Perfluoroalkyl(dithiocarbamato) tellurium(II) compounds†

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$[NMe_4][R_fTe(SC(S)NR_2)_2]$ derivatives are selectively formed by the oxidation of $[NMe_4]TeR_f$ ($R_f = CF_3$, C_2F_5) with $[R_2NC(S)S]_2$ ($NR_2 = NEt_2$, NBz_2, $N(CH_2)_4$) in almost quantitative yields. An alternative route to obtain the dithiocarbamato complex anions offer reactions of $Te[SC(S)NR_2]_2$ ($NR_2 = NEt_2$, NBz_2) with equimolar amounts of Me_3SiR_f and $[NMe_4]F$. Some of the derivatives were recrystallized with bulky cations in order to determine the crystal structures. Structural elucidation by diffraction methods exhibit the structural feature of a distorted pentagonal planar environment (resembling "butterflies") around the tellurium centres. The carbamato tellurates can be transferred easily into the neutral derivatives, $R_fTeSC(S)NR_2$, upon treatment with $Ag[BF_4]$. In solution they equilibrate with $Te_2(R_f)_2$ and $[R_2NC(S)S]_2$ and finally are transformed into $Te(R_f)_2$, $Te[SC(S)NR_2]_2$, and $Te[SC(S)NR_2]_4$, respectively. All compounds are fully characterized by NMR spectroscopic methods (^1H, ^{13}C, ^{19}F, ^{125}Te). Additionally, synthesis and characterization of the hitherto unknown derivative $[NMe_4]TeC_2F_5$ are described.

Introduction

Due to the similar characters of sulfur and tellurium, interchalcogen compounds have attracted attention during the past decades. The lack of low-valent tellurium containing starting materials allowed investigations mainly on tellurium (IV) species clearly revealing the focus on dithiocarbamates as the prominent ligands for these systems. In the 1980s and early 1990s, numerous organotellurium(IV) dithiocarbamates were synthesized and characterized by spectroscopic and diffractional methods.[1] In contrast, examples of organotellurium(II) dithiocarbamates are rare and, to our knowledge, structural determinations are limited to three examples, dimethyldithiocarbamato(2-phenylazophenyl-*C*,*N*′)tellurium(II),[2] dimethyldithiocarbamato[2-(2-pyridyl)-phenyl]tellurium(II),[3] and diethyldithiocarbamato{8-[(dimethyl-amino)-1-naphthyl]}tellurium(II).[4]

The inherent properties of trifluoromethyl-[5] and pentafluoroethyltellurates(0) in combination with their convenient oxidizability[6] leads to interesting aspects of further studies.

Here, we report on the synthesis and characterization of $[NMe_4]TeC_2F_5$, the oxidations of the anions $TeCF_3^-$ and $TeC_2F_5^-$ by dithiuramdisulfides, and an alternative route to obtain compounds with the anions $[R_fTe(SC(S)NR_2)_2]^-$. Furthermore, the aspect of their conversion into neutral species is reported, corroborated by NMR spectroscopy and structural characterization for selected examples.

Results and discussion

Tetramethylammonium pentafluoroethyltellurate(0), $[NMe_4]TeC_2F_5$ (1b)

$[NMe_4]TeC_2F_5$ **1b** is prepared in a similar manner as described for the lighter homologue[5] $[NMe_4]TeCF_3$ **1a** according to eqn (1) in more than 90% yield.

$$[NMe_4]F + Me_3SiC_2F_5 + Te \rightarrow [NMe_4]TeC_2F_5 + Me_3SiF \qquad (1)$$

The salt **1b** was obtained as a pale ochre, moderately light-sensitive solid which can be handled in ambient atmosphere for at least some minutes. In comparison with **1a**, it shows the same spectroscopic characteristics.

It must be noted that extension of the reaction (eqn (1)) to higher perfluoroalkylsilanes did not give any evidence for the homologous compounds, $[NMe_4]Te(n\text{-}C_3F_7)$ and $[NMe_4]Te(n\text{-}C_4F_9)$, but for perfluorinated carbanions of a composition that will be discussed elsewhere.[7]

Oxidations of 1 with dithiuramdisulfides

Oxidations of $[NMe_4]TeR_f$ (R_f = CF_3 (**1a**), C_2F_5 (**1b**)) with dithiuramdisulfides proceed selectively and quantitatively to give the title compounds (*cf.* Scheme 1; top left to centre). Products were obtained as yellow crystalline to waxy materials. Attempted crystallization carried out in open glass beakers at ambient atmosphere gave inhomogeneous products from which crystals of $[NMe_4][R_fTe(SC(S)NR_2)_2]$ (yellow) and $Te[SC(S)NR_2]_2$ (red) were selected for X-ray diffraction studies. Furthermore, a not yet identified derivative (colourless) has been observed implying a decomposition process by loss of CF_3H. The dithiocarbamato compounds are stable on exposure to daylight in ambient atmosphere and can be stored in ordinary glassware. The compounds **3a–f** were characterized by NMR spectroscopic methods and data obtained for the anions did not deviate from those measured for the crystalline derivatives described below (Table 1). Negative ESI-mass spectra did not show the anion peak but were dominated by ions of the carbamate and $\{[NMe_4](SC(S)NR_2)_2]\}^-$. Also, EI mass spectra (20 eV) did not give a deeper insight into the molecular structure. The peak $[R_fTeSC(S)NR_2]^+$ was detected in all spectra with an intensity below 8%; $[Te_2(R_f)_2]^+$ was always found as the 100%-peak.

^{19}F NMR chemical shifts of $[CF_3Te(SC(S)NR_2)_2]^-$ (**3a-c**) are located around −20 ppm for the carbamato compounds and are

