**Review**

**Polyhedral nine-atom clusters of tetrel elements and intermetalloid derivatives**

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Homoatomic polyanions have the basic capability for a bottom-up synthesis of nanostructured materials. Therefore, the chemistry and the structures of polyhedral nine-atom clusters of tetrel elements \([E_9]^{4-}\) is highlighted. The nine-atom Zintl ions are available in good quantities for \(E = \text{Si–Pb}\) as binary alkali metal (A) phases of the composition \(A_4E_9\) or \(A_{12}E_{17}\). Dissolution or extraction of the neat solids with aprotic solvents and crystallization with alkali metal-sequestering molecules or crown ethers leads to a large variety of structures containing homoatomic clusters with up to 45 E atoms. Cluster growth occurs via oxidative coupling reactions. The clusters can further act as a donor ligand in transition metal complexes, which is a first step to the formation of bimetallic clusters. The structures and some nuclear magnetic resonance spectroscopic properties of these so-called intermetalloid clusters are reviewed, with special emphasis on tetrel clusters that are endohedrally filled with transition metal atoms.

**Keywords:** Zintl ions; intermetalloid cluster; polyhedron; wade rules; nano-materials; main group element

**1. Introduction**

In 1891, Joannis described the beginning of the fascinating field of the chemistry of polyanions of main group elements in *Comptes Rendues*: ‘Lorsque l’on met une baguette de plomb pur en excés, en presence du sodammonium, on constate que la liquour mordorée ne trade pas à venir bleue au contact du plomb, puis verde’ (Joannis 1891). This report debuted the first surveillance of the green polyanion—later determined as \([\text{Pb}_9]^{4-}\)—from the reaction of Na and Pb in liquid ammonia and opened the important field of deltahedral anions. These homoatomic clusters are not only fascinating because of the aesthetic simplicity of their polyhedral structures, but comprise an enormous synthetic potential. The investigation of the versatile chemical reactivity of the anions revealed their capability as precursors for the synthesis of nanostructured materials or large, intermetalloid clusters.

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One contribution of 13 to a Theme Issue ‘Metal clusters and nanoparticles’.
2. Homoatomic clusters of tetrel elements

(a) Brief review of homoatomic polyanions

Since Joannis, the successive research work of Kraus, Smyth and Zintl (Smyth 1917; Kraus 1924; Zintl & Harder 1931) established the existence of highly charged element particles. The imagination of tetrel element polyanions was finally verified by the crystal structure determination of a \([Sn_9]^{4−}\) ion in 1976 (Kummer & Diehl 1970) and ever since has developed into a fast growing research field (Corbett 1985; Fässler 2001).

The smallest deltahedral clusters \([E_4]^{4−}\) were first observed in alloys of alkali metals (A = Na, K, Rb, Cs) and tetrels (E = Si, Ge, Sn, Pb) in a 1 : 1 ratio, with NaPb being the first reported representative (Marsh & Shoemaker 1953). Applying a salt-like description (Zintl–Klemm–Busmann concept) to these AE phases (Zintl 1939; Klemm 1958), the valence electron of the alkali metal is formally transferred to an anionic substructure. According to the \((8 − N)\) rule, the tetrel elements form \(P_4\)-analogous tetrahedral clusters \([E_4]^{4−}\), which are retained in a liquid ammonia solution of RbPb as shown by Korber and co-workers, who recently obtained the ammoniate \(Rb_4Pb_4(NH_3)_2\) (Wiesler et al. 2009).

In order to promote the crystal growth of compounds containing polyanions, alkali metal ion-sequestering agents such as \([2.2.2]\)crypt \((= 4,7,13,16,21,24\)-hexaaza-1,10-diazabicyclo-[8.8.8]hexacosane) (Corbett & Edwards 1977) or alkali metal ion-complexing molecules such as \([18]\)crown-6 \((= 1,7,10,13,16\)-hexaoxacyclooctadecane) and its derivatives (Fässler & Hoffmann 1999) were introduced.

The crystal structures of the \(D_{3h}\)-symmetric \([Sn_5]^{2−}\) and \([Pb_5]^{2−}\) anions were elucidated as long ago as 1977 (Edwards & Corbett 1977) and \([Ge_5]^{2−}\) was discovered 20 years later (Campbell & Schrobilgen 1997). They were obtained from ethylenediamine solutions of A–E alloys with different ratios of A : E under the stoichiometric deficiency of \([2.2.2]\)crypt. For the synthesis of \([Si_5]^{2−}\), the binary compound \(Rb_{12}Si_{17}\) was extracted with liquid ammonia in the presence of \([2.2.2]\)crypt and subsequently treated with triphenylphosphine (Suchentrunk & Korber 2006). Intermetallic compounds of the general composition \(A_{12}E_{17}\) contain tetrahedral \([E_4]^{4−}\) and \([E_9]^{4−}\) polyanions in the ratio 2 : 1 (A = Na, K, Rb, Cs; E = Si, Ge, Sn) (von Schnering et al. 1997; Hoch et al. 2003).

The largest unfilled representative of a homoatomic tetrel element cluster is the 10-vertices closo cluster \([Pb_{10}]^{2−}\), which was obtained after the oxidation of an ethylenediamine solution of \(K_4Pb_9\) with \(PPh_3Au(I)Cl\) (Spiekermann et al. 2006).

