

Excursions Beyond the Zintl Border: Anionic Clusters of the Heavier Group 13 Metals

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Several electronegative metals of the p-block are capable of forming anionic clusters or networks upon reduction by an alkali or alkaline earth metal. The first examples, tin and lead polyanion clusters such as Sn_9^{4-} and Pb_5^{2-} in ammonia solution, were characterized by Eduard Zintl in 1931.¹ By definition,² Zintl ions and solid phases derived from them are closed-shell valence compounds, distinct from intermetallic phases,³ whose electrons are globally delocalized. Since electron transfer from the electropositive metal to the p-block metal takes place, these compounds are classified as salts. Unlike intermetallic phases, Zintl phases are semiconductors, and examination of resistivity behavior is one way of distinguishing them.

Even in modern times, simple ideas originally proposed by Zintl can help to explain the structure of these species. The Zintl concept^{2,4,5} considers an element to behave as an isoelectronic one from a different family (a pseudoatom) based on its oxidation state. For example, thallium is a member of Group 13, the triel family, and has three valence electrons. When Tl is in the -1 oxidation state, it behaves as a pseudo-Group 14 (tetrel family) element, and forms four covalent bonds like C or Si. The Zintl concept, which originally assumed octet configurations for each atom, has since been modernized with MO theory to consider the electrons delocalized but still closed-shell. Another useful concept is the extension of Wade's electron counting rules developed for boranes to predict the structure of Zintl polyanions as *closo*, *nido*, or *arachno* polyhedra^{2,4,5}. The total number of valence electrons in the cluster is counted, and in a cluster of n atoms, $2n + 2$ electrons will result in a *closo* structure, while $2n + 4$ electrons will produce a *nido* structure, a polyhedron missing one vertex. Two more electrons result in an *arachno* structure, a polyhedron missing two vertices.

Zintl proposed that elements earlier than Group 14 could not form polyanion clusters, and the line between Groups 13 and 14 was later named the Zintl Border. Many counterexamples have been found in modern times, and the metals of the triel group are currently an exciting area of research due to their formation of novel, unpredictable structures.^{2,5} The structures tend to be hypoelectronic with respect to Wade's rules and are often more condensed than those of the later p-block. Distortions resulting in a more favorable MO structure are often observed in hypoelectronic clusters; extended Hückel calculations are often employed to better understand their bonding.

In recent years, new techniques^{2,5} have been developed to synthesize Zintl phases in the solid state. Typically, powders or pieces of the pure metals are placed in a tantalum tube, which is closed by arc welding and heated under vacuum for a long period. Tantalum vessels allow the escape of hydrogen, a frequent contaminant in the

starting materials. The products are characterized mainly by X-ray techniques, as well as measurements of magnetic susceptibility and electrical resistivity.

The electropositive alkali and alkaline earth metals are typically used as reducing agents in Zintl phase synthesis. The selection of a cation radius that will allow tight packing in the solid state is desirable since the Madelung energy strongly affects the stability of a phase.^{2,5} The employment of more than one cation, and variance of their proportions, has led to the formation of new and interesting phases, such as KNa_3In_9 .⁶ Triel clusters require high negative charges for stability, which results in high Madelung energies and negligible solubilities.

In addition to hollow cages, centered clusters have also been synthesized (Figure 1). The presence of a centering heteroatom helps to stabilize electron-deficient triel clusters, such as $\text{Tl}_{12}\text{Cd}^{12-}$,⁷ $\text{In}_{10}\text{Zn}^{8-}$,⁸ and $\text{Tl}_{11}\text{Pd}^{8-}$.⁹ Typically, members of the Ni or Zn groups play this role. The self-centered cluster Tl_{13}^{11-} has also been prepared¹⁰ and can be thought of as Tl_{12}^{14-} icosahedron (which does not exist by itself) centered by a Tl^{3+} cation.

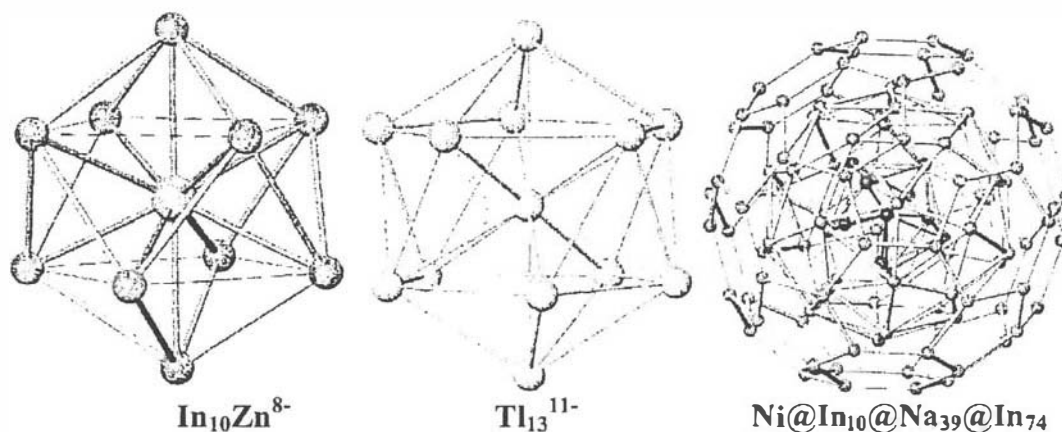


Figure 1. Examples of centered cluster structures.

One of the most interesting developments in Zintl chemistry is the discovery of “onion” compounds such as $\text{Ni@In}_{10}@Na_{39}@In_{74}$.¹¹ The cluster consists of nested fullerene-like spheres of indium separated by sodium cations and centered by a Ni, Pd, or Pt atom. The sodium cations are connected in the figure only to show their positions, not to imply the presence of Na-Na bonds. An In_{72} fullerene-like shell centered by a $\text{Cd}_{12}\text{In}_6$ cylinder has also been discovered,¹² as well as the “dented fullerene” tetrel cluster Sn_{56} .¹³ In contrast to carbon fullerenes, π -bonding is not observed in these clusters.

The distinction between Zintl phases and intermetallic compounds has been explored with phases such as $\text{Na}_3\text{K}_8\text{Tl}_{13}$ ¹⁰ and K_{10}Tl_7 ,¹⁴ as well as examples from the later p-block.¹⁵ The Tl_7^{10-} cluster is isostructural to the previously characterized Tl_7^{7-} , but the additional electrons are globally delocalized in what is thought to be a potassium-centered antibonding MO. Although this compound is not a true Zintl phase, it bridges the gap between Zintl phases and intermetallic phases, and is part of a new family of “metallic” Zintl phases.

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