Synthesis and Structures of Triorganotelluronium Pseudohalides

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Dedicated to Professor D. Naumann on the occasion of his 60th birthday

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The syntheses of $[(CH_3)_3Te]X$ {X = N_3 (**1**), OCN (**2**), SCN (**3**), SeCN (**4**), $[Ag(CN)_2]$ (**5**)} and $[(C_6H_5)_3Te]X$ {X = N_3 (**6**), SeCN (**7**), $[Ag(CN)_2]$ (**8**)}, their NMR spectroscopic data, vibrational spectra and single crystal structures are described. Compounds **1**–**4** are the first trimethyltelluronium pseudohalides, while the known compounds **6** and **7** have been prepared for completion of their analytical and structural properties. The occurrence of intermolecular Te···N, Te···O, Te···S and Te···Se contacts is thoroughly studied. The dicyanoargentates **5** and **8** were obtained in an attempt to prepare telluronium cyanides. Low-temperature ^{13}C NMR spectroscopy of the $[Ag(CN)_2]^-$ ion in solution has been carried out, with determination of the ^{13}C–$^{107/109}Ag$ coupling.

Introduction

Telluronium salts $[R_3Te]X$ have been known for more than a hundred years.[1,2] Some experimental work has been carried out since then, synthesizing telluronium cations with various substituents. In the 1970s Ziolo reported on the first telluronium pseudohalides $[(C_6H_5)_3Te]X$ (X = N_3, CN, OCN, SCN, SeCN),[3,4] with no NMR spectroscopic characterization, but single-crystal X-ray data for $[(C_6H_5)_3Te]OCN$ and $[(C_6H_5)_3Te]SCN$.[5–7]

The preparation and characterization of tris(perfluorophenyl)tellurium(IV) halides $(R_F)_3TeCl$ and $(R_F)_3TeBr$ (R_F = C_6F_5, $CF_3C_6F_4$) was achieved recently.[8] Their X-ray crystallographic analysis and properties revealed structures consistent with a rather covalent constitution.

Telluronium halides and pseudohalides bearing nonfluorinated substituents are in most cases widely ionic and show strong electrolyte behavior in solution.[9,10] Dihalotelluranes R_2TeX_2 feature intermolecular interactions in the solid state, whose distances lie between those of the sum of covalent and van der Waals radii.[11–13] Similar secondary interactions[14] have also been found in telluronium salts.[15,16]

To the best of our knowledge, no trimethyltelluronium pseudohalide has been reported, and continuing our efforts to explore the chemistry of main-group element azides, we report here on the first single-crystal structural determination of telluronium azides. $[(CH_3)_3Te]N_3$ (**1**) and $[(C_6H_5)_3Te]N_3$ (**6**) complete the series $R_nTe(N_3)_{4-n}$ (R = CH_3 or C_6H_5; n = 1, 2, 3), of which both $(CH_3)_2Te(N_3)_2$ and $CH_3Te(N_3)_3$, as well as $(C_6H_5)_2Te(N_3)_2$ and $C_6H_5Te(N_3)_3$ were recently synthesized and characterized.[17,18]

Pursuing the work of Ziolo, we intended to complete his examinations of **6** and **7** with modern spectroscopic and crystallographic methods. Moreover, the scope of telluronium pseudohalides should be extended to the smallest compounds, trimethyltelluronium salts. Thus, the preparation of a series of trimethyltelluronium chalcogenocyanates **2**−**4** was of further interest.

An attempt to prepare telluronium cyanides, omitting the use of an anion exchange resin,[4] will be reported. This work can be seen in context with a very recent report, dealing with structural investigations of several triphenyltelluronium transition metallates.[19]

Results and Discussion

Synthesis

Suitable precursors for the synthesis of telluronium compounds $[R_3Te]X$ are the corresponding telluronium halides. These can be obtained either by the reaction of Grignard reagents with tellurium tetrachloride,[2] or the aqueous ha-

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[‡] X-ray structure analyses
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logenation of tetraalkyl- or tetraaryltelluranes, generated in situ [Equation (1)].[20]

$$\mathrm{TeCl_4} + 4\,\mathrm{RLi} \xrightarrow[-\,4\,\mathrm{LiCl}]{\mathrm{Et_2O},\,-70\,^{\circ}\mathrm{C}} \mathrm{R_4Te} \xrightarrow[-\,\mathrm{RH}]{\mathrm{H_2O/KI}} [\mathrm{R_3Te}]\mathrm{I} \qquad \mathrm{R} = \mathrm{CH_3},\ \mathrm{C_6H_5} \tag{1}$$

Another method for the preparation of $[(C_6H_5)_3Te]Cl$ is the Friedel−Crafts type arylation of tellurium tetrachloride with benzene and aluminum trichloride.[21] Some references stated this as a method suitable for the preparation of $[(C_6H_5)_3Te]Cl$. However, it was found by tracing this reaction at different temperatures up to 90 °C, that the latter approach is somewhat slower than reported.[21] Additionally, minor impurities of $(C_6H_5)_2TeCl_2$ are always present in the isolated product, which was proven by ^{125}Te NMR spectroscopy with a resonance at $\delta = 920$ ppm.

The synthesis of trimethyltelluronium pseudohalides **1−4** is achieved by reaction of the corresponding silver pseudohalides with trimethyltelluronium iodide in aqueous or ethanolic solutions [Equation (2)].

$$[(\mathrm{CH_3})_3\mathrm{Te}]\mathrm{I} + \mathrm{AgX} \xrightarrow[-\,\mathrm{AgI}]{\mathrm{H_2O\ or\ EtOH}} [(\mathrm{CH_3})_3\mathrm{Te}]\mathrm{X} \qquad \mathrm{X} = \underset{(\mathbf{1})}{\mathrm{N_3}},\ \underset{(\mathbf{2})}{\mathrm{OCN}},\ \underset{(\mathbf{3})}{\mathrm{SCN}},\ \underset{(\mathbf{4})}{\mathrm{SeCN}} \tag{2}$$

The trimethyltelluronium pseudohalides are colorless salt-like substances which slowly release dimethyltellane as a product of their reductive decomposition [Equation (3)].

$$[(\mathrm{CH_3})_3\mathrm{Te}]\mathrm{X} \xrightarrow{\text{slow dec., }25\,^{\circ}\mathrm{C}} (\mathrm{CH_3})_2\mathrm{Te} + \mathrm{CH_3X} \tag{3}$$

Another method of preparation of telluronium pseudohalides is employed for the preparation of **6** and **7**. As previously described,[4] they can be obtained by a two-phase exchange reaction of $[(C_6H_5)_3Te]Cl$ with an excess of NaN_3 (**6**), and by simply precipitating a hot aqueous solution with excess KSeCN (**7**) [Equation (4)]. Since **6** and **7** are known compounds, they have been prepared for further spectroscopic and structural characterization and in order to compare the properties of telluronium pseudohalides with different cations.

$$[(\mathrm{C_6H_5})_3\mathrm{Te}]\mathrm{Cl} \; \begin{cases} \xrightarrow[-\,\mathrm{NaCl}]{\mathrm{NaN_3/H_2O/CHCl_3}} [(\mathrm{C_6H_5})_3\mathrm{Te}]\mathrm{N_3} \quad (\mathbf{6}) \\[2ex] \xrightarrow[-\,\mathrm{KCl}]{\mathrm{KSeCN/H_2O}} [(\mathrm{C_6H_5})_3\mathrm{Te}]\mathrm{SeCN} \quad (\mathbf{7}) \end{cases} \tag{4}$$

