CHAPTER 11

Metal-Π Complexes:

❖ Metal Carbonyls: Structure and Bonding

The bonding in coordination compounds is usually visualized as the donation of ligand electron pair to the metal center only. However, there are some ligands which not only have filled atomic orbitals (donor orbitals) but also have some empty orbitals (acceptor orbitals) of appropriate symmetry and energy to accept electron density from a central metal atom or ion. This interaction is called π-backbonding or π-backdonation; and is generally shown by CO, NO, PR_3 and alkene-alkyne type ligands. Two of the most common examples where π-backbonding occurs include $Ni(CO)_4$ and Zeise's salt.

Furthermore, metal carbonyls are one of the most widely studied types of metal-π complexes, that can simply be defined as the coordination compounds of transition metals with carbon monoxide as a ligand. Metal carbonyls are very useful in synthetic organic chemistry and in homogeneous catalysis, like the process of hydroformylation. In the Mond process, nickel carbonyl is used to produce pure nickel. In organometallic chemistry, metal carbonyls act as precursors for the synthesis of many organometallic compounds. Metal carbonyls are toxic by inhalation, skin contact, or ingestion, in part due to their ability to attach to the iron of hemoglobin to give carboxyhemoglobin, which inhibits the binding of dioxygen. Metal carbonyls can be classified on the basis of the number of metal centers; mononuclear carbonyls have only one metal atom or ion such as $Fe(CO)_5$, while polynuclear carbonyls contain more than one metal center like homonuclear $Fe_2(CO)_9$ and heteronuclear $MnRe(CO)_{10}$. One more categorization basis of metal carbonyls is the bonding profile of carbonyl ligand; non-bridging carbonyls and bridging carbonyls. Non-bridging carbonyls may or may not contain metal-metal bonds. For instance, $Ru(CO)_5$ and $Mn_2(CO)_{10}$ both have only terminal carbonyl groups but $Mn_2(CO)_{10}$ has one metal-metal bond also. On the other hand, bridging metal carbonyls like $Fe_3(CO)_{12}$, in addition to terminal CO groups, do have CO groups bridged to more than one metal center.

➢ *General Methods of Preparation*

1. By direct reaction: Some of the mononuclear carbonyls can be prepared by the direct reaction of carbon monoxide with metal powder.

$$Ni + 4CO \xrightarrow[1\ atm]{25°C} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[200\ atm]{200°C} Fe(CO)_5$$

$$2Co + 8CO \xrightarrow[35\ atm]{150°C} Co_2(CO)_8$$

2. By reduction: One of the most widely used methods to synthesize metal carbonyls is the reduction of corresponding metal salts in the presence of carbon monoxide.

$$CrCl_3 + Al + 6CO \xrightarrow[\text{benzene}]{AlCl_3} Cr(CO)_6 + AlCl_3$$

$$VCl_3 + 4Na + 6CO \xrightarrow[\text{high pressure}]{\text{diglyme, } 100°C} [(\text{diglyme})_2Na][V(CO)_6] + 3NaCl$$

$$2CoI_2 + 4Cu + 8CO \xrightarrow[200\text{ atm}]{200°C} Co_2(CO)_8 + 4CuI$$

$$2CoCO_3 + 2H_2 + 8CO \xrightarrow[250-300\text{ atm}]{120-200°C} Co_2(CO)_8 + 2H_2O + 2CO_2$$

$$Re_2O_7 + 17CO \xrightarrow[350\text{ atm}]{250°C} Re_2(CO)_{10} + 7CO_2$$

In the last reaction, carbon monoxide is the reducing agent on its own.

3. From mononuclear carbonyls: Iron pentacarbonyl is sensitive to light and air and can be used to synthesize $Fe_2(CO)_9$ by direct photolysis.

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

Similarly

$$2Os(CO)_5 \xrightarrow{h\nu} Os_2(CO)_9 + CO$$

$$2Ru(CO)_5 \xrightarrow{h\nu} Ru_2(CO)_9 + CO$$

4. From iron pentacarbonyl: Carbon monoxide ligands in $Fe(CO)_5$ are labile and therefore can be used to synthesize other metal carbonyls.

$$MoCl_6 + 3Fe(CO)_5 \xrightarrow[\text{ether}]{110°C} Mo(CO)_6 + 3FeCl_2 + 9CO$$

$$WCl_6 + 3Fe(CO)_5 \xrightarrow[\text{ether}]{110°C} W(CO)_6 + 3FeCl_2 + 9CO$$

5. From metathesis reaction: Mixed-metal carbonyls can successfully be prepared via a metathesis reaction route as:

$$KCo(CO)_4 + [Ru(CO)_3Cl_2]_2 \longrightarrow 2RuCo_2(CO)_{11} + 4KCl$$

➢ ***Structures of Metal Carbonyls***

The structure of metal carbonyls can mainly be classified into three categories; first, as the mononuclear systems that contain only one metal atom, the second one as binuclear systems that may or may not contain bridging carbonyls, and the last one as the polynuclear systems which contain more than two metal centers with all terminal, all bridging, or a mixture of two types of carbonyl groups.

1. Mononuclear metal carbonyls: The structure of mononuclear metal carbonyls is pretty simple and easy to visualize. This is definitely due to the presence of only one metal center. The general examples of mononuclear metal carbonyls include tetrahedral $Ni(CO)_4$ and $Pd(CO)_4$; the trigonal bipyramidal case of $Fe(CO)_5$, $Ru(CO)_5$ and $Os(CO)_5$; and the octahedral geometries of $V(CO)_6$, $Cr(CO)_6$, $Mo(CO)_5$ and $W(CO)_6$.

