Octachalcogen Cations $\text{Te}_8^{2+}$, $\text{Se}_8^{2+}$, and Mixed ($\text{Te}_x\text{Se}_{10-x}$), $x^{2+}$ Stabilized by Chlorometallates of Bi, Zr, and Hf: Synthesis and Crystal Structures of $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$ and $\text{E}_8[\text{MCl}_6]$ (E = Se, Te; M = Zr, Hf)

A. Baumann, J. Beck*, and T. Hilbert

Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany

* Reprint requests to Professor J. Beck. Fax: (49) 228 73 56 60. E-mail: j.beck@uni-bonn.de

Z. Naturforsch. 54b, 1253-1259 (1999); received July 15, 1999

Octaselenium(2+), Octatellurium(2+), Chalcogen Polycations, Halogenobismutates(III), Crystal Structure

The title compounds were obtained by the reaction of elemental chalcogens E (E = Se, Te) with the respective tetrachlorides ECl$_4$ and the Lewis acidic metal halides ZrCl$_4$, HfCl$_4$, and BiCl$_4$. An alternative way, particularly for the preparation of mixed Se/Te-species, is the enlargement of smaller cationic rings in E$_2$[MCl$_6$] ($M = Zr, Hf$) by adding the respective complementary chalcogen. All reactions were carried out in sealed, evacuated glass ampoules at temperatures between 120 °C and 220 °C, and yielded black crystals of $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$, ($\text{Te}_6\text{Se}_{30}$)[HfCl$_6$], ($\text{Te}_6\text{Se}_{27}$)[ZrCl$_6$], ($\text{Te}_6\text{Se}_{15}$)[ZrCl$_6$] and $\text{Te}_8[\text{HfCl}_6]$, which have been identified by crystal structure analyses. All five compounds contain eight-membered chalcogen rings in an endo-exo-conformation which are isostrophic to the known octachalcogen dications E$_8^{2+}$ (E = S, Se, Te). While in ($\text{Te}_6\text{Se}_{30}$)[HfCl$_6$], ($\text{Te}_6\text{Se}_{27}$)[ZrCl$_6$], ($\text{Te}_6\text{Se}_{15}$)[ZrCl$_6$] and $\text{Te}_8[\text{HfCl}_6]$ the molecular polycations are surrounded by discrete, octahedral [MCl$_6$]$^{2-}$-counters, $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$ contains a two-dimensional polymeric anion ([Bi$_4$Cl$_{14}$]$^{2-}$)- built off of a variety of vertex and edge-sharing BiCl$_4$-polyhedra ($x \approx 6, 7$). The Bi-Cl bond lengths are spread over a wide range between 250 and 350 pm.

**Introduction**

Polycationic clusters of the chalcogens sulfur, selenium, and tellurium have been known for a long time. In the last 25 years a large number of these species with different composition, charge and a wide structural diversity have been synthesized and characterized [1 - 4]. Within this field the ions $E_8^{2+}$ (with $E = S$, Se, Te, S/Te, Se/Te) have proven to be the most versatile, as there exist a couple of isomers. One of these has a strong resemblance to the rings found in cycloocta-sulfur [5], red selenium [6] and Teg$_2^+$ in Teg$_4$[W$_6$C$_4$H$_7$] [13] built analogously to the structure of bicyclo[3.3.0]octane, and $\text{Te}_2\text{Se}_5^{2+}$ in ($\text{Te}_2\text{Se}_6$)($\text{Te}_2\text{Se}_3$)[AsF$_6$]$_4$ - 2 SO$_2$ [14] with a bicyclo[2.2.2]octane structure.

We now succeeded in preparing several new compounds containing $\text{Se}_8^{2+}$, $\text{Te}_8^{2+}$ and mixed (Se/Te)$_x^{2+}$ ions, which all have a discrete molecular ring structure [15].