Of further interest in this study would be a telluronium cyanide. The only report of such a compound was also given by Ziolo, who stated that its synthesis had succeeded with the use of an anion exchange resin.[4] Applying the methods mentioned before, mostly led to the formation of an unidentified red decomposition product, after trimethyl- or triphenyltelluronium chloride had been treated with excess of KCN and evaporated subsequently. The use of silver cyanide produced the highly stable dicyanoargentate salts $[(CH_3)_3Te][Ag(CN)_2]$ (**5**) and $[(C_6H_5)_3Te][Ag(CN)_2]$ (**8**), since the complex dicyanoargentate anion formed during the reaction is more stable than the corresponding silver halides [Equation (5)]. Although their synthesis was not an initial goal, they were fully characterized including X-ray crystallography.

$$[\mathrm{R_3Te}]\mathrm{I} + 2\,\mathrm{AgCN} \xrightarrow[-\,\mathrm{AgI}]{\mathrm{H_2O}} [\mathrm{R_3Te}][\mathrm{Ag(CN)_2}] \qquad \mathrm{R} = \underset{(\mathbf{5})}{\mathrm{CH_3}},\ \underset{(\mathbf{8})}{\mathrm{C_6H_5}} \tag{5}$$

Vibrational Spectra

In their IR (strong), as well as their Raman (weak) spectra, the antisymmetric stretching vibration $\nu_{as}N_3$ is visible for both telluronium azides **1** and **6**. They are found in the region of 2030−2000 cm^{-1} similar as found for the $\nu_{as}N_3$ of covalent tellurium(IV) azides.[17,18] Since **1** and **6** exhibit ionic character, the difference between their $\nu_{as}N_3$ frequencies and that of ionic azide ion in NaN_3 ($\nu_{as}N_3 = 2041$ cm^{-1}, $\nu_sN_3 = 1344$ cm^{-1})[22] is negligible. The symmetric stretching vibration, ν_sN_3, is visible in the Raman spectra at 1376 cm^{-1} for **1**, and 1328 cm^{-1} for **6** with medium intensity and in the IR spectra with weak intensity.

Compounds **2−4** and **7** are chemically related and may be described together. Again, comparison of their vibrational spectra, namely the ν_{as}XCN vibration, shows only minor differences from the precursors. As found for **1** and **6**, the telluronium chalcogenocyanates exhibit ionic nature as well. No coordination effects in solution have been proven (NMR section), but the coordination in the solid state shows a significant effect, accounting for a shift of 20 cm^{-1} on the S−C stretching vibration of the SCN$^-$ moiety in the Raman spectrum of **3** (732 cm^{-1}), compared to 749 cm^{-1} in KSCN (Table 1).

Table 1. IR/Raman vibrational frequencies of trimethyltelluronium pseudohalides

[a]	**1**	**2**	**3**	**4**
ν_3	2027, 1998/1999	2170/2135	2076, 2058/2058	2065/2065
$\nu_3(KN_3/KXCN)$	1998[b]/[c]	2155[23]	2060/2058[24] [d]	2071/2076[25]
ν_1	−/1323	1288/1290	732	[e]
$\nu_1(NaN_3/KXCN)$	1342[b]	1282[23]	741/749[24] [d]	561[25]/556

[a] In cm^{-1}. [b] See ref.[26] and references therein. [c] Inactive. [d] Refers to $[Me_4N]NCS$. [e] Not observed due to overlapping with other vibrations.

Table 2. NMR spectroscopic data

[a][b]		1	2	3	4	5	6	7	8[c]
^{1}H		2.29	2.28	2.31	2.31	2.30	7.79−7.31	7.79−7.31	7.61−7.48
	$^{2}J_{\mathrm{H-Te}}$	23.7	23.7	24.6	23.7	23.7			
^{13}C		4.4	128.8 (OCN), 4.5 (CH_3)	133.7 (SCN), 4.5 (CH_3)	120.6 (SeCN), 4.5 (CH_3)	149.0 (CN), 4.4 (CH_3)	134.3 (C2), 131.3 (C4), 130.2 (C3), 127.9 (C1)	134.7 (C2), 131.9 (C4), 130.7 (C3), 125.9 (C1), 117.3 (SeCN)	147.0 (CN), 134.7 (C2), 132.7 (C4), 131.1 (C3), 123.5 (C1)
	$^{1}J_{\mathrm{C-Te}}$	158.3	147.6	147.6	147.6	150.6	249.3	247.5	245.6
	$^{2}J_{\mathrm{C-Te}}$						30.8	31.6	33.1
	$^{1}J_{\mathrm{C-N(Se)}}$		21.1		268.7			256.2	
^{14}N ($\Delta\nu_{1/2}$)		−132 (N_β, 20), −266 ($N_{\alpha\gamma}$, 60)	−304 (10)	−176 (90)	−144 (140)	−106 (400)	−133 (N_β, 50), −260 ($N_{\alpha\gamma}$, 20)	−130 (1000)	−110 (>2000)
^{77}Se					−324			−144 (br)	
^{125}Te		456	443	δ = 441	441	441	795	759	773
	$^{2}J_{\mathrm{Te-H}}$	24.6	24.1	23.7	23.6	23.6			

[a] **1−5** in D_2O, **6−8** in $CDCl_3$. [b] J and $\Delta\nu_{1/2}$ in Hz. [c] ^{109}Ag shift δ = 593 ppm.

Comparison of the Raman spectra of $[(CH_3)_3Te][Ag(CN)_2]$ (**5**) and $[(C_6H_5)_3Te][Ag(CN)_2]$ (**8**) with the Raman spectrum of crystalline $K[Ag(CN)_2]$ (νCN = 2140 cm^{-1})[27] shows that νCN is slightly shifted to 2132 cm^{-1} (**5**) and 2135 cm^{-1} (**8**). Further deviations are not detected.

The vibrational data indicate that all compounds consist of discrete ions in the solid state.

NMR Spectra

The NMR spectroscopic data (Table 2) confirm the salt-like nature of the compounds. In case of the azides, two resonances were observed in the ^{14}N NMR spectra at δ = −132 (N_β) and −266 ($N_{\alpha\gamma}$) ppm for **1** and δ = −132 (N_β) and −272 ($N_{\alpha\gamma}$) ppm for **6**. This strongly suggests, that in solution **1** and **6** are completely dissociated into telluronium cations and azide anions, since for covalently bound azides, three distinct ^{14}N resonances are observed.[17,18] The ^{125}Te NMR spectra show resonances at δ = 443 ppm (D_2O) and δ = 456 ppm ($CDCl_3$) for **1** and δ = 795 ppm ($CDCl_3$) for **6**, which, as expected, are very similar to the shifts of the starting materials $[(CH_3)_3Te]I$ [δ = 441 ppm (D_2O)] and $[(C_6H_5)_3Te]Cl$ [δ = 759 ppm ($CDCl_3$)], respectively. The corresponding triorganoselenonium azides are discrete ions in solution as well.[28]

For compounds **2−5**, **7**, and **8**, only minor variations of the ^{125}Te chemical shift are found, proving the negligible effect of the counterion on the telluronium cation in solution. This is consistent with the ^{125}Te NMR spectroscopic data of $[(C_6H_5)_3Te]_2[MCl_6]$ (M = Ir, Pt) and $[(C_6H_5)_3Te][AuCl_4]$.[19]

The ^{77}Se NMR shift of $[(CH_3)_3Te]SeCN$ (**4**) in D_2O is δ = −324 ppm, which is very similar to that of KSeCN in D_2O (δ = −340 ppm) and $[(CH_3)_3Se]SeCN$ [δ(SeCN) = −328 ppm],[28] but notably different to that of $[(C_6H_5)_3Te]SeCN$ (**7**) in $CDCl_3$ (δ = −144 ppm). This is believed to be mainly a solvent effect.[10] On going from cyanate **2** to thiocyanate **3** and selenocyanate **4**, the linewidth of the ^{14}N NMR resonance increases with the chemical shift. This reflects the change in electronegativity and shielding properties of the chalcogen atom in the chalcogenocyanate moiety.

