

LESSON STRUCTURE

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1B.0 Objective

The studies of Boranes, which are compounds of Boron and Hydrogen has helped the chemists to understand the principles of chemical bonding and structure. The study of Boranes also open a versatile and extensive reaction chemistry.

1B.1 Introduction

Although B does not combine directly with H, a number of hydrides of B are known. These hydrides are covalent compounds and also called Boranes by analogy with alkanes. These are electron deficient compounds.

The 1976 Nobel Prize in chemistry was awarded to W.N.Lipscomb for his studies of Boranes.

Carboranes are derived from $B_nH_n^{2-}$ by replacing BH^- by isoelectronic and isostructural CH. It's structure can be explained on the basis of the structure of Boranes.

Wade's Rule gives a corelation between the number of electrons, the formula and the shape of the molecule.

Metal-metal multiple bonds follow the same symmetry as those in organic chemistry.

1B.2 Electron Deficient Compounds–Boranes

Electron deficient compounds are those in which the total number of atomic orbitals available on all the atoms of the compound is more than the total number of valence shell electrons. Or in other words, the molecules which do not contain enough electrons to form two electron covalent bonds between all the atoms are called electron deficient molecules.

Examples–

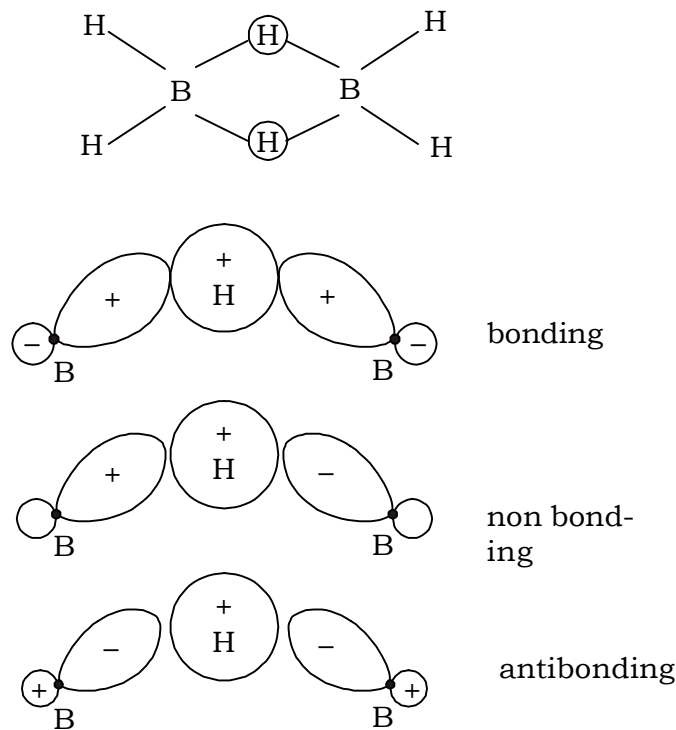


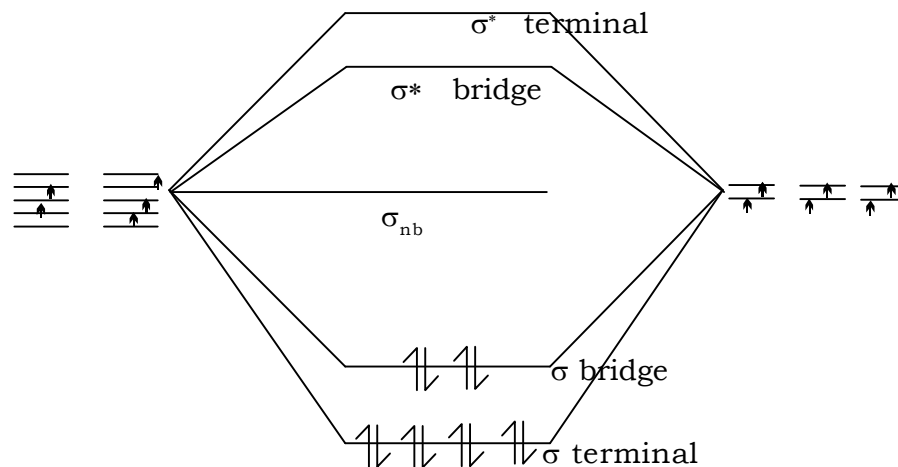
There are 12 valence electrons (6 from 2 B atom, and 6 H atom) but needs 14 electrons to form covalent bonds.



