Synthesis and Crystal Structure of $Te_6[MCl_6]$ (M = Zr, Hf), Containing a Polymeric Chalcogen Cation $(Te_6^{2+})_n$

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Dedicated to Professor Michael Veith on the Occasion of his 60th Birthday

Abstract. The reaction of tellurium, tellurium tetrachloride, and ZrCl₄ or HfCl₄, respectively, under the conditions of chemical vapour transport in a temperature gradient 220 \rightarrow 200 °C yields black crystals of Te₆[ZrCl₆] and Te₆[HfCl₆]. While Te₆[ZrCl₆] is formed almost quantitatively, Te₆[HfCl₆] is always accompanied by neighbored phases such as Te₄[HfCl₆] and Te₈[HfCl₆]. The crystal structures of Te₆[ZrCl₆] (orthorhombic, *Pbcm*, *a* = 1095.4(1), *b* = 1085.2(1), *c* = 1324.5(1) pm) and Te₆[HfCl₆] (*a* = 1094.8(2), *b* = 1086.3(2), *c* = 1325.0(2) pm) are isotypic and consist of one-dimensional polymeric (Te₆²⁺)_n cations and of discrete, only slightly distorted octahedral [MCl₆]²⁻ anions (M = Zr, Hf). The cations are build of five membered rings which are connected via single Te

atoms to a polymer $-Te-Te_5-Te-Te_5-$. Out of the six Te atoms of the asymmetric unit of the chain four atoms exhibit two bonds and two atoms exhibit three bonds. The connecting, threefold coordinated Te atoms of the five membered rings carry formally the positive charges. In consistence with the assumption of the presence of throughout localized bonds eH band structure calculations for Te₆[ZrCl₆] show semiconducting behaviour with a band gap of 1.8 eV.

Keywords: *catena*-Hexatellurium(2+); hexachlorozirconate(IV); hexachlorohafnate(IV); chalcogen polycations; main group element cluster; inorganic polymer; crystal structure

Synthese und Kristallstruktur von Te₆[MCl₆] (M = Zr, Hf) mit einem polymeren Kation $(Te_6^{2+})_n$

Inhaltsübersicht. Die Reaktion von Tellur, Tellurtetrachlorid und ZrCl₄ bzw. HfCl₄ unter den Bedingungen des chemischen Gasphasentransports ergibt bei 220 \rightarrow 200 °C schwarze Kristalle von Te₆[ZrCl₆] und Te₆[HfCl₆]. Während Te₆[ZrCl₆] nahezu einphasig gebildet wird, entstehen im System Te/TeCl₄/HfCl₄ die Phasen Te₄[HfCl₆], Te₆[HfCl₆] und Te₈[HfCl₆] nebeneinander. Die Kristallstrukturen von Te₆[ZrCl₆] (orthorhombisch, *Pbcm*, *a* = 1095,4(1), *b* = 1085,2(1), *c* = 1324,5(1) pm) und Te₆[HfCl₆] (*a* = 1094,8(2), *b* = 1086,3(2), *c* = 1325,0(2) pm) sind isotyp und bestehen aus eindimensional-polymeren (Te₆²⁺)_n-Kationen und diskreten, nur

gering verzerrt oktaedrischen $[MCl_6]^{2-}$ -Anionen (M =Zr, Hf). Die Kationen sind aus fünfgliedrigen Ringen aufgebaut, die über einzelne Te-Atome zu einem Polymer $-Te-Te_5-Te-Te_5-$ verknüpft sind. Von den sechs Te-Atomen der asymmetrischen Einheit der Kette sind vier zweibindig und zwei dreibindig. Die dreibindigen Te-Atome in den Te₅-Ringen tragen formal die positiven Ladungen. In Übereinstimmung mit der Annahme nur lokalisierter Bindungen zeigen eH-Bandstrukturrechnungen für Te₆[ZrCl₆] Halbleiterverhalten mit einer Bandlücke von etwa 1,8 eV.

