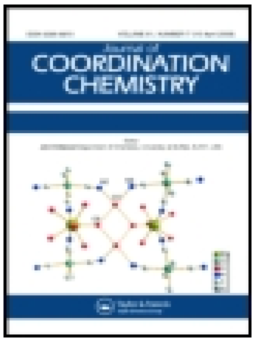

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Syntheses and molecular structures of organo-tellurium(IV) halides *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$, *cis*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$, $[(p\text{-}MeC_6H_4)_2TeBr_2]$, and $[\{(p\text{-}MeC_6H_4)_2TeBr\}_2(\mu\text{-}O)]$

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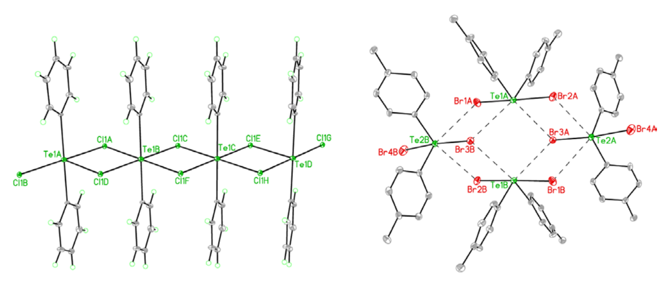
ABSTRACT

Treatment of Ph_2Te with aqueous hydrogen chloride under air in refluxing THF gave *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**), whereas interaction of Ph_2Te with ammonium chloride under similar condition afforded *cis*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**2**). Reaction of $(p\text{-}MeC_6H_4)_2Te$ and bromine in refluxing THF resulted in formation of a discrete complex $[(p\text{-}MeC_6H_4)_2TeBr_2]$ (**3**) with a step-like tetrameric structure, which further reacted with sodium hydroxide in refluxing THF to give a dinuclear tellurium oxide $[\{(p\text{-}Me\text{-}C_6H_4)_2TeBr\}_2(\mu\text{-}O)]$ (**4**) with a bridging oxygen atom. Complexes **1–4** have been spectroscopically characterized and their crystal structures have been established by X-ray crystallography.



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Tellurium; halide; organotellurium; synthesis; crystal structure

1. Introduction

The coordination chemistry of organotellurium compounds has attracted considerable attention in recent years because of their potential application for organic syntheses [1] and utilization in the semiconductor industry [2], along with their fascinating molecular and supramolecular structures [3]. Owing to their inherent propensity, organotellurium compounds can form non-covalent Te···X bonds (X=F, Cl, Br, I, N, O, S) in solution [4] and thus produce secondary Te–X interactions affecting the coordination geometry of the tellurium atoms [5]. In typical organotellurium halides and oxides, the tellurium can adopt different

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equally stable valence states and coordination modes [6–11]. The variation of number and size of the organic substituents also influence the behavior, and these two factors may result in the crystal engineering of organotellurium derivatives [12]. As part of our interest in this chemistry, we have synthesized various organic tellurolate compounds [13]. In the course of this work, we have isolated a series of organotellurium compounds from reactions in solution. In this paper, syntheses and molecular structures of a series of organotellurium(IV) halides *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$, *cis*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$, $[(p\text{-}MeC_6H_4)_2TeBr_2]$, and $[\{(p\text{-}MeC_6H_4)_2\text{-}TeBr\}_2(\mu\text{-}O)]$ are reported, which can be placed into the pool of organotellurium reagents.

2. Experimental

2.1. General considerations

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents of tetrahydrofuran and chloroform, and the chemicals of ammonium chloride, concentrated hydrochloric acid, bromine, sodium hydroxide, PhBr, and $p\text{-}MeC_6H_4Br$ were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Ph_2Te and $(p\text{-}MeC_6H_4)_2Te$ were prepared according to the literature methods [6, 14]. NMR spectra were recorded on a BrukerALX400 spectrometer operating at 400 and 126.2 MHz for ^1H and ^{125}Te, respectively, at room temperature. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and Me_2Te (^{125}Te). Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. Synthesis of polymeric trans-phenyl-tellurium(IV) dichlorides trans-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (1)

To a solution of Ph_2Te (141 mg, 0.50 mmol) in THF (20 mL) was added an aqueous solution of HCl (1.0 M, 1.0 mL), and the reaction mixture was refluxed for 4 h, producing a red solution. The solvent was evaporated *in vacuo* and the residue was extracted with chloroform (5 mL × 3). The filtrate gradually deposited well-formed crystals of **1** at room temperature in two days. Yield: 166 mg, 94% (based on Te). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.83\text{–}7.89$ (m, 10H, *Ph*) ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 920$ ppm. Anal. for $C_{12}H_{10}Cl_2Te$: calcd C 40.86, H 2.86%; found C 40.83, H 2.89%.

