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# Contributions to bis(perfluoroalkyl) chalkogenide chemistry: preparation of $(R_f)_2SeO$ [$R_f = C_2F_5$, $(CF_3)_2CF$, $n$-$C_4F_9$], $(R'_f)_2TeX_2$ [X = F, Cl: $R'_f = n$-$C_3F_7$, $(CF_3)_2CF$, $n$-$C_4F_9$; X = Br: $R'_f = n$-$C_3F_7$, $n$-$C_4F_9$], $(CF_3)_2Te(NSO)_2$ and $(C_2F_5)_2Te(OH)NO_3$

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Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

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## Abstract

The reaction between perfluoroalkyl iodides with a threefold excess of a 1 : 1 molar mixture of Se and Cu is a new method for the preparation of corresponding monoselenides (**1a–c**) and diselenides (**2a–d**). They are oxidised with HOF without a solvent to bis(perfluoroalkyl) selenium(IV) oxides (**3a–d**). Halogenation of $(R_f)_2Te$ with $XeF_2$, $Cl_2$ or $Br_2$ yielded $(R_f)_2TeF_2$ (**7a–c**), $(R_f)_2TeCl_2$ (**8a–c**) and $(R'_f)_2TeBr_2$ (**9a**, **9c**). Oxidation of $(C_2F_5)_2Te$ with conc. $HNO_3$ gave $(C_2F_5)_2Te(OH)NO_3$ (**4**). When $(CF_3)_2TeCl_2$ is treated with AgNSO metathesis took place forming $(CF_3)_2Te(NSO)_2$ (**6**). Two $(C_6F_5)_2Te(VI)$ derivatives with the general formula $(C_6F_5)_2TeX_4$ with $X = CF_3C(O)O$ (**5**) and F are made from $(C_6F_5)_2TeO_2$ and $CF_3C(O)OH$ or $SF_4$, respectively. The monotelluride $(n$-$C_6F_{13})_2Te$ was synthesised similarly from $n$-$C_6F_{13}I$, Te and Cu. X-ray structures for **3d**, **8a**, and **8b** are provided. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Perfluoroalkyl; Selenide; Diselenide; Telluride; Selenium(IV) oxide; Tellurium(IV) hydroxide; Nitrate; Sulfinylamide; Bis(pentafluorophenyl); Tellurium(VI); Trifluoroacetate; Fluoride

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## 1. Introduction

Perfluoroorganoselenonic acids $R_fSeO_2OH$ ($R_f = CF_3$ [1], $C_2F_5$ [2], $C_6F_5$ [3]) and some derivatives are only known since 1985. Bis(perfluoroorgano) selenones [$(R_f)_2SeO_2$] are still unknown. A new and general applicable synthesis for bis(perfluoroorgano) tellurides also provided access to long chain alkyl- and phenyl-derivatives [4]. The aim of this paper is to describe the preparation of new $(R_f)_2Se$ compounds from $R_fI$ and a threefold excess of Se and Cu as well as their oxidation with HOF [5,6]. In addition the halogenation of $(R_f)_2Te$ and oxidation of $(C_2F_5)_2Te$ with $HNO_3$ have been investigated.

## 2. Preparation of $(R_f)_2Se_x$ and their oxidation with HOF

It could be shown that the success and general applicable synthesis of $(R_f)_2Te$ and partly $(R'_f)_2Te_2$ from $R_fI$, Te and Cu can also be transferred to selenium. Heating $R_fI$ with a threefold excess of a 1 : 1 molar mixture of Se and Cu provided in general an approximately 1 : 1 mixture of corresponding mono- and diselenides contrary to reactions with tellurium where mainly monotellurides are formed. In case of $n$-$C_6F_{13}I$ only $(n$-$C_6F_{13})_2Se_2$ or $(n$-$C_6F_{13})_2Te$ is obtained. The mixtures of mono- and diselenides are separated by shaking them with mercury yielding $Hg(SeR_f)_2$ and unchanged $R_fSeR_f$. The latter are liquids and can be removed from the solid mercurial by fractional condensation in vacuo. Surprisingly the mixture of $(n$-$C_4F_9)_2Se_x$ ($x = 1,2$) does not react with Hg and was characterised NMR spectroscopically as such. Treatment of the mercurials with

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iodine yielded the corresponding diselenides which are not investigated any further (Eq. (1)) [14,15].

$$R_fI + 3\,Se + 3\,Cu \longrightarrow \underset{\mathbf{1}}{R_fSeR_f} + \underset{\mathbf{2}}{R_fSeSeR_f}$$

$$R_f = C_2F_5\ (\mathbf{1a, 2a}),\ (CF_3)_2CF\ (\mathbf{1b, 2b}),\ n\text{-}C_4F_9\ (\mathbf{1c, 2c}),\ n\text{-}C_6F_{13}\ (\text{--},\ \mathbf{2d})$$

$$n\text{-}C_6F_{13}I + 3\,Te + 3\,Cu \longrightarrow n\text{-}C_6F_{13}TeC_6F_{13}\text{-}n \qquad (1)$$

$$R_fSeSeR_f \underset{I_2}{\overset{Hg}{\rightleftharpoons}} Hg(SeR_f)_2 \qquad R_f = C_2F_5,\ (CF_3)_2CF,\ n\text{-}C_6F_{13}$$

Attempts to oxidise bis(perfluoroalkyl) monoselenides with HOF in $CH_3CN$ solution failed; the educt could be recovered almost quantitatively. In order to avoid heavy explosions, which occurred already within a few seconds after condensing pure HOF on $(R_f)_2Se$, the procedure was reversed. In order to reduce the number of explosions it is necessary to use larger PTFE-tubes (75 ml) equipped with two Kel–F valves as a reaction vessel. HOF is prepared on a 300 mg scale and stored at $-80^\circ C$. Into this vessel $R_fSeR_f$ is condensed and the mixture is warmed in-between 12 h to room temperature. This procedure was rather safe and the reaction products can be isolated by removing the volatiles in vacuo and purifying the residues by sublimation in vacuo (Eq. (2)).

$$R_fSeR_f + HOF \longrightarrow R_fSe(O)R_f + HF$$

$$\begin{array}{ll} R_f = CF_3,\ C_2F_5\ (\mathbf{1a}),\ n\text{-}C_3F_7\ (\mathbf{1b}), & Rf = CF_3\ (\mathbf{3a}),\ C_2F_5\ (\mathbf{3b}), \\ n\text{-}C_4F_9\ (\mathbf{1c + 2c}) & n\text{-}C_3F_7\ (\mathbf{3c}),\ n\text{-}C_4F_9\ (\mathbf{3d}) \end{array} \qquad (2)$$

A blank oxidation of $CF_3SeSeCF_3$ with HOF without solvent provided only $(CF_3)_2SeO$. Similarly $(n\text{-}C_4F_9)_2SeO$ is yielded by oxidising a mixture of **1c** and **2c** under analogous conditions with HOF. The formation of $(R_f)_2SeO_2$ could not be excluded by $^{19}F$ NMR investigations, as the $^{19}F$ NMR-spectra of **3b–d** were too complicated. The F-atoms of the $CF_2$ group linked to Se are magnetically not equivalent, because of reduced free rotation of the $CF_2$ group caused by the free electron pair at Se(IV) and the doublets expected are broadened by additional $^{77}Se$–$^{19}F$ coupling. The spectra of this two-spin system are not any more of first order, $^2J_{Se-F}$ cannot be measured and compared with corresponding coupling constants of $RCF_2Se(VI)$ compounds. Therefore evidence for the $(R_f)_2Se$ to $(R_f)_2SeO$ oxidation are provided by two different arguments.

- (a) The $(CF_3)_2SeO$, synthesised from $(CF_3)_2Se$ and 4-Cl-$C_6H_4C(O)OOH$ [7] and the one obtained from $(CF_3)_2Se$ and HOF are entirely identical.
- (b) The X-ray structure determination for **3d** proved unambiguously a selenium monoxide moiety.

These experiments supply evidence that oxidation of $(R_f)_2Se$ with HOF stopped at the $(R_f)_2SeO$ level. Compounds of the type $(R_f)_2SeO_2$ are still unknown.

