

Chapter 6

Zintl Phases

Slavi C. Sevov

Department of Chemistry and Biochemistry, University of Notre Dame, IN, USA

1. Introduction

The subject of this chapter is a special class of intermetallics called 'Zintl phases' named after Edward Zintl who pioneered their exploration and the rationale for their structures (Zintl and Dullenkopf, 1932; Zintl and Brouer, 1933; Zintl, 1939). Zintl's view applied to the classical Zintl phase NaTl assumes complete electron transfer from the more electropositive sodium to the more electronegative thallium (Zintl and Woltersdorf, 1935), just as in genuine ionic salts such as NaCl. The difference is that the resulting anions do not necessarily achieve an electronic octet as isolated species but may rather bond to each other in order to do so. Thus, Tl^- in Na^+Tl^- behaves like an element of the group to the right, group 14, and forms a diamond network, typical for the elements of that group, that is stuffed by the Na^+ cations. Such phases are the link between the metallic, alloy-type intermetallics on the one hand and the typical valence compounds on the other. The number of Zintl phases has increased many-fold since Zintl's time, and a number of reviews on the subject have been published in recent years (Corbett, 1996, 1997, 2000a; Miller, 1996; Eisenmann and Cordier, 1996; van der Lugt, 1996; Belin and Tillard-Charbonnel, 1993). Since the definition of a 'Zintl phase' has never been very exact, often compounds that include nonmetals have been considered in this class. The intent here is to concentrate more on clearly intermetallic Zintl phases, i.e. phases that contain main-group metals, semimetals, or semiconductors only. Thus, only compounds of the alkali metals with groups 13 (without B and Al), 14 (without C), and 15 (without N and P) will be discussed here.

1.1 Definition and Synthesis

For the purposes of this chapter 'classical' or true Zintl phases are defined as follows. They are compounds that:

1. contain an alkali or alkaline-earth metal and a p-element (or elements) that is a metal, semimetal, or small-gap semiconductor;
2. are electronically balanced or closed-shell compounds, i.e. the number of electrons provided by the constituting elements equals the number of electrons needed for covalent bonding in the structure;
3. have very narrow or no homogeneity width, i.e. they are line compounds;
4. are semiconductors or poor conductors;
5. are diamagnetic or show very weak, temperature-independent paramagnetism;
6. are brittle.

Criteria (2) through (6) are the same as for normal valence compounds, while (1) provides the connection to the general class of intermetallics. Requirement (2) needs to be explained in some more detail, especially the meaning of 'number of electrons needed for covalent bonding'. For structures with 'normal' 2-center-2-electron localized bonds this number is simply the sum, $2 \times (\text{number of bonds}) + 2 \times (\text{number of lone pairs})$, where all atoms follow the octet rule. For compounds with delocalized bonding, on the other hand, the valence rules are different. The bonding electrons in compounds with deltahedral clusters are calculated by Wade's rules (Wade, 1972, 1976) that have been developed for the borane cages but also work equally well for naked main-group clusters. Furthermore, there are combinations of the two, i.e.

compounds that contain networks of deltahedral clusters bonded to each other via localized bonds, and the sum of bonding electrons for such systems will include the electrons for cluster bonding, those for intercluster bonding, and the lone pairs (usually on cluster atoms not involved in intercluster bonding).

Since the Zintl phases usually contain alkali or alkaline-earth metals and are also air- and moisture-sensitive themselves, their synthesis and handling is carried out in vacuum or inert atmosphere. Typically, they are synthesized by heating (anywhere between 300 and 900 °C) mixtures of the constituting elements sealed in containers made of ductile and high-melting niobium or tantalum. Since the latter are easily oxidized at these temperatures they are additionally 'jacketed' in evacuated ampules of fused silica.

1.2 Historical Overview

For alloys and intermetallic compounds made of similar elements, the correlation between structure and valence electron concentration (VEC) had been established before Zintl's time. The rules developed by Hume-Rothery and Westgren were already stated, and explained why different structures form for different VECs (Hume-Rothery, 1926; Westgren and Phragmen, 1926). Also prior to Zintl the Grimm-Sommerfeld rule for tetrahedral frameworks was suggested (Grimm and Sommerfeld, 1926). Zintl also studied intermetallic compounds but only those made of elements with very different electronegativities, i.e. combinations of the very electropositive alkali or alkaline-earth metals with the post-transition elements. It was clear that the phases in these systems behaved quite differently than Hume-Rothery's metallic phases and were rather saltlike since they had melting points higher than the elements, were brittle, and conducted poorly. It was also noticed that all compounds that were not Hume-Rothery phases exhibited atomic volume contraction, presumably due to contraction of the more electropositive atoms. This suggested that the latter were cations in the structure, or in other words, they have transferred their electrons onto the more electronegative atoms. This was realized by Zintl and became the basis for rationalizing the electronic structure and bonding in the new class of compounds, now called Zintl phases. Thus, instead of using VEC for the prediction of the structure, it was proposed to look at the electronic state of the more electronegative element after assuming complete transfer of the valence electrons from the more electropositive element (Zintl and Woltersdorf, 1935). Later, Klemm

developed the idea further into what is known as the 'pseudo-atom' concept, the negatively charged atom would behave structurally similar to the corresponding isoelectronic neutral element of a group to its right (Klemm, 1956, 1959). This concept, combined nowadays with the electronic requirements for delocalized bonding in closed-shell clusters, is a very powerful tool correlating the structures of the Zintl phases with their stoichiometries.

2. Zintl Phases with Delocalized Bonding

2.1 Isolated Clusters

Usually deltahedral clusters are associated with the borane cages and their derivatives of the type $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, etc. The bonding electrons in such species are delocalized, i.e. they are shared by all atoms of the cluster. Therefore, the electronic requirements in such species can not be described by simple 2-center-2-electron bonding but rather by rules developed by Wade (Wade, 1972, 1976) and known as Wade's rules. The latter postulate that *closo*- (no vertices missing), *nido*- (one vertex missing), and *arachno*- (two vertices missing) species require $2n+2$, $2n+4$, and $2n+6$ electrons for bonding, respectively, where n is the number of vertices of the cluster. The same rules can be applied for main-group 'naked' deltahedral clusters, i.e. clusters without ligands, where one has to consider the fact that each vertex will carry a lone pair of electrons. With this requirement in mind we can review the suitability and potential problems for forming such clusters from different main-group elements. The isolated borane-type deltahedral clusters of the *closo*-type of groups 13, 14 and 15 will have formulas $E_n^{(n+2)-}$, E_n^{2-} , and $E_n^{(n-2)+}$, respectively. The *nido*-species will have charges of $(n+4)-$, $4-$, and $(n-4)+$, respectively, and the charges for the corresponding *arachno*-species will be $(n+6)-$, $6-$, and $(n-6)+$, respectively. One can clearly see that formation of negatively charged clusters of group 15 is basically impossible. The only two possibilities for elements of this group are *arachno* E_4^{2-} (square) and E_5^- (pentagon). None of them has been observed in neat solids (solids made directly by solid-state reactions from the elements and that do not contain organic or similar moieties), although the former anion can be crystallized from ethylenediamine solutions of K_xBi_y in the compound $[K\text{-crypt}]_2Bi_4$ where crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Cisar and Corbett, 1977). For

clusters of group 13, on the other hand, the negative charges are going to be too high. For example, a *closo*-cluster of 11 atoms will require the enormous charge of 13⁻. Its 10 and 9 atom *nido*- and *arachno*-versions will have even higher charges of 14⁻ and 15⁻, respectively. Therefore, it is very unlikely that such clusters will form for this group either. The charges in group 14 are independent of the cluster size, they are always 2⁻, 4⁻, and 6⁻, for *closo*, *nido*, and *arachno* species. The charge of 2⁻ is perhaps too small for a relatively large cluster since it will require only two counteranions in a compound such as $A_2[E_n]$. The two cations will be too few and too small for packing efficiently with the large clusters and for separating and screening them effectively from each other. No such clusters have been found in neat solids, although they exist in compounds precipitated from ethylenediamine solutions with huge counteranions such as [A-crypt]. Known in such compounds are E_5^{2-} trigonal bipyramids (Edwards and Corbett, 1977; Campbell and Schrobilgen, 1997), and E_3^{2-} tricapped trigonal prisms (Belin *et al.*, 1977). Until recently, the *nido* and *arachno* clusters of group 14 were also thought to have charges too low for formation in neat solids. However, in recent years this concept has been proven wrong with the synthesis of a number of Zintl phases with stoichiometry A_4E_9 that contained the *nido*- E_3^{4-} clusters (Queneau and Sevov, 1997a, 1998a,b; Todorov and Sevov, 1998; von Schnering *et al.*, 1997).

2.1.1 Group 14

Small tetrahedral species E_4^{4-} in the equimolar Zintl compounds $AE (= A_8E_4)$ are known for all elements of this group (Schäfer and Eisenmann, 1985). Counting electrons in the tetrahedron is somewhat debatable, since there are two different, but equally satisfactory, ways to do that. One way to look at it is as a *nido* deltahedron derived from the *closo* trigonal bipyramid E_5^{2-} by removing a vertex, despite the fact that all of its faces are triangular and that it does not really look like a geometrical body with a missing vertex. Nevertheless, when taken as such, i.e. assuming delocalized bonding, its charge is going to be 4⁻ as for any *nido* species of this group. The second rationalization of the electron count is to assume simple 2-center-2-electron localized bonding between all the vertices. Thus, the tetrahedron has 6 edges which require a total of $6 \times 2 = 12$ bonding electrons. When the 8 electrons for the 4 lone pairs are included, the total for the cluster becomes 20 electrons, or the available $4 \times 4 = 16$ electrons provided by the 4

atoms are again 4 electrons short from the 20 needed by the cluster. Yet a third and perhaps the best way to view these compounds is to use the pseudo-atom concept where E^- in AE is a pseudo-element of group 15 such as phosphorus, and as such it forms tetrahedra that are typical for one of the allotropic forms of that element. It should also be mentioned here that pseudo-phosphorus can be made not only from atoms of the neighboring group, but also from atoms of group 13, i.e. two groups to the left of phosphorus. Thus the compounds $A_2E (= A_8E_4)$ where $E = In$ or Tl contain the same tetrahedral species although with a doubled charge, E_4^{8-} (Smith and Hansen, 1967; Sevov and Corbett, 1993a).

Larger deltahedral clusters of this group have been known for quite some time but all in compounds crystallized from ethylenediamine solutions with cryptated alkali metal counteranions (Corbett, 1997, 2000a, and references therein). The synthetic methodology starts usually with the preparation of a precursor A_xE_y by melting the two elements. It was always thought that these precursors were simple featureless melts or alloys with no particular structure, or even less likely, structures with clusters. The precursor is dissolved in ethylenediamine which usually also contains 2,2,2-crypt as an additive designed to capture the alkali metal. It was thought that the cluster formation always occurred at this step during the dissolution of the precursor. Nevertheless, our and others' studies have shown that many of the precursors in these systems are Zintl phases with already pre-existing clusters, and that the dissolution process often is reduced to simply extracting them into the solution (Queneau and Sevov, 1997a, 1998a,b; Todorov and Sevov, 1998; von Schnering *et al.*, 1997; Somer *et al.*, 1998; Xu and Sevov, 1999).

