

Coordination compounds & Organometallics

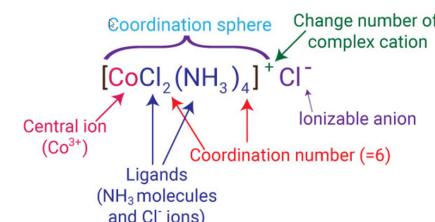
Coordination compounds

Outline

- ❖ Coordination compounds
 - Shapes of inorganic compounds
 - Crystal field theory (CFT)
 - Molecular orbital (MO) theory
- Organometallic chemistry (Metal carbonyls)

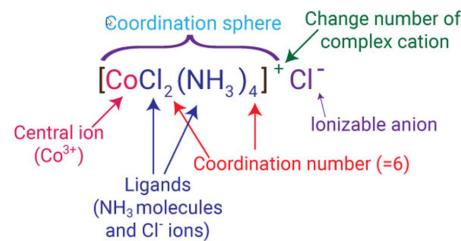
Introduction

- ❖ Addition compounds which retain their identity in solution are called complex compounds.
- ❖ A coordination complex compound consists of a central atom (metal ion) and attached groups (ligands) and all of them are written inside the square brackets.



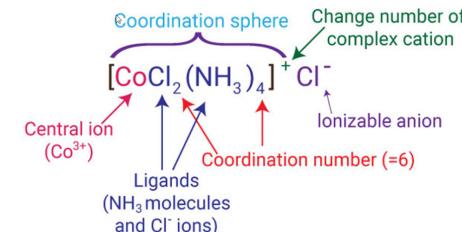
Introduction

- ❖ Each ligand donates an electron pair to the central metal ion and thus it forms a coordinate bond.



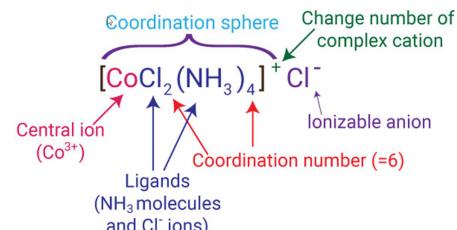
Introduction

- ❖ The total number of ligands (inside the square bracket) bonded to the central atom is the coordination number.



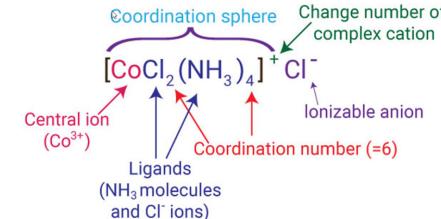
Introduction

- ❖ Central metal ion acts as Lewis acid or electron pair acceptor.
- ❖ Ligands act as Lewis base or electron pair donors.



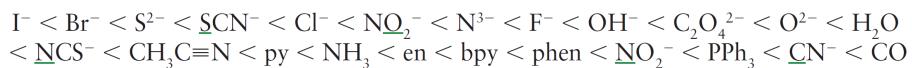
Introduction

- ❖ Primary valence is the oxidation state of the central metal atom.
- ❖ Secondary valence is the coordination number.



Strength of ligands – Spectrochemical series

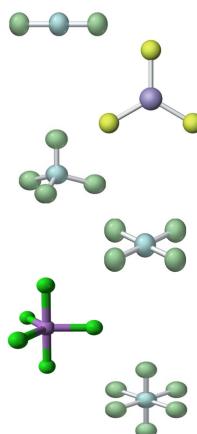
- Based on the experimental data, ligands strength is decided and arranged in the following order. It is spectrochemical series



Shapes of inorganic compounds Valence bond theory

Valence bond theory

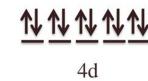
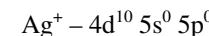
Coordination No.	Geometry	Hybridisation	Examples
2	Linear	sp	$[\text{Ag}(\text{NH}_3)_2]^+$
3	Trigonal planar	sp^2	$[\text{HgI}_3]^-$
4	Tetrahedral	Sp^3	$[\text{NiCl}_4]^{2-}$
4	Square planar	dsp^2	$[\text{Ni}(\text{CN})_4]^{2-}$
5	Trigonal bipyramidal	sp^3d	$\text{Fe}(\text{CO})_5$
6	Octahedral	d^2sp^3	$[\text{Co}(\text{NH}_3)_6]^{3+}$
6	Octahedral	sp^3d^2	$[\text{CoF}_6]^{4-}$



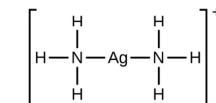
Linear



$$\mathbf{Ag = 47}$$



sp hybridization



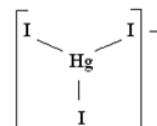
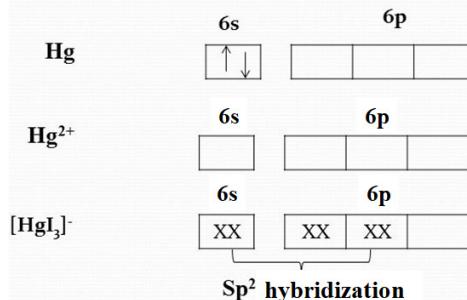
Therefore the structure of $[\text{Ag}(\text{NH}_3)_2]^+$ is linear with sp-hybridization.

Trigonal planar

$[\text{HgI}_3]^-$

$\text{Hg} = 80$

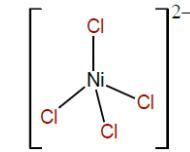
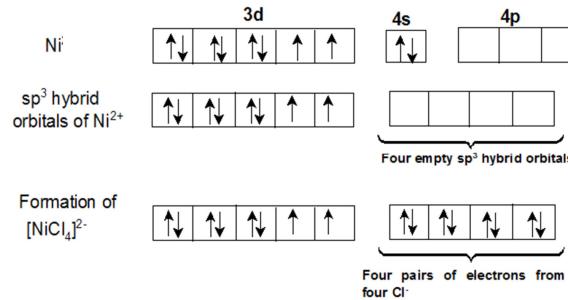
Hg^{80} $[\text{Xe}]^{54} 4f^{14} 5d^{10} 6s^2 6p^0$
 Hg^{2+} $[\text{Xe}]^{54} 4f^{14} 5d^{10} 6s^0 6p^0$



