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# Preparation and X-ray Structure Analysis of 1,1,5,5,9,9-Hexachloro-1,5,9-tritelluracyclododecane ($Cl_6$([12]ane$Te_3$)) and Its Redox Behavior

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The first synthesis and structure determination of 1,1,5,5,9,9-hexachlorotritelluracyclododecane (**1**), a monocyclic multitellurium moiety which is composed of three hypervalent tellurium(IV) atoms, along with redox studies were presented. The pyrolysis of ditellurane (**2**) in dimethylformamide at 160 °C afforded the ring-expansion products **1**, $Cl_6$([12]ane$Te_3$), in 44% yield. The structure of **1** was determined by X-ray diffraction analysis. Each tellurium atom is involved in four bonding contacts, and with the lone pair of electrons the central atoms exhibit a trigonal bipyramidal geometry (TBP). The more electronegative chloride atoms are located in the apical positions, while the lone pair and the two alkyl carbons are in the equatorial position. Compound **1** (1 equiv) reacted with thiophenol (6 equiv) in the presence of triethylamine in dimethyl sulfoxide (DMSO) under an Ar atmosphere at 50 °C for 10 min to give neutral 1,5,9-tritelluradodecane (**3**), [12]ane$Te_3$, in 90% yield. Compound **3** reacted with $Cl_2$ in $CH_2Cl_2$ at room temperature to afford the tris(tellurane) **1** in quantitative yield. The results described herein show a new type of chlorine adduct of a telluromacrocycle, as organotellurium compounds consisting of three hypervalent telluriums are hitherto unknown.

## Introduction

Organic hypervalent compounds of chalcogens have received considerable attention in the past two decades.[1−3] Although the structural and theoretical features of hypervalent sulfuranes and selenuranes have been studied extensively, much less is known about the chemistry of telluranes.[1,3−5] Recently, we reported that 1,5-ditelluracyclooctane gave the first insolable ditellurane (**2**) upon treatment with chlorine.[6] On the other hand, a number of macrocyclic polythioethers[7,8] and a few polyselenoethers[1,9] have been described. However, the macrocyclic polytelluroethers have received less attention.[10] Particularly, X-ray structural determination of the macrocyclic polytelluroethers are quite rare. The lower electronegativity and hence the greated s electron-donating properties of Te compared to Se and/or S suggest that incorporation of telluroether as donors ($TeR_2$) in a macrocyclic arrangement should yield ligands capable of an unmeasurably rich coordination chemistry. One disadvantage of polythia macrocyclic chemistry is the absence of a suitably NMR-active nucleus with which to detect structural and conformational behaviors in solution. However, telluroether chemistry is much more attractive in this context owing to the availability of $^{125}$Te NMR spectroscopy as a powerful structural probe ($^{125}$Te $I = -{}^1/_2$, 6.99%, $D_c = 12.5$). The complexation chemistry of multidentate acyclic ligands with cations has developed steadily over the last century; during the past two decades it has expanded rapidly to macrocyclic ligands. In contrast, reports on studies of the chemistry of the complementary multidentate acids have only recently appeared.[11] Furthermore, macrocycles having hypervalent chalcogen centers have hitherto been unknown. In this paper we report the first synthesis and structure determination

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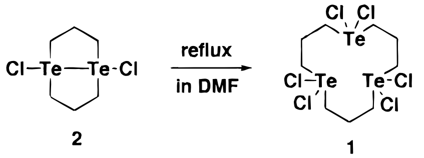
**Scheme 1. Pyrolysis of Ditellurane 2 in DMF**



of 1,1,5,5,9,9-hexachlorotritelluracyclododecane (**1**), a monocyclic multitellurium moiety which is composed of three hypervalent tellurium(IV) atoms, along with redox studies.

## Results and Discussions

Surprisingly, the pyrolysis of ditellurane (**2**) in dimethylformamide at 160 °C afforded the ring-expansion product 1,1,5,5,9,9-hexachloro-1,5,9-tritelluracyclododecane (**1**), $Cl_6([12]aneTe_3)$, in 44% yield; *i.e.* the 8-membered ring of compound **2** has expanded to the 12-membered ring of compound **1** evidently as a result of a deep-seated fragmentation of recombination (Scheme 1). Probably, **2** is initially converted into $(Te(CH_2)_3Te)_n$ by pyrolysis. Subsequently, detellurization and chlorination take place to give **1**. An analogous reaction has been observed by Wudl *et al.*[12] Compound **1** is a white solid that displays limited solubility in noncoordinating solvents. This suggests that these compounds form polymeric networks in the solid state by intermolecular chlorine bridges.