The first structurally characterized compound with isolated 9-atom deltahedral clusters was Cs_4Ge_9 (*tP208*) shown in Figure 1 (Queneau and Sevov, 1997a). Choice of this particular combination of elements for study was not accidental; it combines the largest cation, Cs, and the smallest element of this group, Ge, for which a 9-atom cluster has been characterized from solution. As already discussed, it was thought that E_9^{4-} clusters cannot exist in neat solids due to the mismatch of large clusters and small cations, and therefore the best chance for formation of such species had the smallest clusters combined with the largest cations.

With the knowledge that at least Ge_9^{4-} exist in neat solids it was more than logical to test the possibilities for similar clusters of the heavier analogs Sn and Pb.

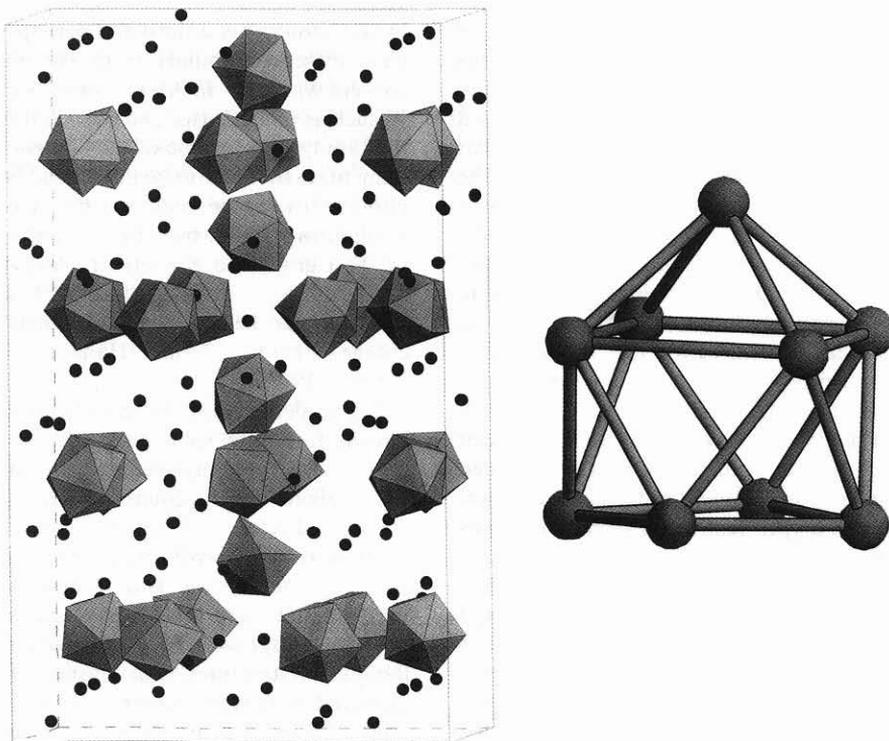


Figure 1 The structure of Cs_4Ge_9 (left), the first Zintl phase with isolated 9-atom clusters of group 14. The clusters Ge_9^{4-} (right) are *nido* deltahedra with the shape of monocapped square antiprisms. There are 208 atoms in the unit cell

Thus, the next step was to investigate the combination of the largest cation and the largest cluster, Cs_4Pb_9 (*mP52*) (Todorov and Sevov, 1998). Again, it was somewhat surprising to discover that the corresponding Zintl phase can be synthesized. Although the atomic ratio is the same as in Cs_4Ge_9 , the packing and therefore the structure of Cs_4Pb_9 is different.

Lastly, the other extreme combination of cation and anion, K_4Pb_9 (*mP52*), with a very small cation and the largest cluster was tried (Queneau and Sevov, 1998a). The compound forms, the structure is different from the above two (Figure 2), and contains two different types of Pb_9^{4-} clusters, labeled A and B (Figure 3). The clusters of type A have the expected geometry for this charge, i.e. monocapped square antiprisms, but those of type B are rather like tricapped trigonal prisms. This latter geometry indicates, of course, *closo* species of 9-atoms, and those therefore should rather

carry a charge of $2-$. Nevertheless, this particular cluster is elongated along the three-fold axis, and, as a result of this, one otherwise antibonding and empty orbital becomes bonding and filled, and the charge is again $4-$.

It should be mentioned here that compounds with Sn_9^{4-} clusters were also made. Furthermore, in addition to the structural characterization most compounds were also studied by Raman spectroscopy (von Schnering *et al.*, 1997). It was shown that the 9-atom clusters exhibit a very characteristic set of vibrations that can be easily recognized in these spectra. Thus, Raman spectroscopy can be a very useful tool for identification of compounds with isolated ionic clusters of different sizes by simply matching experimental spectra with spectra from a database.

All the 9-atom clusters of group 14 mentioned so far, Ge_9 , Sn_9 , and Pb_9 , were known from solution work

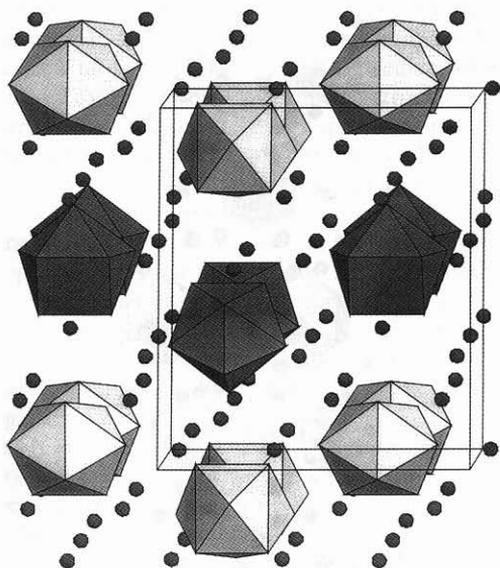


Figure 2 The structure of K_4Pb , with two different types of Pb_9^{4-} clusters, monocapped square antiprisms (darker polyhedra) and elongated tricapped trigonal prisms (lighter polyhedra). The potassium cations are shown as isolated spheres

prior to finding them in Zintl phases. The element missing from this collection is obviously silicon since no silicon clusters (larger than the tetrahedra found in A_4Si_4) had ever been made either from solution or in the solid state. Nevertheless, with the knowledge that clusters of the heavier analogs can be made in neat solids, it was natural to explore the possibility for similar silicon clusters. Thus, reactions with stoichiometry A_4Si_9 were carried out, and the resulting phase indeed contained Si_9^{4-} deltahedral clusters although the stoichiometry of the compound was somewhat different (Queneau and Sevov, 1998b). The new compound, $A_{12}Si_{17}$ where $A = K, Rb, Cs$ (*mP464*), contains not only 9-atom clusters but also the tetrahedral species Si_4^{4-} (Figure 4). The formula can therefore be rewritten as $12A^+ + 2(Si_4^{4-}) + Si_9^{4-}$.

2.1.2 Group 13

Although this group was initially thought to be not very promising for deltahedral clusters (see above), it turns out that it actually provides the largest and most diverse collection of clusters with delocalized bonding. The first cluster of this group was found in a phase which, ironically, is not exactly a true Zintl phase

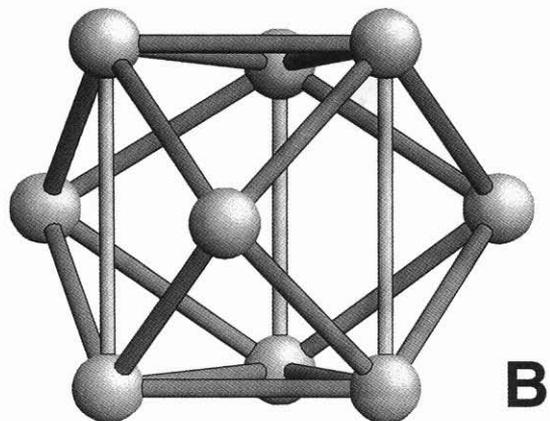
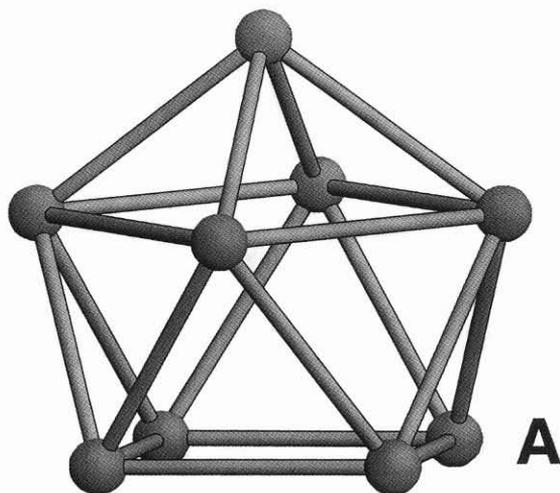


Figure 3 Closer view of the two types of Pb_9^{4-} clusters found in K_4Pb : A) monocapped square antiprism; and B) elongated tricapped trigonal prism

according to the definition given in the Introduction (above), and the cluster itself is not of borane-type geometry. It is an 11-atom cluster of indium, In_{11}^{7-} , found in the compound K_8In_{11} (*hR114*) shown in Figure 5 (Sevov and Corbett, 1991). The discrepancy between charge and number of cations means that there is an extra electron per formula. Therefore, it is not an electronically balanced phase and cannot be called a true Zintl phase according to our rules. It better fits a group of phases which can be called 'almost Zintl phases' or 'metallic Zintl phases', discussed later on. The extra electron is apparently

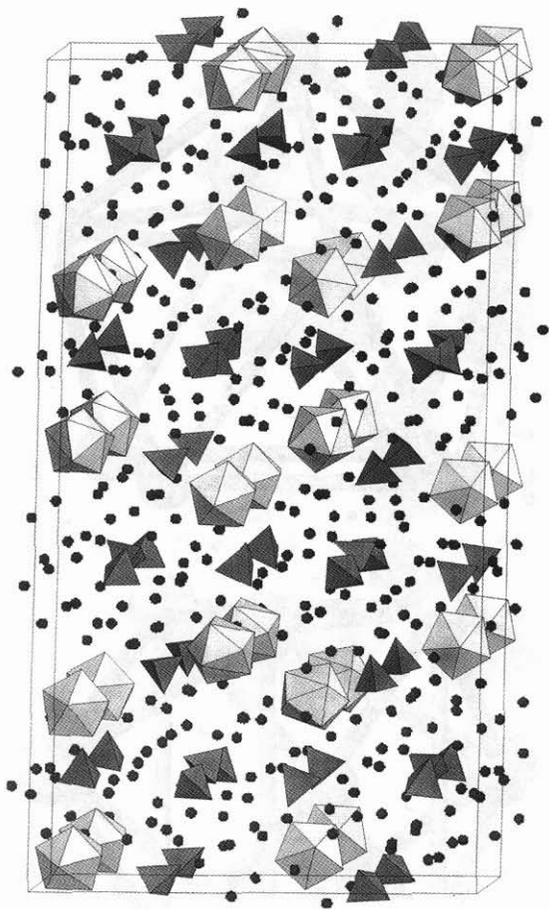


Figure 4 Shown is the structure of $\text{Rb}_{12}\text{Si}_{17}$ which contains 9- and 4-atom clusters of silicon, Si_9^{4-} and Si_4^{4-} in ratio 1:2 shown as lighter and darker polyhedra, respectively. The rubidium cations are shown as isolated spheres. This structure and other Zintl structures may be viewed in color at www.nd.edu/~sbobev/interm.html

delocalized over the alkali-metal atoms and perhaps the cluster antibonding orbitals, and the compound is Pauli-paramagnetic and metallic. Nevertheless, the cluster is deltahedral and exhibits delocalized bonding. Yet, its geometry and electron count differ from that expected for a borane cage of 11 atoms. The cluster in this case is a pentacapped trigonal prism that has been compressed along the three-fold axis (Figure 6), and the number of electrons needed for skeletal bonding within the cluster is not $2n+2$ but rather $2n-4=18$. Thus, instead of carrying the enormous charge of $13-$ corresponding to $(n+2)-$ for *closo* species of group 13 (see above), its charge is the more reasonable $7-$.

