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Bis(sulfinylamido)tellurium(IV) fluoride: a versatile synthon in tellurium–nitrogen chemistry

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Dedicated to Dr. Karl Christe on the occasion of his 65th birthday

Abstract

Halogen exchange reactions between $F_2Te(NSO)_2$ and Me_3SiX provide $X_2Te(NSO)_2$ ($X = Cl$, Br). The brominated derivative can also be made from $Te(NSO)_2$ and Br_2 or from Te and BrNSO. Pyrolysis of $F_2Te(NSO)_2$ gives $F_2\overline{TeNSNS}$ which reacts with MF_5 to salt like $[F\overline{TeNSNS}]^+[MF_6]^-$ ($M = As$, Sb). Halogenation of $F_2Te(NSO)_2$ with Cl_2 or Br_2, ratio 2:1, provides $X_2Te(N{=}S{=}N)_2TeX_2$. The corresponding $F_2Te(N{=}S{=}N)_2TeF_2$ is made by decomposition of $F_2Te(NSO)_2$ dissolved in THF at room temperature during 10 days. It can be transferred by Cl_2, Br_2 or Me_3SiX, respectively to $X_2Te(N{=}S{=}N)_2TeX_2$ ($X = Cl$, Br). When $F_2Te(NSO)_2$ is reacted with X_2 in an 1:1 molar ratio or with TeX_4, then the bicyclus $X_2\overline{TeX_2Te(X_2)N{=}S{=}N}$($X = Cl$, Br) is formed. Ionic moieties with a cage type cation **5** are obtained by treating $F_2Te(NSO)_2$ (molar ratio 1:1) or F_2Te $(N{=}S{=}N)_2TeF_2$ with MF_5 ($M = As$, Sb) (molar ratio 1:2) in SO_2 solution. A 1:1 mixture of $F_2Te(NSO)_2$ and MF_5 reacts in CH_2Cl_2 giving $[FTe(NSO)_2]^+[MF_6^-]$. In SO_2 solution, $F_2Te(NSO)_2$ reacted with AsF_5, molar ratio 1:2, to $[Te(NSO)_2]^{++}[AsF_6^-]_2$. Metathetical reactions between $F_2Te(NSO)_2$ and $[CF_3C(O)]_2O$ or $Me_3Si\text{-}OC(O)CF_3$ as well as $Me_3SiOS(O_2)CF_3$ yield the novel compounds $[CF_3C(O)O]_2Te(NSO)_2$ and $(CF_3SO_2O)_2Te(NSO)_2$, respectively. X-ray structure for **9** is provided. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dihalogeno; Bis(sulfinylamido)tellurium(IV); Preparation; Chemical reactions; Fluorodithiatelluradiazole; Diazolium; Tetrahologeno-bis [−]; Hexahalogeno[η-sulfurdimidato(2−)]-ditellurium(IV); Difluorodithiaditelluratetrazociniium; Fluoro-bis(sulfiniylamido)tellurium(1+); Bis(sulfinylomido)-tellurium(2+); Hexafluoroarsenate-antimonate; Trifluoracetate; Trifluoromethanesulfonate

1. Introduction

The easy access to the simple compounds $Se(NSO)_2$ [1], $Te(NSO)_2$ [2], $Cl_2Te(NSO)_2$ [3], and $F_2Te(NSO)_2$ [4] opened new synthetic routes for the preparation of new neutral or ionic, ring- and cage-like chalcogen–nitrogen compounds. The reactions applied provided so far only exocyclic chlorine or bromine substituted moities and two iodo derivatives [5], as far as fluorine is concerned in these investigations, only one substituted cationic cage [3], has been synthesized. All attempts to replace halogen by fluorine applying metathetical reactions with fluorinating reagents failed [6]. Therefore, new strategies are persued. The aim of this paper is to elucidate the chemical reactions of bis(sulfinylamido)tellurium(IV) fluoride (**1a**) and to demonstrate its utility as a versatile precursor for the preparation of cyclic and non-cyclic tellurium containing compounds. These studies should also provide results for a better understanding of reaction pathways in this complicated by far not completely understood, chalcogen–nitrogen chemistry.

2. Preparation of $X_2Te(NSO)_2$ ($X = F$, Cl, Br) and their reactivity

For the preparation of **1a**, instead of gas chromatographically purified Me_3SiNSO, a mixture of Me_3SiNSO and $Me_3SiOSiMe_3$, as obtained from $(Me_3Si)_2NH$ and SO_2 [7], is applied and the reaction with TeF_4 is carried out at −20 °C giving almost quantitative yields. Halogen exchange reactions with Me_3SiX transfer **1a** into $X_2Te(NSO)_2$ [$X =$ *Cl* **1b** [3], Br **1c**]. Alternative routes to **1c** are reactions of $Te(NSO)_2$ with Br_2 or Te with BrNSO. Defluorination of **1a** with $(C_6H_5)_3Sb$ yields $Te(NSO)_2$ [2]. These reactions are

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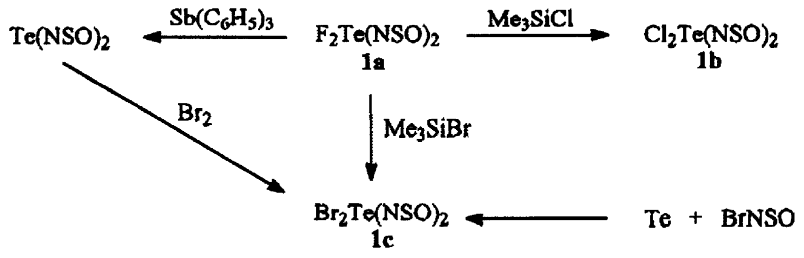
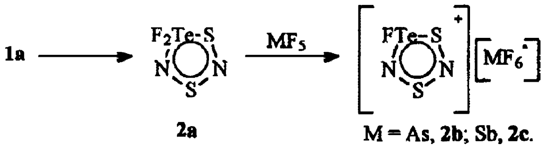
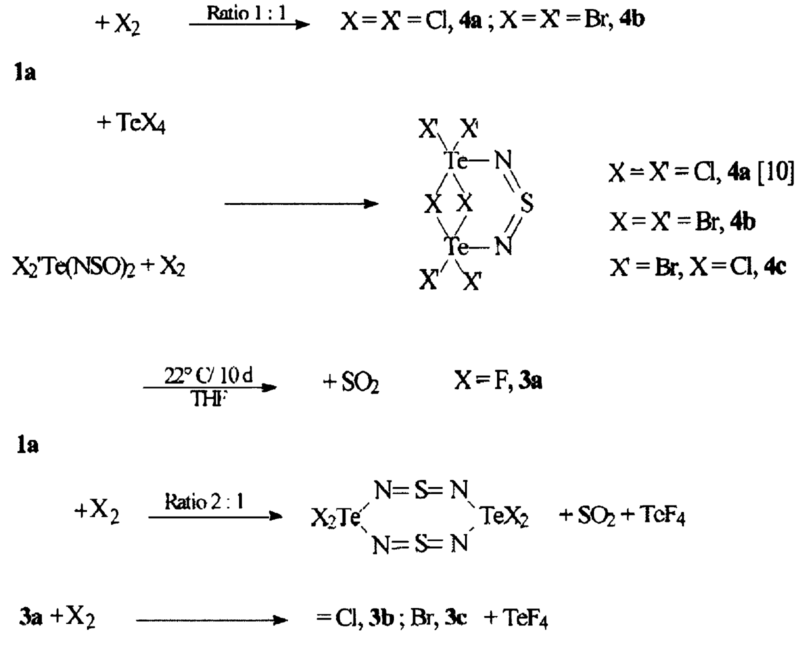


Scheme 1.

