

**Module-2:**  
**Metal Complexes and**  
**Organometallics**

## **Contents.....(6 hours)**

---

**Inorganic complexes** - structure, bonding and applications

**Organometallics** – introduction, stability, structure and applications of metal carbonyls and ferrocene

**Metals in biology:** haemoglobin and chlorophyll- structure and property

# Inorganic Complexes

- Inorganic/coordination complex is a molecule containing one or multiple metal centers that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal).
- These complexes can be neutral or charged. The examples are:

**Neutral Complexes:**  $[\text{CoCl}_3(\text{NH}_3)_3]$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , etc.

**Cationic Complex** :  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and **Anionic Complex** :  $[\text{CoCl}_4(\text{NH}_3)_2]^-$

## Selected examples of metal complexes with names:

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  --- Chloropentaamminecobalt(III) chloride

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$  --- Dichlorotetraaquo chromium(III) chloride

$\text{K}[\text{PtCl}_3(\text{NH}_3)]$  --- Potassiumtrichloroammineplatinate(II)

$[\text{PtCl}_2(\text{NH}_3)_2]$  --- Dichlorodiammineplatinum(II)

$[\text{Co}(\text{en})_3\text{Cl}_3]$  --- tris(ethylenediamine)cobalt(III)chloride

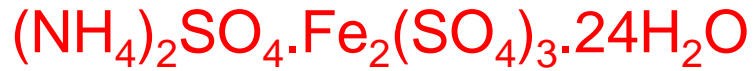
$[\text{Ni}(\text{PF}_3)_4]$  --- tetrakis(phosphorus(III)fluoride)nickel(0)

# Structure and Bonding

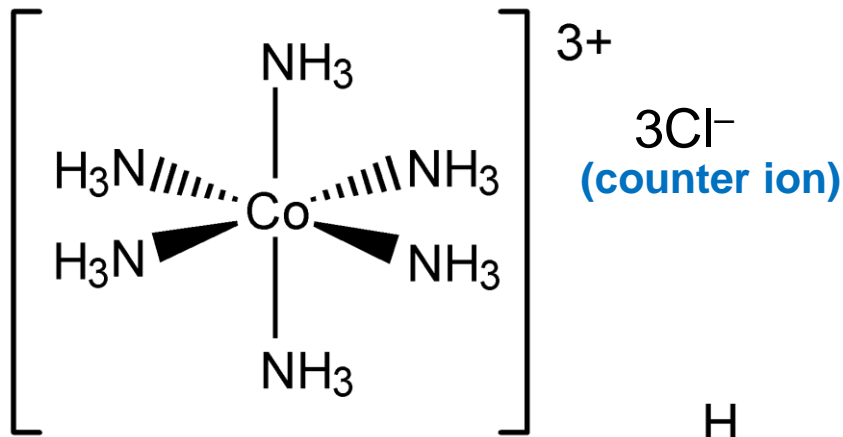
## ❖ Double Salt:

## Double Salts Vs Coordination Compounds

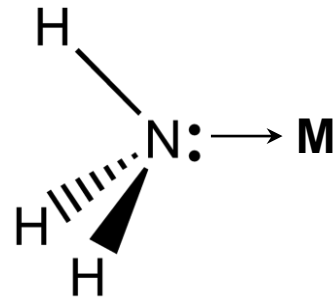
Ferric alum



In water:  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{3+}$

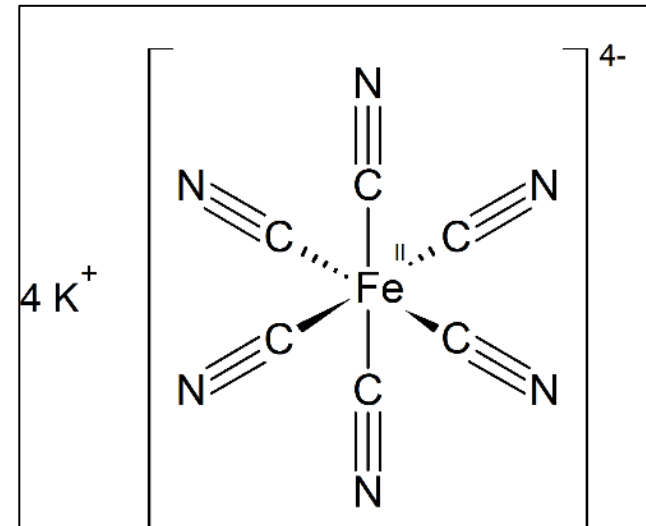
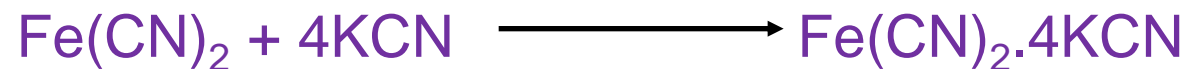


ligand  
(coordination sphere)



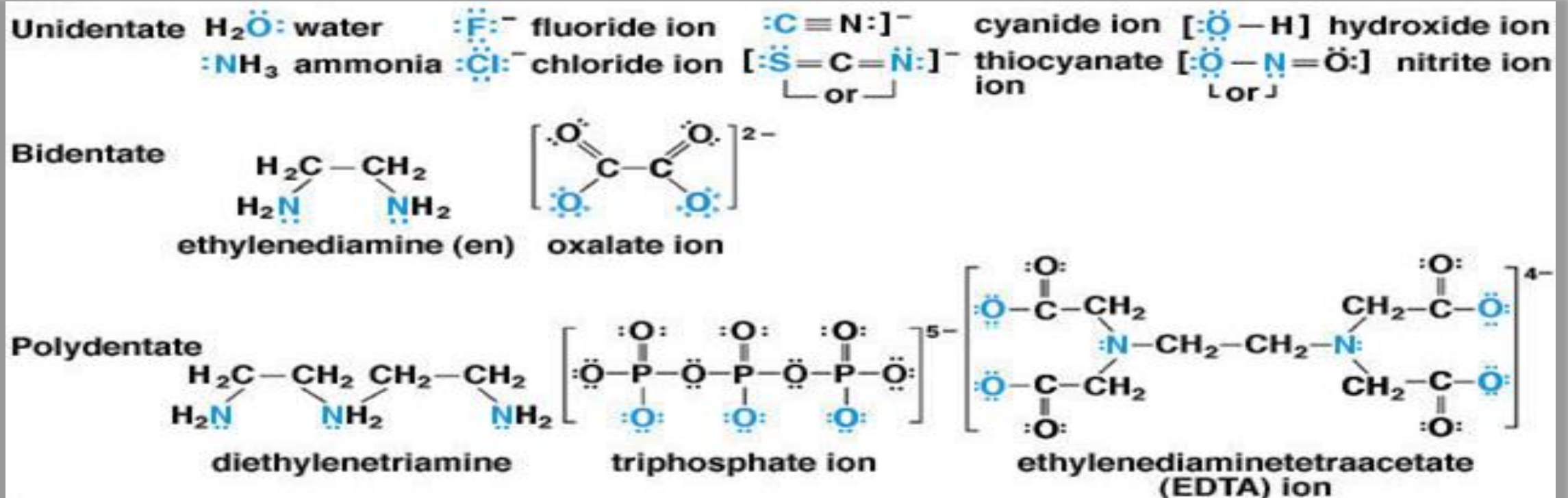
N forms a coordinate covalent bond  
to the metal

## ❖ Co-ordination Compounds



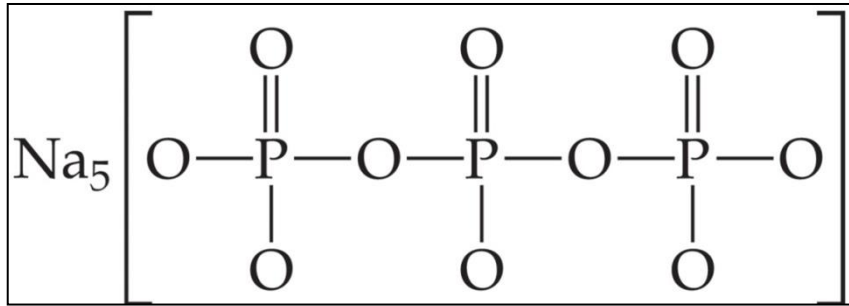
# Ligands

- Molecule or ion having **a lone electron pair with an atom (donor)** that can be donated to a metal atom forming **a dative bond** is called a **Lewis base**.
- coordinate covalent bond: **metal-ligand bond**
- monodentate : **one bond to metal ion**
- bidentate : **two bonds to metal ion**
- polydentate : **more than two bonds to a metal ion possible**

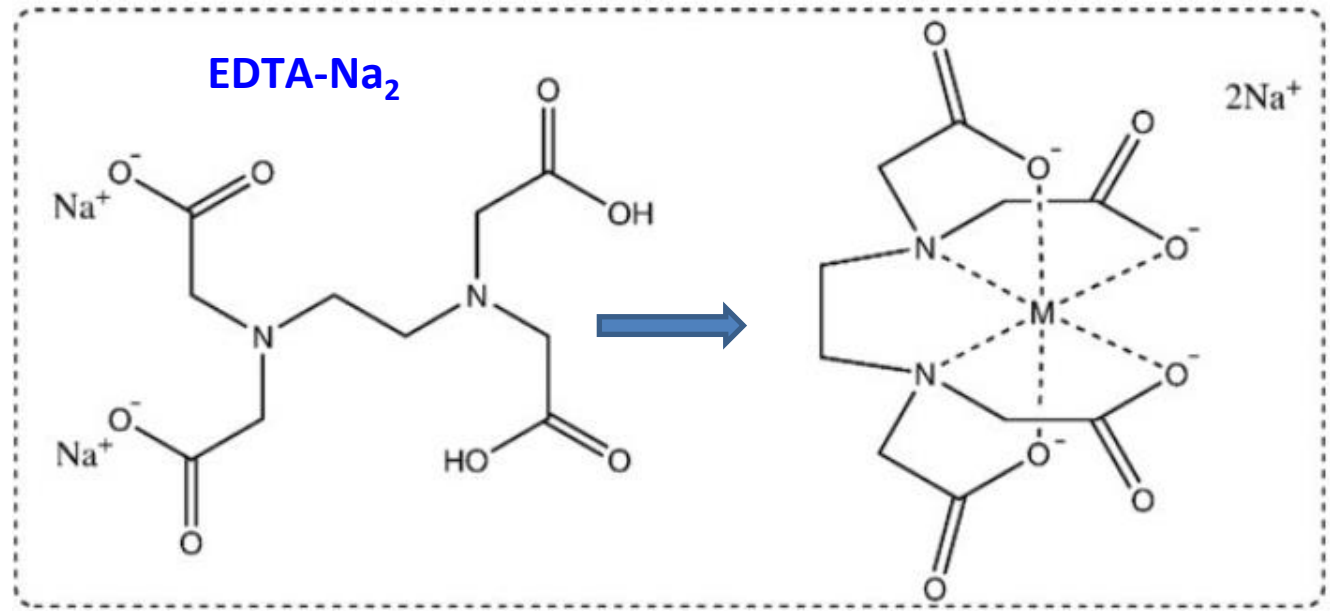
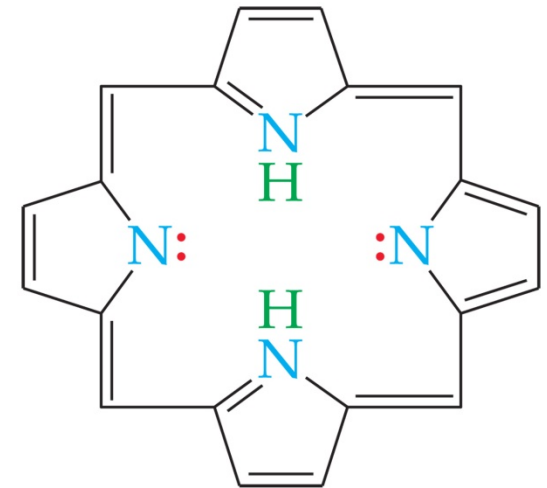


# Chelating Agents

- Bind to metal ions removing them from solution.
- Phosphates are used to tie up  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in hard water to prevent them from interfering with detergents.



- Important biomolecules like heme and chlorophyll are porphyrins



EDTA-Metal  
complex

# Lewis Acid Base Theory - Gilbert N. Lewis, 1920s

---

- ❖ Lewis Acid/Base reactions: Base: electron pair donor; Acid: electron pair acceptor
- ❖ Ligands: Lewis bases ; Metals: Lewis acids ; Coordinate covalent bonds
- ❖ Metal Complexes - Formation of a complex was described as an acid - base reaction according to Lewis

## Sidgwick's Rule

---

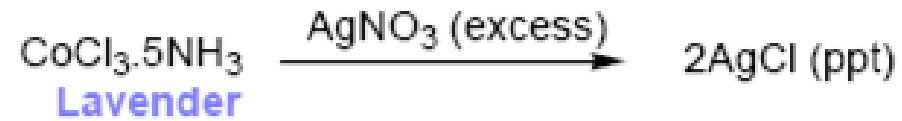
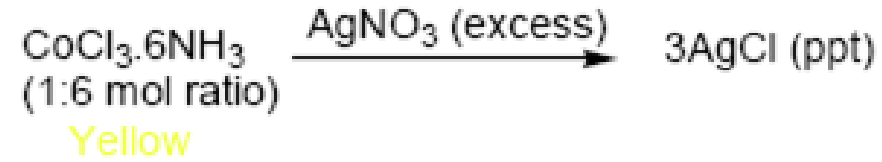
- ❖ Sidgwick's Effective atomic number (EAN) rule is based on the octet theory of Lewis and this is the first attempt to account for the bonding in complexes.

# Werner Coordination Theory

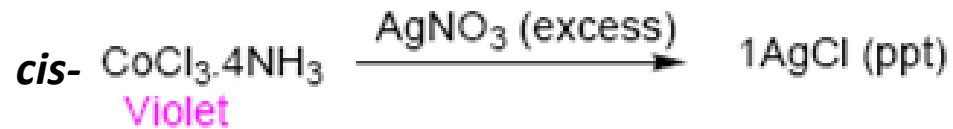
**Werner's Theory:** Alfred Werner, Swiss chemist put forward **a theory to explain the formation of complex compounds.**

Werner studied the following metal complexes:

- $\text{CoCl}_3$  forms four different compounds with  $\text{NH}_3$ .



One Cl does not react



**Limitations:**



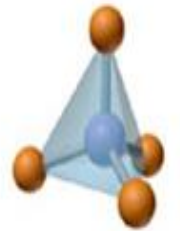
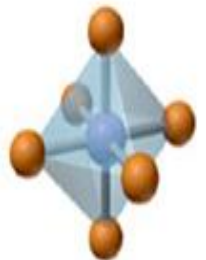
1. Bonding within coordination sphere.
2. Square planar (or) Tetrahedral



# Valence Bond Theory (Linus Pauling, 1931)

**Valence bond theory** predicts that the bonding in a metal complex arises from overlap of filled ligand orbitals and vacant metal orbitals.

Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{CN})_2]^-$
3	$\text{sp}^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$\text{sp}^3$	Tetrahedral	$[\text{Ni}(\text{CO})_4]$ , $[\text{NiCl}_4]^{2-}$
4	$\text{dsp}^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$
5	$\text{dsp}^3$ ( $d_{x^2-y^2}$ orbital is involved)	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$
6	$\text{d}^2\text{sp}^3$ ( $d_z^2$ and $d_{x^2-y^2}$ orbitals of inner shell are involved)	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{Fe}(\text{CN})_6]^{2-}$ , $[\text{Fe}(\text{CN})_6]^{3-}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$ (Inner orbital complexes)
6	$\text{sp}^3\text{d}^2$ ( $d_z^2$ and $d_{x^2-y^2}$ orbitals of the outer shell are involved)	Octahedral	$[\text{FeF}_6]^{4-}$ , $[\text{CoF}_6]^{4-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (Outer orbital complexes)

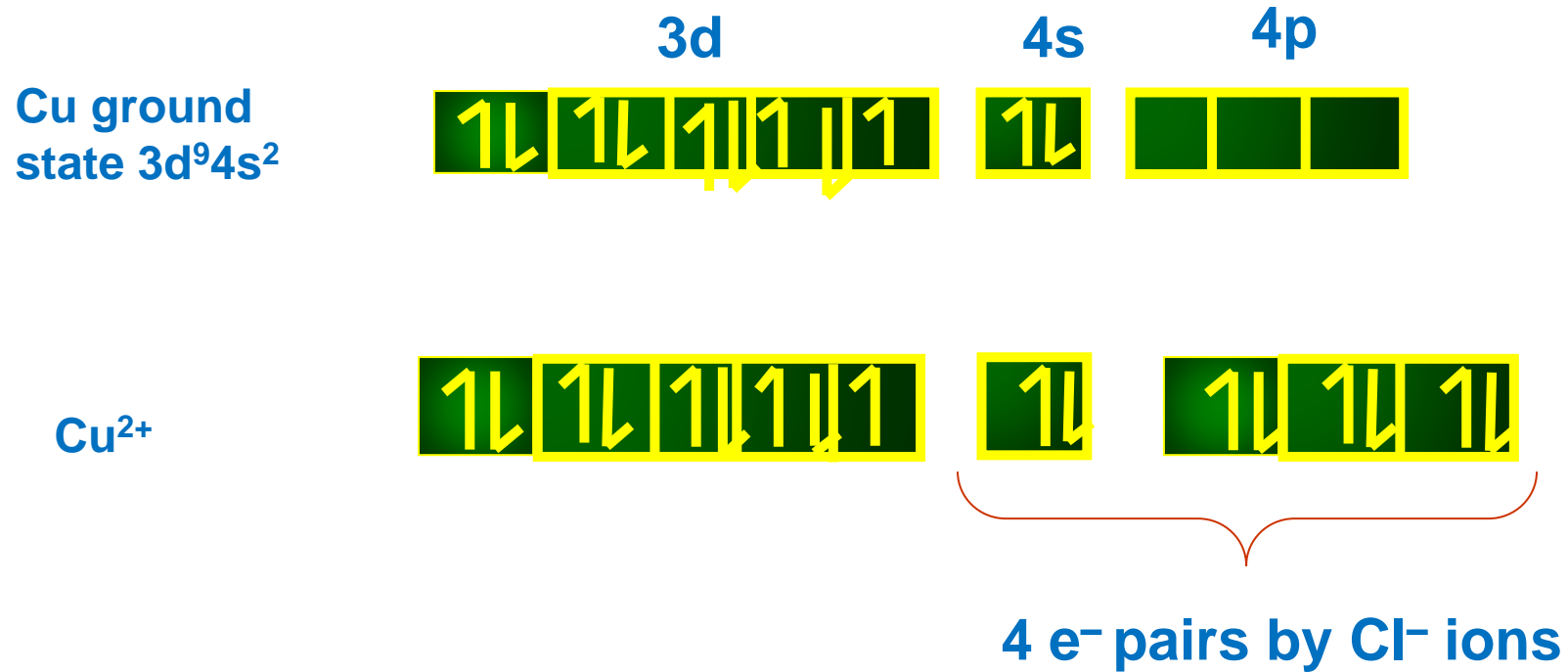
Coordination Number	Shape		Examples
2	Linear		$[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{AuCl}_2]^-$
4	Square planar		$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{PdCl}_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral		$[\text{Cu}(\text{CN})_4]^{3-}$ , $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , $[\text{CdCl}_4]^{2-}$ , $[\text{MnCl}_4]^{2-}$
6	Octahedral		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{V}(\text{CN})_6]^{4-}$ , $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ , $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{FeCl}_6]^{3-}$ , $[\text{Co}(\text{en})_3]^{3+}$

It does not explain the color indicated by coordination compounds, the thermodynamic/kinetic stabilities of coordination complexes. Also, it does not differentiate between weak/strong ligands.

## Limitations

# Tetrahedral Geometry

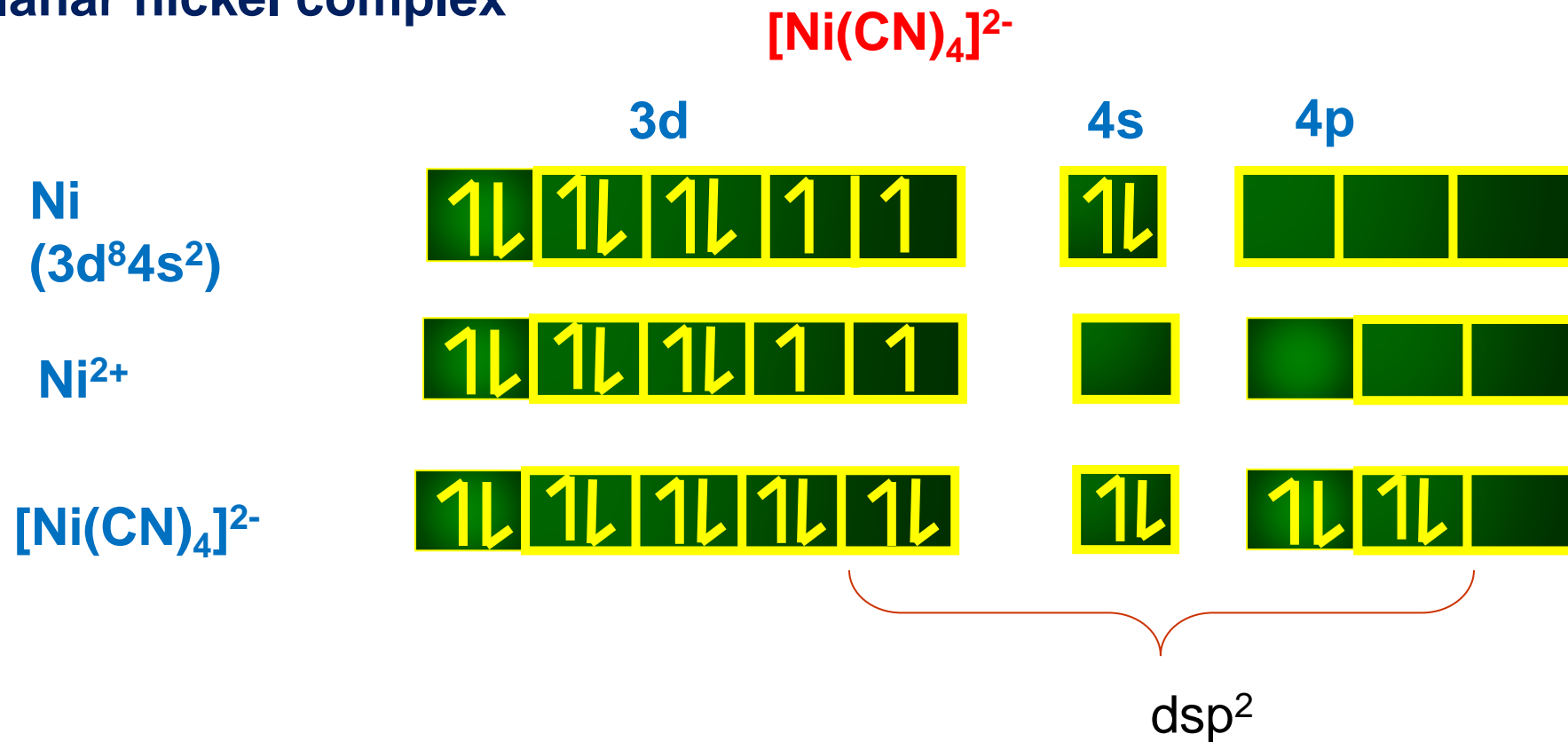
- Tetrahedral copper complex



- One unpaired electron - paramagnetic and attracted by magnets—  
High spin complexes

# Square Planar Geometry

- Square planar nickel complex

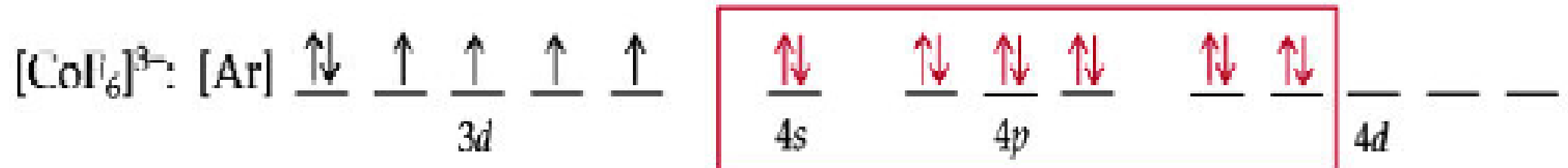


- All paired electrons – diamagnetic - weakly repelled by magnets –  
Low spin complexes

# Octahedral $sp^3d^2$ Geometry

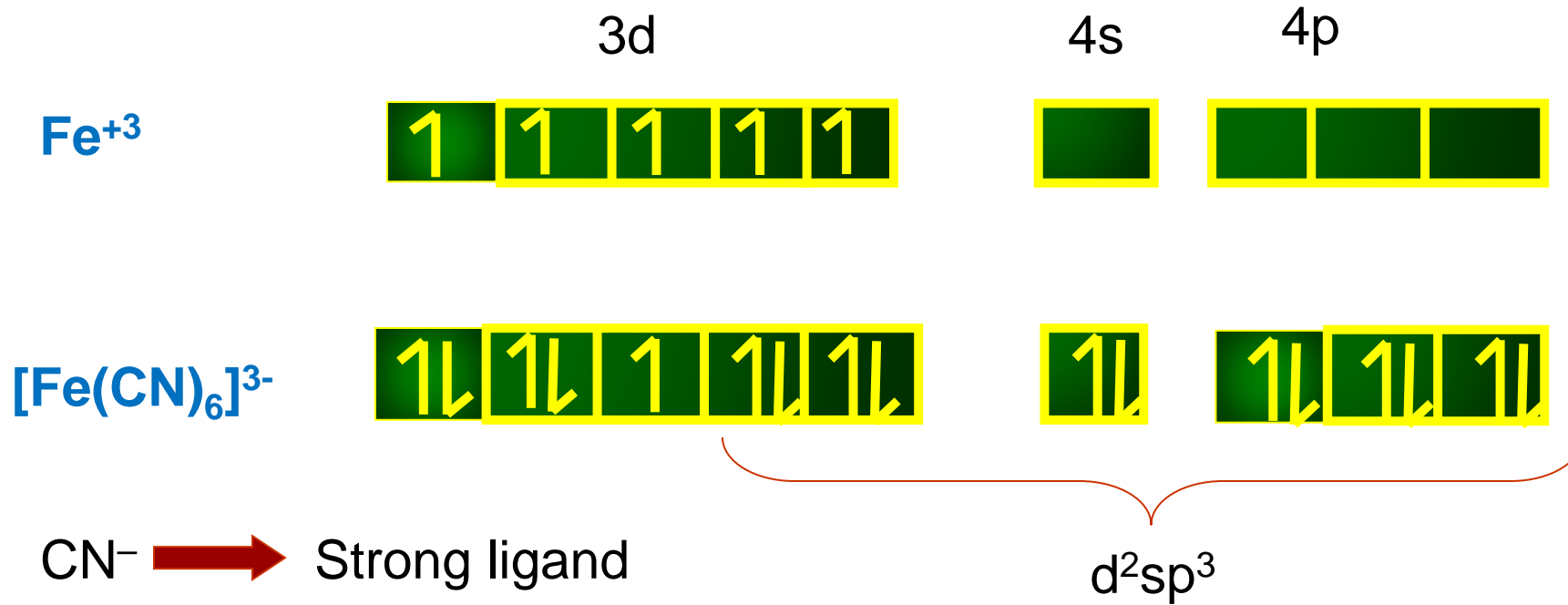
Gives  $[\text{CoF}_6]^{3-}$  four unpaired electrons, which makes it paramagnetic and is called a *high-spin complex*.

Ground state Co =  $(3d^7 4s^2)$



Six  $sp^3d^2$  bonds to the ligands

# Octahedral $d^2sp^3$ Geometry



# Bonding in Coordination Compounds

---

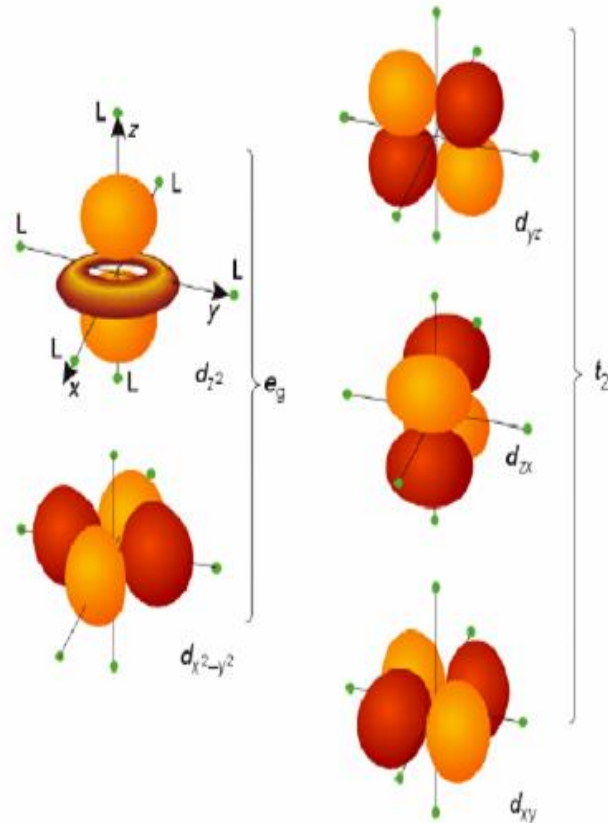
- ❖ Many of the properties of metal complexes are dictated by their electronic structures.

## Crystal field theory (CFT)

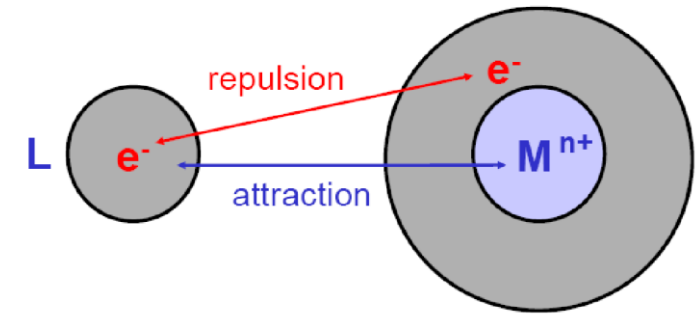
- ❖ Electronic structure can be explained by an ionic model that attributes formal charges on to the metals and ligands. This forms basis of crystal field theory (CFT), which is considered as the core concept in inorganic chemistry.
- ❖ Consider bonding in a complex to be an electrostatic attraction between a positively charged nucleus and the electrons of the ligands.
  - **Electrons on metal atom repel electrons on ligands.**
  - **Focus particularly on the  $d$ -electrons on the metal ion.**
- ❖ Ligand field theory (LFT) and the molecular orbital theory (MO) are considered sophisticated models as compared to CFT. LFT explains complexes, wherein, the interactions are covalent.

# CFT Assumptions

- Interaction between the metal ion and the ligands are purely electrostatic (ionic)
- Ligands are considered as point charges
- Ion-ion interaction, if the ligand is negatively charged and ion-dipole interaction, if the ligand is neutral
- Electrons on the metal are under repulsive from those on the ligands
- Electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands.

