1,2-Dichalcogenolylium Ions $(C_3Cl_3E_3)^+$ from Equilibria Involving Dichalcogen Dichlorides E_2Cl_2 (E = S, Se, Te) − Syntheses and Crystal Structures of $(C_3Cl_3S_2)Cl$, $(C_3Cl_3Se_2)Cl$, and $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$

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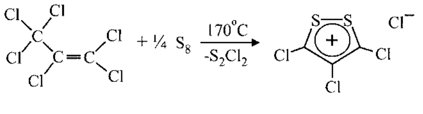
The reaction of tetrachlorocyclopropene with $SeCl_4$ or $TeCl_4$ in CH_2Cl_2 under solvothermal conditions at 120 °C and 90 °C, respectively, is a suitable route to 1,2-dichalcogenolylium ions. Yellow crystals of $(C_3Cl_3Se_2)^+Cl^-$ or red crystals of $\{(C_3Cl_3Te_2)^+\}_2[Te_2Cl_{10}]^{2-}$ are formed in such reactions. The reaction of hexachloropropene with elemental sulfur — the well-known route to 3,4,5-trichloro-1,2-dithiolylium chloride $(C_3Cl_3S_2)Cl$ — turned out not to be transferable to selenium and tellurium chemistry. NMR investigations of the reaction solutions allowed to set up reaction equilibria also involving hexachloropropene and dichalcogen dichlorides E_2Cl_2. The crystal structures of all three compounds were determined by X-ray diffraction. All contain planar, five-membered ring shaped cations $(C_3Cl_3E_2)^+$ (E = S, Se, Te). Short E–E bonds (S–S 201, Se–Se 231, Te–Te 266 pm) indicate substantial π-bonding and charge delocalisation. The anion in $(C_3Cl_3Te_2)_2$-$[Te_2Cl_{10}]$ consists of two tetragonal pyramidal $[TeCl_5]^-$ units linked by long Te–Cl bridges to centrosymmetric dimers in the form of edge-sharing double octahedra.

Introduction

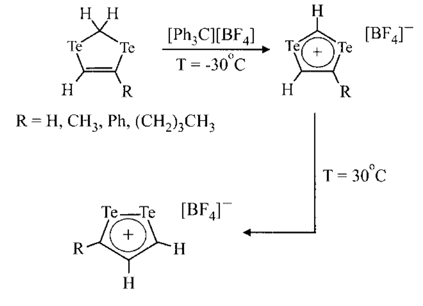
The 1,2-dithiolylium ion is a well-known aromatic planar five-membered ring system. Molecular orbital calculations were carried out on the unsubstituted 1,2-dithiolylium ion by Bergson,[1] and these showed that one 3p electron pair of each sulfur atom is involved in a 6π-electron aromatic system.

Syntheses leading to a variety of differently substituted 1,2-dithiolylium ions have been developed. The reaction of hexachloropropene with sulfur at 160 °C was described by Boberg[2] to yield 3,4,5-trichloro-1,2-dithiolylium chloride (Scheme 1), a stable yellow solid with a decomposition temperature of 235 °C but unknown crystal structure.



Scheme 1. Synthesis of 1,2-dithiolium chloride from hexachloropropene and sulfur

Although a lot of stable 1,2-dithiolylium salts are known much less work has been done on the respective 1,2-ditellurolylium ions. Bender et al. obtained the unsubstituted 1,3-ditellurolylium ion $(C_3H_3Te_2)^+$ by oxidation of 1,3-ditellurol at low temperatures.[3] NMR studies at ambient temperature indicated a rapid rearrangement to the 1,2-ditellurolylium ion (Scheme 2). Alkyl or aryl substituents caused an acceleration of the rearrangement from 1,3- to 1,2-ditelluroles with the consequence that the intermediate 1,3-ditellurolylium ions could not be detected on the NMR time scale. The 1,2-ditellurolylium ion was supposed to be planar with a delocalized positive charge. Above room temperature rapid decomposition with precipitation of tellurium occurs for solutions containing alkyl- or aryl-substituted $(C_3R_3Te_2)^+$ ions. No reports on 1,2-diselenolylium ions have been published.