## 3. Halogenation of $(R_f)_2Te$ to $(R_f)_2TeX_2$ and oxidation of $(C_2F_5)_2Te$ with $HNO_3$

The easy access to $(R_f)_2Te$ [$R_f = n\text{-}C_3F_7$, $(CF_3)_2CF$ and $n\text{-}C_4F_9$] allows to study their chemistry and to synthesise new compounds of preparative interests. Among the many fold possibilities, halogenations and reactions with conc. $HNO_3$ received preferential treatment. According to literature methods [8] the fluorination of $(R_f)_2Te$ is best accomplished by using $XeF_2$ as the fluorinating agent. In $CH_2Cl_2$ solution at $-78^\circ C$ $XeF_2$ acts as a mild educt providing analytical pure $(R_f)_2TeF_2$ (**7a–c**) in about 90% yield without formation of side products. A slightly altered literature procedure [9] is used for the preparation of corresponding tellurium dichlorides (**8a–c**). The reactions were carried out in a sealed tube in $CH_2Cl_2$ solution with $(R_f)_2Te$ and stochiometrical amounts of chlorine at $-30^\circ C$ providing 80 to 90% yield. Analogously the bromination of $(R_f)_2Te$ with $Br_2$ (molar ratio 1 : 1) is accomplished. In order to suppress side reactions, the procedure is started at $-60^\circ C$ and the solution is gradually heated to 22°C. In this way $(n\text{-}C_3F_7)_2TeBr_2$ (**9a**) and $(n\text{-}C_4F_9)_2TeBr_2$ (**9c**) are made. Attempts to prepare $[(CF_3)_2CF]_2TeBr_2$ failed. It might be formed as an intermediate but decomposes fast to be isolated (Eq. (3)).

$$\begin{array}{lll} & + XeF_2 \longrightarrow & (R_f)_2TeF_2 + Xe \\ & & R_f = n\text{-}C_3F_7\ (\mathbf{7a}),\ (CF_3)_2CF\ (\mathbf{7b}),\ n\text{-}C_4F_9\ (\mathbf{7c}) \\ (R_f)_2Te & + Cl_2 \longrightarrow & (R_f)_2TeCl_2 \\ & & R_f = n\text{-}C_3F_7\ (\mathbf{8a}),\ (CF_3)_2CF\ (\mathbf{8b}),\ n\text{-}C_4F_9\ (\mathbf{8c}) \\ & + Br_2 \longrightarrow & (R_f)_2TeBr_2 \\ & & R_f = n\text{-}C_3F_7\ (\mathbf{9a}),\ n\text{-}C_4F_9\ (\mathbf{9c}) \end{array} \qquad (3)$$

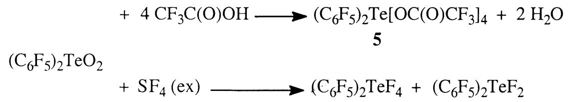
No reaction took place between $(R_f)_2Te$ and iodine. The oxidation of $(C_2F_5)_2Te$ with conc. $HNO_3$ provided $(C_2F_5)_2Te(OH)NO_3$ (**4**), which is unstable and decomposes with elimination of nitrogen oxides to a completely insoluble, nonmelting material of unknown formula. It can be assumed that polycondensation through the two functional groups OH and $ONO_2$ yields finally a polymeric compound.

In analogy to the many-sided chemistry of $Se(NSO)_2$ [10], $Te(NSO)_2$ [11,12] and $X_2Te(NSO)_2$ (X = F, Cl [13]) it was reasonable to assume that $(CF_3)_2Te(NSO)_2$ is a starting material of comparable potential. For its preparation two routes were pursued: Fluorine/$CF_3$ metathesis and halogen substitution in $(CF_3)_2TeCl_2$ by $Hg(NSO)_2$, AgNSO and $(CH_3)_3SiNSO$. No reaction took place between $F_2Te(NSO)_2$ and $(CH_3)_3SiCF_3$ or $(CF_3)_2TeCl_2$ with neither $Hg(NSO)_2$ nor $(CH_3)_3SiNSO$. But when $(CF_3)_2TeCl_2$ is treated with AgNSO in $CH_2Cl_2$, lemon yellow, air and water sensitive $(CF_3)_2Te(NSO)_2$ (**6**) is formed. Its stability in $CH_2Cl_2$ or THF solution is limited to approximately 1 h decomposing with $SO_2$-elimination to unknown compounds (Eq. (4)).

$$(C_2F_5)_2Te + HNO_3 \longrightarrow \underset{\mathbf{4}}{(C_2F_5)_2Te(OH)NO_3}$$

$$(CF_3)_2TeCl_2 + 2\,AgNSO \longrightarrow \underset{\mathbf{6}}{(CF_3)_2Te(NSO)_2} + 2\,AgCl \qquad (4)$$

Additional evidence for the oxidation state of Te(VI) in $(C_6F_5)_2TeO_2$ [2] are provided. It forms with $CF_3C(O)OH$ similar to the reaction with $CF_3SO_2OH$ [2] $(C_6F_5)_2Te[O\text{-}C(O)CF_3]_4$ and is fluorinated with $SF_4$ to the main product $(C_6F_5)_2TeF_4$ and minor amounts of $(C_6F_5)_2TeF_2$ (Eq. (5))



$$(C_6F_5)_2TeO_2 \begin{cases} + 4\,CF_3C(O)OH \longrightarrow \underset{\mathbf{5}}{(C_6F_5)_2Te[OC(O)CF_3]_4} + 2\,H_2O \\ + SF_4\,(ex) \longrightarrow (C_6F_5)_2TeF_4 + (C_6F_5)_2TeF_2 \end{cases} \quad (5)$$

## 4. Crystal and molecular structure of compounds $(n\text{-}C_3F_7)_2TeCl_2$ and $(n\text{-}C_4F_9)_2SeO$

Sublimation of the compounds **8a** and **3d** provided crystals suitable for X-ray structural investigations. In addition crystals of $[(CF_3)_2CF]_2TeCl_2$ are also obtained but the structural data measured did not fulfill standard requirements and therefore only cell dimensions will be published. But without reservations it can be said that the $C_2TeCl_2$-frames of **8a** and **8b** are isostructural. For the first time structure parameters for compounds of the type bis(perfluoroalkyl)tellurium dichloride became available (see Fig. 1). Molecule **8a** has a ψ-trigonal-bipyramidale structure with the two Cl-atoms occupying axial and the two $R_f$-groups including the free electron pair equatorial positions. Considerable deviations 28° for the C–Te–C and 9.5° for the Cl–Te–Cl angle from the ideal trigonal bipyramidal arrangements are observed for the $C_2TeCl_2$ moiety. The substantial reduction of ∠ C–Te–C cannot be explained only by the local requirements of the free electron pair because in that case the axial ∠ Cl–Te–Cl should show a comparable deviation from the ideal geometry. These remarkable distortions can also be caused by intermolecular Te···Cl···Te bonding as shown in Fig. 2. These interactions lead to four membered heterocycles restoring octahedral coordination at the Te atom. Selected bond distances and angles in comparison with $(C_6F_5)_2TeCl_2$ [23] and $(CH_3)_2TeCl_2$ [24] are provided in Table 1. The crystal structure of $(C_4F_9)_2SeO$ deserves some special attention because there exist very remarkable features. First the ideal all-*trans* conformation of the *n*-butyl chains is not pertained and the torsion angles C1–C2–C3–C4 and C5–C6–C7–C8 are 173°. This is obviously not an effect of intermolecular interactions because we found an average torsion angle in the CSD [25] for all molecules containing four $CF_2$ groups in a chain at approximate all-*trans* conformation at 170°. In such a conformation, the intramolecular fluorine–fluorine β-interactions are at 2.65 Å, which resemble distances much below the sum of van der Waals radii (2.94 Å) [26]. These repulsive interactions cause the torsion of the carbon frame albeit to a much lower extent than anticipated by MO calculations (165.5°) and matrix-isolation IR spectra [27]. The packing of the molecules (Fig. 3) are similar to that found in perfluorohex-

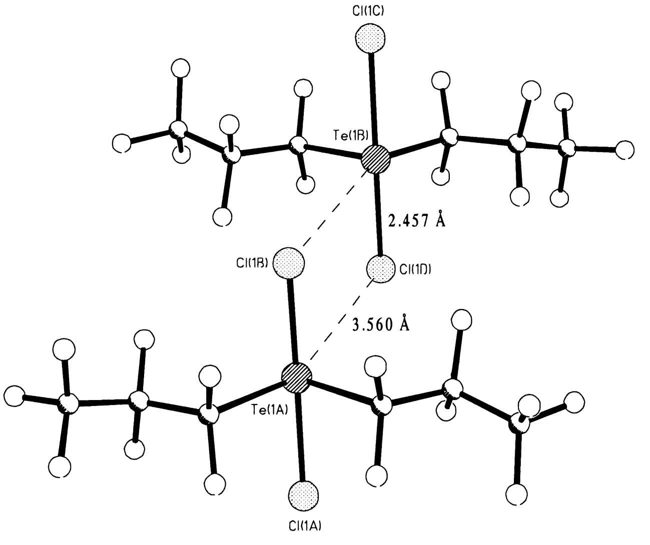


Fig. 1. Molecular structure of $(n\text{-}C_3F_7)_2TeCl_2$ with inter- and intramolecular Te–Cl distances.

