observed for all complexes. The large number of shifted resonances indicates that many residues in addition to those directly coordinated to the metal center are affected via dipolar interactions. Further studies will be necessary to assign the spectra and to attempt to locate additional resonances that are more dramatically shifted. Nonetheless, the spectra clearly support the assignment of the Ni^{2+} complexes as paramagnetic and, hence, distorted tetrahedral rather than diamagnetic and square planar. The relatively broad lines of the Fe^{2+} complex are consistent with high-spin d^6 complexes.

The affinities of CP-1 for Ni^{2+} and Fe^{2+} were determined by metal ion titrations similar to those described previously.[8,17] Fitting the results of these experiments revealed dissociation constants (with estimated standard deviations in parentheses) of $K_d^{Ni} = 1.6\ (\pm 0.9) \times 10^{-6}$ M and $K_d^{Fe} = 2.5\ (\pm 0.8) \times 10^{-6}$ M for CP-1 and $K_d^{Ni} = 1.2\ (\pm 0.4) \times 10^{-6}$ M and $K_d^{Fe} = 2.4\ (\pm 0.8) \times 10^{-6}$ M for CP-1(H24C). Competition experiments with Co^{2+}, Fe^{2+}, and Ni^{2+} with CP-1 suggested that $K_d^{Mn} > 10^{-5}$ M. Zn^{2+}, which binds to CP-1 with $K_d^{Zn} = 2 \times 10^{-12}$,[17] is bound 6 to 9 kcal/mol more tightly than are the other metal ions. The trends in these values are somewhat reminiscent of the corresponding trends for formation of a series of MCl_4^{2-} ions.[23] This behavior has been interpreted in terms of changes in ligand field stabilization energy being a significant component in determining the heats of formation although other factors are also important. The relative ion affinities we have observed indicate that the specific reactivation of TFIIIA by zinc can be accounted for by metal ion affinity without requiring any significant structural differences in the metal complexes once they are formed. Moreover, these initial observations reveal that zinc finger peptides such as CP-1 and CP-1-(H24C) should be useful in studying the properties of a variety of metal ions in distorted tetrahedral mixed sulfur–nitrogen coordination environments.

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Reactions of Tellurium Halides with Sulfur *N,N'*-Bis(trimethylsilyl)diimide—Preparation of the First Fluorotellurium Nitride

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Introduction

The use of sulfur diimides as versatile synthetic reagents in sulfur–nitrogen chemistry is well documented.[1] In addition, they have been found to be excellent precursors in synthesizing novel transition-metal-containing heterocycles.[2] Recently, we reported on the synthesis of $(ClTeNSN)_3N$, the first example of a tellurium nitride stable at room temperature, from reaction of tellurium(IV) chloride with sulfur *N,N'*-bis(trimethylsilyl)diimide (**1**).[3] Herein we report the synthesis and X-ray structural characterization of $(FTeNSN)_3N$ (**2**) using a similar synthetic route involving **1** and tellurium(IV) fluoride.

Experimental Section

Experimental manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried according to standard methods. Tellurium(IV) fluoride[4] and sulfur *N,N'*-bis(trimethylsilyl)diimide[5] (**1**) were prepared by known methods.

For the ^{19}F NMR spectrum $CFCl_3$ was used as an external standard. The ^{125}Te NMR spectrum was determined at ambient temperature with Me_2Te as an external standard. The IR spectrum was obtained as a Nujol mull between sodium chloride windows. Only strong (s) and very strong (vs) bands are reported.

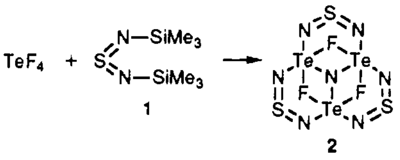
Crystal Data for 2·2(pyridine): $C_{10}H_{10}F_3N_9S_3Te_3$, MW = 792.3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.848\ (2)$ Å, $b = 10.040\ (3)$ Å, $c = 12.598\ (3)$ Å, $\alpha = 69.15\ (1)°$, $\beta = 82.99\ (2)°$, $\gamma = 68.73\ (1)°$, $V = 974.6\ (4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.700$ Mg m^{-3}, $\mu = 4.83$ mm^{-1}, crystal dimensions 0.2 × 0.3 × 0.4 mm. The X-ray structure determination was carried out on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 4516 reflections was measured at −120 °C with a profile-fitting method for $2\theta < 55°$. A semiempirical absorption correction was applied. After equivalents were merged, 4294 independent data with $F > 4\sigma(F)$ were used for all calculations. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. A riding model with idealized hydrogen geometry was employed for H-atom refinement. The full-matrix least-squares refinement converged to final residues $R(F_o) = 0.0216$, $R_w(F_o) = 0.0245$ with $w^{-1} = \sigma^2(F) + 0.0001F^2$. All calculations were performed with SHELXS[6] and SHELXTL.