Scheme 2. Synthesis of 1,3-ditellurolylium salts by oxidation of 1,3-ditelluroles, and their rearrangement to 1,2-ditellurolylium salts

In our studies on the reactivity of tetrachlorocyclopropene toward Lewis acidic metal halides we discovered a straightforward method for the synthesis of 1,2-dichalcogenolylium ions, including the previously unknown diseleno derivative.

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Results and Discussion

Synthesis of $(C_3Cl_3E_2)^+$ Ions (E = Se, Te) from Tetrachlorocyclopropene and ECl_4

Heating $SeCl_4$ and tetrachlorocyclopropene in CH_2Cl_2 under solvothermal conditions in a molar ratio of 1:2 yields yellow crystals of 3,4,5-trichloro-1,2-diselenolylium chloride, $(C_3Cl_3Se_2)Cl$, as well as a black precipitate of elemental selenium. The composition of the crystals was checked by energy dispersive X-ray fluorescence. ^{77}Se NMR spectroscopy of the filtered red reaction solution showed one signal with a chemical shift of $\delta = 1257$ ppm, which is ascribed to Se_2Cl_2.[4] The ^{13}C NMR spectrum showed the signals of hexachloropropene ($\delta = 92.7$, 127.4, and 131.8 ppm[5]), and tetrachlorocyclopropene ($\delta = 62.4$ and 122.6 ppm[5]). Due to the very low solubility, signals attributable to the Se atoms of the 1,2-diselenolylium cation could not be detected. A two-step reaction mechanism is supposed: the first step is a redox equilibrium between tetrachlorocyclopropene/$SeCl_4$ and hexachloropropene/selenium (Scheme 3), and the second step yields $(C_3Cl_3Se_2)Cl$ and Se_2Cl_2 analogous to the reaction of hexachloropropene and sulfur described by Boberg.[3]

$$2\,C_3Cl_4 + ECl_4 \rightleftharpoons 2\,C_3Cl_6 + E$$

$$C_3Cl_6 + 4\,E \rightleftharpoons (C_3Cl_3E_2)Cl + E_2Cl_2$$

$$C_3Cl_4 + E_2Cl_2 \rightleftharpoons C_3Cl_6 + 2\,E$$

Scheme 3. Equilibria in the reactions between chalcogen tetrachlorides and tetrachlorocyclopropene (E = Se, Te)

Heating equimolar amounts of $TeCl_4$ and tetrachlorocyclopropene in CH_2Cl_2 yields deep-red 3,4,5-trichloro-1,2-ditellurolylium pentachlorotellurate(IV) $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$. Energy dispersive X-ray fluorescence confirmed the composition. The ^{125}Te NMR spectrum of the deep-red solution shows one signal at $\delta = 1830$ ppm and a second very weak signal at $\delta = 1000$ ppm. It was verified by comparative measurements that the signal occurring at $\delta = 1830$ ppm was not from $TeCl_4$. This signal can therefore be assigned to tellurium in $(C_3Cl_3Te_2)^+$. Only one signal for both tellurium atoms is expected for chemically equivalent nuclei, consistent with the mirror symmetry of the cation. The second signal might be due to Te_2Cl_2 as an intermediate in the reaction equilibrium. Te_2Cl_2 has recently been prepared from Te, $LiBHEt_3$ and $TeCl_4$,[6] and a ^{125}Te NMR resonance at $\delta = 1336$ pm in CS_2 and $\delta = 1287$ ppm in toluene has been reported. Since it is known that ^{125}Te NMR signals are very dependent on the solvent, we can tentatively propose that the reaction of $TeCl_4$ and C_3Cl_4 incorporates the same equilibria as for the reaction of $SeCl_4$ (Scheme 3). In the ^{13}C NMR spectrum four resonances between $\delta = 172.4$ and 160.3 ppm were present, indicating equilibria between cationic species. The unsubstituted dithiolylium cation $(C_3H_3S_2)^+$ shows two signals at $\delta = 142.6$ and 176.7 ppm in this region, corresponding to the central and the terminal carbon atoms of the allylic group.[7]

