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1. Learning Outcomes

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

- The metal-metal bonds
- Overlapping of *d*-orbitals
- π-backbonding and its effects on various properties of molecule
- Bridge bonding and its type

2. Introduction

$d\pi$ - $p\pi$ Bonding

Though the p - p- π bonding is important for the second period elements, it is of little importance for heavier elements, which give multiple bonds through the use of d orbitals. Thus the bond order of 1.8 in the SO₄²⁻ ion (having no vacant p orbitals) indicates 80% π bonding, due to the overlap of filled p_z orbitals on an oxygen atom with the vacant low energy d_{sz} orbital on sulphur atom (Fig. 4.11).

The $d\pi$ - p- π bonding is more favourable as the d orbitals project into the general direction of the bond formations giving, a better overlap than the purely side overlap of p - p orbitals. The extent of the double bond formation increases in the series

 $PO_4^{3-} < SO_4^{2-} < ClO_4^{--}$

as the formal charge on the central atom increases, Oxyanion of fluorine is not stable as positive charge cannot reside on fluorine atom due to its high electro-negativity and the absence of any low energy orbitals rules out the possibility for the double bond formation)

2.1 Metal-Metal bonding

The general classes of metal-metal bonding are:

- 1. *Covalent bonding:* It is the most common type of metal-metal bonding. In this bond one electron is count from each metal center.
- 2. **Dative bonding:** In this type of bonding one metal make use of filled *d* orbital (lone pair) to coordinate to an empty orbital of the other metal. In most of the situations dative bonds are counted as covalent bonds.
- 3. *Symmetry bonding:* This type of bonding is not common as it is a weak metal-metal interaction caused by molecular orbital symmetry interactions of filled and empty metal-

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metal bonding or/and antibonding orbitals. This type of bonding is found in metals having d^8 configuration.

2.2 Overlapping of d-orbitals

The overlapping of d orbitals makes different types of metal-metal covalent bonds. Fig1 shows the types of covalent M-M interaction from strongest to weakest.



Overlap of two d_z^2 orbitals form a sigma bond which is stronger than the π bond formed by overlap of two d_{yz} or d_{xz} orbitals. Overlapping of d_{x2-y2} orbitals is not shown as it results in M-L bond formation.

Molecular orbital diagram for the interaction of two square planar metal centers is shown in fig 2.



Fig.2 The interaction of two square planar metal centers

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Initially electron fills the bonding orbitals but if more than 8 electrons is added, metal-metal bonds starts canceling and antibonding orbitals are began to form. The energy of antibonding orbitals is higher than the bonding orbitals therefore, antibonding orbitals are less stable.

The table given below shows the bonding between two square-planar metals. The metals having different geometry may have different bond orders.

| No. of | M-M bond |
|--|-------------|
| electrons | |
| d ¹ -d ¹ overlap | Single bond |
| d ² -d ² overlap | Double bond |
| d ³ -d ³ overlap | Triple bond |
| d ⁵ -d ⁵ overlap | Triple bond |
| d ⁶ -d ⁶ overlap | Double bond |
| d ⁷ -d ⁷ overlap | Single bond |
| d ⁸ -d ⁸ overlap | No bond |

 $*d^4 - d^4$ is the optimum case as it results in the formation of quadruple bond.

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Double Bonds t-Bu Ta=Ta=2.68 Å **Triple Bonds** d^sd^sTriple Bond Chisholm dsdsTriple Bond PhH₂C CH₂Ph PhH₂C/ PhH₂Ć CH₂Ph

Mo=Mo=2.17 Å

Os=Os=2.30 Å

Cr=Cr=2.27 Å

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Some examples of multiple covalent bonds:



3. π backdonation or π backbonding

When an electron is move from an atomic orbital of an atom to a π^* -antibonding orbital of a π -acceptor ligand this is known as π -backdonation or π -backbonding. It is found in the transition metals with multi-atomic ligands such as ethylene, carbon monoxide and nitrosonium. In this process the metal having excess of negative charge is used to bind the ligand. Complexes such as Ni(CO)₄ and Zeise's salt exhibit backbonding. It involves a synergic process in which the electrons from the filled π -orbitals or lone pair of the ligand are donated into an empty orbital of the metal and at the same time back donation of electrons take place from the *nd* orbital of the metal to the empty π^* -antibonding orbital of the ligand.