The structure of **1** was confirmed by $^1H$, $^{13}C$, and $^{125}Te$ NMR spectroscopy and elemental analysis. Particularly, the $^{125}Te$ spectroscopy is a diagnostic method to estimate the structure of tellurium compounds. The $^{125}Te$ NMR shift of $Cl_6([12]aneTe_3)$ (**1**) appears at 1005 ppm (in DMSO-$d_6$) relative to neat $Me_2Te$ ($\delta$ 0), which is an intermediate value between that of $Me_2TeCl_2$ in $CH_2Cl_2$ (749 ppm)[13] and in $PhCH_3$ (1218 ppm).[14] The $^1H$ NMR (270 MHz) spectrum of **1** in DMSO-$d_6$ exhibits absorptions at $\delta$ 2.42–2.58 (m, 6H), 3.23–3.29 (m, 12H). The $^{13}C$ NMR spectrum of **1** in DMSO-$d_6$ shows only two peaks at $\delta$ 30.7, 35.7 which is consistent with a symmetrical structure.

In view of the lack of examples of macrocycles having hypervalent chalcogen centers, we undertook a single-crystal X-ray diffraction analysis. Crystals were obtained by slow evaporation of a solution of dimethylformamide containing dissolved **1**. The asymmetric unit consists of two similar Te trimers, one dimethylformamide, and distorted water molecules. An ORTEP plot (Figure 1) of one of the tellurium trimers shows the numbering scheme employed, and Table 1 gives a list of selected bond distances and angles. Each tellurium atom is involved in four bonding contacts, and with the lone pair of electrons the central atoms exhibit a trigonal bipyramidal geometry (TBP). The more electronegative chloride atoms are located in the apical positions, while the lone pair and the two alkyl carbons are in the equatorial position. As shown in Table 1, the Cl–Te–Cl bond angles are close to 180° and the Cl–Te–C bond angles are nearly 90°. The approximate TBP geometry about the tellurium atoms is similar to that of dichlorodimethyltellurane as reported by Christofferson *et al.*[15]

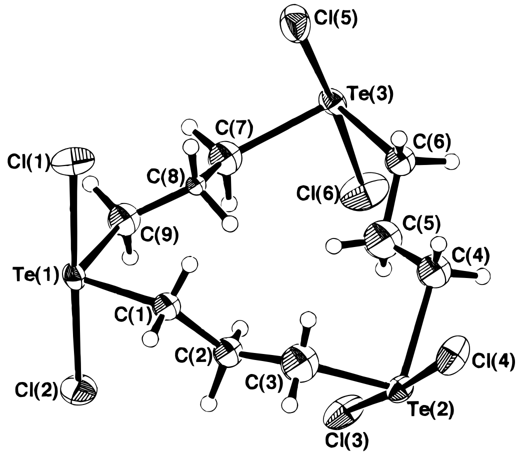


**Figure 1.** ORTEP plot (50% probability) of the structure of **1**.

**Table 1. Non-Hydrogen Bond Distances (Å) and Angles (deg) of $Cl_6([12]aneTe_3)$ (1)**

| | | | | | |
|---|---|---|---|---|---|
| Te(1)–Cl(1) | 2.50(1) | Te(2)–C(3) | 2.10(5) | C(1)–C(2) | 1.58(5) |
| Te(1)–Cl(2) | 2.49(1) | Te(2)–C(4) | 2.26(4) | C(2)–C(3) | 1.49(6) |
| Te(1)–C(1) | 2.11(4) | Te(3)–Cl(5) | 2.50(1) | C(4)–C(5) | 1.40 (6) |
| Te(1)–C(9) | 2.13(4) | Te(3)–Cl(6) | 2.50(1) | C(5)–C(6) | 1.50(6) |
| Te(2)–Cl(3) | 2.45(1) | Te(3)–C(6) | 2.15(4) | C(7)–C(8) | 1.52(5) |
| Te(2)–Cl(4) | 2.58(1) | Te(3)–C(7) | 2.17(4) | C(8)–C(9) | 1.45(5) |