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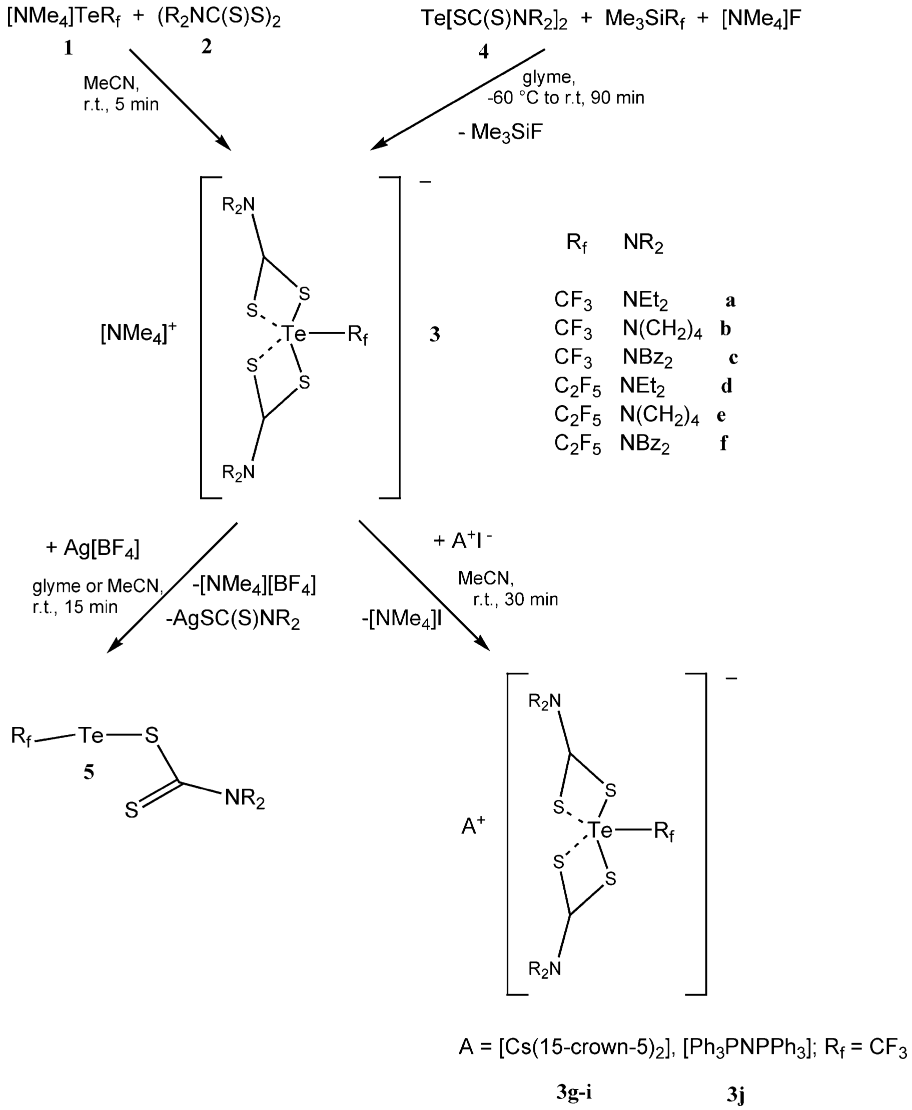
† Dedicated to Professor Alois Haas on the occasion of his 75th birthday.



Scheme 1

significantly shifted from the resonance of the parent ion $TeCF_3^-$ ($\delta \approx +1$)[5] and known CF_3TeSR derivatives ($\delta \approx -27$).[8] This is in perfect agreement with shifts of other trifluoromethyltellurates(II).[6] Exceptionally large couplings for Te(II) derivatives confirm values previously reported for $[CF_3TeI_2]^-$.[6] Similar relations might be applied to the C_2F_5-compounds **3d–f** ($\delta \approx -83.4 \pm 0.3$ (CF_3); -86.5 ± 0.7 (CF_2)) irrespective of the solvent (acetonitrile or DMF), although reference values for comparison purposes are missing (Table 1).

^{13}C NMR signals of the CF_3 group in CF_3Te derivatives and of the CF_2 group in C_2F_5Te derivatives are shifted downfield by approximately 30 ppm compared with the parent ions.[5,9] All signals (^{13}C, ^1H) for the dithiocarbamato ligands are detected in the expected region. The chemical shift of the NCS_2 group of about 205 ± 2.5 ppm implies an ionic rather than a covalent character of the carbamate ligand.[10,11]

^{125}Te NMR signals are located between the resonances of $Te(R_f)_2$ and $Te[SC(S)NR_2]_2$ at approximately 960 ppm ($[CF_3Te(SC(S)NR_2)_2]^-$) and 920 ppm ($[C_2F_5Te(SC(S)NR_2)_2]^-$) representing roughly the arithmetic mean value of $\delta(Te(R_f)_2)$[12,13] and $\delta(Te[SC(S)NR_2]_2)$[14] in the ratio 1 : 2.

Reactions of tellurium(II) dithiocarbamates with the system Me_3SiR_f/F^- ($R_f = CF_3, C_2F_5$)

The compounds **3a–f** were alternatively prepared starting from the corresponding tellurium(II) dithiocarbamates and Me_3SiR_f/F^- as equivalents for perfluoroalkyl anions (*cf.* Scheme 1; top right to centre). These reactions proceed selectively and quantitatively under the chosen conditions. Thereby the exclusive attachment of one perfluoroalkyl group to the tellurium(II) centre is achieved. No evidence for the replacement of the dithiocarbamate ligands by perfluoroalkyl groups was found.

Synthesis of 3g–j and crystal structures of 3h, 3j and bis(triphenylphosphoranyliden)ammonium trifluoromethyl(chloro)-(dibenzyldithiocarbamato)tellurate(II) (3k)

The salts **3g–j** were selectively prepared from the exchange reactions of **3a–c** by the bulky cations $[Cs(15\text{-crown-}5)_2]^+$ and

Table 1 Compilation of NMR data of tetramethylammonium perfluoroalkylbis(dithiocarbamato)tellurates(II), $[NMe_4][R_fTe(SC(S)NR_2)_2]$ **3**

Compound	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**
Solvent	$MeCN/CD_3CN$	DMF-d_7	CD_3CN	$MeCN/CD_3CN$	DMF-d_7	$MeCN/CD_3CN$
^{19}F						
$\delta(CF_3)$	−20.0, s	−20.3, s	−19.6, s	−83.7, t[a]	−83.0, t[b]	−83.5, t[a]
$\delta(CF_2)$				−86.3, q	−85.9, br	−86.1, q
^2J(Te,F)/Hz	287	289	285	160	163	158
^1J(F,C)/Hz	381	381	379	285/322[c]	288/321[c]	287/325[c]
^{125}Te						
δ	955	979	952	883	936	918
^{13}C						
$\delta(CF_3)$	125.3	123.4	124.3	121.4	121.6	121.3
$\delta(CF_2)$				117.8	116.7	117.7
$\delta(CS_2)$	203.2	199.9	207.4	202.5	200.4	206.5
$\delta(NCH_2)$	47.7	52.5	55.6	47.1	52.4	54.5
δ(other)	12.5	25.7	128.1; 128.3; 129.5; 137.9	11.6	25.6	127.2; 127.5; 128.6; 137.1
$\delta(NMe_4)$	56.1	54.9	56.1	55.3	54.8	55.3
^1H						
$\delta(NCH_2)$	4.0, 8H	3.7, 8H	5.2, 8H	3.9, 8H	3.7, 8H	5.2, 8H
δ(other)	1.2, 12H	2.0, 8H	7.4,[d] 20H	1.2, 12H	2.0, 8H	7.4,[d] 20H
$\delta(NMe_4)$	3.1, 12H	3.4, 12H	3.1, 12H	3.1, 12H	3.4, 12H	3.1, 12H

[a] $^3J_{F,F}$ = 3.1 Hz. [b] $^3J_{F,F}$ = 2.5 Hz. [c] First value $^1J_{F,C}$ of CF_3 group; second of CF_2 group. [d] Centre of overlapping multiplets.