An interesting temperature-dependent behavior is observed for the ^{13}C NMR resonance of $[(C_6H_5)_3Te][Ag(CN)_2]$ (**8**). At 25 °C, a single resonance at δ = 143 ppm is detected for the cyano resonance. Variable-temperature measurements of the ^{13}C NMR spectra of **8** between −100 °C and 60 °C in [D$_8$]THF show, that below 25 °C the CN resonance broadens, and at ca. −80 °C two resonances become visible (Figure 1a). Finally, at −100 °C, both the $^{1}J^{13}{}_{\mathrm{C-}}{}^{107}{}_{\mathrm{Ag}}$ (J = 183 Hz) and the $^{1}J^{13}{}_{\mathrm{C-}}{}^{109}{}_{\mathrm{Ag}}$ (J = 209 Hz) coupling is resolved (Figure 1b). A similar feature has been reported for $K[Ag(CN)_2]$ in DMF upon cooling below −50 °C.[29]

The coupling with silver isotopes ^{107}Ag (I = −1/2, 51.82%) and ^{109}Ag (I = −1/2, 48.18%)[30] can be observed only at low temperatures, often explained as a result of fast exchange mechanisms.[31−34] For **8**, the calculated ratio of the coupling constants 0.876 is very close to that predicted by the theoretical ratio of the gyromagnetic constants $\gamma^{107}{}_{\mathrm{Ag}}/\gamma^{109}{}_{\mathrm{Ag}} = 0.869$.

Crystal Structures

As indicated earlier, the crystal structures of $[Ph_3Te]X$ (X = OCN, SCN)[5−7] are known, but for X = N_3 (**6**) and X = SeCN (**7**) only powder diffraction data existed.[3] Hence, for all compounds described in the synthesis section, single-crystal structure determinations have been carried out. Our focus has been set especially on the interactions between the telluronium cations and the different anions, leading to an extended coordination sphere around the tellurium centre (Table 3). The concept of secondary interactions[14] also applies for telluronium compounds[5,6,19,35,36] and was subject to a detailed study.[15,16]

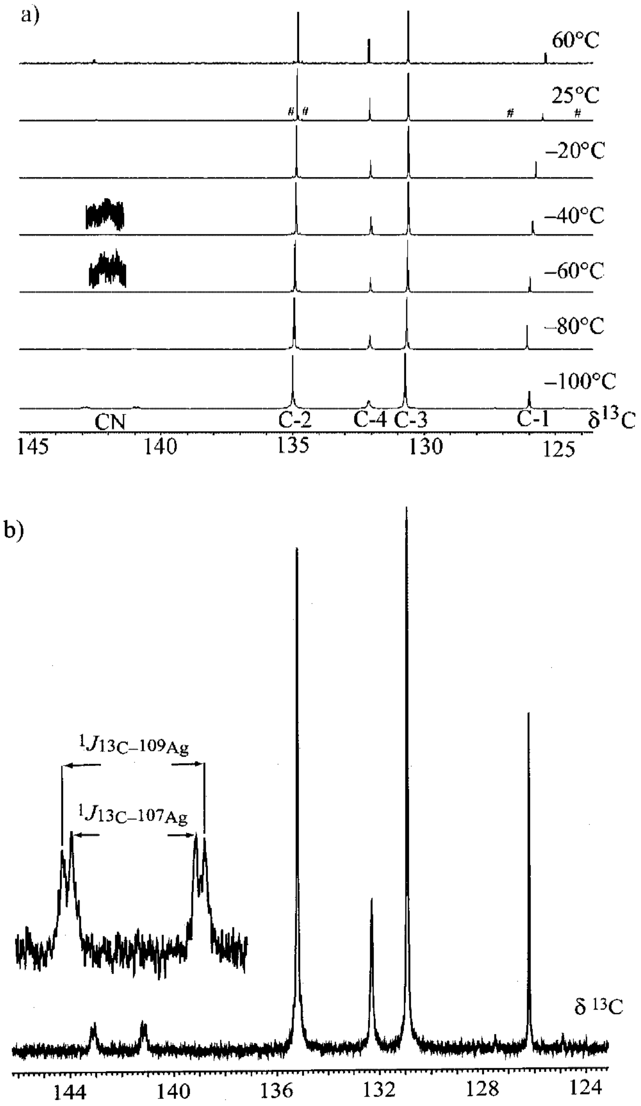

Figure 1: (a) Variable-temperature ^{13}C NMR spectra of [Ph$_3$Te][Ag(CN)$_2$] (**8**) in [D$_8$]THF; asterisks denoting ^{125}Te satellites; (b) ^{13}C NMR spectrum of **8** in [D$_8$]THF at −100 °C

In covalent tellurium azides, R$_2$Te(N$_3$)$_2$ and RTe(N$_3$)$_3$, including the free electron pair at the tellurium centre, hepta- and octacoordination of Te is found,[17,18] containing almost linear azide groups connected to the tellurium ion with Te−C bond lengths of ca. 2.2 Å. The interatomic Te···N distances are in the range of 2.7−3.5 Å.

In contrast, the structures of [(CH$_3$)$_3$Te]N$_3$ (**1**) (Figure 2) and [(C$_6$H$_5$)$_3$Te]N$_3$ (**6**) (Figure 3) show almost perfectly linear azide groups connected on both sides to different layers of telluronium cations. The azide **6** crystallizes as a chloroform solvate (see Table 4). In both azides **1** and **6**, the N−N bond lengths (1.15−1.18 Å) differ only slightly from each other. This is in agreement with the crystal structure of the azide anion in [(CH$_3$)$_4$N]N$_3$, and demonstrates the minor influence of the secondary bonds on the bonding situation of the azide group.[26] The average secondary bonding Te···N distances amount to 3.0 Å, which is well below the sum of the tellurium−nitrogen van der Waals radii (ΣvdWr Te−N 3.61 Å).[37] This leads mostly to a monocapped distorted octahedral AX$_3$Y$_3$E environment and a complex three-dimensional network of cations and anions (Figure 2).

The Te−C bond lengths for the telluronium cations [(CH$_3$)$_3$Te]$^+$ (in **1**−**5**) and [(C$_6$H$_5$)$_3$Te]$^+$ (in **6**−**8**) span ranges between 2.11 and 2.14 Å, and are together with the resulting bond angles in good agreement with those of [(CH$_3$)$_3$Te]I[38] and [(C$_6$H$_5$)$_3$Te]SCN.[7] Regarding only Te−C bonds, a typical AX$_3$E trigonal-pyramidal arrangement around the tellurium centre is formed.

Similarly, the C−N and C−O(S)(Se) bond lengths in the chalcogenocyanate anions of **2**−**4** and **7** exhibit only marginal deviations to those found in the potassium salts. The bond lengths of the cyanate anions in **2** [C−N 1.168(4) Å, C−O 1.217(4) Å] are very similar to those of [(C$_6$H$_5$)$_3$Te]OCN·1/2CHCl$_3$[5] and KOCN.[39] For [(CH$_3$)$_3$Te]SCN (**3**), the distances are very similar, the C−N [1.143(8) Å] and C−S [1.662(5) Å] bonds being negligibly shortened when compared to KSCN [C−N 1.15(1) Å, C−S 1.69(1) Å].[40] The selenocyanate ions in **4** [C−N 1.146(7) Å, C−Se 1.816(5) Å] and **7** [C−N 1.142(8)/1.148(6) Å, C−Se 1.804(5)/1.817(6) Å] feature bond lengths, which also cannot be considered significantly different from those in KSeCN.[41] As discussed for AgSeCN,[42] this is in agreement with a slightly elongated C−N triple bond and a C−Se bond with minor multiple bond contribution.