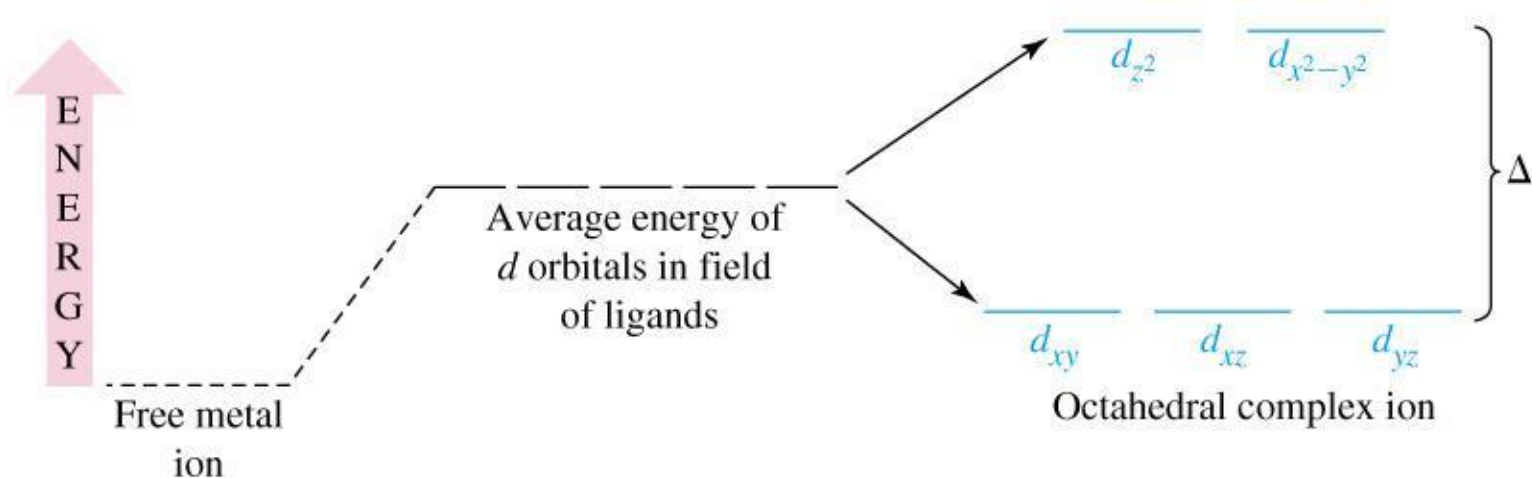


## Crystal Field Theory

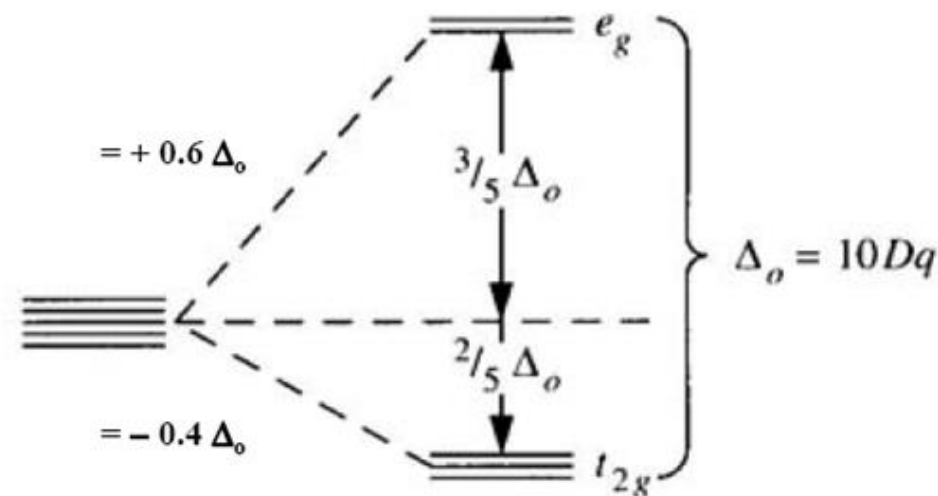


- Interaction between electrons of the cation and those of ligands are entirely repulsive. This is responsible for splitting of d orbitals.
- CFT does not consider the overlapping between metal and ligand orbitals.
- The d-orbitals lose their degeneracy due to the approach of ligands during the formation of complex.

# Octahedral Complex and $d$ -Orbital Energies



- For the  $O_h$  point group, the  $dx^2-y^2$ ,  $dz^2$  orbitals belong to the  $e_g$  irreducible representation and  $xy$ ,  $xz$ ,  $yz$  belong to the  $T_{2g}$  representation.
- The splitting extent of these two sets of orbitals is denoted by  $\Delta_0$  or  $10 Dq$ . As the barycenter must be conserved on going from a spherical field to an octahedral field, the  $t_{2g}$  set must be stabilized as much as the  $e_g$  set is destabilized.





# CFSE and electronic arrangements in octahedral complexes

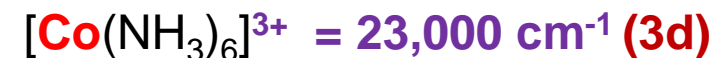
Number of <i>d</i> electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	<i>t</i> <sub>2g</sub>	<i>e</i> <sub>g</sub>	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$	<i>t</i> <sub>2g</sub>	<i>e</i> <sub>g</sub>	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$
<i>d</i> <sup>1</sup>	↑ □ □ □	□ □	-0.4	1.73	↑ □ □ □	□ □	-0.4	1.73
<i>d</i> <sup>2</sup>	↑ ↑ □ □	□ □	-0.8	2.83	↑ ↑ □ □	□ □	-0.8	2.83
<i>d</i> <sup>3</sup>	↑ ↑ ↑ □	□ □	-1.2	3.87	↑ ↑ ↑ □	□ □	-1.2	3.87
<i>d</i> <sup>4</sup>	↑ ↑ ↑ ↑	□ □	-1.2 +0.6 = -0.6	4.90	↑ ↓ ↑ ↑	□ □	-1.6	2.83
<i>d</i> <sup>5</sup>	↑ ↑ ↑ ↑	↑ ↑	-1.2 +1.2 = -0.0	5.92	↑ ↓ ↑ ↓ ↑	□ □	-2.0	1.73
<i>d</i> <sup>6</sup>	↑ ↓ ↑ ↑	↑ ↑	-1.6 +1.2 = -0.4	4.90	↑ ↓ ↑ ↓ ↑	□ □	-2.4	0.00
<i>d</i> <sup>7</sup>	↑ ↓ ↑ ↓ ↑	↑ ↑	-2.0 +1.2 = -0.8	3.87	↑ ↓ ↑ ↓ ↑	↑ □	-2.4 +0.6 = -1.8	1.73
<i>d</i> <sup>8</sup>	↑ ↓ ↑ ↓ ↑	↑ ↑	-2.4 +1.2 = -1.2	2.83	↑ ↓ ↑ ↓ ↑	↑ ↑	-2.4 +1.2 = -1.2	2.83
<i>d</i> <sup>9</sup>	↑ ↓ ↑ ↓ ↑	↑ ↓ ↑	-2.4 +1.8 = -0.6	1.73	↑ ↓ ↑ ↓ ↑	↑ ↓ ↑	-2.4 +1.8 = -0.6	1.73
<i>d</i> <sup>10</sup>	↑ ↓ ↑ ↓ ↑	↑ ↓ ↑	-2.4 +2.4 = 0.0	0.00	↑ ↓ ↑ ↓ ↑	↑ ↓ ↑	-2.4 +2.4 = 0.0	0.00

$\Delta_o$  is dependent on:

- Nature of the ligands
- The charge on the metal ion
- Whether the metal is a 3d, 4d, or 5d element



27  
Co



45  
Rh



77  
Ir

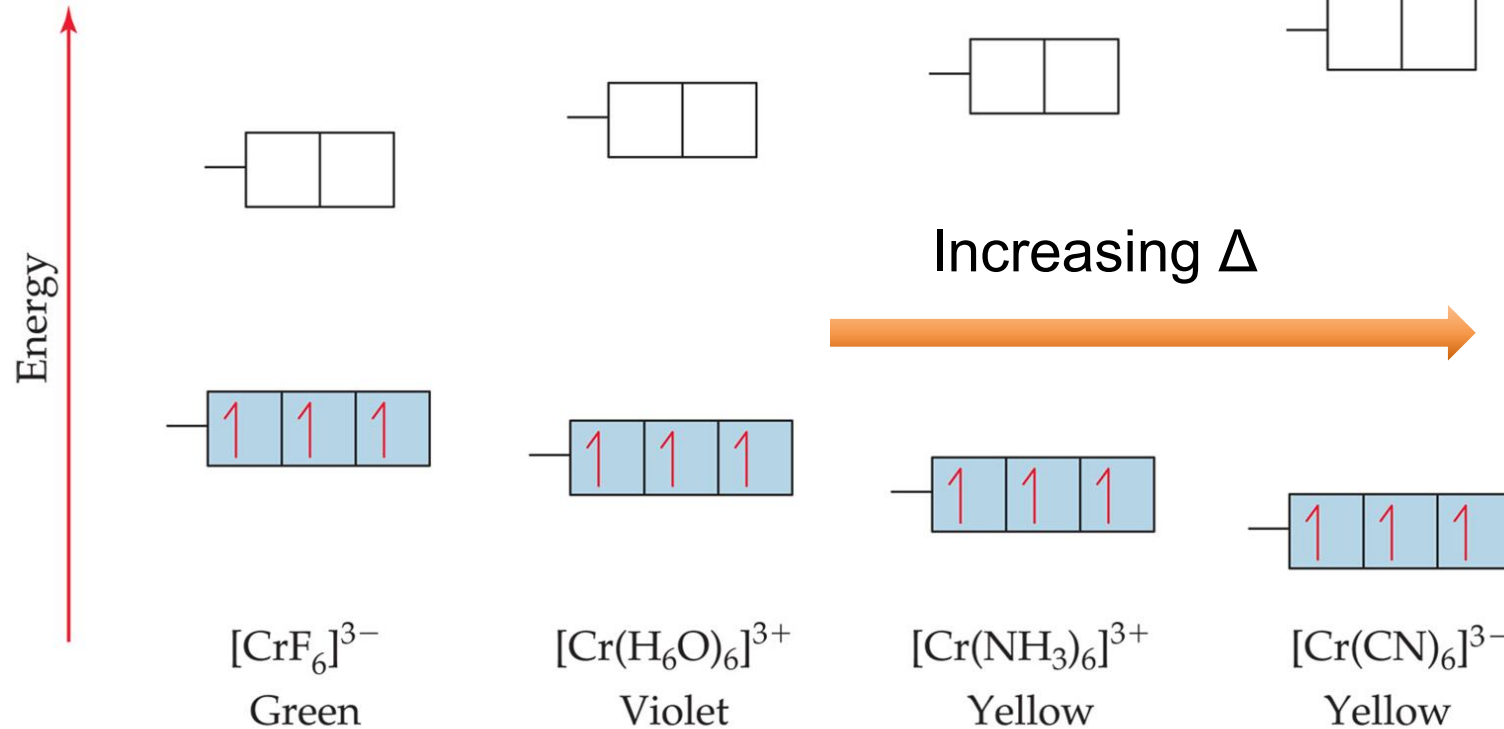
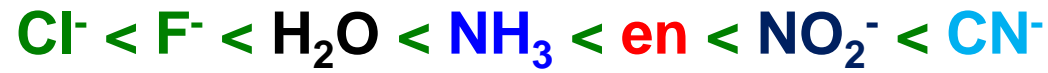


# Spectrochemical series (strength of ligand interaction)

Effect of ligand on splitting energy



Increasing  $\Delta$

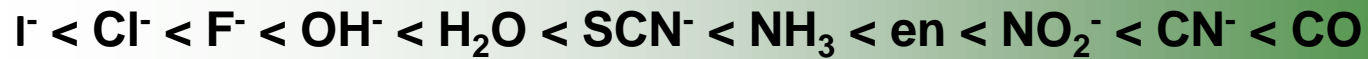


Copyright © 2006 Pearson Prentice Hall, Inc.

Low spin – color variations shown with increasing CFSE  **$(\text{Cr}^{3+} = 24 - 3 - 18 = d^3)$**

# Spectrochemical Series

- For a given ligand, the color depends on the oxidation state of the metal ion.



WEAKER FIELD

STRONGER FIELD

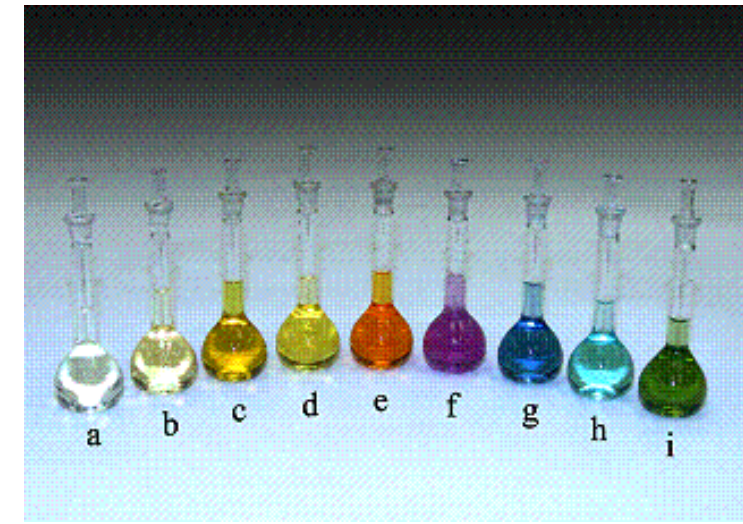
SMALLER  $\Delta$

LARGER  $\Delta$

LONGER  $\lambda$

SHORTER  $\lambda$

- For a given metal ion, the color depends on the ligand.



- ❖ Complexes of cobalt (III) show the shift in color due to the ligand.
- ❖ (a)  $\text{CN}^-$ , (b)  $\text{NO}_2^-$ , (c) phen, (d) en, (e)  $\text{NH}_3$ , (f) gly, (g)  $\text{H}_2\text{O}$ , (h)  $\text{ox}^{2-}$ , (i)  $\text{CO}_3^{2-}$

# Examples

Hybridisation	Shape of coordination compound	Examples
$sp$	linear	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]$
$sp^2$	trigonal planar	$[\text{HgI}_3]^-$
$sp^3$	tetrahedral	$[\text{CuCl}_4]^{2-}$ , $[\text{ZnCl}_4]^{2-}$ , $[\text{Ni}(\text{CO})_4]$
$dsp^2$	square, planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$
$sp^3d$	trigonal bipyramidal	$[\text{CuCl}_5]^{3-}$
$dsp^3$	trigonal bipyramidal	$[\text{Ni}(\text{CN})_5]^{3-}$ $[\text{Fe}(\text{CO})_5]$

Complex Compound or Ion	Magnetic Behaviour	Hybridisation	Shape
$[\text{Fe}(\text{CN})_6]^{3-}$	Paramagnetic	$d^2sp^3$	Octahedral
$[\text{Fe}(\text{CN})_6]^{4-}$	Diamagnetic	$d^2sp^3$	Octahedral
$[\text{Ni}(\text{CN})_4]^{2-}$	Diamagnetic	$dsp^2$	Square Planar
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	Paramagnetic	$dsp^2$	Square Planar
$[\text{Ni}(\text{NH}_3)_4]\text{SO}_4$	Paramagnetic	$sp^3$	Tetrahedral
$[\text{Cu}(\text{CN})_4]^{2-}$	Paramagnetic	$dsp^2$	Square Planar
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	Paramagnetic	$d^2sp^3$	Octahedral
$[\text{Cr}(\text{CN})_6]^{3-}$	Paramagnetic	$d^2sp^3$	Octahedral
$[\text{Co}(\text{CN})_6]^{3-}$	Diamagnetic	$d^2sp^3$	Octahedral
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Diamagnetic	$d^2sp^3$	Octahedral



## Some **limitations of CFT** are as follows:

---

- This theory **only considers the d-orbitals** of a central atom. The **s and p orbits are not taken into account** in this study.
- The theory **fails to explain the behaviour of certain metals**, which exhibit large splitting while others exhibit minor splitting. For example, the theory provides no explanation for why  $\text{H}_2\text{O}$  is a stronger ligand than  $\text{OH}^-$ .
- The theory **excludes the possibility of p bonding**. This is a significant disadvantage because it is found in many complexes.
- **The orbits of the ligands have no significance** in the theory. As a result, it cannot explain any properties of ligand orbitals or their interactions with metal orbitals.