2.3. Synthesis of polymeric cis-phenyl-tellurium(IV) dichlorides cis-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (2)

To a solution of Ph_2Te (141 mg, 0.50 mmol) in THF (15 mL) was added a saturated aqueous solution of NH_4Cl (1.0 mL), and the reaction mixture was refluxed for 6 h, producing a red solution. The solvent was evaporated *in vacuo* and the residue was extracted with chloroform (5 mL × 3). The filtrate gradually deposited well-formed crystals of **2** at room temperature in a week. Yield: 159 mg, 90% (based on Te). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.92\text{–}7.85$ (m, 10H, *Ph*) ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 926$ ppm. Anal. for $C_{12}H_{10}Cl_2Te$: calcd C 40.86, H 2.86%; found C 40.81, H 2.84%.

2.4. Synthesis of di(4-methylphenyl)-tellurium(IV) dibromides [(p-MeC$_6$H$_4$)$_2$TeBr$_2$] (3)

To a solution of (*p*-MeC$_6$H$_4$)$_2$Te (155 mg, 0.50 mmol) in THF (15 mL) was added a THF solution of bromine (1.0 M, 0.5 mL), and the reaction mixture was refluxed for 4 h, producing a dark red solution. The solvent was evaporated *in vacuo* and the residue was extracted with chloroform (5 mL × 3). The filtrate gradually deposited well-formed crystals of **3** at room temperature in two days. Yield: 202 mg, 86% (based on Te). ^{1}H NMR (400 MHz, *C*DCl$_3$): $\delta = 2.36$ (s, 6H, CH$_3$), 6.83–7.89 (m, 8H, *Ph*) ppm. ^{125}Te NMR (126 MHz, *C*DCl$_3$): $\delta = 930$ ppm. Anal. for C$_{14}$H$_{14}$Br$_2$Te: calcd C 35.80, H 3.00%; found C 35.62, H 2.95%.

2.5. Synthesis of oxygen-bridged di(4-methylphenyl)-tellurium(IV) bromide [{(p-MeC$_6$H$_4$)$_2$TeBr}$_2$(μ-O)] (4)

To a solution of **3** (94 mg, 0.20 mmol) in THF (20 mL) was added an aqueous solution of sodium hydroxide (1.0 M, 0.1 mL), and the reaction mixture was refluxed for 2 h, producing a dark red solution. The solvent was evaporated *in vacuo* and the residue was extracted with chloroform (5 mL × 3). The filtrate gradually deposited well formed crystals of **4** at room temperature in three days. Yield: 65 mg, 82% (based on Te). ^{1}H NMR (400 MHz, *C*DCl$_3$): $\delta =$ 2.28 (s, 12H, CH$_3$), 6.97–8.26 (m, 16H, *Ph*) ppm. ^{125}Te NMR (126 MHz, *C*DCl$_3$): $\delta = 932$ ppm. Anal. for C$_{28}$H$_{28}$OBr$_2$Te$_2$: calcd C 42.27, H 3.55%; found C 42.23, H 3.58%.

2.6. X-Ray crystallography

A summary of crystallographic data and experimental details for *trans*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**1**), *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**), [(*p*-MeC$_6$H$_4$)$_2$TeBr$_2$] (**3**), and [{(*p*-MeC$_6$H$_4$)$_2$TeBr}$_2$(μ-O)] (**4**) is presented in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer equipped with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) by using a ω scan technique ($2.29° < \theta < 27.71°$ for **1**, $2.29° < \theta < 24.97°$ for **2**, $1.60° < \theta < 27.56°$ for **3**, and $1.85° < \theta < 25.00°$ for **4**) at 296(2) K. The collected frames were processed with the software SAINT [15]. The data were corrected for absorption using the program SADABS [16]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [17, 18]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C$_{sp3}$-H = 0.97 and C$_{sp2}$-H = 0.93 Å), assigned isotropic displacement parameters, and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

Crystallographic data for *trans*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**1**), *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**), [(*p*-MeC$_6$H$_4$)$_2$TeBr$_2$] (**3**) and [{(*p*-MeC$_6$H$_4$)$_2$TeBr}$_2$(μ-O)] (**4**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1451907/1451908/1451909/1451910. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1233–336-033; E-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

As shown in Scheme 1, treatment of Ph$_2$Te with hydrogen chloride, under air, in refluxing THF gave *trans*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**1**), whereas the interaction of Ph$_2$Te with ammonium chloride in refluxing THF afforded *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**). Both **1** and **2** were confirmed to be of