Introduction

The tetrahalides of group 14 metals Zr and Hf have strong Lewis acidic properties. Predominantly discrete, octahedral $[MX_6]^{2-}$ anions (M = Zr, Hf; X = halogen) are formed which consequently exhibit only weakly basic properties. These anions are able to stabilize "naked" polycationic clusters. Several compounds made up of polycationic clusters and group 14 halometalate anions are meanwhile known. Bi₉⁵⁺ clusters are present in the hexagonal structures of Bi(Bi₉)[MX₆]₃ (M = Zr, Hf, Nb; X= Cl, Br) [1–5]. Square-

Inst. f. Anorg. Chemie d. Universität Gerhard-Domagk-Str. 1 D-53121 Bonn e-mail: j.beck@uni-bonn.de planar Se₄²⁺ and Te₄²⁺ cations were found in the structures of Se₄[ZrCl₆], Se₄[HfCl₆], and Te₄[HfCl₆] [6, 7]. The octaatomic chalcogen cations Se₈²⁺ and Te₈²⁺ are present in the structures of the respective hexachlorozirconates and hafnates E₈[MCl₆] (E = Se, Te; M = Zr, Hf) [8]. Te₄[Zr₂Br₁₀] occurs as a polycation-containing phase in the system Te/ TeBr₄/ZrBr₄ [9].

The fact that two different tellurium cations Te_4^{2+} and Te_8^{2+} are formed in the system $Te/TeCl_4/MCl_4$ (M = Zr, Hf) stimulated us to search for additional phases. We were able to isolate $Te_6[MCl_6]$ (M = Zr, Hf) containing a novel polymeric tellurium polycation Te_6^{2+} on which we report here.

Experimental

Te (99,5 %, Johnson-Matthey) was molten in an evacuated glass ampoule and decanted from oxidic impurities. The crystallized sil-

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Table 1 Crystallographic data and details of the structure refinement for $Te_6[ZrCl_6]$ and $Te_6[HfCl_6]$. Standard deviations given in brackets refer to the last significant digit.

Formula		Te ₆ [ZrCl ₆]	Te ₆ [HfCl ₆]
Crystal system/space group		orthorhombic <i>Pbcm</i> (No. 57)	
Lattice constants	a / pm	1095.4(1)	1094.8(2)
	b / pm	1085.2(1)	1086.3(2)
	c /pm	1324.5(1)	1325.0(2)
Unit cell volume	$V/10^{6} \text{ pm}^{3}$	1574.4(2)	1575.8(3)
Number of formula units	Z	4	4
Density (calculated)	$/ \text{g} \cdot \text{cm}^{-3}$	4.51	4.88
Temperature	/ K	293(2)	293(2)
Range of data collection		$6.1^{\circ} < 2\Theta < 56^{\circ}$	$10.3^{\circ} < 2\Theta < 55.9^{\circ}$
Number of measured reflections		14340	14058
Number of independent reflections		1980, $R_{\rm int} = 0.091$	1955, $R_{\rm int} = 0.117$
Number of reflections in least squares		1980	1955
Number of refined parameters		67	67
Absorption correction		Numerical, description of the crystal shape by	
*		15 faces, $\mu = 125.8 \text{ mm}^{-1}$	10 faces, $\mu = 184.9 \text{ mm}^{-1}$
Reliability factors	R(F) for [number] reflections with		
-	$F_{\alpha} > 4\sigma(F_{\alpha})$	0.028 [1903]	0.038 [1892]
	all reflections	0.029	0.039
	$wR(F^2)$	0.070	0.090
Final difference fourier	$/ e/10^{6} \text{ pm}^{3}$	+1.08 / -1.02	+2.25 / -3.39

very material was finely ground in an argon atmosphere. TeCl₄ was prepared from purified Te and dry chlorine. It was freshly sublimated before use. ZrCl₄ and HfCl₄ (both Aldrich, 99,5 % and 98 %, respectively) were sublimated in closed evacuated glass ampoules before use.

