

Polyanions of Group 14 and Group 15 Elements in Alkali and Alkaline Earth Metal Solid State Compounds and Solvate Structures

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Abstract The chapter discusses the formation of discrete polyanions of group 14 and group 15 elements in solid state structures of alkali and alkaline earth metal compounds depending on the degree of reduction and the cation radii. Applying this concept reveals areas of stability of polyanions of different nature. The mapping of the compounds in one diagram presents a comprehensive overview for the regions of existence of the polyanions in the discussed materials. Additionally, solvate structures are summarized, which provide a promising possibility to adjoin new polyanionic arrangements.

Keywords Cation radii · Group 14 · Group 15 · Homoatomic polyanions · Solid state · Solution · Zintl

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1 Introduction

The existence of polyanions is well known since Joannis first observed the change of color of the characteristic blue sodium ammonia solutions, which turned green in the presence of elemental lead [1, 2]. This was due to the formation of enneaplumbide clusters in solution, and one of the first experimental hints for the availability of metals in negative oxidation states. In the 1930s, Zintl and coworkers were able to identify the compositions of a large number of compounds with negatively charged main group metals and semi-metals using potentiometric titration methods in alkali metal liquid ammonia solutions [3, 4]. This low temperature route of reducing elements of group 14 and group 15 in solution is limited to the temperature range of liquid ammonia between -33 and -77°C . Higher reduced and thus more electron-rich solid state compounds can be obtained by reacting electropositive elements with elements beyond the *Zintl* border in solid state reactions at high temperatures. This route is especially important for elements that cannot be directly reduced at low temperatures, as is the case for silicon or germanium. From the last century until now, a large and still growing number of so-called *Zintl* phases have been reported for alkali or alkaline earth metals in combination with heavier homologues of group 14 and group 15. They all contain polyanionic partial structures of (semi)metal, which range from three-dimensionally extended networks and layers in two dimensions to infinite chains and molecular, discrete polyanions, depending on the degree of reduction. These polyanions feature homopolar element–element bonds exclusively and are connected by electrostatic interactions with the ions of the electropositive metal; the compounds can therefore be understood as polyanionic salts. Using polar solvents which are resilient against reduction and which are able to stabilize high charges, some of these polyanions can be extracted into solution. Liquid ammonia or ethylenediamine can be used as solvents. In solution, polyanions become more and more popular as molecular building blocks for further chemical transformations, e.g., reaction with transition metal complexes [5] or oxidation to bigger aggregates [6–9] and even new elemental modifications [10]. Besides their growing role in solution chemistry, polyanions continue to be the focus of interest in solid state sciences due to their interesting electronic properties and the possibility of

studying the transition from (semi)metallic to ionic structures. It became evident that the use of different or different combinations of electropositive metals led to variations in size and shape of the polyanionic moiety. For some elements this was extensively studied, and a direct influence of cation-element interaction on size, structure, and functionality of the polyanions was emphasized. These interactions are naturally strong for small cations and become less strong the higher the period, in accord with the corresponding radii.

The second important variable for size, structure, and functionality is the degree of reduction of the compound. In *Zintl* phases, there exists a well-defined relationship between chemical and electronic structures [11]. Assuming complete electron transfer from the electropositive to the electronegative metal restates the classical valence rules by giving an average number of valence electrons per anion atom (1). Combined with the 8-N rule, this gives the average number of E–E contacts b_e that occur in the structure (2). Zintl's proposal led to the pseudoatom concept for the charged unit, introduced by Klemm, which relates the structural characteristics of the polyanion to the isoelectronic element structure. The combination of these approaches is well established as the *Zintl–Klemm(–Busmann)* concept [11, 12].

$$N_E = (m \cdot n_M + e \cdot n_E) / e = m / e \cdot n_M + n_E, \quad (1)$$

$$b_e = 8 - N_E, \quad (2)$$

where N_E is the valence electron number per anion atom; m the number of valence electrons of the electropositive element, $m = 1$ for alkali metal, $m = 2$ for alkaline earth metal; n_M the number of electropositive atoms in sum formula; e the number of valence electrons of the electronegative element, $e = 4$ for group 14 element, $e = 5$ for group 15 element; n_E the number of electronegative atoms in sum formula; b_e the average number of E–E contacts.

In the early 1970s, Parthé introduced the valence electron concentration as a powerful systematic tool to explain and predict tetrahedral structures [13]. This concept made it possible to understand structural aspects by only knowing the chemical formula. It has to be noted that the complete electron transfer has to be handled with care, especially for small cations and lighter main group elements, due to not exclusively ionic interactions in this case. The bonding situation of various compounds has been discussed elsewhere [11, 14, 15] and will not be matter of detailed discussion in the overview presented here. We rather concentrate on a systematic consideration of discrete polyanions of group 14 and group 15 elements in solid state compounds. Therefore, the different homoatomic group 14 and group 15 polyanions are summarized and their structural properties will be briefly presented. Because it is of interest to have formalisms by which structural features can be expressed in terms of the chemical formula of the compound, we use the valence electron number per anion atom N_E as an average degree of reduction of the compound. Additionally, the (average) ionic radii of the involved electropositive element cations are taken into account. The scope of this chapter is to give an overview of the known homoatomic molecular polyanions in alkali and alkaline

earth metal solid state compounds of group 14 and group 15 elements to find regions of stability for certain polyanions with respect to the average degree of reduction and the counter ion size. In the end of the chapters of solid state compounds, a map of the differently natured polyanions in certain (N_E ; $r(M^{I/II})_{av}$) areas is provided.

Some of the homoatomic polyanions formulated for solid state compounds are also stable in solution, and even new polyanions are accessible by crystallization from these approaches. The final chapter summarizes homoatomic polyanions of group 14 and group 15, which have been reported in solvate structures.

2 Homoatomic Polyanions of Group 14 Elements in Solid State Compounds

2.1 Clusters of Group 14 Elements in Compounds with $4.4 \leq N_E \leq 5$

The rather low degree of reduction between 4.4 and 5.5 e/atom implicates that atoms of group 14 are bound to three or more bonding partners in average. Coming from the fourfold-bound atoms in the elemental structures ($N_E = 4$), isolated polyanions compete with extended anionic partial structures in compounds, which of course also exhibit these low N_E values close to $N_E = 4$. The most common polyanions of group 14 elements are homoatomic clusters, in particular the tetrahedrally shaped E_4^{4-} and the distorted monocapped square antiprismatically shaped E_9^{4-} clusters [5]. The nine-atom clusters are found in binary alkali metal compounds with the composition $M_4^IE_9$ and $M_{12}^IE_{17}$. Table 1 gives an overview of the hitherto known E_9^{4-} -containing compounds. Calculating the valence electron per anion atom, N_E shows the nonatetretride clusters being part of crystal structures with $N_E = 4.4$ – 4.7 e/atom. With an average cation radius between 0.133 and 0.167 nm [27], compounds containing these nine-atom clusters tend to be stabilized in crystal structures by rather large and therefore polarizable counter ions. This is in accordance with the HSAB principle (for a recent review on HSAB principle, see [28]). $Na_{12}Ge_{17}$ represents an exception; the crystallization of nonagermanide cages together with small sodium cations ($r_{Na^+} = 0.098$ nm) results in huge unit cell dimensions and very poor intensity data [25]. This gives an idea about the still missing crystal structures of small cations and nonatetretride cage anions. Presumably, these phases do not form at all or do not form suitable crystalline products for X-ray structure analysis.

The second most common cluster species are represented by the tetrahedrally shaped fourfold negatively charged E_4^{4-} cages, which can be found together with E_9^{4-} anions in $M_{12}^IE_{17}$ compounds. Additionally, they represent the single anionic moiety in $M_4^IE_4$ and $M^{II}E_2$ materials with a N_E value of 5, corresponding to threefold bound group 14 atoms. The average radius of the cations in this sort of compounds ranges from 0.098 to 0.167 nm and covers a wider area compared to the

Table 1 Solid state compounds that contain nonatetretride clusters

		Compound	N_E	$r(M^I)_{av}$	References
E_9^{4-}	Si	—			
	Ge	K_4Ge_9	4.4	0.133	[16]
		Cs_4Ge_9	4.4	0.167	[17]
	Sn	K_4Sn_9	4.4	0.133	[18]
	Pb	K_4Pb_9	4.4	0.133	[19]
		Rb_4Pb_9	4.4	0.148	[20]
		Cs_4Pb_9	4.4	0.167	[21]
		$Cs_{10}K_6Pb_{36}$	4.4	0.154	[20]
E_9^{4-}/E_4^{4-} (6:7)	Sn	$K_{52}Sn_{82}$	4.63	0.133	[22]
		$Cs_{52}Sn_{82}$	4.63	0.167	[22]
E_9^{4-}/E_4^{4-} (1:2)	Si	$K_{12}Si_{17}$	4.7	0.133	[23]
		$Rb_{12}Si_{17}$	4.7	0.148	[24]
	Ge	$Na_{12}Ge_{17}$	4.7	0.098	[25]
		$K_{12}Ge_{17}$	4.7	0.133	[26]
	Sn	$K_{12}Sn_{17}$	4.7	0.133	[23]
		$Rb_{12}Sn_{17}$	4.7	0.148	[23]

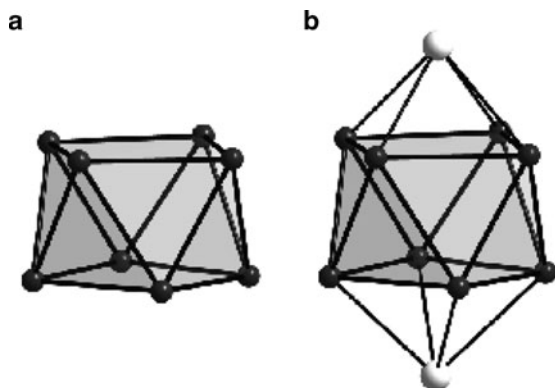
nine-atom species discussed above. Below $N_E = 0.098$, only three-dimensionally extended network structures are observed. But as mentioned before, the compounds with molecular anions compete with those with extended networks, and the kind of observed anionic moiety is sensitive toward the pressure applied during synthesis [29–31] (Table 2).

In addition to these well-known clusters, a third interesting cluster family has been described by Sevov et al. [50]. In ternary compounds with the composition $M_4^ILi_2Sn_8$ ($A = K$ or Rb), a square antiprismatically shaped Sn_8 cluster is present. The valence electron number per tin atom equals 4.75 and lies between the values for nine- and four-atom clusters. The use of small lithium combined with the larger potassium or rubidium ions leads to the formation of square antiprisms Sn_8^{6-} , in which the two square faces are capped by lithium cations, and two edges of the cluster are additionally spanned by lithium cations. The average radius adds up to 0.111 ($M^I = K$) and 0.121 ($M^I = Rb$). The authors give two approaches to the interpretation of the shape of the cluster. Assuming complete electron transfer, the Sn_8 cluster is sixfold negatively charged and therefore an *arachno* species according to Wade's rules [51–53]. The second approach sees lithium interacting partial covalently, which results in a fourfold negatively charged ten-atom *closo*-cluster (Fig. 1).