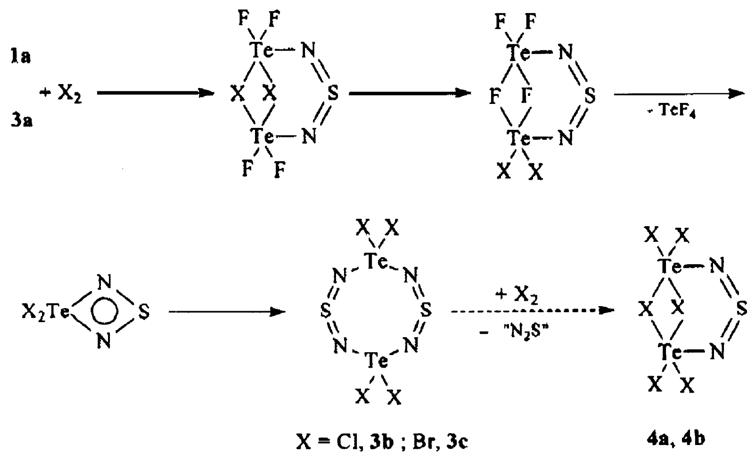


Scheme 2.

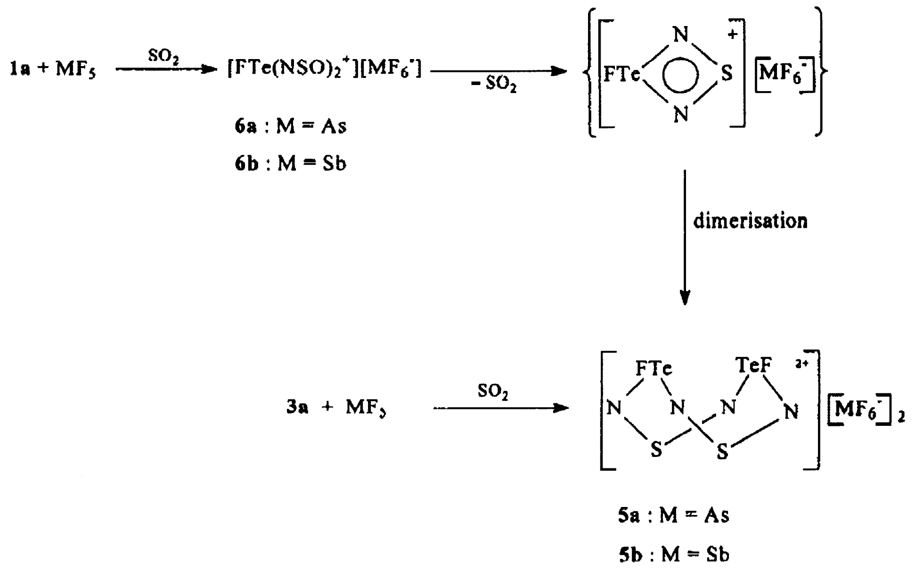
illustrated in Scheme 1. A fluorinated, neutral tellura–chalcogena–nitrogen ring is obtained by gentle pyrolyses of **1a** providing 4,4-difluoro-1,3,4λ^4,2,5-dithiatellura-diazol (**2a**). With strong Lewis-acids, such as AsF_5 or SbF_5 compound **2a**, forms the corresponding hexafluoroarsenates and antimonates **2b** and **c**, respectively according to Scheme 2. The former **2b** is also yielded by pyrolysis of **5a**. In THF, DMF or toluene solution, **1a** is rather unstable and decomposes at 22 °C slowly with elimination of SO_2 forming compound **3a**. The procedure is terminated after 10 days. Both compounds **1a** and **3a** show unexpected behavior towards halogens and **1a** especially towards TeX_4. The reactions with halogens are stochiometrical dependent and if **1a** is treated with X_2 in a 1:1 molar ratio then the bicyclic rings **4a** and **b** are formed. A 2:1 ratio provided the eight membered ring **3** that is for X = Cl, **3b** and for X = Br, **3c**. They are also obtained from **3a** and X_2. The reactions of compound **1a** with TeX_4 lead to **4a** and **b** as shown in Scheme 3. Surprisingly, **1a** forms not only with Cl_2 or Br_2, but also with TeX_4 the unique substituted bicyclus **4a** or **b**. No tetrafluorosubstituted halogen bridged bicycli are observed when reacting **1a** with X_2 (X = Cl, Br). A tentative explanation for this result is a possible instability of the mixed fluorine substituted derivatives rearranging to fluorine bridge moieties, which decompose under elimination of TeF_4 to the corresponding dihalogenated four-membered ring as an intermediate. Their dimerization provide **3b** or **c** which can be further halogenated by excess X_2 to **4a** and **b** as was proved before [14]. This complex chemical procedure is illustrated in Scheme 4. An entirely different reactivity of **1a** with MF_5 (M = As, Sb) is observed in SO_2 solution or CH_2Cl_2 suspension. In SO_2 solution, **1a** forms with MF_5 the insoluble dicationic cages **5a** and **b**, which are also yielded from **3a** and MF_5 under similar conditions



Scheme 3.

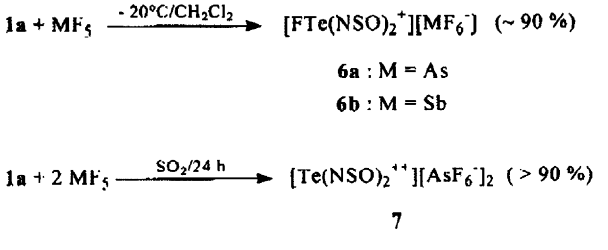


Scheme 4.



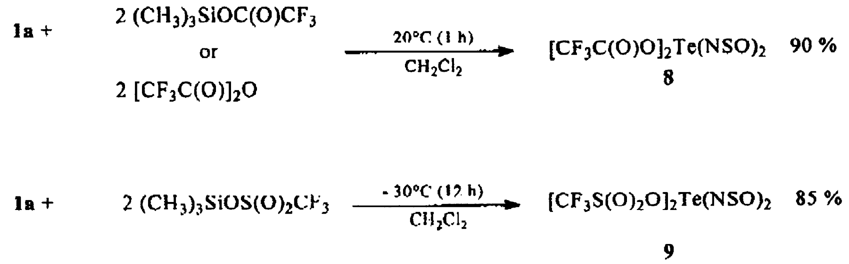
Scheme 5.

as demonstrated in Scheme 5. In order to explain the reaction pathway going from the starting material **1a** to the end-products **5a** and **b** the formation of intermediates such as $[FTe(NSO)_2^+][MF_6^-]$ have to be postulated. Their formation has been be proved by targeted analogous synthesis in CH_2Cl_2 where insoluble **6a** and **b** could be isolated by treating **1a** with 1 mol MF_5 (M = As, Sb) (see Scheme 6).



