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Study Notes on Metal Clusters

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Metal clusters

Metal clusters: These are compounds that contain metal-metal bond. Here, those compounds are considered which contain two or more metals in a closed array. CO is the most common ligand but there are other ligands also which can bound to clusters. In the presence of several metals, bonding arrangements takes place for the ligand which is not possible for monometallic compounds. There are variety of metal arrays that can be seen in cluster compounds like triangular, tetrahedral, and octahedral. These three are the most common metal arrays.

Types of metal clusters:

1. Clusters composed of three or more metals: These clusters get stabilized by small molecules that act as ligands and can be characterized by metal-metal bonds that can be either localized or delocalized over the metal framework.

2. Naked clusters: These clusters have no ligands, are electronically unsaturated, extremely reactive, their formation takes place in atomic beams.

Structure and bonding:

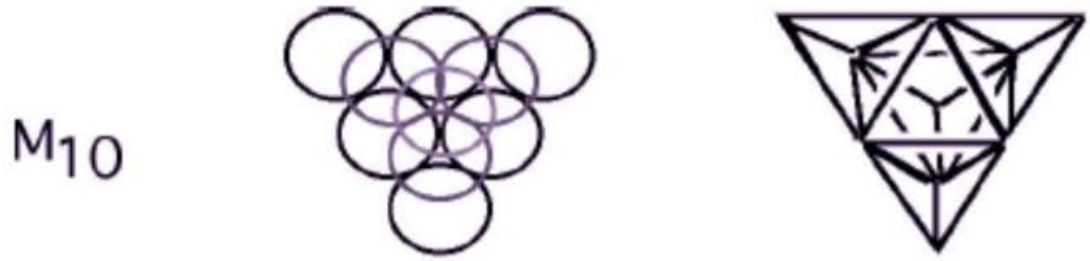
(1) Types of clusters

(i) π-Donor clusters: In this, early transition metals having oxidation states +2 or +3 form bond with π-Donor ligands such as Cl^-, Br^-, S^{2-}, O^{2-}. These clusters generally form triangular or octahedral geometries.

(ii) π-acceptor clusters: In this, late transition metals having oxidation state 0 or nearly 0 form bond with π-acceptor ligands such as CO, CNR, NO.

(2) Cluster geometries:

- **High symmetry**: It generally defines regular polyhedra as octahedra, tetrahedra, triangle.
- **Positions of metals** generally define triangular faces, square planar, trigonal prismatic.
- There are many clusters that represent fragments of ccp arrays of metal atoms like hcp, bcc.



tetracapped octahedron

octahedron less 1 vertex

- **Forms interstitial complexes** that contain H, C, S, N along with other metals. This is the case of high-nuclearity clusters.

Wade's rule: This rule is used to predict the shapes of boron clusters by determining the total number of skeletal electron pairs (SEP) that are available for bonding.

The general method to determine the type of boron cluster is:

- First determine the total number of valence electrons by using chemical formula- 3 electrons per B and 1 electron per H.
- Subtract 2 electrons from each B-H unit.
- In order to get skeletal electron pair, divide the remaining electrons by 2.
- For closo borane, a cluster has n vertices and n+1 SEP for bonding.
- For nido borane, a cluster has n-1 vertices and n+1 SEP for bonding.
- For arachno borane, a cluster has n-2 vertices and n+1 SEP for bonding.

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