Formation and Crystal Structure of Polymeric (MeTeCl₃)ᵣ

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Tellurium Chlorides, Polymeric (MeTeCl₃)ᵣ

The reaction of hexamethyldisilane with tellurium tetrachloride in carbon disulfide afforded polymeric (MeTeCl₃)ᵣ (I) that was characterized by TOF ES mass spectroscopy, ¹²⁵Te NMR spectroscopy, and X-ray crystallography. Pale brown, air- and moisture-sensitive crystals of I are monoclinic, space group P₂₁/n with a = 1030.69(5) Å, b = 643.61(2) Å, c = 1041.68(5) Å, β = 119.236(5)°, V = 0.60299(5) nm³, and Z = 4. The crystal structure consists of infinite helical chains of the MeTeCl₃ units linked by bridging chlorine atoms. The polymeric chains are linked together by Te···Cl and Cl···Cl close contacts. The possible routes for the formation of (MeTeCl₃)ᵣ are discussed.

Introduction

Disulfur and diselenium dihalogenides are relatively stable [1–15] and form a useful class of reagents for many synthetic applications. SCl₂ is also a common synthon that can be prepared directly from elemental selenium and SO₂Cl₂ and can be stabilized in coordinating solvents like THF and acetonitrile [18].

Information on tellurium halogenides is rather sparse. Ditellurium dibromide 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 TeCl₂ by refluxing an equimolar mixture of tellurium tetrachloride and hexamethyl disilane 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 TeCl₄ in neat (Me₃Si)₂, we stirred the reagents in CS₂ at room temperature. In these conditions we obtained polymeric (MeTeCl₃)ᵣ. 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 CS₂ (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): δ = 1790 ppm. – MS (TOF ES): m/z (%) = 305 (13, TeCl₂⁻), 270 (8, TeCl₃⁻), 251 (29, MeTeCl₃⁻), 235 (90, MeTeCl₄⁻), 198 (100, TeCl₄⁻), 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. D₂O 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 Me₆Te [δ(Me₆Te) = δ (H₆TeO₆) + 712].

Diffraction data were collected on a Nonius kappa CCD diffractometer at 120 K using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) by recording 360 frames via ϕ-rotation (Δϕ = 1°; two times 20 s per frame). Crystal data and the ydisilane 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 TeCl₄ in neat (Me₃Si)₂, we stirred the reagents in CS₂ at room temperature. In these conditions we obtained polymeric (MeTeCl₃)ᵣ. The product was characterized by NMR and MS spectroscopy as well as by X-ray crystallography.
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 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 (MeTeCl₃)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 MeTeCl₃ 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 (Σ < Cl–Te–Cl = 359.73°) and the apical methyl group leans slightly towards the bridging basal ligands. Similar structural features are observed in (PhTeCl₃)ₙ [24, 25] and (ClC₂H₄TeCl₃)ₙ [26], which also crystallize as polymeric chains as exemplified by (PhTeCl₃)ₙ [24, 25] and (ClC₂H₄TeCl₃)ₙ [26].

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

![Fig. 1. The molecular structure of (MeTeCl₃)ₙ indicating the numbering of the atoms. Thermal ellipsoids have been displayed at 50% probability level.](image)
Table 2. Selected bond lengths (pm) and angles (°) in (MeTeCl₃)_n.

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<th>Bond length</th>
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<tr>
<td>Te(1)–Cl(1)</td>
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<td>Cl(1)–Te(1)–Cl(1)</td>
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<td>Cl(1)–Te(1)–Cl(2)</td>
<td>Cl(3)–Te(1)–Cl(3)a</td>
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<tr>
<td>Te(1)–Cl(3)–Te(1)b</td>
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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 (MeTeCl₃)_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 (MeTeCl₃)_n, the packing in (PhTeCl₃)_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 (MeTeCl₃)_n range 334.2(3)–360.6(2) pm. In addition there is a weak hydrogen bond [C(1)···Cl(2) = 338.7(6) pm] between the polymer chains.

The ¹²⁵Te NMR spectrum of the reaction solution showed one major resonance at Δ = 1790 ppm with a half width of approximately 3400 Hz. Such a broad resonance is consistent with the expected aggregation of the MeTeCl₃ 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 ¹²⁵Te chemical shift is consistent with the ⁷⁷Se chemical shift of 995 ppm observed for EtSeCl₃ [33], when the reported relationship between the ¹²⁵Te and ⁷⁷Se chemical shifts in analogous compounds [34] is taken into account. The observed value can also be compared to the ¹²⁵Te chemical shift of 1238 ppm observed for PhTeCl₃ in DMSO [35]. It is worth noting, however, that the ¹²⁵Te chemical shift of 758 ppm reported earlier for MeTeCl₃ by Schumann and Magerstädt [36] lies at significantly higher field.

Paul et al. [21] have suggested that TeCl₂ 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:

\[
\text{TeCl}_4 + \text{Me}_3\text{Si-SiMe}_3 \rightarrow \text{TeCl}_2 + 2\text{Me}_3\text{SiCl}
\]

While neither ¹H, ¹³C, nor ²⁹Si NMR spectra indicate the formation of Me₃SiCl in our reaction, the ²⁹Si NMR spectrum of the final reaction solution exhibits the resonance due to SiCl₄ together with that of unreacted Me₃SiMe₃.

\[
13\text{TeCl}_4 + 2\text{Me}_3\text{Si-SiMe}_3 \rightarrow (12/n) (\text{MeTeCl}_3)_n + \text{Te} + 4\text{SiCl}_4
\]

One alternative route for the formation of (MeTeCl₃)_n might involve a simple exchange of substituents in the starting materials:

\[
\text{TeCl}_4 + \text{Me}_3\text{Si-SiMe}_3 \rightarrow (1/n) (\text{MeTeCl}_3)_n + \text{Me}_3\text{Si-SiClMe}_2
\]

While attempts to identify Me₃Si-SiClMe₂ in the reaction solution by ¹H, ¹³C, and ²⁹Si NMR spectroscopy have been unsuccessful, its formation finds support in its convenient preparation from Me₃Si–SiMe₃ and anhydrous hydrogen chloride involving an AlCl₃ catalyst [37]. A detailed study of the dependence of the reaction pathway on the reaction conditions is currently in progress.

Acknowledgment

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