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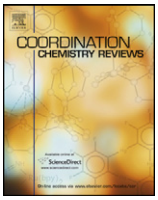

Review

Homo- and heteroatomic polycations of groups 15 and 16. Recent advances in synthesis and isolation using room temperature ionic liquids

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ABSTRACT

Polycations of the electron-rich main group elements are interesting in terms of their diverse structural chemistry and chemical bonding. They constitute a well-established class of compounds of intrinsic fascination and have been widely studied in the past. In this contribution, different routes for the synthesis of polycations of groups 15 and 16 are reviewed and their advantages and limitations are briefly compared. It is concluded that the most recent synthesis procedure in ionic liquid media is a good alternative approach due to mild reaction conditions, process economics, simple treatment, high yield and little influence on environment.

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1. Introduction

The first synthesis of a chalcogen polycation was possibly carried out in 1798, when Klaproth described that tellurium gradually dissolves in sulfuric acid to give a red solution [1]. Following him, in the early 19th century, Bucholz and Magnus prepared colored solution for sulfur and selenium in sulfuric acid and oleum respectively [2]. It took more than 150 years until the true nature of the species responsible for such coloration was interpreted when Bjerrum et al. and Gillespie et al. confirmed spectroscopically that the species are polycations, e.g. Te_4^{2+}, S_4^{2+}, or Se_4^{2+} [3,4]. However, the first chalcogen polycation was isolated in 1962 by Bartlett et al. by reacting oxygen and PtF_6, yielding $O_2[PtF_6]$ containing the oxygen polycation O_2^+ [5]. Later, X-ray crystallographic studies proved the existence and revealed the shape of other chalcogen polycations thereby opening the way to an understanding of the relations between composition, charge, structure, and bonding.

As far as the polycations of group 15 are concerned, the early investigations into the nature of “BiCl” led to the discovery of the first bismuth polycation Bi_9^{5+}. In 1908, Eggink carried out the reduction of bismuth trichloride with elemental bismuth to synthesize “BiCl” [2]. About 60 years later, X-ray crystallographic investigations by Corbett and co-workers revealed the true composition to be $Bi_{24}Cl_{28} = Bi_6Cl_7$ [6,7]. In the crystal structure they found tri-capped trigonal prismatic Bi_9^{5+} polycations accompanied by chlorido-bismuthate(III) anions.

In the early 1970s, Paul et al. and Gillespie et al. provided spectroscopic evidence for antimony, arsenic and phosphorus homoatomic polycations by analyzing different colored solutions, obtained by oxidizing the respective element in protic acids or liquid SO_2 [8,9]. However, the first structurally characterized antimony polycation appeared in 2004, when Kloo and co-workers managed to isolate Sb_8^{2+} from $Ga/GaCl_3$–benzene media [10]. In addition to homoatomic, a number of heteroatomic polycations were also reported by several research groups.

There are plenty of well-established methods for the synthesis of such polycations, all of which need strongly polar media such as H_2SO_4, anhydrous HF, HSO_3F, liquid SO_2, molten salts, e.g. $Na[AlCl_4]$, or GaX_3–benzene media (X = Br, Cl). The particular species are converted to the polycationic clusters through;

- oxidation using appropriate oxidants such as AsF_5, SbF_5, WCl_6, or $MoOCl_4$ [11–13],
- synproportionation in the presence of a strong halogenide ion acceptor such as AlX_3, ZrX_4 or BiX_3 (X = Cl, Br, I) [13–15],
- reduction with elemental Ga or oxidation by GaX_3 in benzene (X = Cl, Br) [16].

Recently room temperature ionic liquids have been introduced as a new alternative reaction medium for the synthesis of polycations and cluster compounds [17–23].

A number of review articles on the synthesis of polycations have been published by Gillespie and co-workers, in which they highlighted the route using highly acidic media or liquid SO_2 and elucidated the structures of the several polycations [11]. Corbett reviewed the homoatomic polycations of main group elements synthesized through the molten salts approach [14c]. In 1989, Passmore et al. discussed in detail the nature of bonding and charge delocalization in some of the unusual non-classically bonded homoatomic polycations [24]. The latest reviews date from 2000, Passmore and co-workers surveyed all known homoatomic polycations of the chalcogens and halogens, studied their bonding, reaction kinetics and thermodynamics to estimate the stabilities using Born–Fajans–Haber cycles [25]. Meanwhile, Beck contributed two review articles, first in 1994, on the preparation of chalcogen polycations via chemical vapor transport, a new synthetic route leading to novel polycations [12], and second in 1997, in which he treated the chalcogens polycations with respect to their structure and bonding according to the Zintl concept [13]. In 1999, Kloo et al. reviewed different preparation routes for the naked clusters of the post-transition elements and explained their structure and bonding [26]. A review article on sub-valent bismuth compounds was published by Ruck in 2001, which covers the whole spectrum from partially oxidized porous metals, through one- and two-dimensional metals, to semiconducting ionic or molecular cluster compounds including new bismuth polycations [27]. In 2004, two comprehensive accounts were presented separately by Krossing and Sheldrick, focusing on the cages and clusters of the group 15 elements and chalcogens respectively [28,29]. They concentrated mainly on the bonding and geometries of the isolated cationic, neutral, and anionic homoatomic cages and clusters.

The focus of this review is to assess critically past and present preparative procedures and to outline new research on the homo- and heteroatomic polycations of groups 15 and 16. Briefly, the modes of synthesis and the structures of the well characterized polycations as well as the physical properties of newly discovered polycationic compounds will be discussed. Further, the article will point out the suitable reaction conditions, e.g. deliberate choice of the nature of oxidants or reductants as well as the acidity needed to stabilize polycationic species in solution and then to isolate solid products containing these species from solution. It will assist in ‘setting the conditions’ to study new reactions and to isolate new compounds.

The last 12 years have provided three new homoatomic polycations, i.e. Bi_5^+, Bi_6^{2+}, Sb_8^{2+}, and 14 new heteroatomic polycations with hitherto unprecedented structures e.g. $(Bi_4E_4)^{4+}$ (E = S, Se, Te), $[Sb_2Te_2]_n^+$, $(Pd@Bi_{10})^{4+}$, $(Au@Bi_{10})^{5+}$, $(Bi_{10}Au_2)^{6+}$, $(Bi_8Si_2)^{3+}$, $(Sb_7S_8Br_2)^{3+}$, $[A_2Te_2Br]_n^+$ (A = Bi, Sb), $(As_3S_5)^+$, $(Bi_3GaS_5)^{2+}$, and $(Sb_{10}Se_{10})^{2+}$. The synthetic schemes for the polycationic clusters are regrettably limited, because they need large, weakly basic, weakly coordinating and non-oxidizing anions to stabilize them in solution and in solid state. Until now, four different successful preparative methods have been reported in literature.

2. Synthesis in inorganic solvents

The superacid route to polycationic clusters was first introduced by Klaproth for the synthesis of Te_4^{2+} by the oxidation of the elemental tellurium in concentrated sulfuric acid where one-component superacids were exercised simultaneously as the oxidizing agent and as the source of the necessary weak Lewis base [1]. The superacids are practical and successful for the synthesis of polycations in solution but several difficulties are associated with crystallization and isolation of solid cluster phases [30]. Gillespie, Passmore and co-workers put their efforts to overcome these difficulties by using highly oxidizing agents like AsF_5 and SbF_5 in superacids or in inert solvents (most often liquid SO_2) to prepare ligand-free “naked” clusters of post-transition elements. This method proved to be very promising and resulted in the fabrication of several new compounds containing variety of polycations of chalcogens, bismuth, and halogens [11,24,25].