| | | | |
|---|---|---|---|
| Cl(1)–Te(1)–Cl(2) | 178.2(2) | Cl(5)–Te(3)–Cl(6) | 173.5(5) |
| Cl(1)–Te(1)–C(1) | 87(1) | Cl(6)–Te(3)–C(6) | 89(1) |
| Cl(1)–Te(1)–C(9) | 90(1) | Cl(6)–Te(3)–C(7) | 86(1) |
| Cl(2)–Te(1)–C(1) | 92(1) | C(6)–Te(3)–C(7) | 107(2) |
| Cl(2)–Te(1)–C(9) | 89(1) | Te(1)–C(1)–C(2) | 116(2) |
| C(1)–Te(1)–C(9) | 101(1) | C(1)–C(2)–C(3) | 110(3) |
| Cl(3)–Te(2)–Cl(4) | 176.1(4) | Te(2)–C(3)–C(2) | 123(3) |
| Cl(3)–Te(2)–C(3) | 91(1) | Te(2)–C(4)–C(5) | 114(3) |
| Cl(3)–Te(2)–C(4) | 91(1) | C(4)–C(5)–C(6) | 109(4) |
| Cl(4)–Te(2)–C(3) | 86(1) | Te(3)–C(6)–C(5) | 116(3) |
| Cl(4)–Te(2)–C(4) | 86(1) | Te(3)–C(7)–C(8) | 120(3) |
| C(3)–Te(2)–C(4) | 96(2) | C(7)–C(8)–C(9) | 111(3) |
| Cl(5)–Te(3)–C(6) | 88(1) | Te(1)–C(9)–C(8) | 119(3) |
| Cl(5)–Te(3)–C(7) | 90(1) | | |

The Te–Cl distances range from 2.44 to 2.58 Å, which is characteristic of hypervalent bonding (2.511 and 2.528 Å),[15,16] and are significantly longer than the sum of the tellurium and chloride covalent radii (2.36 Å), and longer than the Te–Cl single covalent bonds of 2.31 and 2.33 Å ($TeCl_4$).[17,18] The structural data of $Cl_6([12]aneTe_3)$ (**1**) can be understood on the basis of Musher's theory assuming hypervalent three-center four-electron bonds in the axial array. The transannular Te···Te contacts, 6.252(3) Å for Te(1)–Te(2), 6.299(3) Å for Te(1)–Te(3), and 6.185(3) Å for Te(2)–Te(3), are notably longer than the sum of the van der Waals radii (4.4 Å). Therefore, there is no interaction between the intramolecular tellurium atoms. On the other hand, there are a number of intermolecular contacts between tellurium and chlorine atoms in range of 3.35(1) to 3.81(1) Å which are shorter than the sum of the van der Waals radii

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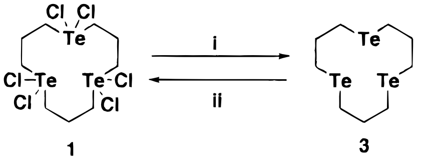
**Scheme 2. Redox Behavior of 1**[a]



[a] Reagents and solvents: (i) PhSH in DMSO; (ii) $Cl_2$ in $CH_2Cl_2$

(3.95 Å). In conclusion, the molecular structure of $Cl_6$([12]ane$Te_3$) (**1**) is composed of a three hypervalent tellurium(IV) moiety which is a normal dialkyltellurium dichloride. To our knowledge, compound **1** represents the first example of an organotellurium compound which contains three hypervalent tellurium centers.

Furthermore, the reactivity of the tris(tellurane) **1** was examined as follows. Thiophenol (**4**) (6 equiv) reacted with **1** (1 equiv) in the presence of triethylamine in dimethyl sulfoxide (DMSO) under an Ar atmosphere at 50 °C for 10 min to give a disulfide (**5**) (90%) as the oxidation product and neutral 1,5,9-tritelluradodeane (**3**), [12]ane$Te_3$ (90%), as the reduction product as shown in Scheme 2. Thus, the tris(tellurane) **1** acts as an oxidant.

The structure **3** was confirmed by $^1H$, $^{13}C$, and $^{125}Te$ NMR spectroscopy, mass spectroscopy, and elemental analysis. The $^{125}Te$ NMR shift of tris(telluride) **3** appears at 213 ppm ($CDCl_3$) relative to neat $Me_2Te$ ($\delta$ 0), similar to the shifts of dipropyl telluride (**8**) (213 ppm in $CDCl_3$).[18] The large upfield shift observed upon reduction with thiophenol **4** is consistent with the neutral telluride structure. The $^1H$ NMR (270 MHz) spectrum of **3** in $CDCl_3$ exhibits absorptions at $\delta$ 2.12 (quint, $J = 7.29$ Hz, 6H), 2.74 (t, $J = 7.29$ Hz, 12H). The $^{13}C$ NMR spectrum of **3** in $CDCl_3$ shows only two peaks at $\delta$ 4.85, 34.0 which consist with a symmetrical structure. On the other hand, the mass spectrum of **3** shows peaks with the correct isotopic distributions at $m/z$ 510 ($M^+$).