Homoatomic, ligand-free tetrel clusters with six, seven, eight or more than 10 vertices have not been detected in solutions so far. Octahedral \([E_6]^{2−}\) clusters have been isolated only by an organometallic synthetic route as transition metal-stabilized species \([\{EM(CO)_5\}_6]^{2−}\) (E = Ge, Sn; M = Cr, Mo, W) consisting of an almost perfect \(E_6\) octahedron with each E atom coordinated to an \(M(CO)_5\) fragment, as shown for the first time for \(E = Sn\) and \(M = Cr\) (Schiemenz & Huttner 1993). However, the anion \([\{SnCr(CO)_5\}_6]^{2−}\) was produced when \(Na_2[Cr_2(CO)_{10}]\) was treated with \(SnCl_2\) in the presence of bipy (bipy = 2,2′-bipyridine) (Kircher et al. 1998) and not from Zintl ion solutions. From gas-phase experiments as well as from theoretical investigations, a particular
stability is expected for the stannaspherene \([\text{Sn}_{12}]^{2−}\) and the plumbaspherene \([\text{Pb}_{12}]^{2−}\), although these species have not been obtained in solid state up to now (Cui et al. 2006).

The structures of tetrahedral \([\text{E}_4]^4−\), trigonal bipyramidal \([\text{E}_5]^2−\) and bicapped quadratic antiprismatic \([\text{E}_{10}]^2−\) clusters strictly follow Wade’s rules corresponding to a 12 skeletal electron (ske) \(\text{nido}\), 12 ske \(\text{closo}\) and 22 ske \(\text{closo}\) cluster, respectively (Wade 1976). Each group 14 atom possesses four valence electrons, two of which remain as one ‘lone pair’ at each vertex equivalent to the covalent exo-BH bonds in boranes.

Nine-atom Zintl clusters of tetrel elements are most frequently examined and best described. They display a complex and exciting structural flexibility, which is described in detail in the following section.

\(\text{b) Nine-atom clusters}\)

Nine-atom clusters are prominent in the intermetallic compounds \(\text{A}_4\text{E}_9\) (\(\text{A} = \text{Na, K, Rb, Cs; E} = \text{Ge, Sn, Pb}\)), of which \(\text{Cs}_4\text{Ge}_9\) was the first one described in solid state by Sevov and co-workers in 1997 ( Quéneau & Sevov 1997). The crystals often show twinning problems and disordered and distorted \(\text{E}_9\) clusters (Ponou & Fässler 2007). Extraction of these intermetallic compounds with polar aprotic solvents such as ethylenediamine (en), liquid ammonia and dimethylformamide (dmf) leads to highly concentrated and intensively coloured solutions of the nine-atom clusters. However, all reported experiments for the isolation of nine-atom silicon clusters from solutions started from \(\text{A}_{12}\text{Si}_{17}\) (\(\text{A} = \text{K, Rb or K/Rb}\)) Zintl phases (Goicoechea & Sevov 2006b; Sevov & Goicoechea 2006).

The nine-atom deltahedral \(\text{closo}\) cluster \((n = 9)\) corresponds to a tricapped trigonal prism \(\text{I}\) with \(\text{D}_{3h}\) point group symmetry (figure 1) if \(2n + 2 = 20\) ske are available for the cluster skeleton bonding. Hence, clusters with a twofold negative charge \([\text{E}_9]^{2−}\) are appropriate to adopt a \(\text{closo}\) structure. Consequently, \([\text{E}_9]^4−\) is on a par with a \(\text{nido}\)-type cluster owing to \(2n + 4 = 22\) ske forming a \(\text{C}_{4v}\)-symmetric monocapped square anti-prism \(\text{IV}\) (figure 1). The shape of a 21 ske cluster \([\text{E}_9]^{3−}\) therefore should appear between these two boundary structures.

Distortions forming the boundary structures \(\text{I}\) and \(\text{IV}\) are also observed for 22 ske clusters \([\text{E}_9]^{12}\) in neat solids \(\text{A}_4\text{E}_9\) as well as in clusters crystallized from solution. Since the lowest unoccupied molecular orbital (LUMO) of the hypothetical ideal \(\text{D}_{3h}\)-symmetric \([\text{E}_9]^{2−}\) cluster has anti-bonding character along the trigonal prism heights, the addition of further electrons (formal reduction) leads to a prism elongation, and distorted \(\text{C}_{2v}\)-symmetric trigonal prisms with one (\(\text{III}\)), two (\(\text{II}\)) or three elongated heights result (figure 1). One strongly elongated height leads—after relaxation of all atomic positions—to structure \(\text{IV}\), while three equally elongated bonds preserve the \(\text{D}_{3h}\) symmetry of the cluster. The two examples \([\text{K}([18]\text{crown-6})]_3\text{K}[\text{Sn}_9]\) (Fässler & Hoffmann 1999a) and \([\text{K}([18]\text{crown-6})]_4[\text{Pb}_9]\) (Fässler & Hoffmann 1999b) show that, in spite of their unambiguously determined fourfold negative charge, \(\text{E}_9\) clusters can occur either with perfect \(\text{C}_{4v}\)-symmetric \(\text{nido}\) structures or with those closer to \(\text{D}_{3h}\) symmetry (figure 2).