**Experimental**

$\text{SeCl}_4$, $\text{Se}_2\text{Cl}_2$, $\text{TeCl}_4$, ZrCl$_4$, HfCl$_4$ and BiCl$_4$ were obtained from the elements [16] and purified by sublimation. Tellurium (Riedel-de Häën, 99.5%) was separated from oxidic impurities by melting and decanting, selenium (Riedel-de Häën, > 99.5%) was used without further treatment. $\text{Te}_4[\text{HfCl}_6]$ and $\text{Se}_4[\text{MCl}_6]$ ($M = Zr, Hf$) were prepared as described [17].

All compounds were handled in an argon-filled glove box. The reactions were carried out in evacuated and sealed glass ampoules of 1 cm in diameter and of 10 - 15 cm length, which were placed in horizontal tube furnaces.

0932-0776/99/1000-1253 $06.00$ © 1999 Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com
Table I. Crystallographic data and details of structure refinement for compounds I to V. Standard deviations are given in parentheses.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Lattice constants [pm, °]</th>
<th>Unit cell volume [Å³]</th>
<th>Density (calc.) [g·cm⁻³]</th>
<th>Crystal dim. [mm]</th>
<th>Absorpt. coeff. µ [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se₈⁻{Bi₄Cl₄} (I)</td>
<td>Bi₄Cl₄Se₈</td>
<td>triclinic</td>
<td>PI</td>
<td>a = 1048.1(2)</td>
<td>1503.8(4)</td>
<td>4.34</td>
<td>0.32</td>
<td>342.5</td>
</tr>
<tr>
<td>(Te₅.5Se₃.5)⁻{HfCl₆} (II)</td>
<td>Cl₆Hf⁻</td>
<td>monoclinic</td>
<td>P2₁/c</td>
<td>b = 1170.1(2)</td>
<td>1844(2)</td>
<td>4.56</td>
<td>0.23-0.15-0.39</td>
<td>4.26</td>
</tr>
<tr>
<td>(Te₆.5Se₁.5)⁻{ZrCl₆} (III)</td>
<td>Cl₆Se₁.5</td>
<td>monoclinic</td>
<td>P2₁/c</td>
<td>c = 1364.3(2)</td>
<td>1861.3(2)</td>
<td>4.26</td>
<td>0.19-0.15-0.50</td>
<td>4.36</td>
</tr>
<tr>
<td>(Te₅.3Se₂.7)⁻{Zr} (IV)</td>
<td>Cl₆Te₅.3</td>
<td>monoclinic</td>
<td>P2₁/c</td>
<td>α = 76.04(2)</td>
<td>1486.8</td>
<td>4.39</td>
<td>0.19-0.15-0.15</td>
<td>4.36</td>
</tr>
<tr>
<td>Te₇⁺{HfCl₆} (V)</td>
<td>Cl₆HfTe₇</td>
<td>triclinic</td>
<td>P1</td>
<td>β = 86.28(2)</td>
<td>139.9</td>
<td>4.26</td>
<td>0.15</td>
<td>179.4</td>
</tr>
</tbody>
</table>

The reaction of Se, SeCl₄ and BiCl₃ in a molar ratio of 3 : 1 : 6 (120 mg total amount) resulted in black crystals after two weeks at 120 °C. Higher yields of (I) were obtained within several days at room temperature, when Se₂Cl₂ was added as a solvent.

II is formed by reaction of Te and Se₄[HfCl₆] or Se and Te₄[HfCl₆] in a molar ratio of 4 : 1 (136 mg and 171 mg total amount). III is obtained from Te and Se₄[ZrCl₆] in a molar ratio of 4 : 1 (113 mg total amount). IV is formed from Te and Se₄[ZrCl₆] in a molar ratio of 5 : 1 (148 mg total amount), and V from Te and Te₄[HfCl₆] in a molar ratio of 4 : 1 (76 mg total amount) or alternatively from Te, TeCl₄ and HfCl₆ in a molar ratio of 11 : 1 : 2 (165 mg total amount).