3.1 Types of backbonding

Back bonding is basically of two type i.e. central atom to side atom and side atom to central atom. As if central atom has lone pair of electrons or filled π -orbitals and side atoms have vacant orbitals then central to side backbonding takes place. For example in N(SiH₃)₃ where lone pair on nitrogen atom are involve in back bonding with empty orbitals of silicon. Opposite is the case with side to central atom backbonding. For example in BF₃ where, electrons from filled π -orbitals of fluorine are involve in backbonding with empty orbitals of boron atom.



Now backbonding can take place in three ways i.e. overlapping of $2p\pi$ - $2p\pi$ (metal-ligand), $2p\pi$ - $3p\pi$ (metal-ligand) and $3p\pi$ - $2p\pi$ (metal-ligand) orbitals. Since in $2p\pi$ - $2p\pi$ overlapping, the energy and symmetry of orbitals of both metal and ligands are same therefore effective overlapping will take place hence the $2p\pi$ - $2p\pi$ backbonding is highly stable. Therefore, with respect to effective overlapping of the orbitals, the order of stability of backbonding is $2p\pi$ - $2p\pi$ > $2p\pi$ - $3p\pi$ > $3p\pi$ - $2p\pi$.

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Note that $3p\pi$ - $3p\pi$ backbonding is not possible as if metal and ligand both are from 3rd period the size of both the atoms will be very large and effective overlapping will not take place.

3.2 Conditions of backbonding

The following conditions should be fulfilled for effective overlapping of atomic orbitals and formation of backbonds:

- 1. Metal atom should have vacant orbitals
- 2. Ligand should have lone pair of electrons or filled π -orbital.
- 3. At least one of the atoms should be from 2nd period. As if both are from 3rd period then effective overlapping will not take place.

4. Effects of backbonding

4.1 Bond length

Bond length of the molecule always decreases whether the backbonding is from central atom to side atom or from side atom to central atom. As due to backbonding partial double bond character is induced in the molecule as a result of which bond order increases and hence bond length decreases. This is the reason for short B-F bond length in BF₃ as compared to $[BF_4]$ ion.



4.2 Hybridization, shape and bond angle

Taking an example of BF₃ molecule, here lone pair on fluorine atom is donated to vacant π -orbital of boron and results in side to central atom backbonding. In this the hybridsation of molecule will not change and it remains sp^2 hybridised. Also the shape of the molecule remains trigonal planar.

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But in N(SiH₃)₃ as lone pair on nitrogen atom is donated to empty orbital of the silicon and central to side atom backbonding take place, the lone pair on nitrogen atom is no more in hybridization and hence the hybridization of the molecule is changes from sp^3 to sp^2 (percentage *s* character increases) and hence the geometry of the molecule also changes from pyramidal to trigonal planar. Now as the geometry of the molecule changes by change in hybridization. Bond angle of the molecule also changes.



4.3 Lewis acidic and Lewis basic character

Back bonding is nothing but intramolecular Lewis acid base interaction. For example on comparing the Lewis acidic character of BF_3 and BH_3 molecule, the Lewis acidic character of BF_3 .

is less than that of BH₃ because it undergoes backbonding due to which the π - orbital of the boron atom is no longer vacant and hence BF₃ cannot act as a Lewis acid.



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Similarly, in the case of $N(SiH_3)_3$ the lone pair of electron on nitrogen atom is involved in backbonding with vacant π - orbitals of Si atom. They are no longer available for further donation and hence N(SiH₃)₃ is less basic than N(CH₃)₃ which do not involve in backbonding as carbon atom do not have vacant π - orbitals.



This is the reason of better Lewis basic character of ethers than that of $(SiH_3)_2O$.



Either the lone pair or the vacant π -orbital of the molecules are involved in backbonding. In both the cases the efficiency of bond formation decreases. This is the reason for poor adduct of (SiH₃)₂O and BF₃ as both are involved in back bonding.

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Similarly NH₃ and BBr₃ forms good adducts because none of them are involved in backbonding. Therefore, we can say that the molecules which are better Lewis base can form better adducts.



4.5 Backbonding in borazine (Inorganic benzene)

Borazine is also known as inorganic benzene because its structure is similar to that of benzene. In borazine nitrogen and boron are bonded as a 6 membered ring or has 6π electron system similar to that of benzene. But as compared to benzene, borazine is kinetically less stable and thermodynamically more stable. This is due to backbonding between boron and nitrogen atoms which induced polarity within the molecule and the bond between nitrogen and boron become ionic.