The energy barrier for the intermolecular conversion between the \(\text{D}_{3h}\)-\(\text{closo}\) and the \(\text{C}_{4v}\)-\(\text{nido}\) structure is indeed very low (Rosdahl et al. 2005), and \(^{119}\text{Sn}\) and \(^{207}\text{Pb}\) nuclear magnetic resonance (NMR) experiments on \([\text{Sn}_9]^{4−}\) and \([\text{Pb}_9]^{1−}\) solutions show only a single resonance indicating a fast atom exchange on the
NMR time scale (Rudolph et al. 1978). The results of a large number of crystal structure determinations of $[E_9]^{4−}$-containing representatives (E = Si, Ge, Sn, Pb) obtained from liquid ammonia and ethylenediamine solutions reveal the large flexibility of the polyhedral cages (Fässler 2001). Careful examination of the atomic displacement parameters of the E atoms in many cases shows that the static structure usually obtained by this method does not allow a distinct assignment to one of the boundary structures (Risdahl et al. 2005). In particular, the cluster charge cannot be clearly assigned on the basis of the appearing structures.

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Structures of [E₉]³⁻ with a singly occupied LUMO of [E₉]²⁻ anions should integrate between the closo and the nido form, and adopt a C₂ᵥ-symmetric shape that derives from a tricapped trigonal prism with one or two elongated prism heights (figure 1; II and III). Indeed, all these [E₉]³⁻ units adopt the shape of a distorted tricapped trigonal prism tending towards C₂ᵥ symmetry, except for [Sn₉]³⁻, which surprisingly retains almost perfect D₃h symmetry with three elongated prism heights. Nine-atom clusters with a threefold negative charge [E₉]³⁻ were isolated from solution for all heavier group 14 elements (E = Si to Pb) exclusively as [A⁺([2.2.2]crypt)] salts (Fässler et al. 2000; Fässler 2001; Goicoechea & Sevov 2004; Yong et al. 2005). Bonding interactions between the anionic and the cationic units do not occur in these compounds. Cation–anion contacts stabilize higher charged clusters [E₉]⁴⁻ or support the formation of dimers. An [E₉]²⁻ cluster was unambiguously isolated and structurally characterized only in the case of K([18]crown-6)₂Si₉(py) (py = pyridine) for E = Si. This compound is obtained again by the extraction of K₁₂Si₁₇. The closo-[Si₉]²⁻ cluster noticeably deviates from an ideal D₃h-symmetric structure expected according to its 20 ske. The [Si₉]²⁻ cluster interacts with two K counterions via two deltahedral cluster faces, and the shape of the cluster is best described as a distorted tricapped trigonal prism with one elongated prism height (Goicoechea & Sevov 2005c).

Powdered samples of [K⁺([2.2.2]crypt)] salts of [E₉]³⁻ show anisotropic electron paramagnetic resonance (EPR) signals with increasing line widths from Ge to Pb. Magnetic measurements of [K([2.2.2]crypt)]₆E₉E₉(en)₁.₅(tol)₀.₅ (E = Sn, Pb; tol = tolyl) with one ordered and one disordered E₉ cluster per asymmetric unit reveal that only 50 per cent of the clusters are paramagnetic. In consequence, a threefold negative charge was assigned to the ordered clusters and a superposition of diamagnetic [E₉]²⁻ and [E₉]⁴⁻ species was assumed for the disordered (Fässler & Schütz 1999; Fässler et al. 2000).

3. Reactions of E₉ clusters

(a) Oxidative coupling reactions

The formation of stable radicals [E₉]³⁻ also offers the possibility of a cluster dimerization. To date, such oxidative coupling reactions have been reported solely for Ge₉ clusters (figure 3), which mostly contain isomer A (Sevov & Goicoechea 2006).

Two different isomers (A and B) were observed in K₆(Ge₉–Ge₉)(dmf)₁₂ (Nienhaus et al. 2006). Conformer A is the result of linking two nido-shaped Ge₉ clusters via an exo-bond at one atom of the open rectangular cluster face. The shape of the clusters deviates slightly from C₄ᵥ symmetry, and in general the diagonal of the open face that points towards the exo-bonded atom is significantly shorter than the second diagonal. The interconnecting exo-bond is collinear with the shorter diagonal of the open rectangular face of each cluster. In B, the connecting exo-bond between the Ge₉ clusters approximately points to both cluster centres. The shape of these clusters derives from a tricapped trigonal prism with two strongly elongated prism heights leading to two rectangular cluster faces according to II (two elongated heights). The connection occurs through the Ge atom that links the related rectangular faces.
Figure 3. (a,b) Two different dimeric [Ge$_9$–Ge$_9$]$^{6-}$ units with the next four coordinated alkali metal atoms (Nienhaus et al. 2006). (c) Polymeric $\frac{1}{\infty}$[[Ge$_9$]$^{2-}$] with coordinated alkali metal atoms (Downie et al. 2000).

In all cases several alkali cations coordinate with the atoms of [Ge$_9$–Ge$_9$]$^{6-}$. Consequently, the complete encapsulation of the alkali metal atoms by the sequestering agent seems to be the crucial factor for the stabilization of free cluster radicals in the crystals.