Scheme 6.

Additionally, it can be shown spectroscopically, that in SO_2 solution **6a** and **b** show above −40 °C ^{19}F NMR signals $\delta(Te–F) = -39.8$ for **6a** and −39.9 for **6b**. The signals disappear on warming providing colorless solids. Their IR spectra are identical with those of **5a** and **b**. The formation of **6a** and **b** in SO_2 solution can also be assumed as an intermediate by reacting **1a** with 2 mol AsF_5 in SO_2 where insoluble **7** is formed (see Scheme 6). The lack of structural data for the insoluble compounds **3a–c** and **5a** and **b** do not allow to assign exact structures to these molecules. In order to overcome this insufficiency, attempts were made to replace halogens by fluorinated organic substituents in F_2-$Te(NSO)_2$ and to study their chemistry. It was found that **1a** undergoes metathetical reactions with $[CF_3(O)]_2O$ or Me_3-$SiOC(O)CF_3$ and $Me_3SiOS(O_2)CF_3$ yielding $[CF_3C(O)O]_2$-$Te(NSO)_2$ (**8**) and $[CF_3S(O_2)O]_2Te(NSO)_2$ (**9**) according to Scheme 7.



$$\mathbf{1a} + \begin{matrix} 2\,(CH_3)_3SiOC(O)CF_3 \\ \text{or} \\ 2\,[CF_3C(O)]_2O \end{matrix} \xrightarrow[CH_2Cl_2]{20^\circ C\ (1\ h)} \underset{\mathbf{8}}{[CF_3C(O)O]_2Te(NSO)_2} \quad 90\ \%$$

$$\mathbf{1a} + 2\,(CH_3)_3SiOS(O)_2CF_3 \xrightarrow[CH_2Cl_2]{-30^\circ C\ (12\ h)} \underset{\mathbf{9}}{[CF_3S(O)_2O]_2Te(NSO)_2} \quad 85\ \%$$

Scheme 7.

2.1. Crystal structure of $[CF_3C(O)O]_2Te(NSO)_2$

The molecular structure with molecule parameters is presented in Fig. 1 and the molecular packing with inter-atomic interactions of $[CF_3C(O)O]_2Te(NSO)_2$ is shown in Fig. 2. This is the first determined structure of an $X_2Te(NSO)_2$ molecule. Therefore distances and angles of the $Te(NSO)_2$ moiety in **8** can only be compared with corresponding data of the compound $Te(NSO)_2$ [4]. While δ(Te–N) is shorted for $Te(NSO)_2$ from 2.039(7) to 2.001(4) Å for **8** δ(N–S) is lengthened from 1.492(7) Å to 1.510 Å and δ(S–O) again shortened from 1.460(7) to 1.417(5) Å. The angles are widened for about 2° going from $Te(NSO)_2$ to **8**, e.g. < N–Te–N 87.3(3)–89.8(2)°, < Te–N–S 122.04–89.8(2)° and < N–S–O 116.6(4)–118.2(3)°. The molecule parameters for the $CF_3C(O)O$-group are comparable with literature data for telluriumtrifluoroacetates [15,16]. From Fig. 1, it is obvious that **8** has a ale-trigonal-bipyramid structure with the two O-atoms occupying axial (< O–Te–O 157°) and the two N-atoms including the free electron pair equatorial (< N–Te–N 90°) positions. Considerable deviations 23° for the O–Te–O and 30° for the N–Te–N angle from the ideal trigonal-bipyramidale arrangements are observed for the O_2TeN_2 moiety. These remarkable distortions can be caused by intermolecular

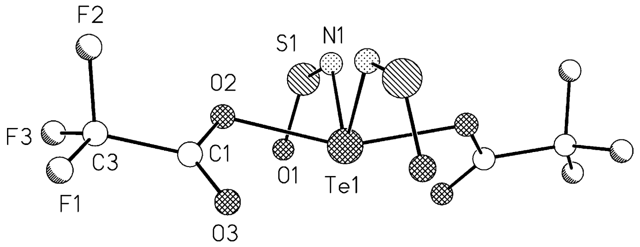


Fig. 1. Molecular structure of $[CF_3C(O)O]_2Te(NSO)_2$.

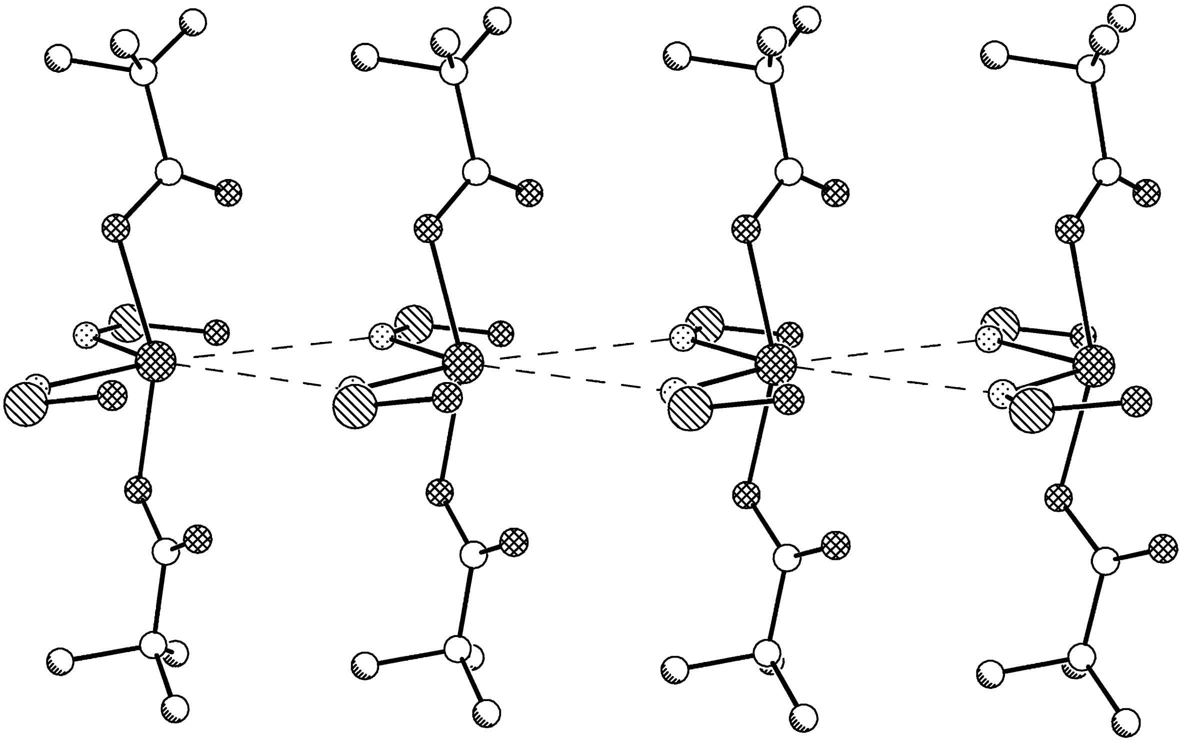


Fig. 2. Molecular packing of $[CF_3C(O)O]_2Te(NSO)_2$ with inter-atomic interactions.