Caution: Compound **2** may decompose violently when exposed to mechanical strain!

To a suspension of 0.94 g (4.6 mmol) of tellurium(IV) fluoride in ether (30 mL) was added dropwise at ambient temperature a solution of 1.04 g (5.1 mmol) of **1** in the same solvent (30 mL). A white precipitate was formed instantaneously. When the reaction mixture was stirred for another 8 h, the color of the precipitate was found to turn to red. The solid was filtered off, redissolved in pyridine/toluene (3:1) and allowed to crystallize at −10 °C, giving 0.50 g (0.8 mmol) of **2** (51%) after drying in vacuo. Recrystallization from the same solvent mixture gave crystals suitable for X-ray structure determination. Mp: 112 °C dec. IR spectrum: 1205 (s), 1149 (vs), 1056 (vs) cm^{-1}. ^{19}F NMR (pyridine-/C_6D_6): −42.6 ppm (s). ^{125}Te NMR (pyridine/C_6D_6): 1157 ppm. Anal. Calcd for **2**, $F_3N_7S_3Te_3$: N, 15.46; F, 9.0. Found: N, 14.7; F, 10.6.

Results and Discussion

A reaction of tellurium(IV) fluoride with a slight excess of sulfur *N,N'*-bis(trimethylsilyl)diimide (**1**) in ether at room temperature proceeds readily with the formation of the novel tellurium nitride **2**.



During the reaction, initially the formation of a white precipitate is observed, which on stirring for some time turns red. To investigate whether the white solid might be an intermediate, this reaction was carried out again at −5 °C and stirred for only 30 min. The white solid was filtered off. A comparison of the IR spectra of the red and white reaction products showed identical absorptions due to the NSN units as broad absorption bands (1149 and 1056 cm^{-1}).

The ^{19}F NMR chemical shift of compound **2** was found about 17 ppm higher than the signal reported for tellurium(IV) fluoride.[7] No ^{125}Te satellites have been observed. However, no attempt was made to detect such couplings by recording the spectrum at lower temperature. The ^{125}Te NMR spectrum shows a very broad signal ($\Delta\nu_{1/2} = 505$ Hz, 1157 ppm). The shift of the analogous chloride $(ClTeNSN)_3N$ in the same solvent was found at 1212 ppm.[8] No coupling with the directly bonded F atoms is observed, indicating

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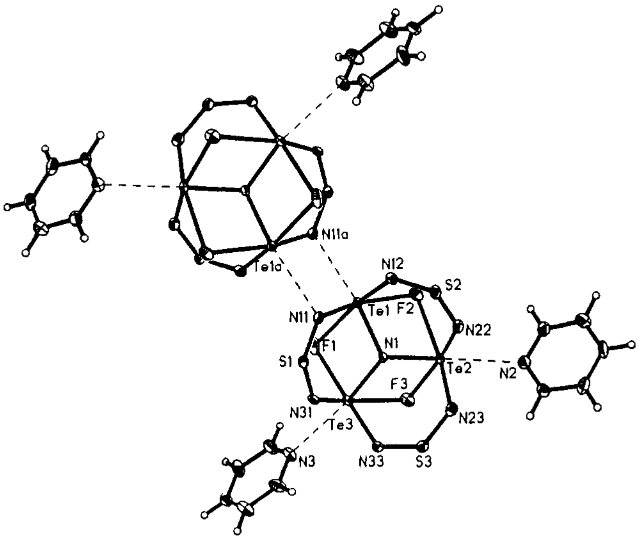

Figure 1. Structure of **2** showing 50% probability thermal motion ellipsoids. Selected mean bond distances (Å) are as follows: Te–N (NSN) (mean) = 2.048 (3), Te–N(1) (mean) = 2.031 (3), Te–F (mean) = 2.331 (3). The nitride N(1) atom is situated about 0.46 Å above the plane built by the three Te atoms.

fast exchange reactions in solution.

The deviation of the calculated elemental analysis from the values required is due to hydrolytic decomposition of compound **2**.

