

Formation and Crystal Structure of Polymeric (MeTeCl_3)_n

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Z. Naturforsch. **56b**, 1369–1372 (2001);
received September 5, 2001

Tellurium Chlorides, Polymeric (MeTeCl_3)_n

The reaction of hexamethyldisilane with tellurium tetrachloride in carbon disulfide afforded polymeric (MeTeCl_3)_n (**1**) that was characterized by TOF ES mass spectroscopy, ¹²⁵Te NMR spectroscopy, and X-ray crystallography. Pale brown, air- and moisture-sensitive crystals of **1** are monoclinic, space group $P2_1/n$ with $a = 1030.69(5)$, $b = 643.61(2)$, $c = 1041.68(5)$ pm, $\beta = 119.236(5)^\circ$, $V = 0.60299(5)$ nm³, and $Z = 4$. The crystal structure consists of infinite helical chains of the MeTeCl_3 units linked by bridging chlorine atoms. The polymeric chains are linked together by $\text{Te}\cdots\text{Cl}$ and $\text{Cl}\cdots\text{Cl}$ close contacts. The possible routes for the formation of (MeTeCl_3)_n are discussed.

Introduction

Disulfur and diselenium dihalogenides are relatively stable [1–15] and form a useful class of reagents for many synthetic applications. SCl_2 is also a common synthon that can be prepared directly from the elements or by chlorination of S_2Cl_2 [16, 17]. Analogous selenium dichloride can be made from elemental selenium and SO_2Cl_2 and can be stabilized in coordinating solvents like THF and acetonitrile [18].

Information on tellurium halogenides is rather sparse. Ditellurium dichloride and dibromide can be prepared as yellow liquids and stored for hours in organic non-chlorinated solvents under an inert atmosphere [19]. While tellurium dichloride is stable in the gas phase, it disproportionates upon condensation to elemental tellurium and tellurium tetrachloride [20]. Paul *et al.* [21] have reported a preparation of TeCl_2 by refluxing an equimolar mixture of tellurium tetrachloride and hexameth-

ylsilane for five hours. The dichloride thus produced can be used *in situ* for synthetic applications.

In this work we have reinvestigated the reaction of Paul *et al.* [21] as a part of systematic study of the preparation and properties of chalcogen halogenides. Instead of refluxing TeCl_4 in neat $(\text{Me}_3\text{Si})_2$, we stirred the reagents in CS_2 at room temperature. In these conditions we obtained polymeric (MeTeCl_3)_n. The product was characterized by NMR and MS spectroscopy as well as by X-ray crystallography.

Experimental Section

Tellurium tetrachloride (0.509 g, 1.89 mmol; Aldrich) and hexamethyl disilane (0.283 g, 1.93 mmol; Aldrich) were stirred together in 20 ml of dry CS_2 (Merck) under an argon atmosphere for 3 h during which time the precipitation of elemental tellurium was observed. The reaction mixture was filtered and the filtrate was stored overnight at -20°C with subsequent formation of brownish crystals. The solution was decanted and the crystals were dried under dynamic vacuum. Yield 0.203 g (43% based on tellurium tetrachloride). The extreme air and moisture sensitivity precluded satisfactory elemental analysis. ¹²⁵Te NMR (126.241, THF): $\delta = 1790$ ppm. – MS (TOF ES): m/z (%) = 305 (13, TeCl_5^-), 270 (8, TeCl_4^-), 251 (29, MeTeCl_3^-), 235 (90, MeTeCl_2^-), 198 (100, TeCl_2^-), 161 (85, TeCl^-). In all fragments the observed and calculated isotopic distributions were in good agreement.

The TOF MS ES negative ion mass spectrum was recorded using a Micromass LCT spectrometer. The ²⁹Si and ¹²⁵Te NMR spectra were recorded at 300 K on a Bruker DPX 400 spectrometer operating at 79.495 and 126.241 MHz, respectively. The respective spectral widths were 47.62 and 100.00 kHz and the pulse widths were 15.0 and 6.67 μs . The ²⁹Si accumulation contained *ca.* 2500 transients and the ¹²⁵Te accumulation *ca.* 50,000 transients. D_2O was used as an external ²H lock. The ²⁹Si chemical shifts are reported relative to TMS and the ¹²⁵Te chemical shifts are reported relative to neat Me_2Te [$\delta(\text{Me}_2\text{Te}) = \delta(\text{H}_6\text{TeO}_6) + 712$].