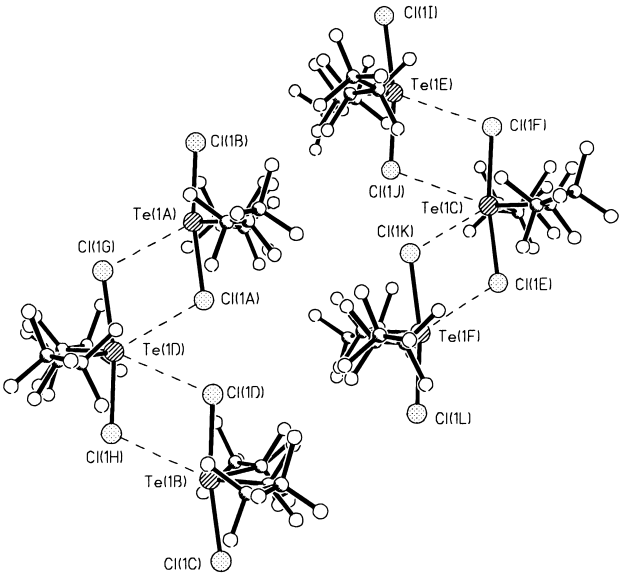


Fig. 2. Molecular packing of $(n\text{-}C_3F_7)_2TeCl_2$ with interatomic interactions.

Table 1
Selected bond distances and -angles

| | $(n\text{-}C_3F_7)_2TeCl_2$ | $(C_6F_5)_2TeCl_2$ | $(CH_3)_2TeCl_2$ |
|---|---|---|---|
| *d*(Te–Cl) | 2.457 | 2.485 | 2.480 |
| | | 2.478 | 2.541 |
| *d*(Te···Cl) | 3.560 | 3.589 | 3.52 |
| | | 3.478 | 3.46 |
| *d*(Te–C) | 2.274 | 2.118 | 2.08 |
| | | 2.127 | 2.10 |
| ∠ (Cl–Te–Cl) | 170.54 | 175.33 | 172.3 |
| ∠ (C–Te–C) | 91.2 | 100.4 | 98.2 |
| ∠ (Cl–Te–C) | 86.8 | 88.1 | 87.6 |
| | | 89.3 | 88.0 |
| | 86.5 | 89.5 | 86.4 |
| | | 87.2 | 88.0 |

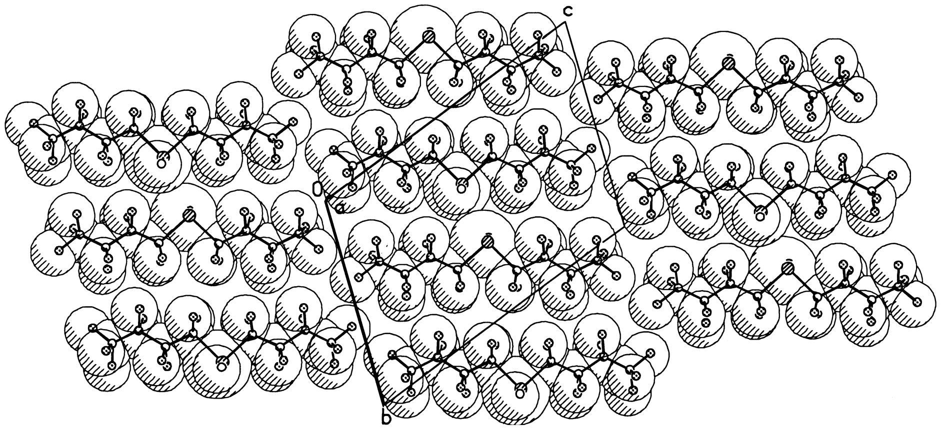


Fig. 3. Presentation of the molecular packing of $(C_4F_9)_2SeO$ viewing down [1 0 0] in an overlap of a space filling and a ball and stick model.

ane [28] with an intergroving of the $CF_2$ groups in the cavities of the neighbouring chains. The distances of the parallel chains are 5.88 Å, similar to those of perfluorohexane with 5.59 Å. In the latter, we find a parallel shift of the chains so that the $CF_3$ groups fit into the hollows between two $CF_2$ groups of the adjacent chains. This is not the case in the structure presented here, the $CF_3$ groups fit into the cavities between a $CF_3$ and a $CF_2$ group of the neighbouring chains, so that the SeO groups achieve pairwise $Se\cdots Se$ contacts of 3.616 Å (sum of van der Waals radii 3.80 Å [25]) within a layer with the oxygen atoms pointing in opposite directions. These data are important for the understanding of fluorine interactions in solids such as perfluorinated alkanes which are currently under investigation.

## 5. Experimental

Air and moisture sensitive compounds were handled in a vacuum line with Young valves or in a Glove box (M. Braun, München) under argon. Solvents were distilled before use and dried according to published procedures [20]. Microanalysis: Carbo Erba Elementanalyser model 1106. IR: Bruker FT-IR IFS 66 (4000 to 400 $cm^{-1}$), solids as KBr pellets, liquids as capillary film. Ra: solids in sealed glass capillaries, Bruker FT IFS 66 with Raman device FRA 106 (Neodym-YAG Laser 1064 nm). NMR: $CDCl_3$ solution unless noted otherwise, Bruker WP 80 PFT, WM 250 PFT, standards used: $Si(CH_3)_4(^{13}C)$, $CFCl_3(^{19}F)$, $(CH_3)_2Se(^{77}Se)$ and $(CH_3)_2Te(^{125}Te)$. MS: Varian MAT CH7. GC/MS: Hewlett Packard 5989 A Quadrupol MS, HP-GC 5890 (70 eV, emission 100 A). X-ray crystal structure determination (see Table 2).

Starting materials: $(CF_3)_2Se$ [14], $(n\text{-}C_3F_7)_2Se$ [14]; $^{19}F$ NMR: $-80.5$ (6F, s, $CF_3$), $-122.7$ (4F, s, $CF_2$), $-87.6$ (4F, s, $CF_2Se$), $Hg(CF_3)_2$ [19], $(CF_3)_2Te$ [4], $(R_f)_2Te$ [$R_f = n\text{-}C_3F_7$, $(CF_3)_2CF$, $n\text{-}C_4F_9$] [4], $(C_6F_5)_2TeO_2$ [2], $(CH_3)_3SiNSO$ [21], AgNSO [22] were prepared by published methods.

### *5.1. Bis(perfluoroalkyl) mono- (1) and -diselenides (2)*

In all procedures, seleninium and copper (1 : 1 molar ratio) were used in a threefold excess with respect to the perfluoroalkyl iodide. All reactions were carried out in glass ampoules (50 $cm^3$) sealed in vacuo and heated to 220–230°C for 15 h in a tube oven. Reagents, amounts in g (mmol), products and yields are given in Scheme 1. The volatile reaction products are removed in vacuo and separated by fractional condensation (20, $-30$ and $-196$°C). A mixture of corresponding monoselenides and diselenides condensed in a trap cooled to $-30$°C and was separated by shaking with mercury yielding pure $R_fSeR_f$ and $Hg(SeR_f)_2$. The liquid monoselenide was removed from the solid mercurial in vacuo. The diselenides can be recovered by treating $Hg(SeR_f)_2$ with $I_2$ according to Lit. method [14,15]. Spectroscopic data for new compounds and unknown data for published ones are given in Table 3.