# Applications of Coordination Compounds

---

- ❖ Coordination compounds are of great importance.
- ❖ Play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.
- **Catalysis**
- **Extraction of metal ions**
- **Analytical chemistry (development of numerous analytical methods)**
- **Hardness estimation -**
- **Biological importance**
- **Medicinal application**
- **Industrial application**

# Extraction / Purification of Metals

---



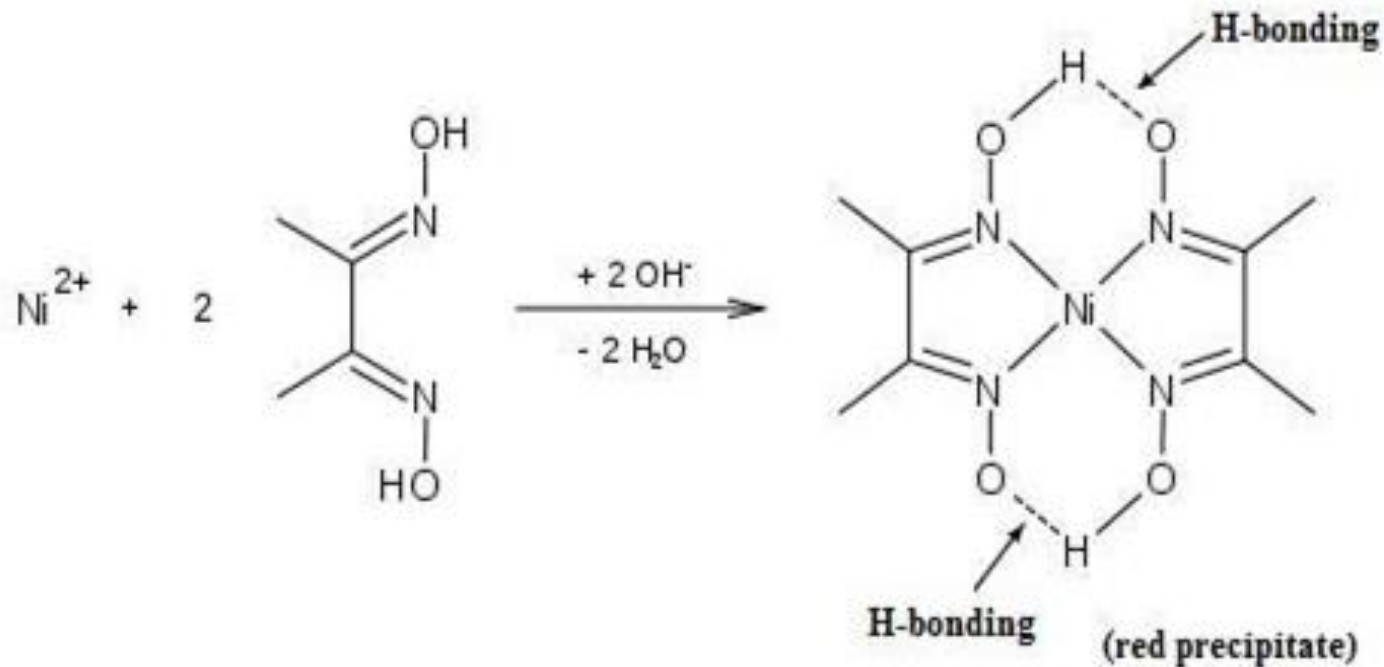
## ➤ Extraction

- ❖ processes of metals, like those of **silver and gold**, make use of complex formation.
- ❖ These noble metals are extracted from their ore by the formation of cyanide complexes - dicyanoargentite(I) -  $[\text{Ag}(\text{CN})_2]^-$  and dicyanoaurate (I) -  $[\text{Au}(\text{CN})_2]^-$  in the presence of oxygen and water, from which the metallic forms can be separated by the addition of zinc.
  - $\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$
  - $2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}\downarrow$
- ❖ **Purification of metals** can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to  **$[\text{Ni}(\text{CO})_4]$** , which is decomposed to yield pure nickel (**the Mond process**).

# Detection of Complex Formation

❖ In the qualitative methods of analysis, complex formation is of immense importance in the identification by color change and separation of most inorganic ions.

❖ Formation of Precipitate

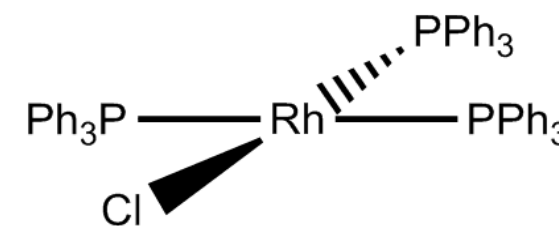
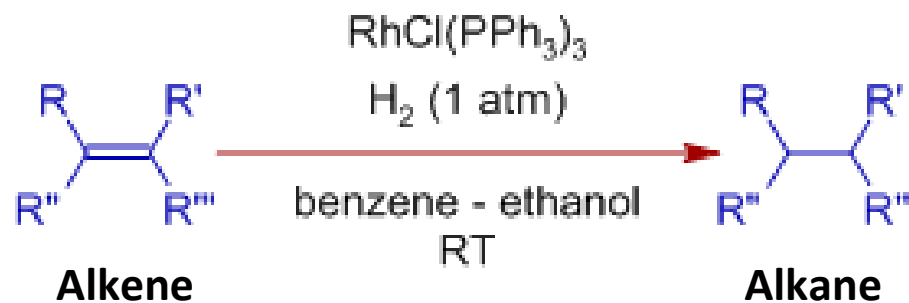


❖  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$  form insoluble colored precipitates with dimethylglyoxime



# Industrial Applications

- Coordination compounds are used as catalysts for many industrial processes. Examples rhodium complex,  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ , a Wilkinson catalyst – Catalytic hydrogenation of alkenes.



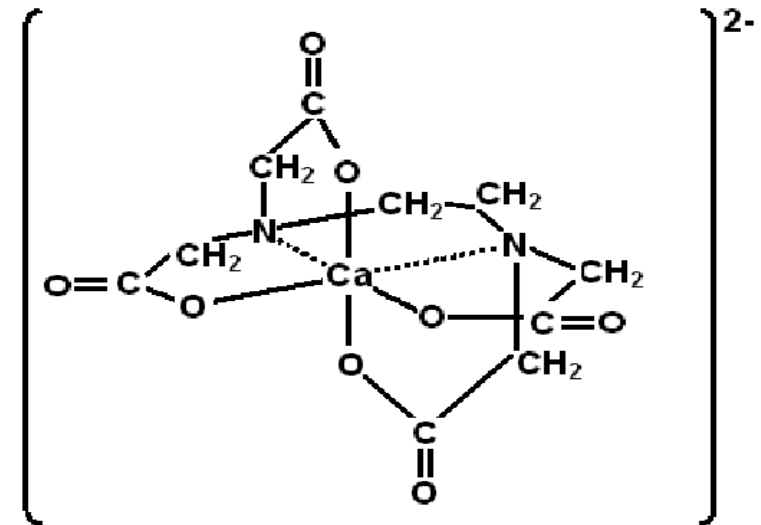
Wilkinson catalyst

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes,  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the non decomposed  $\text{AgBr}$  to form a complex ion,  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ .
- Prussian blue – Mixture of hexacyano $\text{Fe}(\text{II})$  and  $\text{Fe}(\text{III})$  -  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  inks, blueprinting, cosmetics, paints (commercial coloring agents)



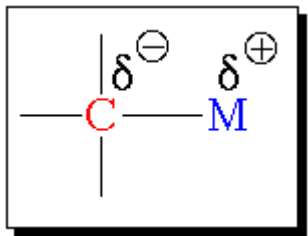
# Hardness of water

- ❖ Hardness of water is estimated by titration with the sodium salt of EDTA.
- ❖ During titration, the calcium and magnesium ions in hard water form the stable complexes, Calcium EDTA and Magnesium EDTA.
- ❖ Hardness of water is estimated by simple titration with  $\text{Na}_2\text{EDTA}$ .
- ❖ The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.



# Organometallics – Introduction, stability, structure and applications of metal carbonyls and ferrocene

# What are Organometallics?



- ❖ An area which bridges organic and inorganic chemistry.
- ❖ A branch of coordination chemistry where the complex has one or more metal-carbon bonds.

**C** always is more electronegative compared to **M**.

- ❖ The leading journals of the field define an "organometallic" compound as one in which there is a bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms)
- ❖ Following longstanding tradition, organic derivatives of metalloids such as **boron (B)**, **silicon (Si)**, **germanium (Ge)**, **arsenic (As)**, **tellurium (Te)** are also included in this definition.

**Zeise's Salt- The first transition metal organometallic compound:**

❖ **Discovery 1827**

❖ **Structure ~ 150 years later**



**First  $\sigma$ -bonded Organometallic Compound- Diethyl Zinc:**

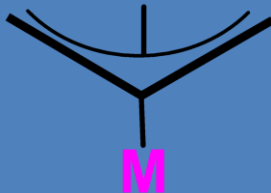


# Nomenclature of Ligands

$\eta^x$

“eta- $x$ ” was originally developed to indicate how many carbons of a  $\pi$ -system were coordinated to a metal center. **Hapticity** is another word used to describe the bonding mode of a ligand to a metal center. An  $\eta^5$ -cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

- $\eta^x$  values for carbon ligands where the  $x$  value is odd usually indicate *anionic* carbon ligands (e.g.,  $\eta^5$ -Cp,  $\eta^1$ -CH<sub>3</sub>,  $\eta^1$ -allyl or  $\eta^3$ -allyl,  $\eta^1$ -CH=CH<sub>2</sub>)
- The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to  $x + 1$
- Even  $\eta^x$  values usually indicate *neutral* carbon  $\pi$ -system ligands (e.g.,  $\eta^6$ -C<sub>6</sub>H<sub>6</sub>,  $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>,  $\eta^4$ -butadiene,  $\eta^4$ -cyclooctadiene)
- Number of electrons donated by the ligand in the even (*neutral*) case is usually just equal to  $x$ .

			
$\eta^5$ -Cp	$\eta^3$ -Cp	$\eta^3$ -allyl	$\eta^1$ -allyl

❖ **Organometallic compounds are classified into three types.**

- **(i) Sigma ( $\sigma$ ) bonded organometallic compounds:** In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, For Example:

- **(a) Grignard reagents,  $R-Mg-X$**  where R is an alkyl or aryl group, and X is a halogen.

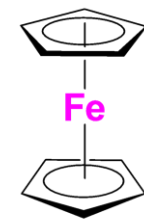
- **(b) Zinc compounds of the formula  $R_2Zn$**  such as  $(C_2H_5)_2Zn$

**(ii) Pi ( $\pi$ ) bonded organometallic compounds:**

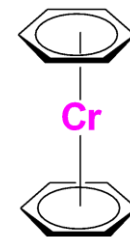
These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the  $\pi$ -electrons of the ligand.

**(iii) Sigma and  $\pi$ -bonded organometallic compounds**

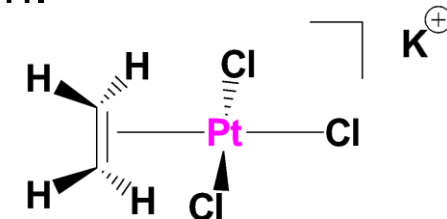
Metal-carbonyl compounds formed between metal and carbon monoxide possess both  $\sigma$ -and  $\pi$ -bonding. Generally, oxidation state of metal atoms in these compounds is zero.



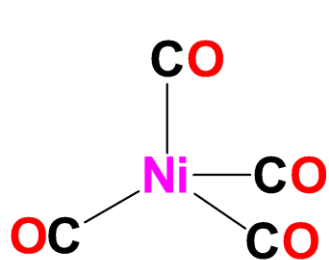
Ferrocene  
 $Fe(\eta^5-C_5H_5)_2$



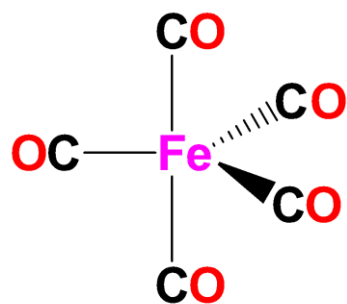
Dibenzene chromium  
 $Cr(\eta^6-C_6H_6)_2$



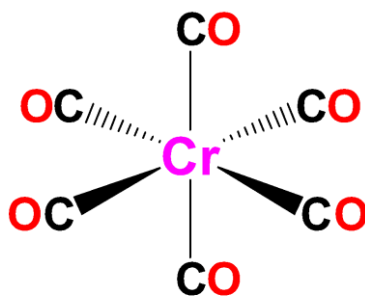
Zeise's salt



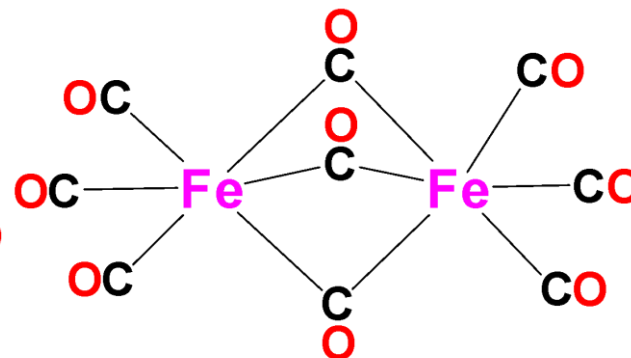
$Ni(CO)_4$



$Fe(CO)_5$



$Cr(CO)_6$



$Fe_2(CO)_9$

# Stability of Organometallic Compounds

- ❖ In general terms, the stability of an organometallic compound may refer to either its thermal stability, or resistance to chemical attack (by air and moisture). Obviously, these different types of stabilities would depend both on **thermodynamic** as well as **kinetic** factors.

The organometallic compounds are generally **hydrolysed** via nucleophilic attack by water, which is facilitated by:

- (1) the presence of empty low-lying orbitals on the metal
- (2) the polarity of metal-carbon bonds. Rate of hydrolysis is dependent on M-C bond polarity – greater the polarity, faster will be the rate

# The 18-electron Rule or Effective atomic number (EAN)

- ❖ The 18e rule is a way to help us decide whether a given d-block transition metal organometallic complex is likely to be stable. Not all the organic formulas we can write down correspond to stable species. **Recall:** Second row elements (B, C, N, O, F) have 4 valence orbitals ( $1s + 3p$ ) so they can accommodate up to 8 valence electrons--*the octet rule*.
- For example,  $\text{CH}_5$  requires a 5-valent carbon and is therefore not stable. Stable compounds, such as  $\text{CH}_4$ , have the noble gas octet, and so carbon can be thought of as following an 8e rule.
- **The 18e rule**, which applies to many low-valent transition metal complexes, follows a similar line of reasoning. *The metal now has one s, and three p orbitals, as before, but now also five d orbitals.* We need 18e to fill all nine orbitals; some come from the metal, the rest from the ligands. Therefore, we can expect that the low-lying MOs can accommodate up to 18 valence electrons--*The 18-Electron Rule*.
- ❖ The rule states that “***thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18***”



# Counting electrons of a metal complex

To count the electrons of a metal complex, one must:

*a) note any overall charge on the metal complex*

*b) know the charges of the ligands bound to the metal center (ionic ligand method)*

*c) know the number of electrons being donated to the metal center from each ligand (ionic ligand method)*

Similarly for a **transition metal complex**, the electron count is the sum of the metal valence electrons + the ligand centered electrons.

❖ **Covalent Model:** # e = # metal electrons (zero valent) + # ligand electrons - complex charge

**Metal:** The number of metal electrons equals its column number (i.e., Ti = 4e, Cr = 6e, Ni = 10e)

**Ligands:** In general L donates 2 electrons, X donates 1 electron.

❖ **Ionic Model:** # e = # metal electrons ( $d^n$ ) + # ligand electrons

**Metal:** Determined based on the number of valence electrons for a metal at the oxidation state present in the complex

**Ligands:** In general and L and X are both 2 e donors.

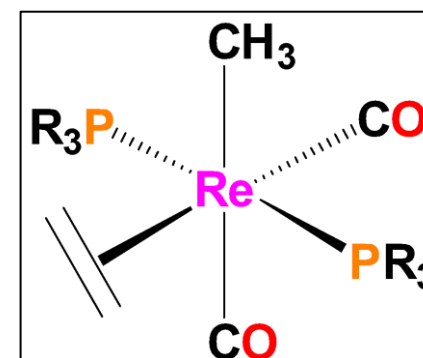
❖ Complexes with 18 e- count are referred to as **saturated**.

❖ Complexes with count lower than 18e- are called **unsaturated**.

## Example 1

Please note that we are using the *Ionic Method* of electron-counting. 95% of inorganic/organometallic chemists use the ionic method. The ionic method assigns formal charges to the metal and ligands in order to keep the ligands with an even # of electrons and (usually) a filled valence shell. Synthetically, the ionic method generally makes more sense and the one that we will use in this course.

- 1) There is no overall charge on the complex
- 2) There is one anionic ligand ( $\text{CH}_3^-$ , methyl group)
- 3) Since there is no overall charge on the complex (it is neutral), and since we have one anionic ligand present, the Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. The +1 charge on the metal is also its oxidation state. So the Re is in the +1 oxidation state. We denote this in two different ways:  $\text{Re}(+1)$ ,  $\text{Re}(\text{I})$ , or  $\text{Re}^{\text{I}}$ .