$[PNP]^+$ using the corresponding iodides (*cf.* Scheme 1; centre to bottom right). $[NMe_4]I$ was filtered off and all volatile components were distilled off *in vacuo* yielding salts **3g–j** nearly quantitatively as bright yellow solids. Recrystallization from CH_2Cl_2/Et_2O mixtures in open glass beakers gave yellow crystals of **3h** and **3j**. These crystals were of the required quality for crystal structure determinations.

Attempted cation exchange of **3c** and [PNP]Cl was unsuccessful. Instead of $[PNP][CF_3Te(SC(S)NBz_2)_2]$, some crystals of $[PNP][CF_3TeCl(SC(S)NBz_2)]$ (**3k**) were collected after crystallization of the raw material from a CH_2Cl_2/Et_2O mixture.

The ligand arrangement around the tellurium centres in the structures of **3h** (Tables 2 and 3, Fig. 1 and 2) and **3j** (Tables 2 and 3, Fig. 3) is almost planar in a distorted pentagonal fashion with two shorter and two longer Te–S contacts (**3h**: 2.696(2)/3.022(2) Å; 2.703(2)/3.082(2) Å; **3j**: 2.711(1)/3.154(1) Å; 2.687(1)/3.069(2) Å). The carbon tellurium bond (**3h**: 2.251(6) Å; **3j**: 2.237(5) Å) is slightly longer with respect to related motifs found in the dimeric $[CF_3TeI(\mu\text{-}I)]_2^{2-}$ dianion (2.205(3) Å).[6] The angular sums around tellurium are 360.0° (**3h**) and 360.1° (**3j**), respectively, again proving the planar ligand arrangement. As a consequence, the anions must be regarded as "hypervalent" [14-Te-5] species with two lone electron pairs occupying axial sites. A similar motif has also been found for the hemi-adduct of bis(diethyldithiocarbamato)tellurium(II) with 4,4′-bipyridyl.[15] A slight tendency towards planar five-coordination by intermolecular Te–S contacts is also discussed for the molecular structures of some bis(dithiocarbamato)tellurium(II) derivatives.[16,17]

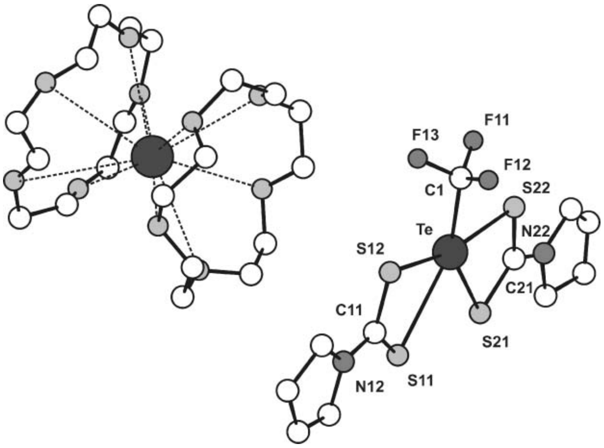


Fig. 1 Molecular structure and labelling scheme of $[Cs(15\text{-crown-}5)_2][CF_3Te(SC(S)N(CH_2)_4)_2]$ **3h**.

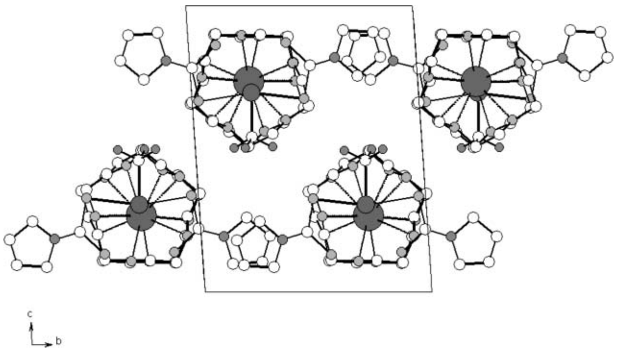


Fig. 2 Perspective view of the unit cell of compound **3h** along the *a*-axis.

In comparison with the parent molecule **4** (see below), Te–S bonds are elongated by up to approximately 0.2 Å due to the

Table 2 Crystal data and structure refinement parameters for **3h**, **3j**, **3k**, **4b** and **6c**

	3h	**3j**	**3k**	**4b**	**6c**
Empirical formula	$C_{31}H_{56}N_2F_3O_{10}S_4CsTe$	$C_{47}H_{46}N_3F_3P_2S_4Te$	$C_{52}H_{44}N_2F_3P_2S_2ClTe$	$C_{10}H_{16}N_2S_4Te$	$C_{60}H_{56}N_4S_8Te$
Formula mass/g mol^{-1}	1062.53	1027.65	1043.00	420.09	1217.17
Rotation angle range	$0° \le \omega \le 180°$; $\psi = 0°$ $0° \le \omega \le 180°$; $\psi = 90°$	$0° \le \omega \le 180°$; $\psi = 0°$ $0° \le \omega \le 180°$; $\psi = 90°$	$0° \le \omega \le 180°$; $\psi = 0°$ $0° \le \omega \le 180°$; $\psi = 90°$	$0° \le \varphi \le 250°$	$0° \le \varphi \le 250°$
Increment	$\Delta\omega = 2°$	$\Delta\omega = 2°$	$\Delta\omega = 2°$	$\Delta\varphi = 2°$	$\Delta\varphi = 2°$
No. of images	180	180	180	125	125
Exposure time/min	6	10	3	4	5
Detector distance/mm	120	120	120	60	60
2θ range/°	1.9–54.8	1.9–54.8	1.9–54.8	3.8–56.3	3.8–56.3
Temperature/K	170(2)	150(2)	150(2)	293(2)	293(2)
Index range	$-16 \le h \le 15$ $-16 \le k \le 16$ $-19 \le l \le 19$	$-19 \le h \le 19$ $-18 \le k \le 17$ $-23 \le l \le 23$	$-17 \le h \le 19$ $-18 \le k \le 18$ $-26 \le l \le 26$	$-10 \le h \le 10$ $-15 \le k \le 15$ $-21 \le l \le 21$	$-20 \le h \le 20$ $-20 \le k \le 20$ $-15 \le l \le 16$
Total data collected	34762	64295	73923	17701	32889
Unique data	9754	9021	10567	3635	3484
Observed data	7375	5859	8412	2472	2203
R_{merg}	0.0390	0.0947	00513	0.0530	0.1002
Transmission min/max	0.4023/0.7632	0.6679/0.8771	0.6956/0.8778	0.6382/0.7575	0.7701/0.9051
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{4}2_1c$ (no. 114)
a/Å	13.192(1)	15.860(1)	15.394(1)	8.094(1)	15.406(2)
b/Å	13.178(1)	14.887(1)	14.710(1)	11.727(1)	
c/Å	14.939(2)	19.424(2)	20.959(2)	16.101(2)	12.161(2)
α/°	87.97(1)				
β/°	78.72(1)	91.20(1)	94.08(1)	92.15(1)	
γ/°	61.22(1)				
Z, Volume/Å^3	2, 2226.9(4)	4, 4584.9(6)	4, 4734.2(5)	4, 1527.1(3)	2, 2886.4(5)
R indexes [$I > 2\sigma I$]	$R_1 = 0.0689$ $wR_2 = 0.1893$	$R_1 = 0.0496$ $wR_2 = 0.1166$	$R_1 = 0.0383$ $wR_2 = 0.1027$	$R_1 = 0.0333$ $wR_2 = 0.0615$	$R_1 = 0.0436$ $wR_2 = 0.0756$
R indexes (all data)	$R_1 = 0.0871$ $wR_2 = 0.2030$	$R_1 = 0.0824$ $wR_2 = 0.1308$	$R_1 = 0.0499$ $wR_2 = 0.1107$	$R_1 = 0.0624$ $wR_2 = 0.0676$	$R_1 = 0.0851$ $wR_2 = 0.0874$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma\ |F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$, $S_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$, with $w = 1/[\sigma^2 (F_o)^2 + (0.1000P)^2]$ for **3h** $w = 1/[\sigma^2 (F_o)^2 + (0.0801P)^2]$ for **3j**, $w = 1/[\sigma^2 (F_o)^2 + (0.0728P)^2 + 0.8236P]$ for **3k**, $w = 1/[\sigma^2 (F_o)^2 + (0.0284P)^2]$ for **4b** and $w = 1/[\sigma^2 (F_o)^2 + (0.0366P)^2]$ for **6c**, were $P = (F_o{}^2 + 2F_c{}^2)/3$. $F_c{}^* = kF_c[1 + 0001 \times |F_c|^2\ \lambda^3/\sin(2\theta)]^{-1/4}$.