2.1. Homoatomic polycations from inorganic solvents

Numerous homoatomic polycations were synthesized using superacidic media and liquid SO_2. They were characterized spectroscopically in solution and through X-ray crystallography in the form of solid phases. The tetraatomic cations E_4^{2+} (E = S, Se, Te) were the earliest to be characterized. In 1971, the first compound $Se_4(HS_2O_7)_2$ was crystallized from oleum in the form of orange needles containing Se_4^{2+} polycations. Originally, the synthesis was performed according to Klaproth; by the oxidation of selenium in disulfuric acid [4a,31], Eq. (1).

$$4\mathrm{Se} + 6\mathrm{H_2S_2O_7} \rightarrow \mathrm{Se_4}^{2+} + 2\mathrm{HS_3O_{10}}^{-} + 5\mathrm{H_2SO_4} + \mathrm{SO_2} \qquad (1)$$

Other chalcogen polycationic compounds were more difficult to isolate from the solution, and it was in early 1980s that the colorless crystals of $S_4[AsF_6]_2{\cdot}0.6SO_2$ were obtained by reacting S_8 with AsF_5 in the presence of traces of bromine in liquid SO_2. Hence, the square planar and discrete molecular entity S_4^{2+} was finally characterized [32]. The tellurium homologue Te_4^{2+} had already been isolated in 1970 as $Te_4[AlCl_4]_2$ through a melting reaction and its crystal structure was determined by Corbett and co-workers [14b]. The same polycation was also found in $Te_4[SbF_6]_2$ as dark red crystals by reacting a mixture of tellurium and germanium with SbF_5 in liquid SO_2 [33]. The tetraatomic E_4^{2+} polycations show charge delocalization and are incompatible with the Zintl concept. The E_4^{2+} polycations carry 22 valence electrons and, according to the Zintl concept, they should contain two double and two triple bound chalcogen atoms in a butterfly conformation where both positive charges are formally localized. Instead, the E_4^{2+} cations show delocalization, which was confirmed by a series of theoretical investigations [34]. The considerable aromatic π stabilization of E_4^{2+} polycations was concluded from all calculations.

The trigonal prismatic Te_6^{4+} polycation had first appeared in 1979 as $Te_6[AsF_6]_4{\cdot}2AsF_3$ and $Te_6[AsF_6]_4{\cdot}2SO_2$ by the oxidation of elemental tellurium with AsF_5 in AsF_3 or liquid SO_2 (Fig. 1a) [35]. Te_6^{4+} is also an example of non-classical structure which has 32 valence electrons. In accordance with the Zintl concept, the number of triple bonded Te atoms should be reduced from six to four but Te_6^{4+} shows the phenomenon of bond delocalization and therefore adopts a non-classical structure.

The heptaatomic tellurium polycation is known as the repetition unit of the polymeric chain $[Te_7^{2+}]_n$. $Te_7[AsF_6]_2$ was synthesized by reacting $Te_4[AsF_6]_2$ with $Fe(CO)_5$ in liquid SO_2, in which the iron carbonyl is presumably responsible for the reduction of Te_4^{2+} to Te_7^{2+}. The infinite chain of the polycation consists of six-membered tellurium rings connected through bridging, triply bonded tellurium atoms which carry the formal positive charges and represent a Zintl precise structure (Fig. 4d) [36].

The eight-membered E_8^{2+} homologues of sulfur and selenium polycations were also prepared. They have similar bicyclic structures derived from the crown shaped ring of the neutral S_8 or Se_8 molecules. Flipping one atom from the *exo* to the *endo* position, excluding an electron pair and deformation of the ring to an oval leads to a bicyclic structure which shows slight distortion from C_s symmetry. The S_8^{2+} polycation was obtained in 1971 as $S_8[AsF_6]_2$ by the oxidation of sulfur with AsF_5 in HF (Fig. 1c) [37], but the crystallization of compounds containing Se_8^{2+} polycations was finally successful in 1987, when elemental tellurium and selenium were oxidized by AsF_5 in liquid SO_2 to get dark green crystals of $(Te_6)(Se_8)[AsF_6]_6{\cdot}SO_2$ [38]. However, Se_8^{2+} had already been isolated through molten salts approach as $Se_8[AlCl_4]_2$ and structurally characterized by Corbett et al. in 1969 [39].

The Se_{10}^{2+} polycation was found as a six-membered twisted ring that is linked across the 1,4-positions by a chain of four Se atoms leading to a bicyclo[4.2.2]decane type structure. It was prepared by oxidizing selenium with AF_5 (A = As, Sb) in liquid SO_2 [40]. The Se_{10}^{2+} polycation has an electron-precise, localized bond structure (Fig. 1d).

S_{19}^{2+} is the heaviest homoatomic polycation synthesized by this approach, here by reacting elemental sulfur with AsF_5 in a mixture of SO_2ClF and liquid SO_2 [41]. Its structure consists of two seven-membered rings in the chair conformation connected by a S_5-chain (Fig. 1e). The two triple bound sulfur atoms hold the formal positive charges and adopt a classical structure.

Besides the spectroscopic evidence for arsenic (e.g. As_4^{2+}, As_2^{2+}), phosphorus (P_8^{2+}, P_4^{2+}), and antimony (Sb_8^{2+}, Sb_4^{2+}) polycations in protic acids or liquid SO_2 [8,9], the trigonal bipyramidal Bi_5^{3+} remained the only group 15 polycation that could be isolated by this route and characterized. It was obtained as $Bi_5(AsF_6)_3{\cdot}2SO_2$ by the oxidation of elemental bismuth with AsF_5 in liquid SO_2 [42] Eq. (2).

$$10\mathrm{Bi} + 9\mathrm{AsF_5} \xrightarrow{\mathrm{SO_2}} 2\mathrm{Bi_5[AsF_6]_3} \cdot 2\mathrm{SO_2} + 3\mathrm{AsF_3} \qquad (2)$$

2.2. Heteroatomic polycations from inorganic solvents

Besides plenty of homoatomic polycations of groups 15 and 16, a small number of heteroatomic polycations have been discovered. Among them, polycations that are built by two different kinds of chalcogen atoms (E) represent the largest group. Gillespie et al. synthesized a variety of such mixed polycations from liquid SO_2 or in a liquid mixture of SO_2ClF/SO_2 and structurally characterized them by means of X-ray crystallography.

For the square E_4^{2+} polycations, a number of mixed group 16 polycations were isolated e.g. $(Te_2Se_2)^{2+}$, $(Te_3Se)^{2+}$, or $(S_3Se)^{2+}$ [43]. The non-classical $(E_4)^{2+}$ polycations show significant deviations from the square-planar conformation. They were obtained as salts of either fluorido-stibates(III) or fluorido-arsenates(III) by reacting the respective elements with SbF_5 or AsF_5 in liquid SO_2.

The six-membered E_6^{2+} species are also known, e.g. $(Te_3S_3)^{2+}$, $(Te_2S_4)^{2+}$, or $(Te_xSe_{6-x})^{2+}$ [44], they are almost isostructural having a six-membered ring in boat-conformation (Fig. 2b and f). A series of heteroatomic $(Te_xSe_{6-x})^{2+}$ polycations were prepared as described above, but for the synthesis of $(Te_3S_3)^{2+}$ two different methods were applied using liquid SO_2 as the reaction medium: (i) by reacting $Te_4[AsF_6]_2$ and $S_8[AsF_6]_2$, (ii) by reacting a mixture of Te/S with AsF_5. All six-membered heteroatomic $(E_6)^{2+}$ cations follow the Zintl concept and exhibit classical structures with localized bonds.

Only two interchalcogen $(E_8)^{2+}$ polycations, $(Te_4S_4)^{2+}$ and $(Te_2Se_6)^{2+}$, were obtained by this synthetic route. The $(Te_2Se_6)^{2+}$ polycation has a bicyclo[2.2.2]octane structure with the two tellurium atoms occupying the bridgehead positions. The triple bonded tellurium atoms bear the formal positive charges and reveal an electron-precise structure (Fig. 2g). Dark brown crystals of $(Te_2Se_6)(Te_2Se_8)[AsF_6]_4{\cdot}(SO_2)_2$ resulted from the reaction of tellurium, selenium, and sulfur with AsF_5 in liquid $2SO_2$ [45]. The realgar-like $(Te_4S_4)^{2+}$ polycation was prepared by a reaction of a mixture of tellurium and tin powder with AsF_5 in liquid SO_2 [46]. For the cage structures, normally a count of 44 valence electrons is realized, however, the $(Te_4S_4)^{2+}$ cation has two extra electrons. According to the Zintl concept, for the four triple bonded Te atoms, the cage structure should bear a positive charge $(Te_4S_4)^{4+}$. Consequently, the $(Te_4S_4)^{2+}$ cation structure was suggested with a pair of delocalized electrons trapped inside the cluster (Fig. 2a).

The ten-membered E_{10}^{2+} heteroatomic polycations, such as $(Te_2Se_8)^{2+}$, $(Te_{3.7}Se_{6.3})^{2+}$ or, $(Te_{4.5}Se_{5.5})^{2+}$, are the heaviest species synthesized employing this route [45,47]. The structure of these cations is similar to Se_{10}^{2+} (Fig. 2e).