Although mild ionization methods (field desorption) were used, no fragments related to **2** could be found in the mass spectrum. A peak observed at m/z 256 can be attributed to S_8. Whether this peak is due to sulfur formation in the reaction or due to fragmentation of the molecule in the mass spectrum is unclear. The only byproduct detectable by ^1H NMR spectroscopy is Me_3SiF. No mechanism for the formation of **2** can be given. However, cleavage of S–N bonds is a well-known possibility in reactions of sulfur diimides.[2,9]

Figure 1 shows the content of the unit cell. Atomic parameters are given in Table I. In the crystalline state two molecules of **2** are connected by two intermolecular coordinations between N and Te atoms with Te- - -N distances of 2.955 Å. The distorted-octahedral coordination sphere is completed by short contacts to pyridine molecules. The bond distances do not differ significantly from those in the analogous chloride $(ClTeNSN)_3N$. Te–F bonds are significantly longer than the bridging and nonbridging Te–F bonds in tellurium(IV) fluoride (2.331 compared to 2.17 or 1.86 Å, respectively).[10] A structure similar to **2** and $(ClTeNSN)_3N$ is found in the phosphazene $(ClPNPCl_2N)_3N$.[11]

Compound **2** is the second structurally characterized tellurium nitride. Binary nitrides of tellurium are known from the literature, but they are—due to their violently explosive nature—only poorly characterized.[12,13] $(ClTeNSN)_3N$ and **2** are rather stable molecules, except that **2** may decompose violently under mechanical strain. The surprising kinetic stability of these two products can be explained with the steric shielding of the nitride N(1) atom by the sulfur diimide units on the one side and the halogen atoms on the other side of the molecules. Although a brown solid was obtained from a reaction involving tellurium(IV) fluoride and **1** in 1:4 molar ratio in THF, no information with respect to its identity could be obtained since it was found to explode violently on treatment with a spatula.

Table I. Atomic Parameters (×10^4) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3) for **2**[a]

	x	y	z	U(eq)
Te(1)	5385 (1)	1726 (1)	5383 (1)	12 (1)
Te(2)	7971 (1)	3085 (1)	6146 (1)	12 (1)
Te(3)	6985 (1)	4105 (1)	3334 (1)	12 (1)
S(1)	7212 (1)	904 (1)	3197 (1)	14 (1)
S(2)	8257 (1)	−439 (1)	7186 (1)	17 (1)
S(3)	10606 (1)	3320 (1)	4161 (1)	18 (1)
F(1)	4600 (3)	3628 (2)	3618 (2)	23 (1)
F(2)	5522 (3)	2576 (2)	6832 (2)	21 (1)
F(3)	7241 (3)	5259 (2)	4645 (2)	20 (1)
N(1)	7221 (3)	2552 (3)	4940 (2)	11 (1)
N(11)	6236 (3)	496 (3)	4296 (2)	15 (1)
N(12)	6777 (4)	−232 (3)	6547 (2)	17 (1)
N(22)	8929 (3)	804 (3)	7070 (2)	16 (1)
N(23)	10187 (3)	2886 (3)	5425 (3)	18 (1)
N(31)	7610 (3)	2372 (3)	2697 (2)	14 (1)
N(33)	9415 (3)	3803 (3)	3191 (2)	17 (1)
N(2)	10081 (4)	2638 (3)	7877 (3)	21 (1)
C(1)	9565 (5)	2213 (5)	8938 (3)	28 (2)
C(2)	10587 (6)	1476 (5)	9888 (3)	33 (2)
C(3)	12196 (5)	1167 (5)	9722 (3)	31 (2)
C(4)	12793 (5)	1589 (4)	8618 (3)	26 (2)
C(5)	11677 (5)	2337 (4)	7728 (3)	21 (1)
N(3)	6828 (4)	5376 (3)	1069 (3)	21 (1)
C(6)	7964 (5)	5031 (4)	316 (3)	27 (1)
C(7)	7698 (5)	5699 (5)	−838 (3)	31 (2)
C(8)	6208 (5)	6756 (4)	−1242 (3)	26 (2)
C(9)	5002 (5)	7110 (5)	−460 (3)	30 (2)
C(10)	5387 (5)	6408 (4)	682 (3)	26 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Attempts to generate an analogous bromide to **2** however were unsuccessful. Tellurium(IV) bromide does not react either with **1** or sulfur *N,N'*-bis(trimethylstannyl)diimide under similar conditions.

Other Te compounds containing sulfur diimide units are known from the literature,[14-16] but except $(ClTeNSN)_3N$ no other compound containing a nitride N atom has been reported. Compound **2** is one of the first fluorides of tellurium(IV) to be structurally characterized.

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Registry No. **1**, 18156-25-7; **2**, 140874-49-3; **2**·2(pyridine), 140874-50-6.

Supplementary Material Available: Listings of positional parameters, anisotropic displacement parameters, and bond distances and angles for $(FTeNSN)_3N$ (3 pages); a listing of structure factor amplitudes for $(FTeNSN)_3N$ (14 pages). Ordering information is given on any current masthead page.

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A Chloroalkane–Silver Complex with a Monodentate RCl→Ag(I) Interaction

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Introduction

During the last 4 years a number of metal complexes containing chloroalkane ligands have been prepared and structurally char-

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