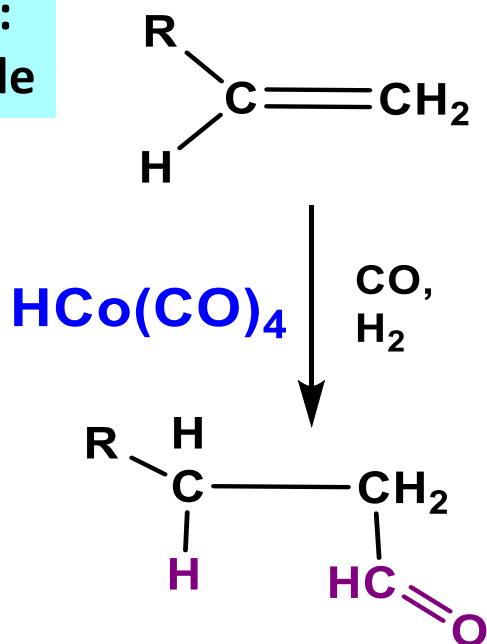


Why study metal carbonyls ?

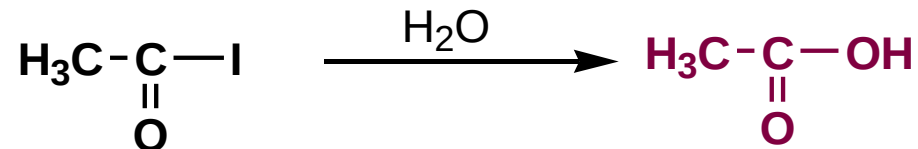
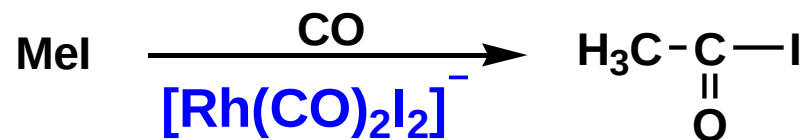
- Simplest of organometallic compounds where M–C σ – bonding is well understood.
- CO is one of the strongest π acceptor ligands.
- Back bonding (π bonding) and variation in electronic properties of CO can be monitored very efficiently by **Infrared spectroscopy**

A range of metal carbonyls are used as **catalysts in Chemical Industry**

Hydroformylation: Alkene to Aldehyde

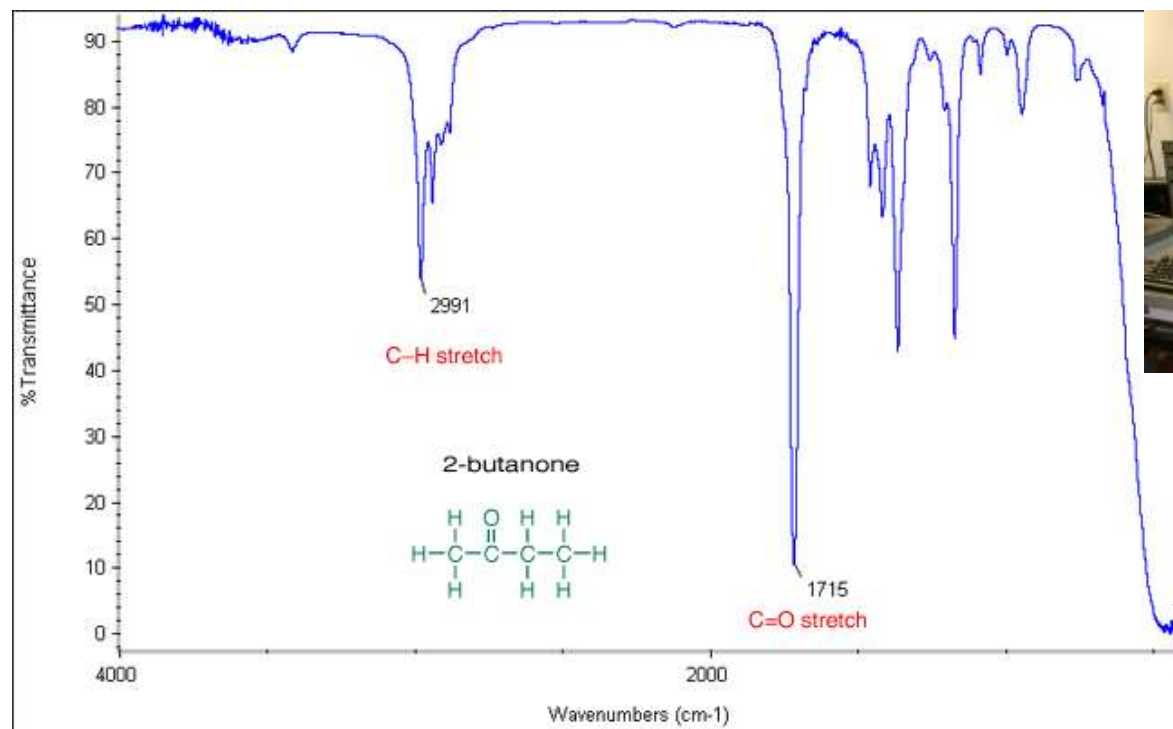


Methanol to Acetic acid Process:



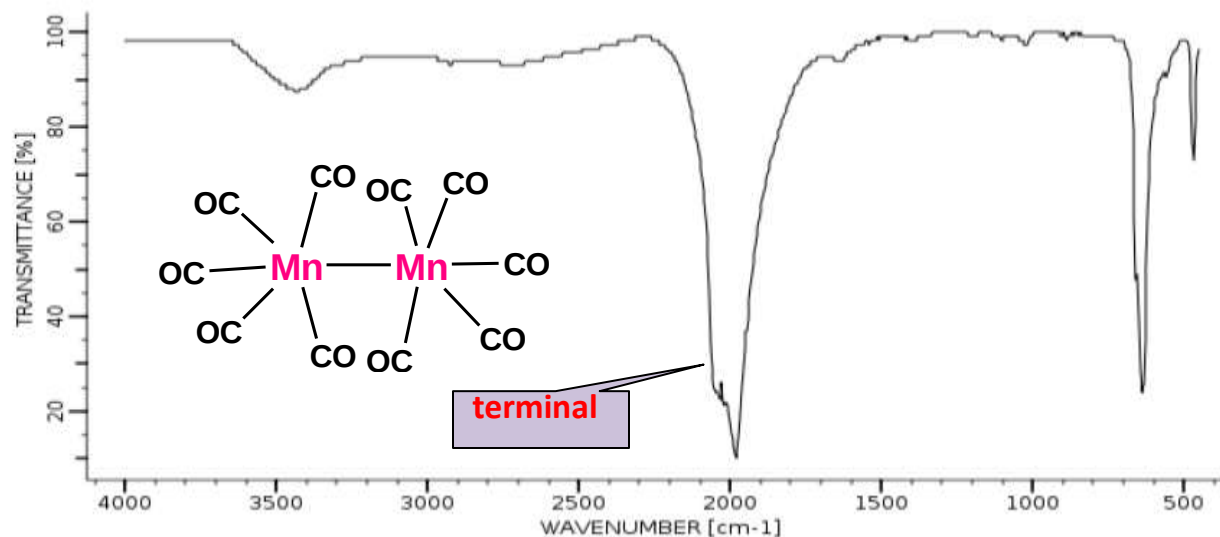
Infrared Spectroscopy- An analytical tool in chemistry

- Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists.
- Simply, it is the absorption measurement of different IR frequencies by a compound positioned in the path of an IR beam.
- **The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample.**