Very few heteroatomic polycations that contain elements of groups 15 and 16 are known. The mixed arsenic/chalcogen polycations, $(As_3S_4)^{+}$ and $(As_3Se_4)^{+}$, were also found by Gillespie et al. [48a]. For the synthesis of $(As_3S_4)^{+}$, they treated β-As_4S_4 with AsF_5 or SbF_5 to get the corresponding salts, while in case of $(As_3Se_4)^{+}$, the related amounts of 1:1 or 4:3 As–Se-melts were reacted with either AsF_5 or SbF_5. Both $(As_3S_4)^{+}$ and $(As_3Se_4)^{+}$ cations have C_s symmetry and are isostructural to P_4S_3 or P_7^{3-} [49], which can be considered to be derived from a tetrahedron of three arsenic atoms and one sulfur or selenium atom with three of its edges bridged by sulfur

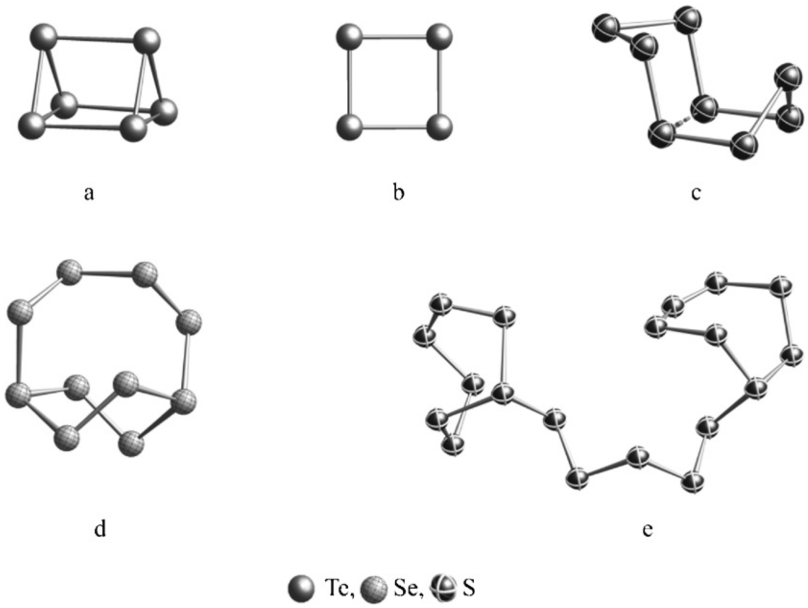

Fig. 1. The structures of the homoatomic polycations. (a) Te_6^{4+}, (b) Te_4^{2+}, (c) S_8^{2+}, (d) Se_{10}^{2+}, and (e) S_{19}^{2+}.

or selenium atoms (Fig. 2c). These heteroatomic polycations show classical, electron-precise structures. Some mixed nitrogen/sulfur polycations were also reported e.g. $(S_4N_4)^{2+}$, $(S_6N_4)^{2+}$, or $(S_5N_5)^{+}$, they were isolated from liquid SO_2, HSO_3Cl, or $SOCl_2$ using a variety of counter ions like $AlCl_4^-$, SbF_6^-, AsF_6^-, or $SbCl_6^-$ etc. [48b–48d]. The phenomenon of bond delocalization was observed in such heteroatomic polycations (Fig. 2d and h).

2.3. Synthesis in inorganic solvents: advantages and limitations

Gillespie et al. and Passmore et al. were successful to establish a new strategy, which could overcome the difficulties associated with the crystallization of polycations. The use of highly oxidizing agents, such as pentafluorides of antimony and, even better, arsenic in superacids or inert solvents (most often liquid SO_2), resulted in the fabrication of several new salt-like compounds containing a variety of polycations of chalcogens, bismuth, and halogens. This synthetic procedure has numerous additional advantages:

- Reactions may be carried out in protic acids or in liquid SO_2 at ambient or lower temperature.
- Study of polycations in solution, using UV–vis and Raman spectroscopy.
- Some reaction by-products as well as the solvents are volatile and can easily be separated, allowing easy recovery of solid phases
- In some cases, well crystallized samples can be obtained.
- The yield was essentially quantitative on the basis of the amount of oxidizing agent used.

However, there are some demerits, which undermine this synthetic approach:

- The use of highly toxic (and expensive) substances like AsF_5 or SbF_5.
- The prerequisite for sophisticated equipment and glassware.
- Crystal growth requires a couple of weeks and sometimes experimental tricks have to be applied in order to obtain crystals with

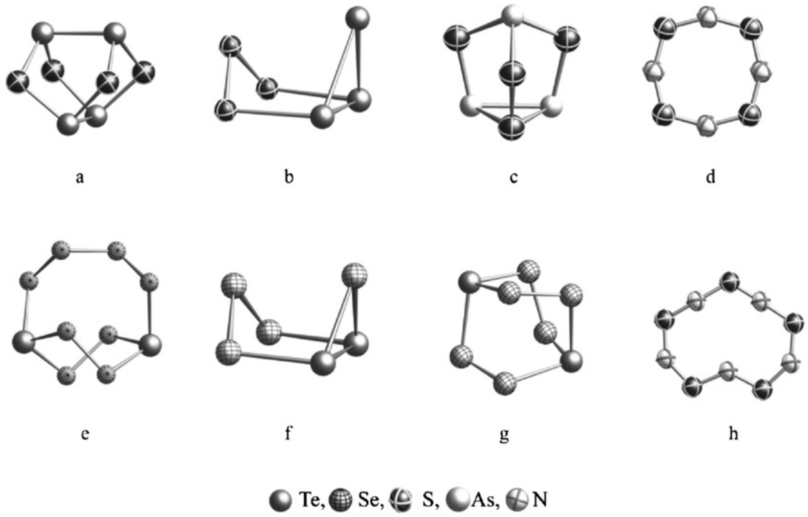

Fig. 2. The structures of the heteroatomic polycations. (a) $(Te_4S_4)^{2+}$, (b) $(Te_3S_3)^{2+}$, (c) $(As_3S_4)^{+}$, (d) $(S_4N_4)^{2+}$, (e) $(Te_2Se_8)^{2+}$, (f) $(Te_2Se_4)^{2+}$, (g) $(Te_2Se_6)^{2+}$, and (h) $(S_5N_5)^{+}$.

sizes suitable for X-ray crystallography. In some cases only microcrystalline powders are accessible.

- The production of less-volatile by-products, especially SbF_3, on reduction is also a troublesome because it can accept fluoride ions to form SbF_6^- or $Sb_2F_{11}^-$ as counter-ions. In this perspective, the syntheses of single-phase products have frequently been made difficult or impossible by co-precipitation of the SbF_3 or by mixed oxidation state anion formation between SbF_5, SbF_3, and fluoride ions. Otherwise reactions, which lead to a solid residue, yielded contaminated products because of the very low volatility of SbF_3 [30].

3. High-temperature synthesis in melts and by chemical vapor transport

The early investigation into the nature of the subchloride “BiCl” fascinated synthetic chemists to explore a new approach to prepare, isolate and characterize the polycationic cluster compounds. This inspiration resulted in the discovery of the high temperature route or molten salts approach, which was mainly developed by Corbett and co-workers [14]. This route gifted not only novel polycations, but also assisted to isolate known species, which were not yet well characterized. Low-melting halogenides with melting points above room temperature (e.g. $SbCl_3$: mp = 73 °C, $AlCl_3$: mp = 193 °C, or $GaCl_3$: mp = 80 °C) were used as the reaction media. The most frequently used method to synthesize polycations in melts is the synproportionation, which also proved helpful to solve the issue of “BiCl”. The single crystals analysis proved the existence of $Bi_{24}Cl_{28} = Bi_6Cl_7$ instead of BiCl, which has a structure consisting of tri-capped trigonal prismatic Bi_9^{5+} polycations accompanied by chlorido-bismuthate(III) anions (Fig. 3e) [6,7]. Later, Krebs et al. managed to modify the scheme by altering the proportion of molten salts to isolate other bismuth polycations [50]. A major obscurity with the synproportionation reaction is that the number of redox reactions that can take place is limited.

Beck brought key improvement in this scheme, which shows apparently similarities to the traditional molten salt route, but it avoids the limitations of synproportionations. This upgraded and advanced strategy is known as chemical vapor transport (CVT), in which a volatile, high-valent transition metal halogenide acts both as halide acceptor and as oxidizing agent [12]. Ruck et al. further expanded the scope of the higher temperature route by incorporating transition metals in the structure of the bismuth polycations [51]. To summarize, by the higher temperature route, besides known polycations, novel homo- and heteroatomic polycations of groups 15 and 16 also became accessible.