### *5.2. Oxidation of bis(perfluoroalkyl) mono-selenides with HOF: general procedures for the preparation of bis(perfluoroalkyl) seleniumoxides $(R_f)_2SeO$ ($R_f = CF_3$ (**3a**), $C_2F_5$ (**3b**), $n\text{-}C_3F_7$ (**3c**) and $n\text{-}C_4F_9$ (**3d**))*

For every reaction 300 mg (8.3 mmol) HOF were prepared separately and condensed in a 75 ml U-type PTFE trap equipped with two Kel–F greaseless Teflon valves at $-80$°C. Into this trap, now kept at $-50$°C with a trichloroethylene bath, $(R_f)_2Se$ is condensed within 5 min and then warmed to 20°C during 12 h. Volatile compounds are removed at 20°C in vacuo and the corresponding selenoxide is purified by vacuo sublimation at 30°C providing colourless, clogged needles. Educts in g (mmol) and spectroscopical data of newly prepared compounds as well as missing informations for already described substances are given in Table 4.

Table 2

| Compound | $(n\text{-}C_3F_7)_2TeCl_2$ | $(i\text{-}C_3F_7)2TeCl_2$ | $(n\text{-}C_4F_9)_2SeO$ |
|---|---|---|---|
| Crystal system | monoclinic | monoclinic | triclinic |
| Space group | *C2/c* | $P2_1/c$ | *P* |
| Unit cell dimensions | | | |
| *a* (Å) | 19.495 (4) | 7.810 (2) | 5.0482 (9) |
| *b* (Å) | 9.222 (4) | 21.993 (3) | 10.470 (2) |
| *c* (Å) | 8.230 (3) | 8.199 (3) | 14.655 (3) |
| α (°) | 90° | 90° | 109.948 (3)° |
| β (°) | 106.16 (2)° | 103.98 (3)° | 94.508 (3)° |
| γ (°) | 90° | 90° | 93.810 (3)° |
| Volume ($Å^3$) | 1421.2 (9) | 1366.6 (6) | 722.9 (2) |
| *Z* | 4 | 4 | 2 |
| Density (calculated) (g $cm^{-3}$) | 2.508 | 2.608 | 2.449 |
| Absorption coefficient ($mm^{-1}$) | 2.619 | 2.720 | 2.811 |
| Crystal size (mm) | 0.52 × 0.48 × 0.37 | 0.3 × 0.3 × 0.2 | 0.17 × 0.11 × 0.02 |
| Temperature (K) | 293 | 203 | 293 |
| Radiation | Mo $K_\alpha$ | Mo $K_\alpha$ | Mo $K_\alpha$ |
| Theta range for data collection | 2.18–24.99° | | 2.08–25.71° |
| Index ranges | $0 \leq h \leq 18$, $0 \leq k \leq 10$, $-9 \leq l \leq 9$ | | $-6 \leq h \leq 6$, $-12 \leq k \leq 12$, $-12 \leq l \leq 17$ |
| Reflections collected | 1164 | | 3207 |
| Independent reflections | 1130 | | 2357 |
| Refinement method | Full-matrix least-squares on $F^2$ | | |
| Data/parameters | 1124/106 | | 1068/181 |
| Goodness-of-fit | 1.000 | | 1.021 |
| Final *R* indices [$I > 2\sigma(I)$] | 0.0388 | | 0.0954 |

### 5.3. *Bis(pentafluoroethyl)tellurium(IV) acid nitrate (**4**)*

A sample of 1.75 g (4.8 mmol) $(C_2F_5)_2Te$ is deposited in a 100 ml Carius tube equipped with a Teflon-stemmed Young valve and cooled to 0°C. Conc. nitric acid (6 ml) is added and the closed evacuated tube is stirred at 22°C for 2 h. Nitrogen oxides and a colourless solid are formed immediately. Volatile compounds, formed $H_2O$ and excess $HNO_3$ are removed in vacuo ($10^{-3}$ Torr). The final product is dried in vacuo for 24 h. The amorphous compound is soluble in $CH_3CN$ and eliminates nitrogen oxides from air but also under argon forming a completely insoluble, non melting derivative of unknown composition. In vacuo and exclusion of light, **4** can be stored at −78°C for several days. Yield: 1.86 g (88%); m.p. 121°C. Anal. Found: C, 10.7; H, 0.3; N, 3.0. Calc. for $C_4HF_{10}NO_4Te$: C, 10.8; H, 0.2; N, 3.1%. $^1H$ NMR ($CD_3CN$): 3.7 (1H, s, OH); $^{19}F$ NMR: −77.6 (6F, m, $CF_3$), −99.6 (4F, m, $CF_2$); $^{125}Te$ NMR ($CD_3CN$): 1248.4 [1Te, m, Te(IV)]. MS *m/z* ion (rel. int.): 430, $(C_2F_5)_2TeNO_3^+$ (5); 368, $(C_2F_5)_2Te^+$ (4); 249, $C_2F_5Te^+$ (22); 149, $TeF^+$ (48); 130, $Te^+$ (34); 119, $C_2F_5^+$ (61); 100, $C_2F_4^+$ (28); 69, $CF_3^+$ (100); 46, $NO_2^+$ (31); 31, $CF^+$ (38); 30, $NO^+$ (24). IR (KBr): 1456 (m), 1383 (s), 1308 (vs), 1202 (s), 1111 (m), 1023 (w), 908 (m), 741 (m), 656 (m), 621 (w), 539 (w). Ra (solid): 1321 (w), 1291 (w), 1203 (w), 1094 (w), 1023 (m), 934 (w), 905 (w), 749 (m), 656 (s), 591 (w), 541 (w), 369 (w), 279 (m), 232 (vs), 216 (m), 135 (m), 103 (m), 83 (m).

### 5.4. *Bis(pentafluorophenyl)tellurium-terakistrifluoroacetat(5)*

As described above 1.0 g (2.0 mmol) $(C_6F_5)_2TeO_2$ are reacted with 1.5 g ( 12.0 mmol) $CF_3C(O)OH$ with stirring at 22°C for 12 h. Volatile materials are removed in vacuo and **5a** is dried at $10^{-3}$ Torr for 24 h. Yield: 1.2 g (66%); m.p. 118°C. Anal. Found: C, 26.3. Calc. for $C_{20}F_{22}O_8Te$: C, 26.3%. $^{19}F$ NMR: −75.4 (12F, s, $CF_3$), −125.7 (4F, d, 2-, 6-F), −146.0 (2F, t, 4-F), −159.1 (4F, t, 3-, 5-F). MS *m/z* ion (rel. int.): 577, $(C_6F_5)_2TeOC(O)CF_3^+$ (14); 483, $(C_6F_5)_2TeF^+$ (8); 464, $(C_6F_5)_2Te^+$ (33); 410, $C_6F_5TeOC\text{-}(O)CF_3^+$ (8); 316, $C_6F_5TeF^+$ (13); 297, $C_6F_5Te^+$ (57); 167, $C_6F_5^+$ (42); 149, $TeF^+$ (23); 130, $Te^+$ (21); 98, $C_5F_2^+$ (18); 79, $C_5F^+$ (10); 69, $CF_3^+$ (50), 44, $CO_2^+$ (7). IR (KBr): 1726 (m), 1639 (m), 1520 (vs), 1495 (vs), 1394 (m), 1294 (w), 1221 (m), 1161 (s), 1092 (s), 980 (s), 856 (w), 805 (m), 731 (m), 669 (w), 606 (w), 492 (w), 418 (w). Ra (solid): 1723 (w), 1639 (w), 1406 (w), 859 (w), 647 (m), 611 (w), 586 (m), 493 (s), 444 (m), 387 (m), 351 (w), 213 (m), 148 (s), 123 (vs), 84 (m).