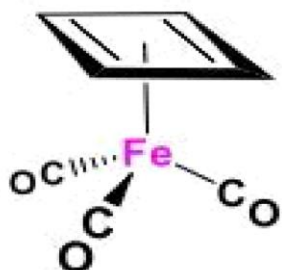


Now we can do our electron counting:

<b>Re(+1)</b>	<b>d<sup>6</sup></b>
<b>2 PR<sub>3</sub></b>	<b>4e<sup>-</sup></b>
<b>2 CO</b>	<b>4e<sup>-</sup></b>
<b>CH<sub>3</sub><sup>-</sup></b>	<b>2e<sup>-</sup></b>
<b>CH<sub>2</sub>=CH<sub>2</sub></b>	<b>2e<sup>-</sup></b>
<hr/>	
<b>Total: 18e<sup>-</sup></b>	

# Other examples

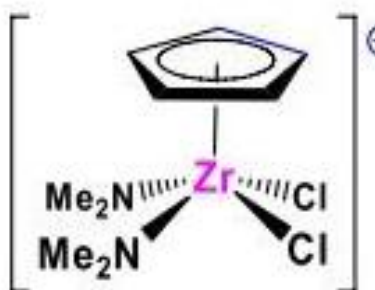
a)  $\text{Fe}(\eta^4\text{-C}_4\text{H}_4)(\text{CO})_3$



Fe(0)	d8
$\eta^4\text{-C}_4\text{H}_4$	4e-
3 CO	6e-
Total	18e-

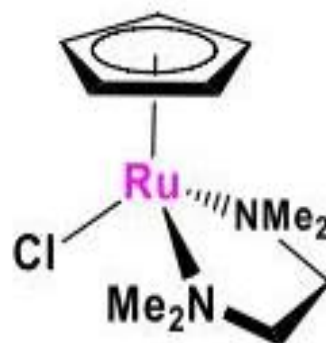
*C<sub>4</sub>H<sub>4</sub> is cyclobutadiene, a neutral 4e- donor*

b)  $\text{cis-}[\text{CpZrCl}_2(\text{NMe}_2)_2]^-$

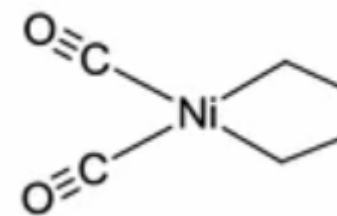


Zr(+4)	d0
Cp <sup>-</sup>	6e-
2 NMe <sub>2</sub> <sup>-</sup>	8e-
2 Cl <sup>-</sup>	4e-
Total	18e-

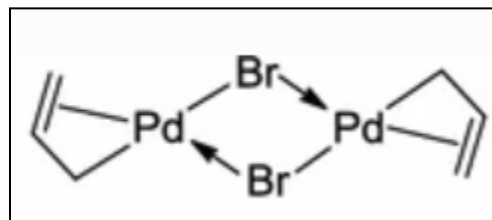
$\text{CpRuCl}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)$



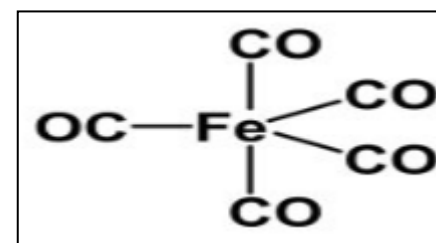
Ru(+2)	d6
Cp <sup>-</sup>	6e-
2 NR <sub>3</sub>	4e-
Cl <sup>-</sup>	2e-
Total	18e-



16 e<sup>-</sup>

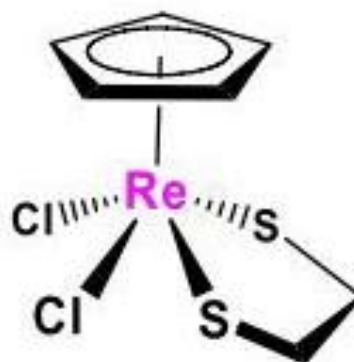


16 e<sup>-</sup>

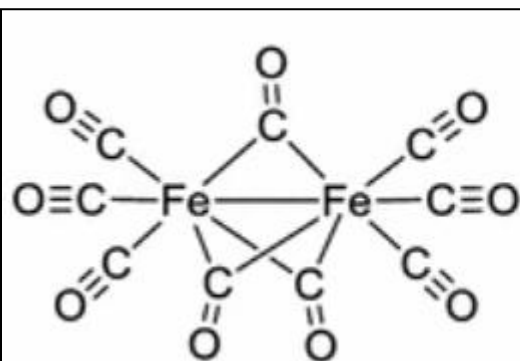


18 e<sup>-</sup>

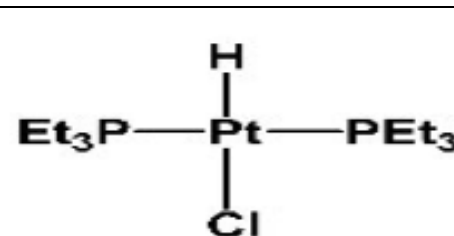
$\text{CpReCl}_2(\eta^2\text{-SCH}_2\text{CH}_2\text{S})$



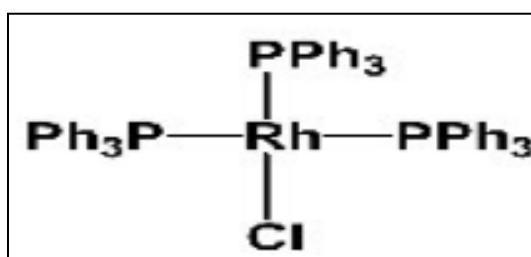
Re(+5)	d2
Cp <sup>-</sup>	6e-
2 SR <sup>-</sup>	4e-
2 Cl <sup>-</sup>	4e-
Total	16e-



Fe(0)	d <sup>8</sup>	8 e <sup>-</sup>
CO	2 e <sup>-</sup> x 3	6 e <sup>-</sup>
μ-CO	1 e <sup>-</sup> x 3	3 e <sup>-</sup>
M-M	1 e <sup>-</sup>	1 e <sup>-</sup>
		18 e <sup>-</sup>

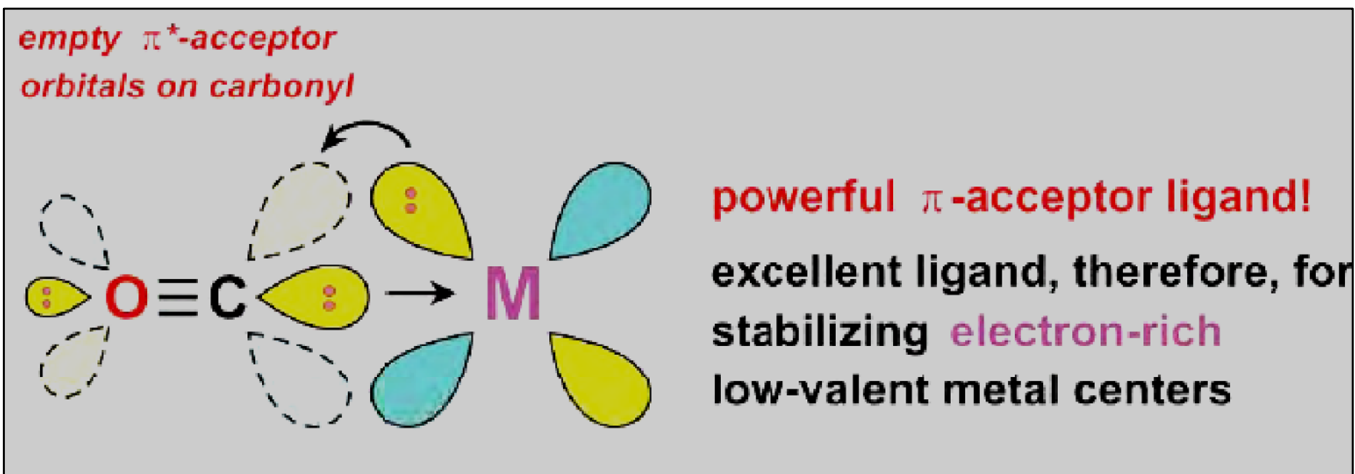


16 e<sup>-</sup>



16 e<sup>-</sup>

# Metal-Carbonyls

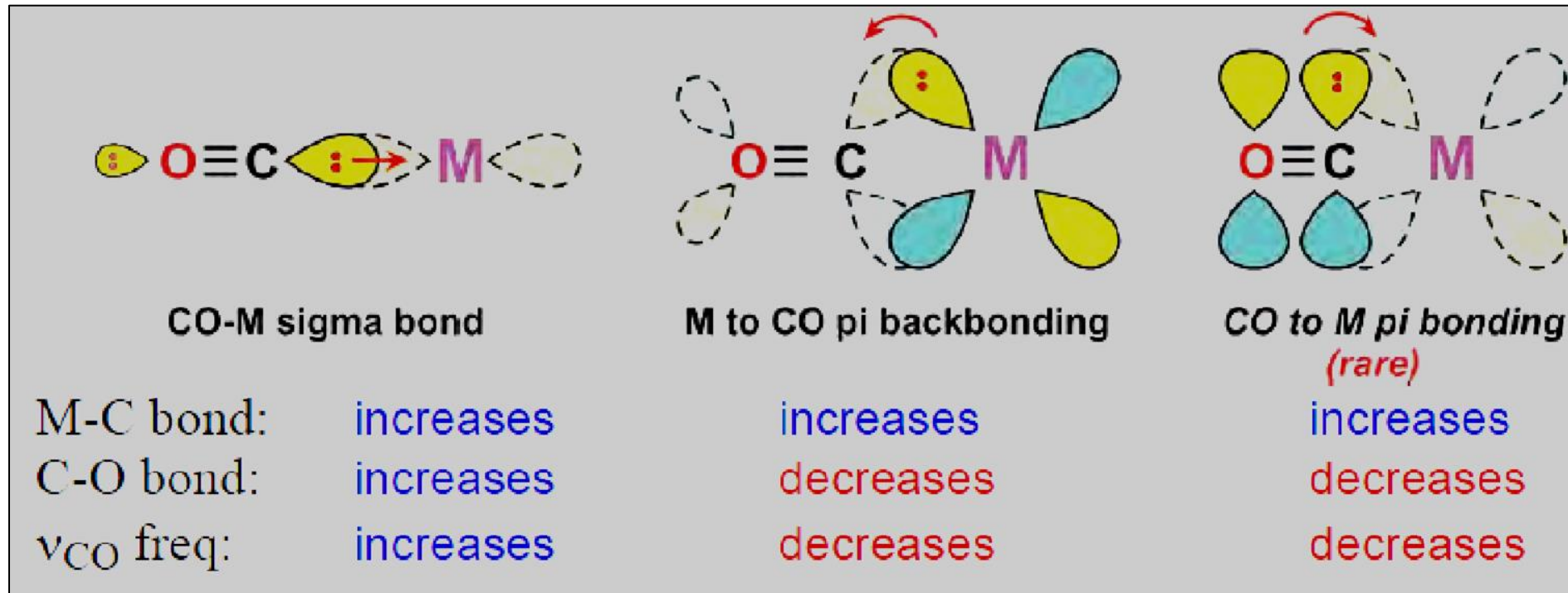


As one goes from a terminal CO-bonding mode to  $\mu_2$ -bridging and finally  $\mu_3$ -bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.

## ❖ Standard Bonding Modes

	free CO	terminal mode	$\mu_2$ -bridging	$\mu_3$ -bridging
$\nu_{CO}$ IR ( $\text{cm}^{-1}$ )	2143	2120 - 1850	1850 - 1720	1730 - 1500
(for neutral metal complexes)		2e <sup>-</sup> neutral donor	2e <sup>-</sup> neutral donor	3e <sup>-</sup> neutral donor

# Types of CO-Metal bonding interactions



## ❖ Formation of $\sigma$ -bond:

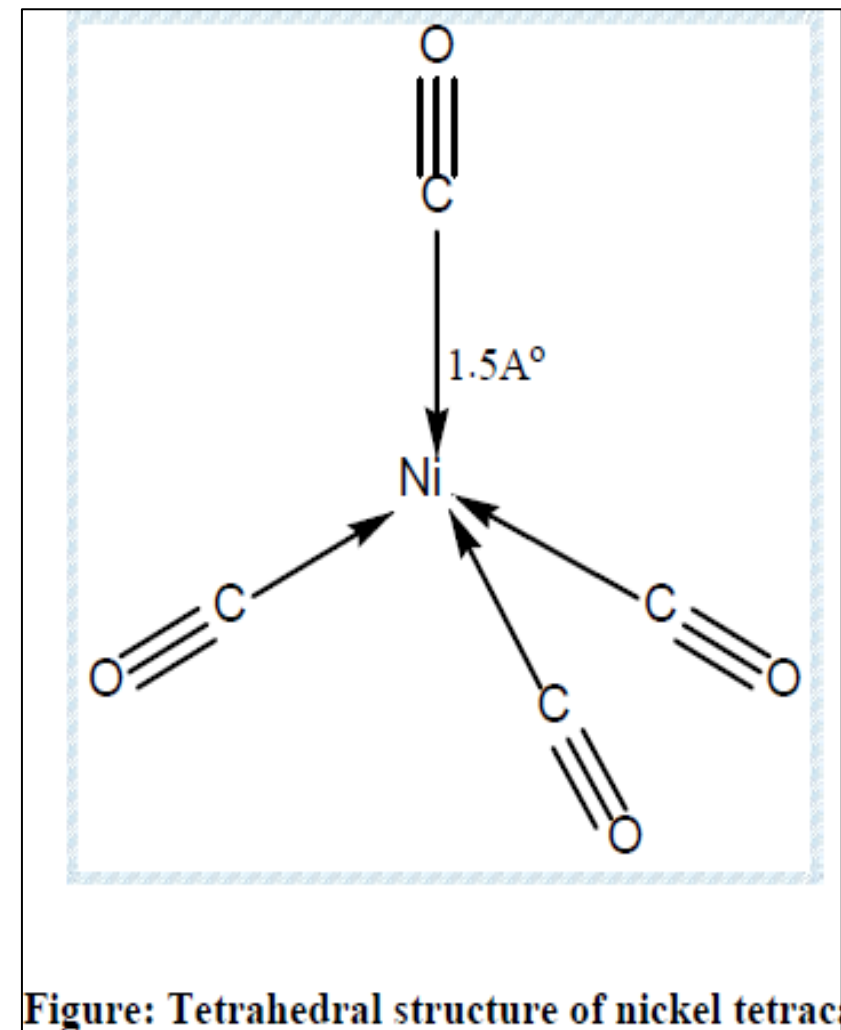
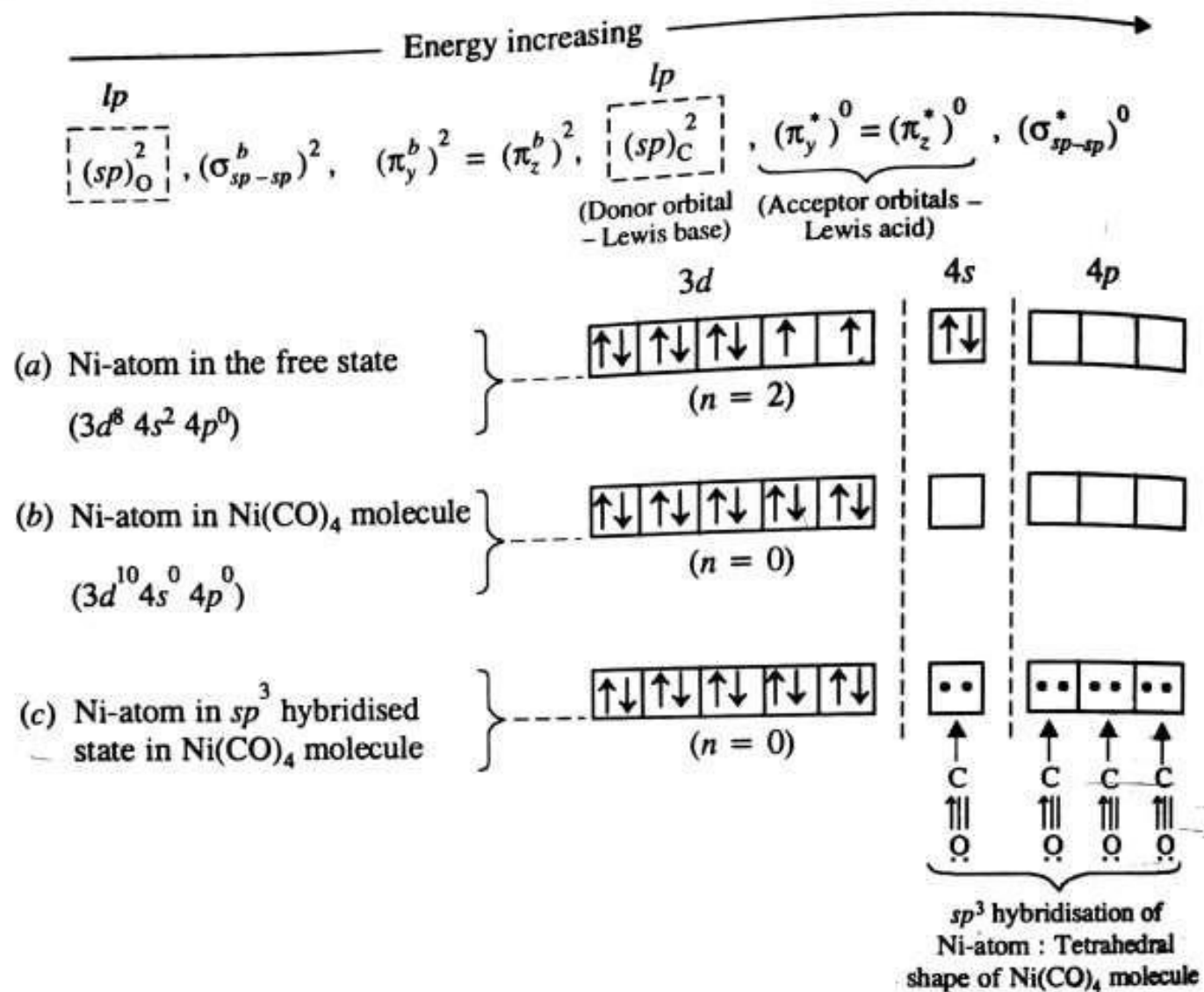
- The overlapping of empty hybrid orbital on metal atom with the filled hybrid orbital on carbon atom of carbon monoxide molecule through lone pair electrons results into the formation of a  $M \leftarrow CO$   $\sigma$ -bond.