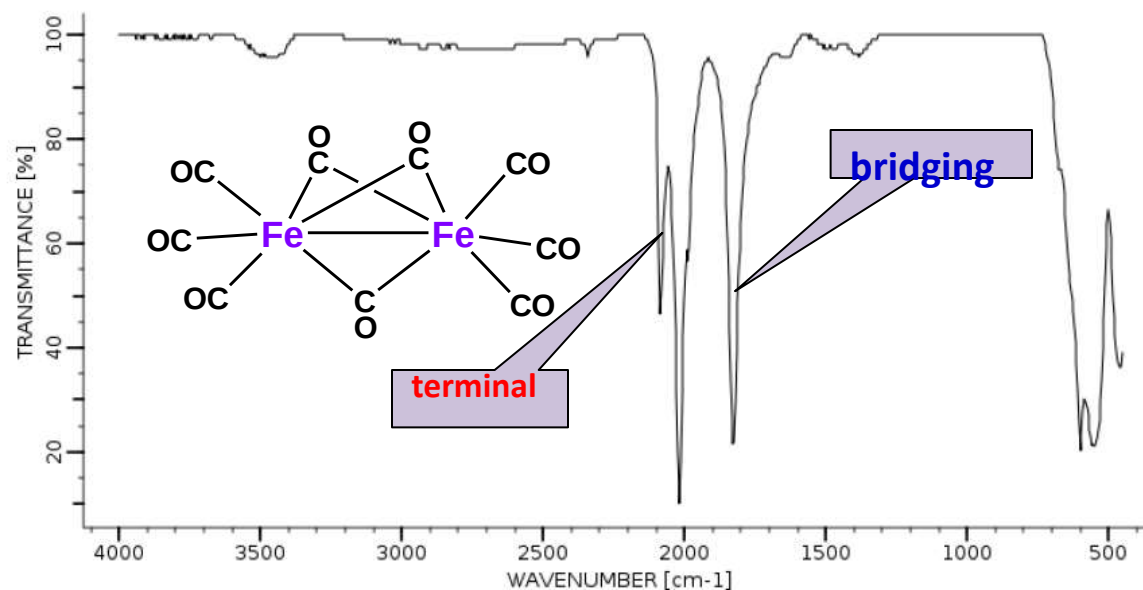


- **Functional groups** are identified based *on vibrational modes of the groups such a stretching, bending etc. Different vibrational modes absorb characteristic frequencies of IR radiation.*
- An infrared spectrophotometer is an instrument that passes infrared light through a molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis. Absorption of radiation lowers the percentage transmittance value.

Infrared Spectroscopy- Spectra of Metal Carbonyls



The range in which the band appears decides bridging or terminal .



The number of bands is only related to the symmetry of the molecule

Terminal versus bridging carbonyls



Free

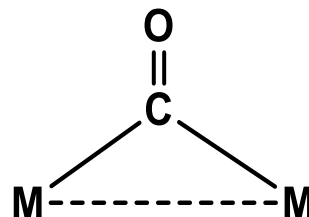
ν_{CO}

2150-2250 cm^{-1}



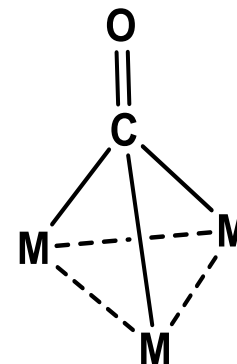
Terminal

2120-1850 cm^{-1}



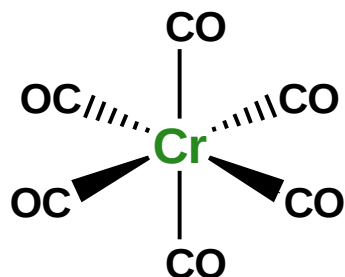
Bridging μ_2

1850-1720 cm^{-1}

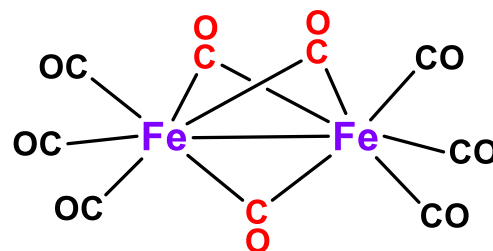


Bridging μ_3

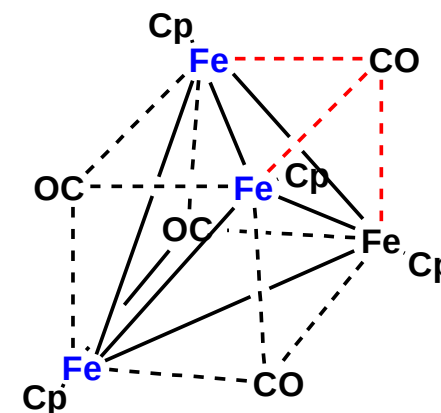
1730-1620 cm^{-1}



2000 cm^{-1}



2018, 1826 cm^{-1}

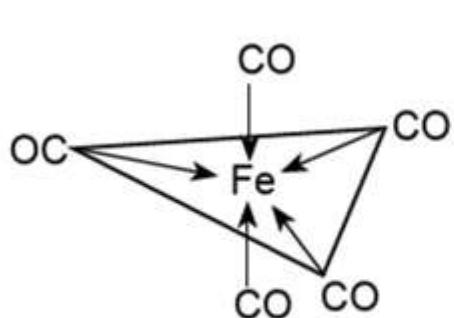


1620 cm^{-1}

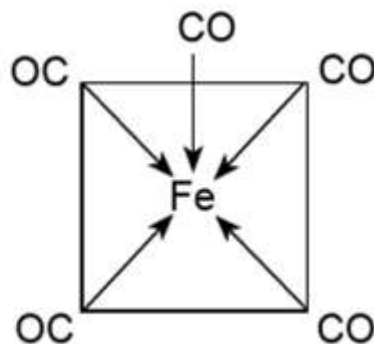
IR Applications-Metal carbonyls

1. Determination of geometries of Carbonyls

through calculating number of IR active bands



Trigonal bipyramidal



Square pyramid

- $\text{Fe}(\text{CO})_5$ adopts a **trigonal bipyramidal** structure - three CO ligands in equatorial positions and two axially bound. The Fe–C–O linkages are each linear.
- ν_{CO} bands in the IR spectrum at **2034 and 2014 cm^{-1}**

