Chalcogen Polycations with Mononuclear Divalent Anions from Chalcogen Subhalides and Tetrachlorides of Zr and Hf: Syntheses and Crystal Structures of $Se_4(MCl_6)$ (M = Zr, Hf) and $Te_4(HfCl_6)$

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Selenium, $SeCl_4$, and MCl_4 (M = Zr, Hf) react in a sealed evacuated glass ampoule at 130°C to afford red, moisture sensitive crystals of $Se_4^{2+}(ZrCl_6^{2-})$ and $Se_4^{2+}(HfCl_6^{2-})$. The isotypic crystal structures (tetragonal, $P4_2/ncm$, Z = 4) consist of square-planar Se_4^{2+} cations and slightly distorted octahedral MCl_6^{2-} (M = Zr, Hf) anions. The ions are packed corresponding to the NaCl structure type with the centres of gravity of the Se_4 rings and the metal atoms of the MCl_6 octahedra in the Na and Cl positions. From Te, $TeCl_4$, and $HfCl_4$ one obtains under similar conditions at 200°C $Te_4^{2+}(HfCl_6^{2-})$ in form of dark violet crystals. The crystal structure (triclinic, $P\bar{1}$, Z = 1) is built of nearly square-planar Te_4^{2+} ions and octahedral $HfCl_6^{2-}$ ions. The packing of the ions corresponds to a rhombohedrally distorted CsCl structure type.

Chalcogen polycations can be synthesized either by oxidation of elemental chalcogens by main group or transition metal halides or by Lewis acid-base reactions between chalcogen subhalides and suitable halogenide acceptors. To obtain tetrachalcogen(2+) ions the elemental chalcogens can be oxidized with AsF_5 or SbF_5 in liquid SO_2 as solvent[1] or in vapour transport reactions with $MoOCl_4$[2] or WCl_6[3]. $AlCl_3$[4] and $NbCl_5$[5] turned out as suitable Lewis acids in reactions with mixtures of Te and $TeCl_4$. $ZrBr_4$ showed similar properties in the reaction with Te_2Br which leads to the formation of $Te_4^{2+}(Zr_2Br_{10}^{2-})$[6]. In continuation of our studies of chalcogen polycations we performed reactions of $Se/SeCl_4$ and $Te/TeCl_4$ mixtures with $ZrCl_4$ and $HfCl_4$ and obtained $Te_4(Zr_2Cl_{10})$[7], $Te_4(HfCl_6)$, $Se_4(ZrCl_6)$, and $Se_4(HfCl_6)$ of which the latter three are described in this article. They are the first compounds consisting of chalcogen polycations and mononuclear divalent anions and adopt simple basic structure types.

Preparation of $Se_4(MCl_6)$ (M = Zr, Hf) and $Te_4(HfCl_6)$

The tetrachlorides of zirconium and hafnium react with mixtures of $Se/SeCl_4$ and $Te/TeCl_4$ with formation of tetrachalcogen(2+) and hexachlorometallate ions.

$$7\ Se + SeCl_4 + 2\ ZrCl_4 \rightarrow 2\ Se_4^{2+}(ZrCl_6^{2-})$$

$$7\ Se + SeCl_4 + 2\ HfCl_4 \rightarrow 2\ Se_4^{2+}(HfCl_6^{2-})$$

$$7\ Te + TeCl_4 + 2\ HfCl_4 \rightarrow 2\ Te_4^{2+}(HfCl_6^{2-})$$

The reactions were carried out in sealed evacuated glass ampoules in a temperature gradient 135–120°C for $Se_4(MCl_6)$ and 215–195°C for $Te_4(HfCl_6)$. The light red crystals of $Se_4(MCl_6)$ show predominantly the shape of needles with a square cross-section and are deposited from the vapour on the cooler side of the ampoule within two days while crystals of $Te_4(HfCl_6)$ are dark violet with a shape of elongated cubes and are formed within two weeks. All three compounds are easily hydrolyzed in moist air and are formed in nearly quantitative yield.