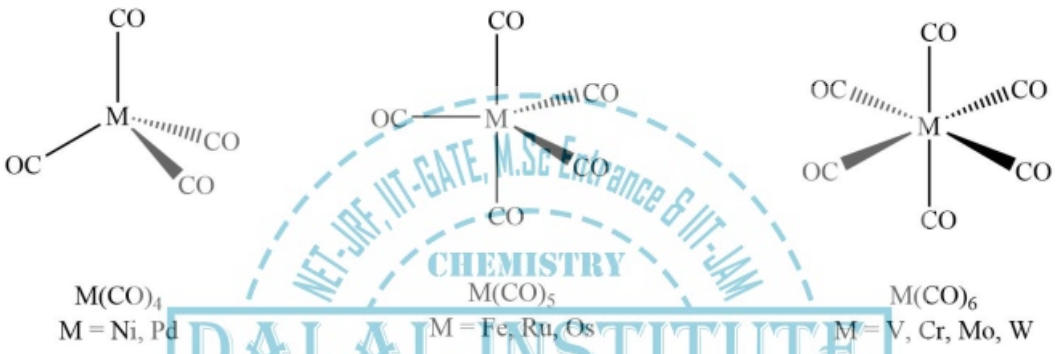
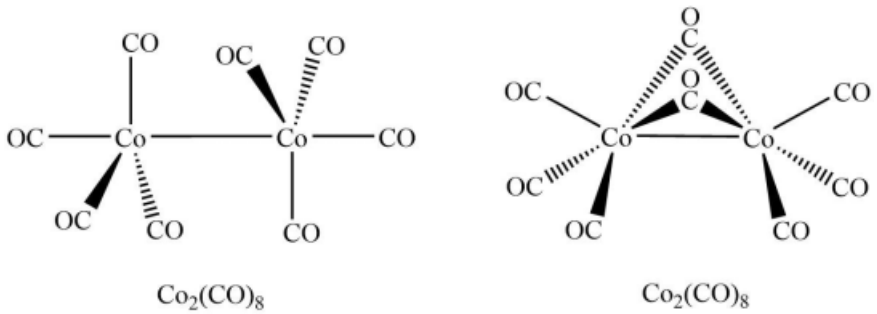


Figure 1. The structures of some mononuclear metal carbonyls.

2. Binuclear metal carbonyls: The structure of the binuclear metal carbonyls comprises of two metal centers and involve either metal-metal bonds or bridging CO groups or both. For example, the $Co_2(CO)_8$ is known to exist in two isomers. The first one has a D_{3d} symmetry with one metal-metal bond with zero bridging carbonyls; the second one is of C_{2v} symmetry and has two bridging CO ligands along with one metal-metal bond. The structure of $Fe_2(CO)_9$ exist with D_{3h} symmetry and contains three bridging CO ligands and six terminal CO groups attached. Furthermore, M_2CO_{10} (M = Mn, Tc, Re) exists with D_{4d} symmetry with one metal-metal bond and four CO ligands attached to each of the metal centers.



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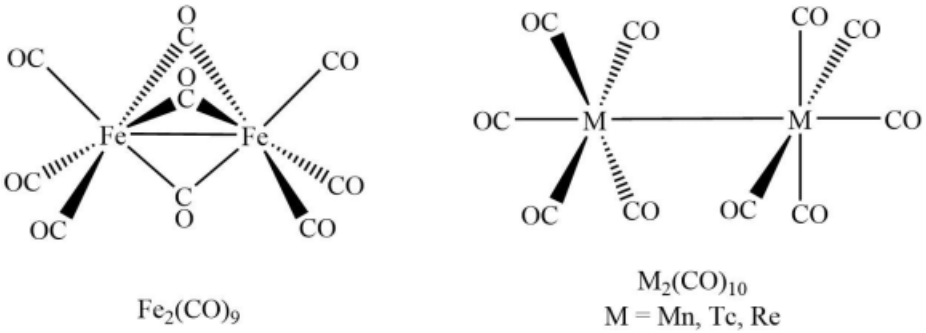
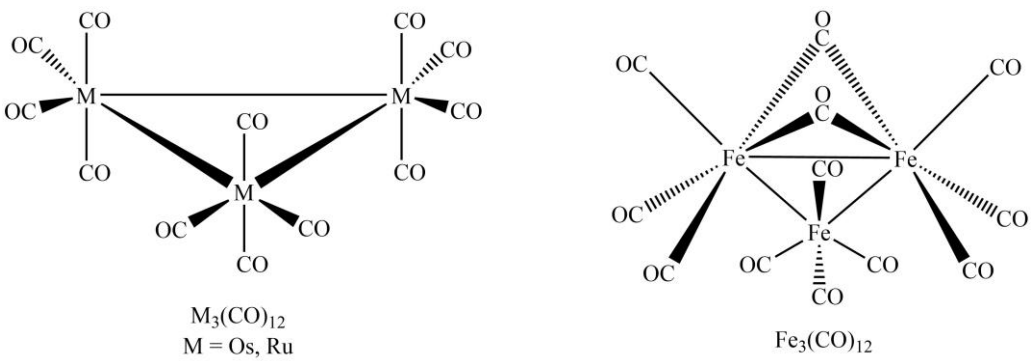


Figure 2. The structures of some binuclear metal carbonyls.

3. Polynuclear metal carbonyls: The structures of the polynuclear metal carbonyls comprises of three or more metal centers and involve all bridging, all terminal, or a mixture of two types of CO groups. For example, the $Ru_3(CO)_{12}$ cluster has D_{3h} symmetry, comprises of an equilateral triangle of Ru centers, each of which has two axial and two equatorial CO ligands. $Os_3(CO)_{12}$ has the same structure, whereas $Fe_3(CO)_{12}$ is different, with two bridging CO ligands, resulting in C_{2v} symmetry. M_4CO_{12} (M = Co, Rh) is consisted of a tetrahedral M_4 core, but the molecular symmetry is C_{3v}. Three carbonyl ligands are bridging ligands and nine are terminal. However, $Ir_4(CO)_{12}$ has perfect T_d symmetry with no bridging CO ligands groups. The Rh_4 and Ir_4 clusters are more thermally robust than that of the Co_4 compound, reflecting the usual trend in the strengths of metal-metal bond for second and third-row metals vs those for the first row metals. Furthermore, $[Re_4(CO)_{16}]^{2-}$ has D_{2h} symmetry with no bridging carbonyl. Furthermore, the structure of $Os_4(CO)_{16}$, $Os_4(CO)_{15}$ and $Os_4(CO)_{14}$ are somewhat more complex because of non-rigidity. The tetranuclear $Os_4(CO)_{16}$ is analogs to the cyclobutane with a puckered structure. The X-ray diffraction analysis of $Os_4(CO)_{14}$ unveiled an irregular tetrahedral Os_4 skeleton with four weakly semi-bridging CO groups and four different Os–Os bond lengths. The experimental structure of $Os_4(CO)_{15}$ was determined to have a planar butterfly-like geometry consisting of two triangles sharing an edge. The hexanuclear $M_6(CO)_{16}$ (M = Rh, Co) exists with an octahedral core with alternate faces participating in the bridging; i.e. with four triply bridged and twelve terminal carbonyls.