Table 3. Summary of Te···X interactions [Å]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Te···N	2.938(4) 3.006(4) 3.032(3) 3.018(5) 3.037(3)	2.983(3) 3.103(3)	3.185(3)	3.252(4)	3.154(5) 3.270(5) 3.407(6)	2.772(4) 2.867(4) 2.946(4) 3.000(4) 3.027(4)	3.122(5)	3.162(4) 3.346(5) 3.501(5)
Te···O		3.095(2)						
Te···S			3.390(1) 3.488(1)					
Te···Se				3.4712(5) 3.5534(6)			3.4424(6) 3.5413(6)	

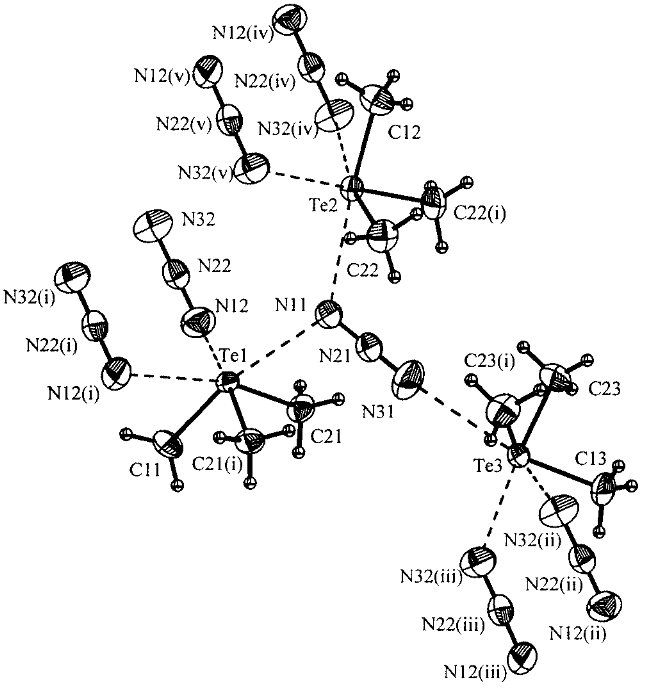

Figure 2. ORTEP plot of **1**; selected bond lengths [Å] and angles [°]: N12−N22 1.164(4), N22−N32 1.173(4), Te1−C11 2.112(4), Te1−C21 2.114(3), Te2−C12 2.143(5), Te2−C22 2.122(3), Te3−C13 2.107(5), Te3−C23 2.111(3), Te1···N11 3.006(4), Te1···N12 3.032(3), Te2···N11 2.938(4), Te3···N31 3.018(5), Te3···N32(*ii*) 3.037(3), N12−N22−N32 179.3(4), C11−Te1−C21 93.9(1); with *i* = *x*, 1/2 − *y*, *z*; *ii* = 1 + *x*, *y*, *z*; *iii* = 1 + *x*, 1/2 − *y*, *z*; *iv* = −*x*, −*y*, −*z*; *v* = −*x*, 1/2 + *y*, −*z*

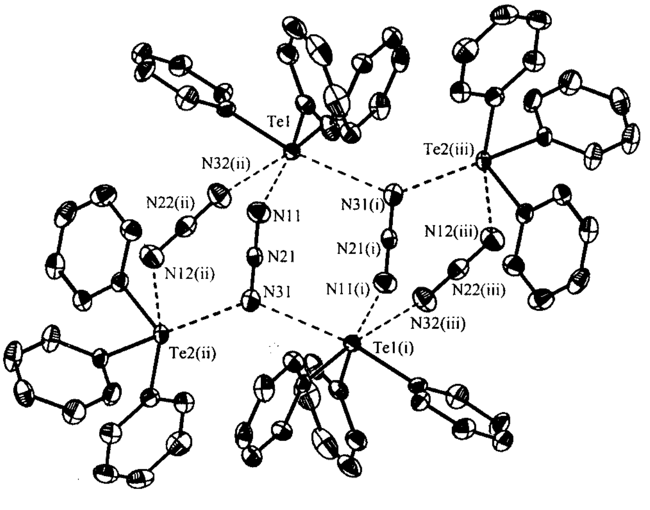

Figure 3. ORTEP plot of **6**; solvate molecules and H atoms omitted for clarity; selected bond lengths [Å] and angles [°]: Te−C 2.121(4)−2.146(4), N11−N21 1.181(5), N21−N31 1.161(5), N12(*ii*)−N22(*ii*) 1.184(5), N22(*ii*)−N32(*ii*) 1.170(5), Te1···N11 2.867(4), Te2(*ii*)···N12(*ii*) 2.772(4), Te2(*ii*)···N31 3.027(4), C−Te−C 92.6(2)−98.8(2), N11(*ii*)−N21(*ii*)−N31(*ii*) 179.6(5), N12−N22−N32 179.1(5); with *i* = −*x*, −*y*, 1 − *z*; *ii* = −1 + *x*, *y*, *z*; *iii* = 1

For compounds **2−4** and **7** (Figure 4−7), similar network-like structures as for the azides **1** and **6** exist. Distorted monocapped octahedral AX_3Y_3E environments indicate secondary bonding between cations and anions as well. An analogous structure was reported for β-[$TeCl_3$][$AlCl_4$], considering primary Te−Cl and secondary Te···Cl bonds.[15] As chalcogenocyanates are ambidentate ligands, it is of interest, whether Te···X [X = O, S, Se; ΣvdWr TeO(S)(Se) 3.58, 3.86, 3.96 Å)], or Te···N contacts or both are preferred. The crystal structures show, that Te···N as well as Te···X coordination is present. Compounds **3**, **4** and **7** exhibit two Te···S(Se) and one Te···N contact each, **3** and **4** crystallize isotypically. The cyanate ion in **2**, which has the oxygen atom as its "hard end", shows an inverted situation. This can be explained according to the HSAB concept,[43,44] considering a telluronium cation as a rather weak acid, preferring coordination to the softer ends of the particular anions. In the solid state the N···Te contacts in **2−4**

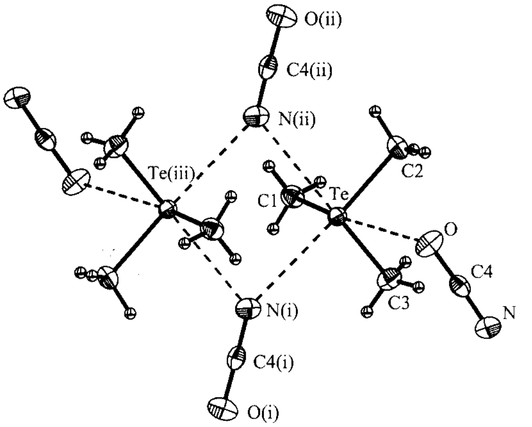

Figure 4. ORTEP plot of **2**; selected bond lengths [Å] and angles [°]: Te−C1 2.113(3), Te−C2 2.121(3), Te−C3 2.110(3), O−C4 1.217(4), N−C4 1.168(4), Te···O 3.095(2), Te···N(*i*) 2.983(3), Te···N(*ii*) 3.103(3), C1−Te−C2 94.8(1), C3−Te−C1 93.3(1), C3−Te−C 2 95.4(1), N−C4−O 178.5(3), Te···N(*i*)···Te(*iii*) 83.14(7), N(*i*)···Te···N(*ii*) 96.86(7); with *i* = 11/2 − *x*, *y* − 1/2, −1/2 − *z*; *ii* = *x* − 1/2, 1/2 − *y*, 1/2 + *z*; *iii* = 1 − *x*, −*y*, −*z*

