ELSEVIER

Coordination Chemistry Reviews
163 (1997) 55–70

COORDINATION CHEMISTRY REVIEWS

Rings, cages and chains – the rich structural chemistry of the polycations of the chalcogens

Johannes Beck

Institut für Anorganische und Analytische Chemie der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, 35392 Gießen, Germany

Received 26 September 1996; accepted 21 November 1996

Contents

Abstract

The review, with 64 references and 17 figures, reports on the structures of chalcogen polycations and covers the literature since 1988 together with some unpublished work. The structures of the polycations are discussed by the application of basic electron counting rules according to the Zintl concept and are compared with already known cations. A new method of preparation is the chemical vapor transport which leads to novel types of cations and a great increase in the formerly limited number of anions. Recent findings in this field of research are the existence of several isomeric forms of one polycation and the occurrence of polymeric chains as a novel structural feature.

---

1. Introduction

It was a historical discovery in the early nineteenth century that the elements sulfur, selenium and tellurium are soluble in concentrated sulfuric acid to give intensively colored solutions. The compositions of these solutions or the chemical nature of the colored species remained unknown until the mid-1960s. Pioneering work by the research groups of N. Bierrum, R.J. Gillespie and J. Corbett showed that polyatomic, positively charged clusters are responsible for the coloring. A variety of methods have been successfully employed to prepare such polycations.

PII S0010-8545(97)00009-X

All of these involve highly electrophilic and acidic media such as H_2SO_4, HSO_3F, anhydrous HF, molten salts like $Na[AlCl_4]$, or liquid SO_2. The elemental chalcogens are oxidized by suitable oxidants like $S_2O_6F_2$, AsF_5, or by a higher halide of the chalcogen itself in the sense of a synproportionation reaction in the presence of a strong halide ion acceptor. In this way, salt-like compounds are formed whose anions like $[AsF_6]^-$, $[SbF_6]^-$, $[SO_3F]^-$ or $[AlCl_4]^-$, as weak conjugate bases of very strong Lewis acids, stabilize the naked polycationic clusters. The first confirmed chalcogen polycation was prepared in 1962 by N. Bartlett from oxygen and PtF_6, yielding $O_2[PtF_6]$ with the ion O_2^+ [1]. R.J. Gillespie and coworkers prepared a large number of polycations in the 70s and 80s. The variety increases with atomic weight. There are only a few examples for sulfur polycations but a plethora of tellurium polycations.

Several review articles appeared on this topic by R.J. Gillespie and coworkers in 1975 [2] followed by an article in 1979, in which the structures of polycations are treated in the context of general structural principles of cluster chemistry of the main group elements [3]. A review article on homopolyatomic cations of main group elements with special emphasis on the molten salt preparation route was published in 1976 by J. Corbett [4]. The latest reviews date from 1989. N. Burford, J. Passmore and J.C.P. Sanders surveyed all known polycations of the chalcogens and halogens, models for bonding and estimations on the stability using Born–Haber cycles [5]. Since stable binary compounds of iodine with sulfur and selenium are not known, the discovery of S–I and Se–I polycations such as S_7I^+ or $Se_2I_4^{2+}$ was quite spectacular. A review by T. Klapötke and J. Passmore treats sulfur and selenium iodine cations known until 1989 [6]. More recently, the preparation of chalcogen polycations by oxidation with transition metal halides with the metal in high oxidation states via chemical vapor transport opened up a new synthetic route leading to novel polycations. This work was reviewed in 1994 [7].

The aim of this article is to present new research on the polycations of the chalcogens published since 1988 together with some yet unpublished work. The structures are rationalized by application of basic electron counting rules according to the Zintl concept and are compared with already known cations.

2. The ions S_4^{2+}, Se_4^{2+} and Te_4^{2+} in delocalized and localized forms

Tetraatomic cations Ch_4^{2+} (Ch = S, Se, Te) were the first to be characterized. Crystal structures of $Se_4[HS_2O_7]_2$ [8] and $Te_4[AlCl_4]_2$ [9] showed these ions to be square planar, discrete molecular entities. Isolable compounds with S_4^{2+} are more difficult to obtain. It was not until 1980 that the first compound with a S_4^{2+} ion was structurally characterized [10].

The Zintl concept allows a prediction of the structure of a polycation with given composition when the charge is known. Alternatively, the known structure of a polycation can be interpreted by applying the concept [11]. If no violation of the octet rule by hypervalence occurs, one expects the formal charge −1 for a single bound chalcogen atom, a double bound should be neutral and a triple bound should carry the formal charge +1. Additionally, applying the Gillespie–Nyholm concept [12] one can predict the stereo-chemistry of the double and triple bound chalcogen atoms: the former is expected to be in a bent, the latter in a trigonal pyramidal environment with bond angles around 100° (Fig. 1).

The observed structure of the Ch_4^{2+} (Ch = S, Se, Te) ions are inconsistent. Ch_4^{2+} carries 22 valence electrons and should contain two double and two triple bound chalcogen atoms. Such a bicyclic structure is observed in Ba_3Si_4, a classical Zintl phase. The anion Si_4^{6-} has 22 valence electrons and a butterfly shaped structure with C_{2v} point symmetry [13]. Another possibility is a one-dimensional band of connected four-membered rings (Fig. 2). In both cases the positive charges are formally localized in the triple bound positions. The observed structure, however, shows no localization of charges and bonds, but delocalization, which was confirmed by a series of theoretical investigations at various computational levels [14]. The substantial π stabilisation of Ch_4^{2+} is concluded from all calculations.

The new synthetic route of oxidation of elemental chalcogens by highly oxidized transition metal halides or by the use of metal halides as halide ion acceptors towards chalcogen subhalides yielded compounds of Se_4^{2+} and Te_4^{2+} with a whole variety of counter ions such as $[\{MoOCl_4\}_2]^{2-}$ [15], $[WCl_6]^-$, $[Zr_2Br_{10}]^{2-}$ [16], $[ZrCl_6]^{2-}$, $[HfCl_6]^{2-}$, $[NbCl_6]^-$ [17], $[TaCl_6]^-$ [17], $[TaBr_6]^-$ [17], $[Ta_2OBr_{10}]^{2-}$ [17], $[AlBr_4]^-$ [18], $[AlI_4]^-$ [18], $[ReCl_6]^{2-}$ [19] or $[Bi_2Cl_8]^{2-}$ [20].