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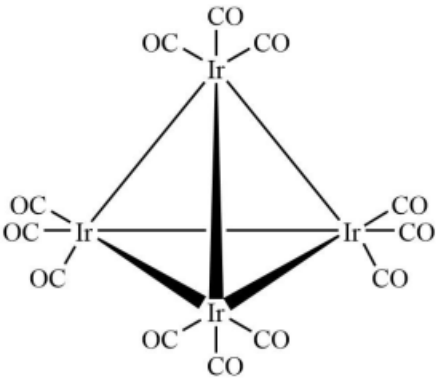
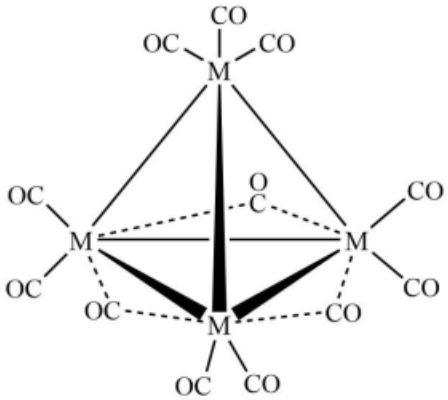


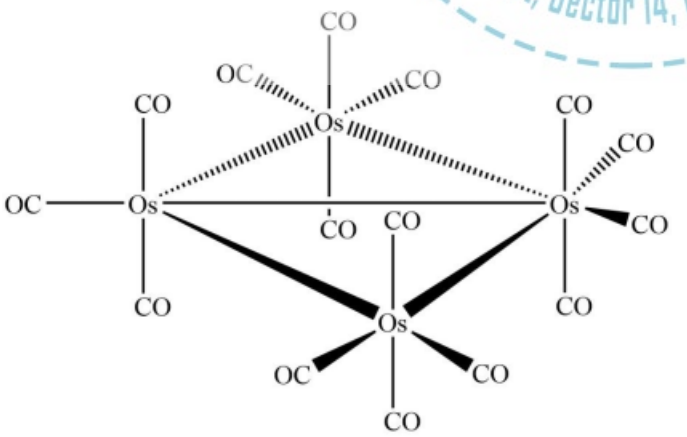
$Ir_4(CO)_{12}$



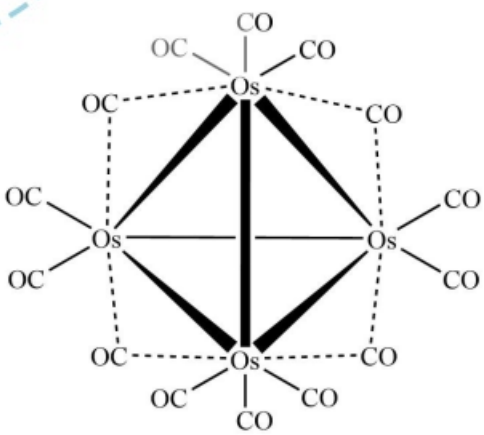
$M_4(CO)_{12}$
M = Co, Rh

$[Re_4(CO)_{16}]^{2-}$

$Os_4(CO)_{16}$



$Os_4(CO)_{15}$



$Os_4(CO)_{14}$

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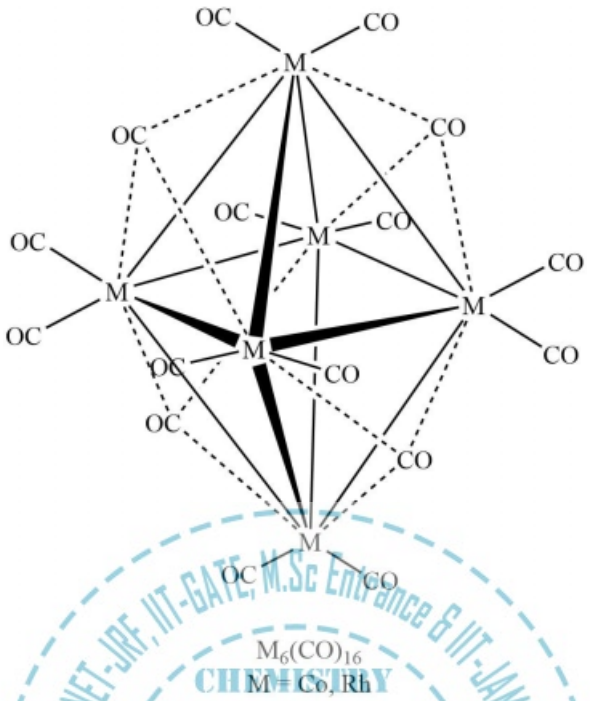


Figure 3. The structures of some polynuclear metal carbonyls.

➢ ***Bonding in Metal Carbonyls***

In order to rationalize the nature of the bonding between the metal center and the carbonyl ligand, we must understand the bonding within the carbonyl ligand itself first. It is a quite well-known fact that the CO group acts as a good sigma donor as well as a good π-acceptor ligand. Two popular approaches to study the bonding in carbon monoxide, as well as metal carbonyls, are discussed below.