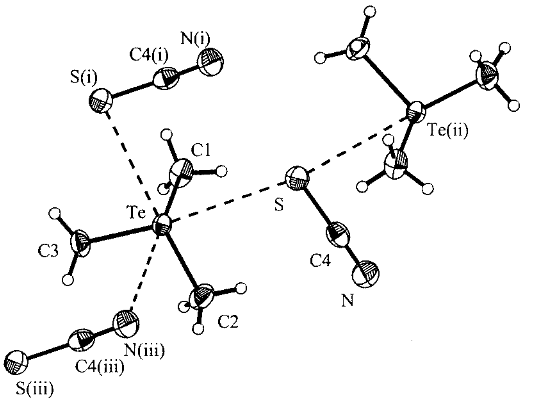

Figure 5. ORTEP plot of **3**; selected bond lengths [Å] and angles [°]: Te−C1 2.115(3), Te−C2 2.113(4), Te−C3 2.120(3), Te···S 3.488(1), Te···S(*i*) 3.390(1), Te(*ii*)···S 3.390(1), Te···N(*iii*) 3.185(3), S−C4 1.662(5), N−C4 1.143(8), C1−Te−C3 92.7(2), C2−Te−C1 93.7(2), C2−Te−C3 96.7(2), N−C4−S 178.5(4), Te···S···Te(*ii*)···167.83(3); with *i* = 1 − *x*, 1 − *y*, 1/2 + *z*; *ii* = 1 − *x*, 1 − *y*, *z* − 1/2; *iii* = 1 − *x* + 1/2, 2 − *y*, 1/2 + *z*

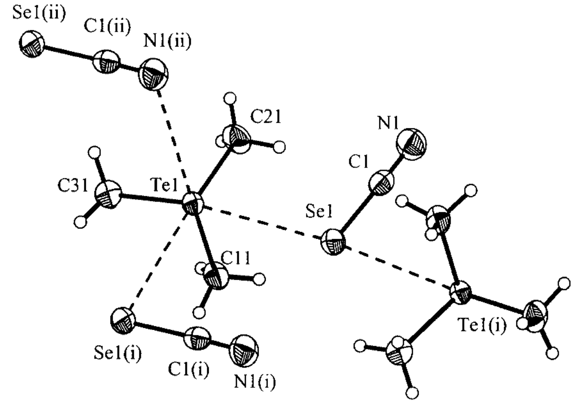

Figure 6. ORTEP plot of **4**; selected bond lengths [Å] and angles [°]: Te1−C11 2.107(3), Te1−C21 2.124(4), Te1−C31 2.121(4), C1−N1 1.146(7), Se1−C1 1.816(5), Te1···N1(*ii*) 3.252(4), Te1···Se1 3.5534(6), Te1···Se1(*i*) 3.4712(5), C11−Te1−C21 93.5(2), C11−Te1−C31 93.3(2), C31−Te1−C21 96.6(2), N1−C1−Se1 178.0(4); with *i* = 1 − *x*, 1 − *y*, −1/2 + *z*; *ii* = 1 − *x*, −*y*, −1/2 + *z*; *iii* = 1 − *x*, 1 − *y*, 1/2 + *z*

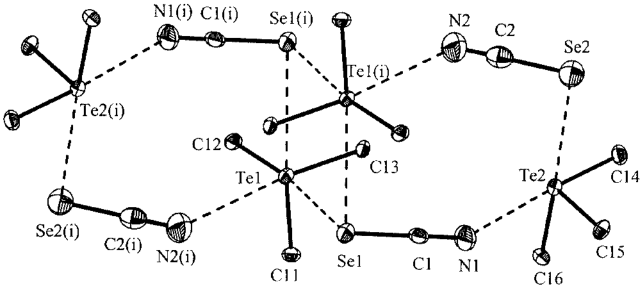

Figure 7. ORTEP plot of **7**; only *Te*-bonded atoms of phenyl groups shown; selected bond lengths [Å] and angles [°]: Te1−C11 2.126(5), Te1−C12 2.139(5), Te1−C13 2.137(4), Te2−C14 2.128(5), Te2−C15 2.120(5), Te2−C16 2.128(5), N1−C1 1.148(6), N2−C2 1.142(8), Se1−C1 1.804(5), Se2−C2 1.817(6), Te1···N2(*i*) 3.122(5), Te2···N1 2.810(5), Te1···Se1 3.4424(6), Te1···Se1(*i*) 3.5413(6), Te2···Se2 3.4321(7), C11−Te1−C12 94.8(2), C11−Te1−C13 93.4(2), C13−Te1−C12 99.9(2), C14−Te2−C15 97.5(2), C14−Te2−C16 94.8(2), C15−Te2−C16 95.3(2), N2−C2−Se2 179.2(6), N1−C1−Se1 177.6(5); with *i* = 1 − *x*, −*y*, 1 − *z*

and in **7** are always shorter than the Te···O/S/Se contacts. The latter have approximately the same distance as reported for Te···Se contacts in $[R_3Te][SeR]$.[36] The coordination sphere of azide **1**, and the other pseudohalides **2−4** and **7** are very similar, with all anions being threefold coordinated (e.g. in **1**: Te1···N11, Te2···N11, Te3···N31 (Figure 2)].

The crystal structures of the dicyanoargentates $[(CH_3)_3Te][Ag(CN)_2]$ (**5**) and $[(C_6H_5)_3Te][Ag(CN)_2]$ (**8**) contain short Ag···Ag contacts that account for 3.167 Å and 2.985 Å, respectively, which is at the lower distance limit of known Ag···Ag contacts (2.99−4.2 Å),[45−47] but no significant effect on the bonding parameters of both the telluronium cation and the dicyanoargentate anion are found. The rod-like dicyanoargentate anions are able to mediate interactions between ions in the crystal which are far away from each other. In the structure of the methyl derivative **5** (Figure 8), infinite chains of two crystallographically independent perfectly linear $[Ag(CN)_2]^-$ ions (C−Ag−C 180°) are oriented staggered in an angle of 75° to each other, alternately coordinated to telluronium cations. In the phenyl derivative **8**, the corresponding angle is 84° (Figure 9). The coordination sphere around tellurium consists of two shorter and one longer Te···N contacts, the latter being only 0.1 Å below the sum of the van der Waals radii of Te−N 3.61 Å. This again can be regarded as a distorted monocapped octahedral AX_3Y_3E arrangement.