Diffraction data were collected on a Nonius kappa CCD diffractometer at 120 K using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by recording 360 frames *via* φ -rotation ($\Delta\varphi = 1^\circ$; two times 20 s per frame). Crystal data and the



details of the structure determination are shown in Table 1. The reflection data were corrected for Lorentz and polarization effects and the empirical absorption correction was applied for the net intensities. The structure was solved by direct methods using SHELXS-97 [22] and refined using SHELXL-97 [23]. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters the hydrogen atoms were placed in calculated positions in the methyl group ($C-H = 98$ pm). In the final refinement the hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal parameters of the hydrogen atoms in the methyl group were fixed at 1.5 times that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the programs.

Crystallographic information (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 169761. Copies

Table 1. Details of the structure determination of $(MeTeCl_3)_n$.

<i>Crystal data</i>	
Formula	CH_3Cl_3Te
Relative molecular mass	248.98
Crystal system	monoclinic
Space group	$P2_1/n$
a (pm)	1030.69(5)
b (pm)	643.61(2)
c (pm)	1041.68(5)
β (deg)	119.236(5)
V (nm 3)	0.60299(5)
Z	4
$F(000)$	448
D_c (g cm $^{-3}$)	2.743
$\mu(Mo-K_{\alpha})$ (mm $^{-1}$)	6.108
θ -range for data collection	3.88–25.00
<i>Structure determination</i>	
Crystal size (mm 3)	0.20 * 0.10 * 0.05
Number of reflections collected	6388
Number of unique reflections	1016
Number of observed reflections ^a	967
Number of parameters/restrains	47/0
R_{INT}	0.0506
R_1^b	0.0326
wR_2^b	0.0859
R_1 (all data)	0.0343
wR_2 (all data)	0.0870
Goodness-of-fit	1.114
Max and min heights in final difference Fourier synthesis (e Å $^{-3}$)	1.165 – 1.991

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$

of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax. +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The molecular structure of $(MeTeCl_3)_n$ with the numbering of the atoms is shown in Fig. 1 and the selected bond parameters in Table 2. The tellurium atom exhibits approximate square pyramidal coordination with the methyl carbon occupying the apical position. The $MeTeCl_3$ units are linked into infinite helical chains by two basal *cis*-chlorine atoms [$Cl(3)$ and its symmetry-related counterpart]. The coordination polyhedron is completed by two terminal chlorine atoms $Cl(1)$ and $Cl(2)$. The tellurium atom lies approximately on the basal plane ($\Sigma < Cl-Te-Cl = 359.73^\circ$) and the apical methyl group leans slightly towards the bridging basal ligands. Similar structural features are observed in $(PhTeCl_3)_n$ [24, 25] and $(ClC_2H_4TeCl_3)_n$ [26], which also crystallize as polymers with the chain propagating through single *cis*-chlorine bridges, as well as in dimeric $(4-ROC_6H_4TeCl_3)_2$ ($R = Et$ [27] or Ph [28]).

The terminal $Te-Cl$ bond lengths $Te(1)-Cl(1)$ and $Te(1)-Cl(2)$ [236.6(2) and 235.2(1) pm, respectively] are typical for single bonds (the sum of the covalent radii of tellurium and chlorine is 236 pm [29]). Conversely, the two crystallographically independent bridging $Te-Cl$ bonds are significantly longer [275.9(2) and 281.4(1) pm]. These values are in good agreement with those of the corresponding bonds in related compounds, as exemplified by $(PhTeCl_3)_n$ [24, 25] and $(ClC_2H_4TeCl_3)_n$ [26].

The polymeric chains exhibit several close contacts as shown in Fig. 2. The $Te(1)\cdots Cl(3)$ contact of 366.2(1) pm expands the coordination polyhedron around each tellurium atom into an approximate octahedron ($< C(1)-Te(1)\cdots Cl(3) = 162.9^\circ$). This is a typical example of a concept of secondary

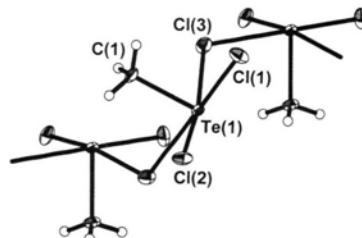


Fig. 1. The molecular structure of $(MeTeCl_3)_n$ indicating the numbering of the atoms. Thermal ellipsoids have been displayed at 50% probability level.

Bond length		Bond angle	
Te(1)–C(1)	211.4(5)	C(1)–Te(1)–Cl(3)	78.0(2)
Te(1)–Cl(1)	236.6(2)	C(1)–Te(1)–Cl(3) ^a	85.3(2)
Te(1)–Cl(2)	235.2(1)	Cl(1)–Te(1)–Cl(2)	89.43(6)
Te(1)–Cl(3)	281.4(1)	Cl(1)–Te(1)–Cl(3)	90.03(5)
Te(1)–Cl(3) ^a	275.9(2)	Cl(2)–Te(1)–Cl(3)	171.32(5)
C(1)–Te(1)–Cl(1)	93.4(2)	Cl(1)–Te(1)–Cl(3) ^a	175.39(5)
C(1)–Te(1)–Cl(2)	91.4(2)	Cl(2)–Te(1)–Cl(3) ^a	86.21(5)
		Cl(3)–Te(1)–Cl(3) ^a	94.06(3)
		Te(1)–Cl(3)–Te(1) ^b	119.61(5)

Table 2. Selected bond lengths (pm) and angles ($^{\circ}$) in $(\text{MeTeCl}_3)_n$.