Table 3 Interatomic distances (Å) and angles (°) for **3h**, **3j**, **3k**, **4b** and **6c** (with estimated standard deviations in parentheses)

3h		**3j**		**3k**		**4b**		**6c**	
Te–S11	3.022(2)	Te–S111	3.154(1)	Te–S1	3.083(1)	Te–S111	2.898(1)	Te–S11	2.755(1) 4x
Te–S12	2.696(2)	Te–S112	2.711(1)	Te–S2	2.570(1)	Te–S112	2.518(1)	Te–S12	2.723(1) 4x
Te–S21	3.082(2)	Te–S211	3.069(2)			Te–S211	2.896(1)		
Te–S22	2.703(2)	Te–S212	2.687(1)			Te–S212	2.495(1)		
Te–C1	2.251(6)	Te–C1	2.237(5)	Te–C1	2.204(3)				
C1–F11	1.263(10)	C1-F11	1.329(7)	C1–F11	1.324(4)				
C1–F12	1.251(10)	C1–F12	1.343(7)	C1–F12	1.331(4)				
C1–F13	1.335(10)	C1–F13	1.358(6)	C1–F13	1.353(4)				
C11–S11	1.695(6)	C11-S111	1.692(5)	C2–S1	1.689(3)	C11–S111	1.688(3)	C1–S11	1.707(5)
C11–S12	1.726(7)	C11–S112	1.732(5)	C2–S2	1.745(3)	C11–S112	1.733(4)	C1–S12	1.714(5)
C21–S21	1.702(7)	C21–S211	1.696(5)			C21–S211	1.686(4)		
C21–S22	1.729(7)	C21–S212	1.719(5)			C21–S212	1.737(4)		
C11–N12	1.345(8)	C11–N12	1.347(6)	C2–N1	1.352(4)	C11–N12	1.325(5)	C1–N1	1.357(6)
C21–N22	1.337(9)	C21–N22	1.346(7)			C21–N22	1.316(5)		
				Te–Cl	2.726(1)				
S11–Te–S12	62.8(1)	S111–Te–S112	61.0(1)	S1–Te–S2	63.0(1)	S111–Te–S112	65.9(1)	S11–Te–S12	65.2(1) 4x
S21–Te–S22	62.1(1)	S211–Te–S212	62.1(1)			S211–Te–S212	66.1(1)		
S11–Te–S21	71.3(1)	S111–Te–S211	162.1(1)			S111–Te–S211	145.4(1)		
S11–Te–S22	133.4(1)	S111–Te–S212	135.8(1)			S111–Te–S212	148.5(1)		
S12–Te–S21	134.1(1)	S112–Te–S211	136.6(1)	S2–Te–C1	149.1(1)	S112–Te–S211	79.5(1)		
S12–Te–S22	163.8(1)	S112–Te–S212	74.9(1)	S2–Te–Cl	127.5(1)	S112–Te–S212	145.6(1)		
S12–Te–C1	81.4(2)	S111–Te–C1	78.4(2)	S1–Te–C1	86.4(1)				
S22–Te–C1	82.4(2)	S211–Te–C1	83.7(2)	S1–Te–Cl	169.5(1)				
				C1–Te–Cl	83.2(1)				
	Σ360.0		Σ360.1		Σ360.1				

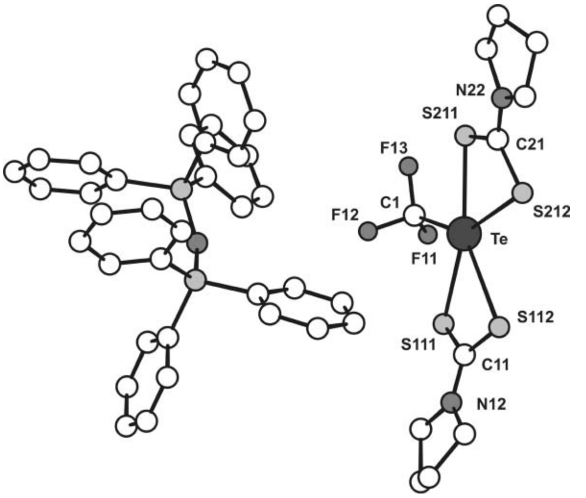
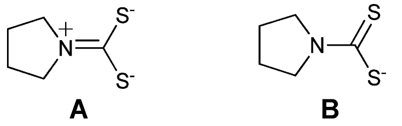


Fig. 3 Molecular structure and labelling scheme of [PNP][$CF_3Te(SC(S)N(CH_2)_4)_2$] **3j**.

additional coordination by the electronegative trifluoromethyl group. C–S and C–N bond lengths indicate an electron distribution in the ligand somewhere in between the canonical forms A and B (Scheme 2) which is in absolute agreement with estimations made on the basis of ^{13}C NMR data in solution.



Scheme 2

The pyrrolidine rings appear to be planar in the crystal structure of **3h**, while significant folding is found for it in **3j**. Alternate stacking of the anions and cations occurs along the *a*-axis leading to the exceptional planar molecular structure of the whole anion due to lattice effects produced by this stacking. In the crystal structure of **3j**, the anions are incorporated in the [PNP] framework allowing the pyrrolidine rings to exhibit their characteristic folding.

No peculiarities are found concerning interatomic distances and angles in both cations [Cs(15-crown-5)$_2$] *e.g.* ref. 18 and 19 and [PNP] *e.g.* ref. 6 and 20 in comparison with known structures. However, it should be noted that a disorder problem in the crown ethers is possibly responsible for the *R*-values obtained for **3h**.