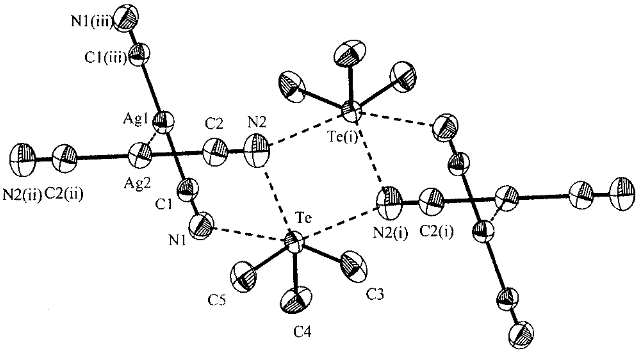

Figure 8. ORTEP plot of **5**; selected bond lengths [Å] and angles [°]: Te−C3 2.102(5), Te−C4 2.100(5), Te−C5 2.109(6), C1−N1 1.098(6), C2−N2 1.143(7), Ag1−C1 2.074(5), Ag2−C2 2.055(6), Te···N1 3.270(5), Te···N2 3.407(6), Te···N2(*i*) 3.154(5), Ag1···Ag2 3.1670(3), C4−Te−C3 95.9(2), C4−Te−C5 95.1(3), C3−Te−C5 93.6(3), C1−Ag1−C1(*iii*) 180.000(1), C2−Ag2−C2(*ii*) 180.000(1), N1−C1−Ag1 178.3(5), N2−C2−Ag2 178.6(5), C1−Ag1−Ag2−C2 −74.9(2); with *i* = −*x*, −*y*, 1 − *z*; *ii* = 1 − *x*, −*y*, 2 − *z*; *iii* = −*x*, −*y*, 2 − *z*

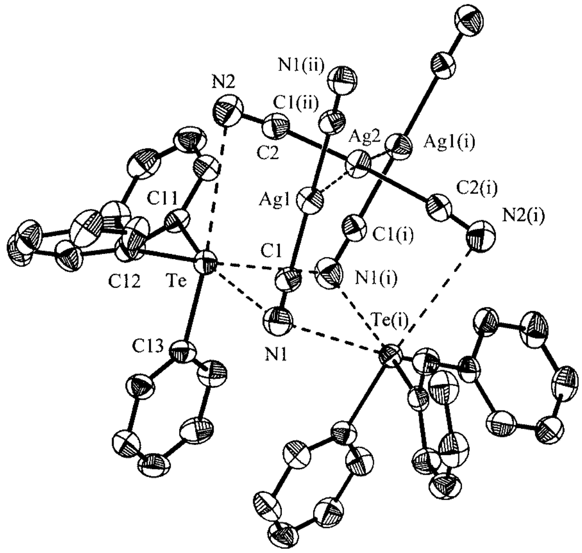

Figure 9. ORTEP plot of **8**; selected bond lengths [Å] and angles [°]: Te−C11 2.119(5), Te−C12 2.121(5), Te−C13 2.120(5), N1−C1 1.142(6), N2−C2 1.138(7), Ag1−C1 2.055(5), Ag2−C2 2.069(6), Te···N1 3.346(5), Te1···N1(*i*) 3.162(4), Te···N2 3.501(5), Ag1···Ag2 2.9847(1), C11−Te−C13 94.4(2), C11−Te−C12 99.5(2), C13−Te−C12 96.0(2), N1−C1−Ag1 174.8(5), N2−C2−Ag2 173.7(5), C1−Ag1−C1(*ii*), 180.0, C2−Ag2−C2(*i*) 175.9(3), Te−N1−Te(*i*) 92.8(1) Ag1−Ag2−Ag1(i) 170.63(2), C1−Ag1−Ag2−C2 91.6(2); with *i* = 1 − *x*, *y*, 1/2 − *z*; *ii* = 1 − *x*, 1 − *y*, 1 − *z*

Conclusion

The syntheses, spectroscopic, and structural studies of triorganotelluronium azides, pseudohalides, and dicyanoargentates have been described. Multinuclear NMR spectroscopy established that total dissociation occurs in solution. Variable-temperature ^{13}C NMR studies of the $[Ag(CN)_2]^-$ ion in solution revealed discrete couplings of ^{13}C to both silver isotopes (^{107}Ag and ^{109}Ag). In the crystal structures of all compounds, secondary interactions, Te···N(O)(S)(Se), are present between cations and anions.

Experimental Section

General Remarks: Commercially available chemicals ($TeCl_4$, 1.6 M MeLi in diethyl ether, 1.8 M PhLi in cyclohexane/diethyl ether) were used without further purification. The silver salts AgX (X = N_3, OCN, SCN, SeCN) were obtained by precipitation of aqueous solutions of silver nitrate with the corresponding Na/K pseudohalides. $[Me_3Te]I$ was prepared according to a standard procedure,[20,48] $[Ph_3Te]Cl$ by a similar reaction or according to ref.[21] IR: Perkin−Elmer Spektrum One FT-IR or Nicolet 520 FT-IR Spektrometer (as KBr pellets or between KBr plates). Raman: Perkin−Elmer Spectrum 2000 NIR FT-Raman (Nd:YAG laser, 1064 nm, 200 mW). NMR spectroscopy: JEOL Eclipse 400 and EX400 instruments; chemical shifts are reported with respect to $(CH_3)_4Si$ (^{1}H, 399.8 MHz; ^{13}C, 100.5 MHz), CH_3NO_2 (^{14}N, 28.9 MHz), $(CH_3)_2Se$ (^{77}Se, 76.3 MHz), aqueous $AgNO_3$ (^{109}Ag, 18.6 MHz), $(CH_3)_2Te$ (^{125}Te, 126.1 MHz). The ^{77}Se and ^{125}Te spectra were recorded at 25 °C. All chemical shifts are presented in Table 2. MS: JEOL MStation JMS 700 Spektrometer. Multi-isotope containing fragments refer to the isotope with the highest natural abundance (for example ^{130}Te). The FAB mass spectra were recorded using 3-nitrobenzyl alcohol (NBA) as matrix. Elemental analyses: in-house.

X-ray Crystallography: For compounds **1**−**4** and **8** a Nonius Kappa CCD, and for **5**−**7** a STOE IPDS area detector device was employed for data collection using Mo-K_α radiation. All structures were solved by direct methods using SIR97[49] (**1**−**4**, **7**, **8**) and SHELXS (**5**, **6**) and refined by means of the full-matrix least-squares procedures using SHELXL-97[50] (Table 4). CCDC-184294 (**1**), -184288 (**2**), -184289 (**3**), -184293 (**4**), -184290 (**5**), -184295 (**6**), -184291 (**7**) and -184292 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

CAUTION! Silver azide is potentially explosive. This necessitates meticulous safety precautions during its preparation and handling. Although both azides **1** and **6** reported in this section are ionic, they do exhibit a noticeable fizzling when exposed to heat!

Trimethyltelluronium Azide, $[Me_3Te]N_3$ (1): Into a solution of 3 mmol of trimethyltelluronium iodide in 40 mL of H_2O, was added 4.2 mmol of moist AgN_3 in one portion. After stirring for 4 h at ambient temperature, the mixture was filtered and the solvent removed from the filtrate in vacuo. After recrystallization from ethanol/diethyl ether, **1** was obtained as colorless, hygroscopic powder (84%), m.p. 110 °C. IR (KBr): $\tilde{\nu}$ = 3009 s, 2027 vs/1998 s ($\nu_{as}N_3$), 1416 m, 1376 m, 1216 w, 1115 vs, 1054 s, 906 s, 618 s, 594 w, 543 m, 439 w cm^{-1}. Raman: $\tilde{\nu}$ = 3023 (5), 2924 (20), 1999 (5, $\nu_{as}N_3$), 1990 (5), 1414 (5), 1323 (35, ν_sN_3), 1225 (5), 1042 (5), 546 (100), 528 (90), 226 (10), 135 (25) cm^{-1}. FAB$^+$ MS: *m*/*z* (%) = 328 (10) $[Me_3Te^+ + NBA]$, 175 (100) $[Me_3Te^+]$. $C_3H_9N_3Te$ (214.72): calcd. C 16.8, H 4.2, N 19.6; found C 16.5, H 4.1, N 18.3.