3.1. *Homoatomic polycations from high-temperature synthesis*

Employing the high temperature synthetic route allowed the isolation and subsequent structure determination of polycationic compounds. Bi_5^{3+} and Bi_8^{2+} polycations were first reported by Bjerrum et al. in 1967 during the spectrochemical investigation of bismuth metal in dilute solutions of $BiCl_3$ in liquid NaCl–$AlCl_3$ and KCl–$ZnCl_2$ mixtures [52]. Corbett attempted to crystallize $Bi_5[AlCl_4]_3$ and $Bi_8[AlCl_4]_2$ from $NaAlCl_4$ melts but due to slow equilibration, supercooling phenomena, and problems with twinning, no suitable single-crystals were obtained in the early investigations [14a]. Krebs and co-workers reconsidered and refined this synthetic route successfully to obtain good quality single-crystals, which allowed a better structural characterization of the salts $Bi_5[AlCl_4]_3$ and $Bi_8[AlCl_4]_2$. The Bi_5^{3+} polycation possesses trigonal bipyramidal conformation, while Bi_8^{2+} is a square antiprism (Fig. 3a and d) [50].

Later, the square pyramidal Bi_5^+ and the distorted octahedral Bi_6^{2+} polycations were found simultaneously in the compounds $Bi_{34}Ir_3Br_{37}$ and $Bi_{12-x}MX_{13-x}$ (M = Rh, Ir; X = Cl, Br; $x \leq 1$) (Fig. 3b and c) [53]. A better structural characterization of the Bi_6^{2+} cation, as a distorted octahedron with an opened edge, became possible with the discovery of $Bi_6[PtBi_6Cl_{12}]$ [54].

Modified Wade’s rules have proven to be a very convenient tool for qualitative estimation of the geometries of homoatomic bismuth clusters, where the 6s electrons form the lone pairs and only the 6p electrons are used in cluster bonding. The geometries of the well-known bismuth polycations are in agreement with the prescribed skeletal electrons (SE) e.g. Bi_5^+ (*nido*, 14 SE) [53], Bi_5^{3+} (*closo*, 12 SE) [14a,15,16b,16c,50a], Bi_6^{2+} (*nido*, 16 SE) [53,54], Bi_8^{2+} (*arachno*, 22 SE) [50b,55], Bi_{10}^{4+} (*arachno*, 26 SE) [51b–51f]. However, according to Wade’s rules, the Bi_9^{5+} polycation with 22 SE should adopt a *nido* conformation with the shape of a monocapped square antiprism (C_{4v}), while in most of the crystal structures it is rather close to the tri-capped trigonal prism (D_{3h}), that is a *closo* polyhedron (Fig. 3e) [6,7,50c,56]. Quite recently, for the first time a C_{4v} symmetric Bi_9^{5+} polycation was reported in the polar structure of $Bi_{18}Sn_7Br_{24}$ [57]. In agreement with Wade’s rules and quantum chemical calculations, the homoatomic *nido* cluster Bi_9^{5+} is a monocapped square antiprism (C_{4v}) (Fig. 3f).

The square-planar Te_4^{2+} polycation was first isolated by the molten salts approach in 1971 in the form of dark red or violet crystals of $Te_4[AlCl_4]_2$ and $Te_4[Al_2Cl_7]_2$ [14b]. Other known square-planar Se_4^{2+} species were also obtained easily by this route [58].

The boat-shaped Te_6^{2+} polycation was trapped in $Te_6[WOCl_4]_2$ through CVT (Fig. 4a) [59]. A polymeric form, the $[Te_6^{2+}]_n$ polycation, has been found in $Te_6[MCl_6]_2$ (M = Zr, Hf) [60]. In this case, five-membered rings are connected via single tellurium atoms to a chain (Fig. 4b). Like trigonal prismatic Te_6^{4+} polycation, Te_6^{2+} also shows a non-classical structure with delocalized bonds but for the polymeric form $[Te_6^{2+}]_n$, the Zintl concept can be applied to explain the relation between charge and structure. In the cationic chain, there are two threefold coordinated Te atoms, which exhibit three bonds and carry formally the positive charge.The Te_7^{2+} has been known merely as a polymeric cation. In $Te_7[AsF_6]_2$, the infinite chain of the polycation consists of six-membered tellurium rings connected through bridging tellurium atoms (Fig. 4d) [36], while in $Te_7[MOX_4]X$ (M = Nb, W; X = Cl, Br) the $[Te_7^{2+}]_n$ strands are made up from centrosymmetric planar Te_7-groups linked by a *spiro* fragment of Te–Te bonds to give a folded band [61]. The structure has been rationalized as containing four triple bound Te atoms bearing a formal positive charge, the central Te atom is in a tetra-coordination with two lone pairs *trans* to each other and having a formal charge of −2. As a result, the polycation was interpreted as Te_7^{2+} (Fig. 4c).

The Te_8^{2+} polycations are found in different conformations. In $Te_8[WCl_6]_2$, it shows a bicyclic structure composed of two five-membered rings each in an envelope conformation (Fig. 5a) [62], while a quasi-bicyclic *exo–endo* conformed Te_8^{2+} ring similar to S_8^{2+} was characterized in $Te_8[ReCl_6]$ (Fig. 1c) [63]. Moreover, a bicyclo[2.2.2]octane structure for Te_8^{2+} polycation has also been described in the compounds $(Te_6)(Te_8)[MCl_6]_4$ (M = W, Nb) (Fig. 4e) [13]. An other structural isomer of Te_8^{2+} has been discovered in $Te_8[U_2Br_{10}]$ and $Te_8[Bi_4Cl_{14}]$, which contain a polymeric chain $[Te_8^{2+}]_n$ of six-membered tellurium rings in chair conformation connected through a Te_2 bridge (Fig. 5b) [64]. Te_8^{4+}, a higher oxidized polycation stabilized in the salt $Te_8[VOCl_4]_2$, can be interpreted as a dimer formed by a pair of coplanar Te_4^{2+} rings. In fact, the Te_8^{4+} forms a cube with two opened edges, leaving four of the eight Te atoms triple bonded (Fig. 4f) [65]. Among different Te_8^{n+} forms, the bicyclo[2.2.2]octane-type Te_8^{2+}, the higher oxidized Te_8^{4+}, and polymeric chain found in $Te_8[U_2Br_{10}]$ and $Te_8[Bi_4Cl_{14}]$ show classical, Zintl precise structures and possess tricoordinated tellurium atoms bearing the formal positive charges.

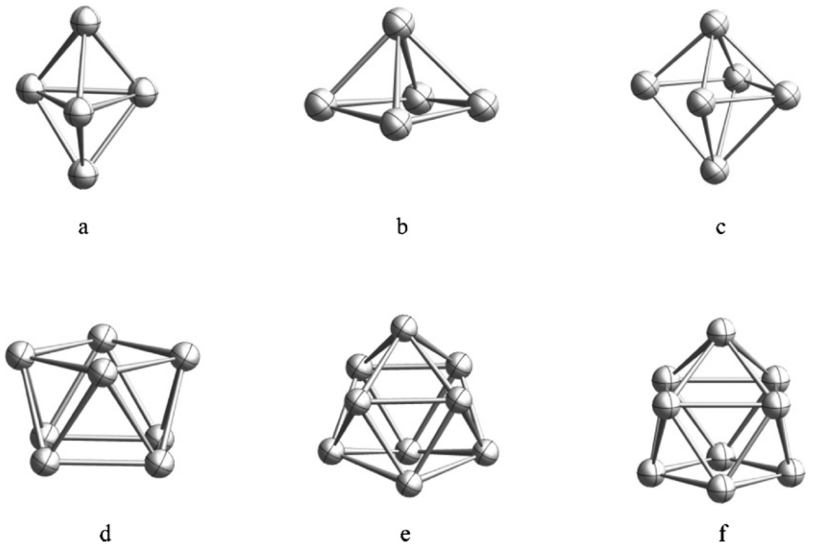

Fig. 3. The structures of the bismuth homopolycations. (a) Bi_5^{3+}, (b) Bi_5^{+}, (c) Bi_6^{2+} with an open edge, (d) Bi_8^{2+}, (e) Bi_9^{5+}, a tri-capped trigonal prism (D_{3h}), and (f) Bi_9^{5+}, a monocapped square antiprism (C_{4v}).