This Sn_8 cluster is also found in the compound $Ba_{16}Na_{204}Sn_{310}$ [54], where it is only coordinated by sodium cations. The number of valence electrons per atom of 4.76 in this compound is only slightly different from the one in the $Li_2M_4^ILi_2Sn_8$ phases, and the average radius of the cations lies with 0.101 nm in the same range as well. This supports the introduced formalism of anion characteristic $[N_E; r(M)_{av}]$ tuples. Beside the Sn_8 cages, $Ba_{16}Na_{204}Sn_{310}$ also contains gigantic clusters of 56 tin atoms with a charge of -44 . They are endohedrally stabilized by four Ba^{2+} cations. The third cluster in this complex compound is represented by interstitially sodium-stabilized Sn_{16-n} clusters with the shape of a capped truncated tetrahedron (*Frank–Kasper* polyhedron) (Fig. 2).

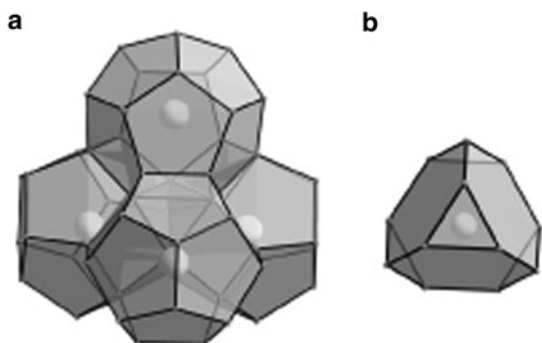
Table 2 Solid state compounds that contain E_4^{4-} clusters, in addition to those mentioned in Table 1

		Compound	N_E	$r(M^{I/II})_{av}$	References
E_4^{4-}	Si	Na_4Si_4	5	0.098	[32, 33]
		K_4Si_4	5	0.133	[34, 35]
		Rb_4Si_4	5	0.148	[34, 35]
		Cs_4Si_4	5	0.167	[34, 35]
		K_7LiSi_8	5	0.125	[36]
		K_3LiSi_4	5	0.117	[36]
		$BaSi_2$	5	0.143	[37]
		$Sr_{1-x}Ba_xSi_2$ $x = 0.2-1.0$	5	0.130	[38]
	Ge	Na_4Ge_4	5	0.098	[32]
		K_4Ge_4	5	0.133	[34, 39]
		Rb_4Ge_4	5	0.148	[34, 39]
		Cs_4Ge_4	5	0.167	[34, 39]
		Rb_7NaGe_8	5	0.142	[40]
		$Na_2Cs_2Ge_4$	5	0.133	[41]
		K_7NaGe_8	5	0.129	[40]
		$SrGe_2$	5	0.127	[42]
		$BaGe_2$	5	0.143	[42]
	Sn	Na_4Sn_4	5	0.098	[43, 44]
		K_4Sn_4	5	0.133	[44, 45]
		Rb_4Sn_4	5	0.148	[46]
		Cs_4Sn_4	5	0.167	[46]
	Pb	Na_4Pb_4	5	0.098	[47]
		K_4Pb_4	5	0.133	[48]
		Rb_4Pb_4	5	0.148	[49]
		K_3LiPb_4	5	0.117	[20]
		Rb_3LiPb_4	5	0.128	[20]
		Cs_4Pb_4	5	0.167	[49]
		Cs_3LiPb_4	5	0.142	[20]
		Cs_3NaPb_4	5	0.149	[20]

Fig. 1 (a) *Arachno*- $[Sn_8^{6-}]$;
(b) *closo*- $[Li_2Sn_8]^{4-}$ cluster
in $M_4^ILi_2Sn_8$ 

Obviously, it is possible to produce bigger clusters at $N_E = 4.76$ by stabilizing them with suitably sized cations, available by electroequivalent substitution of alkali metal by alkaline earth metal cations.

Fig. 2 (a) Sn_{56}^{44-} cluster filled with four Ba^{2+} cations in $\text{Ba}_{16}\text{Na}_{204}\text{Sn}_{310}$; (b) interstitially metal stabilized $\text{M}@\text{E}_{12}^{12-}$ capped truncated tetrahedra in $\text{Ba}_{16}\text{Na}_{204}\text{Sn}_{310}$ ($\text{E} = \text{Sn}$, $\text{M} = \text{Na}$), $\text{M}^{\text{II}}\text{Na}_{10}\text{Sn}_{12}$ ($\text{E} = \text{Sn}$, $\text{M} = \text{Ca}$, Sr), and Li_7RbGe_8 ($\text{E} = \text{Ge}$, $\text{M} = \text{Li}$)



The concept of mixed alkali/alkaline earth metal cations made it also possible to generate compounds of tin with $N_{\text{E}} = 5$ and $r(\text{M})_{\text{av}} < 0.098$ nm in $\text{CaNa}_{10}\text{Sn}_{12}$ and $\text{SrNa}_{10}\text{Sn}_{12}$ [55]. The cluster species one finds in these compounds are again capped truncated tetrahedra, which are stabilized by the endohedral M^{II} cations calcium and strontium. Analogous germanium cages are observed in Li_7RbGe_8 ($N_{\text{E}} = 5$, $r(\text{M})_{\text{av}} = 0.078$ nm), where lithium is interstitially bound. Additional Ge_4^{4-} tetrahedra, which possess the same N_{E} value, can be found in the crystal structure [56].

2.2 In Between Group 14 Clusters and Rings: $N_{\text{E}} = 5.5$

According to the *Zintl–Klemm* concept, an increased degree of reduction of $N_{\text{E}} = 5.5$ means that one atom is in average bound to 2.5 neighbors. This N_{E} value represents the border between clusters ($N_{\text{E}} < 5$) and rings ($N_{\text{E}} > 5.6$), of course competing with two-dimensionally extended layers and one-dimensionally extended strands. In the binary system Ba–Si, this can be well demonstrated with the help of Ba_3Si_4 [57, 58]. This compound contains anions shaped like a butterfly with the formal charge distribution $[\text{Ba}^{2+}]_3[(3\text{b})\text{Si}^{1-}]_2[(2\text{b})\text{Si}^{2-}]_2$. Two silicon atoms are threefold bound like in the previously introduced E_4^{4-} tetrahedra. The remaining two silicon atoms only possess two bonding partners, as one would expect in rings, and they are assigned a charge of -2 in accordance with the 8-N rule. In other words, due to the two-electron reduction of the Si_4^{4-} tetrahedra, one Si–Si bond is broken yielding a butterfly shaped Si_4^{6-} anion. The peritectic temperature of Ba_3Si_4 was determined to be 1,307(5) K, and the material is stable at room temperature [58]. The case is different in the Ba–Ge system, where two modifications of Ba_3Ge_4 are found [59]. The room temperature phase $\alpha\text{-Ba}_3\text{Ge}_4$ crystallizes in a new structure type which is not isotypic but related to Ba_3Si_4 with one-dimensional chains built of distorted Ge_4 rings. At temperatures above 630 K, a phase is detected which is isotypic to Ba_3Si_4 with quasi-isolated Ge_4^{6-} anions.

2.3 Rings of Group 14 Elements in Compounds with $5.66 \leq N_E \leq 6$

The subsequent region above $N_E = 5.5$ e/atom comprises the narrow area of stability of homoatomic rings of group 14 elements. For silicon, the majority of results has been reported by von Schnering and Nesper, whereas Sevov et al. focused on the heavier homologues tin and lead. The number of ring constitutive atoms in all compounds either sums up to five or six, and for silicon additional derivatives of the six-atom ring are reported. Table 3 contains solid state compounds that contain homoatomic rings of group 14 elements.

The lithium and five-atom ring containing compounds ($\text{Li}_{12}\text{Si}_7$, Li_8MgSi_6 , $\text{Ge}_6\text{Li}_{11}$) all show ecliptically stacked quasi-aromatic E_5 rings, where lithium is inserted between adjacent rings. This was called an *infinite sandwich complex* [62]. The same structural motif is found in Na_8BaSn_6 and Na_8BaPb_6 , where contrary to the silicon or germanium compounds the infinite sandwich is built by coordination of the ring plane by the alkaline earth metal. The interchanged positioning concerning alkali/alkaline earth metal was attributed to the different size of the cations, and the ring plane seems to be preferably coordinated by the larger provided cation [65]. This holds true as well for the structures of $\text{Li}_5\text{CaSn}_{11}$ and $\text{Li}_{8.84}\text{CaSn}_{6.16}$, where calcium acts as bridging atom. These observations support the major influence of size with respect to the position of cations toward the anion.

A second remarkable observation is that all crystal structures which contain five-atom rings additionally include higher reduced anionic species. These auxiliary anions seem to be obligatory for the stabilization of the ring structures and become intelligible by taking the N_E value into account. The N_E value of pure quasi-aromatic E_5^{6-} rings sums up to 5.2, which is quite close to the value for homoatomic clusters. At this N_E value, ring formation is not favored due to the remarkable stability of the clusters. Therefore, the ring-containing compounds rather fill the gap between rings and chains at N_E values between 5.6 and 6, but to achieve this high degree of reduction, further and higher reduced anionic species are compulsory in

Table 3 Reported homoatomic rings in alkali/alkaline earth metal containing solid state compounds of group 14 elements

		Compound	Add. anion	N_E	$r(\text{M}^{1/\text{II}})_{\text{av}}$	References
E_5 ring	Si	$\text{Li}_{12}\text{Si}_7$	Si_4^{12-}	5.71	0.068	[60, 61]
		Li_8MgSi_6	Si^{4-}	5.66	0.069	[62]
	Ge	$\text{Ge}_6\text{Li}_{11}$	Ge^{4-}	5.83	0.068	[63]
	Sn	Na_8BaSn_6	Sn^{4-}	5.66	0.103	[64]
		$\text{Li}_5\text{Ca}_7\text{Sn}_{11}$	Sn_6 chain	5.73	0.090	[65]
		$\text{Li}_{8.84}\text{CaSn}_{6.16}$	Sn^{4-}	5.76	0.072	[64]
E_6^{10-} ring	Pb	Na_8BaPb_6	Pb^{4-}	5.66	0.103	[65]
	Si	$\text{Ba}_4\text{Li}_2\text{Si}_6$	–	5.66	0.118	[66]
		$\text{Sr}_4\text{Li}_2\text{Si}_6$	–	5.66	0.107	[67]
	Ge	$\text{Ba}_4\text{Li}_2\text{Ge}_6$	–	5.66	0.118	[66]
		$\text{Ca}_7\text{Mg}_{7.5+/-8}\text{Si}_{14}$	Si^{4-}	6.07	0.090	[68]
Si_{12}^{21-} Si_{10}^{20-}		SiSr	–	6	0.127	[69]

the phases. For E_6^{10-} rings the case is different. The N_E values for these polyanions amounts to 5.66 without any additional anion in the crystal structure; therefore, these rings may be found as the exclusive anionic moiety in $M_4^{II}Li_2E_6$ compounds. The chemical bonding in these highly reduced polyanions is not trivial at all. In 1985, Corbett stated (...) *Such inexplicable bonding arrangements between the heavy elements boggle the mind!* (...) [70], and up to now this still is a fascinating area of research for experimental as well as theoretical chemists. The *Zintl-Klemm* and 8-N rule do not apply simply because of multiple bonding between the main group elements. The bonding in the E_6^{10-} 34-electron systems can be elucidated in terms of the Hückel formalism: 24 electrons form six σ bonds and six nonbonding electron pairs. Ten electrons are remaining and contribute to the π -system by filling three bonding and two antibonding MOs. Based on the total wave function, the electron localization function (ELF [71, 72]) was calculated, which indicated a formally aromatic character of the ring [66].

