Subject	**Chemistry**
Paper No and Title	**11, Inorganic Chemistry –III (Polyatomic zintl cations & anions and chevrel phases)**
Module No and Title	**34: Polyatomic zintl cations & anions and chevrel phases**
Module Tag	**CHE_P11_M34**

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1. Learning Outcomes

After studying this module, you shall be able to know about

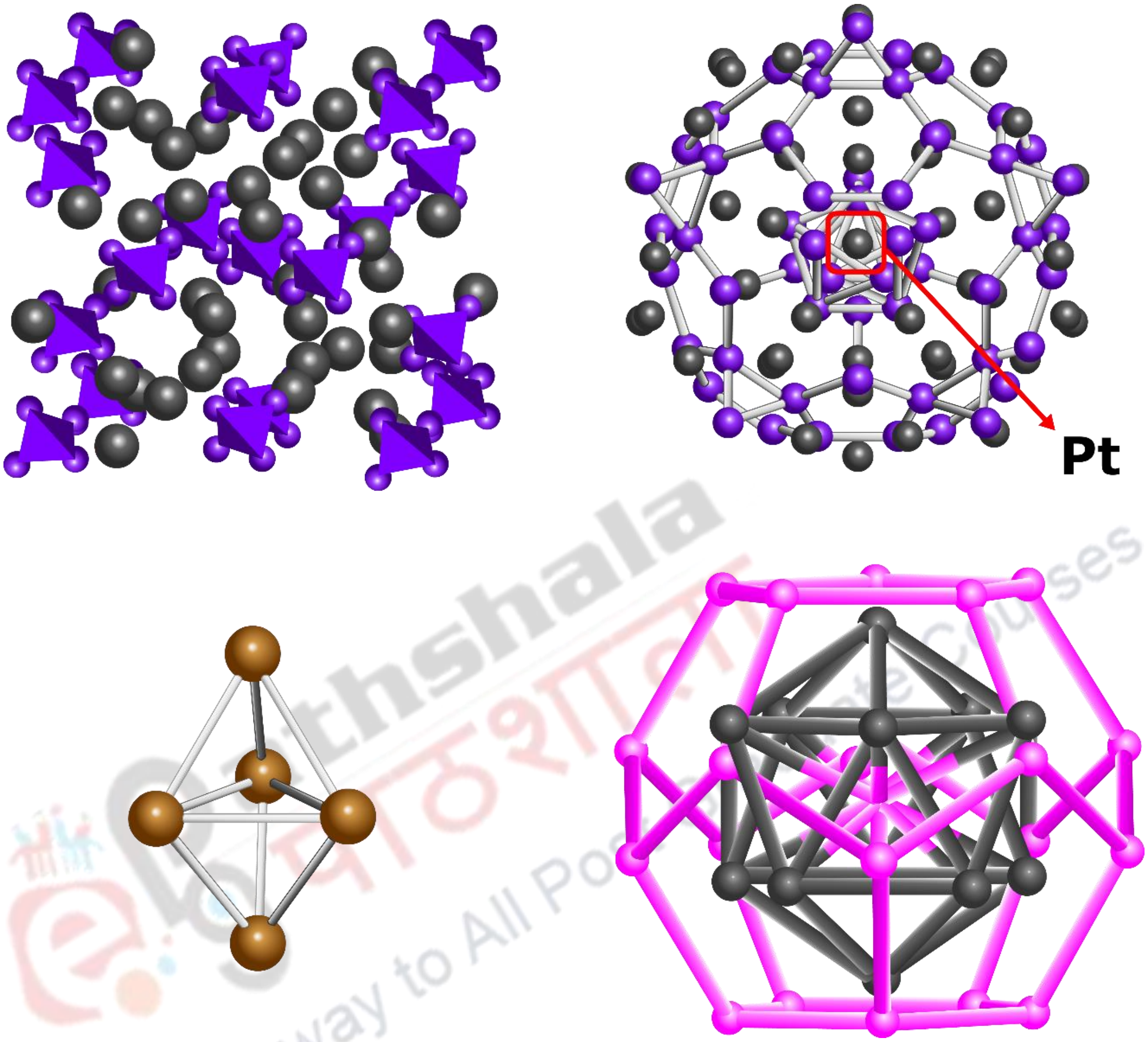
- Zintl phases and their structural features.
- Wade-Mingo rules to elucidate the structures of Zintl phases.
- Chevrel phases and their structures.