Interestingly, compound **3** reacts with $Cl_2$ in $CH_2Cl_2$ at room temperature to afford the tris(tellurane) **1** in quantitative yield as shown in Scheme 2.[20]

The results described herein show a new type of chlorine adduct of a telluromacrocycle having a hypervalent tellurium(IV) bond, as organotellurium compounds consisting of three hypervalent tellurium were hitherto unknown. Further work is in progress to explore applications and advantages of the macrocyclic polytelluroether.

## Experimental Section

**General Data.** All melting points were uncorrected and were taken on a Laboratory Devices Mel-Temp II and a Yanaco micro melting point apparatus. All NMR spectra were measured on a JEOL LMN-EX-270 of a Bruker MSL-400 spectrometer. Mass spectra were taken with a Hitachi RU-6MG, a Shimizu QP-2000, and a JEOL JMX SX102 mass spectrometer. Elemental analysis was carried out by the Chemical Analysis Center at the University of Tsukuba.

All reagents were obtained from Wake Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

**Table 2. Experimental Data for the X-ray Diffraction Studies on $Cl_6$([12]ane$Te_3$) (1)**

| | |
|---|---|
| (a) Crystal Data | |
| formula | $C_{21}H_{46}Cl_{12}NO_{2.5}Te_6$ |
| MW | 1543.6 |
| cryst system, space group | triclinic, $P1$ (No. 1) |
| $a-c$ (Å); $\alpha-\gamma$ (deg) | 8.782(1), 12.426(5), 12.723(4); 60.83(3), 87.65(3), 85.37(3) |
| $V$ (Å$^3$) | 1208.4(7) |
| $Z$ | 1 |
| $d_{calcd}$ (g cm$^{-3}$) | 2.121 |
| $F(000)$ | 715.00 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 42.58 |
| (b) Data Collection | |
| $T$ (K) | 296 |
| radiation; $\lambda$ (Å) | Mo K$\alpha$ (Zr filtered); 0.710 73 |
| scan type, $\Delta\omega$ (deg) | $\omega/2\theta$, 1.20 + 0.65 tan $\theta$ |
| hor and vert aperture (mm) | 2.0–2.5, 4.00 |
| tot. data | 4543 |
| (c) Refinement | |
| reflcns included | 4037 with $I > 5\sigma(I)$ |
| no. of refined params | 256 |
| final $R$, $R_w$, $S$ | 0.079, 0.092, 12.01 |
| resid density (max, min) (e Å$^{-3}$) | +2.5, −2.0 |

**Synthesis of 1,1,5,5,9,9-Hexachloro-1,5,9-tritelluracyclododecane (1).** A solution of dichloroditellurane **2** (500 mg, 1.21 mmol) in DMF (5 mL) was heated for 5 min at 160 °C whence a black precipitate was formed. After filtration, the dimethylformamide was removed slowly in vacuo to give colorless needles of **1** (384 mg, 0.53 mmol) in 44% yield. Compound **1**: Mp 180 °C (dec); $^1H$ NMR (DMSO-$d_6$) $\delta$ 2.42–2.58 (m, 6H), 3.23–3.29 (m, 12H); $^{13}C$ NMR (DMSO-$d_6$) $\delta$ 30.7, 35.7; $^{125}Te$ NMR (DMSO-$d_6$) $\delta$ 1005. Anal. Calcd for $C_{12}H_{25}Cl_6NOTe_3$: C, 18.13; H, 3.17; N, 1.76. Found: C, 18.18; H, 3.01; N, 1.60.