For silicon, two exotic ring structures have been reported. In $Ca_7Mg_{7.5+/-\delta}Si_{14}$, six atoms form a ring, and each atom is substituted by an additional Si atom to form a planar Si_{12} group of D_{6h} symmetry, for which a charge of $-21 \pm 2\delta$ is reported due to not fully occupied magnesium positions. This is compatible neither with a benzene-like unit (Si_{12}^{18-}) nor with an exclusively single-bonded unit (Si_{12}^{24-}). The intraring bond distances indicate a partial double-bonding character because they are somewhat shorter than Si-Si single bonds, and according to the filled π -states for the planar system this means 1.75 double bonds are distributed over the whole six-membered ring [68].

For the binary alkaline earth silicide SiSr, two different structures have been reported. One contains one-dimensionally extended zigzag chains beside isolated Si^{4-} atoms [73]. Schäfer et al. prepared a modification with the same composition, which instead contained isolated silicide units of ten atoms. In these units, planar hexagons are substituted in the 1-, 2-, 4-, and 5-ring positions by four additional Si atoms. An isostructural compound was found for germanium as well, but showing defects in this unit in the positions 1, 2, 4, and 5. Both materials could not be obtained from stoichiometric approaches, and their formation obviously is coupled to strontium excess [69] (Fig. 3).

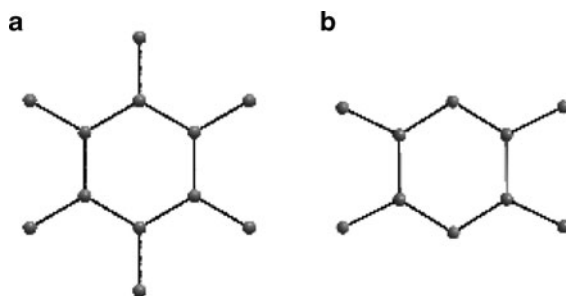


Fig. 3 (a) $Si_{12}^{(21+/-2\delta-)}$ ring in $Ca_7Mg_{7.5+/-\delta}Si_{14}$; (b) Si_{10}^{20-} ring in SiSr

2.4 E_n Chains ($n > 2$) of Group 14 Elements in Compounds with $6 < N_E \leq 6.6$

A further enhanced degree of reduction leads to chains of group 14 elements with N_E values between 6 and 6.6 e/atom. These N_E values cover the range between twofold bound silicon atoms in one-dimensionally extended zigzag chains and E_2^{6-} dumbbells. Isolated chains reside in between these border structures and therefore compete with them [14]. This leads to the expectation of an extreme cation size dependence of the anion formation. Table 4 contains the reported isolated homoatomic chains in solid state compounds.

By having a closer look at the N_E values and the average radii of the cations, it becomes evident that in contrast to the rings discussed above, the degree of reduction plays a subordinate role, within the given borders, for the constitution of the anions. For example, a four-atom chain is observed in $Ca_8Li_{0.969}Mg_{2.031}Si_8$ with an N_E value of 6.63 due to additional monoatomic Si^{4-} anions in the crystal structure. The same length of the chain is also present in $Ba_6Mg_{5.3}Li_{2.7}Si_{12}$ as the exclusive anionic moiety with a N_E value of 6.11. At nearly identical (N_E ; $r(M^{I/II})_{av}$) pair $Sr_{12}Mg_{17.8}Li_{2.2}Si_{20}$ was reported, which includes a three-atom chain and monoatomic Si^{4-} ions. This demonstrates the sensitive relationship between cation properties and anion formation. The majority of chains have up to now been observed within a very narrow range of averaged cation radii between 0.097 and 0.106. Two compounds have been reported for which the cation radius lies quite far away from this region. In $Sr_{11}Mg_2Si_{10}$, eight-atom chains could be realized with a corresponding averaged cation radius of $r(M^{I/II})_{av} = 0.119$ [14]. In monoclinic Li_7Sn_3 , three-atom chains of tin are observed, which are exclusively coordinated by lithium. The arrangement of all atoms together in the unit cell is reminiscent of the structure of metallic lithium. Therefore, the structure of Li_7Sn_3 can be understood as variant of the cubic body-centered metal lattice [80].

Homoatomic chains are a fascinating group of polyanions, due to the possibility to study multiple bonding of heavier main group elements in the solid state and the coordination behavior of differently charged atoms in the same molecular structure.

Table 4 Homoatomic chains of group 14 elements in solid state compounds

	Chain length	Compound	Add. anion	N_E	$r(M^{I/II})_{av}$	References
Si	$n = 3$	$Sr_{12}Mg_{17.8}Li_{2.2}Si_{20}$	Si^{4-}	6.11	0.104	[74]
	$n = 6$	$Ba_2Mg_3Si_4$	Si_2^{6-}	6.5	0.104	[75]
		$Ba_6Mg_{5.3}Li_{2.7}Si_{12}$	–	6.11	0.104	[76]
		$Ca_8Li_{0.969}Mg_{2.031}Si_8$	Si^{4-}	6.63	0.097	[77]
	$n = 8$	$Sr_{11}Mg_2Si_{10}$	Si^{4-}	6.60	0.119	[14]
Ge	$n = 4$	Ca_7Ge_6	Ge_2^{6-}	6.33	0.106	[78]
	$n = 6$	$Ca_8Ge_8Li_{1.18}Mg_{1.82}$	Ge^{4-}	6.60	0.097	[77]
		$Ba_6Ge_{12}Li_{3.1}Mg_{4.9}$	–	6.07	0.103	[79]
Sn	$n = 3$	Li_7Sn_3	–	6.33	0.068	[80]
	$n = 4$	Ca_7Sn_6	Sn_2^{6-}	6.33	0.106	[81]
	$n = 6$	$Li_5Ca_7Sn_{11}$	Sn_5^{6-}	5.73	0.090	[65]

Table 5 Charge of group 14 chains in solid state compounds according to the chemical formula compared to the charge expected for *Zintl*-compliant σ -bonded chains

Chain	Charge according formula q	Charge according Zintl z	Compound
Si ₃	−7.45	−8	Sr ₁₂ Mg _{17.8} Li _{2.2} Si ₂₀
Si ₆	−14	−14	Ba ₂ Mg ₃ Si ₄
	−12.65	−14	Ba ₆ Mg _{5.3} Li _{2.7} Si ₁₂
	−13.03	−14	Ca ₈ Li _{0.969} Mg _{2.031} Si ₈
Si ₈	−18	−18	Sr ₁₁ Mg ₂ Si ₁₀
Ge ₄	−8	−10	Ca ₇ Ge ₆
Ge ₆	−12.82	−14	Ca ₈ Ge ₈ Li _{1.18} Mg _{1.82}
	−12.45	−14	Ba ₆ Ge ₁₂ Li _{3.1} Mg _{4.9}
Sn ₃	−7	−8	Li ₇ Sn ₃
Sn ₄	−8	−10	Ca ₇ Sn ₆
Sn ₆	−13	−14	Li ₅ Ca ₇ Sn ₁₁

Nesper et al. intensively studied silicide chains in ternary and quaternary alkali and alkaline earth metal compounds [82]. It could be shown that the more highly charged terminating silicon atoms prefer coordination by small and hard Li and Mg atoms, whereas the less-charged Si atoms in between obviously tend to be coordinated by larger and soft cations [14, 15]. The charge distribution in the chains is not trivial, and multiple bonding between the heavy elements has to be taken into account. To obtain a first hint on the degree of reduction, one can count the formal charges of the chains from the chemical formula, adopting a charge of -4 for monoatomic anions, -6 for dumbbells, -8 for three-atom chains, and so on, and compare the result with the expected value according to the *Zintl–Klemm* concept which gives the value for single-bonded chains (Table 5).

The discrepancy between the charge according to the chemical formula q and the charge according to single-bonded atoms z gives the double bond contribution to the total bonding x as $x = z - q$, whereby x electrons are taken out of the anti-bonding π^* orbitals. Therefore, smaller bonding distances are expected which are observed more or less distinctively in the latter compounds. This also fits with the observed planarity and the near 120° bonding angles of the building blocks. For the case where $q = z$, one would expect only σ -bonded chains, but here also planar units and bonding angles near 120° are observed, which may mean that the electron pairs at the twofold bound atoms tend to feature sp^2 and p character due to orbital symmetry reasons [14].

Attention has to be drawn to the solid state compound Li₅Ca₇Sn₁₁, which includes Sn₅^{6−} rings (see Sect. 2.3) besides Sn₆ chains. All distances in the Sn₅ ring are shorter than single bonds. Calculations performed on one of the rings resulted in three filled π -bonding orbitals and two empty π -antibonding orbitals, which define a HOMO-LUMO gap of about 2.25 eV for Sn₅^{6−} [64]. The average distance within the five-membered ring is slightly elongated compared to an electronically balanced Na₈EuSn₆, but one distance is reported to be very short. Therefore, some degree of localization of the π -bonding is to be assumed. To the Sn₆ chain, a charge of -12 is assigned due to one significantly shorter Sn–Sn bond. The total amount of electrons from the electropositive metals in this material adds

up to 19. Consequently, there is one electron left unassigned to the polyanions, which is in agreement with magnetic and conductivity measurements. The extra electron is reported to be delocalized over π -antibonding tin orbitals of the pentagon and the Sn_6^{12-} hexamers. Calcium s orbitals are also reported to be involved in the delocalization.