2. Introduction

The polyanions are well known in the literature which was observed by the change in characteristic blue color of the sodium ammonia solution on addition of an external metal. Zintl and coworkers were able to identify the composition of a large number of such compounds containing negatively charged main group metals and semi-metals. These were the first examples of compounds having metals in negative oxidation state. The zintl clusters or zintl phases are intermetallic compounds that are named after Edward Zintl who pioneered the exploration and structural rationale of such type of compounds. Zintl phases are not alloys. The main characteristics of zintl clusters are:

1. They consist of an alkali or alkaline-earth metal and a p-block element (or elements) which can be a metal, semi-metal or a small-gap semi-conductor.
2. They are closed shell compounds which are electronically balanced such that the number of electrons needed for covalent bonding in the structure is equal to the total number of electrons provided by the constituent elements.
3. They are semi-conductors or poor conductors.
4. They are either diamagnetic or possess very weak, temperature-independent paramagnetism.

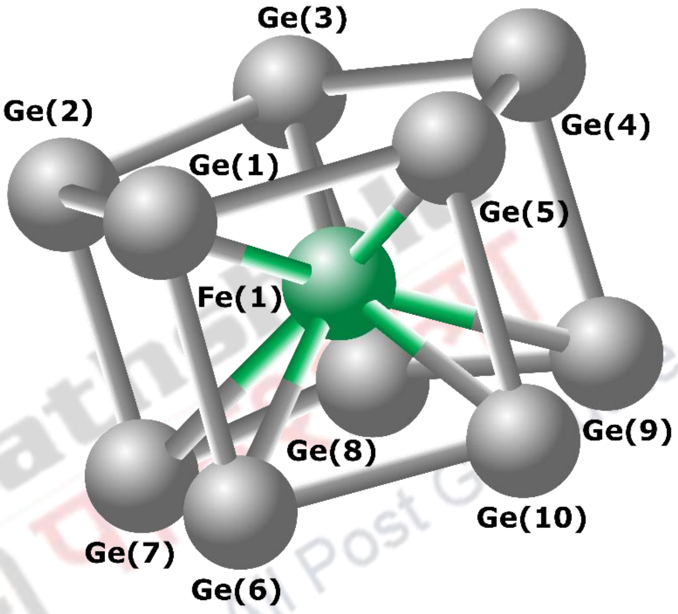
Basically zintl clusters are inter-metallic compounds that are the combinations of elements with very different electronegativity i.e., the very electropositive alkali or alkaline-earth metals and the post-transition elements. Since alkali/alkaline metals are strongly reducing and form zintl phases which contain the alkali metal cation together with a reduced, complex anionic species. Therefore Group 1 zintl phases are ionic compounds where there is an electron transfer from the alkali metal atom to a p-block atomic cluster to form a polyanion. The anions in these compounds are referred to as the ‘Zintl ion’ having a complete octet of valence electrons and are polymeric in nature, the cations are located within the anionic lattice. Depending upon the extent of reduction, the polyanionic structures of metals have wide range of structures such as 3D extended networks and 2D layers, two dimensional infinite chains, discrete polyanionic cages and intercalated compounds. These poyanions remain in solution and some of them have been isolated for structural characterizations. For example, the Group 14 elements (A) form compounds of stoichiometry M_4A_4 and M_4A_9 such as the K_4Ge_4 and Cs_4Ge_9. The Cs_4Ge_9 cluster consists of a monocapped square antiprismatic Ge_4^{9-} anion. The Group 13 elements form compounds like Rb_2In_3 and KGa containing the In_6 octahedra and Ga_8 polyhedral anions respectively. Group 13 elements also form compounds such as Al_5CuLi_3, $RbGa_7$, and K_3Ga_{13}. The compounds like Cs_5Bi_4 contain tetrameric chains of stoichiometry Bi_4^{4-}. Moreover the zintl clusters obtained from Group 1 cations such as $Na_{96}In_{91}M_2$ and $Na_{172}In_{192}M_2$, M = Ni, Pd, Pt display fullerene-shaped structures. The fullerene type cages in these phases comprises of pentagonal and hexagonal faces with one sodium atom per face of the fullerene. In the Nickel-centered cluster of the formula $K_{10}[In_{10}Ni]$, the Ni atoms are found inside the indium spheres. Therefore the formula of such type of intercalated compound is written as $Ni@In_{10}@Na_{36}@In_{74}$ where the symbol @ is used for ‘within’. Some of the structures are:



Top Left: The structure of K_4Ge_4 showing the K ions ad grey balls and Ge_4^{4-} tetrahedral in blue. Top right: The Part of the structure of $Na_{172}In_{192}Pt_2$ showing the complex fulleride-like networks formed by the In ions (blue) around Na (grey) ions and the Pt ion.

Botton left: The Zintl ion $[Sn_5]^{2-}$ has a trigonal bipyramidal cluster structure.
Bottom right: The Ni_{12} icosahedron inside the As_{20} dodecahedron in the icosahedrally symmetric $[As@Ni_{12}@As_{20}]^{3-}$.

An extremely interesting example is that of encapsulation of iron atom inside a pentagonal prismatic zintl ion $[FeGe_{10}]^{3-}$, the structure of which is shown below. At present, a large number of intercalated metal polyanions have been known which have been structurally characterized in detail.



$[FeGe_{10}]^{3-}$

One more interesting example of two clusters $Na_{96}In_{97}Ni_2$ and $Na_{96}In_{96}$, the stoichiometry of the two clusters have negligible difference of two additional Ni atom per 200 atoms of sodium and indium but the structures of the two compounds have nothing in common. The Ni containing cluster is fullerene-shaped whereas the other one diamond-shaped.

3. Group 14 zintl ions such as Germides, stannides and plumbides.

Unlike Carbon and Silicon, the other Group 14 elements such as germanium, tin and lead do not form binary compounds with metals. These metals instead form zintl phases and zintl ions which consist of clusters of these metal atoms. Some of the diamagnetic zintl ions of this Group are $[Ge_9]^{2-}$, $[Ge_{10}]^{2-}$, $[Sn_8Tl]^{3-}$, $[Sn_9Tl]^{3-}$ and

$[Pb_2Sb_2]^{2-}$ whereas the $[Ge_9]^{3-}$ and $[Sn_9]^{3-}$ are exemplified as paramagnetic. The general synthetic route to achieve zintl phases is by the reduction of Ge, Sn and Pb in solution of Na in liquid NH_3.

$$\mathrm{Sn} \xrightarrow{\text{Na in liquid NH}_3} \underset{\text{Zintl phase}}{\mathrm{NaSn}_{1.0-1.7}}$$

4. Wade's rule to elucidate the structure of zintl phases

Wade's rules were developed to define the structures of the borane clusters where a BH- unit contributes two electrons to the cluster bonding. In **zintl phases,** there exists a well-defined relationship between chemical and electronic structure which can be explained by applying Wade's rules.

1. Each group 13, 14 and 15 atom contributes one, two and three electrons to cluster bonding. Thus in the polyanionic cluster bare Ga, In, Tl vertices contribute one skeletal electron, bare Si, Ge, Sn or Pb atom contribute two electrons whereas the bare As, Sb and Bi units provide three electrons to the cluster. On similar line, the bare Se and Te provide four skeletal electrons.
2. Thus, a Si, Ge, Sn or Pb atom can mimic a BH^- unit. It can be said that the each group 14 elements is *isolobal* with a BH^- unit. Similarly the As, Sb and Bi vertices are isoelectronic with CH vertices.
3. The post-transition metals make use of a four orbital *sp*^{3} valence orbital set assuming that the inner shell d-orbitals are not involved in bonding but instead comprise non-bonding lone pair.