While $(C_3Cl_3S_2)Cl$ can readily be obtained from hexachloropropene and sulfur, neither $(C_3Cl_3Se_2)Cl$ nor $(C_3Cl_3Te_2)Cl$ could be synthesized in this way with the respective elemental chalcogen; only the reaction of tetrachlorocyclopropene and the respective chalcogen tetrahalide yields the cyclic cations incorporating Se and Te. This is probably caused by the insolubility of selenium and tellurium in organic solvents. The stability of the chalcogen tetrachlorides ECl_4 (E = S, Se, Te) increases from S to Te, while the stability of the dichalcogen dichlorides E_2Cl_2 decreases. The equilibria set up according to Scheme 3 are thus strongly dependent on the kind of chalcogen used. S_2Cl_2 is a favored product in the reaction of C_3Cl_6 with sulfur and it is not reduced to the element by tetrachlorocyclopropene. In the case of selenium this reduction occurs, since a precipitate of finely dispersed elemental selenium is observed. More complex equilibria are present in the case of tellurium. $(C_3Cl_3Te_2)Cl$ could not be isolated, only the less soluble $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$, formed from $(C_3Cl_3Te_2)Cl$ and $TeCl_4$; no precipitation of elemental tellurium was observed at temperatures below 100 °C. Temperatures higher than 110 °C generated a mixture of products which could not be separated or individually characterized.

Crystal Structures

The crystal structures of $(C_3Cl_3S_2)Cl$, $(C_3Cl_3Se_2)Cl$ and $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$ all contain nearly planar, five-membered ring shaped cations $(C_3Cl_3E_2)^+$ (E = S, Se, Te; Figure 1). Only $(C_3Cl_3Se_2)^+$ has a crystallographic mirror plane bisecting the ion. $(C_3Cl_3S_2)^+$ and $(C_3Cl_3Te_2)^+$, however, do not deviate substantially from C_s symmetry despite not possessing crystallographic symmetry. In all three ions the C−C and C−Cl bond lengths are almost identical, except for the central C2−Cl2 bond, which increases slightly from S to Te (Table 1). As expected, the chalcogen-C and chalcogen-chalcogen bonds increase in the same direction; they are all shorter than expected for single bonds. In the dithiolylium ion the S−S bond is 200.93(7) pm long, shorter than the expected bond length for a *cis*-planar S−S single bond (210 pm),[8] although it is similar to the bond lengths found in square-planar S_4^{2+} polycations ($S_4[Sb_9F_{39}]$ 197.5−199.5 pm,[9] $S_4[AsF_6]\cdot SO_2$ 201.4 pm[10]) and even shorter than in differently substituted 1,2-dithiolylium ions (3,5-diamino-1,2-dithiolylium iodide 208 pm,[11] 3,5-dimethyl-1,2-dithiolylium tetrachlorocobaltate 202 pm,[12] phenyl-1,2-dithiolylium chloride 202 pm [13]). In the homologous 1,2-diselenolylium ion the Se−Se bond length measures 231.1(2) pm. This is shorter than a normal Se−Se single bond (e.g. 233 pm in Se_8 [14]) and in the typical region for Se_4^{2+} cluster ions ($Se_4[Sb_9F_{39}]$ 224.7−227.6 pm;[15] $Se_4[MoOCl_4]_2$ 226−230 pm[16]). In the 1,2-tellurolylium ion the Te−Te bond is 265.6(2) pm long, which is shorter than in Te_4^{2+} polycations (266−270 pm[17]). The remarkably short chalcogen-chalcogen bonds in this series of trichlorodichalcogenolylium ions indicate bond orders higher than one. The presence of electron-withdrawing substituents strengthens the partial double bond character: on going from E = S to Te in the series $(C_3Cl_3E_2)^+$ the bonding character changes from an almost equally delocalized system to a separation of a partially localized E−E double bond and the formation of an allylic system [RC=C(R)−CR]$^+$.

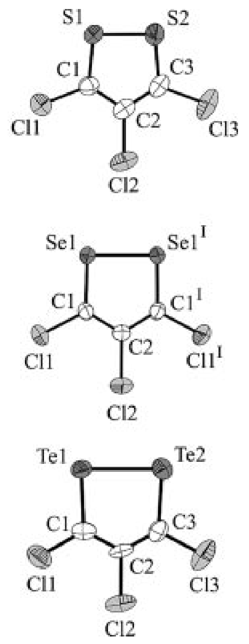

Figure 1. The cations in the structure of $(C_3Cl_3S_2)Cl$ (top), $(C_3Cl_3Se_2)Cl$ (middle), and $(C_3Cl_3Te_2)_2\,[Te_2Cl_{10}]$ (bottom).; the molecules are drawn to the same scale; the displacement ellipsoids represent a probability density of 50%; the $(C_3Cl_3Se_2)^+$ ion is located with its atoms C2 and Cl2 in a mirror plane, the exponent I refers to the symmetry operation x, $0.5 - y$, z.