1. Valence bond theory: According to this model, the bonding within the CO molecule can be best shown as:

$$O \equiv\!\!\rightarrow C$$

The carbon and oxygen atoms in CO are *sp*-hybridized with the following electronic configurations.

$$C \text{ (ground state)} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$$

$$C \text{ (hybridized state)} = 1s^2, (sp_x)^2, (sp_x)^1, 2p_y^1, 2p_z^0$$

Similarly,

$$O \text{ (ground state)} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^2$$

$$O \text{ (hybridized state)} = 1s^2, (sp_x)^2, (sp_x)^1, 2p_y^1, 2p_z^2$$

Now, the one half-filled sp_x-hybridized orbital of carbon atom overlap with half-filled sp_x-hybridized orbital of the oxygen atom to form a σ bond, while sp_x-hybridized lone pairs on both atoms remain non-bonding in nature. Moreover, two π bonds are formed as a result of the sidewise overlap; one between half-filled $2p_y$ orbitals, and the second one as dative or coordinative interaction of fully filled $2p_z$ orbital of oxygen with empty $2p_z$ orbital of carbon.

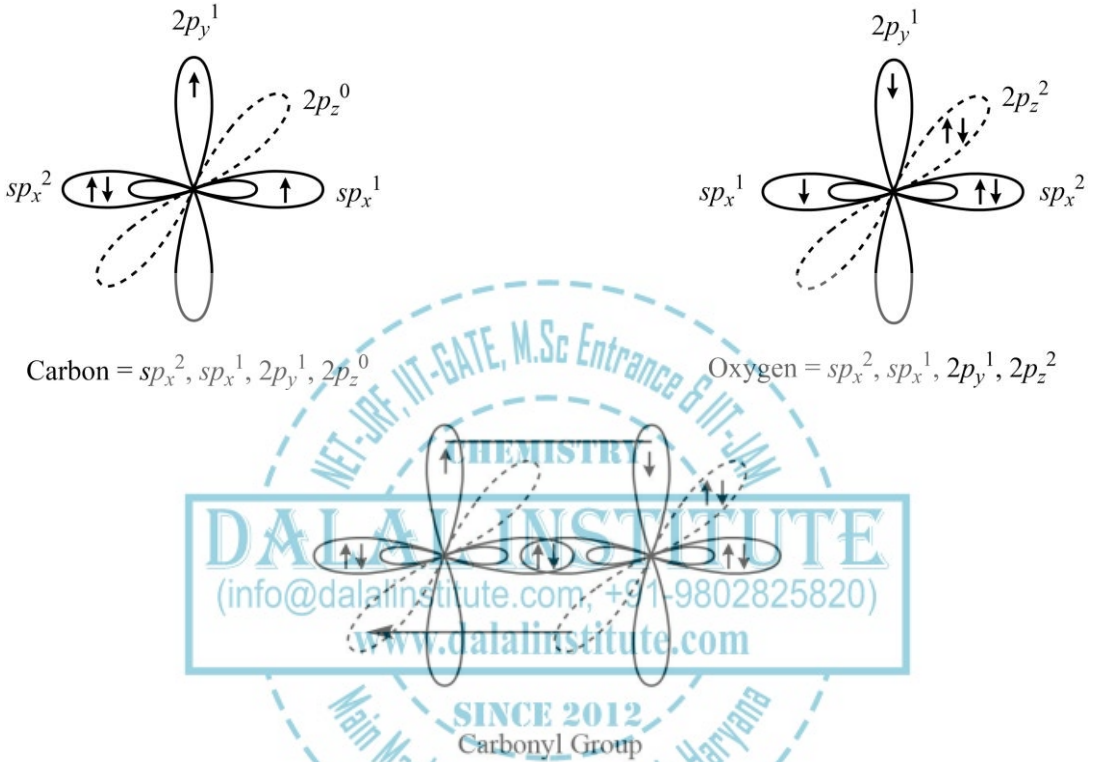


Figure 4. Bonding behavior in CO ligand according to the valence bond method.

Furthermore, the valence bond theory treats the bonding mode of the carbonyl with the metal center in terms of hybridization and resonance phenomena. The central metal atom or ion provides the required number of empty hybrid orbitals with proper orientation to accept the electron pair from surrounding ligands. For instance, in $Cr(CO)_6$ the chromium atom undergoes a d^2sp^3 hybridization to generate six empty hybrid orbital of equivalent shapes and the same energy. When one of the carbonyl ligands approaches this metal ion with its internuclear axis along x-axis, the filled hybrid lone pair of electron on carbon atom overlap with one of the two empty hybrid orbitals orientated oppositely in x-direction. The metal-carbon multiple bonds is explained in terms of various resonating structures which consequently reduces the bond strength of the carbon-oxygen bond. It should also be noted that, though there are two hybrid lone pairs (one on carbon and the other on the oxygen); the bonding of carbonyl group with metal takes place via a donation through carbon end always. This can be explained in terms of the higher energy of hybrid lone pair carbon than oxygen.