2. Determination of Bond orders

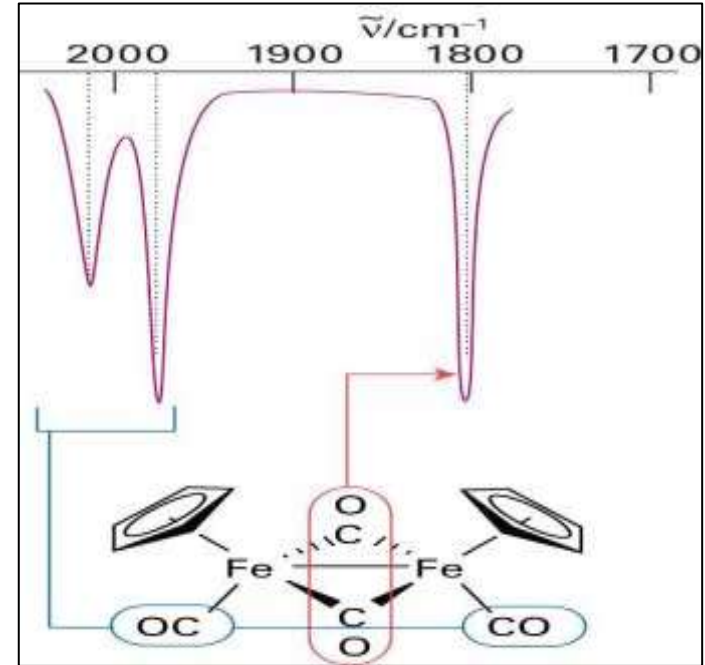
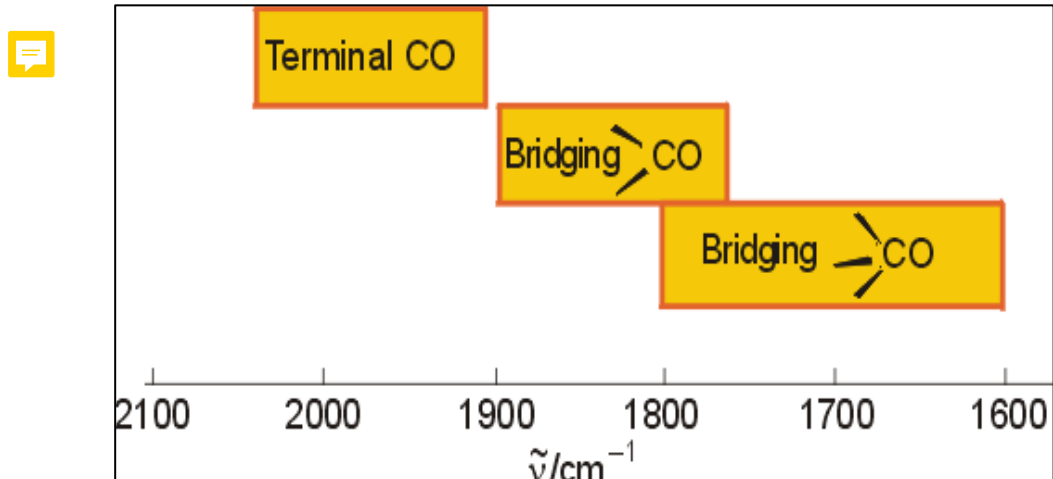
- It has been seen that **I.R. absorption frequency of ligated CO is directly proportional to its B.O.**
- In other words, the I.R. absorption band due to the stretching vibration of **ligated CO with a higher B.O. would occur at a higher frequency** and the **I.R. absorption band of ligated CO with a lower B.O. would occur at a lower frequency.**
- Since the absorption frequency for **free CO is equal to 2250 cm^{-1}** while that for **ligated CO lies between $2220\text{--}1700 \text{ cm}^{-1}$** , **ligated CO has lower B.O.**

The lower B.O. is due to the transfer of metal $d\pi$ electrons into the π^* orbitals of ligated CO. Let us study the following examples.

- Since the presence of **positive charge on $[\text{Mn}(\text{CO})_6]^+$ resists the flow of metal $d\pi$ electrons into the π^* orbitals of CO, the B.O. of CO increases.** Due to the increase in B.O., the absorption band of ligated CO occurs at higher frequency ($= 2090 \text{ cm}^{-1}$)

Metal Carbonyl	$[\text{V}(\text{CO})_6]^-$	$[\text{Cr}(\text{CO})_6]$	$[\text{Mn}(\text{CO})_6]^+$
Charge on Metal	-1	0	+1
Absorption frequency for CO (cm^{-1})	1860	1980	2090

3. To differentiate between terminal and bridging carbonyl groups



4. To study reaction rates

The measurement of the rates of disappearance of the intensity of CO absorption bands in the I.R. spectra can be used to study the rates of substitution reaction of metal carbonyls

Other Applications

- ❖ 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.
- ❖ $\text{Fe}(\text{CO})_5$ 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.
- ❖ 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.

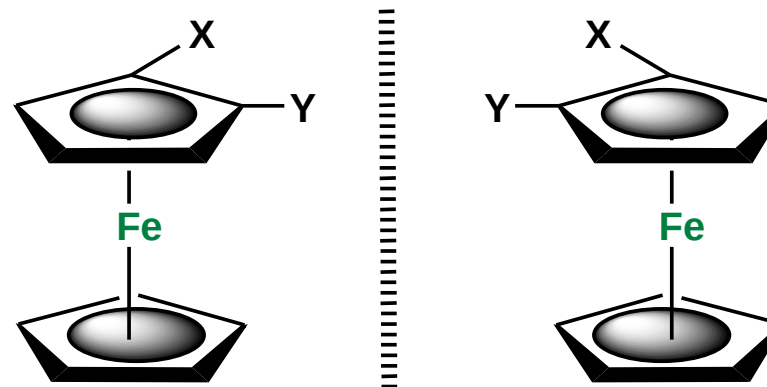


- ❖ Several other Metal-Carbonyl complexes have been employed in the hydrocarboxylation and hydrogenation reactions. Dicobalt octacarbonyl $[\text{Co}_2(\text{CO})_8]$ can be used for hydrosilylation of olefins also.
- ❖ Metal carbonyls serve as precursors for the preparation of other organometallic complexes. i.e., pure metal particles/ metal coatings using Chemical Vapour Deposition (CVD) process.

Why metal – sandwich compounds are important?

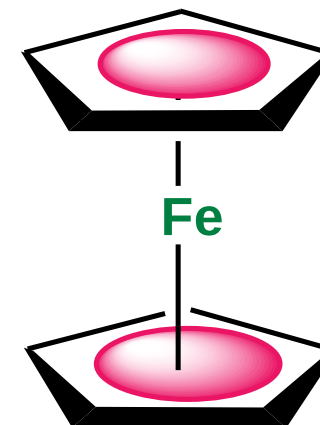
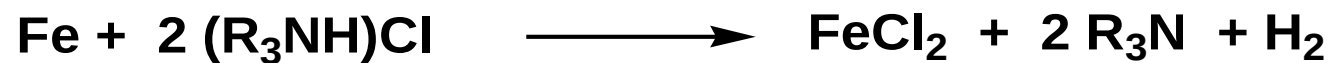
1. Transition metal/metal ion embedded inside an organic matrix: **Makes a metal ion soluble even in hydrocarbon solvents.**
E.g. Ferrocene is soluble in hexane while Fe^{2+} as such is not. Outcome: a hydrocarbon soluble additive/catalyst .
2. Coordination to an electropositive metal often changes the reactivity and electronic properties of the π system bound to it (**benzene vs ferrocene**)
3. A sterically protected metal site where a wide range of catalytic applications are possible.
E.g. alkene polymerization
2. Metal sandwich compounds are excellent substrates **to make planar chiral compounds.**
Applications as chiral catalysts in asymmetric catalysis

Planar chirality:
Non- super-imposable mirror images



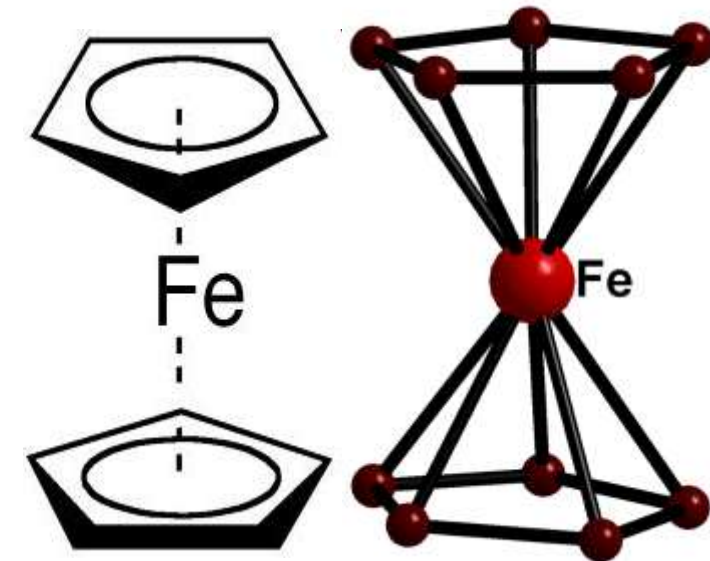
Ferrocene: synthesis

Lab Synthesis

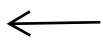


Structure and Bonding Ferrocene

- 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 π -electrons on each ring is then six, which makes it aromatic according to Hückel's rule. These twelve π -electrons are then shared with the metal via covalent bonding.
- Since 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.**

Fuel additive, smoke suppressant and 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 increases mileage from between 10 and 20% while also significantly reducing harmful emissions.