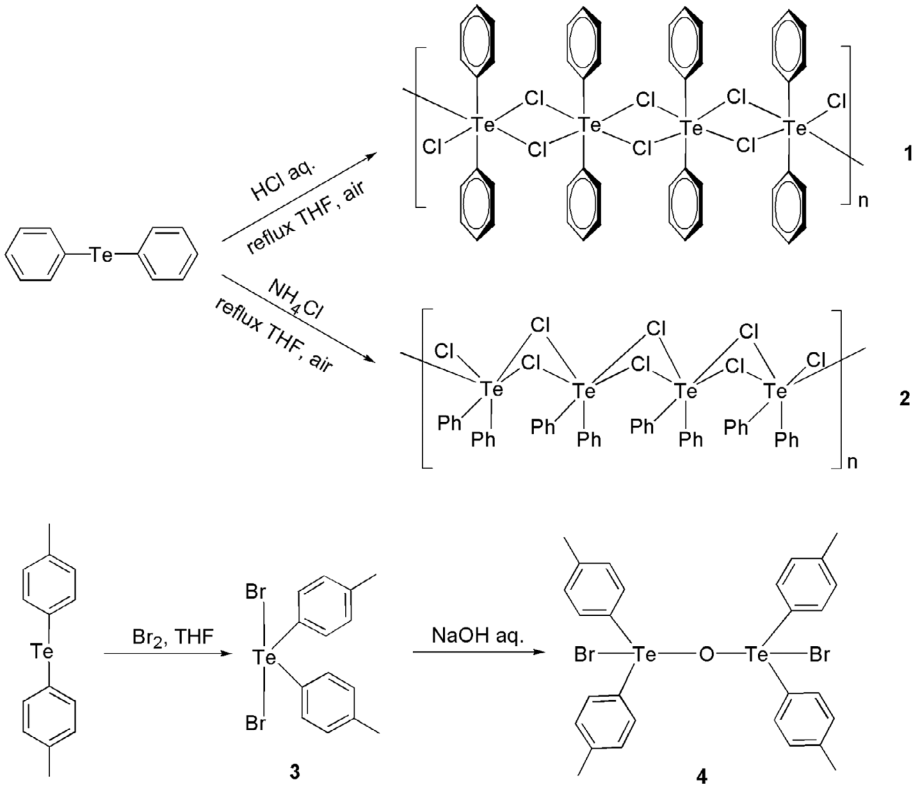
Table 1. Crystallographic data and experimental details for *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**), *cis*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**2**), $[(p\text{-}MeC_6H_4)_2TeBr_2]$ (**3**) and $[\{(p\text{-}MeC_6H_4)_2TeBr\}_2(\mu\text{-}O)]$ (**4**).

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{12}H_{10}Cl_2Te$	$C_{12}H_{10}Cl_2Te$	$C_{14}H_{14}Br_2Te$	$C_{28}H_{28}OBr_2Te$
Formula weight	352.70	352.70	469.67	795.52
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2$	$P2_1/n$	$C2/c$
a, Å	3.8198(12)	18.109(9)	16.5963(18)	21.0711(15)
b, Å	8.659(3)	8.668(4)	10.2473(11)	13.0240(9)
c, Å	17.762(6)	3.8245(18)	17.8978(19)	10.7900(8)
β, deg	91.571(5)	100.950(8)	95.725(2)	100.566(2)
V, Å^3	587.3(3)	589.4(5)	3028.6(6)	4417(7)
Z	2	2	8	4
$D_{calc.}$, g cm^{-3}	1.995	1.987	2.060	1.815
Temperature, K	296(2)	296(2)	296(2)	296(2)
$F(000)$, e	336	336	1760	1512
μ(MoKα), mm^{-1}	2.949	2.939	7.219	4.767
Total refln.	3552	1557	19,312	9966
Independent refln.	1333	998	6893	3821
R_{int}	0.0542	0.0209	0.0285	0.0210
Parameters	70	57	311	152
$R_1{}^a$, $wR_2{}^b$ [$I \geq 2\sigma(I)$]	0.0794, 0.1973	0.0606, 0.1620	0.0465, 0.1353	0.0348, 0.0993
R_1, wR_2 (all data)	0.0872, 0.1999	0.0606, 0.1620	0.0706, 0.1526	0.0481, 0.1082
Goodness of fit (GoF)^c	1.511	1.141	1.032	1.011
Final max/min diff. peaks, e Å^{-3}	+2.680/−2.287	+2.779/−1.914	+0.777/−1.674	+1.112/−1.158
Flack parameter	–	0.5(1)	–	–

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.
[c] $GoF = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

