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| <b>Chemistry</b> | <b>PAPER No.11 : Inorganic Chemistry-II</b>  |
|                  | <b>MODULE No.1 : <math>\pi</math>-acceptor ligand, metal carbonyls, bonding modes of CO, classification of metal carbonyls</b> |

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## 1. Learning Outcomes

After studying this module, you shall be able to:

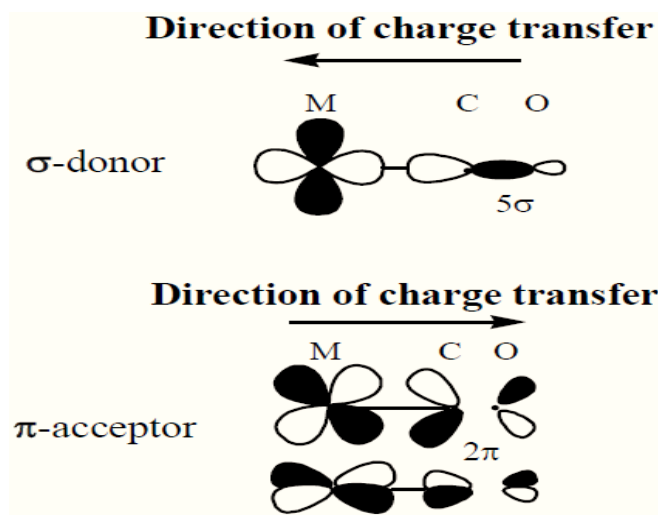
- Know about  $\pi$ -acceptor ligand.
- Learn different bonding modes of metal-carbonyl complexes.
- Identify types of bonding modes of CO-ligand.
- Analyse different symmetry properties.

## 2. Introduction

The  $\pi$ -acceptor ligands are a special class of ligands which contain  $\pi$ -bonds. The anti-bonding type  $\pi$ -orbitals in these ligands, if vacant and of comparable energy, may receive electron density from the filled metal orbitals with which the ligand is coordinated. Therefore, the ligand may act as a  $\sigma$ - or  $\pi$ -donor of the electron density to the metal ion and at the same time, it acts as a  $\pi$ -acceptor ligand. This process of  $\pi$ -acceptance of electron density of a ligand from the metal ion in a complex is an extremely important phenomenon in metal complexes which gives rise to a large number of chemical properties and applications. The  $\pi$ -back donation of electron density results in variations in the bonding properties of the ligand such as bond energy, this change in bond energy can be detected by various spectroscopic techniques and therefore the intensity of charge donation from metal to the ligand can be estimated in order to quantify various properties of the metal complex under consideration. Few examples of the  $\pi$ -acceptor ligands are ethylene, cyclic  $\pi$ -systems such as cyclopentadiene and carbonyls etc.

## 3. $\pi$ -acceptor Ligand or $\pi$ -acidity

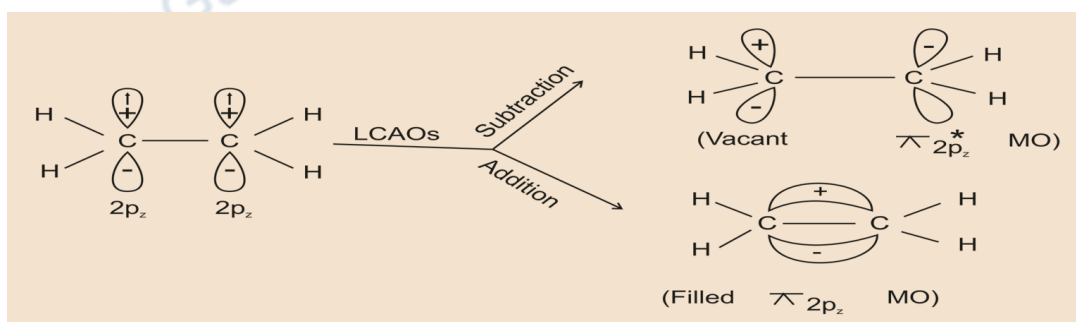
Ligands having empty orbitals which can interact with metal  $d$ -orbitals for the formation of  $\pi$ -bond are called  $\pi$ -acceptor ligands. These ligands possess vacant  $\pi^*$  anti-bonding molecular orbitals or empty  $d$ -orbitals of metals along with filled  $\sigma$ -orbitals. On bonding metal  $d$ -orbital donates its electron density to empty  $\pi$ -orbital of these ligands and this type of bonding is called  $\pi$ -backbonding.