Tetrahedral

$[\text{Ni}(\text{Cl})_4]^{2-}$

$\text{Ni} = 28$



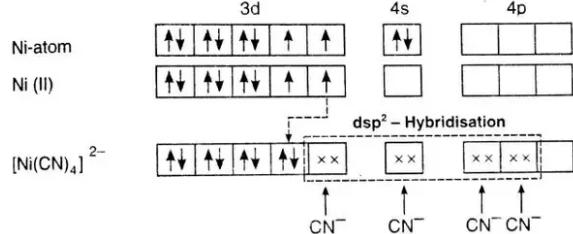
$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_2^- < \text{N}^{3-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{C}\equiv\text{N} < \text{py} < \text{NH}_3 < \text{en} < \text{bpy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

'Cl-' ligands are weak ----- no electron pairing takes place in the metal ion orbitals
 sp³ hybridization
 Tetrahedral
 High-spin complex

Square planar

$[\text{Ni}(\text{CN})_4]^{2-}$

$\text{Ni} = 28$



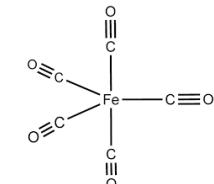
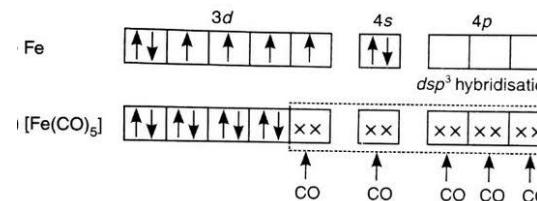
$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_2^- < \text{N}^{3-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{C}\equiv\text{N} < \text{py} < \text{NH}_3 < \text{en} < \text{bpy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

'CN' ligands are strong ----- electron pairing takes place in the metal ion orbitals
 dsp²-hybridization
 Square planar
 Low-spin complex

Trigonal bipyramidal

$[\text{Fe}(\text{CO})_5]$

$\text{Fe} = 26$



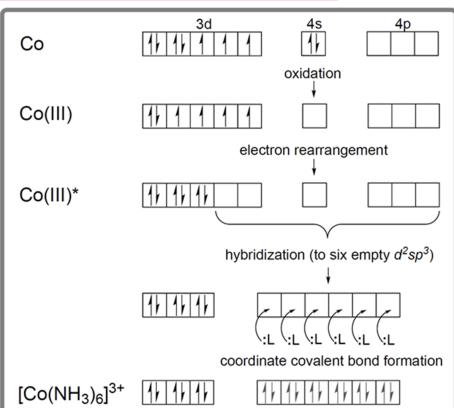
$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_2^- < \text{N}^{3-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{C}\equiv\text{N} < \text{py} < \text{NH}_3 < \text{en} < \text{bpy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

'CO' ligands are strong ----- electron pairing takes place in the metal ion orbitals
 dsp³ - hybridization
 Trigonal bipyramidal
 Low-spin complex

Octahedral



Co = 27

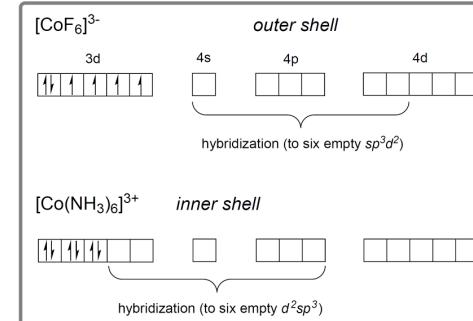


'NH₃' ligands are strong ----- electron pairing takes place in the metal ion orbitals
 d^2sp^3 hybridization
 Low-spin complex
 Octahedral

Octahedral



Co = 27



sp^3d^2 hybridization (outer shell)
 High-spin complex
 Octahedral

d^2sp^3 hybridization (inner shell)
 Low-spin complex
 Octahedral

'NH₃' ligands are strong ----- electron pairing takes place in the metal ion orbitals

'F-' ligands are weak ----- no electron pairing

Failures of VB theory

- ❖ Could not explain the color and spectra of coordination complexes
- ❖ Could not explain the magnetic properties
- ❖ Could not explain the spectrochemical series

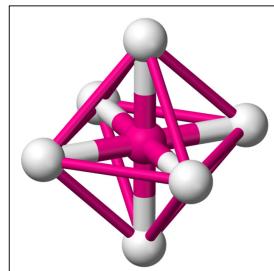
Crystal field theory (CFT)

CFT - Assumptions

- ❖ The attraction between the central metal and ligands is considered as purely electrostatic.
- ❖ Ligands are treated as point charges.
- ❖ There is no interaction between metal orbitals and ligand orbitals.
- ❖ All the d-orbitals on the metal have the same energy (degenerate) in the free atom.
- ❖ However, when a complex is formed (ligand interaction with metal ion), the ligands destroy the degeneracy of these orbitals, i.e. the orbitals now have different energies.

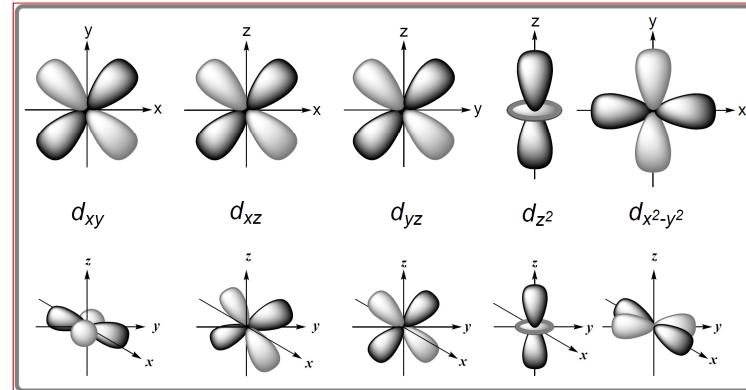
Crystal field theory (CFT)

Octahedral field



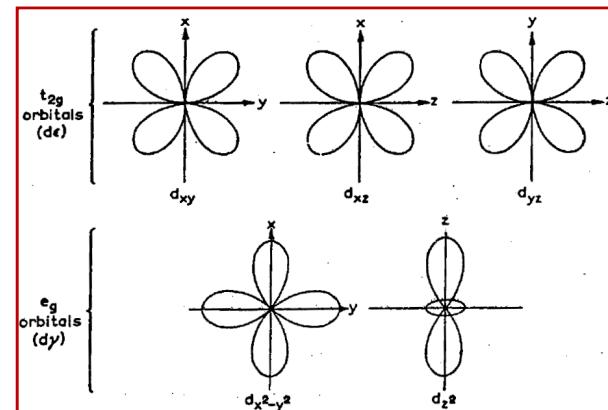
d-orbitals ---- degenerate in free atom

- ❖ All the five d-orbitals of the metal ion posses equal energy (degenerate) when they are empty and without ligand effect. Here there is no field and no coulombic repulsions.