$Se_4[\{MoOCl_4\}_2]$ undergoes a first order phase transition at −21 °C leading to a structure with a doubled unit cell volume. Cations and anions are slightly reoriented with respect to each other [21]. $Te_4[WCl_6]_2$ has been found to exist in two polymorphic forms with a different packing of the ions [22,23]. $Se_4[MCl_6]$, (M = Zr, Hf) and $Te_4[HfCl_6]$ [24] contain mononuclear dianions for the first time, leading to a 1:1 ratio of cations and anions. The structures are simple: $Te_4[HfCl_6]$ adopts the CsCl structure with eight anions surrounding one cation and $Se_4[MCl_6]$ with the smaller Se_4^{2+} ion, the NaCl structure with six anions surrounding one cation. $Se_4[ReCl_6]$ is nearly isostructural to the tetragonal $Se_4[MCl_6]$ (M = Zr, Hf) but crystallizes with lower symmetry in the orthorhombic crystal system. Actually $Se_4[ZrCl_6]$ undergoes a second order phase transition to the orthorhombic system

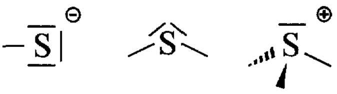


Fig. 1. Valence dash formula and formal charge for single, double and triple bound chalcogen atoms.

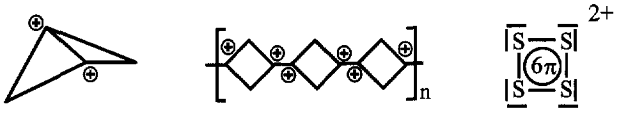


Fig. 2. A schematic representation of the expected structure of a molecular form of Ch_4^{2+} (Ch = S, Se, Te) in analogy to Si_4^{6-}, of a polymeric chain with the formula $(Ch_4^{2+})_n$, and of the known molecular form of Ch_4^{2+}.

with $T_c = -80$ °C and becomes isostructural with $Se_4[ReCl_6]$ [25]. So far we have only observed solid state phase transitions for compounds with Se_4^{2+} and not with Te_4^{2+} ions. The smaller Se_4^{2+} has more possibilities of being embedded in a environment of anions. Ch_4^{2+} ions have a very specific coordination. There are always four halogen atoms of surrounding anions that bridge the edges of the square with the shortest Ch–halogen distances. Electron density is transferred into the σ* orbitals of the cations with the effect of substantial Ch–Ch bond lengthening. Clear correlations can be seen between Te–Te bond lengths in a series of compounds and Te–halogen bond lengths: the shorter the Te–halogen distances the longer the Te–Te distances [17,26]. Moreover Te–Te distances increase with lowering electronegativity of the halogens. An example is the series $Te_4[SbF_6]_2$ (Te–Te = 267.3 pm) [27], $Te_4[TaCl_6]_2$ (Te–Te = 267.8 pm) and $Te_4[TaBr_6]_2$ (Te–Te = 268.4 pm) [27]. Te–halogen bonding is therefore stronger with the heavier halogens.

$BiCl_3$ turned out to be a suitable Lewis-acidic reagent towards tellurium subhalides. The reaction of $Te/TeCl_4/BiCl_3$ at 170 °C yielded $(Te_4)(Te_{10})[Bi_2Cl_8]_2$ [20] containing a Te_4^{2+} ion with a novel, polymeric structure (Fig. 3). The four-membered rings have Te–Te bonds in the range of single bonds (275 and 281 pm) and are connected by 298 pm long Te–Te bonds.

This chain fulfils the requirements for a "Zintl-precise" structure. It has a balanced number of double and triple bound Te atoms and a formal charge localization in the three coordinate positions. There is now a classical Te_4^{2+} beside the well-known non classical, delocalized molecular Te_4^{2+}. In an analogy with Zintl anion chemistry a polymer chain form of the Si_4^{6-} ion type was recently discovered. Ba_3Ge_4 [27] contains simultaneously isolated butterfly-shaped Ge_4^{6-} ions and linked four-membered Ge_4 rings, which also fulfil the Zintl concept as $(Ge_4^{6-})_n$.

3. The six- and eight-atomic chalcogen polycations – further examples for delocalized and localized systems

The structures of the known six atomic polycations can be derived from a hexagonal prism with more or less open edges. $Te_3S_3^{2+}$ [28] and $Te_2Se_4^{2+}$ [29] have structures which are in accordance with the Zintl concept (Fig. 4). In both ions two edges of the prism are opened and in both there are two Te atoms with three bonds formally carrying the positive charges. A clear tendency can be seen to localize charge on the heavier chalcogen atoms.

Te_6^{4+} was first prepared in 1979 as $Te_6[AsF_6]_4$ [30] and in 1988 found again in $(Te_6)(Se_8)[AsF_6]\cdot SO_2$ [31], a unique compound with two different and not mixed

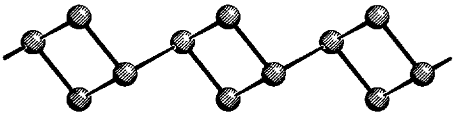


Fig. 3. The structure of the polymeric $(Te_4^{2+})_n$ cation in $Te_7Bi_2Cl_8$ [64].