There are 6 valence electrons from 2 Al and 6 electrons from 6 Cl, but needs more than that.

Boron combines with HYdrogen to form a number of boranes. As BH_3 , is not formed, the simplest borane is diborane B_2H_6 . This is an electron deficient molecule. The evidence of bond lengths and angles, the infrared stretching frequency suggest that the terminal B–H are normal single bonds. The two bridging H atoms are formed as $2e-3C$ bonds. The three A.Os of 2B and 1H combine to form one bonding, one nonbonding and one antibonding M.Os.





A.O. of B + B

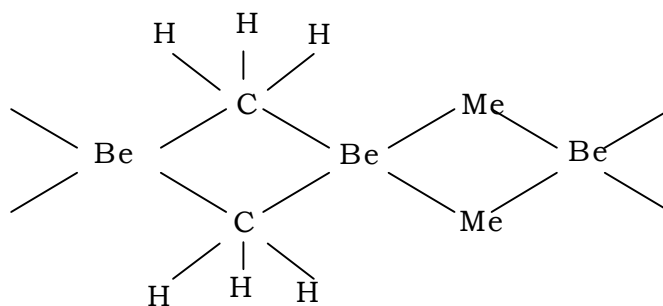
A.O. of 6H

M.O. of B_2H_6

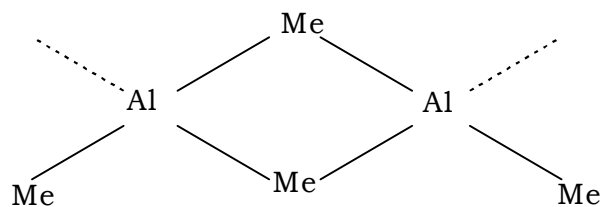
Molecular Orbital diagram of diborane

About 25 neutral Boranes and a large number of Borane anions are known to be present.

Other examples of electron deficient compounds are beryllium dialkyls and aluminium trialkyls.



X-ray analysis reveals a chain polymeric structure for dimethyl beryllium $Be(Me)_2$ as shown above.



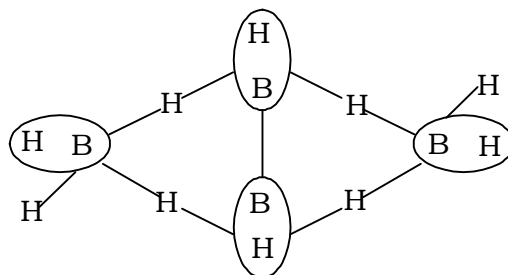
Aluminium trialkyl Al_2Me_6 is a dimer which contains two bridging groups of Me as shown above.

1B.4 Wade's Rules

A correlation between the number of electrons, the formula and the shape of the molecule was established by the British Chemist Kenneth Wade in 1970. Wade's rule apply to a class of polyhedra called deltahedra. A deltahedron is a polyhedron with all faces that are equilateral triangles. For molecular and anionic boranes, this rule helps us to predict the general shape of the molecule or ion from its formula. This rule is extended to other p block clusters and carboranes as it can be expressed in terms of electrons.