Further oxidation formally leads to [Ge$_9$]$^{2-}$ species, which in principle can be interconnected in two ways. (i) In analogy to the formation of dimers, a further linkage leads to a one-dimensional cluster polymer $\frac{1}{\infty}$[[Ge$_9$]$^{2-}$] (figure 3c) with two external two-electron–two-centre bonds at each cluster (Downie et al. 2000). The connection proceeds via two opposite vertex atoms of the open faces of the nido clusters. In the structure of [K([18]crown-6)]$_2$[1/∞[[Ge$_9$]$^{2-}$]](en), one K atom of the two [K([18]crown-6)] units caps a triangular cluster face, while the other one serves as spacer, causing a separation of the polymeric chains of more than 14 Å. (ii) An alternative connection between formal [Ge$_9$]$^{2-}$ clusters occurs in the linear trimeric anion [Ge$_9$=Ge$_9$=Ge$_9$]$^{6-}$ (Ugrinov & Sevov 2002; Yong et al. 2005a) and the linear tetrameric anion [Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]$^{8-}$ (Ugrinov & Sevov 2003; Yong et al. 2004). In these units (figure 4), the cluster contacts are in the range from 2.546 Å to 2.752 Å and thus exceed the length of typical Ge–Ge single bonds as found in Ge$_9$–Ge$_9$ dimers (mean 2.477 Å) or elemental germanium (2.445 Å). Further, the two almost parallel exo-bonds lead to a very unusual coordination of the corresponding Ge atoms with Ge–Ge–Ge bond angles of approximately 90°. Quantum chemical calculations demonstrate that the exo-bonds participate in a
Figure 4. Oligomeric structures of linked Ge₉ clusters including coordinated alkali metal atoms A in (a) [K([18]crown-6)]₆[Ge₉=Ge₉=Ge₉](en)(tol) (Yong et al. 2005a) and also in (b) [Rb([18]crown-6)]₈[Ge₉=Ge₉=Ge₉=Ge₉](en)₂ (Ugrinov & Sevov 2003).

delocalized electron system that comprises the whole anion (Yong et al. 2004). The individual clusters in [Ge₉=Ge₉=Ge₉]₆⁻ and [Ge₉=Ge₉=Ge₉=Ge₉]₈⁻ adopt the shape of tricapped trigonal prisms, and since they are interconnected collinearly to two of their three prism heights, the clusters are elongated along these heights towards a $C_{2v}$-symmetric polyhedron (see figure 1, II). It is worth mentioning that most of the dimeric, oligomeric and polymeric cluster compounds can also be obtained from solutions without the addition of any oxidation agent.

(b) Homoatomic E₉ clusters bonded to d-block metals

Structural units with less than nine tetrel element atoms that serve as ligands for d-block elements are reported rarely in the literature. As already pointed out, the anion $[[\text{SnCr(CO)}₅]₆]^{12−}$ contains the octahedral subunit $[\text{Sn₆}]^{12−}$ in which each tin atom coordinates to a Cr(CO)₅ fragment (figure 5a; Kircher et al. 1998). This example shows that the extended Wade’s rules for pure main group element clusters are obeyed when the four valence electrons of each Sn atom are considered as two ske and one electron ‘lone pair’. The ‘lone pair’ completes the 18-electron configuration of the transition metal. In consequence, the central unit corresponds to a 14-ske closo cluster ($6 \times 2 + 2$ including the two negative charges). The ‘lone pair’ points to the outside of the cluster and shows nicely that it can be treated as the external B–H bond in boranes in the skeletal electron pair formalism (Wade’s rules).

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An anionic Pb$_5$ unit has been stabilized in [Pb$_5${Mo(CO)$_3$}$_2$]$^{4-}$ synthesized from an ethylenediamine solution of [Pb$_9$]$^{4-}$ and (η$^6$-mesityl)Mo(CO)$_3$ (figure 5b). In this molecule, a planar Pb$_5$ ring binds to two {Mo(CO)$_3$} fragments in a η$^5$ fashion (Yong et al. 2005d). Density functional theory (DFT) calculations support that the anion is best described formally as a complex of an aromatic 2π electron system [Pb$_5$]$^{2-}$ and two [Mo(CO)$_3$]$^{1-}$ moieties. As mentioned in §2(a), a ‘naked’ [Pb$_5$]$^{2-}$ unit was obtained from ethylenediamine solutions of [Pb$_9$]$^{4-}$ as [K$^+$(2,2,2-crypt)] salt, and adopts—in contrast to the Pb$_5$ ring in [Pb$_5${Mo(CO)$_3$}$_2$]$^{1-}$—a close D$_{3h}$-symmetric trigonal bipyramidal structure (figure 1; Edwards & Corbett 1977).

Owing to their facile accessibility, soluble homoatomic [E$_9$]$^{1-}$ Zintl ions (E = Ge, Sn, Pb) offer an excellent possibility for heteroatomic cluster formation. The elements are fused at high temperatures, in most cases, with K in metal ampoules in the ratio of K:E = 4:9. The resulting K$_4$E$_9$ phases are soluble in liquid ammonia, and—more conveniently—in ethylenediamine or dmf, as introduced in 1970 (Kummer & Diehl 1970) and 2006 (Nienhaus et al. 2006),

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A simple and efficient one-pot synthesis for Sn₉ and Pb₉ clusters is the reduction of the corresponding elements with Na or K in liquid [18]crown-6 at 40°C (Fässler & Hoffmann 1999a), or by applying electrochemical methods (Pons et al. 1981; Eisenmann 1993).