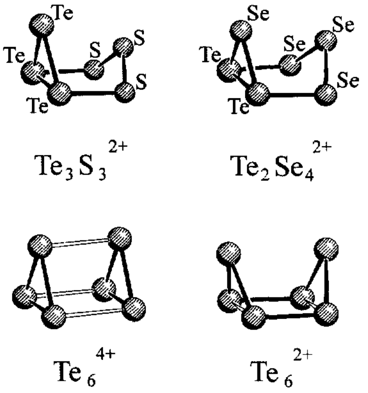


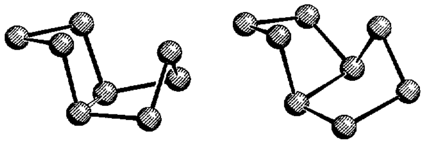
Fig. 4. The structures of the six-atomic polycations $Te_3S_3^{2+}$, $Te_2Se_4^{2+}$, Te_6^{4+} and Te_6^{2+}.

cations. Te_6^{4+} has the structure of an elongated prism with six very short bonds of 267 pm between the Te atoms of the triangular faces and three very long Te–Te bonds of about 312 pm which link the triangular faces. Te_6^{4+} has 32 valence electrons, two more than required for a prismane shaped molecule. The hypothetical Te_6^{6+} is expected to have a regular prismane structure with all six Te atoms triply bound and each carrying one formal positive charge. The two excess electrons should cause the breaking of one prism edge or in terms of Zintl's concept, reduce the number of triple bound Te atoms from six to four. A recent theoretical investigation based on density functional methods has shown that the elongated trigonal-prismatic D_{3h} structure actually represents the ground state of Te_6^{4+} [32]. The extra pair of electrons causes the simultaneous lengthening of all three bonds parallel to the C_3 axis, as found experimentally.

Te_6^{2+} was first obtained by the oxidation of elemental tellurium with $WOCl_4$ [33]. $Te_6^{2+}([WOCl_4]^-)_2$ contains boat shaped cations and square-pyramidal anions which are linked to linear chains by asymmetric $W{=}O\cdots\cdots W$ bridges. $NbOCl_3$ is a suitable Lewis-acid to remove chloride anions from the tellurium subhalide Te_3Cl_2 yielding the analogous compound $Te_6^{2+}([NbOCl_4]^-)_2$ [34]. In both structures the Te_6^{2+} ions form one-dimensional strands facing towards each other with the triangular prism faces. The shortest Te–Te distances between individual ions are 461 pm for $Te_6[WOCl_4]_2$ and 482 pm for $Te_6[NbOCl_4]_2$ and indicate no cation–cation interactions. For Te_6^{2+} to adopt a structure according to the Zintl concept there would be two triple bound Te atoms or two edges of the prism would be opened since two excess electron pairs are present with respect to Te_6^{6+}. Instead only one prism edge is fully opened and two prism edges in the triangular faces are "half opened" with Te–Te distances between 321 and 338 pm, while all other Te–Te bonds are in the normal single bond range (mean 272 pm) (Fig. 4). The two positive charges are thus delocalized over four Te centers.

Only the six atomic mixed polycations have classical structures with localized bonds, the homoatomic ions Te_6^{2+} and Te_6^{4+} show the phenomenon of bond delocalization and adopt non-classical structures.

Te_8^{2+} was a missing link in the series of eight atomic chalcogen polycations since its lighter homologues S_8^{2+} and Se_8^{2+} were well known. Te_8^{2+} could not be prepared by the route of oxidizing tellurium with AsF_5/SbF_5 in liquid SO_2. Te_8^{2+} in an isostructural form like its lighter homologues became available by a Lewis-acid–base reaction between Te_3Cl_2 and $ReCl_4$ at 200 °C. $Te_8[ReCl_6]$ contains the typical quasi-bicyclic *exo–endo* conformed eight-membered rings (Fig. 5) [35]. Since the discovery of S_8^{2+} [36] and Se_8^{2+} [37] bonding in the Ch_8^{2+} cluster ions is a matter of discussion. Their structure can be derived from the crown shaped ring of the neutral molecules S_8, Se_8 and very recently Te_8, observed embedded in the structure of the polytelluride Cs_3Te_{22} [38]. Flipping one atom from the *exo* to the *endo* position, removal of two electrons and a deformation of the ring to an oval leads to a bicyclic structure. The shortest transannular bonds, however, are very long in all cases (S_8^{2+}: 283 pm; Se_8^{2+}: 284 pm; Te_8^{2+}: 315 pm). Recent models for the interpretation of bonding take for each ion the first three closest cross-ring contacts into account and view the bonding as a six-center, two electron π^*–π^* bond [5]. A structurally closely related form of Te_8^{2+} was already known in $Te_8[WCl_6]_2$ [39]. The structure of this isomeric form shows marked differences to the ion in $Te_8[ReCl_6]$. It has a bicyclic structure composed of two five-membered rings each in an envelope conformation. The transannular bond is 299 pm long and is much shorter than in $Te_8[ReCl_6]$, giving the ions in $Te_8[WCl_6]_2$ a pronounced bicyclic character (Fig. 5). A remarkable feature in the structure of $Te_8[WCl_6]_2$ is the association of the Te_8^{2+} ions into an undulated chain (Fig. 5). The shortest interionic contacts are 343 pm and are still within the range of weak bonding. The 299 pm transannular bond is not a full single bond with an expected length of 275 pm. The four additional weak bonds of each ion to its neighbors indicate a partial charge delocalization leading to a polymeric tellurium cation $(Te_n)^{n/4+}$.



Te_8^{2+} in $Te_8[ReCl_6]$ Te_8^{2+} in $Te_8[WCl_6]_2$

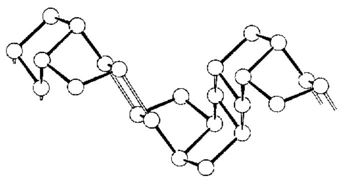


Fig. 5. The structures of the eight-atomic polycations Te_8^{2+} in $Te_8[ReCl_6]$ and in $Te_8[WCl_6]_2$, and the association of Te_8^{2+} ions in the structure of $Te_8[WCl_6]_2$ leading to an undulated chain $(Te_n)^{n/4+}$.