Original metal  $d$ -orbital have lower energy than the acceptor  $\pi$ -orbital of the ligand, therefore the resulting MOs are of lower energy than the metal  $d$ -orbitals and antibonding orbitals are of higher energy. Hence, the ability of ligands to accept  $\pi$ -electron density from the metal into their low-lying empty  $\pi$  orbitals is called  $\pi$ -acidity and such ligands are called  $\pi$  acceptor ligands or  $\pi$ -acids in the Lewis sense. The  $\pi$ -acidity of various ligands increases with increase in the electronegativity of their atoms because it decreases the energy of vacant  $\pi^*$  molecular orbitals and make them more suitable to accept  $\pi$  electron density from metal  $d_\pi$  orbitals.

$\pi$ - acceptor or  $\pi$ -acidic ligand form two types of bonding with metal  $d$ - orbital.

i) Filled  $\pi_{2p_z}$  bonding molecular orbital & ii) Vacant  $\pi_{2p_z}^*$  antibonding molecular orbital



**Figure 1:** Showing two types of bonding done by  $\pi$ -acceptor ligands

## 4. Metal -Carbonyl Complexes

Metal carbonyls are important class of organometallic compounds that have been studied for a long time. CO is an unsaturated ligand, by virtue of C-O multiple bond. Such ligands are capable of accepting metal  $d_\pi$  electron by back bonding, i.e. these ligands are  $\pi$ -acceptor and therefore also called as hard ligands.

Being  $\pi$ -acidic in nature, CO is a strong field ligand that achieves greater  $d$ -orbital splitting through the metal to ligand  $\pi$ -back donation. A metal-CO bonding interaction thus comprises of a CO to metal  $\sigma$ -donation and a metal to CO  $\pi$ -back donation (Figure 2). Interestingly enough, both the spectroscopic measurements and the theoretical studies suggest that the extent of the metal to CO  $\pi$ -back donation is almost equal to or even greater than the extent of the CO to metal  $\sigma$ -donation in metal carbonyl complexes. This observation is in agreement with the fact that low valent-transition metal centers tend to form metal carbonyl complexes.

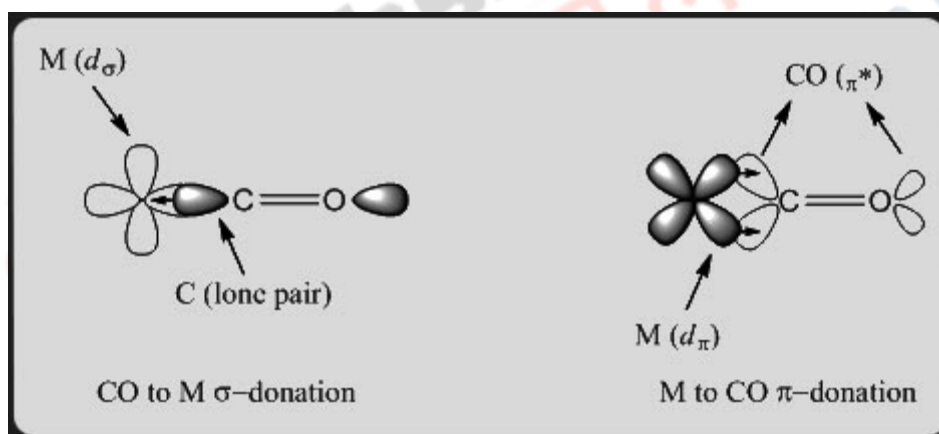


Figure 2: Showing  $\sigma$  and  $\pi$  bonding in metal-carbonyl complexes

In the metal carbonyl complexes, the direct bearing of the  $\pi$ -back donation is observed on the M-C bond distance that becomes shorter as compared to that of a normal M-C single bond distance.