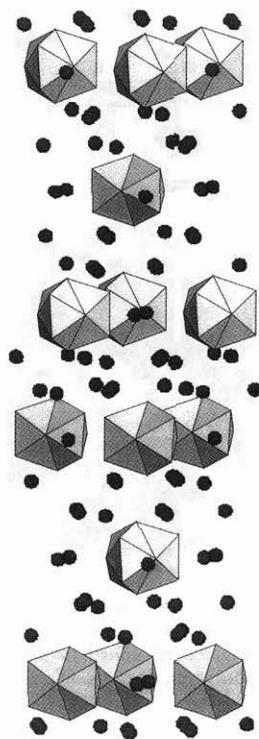


Figure 5 The structure of K_8In_{11} (rhombohedral, $R\bar{3}c$) is of close-packed layers of In_7^{7-} clusters (polyhedra) stacked in a cubic fashion along the c axis (vertical) and separated by double layers of potassium cations (spheres)

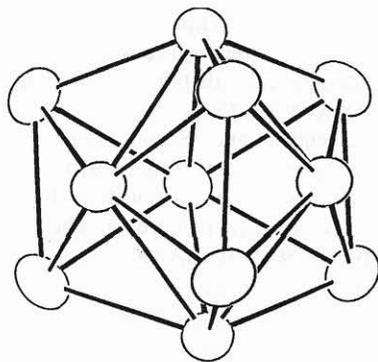


Figure 6 A closer view of the indium cluster in K_8In_{11} . Its shape can be considered as a pentacapped trigonal prism that has been compressed along the three-fold axis (vertical). Three of the capping atoms cap rectangular faces at the waist of the prism, and the remaining two cap the two triangular bases, top and bottom of the figure

Molecular orbital calculations clearly show that a good size HOMO-LUMO (Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital) gap of 1.2 eV opens at 18 bonding electrons for this geometry, i.e. the cluster is hypo-electronic with respect to the classical *closo* geometry. It can be rationalized in the following way. Starting from a classical tricapped trigonal prism with $2n+2=20$ electrons, i.e. In_9^{1-} , we add two more indium vertices to cap the triangular bases. This addition does not bring new orbitals, i.e. the number of required electrons remains 20, but only two additional electrons, the p-electrons of the indium atoms, and the cluster becomes In_{11}^0 . Next, the cluster is compressed along the three-fold axis, and this distortion makes a formerly bonding a_1' orbital into an antibonding and empty one (Figure 7). This translates into the lower charge for the cluster, In_{11}^{7-} .

Besides K_8In_{11} the clusters In_{11}^{7-} also exist in $\text{Rb}_8\text{In}_{11}$ and $\text{Cs}_8\text{In}_{11}$. Clusters with the same geometry and charge were later found for thallium in A_8Tl_{11} where $\text{A}=\text{K}, \text{Rb}, \text{or Cs}$ (Dong and Corbett, 1995a), $\text{A}_{15}\text{Tl}_{27}$ (*hP42*) where $\text{A}=\text{Rb}$ or Cs (Dong and Corbett, 1996a), and $\text{K}_{18}\text{Tl}_{20}\text{Au}_3$ (*hP41*) (Dong and Corbett, 1995b), and for gallium in $\text{Cs}_8\text{Ga}_{11}$ (Henning and Corbett, 1997). Furthermore, it should be pointed out that these A_8E_{11} phases can be made electronically balanced by 'controlled' one-electron oxidation without changing their structures. Thus, the chlorine-intercalated derivatives $\text{Cs}_8\text{Ga}_{11}\text{Cl}$ and $\text{Cs}_8\text{In}_{11}\text{Cl}$ (*hR120*) contain the same 11-atom clusters and the same overall structure but are semiconducting and diamagnetic (Henning and Corbett, 1997). The chlorine occupies an available site that is empty in the A_8E_{11} structure. These two phases satisfy all but one requirement in our definition of Zintl phases (see above). Criterion (1) is violated since chlorine is obviously a nonmetal. Nevertheless, Cl is one atom out of 20, and furthermore the phase can exist without it. This clearly shows how complicated defining Zintl phases can be!

In addition to these compounds, there is also a substitutional phase that is electronically balanced. This is $\text{K}_8[\text{In}_{10}\text{Hg}]$ (*hP38*) with the same 11-atom cluster as in K_8In_{11} but with one indium atom substituted by Hg, an element from the group to the left (Sevov *et al.*, 1993). Due to the substitution the cluster assumes charge $8-$, i.e. $[\text{In}_{10}\text{Hg}]^{8-}$, and the compound is a true Zintl phase. Although here we have a ternary system, the heteroatom does not cause changes in the cluster shape. It rather acts only as an electron gatherer and causes localization on the cluster of the otherwise delocalized extra electron.

Similarly, there are two derivatives of substitution in the Tl_{11}^{7-} clusters. The isoelectronic $[\text{Tl}_8\text{Cd}_3]^{10-}$ is the result of three thallium atoms substituted by an element to the left, and the cluster keeps the same overall geometry (Huang and Corbett, 1999). Nevertheless, the compound in which it is found, $\text{Na}_9\text{K}_{16}\text{Tl}_{18}\text{Cd}_3$ (*hP92*), is not a classical Zintl phase since it has an extra electron which makes the compound paramagnetic. Another derivative is $[\text{Tl}_9\text{Au}_2]^{9-}$ which has even fewer electrons, $2n-6$ rather than $2n-4$ (Dong and Corbett, 1995b). The pentacapped trigonal prism in this case is compressed even further, so much so that a bond is formed

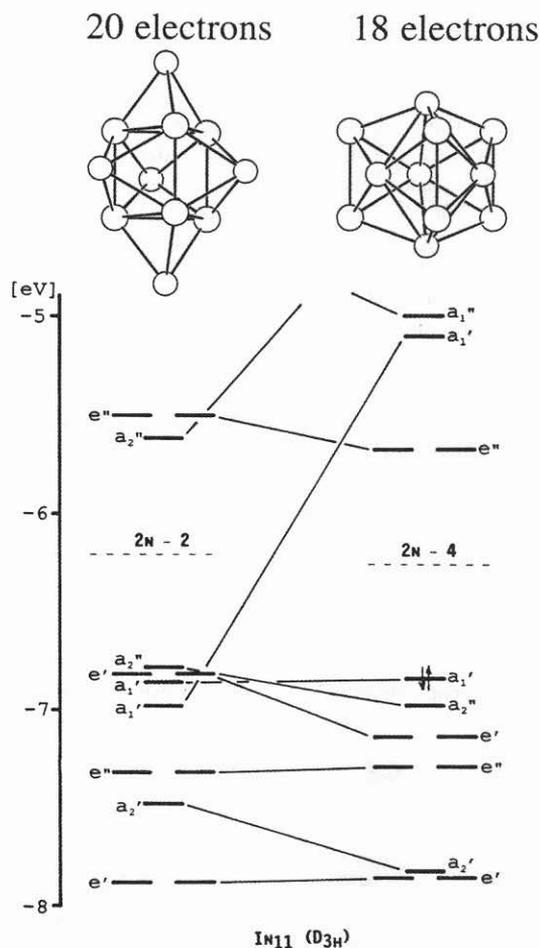


Figure 7 The molecular orbital levels for p orbitals in In_{11} clusters with D_{3h} symmetry: left, the classical pentacapped trigonal prism with 20 electrons; and right, the observed axially compressed cluster with 18 electrons. The HOMO-LUMO separations are shown with broken lines

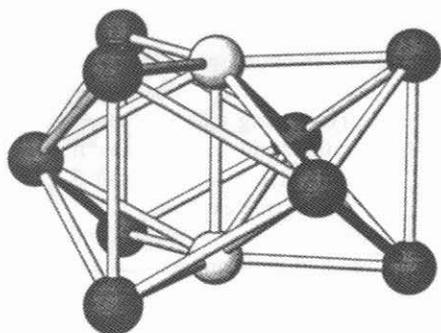


Figure 8 The cluster Tl_9Au_2 in $K_{18}Tl_{20}Au_3$. It can be considered as an extremely compressed pentacapped trigonal prism (see also Figures 6 and 7) with the gold atoms (light) capping the two triangular bases. The compression leads to the formation of a bond between the two gold atoms

between the gold atoms capping the bases (Figure 8). Alternatively, the shape can be considered as made of three face-fused octahedra, all sharing an edge, the Au–Au bond. Again, compression and condensation lead to a decrease of the number of electrons needed for bonding and a lower charge.

For indium and gallium it seems the 11-atom cluster is the only isolated species. Thallium, on the other hand, forms five additional isolated clusters: Tl_5^{7-} in $Na_2K_{21}Tl_{19}$ (*oC168*) (Dong and Corbett, 1994), $Na_{23}K_9Tl_{15.33}^*$ (*hP96*) (Dong and Corbett, 1996c) and $Na_9K_{16}Tl_{18}Cd_3$ (Huang and Corbett, 1999), Tl_6^{6-} in ATl where $A = K$ or Cs (Dong and Corbett, 1993, 1996b), Tl_8^{8-} in $Na_{14}K_6Tl_{18}M$ (*hP39*) for $M = Mg, Zn, Cd, \text{ or } Hg$ (Dong and Corbett, 1996d), Tl_7^{7-} in $K_{10}Tl_7$ (*mP68*) (Kaskel and Corbett, 2000) and $Na_{12}K_{38}Tl_{48}Au_2$ (*hP100*) (Huang *et al.*, 1998), and Tl_9^{9-} in $Na_2K_{21}Tl_{19}$ (Dong and Corbett, 1994) and $Na_{12}K_{38}Tl_{48}Au_2$ (Huang

et al., 1998). Two of these, Tl_5^{7-} and Tl_8^{8-} , follow Wade's rules and carry the prescribed charges of $(n+2)-$. The geometries, as one might expect, are also borane-like, a trigonal bipyramid and an octahedron for the two, respectively. The other three species are again hypoelectronic with nonclassical shapes: Tl_6^{6-} and Tl_7^{7-} are compressed square and pentagonal bipyramids, respectively, with bonds between the two axial vertices, and Tl_9^{9-} has a strange geometry that is best described as the imaginary product of the removal of four neighboring vertices from a Tl-centered icosahedron (Figure 9).

