Solid State Polyselenides and Polytellurides: A Large Variety of Se–Se and Te–Te Interactions

Christian Graf, Abdeljalil Assoud, Oottil Mayasree and Holger Kleinke *

Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, Canada

* Author to whom correspondence should be addressed; E-mail: kleinke@uwaterloo.ca.

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Abstract: A large variety of different interactions between the chalcogen atoms, $Q$, occur in the solid state structures of polyselenides and polytellurides, including both molecular and infinite units. The simplest motifs are classical $Q_2^{2-}$ dumbbells and nonlinear $Q_n^{2-}$ chains ($n = 3, 4, 5, ..$), e.g. found in alkali metal polychalcogenides. In addition, nonclassical so-called hypervalent motifs exist in the form of linear $Q_3^{4+}$ units or within larger units such as $Q_4^{4+}$ and $Q_5^{4+}$. Infinitely extended $Q$ units include zigzag, cis/trans and linear chains, as well as planar and slightly puckered layers. Several of those are susceptible to Peierls distortions, leading to the formation of both commensurate and incommensurate superstructures and anomalies in transport properties, including metal-nonmetal transitions.

Keywords: selenium; tellurium; bonding; hypervalent

1. Introduction

Solid state materials based on chalcogenides, *i.e.*, sulfides, selenides and tellurides, play a large role in today's society. Examples include semiconductor devices, e.g. in solid state electronics [1], fast-ion conductors [2,3], rechargeable batteries [4], data storage including phase-change materials [5-7], chalcogenide glasses [8], and the thermoelectric energy conversion [9-12]. Polychalcogenides, like the potential thermoelectric material HfTe$_5$, are materials that comprise homonuclear bonds between negatively charged chalcogen atoms, e.g. a Se–Se bond within Se$_2^{2-}$ pairs of Rb$_2$Se$_2$ [13]. These bonds occur in chalcogen-rich materials, where the chalcogen atom cannot be reduced to attain the closed-shell formation as in $Q^2$. For example, Se carries a charge of −1 in Rb$_2$Se$_2$, like O in SrO$_2$, and
therefore forms one Se–Se bond. As such, Rb₂Se₂ is a typical Zintl phase. Zintl phases AXₓ consist of an electropositive element A (here: Rb) and a more electronegative element X of the later (post transition) main groups (here: Se). Assuming a complete charge transfer of all of A’s valence-electrons to X, the cation A⁺ possesses a full octet, and the (formal) anion Xₓ⁻ attains the octet by forming homonuclear X–X bonds in addition to the reduction by A. In most cases, these bonds are classical single bonds (two-center two-electron, 2c-2e), i.e. exactly one bond is formed for each electron missing to complete the octet of X [14-16].

The rich structural chemistry in particular of the polyselenides and polytellurides is the scope of this review, going beyond the common 2c-2e bonds: hypervalent interactions as found in XeF₂ [17] or SF₆ [18] are often observed in various fragments of these materials [19]. In addition, weaker fractional bonds or cohesive interactions of different lengths, as in elemental tellurium, render the Se/Te substructures intriguingly complex [20,21], which in turn may be beneficial for the thermoelectric energy conversion [22]. Four reviews about polychalcogenides from the years 1995 to 2000 underline the importance of this field [20,23-25].

2. Results and Discussion

2.1. Molecular units in polyselenides and polytellurides

2.1.1. Oligomeric Qₙ²⁻ motifs

The simplest polychalcogenide motif is the dumbbell unit Q₂⁻, occurring for example in Na₂Se₂ [26], Rb₂Se₂ and Rb₂Te₂ with Se–Se and Te–Te distances of 2.38 Å, 2.47 Å and 2.78 Å, respectively (Figure 1). These dumbbells are also found in organic compounds with similar bond lengths, e.g. in [N(CH₃)₄]₂Te₂ (d₁e–Te = 2.74 Å) [27] and [Na(CH₃OH)₃]₂Te₂ [28]. Assigning charges is straightforward in these examples, e.g. (Na⁺)₂Se₂⁻, with Se₂⁻ being isostructural to Br₂ and I₂, with 14 valence-electrons for the dumbbells, which are therefore held together by one 2c-2e bond. While generally these distances compare well with the sum of the single bond radii, r₆e = 1.17 Å and r₇e = 1.37 Å [29], the influence of the cations is evident, for the Se–Se bond in Rb₂Se₂ is approximately 0.1 Å longer than in Na₂Se₂.