Some simple examples of homonuclear bare ionic post-transition metal clusters are mentioned as :

1. *Square shaped*: In Bi_4^{2-}, Se_4^{2+} and Te_4^{2+}, they all have 14 skeletal electrons. For example, in Bi_4^{2-} (4x3+2 = 14), the 14 electrons can corresponds to eight electrons for the four σ-bonds and four electrons to the two π-bonds whereas remaining two electrons constitute the two formal charges. Hence the structures of these polyanions are isoelectronic and isolobal with the delocalized planar cyclobutadiene dianion.

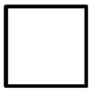
2. *Butterfly shaped*: In $Tl_2Te_2^{2-}$, the skeletal electron count is 2x1+2x4+2=12. Hence the structure consists of four σ-bonds and two π-bonds, isoelectronic and isolobal with neutral cyclobutadiene. However, the structure undergoes a Jahn-Teller type distortion at one of the four vertices leading to a butterfly-like structure.

3. *Tetrahedral*: For example $Sn_2Bi_2^{2-}$ and $Pb_2Sb_2^{2-}$ have 2x2+2x3+2= 12 skeletal electrons which is isoelectronic with a tetrahedron analogous to P_4.

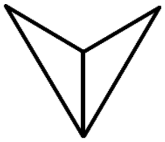
4. *Trigonal Bipyramidal*: Sn_5^{2-}, Pb_5^{2-} and Bi_5^{3+} have 12 skeletal electrons to make it analogous to a trigonal bipyramidal structure like that of a $C_2B_3H_5$ carborane.

5. *Seven vertex structures*: As_7^{3-} and Sb_7^{3-} have a different kind of skeletal electron count (4x3+3x1+3 = 18) for seven edges with three vertices of degree 3 (three bonds) and three vertices of degree 2 (two bonds).

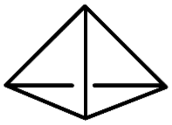
6. *Bicapped square antiprism*: Pb_{10}^{2-} has the 10x2+2 = 22 (2n+2 with n = 10). A 10 vertex structure is a D_{4d} detahedron analogous to that of $B_{10}H_{10}^{2-}$. $TlSn_9^{3-}$ is isoelectronic with Pb_{10}^{2-} and has similar structure. These structures are shown as:



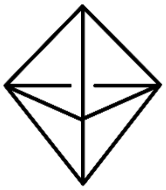
Square: Bi_4^{2-}, Se_4^{2+}, Te_4^{2+}



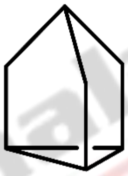
Butterfly: $Tl_2Te_2^{2-}$



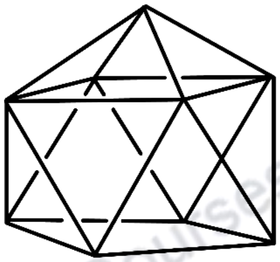
Tetrahedron: $Sn_2Bi_2^{2-}Pb_2Sb_2^{2-}$



Trgonal Bipyramid: Sn_5^{2-},Pb_5^{2-},Bi_5^{3+}



As_7^{3-},Sb_7^{3-}



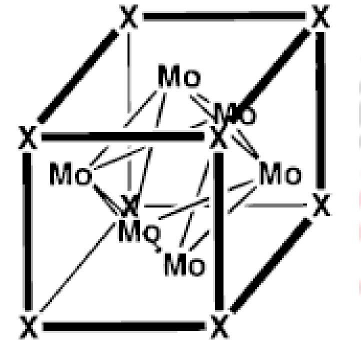
Capped Square Antiprism: Ge_9^{4-},Sn_9^{4-},Pb_9^{4-}