Te–N–Te bonding as shown in Fig. 2. These interactions lead to four membered heterocycles restoring octahedral coordination at the Te-atom. The intermolecular Te···N distance (3.502 Å) is shorter than the sum of van der Waals radii (3.65 Å).

3. Experimental

All reactions are carried out in a standard vacuum line with Teflon-stemmed Young valves or in a glove box (Fa. M. Braun GmbH, München) under argon (dried with Sicapent); solvents are dried according to standard methods and transferred from activated molecular sieves. Microanalyses: Carlo-Erba Element analyser model 1106. IR: KBr-discs, Bruker FT-IR IFS 85 (400–4000 cm^{-1}). Very weak bands are not recorded. Raman: solids in sealed glass capillaries, Bruker FRA 106 (4000–100 cm^{-1}). MS: Varian MAT-CH7, 70 eV, emission 100 μA. NMR spectra were recorded for SO_2 solutions unless stated otherwise using a Bruker WP 80 (^{19}F), WM 250 PFT (^{125}Te). Standards: ^{19}F:$CFCl_3$, ^{125}Te:$Te(CH_3)_2$ (exterior) $\delta = 0$.

TeF_4 [8], Me_3SiNSO [7], BrNSO [9] and $Te(NSO)_2$ [2] are prepared by known methods, all other substances are commercially available and are used without other treatment.

3.1. X-ray analysis

The intensities were measured with a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS-97) [12]. Refinements were carried out with the SHELXL-97 [13] package. All atoms were refined with anisotropic temperature factors. All refinements were made by full-matrix least-squares on F^2. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary. Copies of the data can be obtained free of charge on application to CCDC, reference number 172 468 12 Union Road, Cambridge CB2 1EZ, UK[1] (Table 1).

3.2. Bis(sulfinylamido)tellurium(IV) fluoride (**1a**)

In an apparatus consisting of two bulb-shaped glass vessels equipped with a medium-sintered glass frit and Teflon-stemmed Young valves a mixture of TeF_4 (0.6 g, 3.0 mmol) in CH_2Cl_2 (5–10 ml) are placed in one of the bulbs. Into this mixture, $(CH_3)_3SiNSO$ (0.8 g, 6.0 mmol) in $((CH_3)_3Si)_2O$ (10–15 ml) are condensed and the suspension is stirred at −20°C (4 h). Formation of $(CH_3)_3SiF$ is confirmed by its IR spectrum in the gas phase. The solution is separated by filtration and the remaining colorless, bulky precipitate is washed several times with about 10 ml CH_2Cl_2 at −20 °C. The solvent is removed in vacuo and the residue dried at −10 °C (24 h). Yield **1a** (0.87 g, ~100%). **1a**: Anal. Found: N, 9.5; S, 21.9. Calc. for $F_2N_2O_2S_2Te$ (289.7): N, 9.67; S, 22.15%; physical and spectroscopical data are in agreement with those reported in [3].

Table 1
Experimental details of the crystallographic studies

Chemical formula	$C_4F_6N_2O_6S_2Te$
Formula weight	477.78
Crystal system	Hexagonal
Space group	*P*6(4)
μ(Mo Kα) (cm^{-1})	2.574
a (Å)	16.018(2)
b (Å)	16.018(2)
c (Å)	4.6220(10)
β (°)	120
V (Å^3)	1027.0(3)
Z	3
T (K)	293
Number of data collected	2380
Number of unique data	1064
R_{int}	0.0287
Final $R(F^2)$ for all data	0.0652
Final $R(F)$ for $F_0 > 4\sigma(F_0)$	0.0265

3.3. Bis(sulfinylamido)tellurium(IV) chloride (**1b**)

In an apparatus as described before, compound **1a** (0.82 g, 2.8 mmol) suspended in CH_2Cl_2 (20 ml) is treated with Me_3SiCl (0.62 g, 5.7 mmol) and reacted at −20 °C for 2 h with stirring. In the gas phase, the formation of Me_3SiF is detected by IR-spectroscopy. The bright yellow solid is separated by filtering the suspension into the other Carius-tube and the residue is washed five times with CH_2Cl_2 (about 5 ml). The volatile components are removed in vacuo and dried for 14 h at 20 °C providing $Cl_2Te(NSO)_2$ (0.91 g, ~100%); spectroscopical data are identical with those published [3,10].

3.4. Bis(sulfinylamido)tellurium (IV) bromide (**1c**)

3.4.1. From **1a** and Me_3SiBr

As described before **1a** (0.56 g, 1.9 mmol) suspended in CH_2Cl_2 (20 ml) are reacted with Me_3SiBr (0.6 g, 3.9 mmol) at −40 °C yielding spontaneously $Br_2Te(NSO)_2$ (0.79 g, ~100%).

3.4.2. From $Te(NSO)_2$ and Br_2

In a 100 ml Carius tube closed with a Teflon valve a suspension of $Te(NSO)_2$ (0.42 g, 1.7 mmol) in CH_2Cl_2 (20 ml) is oxidized with Br_2 (0.26 g, 1.7 mmol) at 0 °C with stirring. The color changed from red to yellow and after 5 h, the volatile materials are removed, the solid residue is dried for 16 h in vacuo giving **1c** (0.65 g, 93%).

3.4.3. From Te and BrNSO

As described before to a mixture of tellurium (0.15 g, 1.2 mmol) and CH_2Cl_2 (5 ml) a solution of BrNSO (0.35 g,

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2.5 mmol) in CF_2ClCF_2Cl (15–20 ml) are condensed in vacuo. The reaction mixture is warmed to 0 °C and stirred for 5 days. Afterwards volatile components of the yellow colored suspension are removed and $Br_2Te(NSO)_2$ (0.48 g, 97%) is dried at 0 °C (16 h). It decomposes at 22 °C with SO_2 elimination and should, therefore, be stored under Argon in closed systems. In the presence of air decomposition takes place accompanied by a color change from yellow into black. It is slightly soluble in CH_2Cl_2, but insoluble in common organic and inorganic solvents. Mp 105 °C. Anal. Found: N, 6.7; S, 15.3. Calc. for $Br_2N_2S_2O_2Te$ (411.6): N, 6.8; S, 15.5%. IR (KBr): 1204 vs, 1081 m, 1070 s, 606 m, 591 s, 408 w; Raman: 1202 w, 1079 m, 594 w, 404 m, 242 w, 224 s, 167 vs, 95 m; MS *m/z* (rel. int., ion): 414 (3, M^+), 380 (2, $Br_2N_2S_2Te^+$), 335 (2, $BrO_2N_2S_2Te^+$), 301 (12, $BrN_2S_2Te^+$), 288 (42, Br_2Te^+), 222 (10, $N_2S_2Te^+$), 209 (68, $BrTe^+$), 176 (8, $NSTe^+$), 130 (9, Te^+), 92 (84, $N_2S_2{}^+$), 79 (9, Br^+), 64 (9, $SO_2{}^+$), 48 (7, SO^+), 46 (100, NS^+), 32 (29, S^+).