Table 1. Selected distances (pm) and angles (°) in the $(C_3Cl_3E_2)^+$ (E = S, Se, Te) cations

	$(C_3Cl_3S_2)^+$	$(C_3Cl_3Se_2)^+$	$(C_3Cl_3Te_2)^+$
E−E	200.93(7)	231.1(2)	265.6(2)
E−C	169.1(2); 169.9(2)	184.1(3)	205(2); 206(2)
C−C	138.9(3); 137.9(3)	138.3(3)	137(2); 141(2)
C−Cl(terminal)	168.6(2); 169.1(2)	169.2(3)	169(2); 168(2)
C−Cl(central)	170.8(2)	171.5(4)	174(2)
E−E−C	95.31(7); 95.05(8)	90.93(8)	87.5(4); 86.2(4)
C−C−C	113.6(2)	118.0(3)	123(2)
E−C−C	118.0(2); 118.11(2)	120.0(2)	122.4(9); 121(1)

In the structure of $(C_3Cl_3S_2)Cl$ the cations are arranged in layers. The chloride ions are located in the layers which are stacked with an interlayer distance of 341 pm along the crystallographic *a*-axis in an ABAB.... sequence (Figure 2). The chloride ion interacts with the cation via short, nearly symmetrical contacts to the sulfur atoms of the disulfide group, with S−Cl distances of 292.5 and 293.3 pm. Additionally, the chloride ion is η^5-coordinated by two cations belonging to adjacent planes with distances of 341 pm to the centres of the rings.

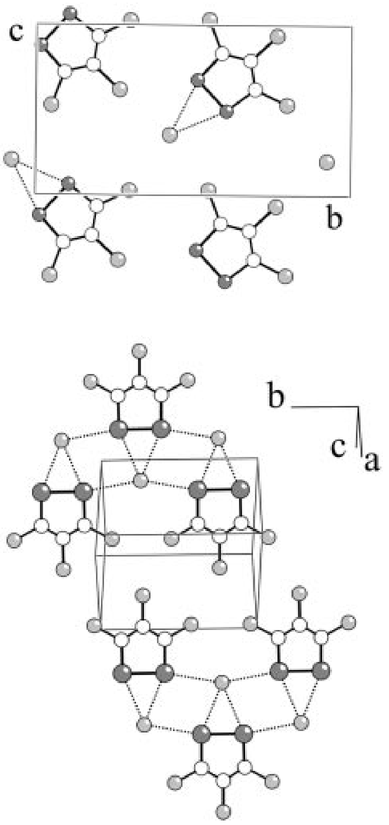

Figure 2. The crystal structures of $(C_3Cl_3S_2)Cl$ (top) and $(C_3Cl_3Se_2)Cl$ (bottom); for both structures only one layer of cations and chloride ions is shown

The structure of $(C_3Cl_3Se_2)Cl$ is substantially different from the structure of its sulfur-containing congener. Again, the cations and the chloride anions are located in planes. These planes are stacked along the [101] direction in an ABCABC... sequence with an interlayer distance of 342 pm (Figure 2). Three chloride ions approach the diselenide group of each cation giving rise to triangular Se_2Cl groups with Se−Cl contacts of 305.3 pm lengths and to almost linear $ClSe_2Cl$ groups with Se−Cl distances of 320.7 pm. These interactions link the cations to bands running along the crystallographic *b*-axis. An equivalent arrangement was found in the structure of 4-phenyl-1,2-dithiolylium chloride.[18]

The structure of $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$ contains binuclear $[Te_2Cl_{10}]^{2-}$ ions (Figure 3). Two tetragonal pyramidal $[TeCl_5]^-$ units are linked via long Te−Cl bridges (Te3−Cl4 290.0 pm) to centrosymmetric dimers. The Cl−Te3−Cl angles deviate by a maximum of 6° from rectangularity. The Te−Cl bonds, however, show marked differences. There is always a short Te−Cl bond (Te3−Cl6, Te3−Cl7, Te3−Cl8 234.1−244.3 pm) in the *trans* position to a long bond (Te3−Cl4, Te3−Cl4^I, Te3−Cl5 261.6−290.0 pm). The structure of the $[Te_2Cl_{10}]^{2-}$ ion in $(C_3Cl_3Te_2)_2\,[Te_2Cl_{10}]$ is almost identical to the respective ion in $[Ph_4As]_2\,[Te_2Cl_{10}]$.[19]