The first representative of E₉ complexes in which the nido cluster coordinates with four atoms of its open face to a transition metal of group 6 [(η⁴-E₉)M(CO)₃]⁻ (E = Sn, Pb; M = Cr, Mo, W) was already presented in 1988 with E = Sn and M = Cr (Eichhorn & Haushalter 1988) and the whole series was completed in 2005 (Eichhorn & Haushalter 1990; Kesanli et al. 2001; Campbell et al. 2002; Yong et al. 2005c; figure 5c). The isomerization of the resulting closo clusters with η⁴ coordination leads to η⁵-E₉ complexes analogous to the above-mentioned [(η⁵-Pb₅){Mo(CO)₃}₂]⁻ unit (figure 5b). Recently, other complexes involving d-block elements have been isolated: [Sn₉-Ir(cod)]₃⁻ (cod = cyclooctadiene) (Wang et al. in press), [Ge₉-Cu(PiPr)₃]³⁻ (Scharfe & Fässler in press), [E₉–Zn(C₆H₅)]³⁻ (E = Si–Pb) (Sevov & Goicoechea 2006) and [Sn₉–Cd(SnBu₃)]³⁻ (Zhou et al. 2009a). All these compounds exclusively adopt an η⁴ coordination in the solid state (figure 5d–f).

According to the isolobal concept, M(CO)₃ fragments with M = Cr, Mo and W as well as Ir(cod)⁺, CuPR₃⁺ and MR⁺ (M = Zn, Cd and R = C₆H₅ and Sn(alkyl)₃) units act as zero electron building blocks. Therefore, and based on the Wade/Mingos rules, the cluster expansion by a transition metal fragment corresponds to the transformation of a nine-atom nido cluster to a 10-atom closo cluster with 2×9 = 18 + 4 = 22 skeletal electrons and 2×10 = 20 skeletal electrons, respectively, since the number of cluster vertices is increased by one but the number of delocalized skeleton electrons remains unchanged.

(c) Ligand-free heteroatomic cluster: intermetalloid

The first ligand-free complex of a Zintl ion with a d-block element was obtained as a polyanionic polymer chain {[HgGe₉]}₂⁻ (figure 6a; Nienhaus et al. 2002). Ever since, the formation of heterometallic ligand-free anions allows an approach of intermetallic phases from a bottom-up synthesis using E₉ Zintl clusters as building blocks. In {[HgGe₉]}₂⁻ Ge–Hg contacts covalently bridge the Ge₉ nido clusters. Each exo-bond of the [Ge₉]⁺⁻ nido cluster reduces the charge by one. With two exo-bonds, the clusters carry a charge of −2.

The anion [(η⁴-Ge₉)Cu(η¹-Ge₉)]⁷⁻ (figure 6b) is closely related to [(η⁴-Ge₉)Cu–P(Pr)₃]⁻ (figure 5c; Scharfe & Fässler in press). Both are synthesized from K₄Ge₉ and Pr₃PCu(I)Cl, and [(η⁴-Ge₉)Cu(η¹-Ge₉)]⁷⁻ represents a rare example where a homoatomic E₉ cluster acts as a two-electron σ-donor ligand similar to [{SnCr(CO)₅}₆]²⁻ (Schiemenz & Huttner 1993).

Similar reactions starting from the analogous gold compound Ph₃PAu(I)Cl lead to the related cluster [Ge₉Au₃Ge₉]⁵⁻ shown in figure 6c (Spiekermann et al. 2007b), in which three singly positively charged Au atoms bridge two Ge₉ clusters via triangular Ge faces. As a result, the Au atoms form a triangle that is almost coplanar with the two deltahedral faces of the interconnected [Ge₉]¹⁻ clusters. Rather short Au–Au contacts hint at aurophilic interactions (Schmidbaur 1999). The positive charge of the Au atoms was confirmed by DFT calculations.
A combination of the oxidative coupling reaction described in §3(a) and the complexation of the resulting polyanion reported in §3(b) leads to larger clusters reaching the nanometre scale. [Au₃Ge₄₅]⁹⁻ was found as a by-product of the reaction of ethylenediamine solutions of K₄Ge₉ and Ph₃PAu(I)Cl (figure 6d; Spiekermann et al. 2007a). By changing the reaction conditions, the yield of this fascinating large cluster can be raised. Within this anion, four deltahedral Ge₉ clusters are covalently connected by a unit of nine Ge atoms. The cluster displays a variety of bonding schemes reminiscent of the structural chemistry of boranes: multi-centre bonds arise in the deltahedral clusters, and covalent two-centre–two-electron bonds link them together. Long Ge–Ge contacts within a triangle of five-coordinated Ge atoms shown as dashed lines in figure 6d correspond to three-centre–two-electron bonds. Furthermore, five-membered Ge faces resemble

**Figure 6.** Zintl ions with ligand-free d-block metal atoms: (a) \(\{\infty[HgGe₉]\}^{2-}\) (Nienhaus et al. 2002); (b) \([\eta^1\cdot Ge₉]Cu(\eta^1\cdot Ge₉)\]^{2-}\) (Scharfe & Fässler in press); (c) \([Ge₉Au₃Ge₉]\]^{5-}\) (Spiekermann et al. 2007b); and (d) \([Au₃Ge₄₅]\]^{9-}\) (Spiekermann et al. 2007a).
Review. Clusters of tetrel elements

Figure 7. Representative Zintl ions with one endohedral metal atom: (a) \([\text{Cu@E}_9]^{3-}\) (Scharfe et al. 2008); (b) \([\text{Ni@Pb}_{10}]^{2-}\) (Esenturk et al. 2005); (c) \([\text{M@Pb}_{12}]^{2-}\) (Esenturk et al. 2006a); and (d) \([\text{Co@Ge}_{10}]^{3-}\) (Wang et al. 2009).

A structural motif found in three-dimensional solids, such as alkali metal and alkaline earth metal germanides with clathrate structures. Ge–Au contacts in \([\text{Au}_3\text{Ge}_{45}]^{9-}\) confine the cluster to a more or less spherical shape. Interestingly, \([\text{Au}_3\text{Ge}_{45}]^{9-}\) exhibits no Au–Au contacts, despite the presence of a largely negative cluster charge (Spiekermann et al. 2007a).