4. Chevrel phases

Chevrel phases are an important class of materials displaying spectacular physical and chemical properties such as high-temperature superconductance (14 to 15 K), extraordinary electrical and magnetic properties (remarkably high fields of 60 T at zero temperature). The general formula of clusters containing chevrel phases $M_XMo_6X_8$ where M can be a monovalent, divalent or trivalent element where x can vary from 0 to 4. The X is a chalcogenide anion (S, Se and Te) which can be substituted by a halogen or a oxygen anion. The main cation Mo can also be sometimes replaced by another transition metals like Nb, Ta, Re, W and others. The remarkable chemical and physical are closely related to the structural features of these clusters such as hosting a large number of external elements into the crystal structure.

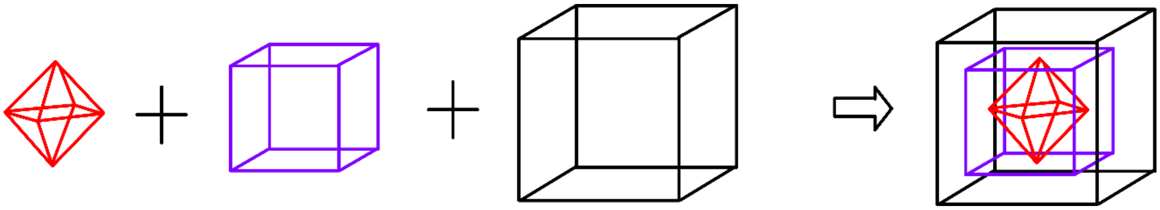
4. Structures of Chevrel phases

The metal clusters of molecular formula $M_XMo_6X_8$ are known as Chevrel phases. These are the first compounds possessing high temperature superconductivity and high critical fields. A common feature of the structure of these clusters compounds is a Mo_6 octahedron consisting of 6 tightly packed Mo atoms (Mo-Mo distances in the range of 2.67 and 2.78 Ǻ). Each face of the octahedron is capped by a sulphur atom forming a S_8 cube around the Mo_6 octahedron, thus there is a Mo_6 octahedron within a S_8 cube.



An Mo_6 octahedron inside a X_8 cube.

Thus each X atoms forms a nearly perfect cube encapsulating a Mo octahedron. Moreover, this Mo_6X_8 unit is contained within a larger cube of M atoms in such a way that all the three polyhedrons share a common threefold rotational axis.



In the real situation, the inner two polyhedra are rotated about a common threefold axis. For example, in the $PbMo_6S_8$ the inner two polyhedral are turned at an angel of 25°. In the Chevrel phases, each M atom is coordinated with X atoms cubically with two short and six longer M-X bonds. Hence, each X atom is tetrahedrally coordinated by three Mo atoms and one M atom.

5. Summary

1. Metal clusters are an important class of compounds displaying interesting physical and chemical properties. Among these, the zintl and chevrel phases are unique class of metal clusters. Zintl phases consist of an alkali or alkaline-earth metal and a p-block element (or elements) which can be a metal, semi-metal or a small-gap semi-conductor.
2. Group 1 zintl phases are ionic compounds where there is an electron transfer from the alkali metal atom to a p-block atomic cluster to form a polyanion. These polyanionic structures of metals have wide range of structures such as 3D extended networks and 2D layers, two dimensional infinite chains, discrete polyanionic cages and intercalated compounds.
3. The zintl clusters are commonly synthesized by the reduction of Ge, Sn and Pb in solution of Na in liquid NH_3.
4. Taking advantage of the relationship between chemical and electronic structure of the zintl phases, Wade-Mingo rules can be applied to elucidate the structural features.
5. Chevrel phases are an important class of materials displaying spectacular physical and chemical properties such as high-temperature superconductance (14

to 15 K), extraordinary electrical and magnetic properties (remarkably high fields of 60 T at zero temperature).

- The types of reactions that cluster complexes undergo are reactions with electrophiles and nucleophiles, oxidative addition reactions and reactions on the metal-metal multiple bonds.