3.5. *4,4-Difluoro-1,3,4λ^4,2,5-dithiatellurradiazole (**2a**)*

Compound **1a** (1.25 g, 4.32 mmol) is deposited in a 50 ml glass ampoule, which is sealed in vacuo (10^{-3} Torr). Afterwards, it is heated at 60 °C for 24 h which continued at 95 °C for 7 days. The tube is opened and volatile materials (SO_2, N_2) are removed in vacuo. The orange solid is then transferred in a glove box and filled into an apparatus as described before. Onto the solid THF (30 ml) are condensed in vacuo and the suspension is stirred for 24 h forming an orange liquid and a brown solid phase. The solution is filtered in the second tube and evaporated to dryness. The resulting dark orange oil is dissolved in CH_2Cl_2 and the solution stirred for 48 h yielding **2a** as an yellow orange solid which is dried in vacuo for 24 h (0.42 g, 70%). Mp 165 °C; Anal. Found: N, 10.5; S, 24.4. Calc. for $F_2N_2S_2Te$ (257.7) N, 10.9; S, 24.9%. IR (KBr): 1035 vs, 939 m, 699 s, 623 m, 519 w, 480 s; ^{19}F NMR (THF): −41.5 [2F, s]; ^{125}Te NMR: 1254 [1Te, s]; MS *m/z* (rel. int., ion): 260 (18, M^+), 241 (36, $FN_2S_2Te^+$), 222 (7, $N_2S_2Te^+$), 214 (9, F_2NSTe^+), 195 (35, $FNSTe^+$), 187 (57, F_3Te^+), 176 (12, $NSTe^+$), 168 (24, F_2Te^+), 149 (15, FTe^+), 130 (20, Te^+), 92 (17, $N_2S_2{}^+$), 78 (8, $NS_2{}^+$), 64 (12, $S_2{}^+$), 46 (100, NS^+), 32 (37, S).

3.6. *4-Fluoro-1,3,4λ^3,2,5-dithiatelluradiazolium hexafluoroarsenate (**2b**)*

3.6.1. *From **2a** and AsF_5*

In the glass apparatus described earlier **2a** (0.23 g, 0.9 mmol) is treated with AsF_5 (0.15 g, 0.9 mmol) in SO_2 (20 ml). The mixture is kept at 0 °C for 24 h and **2b** is isolated by evaporating the volatile materials in vacuo to dryness providing a dark red highly viscose oil. It is treated with CH_2Cl_2 (20 ml) for 4 h yielding an orange solid. After additional stirring for 36 h, the suspension is filtered and is washed with CH_2Cl_2 (3–5 ml) for three times. After removing the solvent **2b** is dried in vacuo for 16 h (0.36 g, 86%).

3.6.2. *By pyrolysis of **5a***

The synthesis is carried out in a glass apparatus analogous to that employed for the preparation of **1a**. Compound **5a** (0.34 g, 0.4 mmol) is treated at 90 °C for 8 days giving N_2 as a non-condensable gas, SiF_4 and a solid mixture. After removing the volatile products, the solid is treated with liquid SO_2 yielding a red solution and a brown residue. According to IR and mass spectroscopical investigations, the solid is a mixture of unidentified SN-compounds, sulfur and TeF_4. The liquid phase is filtered into the second tube and the solvent is removed in vacuo leaving a red oil which is worked-up as described before (0.26 g, 64%). Mp 92 °C (decomp.); Anal. Found: N, 6.5; S, 14.8. Calc. for $AsF_7N_2S_2Te$ (427.6): N, 6.6; S, 15.0%. IR (KBr): 1032 m, 943 m, 702 vs, 593 w, 571 w, 514 w; Raman: 1034 w, 957 m, 709 vs, 672 m, 672 m, 627 w, 572 w, 518 vs, 349s, 286 vs, 274 m, 157 w, 84 w; ^{19}F NMR: −41.9 [1F, s], −53.6 [6F, s, br]; ^{125}Te NMR: 2532 [1Te, s]; MS *m/z* (rel. int., ion): 241 (18, $FN_2S_2Te^+$), 222 (6, $N_2S_2Te^+$), 214 (4, F_2NSTe^+), 195 (15, $FNSTe^+$), 187 (50, F_3Te^+), 176 (3, $NSTe^+$), 168 (13, F_2Te^+), 149 (10, FTe^+), 132 (11, $AsF_3{}^+$), 130 (13, Te^+), 113 (33, $AsF_2{}^+$), 94 (7, AsF^+), 92 (37, $N_2S_2{}^+$), 78 (13, $NS_2{}^+$), 75 (5, As^+), 64 (6, S^+), 46 (100, NS^+), 32 (24, S^+).

3.7. *4-Fluoro-1,3,4λ^3,2,5-dithiatelluradiazolium hexafluoroantimonate (**2c**)*

Analogous to the preparation of **2b** compound, **2a** (0.34 g, 1.3 mmol) is treated with SbF_5 (0.29 g, 1.3 mmol) dissolved in SO_2 (20 ml) forming a light brown solution which is stirred for 24 h at 20 °C. After evaporating the solution to dryness, a brown oil remained which is worked-up as mentioned before providing **2c** (0.42 g, 68%); mp 104 °C (decomp.); Anal. Found: N, 6.1; S, 13.1. Calc. for $F_7N_2S_2SbTe$ (474.5): N, 5.9; S, 13.5%. IR (KBr): 1030 m, 950 m, 713 w, 661 vs, 594 w, 565 m, 520 w; Raman: 1025 w, 958 w, 713 w, 648 s, 630 w, 556 m, 528 s, 372 w, 349 s, 278 s, 165 w, 142 w; ^{19}F NMR: −43.2 [1F, s], −108.6 [6F, s, br]; ^{125}Te NMR: 2551 [1Te, s]; MS *m/z* (rel. int., ion): 241 (6, $FN_2S_2Te^+$), 222 (12, $N_2S_2Te^+$), 197 (7, F_4Sb^+), 195 (3, $FNSTe^+$), 187 (60, F_3Te^+), 178 (3, F_3Sb^+), 168 (19, F_2Te^+), 159 (100, F_2Sb^+) 149 (21, FTe^+), 140 (16, FSb^+), 130 (18, Te^+), 121 (24, Sb^+), 92 (14, $N_2S_2{}^+$), 64 (64, $S_2{}^+$), 46 (95, NS^+), 32 (24, S^+).

3.8. *Tetrafluoro-1κ^{2}F,2κ^{2}F-bis[μ-sulfurdiimidato(2-)-1κN,2κN']-ditellurium(IV) (3a)*

In an apparatus as described for the preparation of **1a**, a solution of compound **1a** (2.1 g, 7.3 mmol) in THF (20 ml) is placed in one tube and stirred at 20 °C. Already after 30 min the formation of SO_2 (characterized by its IR-spectrum) and an orange solid is observed. The reaction is stopped after 10 days, the residue is separated by filtration in the second tube and washed several times with THF (10 ml). It is dried in vacuo at 20 °C for 24 h providing pure **3a** (1.32 g, 80%); mp 161 °C (decomp.); Anal. Found: N, 12.8; S, 14.3. Calc. for $F_4N_4S_2Te_2$ (451.3): N, 12.4; S, 14.2%. IR (KBr): 1147 vs, 1059 s, 713 s, 587 m, 566 s, 428 s; Raman: 1070 m, 713 w, 586 m, 565 w, 430 s, 359 vs, 276 w, 206 s, 161 w, 120 m, 94 m; MS *m/z* (rel. int., ion): 260 (10, $F_2N_2S_2Te^+$), 241 (1, $FN_2S_2Te^+$), 222 (4, $N_2S_2Te^+$), 214 (5, F_2NSTe^+), 195 (10, $FNSTe^+$), 187 (31, F_3Te^+), 176 (6, $NSTe^+$), 168 (11, F_2Te^+), 149 (4, FTe^+), 130 (5, Te^+), 92 (55, $N_2S_2{}^+$), 64 (9, $S_2{}^+$), 46 (100, NS^+), 32 (13, S^+).