Te₆[MCl₆] (M = Zr, Hf). In an argon filled glove box 500 mg Te (3.92 mmol), 151 mg TeCl₄ (0.56 mmol), and 261 mg ZrCl₄ (1.12 mmol) or 359 mg HfCl₄ (1.12 mmol), respectively, were filled in a glass ampoule of 15 cm length and 1.5 cm internal diameter. The ampoules were evacuated and flame-sealed, and placed in a horizontal tube furnace. The furnace was heated to 220 °C and the ampoule placed asymmetrically, so a temperature gradient of 20 °C from the hot, charged end to the empty tip of the ampoule was established. Within 3 weeks black, shiny crystals of Te₆[ZrCl₆] formed in almost quantitative yield which were deposited in the colder part of the reaction ampoule. Using HfCl₄ always a mixture of the phases Te₄[HfCl₆], Te₆[HfCl₆], and Te₈[HfCl₆] was formed. The visual distinction is difficult and can be made only for Te₄[HfCl₆] the crystals of which exhibit a typical dark violet luster.

Crystal Structure Analyses

Since all compounds are sensitive towards hydrolysis by moist air, opening of the reaction ampoules and selection of crystals was performed in an argon filled glove box. Crystals were filled into glass capillaries, which were sealed. The crystals selected had the size 0.34 \cdot 0.30 \cdot 0.53 mm for M = Zr and 0.27 \cdot 0.30 \cdot 0.30 mm for M = Hf. Preliminary examinations by precession photographs revealed the orthorhombic crystal system for both crystals. Data sets were recorded at ambient temperature using a STOE IPDS diffractometer with graphite monochromatized Mo-K α radiation. The systematic absences: 0kl only present for k = 2n, and h0l only present for l = 2n lead to the possible space groups $Pbc2_1$ and Pbcm of which the centrosymmetric group turned out as correct through the refinement calculations. Structure models were obtained by direct methods [10] and refined against F^2 with anisotropic displacement parameters for all atoms [11]. A numerical absorption correction was applied to both data sets [12]. Crystallographic data and details of the structure analyses are given in Table **Table 2** Positional coordinates and equivalent isotropic displacement parameter $B_{eq}/10^4$ pm² for the atoms in the structures of Te₆[ZrCl₆] and Te₆[HfCl₆]. Standard deviations refer to the last significant digit. The respective values for Te₆[HfCl₆] are given in *italics* in the respective second line.

Atom	X	у	Z	B_{eq}
Te1	0.18058(3)	0.40191(3)	-0.10084(2)	1.831(8)
	0.18047(4)	0.40209(4)	-0.10088(4)	1.47(1)
Te2	0.38569(3)	0.37089(3)	0.02268(2)	1.907(8)
	0.38545(4)	0.37088(4)	0.02304(4)	1.55(1)
Te3	0.01882(4)	0.25	0	1.92(1)
	0.01866(6)	0.25	0	1.56(1)
Te4	0.26536(4)	0.23851(5)	-0.25	2.22(1)
	0.26554(7)	0.23846(6)	-0.25	1.84(1)
Zr	0.73864(5)	0.20112(6)	0.25	1.37(1)
Hf	0.73876(3)	0.20100(3)	0.25	1.35(1)
Cl1	0.5695(3)	0.0556(2)	0.25	2.58(3)
	0.5698(3)	0.0569(3)	0.25	2.80(5)
C12	0.9141(2)	0.3384(2)	0.25	2.03(3)
	0.9133(2)	0.3378(2)	0.25	2.10(5)
Cl3	0.6438(1)	0.3291(1)	0.1191(1)	2.88(2)
	0.6442(2)	0.3283(2)	0.1201(2)	2.54(3)
Cl4	0.8435(1)	0.0731(1)	0.3801(1)	2.70(2)
	0.8432(2)	0.0735(1)	0.3797(2)	2.34(3)

1, positional parameters in Table 2, selected bond lengths and angles in Table 3. Further information on the crystal structure analyses have been deposited with the FIZ Karlsruhe, D-76344 Eggenstein-Leopoldshafen form where they can be obtained by quoting the deposit numbers CSD-414293 for $Te_6[ZrCl_6]$ and CSD-414294 for $Te_6[HfCl_6]$.