### 5.5. *Bis(pentafluorophenyl)tellurium tetrafluoride*

To 1.0 g (2.0 mmol) $(C_5F_5)_2TeO_2$placed in a 50 ml Monell autoclave 4.8 g (44.0 mmol) $SF_4$ are condensed at −196°C and after warming to room temperature the mixture is heated for 18 h at 60°C. After cooling to 20°C excess $SF_4$

Table 3
Spectroscopic data

| Compound | IR (gas) (cm$^{-1}$) [Ra (liquid)] | $^{13}$C NMR ($\delta$, J/Hz) | $^{19}$F NMR ($\delta$, J/Hz) | $^{77}$Se NMR ($\delta$) | Mass spectra *m/z*, fragment (%) |
|---|---|---|---|---|---|
| **1a**[a] | – | 115.9 (2C, qt, $^1J_{C–F} = 315$, $^2J_{C–F} = 30$, $CF_2$)<br>120.4 (2C, tq, $^1J_{C–F} = 285$, $^2J_{C–F} = 19$, $CF_3$ | – | 629 (1Se) | |
| **1b**[b] | 1889 (m), 1821 (m), 1335 (s), 1257 (vs), 1154 (s), 1131 (s), 1104 (s), 1075 (m) , 961 (m), 899 (m), 825 (s), 737 (vs) | 88.3 (2C, sptd, $^1J_{C–F} = 192.6$ $^2J_{C–F} = 36.2$, CF)<br>120.2 (4C, dq, $^1J_{C–F} = 185$, $CF_3$) | −80.3 (12F, d, $^3J_{F-F} = 12$, $CF_3$)<br>−162.9 (2F, spt, CF) | 654.7(1Se, m) | – |
| **1c**[c] | 1349 (s), 1256 (vs), 1151 (vs), 1099 (s), 1005 (m), 956 (m), 884 (m), 854 (m), 796 (m), 779 (s), 746 (s), 720 (s), 534 (m) | 105.4 (2C, m, $CF_2$),<br>109.6 (2C, m, $CF_2$),<br>110.2 (2C, m, $CF_2$),<br>199.5 (2C, tq, $^1J_{C–F} = 288.1$, $^2J_{C–F} = 36.4$, $CF_3$) | −81.5 (6F, s, $CF_3$)<br>−125.9 (4F, s, $CF_2$)<br>−118. (4F, s, $CF_2$)<br>−85.8 (4F, s, $CF_2$) | 665 (1Se, m) | 598, $M^+$ (6.5); 379, $C_4F_9Se_2^+$ (10); 299, $C_4F_9Se^+$ (2); 280, $C_4F_8Se^+$ (4); 219, $C_4F_9^+$ (6.5); 160, $Se_2^+$ (54.6); 131, $C_3F_5^+$ (16.4); 119, $C_2F_5^+$ (14); 69, $CF_3^+$ (100); 50, $CF_2^+$ (5) |
| **2c** | | 108.2 (2C, m, $CF_2$),<br>110.3 (2C, m $CF_2$),<br>110.7 (2C, m $CF_2$),<br>114.3 (2C, tg, $^1J_{C–F} = 287.5$, $^2J_{C–F} = 31.3$, $CF_3$) | −81.2 (6F, s, $CF_3$),<br>−86.2 (4F, s, $CF_2$),<br>−118.6 (4F, s, $CF_2$),<br>−126.5 (4F, s, $CF_2$) | 535 (2Se, m) | |
| **2d** | 1632 (m), 1245 (s), 1206 (s) 1098 (m), 1005 (m), 789 (m) 735 (m), 721 (m)<br>[1365 (m), 1113 (w), 876 (w) 758 (vs), 723 (vs), 584 (s)] | – | −121.9 (6F, s, $CF_3$)<br>−85.5, −118.1, −121.9, −123.0, −126.4 [10F, s, $(CF_2)_5$] | – | 798, $M^+$ (4); 779, $M^+$–F (2); 718, $C_{12}F_{25}Se^+$ (4.5); 669, $C_{12}F_{25}Se^+$ 3); 449, $C_7F_{15}Se^+$ (6.5); 380, $C_6F_{12}Se^+$ (3); 319, $C_6F_{13}^+$ (10); 169, $C_3F_7^+$ (35); 160, $Se_2^+$ (5); 119, $C_2F_5^+$ (60); 80, $Se^+$ (1); 69, $CF_3^+$ (100) |

[a] For $^{19}$F NMR spectrum see also [16].

[b] IR- and $^{19}$F NMR-spectra see [15,16].

[c] According to a elemental analysis – found: C, 17.4; **1c** requires 18.6 and **2c** 16.1% – this is approximately a 1:1 molar mixture. All spectroscopic data are measured with this mixture.

Table 4
Reagents, amounts, yields and spectroscopic data

| Compound (yield%) | Educts (amounts/g; mmol) | IR (KBr) (cm$^{-1}$) [Ra (solid)] | $^{19}$F NMR ($\delta$, J/Hz) | $^{77}$Se NMR ($\delta$) | Mass spectra: *m/z*, fragment (%) |
|---|---|---|---|---|---|
| $(CF_3)_2SeO$[a] **3a** (91) | $(CF_3)_2Se$ (1.30; 6.0) | 1210 (s), 1122 (s), 1043 (s), 870 (m), 854 (m), 830 (m), 787 (s), 747 (s)<br>[1146 (m), 1072 (m), 1059 (m), 852 (vs), 838 (vs), 747 (vs), 741 (m), 368 (s), 307 (s), 250 (vs)] | – | – | 254, $M^+$ (4); 218, $C_2F_6Se^+$ (10); 199, $C_2F_5Se^+$ (15); 165, $CF_3SeO^+$ (5); 149, $CF_3Se^+$ (50); 130, $CF_2Se^+$ (35); 96, $SeO^+$ (6); 80, $Se^+$ (10); 69, ${CF_3}^+$ (100); 50, ${CF_2}^+$ (60) |
| $(C_2F_5)_2SeO$[b] **3b** (71) | $(C_2F_5)_2Se$ (1.32, 4.2) | 1327 (m), 1214 (vs), 1167 (vs) 1084 (s), 1032 (s), 744 (vs), 475 (s)<br>[–] | $-83.6$ (6F, s, $CF_3$),<br>$-106.3$ (2F, d, $J_{CF–CF} = 213.6$, CF)<br>$-109.7$ (2F, d, $J_{CF–CF} = 213.6$, CF) | 1093 (Se, m) | 334, $M^+$ (2); 318, $M^+$–O (418); 215, $C_2F_5SeO^+$ (20); 199, $C_2F_5Se^+$ (20); 180, $C_2F_4Se^+$ (10); 119, ${C_2F_5}^+$ (95); 100, ${C_2F_4}^+$ (35); 96, $SeO^+$ (20); 80, $Se^+$ (40); 50, ${CF_2}^+$ (28) |
| $(n\text{-}C_3F_7)_2SeO$ **3c** (47) | $(n\text{-}C_3F_7)_2Se$ (1.73, 4.1) | 1108 (m), 1061 (m), 862 (s), 667 (s), 483 (s)<br>[1085 (w), 1070 (w), 870 (s), 741 (s), 380 (w), 278 (s), 157 (s) 117 (s), 85 (s)] | $-80.5$ (6F, $CF_3$),<br>$-122.9$ (4F, $CF_2$)<br>$-104.7$ (4F, dd, $J_{CF–CF} = 231.9$, $CF_2$) | – | 434, $M^+$ (1.5); 418, $M^+$–O (1); 265, $C_3F_7SeO^+$ (4); 249, $C_3F_7Se^+$ (7); 169, ${C_3F_7}^+$ (60); 119, ${C_2F_5}^+$ (35); 96, $SeO^+$ (25); 80, $Se^+$ (3); 69, ${CF_3}^+$ (100) |
| $(n\text{-}C_4F_9)_2SeO$ **3d** (51) | $(n\text{-}C_4F_9)_2Se$ (2.10, 3.8)[c] | 1204 (s), 1144 (m), 1102 (s), 998 (s), 867 (s), 776 (m), 673 (s) 629 (m), 568 (m), 534 (m)<br>[1130 (s), 1010 (m), 868 (vs), 727 (s), 671 (m), 384 (s), 337 (s), 286 (m), 98 (s)] | $-81.1$ (6F, $CF_3$),<br>$-125.9$ (4F, $CF_2$),<br>$-119.1$ (4F, $CF_2$),<br>$-106.4$ (4F, dd, $J_{CF–CF} = 232.3, 94.5$, $CF_2$) | 1119 (Se, m) | 534, $M^+$ (6); 518, $M^+$–O (1); 315, $C_4F_9SeO^+$ (3); 299, $C_4F_9Se^+$ (6); 219, ${C_4F_9}^+$ (22); 169, ${C_3F_7}^+$ (18); 96, $SeO^+$ (15); 80, $Se^+$ (3); 69, ${CF_3}^+$ (100) |

[a] NMR-data published in [7,17].