Another possibility for a chalcogen polycation Ch_8^{2+} is a bicyclo[2.2.2]octane structure, which was first found as the cation $Te_2S_6^{2+}$ in $(Te_2Se_6)(Te_2Se_8)[AsF_6]_4 \cdot 2SO_2$ [40] (Fig. 6). The two tellurium atoms are in the triple bound bridgehead positions, the selenium atoms form three Se_2 bridges between the Te atoms. As in $Te_2Se_4^{2+}$ or $Te_3S_3^{2+}$ this structure conforms to the Zintl concept without charge and bond delocalization. The solvothermal reaction of Te with WCl_6 and of Te, $TeCl_4$ and $NbCl_5$ in $SnCl_4$ at 150 °C yields the compounds $(Te_6)(Te_8)[MCl_6]_4$ (M = W, Nb) [18]. The structures contain boat shaped Te_6^{2+} ions, analogous to those described above, and Te_8^{2+} ions, which are isostructural to $Te_2Se_6^{2+}$ (Fig. 6). This is now the third form of Te_8^{2+} besides $Te_8[ReCl_6]$ and $Te_8[WCl_6]_2$. Although homoatomic, it has a classical structure with two triply bound Te atoms which carry the formal positive charges and six neutral Te atoms with two bonds. The structures of these eight-atomic polycations can easily be derived from a cube with three open edges [40]. A cube-like chalcogen polycation consists only of triple bound atoms and is thus expected to have eight positive charges Ch_8^{8+}. Adding six electrons or three pairs respectively leads to the opening of three bonds in a bicyclo[2.2.2]octane structure.

Another eight-atomic mixed polycation with an unexpected structure was obtained from Te/Sn and AsF_5 in liquid SO_2. The presence of metallic tin causes the reduction of SO_2 to elemental sulfur which yields with tellurium $(Te_4S_4)[AsF_6]_2 \cdot 2SO_2$ [41]. $Te_4S_4^{2+}$ has the closed cage structure of S_4N_4 (Fig. 7). The Te–Te distances of 271 pm are in the range of single bonds while the Te–S bonds of mean 230 pm are substantially shorter than other Te–S bonds (e.g. 245 pm in $Te_3S_3^{2+}$ [28]). The closed cage structure is normally realized at a count of 44 valence electrons but $Te_4S_4^{2+}$ has two electrons more. In terms of the Zintl concept one expects for the four triple bound Te atoms a charge of $Te_4S_4^{4+}$.

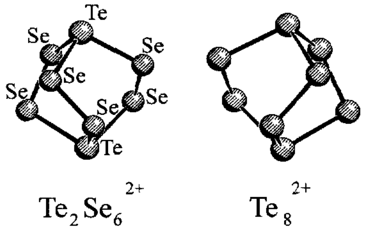


Fig. 6. The structures of $Te_2Se_6^{2+}$ and of Te_8^{2+} in $(Te_6)(Te_8)[WCl_6]_4$.

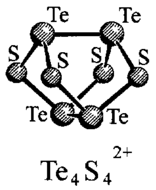


Fig. 7. The structure of $Te_4S_4^{2+}$.

The structure was therefore interpreted with a pair of delocalised electrons trapped inside the cluster [41]. On the other hand, theoretical investigations at the density functional level have shown the $Te_4S_4^{2+}$ to have a half filled doubly generate highest occupied molecular orbital which is strongly antibonding between the tellurium atoms. An optimized geometry for the 46 valence electron cluster lead to a geometry differing substantially from the experiment. The cleavage of one Te–Te bond is predicted to produce a structure similar to the isoelectronic S_8^{2+}/Se_8^{2+}/Te_8^{2+} ions [32]. This conflict would be solved with one atom of tin on one of the four Te positions and the respective formula $Te_3SnS_4^{2+}$. The Sn atom probably may not have been detected in the X-ray study because it has a scattering power very similar to Te and could be disordered over all four Te positions [42]. A triply bound ψ-tetrahedrally coordinated Sn atom has a formal charge of −1, which gives with the three +1 charges of the Te atoms an overall charge of +2 for the cationic cluster.

A higher oxidized cation became available by the reaction of tellurium with $VOCl_3$. At 200 °C green $VOCl_2$ and silvery Te_3Cl_2 are formed by a redox process. At 270 °C $Te_8[VOCl_4]_2$ is then formed in a Lewis-acid–base reaction [43]. The oxidation state +IV was confirmed by a magnetic measurement which delivered the paramagnetism expected for one unpaired electron per $[VOCl_4]^{2-}$ group. The structure of the Te_8^{4+} ion (Fig. 8) is according to the charge. The cage-like structure of S_4N_4 can be expected for this 44 electron molecule, but another possibility is realized. Te_8^{4+} forms a cube with two open edges, leaving four of the eight Te atoms triple bound in a ψ-tetrahedral geometry. As in the structures of $Te_8[WCl_6]_2$ [39] and $Te_6[MOCl_4]_2$ (M = Nb, W) [33,34] relatively short cation–cation contacts are observed. The cations form a linear strand reminiscent of a stack of cubes (Fig. 8) surely favored by the rigid framework provided by the polymeric $[VOCl_4]^{2-}$ counterions. The cationic strand is also reminiscent of a stack of Te_4^{2+} cations. The delocalized

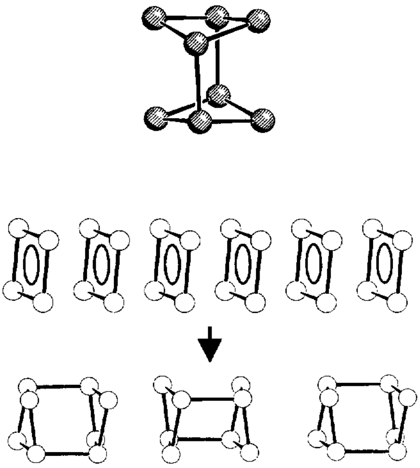


Fig. 8. The structure of Te_8^{4+}. The ions form one-dimensional strands which can be derived from a stack of equidistant Te_4^{2+} ions, which are paired and form $(Te_4^{2+})_2$ dimers.

character of the Te_4^{2+} ions including their planarity is lost through the formation of $(Te_4^{2+})_2$ pairs with localized bonding (Fig. 8).