**Figure 1.** From left to right: Oligomeric Qₙ²⁻ motifs in Na₂Se₂, K₂Se₃, Na₂Se₄, and K₂Se₅.

The dumbbells can formally be extended to oligomeric chain-like units Qₙ²⁻ (with n = 3, 4, 5, 6, 12, 13) by adding neutral Q atoms to the chain, wherein the terminal Q atoms remain negatively charged. Each neutral Q atom participates in two 2c-2e bonds, comparable to the elemental structures of
selenium and tellurium. \( \text{Se}_3^{2-} \) groups (with one central neutral Se atom) occur for example in, \( \text{K}_2\text{Se}_3 \) \[30\], \( \text{Sr}_2\text{SnSe}_5 \) \[31\] and \( \text{Ba}_2\text{SnSe}_5 \) \[32\], with bond lengths of approximately 2.4 Å, and \( \text{Te}_3^{2-} \) groups in \( \text{K}_2\text{Te}_3 \) with \( d_{\text{Te}-\text{Te}} = 2.80 \) Å \[33\] and in \( \text{Ba}_2\text{Au}_2\text{Te}_{14} \) with \( d_{\text{Te}-\text{Te}} = 2.89 \) Å \[34\]. It is evident that the lengths of regular single (2c-2e) bonds may vary substantially, noting that these bonds are significantly elongated compared to single \( r_{\text{Se}} = 2.34 \) Å and \( r_{\text{Te}} = 2.74 \) Å, respectively.

The \( \text{Q}_3^{2-} \) anions are bent, ideally exhibiting \( C_2h \) symmetry, with typical \( Q-Q-Q \) bond angles of 105° - 110°, in accordance with the VSEPR concept, which suggests tetrahedral arrangement of the two bonds and two free electron pairs around the central \( Q \) atom. The packing of the three-dimensional structure may cause a severe distortion of the angle as well, e.g. down to 92° in \( \text{Ba}_2\text{Au}_2\text{Te}_{14} \).

Anions with larger \( n \), such as \( \text{Se}_4^{2-} \) in \( \text{Na}_2\text{Se}_4 \) \( d_{\text{Se-Se}} = 2.35 \) Å and \( 2.36 \) Å \[35\], \( \text{Te}_4^{2-} \) in \( (\text{Ph}_3\text{P})_2\text{Te}_4:2\text{CH}_3\text{OH} \) \( d_{\text{Te-Te}} = 2.72 \) Å and \( 2.76 \) Å \[36\], \( \text{Se}_5^{2-} \) in \( \text{K}_2\text{Se}_5 \) \( 2.34 \) Å \( \leq \) \( d_{\text{Se-Se}} \leq 2.37 \) Å \[37\], and \( \text{Se}_6^{2-} \) in \( [\text{Me}_3\text{N}(\text{CH}_2)_{13}\text{CH}_3]\text{Se}_6 \) \( 2.27 \) Å \( \leq \) \( d_{\text{Se-Se}} \leq 2.35 \) Å \[38\] are best described as oligomeric zigzag or helical chain fragments. Larger chain-like polychalcogenide anions, though extremely rare, do exist, like \( \text{Te}_{12}^{2-} \) in \( [\text{N}(\text{C}_2\text{H}_5)_4]\text{Te}_{12} \) \[39\] and \( \text{Te}_{13}^{2-} \) in \( \text{Cs}_2\text{Te}_{13} \) \[40\] (Figure 2), and they are often - as in these two examples - interconnected via longer interchain interactions (here: 3.14 Å and 3.18 Å). These interactions are much shorter than twice the van der Waals radius and will be discussed later in this review.