3.9. *Tetrachloro-1κ^2Cl,2κ^2Cl (**3b**) and tetrabromo-1κ^2Br,2κ^2Br-bis[μ-sulfurdiimidato(2-)-1κN,2κN']-ditellurium(IV) (**3c**)*

As already described before compounds **3b** and **3c** are synthesized either from (1) **3a** and X_2 (X = Cl, Br), (2) **3a** and Me_3SiX, and (3) **1a** and X_2 (molar ratio 2:1).

1. A suspension of compound **3a** (0.52 g, 1.15 mmol) in CH_2Cl_2 (20 ml) is stirred with Cl_2 (0.08 g, 1.15 mmol) or Br_2 (0.18 g, 1.15 mmol) for 10 days at 22 °C, filtered and the residue washed several times with CH_2Cl_2 (10 ml). After drying the compounds in vacuo for 16 h pure **3b** (0.21 g, 71%) or **3c** (0.29 g, 72%), respectively are obtained.
2. Analogous compound **3a** (0.45 g, 1.0 mmol) is treated either with Me_3SiCl (0.44 g, 4.1 mmol) or Me_3SiBr (0.61 g, 4 mmol) and the mixtures are stirred at 22 °C for 7 days. Pure **3b** (0.47 g, 91%) or **3c** (0.61 g, 88%), respectively are isolated. Spectroscopical data for **3b** are identical with published spectra [3] **3c**: mp 187 °C (decomp.); Anal. Found: N, 7.8; S, 8.8. Calc. for $Br_4N_4S_2Te_2$ (695.2): N, 8.0, S, 9.2%. IR (KBr): 1128 vs, 1060 s, 1046 s, 670 s, 557 m, 537 s; Raman: 1058 w, 669 w, 556 m, 535 w, 381 s, 365 m, 326 w, 222 s, 200 vs, 102 s; ^{125}Te NMR: 1227 [2Te, s]; MS *m/z* (rel. int., ion): 416 (4, $Br_2Te_2{}^+$), 339 (4, $BrTe_2{}^+$), 303 (15, Br_2NTe^+), 288 (61, Br_2Te^+), 255 (4, $BrNSTe^+$), 241 (7, $BrSTe^+$), 222 (15, $N_2S_2Te^+$), 209 (82, $BrTe^+$), 176 (9, $NSTe^+$), 144 (4, NTe^+), 130 (55, Te^+), 92 (54, $N_2S_2{}^+$), 79 (66, Br^+), 64 (18, $S_2{}^+$), 46 (100, NS^+), 32 (47, S^+).
3. In a typical experiment **1a** (0.81 g, 2.8 mmol) suspended in CH_2Cl_2 (20 ml) was treated with Cl_2 (0.10 g, 1.4 mmol) or Br_2 (0.22 g, 1.4 mmol), respectively and stirred at 22 °C for 5 days. Formation of SO_2 was confirmed by its IR spectrum in the gas phase. The precipitate was filtered and washed with CH_2Cl_2 (5 ml) and then with SO_2 for several times and dried in vacuo for 16 h yielding **3b** [3] (0.31 g, 85%) or **3c** (0.30 g, 88%). Spectroscopical data for **3b** and **3c** are identical with published results. The yields are calculated on the base that 4 mol **1a** form with $2X_2$ 1 mol **3**, $2TeF_4$, SO_2 and others.

3.10. *Di-μ-chlorotetrachloro-1κ2Cl,2κ2Cl (**4a**) and di-μ-bromotetrabromo-1κ2Br,2κ2Br-μ-[sulfur-diimidato(2-)-1κN,2κN']ditellurium(IV) (**4b**)*

3.10.1. *From **1a** and $TeCl_4$ or $TeBr_4$*

Compound **1a** (0.36 g, 1.24 mmol) in CH_2Cl_2 (20 ml) is treated with $TeCl_4$ (0.33 g, 1.24 mmol) or $TeBr_4$ (0.56 g, 1.24 mmol) with stirring at 22 °C for 10 days. Formation of SO_2 is confirmed by its IR spectrum in the gas phase. The precipitate is filtered and washed with CH_2Cl_2 as well as with SO_2 for several times and dried in vacuo for 16 h yielding **4a** (0.19 g, 29%) or **4b** (0.33 g, 34%). Spectroscopical data for **4a** [11] and **4b** [3] are identical with published results.

3.10.2. *From **1a** and Cl_2 or Br_2*

As mentioned above, compound **1a** (0.47 g, 1.6 mmol) suspended in CH_2Cl_2 (20 ml) is treated with Cl_2 (0.11 g, 1.6 mmol) or Br_2 (0.26 g, 1.6 mmol), respectively and stirred at 22 °C for 7 days. Formation of SO_2 is detected IR spectroscopically in the gas phase. The suspension is filtered and the residue washed with CH_2Cl_2 (5 ml) followed by extraction with liquid SO_2. After removing the volatile components, the residues are dried in vacuo for 16 h providing **4a** (0.15 g, 70%) and **4b** (0.21 g, 92%). The yields were calculated on the base that 4 mol **1a** form with $3X_2$ 1 mol **4**, $2TeF_4$, SO_2 and others.

3.11. *3,7-Difluoro-1$\lambda^4\delta^2$,5$\lambda^4\delta^2$-1,5,3,7,2,4,6,8-dithiaditelluratetrazociniium-bis(hexafluoro-arsenate) (**5a**) and bis(hexafluoroantimonate) (**5b**)*

3.11.1. *From **1a** and AsF_5 or SbF_5*

To compound **1a** (0.42 g, 1.5 mmol) placed in one tube of the apparatus described for the preparation of **1a**, AsF_5 (0.26 g, 1.5 mmol) or SbF_5 (0.34 g, 1.6 mmol) and SO_2 are condensed in vacuo at −196 °C. The mixtures are slowly warmed to 22 °C and stirred for 5 days. The colorless residues are separated from the red or dark green solution by filtration into the second tube and washed several times with SO_2 (5 ml). Compound **5a** (0.52 g, 80%) and **5b** (0.62 g, 88%) are neither soluble in common organic nor in inorganic solvents and are extremely sensitive to hydrolyses.