4. Towards larger clusters – chalcogen polycations with more than eight atoms

Only a few examples of discrete chalcogen polycations composed of more than eight atoms are known. The ten-atomic cations $Te_2Se_8^{2+}$ and Se_{10}^{2+} were obtained as $(Te_2Se_8)[AsF_6]_2$ and $(Te_2Se_6)(Te_2Se_8)[AsF_6]_4 \cdot 2SO_2$ [40], $(Te_2Se_8)[AsF_6]_2 \cdot SO_2$ [44], and as $Se_{10}[SO_3F]_2$ [45]. Their structures (Fig. 9) are isomorphous. A six-membered twisted ring is linked across the 1,4 positions by a chain of four Se atoms leading to a bicyclo[4.2.2]decane type structure. In $Te_2Se_8^{2+}$ the Te atoms are localized in the triply bound positions in analogy to $Te_3S_3^{2+}$, $Te_2Se_4^{2+}$ and $Te_2Se_6^{2+}$. Even Se_{10}^{2+} has an electron-precise, localized bond structure although it is homoatomic. This could be due to the lattice energy in the solid state, since ^{77}Se NMR studies showed evidence for an intramolecular exchange and thus a non-rigid structure in solution [46].

The largest non-polymeric cations known are Se_{17}^{2+} and S_{19}^{2+}. Se_{17}^{2+} became first available as $Se_{17}[WCl_6]_2$ by a chemical vapor-transport reaction of selenium and WCl_6 at 100 °C [47]. Meanwhile the isotypic $Se_{17}[NbCl_6]_2$ and $Se_{17}[TaBr_6]_2$ could be prepared from selenium and $NbCl_5$, and $TaBr_5$ by solvothermal reaction in $SnCl_4$ and $SiBr_4$ as solvent, respectively [48]. S_{19}^{2+} was prepared by oxidation of elemental sulfur with AsF_5 or SbF_5 in liquid SO_2 [49]. Their structures are very closely related. Both ions consist of two seven-membered rings in the chair conformation connected by a Se_3 chain and by a S_5 chain, respectively (Fig. 10). Both ions contain two triple bound chalcogen atoms that carry the two formal positive charges. Another typical feature are the marked bond lengths alternations in the seven-membered rings of both ions.

The reaction of selenium with $NO[SbCl_6]$ as an oxidant in liquid SO_2 yields $(Se_9Cl)[SbCl_6]$ [50]. The Se_9Cl^+ ion consists of a seven-membered ring with an Se_2Cl group attached to one of the Se atoms of the ring (Fig. 11). The ring is in the chair conformation and shows the typical bond lengths alternation between 227 and 243 pm. The Se_9Cl^+ ion is strikingly similar to the respective fragments of S_{19}^{2+} and Se_{17}^{2+} and one can speculate that Se_{17}^{2+} was formed in the reaction initially,

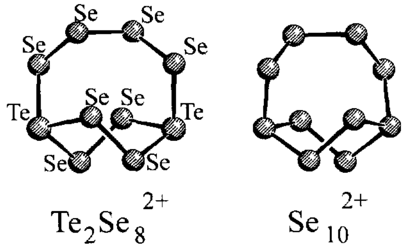


Fig. 9. The structures of $Te_2Se_8^{2+}$ and Se_{10}^{2+}.

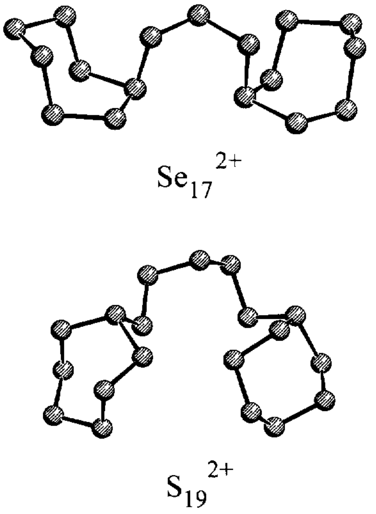


Fig. 10. The structures of Se_{17}^{2+} and S_{19}^{2+}.

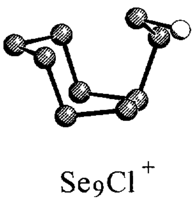


Fig. 11. The structure of Se_9Cl^+.

followed by the oxidative cleavage of a Se–Se bond in the Se_3 bridge by traces of $SbCl_5$ present in the reaction mixture.

5. Polymers in the form of chains – a novel type of chalcogen polycations

A new structural feature among the chalcogen polycations are polymeric, chain-like entities, known only since 1991. The tellurium subhalides Te_3Cl_2 and Te_2Br already contain one-dimensional Te substructures, a spiral chain in Te_3Cl_2 and a chain of fused six-membered rings in Te_2Br [51]. The new structure type $(Te_{15}X_4)_n[MOX_4]_{2n}$ (M = Mo, W; X = Cl, Br) contains a modified Te_2Br structure [52]. The cations form strands in which one of the two rows of halogen atoms that bridges the band of condensed Te_6 rings is stripped off by the Lewis acids $MoOCl_3$, $MoOBr_3$ and $WOBr_3$. Additionally, one Te position is only occupied by 75%, so one out of every four of these Te atoms is removed (Fig. 12). In a cationic strand with all Te positions fully occupied there would be one positive charge for every repeating Te_4X unit. Since there are two cationic strands for only one anionic

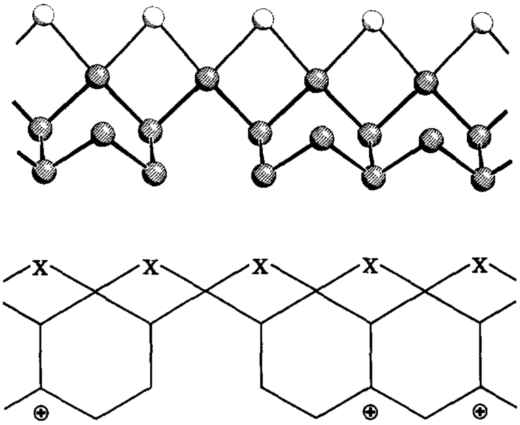


Fig. 12. A section of the chain structure of $(Te_{15}X_4^{2+})_n$ (X=Cl, Br) and a schematic representation of the cationic strand. The removal of one fourth of one type of Te atoms in the Te_6 rings halves the number of positive charges on each polycationic strand.

strand and thus two Te_4X units for one $[MOX_4]^-$ unit the compounds would have no charge balance between cations and anions. The removal of one Te atom in every fourth Te_4Br unit leaves the neighboring Te atoms only double bound and with no formal charge. The result is a $(Te_{15}X_4)^{2+}$ chain and the charge balance in the structure.