Black crystals of II, III and IV were obtained within three weeks at 185 °C with Se₂Cl₂ as byproduct. Independent of the synthetic approach at 170 °C or 220 °C, respectively, black crystals of V were formed within one week along with crystals of the starting material Te₄[HfCl₆] and another yet unidentified phase.

Crystal structure analyses

Since all compounds are moisture-sensitive the selected crystals were sealed under argon in glass capillaries. Table I contains the crystallographic data and further details of the data collection and refinement. The data sets were collected with a STOE AED 2 four circle or with a STOE IPDS image plate diffractometer at room temperature using Mo-Kα radiation. The structures were solved by direct methods [18] and refined with anisotropic displacement parameters for all atoms [19]. A numerical absorption correction was applied to all data sets. The crystal shapes were optimized with the aid of the program HABITUS [20]. The compositions of the mixed cations were derived from refinement of the site

Se₈⁻{Bi₄Cl₄} (I)

The reaction of Se, SeCl₄ and BiCl₃ in a molar ratio of 3 : 1 : 6 (120 mg total amount) resulted in black crystals after two weeks at 120 °C. Higher yields of (I) were obtained within several days at room temperature, when Se₂Cl₂ was added as a solvent.
occupation factors. Further details of the crystal structure analyses have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, and are available by quoting the authors, the literature citation and the deposit number CSD-410302 for I, CSD-410303 for II, CSD-410304 for III, CSD-410305 for IV, and CSD-410306 for V.

**Results and Discussion**

**Syntheses**

The formation of compounds I and V with homonuclear polycations can be interpreted as a comproportionation of the chalcogen and the corresponding tetrachloride to a subvalent intermediate followed by a Lewis acid base reaction of this intermediate with the respective metal chloride.

\[
15 \text{Se} + \text{SeCl}_4 + 8 \text{BiCl}_3 \rightarrow 2 \text{Se}_8[\text{Bi}_4\text{Cl}_{14}] \quad (I)
\]

\[
15 \text{Te} + \text{TeCl}_4 + 2 \text{HfCl}_4 \rightarrow 2 \text{Te}_8[\text{HfCl}_6] \quad (V)
\]

Another way of synthesis is the reaction of a polycation containing compound with an excess of elemental chalcogen. Thus, V and the heteronuclear polycations in the compounds II - IV were formed by formal enlargement of smaller cationic rings.

\[
\text{Se}_4[\text{MCl}_6] \quad (\text{M = Hf, Zr}) + 4 \text{Te} \\
\rightarrow (\text{Te}_{8-x}\text{Se}_x)_8[\text{MCl}_6] \quad (II - IV)
\]

\[
\text{Te}_4[\text{MCl}_6] \quad (\text{M = Hf, Zr}) + 4 \text{Se} \\
\rightarrow (\text{Te}_{8-x}\text{Se}_x)_8[\text{MCl}_6] \quad (II - IV)
\]

\[
\text{Te}_4[\text{HfCl}_6] + 4 \text{Te} \rightarrow \text{Te}_8[\text{HfCl}_6] \quad (V)
\]

All reactions yielded significant amounts of byproducts such as subhalides of the chalcogens or phases containing other polycations of selenium and/or tellurium.

**Cation structures**

The removal of two electrons from the neutral, crown-shaped rings which occur in the structures of sulfur and red selenium with approximate $D_{4d}$ symmetry is accompanied by a contraction of the ring between two opposite atoms. The Zintl-Klemm concept states that the positive charges should be localized at these triply coordinated bridgehead atoms. Geometrical strains are avoided by flipping one atom from an endo to an exo position. The rings are deformed to an oval, which allows weak transannular bonds.

![Fig. 1. The structures of the $E_8^{2+}$ polycations in the structures of compounds I to V. Bond lengths and transannular distances are given in pm (mean standard deviations 0.3 pm). Relative Te/Se occupations on the different sites in the mixed species are given in percent in italic letters. Thermal ellipsoids are scaled to enclose 50% of the probability density (ORTEP [26]).](image-url)
Table II. Comparison of bond lengths in octaatomic chalcogen cations.