There are a number of observations that can be made at this stage for both groups 13 and 14. One is that clearly *nido* and *arachno* species of group 14 have the 'right' charges and can form in the solid state. Two, the problem of high negative charges of group 13 has been solved by simply forming deltahedral clusters with nonclassical shapes that require fewer electrons for skeletal bonding, i.e. hypoelectronic clusters. This, however, is only one of the solutions of the problem.

Another solution is to form centered clusters where the centering atom brings additional electrons and/or causes geometrical distortions that lead to hypoelectronic species. This is the case in $K_8E_{10}Zn$ (*tP38*) for $E = In$ or Tl (Sevov and Corbett, 1993b; Dong *et al.*, 1997), $K_{10}E_{10}M$ (*oP252*) for $E = In$ or Tl and $M = Ni, Pd, \text{ or } Pt$ (Sevov and Corbett, 1993c; Corbett, 2000a), and $Na_{10}Ga_{10}Ni$ (Henning and Corbett, 1999). The Zn-centered clusters $[E_{10}Zn]^{8-}$ are close to the classical shape expected for 10-atom species (Figure 10), a bicapped square antiprism, but again compressed along the four-fold axis. The compression is clearly a result of the equidistant positioning of all cluster atoms from the central zinc. The effect of the compression is the same as in all compressed clusters described so far, i.e. molecular orbitals that are otherwise bonding and filled become antibonding and empty, and the charge on the cluster is lowered. Thus, instead of $2n+2$ the

*Non-integral proportions indicate presence of vacancies in the position.

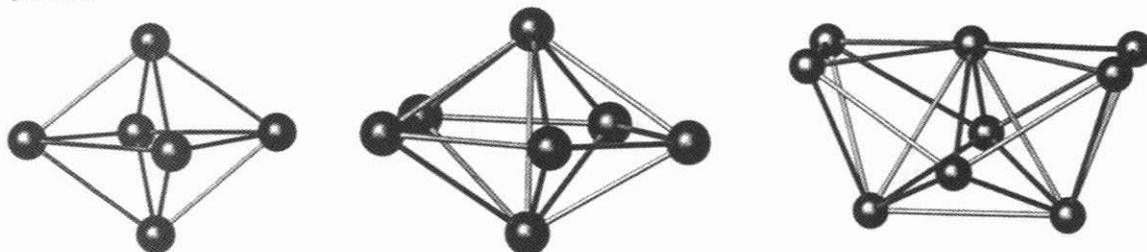


Figure 9 Shown are three thallium clusters: left Tl_6^{6-} with the shape of a compressed square bipyramid; center, Tl_7^{7-} with the shape of a compressed pentagonal bipyramid; and right, Tl_9^{9-} with the shape of a self-centered icosahedron of thallium where four vertices have been removed

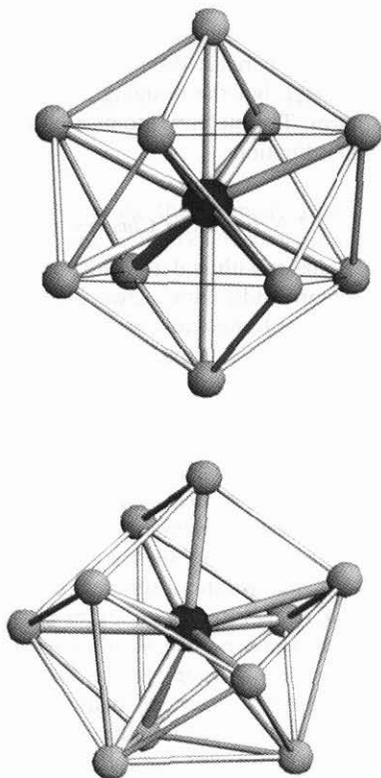


Figure 10 Two centered In_{10} clusters: top, $\text{In}_{10}\text{Zn}^{8-}$ with the shape of a compressed bicapped square antiprism; and bottom, $\text{In}_{10}\text{Ni}^{10-}$ with the shape of a compressed tetracapped trigonal prism (capped are the three rectangular faces and the upper triangular base)

Zn-centered cluster requires just $2n = 20$ electrons for bonding. The central Zn and the 10 In atoms provide $2 + 10 = 12$ electrons (lone pairs are not counted), and the resulting charge is $20 - 12 = 8-$. Exactly the same is observed in the $[\text{E}_{10}\text{M}]^{10-}$ clusters. The clusters are tetracapped trigonal prisms that have been compressed along the three-fold axis (Figure 10). The cause for the distortion is again the central Ni, Pd, or Pt atom being equidistant from the cluster atoms. The distortion makes the cluster again hypoelectronic with $2n = 20$ electrons. In this case the central atoms do not provide bonding electrons, and consequently the charge is $20 - 10 = 10-$.

Isolated and centered clusters of thallium are again more numerous than those of the lighter analogs. In addition to the above-mentioned centered species it also forms self-centered icosahedra $(\text{Tl}_{12}\text{Tl})^{10-}$ and $(\text{Tl}_{12}\text{Tl})^{11-}$ (Dong and Corbett, 1995c), Na- and H-centered icosahedra $(\text{Tl}_{12}\text{Na})^{13-}$ and an octahedron $(\text{Tl}_6\text{H})^{7-}$ (Dong and Corbett, 1995d), and icosahedra

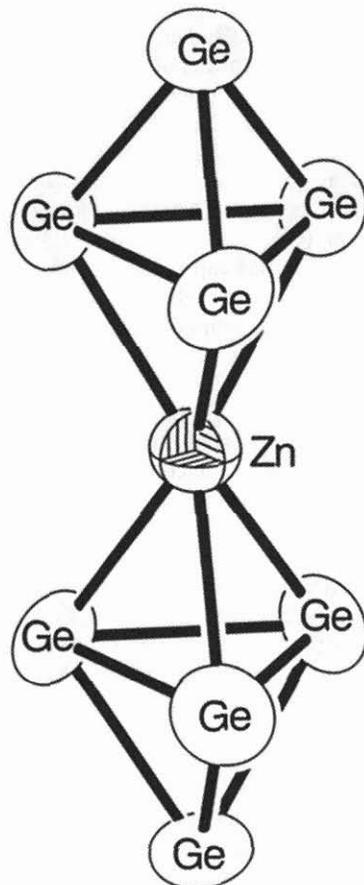


Figure 11 The dimer of corner-sharing, the zinc atom, trigonal bipyramids of $\text{Ge}_6\text{Zn}^{6-}$ found in $\text{Cs}_8\text{Ge}_6\text{Zn}$. It can also be considered as two germanium tetrahedra linked by a zinc atom. The two Zn-capped faces are eclipsed making the zinc in a trigonal prismatic environment

centered by two-electron donors $(\text{Tl}_{12}\text{M})^{12-}$ where $\text{M} = \text{Mg}, \text{Zn}, \text{Cd},$ or Hg (Dong and Corbett, 1996d). Notice that the self-centered icosahedra can exist with different charges, $10-$ and $11-$, and therefore with both even and odd numbers of electrons. More importantly, the cluster with the odd number of electrons (49), $(\text{Tl}_{12}\text{Tl})^{10-}$, is one electron short of the required number for a closed shell. This has apparently been explained with an electron hole localized on the cluster, since the compound is paramagnetic.

2.1.3 Heteroatomic

The substituted 11-atom clusters of group 13, $[\text{In}_{10}\text{Hg}]^{8-}$, $[\text{Tl}_9\text{Au}_2]^{9-}$ and $[\text{Tl}_8\text{Cd}_3]^{10-}$ have been

discussed already. For group 14 there are no such substituted species. Rather, all attempted similar substitutions with elements of group 12 lead to species made of tetrahedra of group 14 that are connected by the heteroatom. Thus, $\text{Cs}_6[\text{Ge}_8\text{Zn}]$ (*oF150*) (Figure 11) contains isolated $[\text{Ge}_8\text{Zn}]^{6-}$ clusters that can be considered as corner sharing (the Zn atom) trigonal bipyramids or as two Ge_4 -tetrahedra joined together via a zinc atom (Queneau and Sevov, 1997b). For the latter, the zinc atoms cap faces of tetrahedra that are eclipsed with respect to each other so that the zinc is in trigonal prismatic coordination. Coincidentally, had the zinc substituted for a germanium atom in the Ge_5^{4-} clusters, the resulting species would have had the same stoichiometry and charge, $[\text{Ge}_8\text{Zn}]^{6-}$. The explanation of why zinc does not substitute in Ge_5^{4-} and In_11^8- clusters is perhaps the fact that it carries only two electrons and its s-orbital is not inert (stable) enough. Mercury, for example, can and does substitute for In in In_{11} . The zinc atom prefers a position with rather a spherical environment, a geometry that does not require a lone pair. Cadmium and mercury also do not substitute in the 9-atom clusters of group 14. Instead, they form compounds that are structurally different from $\text{Cs}_6[\text{Ge}_8\text{Zn}]$ but stoichiometrically equivalent with it. The cadmium analog, $\text{K}_6[\text{Pb}_8\text{Cd}]$ (*mC90*) (Todorov and Sevov, 1999), contains isolated Pb_4^{4-} -tetrahedra as well as tetramers of Pb_4 -tetrahedra connected via cadmium atoms, $[(\text{Pb}_4)\text{Cd}(\text{Pb}_4)\text{Cd}(\text{Pb}_4)\text{Cd}(\text{Pb}_4)]^{10-}$ (Figure 12). The latter can be also viewed as made of a pair of $[\text{Pb}_8\text{Cd}]^{6-}$ species analogous to $[\text{Ge}_8\text{Zn}]^{6-}$ that have been further linked by the third cadmium. All tetrahedra are linked via faces, but the faces are

staggered with respect to each other, so that the cadmium atoms are in a trigonal antiprismatic environment. Lastly, Hg-connected dimers of tin tetrahedra exist in $\text{Cs}_6[\text{Sn}_8\text{Hg}]$, but the bridging is between edges rather than faces. The mercury atoms are in elongated tetrahedral coordination.

2.2 Networks of Clusters

Besides Zintl phases with isolated clusters there are a number of compounds with networks of interconnected clusters, predominantly in the systems group 13 – alkali metal. Such compounds combine two different types of bonding, delocalized within the clusters and localized between them. Naturally, the intercluster bond distances (*exo*-bonds) are shorter than those within the clusters (*endo*-bonds) since the former are ‘normal’ 2-center–2-electron bonds while the latter is delocalized bonding.