Metal binds to C, not O, because the ligand HOMO is the Carbon, not the Oxygen-lone pair, this is because oxygen is more electronegative & so its orbitals have lower energy.

Dipole moment of free CO molecule is close to zero.

#### 4.1 Nomenclature in metal carbonyls:

The metal carbonyls are coordination compounds and hence their IUPAC names are written as per the rules approved for the nomenclature of coordination compounds. These rules are:

- 1.) The name of compound is written as one word. But if it is in ionic form then the ligands present in coordination sphere is written alongwith the type of ionic species attached to it e.g. if a cation is attached to it then it is written first then constituents in coordination sphere and if anion is attached then entities in coordination sphere and then the anion.
- 2.) In the coordination sphere, the ligands are named first but in alphabetical order before the name the name of the metal ion or atom. The numerical prefixes such as di, tri, etc. which indicate number of a particular ligand should be ignored.
- 3.) Oxidation state of metal atom is written in Roman numeral in parenthesis next to it without leaving any space between them.

| Metal carbonyl           | Common name          | IUPAC name                       |
|--------------------------|----------------------|----------------------------------|
| Ni (CO) <sub>4</sub>     | Nickel tetracarbonyl | Tetracarbonylnickel(0)           |
| Fe (CO) <sub>5</sub>     | Iron pentacarbonyl   | Pentacarbonyliron(0)             |
| [Mn(CO) <sub>6</sub> ]Cl |                      | Hexacabonylmanganese(I) chloride |

#### 4.2 Classification of Metal Carbonyl complexes :

The metal carbonyls can be classified in a number of ways.

##### 4.2.1 On the basis of nature of ligands:

On this basis metal carbonyls are of two types.

##### a) Homoleptic metal carbonyls:

The metal carbonyls which contain only carbon monoxide molecule as ligand are called homoleptic metal carbonyls. Examples- [Ni (CO)<sub>4</sub>], [Fe(CO)<sub>5</sub>], [Cr (CO)<sub>6</sub>], etc.

##### b) Heteroleptic metal carbonyls:

The metal carbonyls which contain some other ligands also in addition to carbon monoxide are called heteroleptic metal carbonyls. Examples-[CoH(CO)<sub>4</sub>], [Rh(CO)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>, [Rh(CO)H(PPh<sub>3</sub>)<sub>3</sub>], [Pt(CO)<sub>2</sub>Cl<sub>2</sub>], etc.

#### 4.2.2 On the basis of number of metal atoms present per molecule:

On this basis metal carbonyls are of two types.

##### a) Mononuclear metal carbonyls:

The metal carbonyls which contain only one metal atom per molecule are called mononuclear metal carbonyls. Examples- $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Cr}(\text{CO})_6]$ , etc.

##### b) Polynuclear metal carbonyls:

The metal carbonyls which contain more than one metal atom per molecule are called polynuclear metal carbonyls. Examples-  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Co}_4(\text{CO})_{12}$ ,  $\text{Ir}_6(\text{CO})_{16}$ , etc.

Polynuclear metal carbonyls are further of two types.

##### i) Homonuclear metal carbonyls:

The polynuclear metal carbonyls which contain identical metal atoms are called homonuclear metal carbonyls. Examples,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Co}_4(\text{CO})_{12}$ ,  $\text{Ir}_6(\text{CO})_{16}$ , etc.

##### ii) Heteronuclear metal carbonyls:

The polynuclear metal carbonyls in which different metal atoms are present are called heteronuclear metal carbonyls. Examples,  $\text{MnRe}(\text{CO})_{10}$ ,  $\text{MnTc}(\text{CO})_{10}$ , etc.

#### 4.2.3. On the basis of charge on the coordination sphere:

On this basis metal carbonyls are of three types.