The [$CF_3TeCl(SC(S)NBz_2)$]$^-$ anion in **3k** (Tables 2 and 3; Fig. 4) exhibits a distorted square planar ligand arrangement at tellurium. As to be expected, ligand–Te–ligand angles vary from 63.0(1)° (S1–Te–S2)—due to the chelating bidentate character of the dithiocarbamate ligand—to 127.5(1)° (S1–Te–Cl), while only the two angles S1–Te–C1 (86.4(1)°) and C1–Te–Cl (83.2(1)°) are close to the rectangle. As a consequence, the *trans* angles S1–Te–Cl (169.5(2)°) and especially S2–Te–C1 (149.1(1)°) deviate significantly from linearity. However, the angular sum around tellurium is 360.1° suggesting that the lone electron pairs are located above and below the plane as is expected for a [12-Te-4] species. The Te–S2 bond is shorter than in the five-coordinate species (**3h** and **3j**) but significantly longer than in comparable bis(dithiocarbamato)tellurium(II) compounds.[16,17,21]

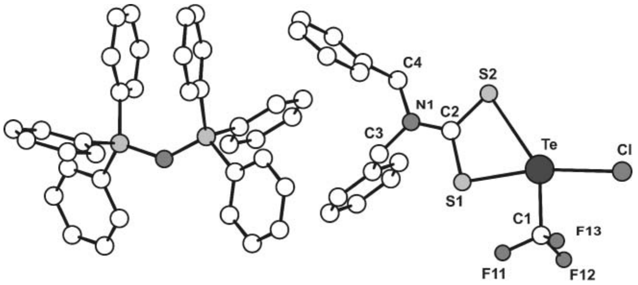


Fig. 4 Molecular structure and labelling scheme of [PNP][$CF_3TeCl(SC(S)NBz_2)$] **3k**.

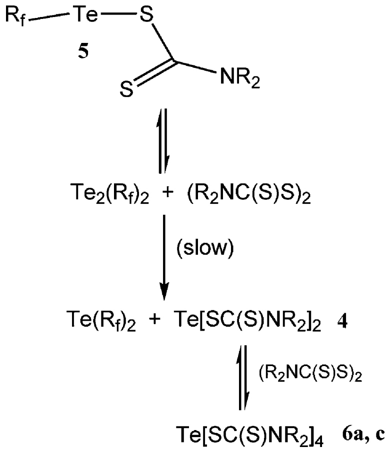
The Te–C bond length of 2.204(3) Å is found in the range of similar crystallographically characterized square-planar trifluoromethyltellurates(II), [$CF_3TeI(\mu\text{-}I)]_2^{2-}$[6] and [$CF_3Te(TeCF_3)(\mu\text{-}X)]_2^{2-}$ (X = Cl, Br, I).[6,22] The Te–Cl bond (2.726(1) Å) is shorter by approximately 0.1 Å in comparison with previously reported data for [$CF_3Te(TeCF_3)(\mu\text{-}Cl)]_2^{2-}$ and related compounds.[23] Again, electron distribution in the dithiocarbamato ligands is best described by the canonical structures depicted in Scheme 2.

Synthesis of perfluoroalkyl(dithiocarbamato)tellurium(II) 5

The reactions of the compounds **3** and Ag[BF_4] proceed selectively in MeCN solution within 15 min to give the corresponding derivatives **5** in quantitative yields. The formation of the sparingly soluble salts [NMe_4][BF_4] and Ag[$SC(S)NR_2$] appears to be the driving force (*cf.* Scheme 1, centre to left). During the reaction the colour of the mixture changes from bright yellow to orange, while a white solid precipitates. Upon filtration and condensing off the solvent *in vacuo*, derivatives **5** were isolated as intensive orange solids unfortunately of insufficient purity.

Concomitant with the formation of **5** an equilibrium begins to establish between the former, $Te_2(CF_3)_2$ and the dithiuram disulfide (Scheme 3). Upon prolonged storing of **5** in solution irrespective of the solvent, a second equilibrium is observed between the former and $Te(R_f)_2$ and Te[$SC(S)NR_2$]$_2$ **4**. Finally, the known[14] equilibrium between **4** and Te[$SC(S)NR_2$]$_4$ **6** and dithiuramdisulfide occurs.

As a consequence, the signals of five tellurium compounds were detected in the $^{125}Te,^{19}F$-HMBC spectra (*cf.* Fig. 5 for



Scheme 3

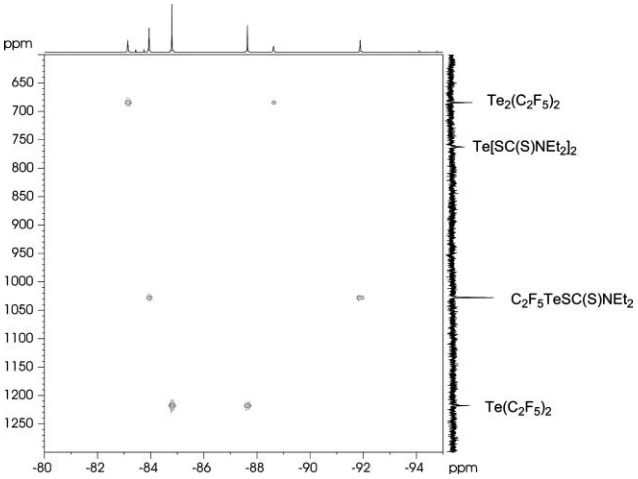


Fig. 5 $^{125}Te,^{19}F$-HMBC spectrum of the decomposition products of **5d** in CD_3CN.

$C_2F_5TeSC(S)NEt_2$ (**5d**) in CD_3CN), while three of the signals gave crosspeaks in the $^{19}F\{^{125}Te\}$ HMBC spectra. The signal of $Te[SC(S)NEt_2]_4$ **6a** occurs at −543 ppm and cannot be displayed in this figure due to technical limitations. The chemical shifts for $Te(C_2F_5)_2$ (1218 ppm)[12], $Te_2(C_2F_5)_2$ (685 ppm)[12], $Te[SC(S)NEt_2]_2$ (763 ppm)[14] and $Te[SC(S)NEt_2]_4$ (−543 ppm)[14] correspond to reported values, while the resonance of **5d** is located at 1028 ppm. Similar relations are found for the corresponding trifluoromethyl derivatives **5a–c** and the other pentafluoroethyl derivatives **5e** and **5f**. In most cases compounds **4** and **6** crystallized from the solutions as dark red (**4**) and yellow to orange (**6**) specimens.

The results of NMR investigations are summarized in Table 4. All 1D NMR spectral data match the expectations and display the typical splitting.

While the ^{19}F NMR signals of the CF_3 (**5a–c**) respectively CF_2 (**5d–f**) groups are shielded by approximately 6 ppm in comparison with the parent ions **3a–f**, the ^{125}Te NMR signals are deshielded by approximately 150 ppm. The ^{13}C NMR signal of the NCS_2 group is detected around 190 ppm whereas 205 ± 2.5 ppm is observed for **3a–f**. These differences express different bonding situations in **3a–f** and **5a–f** and suggest a pronounced covalent nature of the tellurium sulfur bonds in **5a–f**.