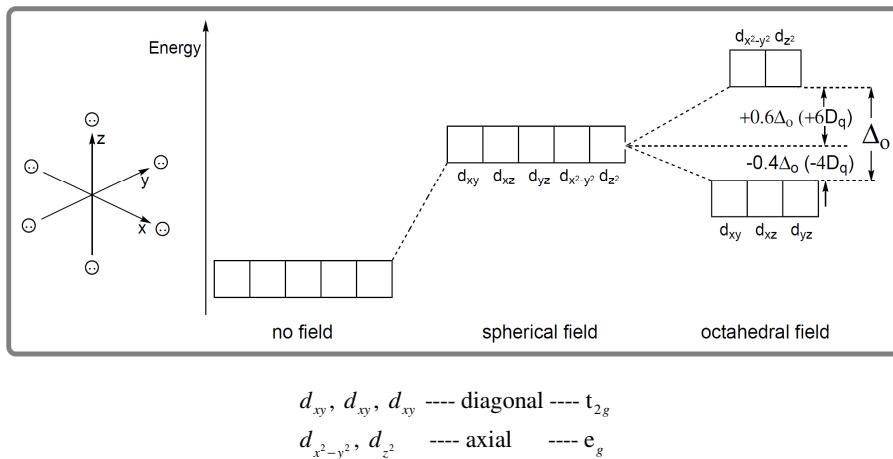
Types of d-orbitals

- ❖ Though all the five d-orbitals have equal energy, they are again two types based on their internal orbital arrangement.



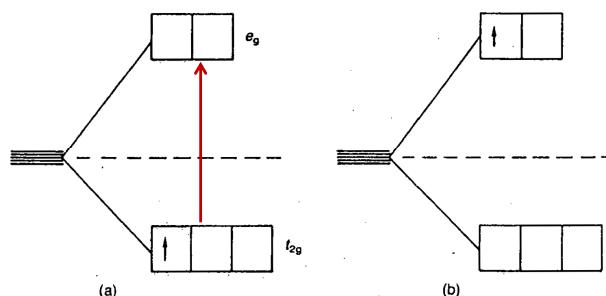
Octahedral field ----- d-orbital splitting

- In a spherical field with symmetric charge density, all five d-orbitals are raised in energy equally, remaining degenerate.
- However, when point charges (ligands) are introduced in octahedral field, this degeneracy is removed.



Color of coordination compounds

- CFT was able to explain the color of the complex compounds using the d-d electron transitions.



d^1 configuration: (a) ground state, (b) excited state.

Spectrochemical series

- The crystal field splitting value, Δ_o depends upon the ligands in the complex compound. Strong field ligands lead to large splitting and more Δ_o value.
 - Based on the experimental data from many complexes, the strength of ligands can be explained which is called spectrochemical series.
- $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_2^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < CH_3C\equiv N < py < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$

Crystal field splitting energy (CFSE)

- The splitting of the five d-orbitals into e_g and t_{2g} energy levels by approaching ligands is called crystal-field splitting.
- The energy difference between e_g and t_{2g} levels (denoted by Δ_o or $10 Dq$) is called Crystal Field Splitting Energy (CFSE).

In Octahedral field, configuration is: $t_{2g}^x e_g^y$

$$CFSE = [-0.4x + 0.6y]\Delta_o$$

x - the number of electrons in t_{2g} orbitals

y - the number of electrons in e_g orbitals

Octahedral field --- CFSE

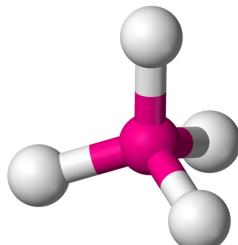
Number of <i>d</i> electrons	Arrangement in weak ligand field			Arrangement in strong ligand field			
	<i>t</i> _{2g}	<i>e</i> _g	CFSE Δ_o	<i>t</i> _{2g}	<i>e</i> _g	CFSE Δ_o	
			Spin only magnetic moment $\mu_s(D)$			Spin only magnetic moment $\mu_s(D)$	
<i>d</i> ¹	↑ [] [] [] []	[] [] [] []	-0.4	1.73	↑ [] [] [] []	-0.4	1.73
<i>d</i> ²	↑↑ [] [] []	[] [] [] []	-0.8	2.83	↑↑ [] [] []	-0.8	2.83
<i>d</i> ³	↑↑↑ [] []	[] [] [] []	-1.2	3.87	↑↑↑ [] []	-1.2	3.87
<i>d</i> ⁴	↑↑↑↑ [] []	[] [] [] []	-1.2 +0.6 = -0.6	4.90	↑↑↑↑ [] []	-1.6	2.83
<i>d</i> ⁵	↑↑↑↑↑ [] []	[] [] [] []	-1.2 +1.2 = -0.0	5.92	↑↑↑↑↑ [] []	-2.0	1.73

Octahedral field --- CFSE

Number of <i>d</i> electrons	Arrangement in weak ligand field			Arrangement in strong ligand field				
	<i>t</i> _{2g}	<i>e</i> _g	CFSE Δ_o	<i>t</i> _{2g}	<i>e</i> _g	CFSE Δ_o		
		Spin only magnetic moment $\mu_s(D)$			Spin only magnetic moment $\mu_s(D)$			
<i>d</i> ⁶	↑↓↑↑↑↑	↑↑↑↑↑↑	-1.6 +1.2 = -0.4	4.90	↑↓↑↑↑↑	↑↑↑↑↑↑	-2.4	0.00
<i>d</i> ⁷	↑↓↑↑↑↑↑	↑↑↑↑↑↑↑	-2.0 +1.2 = -0.8	3.87	↑↓↑↑↑↑↑	↑↑↑↑↑↑↑	-2.4 +0.6 = -1.8	1.73
<i>d</i> ⁸	↑↓↑↑↑↑↑↑	↑↑↑↑↑↑↑↑	-2.4 +1.2 = -1.2	2.83	↑↓↑↑↑↑↑↑	↑↑↑↑↑↑↑↑	-2.4 +1.2 = -1.2	2.83
<i>d</i> ⁹	↑↓↑↑↑↑↑↑↑	↑↑↑↑↑↑↑↑↑	-2.4 +1.8 = -0.6	1.73	↑↓↑↑↑↑↑↑↑	↑↑↑↑↑↑↑↑↑	-2.4 +1.8 = -0.6	1.73
<i>d</i> ¹⁰	↑↓↑↑↑↑↑↑↑↑↑	↑↑↑↑↑↑↑↑↑↑↑	-2.4 +2.4 = 0.0	0.00	↑↓↑↑↑↑↑↑↑↑↑	↑↑↑↑↑↑↑↑↑↑↑	-2.4 +2.4 = 0.0	0.00