**X-ray Analysis for 2[$C_9H_{18}C_{16}Te_6$]·1.5$H_2O$·DMF (1).** A transparent colorless needlelike crystal (0.20 × 0.50 × 1.20 mm$^3$) was mounted on the end of a glass fiber and transferred to an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo K$\alpha$ radiation (Zr filtered, $\lambda$ = 0.710 73 Å). The lattice parameters at 296 K were determined by a least-squares fit to the setting angles of 25 independent reflections ($12.0 < 2\theta < 21.0°$), and their refinement was carried out by SET4 scans. The crystallographic data and numerical details for compound **1** are listed in Table 2. The three reference reflections monitored after every 2 h indicated that 20% decomposition had occurred during the data collection. A total of 4543 reflections ($2\theta_{max} = 49.9°$) collected using an $\omega-2\theta$ scan technique were corrected for Lorentz and polarization effects, nonlinear decay, and absorption (DIFABS,[21] min/max transmission = 0.52/1.00). The space group was determined to be $P1$ (No. 1). The structure was solved by direct methods[22] and expanded using difference Fourier syntheses. All non-carbon and non-hydrogen atoms were modeled anisotropically and the rest isotropically using neutral atom scattering factors. The hydrogen atoms were introduced on calculated positions (C–H, O–H = 0.97 Å) but not refined. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight $w$ was equal to $[\sigma^2c(F_o)]^{-1}$. The absolute structure was determined by the atomic coordinates inversion method.[23] The neutral atom scattering factors used in the refinements were taken from Cromer and Waber[24] and corrected for anomalous dispersion[25] using the $f'$ and $f''$ values determined by Creagh

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(20) It has been known that the reaction of aliphatic monotellurides with halogens gave dialkyltellurium(IV) dihalides, the stability of which depend markedly on the alkyl group and the halogen.[1,4]

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and McAuley.[26] In the final cycle of refinement 4037 reflections with $I > 5.0\sigma(I)$ were used. The final cycle of full-matrix least-squares refinement included 256 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - F_c||/\sum|F_o| = 0.079$ and $R_w = (\sum w(|F_o| - F_c|)^2/\sum wF_o^2)^{1/2} = 0.092$.

The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 2.5 and −2.0 e/Å$^3$, respectively, with the maxima located at a distance of 1.27 Å from a tellurium atom. A more detailed examination showed that each tellurium has two residual peaks (1.7−2.5 e/Å$^3$) at a distance ranging from 0.96 to 1.98 Å$^3$ from the atom center. This indicates that the $Cl_6$([12]aneTe$_3$) molecules are disordered over three sites. The significant difference in calculated and observed densities suggests that the loss of solvent molecules during the data collection caused the decomposition. The disordered water and $Cl_6$([12]aneTe$_3$) molecules and the high degree of crystal decomposition are the major contributing factors for the high *R*-values.

All calculations were performed using the teXsan[27] crystallographic software package. The final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of one molecule of $Cl_6$([12]aneTe$_3$) are given in the Supporting Information. A list of hydrogen atom coordinates and a table of anisotropic thermal parameters have been deposited as Supporting Information.

**Reduction of Tris(tellurane) 1 with Thiophenol.** To a soluton of the $Cl_6$([12]aneTe$_3$) (**1**) (100 mg, 0.14 mmol) in 10 mL of anhydrous dimethyl sulfoxide was added 6 equiv of thiophenol **4** (92 mg, 0.83 mmol) and 6 equiv of triethylamine (84 mg, 0.83 mmol) under an Ar atmosphere at 50 °C. After the mixture was stirred at room temperature for 10 min, water was added. Then $CH_2Cl_2$ was added, and the organic layer was extracted from the NaCl-saturated solution and washed with an $NaHCO_3$-saturated solution and water, successively. After the usual workup, the mixture was purified by HPLC to afford the tris(telluride) **3** (64 mg, 0.13 mmol) in 90% yield and diphenyl disulfide (**5**) (82 mg, 0.38 mmol) in 90% yield. Compound **3**: Mp 116−118 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.12 (quint, $J = 7.29$ Hz, 6H), 2.74 (t, $J = 7.29$ Hz, 12H); $^{13}$C NMR ($CDCl_3$) $\delta$ 4.85, 34.0; $^{125}$Te NMR ($CDCl_3$) $\delta$ 213; MS *m/z* 516 ($M^+$). Anal. Calcd for $C_9H_{18}Te_3$: C, 21.24; H, 3.56. Found: C, 21.03; H, 3.45. The quantitative formation of triethylammonium chloride ($Et_3HN^+Cl^-$) was detected by $^1$H and $^{13}$C NMR spectroscopy.

**Reaction of Tris(telluride) 3 with Chlorine.** Treatment of tris(telluride) **3** (60 mg, 0.12 mmol) with chloride in $CH_2Cl_2$ (30 mL) at room temperature under an Ar atmosphere gave the white solid **1** (82 mg, 0.11 mmol) in 95% yield.

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**Supporting Information Available:** Text describing X-ray procedures and complete tables of X-ray structural data, positional and thermal parameters, and bond lengths and angles for **1** (19 pages). Ordering information is given on any current masthead page.

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