**Figure 2.** Oligomeric \( \text{Te}_n^{2-} \) motifs in \( (\text{NET}_4)_2\text{Te}_{12} \) (left) and \( \text{Cs}_2\text{Te}_{13} \) (right).

2.1.2. Oligomeric \( Q_n^{4-} \) motifs

Since the \( Q_n^{4-} \) fragments comprise two more valence-electrons than their \( Q_n^{2-} \) counterparts, they cannot contain the same 2c-2e bonds. \( n = 2 \) is a hypothetical case only, as it would correspond to two isolated closed-shell \( Q^2- \) anions. \( n = 3 \) is realized in \( \text{Se}_3^{4-} \) units of \( \text{Ba}_2\text{Ag}_4\text{Se}_5 \) \[41\], and \( \text{Rb}_{12}\text{Nb}_6\text{Se}_{35} \) \[42\]. In the former, \( \text{Se}_3^{4-} \) exhibits the highest symmetry possible, namely linearity and equidistant interactions, thus point group \( D_{xbh} \), while \( \text{Rb}_{12}\text{Nb}_6\text{Se}_{35} \) is comprised of two differently distorted, almost linear \( \text{Se}_3^{4-} \) units of \( C_{3y} \) and \( C_1 \) symmetry, respectively. In these two compounds, the Se–Se–Se bond angle of \( \text{Se}_3^{4-} \) varies between 180° and 164°, and the Se–Se bond lengths between 2.59 Å and 2.77 Å (Figure 3).
Figure 3. From left to right: Se$_3^{4-}$ (D$_{sh}$), Se$_3^{4-}$ (C$_{2v}$), Se$_4^{4-}$, cis-Se$_5^{4-}$ and trans-Te$_5^{4-}$.

Ba$_2$Ag$_4$Se$_5$ contains two isolated Se$^{2-}$ anions and one Se$_3^{4-}$ per formula unit, according to the ionic formulation (Ba$^{2+})_2$(Ag$^{+})_4$Se$_3^{4-}$Se$_2^{2-}$. Electronic structure calculations and electrical conductivity measurements confirmed the semiconducting, hence electron precise character of this compound [41]. Rb$_{12}$Nb$_6$Se$_{35}$ is a special case, containing both Se$^{2-}$ and Se$_3^{4-}$ units, according to the formula (Rb$^{+})_{12}$(Nb$^{5+})_6$(Se$_3^{2-})_2$(Se$_2^{2-})_7$(Se$_3^{4-})_3$(Se$_2^{2-})_6$. Since diffuse reflectance measurements supported the semiconducting and thus closed-shell character of Rb$_{12}$Nb$_6$Se$_{35}$ [42], this treatment of Rb$_{12}$Nb$_6$Se$_{35}$ within the Zintl concept is justified.

With 22 valence-electrons, Se$_3^{4-}$ is isoelectronic with hypervalent linear XeF$_2$ and I$_3^{-}$. Several examples are known that contain the linear I$_3^{-}$ motif, including CsI$_3$ [43] and [Ph$_4$As]I$_3$ [44]. Ideally the two I–I distances are equivalent, with a bond angle of 180° as in [Ph$_4$As]I$_3$ (d$_{I-I} = 2.90$ Å), but deviations from the centrosymmetric arrangement are often found with smaller cations, like in CsI$_3$ with I–I bonds of 2.84 Å and 3.04 Å and a bond angle of 178°. The linear arrangement is well understood based on Rundle's model [45], which treats the s orbitals as well as the p orbitals of π symmetry as lone pairs. Then the frontier orbital set consists of one filled σ bonding, one filled nonbonding, and one empty σ antibonding molecular orbital, formed by the $p_z$ orbitals when $z$ corresponds to the molecular axis. The nonbonding orbital contains a nodal plane at the center of the triatomic unit, resulting in a three-center-four-electron (3c-4e) bond. The validity of Rundle's model was - in principle - confirmed for Se$_3^{4-}$ via Gaussian calculations using the B3LYP functional [41].