The octaselenium Se_8^{2+} polycation was first obtained through synproportionation in 1971 in the form of dark reddish brown crystals of $Se_8[AlCl_4]_2$ [66]. Se_8^{2+} is isostructural to S_8^{2+} and possesses a cyclic structure with approximately C_s symmetry (Fig. 1c).

Te_{10}^{2+} was also reported as a polymer. The structure of $(Te_4)(Te_{10})[Bi_4Cl_{16}]$ contains two different polymeric cations i.e. $[Te_4^{2+}]_n$ and $[Te_{10}^{2+}]_n$ [67]. The structure of $[Te_{10}^{2+}]_n$ polycation is similar to $[Te_7^{2+}]_n$ (Fig. 4c) and consists of two tetra-coordinated, six tri-coordinated and two di-coordinated tellurium atoms. The two tetra-coordinated Te atoms are members of two adjacent planar four-membered rings and the six tricoordinated centers link the planar Te_{10}^{2+} units forming an infinite folded band (Fig. 5d).

The largest discrete homoatomic polycation is Se_{17}^{2+}, which was synthesized by the oxidation of elemental selenium with WCl_6 through CVT [68]. The electron-precise structure of Se_{17}^{2+} is similar to S_{19}^{2+} and consists of two seven-membered rings, which are linked by a three-membered selenium chain (Fig. 5c).

3.2. Heteroatomic polycations from high-temperature synthesis

In addition to homoatomic, a number of heteroatomic polycations were obtained through the higher temperature routes. Beck synthesized a small number of mixed polycations of groups 15 and 16, while Ruck et al. focused on the incorporation of transition metals and post transition elements into the bismuth polycations and managed to prepare a couple of novel heteroatomic clusters. A most recent review published by Braunschweig et al. emphasizes on the ability of bismuth species to build mixed clusters with transition metals [69], generating a wide variety of structures containing transition metal–bismuth bonds [70].

A series of mixed polycations $(Bi_4E_4)^{4+}$ were obtained from acidic $NaCl/AlCl_3$ melts (E = S, Se, Te). These mixed polycations reveal crystallographic S_4 symmetry, which is slightly distorted from a regular cube, whose corners are occupied alternately by Bi and E atoms (Fig. 6c) [71].

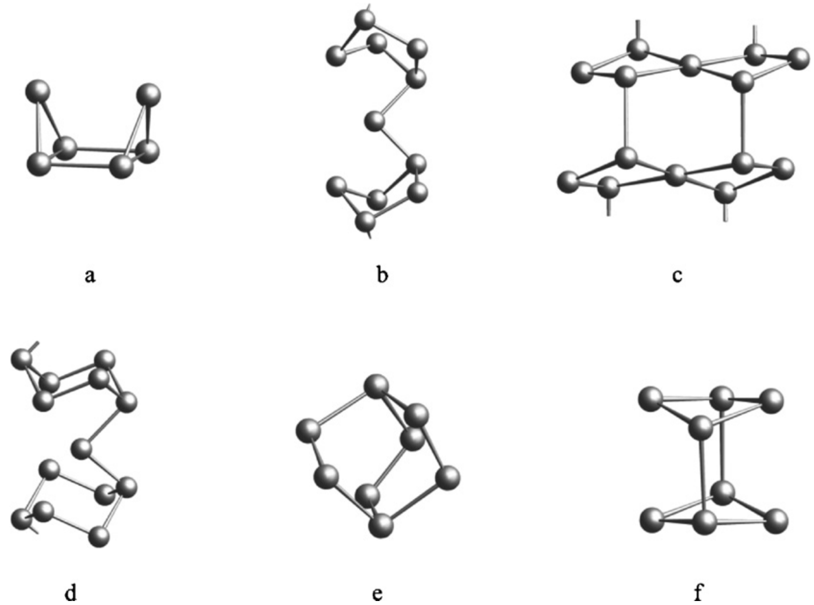

Fig. 4. The structures of the tellurium homoatomic polycations: (a) Te_6^{2+}, (b) $[Te_6^{2+}]_n$ chain, (c) folded band of $[Te_7^{2+}]_n$, (d) polymeric $[Te_7^{2+}]_n$, (e) Te_8^{2+}, and (f) Te_8^{4+}, a cube with two open edges.

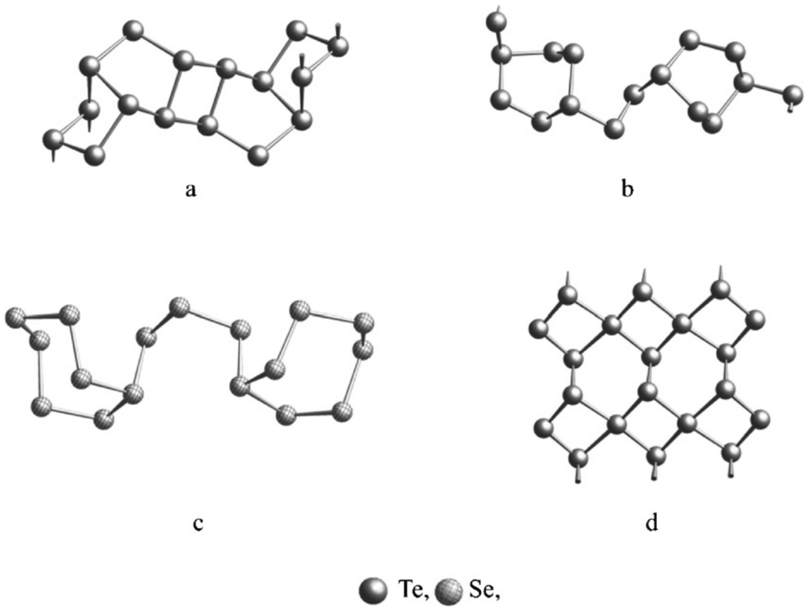

Fig. 5. The structures of homoatomic cations: (a) the association of the Te_8^{2+} ions into an undulated chain, (b) polymeric chain of $[Te_8^{2+}]_n$, (c) Se_{17}^{2+}, and (d) the infinite folded band of $[Te_{10}^{2+}]$n.

$[Sb_2Te_2^{+}]_n$ is a polymeric heteroatomic polycation, which forms strands made up of stacked Sb_2Te_2-rings. These rings are connected with their neighbors alternating via two, three, or four covalent bonds. Mostly Sb–Te bonds are present, in smaller number Sb–Sb bonds, while Te–Te bonds are not observed (Fig. 6d) [72].

The mixed chalcogen polycations $(Se_4Te_3)^{2+}$ and $[Se_{4.85}Te_{3.15}^{2+}]_n$ were obtained by reacting $Te_6[WOCl_4]_2$ with selenium, or Se/Te mixtures with $WOCl_4$ [73]. The $(Se_4Te_3)^{2+}$ polycation is almost similar to polymeric $[Te_7^{2+}]_n$, built by four-membered planar Te_2Se_2 rings connected via three atomic Se–Te–Se bridges in the 1,3 positions of the rings (Fig. 6f). The polymeric cation $[Se_{4.85}Te_{3.15}^{2+}]_n$ consists of five-membered rings that are connected in the 1,3-positions by three-atomic bridges.

The heteroatomic arsenic/sulfur polycation $(As_3S_5)^+$ was synthesized by treating As, S, and $AsCl_3$ in $AlCl_3$ melts at 80 °C to get yellow crystals of $(As_3S_5)[AlCl_4]$ [74]. The polycation $(As_3S_5)^+$ has C_s molecular symmetry (Fig. 6e). The structure of the eight-atomic cage can be derived from an As_3S tetrahedron with four edges capped by sulfur atoms.

The Zintl–Klemm concept is easily applicable to above mentioned heteroatomic $(Bi_4E_4)^{4+}$, $[Sb_2Te_2^{+}]_n$, and $(As_3S_5)^+$ polycations. Each group 15 element has three bonds, which is consistent with neutrality for a group 15 element, while with three bonds E, as an element of group 16, behaves as a pseudo-element of group 15 with a positive charge. Therefore, they belong to the electron-precise species.

The heteroatomic $(Bi_8Si_2)^{3+}$ was found in the semiconducting compounds $Bi_{14}Si_2MI_{12}$ (M = Rh, Ir) [51a]. The polycation reveals a square-antiprism of bismuth atoms of which square faces are capped by two silicon atoms.