2.5 A Branched Four-Atom Tetrelide “Star” ($E = \text{Si}, \text{Ge}$)

Besides clusters, rings, and chains, a highly charged tetrelide anion that takes the shape of a three jagged star has been reported for silicon and germanium in different crystal structures. It was reported for the first time in 1980 by von Schnering et al. for silicon in the compound $\text{Li}_{12}\text{Si}_7$ [61], which additionally contains the before-mentioned Si_5^{6-} rings. In this compound, the four-atom anion is assigned a formal charge of -12 , which is not understandable by the model of formal ions. A first interpretation was given by von Schnering et al., who suggested the formulation $(\text{Li}^+)_{24}(\text{Si}_4^{8-})(\text{Si}_5^{8-})_2$ with the Si_4^{8-} moiety isoelectronic to carbonate and the Si_5^{8-} to cyclopentene [61]. Leuken et al. carried out ab initio localized spherical wave calculations on crystalline $\text{Li}_{12}\text{Si}_7$ and provided new insights into the compound [83]. Their results basically match the interpretation of von Schnering et al., with the major difference that the five-atom ring is assigned a charge of -6 and the two remaining electrons fill the $2s$ shell of the ring coordinating lithium atoms. This yields a formula of $(\text{Li}^+)_{22}(\text{Li}^-)_2(\text{Si}_4^{8-})(\text{Si}_5^{6-})_2$. Anyway, in this compound the “star” acts as accompanying anion which supports the N_E value where rings are stable (see Sect. 2.3).

The same three jagged star anion is reported in $\text{Ba}_5\text{Mg}_{18}\text{E}_{13}$ ($N_E = 7.54$ e/atom; $r(\text{M}_{\text{av}}^{\text{I/II}}) = 0.092$ nm) and $\text{Sr}_{6.33}\text{Mg}_{16.67}\text{E}_{13}$ ($N_E = 7.54$ e/atom; $r(\text{M}^{\text{I/II}})_{\text{av}} = 0.091$ nm) for $E = \text{Si}$ or Ge [84]. The N^E value for these compounds lies quite far away from the other reported values for compounds containing isolated polyanions. The crystal structures of the ternary materials show as additional anionic moieties the presence of monoatomic E^{4-} anions, and a composition of $\text{E}_4:\text{E}^{4-}$ of 1:9 reveals the charge of the four-atom star to be -10 . This gives rise to internal redox capacity of such E_4 groups. Beside mixed cation sites in the second compound, which lead to geometrically unusual positions resulting in very short Sr-E distances of 292 pm (Si) and 293 pm (Ge), the central atoms of the stars feature a very distinctive anisotropic displacement. For germanium, a slightly pyramidal Ge_4 group could be resolved, which is reflected in the electron density distributions. They show two distinct density maxima for the germanium position (Fig. 4a). Corresponding results could not be obtained for Si_4 from X-ray diffraction data, and ordering of the Si_4 group at lower temperatures could also be excluded. Therefore, a static disorder of Si_4 groups is assumed. Consequently, E_4 groups may occur as completely planar E_4^{8-} ions, isostructural and isoelectronic to CO_3^{2-} , or as slightly pyramidal E_4^{10-} ions, depending on the nature of the cations [84].

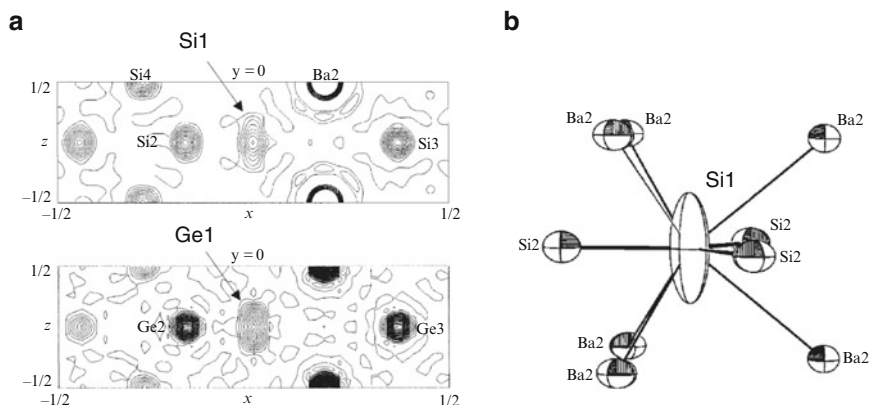


Fig. 4 (a) Charge density distribution and (b) coordination spheres of the star-like E_4 units in $Ba_5Mg_{18}E_{13}$ ($E = Si, Ge$). ([84] Copyright Wiley-VCH Verlag GmbH & Co KGaA. Reproduced with permission)

2.6 Combination of Different Tetrel Elements

Very recently, a mixture of silicon and tin reduced by barium metal yielded the compound Ba_8Si_6Sn , which contains three-atom rings of silicon atoms Si_3^{6-} and monoatomic Sn^{4-} [85]. This shows that the combination of differently sized anionic atoms gives the opportunity to expand into hitherto unknown (N_E ; $r(M)$) regions that contain new polyanions.

2.7 Summarized: Homoatomic Polyanions of Group 14 Elements

To summarize the previously presented anions, the model of the averaged radii of cations in relation to the degree of reduction is applied, which results in areas of stability for the differently natured anions. Concerning clusters, large nine- and eight-atom clusters tend to be stabilized by rather large cations, which is in accordance with simple packing considerations as well as the HSAB principle. In contrast, the smaller tetrahedral E_4^{4-} clusters may be stabilized by a very broad range of cation radii. Compounds that contain tetrahedral anions beside the nonatetretride cages show an expanded cation range compared to the pure nine-atom compounds. In ring-containing compounds, both the average radius of the cationic moieties and the degree of reduction generally are within a smaller array compared to the clusters. Five-membered rings of silicon and germanium are present within 0.06 and 0.08 nm cation size and a degree of reduction between 5.6 and 5.8 e/atom. Around 5.7 e/atom and 0.09–0.11 nm cation radius, the heavier



Fig. 5 Polyanions of group 14 and their dependence on averaged cation radii and degree of reduction

homologue rings of tin and lead are observed. An increased cation radius at a similar degree of reduction yields six-membered rings of silicon and germanium. At a higher degree of reduction, substituted derivatives of the six-atom rings of silicon are obtained. The combination of differently sized anion atoms provides the opportunity to push the limits further to compounds with higher N_E values which contain rings.

Concerning compounds with a still higher charge for the formally anionic structure part, between a degree of reduction of six and seven e/atom chains are present, where four to seven atom chains are stabilized best by an averaged cation radius around 0.1 pm. Three-atom chains are observed either at smaller cation radii or at a higher degree of reduction. Larger cations yield an eight-atom silicon chain. At a very high degree of reduction, the presence of a four-atom star is reported (Fig. 5).

3 Homoatomic Polyanions of Group 15 Elements in Solid State Compounds

Polyphosphide compounds within the scope of this overview rely heavily on contributions by von Schnering et al. (for a review on polyphosphides, see [86]), and major results concerning the heavier homologues As, Sb, and Bi are due to Röhr et al., Eisenmann et al., and Belin et al.

3.1 Clusters of Group 15 Elements in Compounds with $5.2 < N_E < 5.5$

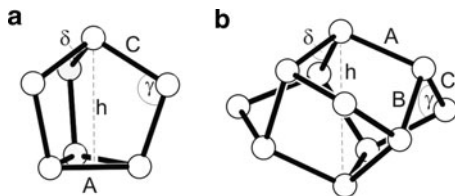
When combining electropositive alkali and alkaline earth metals with group 15 elements, the lowest degree of reduction for molecular polyanions is between 5.2 and 5.5 e/atom. This gives an average of 2.8 to 2.5 E–E contacts according to the 8-N rule, and is therefore less than in elemental structures, where each group 15 atom is threefold bound. For these N_E values, a combination between twofold and threefold bound atoms is expected in crystal structures, which in case of isolated species results in two different homoatomic cluster types. Table 6 contains homoatomic clusters in solid state compounds of group 15 elements.

In contrast to group 14 element clusters, here only two different cluster types are observed. The most common cluster species is represented by the nortricyclane-like E_7^{3-} anions ($E = \text{P–Sb}$), which were structurally characterized for the first time by von Schnering et al. in the compound Sr_3P_{14} in 1972 [94]. The N_E value in these materials adds up to 5.43 e/atom. The existence of the yellow binary alkali metal compounds M_3P_7 with isoelectronic anions was known for a long time [103–105], but crystal structures for Li_3P_7 [90] and Cs_3P_7 [93] were reported only in the middle of the 1980s, which is due to the crystalline to plastic–crystalline transitions of M_3P_7 materials ($\text{M} = \text{Na–Cs}$) [91]. Crystal structures of the analog compounds for the heavier homologue element arsenic even have been reported as late as 2002 [96]. The nortricyclane-like E_7^{3-} anions feature three main distances (A, B, C), and for

Table 6 Homoatomic clusters of group 15 elements in solid state compounds

		Compound	N_E	$r(\text{M}^{\text{I/II}})_{\text{av}}$	References
E_{11}^{3-}	P	Na_3P_{11}	5.27	0.098	[87]
		K_3P_{11}	5.27	0.133	[88]
		Rb_3P_{11}	5.27	0.148	[88]
		Cs_3P_{11}	5.27	0.167	[88]
	As	K_3As_{11}	5.27	0.133	[88]
E_7^{3-}	P	$\text{Rb}_3\text{As}_{11}$	5.27	0.148	[88, 89]
		$\text{Cs}_3\text{As}_{11}$	5.27	0.167	[88, 89]
		Li_3P_7	5.43	0.068	[90]
		Na_3P_7	5.43	0.098	[91]
		K_3P_7	5.43	0.133	[91]
	As	Rb_3P_7	5.43	0.148	[91, 92]
		Cs_3P_7	5.43	0.167	[93]
		Sr_3P_{14}	5.43	0.127	[94]
		Ba_3P_{14}	5.43	0.143	[95]
		Li_3As_7	5.43	0.068	[96, 97]
	Sb	Na_3As_7	5.43	0.098	[96, 98]
		K_3As_7	5.43	0.133	[96]
		Rb_3As_7	5.43	0.148	[96, 99]
		Cs_3As_7	5.43	0.167	[96]
		$\text{Ba}_3\text{As}_{14}$	5.43	0.143	[100]
		Rb_3Sb_7	5.43	0.148	[101]
		Cs_3Sb_7	5.43	0.167	[101, 102]

Fig. 6 E_7^{3-} and E_{11}^{3-} anions with the labels of the bond lengths, pertinent bond angles, and the heights of the polyanions



neutral heptaheteronortricyclanes P_4S_3 and P_4Se_3 $A > B > C$ and $\gamma > \delta$ holds true, whereas for the homoatomic ionic cages here discussed $A > C > D$ and $\delta > \gamma$ applies (Fig. 6a) [86].