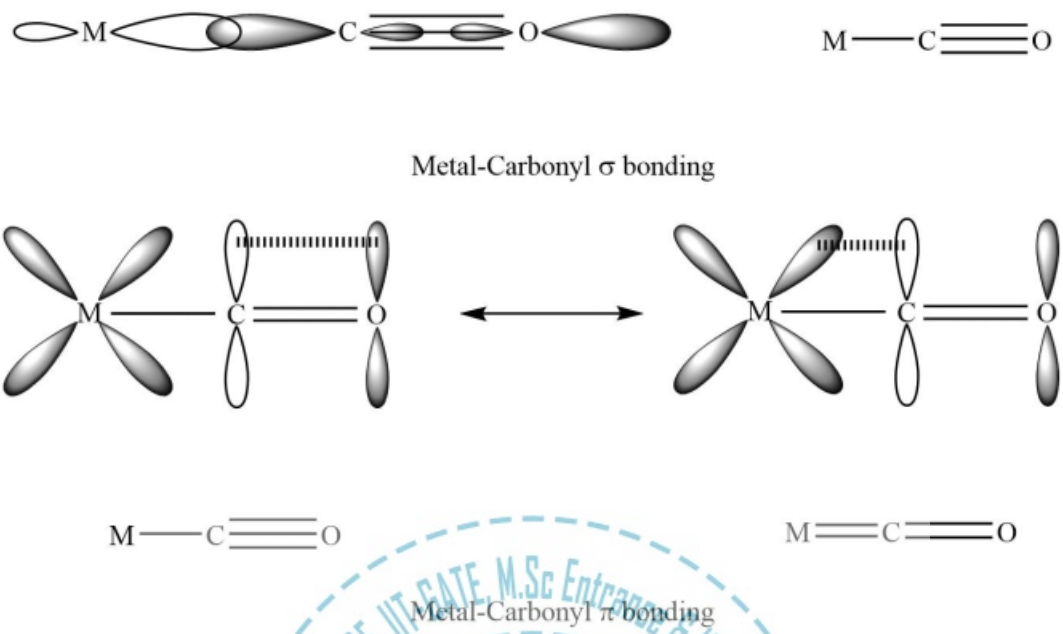


Figure 5. The valence bond nature of σ and π overlap in metal carbonyls.

2. Molecular orbital theory: This is the best model to explain the bonding within the CO ligand as well as in metal carbonyl complexes. There are total three molecular diagrams for carbonyl ligand which were proposed from time to time. Though, all three molecular orbital (MO) diagrams are able to explain the nature of metal-carbonyl π-bonding; the initial treatment was not so effective to explain the σ donation, the second one does also suffer from some minor anomalies. The third molecular orbital diagram is most widely accepted in the scientific community as it gives a logical explanation to what had been a mystery in metal carbonyl chemistry. We will study these MO diagrams in the order they were proposed.

i) The first molecular orbital diagram of carbon monoxide assumes that the atomic orbitals of carbon and oxygen interact with each other to create molecular orbitals. The electronic configurations of C and O are:

$$\text{Carbon} = 1s^2, 2s^2, 2p^2$$

$$\text{Oxygen} = 1s^2, 2s^2, 2p^4$$

The number of outer electrons in carbon and oxygen are four and six, respectively. Thus, a total of 10 electrons are to be filled in the molecular orbitals of the carbon monoxide molecule. The higher energy of corresponding atomic orbitals of carbon is due to its lower electronegativity, which makes the bonding and antibonding molecular orbitals to receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, would be rich in atomic orbitals of carbon. The bonding molecular orbitals will have more characteristics of atomic orbitals of Oxygen and antibonding Molecular orbitals would have more

characteristics of carbon. The electronic configuration of CO molecule will be $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^2$, $\pi 2p_x^2$, $\pi 2p_y^2$ which gives a bond order three i.e. triple bond between carbon and oxygen. The molecular orbital diagram and expected bonding mode of the carbonyl ligand are given below.

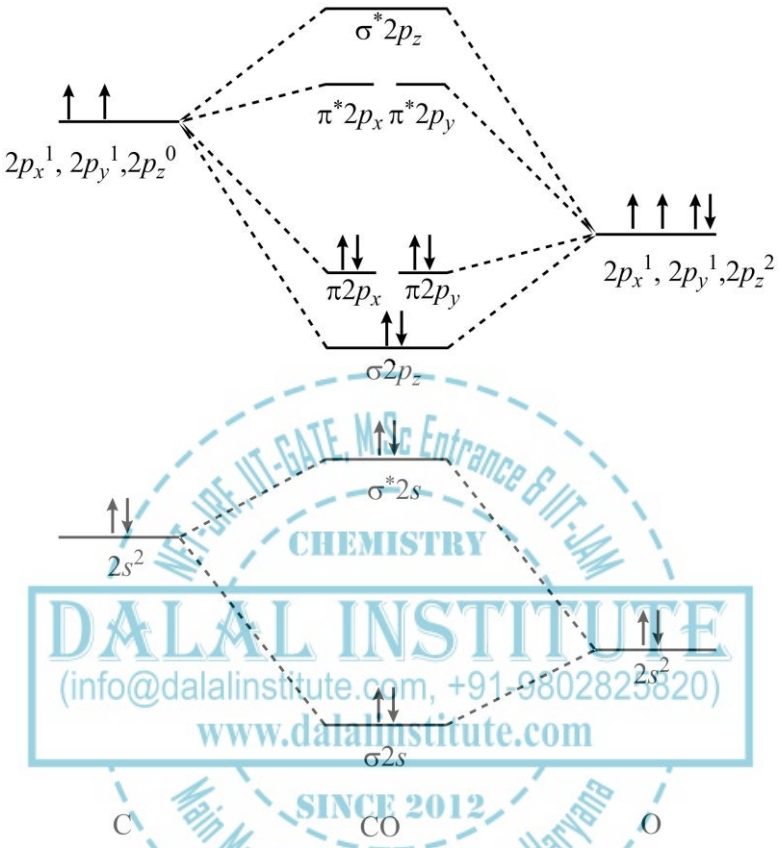
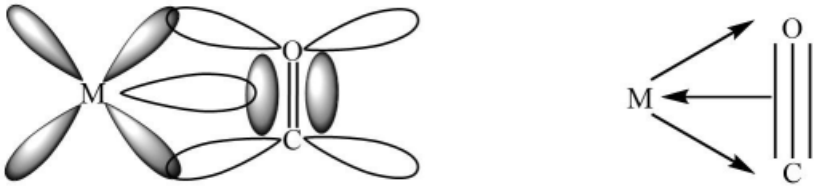


Figure 6. The first generation molecular orbital diagram of carbonyl ligand.