It turns out that many of the network compounds are not electronically balanced but very close to being such. Many of them have a few extra electrons (or holes) relative to those needed for the bonding. Such compounds can be referred to as ‘metallic Zintl phases’, and in order to consider them in this chapter we have to somehow broaden the definition given before. We can extend and paraphrase Hughbanks’ interpretation of Zintl phases as phases with ‘structures for which we can at least *think*’ of as valence compounds (Hughbanks, 1992). We will call ‘metallic Zintl phases’ those compounds that conform to all rules outlined in the Introduction (see above) except rule (2). We modify rule (2) to state that the phases

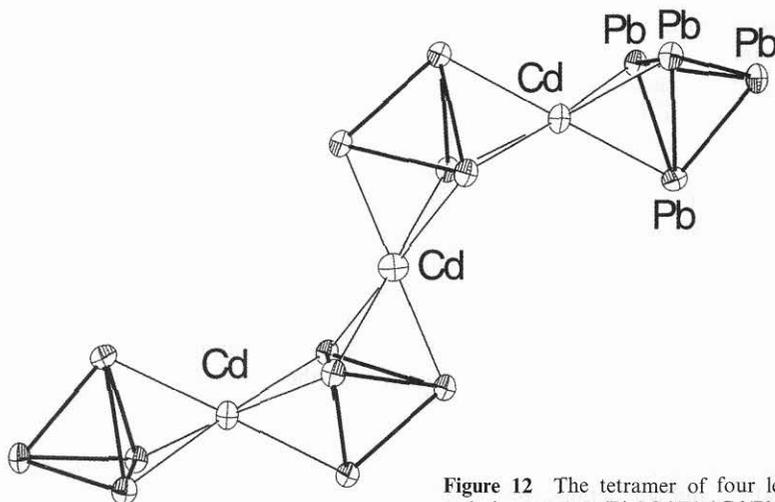


Figure 12 The tetramer of four lead tetrahedra joined by three cadmium atoms, $(\text{Pb}_4)\text{Cd}(\text{Pb}_4)\text{Cd}(\text{Pb}_4)\text{Cd}(\text{Pb}_4)$, found in $\text{K}_6\text{Pb}_8\text{Cd}$

'look like' they were nearly electronically balanced according to their structures but have a few extra electrons or holes.

2.2.1 Group 13

Gallium is perhaps the element with the greatest tendency to form networks of interconnected clusters, while it has only one compound with isolated clusters. The tendency for network formation diminishes drastically on going down the group, with thallium exhibiting only two such compounds, $A_{15}Tl_{27}$ for $A = Rb, Cs$ (Dong and Corbett, 1996a) and K_6Tl_{17} (*oC184*) (Corbett, 2000b), but a large number of isolated clusters. Indium is clearly in between with many examples of both networks and isolated species. The structural chemistry of the systems alkali metal – gallium has been extensively reviewed by Belin (Belin and Tillard-Charbonnel, 1993). A good example of a gallium network is the structure of KGa_3 (*tI24*) (Belin and Ling, 1982) which contains 8-atom clusters of gallium, each with 8 *exo*-bonds, and isolated 4-bonded gallium atoms, the two species in equimolar ratio (Figure 13). The clusters are of the *closo*-type and therefore require $2n+2=18$ electrons for skeletal bonding. Also, since each *exo*-bond is a normal 2-center–2-electron bond, half of the electrons needed for them, i.e. $(8 \times 2)/2 = 8$, are counted for the cluster as well. The total number of electrons required for the *endo*- and *exo*-bonding of the cluster is therefore $18+8=26$. The eight gallium atoms of the cluster bring $8 \times 3 = 24$ electrons and the charge of the cluster is $2-$, i.e. Ga_8^{2-} . The 4-bonded isolated gallium is in tetrahedral coordination and therefore has a formal charge of $1-$, i.e. Ga^{1-} , in order to achieve an octet. Thus, the equimolar combination of Ga_8^{2-} and Ga^{1-} will require 3 potassium atoms to balance the charge, and therefore the formula K_3Ga_9 ($=KGa_3$) can be represented as $3K^+ + Ga_8^{2-} + Ga^{1-}$. The compound is electronically balanced and a true Zintl phase.

Other examples of electronically balanced gallium networks of clusters are: K_3Ga_{13} (*oC128*) with 12- and 11-atom clusters, Li_2Ga_7 (*hR18*) with icosahedra, Na_7Ga_{13} (*hR360*) with icosahedra and 15-atom 'spacers', $RbGa_7$ (*hR32*) with icosahedra connected via 3-center–2-electron bonds, etc. More complex structures with fused deltahedra and/or partially occupied gallium sites also exist, and these are often 'metallic Zintl phases'. Such are Li_5Ga_9 (*oC56*), $Na_{22}Ga_{39}$ (*oP244*), $Li_3Na_5Ga_{19.57}$ (*oF896*), $Li_3K_3Ga_{28.83}$ (*oC328*), $Na_{13}K_4Ga_{49.57}$ (*hR138*), etc.

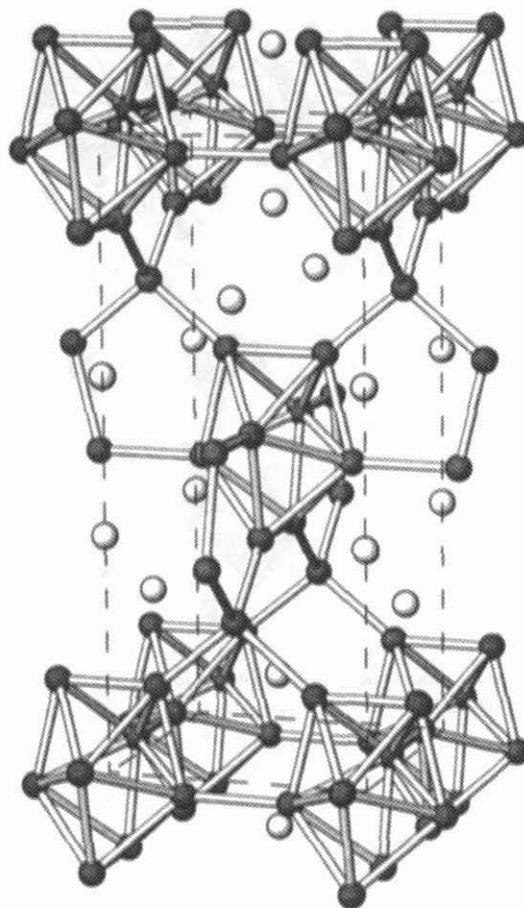


Figure 13 The structure of KGa_3 made of interconnected gallium (dark spheres) 8-atom *closo* deltahedra and isolated atoms

(Belin and Tillard-Charbonnel, 1993, and references therein).

There are also many indium networks made up of interconnected deltahedral clusters. Perhaps the simplest such network is found in Rb_2In_3 ($=Rb_4In_6$) (*tI20*) (Sevov and Corbett, 1993d), layers of 4-bonded octahedra made of indium (Figure 14). The electron count is straightforward: $2n+2=14$ for skeletal bonding, $2 \times 2 = 4$ for lone pairs on the two non-*exo*-bonded vertices, and $(4 \times 2)/2 = 4$ for the 4 *exo*-bonds. This totals 22 electrons required for bonding while the 6 indium atoms of the cluster provide only $6 \times 3 = 18$ electrons. The additional 4 electrons come from the 4 rubidium atoms, and the compound is electronically balanced. This is not the case, however, in $K_3Na_{26}In_{48}$

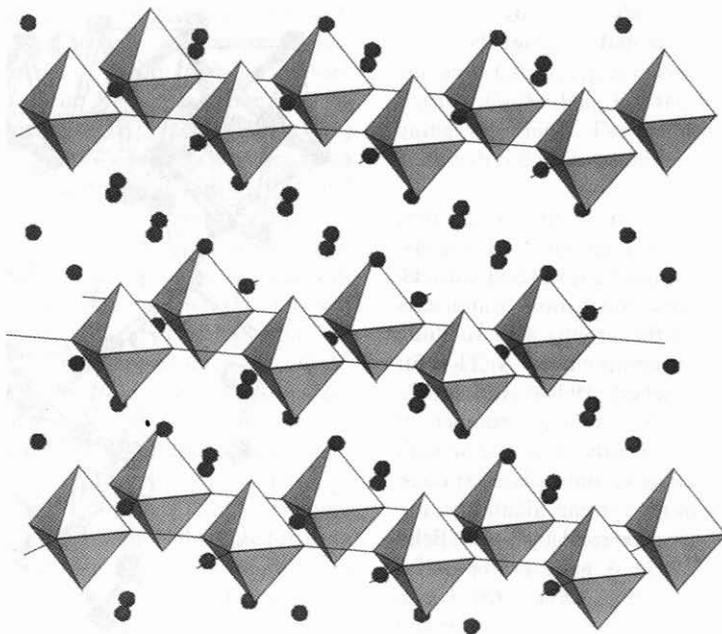


Figure 14 The structure of Rb_2In_3 made of layers of 4-bonded *closo* octahedra of indium and separated by the rubidium cations (isolated spheres)

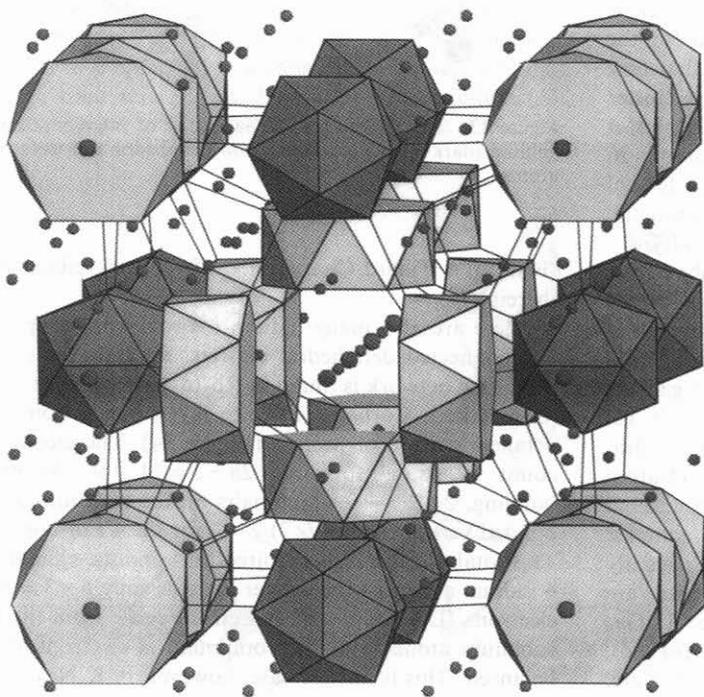


Figure 15 The structure of $\text{K}_3\text{Na}_{26}\text{In}_{48}$. The anionic network is made of interconnected icosahedra (darker polyhedra) and *arachno* 12-atom deltahedra (drum shaped, lighter polyhedra) of indium. The cations of potassium and sodium are shown as larger and smaller isolated spheres, respectively