The stuffed polycation $(Pd@Bi_{10})^{4+}$ was discovered in $Bi_{14}PdBr_{16}$ and $Bi_{16}PdCl_{22}$ [51b,51c]. It consists of a pentagonal antiprism Bi_{10}^{4+} and an uncharged palladium atom at the centre (Fig. 6a).

The $(Au@Bi_{10})^{5+}$ polycation which is isoelectronic and isostructural to $(Pd@Bi_{10})^{4+}$, is a part of the semiconducting compounds $AuBi_{14-\delta}Sn_{2+\delta}X_{21-\delta}$ ($\delta \approx 0.4$) [51e]. The capped polycation $(Bi_{10}Au_2)^{6+}$, a heteroicosahedron with Au^+ cations in 1,12-positions, was found as the central part of the molecule $(Bi_{10}Au_2)[SbBi_3Br_9]_2$ (Fig. 6b) [51d]. The heteroatomic cluster cation $(Bi_{10}Au_2)^{6+}$ was also reported in a series of compounds $(Bi_{10}Au_2)[EBi_3X_9]_2$ (E = As, Bi; X = Cl, Br) [51f]. Disregarding the 6s electrons, which do not contribute because of their stabilization by relativistic effects, the Bi_{10}^{4+} polyhedron with $10 \times 3 - 4 = 26$ electrons in the skeleton meets the expectations for an electron-precise *arachno*-cluster according to the Wade–Mingos classification ($2n + 6 = 26$ electrons for bonding within the cluster).

3.3. High-temperature synthesis: advantages and limitations

This synthetic procedure contributed not only novel polycations, but also supported to isolate crystals of the known species, which had already been investigated only in solution using UV–vis and Raman spectroscopy. The successive developments in this scheme further expanded the scope of the higher temperature route and proved to be successful in synthesizing new solid cluster compounds. Contrary to the synthesis in inorganic solvents, the higher temperature approach avoided the use of toxic substances like AsF_5 or SbF_5. The additional potential advantages of this approach are:

- Improvement in the synthesis of known phases, e.g., Bi_6Cl_7, $Bi_5[AlCl_4]_3$, or $Bi_8[AlCl_4]_2$.
- Reactions are no more limited to synproportionation only.
- In most cases, good quality crystals are obtained. The use of an excess amount of one of the components, e.g. the halogenide, generates a flux immanent to the system.
- The use of different Lewis acids can effectively enhance the number of possibilities of polycationic compounds synthesis.
- In comparison with reactions in high temperature melts, CVT provides better control and reactions are performed at comparatively lower temperature.

Although, the synthesis in melts and by CVT is comparatively successful and provided plenty of novel polycations, there are still some problems associated with the higher temperature approach:

- Contamination with solid by-products, especially in the case of peritectically forming compounds.
- The risk of product decomposition in case of thermally unstable compounds.
- Long annealing time needed for reaction and/or proper crystallization.
- Kinetic hindrance of solid–solid reactions.
- Phase separation in the liquid, e.g. in the Bi/BiX_3 systems (X = Cl, Br, I).
- Complex and widely unknown solid–liquid–gas equilibria.
- Danger of failure of the ampoule due to high vapor pressure.
- Yield, especially in CVT, can be rather low.
- The prerequisite for sophisticated furnaces and ampoules.

4. Synthesis in organic solvents

Kloo and co-workers introduced a new room temperature route in 1995 using Ga/GaX_3–benzene media (X = Cl, Br) [26]. Three different procedures were applied to synthesize polycations; (i) by synproportionation of Bi and BiX_3 in GaX_3-benzene solutions to synthesize bismuth polycations in both chloride and bromide media, (ii) by reduction of the post-transition metal halogenides with a mixture of Ga/GaX_3 in benzene, and (iii) by oxidation of the post-transition metals with GaX_3 in benzene. Kloo et al. synthesized and isolated successfully some homoatomic polycations of antimony, bismuth, and tellurium.

Besides the synthesis of known polycations like Te_4^{2+} [16a,16b,75], Bi_5^{3+} [16c], and Bi_8^{2+} [16b,16c] by this room temperature method [75], for the first time an antimony polycation Sb_8^{2+}, was obtained [10,16b]. All these polycations were isolated as salts of halogenido-gallates(III). The polycation Sb_8^{2+} has square-antiprismatic D_{4d} symmetry, which is analogous to the previously known Bi_8^{2+} cation (Fig. 3d).

Considering the toxicity of benzene in the above mentioned procedure, later Kloo and co-workers used an alternative approach. Here benzene was replaced by dichloromethane to achieve the same goals. Dichloromethane had also been used earlier for the synthesis of some mixed nitrogen/sulfur polycations, e.g. $(SN)^+$ and $(S_2N)^+$ [76a,76b]. To synthesize bismuth clusters, Kloo and co-workers performed a two-step reaction, first to react Ga and $GaCl_3$ in order to get a crystalline adduct, which was subsequently treated with $BiCl_3$ in dichloromethane. Within a couple of weeks, they obtained a red/orange powder of $Bi_5[GaCl_4]_3$. Attempts to get single crystals were not successful. Moreover, the low reaction rate in dichloromethane is believed to be an effect of the significantly lower concentration of gallium metal in this solvent [76c].

4.1. *Synthesis in organic solvents: advantages and limitations*

The use of benzene as solvent in the synthesis of homoatomic polycations was successful in the isolation of several new compounds. The specific important aspects of this procedure are:

- Contrary to synthesis in inorganic solvents or by higher temperature methods, synthesis in benzene or in dichloromethane is relatively economical, easy to handle, and can be performed at room temperature.
- Gallium(III) halogenides have some unique properties, which make them ideal candidates as reagents for the synthesis of main group polycations and transition metal clusters, e.g. high solubility (up to 50 mol% in benzene), Lewis acidity, and the reducing ability of Ga/GaX_3–benzene mixtures (X = Cl, Br).
- Compared to higher temperature synthesis, crystal growth in Ga/GaX_3–benzene media requires only a few days.
- Specially designed glassware or other dedicated laboratory equipment is not mandatory.
- The isolation of solid polycationic compounds from the benzene solutions is conveniently performed by extraction with heptane or mesitylene.

Besides the isolation of various new compounds containing well-known main group polycations, a novel antimony polycation was also synthesized. On the other hand, this route cannot avoid some demerits:

- The use of toxic and cancer causing benzene [77]. The alternative solvent dichloromethane can replace benzene but the solubility problem arises and the reaction rates are often low.
- Limitations in temperature (reactions could only be performed in the liquid range of the solvents).
- General problems with controlled crystallization [16b,16c].
- Growth of single crystals is still difficult from dichloromethane system.
- Seemingly limited to a few systems, since not widely exploited.

5. Synthesis in ionic liquids

Room temperature ionic liquids (RTIL) have opened new opportunities in the field of material synthesis and have provided new soft and low-temperature routes to inorganic solids that are usually prepared by high-temperature reactions. RTIL have distinct physical properties such as high thermal stability, wide liquid range, negligible vapor pressure, good ionic conductivity, and high solubility of both organic and inorganic substances [78,79]. The use of a soft-chemical approach is common in organic synthesis [78], catalysis [80], polymer science [79], nanotechnology [81], and in the synthesis of clathrates [82], and zeolites [83]. However, the application of this technique to prepare polycationic cluster compounds was relatively unexplored. Recently, Ruck et al., Kanatzidis et al., and Feldmann et al. expanded effectively the span of this approach and synthesized a couple of new polycations of groups 15 and 16 [17–23]. The synthesis in ionic liquid media offers an opportunity of conducting one-pot synthesis involving the redox process at low temperature. This low temperature synthesis route eliminates the risk of product decomposition. Moreover modifying the controllable parameters, such as solvent acidity, oxidizing/reducing agent, or halide acceptor, allows the synthesis to be tailored to produce different products. It has been observed that synproportionation, oxidation, and reduction could be easily carried out in RTIL for clusters synthesis e.g. (i) by synproportionation Bi_5^{3+} [17], Te_4^{2+} [19], "$Te_4^{1.78+}$" [84], and Te_8^{2+} [85] polycations were obtained; (ii) by oxidation of elemental tellurium with $WOCl_4$, Te_6^{2+} was prepared [19], and (iii) by reduction of $BiCl_3$ with indium metal Bi_9^{5+} was synthesized [84].