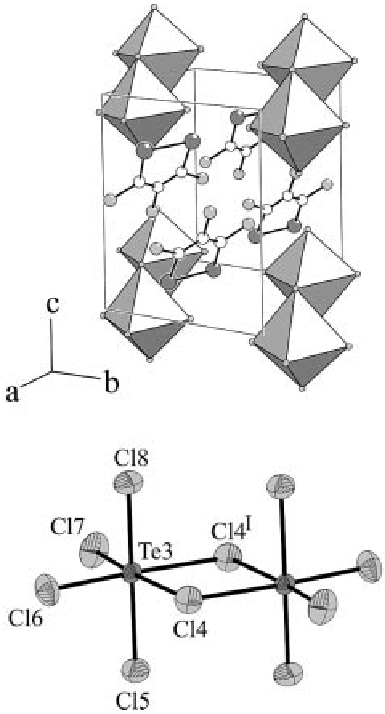

Figure 3. The unit cell of $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$ and a detailed view of the dinuclear $[Te_2Cl_{10}]^{2-}$ anion.; the displacement ellipsoids represent a probability density of 50%; the exponent I refers to the symmetry operation $-x + 1, -y, -z$; selected bond lengths [pm] and angles [°]: Te3−Cl4^I 290.0(3); Te3−Cl4 274.5(4); Te3−Cl5 261.6(3); Te3−Cl6 238.5(3); Te3−Cl7 234.1(3); Te3−Cl8 244.3(4); Te3−Cl4−Te3^I 94.8(1)

Experimental Section

General Techniques: All reactions were carried out in thick-walled glass ampoules of 10 cm length and 10 mm diameter. The ampoules were heated under vacuum to remove traces of water and filled with the starting materials under argon, the solvent was added with a syringe. The contents were frozen with liquid nitrogen, the ampoules were flame-sealed under vacuum and placed in horizontally aligned tube furnaces. Since the products are sensitive towards moisture and oxygen they were opened after the reaction under an argon atmosphere. Liquids were removed with a syringe. Single crystals were prepared under paraffin and mounted in glass capillaries under an argon atmosphere. Tetrachlorocyclopropene (>98%, Fluka) and $SeCl_4$ (Aldrich) were used as purchased. $TeCl_4$ was obtained by chlorinating tellurium powder according to literature procedures.[20] CH_2Cl_2 was dried with P_4O_{10} and freshly distilled before use.

$(C_3Cl_3S_2)Cl$: Heating hexachloropropene (0.1 mL, 7.1 mmol) and sulfur (105 mg, 3.3 mmol) to 170 °C for one day produced yellow needles of $(C_3Cl_3S_2)Cl$. Although the stoichiometry of the reaction (Scheme 1) affords one equivalent of C_3Cl_6 for two equivalents of sulfur, a crystalline product could not be obtained unless a twofold excess of hexachloropropene was used. The yield approached about 70% based on the amount of sulfur used.

$(C_3Cl_3Se_2)Cl$: $SeCl_4$ (270 mg, 1.2 mmol), tetrachlorocyclopropene (0.3 mL, 2.6 mmol), and 1 mL of CH_2Cl_2 were heated slowly at a rate of 10 °C/h to 120 °C. At about 70 °C the $SeCl_4$ dissolved completely with formation of an orange solution. Keeping the temperature at 120 °C for 24 hours and cooling at 10 °C/h to ambient temperature yielded a greyish-black precipitate of elemental selenium and yellow crystals of $(C_3Cl_3Se_2)Cl$. On the basis of $SeCl_4$ the yield reached about 50%.