Since the 3c-4e bonds are electron deficient, containing only one bonding molecular orbital for two bonds (which is why they are often called "half" bonds), they are longer than the regular 2c-2e bonds. Correspondingly, the I–I single bond in I$_2$ of 2.76 Å is much shorter than the above-mentioned I–I bonds (2.84 Å and 3.04 Å), and Se–Se single bonds (2.34 Å) are shorter than the Se–Se bonds of Se$_3^{4-}$ (2× 2.77 Å in Ba$_2$Ag$_4$Se$_5$ and 2.59 Å - 2.65 Å in Rb$_{12}$Nb$_6$Se$_{35}$). In Rb$_{12}$Nb$_6$Se$_{35}$, the bond angles of approximately 164° deviate substantially from linearity, which is likely caused by the packing effect. Despite the distortion, the Se$_3^{4-}$ unit of Rb$_{12}$Nb$_6$Se$_{35}$ can easily be distinguished from the Se$_3^{2-}$ unit occurring in the same structure, which shows bond distances of 2.39 Å and a bond angle of 94°.

While no isolated, linear hypervalent Te$_3^{4-}$ anion has been reported so far, the isoelectronic linear units P$_3^{7-}$, As$_3^{7-}$, Sb$_3^{7-}$, and Bi$_3^{7-}$ all occur in the numerous representatives of the Ca$_{14}$AlSb$_{11}$ type [46], including Ca$_{14-x}$Eu$_x$MnSb$_{11}$, which exhibits colossal magnetoresistance [47], and the high temperature thermoelectric Yb$_{14}$MnSb$_{11}$ [48].

The only $Q_4^{4-}$ representative known to date is Se$_4^{4-}$ in K$_3$CuNb$_2$Se$_{12}$ [49], which is basically an almost linear Se$_3^{4-}$ unit (bond angle: 166°) with an additional Se atom attached via a single bond to one
end. Therefore, its ideal valence-electron number is 28, namely 22 for the Se$^{4-}$ fragment plus six for the additional Se atom. Within this model, we interpret the two bonds of the linear part as 3c-4e bonds and the exo bond as 2c-2e. This is in accord with the 2.73 Å and 2.54 Å distances for the (pseudo) collinear bonds, and the short 2.39 Å bond to the fourth Se atom with a bond angle of 93°. K$_2$CuNb$_2$Se$_{12}$ is another example for a complex selenide with three topologically different Se units, namely tetrameric Se$_4^{4-}$, Se$_2^{2-}$ pairs, and isolated Se$^{2-}$, according to (K$^+$)$_3$Cu$^+$(Nb$^{5+}$)$_2$Se$_4^{4-}$ (Se$_2^{2-}$)$_3$(Se$^{2-}$)$_2$.

Representatives for $Q_n^{4-}$ with $n = 5$ exist both among selenides and tellurides. In all cases, the $Q_n^{4-}$ units contain a central (almost) linear hypervalent unit, with the two remaining $Q$ atoms attached via a single bond to both ends of the linear part, like the fourth atom in Se$_4^{4-}$. By analogy, we conclude an ideal valence-electron number of 34, namely 22 for the $Q_3^{4-}$ fragment plus 2× six for the two additional $Q$ atoms, hence $Q_5^{4-}$: 5× 6 valence-electrons (from the neutral $Q$ atoms) plus four for the negative charges equals 34.