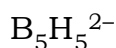
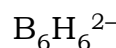
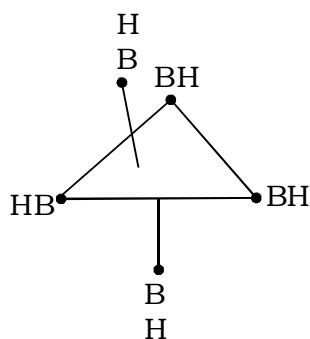
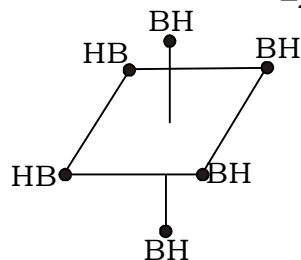
The building block of the deltahedron is BH group. The electrons in the BH group are ignored, but all the other electrons are counted as they help to hold the skeleton together. Each B–H bond is a unit. If B atom is attached to two H atoms, only one is treated as a part of B–H unit.

In B_4H_{10} , there are four BH units, Each BH unit makes two electrons available to the structure. 4 BH unit will contribute 8e and 6e will come from the remaining 6H atoms, making a total of 14e or 7 pairs of electrons.

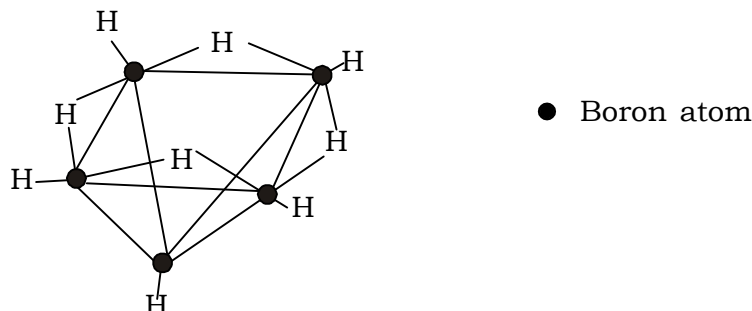


Two pairs of electrons are used for additional terminal B–H bond. Four are used for B–H–B bridge and one is used for B–B bond.

According to the Wade's Rule, Boranes of formula $B_nH_n^{2-}$ with $n+1$ pairs of skeletal electrons have a "closo" structure (Greek closo-cage) with a B atom at each corner of a closed deltahedron. This has no B–H–B bond or B–B bond. The value of n varies from 5 to 12.

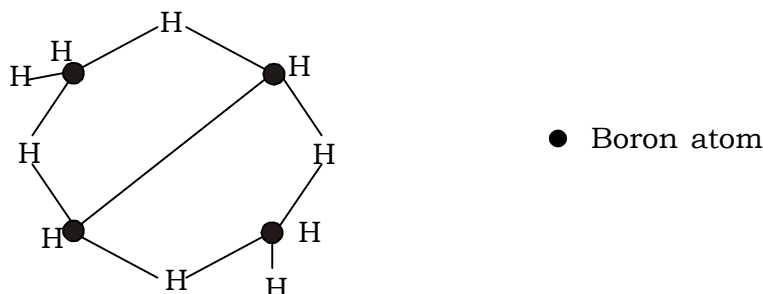

 -2

 -2


Boron clusters of formula B_nH_{n+4} and $n+2$ pairs of skeletal electrons have a "nido" (Latin nido–nest) structure. They are derived from closo borane which has lost one vertex. This has both B–H–B and B–B bond. e.g. B_5H_9



In general the thermal stability of nido borane is in between closo borane and arachno borane.

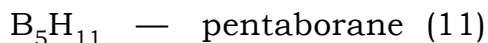
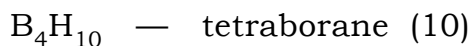
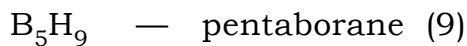
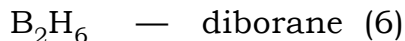
Borane clusters of the formula B_nH_{n+6} and $n+3$ skeletal electron pairs are called "arachno" (Greek-spider) structure. These are regarded as closo borane less two vertices. They have B–H–B and B–B bond. e.g. B_4H_{10}



Most arachno boranes are thermally unstable and highly reactive.