Crystal Structure of $Se_4(MCl_6)$ (M = Zr, Hf)

The isotypic crystal structures of these compounds are built of Se_4^{2+} and of MCl_6^{2-} ions. Tables 1 and 2 contain the crystal data and atomic coordinates; Figure 1 gives a view of the ions [*], Figure 2 shows the unit cell. The planar Se_4^{2+} ions possess $2/m$ (C_{2h}) symmetry with the atoms Se(1) and Se(1^I) located in the mirror plane and the atoms Se(2) and Se(2^I) located on the twofold axis. All four Se–Se distances have the equal length of 229.1(1) pm for M = Zr and 229.2(1) pm for M = Hf. Only the Se–Se–Se angles of 89.52(2) and 90.48(2)° and 89.48(4) and 90.52(4)° for M = Hf show a significant difference from the ideal square (D_{4h}) symmetry. Bond length and angles agree well with other halogenometallates containing Se_4^{2+} ions, e.g. $Se_4(MoOCl_4)_2$[2] or $Se_4(AlCl_4)_2$[8]. The MCl_6^{2-} ions form slightly distorted octahedra and possess $2/m(C_{2h})$ symmetry with the metal atom located on the centre of inversion and Cl(1) and Cl(1^{II}) in the mirror plane. Due to the symmetry only two independent M–Cl distances are observed for the anions which show slight differences. In the $ZrCl_6^{2-}$ ions the Zr–Cl(1) distances are 242.1(1) pm and the Zr–Cl(2) distances 247.2(1) pm, in the $HfCl_6^{2-}$ ions these distances are 241.1(1) and 245.8(1) pm, respectively. Distortions of the halogenometallate ions in compounds with chalcogen polycations are typical and can be explained by strong interactions between the cations and the halogen atom of the anions. The Se_4^{2+} ions in the structures of $Se_4(MCl_6)$ are

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[*] The ions in the structures of $Se_4(ZrCl_6)$ and $Se_4(HfCl_6)$ are very similar, so a separate figure for $Se_4(HfCl_6)$ is dispensable.

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coordinated in the typical way: four Cl atoms with short Se−Cl distances span the edges of the Se_4 square. The shortest contacts are 299.2 pm for $Se_4(ZrCl_6)$ and 299.6 pm for $Se_4(HfCl_6)$. Se···Cl contacts of the same order are observed in $Se_4(MoOCl_4)_2$ (290.1 pm)[2] or $Se_4(AlCl_4)_2$ (310.1 pm)[8].

Figure 1. The Se_4^{2+} and $ZrCl_6^{2-}$ ions in the structure of $Se_4(ZrCl_6)$; thermal ellipsoids are scaled to enclose 70% of the probability density (ORTEP[15]); symmetry operations: I: $-x, -y, -z + 1$, II: $-x, -y, -z$, III: y, x, z, IV: $-y, -x, -z$; selected distances [pm] and angles [°] {respective values for $Se_4(HfCl_6)$ are given in braces}: Se(1)−Se(2) 229.1(1) {229.2(2)}, Zr−Cl(1) 242.1(1) {241.1(1)}, Zr−Cl(2) 247.3(1) {245.8(1)}; Se(2)−Se(1)−Se(2^I) 89.52(2) {89.48(4)}, Se(1)−Se(2)−Se(1^I) 90.48(2) {90.52(4)}

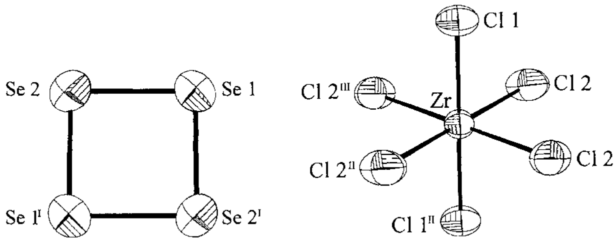
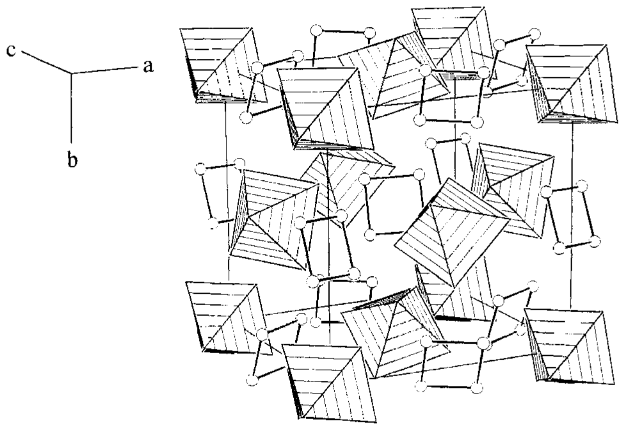


Figure 2. The unit cell of $Se_4(MCl_6)$ (M = Zr, Hf); MCl_6^{2-} ions are drawn as shaded octahedra