The two terminal $Q$ atoms may be in cis or trans conformation. The cis variant is realized in the heavily distorted Se$_5^{4-}$ of Nb$_2$Se$_9$, wherein the hypervalent bonds of 2.64 Å and 2.66 Å exhibit a bond angle of only 143°, and the terminal single bonds of 2.36 Å/2.37 Å are both connected with a 83° bond angle. Considering the presence of a 2.90 Å Nb–Nb bond, Nb is most likely in the 4+ state, and noting the presence of two Se$_2^{2-}$ pairs per formula unit, (Nb$^{4+}$)$_2$Se$_5^{4-}$ (Se$_2^{2-}$)$_2$ is also a closed-shell material [50].

The trans conformation is only known within the tellurides, occurring in NaTe ((Na$^+$)$_6$Te$_5^{4-}$Te$_2^{2-}$) [51] and Ba$_2$SnTe$_5$ ((Ba$^{2+}$)$_6$(Sn$^{4+}$)$_3$Te$_5^{4-}$ (Te$^{2-}$)$_{10}$) [52]. An isoelectronic cationic variant is I$_5^+$ in I$_5$AsF$_6$ [53], while analogous pnictides have not been reported yet.

The largest representative of the series $Q_n^{4-}$ currently known is Te$_5^{4-}$, coordinated to an Ag$^+$ or Hg$^{2+}$ cation via the central Te and the two terminal Te atoms [54,55]. The Te$_5^{4-}$ anion can formally be constructed from adding two neutral Te atoms to a cis-Te$_5^{4-}$. In case of the Ag compound, the central Te$_3$ unit contains hypervalent bonds of 2.87 Å and 3.23 Å with a bond angle of 174°, and the additional Te atoms form regular 2c-2e bonds of 2.71 Å to 2.76 Å.

Two interpenetrating Te$_5^{4-}$ units forming an almost square planar Te$_5^{6-}$ unit with a central four-bonded Te atom are found in K$_2$SnTe$_5$ with distances of 3.02 Å and 3.06 Å [56]. These units can polymerize [57], the products of which will be discussed later in this manuscript. Adding two more Te atoms via single bonds, for example, results in bicyclic Te$_7^{2-}$ [58].

### 2.2. Infinite motifs in polyselenides and polytellurides

#### 2.2.1. One-dimensional motifs: chains

The above-mentioned fragments $Q_n^{2-}$ and $Q_n^{4-}$ can form higher dimensional arrays such as infinite chains, ribbons or layers. At least two bonds are required per $Q$ atom in infinite chains, but the $Q$ atoms may only participate in two 2c-2e bonds, when their oxidation state is 0. Such neutral chains exist in the elements selenium and tellurium. On the other hand, Te is especially well known for its ability to form electron deficient multicenter bonds, thereby producing linear $\underline{4} \{Te^+\}$ chains. These chains occur in CuTe [59], UTe$_2$ [60] and Ca$_{0.66}$K$_4$Te$_3$ [61] with typical intrachain distances between
3.0 Å and 3.1 Å. These interactions are delocalized $2e-1e$ ("half") bonds, wherein one $p$ orbital is half-filled, indicating a one-dimensional metal.

**Figure 4.** Infinite Te$^{1-}$ chains in Ca$_{0.5}$K$_4$Te$_3$ (left) and K$_5$Te$_3$ (right).

Such linear equidistant chains may undergo a Peierls distortion, i.e. exhibit alternating short and long distances, occurring with a metal-insulator transition (Figure 5) [62]. There are also examples of distorted linear chains of Te atoms with a formal charge of –1 such as in Cs$_5$Te$_3$ [63] or K$_5$Te$_3$ [64]. In these compounds, the Te atom chain features two different Te–Te distances, one of around 2.8 Å and the other larger than 3.5 Å. Thus, a description as $\frac{1}{\alpha}[\text{Te}_2^{2-}]$ is more appropriate for these compounds, wherein van der Waals forces connect the pairs to linear chains.