The least-reduced isolated polyanion in a dense solid without alkali metal ligands or solvent molecules is represented by the E_{11}^{3-} anions ($E = P, As$), which feature a N_E value of 5.27 e/atom. For these kinds of trishomocubane-like clusters, a similar but less-pronounced analysis of bonds lengths and angles is applicable (Fig. 6b). The phosphorus compounds and the heavy alkali metal arsenides Rb_3As_{11} and Cs_3As_{11} can be obtained directly from the elements. For the preparation of the potassium analog compound, K_3As_7 is used as reducing agent for stoichiometric amounts of arsenic.

3.2 Rings of Group 15 Elements in Compounds with $N_E = 5.67, 6$

An increased N_E value results in the formation of isolated rings of group 15 elements in solid state structures. Besides these rings, of course two-dimensionally extended layers and one-dimensionally extended chains are observed, according to the 8-N rule for these N_E values. In Table 7, solid state compounds are listed in which homoatomic rings are present in the crystal structure.

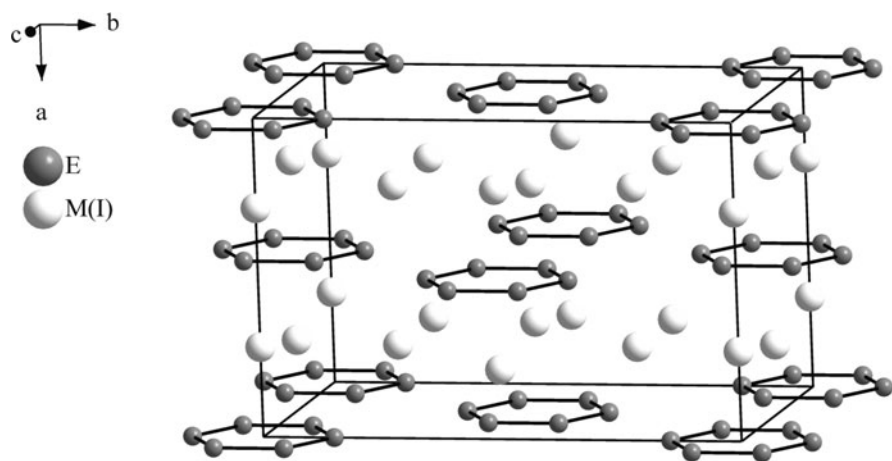
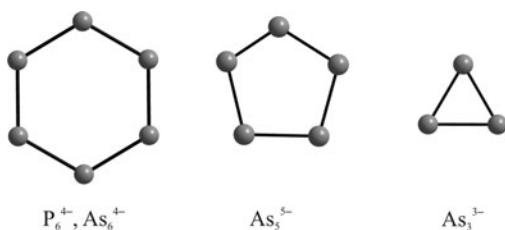
There are three kinds of rings of different nuclearity known for homoatomic group 15 anions (Fig. 7). For arsenic, three-, five-, and six-atom rings are described in solid state compounds, and for phosphorus only the six-atom ring is reported, whereas for antimony and bismuth no homoatomic rings are known in neat solid state materials of alkali and alkaline earth metals.

Rings of six atoms are observed for phosphorus and arsenic as the exclusive anionic moiety in compounds following the formula $M_4^I E_6$. This implies a charge of -4 for the rings, and chemical bonding referring to the Hückel concept was carefully discussed due to planarity of the anion in its crystal structures [107, 111] (Fig. 8).

This planarity is caused by the crystal symmetry of the space group $Fmmm$ ($Fddd$ for β - K_4P_6). Recently, quantum chemical calculations could demonstrate for P_6^{4-} that the ring is slightly distorted in a chair-like conformation, which is

Table 7 Homoatomic rings of group 15 elements in solid state structures

	Compound	N_E	$r(M^{I/II})_{av}$	References
P_6^{4-}	K_4P_6	5.67	0.133	[106]
	Rb_4P_6	5.67	0.148	[107, 108]
	Cs_4P_6	5.67	0.167	[107]
As_6^{4-}	Rb_4As_6	5.67	0.148	[109]
	Cs_4As_6	5.67	0.167	[109]
As_3^{3-}	$CsAs$	6	0.167	[96]
As_5^{5-}	Ba_2KAs_5	6	0.140	[110]
	Ba_2RbAs_5	6	0.145	[110]

Fig. 7 Rings of group 15 elements in solid state compounds of alkali and alkaline earth metals

Fig. 8 Unit cell of $M_4^I E_6$ ($M^I = K-Cs$; $E = P, As$) contains nonaromatic six atom rings

contradictory to the previously assumed aromatic character but fits perfectly to the also missing low field shift of the anions in ^{31}P MAS NMR spectra [112, 113].

With arsenic, five-atom rings in an envelope conformation are observed in compounds with a N_E value of 6, which consequently carry a charge of -5 corresponding to twofold bound atoms. These rings only are present in the mixed alkali/alkaline earth metal ternary materials $Ba_2M^IAs_5$ ($M^I = K, Rb$). Only one binary alkali metal pentelide phase containing isolated anions is reported at the same N_E value, which contains three-atom rings of arsenic together with caesium.

For the compounds with lighter alkali metals which have the same composition, the formation of the isoelectronic one-dimensionally extended chains is favored [96]. This once again demonstrates the effect of cation size beyond the charge compensating function on the nature of the observed anions.

By taking the cation radii into account, it becomes evident that rather large cationic moieties are necessary to stabilize isolated rings of group 15 elements in solid state compounds. Smaller cations lead to extended structures as their size does not suffice to isolate discrete anions. Therefore, rings are only observed in compounds of cations with radii above 0.133 nm for phosphorus and above 0.140 nm for the heavier homologue arsenic. In contrast, group 14 rings are observed up to an averaged cation radius of 0.127 nm.

3.3 Chains of Group 15 Elements in Compounds with $6.11 \leq N_E \leq 6.8$

While the number of differently shaped clusters and rings of group 15 elements is quite limited, compounds with N_E values between 6.11 and 6.8 e/atom display an impressive variety of dissimilar discrete chains. In Table 8, chain-containing solid state structures of group 15 elements are listed.

The charge assignment is straightforward for P_3^{5-} , E_4^{6-} ($E = P, As$), Sb_6^{8-} , and As_8^{10-} by applying the valence bond concept (Fig. 9a). The bonding situation of the electron-deficient chains shown in Fig. 9b is not as trivial. In these cases, on one hand, multiple element–element bonding is discussed, and on the other hand, the possibility of partial protonation cannot be excluded completely, especially for compounds of the sometimes hydrogen-contaminated metal barium.

Table 8 Homoatomic chains of group 15 elements in solid state structures

Chain	Compound	Add. anion	N_E	$r(M^{I/II})_{av}$	Electron precise ^a	References
P_3^{4-}	K_4P_3	—	6.33	0.133	—	[114]
P_3^{5-}	KBa_4P_5	P_2^{4-}	6.8	0.141	+	[115]
P_4^{6-}	Sr_3P_4	—	6.5	0.127	+	[116]
	Ba_3P_4	—	6.5	0.143	+	[116]
P_9^{10-}	Ba_5P_9	—	6.11	0.143	—	[117]
As_4^{5-}	K_5As_4	—	6.25	0.133	—	[118]
As_4^{6-}	Ca_2As_3	As_8^{10-}	6.33	0.106	+	[119]
	Sr_3As_4	—	6.5	0.127	+	[120]
As_8^{10-}	Ca_2As_3	As_4^{6-}	6.33	0.106	+	[119]
Sb_4^{5-}	K_5Sb_4	—	6.25	0.133	—	[121]
	Rb_5Sb_4	—	6.25	0.148	—	[118]
Sb_6^{8-}	Ba_2Sb_3	—	6.33	0.143	+	[122]
	Sr_2Sb_3	—	6.33	0.127	+	[122]
Bi_4^{5-}	K_5Bi_4	—	6.25	0.133	—	[118]
	Rb_5Bi_4	—	6.25	0.148	—	[118]
	Cs_5Bi_4	—	6.25	0.167	—	[118]

^aElectron count according to the (8-N) rule and the Zintl–Klemm concept

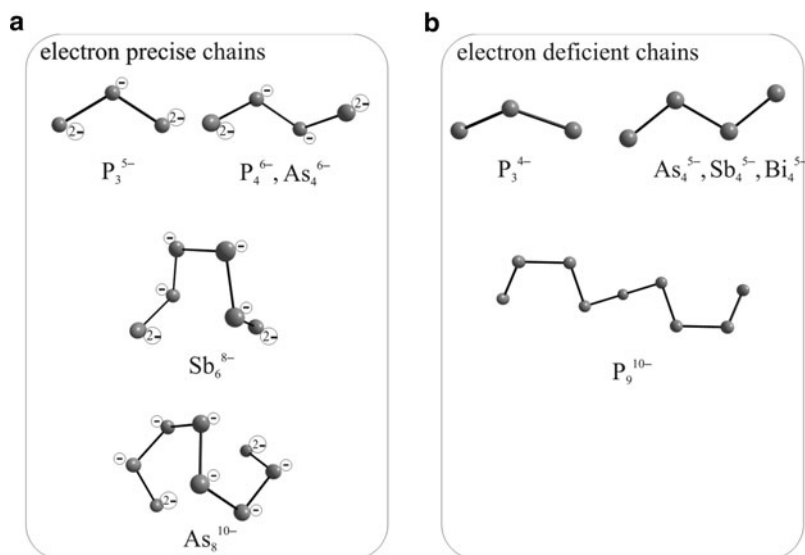


Fig. 9 (a) Electron precise chains of group 15 elements in solid state structures with formal charges assigned by valence count; (b) electron-deficient chains of group 15 elements; all chains are represented in perspective view to convey the helical assemblies

For three- and four-atom chains, electron precise and electron-deficient moieties are known. Three-atom chains are only observed in phosphorus-containing materials. The existence of an electron precise P_3^{5-} chain is reported in the mixed alkali/alkaline earth metal material KBa_4P_5 . The structure exhibits a 50/50 anionic occupational disorder in a single cavity between the cations, and as an additional anion in this cavity, P_2^{4-} dumbbells are described [115]. The second *catena*-triphosphide is present in K_4P_3 , where the three-atom chain is assigned a fourfold negative charge, which implicates that the anion is a radical. The expected paramagnetism was proven. The FIR P–P valence vibrations are shifted 30–40 cm^{-1} toward higher wave numbers compared to other P–P valence vibrations. This is in agreement with the increased bond order [114].