## ❖ Formation of $\pi$ -bond by back donation:

- This bond is formed because of overlapping of filled  $d\pi$  orbitals or hybrid  $dp\pi$  orbitals of metal atom with antibonding  $\pi$  orbitals on CO molecule.



# Structure of $\text{Ni}(\text{CO})_4$



# Applications

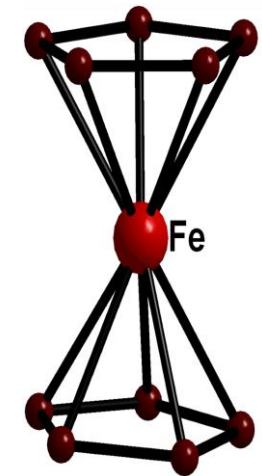
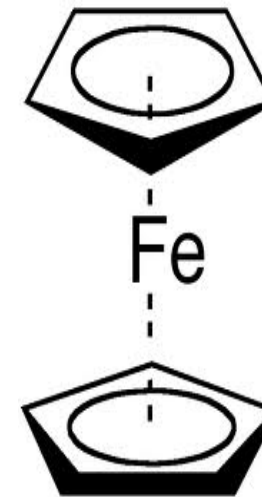
1. Metal carbonyls are used in several industrial processes. Perhaps the earliest application was the extraction and purification of nickel *via* nickel tetracarbonyl by the Mond process.
2.  $\text{Fe}(\text{CO})_5$  is used for the preparation of inductors, pigments, as dietary supplements in the production of radar-absorbing materials in the stealth technology, and in thermal spraying.
3. Metal carbonyls are used in a number of industrially important carbonylation reactions. In the oxo process, an alkene, hydrogen gas, and carbon monoxide react together with a catalyst (such as  $\text{HCo}(\text{CO})_4$ ) to give aldehydes (hydroformylation).



4. Several other Metal-Carbonyl complexes have been employed in the hydrocarboxylation and hydrogenation reactions. Dicobalt octacarbonyl  $[\text{Co}_2(\text{CO})_8]$  can be used for hydrosilylation of olefins also.
5. Many organometallic complexes are the sources for the pure metal particles/ metal coatings using Chemical Vapour Deposition (CVD) process.

# Structure and Bonding in Ferrocene

- Mössbauer spectroscopy indicates that the iron center in ferrocene should be assigned the +2 oxidation state. Each cyclopentadienyl (Cp) ring should then be allocated a single negative charge. Thus ferrocene could be described as iron(II) bis(cyclopentadienide)  $\text{Fe}^{2+}[\text{C}_5\text{H}_5^-]_2$ .
- The number of  $\pi$ -electrons on each ring is then six, which makes it aromatic according to Hückel's rule. These twelve  $\pi$ -electrons are then shared with the metal via covalent bonding. Since  $\text{Fe}^{2+}$  has six d-electrons, the complex attains an 18-electron configuration, which accounts for its stability. In modern notation, this sandwich structural model of the ferrocene molecule is denoted as  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ .
- Crystallography reveals that the cyclopentadienide rings are in staggered conformation.
- Hybridization:  $d^2sp^3$
- Magnetic Nature: Diamagnetic





# Applications of Ferrocene

---

- 1. Fuel additives:** Ferrocene and its derivatives could be used as antiknock agents in the fuel for petrol engines. They are safer than previously TEL.
- 2. Pharmaceutical:** Ferrocene derivatives have been investigated as drugs e.g. one drug has entered clinic trials, Ferroquine (7-chloro-N-(2-((dimethylamino)methyl)ferrocenyl)quinolin-4-amine), an antimalarial. Ferrocene-containing polymer-based drug delivery systems have been investigated.
- 3. Solid rocket propellant:** Ferrocene and related derivatives are used as powerful burn rate catalysts in ammonium perchlorate composite propellant.
- 4. As a ligand scaffold:** Chiral ferrocenyl phosphines are employed as ligands for transition-metal catalyzed reactions. Some of them have found industrial applications in the synthesis of pharmaceuticals and agrochemicals.

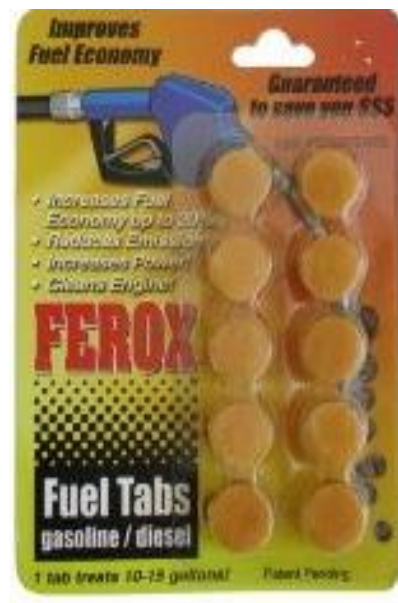
# Applications of Ferrocene as a Fuel additive, a smoke suppressant and a chiral catalyst precursor



Ferrocene powder

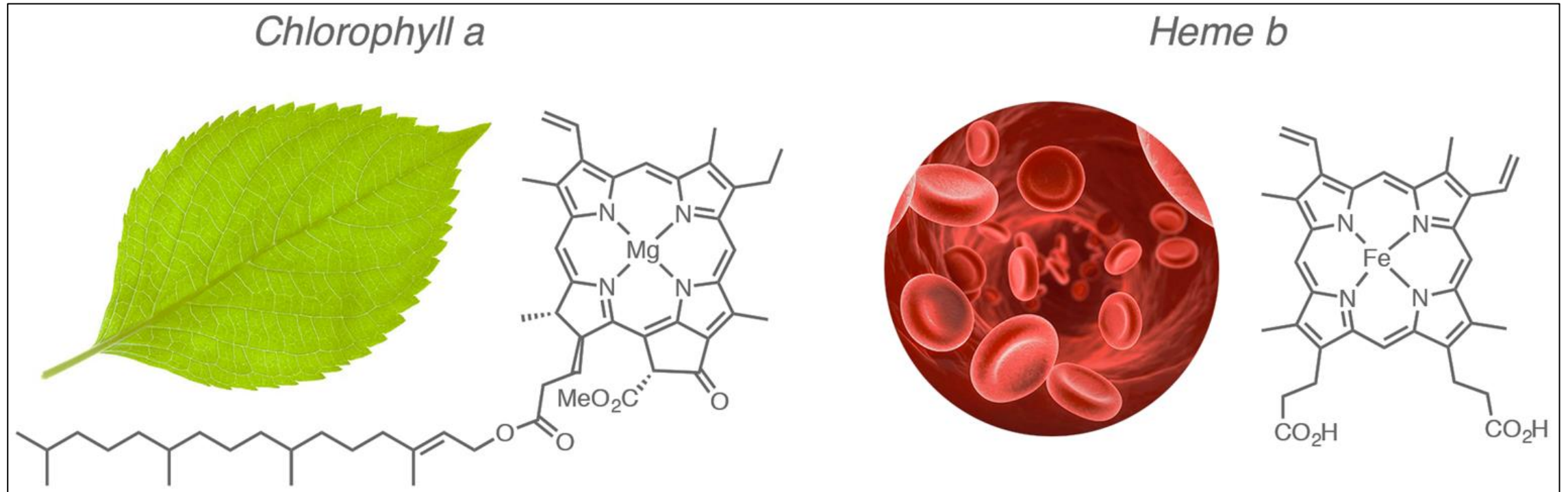


Ferrocene crystals



**Ferox Gas & Diesel Fuel Additive** is a catalyst that is an eco-friendly fuel additive and horsepower booster. It allegedly increases mileage from between 10 and 20% while also significantly reducing harmful emissions.

# Metals in biology

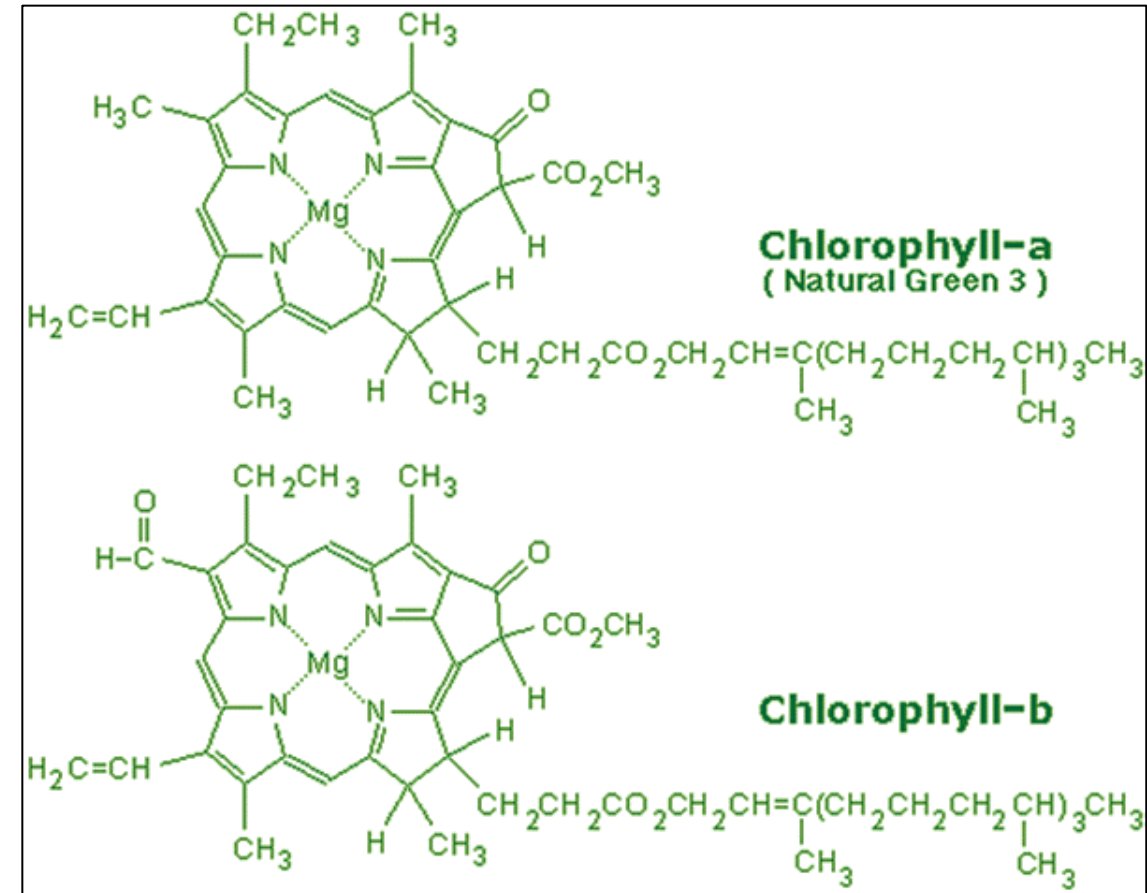


**Contents.....Metals in biology (haemoglobin, chlorophyll-  
structure and property)**

# Chlorophyll- Structure and Property

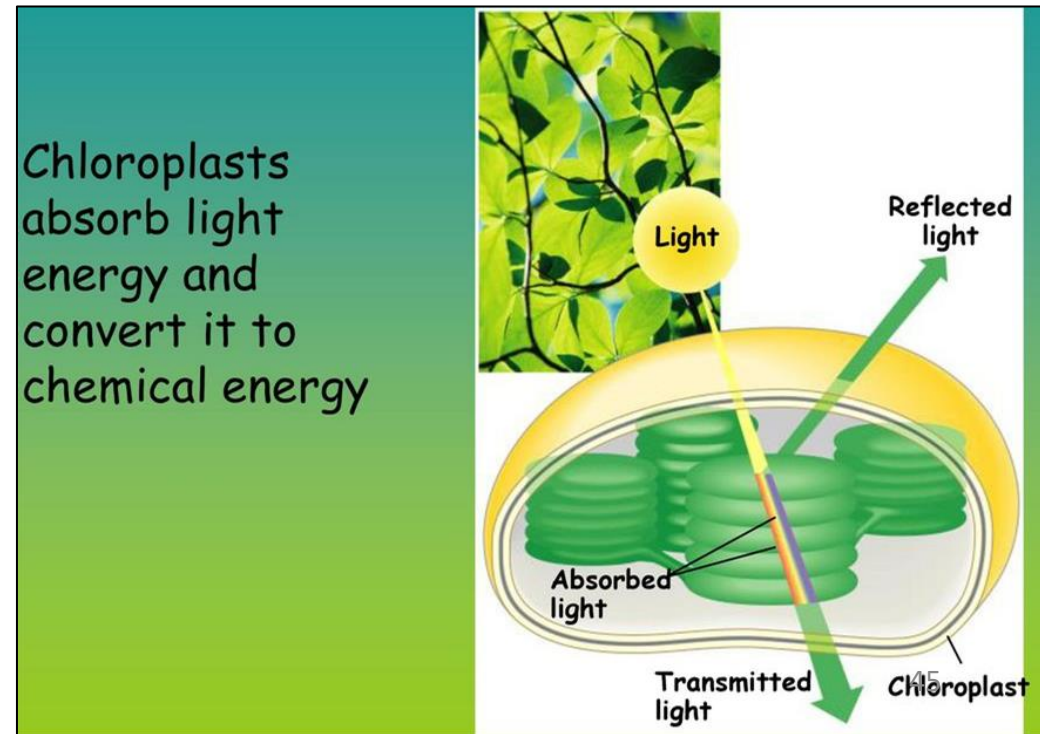
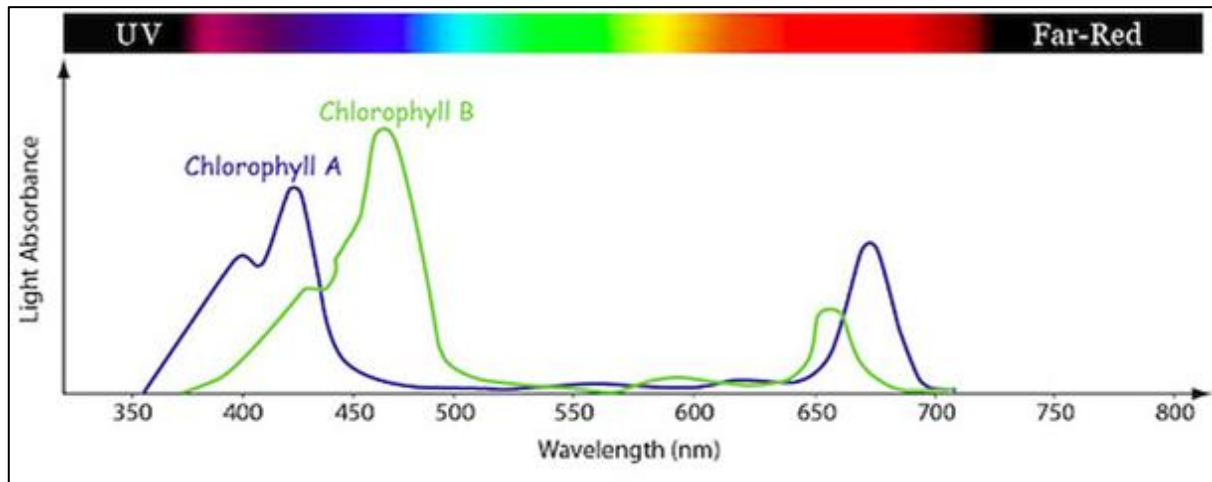
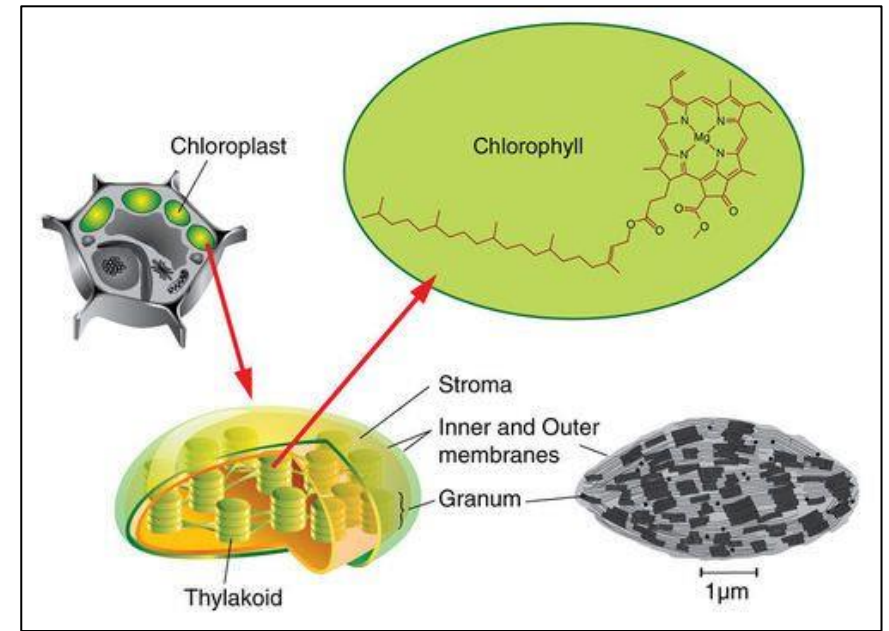
## ❖ Structure of Chlorophyll