EI mass spectra show the respective M^+ peaks with intensities lower than 10% and are dominated by the ions $[Te_2(R_f)_2]^+$, $[Te_2R_f]^+$, $[TeSC(S)NR_2]^+$ and $[R_2NCS]^+$.

Sign determination for the $^2J(^{125}Te,^{19}F)$ couplings in 3a and 3d

The absolute values of the $^2J(^{125}Te,^{19}F)$ coupling constants in **3a–c** and **3d–f** are found to increase for the anionic species compared with the neutral derivatives **5a–c** as well as **5d–f**. From previous investigations,[24] different signs were reported for the $^2J(^{125}Te,^{19}F)$ coupling constants of the molecules $Te(CF_3)_2$ and $Te(C_2F_5)_2$ with an opposite trend of the value when both molecules interact with Lewis bases under the same conditions. Therefore, the sign of the $^2J(^{125}Te,^{19}F)$ coupling constant of **3a** and **3d** was explored.

The sign of this coupling constant can be obtained from $^{13}C,^{19}F$ correlated spectra investigating the crosspeaks of the tellurium satellites of the fluorine signals to the tellurium satellites of the ^{13}C signals. The slope of these crosspeaks provides information on the relative sign of the $^2J(^{125}Te,^{19}F)$ coupling constant compared with the sign of the $^1J(^{13}C,^{125}Te)$ coupling constant. The correlation spectra of **3a** and **3d** exhibit the $^2J(^{125}Te,^{19}F)$ coupling constant

Table 4 Compilation of NMR data of perfluoroalkyl(dithiocarbamato)tellurium(II), $R_fTeSC(S)NR_2$ **5**

Compound	**3h**	**3h**	**3h**	**3h**	**5e**	**5f**
Solvent	CD_3CN (CD_2Cl_2)	CD_3CN (CD_2Cl_2)	CD_3CN (CD_2Cl_2)	CD_3CN	CD_3CN	CD_3CN
^{19}F						
$\delta(CF_3)$	−26.4 (−26.6)	−26.1 (−26.0)	−25.7 (−26.3)	−84.0, t[c]	−84.0, t[c]	−83.9, br
$\delta(CF_2)$				−91.9, q	−91.4, q	−90.0,br
$^{[3]2}J$(Te,F)/Hz	197 (187)	196 (183)	198 (183)	[23] 38	[23] 38	[n.o.] 36
^aJ(F,C)/Hz	371	371	371	283/317	283/317	284/315
^{125}Te						
δ	1100 (1103)	1150 (1162)	1156 (1146)	1028	1078	1082
^{13}C						
$\delta(CF_3)$	119.8	118.7	119.7	120.5	120.5	120.5
$\delta(CF_2)$				115.6	114.8	115.3
$\delta(CS_2)$	193.7	187.9	n.o.	n.o.	195.3	n.o.
$\delta(NCH_2)$	50.0	54.6	58.7	52.4	53.0	58.8
δ(other)	11.5	26.2	128.5; 129.2; 129.9; 135.2	11.4	25.0	128.6; 129.2; 129.9; 135.3
^1H						
$\delta(NCH_2)$	3.8, 4H	3.7, 4H	5.0, 4H	3.8, 4H	3.7, 4H	5.0, 8H
δ(other)	1.3, 6H	2.0, 4H	7.3,[b] 10H	1.3, 6H	2.1, 4H	7.3,[b] 10H

[a] First value $^1J_{F,C}$ of CF_3 group; second of CF_2 group. [b] Centre of overlapping multiplets. [c] $^3J_{F,F}$ = 3.1 Hz.

to have the same sign as the $^{1}J(^{13}C,^{125}Te)$ coupling constant for both anions. This fact explains the increase of the value of the $^{2}J(^{125}Te,^{19}F)$ coupling constant for both compounds.

The sign of the $^{1}J(^{13}C,^{125}Te)$ coupling constant of 419 Hz of $Te(CF_3)_2$ was found to be positive.[24] The values of the $^{1}J(^{13}C,^{125}Te)$ coupling constants are 517 Hz for **3d** and 662 Hz for **3a**. The fact that all three values are found in the same order of magnitude led to the assumption of all three couplings having a positive sign. As a consequence, the sign of the $^{2}J(^{125}Te,^{19}F)$ coupling constant is positive for both derivatives, **3a** and **3d**.

Structures of 4b and 6c

In bis(tetramethylendithiocarbamato)tellurium(II) (**4b**) (Tables 2 and 3; Fig. 6), the two dithiocarbamato moieties act as bidentate chelating ligands as it is found in all the structures of related compounds.[16,17,21] The sulfur coordination around tellurium is best described as a planar trapezoidal configuration with two short (2.518(1); 2.495(1) Å) and two long (2.898(1); 2.896(1) Å) Te–S bonds. Carbon–sulfur bond lengths differ by 0.05 Å as well. Together with the quite short C–N bond the essentially planar dithiocarbamate ligand may be seen somewhere between the canonical forms $R_2N^+{=}CS_2^{2-}$ and $R_2N{-}C(S)S^-$.

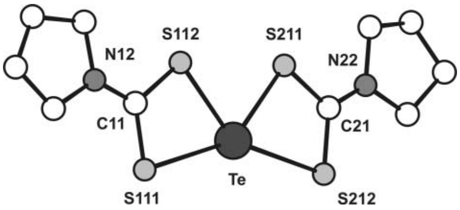


Fig. 6 Molecular structure and labelling scheme of $Te(SC(S)N(CH_2)_4)_2$ **4b**.

Tetrakis(dibenzyldithiocarbamato)tellurium(IV) (**6c**) (Tables 2 and 3; Fig. 7 and 8) crystallizes in the tetragonal space group $P\bar{4}2_1c$. The space group symmetry requires that the Te atoms are found on fourfold inversion axes. They are distorted dodecahedrally coordinated to the 8 S atoms of the 4 dithiocarbamato ligands. The Te–S bond lengths of 2.723(1) and 2.755(1) Å as well as the S–C bond lengths of 1.707(5) and 1.714(5) Å deviate only slightly from each other indicating that the negative charge of the ligand is nearly ideally delocalised. The lone pair of electrons on Te(IV) appears to be stereochemically inactive. Bond lengths and angles match best with those reported for tetrakis[*N*-(2-hydroxyethyl)-*N*-methyldithiocarbamato]tellurium(IV).[25]

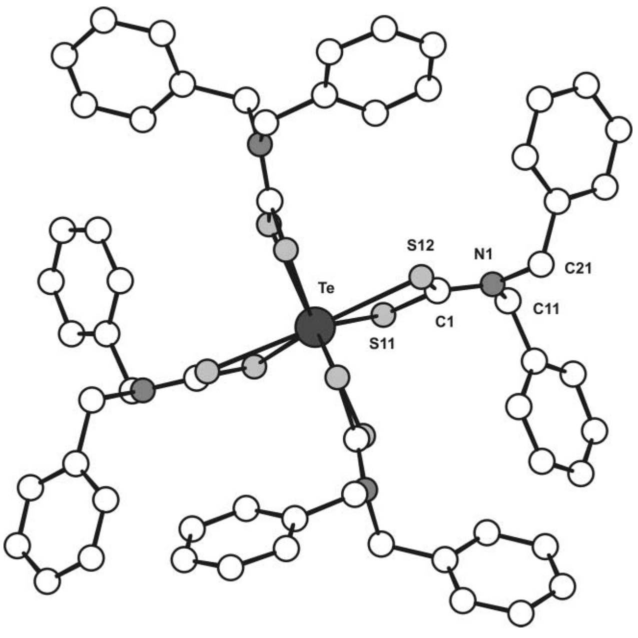


Fig. 7 Molecular structure and labelling scheme of $Te(SC(S)NBz_2)_4$ **6c**.