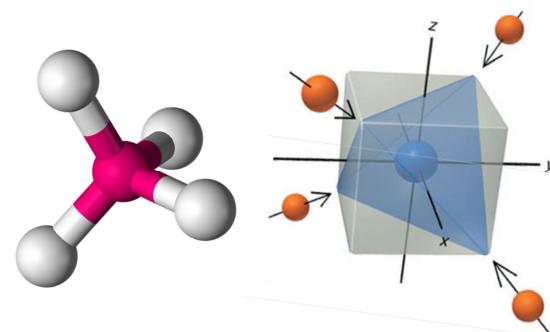
Crystal field theory (CFT)

Tetrahedral field



Tetrahedral field ----- d-orbital splitting

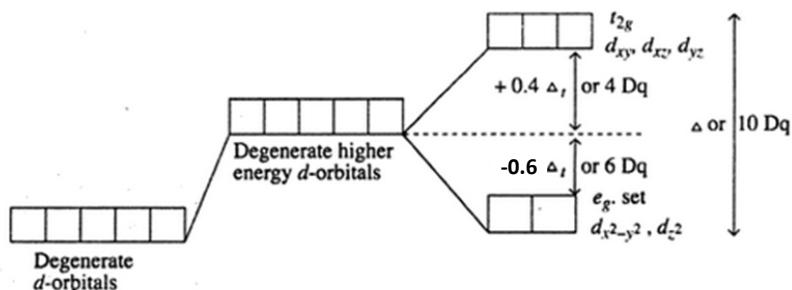
- In a field with symmetric charge density, all five d-orbitals are raised in energy equally, remaining degenerate.
- However, when point charges (ligands) are introduced in tetrahedral field, this degeneracy is removed.



- In the tetrahedral field, the *t*_{2g} orbitals of the metal ion are close to the four ligands when compared to *e*_g orbitals.

Tetrahedral field ----- d-orbital splitting

- The mode of splitting of d-orbitals in a tetrahedral complex is just reverse of that in an octahedral complex.
- The difference between low energy t_{2g} orbitals and high energy e_g orbitals in a tetrahedral complex is called the tetrahedral crystal field splitting energy and is denoted by Δ_t



Tetrahedral CFSE – weak ligand field

Number of d electrons	Arrangement of electrons	Spin only magnetic moment	Tetrahedral CFSE	
	e_g	t_{2g}	$\mu(D)$	Δ_t
d^1			1.73	-0.6
d^2			2.83	-1.2
d^3			3.87	$-1.2 + 0.4 = -0.8$
d^4			4.90	$-1.2 + 0.8 = -0.4$
d^5			5.92	$-1.2 + 1.2 = 0.0$
d^6			4.90	$-1.8 + 1.2 = -0.6$
d^7			3.87	$-2.4 + 1.2 = -1.2$

Electron pairing takes place in case of strong ligand fields

Tetrahedral CFSE

- The difference between low energy t_{2g} orbitals and high energy e_g orbitals in a tetrahedral complex is called the tetrahedral crystal field splitting energy and is denoted by Δ_t

In tetrahedral field, configuration is: $e_g^x t_{2g}^y$

$$\text{CFSE} = (-0.6x + 0.4y)\Delta_t$$

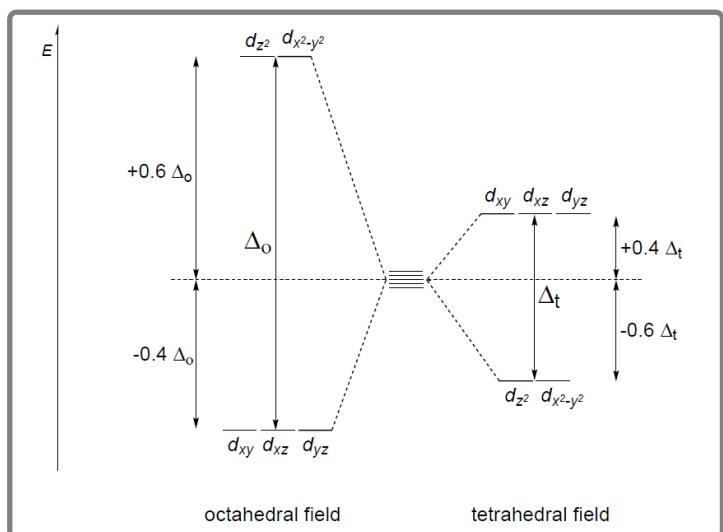
x - number of electrons in e_g orbitals

y - number of electrons in t_{2g} orbitals

Octahedral field Vs Tetrahedral field

- The magnitude of the crystal field splitting in tetrahedral complexes is considerably less than in octahedral fields. There are two reasons for this:
 - There are only four ligands instead of six, so the ligand field is only two thirds the size: hence the ligand field splitting is also two thirds the size.
 - The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.
- Thus the tetrahedral crystal field splitting Δ_t , is roughly $2/3 \times 2/3 = 4/9$ of the octahedral crystal field splitting Δ_o .

Octahedral field Vs Tetrahedral field



CFT – advantages & disadvantages

- ❖ Explained the shapes of coordination complexes
 - ❖ Explained the magnetic properties
 - ❖ Explained the colour exhibited by transition metal complexes
 - ❖ CFSE calculations are quite simple
-
- ❖ Failed to explain spectrochemical series and the position of certain ligands in it. It is due to the non-consideration of nature of ligands.
 - ❖ Compounds in zero oxidation state such as nickel carbonyl $[Ni(CO)_4]$ have no electrostatic attraction between the metal and the ligands. CFT failed to explain the bonding in such complexes

Molecular orbital (MO) theory Octahedral complexes

MO theory on transition metal complexes -- Ligand field theory

- ❖ Incorporates covalent bonding in transition metal complexes
- ❖ Nature of ligands is taken into account. Ligands can also form π -bonds in addition to σ -bonds (electron pair donors)
- ❖ Explained the spectrochemical series using the π -bonding.
- ❖ Explained the formation of complexes with zero metal oxidation state such as in $[Ni(CO)_4]$ using again the π -bonding.
- ❖ Calculations are not that simple.