- Chlorophylls are **green pigments** with polycyclic, planar structures resembling the protoporphyrin system present in haemoglobin
- In chlorophyll,  $Mg^{2+}$  is the metal centre
- The four inward-oriented nitrogen atoms of the porphyrin ring in chlorophyll are coordinated with the  $Mg^{2+}$
- All chlorophylls have a long **phytol** side chain, esterified to a carboxyl-group substituent in ring IV
- Chlorophylls also have a fifth five membered ring not present in heme
- The heterocyclic five-membered ring system that surrounds the  $Mg^{2+}$  has an extended polyene structure, with alternating single and double bonds
- Such polyenes characteristically show strong absorption in the visible region of the electromagnetic spectrum
- Chlorophylls have unusually high molar extinction coefficients (higher light absorbance) and are therefore particularly well-suited for absorbing visible light during photosynthesis



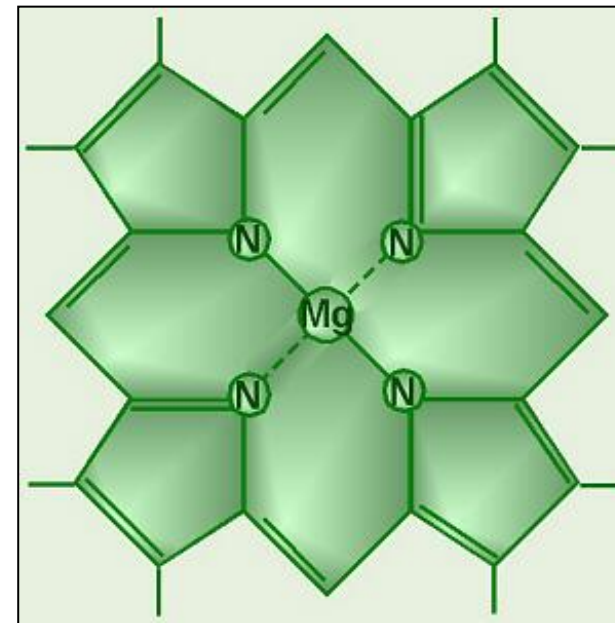
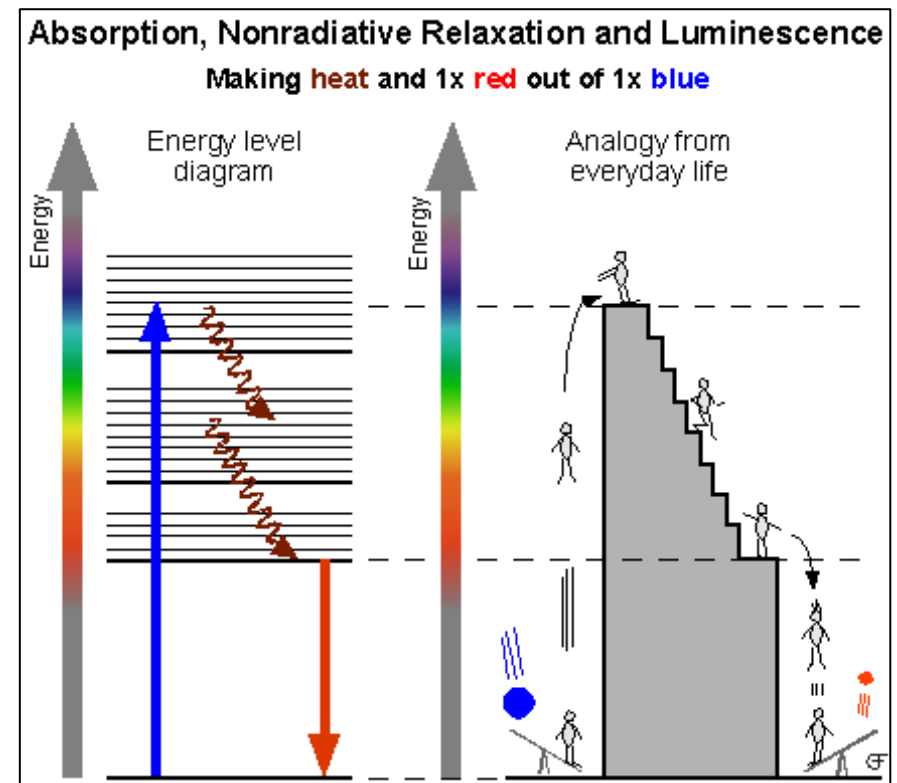


- ❖ Chloroplasts always contain both chlorophyll a and chlorophyll b
- ❖ Both are green, their absorption spectra are sufficiently different that they complement each other's range of light absorption in the visible region
- ❖ Both chlorophyll a & b absorb in the blue and red region so that the remaining green region is transmitted – hence chlorophylls are green in colour
- ❖ Most plants contain about **twice as much chlorophyll a as chlorophyll b**
- ❖ Chlorophyll is always associated with specific binding proteins, forming light-harvesting complexes (LHCs) in which chlorophyll molecules are fixed in relation to each other, to other protein complexes, and to the membrane.



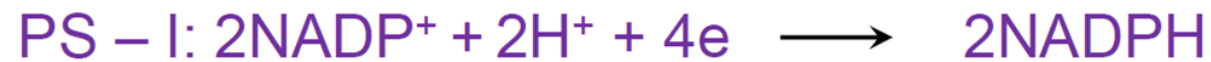
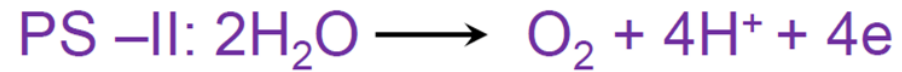
# Role of Mg in chlorophyll

- ❖ Without  $\text{Mg}^{2+}$  the chlorin ring is **fluorescent** – i.e. the absorbed **light energy is emitted** back immediately
- ❖ With  $\text{Mg}^{2+}$  chlorophyll becomes phosphorescent
- ❖ In the case of fluorescence, the absorbed light energy is lost immediately – **will not be used for chemical reaction**
- ❖ In the case of phosphorescence, there will be excited state of **finite life time and the energy can be used for chemical reactions**
- ❖ The  $\text{Mg}^{2+}$  coordination **increase the rigidity of the planar** chlorin ring: The energy loss as heat due to vibration of the ring during light absorption is prevented

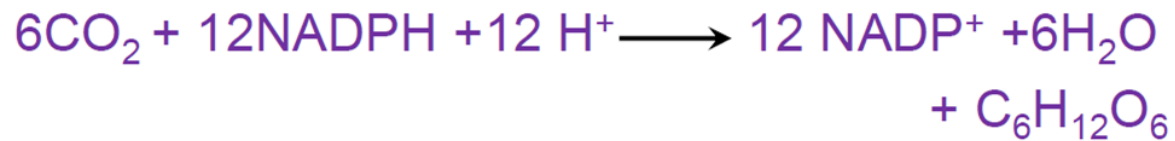


# Photosynthesis Reaction

## Light reaction

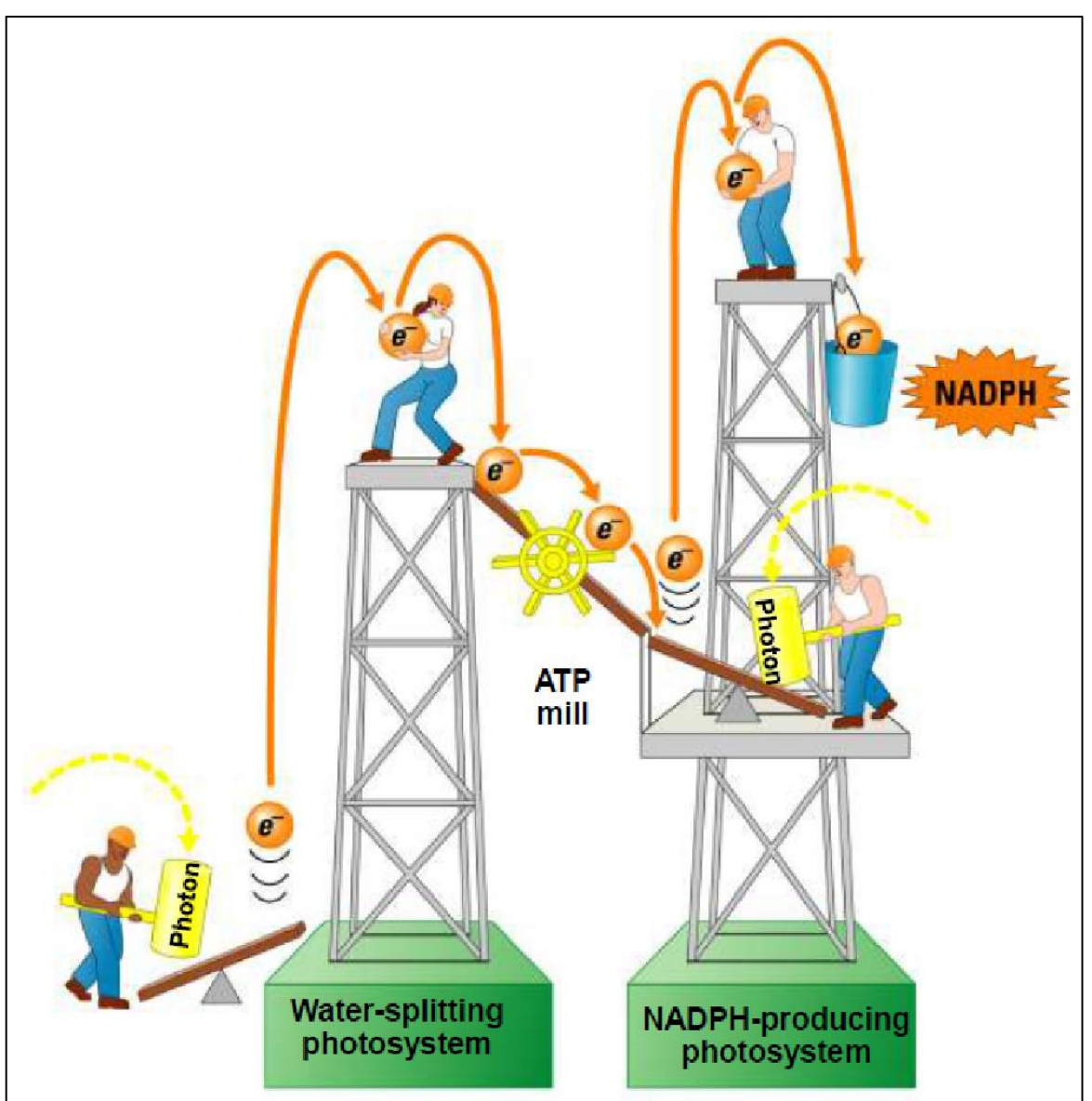
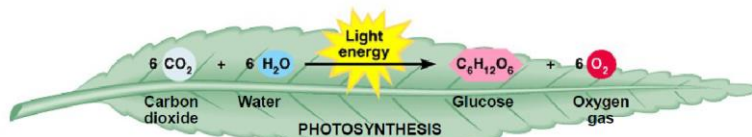


## Dark reaction



### AN OVERVIEW OF PHOTOSYNTHESIS

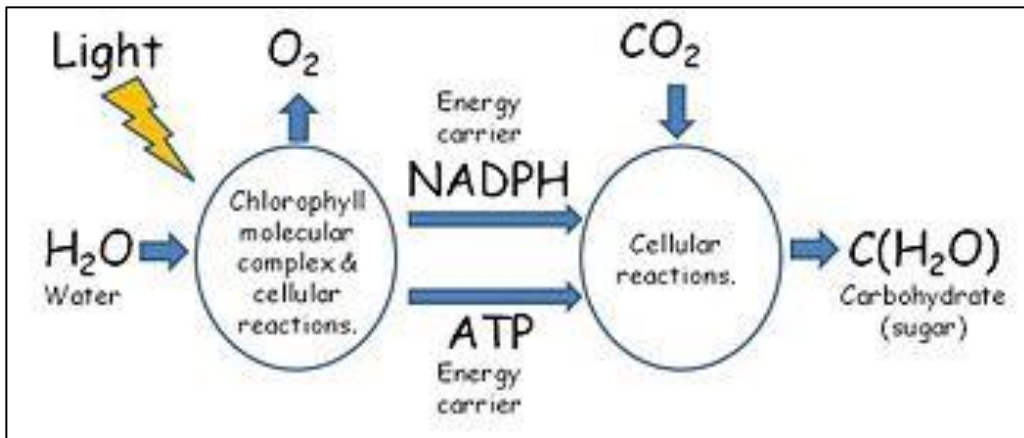
- Photosynthesis is the process by which autotrophic organisms use light energy to make sugar and oxygen gas from carbon dioxide and water



Two types of photosystems cooperate in the light reactions

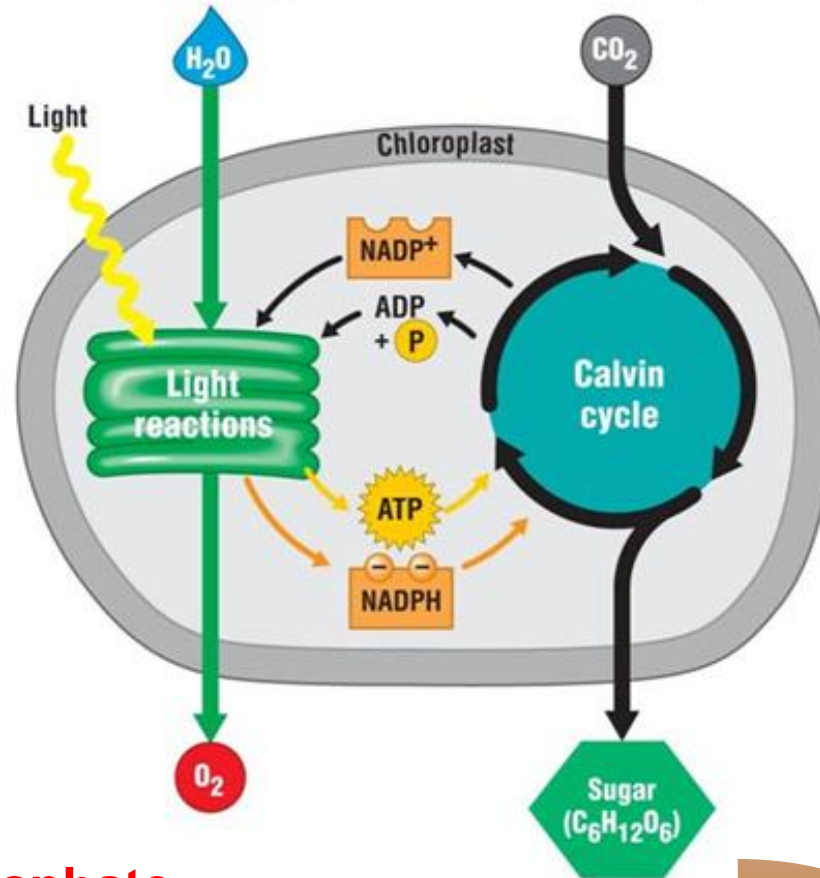


# A Photosynthesis Road Map



**Nicotinamide Adenine Dinucleotide Phosphate**  
**Hydrogen (NADPH)**  
**Adenosine 5'-triphosphate (ATP)**

Photosynthesis is composed of two



- The light reactions convert solar energy to chemical energy.