The ions in the structures of $Se_4(MCl_6)$ are arranged as Na^+ and Cl^- ions in the NaCl structure type. The metal atoms of the MCl_6^{2-} octahedra are located in all corners and in all centres of the faces of the unit cell. The centres of gravity of the Se_4^{2+} ions are located on the middle of all edges and in the centre of the unit cell. The lattice constants are pseudo-cubic [a = 1088.4, c = 1040.9 pm for $Se_4(HfCl_6)$, see Tables 1 and 2] and so every ion is surrounded by six counterions in a nearly regular octahedral fashion. The close relationship between the NaCl and the $Se_4(MCl_6)$ structure is confirmed by the possibility of establishing supergroup-subgroup relations between the respective space groups (Figure 3)[9]. Without changing the unit cell dimensions only three steps of symmetry reduction, on step being *translationengleich* with loss of the threefold axis and two steps being *klassengleich* with loss of centering, lead from $Fm\bar{3}m$ to the actual tetragonal space group $P4_2/ncm$.

Table 1. Crystallographic data, structure determination[a] and fractional atomic coordinates for $Se_4(ZrCl_6)$

Atom	x	y	z
Zr	0	0	0
Se(1)	0.09053(3)	0.09053(3)	0.58039(5)
Se(2)	0.10469(3)	−0.10469(3)	0.5
Cl(1)	0.13915(6)	0.13915(6)	−0.1080(1)
Cl(2)	−0.0614(1)	0.16508(7)	0.14987(9)

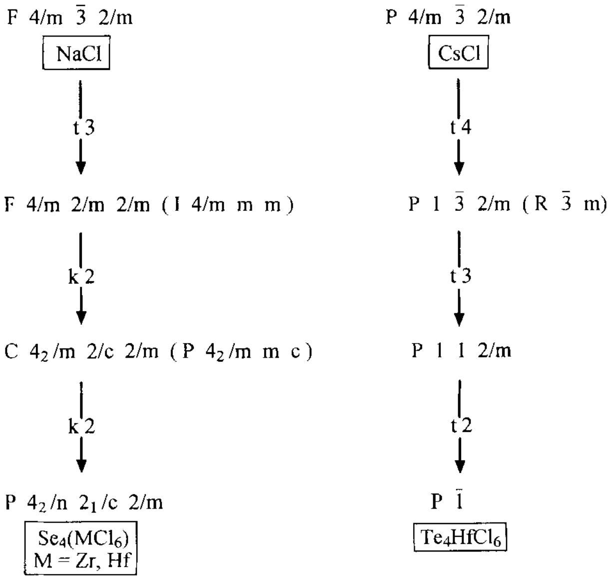
[a] Cl_6Se_4Zr; tetragonal; $P4_2/ncm$; a = 1089.6(1), c = 1041.0(2) pm; $V = 1235.9 \cdot 10^6$ pm³; $Z = 4$; four circle diffractometer STOE AED 2; Mo-K_α; 295 K; 7623 reflections collected in the range $3° < 2\Theta < 60°$; 975 unique reflections; $R_{merge} = 0.055$; 975 reflections in least squares; 32 parameters; $\mu = 138$ cm^{-1}; empirical absorption correction based on 20 ψ-scanned reflections, $wR(F^2) = 0.061$; $R(|F|)$ for 847 reflections with $F > 4\sigma(F) = 0.026$; largest difference peak/hole +0.88/−0.63 e/10⁶ pm³.

Table 2. Crystallographic data, structure determination[a] and fractional atomic coordinates for $Se_4(HfCl_6)$

Atom	x	y	z
Hf	0	0	0
Se(1)	0.09090(5)	0.09090(5)	0.57993(8)
Se(2)	0.10481(5)	−0.10481(5)	0.5
Cl(1)	0.1388(1)	0.1388(1)	−0.1073(2)
Cl(2)	−0.0609(2)	0.1640(1)	0.1494(2)

[a] Cl_6HFSe_4; tetragonal; $P4_2/ncm$; a = 1088.4(2), b = 1040.9(2) pm; $V = 1233.1 \cdot 10^6$ pm³; $Z = 4$; four circle diffractometer STOE AED 2; Mo-K_α; 295 K; 7587 reflections collected in the range $3° < 2\Theta < 60°$; 969 unique reflections; $R_{merge} = 0.109$; 969 reflections in full matrix least squares; 32 parameters; $\mu = 212$ cm^{-1}; empirical absorption correction based on 10 ψ-scanned reflections, $wR(F^2) = 0.075$; $R(|F|)$ for 744 reflections with $F > 4\sigma(F) = 0.032$; largest difference peak/hole +0.89/−0.98 e/10⁶ pm³.