[b] Anal. Found: C, 14.4. Calculated for $C_4F_{10}OSe$: 14.4%; $^{13}$C NMR 117.5 (2C, tq, $^1J_{C–F} = 335.6$, $^2J_{C–F} = 43.1$, $CF_3$), 110.5 (2C, qt, $^1J_{C–F} = 287.9$, $^2J_{C–F} = 29.1$, $CF_2$).

[c] Calculated on a 1 : 1 mixture of **1c** and **2c**.

Table 5
Educts, conditions, yields, melting points, formulas, analysis

| Compound point | Educt Formula [amounts (mmol)] | Conditions Analysis (time, temperature) | Yield (g, %) | Melting (°C) | Formula (mol. weight) | Analysis | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Found (%) | | Calculated (%) | |
| | | | | | | C | Cl | C | Cl |
| $(n\text{-}C_3F_7)_2TeF_2$ | $(n\text{-}C_3F_7)_2Te$ (0.85 g, 1.8) | 2 h, −78°C; 1 h, 0°C; | 0.85 (92) | 103 | $C_6F_{16}Te$ | 13.3 | – | 14.3 | – |
| **7a** | $XeF_2$ (0.31 g, 1.8) | dried: 16 h, −30°C | | | (503.6) | | | | |
| $[(CF_3)_2CF]_2TeF_2$ | $[(CF_3)_2CF]_2Te$ (1.18 g, 2.5) | 2 h, −78°C; 1 h, 0°C; | 1.06 (84) | 68 | $C_6F_{16}Te$ | 12.2 | – | 14.3 | – |
| **7b** | $XeF_2$ (0.43 g, 2.5) | subl.: 22°C/$10^{-3}$ Torr | | | (503.6) | | | | |
| $(n\text{-}C_4F_9)_2TeF_2$ | $(n\text{-}C_4F_9)_2Te$ (1.90 g, 3.4) | 2 h, −78°C; 1 h, 0°C; | 1.81 (89) | 131 | $C_8F_{20}Te$ | 16.0 | – | 15.9 | – |
| **7c** | $XeF_2$ (0.54 g, 3.4) | subl.: 22°C/$10^{-3}$ Torr | | | (603.7) | | | | |
| $(n\text{-}C_3F_7)_2TeCl_2$ | $(n\text{-}C_3F_7)_2Te$ (1.15, 2.5) | 1 h, −30°C; 10 mi*n*; 22°C; | 1.07 (80) | 40 | $C_6Cl_2F_{14}Te$ | 13.2 | 13.0 | 13.4 | 13.2 |
| **8a** | $Cl_2$ (0.18 g, 2.5) | subl.: 22°C/$10^{-3}$ Torr | | | (536.6) | | | | |
| $[(CF_3)_2CF]_2TeCl_2$ | $[(CF_3)_2CF]_2Te$ (1.60 g, 3.4) | 1 h, −30°C; 10 min; 22°C; | 1.47 (79) | 58 | $C_6Cl_2F_{14}Te$ | 13.3 | 12.9 | 13.4 | 13.2 |
| **8b** | $Cl_2$ (0.24 g, 3.4) | subl.: 22°C/$10^{-3}$ Torr | | | (536.6) | | | | |
| $(n\text{-}C_4F_9)_2TeCl_2$ | $(n\text{-}C_4F_9)_2Te$ (1.20 g, 2.1) | 1 h, −30°C; 10 min; 22°C; | 1.20 (90) | 58 | $C_8Cl_2F_{18}Te$ | 15.3 | 11.0 | 15.1 | 11.1 |
| **8c** | $Cl_2$ (0.15 g, 2.1) | subl.: 22°C/$10^{-3}$ Torr | | | (636.6) | | | | |
| $(n\text{-}C_3F_7)_2TeBr_2$ | $(n\text{-}C_3F_7)_2Te$ (1.83 g, 3.9) | 0.5 h, −60°C; 0.5 h, −20°C; | 2.05 (85) | 52 | $Br_2C_6F_{14}Te$ | 10.7 | – | 11.5 | – |
| **9a** | $Br_2$ (0.63 g, 3.9) | 10 min; 22°C; dried: 16 h, −20°C | | (625.5) | | | | | |
| $(n\text{-}C_4F_9)_2TeBr_2$ | $(n\text{-}C_3F_7)_2Te$ (1.14 g, 2.0) | 0.5 h, −60°C; 0.5 h, −20°C; | 0.67 (50) | 52 | $Br_2C_8F_{18}Te$ | 11.7 | – | 13.2 | – |
| **9c** | $Br_2$ (0.32 g, 2.0) | 10 min; 22°C; dried: 16 h, −20°C | | (725.5) | | | | | |