Electron precise angulated four-atom chains are found in the isotypic phosphorus and arsenic alkaline earth metal compounds Sr_3P_4 , Ba_3P_4 , and Sr_3As_4 . $M_3^{II}E_4$ was shown to be strongly related to the α -ThSi₂ structure type in terms of the formulation $M_3^{II}E_4\Box_2$ (\Box represents voids in the anionic partial structure of α -ThSi₂) [116]. Additionally, As_4^{6-} chains are observed in Ca_2As_3 next to As_8^{10-} chains. For the heavier group 15 elements As, Sb, and Bi, a one-electron oxidized variant of the four-atom chain is known. As the chains are flat, a description by single bonds seems implausible. The two possibilities that were discussed are the delocalization of one electron over the isolated anions or over the whole structure. To elucidate the electronic structure, magnetic measurements were carried out, which resulted in the detection of temperature-independent *Pauli*-like paramagnetism. This puts the compounds in the rare class of *metallic salts* [118].

The longest chain of group 15 elements is observed for phosphorus in the compound Ba_5P_9 . For exclusively single-bonded atoms, one would expect a charge of -11 ; so the P_9^{10-} chain is one electron short for a description according to the 8-N rule. The authors discuss two possibilities to explain this feature. On one hand, multiple bonding is possible, but no significant shortening of one P–P bond is observed, and the helical structure of the anion also is contrary to this description. On the other hand, protonation of one phosphorus atom in an electronically balanced P_9^{11-} might be possible and could not be completely excluded [117]. The second description would yield a N_E value of 6.22 e/atom which would nicely fit and narrow the N_E region for chains ($6.22 \leq N_E \leq 6.8$ instead of $6.11 \leq N_E \leq 6.8$).

As is the case for group 14 chains, the N_E values where chain formation is observed span a quite large range. A first comparison between group 14 and group 15 chains concerning the cation radii clearly shows that large cation radii above 0.106 nm are needed to stabilize group 15 element chains. In contrast, group 14 element chains are observed below an averaged cation radius of 0.106 nm.

3.4 A Branched P_8^{10-} Anion at $N_E = 6.25$

Within the N_E region of isolated chain fragments, an additional phosphide anion was observed by Hadenfeldt and Bartels [123]. In Ca_5P_8 , the combination with the small calcium cations ($r(\text{Ca}^{2+}) = 0.106$ nm) results in a polyphosphide that contains fourfold-bound phosphorus atoms beside single-bonded atoms. The centrosymmetric anion P_8^{10-} possesses 50 valence electrons, and it is shaped like ethane in the staggered conformation. This is the first example of a polyphosphide which contains formally positively charged phosphorus atoms beside formally twofold negatively charged (Fig. 10). P_8^{10-} is isoelectronic to the hexathiophosphate anion $\text{P}_2\text{S}_6^{4-}$ and isovalence electronic to staggered $\text{Si}_2\text{Te}_6^{6-}$ as well as staggered or eclipsed $\text{Ga}_2\text{X}_6^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) anions [124].

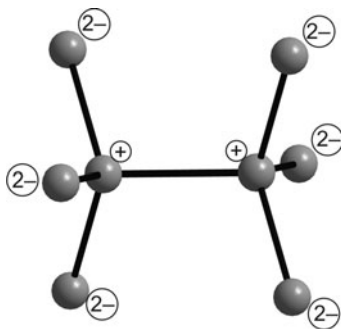


Fig. 10 P_8^{10-} anion in Ca_5P_8 (with assigned formal charges) features an ethane-like staggered conformation

3.5 Summarized: Homoatomic Polyanions of Group 15 Elements

The model of the averaged radii of cations in relation to the degree of reduction is applied, which results in areas of stability for the differently natured anions of group 15, similar to the observations for the group 14 element anions.

Homoatomic group 15 clusters are observed at $N_E = 5.27$ (E_{11}^{3-}) and 5.43 (E_7^{3-}). The larger E_{11}^{3-} clusters tend to be stabilized by larger cations; only for the smaller phosphorus cage E_7^{3-} a crystal structure of a sodium-containing compound is reported, which again is in accordance with simple packing considerations as well as the HSAB principle. Other E_{11} cage compounds ($E = P, As$) are only stabilized from a cation radius of 0.133 nm (potassium) upward. No Sb_{11}^{3-} cluster has been reported in neat solid state compounds. In contrast to this, smaller nortricyclane-like E_7^{3-} clusters are observed for cation radii between 0.068 nm (Li) and 0.167 nm (Cs).

At a N_E value of 5.67 e/atom, six-membered rings E_6^{4-} are present in crystal structures for cation radii between 0.133 nm (K) and 0.167 nm (Cs). Further reduced 1:1 compounds of phosphorus and arsenic for alkali metals yield three- and five-membered rings for large cations. For larger N_E values from 6.11 e/atom (respectively 6.22 e/atom, see Sect. 3.3) on, the field of chain fragments affiliates, followed by phosphorus assemblies containing nine or ten atoms which are present around 6.25 e/atom. For larger cations and heavier group 15 elements, electron-deficient E_4^{5-} chains are observed in binary compounds. Further reduction yields for phosphorus the electron-deficient P_4^{3-} anion, and for arsenic and antimony

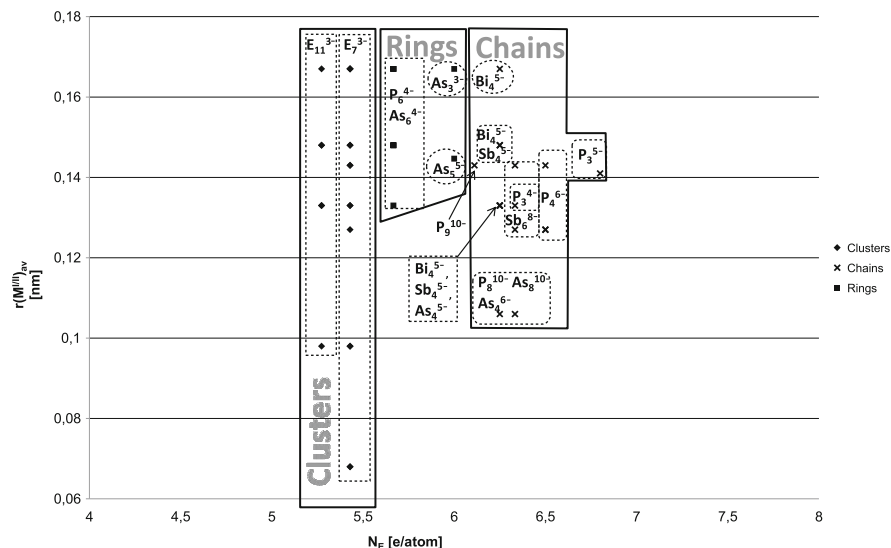


Fig. 11 Homoatomic polyanions of group 15 elements in neat solids

larger electron precise chain fragments of four, six, or eight atoms. At $N_E = 6.5$ e/atom, electron precise E_4^{6-} chains for phosphorus and arsenic are observed. After a large gap in N_E value, KBa_4P_5 is reported, which includes occupational disordered P_2^{4-} dumbbells and P_3^{5-} chains on the same crystallographic site.

4 Combining the Jigsaw Puzzle: Homoatomic Polyanions of Group 14 and Group 15 Elements in Solid State Compounds

We introduced $(N_E; r(\text{M}^{\text{III}})_{\text{av}})$ pairs to organize known solid state compounds which include homoatomic polyanions of group 14 and group 15 elements. The schemata given in Figs. 5 and 11 show regions that designate cluster, ring, and chain formation. Of course, these structures always compete with extended isoelectronic networks. Combining now both diagrams of group 14 and group 15 persuasively shows how homoatomic polyanions of the one group complement and accompany homoatomic polyanions of the other group. Clusters of group 15 elements follow the cluster compounds of group 14, as one would expect due to the 8-N rule. In contrast to that, rings and chains are present for both groups of the periodic table at similar N_E values. This gives a narrow N_E value for rings between 5.6 and 6.2 e/atom for elements of both groups. Subsequently, the formation of chains is observed up to high degrees of reduction of 7.5 e/atom, if one counts

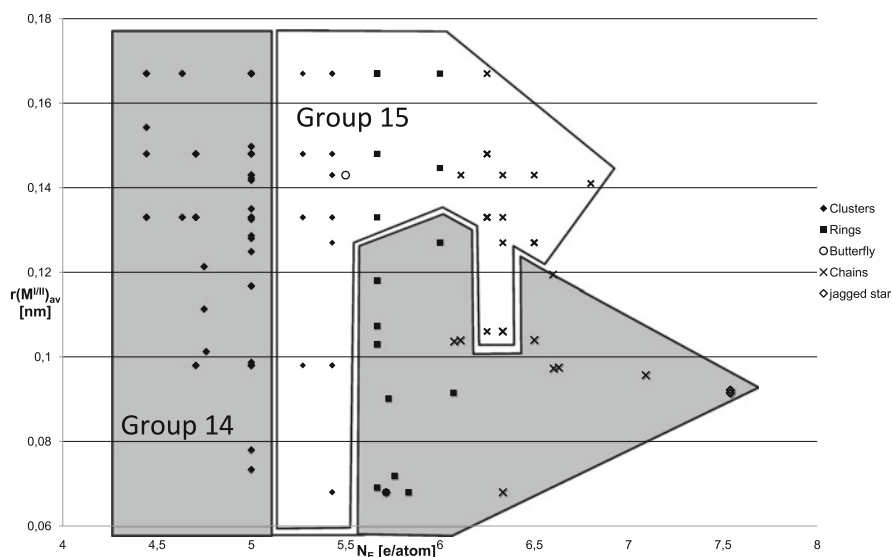


Fig. 12 Group 14 and group 15 compounds of alkali and alkaline earth metals which contain isolated homoatomic polyanions harmonize like parts of a jigsaw puzzle

branched chains as well. The majority of chains are present at N_E values between 6.2 and 6.7 e/atom. In contrast to this similarity, group 14 and group 15 ring- and chain-containing compounds differ significantly in the size of the involved cation radii. This is a remarkable characteristic of the applied structure mapping procedure. With respect to the known polyanionic compounds, no overlap is observable in $(N_E; r(M^{I/II})_{av})$ regions: Group 14 rings and chains crystallize together with small cations, whereas group 15 chains and rings seem to be rather stabilized by larger cations. Both the polyanionic regions of group 14 and group 15 can be seen as part of a jigsaw puzzle, which fits remarkably well and demonstrates the similarities and the differences of neighbors in the periodic table (Fig. 12).

5 Group 14 and Group 15 Polyanions in Solution

The presence of isolated anionic species coordinated by electropositive metal cations suggests the possibility to transfer both congruently in solutions using an appropriate solvent. This transfer is the ultimate test as to whether a polyanion perceived in a solid is really a separate and viable chemical entity, and of course the prerequisite for chemical transformations. The overview on binary and multinary polyanionic compounds given in the Chaps. 1–4 thus has to be complemented by an overview of crystalline solids containing solvent molecules and alkali metal ligands which were obtained from solutions, and which give a good indication of the species available for further chemistry.