a structural type of a one-dimensional polymeric chain. A compound $[Ph_2TeCl_2]$, adopting the 1D *zigzag* chains via the secondary Te···Cl contacts with the chloride of an adjacent molecule, was isolated from the reaction of Ph_2Hg with $TeCl_4$ in refluxing benzene, and a compound $[PhTeCl_3]$ was prepared from the reaction of *in situ* generated $[Ph_2Te]$ with SO_2Cl_2 [19]. It appears that the *trans*-product is formed in acid solution and the *cis*-product in neutral solution in the presence of chloride ion. To our best knowledge, the *trans*-conformation of Ar_2TeCl_2-type (Ar=aryl) complexes is quite rare according to CCDC search results. Treatment of $(p\text{-}MeC_6H_4)_2Te$ with bromine in refluxing THF resulted in the formation of $[(p\text{-}MeC_6H_4)_2TeBr_2]$ (**3**) with a step-like tetrameric structure. This complex reacts with NaOH in refluxing THF to give a dinuclear complex $[\{(p\text{-}Me\text{-}C_6H_4)_2TeBr\}_2(\mu\text{-}O)]$ (**4**) with a bridging oxygen atom. An analogous iodide complex $[(p\text{-}MeOC_6H_4)_2TeI_2]_2(\mu\text{-}O)$ was synthesized from the reaction of $(p\text{-}MeO\text{-}C_6H_4)_2TeO$ and $(p\text{-}MeOC_6H_4)_2TeI_2$ in a ratio of 1:1 in THF [5]. Complexes **1**–**4** are air stable in both the solid state and solution. The ^1H NMR spectra of **1**–**4** show multiple signals at 6.8–8.3 ppm corresponding to the phenyl groups. The ^1H NMR spectra of **3** and **4** show a singlet at 2.36 and 2.28 ppm, respectively, corresponding to the methyl groups of the 4-tolyl moieties. The ^{125}Te-NMR signals for **1**–**4** in $CDCl_3$ range from 920 to 932 ppm, which are comparable to other reported diorganotellurium dichlorides [5].

The crystal structures of **1**–**4** have been established by X-ray crystallography. Selected bond lengths and angles are given in Tables 2–5, respectively. Crystal structure of the reported complex $[Ph_2TeCl_2]$, obtained from the reaction of Ph_2Hg with $TeCl_4$, are orthorhombic, space group *Pbca*, with unit-cell dimensions $a = 7.644(2)$, $b = 18.160(3)$, $c = 18.014(3)$ Å, $Z = 8$ [19]. In this research, **1** crystallized in the monoclinic centrosymmetric space group



Scheme 1. Syntheses of **1**–**4**.

Table 2. Selected bond lengths (Å) and angles (°) for *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**).

Te(1)–C(1)	2.350(9)	Te(1)–Cl(1)	2.656(2)
Te(1)–Cl(1)#2	2.644(3)		
C(1)#1–Te(1)–C(1)	180.0(7)	C(1)–Te(1)–Cl(1)#2	91.2(3)
C(1)–Te(1)–Cl(1)	90.3(2)	C(1)–Te(1)–Cl(1)#1	89.7(2)
C(1)–Te(1)–Cl(1)#3	88.8(3)	Cl(1)#1–Te(1)–Cl(1)	180.0
Cl(1)#2–Te(1)–Cl(1)	87.76(8)	Cl(1)#3–Te(1)–Cl(1)	92.24(8)
Cl(1)#2–Te(1)–Cl(1)#3	180.0	Te(1)#4–Cl(1)–Te(1)	92.24(8)

Note: Symmetry transformations used to generate equivalent atoms: #1 − *x*, −*y*, −*z* + 1; #2 − *x* + 1, −*y*, −*z* + 1; #3 *x* − 1, *y*, *z*; #4 *x* + 1, *y*, *z*.

Table 3. Selected bond lengths (Å) and angles (°) for *cis*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**2**).

Te(1)–C(11)	2.346(9)	Te(1)–Cl(1)	2.654(4)
Te(1)–Cl(1)#2	2.650(4)		
C(11)#1–Te(1)–C(11)	83.3(8)	C(11)–Te(1)–Cl(1)	88.5(3)
C(11)–Te(1)–Cl(1)#1	134.9(3)	C(11)–Te(1)–Cl(1)#2	90.7(7)
C(11)–Te(1)–Cl(1)#2	131.9(3)	Cl(1)#1–Te(1)–Cl(1)#3	63.03(17)
Cl(1)#2–Te(1)–Cl(1)#3	125.85(17)	Cl(1)–Te(1)–Cl(1)#1	125.93(17)
Cl(1)–Te(1)–Cl(1)#3	92.27(12)	Te(1)–Cl(1)–Te(1)#4	92.27(12)

Note: Symmetry transformations used to generate equivalent atoms: #1 −*x*, *y*, −*z* + 2; #2 *x*−1, *y*, *z*; #3 −*x* + 1, *y*, −*z* + 2; #4 *x* + 1, *y*, *z*.

Table 4. Selected bond lengths (Å) and angles (°) for [(p-$MeC_6H_4)_2TeBr_2$] (**3**).

Te(1)–C(11)	2.109(6)	Te(1)–C(21)	2.119(6)
Te(2)–C(31)	2.114(7)	Te(2)–C(41)	2.129(7)
Te(1)–Br(1)	2.6717(10)	Te(1)–Br(2)	2.6946(10)
Te(2)–Br(3)	2.6920(9)	Te(2)–Br(4)	2.6133(12)
C(11)–Te(1)–C(21)	98.6(2)	C(31)–Te(2)–C(41)	98.3(3)
C(11)–Te(1)–Br(1)	89.04(18)	C(21)–Te(1)–Br(1)	91.13(17)
C(11)–Te(1)–Br(2)	89.62(18)	C(21)–Te(1)–Br(2)	89.04(17)
C(31)–Te(2)–Br(4)	88.71(17)	C(41)–Te(2)–Br(4)	91.94(18)
C(31)–Te(2)–Br(3)	87.74(17)	C(41)–Te(2)–Br(3)	92.32(18)
Br(1)–Te(1)–Br(2)	178.66(3)	Br(4)–Te(2)–Br(3)	174.81(4)

Table 5. Selected bond lengths (Å) and angles (°) for [{(p-$MeC_6H_4)_2TeBr\}_2(\mu$-O)] (**4**).