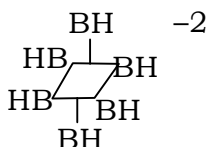
Type	Formula	Skeletal electron pairs	Examples
Closoborane	$B_nH_n^{2-}$	$n+1$	$B_5H_6^{2-}$, $B_6H_6^{2-}$, $B_{12}H_{12}^{2-}$
Nido borane	B_nH_{n+4}	$n+2$	B_2H_6 , B_5H_9 , B_6H_{10}
Arachno borane	B_nH_{n+6}	$n+3$	B_4H_{10} , B_5H_{11}

In naming neutral boranes, the number of B atom in the molecule is indicated with a Latin prefix to borane. The number of H atoms in the molecule is shown by a number in parenthesis. e.g.

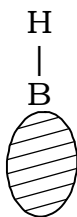


Using Wade's rule the structure of $[\text{B}_6\text{H}_6]^{2-}$ can be inferred from its formula and electron count as below.

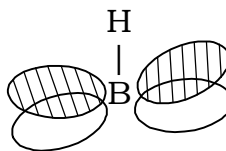
$[\text{B}_6\text{H}_6]^{2-}$ belongs to the closo structure from its formula. From electron count 6 BH will give $6 \times 2 = 12$ electrons + $2e^-$ from its charge making it to 14. This is $2(n+1)$ where $n = 6$. This number of $n + 1$ electron pair is characteristic of closo structure. Thus the structure is an octahedron as below.



Wade's Rule has been justified by Molecular Orbital calculations. In $\text{B}_6\text{H}_6^{2-}$ there is $n + 1$ skeletal electron pair, a B–H bond utilizes one electron and one orbital of the B atom, leaving three orbitals and two electrons for the skeletal bonding. One of these orbitals called a radial orbital can be considered to be a boron sp hybrid.

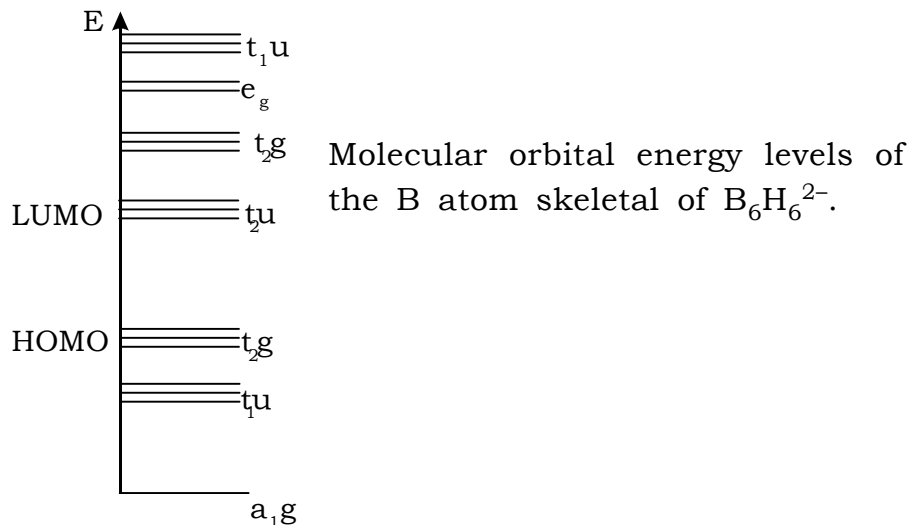


Radial Orbital



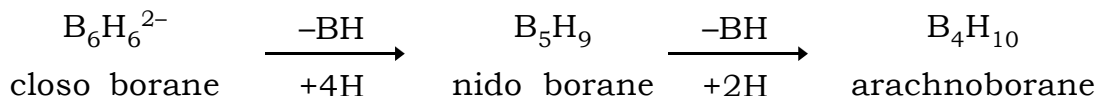
Tangential Orbital

The remaining two B p orbitals, the tangential orbitals are perpendicular to the radial orbital. The shapes of the 18 symmetry adapted linear combinations of these 18 orbitals in an octahedral B_6H_6 cluster.



