of the TeF_5 group,[14] element-nitrogen double bonds become very strong, as indicated by the stretching frequencies shown in Table II. This is especially obvious in the case of $Cl_4W{=}NTeF_5$ as shown by the crystal structure analysis (see Figures 1 and 2 and Table III).

The W–N–Te skeleton is almost linear (171°), and the two tetragonal groupings (Cl_4W and TeF_5) are in an eclipsed configuration. The coordination sphere of tellurium is certainly saturated, as also in $OTeF_5$ compounds.[14] The tungsten coordination sphere, however, is increased by a double chlorine bridge (W–Cl′) between two molecules. All other distances are typical for nonbonding intermolecular forces.

The large thermal parameters for fluorine indicate static or dynamic disorder. If a riding model correction[15,16] is applied, then the Te–F distances increase about 4 pm.

The formation of *cis*-$[(CH_3)_3SiNH]_2TeF_4$ is paralleled by the reaction of $(CH_3)_3SiOTeF_5$ and $(CH_3)SiOSi(CH_3)_3$:[17]

$$(CH_3)_3SiNHTeF_5 + (CH_3)_3SiNHSi(CH_3)_3 \rightarrow (CH_3)_3SiF + cis\text{-}[(CH_3)_3SiNH]_2TeF_4$$

$$(CH_3)_3SiOTeF_5 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow (CH_3)_3SiF + cis\text{-}[(CH_3)_3SiO]_2TeF_4$$

The cis geometry could unambigously be proven by the typical a_2b_2 ^{19}F NMR spectrum of each compound. The formation of cis products in both cases is certainly a result of kinetics, since sterically the trans product should be favored. *cis*-$[(CH_3)_3SiNH]_2TeF_4$ was formed sometimes directly from $(CH_3)_3SiNHSi(CH_3)_3$ and TeF_6, especially when vessels were used that had not previously been cleaned by concentrated nitric acid. *cis*-$[(CH_3)_3SiNH]_2TeF_4$ is a colorless crystalline material that can be sublimed under vacuum. Occasionally explosions have been observed during prolonged heating. The decomposition probably proceeds according to

$$cis\text{-}[(CH_3)_3SiNH]_2TeF_4 \rightarrow 2(CH_3)_3SiF + N_2 + 2HF + Te$$

Once a large amount of this material was left in an unsealed vessel. After several months the material had turned to a yellow product of unknown composition, which exploded, causing severe damage.

Discussion

In spite of the instability of the unknown compound last mentioned, the double-bonded systems containing $>NTeF_5$ are generally surprisingly stable. The TeF_5 group lends some of its electron withdrawal effect to the nitrogen. Some of the compounds listed in Scheme I have analogies in sulfur chemistry such as $O{=}C{=}NSF_5$,[18] $F_2S{=}NSF_5$,[19] $O{=}SF_2{=}NSF_5$,[20] $Cl_2S{=}NSF_5$,[21] and Cl_2NSF_5.[22]

In general the chemistry of the NSF_5 group is much more restricted since sulfur tends to decrease its coordination. The best example may be H_2NSF_5, which readily eliminates HF, forming NSF_3.[4] It should be noted that no corresponding $NSeF_5$ compounds are known so far.

$Cl_2Se{=}NTeF_5$ and $F_2Se{=}NTeF_5$ represent one of the few examples of molecules containing selenium–nitrogen double bonds. Other compounds with such a bond are of the type $RC_6H_4SO_2N{=}SeCl_2$.[23]

The crystal and molecular structure of $Cl_4W{=}NTeF_5$ shows the tendency of the tungsten atom to achieve the coordination number 6. In the related $WOCl_4$ the same effect is obtained by linking the tungsten atoms through oxygen bridges in endless chains.[24] Since the $=NTeF_5$ group is unable to form bridges, the bridging is done by chlorine atoms (see Figure 1). This structural behavior is similar to that of $[Cl_4W{=}NC_2Cl_5]_2$.[25] The saturation of the tungsten coordination sphere is achieved in other compounds by Cl^-, $C_2Cl_5N{=}WCl_5^-$,[26] or by $POCl_3$, $Cl_3POCl_4W{=}NC_2Cl_5$.[26] Related behavior of rhenium and molybdenum complexes is known also.[27,28]

The almost complete linearity of the TeN=W bridge is found also in all the other examples mentioned above. Along with this a rather short tungsten–nitrogen bond distance of 169 pm is observed (171 pm in $[Cl_4W{=}NC_2Cl_5]_2$). This has often been interpreted in terms of metal–nitrogen triple bonds. In $Cl_4W{=}NTeF_5$ the electron density of the lone pair of nitrogen is certainly involved in the bonding toward tungsten *and* tellurium. The eclipsed configuration of the two tetragonal parts of the molecule as seen in Figure 2 strongly favors this model. The $W_2NCl_{10}^{2-}$ anion also has an eclipsed configuration, without having a symmetric WNW bridge.[29]

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Registry No. TeF_6, 7783-80-4; $[(CH_3)_3Si]_2NH$, 999-97-3; $(CH_3)_3SiNHTeF_5$, 42005-82-3; *cis*-$[(CH_3)_3SiNH]_2TeF_4$, 86045-52-5; COF_2, 353-50-4; H_2NTeF_5, 42005-83-4; $O{=}C{=}NTeF_5$, 86024-46-6; $CH_3OC(O)NHTeF_5$, 86024-47-7; CH_3OH, 67-56-1; ClF, 7790-89-8; Cl_2NTeF_5, 86024-48-8; $(CH_3)_3SiNClTeF_5$, 86024-49-9; $(CH_3)_3SiBr$, 2857-97-8; SF_4, 7783-60-0; $F_2S{=}NTeF_5$, 86024-50-2; $Cl_2S{=}NTeF_5$, 86024-51-3; $O{=}S{=}NTeF_5$, 86024-52-4; $O{=}SF_2{=}NTeF_5$, 86024-53-5; $O{=}SF_4$, 13709-54-1; $F_2Se{=}NTeF_5$, 86024-54-6; SeF_4, 13465-66-2; $Cl_2Se{=}NTeF_5$, 86024-55-7; $SeCl_4$, 10026-03-6; $F_3P{=}NTeF_5$, 86024-56-8; PF_5, 7647-19-0; $Cl_3P{=}NTeF_5$, 86024-57-9; PCl_5, 10026-13-8; $Cl_4W{=}NTeF_5$, 86024-58-0; WCl_6, 13283-01-7.

Supplementary Material Available: Listings of anisotropic temperature factors and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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