The formation of molecular orbitals given above is actually an oversimplification of a ticklish problem. This statement is made on the basis of two facts. The first one is that when one electron removed from CO to form CO^+, the bond order actually increases, which is actually the opposite of what is expected if the electron is lost from the highest occupied molecular orbital (HOMO) of bonding nature. Its bond order should be decreased from the removal of an electron from $\pi 2p_x^2$ or $\pi 2p_y^2$, which suggests that the HOMO of carbon monoxide should be of antibonding nature rather bonding. The second anomaly also arises from the MO diagram of CO ligand which clearly shows that in order to donate electron density from π-bonding molecular orbital, the carbonyl ligand must approach the metal center with its carbon-oxygen internuclear axis perpendicular to *x*, *y* or *z*-axis assigned to the central atom. This explains how the empty $\pi^* 2p_x$ and $\pi^* 2p_y$ could be used to accept electron density from filled *d*-orbitals of central metal atom or ion. However, in actual practice, the carbonyl ligand binds to the metal center in linear fashion via carbon end only.



Metal-Carbonyl σ donation and π acceptance

Figure 7. The expected nature of σ and π overlap in metal carbonyls from the first MO of CO.

ii) The second molecular orbital diagram of carbon monoxide was suggested by Coulson which assumes that the first molecular orbital diagram of CO is not correct. According to Coulson, 2*s* and 2p_x atomic orbitals of both carbon and oxygen undergo hybridization before they create molecular orbitals. The carbon and oxygen atoms in carbon monoxide are *sp*-hybridized with the following electronic configurations.

$$\text{C (hybridized state)} = 1s^2, (sp_x)^2, (sp_x)^1, 2p_y^1, 2p_z^0$$

$$\text{O (hybridized state)} = 1s^2, (sp_x)^2, (sp_x)^1, 2p_y^1, 2p_z^2$$

The total number of valence electrons in carbon and oxygen are four and six, respectively; and thus, ten electrons are to be filled in the molecular orbitals of CO molecule. The half-filled sp_x hybrid orbitals of carbon and oxygen interact to form σ and σ* molecular orbitals; while the fully-filled sp_x hybrid lone pair orbitals of carbon and oxygen remain non-bonding. Moreover, doubly degenerate sets of π-bonding and π-antibonding molecular orbitals are also formed due to the sidewise overlap of 2p_y orbitals and 2p_z orbitals.

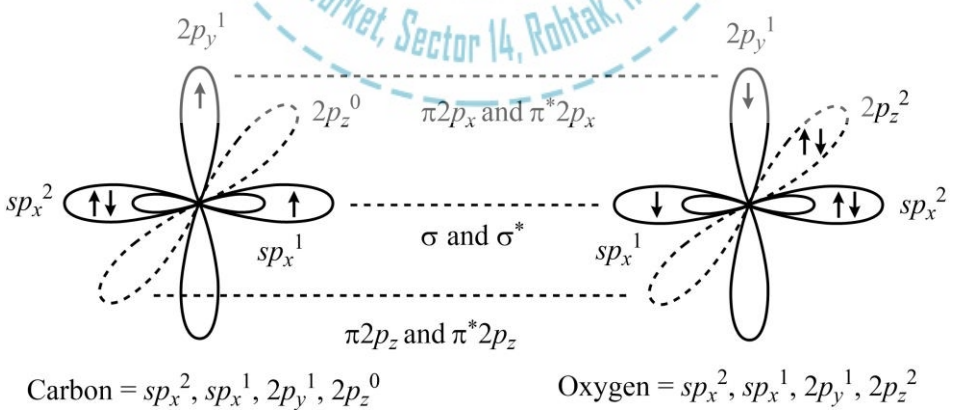


Figure 8. The nature of σ and π in carbonyl ligand.

The bonding molecular orbitals will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, would be rich in atomic orbitals of carbon. The bonding molecular orbitals

will have more characteristics of atomic orbitals of oxygen and antibonding molecular orbitals would have more characteristics of carbon. The molecular orbital diagram carbon monoxide proposed by Coulson is given below.