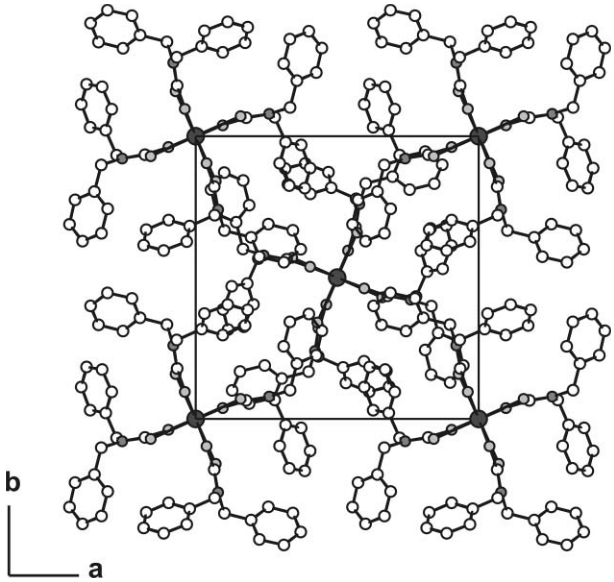


Fig. 8 View of the unit cell of compound **6c**.

Experimental

The following derivatives were prepared according to literature procedures: $[NMe_4]TeCF_3$,[5] $Me_3SiC_2F_5$,[26] $[NMe_4]F$,[27] [PNP]X,[28] $((CH_2)_4NC(S)S)_2$,[29] $[Cs(15\text{-crown-}5)_2]I$,[30] $Te[SC(S)NR_2]_2$.[14] Me_3SiCF_3 (ABCR), elemental tellurium (Acros), and $(Et_2NC(S)S)_2$ (Fluka) were used as received. $(Bz_2NC(S)S)_2$ was received from Prof. Dr Josef Hahn as a gift.

Schlenk techniques were used throughout all manipulations. NMR spectra were recorded on Bruker AC 200 (routine ^{1}H, ^{19}F), AVANCE II 300, AVANCE 400 and DRX500 spectrometers. Assignments were made on the basis of 1D and 2D NMR (HMBC; HMQC) experiments. External standards were used in all cases (^{1}H, ^{13}C: Me_4Si; ^{19}F: CCl_3F; ^{125}Te: Me_2Te). Acetone-d_6 was used as an external lock (5 mm tube) in reaction control measurements while an original sample of the reaction mixture was measured in a 4 mm insert. Due to the sensitivity of NMR parameters to concentration for tellurium compounds, all NMR experiments were performed with saturated solutions. The $^{13}C,^{19}F$-HMQC spectra for sign determination, optimized for the $^{1}J(^{13}C,^{19}F)$ coupling constant, were carried out using a 5 mm inverse broadband probe head. The detection coil was tuned to the fluorine frequency of 470.59 MHz, the decoupling coil to the carbon frequency of 125.76 MHz. The 90° fluorine pulse was 14.0 µs, the 90° ^{13}C pulse 12.5 µs.

Negative ESI mass spectra in MeCN solutions were run on a Finnigan MAT 900 apparatus with a flow rate of 2 µl min^{-1}. Intensities are referenced to the most intense peak of a group.

EI mass spectra (20 eV) were recorded on a Finnigan MAT 95 spectrometer. Isotope patterns for comparison were calculated with the program Isopro.[31] Visible decomposition points were determined using the Stuart melting point apparatus SMP10. C, H, N, and S analyses were carried out with a HEKAtech Euro EA 3000 apparatus. Details of crystal data and structure refinement parameters are summarised in Table 2.

X-Ray crystal structure determinations

Data collection for X-ray structure determinations (Table 2) were performed on a STOE IPDS I/II diffractometer using graphite-monochromated Mo-Kα radiation (0.71073 Å). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data.[32] The programs used in this work are Stoe's X-Area,[33] including X-RED and X-Shape for data reduction and absorption correction,[34] and the WinGX suite of programs,[35] including SIR-92[36] and SHELXL-97[37] for structure solution and refinement. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all of the hydrogen atoms. Selected interatomic distances and angles are given in Table 3.

CCDC reference numbers 614394 (**3h**), 614395 (**3j**), 614396 (**3k**), 614397 (**4b**) and 614398 (**6c**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618240b

Tetramethylammonium pentafluoroethyltellurate(0) (1b). The preparation procedure was the same as that used for **1a**.[5] An amount of 2.00 g (15.7 mmol) elemental tellurium was suspended in a solution of 2.14 g (11.1 mmol) $Me_3SiC_2F_5$ in 80 mL glyme at −60 °C. $[NMe_4]F$ (0.93 g; 10.0 mmol) was added and the reaction mixture was allowed to warm up to ambient temperature overnight. Excess tellurium was filtered off and all volatile components were distilled off *in vacuo* at room temperature giving a waxy solid which was washed twice with n-pentane. After drying *in vacuo*, **1b** was obtained as a malodorous, pale ochre solid in 91% yield (2.92 g).

Mp (decomp.) 115 °C; Found. C, 22.2; H, 4.0; N, 4.4%. $C_6H_{12}NF_5Te$ requires C, 22.5; H, 3.8; N, 4.4%. δ_H (DMF-d$_7$) 3.41 ($[NMe_4]^+$); δ_F (DMF-d$_7$) −66.6 (q, 2F, ^2J(Te,F) = 108 Hz, ^1J(F,C) = 299 Hz, ^3J(F,F) = 10 Hz), −83.5 (t, 3F, ^3J(Te,F) = 12 Hz; ^1J(F,C) = 283 Hz, ^3J(F,F) = 10 Hz), $\delta_{Te\{F\}}$ (DMF-d$_7$) 140, $\delta_{C\{F\}}$ 120.1 (s, ^2J(Te,C) = 76 Hz), 95.1 (s, ^1J(Te,C) = 574 Hz), 54.4 (qdec, ^1J(C,H) = 144 Hz, ^3J(C,H) = 4 Hz).

Synthesis of tetramethylammonium perfluoroalkylbis(dithiocarbamato)tellurates(II) (3a–f).