3.11.2. *From **3a** and AsF_5 or SbF_5*

As described above, compound **3a** (0.36 g, 0.8 mmol) is reacted with either AsF_5 (0.27 g, 1.6 mmol) or SbF_5 (0.06 g, 1.7 mmol) in SO_2 (20 ml) at 22 °C for 6 days with stirring. White precipitate is isolated from the light yellow solutions in both cases by filtration and they are dried for 16 h in vacuo giving **5a** (0.55 g, 80%) or **5b** (0.61, 84%). **5a**: mp 165 °C (decomp.); Anal. Found: N, 7.3; S, 8.5. Calc. for $As_2F_{14}N_4S_2Te_2$ (791.9): N, 7.1; S, 8.1%. IR (KBr): 1131 vs, 1101 m, 1091 m, 1034 vs, 768 vs, 734 w, 721 vs, 715 w, 700 vs, 669 vs, 620 w, 576 s, 562 s, 482 m, 462 w; Raman: 1092 m, 1014 m, 749 w, 718 w, 697 w, 678 m, 619 m, 564 w, 417 s, 392 w, 379 s, 251 w, 219 vs, 179 w, 145 s, 128 w; MS *m*/*z* (rel. int., ion): 260 (4, $F_2N_2S_2Te^+$), 241 (15, $FN_2S_2Te^+$), 222 (6, $N_2S_2Te^+$), 214 (4, F_2NSTe^+), 195 (26, $FNSTe^+$), 187 (40, F_3Te^+), 176 (8, $NSTe^+$), 168 (20, F_2Te^+), 149 (15, FTe^+), 144 (8, NTe^+), 132 (35, AsF_3^+), 130 (21, Te^+), 113 (65, AsF_2^+), 94 (19, AsF^+), 92 (52, $N_2S_2^+$), 78 (9, NS_2^+), 75 (18, As^+), 64 (15, S_2^+), 46 (100, NS^+), 32 (62, S^+). **5b**: mp 195 °C (decomp.); Anal. Found: N, 6.5; S, 7.8. Calc. for $F_{14}N_4S_2Sb_2Te_2$ (884.7): N, 6.3; S, 7.2. IR (KBr): 1124 vs, 1094 w, 1086 w, 1032 s, 751 s, 723 w, 692 m, 683 m, 663 s, 638 m, 622 s, 574 w, 559 m, 463 w, 419 m; Raman: 1086 m, 1028 m, 716 w, 680 w, 656 w, 642 m, 613 m, 561 m, 414 s, 379 s, 278 m, 214 vs, 142 s; MS *m*/*z* (rel. int., ion): 260 (2, $F_2N_2S_2Te^+$), 241 (8, $FN_2S_2Te^+$), 222 (6, $N_2S_2Te^+$), 195 (16, $FNSTe^+$), 187 (23, F_3Te^+), 178 (31, F_3Sb^+), 176 (11, $NSTe^+$), 168 (14, F_2Te^+), 159 (95, F_2Sb^+) 149 (11, FTe^+), 144 (4, NTe^+), 140 (16, FSb^+), 130 (15, Te^+), 121 (18, Sb^+), 92 (92, $N_2S_2^+$), 64 (6, S^+), 46 (100, NS^+), 32 (20, S^+).

*3.12. Fluorobis(sulfinylamido)tellurium(1+)-hexafluoroarsenate (**6a**) and hexafluoroantimonate (**6b**)*

The method used for the preparation of compounds **6a** and **b** is analogous to that employed for the preparation of **1a**. They are synthesized from compound **1a** (0.36 g, 2.2 mmol) and AsF_5 (0.37 g, 2.2 mmol) or **1a** (0.47 g, 1.6 mmol) and SbF_5 (0.35 g, 1.6 mmol) suspended in both cases in CH_2Cl_2 (20 ml). The mixtures are warmed from -196 to -20 °C and stirred for 12 h. The residues are filtered, washed several times with CH_2Cl_2 and dried for 14 h in vacuo. Both compounds are extremely sensitive to hydrolyses and should be stored in an inert atmosphere at -80 °C. They are soluble in liquid SO_2. **6a**: (0.92 g, 91%); mp 48 °C (decomp. to a dark green liquid); Anal. Found: N, 5.8; S, 14.11. Calc. for $AsF_7N_2O_2S_2Te$ (459.7): N, 6.1; S, 13.9%. IR (KBr): 1228 vs, 1202 vs, 1090 s, 790 m, 703 vs, 667 s, 587 m, 568 m, 548 m; Raman: 1234 w, 1214 m, 1117 s, 689 m, 670 m, 584 s, 423 vs, 371 w, 167 s, 132 w, 84 s; ^{19}F NMR: -39.8 [1F, s], -54.5 [6F, s, br]; ^{125}Te NMR: 1321 [1Te, s]; MS *m*/*z* (rel. int., ion): 260 (18, $F_2N_2S_2Te^+$), 241 (4, $FN_2S_2Te^+$), 222 (19, $N_2S_2Te^+$), 214 (8, F_2NSTe^+), 195 (21, $FNSTe^+$), 187 (24, F_3Te^+), 176 (20, $NSTe^+$), 168 (11, F_2Te^+), 151 (13, AsF_4^+), 149 (4, FTe^+), 144 (3, NTe^+), 132 (43, AsF_3^+), 130 (17, Te^+), 113 (62, AsF_2^+), 94 (9, AsF^+), 92 (69, $N_2S_2^+$), 78 (7, NS_2^+), 75 (5, As^+), 64 (31, S_2^+ or SO_2^+), 46 (100, NS^+), 32 (16, S^+). **6b**: (0.72 g, 89%); mp 92 °C (decomp. to a black oil); Anal. Found: N, 5.1; S, 12.8. Calc. for $F_7N_2O_2S_2SbTe$ (506.5): N, 5.5; S, 12.6%. IR (KBr): 1201 vs, 1099 vs, 665 vs, 656 vs, 581 s, 569 s, 554 m, 406 m; Raman: 1237 w, 1214 m, 1119 s, 650 m, 583 s, 420 vs, 374 w, 286 w, 162 s, 99 m, 84 w; ^{19}F NMR: -39.9 [1F, s], -105.6 [6F, s, br]; ^{125}Te NMR: 1329 [1Te, s]; MS *m*/*z* (rel. int., ion): 260 (5, $F_2N_2S_2Te^+$), 241 (2, $FN_2S_2Te^+$), 222 (8, $N_2S_2Te^+$), 195 (7, $FNSTe^+$), 187 (21, F_3Te^+), 178 (36, F_3Sb^+), 176 (12, $NSTe^+$), 168 (7, F_2Te^+), 159 (81, F_2Sb^+) 149 (4, FTe^+), 140 (10, FSb^+), 130 (12, Te^+), 121 (12, Sb^+), 92 (51, $N_2S_2^+$), 64 (25, S_2^+ or SO_2^+), 46 (100, NS^+), 32 (22, S^+).