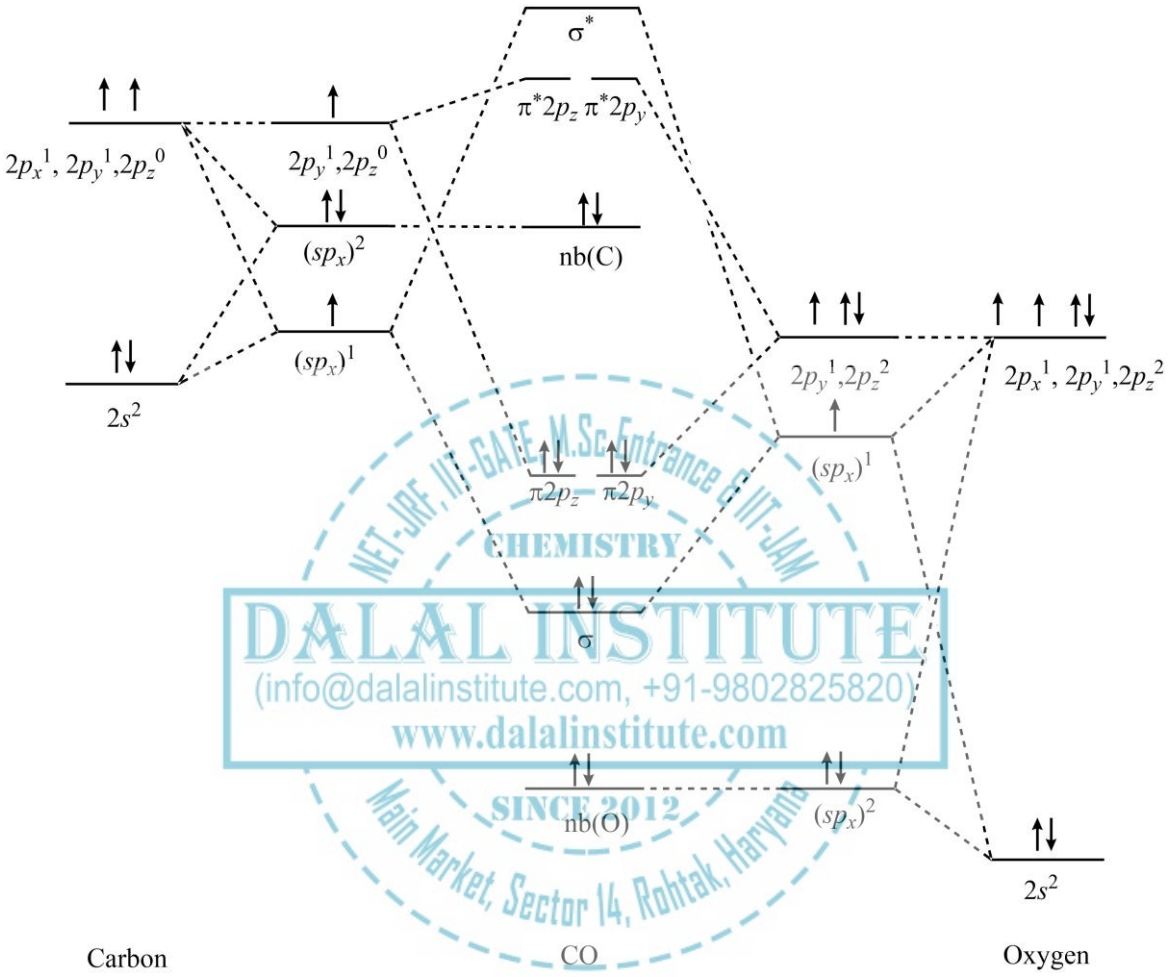


Figure 9. The second molecular orbital diagram of carbonyl ligand.

The MO diagram shown above is very useful in explaining the bonding between the metal center and carbonyl ligand. This diagram eliminates the possibility of sigma donation through bonding molecular orbital and perpendicular orientation CO ligand as the HOMO is now non-bonding hybrid lone pair rather π-bonding. This also explains why the carbonyl group prefers to bond via carbon end in a linear manner. This also explains how the lowest unoccupied molecular orbital (LUMO) π^*2p_z and π^*2p_y could be used to accept electron density from filled *d*-orbitals of central metal atom or ion. Moreover, the reduced CO stretching frequency of metal coordinated carbonyl can be attributed to the reduced bond order due to the transfer of *d*-electron density from metal to π^* orbital carbonyl ligand. However, the increase in bond order when one electron is removed from

CO to form CO^+ is still a mystery because the electron is lost from the highest occupied molecular orbital (HOMO) of nonbonding bonding nature, and the bond order should have remained the same.

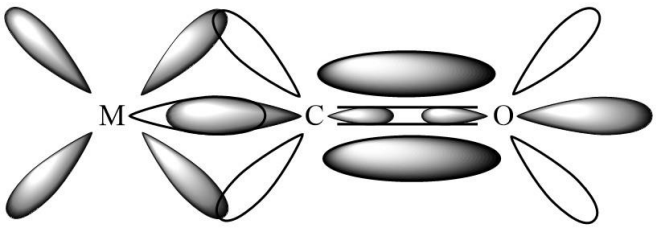


Figure 10. The nature of σ and π overlap in metal carbonyls.

iii) This molecular orbital diagram of carbon monoxide is most widely accepted to rationalize its σ-donor and π-acceptor strength. The total number of valence electrons in carbon and oxygen are four and six, respectively; and thus, ten electrons are to be filled in the molecular orbitals of CO molecule. A total of four singly degenerate σ- molecular orbitals and two doubly degenerate sets of π- molecular orbitals are formed. One doubly degenerate set of π molecular orbitals will be bonding while the other one will be antibonding in nature. The nature of σ molecular orbitals is more complex as three out of four are of bonding character. Initially, the σ_5 was thought to be of antibonding to justify the higher bond order of CO^+. However, the σ_5 is slightly bonding in nature because there is some mixing with the *p* atomic orbitals of the right symmetry. Out of four σ-molecular orbitals, only σ_6 possesses the antibonding character, while σ_5 goes with expected bonding characteristics. The σ_5 is essentially non-bonding and almost centered on the oxygen atom. Moreover, doubly degenerate sets of π-bonding and π-antibonding molecular orbitals are also formed due to the sidewise overlap of $2p_y$ orbitals and $2p_z$ orbitals. The π-bonding molecular orbitals set will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, will be rich in atomic orbitals of carbon atom.

However, the problem that why does the bond order increases when an electron is removed from CO still persists. Because we are removing the electron from a bonding molecular orbital, its bond order must be decreased. The possible explanation for the shortening of the bond after ionization is that the ionization induces a shift of the electron-polarization in CO ligand. In other words, the ionization occurs as the loss of an electron from a σ-HOMO orbital which is mostly carbon-centered; and since the HOMO-σ orbital is only slightly bonding in nature, the loss of bonding character is quite small and could easily be compensated by the advantage in covalent character; i.e. the formation of a positive partial charge on the carbon atom increases the strength of the covalence of the bond and thus decreases the bond length. This enhanced covalent character can also be visualized in terms of better interaction of two atomic orbitals if their energies are comparable. In carbon monoxide molecule the atomic orbitals of oxygen lie energetically a lot below then the atomic orbitals of carbon; But when the CO is oxidized to CO^+, the partial positive charge on carbon shifts the atomic orbitals of carbon down in energy, and thereby makes the energies closer to the related atomic orbitals of oxygen, which leads to a stronger interaction when bonds are made.