Trimethyltelluronium Cyanate, $[Me_3Te]OCN$ (2): Into a solution of 1 mmol of trimethyltelluronium iodide in 50 mL of H_2O, was added

Table 4. Crystal data and structure refinements

	1	**2**	**3**[a]	**4**[b]	**5**	2(**6**·$CHCl_3$)[c]	**7**	**8**
Empirical formula	$C_3H_9N_3Te$	C_4H_9NOTe	C_4H_9NSTe	C_4H_9NSeTe	$C_5H_9AgN_2Te$	$C_{37}H_{31}Cl_3N_6Te_2$	$C_{19}H_{15}NSeTe$	$C_{21}H_{16}AgCl_3N_2Te$
Formula mass	214.72	214.72	230.79	277.68	332.61	921.23	463.89	638.19
Temperature [K]	200(2)	200(2)	200(2)	200(2)	200(2)	200(3)	200(2)	200(2)
Crystal size [mm]	0.56 × 0.24 × 0.20	0.17 × 0.15 × 0.07	0.24 × 0.11 × 0.09	0.16 × 0.10 × 0.02	0.36 × 0.18 × 0.06	0.18 × 0.18 × 0.08	0.33 × 0.26 × 0.20	0.31 × 0.17 × 0.13
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic	orthorhombic	orthorhombic
Space group	*Pnma*	$P2_1/n$	$Pna2_1$	$Pna2_1$	$P2_1/n$	$P\bar{1}$	*Pbca*	*Pbcn*
a [Å]	11.2220(1)	6.5637(2)	11.5352(3)	11.6595(2)	6.3340(6)	12.1279(9)	15.7423(9)	31.0459(5)
b [Å]	9.7746(1)	10.6046(3)	6.5142(2)	6.6326(1)	15.331(1)	12.620(1)	20.363(1)	12.4486(2)
c [Å]	19.2919(3)	9.6477(3)	10.0654(2)	10.1745(2)	9.622(1)	13.648(1)	21.668(1)	11.8989(2)
β [°]	90	93.288(1)	90	90	98.79(1)	114.408(9)	90	90
V [Å^3]	2116.14(4)	670.43(3)	756.34(3)	786.82(2)	923.4(2)	1856.0(3)	6945.8(7)	4598.7(1)
Z	12	4	4	4	4	2	16	8
$\rho_{calcd.}$ [g cm^{-3}]	2.022	2.127	2.027	2.344	2.393	1.649	1.774	1.844
μ [mm^{-1}]	4.116	4.334	4.106	8.307	5.208	1.823	3.805	2.478
$F(000)$	1200	400	432	504	608	900	3552	2448
θ range [°]	3.5−27.5	3.65−23.99	3.53−30.03	3.5−27.5	2.52−24.00	2.14−28.0	1.89−24.0	3.27−24.0
Index ranges	$-14 \le h \le 14$ $-12 \le k \le \le 12$ $-24 \le l \le 25$	$-7 \le h \le 7$ $-12 \le k \le 12$ $-11 \le l \le 10$	$-15 \le h \le 16$ $-9 \le k \le 9$ $-14 \le l \le 14$	$-15 \le h \le 15$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-7 \le h \le 7$ $-16 \le k \le 17$ $-11 \le l \le 11$	$-14 \le h \le 14$ $-16 \le k \le 16$ $-17 \le l \le 17$	$-18 \le h \le 18$ $-23 \le k \le 23$ $-24 \le l \le 24$	$-33 \le h \le 35$ $-14 \le k \le 12$ $-13 \le l \le 10$
Reflections collected	28232	6166	7241	15675	5065	16215	42898	23151
Reflections unique	2569 (R_{int} = 0.0714)	1054 (R_{int} = 0.0422)	2203 (R_{int} = 0.0526)	1808 (R_{int} = 0.0524)	1379 (R_{int} = 0.0426)	8276 (R_{int} = 0.0470)	5451 (R_{int} = 0.0718)	3607 (R_{int} = 0.0667)
$R1$, $wR2$ (2σ data)	0.0250, 0.0580	0.0155, 0.0353	0.0251, 0.0521	0.0213, 0.0442	0.0199, 0.0406	0.0338, 0.0607	0.0277, 0.0596	0.0355, 0.0794
$R1$, $wR2$ (all data)	0.0282, 0.0595	0.0177, 0.0359	0.0333, 0.0546	0.0235, 0.0455	0.0302, 0.0420	0.0673, 0.0663	0.0454, 0.0624	0.0570, 0.0893
Max./min. transm.	0.4377/0.2811	0.7464/0.4819	0.7109/0.4377	0.8184/0.2956	0.7469/0.3413	0.9017/0.7383	0.5321/0.4589	0.7628/0.5196
Data/restr./param.	2569/0/116	1054/0/101	2203/1/65	1808/1/64	1379/0/85	8276/0/557	5451/0/397	3607/0/255
GOOF on F^2	1.153	1.120	1.056	1.071	0.965	0.831	0.938	1.061
Larg. diff. peak/hole [e/Å^3]	0.906/−1.086	0.749/−0.494	1.133/−0.805	0.765/−0.415	0.476/−0.572	0.559/−0.633	0.530/−1.130	0.832/−0.746

[a] Flack parameter: −0.01(3). [b] Racemic twin, volume fraction from refinement: 0.40(1). [c] Compound **6**: α = 95.58(1)°, γ = 97.96(1)°.

2 mmol of freshly precipitated AgOCN in one portion. After stirring for 1 d at ambient temperature, the mixture was filtered and the solvent removed from the filtrate in vacuo. After recrystallization from ethanol/diethyl ether, **2** was obtained as colorless powder (93%), m.p. 141 °C. IR (KBr): $\tilde{\nu}$ = 3011 m, 2916 w, 2170 vs/2138 s/2113 m (ν_{as}OCN), 1414 s, 1318 w, 1301 s, 1288 s, 1269 w, 1249 m, 1237 m, 1224 w, 1206 vs, 1185 w, 907 vs, 900 vs, 831 m, 822 m, 662 w, 638 s, 628 s, 623 s, 580 w, 546 s, 537 s cm^{-1}. Raman: $\tilde{\nu}$ = 3025 (15), 2930 (35), 2135 (20, ν_{as}OCN), 1428 (5), 1290 (15), 1203 (10), 551 (85), 540 (100), 234 (15) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 328 (10) [Me_3Te^+ + NBA], 175 (100) [Me_3Te^+]. C_4H_9NOTe (214.72): calcd. C 22.1, H 4.2, N 6.5; found C 22.4, H 4.2, N 6.5.

Trimethyltelluronium Thiocyanate, [Me_3Te]SCN (3): Into a solution of 1 mmol of trimethyltelluronium iodide in 15 mL of H_2O, was added 2 mmol of freshly precipitated AgSCN in one portion. After stirring for 4 h at ambient temperature, the mixture was filtered and the solvent removed from the filtrate in vacuo. After recrystallization from ethanol/diethyl ether, **3** was obtained as colorless powder (89%), m.p. 86−88 °C. IR (KBr): $\tilde{\nu}$ = 3004 m, 2916 w, 2076 s/2058 vs (ν_{as}SCN), 1793 w, 1759 w, 1631 m, 1515 w, 1412 s, 1385 m, 1262 m, 1251 m, 1228 m, 1214 s, 1096 m, 1022 m, 937 m, 925 m, 894 vs, 822 m, 804 m, 730 s, 544 s, 534 s, 468 m, 463 m cm^{-1}. Raman: $\tilde{\nu}$ = 3018 (5), 2936 (5), 2058 (30, ν_{as}SCN), 1405 (5), 1251 (5), 1232 (5), 1216 (5), 932 (10), 732 (10), 545 (100), 534 (98), 215 (10), 112 (10) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 328 (10) [Me_3Te^+ + NBA], 175 (100) [Me_3Te^+]. C_4H_9NSTe (230.79): calcd. C 20.8, H 3.9, N 6.1, S 13.9; found C 20.7, H 4.0, N 5.9, S 13.2.