Te(1)–O(1)	1.983(2)	Te(1)–C(11)	2.120(4)
Te(1)–C(21)	2.108(4)	Te(1)–Br(1)	2.880(1)
C(21)–Te(1)–C(11)	96.8(2)	C(11)–Te(1)–Br(1)	91.4(1)
C(21)–Te(1)–Br(1)	88.1(1)	O(1)–Te(1)–C(21)	86.7(1)
O(1)–Te(1)–C(11)	89.2(1)	O(1)–Te(1)–Br(1)	174.9(1)
Te(1)–O(1)–Te(1)#1	126.1(2)		

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + ½$.

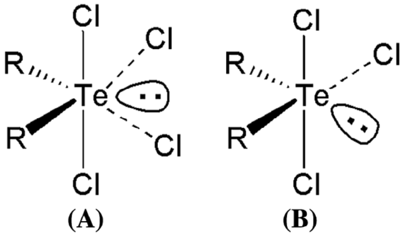


Chart 1. Common coordination modes of diorganotellurium dihalides.

$P2_1/n$ and **2** crystallized in the monoclinic space group $C2$, respectively. Usually diorganotellurium dihalides adopt two coordination geometries taking into account the steric demand of the stereochemically active lone pair, as shown in Chart 1 [5]. The reported polymeric complex [Ph_2TeCl_2] revealed a 5 + 1 coordination geometry in the solid state, with an equatorial lone pair (type B, Chart 1) [19]. In both **1** and **2**, the tellurium atoms adopt the 5 + 2 geometry with an equatorial lone pair. The tellurium atom in the former displays a *trans*-coordinated mode, whereas the central tellurium atom in the latter exhibits a *cis*-coordinated mode, indicated by the angles C-Te-C (180.0(7)° for **1** and 83.3(8)° for **2**) and four angles Cl-Te-Cl at 87.76(8)°, 92.24(8)°, and 180.0° for **1** and at 63.04(17)°, 92.27(12)°, 125.93(17)°, and 125.85(17)° for **2**. Both complexes show one-dimensional polymeric structures, as displayed in Figures 1(b) and 2(b). There is a head-to-head arrangement of phenyl rings located on two sides of the chain in **1**, and there is a face-to-face arrangement of phenyl rings located on one side of the chain in **2**. The average bridging Te-Cl bond lengths are 2.651(2) Å and 2.652(2) Å for **1** and **2**, respectively, slightly longer than the terminal Te–Cl bond lengths in [(p-$MeOC_6H_4)_2TeCl_2$] (av. 2.516(2) Å) [20] and [(p-$MeC_6H_4)_2TeCl_2$] (av. 2.515(2) Å) [5]. The Te–Cl–Te angles are 92.24(8)° and 92.3(1)° for **1** and **2**, respectively. The Te–C bond lengths for **1** (2.350(9) Å) and **2** (2.346(9) Å) are longer than the values reported for other R_2TeX_2