**Figure 5.** Peierls distortion of a linear $\frac{1}{\alpha}[\text{Te}^-]$ chain.

The dimorph TlTe is a nice example of a material exhibiting different Te atom chains [65]. The room temperature (RT) modification of TlTe represents an equidistant $\frac{1}{\alpha}[\text{Te}^-]$ chain with Te–Te distances of 3.08 Å. A parallel running, second linear equidistant Te atom chain within the same structure is more complex, as two additional Te atoms are connected to each chain atom via hypervalent bonds of 3.01 Å, yielding a $\frac{1}{\alpha}[\text{Te}_3^{3-}]$ chain (Figure 6). Thus, the RT modification may be written as $(\text{Tl}^+)_{16}\text{Te}_6^{6-}(\text{Te}_3^{3-})_2(\text{Te}^-)_4$. In the low temperature (LT, 172 K) modification, both chains are distorted. Every second $\frac{1}{\alpha}[\text{Te}_3^{3-}]$ chain is not equidistant with alternation distances of 2.86 Å and 3.30 Å, while the other $\frac{1}{\alpha}[\text{Te}_3^{3-}]$ remain undistorted. Moreover, the linear equidistant $\frac{1}{\alpha}[\text{Te}^-]$ chain of the RT form is slightly bent in the LT form. Overall, the LT phase may be viewed as $(\text{Tl}^+)_{16}\text{Te}_6^{6-}(\text{Te}_3^{3-})_2(\text{Te}^-)_4$. 
By reducing the number of valence electrons from 7 per atom in such a one-dimensional unit, the conditions become more and more complicated. The Te atoms in Tl\textsubscript{2}Te\textsubscript{3}, for example, have a valence electron concentration (VEC(Te)) of 6\textsuperscript{2/3}, forming an infinite Te chain that can be described as polymerized linear Te\textsubscript{3}\textsuperscript{4–} fragments (Figure 7). The bonds between the Te\textsubscript{3}\textsuperscript{4–} units decrease the negative charges, leading to the description \( \frac{3}{2}[\text{Te}\textsubscript{3}\textsuperscript{2–}] \) [66]. Two different distances were found in this chain due to different bonding situations. The short distance of 2.83 Å, a typical length for a 2\textit{c}-2\textit{e} Te–Te bond, is found between the Te atoms of charge –½, the second distance (3.02 Å) occurs between Te\textsuperscript{1–} and Te\textsuperscript{3/2–}, indicative of a 3\textit{c}-4\textit{e} bond.

**Figure 7.** Infinite Te atom chains with different VEC(Te) in Tl\textsubscript{2}Te\textsubscript{3} (left), LiTe\textsubscript{3} (center) and Te (right).

In LiTe\textsubscript{3} [67], the VEC(Te) within the chain is lowered to 6\textsuperscript{1/3}. Consequently, this chain exhibits parts known from the Te atom chains in Tl\textsubscript{2}Te\textsubscript{3} as well as from elemental Te [68], and can therefore be viewed as \( \frac{1}{2}[(\text{Te})\textsuperscript{2–}][(\text{Te}\textsubscript{3})\textsuperscript{2–}] \). The distances within this chain are 2.85 Å for the 2\textit{c}-2\textit{e} bonds in the neutral...
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Te₃ part of the chain, 3.02 Å for the 3c-4e bond in the Te₃²⁻ unit and 2.91 Å for the bond connecting these fragments.

2.2.2. One-dimensional motifs: Ribbons

Only very few polychalcogenides exist that contain one-dimensionally extended Q atom substructures with more than two Q–Q bonds per Q atom. The dialkali pentatellurides show two different forms of intercondensation of above-mentioned Te₅⁶⁻ squares to yield $\frac{1}{3}Q[Te₅²⁻]$ ribbons with VEC(Te) = 6.4, namely the cis conformation in Cs₂Te₅ [69] and the trans conformation in Rb₂Te₅ [70] (Figure 8).

**Figure 8.** Infinite Te ribbons with different modifications in Cs₂Te₅ (top left), Rb₂Te₅ (top right) and In₂Te₅ (bottom center).