Results and Discussion

Synthesis

The formation of $Te_6[M = Zr, Hf)$ can formally be interpreted as a comproportionation of tellurium and telluriumtetrachloride to a subvalent intermediate followed by a Lewis acid base reaction. $ZrCl_4$ and $HfCl_4$ act as Lewis acids, abstracting chloride ions from the intermediate subhal-

Table 3 Selected bond lengths / pm and angles / $^{\circ}$ in the structures of Te₆[ZrCl₆] and Te₆[HfCl₆]. The values for Te₆[HfCl₆] are given in *italics* in the respective second line. Standard deviations refer to the last significant digit. Symmetry operations are given in the legend for Figure 1.

Te1-Te2	279.97(4)	Zr-Cl1	243.4(2)
	289.12(7)	Hf-Cl1	242.4(2)
Te1-Te3	276.43(4)	Zr-Cl2	243.1(2)
	276.67(6)	Hf-Cl2	242.1(2)
Te1-Te4	281.24(5)	Zr-Cl3	245.3(1)
	281.62(7)	Hf-Cl3	243.8(2)
Te2-Te2 ^I	269.18(7)	Zr-Cl4	249.3(1)
	269.63(9)	Hf-Cl4	248.5(2)
Te2-Te1-Te3	99.23(1)	Te1-Te2-Te2 ^I	89.24(1)
	99.06(2)		89.15(2)
Te3-Te1-Te4	100.08(2)	Te1-Te3-Te1 ^I	100.27(2)
	100.01(2)		100.37(3)
Te2-Te1-Te	493.99(1)	Te1-Te4-Te1 ^{III}	89.25(2)
	94.01(2)		89.11(3)

ogenide under formation of the polycationic cluster and the respective hexachlorometalate.

11 Te + TeCl₄ + 2 MCl₄ \rightarrow 2 Te₆[MCl₆] (M = Zr, Hf)

The reaction proceeds via the gas phase in closed evacuated ampoules. Since MCl₄ (M = Zr, Hf) are both volatile and TeCl₂ is known to be a stable gas phase species [13], chemical transport is achieved in a closed system with a temperature gradient from $220 \rightarrow 200$ °C.

A remarkable difference was observed in the reactivity of $ZrCl_4$ and $HfCl_4$. The reaction of Te, $TeCl_4$, and $HfCl_4$ yielded in all experiments simultaneously all three Hf/Te/Cl phases $Te_4[HfCl_6]$, $Te_6[HfCl_6]$, $Te_8[HfCl_6]$, together with other yet unidentified phases. While the crystals of $Te_4[HfCl_6]$ show a typical dark violet luster, the visual distinction between the black crystals of $Te_6[HfCl_6]$ and $Te_8[HfCl_6]$ was not possible. Using Te, $TeCl_4$, and $ZrCl_4$, however, the compound $Te_6[ZrCl_6]$ is formed in almost quantitative yield. The neighboured phases $Te_4[ZrCl_6]$ and $Te_8[ZrCl_6]$ could not be detected.

Crystal Structures

Te₆[ZrCl₆] and Te₆[HfCl₆] crystallize isotypically. The structures contain one-dimensional polycations $(Te_6^{2+})_n$ and discrete octahedral anions $[MCl_6]^{2-}$. No significant diffences in bond lenghts and angles are present between Te₆[ZrCl₆] and Te₆[HfCl₆]. Figure 1 gives a view of a section of the cationic chain and of the anion.