Four one-dimensional, chain-like polycations composed of tellurium or mixed with tellurium/selenium structure are known with a "Zintl precise" structure. $Te_7[AsF_6]_2$ was obtained from the reaction of $Te_4[AsF_6]_2$ and $[Fe(CO)_5]$ in liquid SO_2 [53]. The role of the iron carbonyl is still not clear but most likely it causes the reduction of Te_4^{2+} to Te_7^{2+}. The structure contains besides octahedral $[AsF_6]^-$ ions, a polymeric chain of six-membered tellurium rings in the chair conformation connected through bridging tellurium atoms in the 1- and 4-positions (Fig. 13). Therefore, two of the seven Te atoms are triple bound and carry the formal positive charges.

A very closely related cation is found in $Te_8[Bi_4Cl_{14}]$ which is obtained by a chemical vapor transport reaction from Te/$TeCl_4$ and $BiCl_3$ [20]. The structure contains a two-dimensional polymeric chlorobismutate network $[Bi_4Cl_{14}]^{2-}$ and a polymeric chain of six-membered tellurium rings in a chair conformation connected

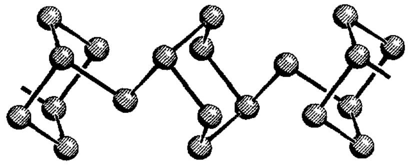


Fig. 13. A section of the chain $(Te_7^{2+})_n$ in the structure of $Te_7[AsF_6]_2$.

through a Te_2 bridge (Fig. 14). This polymeric $(Te_8^{2+})_n$ now is the fourth isomeric form of Te_8^{2+}.

The reactions of $Te_6[WOCl_4]_2$ with selenium or of Te/Se mixtures with $WOCl_4$ are a source for new polymeric cations [54]. $(Se_{4.85}Te_{3.15})[WOCl_4]_2$ contains square-pyramidal $[WOCl_4]^-$ units which are linked by $W{=}O \cdots W$ bridges to linear strands and a polymeric chain, consisting of five-membered rings connected through tri-atomic chalcogen bridges in the 1,3-positions (Fig. 15). The given composition is the result of the refinement of the occupation factors. All positions are simultaneously occupied by tellurium and selenium in a disordered way, but as expected the Te content in the triple bound positions is very high. The overall composition, however, of this cationic strand is $(Ch_8^{2+})_n$ and represents, besides the four other isomeric forms of Te_8^{2+}, a fifth possibility to realize a structure of six double and two triple bound chalcogen atoms.

$(Se_4Te_3)[WOCl_4]_2$ completes the series of connected chalcogen rings [54]. The structure contains four-membered rings connected through three-atomic bridges. Te and Se are well-ordered and alternatively occupy the atomic positions, tellurium again is found in the triple bound positions. This cation of the general formula $(Ch_7^{2+})_n$ is an isomeric form of $(Te_7^{2+})_n$ in $Te_7[AsF_6]_2$.Fig. 16

Another type of polymeric cationic strand occurs in the structure type

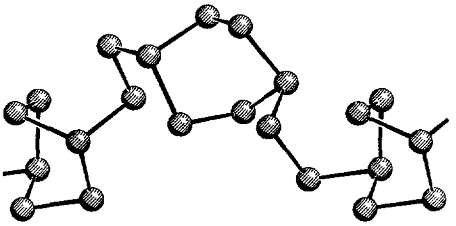


Fig. 14. A section of the chain $(Te_8^{2+})_n$ in the structure of $Te_8[Bi_4Cl_{14}]$.

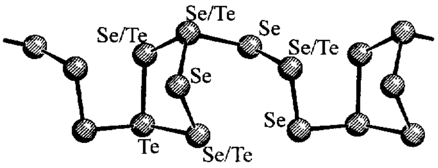


Fig. 15. A section of the chain $(Te_{3.15}Se_{4.85}^{2+})_n$ in the structure of $(Te_{3.15}Se_{4.85})[WOCl_4]_2$. All positions are occupied by selenium and tellurium, but some positions contain predominantly (>85%) only one type of chalcogen. For these positions, only the predominant atom type is labeled.

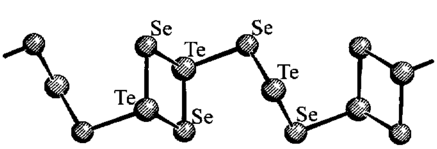


Fig. 16. A section of the chain $(Te_3Se_4^{2+})_n$ in the structure of $(Te_3Se_4)[WOCl_4]_2$.

$Te_7[MOX_4]X$, for which four examples are known so far: $Te_7[WOBr_4]Br$ [55], $Te_7[WOCl_4]Cl$ [56], $Te_7[NbOCl_4]Cl$ and $Te_7[NbOBr_4]Br$ [57]. The polymeric $(Te_7^{2+})_n$ strands are made up from planar Te_7 groups linked by four Te–Te bonds to give a folded band (Fig. 17). Te atoms in this polymeric cationic chain have three different types of bonding. The central Te atoms are in a square planar environment with four relatively long Te–Te bonds between 295 and 300 pm. The Te atoms which connect the Te_7 groups are in a trigonal pyramidal environment and there are two Te atoms in each Te_7 group which are double bound and formally neutral. The four triple bound Te atoms carry a formal charge of $+1$, the central Te atom is interpreted as being in a ψ^2-octahedral coordination with two lone pairs *trans* to each other and having a formal charge of -2. The result is a charge of $+2$ for the Te_7 group. The charge distribution in the $Te_7[MOX_4]X$ structure type was unambiguously clarified by the diamagnetism of the niobium containing compounds which showed that the niobium is in an oxidation state of +V. So there is a $[NbOX_4]^-$ group, and an isolated halide ion X^- in the structure, necessarily charge balanced by a Te_7^{2+} group. The structural motifs of the $(Te_7^{2+})_n$ ion are very unusual in the area of chalcogen polycations but are realized in various ways in compounds with tellurium polyanions. For example the spirocyclic anions Te_7^{2-} [58], Te_8^{2-} [59], $TeSe_{10}^{2-}$ [60] or Te_5^{6-} [61] all contain a square planar coordinated Te atom with 12 valence electrons.