(d) Endohedrally filled clusters: intermetalloids

Backing up Schnöckel’s term ‘metalloid clusters’ (Schnepf & Schnöckel 2002), the expression ‘intermetalloid clusters’ was introduced (Fässler & Hoffmann 2004) for clusters consisting exclusively of atoms of at least two different (semi)metallic elements. The complexes in §3(c) can already be seen as intermetalloids; however, high coordination numbers as observed in intermetallic compounds are better realized in endohedrally filled clusters. Such compounds might even topologically exhibit similar structural motifs as found in related intermetallic compounds.

Endohedral, filled clusters—as shown in figure 7—can be formed by stripping off the ligands in those complexes depicted in figure 5. The smallest transition metal-filled Zintl clusters were found in \([\text{Ni@Ge}_9]^{3-}\) (Sevov & Goicoechea 2006) and \([\text{Cu@E}_9]^{3-}\) for E = Sn and Pb (Scharfe et al. 2008; figure 7a). \([\text{Ni@Ge}_9]^{3-}\) was obtained from reactions of K₄Ge₉ with Ni(cod)$_2$, whereas \([\text{Cu@E}_9]^{3-}\) resulted from reactions of Cu–MeS with the respective Zintl phases K₄Sn₉ and K₄Pb₉ in dmf. In these compounds, the E₉ cluster skeleton is retained, and a transition metal is incorporated into it. Although the structure refinement of \([\text{Ni@Ge}_9]^{3-}\) suffers from an intense disorder, the cluster apparently adopts the shape of a strongly distorted tricapped trigonal prism with unequally elongated prism heights in the range of 3.089–3.560 Å. In \([\text{Cu@E}_9]^{3-}\), the cluster atoms also build a tricapped trigonal prism, but with equally elongated heights (Scharfe et al. 2008), and maximization of the strength of nine Cu–E interactions leads to an almost perfect spherical shape of the nine-atom cluster and not to the nido-type structure typical of 22 skeleton electrons \([\text{E}_9]^{4-}\) clusters. The prism heights in this anion differ from each other by at most 5 per cent (E = Sn) or 6 per cent (E = Pb), but they are extended by 17 per cent and 15 per cent, respectively, compared to empty clusters with a similar skeleton shown in figure 1d. As a result of this elongation,
the Cu–E distances vary in a very narrow range of ±0.05 Å with slightly longer contacts to the capping atoms. The clusters can be considered as paramagnetic [Ni0@(Ge9)3−] as confirmed by EPR measurements (Sevov & Goicoechea 2006), and [Cu+@(E0)4−] reveals sharp 119Sn, 207Pb and 63Cu NMR signals as expected for diamagnetic compounds (Scharfe et al. 2008). NMR experiments on [Cu@E0]3− in solution again nicely illustrate the structural flexibility of the E0 clusters. The 119Sn NMR spectrum of [Cu@Sn0]3− at room temperature (figure 8b) displays a single resonance, which indicates that all Sn atoms are time-averaged in solution. At room temperature, [Cu@Sn0]3− also provides one sharp 63Cu NMR (figure 8c). The high-resolution satellite pattern permits the rare determination of the 63Cu−119Sn coupling constant. The observed resonance frequency of −332 ppm in [Cu@Sn0]3− is in the range of other Cu(I) compounds, and therefore the Cu atom is assumed to have the formal

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Figure 8. NMR spectra of [Cu@Sn9]3−. (a) Spherical shape of the intermetalloid cluster. (b) Experimental 119Sn NMR spectrum (δ = −1440 ppm, 1:1:1 quartet, J(119Sn−63/65Cu) = 286 Hz, two satellites with J(119Sn−117Sn) = 85 Hz). (c) Experimental (δ = −332 ppm, J(119Sn−63Cu) = 280 Hz) and simulated (insert) 63Cu NMR spectrum. The spectra are recorded in acetonitrile at room temperature. Simulations account for coupling to various 119/117Sn isotopomers [Cu@119/117SnxSn(9−x)]3− (with x = 0, 1, . . . , 4) (Scharfe et al. 2008).
oxidation state $+1$. The charge of Cu(I) was also confirmed by DFT calculations. Both the $^{119}$Sn and $^{63}$Cu NMR spectra do not change upon cooling to $-40^\circ C$ (Scharfe et al. 2008).

The endohedral 10-vertices cluster $[\text{Ni@Pb}_{10}]^{2-}$ (figure 7b) was found from the reaction of Ni(cod)$_2$ with K$_4$Pb$_9$ in ethylenediamine (Esenturk et al. 2005). Herein, the Ni atom occupies the centre of a bicapped square anti-prism as predicted from DFT calculations. $^{207}$Pb NMR studies again revealed a fast atom exchange of the cluster in solution, since only one (broad) signal was detected at $-996$ ppm (Esenturk et al. 2005).