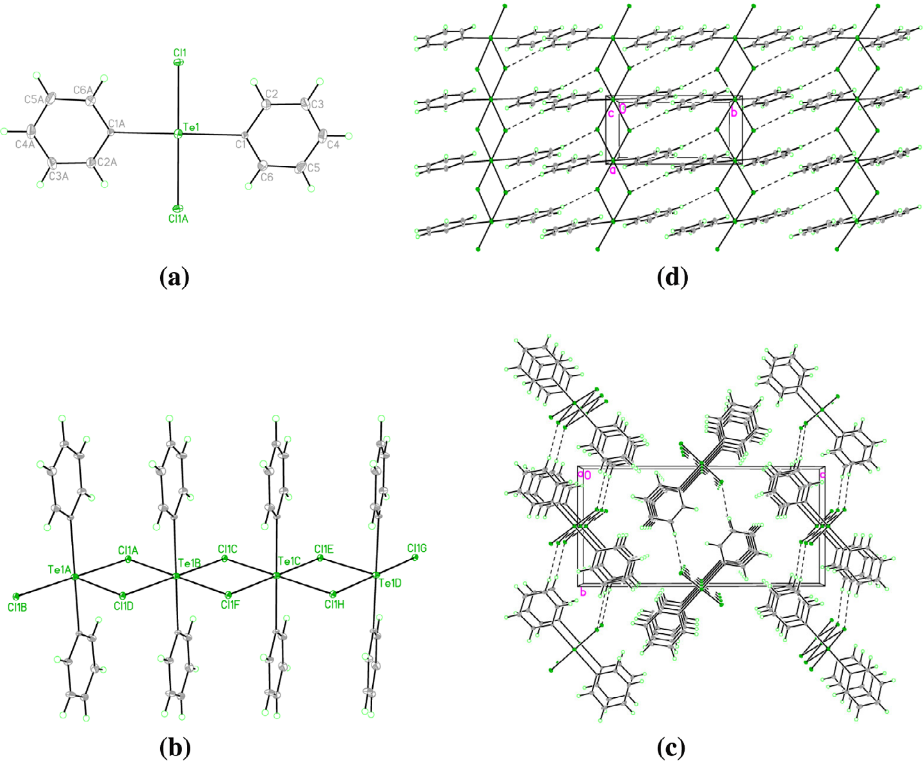


Figure 1. (a) Structure of *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**) showing the atom numbering scheme. The atoms are drawn with 50% probability ellipsoids. (b) Perspective view of *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**) showing chains with head-to-head contacts of benzene rings. (c) Packing diagram of *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**) in the *bc* plane, showing the weak interactions of C–H···Cl van der Waals contacts (dashed lines) between the neighboring chains. (d) Packing diagram of *trans*-$[(Ph_2Te)(\mu\text{-}Cl)_2]_n$ (**1**) in the *ab* plane, showing a two-dimensional framework formed by the C–H···Cl van der Waals contacts (dashed lines).

complexes, such as $[(p\text{-}MeC_6H_4)_2TeCl_2]$ (av. 2.116(3) Å) [5], $[(C_6H_5)_2TeCl_2]$ (av. 2.111(7) Å) [19], $[(p\text{-}MeOC_6H_4)_2TeCl_2]$ (av. 2.113(6) Å) [20], and $[Ph_2TeF_2]$ (av. 2.115(3) Å) [21]. Moreover, the Te–C bond lengths in **1** and **2** are expectedly longer than the corresponding Se–C bond length (1.938(3) Å) in the Se analog $[Ph_2SeCl_2]$ [22]. Packing diagrams of **1** in the *bc* and *ab* planes are presented in Figures 1(c) and (d), respectively, showing weak C-H···Cl van der Waals contacts (H···Cl = 2.879(3) Å, C···Cl = 3.803(3) Å, ∠C–H···Cl = 172.4(2)°) between neighboring chains, which results in the formation of a two-dimensional framework, as displayed in Figure 1(d). Similar interactions were also observed in **2**, as shown in Figures 2(c) and (d). The C···Cl distance and the C–H···Cl angle are 3.806(4) Å and 170.0(4)°, respectively, which are comparable with those in **1**.

Complex **3** crystallized in the monoclinic space group $P2_1/n$ with two crystallographically independent $[(p\text{-}MeC_6H_4)_2TeBr_2]$ molecules associated as symmetry related pairs by secondary Te···Br interactions, as illustrated in Figure 3. Taking into account the steric demand of the stereochemically active lone pair, the geometry of the two tellurium atoms is described as pseudo-pentagonal-bipyramidal (type A, Chart 1), forming a discrete tetramer, which is similar to that observed in complex $[(p\text{-}MeC_6H_4)_2TeCl_2]$ [5]. Actually, this 5 + 2 coordination geometry