The lowest energy $a_1 g$ arises from the contributions of all the radial orbitals, t_{2g} are tangential orbitals. These constitute the seven bonding orbitals which are occupied with seven pair of electrons.

The structural correlation between closo, nido and arachno boranes is based on the fact that clusters with the same number of skeletal electrons are related by removal of successive BH groups and addition of appropriate number of electrons and H atoms.



The concept of three center two electron bonds developed in connection with B_2H_6 was extended to higher boranes by the Noble Prize winner Lipscomb. The bonding scheme depends on the following:

- (i) Terminal 2C-2e B-H bond
- (ii) 2C-2e B-B bond
- (iii) 3C-2e B-H-B bond (bridge)
- (iv) Open 3C-2e B-B-B boron bridge bond



(v) Closed 3C-2C boron bond



The valence structures of boranes may be expressed in terms of their “styx” numbers based on the following code system.

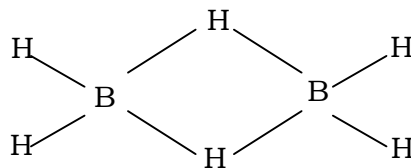
s = number of B-H-B bond

t = number of B-B-B bond

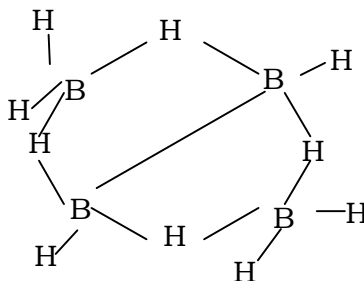
y = number of B-B bond

x = number of BH₂ group

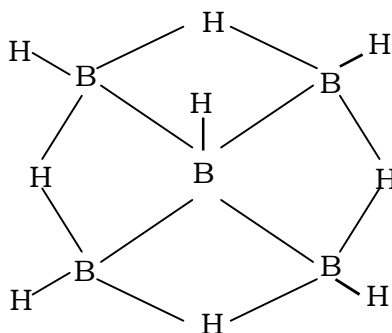
Diborane has styx number 2002



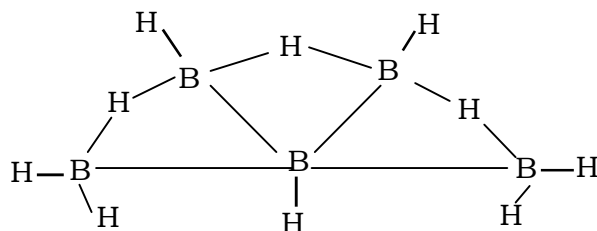
B₄H₁₀ has styx number 4012



B₅H₉ has styx number 4120

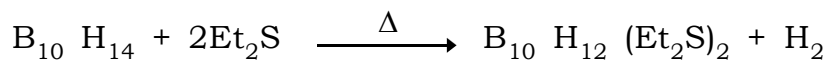


B_5H_{11} has styx number 3203

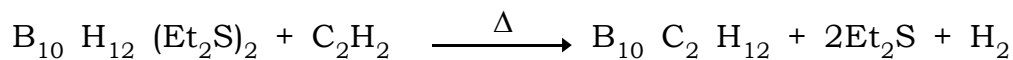


1B.5 Carboranes

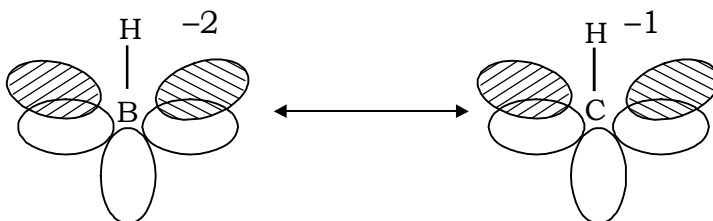
Carboranes are large family of clusters with contain both B and C besides H. These are derived from $B_nH_n^{2-}$ structures replacing BH^- by isoelectronic and isostructural CH. Replacements of $2BH^-$ by two CH results in neutral closo structures $C_2B_{n-2}H_n$.