*3.13. Bis(sulfinylamido)tellurium(2+)-bishexafluoroarsenate (**7**)*

Analogous to the preparation of compound **6a**, to partially dissolved **1a** (0.49 g, 1.7 mmol) in SO_2 (20 ml) AsF_5 (0.58 g, 3.4 mmol) is added and stirred for 1 day at 22 °C. After removing the solvent and volatile materials a dark green highly viscous oil is obtained. It is dried in vacuo at 22 °C for 14 h, but did not solidify. Handling problems prohibited analytical and Raman spectroscopical investigations. Compound **7** (0.98 g, 92%) is soluble in SO_2 and very sensitive to hydolyses, turning black when it come in contact with air. IR (KBr): 1240 s, 1096 s, 861 m, 702 vs, 472 w; ^{19}F NMR: -53.0 [12F, s, br]; ^{125}Te NMR: 2116 [1Te, s]; MS *m*/*z* (rel. int., ion): 222 (8, $N_2S_2Te^+$) 195 (7, $FNSTe^+$), 187 (9, F_3Te^+), 176 (10, $NSTe^+$), 168 (6, F_2Te^+), 149 (3, FTe^+), 144 (2, NTe^+), 132 (39, AsF_3^+), 130 (7, Te^+), 113 (76, AsF_2^+), 94 (28, AsF^+), 92 (39, $N_2S_2^+$), 75 (20, As^+), 64 (19, S_2^+ or SO_2^+), 48 (12, SO^+), 46 (100, NS^+), 32 (24, S^+).

*3.14. Bis(sulfinylamido)tellurium(IV)trifluoracetat (**8**)*

*3.14.1. From **1a** and $(CF_3CO)_2O$*

Compound **1a** (0.45 g, 1.6 mmol) and $(CF_3CO)_2O$ (0.65 g, 3.1 mmol) dissolved in CH_2Cl_2 (20 ml) reacted spontaneously providing a yellow solution. After stirring for 1 h at 22 °C the solvent is cautiously removed by cooling the second tube of the apparatus to 10 °C. Light yellow crystals are formed in the first tube. They are filtered, washed twice with cold CH_2Cl_2 and dried for 12 h at 22 °C in vacuo giving pure **8** (0.63 g, 83%).

*3.14.2. From **1a** and $Me_3SiOC(O)CF_3$*

Similarly compound **1a** (0.75 g, 2.5 mmol) is reacted with $Me_3SiOC(O)CF_3$ in CH_2Cl_2 (20 ml) providing light yellow crystals of **8** (1.19 g, ~100%). The crystals are soluble in CH_2Cl_2. In the presence of moist air, they decompose immediately accompanied by a color change into white. Mp 81 °C (decomp.); Anal. Found: C, 10.1; N, 6.0; S, 13.0. Calc. for $C_4F_6N_2O_6S_2Te$ (477.6): C, 10.1; N, 5.9; S, 13.4%. IR (KBr): 1691 vs, 1580 w, 1391 s, 1214 vs, 1178 vs, 1160 vs, 1103 s, 1095 s, 863 m, 840 w, 804 w, 787 m, 738 s, 729 s, 611 m, 595 m, 521 w, 502 m, 422 m; Raman: 1696 m, 1394 m, 1208 w, 1104 vs, 865 m, 742 w, 613 s, 511 s, 420 vs, 359 m, 309 m, 261 w, 187 s, 151 s, 133 s, 101 s, 85 s; ^{13}C NMR: 118.2 [1C, s, CF_3], 163.9 [1C, s, C=O]; ^{19}F NMR: -75.0 [3F, s, CF_3]; ^{125}Te NMR (CH_2Cl_2): 1307 [1Te, s]; MS *m*/*z* (rel. int., ion): 461 (1, M^+–F), 417 (2, $C_3F_5N_2O_4S_2Te^+$), 367 (8, $C_2F_3N_2O_4S_2Te^+$), 323 (4, $CF_3N_2O_2S_2Te^+$), 304 (3, $CF_2N_2O_2S_2Te^+$), 285 (3, $CFN_2O_2S_2Te^+$), 273 (4, $FN_2O_2S_2Te^+$), 254 (4, $N_2O_2S_2Te^+$), 230 (4, F_2NOSTe^+), 211 (3, $FNOSTe^+$), 192 (7, $NOSTe^+$), 187 (13, F_3Te^+), 168 (4, F_2Te^+), 149 (4, FTe^+), 144 (7, NTe^+), 130 (5, Te^+), 112

(9, $CF_3CO_2^+$), 97 (8, CF_3CO^+), 81 (5, CF_3C^+), 69 (100, CF_3^+), 64 (82, O_2S^+), 50 (46, CF_2^+), 48 (77, OS^+), 46 (81, NS^+), 44 (47, CO_2^+), 32 (22, S^+), 31 (18, CF^+).

*3.15. Bis(sulfinylamido)tellurium(IV)-trifluoromethanesulfonate (**9**)*

Similarly, to the preparation of **8**, compound **1** (0.61 g, 2.1 mmol) and $Me_3SiOSO_2CF_3$ (0.94 g, 4.2 mmol) dissolved in CH_2Cl_2 (20 ml) are stirred at −30 °C for 12 h providing a pine solid which is separated and dried at 22 °C for 14 h in vacuo. Compound **9** is insoluble in CH_2Cl_2 and extremely sensitive to hydrolyses turning black in moist air. Mp 78 °C (decomp.); Anal. Found: C, 4.3; N, 5.3; S, 22.9. Calc. for $C_2F_6N_2O_8S_4Te$ (549.7): C, 4.4; N, 5.1; S, 23.3%. IR (KBr): 1303 s, 1256 s, 1224 vs, 1198 vs, 1106 s, 1097 s, 1086 s, 1018 s, 1011 s, 767 w, 634 s, 597 w, 577 m, 521 m, 418 w; Raman: 1302 w, 1242 w, 1217 w, 1189 w, 1158 m, 1107 s, 1087 m, 1015 s, 767 s, 634 w, 597 s, 577 m, 424 vs, 393 s, 352 w, 320 w, 187 w, 152 s, 117 m; MS *m/z* (rel. int., ion): 465 (4, $CF_3N_2O_3S_2Te_2^+$), 371 (5, $CF_3N_2O_3S_3Te^+$), 354 (3, $F_2N_2STe_2^+$), 335 (4, $FN_2STe_2^+$), 316 (26, $N_2STe_2^+$), 270 (10, NTe_2^+), 257 (24, $FN_2OS_2Te^+$), 256 (12, Te_2^+), 241 (9, $FN_2S_2Te^+$), 222 (20, $N_2S_2Te^+$), 211 (11, $FNOSTe^+$), 192 (6, $NOSTe^+$), 176 (44, $NSTe^+$), 165 (8, $FOTe^+$), 144 (31, NTe^+), 130 (47, Te^+), 92 (10, $N_2S_2^+$), 78 (4, NS_2^+), 69 (82, CF_3^+), 64 (28, SO_2^+), 50 (7, CF_2^+), 48 (30, SO^+), 46 (100, NS^+), 32 (22, S^+).

3.16. Reactions of $Br_2Te(NSO)_2$ with chlorine or bromine

As described for the preparation of **1a** $Br_2Te(NSO)_2$ (0.45 g, 1.09 mmol) suspended in CH_2Cl_2 (20 ml) was reacted with Cl_2 (0.04 g, 0.56 mmol) or Br_2 (0.09 g, 0.56 mmol), respectively at 22 °C (24 h stirring). A yellow solid deposited and SO_2 could be detected in the gas-phase spectroscopically. The precipitate was filtered, washed several times with CH_2Cl_2 and dried in vacuo for 16 h providing **4c** (0.35 g, 90%) and **4b** (0.38 g, 88%). Physical and spectroscopical data are in agreement with literature values [3].

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