π -bonding

- ❖ The main source of π -bonding is between the d_{xy} , d_{yz} and d_{xz} -orbitals on the metal and the d , p or π^* -orbitals on the ligand.
- ❖ Ligands with full p or d -orbitals serve as a π -donors ($L \rightarrow M$).
- ❖ Ligands with empty d or π^* -orbitals serve as a π -acceptors ($M \rightarrow L$) and form **π -back bonding**.

Metals with zero-oxidation state -Complex formation

- ❖ The nature of Metal-Ligand (eg: $M-CO$) bonding can be understood by considering the formation of a dative σ -bond and π -bonding (due to back donation).

Eg: $[Ni(CO)_4]$, $[Fe(CO)_5]$

Metals with zero-oxidation state -Complex formation

Dative σ -bond

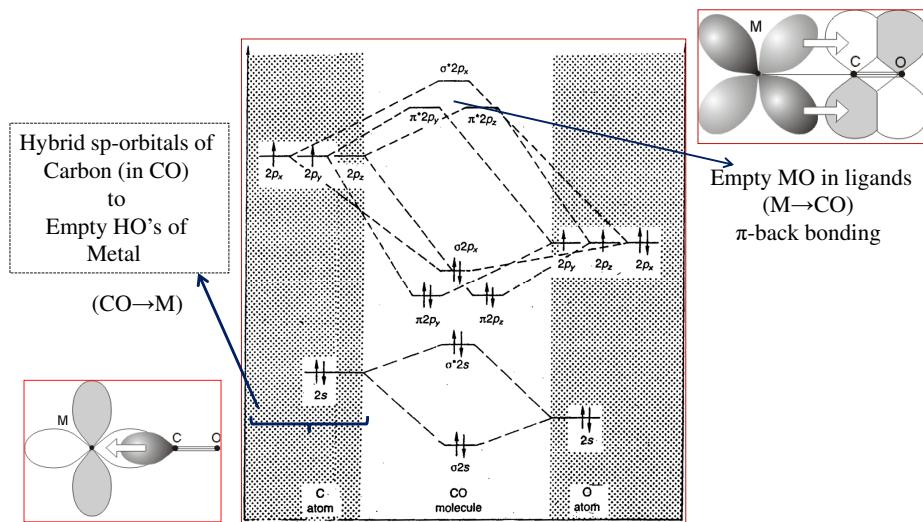
- ❖ The overlapping of empty hybrid orbital (a blend of d, s & p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a $M \leftarrow CO$ σ -bond.

Metals with zero-oxidation state -Complex formation

π -bonding (π -back bonding)

- ❖ In low oxidation states, the electron density on the metal ion is very high.
- ❖ To stabilize low oxidation states of metals, we require ligands which can bind the metal centre and withdraw electron density from it simultaneously.
- ❖ Carbon monoxide (CO) is one of the most important π -acceptor ligand. Because of its π - acidity, it can stabilize zero formal oxidation state of metals in carbonyl complexes. Eg: $[Ni(CO)_4]$, $[Fe(CO)_5]$
- ❖ CO has empty π^* -molecular orbitals which can interact with filled d-orbitals of the metal ($M \rightarrow CO$). This is also called π -back bonding.

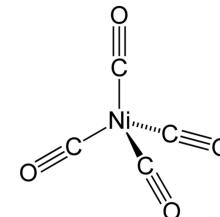
Metals with zero-oxidation state -Complex formation



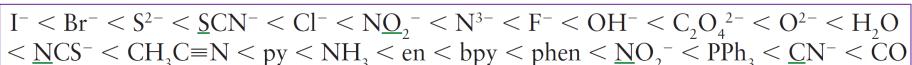
Metals with zero-oxidation state -Complex formation

❖ Thus, MO theory explained the formation of complexes with zero metal oxidation state using the π -bonding.

Eg: $[\text{Ni}(\text{CO})_4]$



Spectrochemical series – explanation



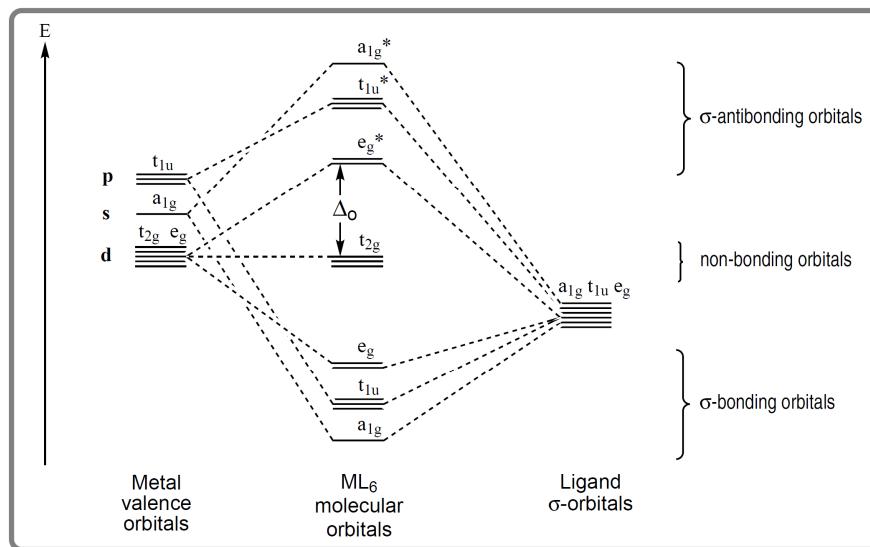
π donor < weak π -donor < σ -only < π -acceptor

- ❖ All ligands are σ -donors. In general, ligands that engage solely in σ -bonding are in the middle of the spectrochemical series.
- ❖ Ligands with filled p or d -orbitals can also serve as π -donors (weak ligands). This results in a smaller value of Δ_o .
- ❖ Ligands with empty p , d or π^* -orbitals can serve as π -acceptors (strong ligands). This results in a larger value of Δ_o .