Table 6
Spectroscopic data

| | IR-frequency (cm$^{-1}$) | Ra-frequency (cm$^{-1}$) | $^{19}$F NMR (ppm) [$^{125}$Te NMR] | Mass spectra: *m/z*, fragment (rel. int.) |
|---|---|---|---|---|
| **7a**[a] | 1336 (s), 1279 (m), 1215 (vs), 1188 (s), 1135 (vs), 1074 (m), 1037 (s), 879 (m), 812 (m), 750 (m), 737 (s), 672 (m), 590 (w), 559 (w), 535 (m), 495 (s) | 1333 (m), 1285 (w), 1220 (w), 1079 (s), 806 (s), 739 (vs), 677 (s), 606 (m), 590 (s), 510 (vs), 379 (s), 346 (s), 276 (vs), 246 (vs), 148 (vs), 104 (vs), 85 (s) | $-79.7$ (6F, s, $CF_3$), $-117.4$ (4F, s, $CF_2$), $-120.5$ (4F, s, $CF_2$), $-98.9$ (2F, s, $TeF_2$) [1251.7 (1Te, m)] | 487, $M^+$–F (13); 468, $(C_3F_7)_2Te^+$ (1); 337, $C_3F_7TeF_2^+$ (15); 318, $C_3F_7TeF^+$ (8); 299, $C_3F_7Te^+$ (25); 169, $C_3F_7^+$ (47); 168, $TeF_2^+$ (7); 149, $TeF^+$ (26); 130, $Te^+$ (15); 100, $C_2F_4^+$ (23); 69, $CF_3^+$ (100); 50, $CF_2^+$ (4); 31, $CF^+$ (15) |
| **7b**[b] | 1284 (vs), 1233 (vs), 1171 (s), 1143 (s), 964 (s), 889 (m), 749 (m), 714 (s), 572 (w), 521 (m) | – | $-69.0$ (12F, s, $CF_3$), $-144.1$ (2F, s, CF), $-96.9$ (2F, s, $TeF_2$) [1273.0 (1Te, m)] | 487, $M^+$–F (13); 337, $C_3F_7TeF_2^+$ (15); 318, $C_3F_7TeF^+$ (26); 299, $C_3F_7Te^+$ (2); 187, $TeF_3^+$ (23); 168, $TeF_2^+$ (23); 149, $TeF^+$ (31); 131, $C_3F_5^+$ (21); 130, $Te^+$ (7); 100, $C_2F_4^+$ (30); 81, $C_2F_3^+$ (9); 69, $CF_3^+$ (100); 50, $CF_2^+$ (4); 31, $CF^+$ (27) |
| **7c** | 1349 (s), 1238 (vs), 1207 (vs), 1174 (s), 1140 (s), 1113 (m), 1099 (m), 998 (m), 796 (w), 776 (w), 745 (w), 721 (m), 682 (m), 668 (m), 630 (w), 571 (w), 532 (w), 472 (w), 451 (w) | 1352 (m), 1287 (m), 1118 (w), 1100 (m), 1003 (s), 779 (m), 747 (s), 724 (vs), 692 (m), 676 (w), 635 (m), 606 (m), 574 (w), 515 (vs), 381 (s), 356 (m), 334 (s), 294 (s), 279 (s), 246 (s), 180 (m), 152 (m), 132 (s), 84 (s) | $-81.2$ (6F, s, $CF_3$)<br>$-96.7$ (2F, s, $TeF_2$)<br>$-114.3$ (4F, s, $CF_2$)<br>$-116.8$ (4F, s, $CF_2$)<br>$-126.2$ (4F, s, $CF_2$) | 587, $M^+$–F (7); 568, $(C_4F_9)_2Te^+$ (1); 387, $C_4F_9TeF_2^+$ (12); 368, $C_4F_9TeF^+$ (4), 349, $C_4F_9Te^+$ (15); 219, $C_4F_9^+$ (17); 169, $C_3F_7^+$ (17); 168, $TeF_2^+$ (6); 149, $TeF^+$ (20); 131, $C_3F_5^+$ (39); 130, $Te^+$ (9); 119 $C_2F_5^+$ (29); 100, $C_2F_4^+$ (20); 69, $CF_3^+$ (100); 50, $CF_2^+$ (3); 31, $CF^+$ (11) |
| **8a**[c] | 1328 (vs), 1274 (vs), 1229 (vs), 1208 (vs), 1192 (vs), 1136 (vs), 1057 (s), 1029 (m), 858 (w), 797 (vs), 723 (vs), 686 (w), 669 (vs), 591 (m), 534 (m), 508 (w) | 1328 (w), 1071 (m), 1057 (m), 796 (w), 735 (s), 721 (m), 678 (w), 592 (w), 379 (w), 285 (vs), 267 (s), 236 (m), 154 (m), 137 (s) | $-80.2$ (6F, s, $CF_3$)<br>$-88.6$ (2F, s, $CF_2$)<br>$-116.9$ (2F, s, $CF_2$)<br>[1131.5 (1Te, m)] | 503, $M^+$–Cl (3); 468, $(C_3F_7)_2Te^+$ (2); 449, $C_6F_{13}Te^+$ (1); 369, $C_3F_7TeCl_2^+$ (5); 353, $C_3F_7TeFCl^+$ (4); 334, $C_3F_7TeCl^+$ (7); 299, $C_3F_7Te^+$ (15); 280, $C_3F_6Te^+$ (3); 200, $TeCl_2^+$ (9); 185, $C_3F_7Cl^+$ (16); 169, $C_3F_7^+$ (16); 165, $TeCl^+$ (26); 149, $TeF^+$ (12); 130, $Te^+$ (32); 119, $C_2F_5^+$ (10); 100, $C_2F_4^+$ (25); 85, $CF_2Cl^+$ (17); 69, $CF_3^+$ (100); 50, $CF_2^+$ (11); 35, $Cl^+$ (26); 31, $CF^+$ (29) |
| **8b**[d] | 1269 (vs), 1233 (vs), 1163 (s), 961 (s), 950 (m), 886 (w), 863 (w), 743 (s), 714 (s), 537 (w) | 863 (w), 751 (m), 538 (w) 349 (w), 293 (vs), 221 (s), 190 (m), 135 (s) | $-65.8$ (12F, s, $CF_3$)<br>$-145.7$ (2F, s, CF)<br>[1162.0 (1Te, m)] | 503, $M^+$–Cl (17); 468, $(C_3F_7)_2Te^+$ (2); 369, $C_3F_7TeCl_2^+$ (7); 334, $C_3F_7TeCl^+$ (32); 299, $C_3F_7Te^+$ (19); 280, $C_3F_6Te^+$ (1); 200, $TeCl_2^+$ (8); 165, $TeCl^+$ (55); 149, $TeF^+$ (30); 131, $C_3F_5^+$ (22); 130, $Te^+$ (25); 100, $C_2F_4^+$ (72); 81, $C_2F_3^+$ (7); 69, $CF_3^+$ (100); 50, $CF_2^+$ (5); 35, $Cl^+$ (10); 31, $CF^+$ |

Table 6 (*Continued*)

| | IR-frequency (cm$^{-1}$) | Ra-frequency (cm$^{-1}$) | $^{19}$F NMR (ppm) [$^{125}$Te NMR] | Mass spectra: *m/z*, fragment (rel. int.) |
|---|---|---|---|---|
| | | | | (31) |
| **8c** | 1357 (s), 1239 (vs), 1207 (vs), 1183 (s), 1141 (vs), 1108 (m), 1079 (s), 984 (m), 934 (w), 836 (w), 773 (m), 740 (m), 715 (s), 674 (s), 645 (w), 632 (m), 603 (w), 574 (m), 531 (m), 456 (w) | 1356 (w), 1287 (w), 1097 (w), 992 (w), 774 (w), 720 671 (w), 636 (w), 531 (w), 382 (w), 334 (m), 288 (vs), 236 (m), 155 (s), 132 (s), 84 (m) | −81.1 (3F, s, $CF_3$)<br>−87.5 (2F, s, $CF_2$)<br>−113.5 (2F, s, $CF_2$)<br>−126.1 (2F, s, $CF_2$)<br>[1142.9 (1Te, m)] | 603, $M^+$–Cl (21); 568, $(C_4F_9)_2Te^+$ (5); 549, $C_8F_{17}Te^+$ (2), 419, $C_4F_9TeCl_2{}^+$ (11); 384, $C_4F_9TeCl^+$ (17); 349, $C_4F_9Te^+$ (18); 330, $C_4F_8Te^+$ (3); 219, $C_4F_9{}^+$ (16); 200, $TeCl_2{}^+$ (8), 180, $TeCF_2{}^+$(7); 165, $TeCl^+$ (38); 149, $TeF^+$ (21); 131, $C_3F_5{}^+$ (39); 130, $Te^+$ (26); 119, $C_2F_5{}^+$ (16); 100, $C_2F_4{}^+$ (24); 69, $CF_3{}^+$ (100); 50, $CF_2{}^+$ (3); 35, $Cl^+$ (2); 31, $CF^+$ (7) |
| **9a** | 1329 (vs), 1273 (vs), 1228 (vs), 1192 (vs), 1134 (vs), 1056 (s), 857 (m), 805 (s), 796 (s), 721 (vs), 687 (m), 589 (m), 534 (m), 505 (w) | 1056 (w), 732 (w), 244 (vs) 224 (s), 197 (s), 170 (vs), 151 (m), 105 (m), 77 (m) | −80.4 (6F, s, $CF_3$)<br>−85.7 (2F, s, $CF_2$)<br>−115.8 (2F, s, $CF_2$)<br>[1516.8 (1Te, m)] | 547, $M^+$–Br (18); 468, $(C_3F_7)_2Te^+$ (9); 449, $C_6F_{13}Te^+$ (3); 378, $C_3F_7TeBr^+$ (15); 299 $C_3F_7Te^+$ (26); 288, $TeBr_2{}^+$ (4); 280, $C_3F_6Te^+$ (7); 209, $TeBr^+$ (33); $TeCF_2{}^+$ (4); 169, $C_3F_7{}^+$ (28); 160, $Br_2{}^+$ (16); 149, $TeF^+$ (12), 130, $Te^+$ (34); 119, $C_2F_5{}^+$ (9), 100, $C_2F_4{}^+$ (48); 79, $Br^+$ (7); $CF_3{}^+$ (100); 50, $CF_2{}^+$ (8); 31, $CF^+$ (2) |
| **9c** | 1354 (s), 1239 (vs), 1207 (vs), 1183 (s), 1141 (vs), 1107 (s), 1096 (s), 981 (m), 802 (w), 772 (w), 739 (w), 713 (m), 673 (m), 633 (w), 602 (w), 573 (w), 531 (w), 457 (w) | 717 (w), 245 (vs), 223(vs), 172 (s), 131 (m), 76 (s) | −81.0 (3F, s, $CF_3$)<br>−84.6 (2F, s, $CF_2$)<br>−112.5 (2F, s, $CF_2$)<br>−126.1 (2F, s, $CF_2$)<br>[1545.0 (1Te, m)] | 647, $M^+$–Br (7); 568, $(C_4F_9)_2Te^+$ (9); 549, $C_8F_{17}Te^+$ (4); 428, $C_4F_9TeBr^+$ (7); 399, $C_4F_9TeCF_2{}^+$ (2); 349, $C_4F_9Te^+$ (21); 330, $C_4F_8Te^+$ (7); 288, $TeBr_2{}^+$ (2); 219, $C_4F_9{}^+$ (14); 209, $TeBr^+$ (17); 180, $TeCF_2{}^+$ (4); 160, $Br_2{}^+$ (18); 149, $TeF^+$ (15); 131, $C_3F_5{}^+$ (28); 130, $Te^+$ (19); 119, $C_2F_5{}^+$ (9); 100, $C_2F_4{}^+$ (23); 79, $Br^+$ (5); 69, $CF_3{}^+$ (100); 50, $CF_2{}^+$ (3); 31, $CF^+$ (11) |