As a minor by-product from the reaction of Ni(cod)$_2$ with K$_4$Pb$_9$, the icosahedral cluster $[\text{Ni@Pb}_{12}]^{2-}$ was found (figure 7c; Esenturk et al. 2006a). For the heavier homologues Pd and Pt, the isostructural clusters $[\text{Pd@Pb}_{12}]^{2-}$ and $[\text{Pt@Pb}_{12}]^{2-}$ were obtained from the reaction of K$_4$Pb$_9$ with Pd(PPh$_3$)$_4$ and Pt(PPh$_3$)$_4$, respectively (Esenturk et al. 2004, 2006a). Apparently, nine-atom clusters must be oxidized during the reaction, which is ascribed to cod and/or PPh$_3$. A comparison of solid-state structures of $[\text{M@Pb}_{12}]^{2-}$ confirms that the smaller the transition metal M is, the more strongly distorted is the Pb skeleton. While the interstitial Pt atom is surrounded by an almost perfect icosahedron with virtually equal Pb–Pb distances, these contacts vary over a larger range with increasing variances for clusters with interstitial Pd and Ni atoms. The cluster distortion manifests in the distribution of the M–Pb distances, whereas for $\text{M} = \text{Ni}$ the 10-vertices cluster is clearly favoured (Esenturk et al. 2006a). In solution, only one $^{207}$Pb NMR resonance was found for $[\text{M@Pb}_{12}]^{2-}$ (Ni: 1167 ppm, Pd: 1520 ppm, Pt: 1780 ppm), which either reflects the high symmetry of the cluster, or can be ascribed to a fluxional behaviour (Esenturk et al. 2006a).

Recently, we succeeded in the synthesis of an endohedral 12-atom tin cluster $[\text{Ir@Sn}_{12}]^{3-}$ (Wang et al. in press). It is apparently formed in a stepwise reaction that starts from an ethylenediamine solution of K$_4$Sn$_9$ and [IrCl(cod)]$_2$. At first, the Ir(cod)-capped Sn$_9$ cluster is formed (figure 5d). If the ethylenediamine solution of this 10-vertices cluster is heated to $80^\circ C$, it is—under the loss of the cod ligand—transformed into $[\text{Ir@Sn}_{12}]^{3-}$. This reaction is accelerated by the addition of PPh$_3$ or dppe (1,2-bis(diphenylphosphino)ethane). The cluster can be formulated as $[\text{Ir}^{1-}@\text{(Sn}_{12})^{2-}]$, and the cluster skeleton fulfils Wade’s rules. The 12 tin atoms form an almost perfect icosahedron, with Sn–Sn distances in a slightly larger range than those found for the Pb–Pb contacts in $[\text{Pt@Pb}_{12}]^{2-}$. No analogous germanium compound displaying a metal atom-centred Ge$_{12}$ cluster has been reported to date.

The family of intermetalloid clusters was recently expanded to electron-poor transition elements such as Co, and a non-deltahedral structure much more similar to structures observed in intermetallic compounds was found. The anion $[\text{Co@Ge}_{10}]^{3-}$ (figure 7d) with an unprecedented structure emerged during the reaction of K$_4$Ge$_9$ with Co(C$_8$H$_{12}$)(C$_8$H$_{13}$) (Wang et al. 2009). Although all the tetrel atom clusters obtained from solution so far have had deltahedral structures, the germanium atoms in $[\text{Co@Ge}_{10}]^{3-}$ build a $D_{5h}$-symmetric pentagonal prism that comprises no triangular faces at all. This unprecedented cluster shape indicates that neither its electron count nor its bonding situation follow conventional rules. From Wade’s rules a $D_{4d}$-symmetric

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bicapped square anti-prism would have been forecast for the shape of this species, and DFT calculations performed for [Co@Ge10]3− revealed that the potential surface for this cluster is rather flat, with an energy difference of 13.3 kcal mol−1 between the stationary points. Therefore, it can easily transform between the favoured $D_{5h}$-symmetric and the energetically unpropitious $D_{4d}$-symmetric arrangement (Wang et al. 2009). The same calculations for [Ni@Ge10]2− revealed an energetic minimum for the $D_{4d}$ geometry, while the pentagonal prism corresponds to a ground state of 5.33 kcal mol−1 (King et al. 2008; Wang et al. 2009). Thus for these clusters the global minimum cannot be determined indisputably, whereas the empty [Ge10]2− unit preferentially adopts a bicapped square anti-prism (King et al. 2006), which was also found for [Cu@Ge10]− and [Zn@Ge10] (King et al. 2008). Natural bond orbital (NBO) analyses of [Co@Ge10]3− pointed to a natural charge of −1.05 for the incorporated Co atom and consequently a d10 electron configuration (Wang et al. 2009). Interatomic Co–Ge and Ge–Ge distances in [Co@Ge10]3− resemble the bonding situation in the binary intermetallic compound CoGe2. In the latter, the Co atom is located in a distorted cubic cavity of eight Ge atoms. Recently, the formation of the cluster [Fe@Ge10]3− was reported in a similar reaction of Fe(2,6-MeS2C6H3)2 with K4Ge9 (Zhou et al. 2009b). Owing to the odd number of electrons, the anion should be paramagnetic; however, no magnetic data have been reported so far.