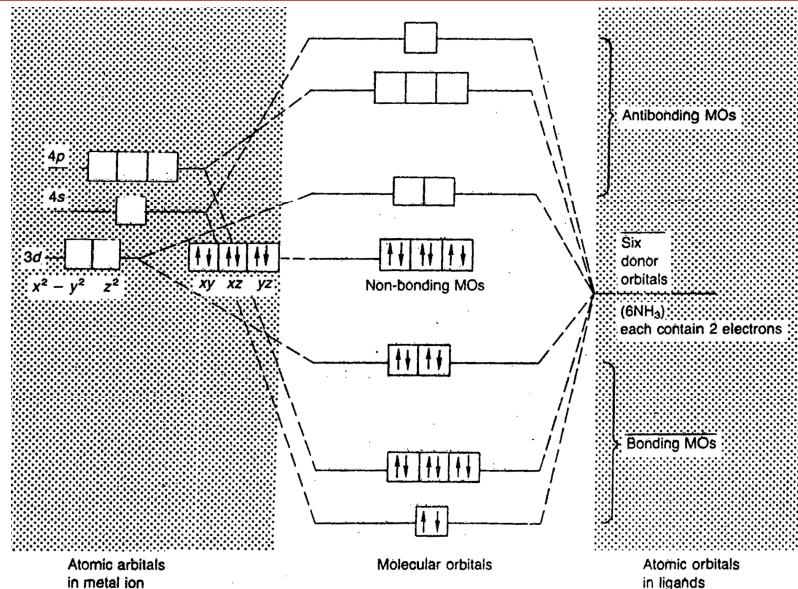
MO diagram for octahedral complexes

Metal orbital	Symmetry label	Degeneracy
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
$d_{x^2-y^2}, d_{z^2}$	e_g	2
d_{xy}, d_{yz}, d_{zx}	t_{2g}	3

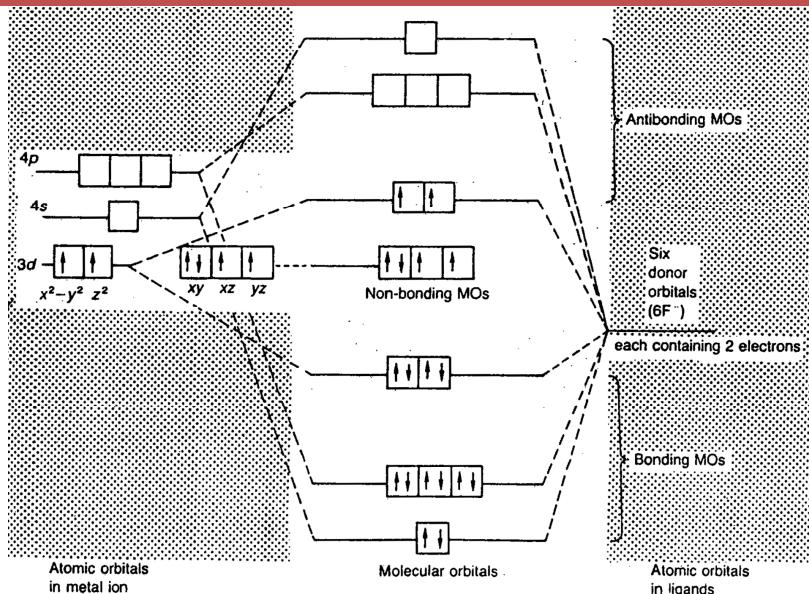
MO diagram for octahedral complexes



MO diagram for [Co(NH₃)₆]³⁺



MO diagram for [CoF₆]³⁻



Organometallics
--
Metal carbonyls

Organometallics --- Metal carbonyls

- Compounds having at least one bond between carbon and metal are known as **organometallic compounds**.
- Metal carbonyls** are the transition metal complexes of carbon monoxide containing metal-carbon bond ($M-C\equiv O$).
- A variety of complexes such as mono nuclear, poly nuclear, homoleptic (similar ligands) and mixed ligands are known.
- Metal carbonyls are widely studied due to industrial importance, catalytic properties and structural interest

Metal carbonyls

formula	Valence electrons	Structure
$Fe(CO)_5$	Fe 8 5(CO) 10 Total 18	
$Co_2(CO)_8$	Co 9 4(CO) 8 M-M 1 Total 18	
$Ni(CO)_4$	Ni 10 4(CO) 8 Total 18	

Bonding in metal carbonyls

- The nature of M-CO bonding in mononuclear carbonyls can be understood by considering the formation of
 - a dative σ -bond ($CO \rightarrow M$)
 - π -bonding due to back donation ($M \rightarrow CO$)

Formation of dative σ -bond:

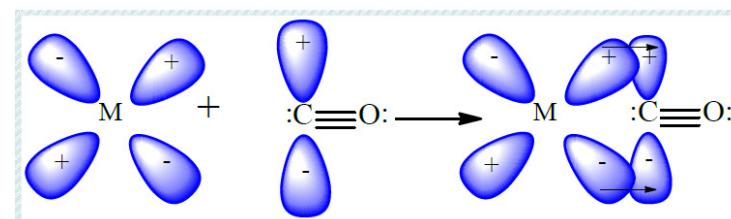
The overlapping of empty hybrid orbital (a blend of d, s & p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a ($CO \rightarrow M$) dative σ -bond.



Bonding in metal carbonyls

Formation of π -bond by back donation (π -back bonding):

CO ligand has empty π^* -molecular orbitals which can interact and withdraw electron density from filled d-orbitals of the metal ($M \rightarrow CO$). This is also called π -back bonding.



Metal carbonyls - Classification

In addition to the linear M-CO groups, the CO ligand is also known to form bridges. This type of bonding is observed in some binuclear and polynuclear carbonyls. It is denoted by μ_n -CO, where 'n' indicates the number of metals bridged.