As the first experiments on polyanionic compounds used liquid ammonia as the reaction medium, using this solvent suggests itself. The application of the ammonia-related solvent ethylenediamine provides the possibility to work at moderate temperatures. Up to now, a quite impressing number of solvate structures has been reported, which contain homoatomic polyanions and demonstrate the stability of these discrete element building blocks outside of a dense cation–anion network. Besides stable polyanions in solution, it has to be noted that due to their high degree of reduction, most higher charged anions are very sensitive toward oxidation. This oxidation may be accompanied by a rearrangement of the polyanions, and therefore some polyanions from the solid state are not observed in solution. In contrast, new polyanions that are not known from solid state compounds may be crystallized from solution and characterized by X-ray diffraction studies.

5.1 Group 14 Polyanions in Solution

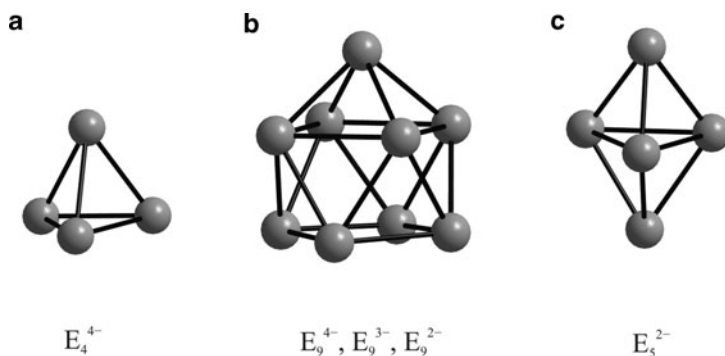
In the past decades, homoatomic polyanions in solid state compounds of group 14 elements have been a powerful starting material toward different kinds of chemical transformations. Recent developments, especially for nine-atom clusters, have been discussed elsewhere [5, 125, 126] and are not within the scope of this review. Here, we concentrate on “neat solvates”, which means that in addition to cation and anion

Table 9 Reported neat solvate structures of polyanions of group 14 elements, which are existent in solid state as well as in solution

Anion	Compound	N_E	References
Si_9^{4-}	$\text{Rb}_4\text{Si}_9 \cdot 4.75\text{NH}_3$	4.44	[127]
	$\text{Rb}_4\text{Si}_9 \cdot 5\text{NH}_3$	4.44	[128]
Ge_9^{4-}	$\text{K}_4\text{Ge}_9 \cdot 9\text{NH}_3$	4.44	[129]
	$\text{Rb}_4\text{Ge}_9 \cdot 5\text{NH}_3$	4.44	[129]
	$\text{Rb}_4\text{Ge}_9 \cdot \text{en}^a$	4.44	[130]
	$\text{Cs}_4\text{Ge}_9 \cdot \text{en}$	4.44	[131]
Sn_9^{4-}	$\text{Na}_4\text{Sn}_9 \cdot 7\text{en}$	4.44	[132, 133]
	$[\text{Li}(\text{NH}_3)_4]_4\text{Sn}_9 \cdot \text{NH}_3$	4.44	[134]
Pb_9^{4-}	$[\text{Li}(\text{NH}_3)_4]_4\text{Pb}_9 \cdot \text{NH}_3$	4.44	[134]
Sn_4^{4-}	$\text{Rb}_4\text{Sn}_4 \cdot 2\text{NH}_3$	5	[135]
	$\text{Cs}_4\text{Sn}_4 \cdot 2\text{NH}_3$	5	[135]
Pb_4^{4-}	$\text{Rb}_4\text{Pb}_4 \cdot 2\text{NH}_3$	5	[135]

Here, only nine-atom cages without sequestering agents like crown ethers or cryptands are listed; for an exhaustive overview on E_9 compounds, see [5, 125, 126]

^aThis compound was obtained by exchange reaction of a solution of “ $\text{NaGe}_{2.25}$ ” (precursor) in ethylenediamine with solid RbI at 363 K

**Fig. 13** Homoatomic polyanions of group 14 elements, which are present in solvate structures; (a) tetrahedral E_4^{4-} ($\text{E} = \text{Sn}, \text{Pb}$); (b) nine-atom cages E_9^{n-} ($n = 2-4$; $\text{E} = \text{Si-Pb}$); (c) trigonal bipyramidal E_5^{2-} ($\text{E} = \text{Si-Pb}$)

from the polyanionic salts, exclusively solvate molecules participate in the crystal structures. Table 9 contains polyanions of group 14 elements, which are present in solvate structures and therefore presumably are stable not only in the solid state but also in the solution.

Having a closer look at the reported solvate structures of homoatomic polyanions of group 14 elements, it becomes evident that only clusters and no rings or chains are stable in solid state as well as in solution (Fig. 13). Higher reduced polyanions with $N_E > 5$, equivalent with a charge higher than -1 per atom, are not reported in solution so far. The nine-atom species is quite well established in solutions of ammonia and ethylenediamine. Their interesting reactivity is intensely studied and is discussed elsewhere [5, 125, 126]. The less-understood cluster

species in solution is represented by the four-atom tetrahedral anions, which are only present in solutions of ammonia for the elements tin and lead. Recently, it was proposed that the four-atom species are the origin of the trigonal bipyramidal five-atom clusters [128]. This cluster species E_5^{2-} ($E = \text{Si}$ [128, 136]; Ge [137, 138]; Sn [139, 140]; Pb [140, 141]) is only known in solvate structures in combination with large alkali metal cryptand complexes in compounds following the compositions $[M^I@crypt]_2E_5$ ($E = \text{Sn}, \text{Pb}$) and $[M^I@crypt]_2E_5 \cdot 4\text{NH}_3$ ($E = \text{Si}, \text{Ge}$). Non-atetrelide cages are known in different oxidation states (E_9^{2-} , E_9^{3-} , E_9^{4-}), where the less-charged cages E_9^{2-} and E_9^{3-} tend to crystallize together with sequestering agents like for example 18-crown-6 or [2.2.2]-cryptand. In all compounds, the number of atoms remains the same, independently from charge, and merely the shapes of the clusters change. Therefore, the nine-atom species represents the most stable cluster species in polyanionic salt solutions, which can compensate oxidation and reduction processes without changing the cluster size. This is also corroborated by ^{119}Sn solution NMR studies, where the signal of the nine-atom clusters at $-1,224$ ppm increases after several days [142, 143]. In contrast, the four-atom cages compensate oxidation processes by rearrangement and enlargement of the cluster.

5.2 Group 15 Polyanions in Solution

In solvate structures of polypentelides, some polyanions are observed which are also present in solid state structures. These polyanions are in most instances limited to the 7- and 11-atom cluster compounds (Table 10). Using ion exchange resins, alkali metal cations can be replaced by quaternary ammonium or phosphonium cations. The shape of the clusters in all compounds is very similar to the ones found in the solid state materials. Only one homoatomic ring which is also known in solid state materials has been found up to now, and it is present in the compound $[\text{Rb}(18\text{-crown-6})]_2\text{Rb}_2\text{As}_6 \cdot 6\text{NH}_3$. In contrast to the solid state compound Rb_4As_6 , where the rings are planar due to space group symmetry, in the solvate structure the rings are slightly distorted. This distortion agrees well with quantum chemical calculations which confirmed the absence of aromaticity in these rings [112].

In addition to the recrystallization of polyanionic salts from solution, the dissolution and oxidation of these compounds provide the possibility of generating new polyanions, which consequently are only accessible by crystallization from solution. The hitherto known compounds that contain new anionic species are listed in Table 11. The formation of new ring anions is observed. Six-membered ring containing A_4P_6 materials dissolve incongruently in liquid ammonia under the formation of heptaphosphide cages and lone-pair aromatic P_4^{2-} rings [112, 145, 169]. Other rings of group 15 elements crystallizing from solution are a Sb_5^{5-} ring in envelope conformation in $[\text{Li}(\text{NH}_3)_4]_3[\text{Li}_2(\text{NH}_3)_2\text{Sb}_5] \cdot 2\text{NH}_3$ and a S_8 -like Sb_8^{8-} anion in $[\text{K}_{17}(\text{Sb}_8)_2(\text{NH}_2)] \cdot 17.5\text{NH}_3$. Additionally, cyclic As_4^{2-} and Sb_4^{2-} anions are also reported (Fig. 14).

Table 10 Polyanions of group 15 in solvate structures, which are also known in solid state compounds

Anion	Compound	N_E	References
P_7^{3-}	$Cs_3P_7 \cdot 3NH_3$	5.43	[144]
	$Rb_3P_7 \cdot 7NH_3$	5.43	[145]
	$Ba_3P_{14} \cdot 18NH_3$	5.43	[146]
	$[NEt_3Me][Cs_2P_7] \cdot NH_3$	5.43	[147]
	$[NEt_4]Cs_2P_7 \cdot 4NH_3$	5.43	[147]
	$[NEtMe_3]Cs_2P_7 \cdot 2NH_3$	5.43	[148]
	$[NMe_4]_2RbP_7 \cdot NH_3$	5.43	[149]
	$[Rb(18-crown-6)]_3P_7 \cdot 6NH_3$	5.43	[145]
	$[K(18-crown-6)]_3K_3(P_7)_2 \cdot 10NH_3$	5.43	[145]
	$Li_3P_7 \cdot 3TMEDA$	5.43	[150]
P_{11}^{3-}	$Cs_3P_{11} \cdot 3NH_3$	5.27	[151]
	$BaCsP_{11} \cdot 11NH_3$	5.27	[152]
	$[NEt_3Me]_2CsP_{11} \cdot 5NH_3$	5.27	[153]
	$[NEtMe_3]_3P_{11}$	5.27	[154]
	$[NEt_4]Cs_2P_{11}$	5.27	[149]
	$[K(18-crown-6)]_3P_{11} \cdot 2en$	5.27	[155]
As_6^{4-}	$[Rb(18-crown-6)]_2Rb_2As_6 \cdot 6NH_3$	5.67	[112]
As_7^{3-}	$[Li(NH_3)_4]_3As_7 \cdot NH_3$	5.43	[156]
	$Cs_3As_7 \cdot 6NH_3$	5.43	[156]
	$Cs_3As_7 \cdot NH_3$	5.43	[157]
	$[Li(TMEDA)]_3As_7 \cdot OEt_2$	5.43	[158]
	$[Li(TMEDA)]_3As_7 \cdot 1.5\ tol$	5.43	[159]
	$[Li(DME)]_3As_7 \cdot OEt_2$	5.43	[160]
	$[NMe_4]_2RbAs_7 \cdot NH_3$	5.43	[161]
	$[Rb(18-crown-6)]_3As_7 \cdot 8NH_3$	5.43	[156]
	$[P(Ph_3)_4]_2CsAs_7 \cdot 5NH_3$	5.43	[156]
	$[K([2.2.2]-crypt)]_{1.5}K_{1.5}As_7$	5.43	[162]
As_{11}^{3-}	$[Cs(18-crown-6)]_2CsAs_{11} \cdot 8NH_3$	5.27	[163]
	$[K([2.2.2]-crypt)]_3As_{11}$	5.27	[164]
	$[Na([2.2.2]-crypt)]_3Sb_7$	5.43	[165]
Sb_7^{3-}	$Na_3Sb_7 \cdot 3en$	5.43	[132]
	$Li_3Sb_7 \cdot 3TMEDA \cdot tol$	5.43	[166]
	$Na_3Sb_7 \cdot 3TMEDA \cdot 3thf$	5.43	[159]
	$Li_3Sb_7 \cdot 6HNMe_2$	5.43	[166]
	$[K([2.2.2]-crypt)]_3Sb_7 \cdot 2en$	5.43	[167]
	$Na_3Sb_7 \cdot 3PMDETA \cdot tol$	5.43	[168]