The distances in these ribbons range from 2.78 Å in Rb₂Te₅ and 2.77 Å in Cs₂Te₅ for the 2c-2e bond between the Te₅ units to 3.04 Å in Rb₂Te₅ and 3.05 Å in Cs₂Te₅ for the 3c-4e bond within the Te₅ units. In₂Te₅ [71] possesses a similar unit with a higher VEC(Te) of $6\frac{2}{3}$, which causes a distortion, namely an alternation of short and long Te–Te distances of 2.83 Å (solid lines) and 3.36 Å (dashed lines). Therefore it is best described as a one-dimensional arrangement of Te₃²⁻ fragments.

2.2.3. Two-dimensional motifs: Layers

Compounds with hypervalently bonded Te atoms that are arranged in planar or puckered layers are often dominated by T-shaped fragments. These building blocks are then either directly connected to each other or bridged via other Te atoms. An overview of (schematic) T nets was published in the year 2004 [72]. One of the simplest examples of a T network containing Te atoms can be found in the planar layers of NbTe₄ [73]. Each Te atom in this layer is surrounded by three other Te atoms in form of a heavily distorted T. Four-membered rings, exhibiting Te–Te distances of 3.30 Å, are connected to surrounding four-membered rings via shorter bonds of 2.88 Å (Figure 9). This hole-style arrangement in NbTe₄ is subject to a distortion, driven by a charge density wave along the Nb atom chains perpendicular to the layer of interest. Considering the large difference of 0.4 Å between these distances, one could view this layer as loosely connected Te₅²⁻ units. This is in contrast to the Sb atom
layer of Hf$_2$Sb$_9$ [74], wherein all bonds are between 2.99 Å and 3.03 Å, i.e. all bonds of that T net are electron deficient multicenter bonds [75].

**Figure 9.** Different T nets in NbTe$_4$ (top left), CsTe$_4$ (top right) and Cs$_3$Te$_{22}$ (bottom center).

CsTe$_4$ [76] also features T-shaped Te atom units forming a layer, which is comprised of a polymerized Te$_4^{4-}$ anion. This anion loses, due to this polymerization, three charges and builds a puckered layer that could be described as $\tilde{2}\varepsilon[\text{Te}_4^{4-}]$. The distances in the original T-shaped fragment in this layer are 2.92 Å and 3.14 Å for the collinear bonds, and 2.84 Å for the perpendicular bond. The connection between two (similar or different) fragments is slightly shorter (2.76 Å). The majority of the Te atoms are twofold coordinated and provide bonding angles between 96° and 103°. Therefore, the bonds within the Te$_4^{4-}$ fragments could be considered as asymmetric 3c-4e bonds and the remaining bonds as 2c-2e bonds.

Cs$_3$Te$_{22}$ provides an example of an electron-poor layer of Te atoms [77]. Cs$_3$Te$_{22}$ contains also neutral eight-membered Te rings, and can be described as $(\text{Cs}^+)_3(\text{Te}_8)_2(\text{Te}_4\text{Te}_4^{2-})^3$. Its planar $\tilde{2}\varepsilon[\text{Te}_4\text{Te}_4^{2-}]$ layer consists of two- and threefold connected Te atoms, with the former being linearly
coordinated and the latter T-shaped. The linearly bonded atoms interconnect the Te₄ squares comprising the T connected Te atoms. All Te–Te distances are between 3.00 Å and 3.07 Å. Band structure calculations indicate that this layer would be semiconducting with a charge of –4, but its actual charge of –3 renders it metallic [78].

2.2.4. Two-dimensional motifs: Chains connected to layers

The previously discussed lower dimensional fragments can be connected to two-dimensional layers in several ways. The binary chalcogenides UTe₂ [79], U₂Te₅ [80], α-UTE₃ [81] and Zr₆Q₃ [82,83] all contain linear chains aligned to form planar layers (Figure 10).