Crystallographic mirror planes bisect the anions. The atoms M (M = Zr, Hf), Cl(1) and Cl(2) are located in the mirror planes giving the anions C_s symmetry. The deviation from the ideal octahedral symmetry is significant. The M-Cl bond lengths range from 242 to 249 pm, the Cl-M-Cl angles from 87° to 93°. These deviations are caused by strong cation-anion interactions. The shortest Te-Cl distances between the Cl atoms of the anions and the Te atoms of the cations are Te(2)····Cl(3) = 313.5(1) pm



Fig. 1 A section of the polymeric $(Te_6^{2+})_n$ cation and the $[HfCl_6]^{2-}$ anion in the structure of $Te_6[HfCl_6]$. Thermal ellipsoides are drawn to include a probability density of 50 %.

Symmetry operations: I = x, $\frac{1}{2} - y$, -z; II = x, y, $\frac{1}{2} - z$; III = x, y, $-\frac{1}{2} - z$.

{314,6(2) pm} and Te(3)····Cl(4) = 314.5(1) pm {314.8(1) pm}. These distances are shorter than the respective shortest Te····Cl contacts in the structures of Te₄[HfCl₆] (324.9 pm [6]) and Te₈[HfCl₆] (322.9 pm [8]).

The cations consist of five-membered rings in a twist conformation which are connected by single Te atoms leading to one-dimensional strands according to the formula $(-Te-Te_5-^{2+})_n$. Crystallographic twofold axes run perpendicular to the direction of the chain through the atoms Te(3) and the centre of the Te(2)–Te(2)^I bond. The atoms Te(4) are located in mirror planes spread out perpendicular to the running direction of the cationic chains. The consequence is that translational equivalence within the $(Te_6^{2+})_n$ strand is reached only with every second Te₅ ring. Figure 2 shows the unit cell and a stereoscopic view of the coordination environment of the five-membered ring of the cations. Eight anions coordinate the Te₅ ring in form of a distorted cube. The structure of $Te_6[MCl_6]$ (M = Zr, Hf) thus adopts the CsCl structure type. This is reflected by the lattice constants, which remind of a tetragonally elongated cubic cell. The elongation of the cell occurs along the c direction which is the direction of the cationic strands.

The Zintl concept can be applied to explain the relation between charge and structure of the cation. In each

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Fig. 2 The unit cell of $Te_6[MCl_6]$ (M = Zr, Hf) in a view inclined to the *b*-axis (top) and a stereoscopic view of the cuboidal coordination of the cationic $-Te-Te_5-Te-$ group by eight $[MCl_6]^{2-}$ anions (bottom).

 $(-Te_5-Te-)^{2+}$ section of the chain there are two threefold coordinated Te atoms (Te(1) and Te(1)^I), while all other Te atoms are twofold coordinated. A chalcogen atom bearing five valence electrons behaves like an atom of group 15 and thus exhibits three bonds and carries formally a positive charge. The bridgehead atoms Te(1) have a trigonal pyramidal coordination environment typical for three bonds of p character and a stereochemically active lone pair. The Te-Te bonds show a pronounced bond lengths alternation. Te-Te bond lengths involving the threefold coordinate Te(1) and the ring linking Te(4) are ranging from 277 to 282 pm. The $Te(2)-Te(2)^{1}$ distance is only 269 pm indicating partial double bond character. The Te-Te-Te angles are all in the typical range between 90° and 100° (Tab. 3) and are thus slightly smaller than in the element structure of tellurium (103,1°) [14].