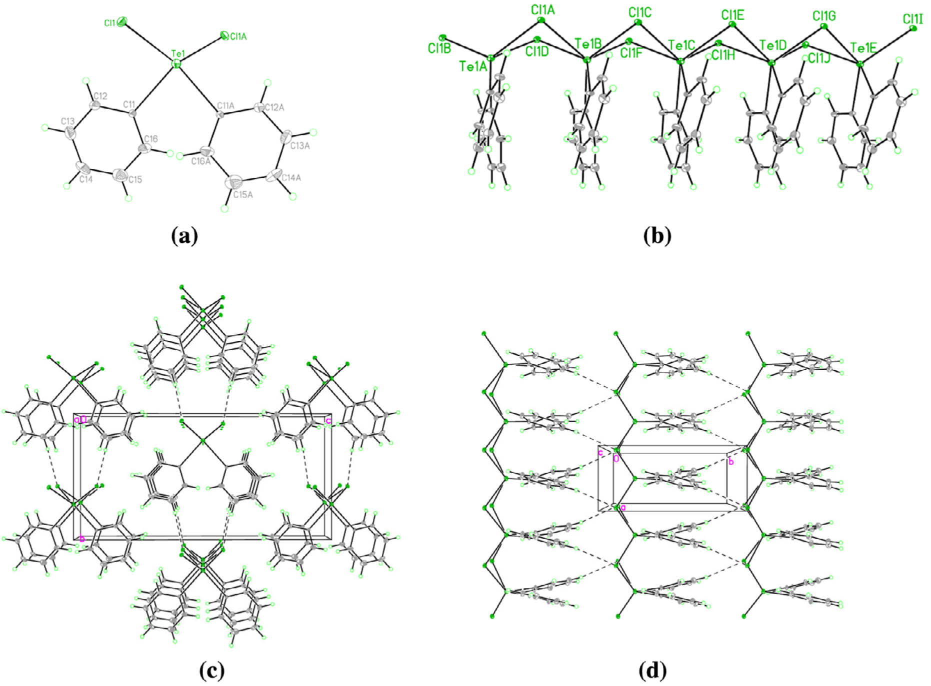


Figure 2. (a) Structure of *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**) showing the atom numbering scheme. The atoms are drawn with 50% probability ellipsoids. (b) Perspective view of *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**) showing chains with the face-to-face contacts of benzene rings. (c) Packing diagram of *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**) in the *bc* plane, showing the weak interactions of C–H···Cl van der Waals contacts (dashed lines) between the neighboring chains. (d) Packing diagram of *cis*-[(Ph$_2$Te)(μ-Cl)$_2$]$_n$ (**2**) in the *ab* plane, showing a two-dimensional framework formed by the C–H···Cl van der Waals contacts (dashed lines).

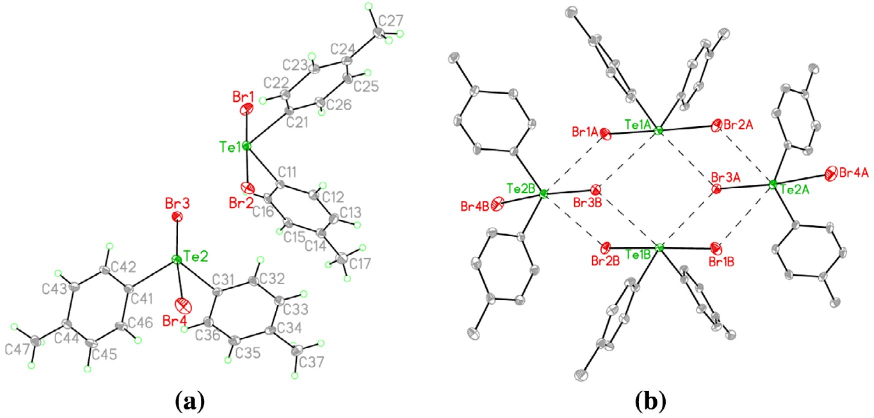


Figure 3. (a) ORTEP plot of the two independent molecules of [(p-MeC$_6$H$_4$)$_2$TeBr$_2$] (**3**). The atoms are drawn with 50% probability ellipsoids. (b) Perspective view of the two pairs of crystallographically independent molecules of [(p-MeC$_6$H$_4$)$_2$TeBr$_2$] (**3**) associated by secondary Te···Br interactions (dashed lines).

is the most frequently encountered for diorganotellurium dihalides [4]. The Br atoms occupy the axial positions with Br–Te–Br angles of 178.66(3)° and 174.81(4)°. The angles between the equatorial aryl groups (98.6(2)°, 98.3(3)°) are less than the normal 120°, presumably due

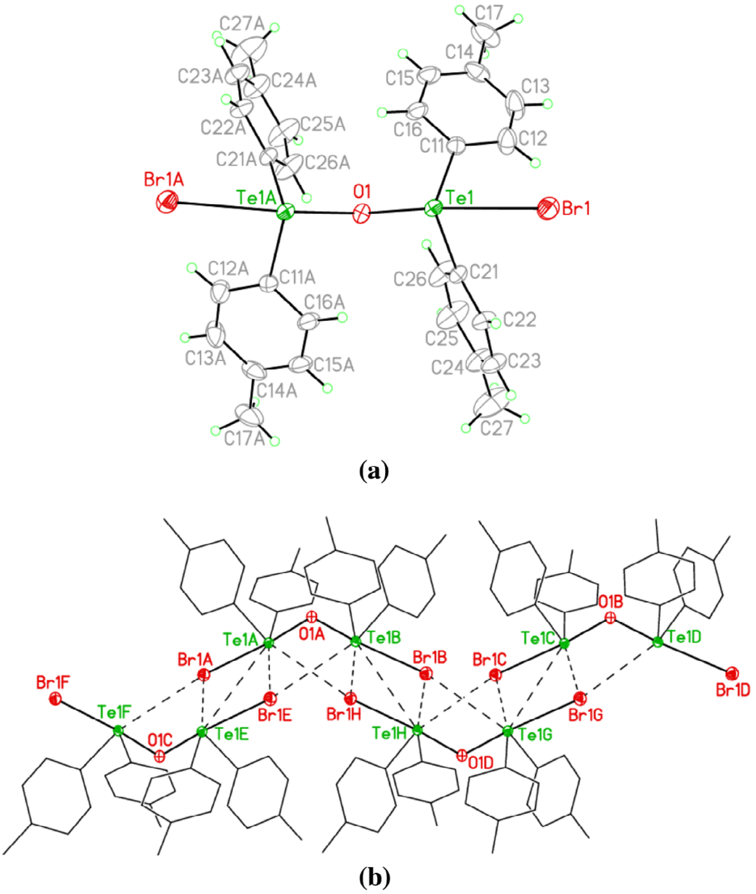


Figure 4. (a) ORTEP drawing of [{(p-MeC$_6$H$_4$)$_2$TeBr}$_2$(μ-O)] (**4**) with 50% probability thermal ellipsoids. (b) Perspective view of four molecules of [{(p-MeC$_6$H$_4$)$_2$TeBr}$_2$(μ-O)] (**4**) showing the association into one-dimensional zigzag chain by secondary Te···Br interactions (dashed lines).