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

- ❖ The 18e rule helps us decide whether a given d-block transition metal organometallic complex is likely to be stable or not.
- 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, CH_5 requires a 5-valent carbon and is therefore not stable. Stable compounds, such as 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**, and in addition now have **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 for 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:** $\# e^- = \text{no. of metal electrons (zero valent)} + \text{no. of ligand electrons (L)} - \text{complex charge}$

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

Ligands: In general L donates two electrons, X donates one electron.

❖ **Ionic Model:** $\# e^- = \text{no. of metal electrons } (d^n) + \text{no. of ligand electrons}$

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

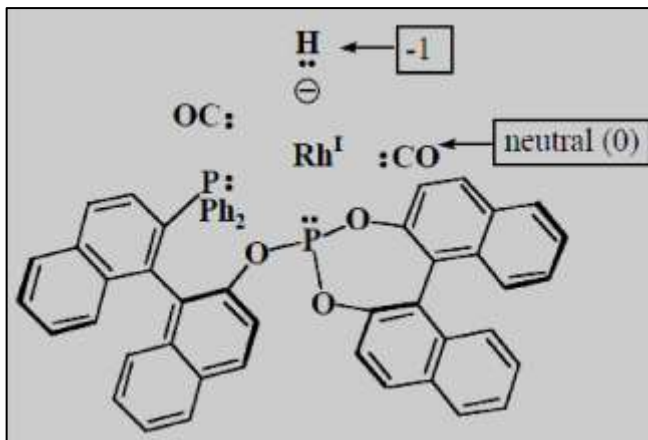
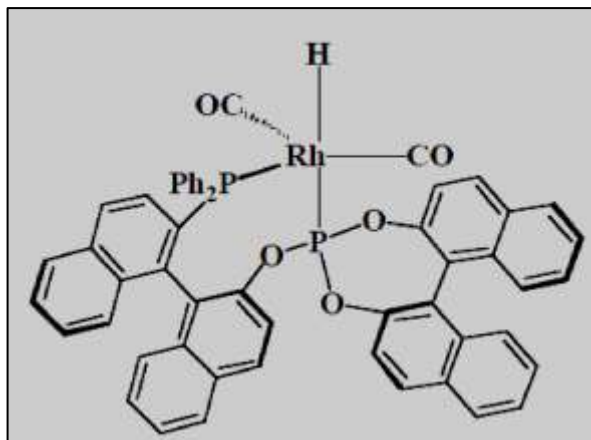
Ligands: In general L and X are both two electron donors.

❖ Complexes with $18 e^-$ counts are referred to as **saturated**.

❖ Complexes with counts lower than $18e^-$ are called **unsaturated**.

Electron Counting

- ❖ **Step 1: Determine the oxidation state of the metal.** To do this, balance the ligand charges with an equal opposite charge on the metal. This is the metal's formal oxidation state.
- To determine ligand charges, create an ionic model by assigning each M-L electron pair to the more electronegative atom (L). This should result in stable ligand species or ones known as reaction intermediates in solution.

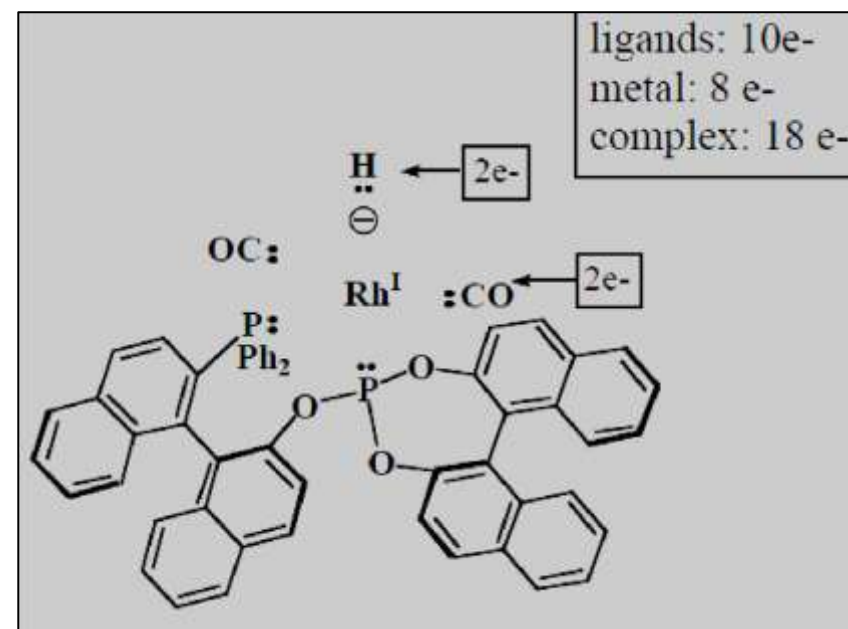


- ❖ **Step 2: Determine the d electron count.** Recall: subtract the metal's oxidation state from its group #.

$$\text{Rh} = 4d^8 5s^1$$

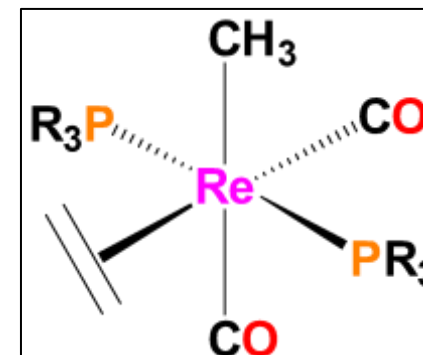
$$\text{Rh}^{+1} = 4d^8 5s^0$$

- ❖ **Step 3: Determine the electron count of the complex** by adding the # of electrons donated by each ligand to the metal's d electron count.



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.

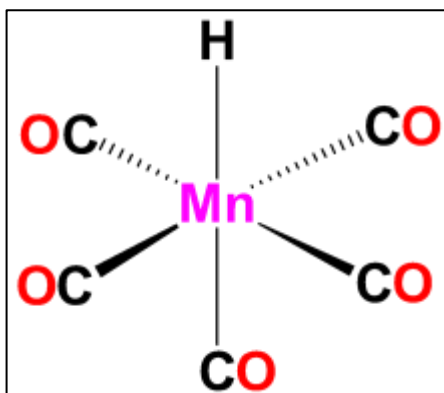


Now we can do our
electron counting:

- 1) There is no overall charge on the complex
- 2) There is one anionic ligand (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 Re^{I} .