##### a) Neutral metal carbonyls:

The metal carbonyls in which there is no charge on the coordination sphere are called neutral metal carbonyl. Examples,  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Cr}(\text{CO})_6]$ , etc.

##### b) Cationic metal carbonyls:

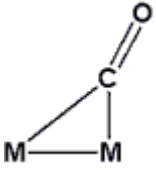
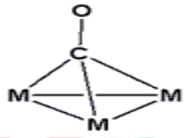
The metal carbonyls in which there is positive charge on the coordination sphere are called cationic metal carbonyl. Example-  $[\text{Mn}(\text{CO})_6]^+\text{Cl}^-$ .

##### c) Anionic metal carbonyls:

The metal carbonyls in which there is negative charge on the coordination sphere are called anionic metal carbonyl. Examples-  $\text{Na}[\text{V}(\text{CO})_6]$ ,  $\text{Na}_2[\text{Fe}(\text{CO})_4]$ ,  $\text{Na}[\text{Co}(\text{CO})_4]$ , etc.



## 5. Bonding modes of carbonyl:

| Bonding Modes of CO   | Range for $\nu(\text{CO})$ in neutral complexe ( $\text{cm}^{-1}$ ) |
|---|---|
| Free CO   | 2143  |
| Terminal M-CO   | 1850-2120   |
| Symmetric $\mu_2\text{-CO}$    | 1700-1860   |
| Symmetric $\mu_3\text{-CO}$  | 1600-1700   |

## 6. Properties in terms of symmetry, IR etc. :

### 6.1 In Terms of Symmetry:

Higher the symmetry of the complex lower the bands in  $\nu(\text{CO})$  stretching frequency of the complex. For example, in  $[\text{M}(\text{CO})_x \text{L}_y]$  complex, where  $x=3,4,5,6$  and  $y=0,1,2,3$  respectively.



| Structure of complex                    | Number of $\nu(\text{CO})$ band | Point group of complex |
|---|---------------------------------|------------------------|
| 1.) $[\text{M}(\text{CO})_6]$           | 1                               | $\text{O}_h$           |
| 2.) $[\text{M}(\text{CO})_5\text{L}]$   | 3                               | $\text{C}_{4h}$        |
| 3.) $[\text{M}(\text{CO})_4\text{L}_2]$ |                                 |                        |
| a.) Trans                               | 1                               | $\text{D}_{4h}$        |
| b.) Cis                                 | 4                               | $\text{C}_{2v}$        |
| 4.) $[\text{M}(\text{CO})_3\text{L}_3]$ |                                 |                        |
| a.) Meridional                          | 3                               | $\text{C}_{2v}$        |
| b.) facial                              | 2                               | $\text{C}_{3v}$        |

**6.2 On the basis of oxidation state of the central metal atom present in the coordination sphere:-**

$\nu(\text{CO})$  stretching frequencies ( $\text{cm}^{-1}$ )

$\text{Mn}(\text{CO})_6^+$  2093

$\text{Cr}(\text{CO})_6$  1995

$\text{V}(\text{CO})_6^-$  1860

Therefore we can say that CO stretching frequencies increases with increase in positive charge on central metal or frequencies decreases with decrease in negative charge on central metal atom.

## 7. Summary

- The  $\pi$ -acceptor ligands constitute an important class of ligands which display a synergism of  $\sigma$ - or  $\pi$ -donation to the metal ion and  $\pi$ -acceptance of the charge density in their anti-bonding orbitals
- Carbonyls are a special of  $\pi$ -accepting ligands which coordinated with the metal ions through  $\sigma$ -donation at the carbon center and simultaneously display  $\pi$ -acceptance behavior as a result of which the carbon-oxygen bond weakens
- The metal-carbonyl complexes can be classified on the basis of the nature of the ligands, the number of metal ions present and the charge on the coordination sphere
- The carbonyl ligands display a variety of bonding modes in their metal complexes such as terminal and bridging and hence have different stretching frequencies.