Precursors for larger intermetalloid units consisting of 17 or 18 tetrel atoms are given by [(η4-Ge9)Cu(P4Pr)3]3− (Scharfe & Fässler in press) as shown in figure 5c, and also by a class of E9 clusters that are filled and are simultaneously capped by a transition metal, such as the anions [(Ni@Sn9)Ni–CO]3− and [(Pt@Sn9)Pt–PPh3]2− (Kesanli et al. 2002) shown in figure 9a,b, respectively, as well as by modified Ge9 clusters [(Ni@Ge9)Ni–R] (R = CO, C–C–Ph, en) (Sevov & Goicoechea 2006). Assuming that a ligand exchange in [Ge9–Cu(P4Pr)3]3− as discussed above also takes places in [(Pt@Sn9)Pt–PPh3]2−,
the formation of a cluster species that includes two transition metals and 18 tetrel atoms (see figure 10d) could be achieved. Four new clusters of higher nuclearity, \([\text{Ni}_2@\text{Sn}_{17}]^{4-}\) (Esenturk et al. 2006b), \([\text{Pt}_2@\text{Sn}_{17}]^{4-}\) (Kesanli et al. 2007), \([\text{Pd}_2@\text{Ge}_{18}]^{4-}\) (Goicoechea & Sevov 2005a) and \([\text{Pd}_2@\text{E}_{18}]^{4-}\) (Goicoechea & Sevov 2005b; Sun et al. 2007), were synthesized in ethylenediamine solution from Ni(cod)_2, Pt(PPh_3)_4 and Pd(PPh_3)_4, respectively (figure 10a, b and d). Cluster formation requires the partial oxidation of the Sn_9 clusters along with the reduction of cyclooctadiene probably also involving the solvent ethylenediamine. In \([\text{Ni}_2@\text{Sn}_{17}]^{4-}\), two \([\text{Ni}@\text{Sn}_9]^{2-}\) subunits are connected via one apex-like, central Sn atom that participates in both Sn_9 clusters (figure 10a; Esenturk et al. 2006b). The cluster shapes deviate significantly from deltahedral structures. With a more open shape, \([\text{Ni}_2@\text{Sn}_{17}]^{4-}\) displays \(D_{2d}\) point group symmetry, and the central Sn atom is surrounded by a pseudo-cube of eight Sn atoms.

The high coordination number of the central Sn atom causes remarkably long Sn–Sn contacts that are more common in solid-state compounds such as BaSn_5, in which the Sn atoms even reach a 12-fold coordination by other tin atoms (Fässler et al. 2001). The dynamic behaviour of this cluster was examined by temperature-dependent \(^{119}\text{Sn}\) NMR experiments in dmf solutions (Esenturk et al. 2006b). At a temperature of −64°C, four resonances appear in the \(^{119}\text{Sn}\) NMR spectrum (−1713, −1049, −1010 and +228 ppm). They are assigned to the different cluster atoms via peak intensity analysis, and the central Sn atom generates the most deshielded signal. At 60°C only one signal is observed at −1167 ppm, indicating fast atom exchange reactions. In contrast, the analogous \([\text{Pt}_2@\text{Sn}_{17}]^{4-}\) unit (figure 10b) generates only one \(^{119}\text{Sn}\) NMR resonance over the whole temperature range (−742.3 ppm) and is apparently fluxional in dmf solution even at −60°C (Kesanli et al. 2007). The solid-state structure of \([\text{Pt}_2@\text{Sn}_{17}]^{4-}\) differs significantly from that of the isoelectronic \([\text{Ni}_2@\text{Sn}_{17}]^{4-}\). In the former, the Sn_{17} cluster encloses two Pt atoms at a distance of 4.244 Å, which does not indicate bonding Pt–Pt contacts (Kesanli et al. 2007).
A similar ellipsoid structure was found for the clusters $[\text{Pd}_2@E_{18}]^{4-}$ (E = Ge, Sn) in which two Pd$^0$ atoms are encapsulated by 18 tetrel atoms that form a prolate deltahedral cluster (Goicoechea & Sevov 2005b; Sun et al. 2007). These units are the largest endohedral tetrel atom clusters with a completely closed cluster shell discovered up to now. The interstitial Pd atoms with d$^{10}$ electron configuration approximately occupy the ellipse foci. Even though the Pd–Pd distance of 2.831 Å is shorter in the smaller Ge cage than in the Sn cage (3.384 Å), no bonding Pd–Pd contacts are to be considered. The $[\text{Pd}_2@\text{Sn}_{18}]^{4-}$ cluster is fluxional at room temperature in ethylenediamine solution, with only one $^{119}\text{Sn}$ NMR resonance at $-751.3$ ppm.

The intermetalloid cluster $[\text{Ni}_3@\text{Ge}_{18}]^{4-}$ displays a somewhat similar structure where a linear trimer of Ni atoms was found to bind to two separated, widely opened Ge$_9$ clusters (Goicoechea & Sevov 2005a). These two Ge$_9$ units feature the same shape as one of the two units found in $[\text{Pd}_2@E_{18}]^{4-}$. Although the Ge atoms of the two cluster units are not connected, the relative orientation of the atoms of each open face is already staggered as required for an 18-vertices cage (Sevov & Goicoechea 2006).

4. Summary

Zintl ions have the basic capability for a bottom–up synthesis of nanostructured materials. The known examples show that such anionic clusters undergo oxidative addition on the one hand, but can also add step-by-step transition metals on the other. Up to now homoatomic clusters, homoatomic complexes and endohedral clusters derived from Zintl tetrel anions reach the size of 36 Ge atoms in $[(\text{Ge}_9)_4]^{8-}$, 45 Ge atoms in $[\text{Au}_3\text{Ge}_{45}]^{8-}$ and 18 E atoms in $[\text{Pd}_2@E_{18}]^{4-}$ (E = Ge and Sn), respectively. Still there is a necessity for a better understanding of the reactivity and the cluster growth mechanisms, since oxidative coupling reactions often proceed even without the addition of an oxidation reagent. Although the chemistry of highly charged anions is still limited to a few polar and aprotic solvents, its high potential has become evident, and has developed into a rapidly growing field.

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