$\text{Re}(+1)$	d^6	6e-
2 PR_3		4e-
2 CO		4e-
CH_3^-		2e-
$\text{CH}_2=\text{CH}_2$		2e-
		Total: 18e-



$\text{Mn}(+1) d^6$

5 CO

H^-

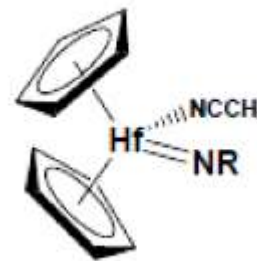
6e-

10e-

2e-

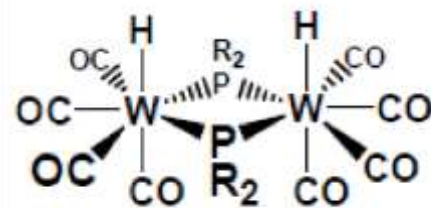
Total: 18e-

b) Hf, Cp, $\text{N}\equiv\text{CCH}_3$, NCH_3



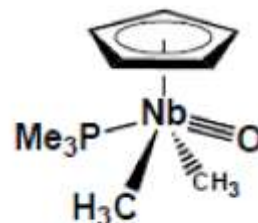
Hf(+4)	0e-
NR^{2-}	4e-
2Cp^-	12e-
NCMe	2e-
Total	18 e-

a) W, $\mu\text{-PR}_2$, CO, H



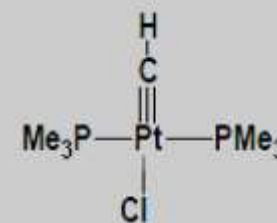
W(+2)	4e-
$2\mu\text{-PR}_2^-$	4e-
H^-	2e-
4CO	8e-
Total	18 e-

d) Nb, O, CH_3 , Cp, PMe_3



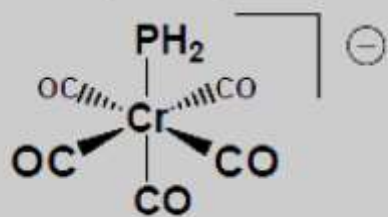
Nb(+5)	0e-
Cp^-	6e-
O^{2-}	6e-
2CH_3^-	4e-
PMe_3	2e-
Total	18 e-

c) Pt, CH, Cl, PMe_3



Pt(+4)	6e-
CH^{3-}	6e-
Cl^-	2e-
2PMe_3	4e-
Total	18 e-

a) $[\text{Cr}(\text{PH}_2)(\text{CO})_5]^-$

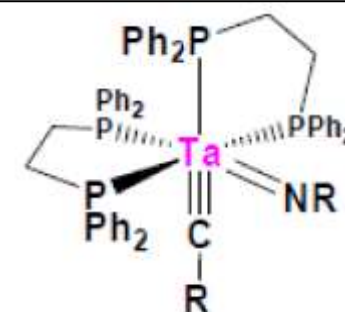


Cr(0)	6e-
PH_2^-	2e-
5 CO	10e-
Total	18 e-

d) Ru, benzene, H, $\text{C}\equiv\text{NMe}$



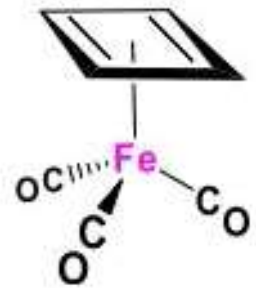
Ru(+2)	6e-
benzene	6e-
2H^-	4e-
$\text{C}\equiv\text{NMe}$	2e-
Total	18 e-



Ta(+5)	0e-
C-R^{3-}	6e-
N-R^{2-}	4e-
2dppe	8e-
Total	18 e-

Other examples

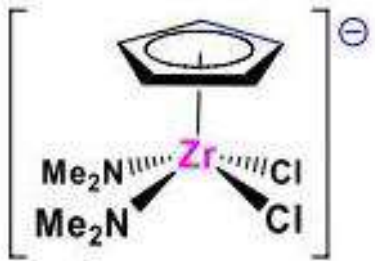
a) $\text{Fe}(\eta^4\text{-C}_4\text{H}_4)(\text{CO})_3$



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

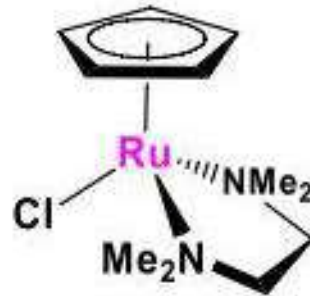
*C₄H₄ is cyclobutadiene
neutral 4e- donor*

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



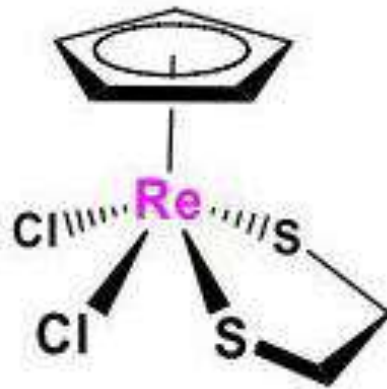
Zr(+4)	d0
Cp ⁻	6e-
2 NMe ₂ ⁻	8e-
2 Cl ⁻	4e-
Total	18e-

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

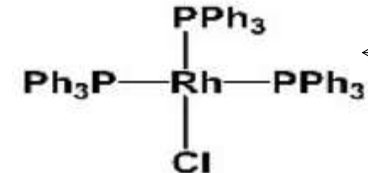
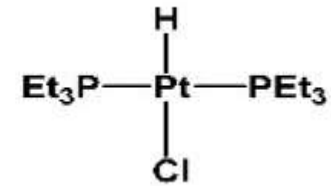
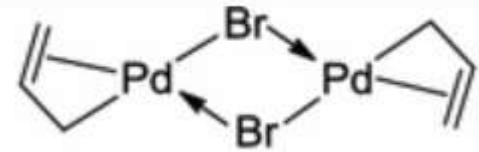
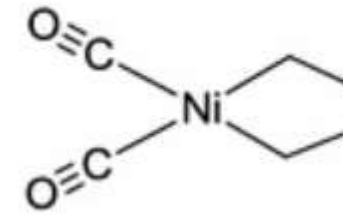


Ru(+2)	d6
Cp ⁻	6e-
2 NR ₃	4e-
Cl ⁻	2e-
Total	18e-

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



Re(+5)	d2
Cp ⁻	6e-
2 SR ⁻	4e-
2 Cl ⁻	4e-
Total	16e-



16 e⁻

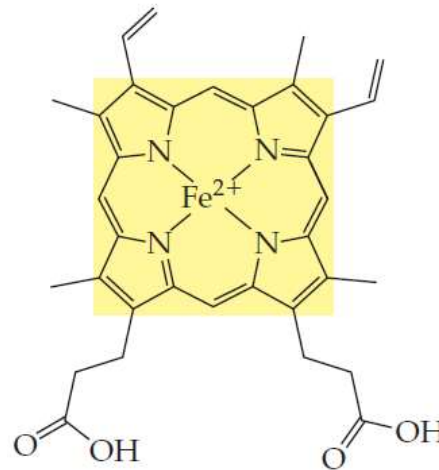
Metals in Living Systems

- Among the most important chelating agents in nature are those derived from the *porphine* molecule.
- This molecule can coordinate to a metal *via its four nitrogen donor atoms*.
- Once porphine bonds to a metal ion, *the two H atoms on the nitrogens are displaced to form complexes called porphyrins*.