Method A. An amount of 0.54 g (2.0 mmol) **1a** (0.32 g (1.0 mmol) **1b**) was dissolved in 15 mL (10 mL) MeCN. 2.0 mmol (1.0 mmol) of the corresponding dithiuramdisulfide **2** was added in one portion. Directly after the addition, the colour of the reaction mixture changed from ochre to bright yellow–orange. Stirring was continued for up to 1 h. The solvent was removed *in vacuo*, giving waxy orange residues. Washing twice with n-pentane and drying *in vacuo* at ambient temperature gave the intensive yellow salts **3a–f** in nearly quantitative yields.

Method B. Due to the low solubility of $Te[SC(S)N(CH_2)_4]_2$ in glyme, the reactions were only performed with $Te[SC(S)NEt_2]_2$ and $Te[SC(S)NBz_2]_2$. To a mixture of 1.0 mmol of **4** and 1.2 mmol of Me_3SiR_f in 10 mL glyme (−60 °C), 1.0 mmol $[NMe_4]F$ was added in one portion. The mixture was stirred overnight, while the temperature rose to room temperature. All volatile components were condensed *in vacuo* giving the salts **3a**, **3c**, **3d**, and **3f** in quantitative yields.

The NMR data are summarized in Table 1.

Tetramethylammonium trifluoromethylbis(diethyldithiocarbamato)tellurate(II), $[NMe_4][CF_3Te(SC(S)NEt_2)_2]$ (3a). Mp (decomp.) 100 °C; Found. C, 31.5; H, 5.8; N, 7.2%. $C_{15}H_{32}N_3S_4F_3Te$ requires C, 31.8; H, 5.7; N, 7.4%.

Tetramethylammonium trifluoromethylbis(tetramethylendithiocarbamato)tellurate(II), $[NMe_4][CF_3Te(SC(S)N(CH_2)_4)_2]$ (3b). Mp (decomp.) 130 °C; Found. C, 32.2; H, 5.1; N, 7.9%. $C_{15}H_{28}N_3S_4F_3Te$ requires C, 32.0; H, 5.0; N, 7.5%.

Tetramethylammonium trifluoromethylbis(dibenzyldithiocarbamato)tellurate(II), $[NMe_4][CF_3Te(SC(S)NBz_2)_2]$ (3c). Mp (decomp.) 101 °C; Found. C, 51.7; H, 5.0; N, 5.4%. $C_{35}H_{40}N_3S_4F_3Te$ requires C, 51.5; H, 4.9; N, 5.2%.

Tetramethylammonium pentafluoroethylbis(diethyldithiocarbamato)tellurate(II), $[NMe_4][C_2F_5Te(SC(S)NEt_2)_2]$ (3d). Mp (decomp.) 70 °C; Found. C, 31.1; H, 5.4; N, 6.7%. $C_{16}H_{32}N_3S_4F_5Te$ requires C, 31.1; H, 5.2; N, 6.8%.

Tetramethylammonium pentafluoroethylbis(tetramethylendithiocarbamato)tellurate(II), $[NMe_4][C_2F_5Te(SC(S)N(CH_2)_4)_2]$ (3e). Mp (decomp.) 159 °C; Found. C, 31.0; H, 4.9; N, 7.0%. $C_{16}H_{28}N_3S_4F_5Te$ requires C, 31.3; H, 4.6; N, 6.9%.

Tetramethylammonium pentafluoroethylbis(dibenzyldithiocarbamato)tellurate(II), $[NMe_4][C_2F_5Te(SC(S)NBz_2)_2]$ (3f). Mp (decomp.) 85 °C; Found. C, 49.2; H, 4.7; N, 4.9%. $C_{36}H_{40}N_3S_4F_5Te$ requires C, 50.0; H, 4.7; N, 4.9%.

Synthesis of bis(15-crown-5)caesium trifluoromethylbis(dithiocarbamato)tellurates(II) (3g–i) and bis(triphenylphosphoranyliden)ammonium trifluoromethylbis(tetramethylendithiocarbamato)tellurate(II) (3j). Equimolar amounts (0.5 mmol) of **3a–c** and [Cs(15-crown-5)$_2$]I or [PNP]I were dissolved in 10 mL MeCN at room temperature. The mixture was stirred for approximately 1 h. Completeness of the exchange was monitored by ^{1}H NMR spectroscopy (missing signal of the $[NMe_4]$ ion). $[NMe_4]I$ was filtered off, and the solvent was evaporated to dryness. The residue was washed with two small portions of n-pentane and recrystallized from CH_2Cl_2/diethyl ether mixtures (v/v = 1 : 1) in open glass beakers. The salts **3g–j** were isolated as pale yellow crystals in better than 90% yields. NMR data of the anions did not deviate from those listed in Table 1.

Bis(15-crown-5)caesium trifluoromethylbis(diethyldithiocarbamato)tellurate(II) (3g). Mp (decomp.) 125 °C; Found. C, 35.3; H, 5.7; N, 3.1%. $C_{31}H_{60}N_2O_{10}S_4F_3TeCs$ requires C, 34.9; H, 5.7; N, 2.6%.

Bis(15-crown-5)caesium trifluoromethylbis(tetramethylendithiocarbamato)tellurate(II) (3h). Mp (decomp.) 135 °C; Found. C, 35.1; H, 5.4; N, 2.9%. $C_{31}H_{56}N_2O_{10}S_4F_3TeCs$ requires C, 35.0; H, 5.3; N, 2.6%.

Bis(15-crown-5)caesium trifluoromethylbis(dibenzyldithiocarbamato)tellurate(II) (3i). Mp (decomp.) 133 °C; Found. C, 46.9; H, 5.4; N, 2.5%. $C_{51}H_{68}N_2O_{10}S_4F_3TeCs$ requires C, 46.6; H, 5.2; N, 2.1%.

Bis(triphenylphosphoranyliden)ammonium trifluoromethylbis(tetramethylendithiocarbamato)tellurate(II) (3j). Mp (decomp.) 120 °C; Found. C, 54.8; H, 4.8; N, 3.7%. $C_{47}H_{46}N_3P_2S_4F_3TeCs$ requires C, 54.4; H, 4.5; N, 4.1%.

Synthesis of perfluoroalkyl(dithiocarbamato)tellurium(II) (5a–f)

To a well stirred solution of 1 mmol **3** either in MeCN or glyme, 1 mmol Ag[BF_4] was added at room temperature. Directly after the addition, the colour of the reaction mixture changed from bright yellow into intensively orange, while [NMe_4][BF_4] and Ag[SC(S)NR_2] precipitated as white solids. Stirring was continued for approximately 30 min and completeness of the reaction was checked by ^{19}F NMR spectroscopy. The precipitate was filtered off and all volatile compounds were removed *in vacuo* giving the derivatives **5** as viscous dark orange materials which were washed with n-pentane. Elemental analyses revealed in all cases impurities by the corresponding dithiuramdisulfide. Due to the decomposition processes in solution, attempts to recrystallize the compounds remained unsuccessful. The results of NMR examinations are given in Table 4.

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