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Now in borazine although nitrogen is more electronegative than boron but due to backbonding there will be a partial negative charge on boron and partial positive charge on nitrogen (nitrogen has lone pair of electron which are backbonded with vacant pi orbital of boron). For example if borazine is going to react with HCl then following reaction will take place:



Bridge bonding is another type of backbonding. It causes polarization in the molecule having vacant orbitals as they participates in hybridization. Due to which hybridization always increases to 1 step (i.e. $sp-sp^2$ and sp^2-sp^3) and percentage s character decreases.

5.1 Types of bridge bonding

Bridge bonding is of two type i.e. 3 centered-2 electron and 3 centered-4 electron bridge bonding. Bridge bonding is only possible if there is no backbonding and no steric crowding with in the molecule. BH₃ involves in bridge bonding and one extra σ bond is formed with another BH₃ molecule. Here, the shared pair electrons of boron and hydrogen atom are donated to the vacant π -orbital of the next boron atom. In this way 2 electrons are shared between 3 atoms i.e. 3centered-2electron bridge bonding will take place. The resultant B₂H₆ molecule is shown below:

| | | L |
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| | 11-4 | |
| | | 4 |
| | | |



The bridge bond of B_2H_6 is also known as banana bond. As the shape of bond is similar to that of banana. This is because of the hybridization (i.e. sp^3-s-sp^3) of boron-hydrogen-boron atom involves in bridge bonding.

On the other hand, $Al(CH_3)_3$ molecule also involves in bridge bonding in which 2 σ bonds are form between 2 molecules of $Al(CH_3)_3$. Here, 4 electrons from 2 of the Al-C bond are shared between 3 atoms and results in 3 centered-4 electrons bridge bonding. The resultant $Al_2(CH_3)_6$ molecule is shown below:



Here, the hybridization of Al-C-Al bridge bond is sp³- sp³-sp³.

To understand the chemistry of molecules involved in bridge bonding, let us take an example of B_2H_6 molecule.



Where, Ht - terminal hydrogen Hb - bridging hydrogen

Here, in the molecule there are two types of bonds i.e. bridge bonds and terminal bonds. Bridge bonds are stronger and longer than that of terminal bonds due to the following reasons:

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- 1. The formation of bridge bonds results in formation of a 4 membered ring and in order to stable the ring structure, the bridge bonds are longer than that of terminal bonds
- 2. Also, the bridge bonds are stronger because there are two electrons shared between three atoms and hence force by which electrons are hold with in the bond is more.

This can be explain by considering methylation of B_2H_6 . As it takes place on terminal bonds instead of bridge bonds and following product is form.



5.2 Cleavage of bridge bonding

There are two types of cleavage possible in molecules i.e. homolytic cleavage and heterolytic cleavage. In homolytic cleavage two electrons in a cleaved bond are divided equally between the products. And in heterolytic cleavage the bond break in such a way that the shared pair of electrons remain with one of the fragments. Taking an example of B_2H_6 , bulkier bases such as N(CH₃)₃ results in homolytic cleavage and form two molecules of BH₃ molecule because the bulky groups (i.e. CH₃) cause steric crowding therefore N(CH₃)₃ cannot attack on boron having more number of terminal hydrogen.



On the other hand lighter base such as NH_3 causes heterolytic cleavage and results in the formation of $[BH_2^+]$ and $[BH_4^-]$ as shown below:



[Heterolytic cleavage]

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6. Summary

- The overlapping of d orbitals makes different types of metal-metal covalent bonds.
- Overlap of two d_z^2 orbitals form a sigma bond which is stronger than the π bond formed by overlap of two d_{yz} or d_{xz} orbitals.
- The energy of antibonding orbitals is higher than the bonding orbitals in a molecular orbital therefore, antibonding orbitals are less stable.
- Backbonding involves a synergic process in which the electrons from the filled π -orbitals or lone pair of the ligand are donated into an empty orbital of the metal and at the same time back donation of electrons take place from the *nd* orbital of the metal to the empty π^* antibonding orbital of the ligand.
- Backbonding is basically of two type i.e. central atom to side atom and side atom to central atom.
- Back bonding can affect the following properties of a molecule:
- 1. Bond length
- 2. Hybridization, shape and bond angle
- 3. Lewis acidic and basic characters
- 4. Adduct formation
- Bridge bonding is another type of backbonding. It causes polarization in the molecule having vacant orbitals as they participates in hybridization.
- It is of two types i.e. 3 centered-2 electron and 3 centered-4 electron bridge bonding.
- Bridge bonding is only possible if there is no backbonding and no steric crowding with in the molecule.

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