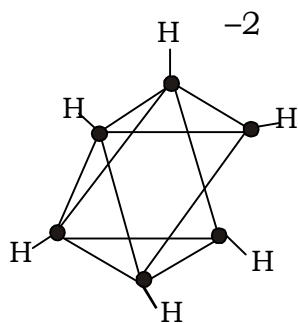
nido borane



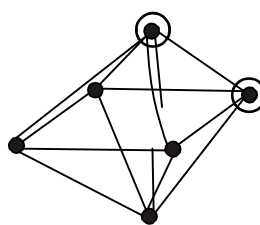
closo carborane



replacement of BH^- by CH



Closo $B_6H_6^{-2}$

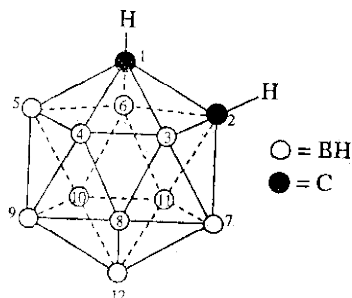
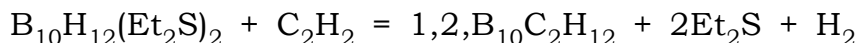
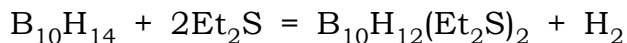


Closo 1, 2, $B_4C_2H_6$

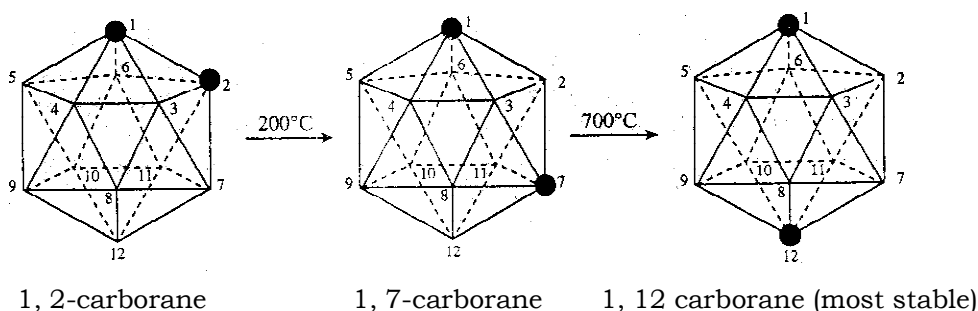
The nomenclature should depict the position of carbon atoms.

The carboranes follow the Wade's electron counting rule as in the case of boranes.

As already mentioned, $B_{10}H_{14}$ the decaborane(14) when heated with diethyl sulphide and acetylen gives 1,2- $B_{10}C_2H_{12}$



1,2. dicarba closo dodecarborane

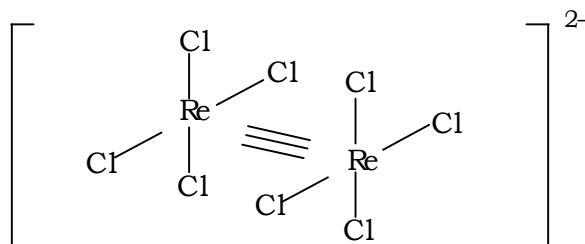


Depending upon the relative position of the two carbon atoms in the icosahedral frame work, three isomers of $B_{10}C_2H_{12}$ are possible. 1, 2 isomer as above rearranges it self to 1, 7 and 1, 2 isomers on heating as shown above.