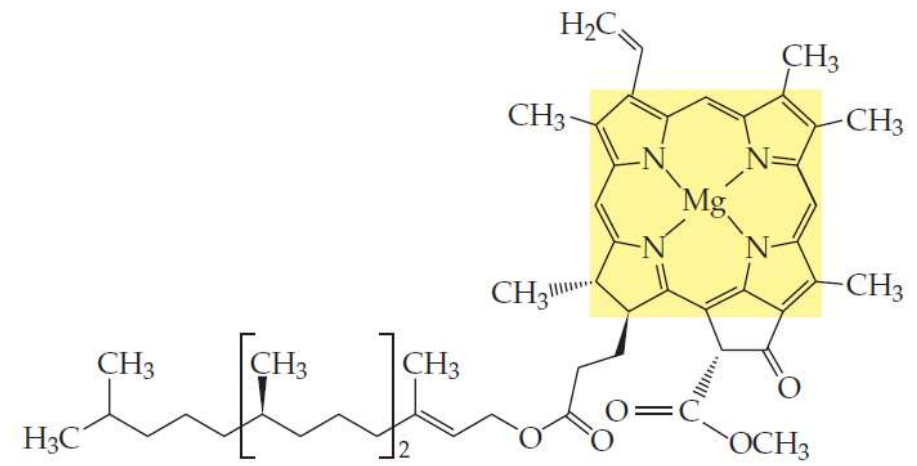


Porphine

- Two important porphyrins are *hemes* [in which the metal ion is **Fe(II)**], and *chlorophylls* [with a **Mg(II)** central ion].