<table>
<thead>
<tr>
<th>Compound [Ref.]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₈[AsF₆]₂ [21]</td>
<td>204.3</td>
<td>283.2</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>203.3</td>
<td>288.9</td>
<td>204.5</td>
<td>1.41</td>
</tr>
<tr>
<td>S₈[Sb_4F_22] [22]</td>
<td>205.0</td>
<td>284.2</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>S₈[AICl₄] [110]</td>
<td>231.8</td>
<td>284.2</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>(Se₈)(Te₆)[AsF₆]₂ [22]</td>
<td>230.6</td>
<td>290.5</td>
<td>233.4</td>
<td>1.24</td>
</tr>
<tr>
<td>S₈[Bi_4Cl_4]</td>
<td>232.3</td>
<td>296.5</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>(Te₆)[HfCl₆]</td>
<td>259.6</td>
<td>301.1</td>
<td>262.6</td>
<td>1.15</td>
</tr>
<tr>
<td>(Te₆.1Se₇)[ZrCl₆]</td>
<td>261.7</td>
<td>301.5</td>
<td>264.3</td>
<td>1.14</td>
</tr>
<tr>
<td>(Te₆.5Se₁.5)[ZrCl₆]</td>
<td>269.0</td>
<td>304.6</td>
<td>271.5</td>
<td>1.12</td>
</tr>
<tr>
<td>Te₈[HfCl₆]</td>
<td>273.3</td>
<td>305.7</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>Te₈[ReCl₆] [12]</td>
<td>272.5</td>
<td>315.3</td>
<td>280.3</td>
<td>1.12</td>
</tr>
<tr>
<td>Te₈[WCl₆] [13]</td>
<td>275.2</td>
<td>299.3</td>
<td>1.06</td>
<td></td>
</tr>
</tbody>
</table>

A: Mean bond length in the outer diameter of the E₈⁺⁺ ring [pm]. B: Shortest transannular bond [pm]. C: E-E single bond lengths in the octaatomic molecular forms of the elements. a Values for the hypothetical mixed neutral species are calculated using the bond lengths in the homonuclear rings and weighting them with the chalcogen ratio found in the corresponding cations. D: Ratio B/C expresses the relative lengthening of the transannular bonds with respect to a covalent single bond.

The shortest transannular distance in the Se₈⁺⁺ ion of compound I is 296.5 pm. The transannular bond is thus weaker in comparison with Se₈[AICl₄]₂ (284.2 pm [11]) or (Te₆)(Se₈)[AsF₆]₂.

Fig. 2. Comparison of the association of adjacent polycationic rings in Te₈[HfCl₆] (top) and Te₈[WCl₆] (bottom). Weak Te-Te bonds longer than 280 pm are drawn as white sticks.

SO₂ (290.5 pm [12]). The bicyclic character resulting from the ring contraction increases in the order S₈⁺⁺, Se₈⁺⁺, Te₈⁺⁺, reflecting a stronger charge localization for the heavier homologues (Table II). In S₈⁺⁺ the transannular bonds are apparently very weak, since the shortest transannular distance is about 50% longer than a covalent single bond. With increasing Te content the transannular contacts become closer and reach 305.7 pm in Te₈[HfCl₆] (V) which is only about 10% longer than the normal single bond between Te atoms. The transannular interaction in the octachalcogen rings of II - V is strong as compared to that in Te₈[WCl₆]₂, which is described with a distinct bicyclic geometry [14]. It is not possible to categorize the transannular interactions in the E₈⁺⁺ ions in a scheme of bond length-bond strength. The existence of transannular bonds.
in $E_8^{2+}$ ions was the subject of various theoretical treatments at different levels of sophistication. The most recent work has presented ab initio calculations on $S_8^{2+}$ and $S_{8-x}^{2+}$ [23]. A definitive answer, however, could not be given since even upon different theoretical approaches it was not possible to reproduce the structures of the ions found in the solid state.