Several cationic tellurium chains are known since about one decade [15, 16]. They can be divided in two kinds. The first kind exhibits hypervalent bonding with square planar coordinated Te atoms, present for example as $(Te_7^{2+})_n$ in the structures of Te₇[WOBr₄]Br [17], Te₇[NbOCl₄]Cl [18] or $(Te_{10}^{2+})_n$ in $(Te_4)(Te_{10})$ [Bi₄Cl₁₆] [19]. The second kind contains only twofold and threefold coordinated Te atoms. The bonding situation can thus be interpreted by simple models. As a common structural feature, caused by the necessity of the presence of threefold coordinated atoms, the structures are all made up of rings which are connected either directly or by short chains of Te atoms. The known representatives



Fig. 3 The structures of the known one-dimensional polymeric chalcogen cations composed of linked rings. The numbers on the left refer to a simple structure designator code (see text).

are depicted in Figure 3. The ring size varies between four and six, the number of atoms in the connecting chains varies between zero in $({Te_4}^{2+})_n$ (Fig. 3a) [19] and three in $(Te_3Se_4^{2+})_n$ and $(Te_{3.15}Se_{4.85}^{2+})_n$ (Figs. 3b and 3d) [20]. $(Te_6^{2+})_n$ with its structure of five-membered rings connected via -Te- bridges fits in this series. A simple structure designator code can be set up since the different chains can unequivocally be termed by the parameters ring size and number of connecting atoms. The first digit gives the number of atoms in the respective rings, the second digit gives the number of bridging atoms. So for $(Te_6^{2+})_n$ the structure designator is 5-1. In Figure 3 the respective structure designation codes are given for all known chainlike chalcogen polycations, ranging from 4-0 in $(Te_4^{2+})_n$ to 6-2 in $(Te_8^{2+})_n$, realized as two isomers in the structures of Te₈[U₂Br₁₀] (Fig. 3 f) [22] and Te₈[Bi₄Cl₄] (Fig. 3 g) [23]. The only other reprensentative known so far having a single atom bridge between the rings was $(Te_7^{2+})_n$ in the structure of $Te_7[AsF_6]_2$ (Fig. 3e) [21]. The structures of $Te_6[MCl_6]$ (M= Zr, Hf) and Te₇[AsF₆]₂ have another unique common feature. They are the only representatives which contain besides a polymeric chalcogen cation discrete monomeric anions. All other compounds composed of polymeric chalcogen cations also contain polymeric anions.



Fig. 4 The total density of states (DOS) for $Te_6[ZrCl_4]$ as obtained by an eH band structure calculation. The dotted line represents the integration over all states, the broken line indicates the niveau of the Fermi energy E_F .

The structure of the cation $(Te_6^{2+})_n$ in Te₆[MCl₆] (M = Zr, Hf) shows distinct differences to the cations in the structures of Te₆[WOCl₄]₂ [24] and Te₆[NbOCl₄]₂ [25]. Both the latter compounds consist of discrete molecular Te₆²⁺ cations in the form of six-membered rings which are in a strongly bent boat conformation and remind of a trigonal prism with two open edges. However, no simple mechanism for a polymerisation of the discrete Te₆²⁺ ions to the polymeric strand of $(Te_6^{2+})_n$ can be set up without substantial rearrangement of the atoms.

Since one-dimensional infinite bonding is present in the structure of Te₆[MCl₆] (M=Zr, Hf) we performed band structure calculations on the extended Hückel level [26] to gain insight into the chemical bonding especially along the polymeric Te chain. In the band structure no electronic bands are crossing the level of the Fermi energy which was calculated to -7.6 eV. The next and unoccupied bands are 1.8 eV higher in energy, indicating that $Te_6[ZrCl_6]$ is a semiconductor. Figure 4 shows the total density of states. The total density of states reaches zero at the Fermi level. The projected DOS shows that the highest occupied band between -7.6 and -12 eV is mainly originated by Te p orbitals indicating the electron dispersion along the Te chain. Since this band is completely filled with electrons the polycationic structure can be termed electron precise. The shape of the first unoccupied band is very acute and corresponds to Zr 5s orbitals. A population analysis gives the charges

on the Te atoms. In line with the formal description the effective charges on the Te atoms Te(2), Te(3), and Te(4) are very low, not exceeding +0.15 units, while the threefold coordinated Te(1) exhibits a charge of +0.83.

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