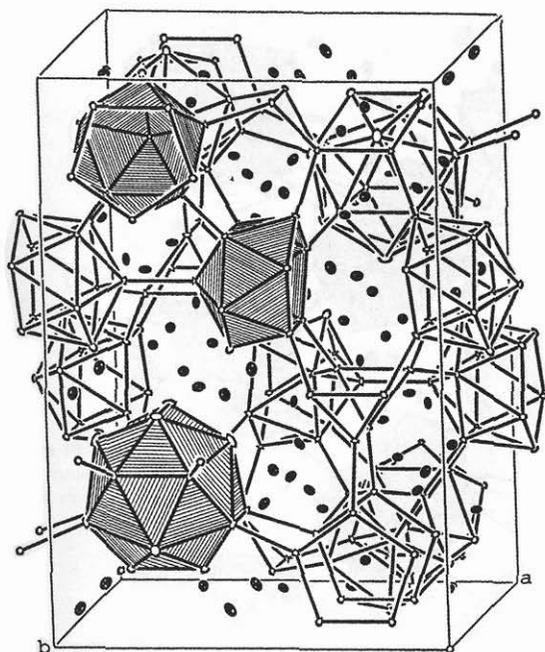


Figure 16 The structure of $\text{Na}_7\text{In}_{11.8}$ which contains 12-bonded *closo*- In_{16} clusters and *nido* icosahedra

(*cP154*) (Sevov and Corbett, 1993e), also with a network of clusters (Figure 15). The network is made of 12-bonded icosahedra (*closo*- In_{12}) and 6-bonded hexagonal antiprisms (*arachno*- In_{12}) in ratio 1:3. Each icosahedron requires $2n+2=26$ and $(12 \times 2)/2=12$ electrons for *endo*- and *exo*-bonding, respectively, while these numbers for the *arachno*- In_{12} are $2n+6=30$ and $(12 \times 2)/2=12$ electrons, respectively. Combined with the available $12 \times 3=36$ electrons from the 12 indium atoms forming the clusters, the charges are $2-$ and $6-$ for the *closo* and *arachno* species, respectively, i.e. *closo*- In_{12}^{2-} and *arachno*- In_{12}^{6-} in ratio 1:3. Thus the number of needed extra electrons to balance the charges of $1 \times 12 + 3 \times 12 = 48$ indium atoms is $1 \times 2 + 3 \times 6 = 20$. However, available are 3 potassium and 26 sodium atoms according to the formula, and therefore the compound is a 'metallic Zintl phase' with 9 extra electrons per formula.

Twelve-atom clusters, icosahedra, are typical for this group which is sometimes called the group of the icosagens. Nevertheless, indium has shown capabilities to form even larger *closo*-species. Sixteen-atom clusters of indium have been found in two different nonstoichiometric compounds, $\text{Na}_7\text{In}_{11.8}$ (*tP228*) and

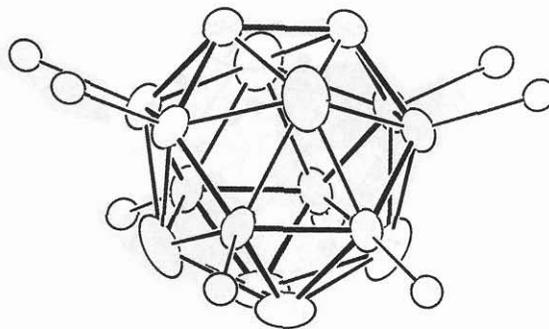


Figure 17 A closer view of the 12-bonded *closo*- In_{16} found in $\text{Na}_7\text{In}_{11.8}$. The shape can be considered as a tetracapped truncated tetrahedron. The 4 capping atoms are 6-bonded within the cluster and do not have *exo*-bonds. The truncated tetrahedron is shown with thicker bonds

$\text{Na}_{15}\text{In}_{27.4}$ (*oC344*) (Sevov and Corbett, 1992, 1993a). The network of the former (Figure 16) is made of three different species, 12-bonded *closo*- In_{16} , 11-bonded *nido*- In_{11} , and 4-bonded isolated indium atoms. The numbers of required and available electrons per cell are 504 and 507, respectively, or only 3 extra electrons (or 0.6%) available per 504 electrons and the compound is metallic, an 'almost Zintl phase'. The 16-atom deltahedral cluster is a new species found for the first time in this compound (Figure 17). Its shape can be understood starting from a tetrahedron, then truncating its 4 corners to form a 12-atom cluster species with 4 hexagonal faces, and finally capping those hexagonal faces with 4 additional indium atoms. It is highly spherical with the ideal geometry of point group T_d . As a result of this particular tetrahedral symmetry, the bonding within the cluster needs rather $2n+4$ electrons instead of the 'normal' $2n+2$ electrons for *closo*-species. The cluster is hyperelectronic.

2.2.2 Heteroatomic

In addition to the described networks of homoatomic clusters there are also many group 13-based networks of heteroatomic ones. Such are $\text{Na}_{102}\text{Cu}_{36}\text{Ga}_{279}$ (*hR417*) and $\text{Na}_{102}\text{Zn}_{72}\text{Ga}_{243}$ (*hR417*) with species of 3 face-fused icosahedra, $\text{Na}_{35}\text{Cd}_{24}\text{Ga}_{56}$ (*cF460*) and $\text{Li}_{38}\text{Zn}_{34}\text{Ga}_{67}$ (*hP834*) with 16-atom tetracapped truncated tetrahedra, and $\text{Li}_{13}\text{Cu}_6\text{Ga}_{21}$ (*cI160*) with interconnected icosahedra (Belin and Tillard-Charbonnel, 1993, and references therein). Indium-based ternary and quaternary compounds with heteroatomic clusters are also numerous, $\text{KIn}_{2-x}\text{Cd}_x$ (*hP90*) and

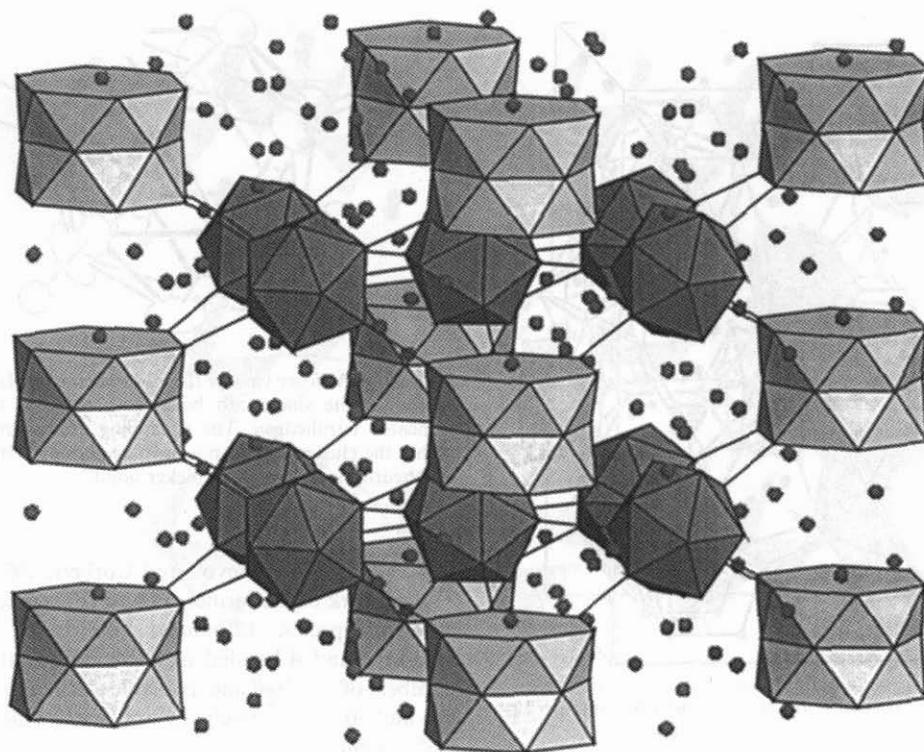


Figure 18 The structure of $\text{KIn}_{2-x}\text{Cd}_x$ with *arachno*- In_{18} deltahedra (lighter polyhedra) in the shape of double drums and icosahedra (darker polyhedra)

$\text{K}_{37}\text{In}_{69-x}\text{Cd}_x$ (*hR636*) (Sevov, 1993) with 12-bonded *arachno* 18-atom clusters (Figure 18), $\text{Na}_{23}\text{In}_{38.4}\text{Zn}_{4.6}$ and $\text{Na}_{23}\text{In}_{39.8}\text{Au}_{3.4}$ (*hP132*) (Sevov, 1993) with 15-bonded *closo* 15-atom clusters that are truncated trigonal prisms (Figure 19), and $\text{Na}_9\text{In}_{16.8}\text{Zn}_{2.3}$ (*cF448*) with 16-bonded *closo* 16-atom clusters (Sevov, 1993). All these are either electronically balanced or very close to being such. Once more, the thallium-based heteroatomic network compounds are only a very few. Known are $\text{K}_{14}\text{Cd}_9\text{Tl}_{21}$ (*hP88*) with interconnected pentagonal bipyramids (Tillard-Charbonnel *et al.*, 1997) and $\text{Cs}_5\text{Tl}_{11}\text{Cd}_2$ with columns of fused Cd-centered pentagonal antiprisms (Corbett, 2000b).

Perhaps the most spectacular ternary Zintl phases based on group 13 elements are those with fused 'fullerene'-like cages made of indium (Figure 20), $\text{Na}_{96}\text{In}_{97}\text{Z}_2$ (*hP195*) (Sevov and Corbett, 1993f) and $\text{Na}_{172}\text{In}_{192}\text{Z}_2$ (*oP732*) for $\text{Z} = \text{Ni}, \text{Pd}, \text{Pt}$ (Sevov and Corbett, 1996). The fullerene cages in these phases are made of pentagonal and hexagonal faces and contain

concentric spheres of sodium where the number of sodium atoms equals the number of fullerene faces (Figure 21). Nickel-centered clusters of In_{10} , just like those in $\text{K}_{10}[\text{In}_{10}\text{Ni}]$ (see above) are found inside the sodium spheres. The formula of one fullerene cage can be written as $\text{Ni}@\text{In}_{10}@\text{Na}_{36}@\text{In}_{74}$ where the symbol @ is used for 'within' (Figure 21). We should point out here that the stoichiometries of these compounds are extremely close to another Zintl phase, NaIn ($=\text{Na}_{96}\text{In}_{96}$) with a diamond framework of indium (Zintl and Dullenkopf, 1932). The difference is just 2 additional nickel atoms per nearly 200 atoms of sodium and indium! Although there is such a negligible difference in stoichiometry, the two structures, those of $\text{Na}_{96}\text{In}_{97}\text{Ni}_2$ and $\text{Na}_{96}\text{In}_{96}$, have nothing in common. Furthermore, although structurally extremely complicated, the $\text{Na}_{96}\text{In}_{97}\text{Z}_2$ compounds are diamagnetic, and therefore true Zintl phases.