5.1. *Homoatomic polycations from ionic liquids*

In addition to the synthesis of some known homoatomic polycations like Te_4^{2+}, Te_6^{2+}, Te_8^{2+}, Bi_5^{3+}, and Bi_9^{5+} by this method, a partially reduced square-planar "$Te_4^{1.78+}$" polycation was also isolated. The "$Te_4^{1.78+}$" polycation, a slightly distorted square similar to Te_4^{2+} [14b,86], was found in $Te_4[Bi_{0.74}Cl_4]$, synthesized by treating Te, $TeCl_4$, and $BiCl_3$ at room temperature in the Lewis-acidic ionic liquid [BMIM]Cl/$AlCl_3$ (mole ratio = 1:2, $[BMIM]^+$: 1-*n*-butyl-3-methylimidazolium). The incommensurately modulated structure of $Te_4[Bi_{0.74}Cl_4]$ consists of one-dimensional stacks $[Te_4^{1.78+}]_n$ and aperiodic sequences of chlorido-bismuthate(III) anions. The excess electrons are delocalized over the ecliptically stacked polycations.

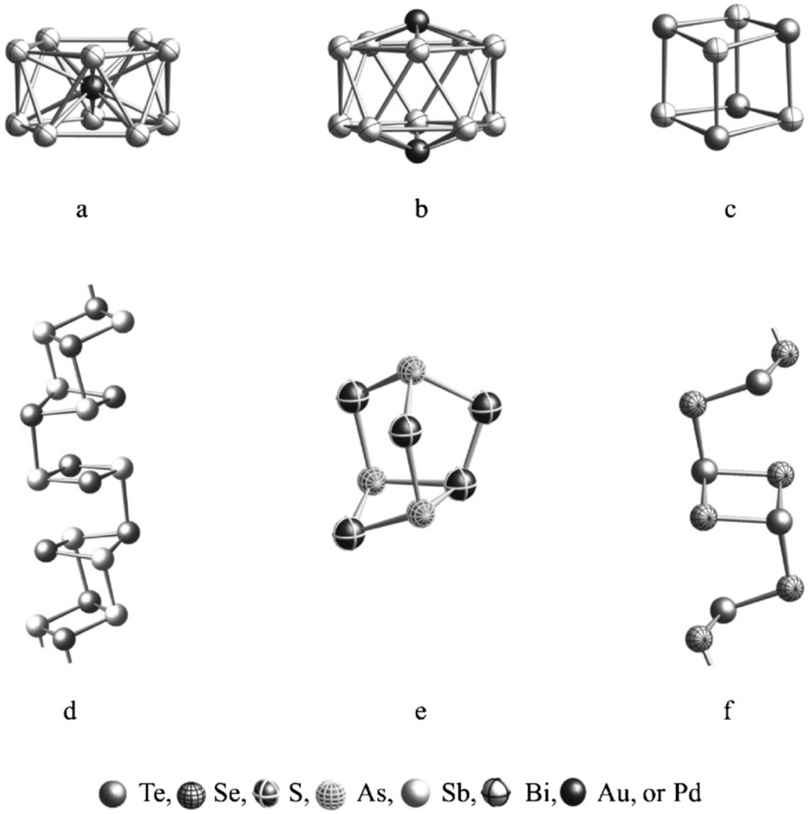

Fig. 6. The structures of the heteroatomic polycations. (a) $(Pd@Bi_{10})^{4+}$, (b) $(Bi_{10}Au_2)^{6+}$, (c) $(Bi_4Te_4)^{4+}$, (d) the polymeric strand of $[Sb_2Te_2{}^+]_n$, (e) $(As_3S_5)^+$, and (f) $[Sb_4Te_2{}^+]_n$.

5.2. Heteroatomic polycations from ionic liquids

To date, a small number of new heteroatomic polycations were also synthesized by means of this soft and sustainable chemical approach. Single crystals of $(Sb_7S_8Br_2)[AlCl_4]_3$ were obtained by reacting elemental sulfur and antimony in the Lewis-acidic ionic liquid [EMIM]Cl/$AlCl_3$ (molar ratio = 1:11, $[EMIM]^+$:1-ethyl-3-methylimidazolium) at 165 °C [21]. The heteroatomic polycation $(Sb_7S_8Br_2)^{3+}$ adopts a double-cubane structure, in which two distorted cubic clusters share one corner (the Sb atom). The other corners are alternately occupied with Sb and S atoms. Two Sb sites have terminal Sb–Br bonds projecting out of the cluster structure (Fig. 7a). The red crystals of $(Sb_7S_8Br_2)[AlCl_4]_3$ exhibit nonlinear optical (NLO) properties, including difference-frequency generation (DFG) and second harmonic generation (SHG).

The two isostructural heteroatomic polymeric cations $[A_2Te_2Br^+]_n$ (A = Bi, Sb) were synthesized by reacting tellurium with bismuth or antimony in the less Lewis-acidic

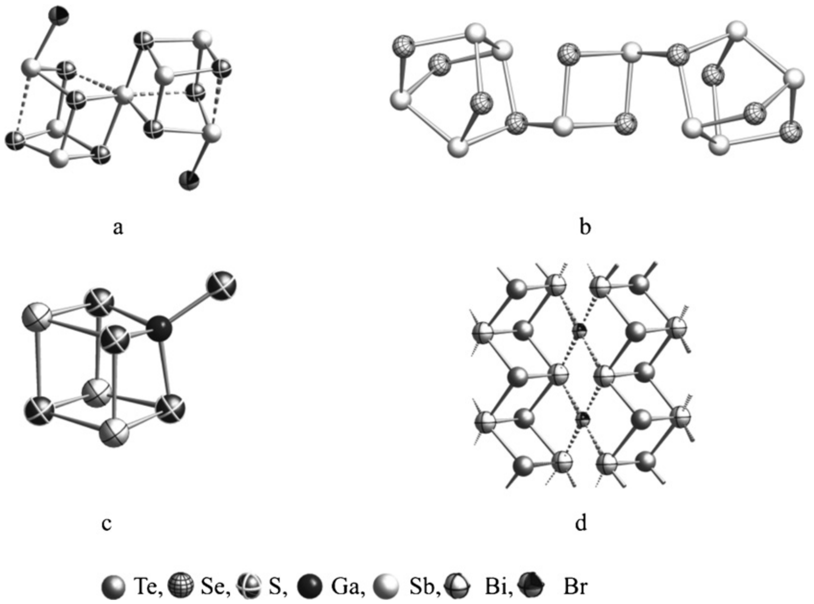

Fig. 7. The structures of the heteroatomic polycations. (a) $(Sb_7S_8Br_2)^{3+}$, (b) $(Sb_{10}Se_{10})^{2+}$, (c) $(Bi_3GaS_5)^{2+}$, and (d) an infinite layer of $[Bi_2Te_2Br^+]_n$.

Table 1
Selected homo- and heteroatomic polycations of groups 15 and 16, synthesized by different routes.