The structure of $(Te_4)(Te_{10})[Bi_2Cl_8]_2$ ([20], see Section 2) contains a novel polycation $(Te_{10}^{2+})_n$ (Fig. 17) besides the polymeric chain $(Te_4^{2+})_n$. It has a striking similarity to $(Te_7^{2+})_n$ and can be discussed in an analogous manner. It consists of two spirocyclic centers, six triple and two double bound Te atoms, giving the charge

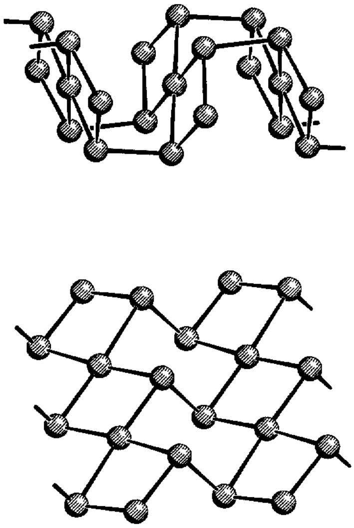


Fig. 17. Sections of the chains $(Te_7^{2+})_n$ in the structures of $Te_7[MOX_4]X$ (M = Nb, W; X = Cl, Br) and $(Te_{10}^{2+})_n$ in the structure of $(Te_4)(Te_{10})[Bi_4Cl_{16}]$.

Table 1
The presently known polyatomic cations of the chalcogens[a]

Number of atoms	4	6	8	10	>10	∞
	S_4^{2+}	$Te_3S_3^{2+}$	S_8^{2+}	Se_{10}^{2+}	S_{19}^{2+}	$(Te_4^{2+})_n$
	Se_4^{2+}	$Te_2Se_4^{2+}$ [c]	Se_8^{2+}	$Te_2Se_8^{2+}$	Se_{17}^{2+}	$(Te_3Se_4^{2+})_n$
	Te_4^{2+} [b]	Te_6^{2+}	$Te_4S_4^{2+}$			$(Te_7^{2+})_n$ [e]
		Te_6^{4+}	$Te_2Se_6^{2+}$			$(Te_{3.15}Se_{4.85}^{2+})_n$
			Te_8^{2+} [d]			$(Te_8^{2+})_n$
			Te_8^{4+}			$(Te_{10}^{2+})_n$

[a] Chalcogen–halogen polycations are not included in this table.
[b] Mixed species such as $Te_2Se_2^{2+}$ and Te_3Se^{2+} are also known [62].
[c] Mixed species of the types $Te_xS_{6-x}^{2+}$ and $Te_xSe_{6-x}^{2+}$ are also known [63].
[d] Three isomeric forms are known.
[e] Two isomeric forms are known.

+2 for the planar Te_{10} group. Again there are hypervalent Te atoms incorporated in a chain of connected repeating units.

6. Summary and Scope

The presently known polyatomic cations of the chalcogens are summarized in Table 1. New methods of syntheses made new types of cations available. Polymeric chains as a novel structural feature have only recently been prepared. Moreover, the new discovery of several isomeric forms of one polycation, for instance the three forms of molecular Te_8^{2+} and the two different types of $(Te_7^{2+})_n$ chains, provide a deeper understanding in this still increasing area of main group element chemistry.

Acknowledgements

I owe many thanks to the coworkers in my research group. It is their diligence which made many beautiful results possible. Thanks also to Dr. M. Serafin for his help with the SCHAKAL plots [64] and to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

References

[1] N. Bartlett, D.H. Lohmann, Proc. Chem. Soc. (1962) 115; J. Chem. Soc. (1962) 5253.
[2] R.J. Gillespie, J. Passmore, Adv. Inorg. Chem. Radiochem. 17 (1975) 49.
[3] R.J. Gillespie, J. Chem. Soc. Rev. 8 (1979) 315.
[4] J.D. Corbett, Prog. Inorg. Chem. 21 (1976) 129.
[5] N. Burford, J. Passmore, J.C.P. Sanders, Mol. Struc. Energ. 11 (1989) 53.
[6] T. Klapötke, J. Passmore, Acc. Chem. Res. 22 (1989) 234.
[7] J. Beck, Angew. Chem. 106 (1994) 172; Angew. Chem. Int. Ed. Engl. 33 (1994) 163.