Symmetry operations: ^a $-x + 3/2, y - 1/2, -z + 1/2$; ^b $-x + 3/2, y + 1/2, -z + 1/2$.

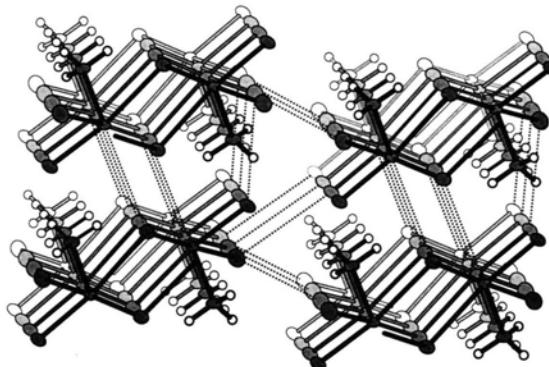


Fig. 2. The packing of the $(\text{MeTeCl}_3)_n$ chains in the lattice.

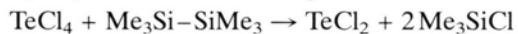
bonding interaction that has been introduced by Alcock [24] and explored recently for a number of triphenyltelluronium salts [30, 31]. It is interesting to note, however, that in contrast to $(\text{MeTeCl}_3)_n$, the packing in $(\text{PhTeCl}_3)_n$ involves virtually no secondary Te···Cl interactions [24, 25]. The polymer chains are stacked together as a result of face-to-face interactions of the phenyl rings and very weak Te···Te contacts (435.8 and 436.9 pm [24]). The presence of only a very weak secondary contact and the resulting virtual five-coordination was proposed by Wynne and Pearson [32] as a consequence of a strong *trans*-bond lengthening caused by the methyl group.

The closest Cl···Cl contacts in $(\text{MeTeCl}_3)_n$ range 334.2(3)–360.6(2) pm. In addition there is a weak hydrogen bond [$\text{C}(1)\cdots\text{Cl}(2) = 338.7(6)$ pm] between the polymer chains.

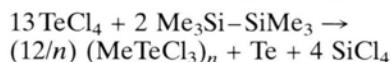
The ^{125}Te NMR spectrum of the reaction solution showed one major resonance at $\delta = 1790$ ppm with a half width of approximately 3400 Hz. Such a broad resonance is consistent with the expected aggregation of the MeTeCl_3 units in solution [32] and can further be understood in terms of isotopic shifts of the three chlorine atoms that are bound

to tellurium. The ^{125}Te chemical shift is consistent with the ^{77}Se chemical shift of 995 ppm observed for EtSeCl_3 [33], when the reported relationship between the ^{125}Te and ^{77}Se chemical shifts in analogous compounds [34] is taken into account. The observed value can also be compared to the ^{125}Te chemical shift of 1238 ppm observed for PhTeCl_3 in DMSO [35]. It is worth noting, however, that the ^{125}Te chemical shift of 758 ppm reported earlier for MeTeCl_3 by Schumann and Magerstädt [36] lies at significantly higher field.

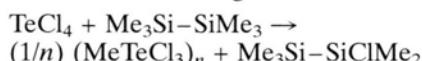
Paul *et al.* [21] have suggested that TeCl_2 is formed by dechlorination of tellurium tetrachloride and by the consequent cleavage of the Si–Si bond in hexamethyldisilane with the formation of trimethylsilyl chloride as a side-product:



While neither ^1H , ^{13}C , nor ^{29}Si NMR spectra indicate the formation of Me_3SiCl in our reaction, the ^{29}Si NMR spectrum of the final reaction solution exhibits the resonance due to SiCl_4 together with that of unreacted $\text{Me}_3\text{SiSiMe}_3$.



One alternative route for the formation of $(\text{MeTeCl}_3)_n$ might involve a simple exchange of substituents in the starting materials:



While attempts to identify $\text{Me}_3\text{Si–SiClMe}_2$ in the reaction solution by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy have been unsuccessful, its formation finds support in its convenient preparation from $\text{Me}_3\text{Si–SiMe}_3$ and anhydrous hydrogen chloride involving an AlCl_3 catalyst [37]. A detailed study of the dependence of the reaction pathway on the reaction conditions is currently in progress.

Acknowledgment

Financial support from Academy of Finland is gratefully acknowledged.

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