Polycations	Inorganic solvents	Higher temperature synthesis	Organic solvents	Ionic liquids
O_2^+		[5]		
S_4^{2+}	[32]	–	–	–
S_8^{2+}	[37]	–	–	–
S_{19}^{2+}	[41]	–	–	–
Se_4^{2+}	[31]	[58]	–	–
Se_8^{2+}	[38]	[39,66]	–	–
Se_{10}^{2+}	[40]	[58]	–	–
Se_{17}^{2+}	–	[68]	–	–
Te_4^{2+}	[33]	[14b]	[16a,16b]	[19]
"$Te_4^{1.78+}$"	–	–	–	[84]
Te_6^{4+}	[35]	–	–	–
Te_6^{2+}	–	[59,60]	–	[19]
Te_7^{2+}	[36]	[61]	–	–
Te_8^{2+}	–	[62–64]	–	[85]
Te_8^{4+}	–	[65]	–	–
Te_{10}^{2+}	–	[67]	–	–
Bi_5^{3+}	[42]	[14a,15,50]	[16c,76c]	[17]
Bi_5^+	–	[53]	–	–
Bi_6^{2+}	–	[53,54]	–	–
Bi_8^{2+}	–	[14a,50]	[16b,16c]	–
Bi_9^{5+}	–	[6,7,50c,56,57]	–	[84]
Sb_8^{2+}	–	–	[10]	–
$(Te_2Se_2)^{2+}$, $(Te_3Se)^{2+}$, and $(S_3Se)^{2+}$	[43]	–	–	–
$(Te_3S_3)^{2+}$ and $(Te_xSe_{6-x})^{2+}$	[44]	–	–	–
$(Se_4Te_3)^{2+}$	–	[73]	–	–
$(Te_2Se_6)^{2+}$	[45]	–	–	–
$(Te_4S_4)^{2+}$	[46]	–	–	–
$(Te_2Se_8)^{2+}$	[45,47]	–	–	–
$(As_3Se_4)^+$ and $(As_3S_4)^+$	[48a]	–	–	–
$(S_4N_4)^{2+}$	[48b]	–	–	–
$(S_5N_5)^+$	[48c]	–	–	–
$(S_6N_4)^{2+}$	[48d]	–	–	–
$(SN)^+$ or $(S_2N)^+$	–	–	[76a,76b]	–
$(As_3S_5)^+$	–	[74]	–	–
$[Sb_2Te_2]_n^+$	–	[72]	–	–
$(Bi_4Te_4)^{4+}$, $(Bi_4Se_4)^{4+}$, and $(Bi_4S_4)^{4+}$	–	[71]	–	–
$(Bi_8Si_2)^{3+}$	–	[51a]	–	–
$(Pd@Bi_{10})^{4+}$ and $(Au@Bi_{10})^{5+}$	–	[51b,51c,51e]	–	–
$(Bi_{10}Au_2)^{6+}$	–	[51d,51f]	–	–
$(Sb_7S_8Br_2)^{3+}$	–	–	–	[21]
$[Bi_2Te_2Br^+]_n$ and $[Sb_2Te_2Br^+]_n$	–	–	–	[22]
$(Bi_3GaS_5)^{2+}$	–	–	–	[23]
$(Sb_{10}Se_{10})^{2+}$	–	–	–	[87]

ionic liquid [EMIM]Cl/$AlCl_3$ with molar ratio = 1:4.8 [22]. The structures of the semiconducting compounds $[Bi_2Te_2Br][AlCl_4]$ and $[Sb_2Te_2Br][AlCl_4]$ contain infinite $[A_2Te_2Br^+]_n$ chains, which consists of $(A\text{Te})_2$ rhombic units that are connected via bromide ions. The *A* atoms are five fold-coordinated by three tellurium atoms and two bridging bromide atoms to form distorted square-pyramidal conformation (Fig. 7d).

The first cationic heterocubane $(Bi_3GaS_5)^{2+}$ was prepared by the reaction of elemental Bi, S, $BiCl_3$, and $GaCl_3$ in [BMIM]Cl at 150 °C. The red transparent crystals of $(Bi_3GaS_5)_2[Ga_3Cl_{10}]_2[GaCl_4]_2{\cdot}S_8$ were obtained within 10 days [23]. The $(Bi_3GaS_5)^{2+}$ polycation is a distorted heterocubane (Fig. 7c), which has localized bonds.

The first mixed antimony/selenium polycation $(Sb_{10}Se_{10})^{2+}$ was obtained by reacting antimony, selenium and selenium tetrachloride at room temperature in the Lewis–acidic ionic liquid [BMIM]Cl/$AlCl_3$ (molar ratio = 1:2) [87]. In $(Sb_{10}Se_{10})[AlCl_4]_2$, the centrosymmetric polycyclic cation consists of two realgar-like $[Sb_4Se_4]^+$ cages, which are connected through three-bonded selenium atoms with the central $[Sb_2Se_2]$ ring (Fig. 7b). $(Sb_{10}Se_{10})^{2+}$ represents an electron-precise structure according to the Zintl concept.

The ionic liquid based low-temperature synthesis facilitated the isolation of a number of known and new main group sub-valent compounds in high yield. This stimulated the investigation of the physical properties. Recently, Sun and co-workers studied the photoluminescence (PL) properties of $Bi_5[AlCl_4]_3$ crystals, synthesized from ionic liquids [88a]. $Bi_5[AlCl_4]_3$ exhibits extremely broad near-infrared (NIR) PL with a full width at the half maximum (FWHM) of >510 nm and an effective PL lifetime of 4.1 μs at 1160 nm. They also investigated Raman and absorption spectra of the ionic liquids containing subvalent bismuth, which confirmed the coexistence of Bi_5^{3+} and Bi^+ in the solution. The Bi_5^{3+} and Bi^+ emitters, stabilized by the Lewis-acidic ionic liquid, demonstrated ultrabroad NIR photoluminescence with a lifetime of around 1 μs [88b].

5.3. *Synthesis in ionic liquids in comparison with other synthetic routes*

The synthesis in IL is based on the extraordinarily high solubility of metal halides in highly polar Lewis acidic systems, which renders pseudo-melt behavior to the saturated solution. Thus, it has been possible to repeat, even at room temperature, several of the reactions previously performed in molten salts at substantially higher temperature [14]. The major advantages of performing reactions in ionic liquids at low temperatures are:

- Performing reactions in ionic liquids generates an efficient one-step route to the inorganic compounds, which does not require particularly stringent temperature control or gradients.

- Very high solubility of main group elements (e.g., Bi, Te, Sb, Se, Ga, In) and their halogenides allow reactions under mild conditions.
- All polycation syntheses previously performed in molten $AlCl_3$ at elevated temperature can also be done in ionic liquids at room temperature.
- Compare to higher temperature methods, reactions are faster, the yields can be rather high, and there is no need to wait for weeks as in CVT. Crystal growth requires only few days and can be further enhanced either by salting out or by adding a slight excess of a Lewis acid. Good quality single crystals are easily obtained.
- Purely inorganic compounds can be synthesized. Organic components of the ionic liquids are not included in the final structures.
- The inherent thermal stability and the comparatively wide liquid range of RTIL permit access to low and moderate temperatures, at which kinetically stabilized phases can be obtained.
- The mild reaction conditions in IL allow the preparation of new solid phases, also of transition elements, which seem to be not accessible via high-temperature routes. Examples are the room temperature syntheses of cluster compounds, such as $(Mo_2Te_{12})I_6$, $Bi[Mo_5Cl_{13}]Cl$, or $Sn(SnCl)[W_3Cl_{13}]$, which could not be obtained from melt or by CVT [18–20].
- Study of polycations in solution, using UV–vis or Raman spectroscopy.
- Ionic liquids render stability to the ionic reaction intermediates.
- The reaction conditions are easily tunable by varying the ionic liquids, the Lewis acidity, and the temperature. The use of different Lewis acids can effectively increase the variety of polycationic compounds.
- Synproportionation as well as redox reactions can be easily carried out in IL for polycations synthesis.
- Very good reproducibility of the products.
- Specifically designed glassware or other dedicated laboratory equipment is not mandatory as in synthesis using inorganic solvents and other higher temperature routes.
- The isolation of solid polycationic compounds from excess IL is conveniently performed by filtration or by decantation and crystals can be washed with dry dichloromethane or chloroform to remove any traces of ionic liquid.
- Compared to other low-temperature synthetic routes, which make use of cancer causing or toxic organic and inorganic substances like benzene, SO_2, and AsF_5, ionic liquids are more convenient, economical and environmental friendly solvents [77,78].

There is enough possibility to target new materials using the chemistry of ionic liquids and the approach, reported here, might be a route for the preparation of many previously unknown materials, which are difficult to prepare in traditional synthesis. Several hundred ionic liquids are commercially available and many of these will be suitable for this type of work, illustrating further, the scope of this method. These features make ionic liquid based synthetic methods convenient chemical procedures that are versatile and general routes for the development of polycations or clusters of high nuclearity.

6. Summary and outlook

Selected homo-and heteroatomic polycations of groups 15 and 16 are summarized in Table 1. Past and recent developments for the synthesis of polycations have been reviewed. From the increasing number of methods and quality of publications in this area, we can conclude that it is a field of growing interest. Moreover, the attractive photophysical properties of materials containing bismuth polycations motivate further attention to design novel photonic materials containing a wide array of p-block elements. Though, the earlier methods of preparation bestowed origin to this promising field of research, the new alternative facile routes have the potential to flourish and promote the richness of this chemistry. The observation that different mixtures of elements in ionic liquids specifically generate new polycations yield spirit for obtaining other polycations with combinations not yet employed. Moreover, ionic liquids offer a promising synthetic strategy towards new chalcogenide species with cationic character rather than the more familiar anionic nature. We anticipate that the investigation of the chemistry of the homo- and heteroatomic polycations of groups 15 and 16 in ionic liquids will go on smoothly with new discoveries.

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