Trimethyltelluronium Selenocyanate, [Me_3Te]SeCN (4): Into a solution of 1 mmol of trimethyltelluronium iodide in 100 mL of H_2O, was added 2 mmol of freshly precipitated AgSeCN in one portion. After stirring for 8 h at ambient temperature, the mixture was filtered and the solvent removed from the filtrate in vacuo. After recrystallization from methanol/chloroform/diethyl ether, **4** was obtained as slightly pinkish powder (58%), m.p. 106−109 °C. IR (KBr): $\tilde{\nu}$ = 3421 (br), 3011 m, 2065 vs/2018 m (ν_{as}SeCN), 1757 w, 1640 w, 1503 w, 1409 s, 1385 m, 1249 m, 1226 m, 1215 s, 890 vs, 826 w, 816 m, 540 s, 530 s, 414 m cm^{-1}. Raman: $\tilde{\nu}$ = 3014 (5), 2918 (15), 2065 (40, ν_{as}SeCN), 1217 (5), 542 (85), 531 (100), 227 (br, 10), 120 (br, 5) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 328 (10) [Me_3Te^+ + NBA], 175 (100) [Me_3Te]$^+$. C_4H_9NSeTe (277.68): calcd. C 17.3, H 3.2, N 5.0; found C 17.5, H 3.3, N 4.9.

Trimethyltelluronium Dicyanoargentate, [Me_3Te][$Ag(CN)_2$] (5): Into a solution of 1 mmol of trimethyltelluronium iodide in 100 mL of H_2O, was added 2 mmol of AgCN in one portion. After stirring for 20 h at 50 °C, the mixture was filtered and the solvent removed from the filtrate in vacuo; **5** was obtained as slightly grayish crystals (85%), m.p. 118−122 °C. IR (KBr): $\tilde{\nu}$ = 3007 m, 2962 m, 2929 m, 2873 m, 2135 s/2126 s (νCN), 1728 m, 1563 m, 1416 m, 1290 m, 1251 m, 1222 m, 1125 w, 898 s, 832 m, 550 m, 537 m, 391 s cm^{-1}. Raman: $\tilde{\nu}$ = 3027 (20), 2932 (50), 2132 (70, νCN), 1412 (10), 1226 (10), 550 (90), 540 (100), 213 (30) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 328 (10) [Me_3Te^+ + NBA], 175 (100) [Me_3Te]$^+$. FAB$^-$ MS: *m/z* (%) = 427 [$Ag_3(CN)_4^-$], 292 [$Ag_2(CN)_3^-$], 159 [$Ag(CN)_2^-$]. $C_5H_9AgN_2Te$ (332.6): calcd. C 18.1, H 2.7, N 8.4; found C 20.9, H 3.1, N 7.6.

Triphenyltelluronium Azide, [Ph_3Te]N_3 (6): Into a solution of 2.5 mmol of triphenyltelluronium chloride in 50 mL of chloroform, was poured in one portion a solution of 20 mmol of NaN_3 in 50 mL H_2O. After stirring for 45 min at ambient temperature, the chloroform extract was separated and dried with anhydrous $MgSO_4$. After removal of the solvent, recrystallization from chloroform or 2-propanol yielded **6** as colorless crystals (82%), m.p. 155 °C (ref.[4] 155.5−156.5 °C). IR (KBr): $\tilde{\nu}$ = 3293 w, 3051 w, 2017 vs/1993 s ($\nu_{as}N_3$), 1572 w, 1478 w, 1434 w, 1182 w, 1055 w, 996 w, 735 m, 688 w cm^{-1}. Raman: $\tilde{\nu}$ = 3145 (10), 3058 (70), 1989 (25, $\nu_{as}N_3$), 1574 (35), 1478 (10), 1328 (40), 1240 (5), 1188 (10), 1160 (10), 1056 (15), 1020 (55), 1001 (100), 655 (50), 614 (10), 464 (5), 365 (10), 284 (45), 269 (40), 258 (70), 233 (40), 134 (70) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 361 (100) [Ph_3Te^+], 284 (10) [Ph_2Te^+], 207 (5) [$PhTe^+$]. $C_{18}H_{15}N_3Te \cdot 1/2CHCl_3$ (460.62): calcd. C 48.2, H 3.4, N 9.1, Cl 11.6; found C 48.7, H 3.4, N 9.0, Cl 11.3.

Triphenyltelluronium Selenocyanate, [Ph_3Te]SeCN (7): Into a solution of 0.5 mmol of triphenyltelluronium chloride in 10 mL of H_2O, was added 1 mL of a hot aqueous solution of 2 mmol of KSeCN in one portion. After stirring for 15 min at 50 °C, filtration of the residue and subsequent rinsing with diethyl ether yielded **7** as a colorless powder (98%), m.p. 164.5−165.5 °C (ref.[4] 164.5−165.5 °C). IR (KBr): $\tilde{\nu}$ = 3048 w, 2960 m, 2077 vs/2062 vs (ν_{as}SeCN), 1572 m, 1477 s, 1436 vs, 1331 w, 1313 w, 1262 s, 1180 w, 1160 w, 1096 vs, 1064 s, 1056 s, 1017 vs, 995 s, 802 vs, 746 s, 730 vs, 685 s, 467 m, 452 m, 403 m cm^{-1}. Raman: $\tilde{\nu}$ = 3142 (10), 3053 (8), 2079 (75, ν_{as}SeCN), 1574 (35), 1479 (10), 1332 (40), 1271 (5), 1188 (10), 1162 (10), 1056 (15), 1020 (55), 1000 (100), 657 (50), 613 (10), 570 (5), 550 (5), 470 (5), 452 (5), 281 (95), 270 (60), 255 (90), 228 (75), 179 (30), 117 (45) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 361 (100) [Ph_3Te^+], 284 (10) [Ph_2Te^+], 207 (5) [$PhTe^+$]. $C_{19}H_{15}NSeTe$ (463.89): calcd. C 49.2, H 3.3, N 3.0; found C 49.0, H 3.2, N 3.0.

Triphenyltelluronium Dicyanoargentate, [Ph_3Te][$Ag(CN)_2$] (8): Into a solution of 1 mmol of triphenyltelluronium chloride in 40 mL of H_2O, was added 1.5 mmol of KI in one portion. The resulting precipitate was collected and washed with water and diethyl ether. To a suspension of this precipitate in 50 mL of H_2O was added 2 mmol of AgCN. After stirring for 20 h at 50 °C, the mixture was filtered and the solvent removed from the filtrate in vacuo. Recrystallization from chloroform/hexane yielded **8** as colorless crystals (42%), m.p. 130−132 °C. IR (KBr): $\tilde{\nu}$ = 3055 w, 2921 w, 2126 s/1999 s (νCN), 1573 s, 1477 w, 1436 s, 1384 m, 1250 m, 1182 w, 1149 w, 1042 m, 1016 s, 994 s, 958 s, 915 m, 817 s, 732 s, 6685 s, 649 s, 502 m cm^{-1}. Raman: $\tilde{\nu}$ = 3056 (55), 2135 (30), 1575 (40), 1020 (45), 1000 (100), 658 (55), 613 (20), 263 (50), 231 (50) cm^{-1}. FAB$^+$ MS: *m/z* (%) = 361 (100) [Ph_3Te^+], 284 (10) [Ph_2Te^+], 207 (5) [$PhTe^+$]. FAB$^-$ MS: *m/z* (%) = 427 [$Ag_3(CN)_4^-$], 292 [$Ag_2(CN)_3^-$], 159 [$Ag(CN)_2^-$].

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