[8] I.D. Brown, D.B. Crump, R.J. Gillespie, Inorg. Chem. 10 (1971) 23.
[9] D.J. Prince, J.D. Corbett, B. Garbisch, Inorg. Chem. 9 (1970) 2731.
[10] J. Passmore, G. Sutherland, P.S. White, J. Chem. Soc. Chem. Comm. (1980) 330.
[11] H.G. von Schnering, Angew. Chem. 93 (1981) 44; Angew. Chem. Int. Ed. Engl. 20 (1981) 33.
[12] R.J. Gillespie, Chem. Soc. Rev. 21 (1992) 59.
[13] B. Eisenmann, K.H. Janzon, H. Schäfer, A. Weiss, Z. Naturforsch. 24b (1969) 457.
[14] M.J. Rothmann, L.S. Bartell, C.S. Ewig, J.R. van Wazer, J. Comput. Chem. 1 (1980) 64 and references therein.
[15] J. Beck, Z. Naturforsch. 45b (1990) 1610.
[16] J. Beck, Chem. Ber. 124 (1991) 677.
[17] J. Beck, G. Bock, Z. Naturforsch. 51b (1996) 119.
[18] J. Beck, A. Fischer, publication in preparation.
[19] J. Beck, K. Müller-Buschbaum, publication in preparation.
[20] J. Beck, A. Stankowski, publication in preparation.
[21] J. Beck, Z. anorg. allg. Chem. 621 (1995) 131.
[22] J. Beck, Z. Naturforsch. 45b (1990) 413.
[23] J. Beck, Z. Naturforsch. 49b (1994) 1159.
[24] J. Beck, K.-J. Schlitt, Chem. Ber. 128 (1995) 763.
[25] J. Beck, A. Leiter, K. Müller-Buschbaum, K.-J. Schlitt, publication in preparation.
[26] G. Cardinal, R.J. Gillespie, J.F. Sawyer, J.E. Vekris, J. Chem. Soc. Dalton Trans. (1982) 765.
[27] F. Zürcher, R. Nesper, Annual Meeting SGK/SKM, University of Zürich, Switzerland, 1996, Coll. Abstr.; VIII. Meeting of Gesellschaft Deutscher Chemiker, Darmstadt, Germany, 1996, Coll Abstr. P II 26.
[28] R.J. Gillespie, W. Luk, W. Maharajh, D.R. Slim, Inorg. Chem. 16 (1977) 892.
[29] R.C. Burns, M.J. Collins, S.M. Eicher, R.J. Gillespie, J.F. Sawyer, Inorg. Chem. 27 (1988) 1807.
[30] R.C. Burns, R.J. Gillespie, W.-C. Luk, D.R. Slim, Inorg. Chem. 11 (1979) 3086.
[31] M.J. Collins, R.J. Gillespie, J.F. Sawyer, Acta Crystallogr. C 44 (1988) 405.
[32] P.D. Lyne, D.M.P. Mingos, T. Ziegler, J. Chem. Soc. Dalton Trans. (1992) 2743.
[33] J. Beck, Chem. Ber. 128 (1995) 23.
[34] J. Beck, G. Bock, Z. anorg. allg. Chem. 622 (1996) 823.
[35] J. Beck, K. Müller-Buschbaum, Z. anorg. allg. Chem. 623 (1997) 409
[36] C.G. Davies, R.J. Gillespie, J.J. Park, J. Passmore, Inorg. Chem. 10 (1971) 2781.
[37] R.K. McMullan, D.J. Prince, J.D. Corbett, Inorg. Chem. 10 (1971) 1749.
[38] W.S. Sheldrick, M. Wachhold, Angew. Chem. 107 (1995) 490; Angew. Chem. Int. Ed. Engl. 34 (1995) 450.
[39] J. Beck, Angew. Chem. 102 (1996) 301; Angew. Chem. Int. Ed. Engl. 29 (1990) 293.
[40] M.J. Collins, R.J. Gillespie, J.F. Sawyer, Inorg. Chem. 26 (1987) 1476.
[41] R. Faggiani, R.J. Gillespie, J.E. Vekris, J. Chem. Soc. Chem. Comm. (1988) 902.
[42] R.J. Gillespie, personal communication.
[43] J. Beck, G. Bock, Angew. Chem. 107 (1995) 2739; Angew. Chem. Int. Ed. Engl. 34 (1995) 2559.
[44] P. Boldrini, I.D. Brown, R.J. Gillespie, P.R. Ireland, W. Luk, D.R. Slim, J.E. Vekris, Inorg. Chem. 15 (1976) 765.
[45] R.C. Burns, W.-L. Chan, R.J. Gillespie, W.-C. Luk, J.F. Sawyer, D.R. Slim, Inorg. Chem. 19 (1980) 1432; M.J. Collins, R.J. Gillespie, J.F. Sawyer, G.J. Schrobilgen, Acta Crystallogr. C 42 (1986) 13.
[46] R.C. Burns, M.J. Collins, R.J. Gillespie, G.J. Schrobilgen, Inorg. Chem. 25 (1986) 4465.
[47] J. Beck, J. Wetterau, Inorg. Chem. 34 (1995) 6202.
[48] J. Beck, A. Fischer, Z. anorg. allg. Chem. 623 (1997) 780
[49] R.C. Burns, R.J. Gillespie, J.F. Sawyer, Inorg. Chem. 19 (1980) 1423;
R. Faggiani, R.J. Gillespie, J.F. Sawyer, J.E. Vekris, Acta Crystallogr. C 45 (1989) 1847.
[50] R. Faggiani, R.J. Gillespie, J.W. Kolis, K.C. Malhotra, J. Chem. Soc. Chem. Comm. (1987) 591.
[51] R. Kniep, D. Mootz, A. Rabenau, Z. anorg. allg. Chem. 422 (1976) 17.
[52] J. Beck, M.A. Pell, J. Richter, J.A. Ibers, Z. anorg. allg. Chem. 622 (1996) 473.
[53] G.W. Drake, G.L. Schimek, J.W. Kolis, Inorg. Chem. 35 (1996) 1740.
[54] J. Beck, Th. Schlörb, publication in preparation.

[55] J. Beck, Angew. Chem. 103 (1991) 1149; Angew. Chem. Int. Ed. Engl. 30 (1991) 1128.
[56] J. Beck, Z. anorg. allg. Chem. 619 (1993) 237.
[57] J. Beck, G. Bock, Z. anorg. allg. Chem. 620 (1994) 1971.
[58] F. Klaiber, W. Petter, F. Hulliger, J. Solid State Chem. 46 (1983) 112.
[59] B. Schreiner, K. Dehnicke, K. Maczek, D. Fenske, Z. anorg. allg. Chem. 619 (1993) 1414.
[60] R. Zagler, B. Eisenmann, Z. Naturforsch. 46 B (1991) 593.
[61] M. Julien-Pouzol, S. Jaulmes, F. Alapini, Acta Crystallogr. 33 B (1977) 2270.
[62] P. Boldrini, I.D. Brown, M.J. Collins, R.J. Gillespie, E. Maharajh, D.R. Slim, J.F. Sawyer, Inorg. Chem. 24 (1985) 4302.
[63] R.C. Burns, M.J. Collins, S.M. Eicher, R.J. Gillespie, J.F. Sawyer, Inorg. Chem. 27 (1988) 1807.
[64] E. Keller, SCHAKAL 92, program for the graphical representation of crystal structures, University Freiburg, F.R.G., 1992.