Another group of compounds containing networks of heteroatomic clusters are based on mixtures of groups 12 and 14. Two compounds, $\text{Na}_{13}\text{Cd}_{20}\text{E}_7$

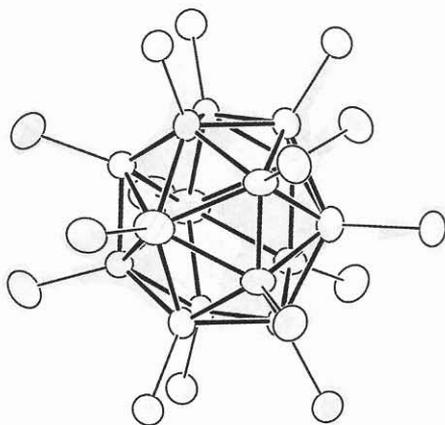


Figure 19 A view of the 15-bonded *closo*-In₁₅ with the shape of a truncated trigonal prism (the three-fold axis is vertical) found in Na₂₃In_{38.4}Zn_{4.6} and Na₂₃In_{39.8}Au_{3.4}

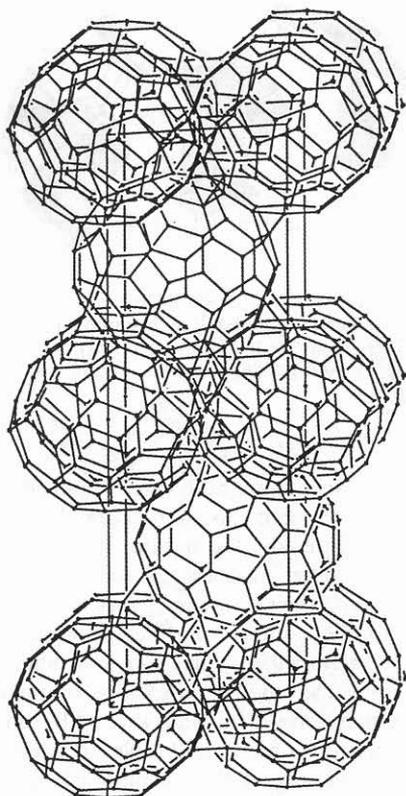


Figure 20 The indium framework in Na₉₆In₉₇Ni₂ made of face-fused fullerene-like cages of 74 and 60 atoms. The spheres are 'stuffed' with sodium cations and Ni-centered In₁₀ clusters (see Figure 21). The layers of cages are stacked in double hexagonal fashion, ABACAB, along the *c*-axis (vertical)

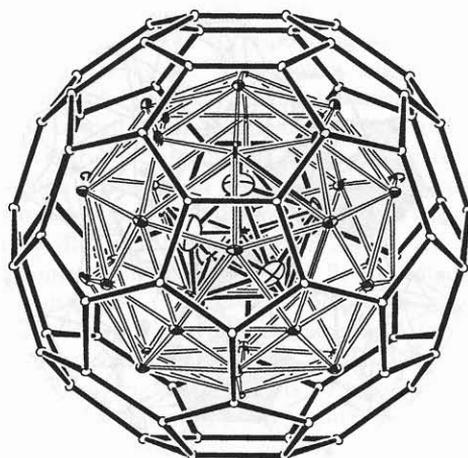


Figure 21 A closer view of a fullerene-like cage of indium made of 74 atoms. A nickel atom centers the sphere, a cluster of 10 indium atoms surrounds the nickel, and a sphere of 36 sodium atoms surrounds the indium cluster. The formation can be written as Ni@In₁₀@Na₃₆@In₇₄

(*cI160*) for E = Pb, Sn (Todorov and Sevov, 1997a) and Na₄₉Cd_{58.5}Sn_{37.5} (*hR580*) (Todorov and Sevov, 1997b), were synthesized recently. Both compounds contain empty icosahedra, the only examples of such species that do not involve group 13 elements. One way to rationalize that is, of course, to consider the isoelectronic relationship between an atom of group 13 and the average of an atom of group 12 and another one of group 14. In addition to the icosahedra, Na₄₉Cd_{58.5}Sn_{37.5} also contains 12-bonded *closo* deltahedra of 18 atoms, the largest *closo* deltahedra known so far (Figure 22). This cluster is also interesting from an electronic point of view since, as in the case of *closo*-In₁₆, it is *hyperelectronic* and requires $2n + 4$ bonding electrons. However, the violation of Wade's rules in this case is not due to the particular symmetry as in the case of In₁₆ but is rather due to the size of the cluster. Since the cluster is rather elongated, an 'extra' orbital that is bonding within the two hemispheres and antibonding between them becomes net-bonding and filled. Also of interest here is that the non-*exo*-bonded atoms of the cluster do not carry lone pairs of electrons, apparently due to the flatness of the coordination of these atoms. The planarity is a direct result of the size of the cluster, and therefore this cluster is beyond or at some critical size, above which atoms without *exo* bonds will have empty *p*-orbitals.

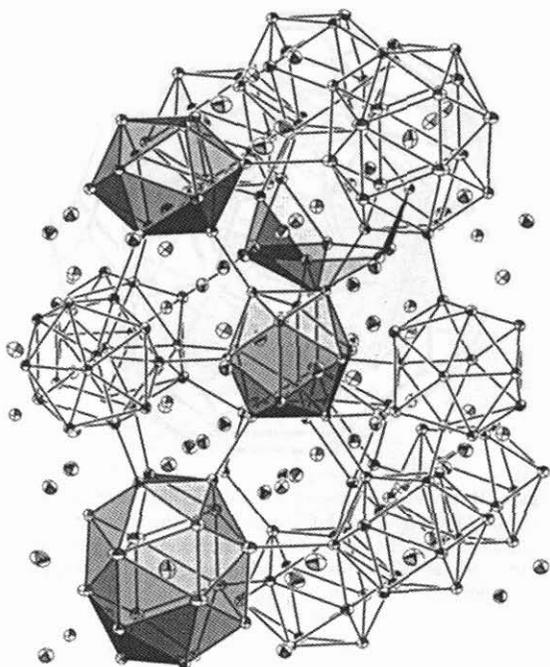


Figure 22 The structure of $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ with the largest *closo* deltahedron of 18 atoms. The cluster is 12-bonded to other cluster species in the structure. The potassium cations are shown as isolated spheres

3. Zintl Phases with Localized Bonding

The compounds in this category contain only regular 2-center–2-electron bonds between the p-elements. Most of them involve the relatively electron-rich p-elements, i.e. elements from the right-hand side of the p-block. The majority of compounds involve at least two p-elements of different groups and alkali metals, and are therefore mostly ternaries. An excellent review of these compounds by Eisenmann *et al.* has appeared recently (Eisenmann and Cordier, 1996). Many of the compounds contain tetrahedral units made of one of the p-elements and centered by the other, and often share corners or edges with each other. For example, isolated Sn-centered tetrahedra of antimony, $[\text{SnSb}_4]^{8-}$, are found in Na_8SnSb_4 (*cF104*) (Eisenmann and Klein, 1988). Chains and higher dimensional motifs of corner-sharing tetrahedra are found in many compounds. Chains characterize the structure of Na_3SnSb_3 , while a 3-D network of tetrahedra is found in $\text{Cs}_7\text{In}_4\text{Bi}_6$ (*aP17*) (Bobev and Sevov, 1999a), for example (Figure 23). There are also structures

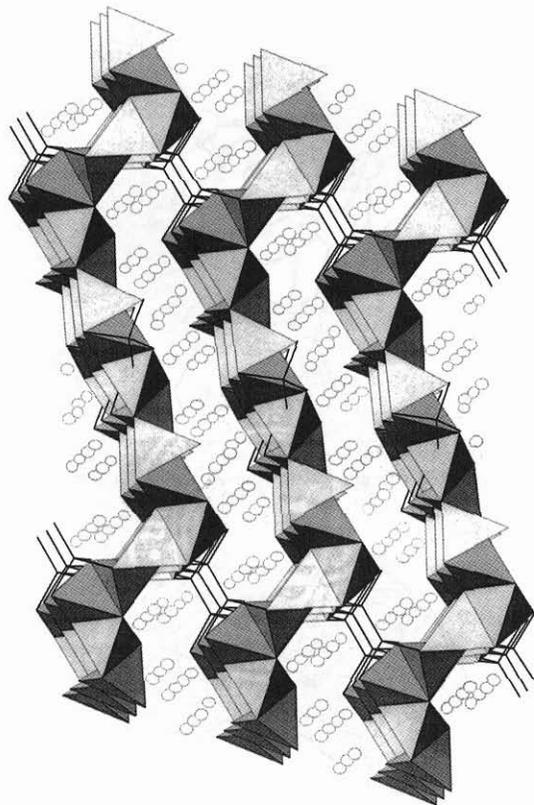


Figure 23 The structure of $\text{Cs}_7\text{In}_4\text{Bi}_6$ with chains of edge-sharing In-centered tetrahedra of bismuth. The chains are interconnected via In–In bonds (shown) to form a 3-dimensional network. The cesium cations are shown as isolated circles

where the tetrahedra are both corner- and edge-shared such as Ga-centered As_4 -tetrahedra in $\text{K}_3\text{Ga}_3\text{As}_4$ (*oP40*), In-centered As_4 -tetrahedra in $\text{K}_3\text{In}_2\text{As}_3$ (*oC64*), etc. The number of such heteroatomic compounds and their structural types is very large. In addition to the number of different ways of interconnecting tetrahedra, there are structures with isolated or connected flat AB_3 units, or mixtures of interconnected tetrahedra and such AB_3 units, etc. (Eisenmann and Cordier, 1996). Nevertheless, despite the structural variety, all these compounds have simple bonding, are easily understood by simple octet rule consideration, and since they have been extensively reviewed already (Eisenmann and Cordier, 1996; von Schnering and Hönle, 1988; Schäfer and Eisenmann, 1985; von Schnering, 1981; Schäfer and Eisenmann, 1981) they will not be discussed any further in this

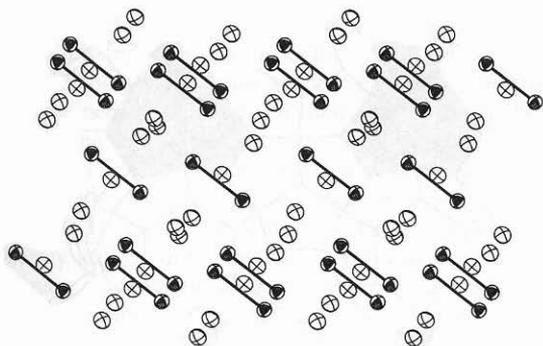


Figure 24 The structure of Cs_3Bi_2 with isolated dimers of Bi_2^{2-} . An extra electron is apparently delocalized on the cesium cations and antibonding Bi-orbitals

chapter. More emphasis will be given to new homoatomic compounds, i.e. one p-element combined with alkali metals.