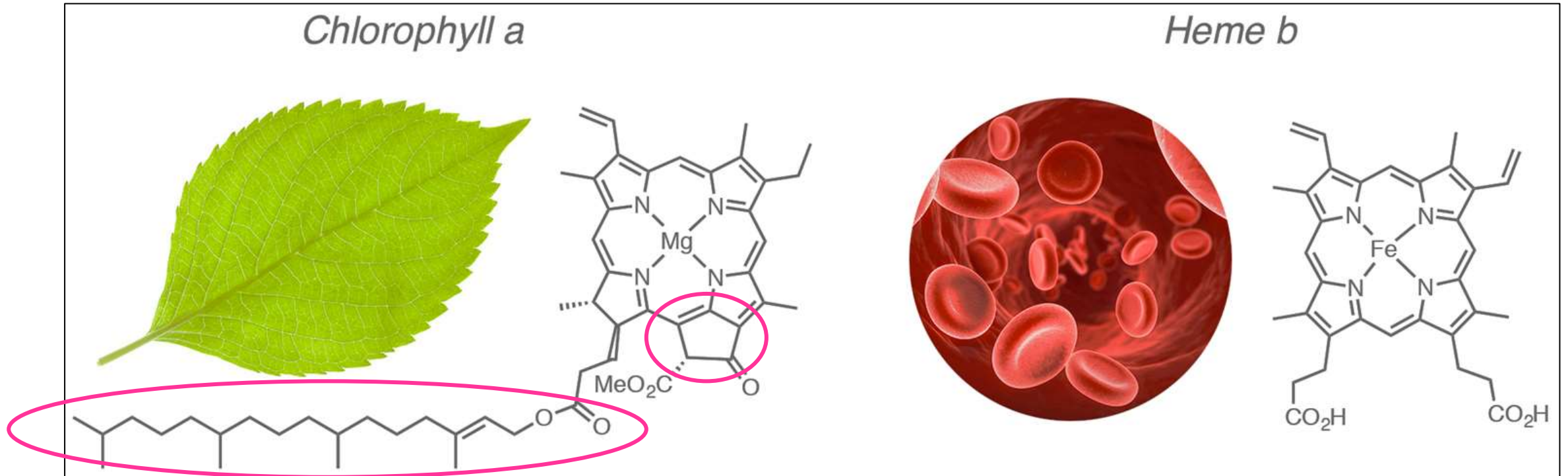


Heme b



Chlorophyll a

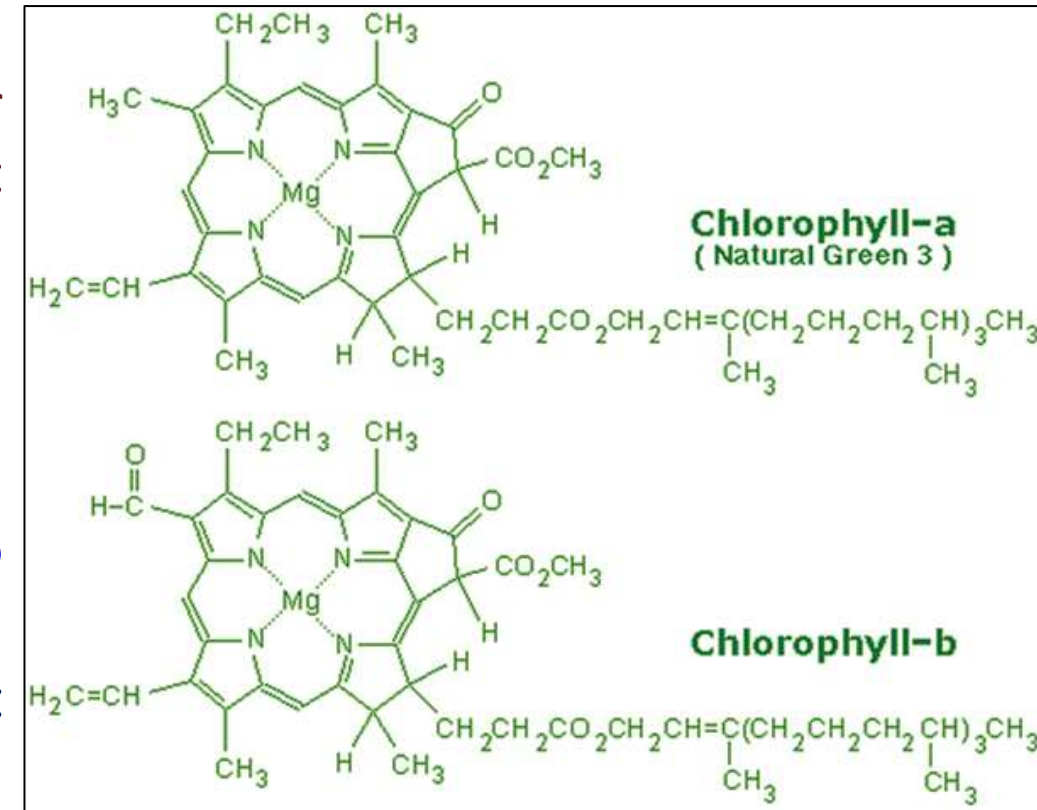
Metals in Living Systems



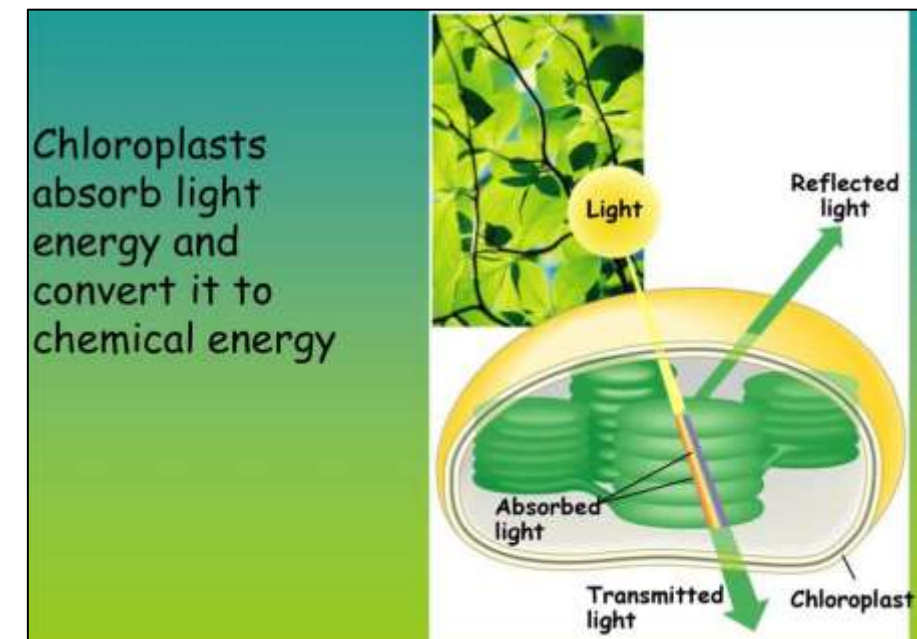
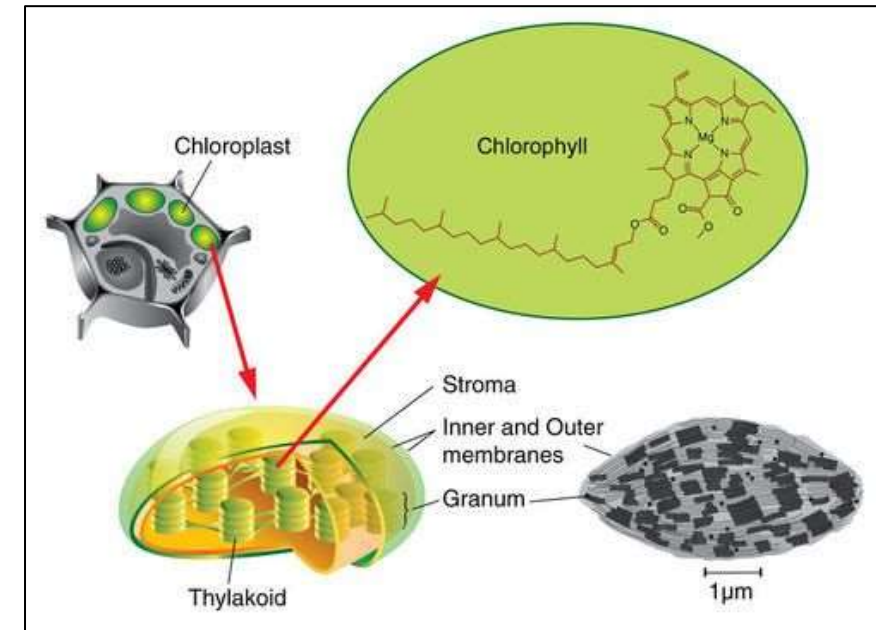
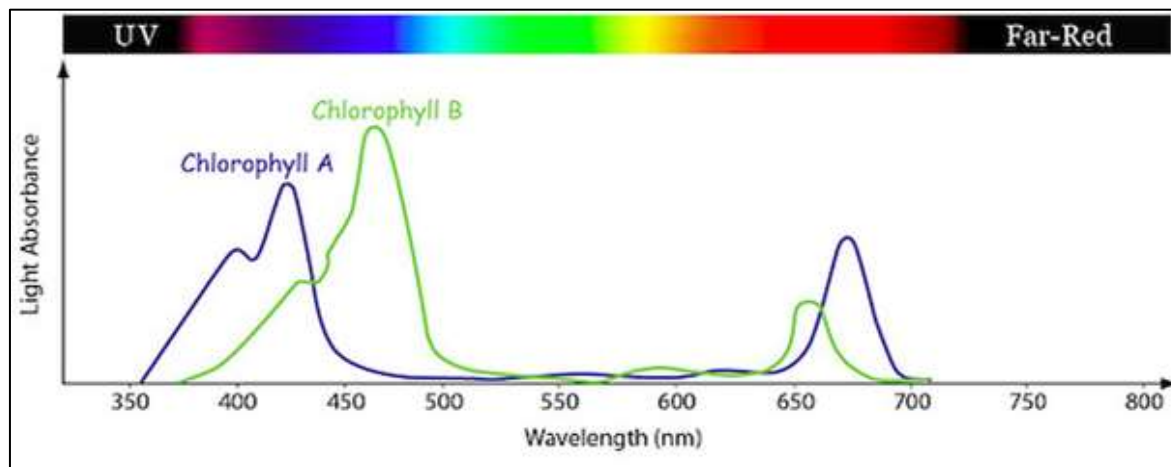
**Contents.....Metals in biology (haemoglobin, chlorophyll-
structure and property)**

Chlorophyll- Structure and Property

- 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 image displays the chemical structures of two types of chlorophylls, Chlorophyll-a and Chlorophyll-b. Both structures feature a central magnesium atom (Mg) coordinated by four nitrogen atoms within a porphyrin-like ring system. The ring is substituted with various groups, including methyl (CH₃), vinyl (H₂C=CH), and a long phytyl ester side chain (CH₂CH₂CO₂CH₂CH=C(CH₃)(CH₂)₃CH₃). Chlorophyll-a is labeled '(Natural Green 3)' and Chlorophyll-b is labeled 'Chlorophyll-b'.
- 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

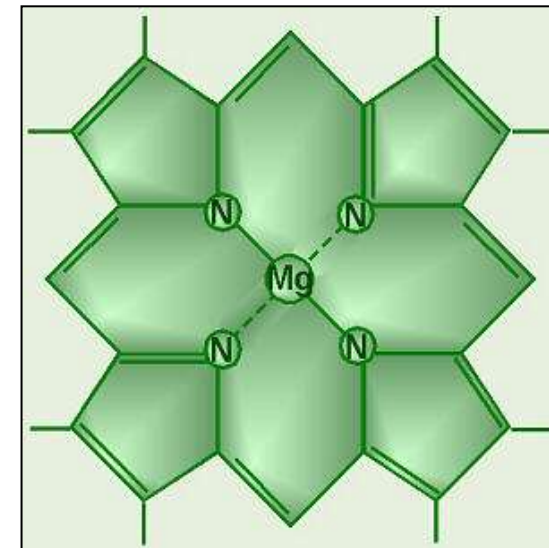
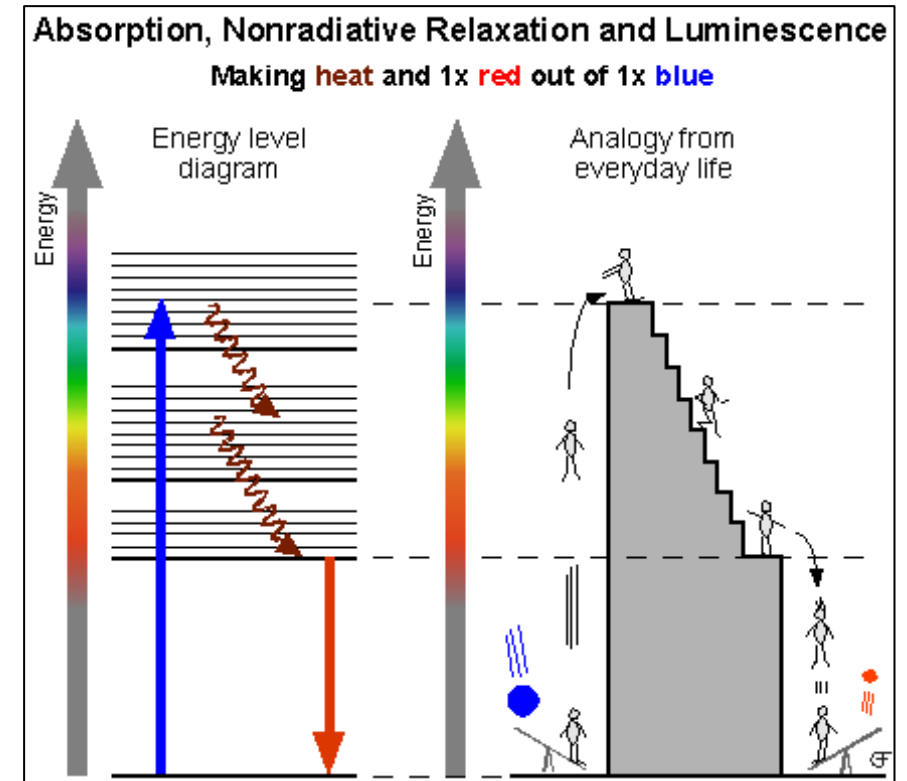