TMEDA tetramethylethylenediamine, *PMDETA* pentamethyldiethylenediamine

Contrary to solid state compounds, where E_{11}^{3-} anions are only known for phosphorus and arsenic, in solution Sb_{11}^{3-} clusters are accessible, which show similar structural features as the lighter homologue As_{11}^{3-} [163]. Using oxidizing agents, P_7^{3-} and As_7^{3-} clusters can be connected by single bonds to form dimeric P_{14}^{4-} and As_{14}^{4-} anions. The same is possible for undecapentelides, and solvate structures of As_{22}^{4-} and P_{22}^{4-} have been reported (Fig. 15).

Protonation of polyanions of group 14 and group 15 elements generally means an oxidation of the latter, due to the higher electronegativity of hydrogen compared to the heavier main group elements. For phosphorus and arsenic, the electronegativities are very similar to the value for hydrogen; therefore, one can expect stable

Table 11 Polyanions that are (up to now) not known in solid state compounds and therefore are only accessible from solution

Anion	Compound	N_E	References
P_4^{2-}	$Cs_2P_4 \cdot 2NH_3$	5.5	[145, 169, 170]
	$(K@18\text{-Krone-6})_2P_4 \cdot 8.5NH_3$	5.5	[145, 169]
P_{14}^{4-}	$[Li(NH_3)_4]_4P_{14} \cdot NH_3$	5.29	[171]
P_{22}^{4-}	$(NEtMe_3)_4P_{22} \cdot 2NH_3$	5.18	[172]
As_4^{2-}	$[Li(NH_3)_4]_2As_4$	5.5	[173]
	$[Na(NH_3)_5]_2As_4 \cdot 3NH_3$	5.5	[173]
	$[Cs_{0.35}Rb_{0.65}(2,2,2\text{-crypt})]_2As_4 \cdot 2NH_3$	5.5	[173]
As_{14}^{4-}	$[Rb(18\text{-crown-6})]_4As_{14} \cdot 6NH_3$	5.29	[171]
As_{22}^{4-}	$[Rb([2.2.2]\text{-crypt})]_4As_{22} \cdot 4DMF$	5.18	[174]
Sb_4^{2-}	$[K([2.2.2]\text{-crypt})]_2Sb_4$	5.5	[167]
Sb_5^{5-}	$[Li(NH_3)_4]_3[Li_2(NH_3)_2Sb_5] \cdot 2NH_3$	6	[175]
Sb_8^{8-}	$[K_{17}(Sb_8)_2(NH_2)] \cdot 17.5NH_3$	6	[176]
Sb_{11}^{3-}	$[K(18\text{-crown-6})(NH_3)_2]_3Sb_{11} \cdot 5.5NH_3$	5.27	[163]
	$[Na([2.2.2]\text{-crypt})]_3Sb_{11}$	5.27	[177]

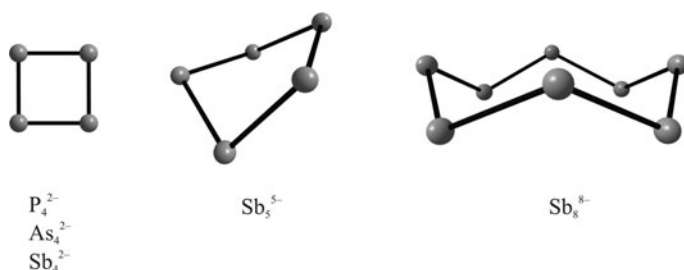


Fig. 14 Group 15 rings crystallized from ammonia or ethylenediamine solutions

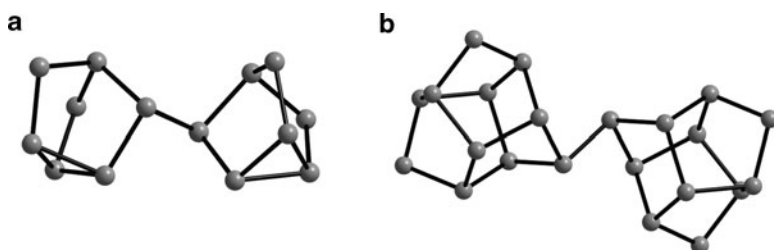
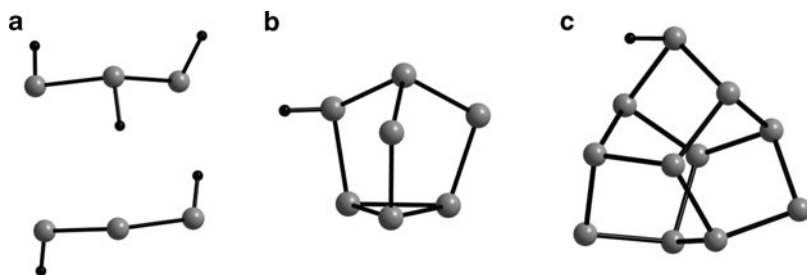


Fig. 15 Connected clusters for $E = P, As$: (a) E_{14}^{4-} , (b) E_{22}^{4-}

hydrogen polyphosphides and arsenides. The existence of hydrogen polypentelides in ammonia or ethylenediamine solution was proven and extensively studied by Baudler et al. using ^{31}P NMR techniques [178, 179]. Some of the predicted polyanions in solution have been crystallized and are summarized in Table 12 (Fig. 16).

Table 12 Hydrogenpentelides crystallized from solution

Anion	Compound	N_E	References
$P_3H_2^{3-}$	$K_3(P_3H_2) \cdot 2.3NH_3$	6	[180]
	$Rb_3(P_3H_2) \cdot NH_3$	6	[180]
$P_3H_3^{2-}$	$[Na(NH_3)_5][Na(NH_3)_3(P_3H_3)]$	5.67	[181]
	$[Rb(18-crown-6)]_2(P_3H_3) \cdot 7.5NH_3$	5.67	[180]
	$[Cs(18-crown-6)]_2(P_3H_3) \cdot 7NH_3$	5.67	[180]
	$[K([2.2.2]-crypt)]_3K(HP_7)_2 \cdot en$	5.28	[182]
HP_7^{2-}	$[K(18-crown-6)]_2HP_7$	5.28	[182]
	$[K(db18-crown-6)]_2HP_7 \cdot tol$	5.28	[182]
	$(PPh_4)_2HP_7 \cdot 3NH_3$	5.28	[183]
	$(PPh_4)H_2P_7$	5.14	[184]
HP_{11}^{2-}	$[K(2,2,2-crypt)]_2HP_{11}$	5.18	[185]
	$(NBnMe_3)_2HP_{11}$	5.18	[154]
	$(PBnPh_3)_2HP_{11}$	5.18	[154]
	$[Sr(NH_3)_8]HP_{11} \cdot NH_3$	5.18	[186]

**Fig. 16** Hydrogenpolyphosphides crystallized from ammonia solutions; (a) $P_3H_3^{2-}$, $P_3H_2^{3-}$; (b) HP_7^{2-} ; (c) HP_{11}^{2-}

In the case of group 14 polyanions, the bond between element and hydrogen is very polarized; therefore, hydrogen features more hydride character. In protic solvents, which of course ammonia and ethylenediamine are to a certain extent, these hydrides are protonated under the formation of elemental hydrogen, which is removed from equilibrium by degassing. This means an oxidation of the cages to the stage of the most stable element modification. The first step, anyway, in this process is amide formation by protonation of the anions. This amide formation is known to be temperature dependent [187] and very sensitive toward catalyzing traces of protons [188, 189]. Therefore, any source of protons has to be strictly avoided when working with homoatomic polyanions of group 14 in solution.

5.3 Summarized: Solvate Compounds of Group 14 and Group 15

If one compares the N_E values of solvate compounds that contain homoatomic polyanions, it becomes evident that there seems to be a border that has not been

transcended so far. Group 14 compounds that have been crystallized from solution show a maximum N_E value of 5, corresponding to one negative charge per atom and threefold bound atoms. Group 15 element anions show a corresponding behavior by covering N_E values below 6, which also means a maximum value of one negative charge per group 15 atom and twofold bound atoms. Protonation of polyphosphides yields hydrogenpolyphosphide compounds, where the N_E value is further reduced compared to the homoatomic anions. For group 14 compounds, no protonated species have been reported so far. Here, different charges in E_9 clusters are compensated without any change in composition, whereas the four-atom tetrahedral clusters lead to larger cluster sizes when oxidized. When working with bare group 14 polyanions in solution, smallest traces of protons have to be avoided due to protonation being equivalent with oxidation of the anions. Smooth oxidation using, e.g., $SbPh_3$ or PPh_3 as catalysts provides the possibility of yielding new polyanionic materials.

6 Conclusions and Outlook

Main group elements in negative oxidation states are very interesting materials, which show all different kinds of anionic arrangements. In this review, we focused on discrete homoatomic polyanions, which have been ordered with respect to the degree of reduction and the averaged cation radii. This arrangement displays certain regions of stability of differently natured polyanions, which of course always compete with isoelectronic extended anionic subunits. It was shown that how regions of group 14 and group 15 polyanions fit like parts of a jigsaw puzzle in a combined diagram.

Polyanionic compounds in solution are a very fascinating and versatile class of compounds, the behavior of which is not understood completely. It is very challenging to tune the degree of oxidation for obtaining bigger discrete polyanionic units. On the other side, the limit for stable highly charged element building blocks in solution needs to be pushed further toward higher reduced species. It will be interesting to see whether the border defined by a maximum of one negative charge per atom can be crossed in the future for dissolved polyanions.

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