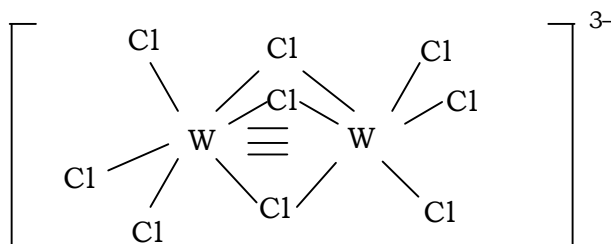
1B.6 Metal-Metal Multiple Bonding

Metal-metal bonds are known from a very long time, but lots of work in this field has been done in the last fifty years. Metal-metal multiple bonds follow the same symmetry as those in organic chemistry, then they go one better by allowing quadruple bond formation. Catenaion which was earlier to be thought only in organic chemistry, has proved very important in Inorganic chemistry.

X-ray diffraction shows that $[\text{Re}_2\text{Cl}_8]^{2-}$ has the structure shown below.



The eclipsed structure of the two sets of equatorial Cl^- ligands, rather than the staggered structure, would minimise Vander Waal's repulsions between the two sets of ligands. The eclipsed configuration is due to d_{xy} orbitals on each of two Re atoms. The short Re-Re bond distance of only 2.24 \AA is due to the presence of δ bonds between the two atoms. Another example is $[\text{W}_2\text{Cl}_9]^{3-}$



Another evidence for the presence of a δ bond is provided by the electronic configuration transition at $15,000 \text{ cm}^{-1}$ in the near IR region. The structure can be assigned to $\delta^* \leftarrow \delta$ transition. All the bonding orbitals in $[\text{Re}_2\text{Cl}_8]^{2-}$ is filled as shown below.

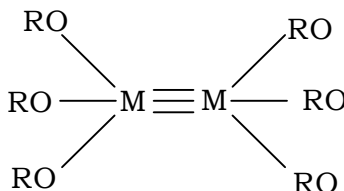
δ^*		
δ	$\uparrow\downarrow$	\uparrow
π	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
σ	$\uparrow\downarrow$	$\uparrow\downarrow$
bond order	4.0	3.5
Example	$[\text{Re}_2\text{Cl}_8]^{2-}$	$[\text{Mo}_2(\text{SO}_4)_4]^{3-}$

Qualitative Molecular Orbital diagram for dinuclear Re and Mo compounds.

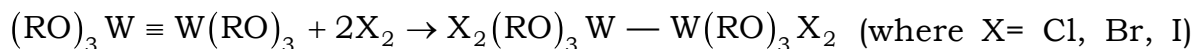
In $[\text{Re}_2\text{Cl}_8]^{2-}$, the bond order of 4 results from one σ , two π and one δ bond.

Cu(II) and Cr(II) also form acetate complexes of similar to $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$.

Among more interesting metal-metal multiple bonded complexes are hexaalkoxo dinuclear W and Mo complexes $[M_2(OR)_6]$ where $M = W, Mo$