Type	Examples
Mononuclear carbonyls	$[\text{Ti}(\text{CO})_6]^{2-}$, $[\text{V}(\text{CO})_6]$, $[\text{Cr}(\text{CO})_6]$, $[\text{Fe}(\text{CO})_5]$, $[\text{Ni}(\text{CO})_4]$
Binuclear carbonyls	$[\text{Mn}_2(\text{CO})_{10}]$, $[\text{Fe}_2(\text{CO})_9]$, $[\text{Co}_2(\text{CO})_8]$
Polynuclear carbonyls	$[\text{Fe}_3(\text{CO})_{12}]$, $[\text{Co}_4(\text{CO})_{12}]$, $[\text{Co}_6(\text{CO})_{16}]$
μ_2 -Bridging carbonyls	$[\text{Fe}_2(\text{CO})_9]$, $[\text{Co}_2(\text{CO})_8]$, $[\text{Fe}_3(\text{CO})_{12}]$, $[\text{Co}_4(\text{CO})_{12}]$
μ_3 -Bridging carbonyls	$[\text{Rh}_6(\text{CO})_{16}]$ (Four triply bridged carbonyl groups)
Carbonyl hydrides	$[\text{HMn}(\text{CO})_5]$, $[\text{HCo}(\text{CO})_4]$, $[\text{H}_2\text{Fe}(\text{CO})_4]$

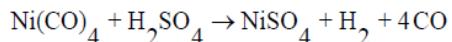
$\text{Ni}(\text{CO})_4$ -- Properties

Physical properties:

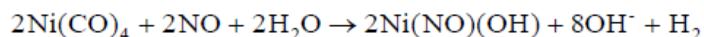
- It is a colourless liquid having melting point -25°C , boiling point 43°C and decomposition temperature in the range of $180\text{--}200^\circ\text{C}$. It is insoluble in water but dissolves in organic solvents.

Chemical properties:

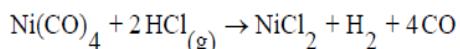
- It reacts with concentrated sulphuric acid along with detonation



- It reacts with moist nitric oxide to give deep blue colored compound

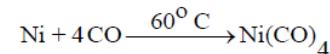


- Passing gaseous hydrochloric acid in the solution of nickel tetracarbonyl results in the decomposition

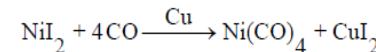


Nickel tetracarbonyl , $\text{Ni}(\text{CO})_4$ --- Preparation

- It can be prepared by passing carbon monoxide over nickel in the temperature range of $60\text{--}100^\circ\text{C}$



- It can be made by heating nickel iodide with carbon monoxide in the presence of copper which acts as a halogen acceptor.



$\text{Ni}(\text{CO})_4$ -- Structure

- Nickel tetracarbonyl has a tetrahedral geometry with Ni-C bond lengths of 1.5 \AA . It is also found to be diamagnetic.

- $\text{OC}\rightarrow\text{Ni}$ bond is a result of the overlap between the empty sp^3 hybrid orbital (LUMO) on Ni-atom and the HOMO on C-atom in CO molecule.

- The nickel atom donates back some electron density from the filled d-orbitals to the empty (LUMO) molecular orbitals on CO molecule resulting into formation of a double bond. i.e. $\text{M} \rightarrow \text{CO} (\pi)$

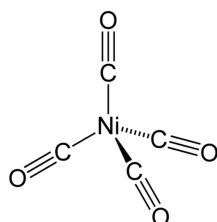
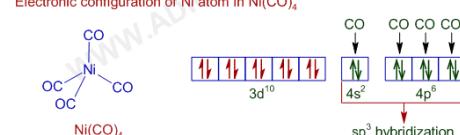
Electronic configuration of Ni atom in ground state



Change in electronic configuration of Ni atom when CO ligands approach it



Electronic configuration of Ni atom in $\text{Ni}(\text{CO})_4$

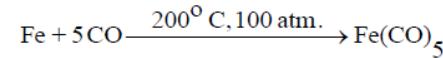


Ni(CO)₄ -- Uses

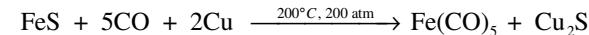
1. Since Ni(CO)₄ on heating decomposes to metallic nickel, it is used in the production of nickel by Mond's process.
2. It is used for plating nickel on other metals.
3. It is used as a catalyst for synthesis of acrylic monomers in plastic industries.

Iron pentacarbonyl, Fe(CO)₅ --- preparation

1. It can be prepared by passing carbon monoxide over iron powder at high temperature and pressure



2. It can also be prepared by carbonylation of ferrous sulphide/iodide in presence of Cu-metal, which acts as a reducing agent



Fe(CO)₅ --- properties

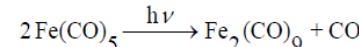
Physical Properties:

- ❖ It is a pale yellow liquid having melting point -20°C, boiling point 103°C and decomposition temperature around 250°C.
- ❖ It is insoluble in water but soluble in glacial acetic acid, methanol, diethyl ether, acetone and benzene.

Fe(CO)₅ --- properties

Chemical properties:

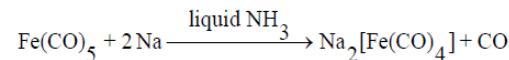
1. Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light.



2. It is readily hydrolysed by water and acids

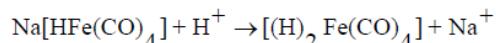
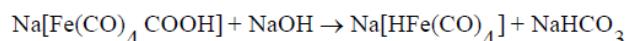
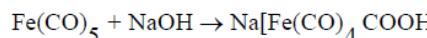


3. It reacts with sodium metal in liquid ammonia to give carbonylate anion. This compound is popularly known as Collman's reagent in organic synthesis. The Collman's reagent is used in aldehyde synthesis.



Fe(CO)₅ --- properties

4. The reaction of sodium hydroxide with iron pentacarbonyl results in nucleophilic attack by hydroxide ion on the carbonyl group to give a metal carboxylic acid complex. Upon further action with sodium hydroxide, the carboxylic acid gives up carbon dioxide to form a hydrido anion. The protonation of this anion results in the formation of iron tetracarbonyl hydride (Heiber base) as shown below:



Fe(CO)₅ --- Structure

The structural studies have suggested trigonal bipyramidal geometry for iron pentacarbonyl. The Fe-C distances are found to be 1.80 Å and 1.84 Å for axial and equatorial bonds respectively. The molecule is also found to be diamagnetic.