Figure 10. Planar layers of linear chains in U₂Te₅ (left), ZrTe₃ (center) and ZrSe₃ (right).
Another planar layer formation only consisting of Te$_2^{2-}$ dumbbells ($d_{\text{Te-Te}} = 2.78$ Å) occurs in the crystal structure of $\text{ALnTe}_4$ [88,89] with an interpair distance of 3.50 Å, which is shorter than a van der Waals contact.

**Figure 11.** Layers of oligomeric Te atom fragments in $\text{Cs}_2\text{Te}_2$ (top left), $\text{ALnTe}_4$ (top right), $\text{RbTe}_6$ (bottom left), and $\text{CrTe}_3$ (bottom right).

The structure of $\text{RbTe}_6$ [90] features a $\text{Te}_6^{2-}$ layer that is puckered because of its bent Te$_3$ units, where the central Te atom takes a position either beneath or above the layer plane. Within these bent Te$_3$ units, the Te–Te distances are 2.78 Å and 2.79 Å, respectively, with a bond angle of 102°, while the distances between these units are 3.20 Å and 3.21 Å. The charge of the $\text{Te}_6^{2-}$ layer cannot be readily understood; ignoring the 3.2 Å distances would indicate a charge of −2 for each Te$_3$ unit, while treating them as hypervalent half bonds would ideally result in neutral Te$_3$ units.

The structure of $\text{CrTe}_3$ contains Te atoms in three different oxidation states in a nearly planar layer [91]. The $\text{Te}_3^{3-}$ layer of this compound contains Te$^{2-}$ ions and Te$_2^{2-}$ and Te$_3^{2-}$ units, with typical Te–Te distances of 2.82 Å. The assignment of charges is straightforward and yields a balanced formula for Cr in its +3 state: (Cr$^{3+}$)$_2$Te$_3^{2-}$Te$_2^{2-}$Te$^{2-}$. 
2.2.6. Three-dimensional motifs

The only known compound that is comprised of a three-dimensional, covalently bonded network of Te atoms is Cs$_4$Te$_{28}$ [40]. The Te atom network is similar to the one in Cs$_3$Te$_{22}$, but in this case, half of the Te$_8$ rings are broken into Te$_4$ units that connect to one of the former linearly bonded atoms (Figure 12), which then assumes an oxidation state of zero.

**Figure 12.** Three-dimensional network of Te atoms in Cs$_4$Te$_{28}$.

This covalently bonded three-dimensional network could be considered as (Cs$^+$)$_4$Te$_8$[(Te$_4$)$_{4/2}$(Te$_4$Te$_4$)$_{2/2}$]$^{4-}$, wherein the neutral Te$_8$ ring is comprised of typical 2e-2e bonds (2.79 Å - 2.83 Å) like elemental sulfur. The Te–Te bonds of the connecting (also neutral) Te$_4$ fragments are comparable (2.77 Å and 2.79 Å), as are the connections of these Te$_4$ units of 2.80 Å with the layer of Te atoms. As a result of the connection with the Te$_4$ units, all Te atoms of the layer are connected in a T-like shape exhibiting hypervalent bonds >2.9 Å, in contrast to the twofold linearly connected Te atoms in the structure Cs$_3$Te$_{22}$.

3. Conclusions

An overview of the variety of Se–Se and Te–Te interactions occurring in the solid state of both inorganic and organic polychalcogenides was presented. In contrast to polysulfides, the Se and Te atoms are capable of forming electron deficient multicenter (hypervalent) bonds. This adds significantly to the connectivity possibilities, e.g. the formation of T-shaped Te motifs or linear Se/Te fragments, which in turn increases the complexity of these polychalcogenides, a desired feature for, e.g., thermoelectric materials.

The tendency of Te towards higher coordination numbers is reflected in the higher abundance of complex Te atom layers, compared to Se. However, within the oligomeric units, the selenides and tellurides are quite comparable, so that more polyselenides with related two-dimensional motifs are likely to be uncovered in the near future as well.
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