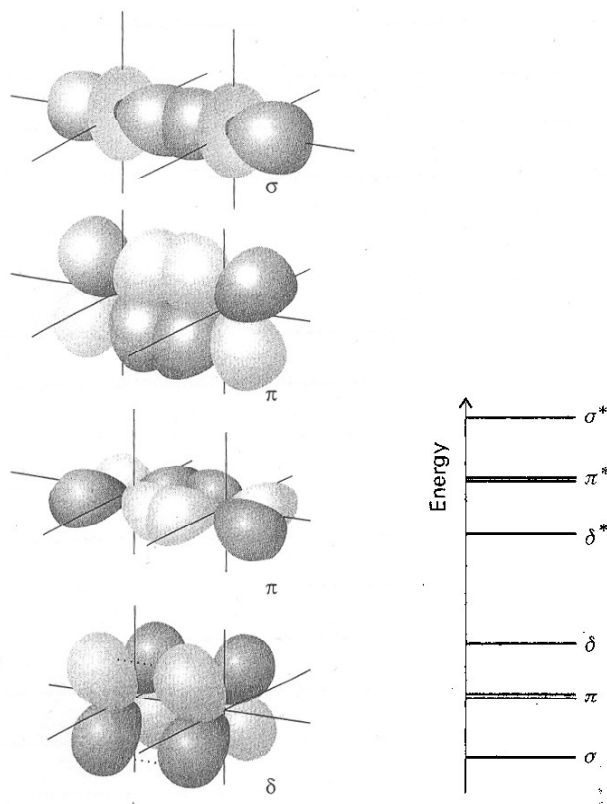


The $M \equiv M$ bonds are somewhat analogous to $C \equiv C$ as they undergo addition reactions.



Going down in the column of transition metal atoms, the increase in the Principal Quantum Number leads to the maximum in the radial distribution function moving farther from the nucleus and consequently the overlaps increase in the order $5d-5d > 4d-4d > 3d-3d$. This has a large effect on the relative strengths of metal bonding.

METAL-METAL BONDED d-METAL COMPOUNDS



The origin of σ , π , and δ interactions between two d-block metal atoms situated along the z-axis. Only the bonding combinations are shown.

Approximate molecular orbital energy level scheme for the M-M interactions in tetragonal-prismatic twometal clusters.

1B.7 Summary

The bonding pattern in electron deficient compounds is very interesting and different. The bonding in Boron hydrides can be approximated by conventional 2C–2e bonds together with 3C–2e bonds.

Boron hydride structures include polyhedral closo compounds and progressively more open nido and arachno structures. Styx number throws light on their structure.

When CH is introduced in place of BH⁻ in a polyhedral borane, the charge on the resulting carborane is one unit more positive. Carborane anions are very useful in boron containing organometallic compounds.

The transition metals form a wide range of compounds containing more than one metal atom. The short metal to metal distance suggest the presence of multiple metal–metal bonds due to the overlap of δ orbitals. The maximum metal–metal bond order may be five i.e one σ , two π and two δ bonds.

1B.8 Questions for Exercise

1. What are electron deficient compounds ? Give the molecular orbital description of diborane.
2. Write a short note on Wade's Rule. Using Wade's Rule infer the structure of $[\text{B}_6\text{H}_6]^{2-}$ from its formula and from its electron count.
3. (i) Draw structural formula of B_4H_{10} and B_5H_9
(ii) Suggest styx number of B_5H_9 and B_5H_{11} and give their IUPAC names.
4. What are boranes ? How are they classified ? Give the structure and bonding in any four of them.
5. (a) Write a short note on Carboranes.
(b) Draw structures of (1, 2), (1, 7) and (1, 12) dicarsa closo dodecarboranes.
6. Write short note on metal metal multiple bonding giving suitable examples.
7. Using Wade's rule predict the structures of the following:
 - (a) B_4H_{10}
 - (b) $[\text{B}_5\text{H}_5]^{2-}$
 - (c) B_6H_{10}

8. Draw the structure of diborane and explain its bonding. In what way it differs from bonding in C_2H_6 ?
9. Write short notes on the following–
 - (a) Classification of boranes with examples
 - (b) Electron deficient compounds with examples.
 - (c) Wade's Rule and its applications.
10. How are carboranes related to boranes ? How are carboranes prepared ?

1B.9 Suggested Readings

1. Advanced Inorganic Chemistry by Cotton and Wilkinson
2. Modern Inorganic Chemistry by Mackay and Mackay
3. Inorganic Chemistry by Shriver and Atkins
4. Inorganic Chemistry by Gary Wulfsberg