[a] $^{13}$C NMR: 118.1 [2C, tq, ($^1J_{C–F} = 288.4$, $^2J_{C–F} = 34.2$)]; 109.4 [2C, tqt, ($^1J_{C–F} = 264.6$, $^2J_{C–F} = 38.6$, $^2J_{C–F'} = 9.1$)]; 126.0 [2C, tt, ($^1J_{C–F} = 327.0$, $^2J_{C–F} = 43.4$)].

[b] $^{13}$C NMR: 104.3 [2C, septd, ($^1J_{C–F} = 271.3$, $^2J_{C–F} = 18.2$]; 120.5 [4C, dq, ($^1J_{C–F} = 286.7$, $^2J_{C–F} = 24.5$)].

[c] $^{13}$C NMR: 116.7 [2C, tq, ($^1J_{C–F} = 289.6$, $^2J_{C–F} = 34.0$)]; 109.2 [2C, tqt, ($^2J_{C–F} = 31.1$)]; 117.9 [2C, tt, ($^1J_{C–F} = 342.6$, $^2J_{C–F} = 43.4$)].

[d] $^{13}$C NMR: 99.1 [2C, septd, ($^1J_{C–F} = 297.0$, $^2J_{C–F} = 36.2$)]; 120.2 [$^1J_{C–F} = 289.4$, $^2J_{C–F} = 36.2$)].

is removed in vacuo, the residue is then treated with 20 ml acetone and the suspension is transferred into a glass apparatus consisting of two tubes closed with Teflon stemmed Young valves and linked with a glass frit. The apparatus is evacuated and the suspension filtered into the second tube. After evaporating the filtrate to dryness $(C_6F_5)_2TeF_4$ contaminated with $(C_6F_5)_2TeF_2$ is obtained. The mixture could not be separated and was characterised as such:. m.p. 69°C; $^{19}$F NMR: $(C_6F_5)_2TeF_4$: −21.1 (2F, m, $TeF_{2\,aqu.}$); −39.4 (2F, m, $TeF_{2\,ax.}$); $(C_6F_5)_2TeF_2$: −102.2 (2F, m, $TeF_2$). IR (KBr) [$(C_6F_5)_2TeF_4 + (C_6F_5)_2TeF_2$]: 1640 (m), 1520 (s), 1492 (vs), 1397 (m), 1293 (m), 1093 (s), 980 (s), 805 (w), 665 (w). $\delta$-values measured are in good agreement with literature data [18].

### 5.6. Bis(trifluoromethyl)tellurium(IV) sulfinylamide (6)

The synthesis of **6** is performed in a glass apparatus fitted with two 50 ml Carius tubes closed with Teflon valves and linked by a medium glass frit. One tube contains a suspension of 1.02 g (6.0 mmol) AgNSO, 1.0 g (3.0 mmol) $(CF_3)_2TeCl_2$, 20 ml $CH_2Cl_2$ and glass bulbs. This mixture is stirred at −20°C (45 min) and then at 22°C (15 min) forming a colourless solid and a yellow solution. The yellow solution is separated by filtration into the second tube cooled to −20°C. The solvent is removed at −20°C/$10^{-3}$ Torr and the solid residue is dried at −20°C for 16 h providing **6**. Yield: 0.62 g (53%); m.p. 87°C. Anal. Found: C, 6.2; N, 7.0; S, 17.8. Calc. $C_2F_6N_2O_2S_2Te$: C, 6.2; N, 7.2; S, 16.8%. $^{19}F$ NMR: −44.7 (6F, s, $CF_3$); $^{125}Te$ NMR: 887.0 (1Te, m). MS *m/z* ion (rel. int.): 330, $M^+$–NSO (28); 287, $(CF_3)_2TeF^+$ (3); 268, $C_2F_4Te^+$ (17); 261, $CF_3TeNSO^+$ (9); 249, $C_2F_5Te^+$ (4); 199, $CF_3Te^+$ (23); 192, $TeNSO^+$ (19); 180, $CF_2Te^+$ (5); 149, $TeF^+$ (6); 144, $TeN^+$ (8); 130, $Te^+$ (18); 69, $CF_3^+$ (7); 64, $SO_2^+$ (79); 50, $CF_2^+$ (8); 48 $NS^+$ (42); 32, $S^+$ (7); 28, $N_2^+$ (12). IR (KBr): 1259 (w), 1207 (s), 1154 (s), 1093 (s), 1073 (s), 1041 (vs), 740 (m), 734 (s), 542 (s), 532 (m). Ra (solid): 1238 (w), 1100 (w), 1061 (s), 1040 (w), 741 (m), 564 (m), 328 (vs), 299 (m), 270 (m), 240 (m), 222 (w), 197 (w), 130 (m), 98 (s).

### 5.7. Bis(perfluoro-n-hexyl)telluride

A well ground mixture of 2.0 g (4.4 mmol) $n$-$C_6F_{13}I$, 1.75 g (13.2 mmol) Te and 0.85 g (13.2 mmol) Cu are placed in a Carius tube (60 ml), which was evacuated and sealed. The reaction vessel is heated in a tube oven at 180°C for 12 h. The tube is opened in vacuo and $(n\text{-}C_6F_{13})_2Te$ condensed at $10^{-3}$ Torr in a trap cooled to −196°C providing air sensitive bright yellow needles, which are only slightly soluble in $CHCl_3$. Yield: 0.7 g (41%). $^{19}F$ NMR: −81.3 (6F, s, $CF_3$), −59.6, −113.4, −121.4, −123.0, −126.4 [10F, s, $(CF_2)_5$]. MS *m/z* ion (rel. int.): 768, $M^+$ (1); 499, $C_6F_{13}TeCF_2^+$ (3); 319, $C_6F_{13}^+$ (20); 269, $C_5F_{11}^+$ (20); 169, $C_3F_7^+$ (70); 130, $Te^+$ (70); 119, $C_2F_5^+$ (70); 69, $CF_3^+$ (100). IR (KBr): 1232 (s, br), 1200 (s), 1150 (s), 1040 (m), 1020 (m), 848 (m, br), 733 (m), 651 (s), 606 (m), 557 (m), 526 (m), 418 (m). Ra (solid): 1107 (w), 746 (s), 651 (s), 461 (s), 366 (s), 202 (s), 118 (s).

### 5.8. General procedure for the preparation of bis(perfluoroalkyl) tellurium(IV) halides $(R_f)_2TeX_2$; $X = F$, **7**; Cl, **8**; Br, **9** and $R_f = n\text{-}C_3F_7$, **a**; $(CF_3)_2CF$, **b**; $n\text{-}C_4F_9$, **c**

Into a carefully in vacuo dried 50 ml Carius tube equipped with a Teflon stemmed valve bis(perfluoroalkyl) tellurides, 20 ml $CH_2Cl_2$ and stochiometrical amounts of halogenating reagents are condensed. The content of the evacuated, closed vessel is stirred at −78°C for 1 h, warmed to 0°C and additionally stirred for another hour. The solvent was removed and the residue was dried or sublimated at $10^{-3}$ Torr at corresponding temperatures. Additional reaction parameters such as educts, conditions, yields, melting points, formulas and analysis are given in Table 5, spectroscopic data are reported in Table 6.

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