Between two neighboring cationic rings in the structures of IV and V a short intermolecular distance of 347 pm is present. This distance is comparable to the one between neighboring rings in Te$_8$[WCl$_6$]$_2$ (342 pm) and the secondary Te-Te interaction in the element (349 pm). In the case of Te$_8$[WCl$_6$]$_2$ this results in a polymeric (Te$_8^{2+}$)$_n$ strand. In IV and V two rings form (Te$_8^{2+}$)$_2$ dimers with no further Te neighbors closer than 384 pm (Fig. 2).

**Anion structures**

In four of the five compounds presented the polycationic rings are surrounded by discrete, slightly distorted octahedral [MCl$_6$]$^{2-}$ anions. In all structures the M-Cl distances vary only between 242.8(1) pm and 249.6(1) pm and are in good accordance with the sum of the covalent radii.

The structures of (Te$_{6.5}$Se$_{1.5}$)[ZrCl$_6$] (IV) and Te$_8$[HfCl$_6$] (V) are isotypic and can be deduced from a simple AB type, namely the CsCl structure. The MCl$_6$ octahedra occupy the eight vertices and the Te$_8$ rings the center of a distorted cube (Fig. 3).

In contrast to compounds II to V the $S_{8-x}^{2+}$ ions in Ses[Bi$_4$Cl$_{14}$] are enclosed sandwich-like by two-dimensionally infinite layers of chlorobismutate anions. In Fig. 4 a detailed view of the anionic layer parallel to the $ac$ plane shows the complex linking of the Bi-Cl polyhedra by shared edges and vertices. The wide range of Bi-Cl distances causes different kinds of coordination for the four crystallographically independent Bi atoms.

Bi(2) and Bi(3) have three short Bi-Cl bonds of about 250 pm with a large gap to the next series of Cl atoms starting at about 300 pm. Bi(1) and Bi(4) do not show such a distinct preference to form BiCl$_3$ molecules. If one defines a first coordination sphere with a radius of 310 pm, Bi(1) and Bi(4) obtain the coordination number five in form of a tetragonal pyramid, Bi(2) forms a distorted BiCl$_6$ octahedron and Bi(3) has coordination number four in very strongly distorted tetrahedral fashion. Enlarging the coordination sphere to a radius of 350 pm around each Bi atom gives coordination number seven in the form of distorted pentagonal bipyramids for Bi(1), Bi(3), and Bi(4).

The complex linking of irregular Bi-Cl polyhedra to an extended chlorobismutate anionic substructure seems to be a typical feature for compounds with polycationic clusters since it was also observed in...
the structures of Te$_4$[Bi$_6$Cl$_{20}$] [24] and the bismuth subhalide Bi$_6$Cl$_7$ = Bi$_9^{5+}$[Bi$_5$Cl$_{14}$]$^{5-}$ [25].

**Cation-anion interactions**

Generally only weak Lewis basic anions are suitable to stabilize naked polycationic clusters against oxidation. In comparison to discrete complex ions the polymeric [Bi$_5$Cl$_{14}$]$^{2-}$ ion has a relatively soft Lewis basic character, resulting in a stronger interaction with the polycations. The shortest chalcogen-halogen distances in Seg$_8$[Bi$_4$Cl$_{14}$] of 306 pm are significantly shorter than the values of 325 pm found in Seg$_8$[AlCl$_4$]. This is accompanied by an effective shielding of the cations against each other, as revealed by the shortest intermolecular Se-Se distance of 413 pm in Seg$_8$[Bi$_4$Cl$_{14}$] compared to 385 pm in Seg$_8$[AlCl$_4$]$_2$ [10]. Moreover, the surrounding anionic chlorobismutate matrix favors a stronger charge delocalization within the cationic ring, which explains a relatively long transannular Se-Se distance and thus a less marked bicyclic character as well as a poorly pronounced alternance of the bond lengths along the ring.

**Acknowledgements**

The support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

---