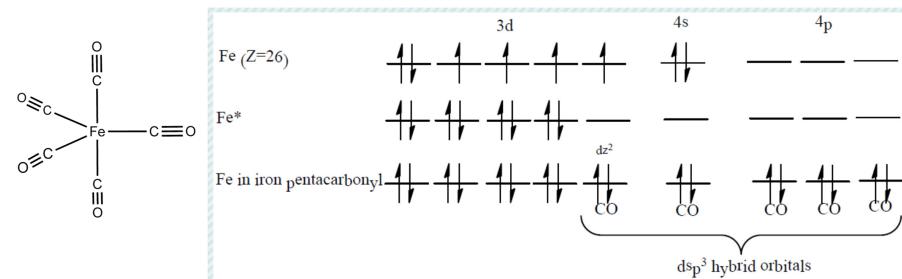


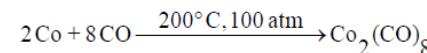
Figure: dsp^3 hybridization in iron pentacarbonyl.

Fe(CO)₅ --- Uses

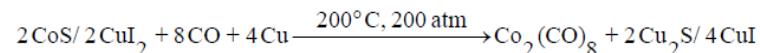
1. Fe(CO)₅ is used in the production of “carbonyl iron”, a finely divided form of Fe, a material used in magnetic cores of high-frequency coils for radios and televisions.
2. Used to manufacture the active ingredients of some radar absorbent materials (e.g. iron ball paint to absorb radio frequency (RF) radiation).
3. It is famous as a chemical precursor for the synthesis of various iron-based nanoparticles.
4. Iron pentacarbonyl has been found to be a strong flame speed inhibitor in oxygen based flames.

diCobalt octacarbonyl, Co₂(CO)₈ --- Preparation

1. It can be prepared by direct combination of carbon monoxide with cobalt metal.



2. It can also be prepared by carbonylation of cobalt iodide/cobalt sulphide/cobalt carbonate using reducing agents like copper metal or hydrogen gas.



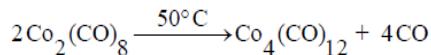
Co₂(CO)₈ --- Properties

Physical Properties:

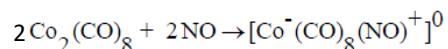
1. It is an orange crystalline substance having melting point 51°C and turns deep violet upon exposure to air.
2. It is soluble in alcohols, ether and carbon tetrachloride.

Chemical Properties:

1. Upon heating at 50°C it forms tetracobalt dodecacarbonyl



2. It reacts with nitric oxide to form cobalt carbonyl nitrosyl.



Co₂(CO)₈ --- Structure

Dicobalt octacarbonyl is known to exist in two isomeric forms. A bridged structure of this molecule is observed in the solid state as well as solution state at a very low temperature.

A non-bridged structure predominates in a solution at temperatures above ambience.

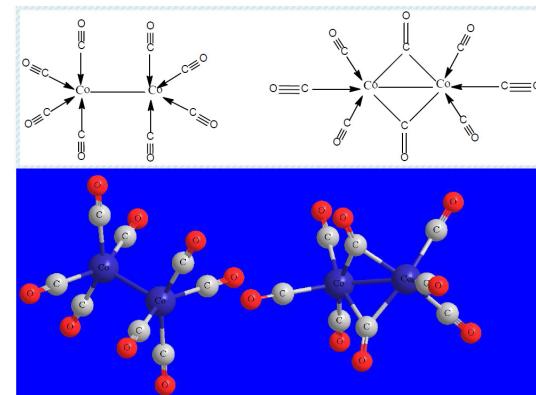


Figure: Structure of dicobalt octacarbonyl (without bridge and with bridge).

Co₂(CO)₈ --- Structure without bridge

In the structure without bridge, the cobalt atoms are in dsp^3 hybrid state. Out of five hybrid orbitals on each cobalt atom, four orbitals on each atom accept a lone pair of electrons from the CO molecules to form 8 CO \rightarrow Co coordinate bonds.

A Co-Co bond is formed by the overlap of two half-filled dsp^3 hybrid orbitals on the cobalt atoms.

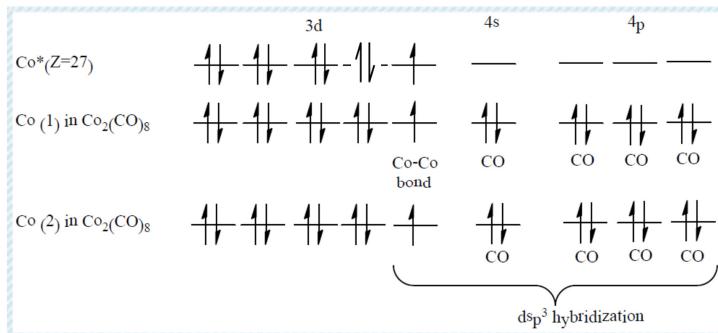


Figure: dsp^3 hybridization in dicobalt octacarbonyl

Co₂(CO)₈ --- Structure with bridge

In the bridged structure, the cobalt atoms are in d^2sp^3 hybrid state. Three such hybrid orbitals on each cobalt atom accept lone pair of electrons from 3 – CO molecules to form a total of six CO \rightarrow Co coordinate bonds.

A Co-Co bond is formed by the overlap of two half-filled d^2sp^3 hybrid orbitals on the cobalt atoms. Remaining two half-filled hybrid orbitals on each Co-atom overlap with appropriate orbital on carbon atom of the carbonyl to form two bridging CO groups.

Thus, all electrons in this molecule are paired and it is diamagnetic.

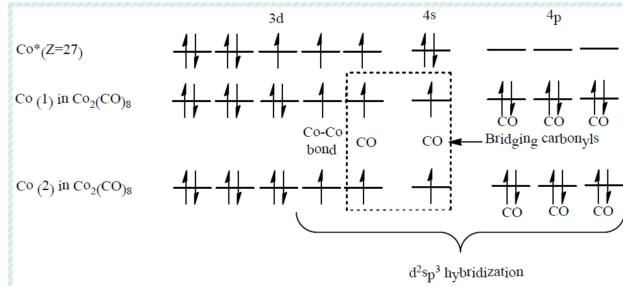


Figure: d^2sp^3 hybridization in dicobalt octacarbonyl

Co₂(CO)₈ --- Uses

1. This metal carbonyl is used as a reagent and catalyst in organometallic chemistry and organic synthesis.
2. It is central to much known organocobalt chemistry.
3. It is the precursor to a hydroformylation catalyst, cobalt tetracarbonyl hydride.

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Reference books

- “Concise Inorganic Chemistry” by J. D. Lee.
- “Inorganic Chemistry” by Atkins and Shriver.
- “Inorganic Chemistry: Principles of Structure and Reactivity” by James E. Huheey.