$(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$: $TeCl_4$ (150 mg, 0.56 mmol), tetrachlorocyclopropene (0.75 mL, 0.65 mmol), and 1.5 mL of CH_2Cl_2 were heated slowly at a gradient of 10 °C/h to 90 °C. After 45 hours the reaction ampoule was cooled to room temperature with a gradient of 5 °C/day. $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$ was obtained as dark-red, needle-shaped crystals in low yield (not exceeding 10%). Pure samples could only be obtained by mechanical separation from unchanged starting materials and by-products. UV/Vis (saturated filtered reaction solu-

Table 2. Crystal data and details of data collection for $(C_3Cl_3S_2)Cl$, $(C_3Cl_3Se_2)Cl$, and $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$

	$(C_3Cl_3S_2)Cl$	$(C_3Cl_3Se_2)$	$(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$
Empirical formula	$C_3Cl_4S_2$	$C_3Cl_4Se_2$	$C_6Cl_{16}Te_6$
Molecular mass/gmol^{-1}	241.97	335.77	1404.91
Space group	$P2_1/n$	$P2_1/m$	$P\bar{1}$
Crystal system	monoclinic	monoclinic	triclinic
a/pm	682.0(1)	542.1(3)	839.77(6)
b/pm	1487.7(1)	861.8(4)	857.9(1)
c/pm	804.5(1)	846.2(5)	1092.12(7)
α/°	90	90	96.940(7)
β/°	96.79(1)	92.77(6)	102.295(7)
γ/°	90	90	99.65(1)
V/10^{6}pm^3	810.6(2)	394.9(4)	748.8(2)
Z	4	2	1
$D_{calcd.}$/gcm^{-3}	1.983	2.824	3.119
μ/cm^{-1}	18.8	106.2	72.0
$2\theta_{max}$	55.7	70.1	50.0
Data(total)	7206	6963	6719
Data(independent)	1830	1845	2625
Refined parameters	82	47	128
Final electron density/e10^{-6}pm^{-3}	+0.37/−0.24	+0.58/−0.48	+2.01/−2.52
$R(\|F\|)$	0.036	0.060	0.077
$wR(F^2)$	0.071	0.071	0.149

tion): λ_{max} = 260 nm, 238, 214. MS (EI): *m*/*z* (%) = 358 (7) $[C_2Cl_2Te_2]^+$, 200 (65) $[TeCl_2]^+$, 165 (65) $[TeCl]^+$, 130 (100) $[Te]^+$, 117 (40) $[CCl_3]^+$, 94 (40) $[C_2Cl_2]^+$.

Energy Dispersive X-ray fluorescence: The composition of all three compounds, $(C_3Cl_3S_2)Cl$, $(C_3Cl_3Se_2)Cl$, and $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$ was checked by electron beam X-ray fluorescence spectra. Crystals were selected in an argon-filled glove box, mechanically broken, placed on a conductive carbon-plated sample holder and transferred into the vacuum chamber of the spectrometer (Zeiss DSM 940, EDAX PV 9800) via an argon-filled gate. Spectra were recorded with a 15 kV acceleration voltage targeting the freshly broken faces of several crystals. Standard deviations are given in brackets and were estimated by the mean error of 10 independent measurements.

$(C_3Cl_3S_2)Cl$, calcd. C 33.3, S 22.2, Cl 44.4; found C 32(2), S 23.8(7), Cl 44(1)

$(C_3Cl_3Se_2)Cl$, calcd. C 33.3,Se 22.2, Cl 44.4; found C 33(2), Se 23(1), Cl 45(2)

$(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$, calcd. C 21.4, Cl 57.1, Te 21.4; found C 20(2), Cl 58(1), Te 22.2(8)

Crystal Structure Analyses: Crystals of all three compounds were tested for diffraction quality by precession photographs. Data were collected at ambient temperature with a STOE Image Plate diffractometer for $(C_3Cl_3S_2)Cl$ and with a STOE AED 2 four circle diffractometer for $(C_3Cl_3Se_2)Cl$ and $(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$ using graphite monochromated Mo-K_α radiation (λ = 71.073 pm). An empirical absorption correction was applied to the data set of $(C_3Cl_3Se_2)Cl$. Structure models were obtained by direct methods using SHELXS-86[21] and were refined based on F^2 by least-squares full-matrix refinements with anisotropic displacement parameters for all atoms using SHELXL-93.[22] Table 2 contains the crystallographic data and further details of data collection and refinement. CCDC-170239 [$(C_3Cl_3S_2)Cl$), CCDC-170240 [$(C_3Cl_3Se_2)Cl$) and CCDC-170241 [$(C_3Cl_3Te_2)_2[Te_2Cl_{10}]$) 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].

Acknowledgments

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