Figure 3. Symmetry relation between the structures of NaCl and $Se_4(MCl_6)$ (left) and CsCl and $Te_4(HfCl_6)$ (right), depicted as a supergroup-subgroup family tree. The conventional settings of the unconventional space group symbols obtained by symmetry reduction are given in parentheses



The ideal ratio of the radii of anion and cation in the NaCl structure type for filling the octahedral interstices in the cubic closest anion packing is 1:0.414 but the structure type is realized in a wide span from 1:0.35 up to 1:1[10]. Although the Se_4^{2+} ions are square-planar they have several orientations and can on average be regarded as a spherical case with a radius of 162 pm[*]. The different orientations of the MCl_6 octahedra also allow a spherical approximation of their structure with a radius equivalent to the mean M−Cl distance of 245 pm. The ratio of the radii of anion to cation for the $Se_4(MCl_6)$ structure is 1:0.66. This falls into the range for the NaCl structure type.

Crystal Structure of $Te_4(HfCl_6)$

The crystal structure is built of discrete Te_4^{2+} and $HfCl_6^{2-}$ ions. Table 3 contains the crystal data and atomic coordinates; Figure 4 shows the structure of the ions, Figure 5 gives a view of the unit cell. The planar, centrosymmetric Te_4^{2+} ions are with Te−Te distances of 267.1(1) and 268.2(1) pm and Te−Te−Te angles of 89.89(3) and 90.11(3)° only slightly distorted from D_{4h} symmetry. The $HfCl_6^{2-}$ octahedra are also centrosymmetric with the Hf atom located on the inversion centre. The three independent Hf−Cl distances of 241.7(1), 245.4(1), and 246.2(1) pm and the Cl−Hf−Cl angles that range from 89.04(7) to 90.96(7)° show the nearly regular octahedral symmetry.

Table 3. Crystallographic data, structure determination[a] and fractional atomic coordinates for $Te_4(HfCl_6)$

Atom	*x*	*y*	*z*
Hf	0	0	0
Te(1)	0.27738(5)	−0.31924(5)	0.45809(5)
Te(2)	0.50408(6)	−0.57980(5)	0.28775(4)
Cl(1)	0.1277(2)	−0.3524(2)	0.1084(2)
Cl(2)	0.2700(3)	0.1270(2)	0.0884(3)
Cl(3)	0.2157(3)	0.0229(3)	−0.3046(2)

[a] Cl_6HfTe_4; triclinic: $P\bar{1}$; $a = 677.6(3)$, $b = 683.3(3)$, $c = 788.0(3)$ pm, $\alpha = 73.93(2)°$, $\beta = 75.71(2)°$, $\gamma = 84.74(2)°$; $V = 339.7 \cdot 10^6$ pm^3; $Z = 1$; four-circle diffractometer STOE AED 2; MoK_α; 295 K; 3986 reflections collected in the range $3° < 2\Theta < 60°$; 1993 unique reflections; $R_{merge} = 0.030$; 1993 reflections in full matrix least squares; 53 parameters; $\mu = 172$ cm^{-1}; empirical absorption correction based on 5 ψ-scanned reflections, $wR(F^2) = 0.063$, $R(|F|)$ for 1934 reflections with $F > 4\sigma(F) = 0.022$; largest difference peak/hole +1.00/−0.72 e/10^6 pm^3.

The shortest interionic contacts are Te(1)···Cl(1) with 324.9 pm and Te(2)···Cl(1) with 330.8 pm and are in same order as in $Te_4(WCl_6)_2$[3] or $Te_4(AlCl_4)_2$[4].

The ions in the structure of $Te_4(HfCl_6)$ are arranged according to a rhombohedrally distorted CsCl structure type. The metal atoms of the $HfCl_6^{2-}$ octahedra are located in all corners and the centre of gravity of the Te_4^{2+} squares in the centre of the unit cell. The lattice constants are close to a rhombohedral cell (Table 3). Every ion in the structure is surrounded by eight counterions in a strongly distorted cubic fashion. The supergroup-subgroup relation is depicted in Figure 3. Only three steps of symmetry reduction lead from the cubic space group $Pm\bar{3}m$ of CsCl to the actual space group $P\bar{1}$ of $Te_4(HfCl_6)$. The ionic radii arguments developed for the NaCl structure analogy of $Se_4(MCl_6)$ also hold for $Te_4(HfCl_6)$ althrough the Te_4^{2+} ions have all the same orientation. The "sphere radius" of Te_4^{2+} is 189 pm and the ratio of the radii of anions to cations is 1:0.77, which is very close to the ideal value 1:0.732 for the CsCl type. Simple crystal chemistry rules allow us to explain the difference between the structures of $Se_4(MCl_6)$ and $Te_4(HfCl_6)$: the enlargement of the cation size from Se_4^{2+} to Te_4^{2+} leads to a new structure type with a higher coordination number.