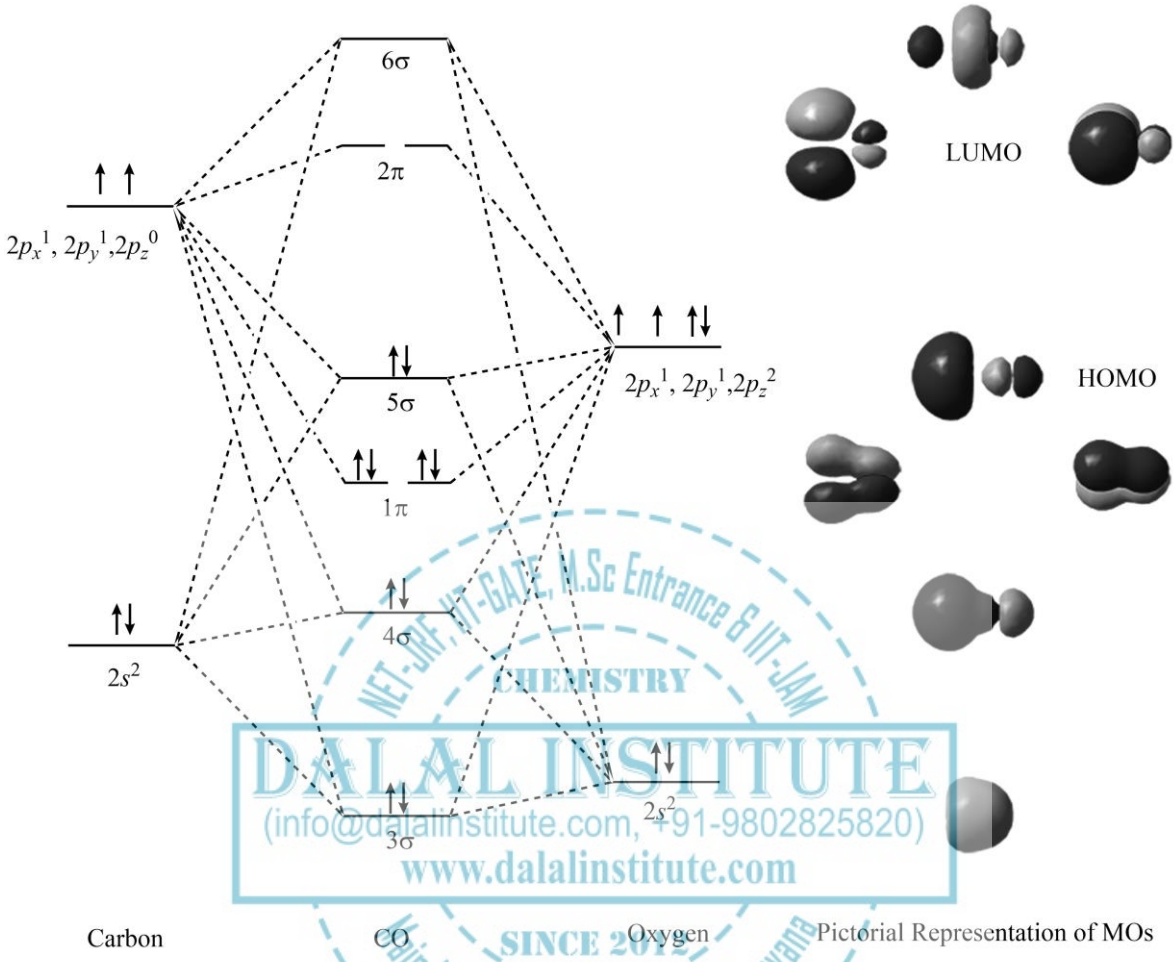


Figure 11. Third molecular orbital diagram of carbonyl ligand.

The MO diagram shown above is very useful in explaining the bonding between the metal center and carbonyl ligand. The carbonyl ligand uses its HOMO for sigma donation while simultaneously accepts electron density from filled metal d-orbital to its π^* LUMO.

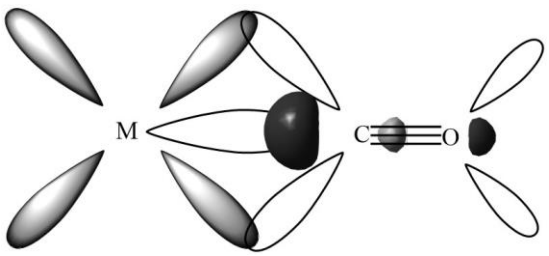


Figure 12. The nature of σ and π overlap in metal carbonyls using third MO diagram of CO.

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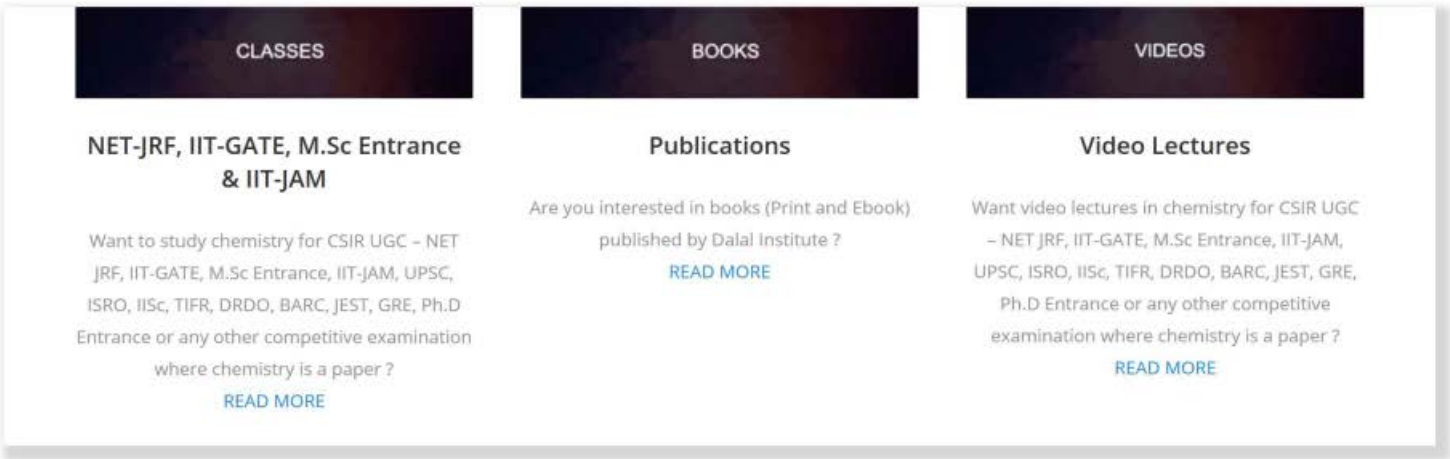

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Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

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