to the repulsion of the aromatic groups by the equatorial lone pair, as predicted by valence shell electron-pair repulsion (VSEPR) theory [5]. The Te$_4$Br$_6$ unit adopts a step-like structure (see Figure 3(b)). A quite similar geometry was also found for the two independent tellurium sites in the crystal structures of [(p-MeC$_6$H$_4$)$_2$TeCl$_2$] [5] and [(p-MeOC$_6$H$_4$)$_2$TeCl$_2$] [20]. The average Te–C bond length for **3** (2.118(6) Å) agrees well with those reported for other R$_2$TeX$_2$ complexes [5, 19–21, 23, 24], but is still shorter than the values for **1** (2.349(8) Å) and **2** (2.368(6) Å). The average C–Te–C bond angle for **3** (98.4(3)°) is comparable with those reported for [(p-MeOC$_6$H$_4$)$_2$TeCl$_2$] (96.46(2)°) [20], [(p-MeC$_6$H$_4$)$_2$TeCl$_2$] (99.16(11)°) [5] and [(C$_6$H$_5$)$_2$TeCl$_2$] (99.01(29)°) [19]. The average Te–Br bond length and Br–Te–Br bond angle in **3** are 2.668(1) Å and 176.74(4)°, respectively. The distances of the Te···Br secondary bonds in **3** are 3.704(8) and 3.713(9) Å, which are shorter than that of 3.936(3) Å in [(C$_6$H$_5$)$_2$TeBr$_2$] [25].

Complex **4** crystallized in the monoclinic space group *C*2/*c*, with crystallographic symmetry as shown in Figure 4(a). The [{(p-MeC$_6$H$_4$)$_2$TeBr}$_2$(μ-O)] units are linked by the bromide ions, leading to association into *zigzag* chains through Te···Br secondary interactions, as illustrated in Figure 4(b). Taking into account the stereochemically active lone pair, the spatial arrangement around the tellurium atoms is *pseudo*-trigonal-bipyramidal with a C_2BrO donor set. The axial Te–Br bond length is 2.880(1) Å and the separation of the Te···Br atoms is 3.540(2) Å. The Te–O bond length of 1.983(2) Å in **4** is in agreement with that of 1.986(6) Å in $[\{(p\text{-MeOC}_6H_4)_2Te\}_2(\mu\text{-O})I_2]$ [7], but is somewhat shorter than the Te–O single bond of the polymeric complex $[(p\text{-MeOC}_6H_4)_2TeO]_n$ (2.063(2) Å) [26]. The average Te-C bond length for **4** (2.114(4) Å) agrees well with those reported for other R_2TeX_2 complexes and **3** (2.118(6) Å), but is still shorter than the values for **1** (2.349(8) Å) and **2** (2.368(6) Å). The Te–O–Te angle of 126.1(2)° is more obtuse than those of 118.8(2)° and 120.2(3)° in $[\{(p\text{-MeOC}_6H_4)_2Te\}_2(\mu\text{-O})I_2]$ [7] and $[(p\text{-MeO-C}_6H_4)_2Te]_2O(O_3SCF_3)_2$ [27], respectively.

4. Conclusion

Four organotellurium(IV) halide complexes, *trans*-$[(Ph_2Te)(\mu\text{-Cl})_2]_n$ (**1**), *cis*-$[(Ph_2Te)(\mu\text{-Cl})_2]_n$ (**2**), $[(p\text{-MeC}_6H_4)_2TeBr_2]$ (**3**), and $[\{(p\text{-MeC}_6H_4)_2TeBr\}_2(\mu\text{-O})]$ (**4**), have been isolated under controlled conditions and characterized by X-ray crystallography. Complexes **1** and **2** show polymeric chain structures, the former with the head-to-head arrangement of phenyl rings located on two sides of chains and the latter with the face-to-face arrangement of phenyl rings located on one same side of the chains, which further form two-dimensional hydrogen-bonded frameworks due to the weak C–H···Cl van der Waals contacts between the neighboring chains. The structure of **3** may be described as a discrete tetramer through Te···Br secondary interactions, with the Te_4Br_6 unit adopting the step-like structural type, while the structure of **4** can be described as $[\{(p\text{-MeC}_6H_4)_2TeBr\}_2(\mu\text{-O})]$ units that are linked by the bromide ions, leading to a *zigzag* chain through the Te···Br secondary interactions.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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