3.1 Group 15

It is quite surprising that until recently there were blank spots of structurally unknown compounds in the simple binary systems alkali-metal-antimony and

alkali-metal-bismuth, and even in alkali-metal-arsenic. Studies of the corresponding liquid systems (van der Aart *et al.*, 2000) have suggested that structural units such as dimers, tetramers, squares, etc., exist in melts with stoichiometries A_3E_4 and A_3E_2 . Recently, structural studies in these systems revealed that similar units exist in the corresponding solid-state compounds (Gascoin and Sevov, 2000). Thus, compounds A_3Bi_2 (*oC15*) were found for $\text{A} = \text{K}, \text{Rb}, \text{or Cs}$. They contain Bi_2 -dimers with a Bi-Bi distance of 2.976 Å in Cs_3Bi_2 (Figure 24). Compounds with the stoichiometry A_3E_4 were characterized for both bismuth and antimony with $\text{A} = \text{K}, \text{Rb}, \text{or Cs}$. They contain planar zig-zag tetramers of bismuth (Figure 25) with end distances of 2.972 Å and a middle one of 3.036 Å. Magnetic and two-probe conductivity measurements suggest that the compounds are metallic. This combined with the stoichiometries and the structures of the compounds (the possible presence of hydrogen has been discarded based on neutron diffraction studies and indirect synthetic evidence) leads to only one possible explanation of their electronic structures. Similar to K_8In_{11} which can be written as $8\text{K}^+ + \text{In}_{11}^{7-} + e^-$ and other similar 'metallic Zintl phases' with extra electrons (see above), the two compounds A_3E_2 (*oC15*) and A_3E_4 (*oC18*) contain the species E_2^{2-} and E_4^{4-} , respectively, and an extra

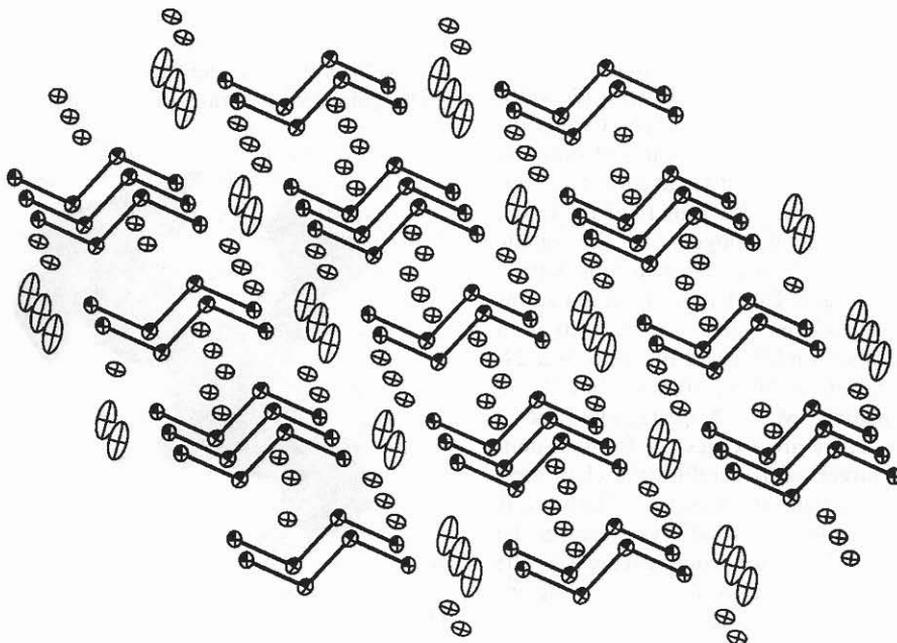


Figure 25 The structure of Cs_3Bi_4 with isolated tetramers of Bi_4^{4-} . Similarly to Cs_3Bi_2 (see Figure 24) there is a delocalized electron that makes the compound metallic

electron each. Their formulas can be written as $3A^+ + E_2^- + e^-$ and $5A^+ + E_4^- + e^-$, respectively. Furthermore, both bismuth compounds dissolve in ethylenediamine, and the compounds that can be crystallized from the solutions contain double-bonded dimeric $[Bi=Bi]^{2-}$ molecules (Xu *et al.*, 2000). This indicates that the dimer in A_3Bi_2 also has a double bond, and that the planar tetramer in A_5Bi_4 has one delocalized double bond with all bismuth atoms in sp^2 hybridization. The extra electrons in both compounds are delocalized over the alkali-metal cations and anti-bonding Bi—Bi orbitals (just as in K_8In_{11} , see above). The latter makes the bismuth distances somewhat longer than for the corresponding multiple bonding.

3.2 Group 14

Species with multiple bonding have been found for the elements of this group as well. Thus planar rings of silicon and germanium, Si_5^{8-} and Ge_5^{8-} , isoelectronic with cyclopentene, have been found in $Li_{12}E_7$ (*oP152*) (von Schnering *et al.*, 1980). Also, planar triangular star-shaped Si_4^{8-} and Ge_4^{8-} are found in the same compounds. These species are isoelectronic with CO_3^{2-} and similarly have a delocalized double bond.

Recently, a class of compounds called clathrates based on group-14 elements have attracted much attention due to their potential for thermoelectric applications. These compounds are A_8E_{46} (*cP54*) and $A_{24}E_{136}$ (*cF160*) (ideal stoichiometries) where A = alkali metal and E = group-14 element, identified as clathrate-I and clathrate-II, respectively (Cros *et al.*, 1965; Kasper *et al.*, 1965). The structures of both are built of fused cages of 4-bonded tetrahedral E-atoms, and the alkali metals occupy the centers of the cages. Clathrate-I type phases (analogous to the zeolite melanophlogite) crystallize in a primitive cubic lattice, space group $Pm\bar{3}n$ (Figure 26). The 46 clathrand atoms form two cages of different sizes: one is a 20-atom pentagonal dodecahedron $[5^{12}]$, and the other is a 24-atom tetrakaidecahedron $[5^{12}6^2]$ (the symbol $[5^{12}6^2]$ denotes a polyhedron with 12 pentagonal and 2 hexagonal faces). There are 8 cages per formula unit, 2 smaller and 6 larger, and therefore the clathrate-I formula can be written as $A_2A'_6E_{46}$. Clathrate-II (analogous to the zeolite ZSM-39) crystallizes in the face-centered cubic $Fd\bar{3}m$ space group (Figure 27). The framework-building atoms also form two different polyhedra. The difference, however, is that here in addition to the pentagonal dodecahedra $[5^{12}]$ the second type of polyhedra are built of 28 atoms, hexakaidecahedra $[5^{12}6^4]$, that have 12 pentagonal

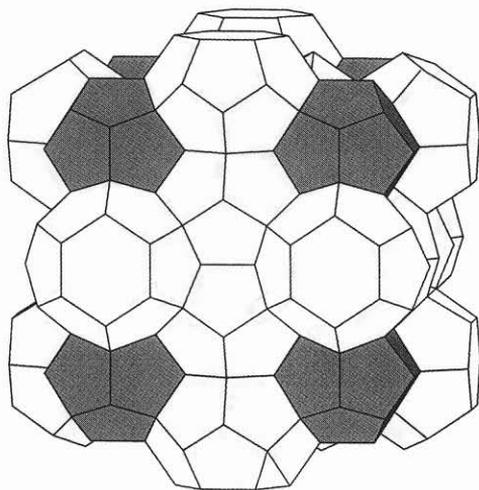


Figure 26 The structure of clathrate-I with cages made of 4-bonded elements of group 14. The clathrate has cages of 20 and 24 atoms shown as gray and white polyhedra, respectively. Alkali-metal cations (not shown) center the cages

and 4 hexagonal faces. The ratio of smaller to larger cavities in clathrate-II is 16:8 and therefore the formula can be written as $A'_{16}A''_8E_{136}$.

Four-bonded atoms of group 14 should have zero formal charge, and therefore both clathrates should be 'metallic Zintl phases' considering a full transfer of electrons from the alkali metal atoms to the framework atoms. Nevertheless, there are ways to achieve electronically balanced clathrates, i.e. to 'stabilize' true Zintl

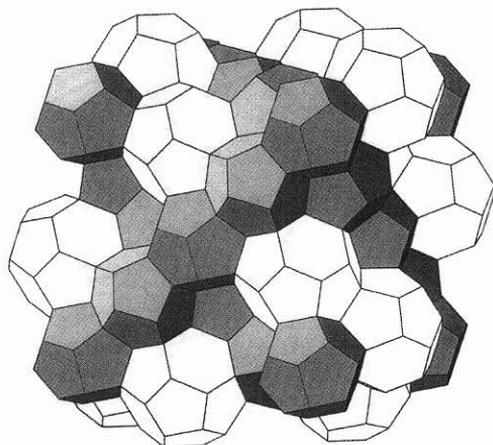


Figure 27 The structure of clathrate-II with cages of 20 and 28 atoms shown as gray and white polyhedra, respectively. Two types of cations with very different sizes such as Cs^+ and Na^+ stabilize this structure by occupying the centers of the two different cages

phases. One way is to form vacancies at the network sites as in $A_8Sn_{44}\square_2$ where \square is a vacancy at a tin site. Each missing tin atom leaves the 4 neighboring atoms with incomplete valence shells, i.e. 4 extra electrons will be needed to complete their octet configurations with lone pairs. Another way to balance the 'extra' electrons from the alkali metals is to substitute group-14 atoms with an electron-poorer element, from groups 13 or 12 for example. This idea has been widely utilized in the last 10–15 years for making new ternary phases with the clathrate-I-structure. The ideal stoichiometries will be $A_8E'_8E_{38}$ and $A_8E''_4E_{42}$ where E' and E'' are group-13 and -12 elements, respectively. The existence of many of these compositions and their compliance with the Zintl concept have been proven.

Even more complicated and difficult for interpretation are the compounds with the clathrate-II-type structure. Until recently, only the non-stoichiometric Na_xSi_{136} and Na_xGe_{136} phases were known in the binary A-E systems (Cros *et al.*, 1965, 1970). The structure of the former was recently refined from X-ray powder diffraction in order to determine the distribution of the sodium atoms within the two available alkali-metal sites, i.e. the centers of the pentagonal dodecahedra and the hexakaidecahedra (Ramachandran *et al.*, 1999; Reny *et al.*, 1998). It was concluded that for $x \leq 8$, the Na-atoms occupy preferably the larger $[5^{12}6^2]$ cage. Until very recently, there was no unequivocal structure determination for compounds with the clathrate-II type structure. The first well-refined structures from single crystal data and reproducible direct syntheses were reported for the stoichiometric and completely-filled silicon and germanium clathrate-II compounds with mixed alkali metals: $Cs_8Na_{16}Si_{136}$, $Cs_8Na_{16}Ge_{136}$, $Rb_8Na_{16}Si_{136}$, and $Rb_8Na_{16}Ge_{136}$ (Bobev and Sevov, 1999b, 2000). These compounds are stoichiometric and due to the extra 24 electrons per 136 group-14 atoms, they are also metallic Zintl phases.

4. Conclusion

Both the true Zintl phases and the 'metallic Zintl phases' are classes of fascinating compounds, some with clusters presenting delocalized bonding and some with 'normal' localized bonds. The variety and structural richness is quite obvious, and this is only a small percent of all possible combinations to be explored. The importance of these intermetallic compounds is primarily in the understanding of the chemistry of the p-elements in their negative oxidation

states. When in such unusual oxidation states many of these elements form bonds between themselves, form clusters and networks of clusters. These phases are potential starting materials for deposition of thin films or formation of nanoparticles of the corresponding element. Some of them may have good thermoelectric and semiconducting properties, and even may show superconductivity. There are definitely many new and more exciting compounds to be found.

5. References

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