- The Calvin cycle adds that chemical energy to carbon dioxide to make the high-energy molecule sugar.

Sugar used for

- Cellular respiration
- Cellulose
- Starch
- Other organic compounds

# Hemoglobin Hb

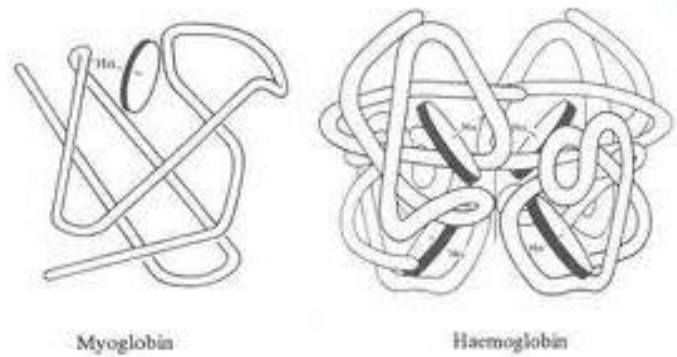
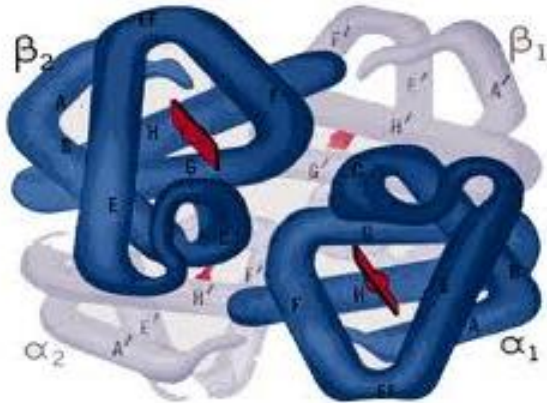


Figure 3 Myoglobin versus haemoglobin

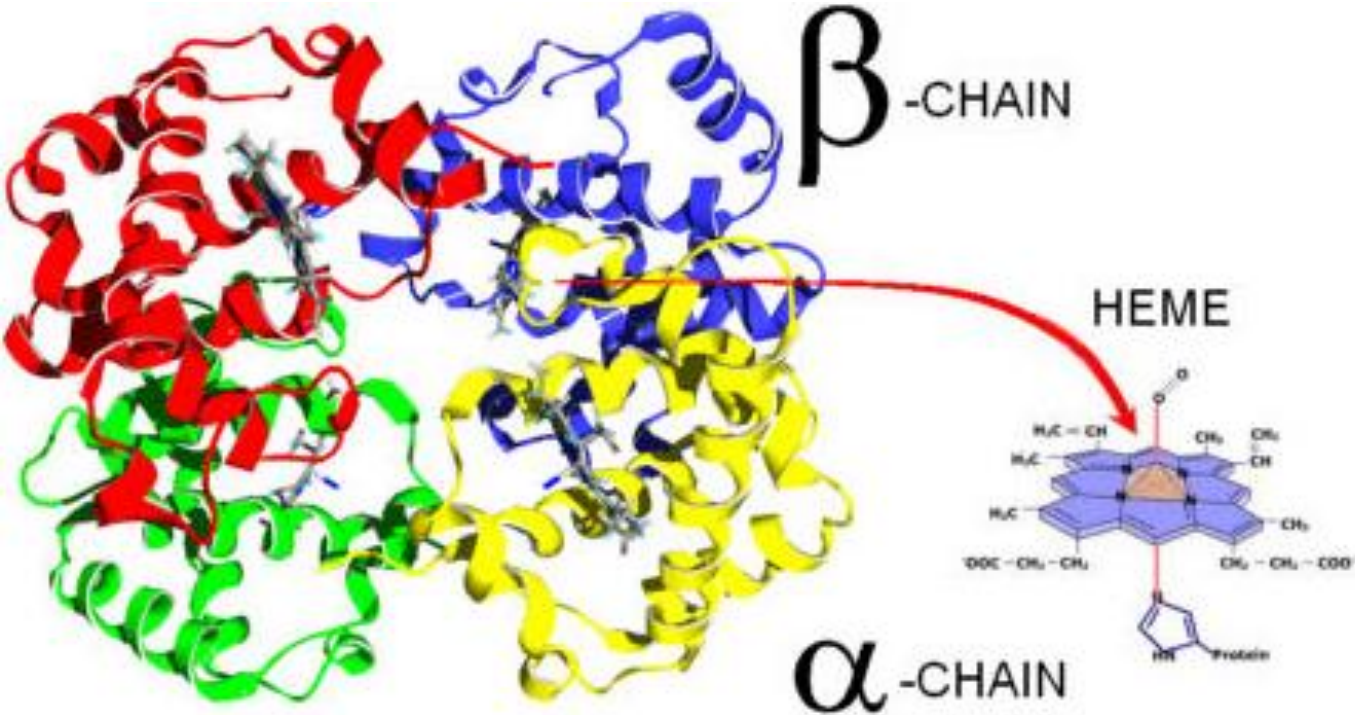
Property	Hemoglobin	Myoglobin
metal	Fe	Fe
M <sup>n+</sup> ox state for deoxy	II	II
Metal:O <sub>2</sub>	Fe:O <sub>2</sub>	Fe:O <sub>2</sub>
Color deoxy	red-purple	red-purple
Color oxy	red	red
Metal coor motif	porphyrin	porphyrin
Molecular weight (Da)	65,000	16,700
# of subunits	4	1

- $\alpha$  141 Amino acid
- $\beta$  146 Amino acid
- Mb 153 Amino acid

Hb is not an exact tetramer of Mb

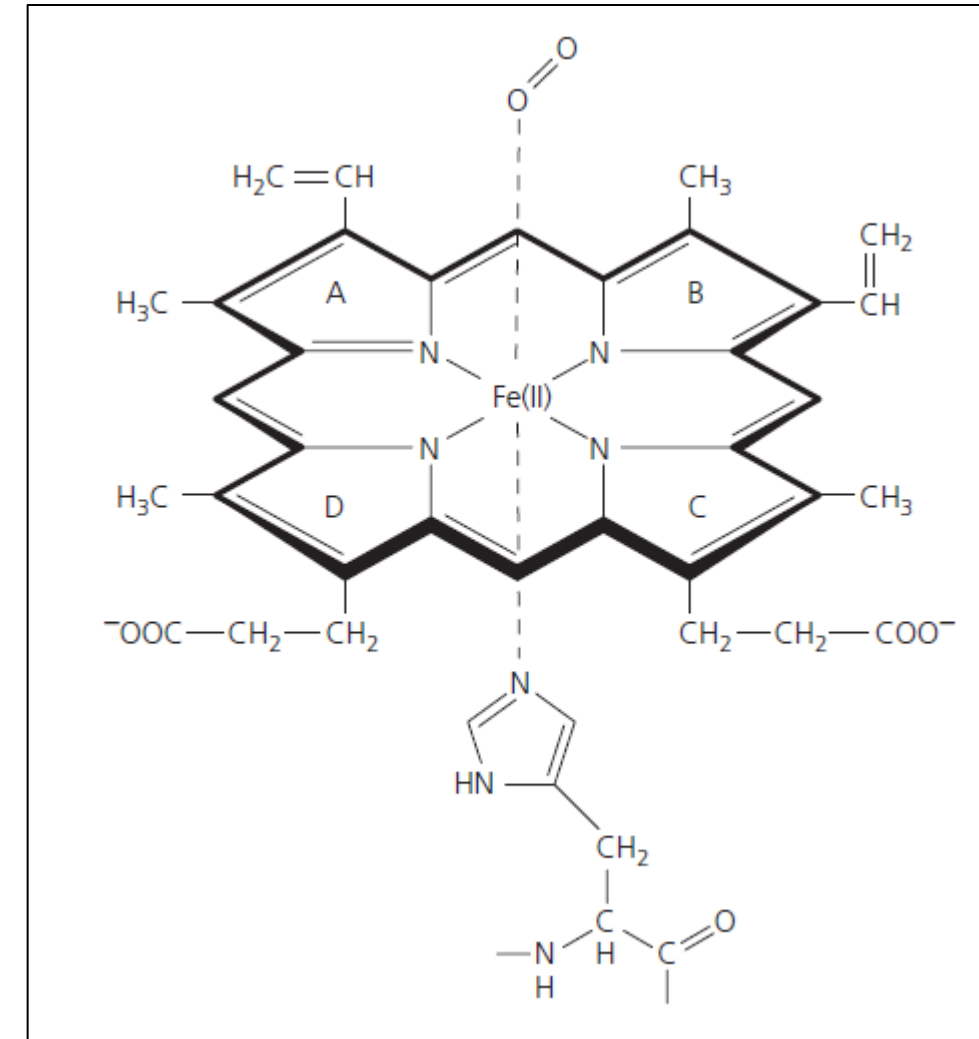


Four units of Hb

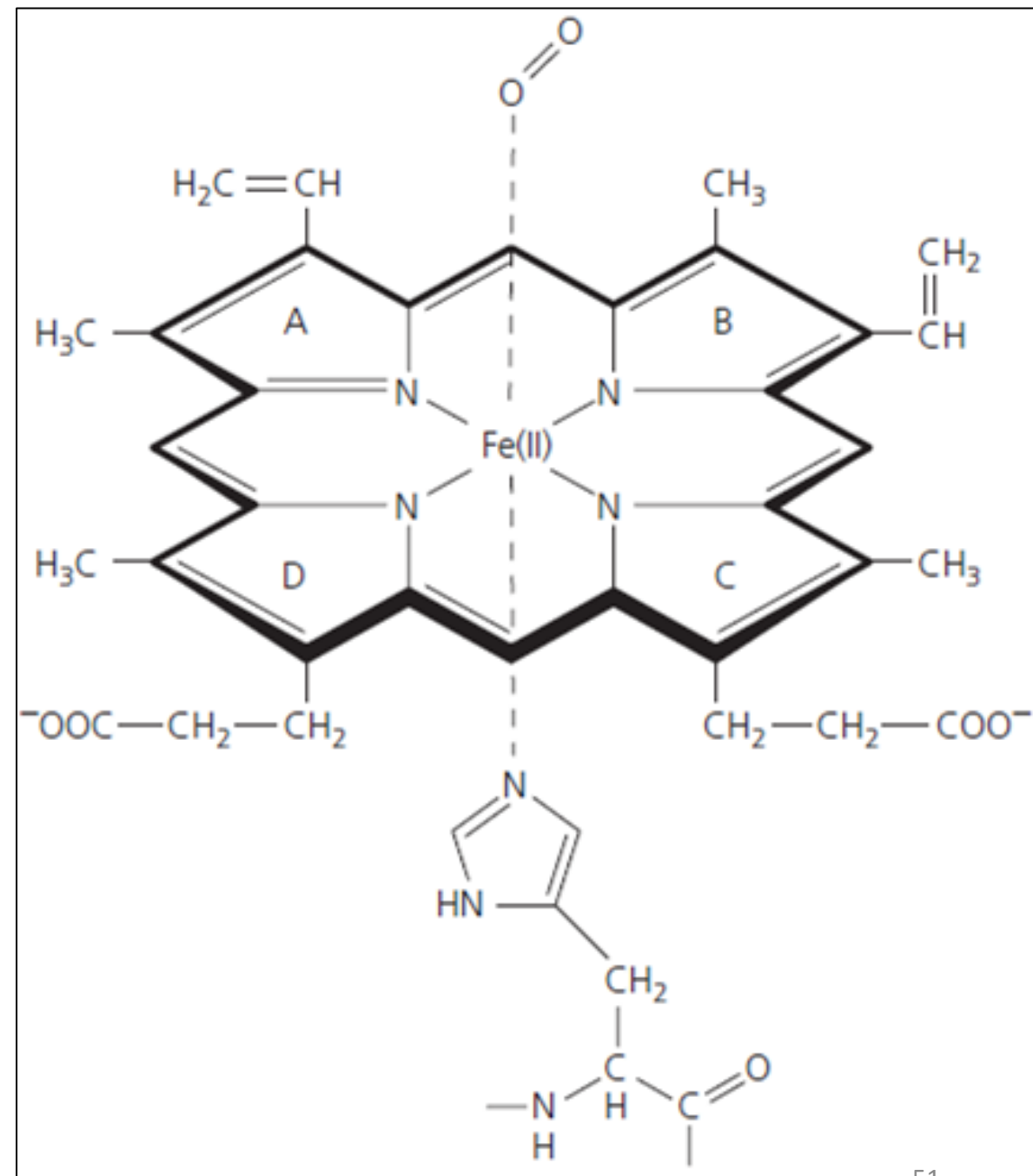


- 3 major types of Hb
- Hb A (Adult)
  - Hb F (Fetal)
  - Hb S (Sickle cell)

- ❖ Each of these subunit polypeptides contains a heme group—an iron atom at the center of a porphyrin ring—which reversibly binds a single  $O_2$  molecule in the ferrous state ( $Fe^{2+}$ ).
- ❖ Whereas free heme binds  $O_2$  irreversibly and is converted to the ferric state ( $Fe^{3+}$ ) in the process, Hb can reversibly bind  $O_2$  because the valence state of the iron atom is protected by encapsulating the heme in the globin protein fold
- ❖ Each tetrameric ( $\alpha_2\beta_2$ ) Hb can therefore reversibly bind four  $O_2$  molecules.
- ❖ Oxygenation changes the electronic state of the  $Fe^{2+}$  heme iron, which is why the color of blood changes from the dark, purplish hue characteristic of venous blood to the brilliant scarlet of arterial blood.



- ❖ The organic component of the heme group—the protoporphyrin—is made up of four pyrrole rings (A, B, C & D) linked by methine bridges to form a tetrapyrrole ring. Four methyl groups, two vinyl groups, and two propionate side chains are attached.
- ❖ The iron atom at the center of the protoporphyrin is bonded to the four pyrrole atoms.
- ❖ Under normal conditions the iron is in the ferrous ( $\text{Fe}^{2+}$ ) oxidation state. The iron atom can form two additional bonds, one on each side of the heme plane, called the fifth and sixth coordination sites.
- ❖ The fifth coordination site is covalently bound by the imidazole side chain of the globin chain (the “proximal histidine,”  $\alpha 87$  and  $\beta 92$ ).
- ❖ The sixth coordination site of the iron ion can bind  $\text{O}_2$  or other gaseous ligands ( $\text{CO}$ ,  $\text{NO}$ ,  $\text{CN}^-$ , and  $\text{H}_2\text{S}$ ).





- Role of distal histidine: Makes  $O_2$  to bind in a bent fashion and makes it difficult for CO to bind in a linear fashion.
- An isolated heme binds CO 25000 times as strongly as  $O_2$  in solution. In the living system binding affinity for oxygen is reduced considerably. For CO to bind strongly, it has to bind linearly which is made difficult by distal histidine