Figure 4. The Te_4^{2+} and $HfCl_6^{2-}$ ions in the structure of $Te_4(HfCl_6)$; thermal ellipsoids are scaled to enclose 70% of the probability density (ORTEP[15]); symmetry operations: I: $-x + 1, -y - 1, -z + 1$, II: $-x, -y, -z$; selected distances [pm] and angles [°]: Te(1)−Te(2) 267.1(1), Te(1)−Te(2^I) 268.2(1), Hf−Cl(1) 246.2(1), Hf−Cl(2) 241.7(1), Hf−Cl(3) 245.4(2); Te(2)−Te(1)−Te(2^I) 89.89(3), Te(1)−Te(2)−Te(1^I) 90.11(3)

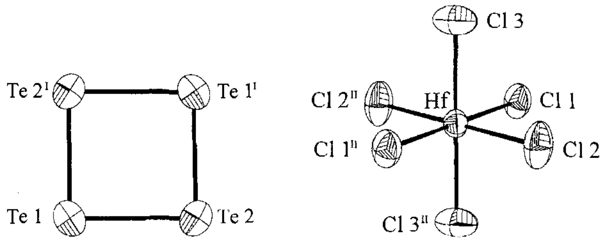
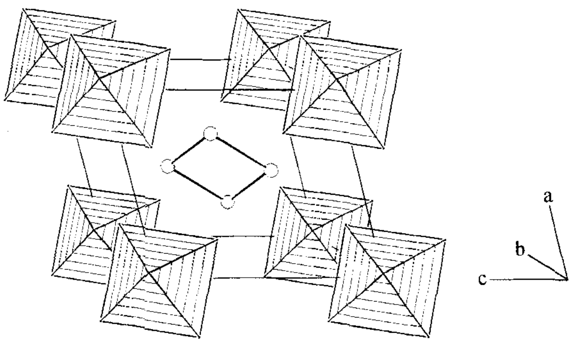


Figure 5. The unit cell of $Te_4(HfCl_6)$; $HfCl_6^{2-}$ ions are drawn as shaded octahedra



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Experimental

All experiments were carried out under dry Ar. Glass ampoules were heated to 300°C before use. Charging and opening of the ampoules were performed in an Ar-filled glove box. $TeCl_4$ and $SeCl_4$ were prepared from the elements according to literature procedures[11], $ZrCl_4$ and $HfCl_4$ were sublimed in vacuo before use, Se and Te (powder; Aldrich Company) were used as obtained.

cyclo-Tetraselenium(2+) Hexachlorozirconate(2−) [$Se_4^{2+}(HfCl_6^{2-})$] *and cyclo-Tetraselenium(2+) Hexachlorohafnate(2−)* [Se_4^{2+}-($HfCl_6^{2-}$)]: Selenium (55.3 mg, 0.7 mmol), $SeCl_4$ (22.1 mg, 0.1 mmol), and $ZrCl_4$ (46.6 mg, 0.2 mmol) or $HfCl_4$ (64.1 mg, 0.2 mmol) were filled in a glass ampoule (20 cm in length and 1.5 cm in diameter) which was evacuated and sealed. The ampoule was

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[*] The assumed radius is the mean distance from the centre of the ring to the four Se atoms.

placed in a horizontal tube furnace (temperature gradient 135 → 120°C). Red needle-shaped crystals were deposited in the cooler part of the ampoule within two days in nearly quantitative yield.

cyclo-Tetratellurium(2+) Hexachlorohafnate(2−) [Te_4^{2+}-($HfCl_6^{2-}$)]: Tellurium (89.3 mg, 0.7 mmol), $TeCl_4$ (26.9 mg, 0.1 mmol), and $HfCl_4$ (64.1 mg, 0.2 mmol) were placed in glass ampoule which was evacuated and sealed. The ampoule was placed in a horizontal tube furnace (temperature gradient 215 → 195°C). Within two weeks dark violet crystals formed on the cooler side of the ampoule in nearly quantitative yield.

Crystal-Structure Determinations of $Se_4(ZrCl_6)$, $Se_4(HfCl_6)$, and $Te_4(HfCl_6)$[12]: Tables 1, 2, and 3 contain the crystallographic data, details of data collection, refinement, and the positional parameters of the atoms. To avoid decomposition by hydrolysis in moist air the crystals were sealed in glass capillaries under Ar. All structures were solved by direct methods[13], all atoms were refined with anisotropic displacement parameters[14].

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