- ❖ Chloroplasts always contain both **chlorophyll a** and **chlorophyll b**
- ❖ Both are green, their absorption spectra are sufficiently different that they complement each other's range of light absorption in the visible region
- ❖ Both chlorophyll a & b absorb in the **blue** and **red** region so 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**



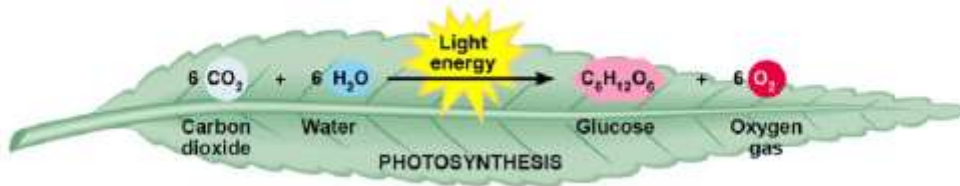
Role of Mg in chlorophyll

- ❖ Without Mg^{2+} the **porphyrin** ring is **fluorescent** – i.e. the absorbed light energy is emitted back immediately
- ❖ With 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 Mg^{2+} coordination **increase the rigidity of the planar porphyrin ring**
- ❖ The energy loss as heat due to vibration of the ring during light absorption is prevented

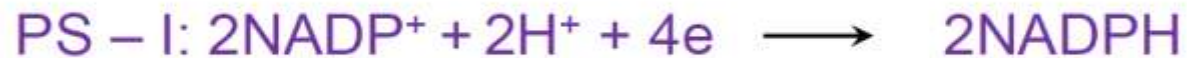


Photosynthesis Reaction

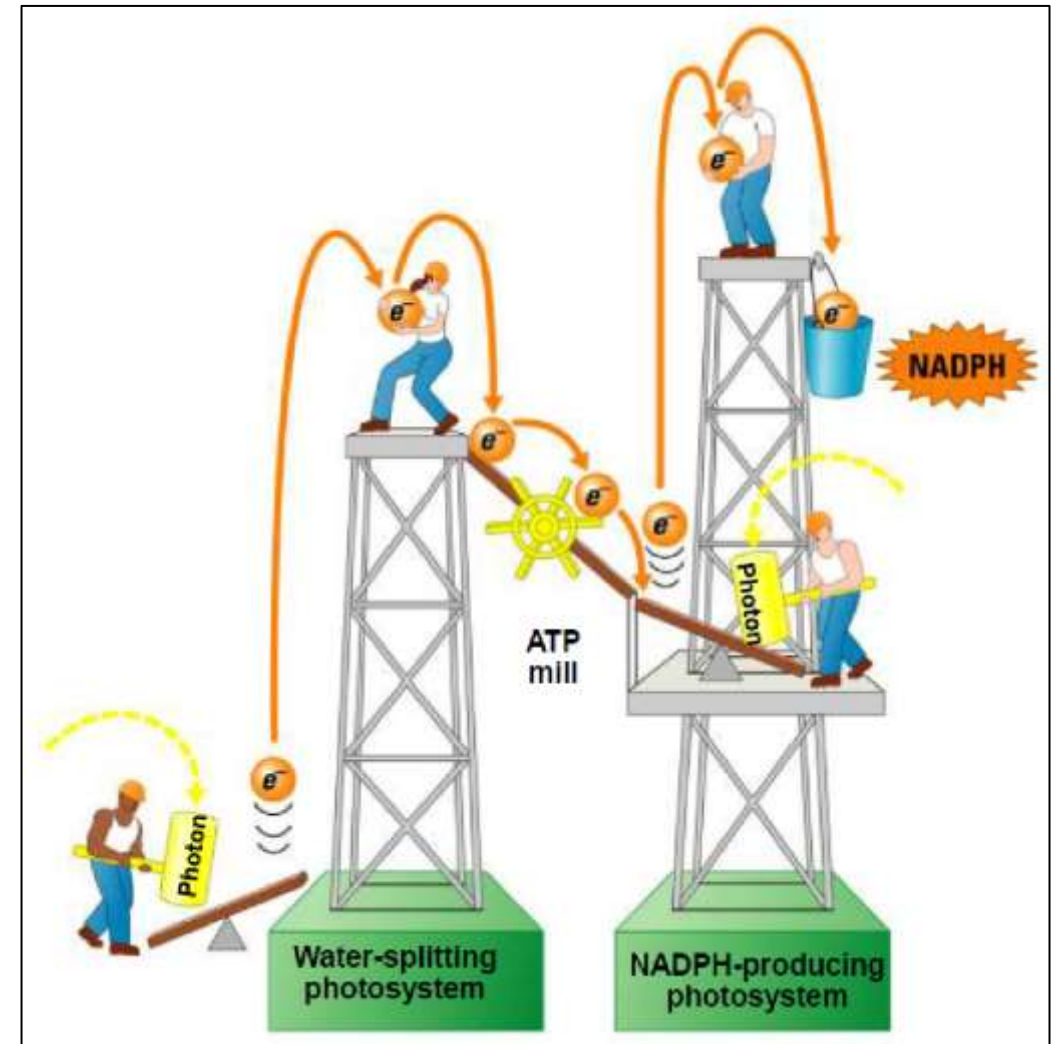
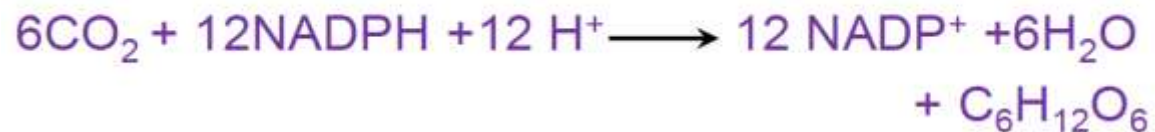
- Photosynthesis is the process by which autotrophic organisms use light energy to make sugar and oxygen gas from carbon dioxide and water



Light reaction

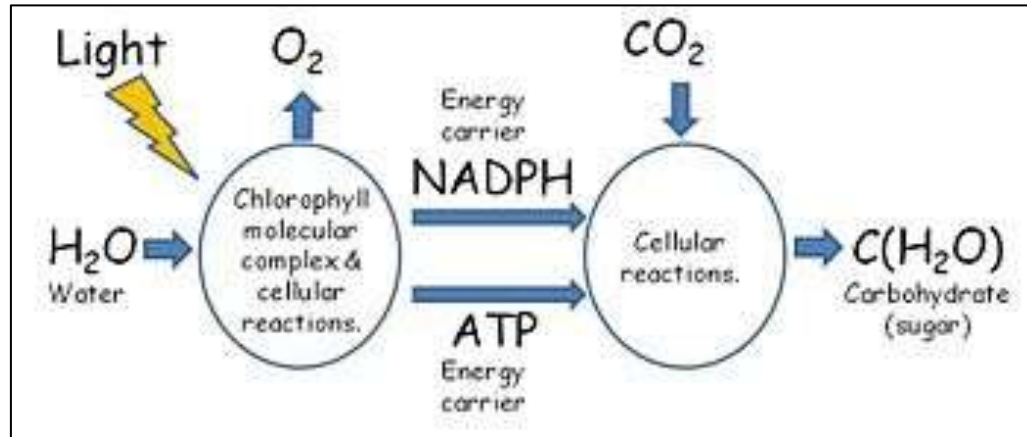


Dark reaction

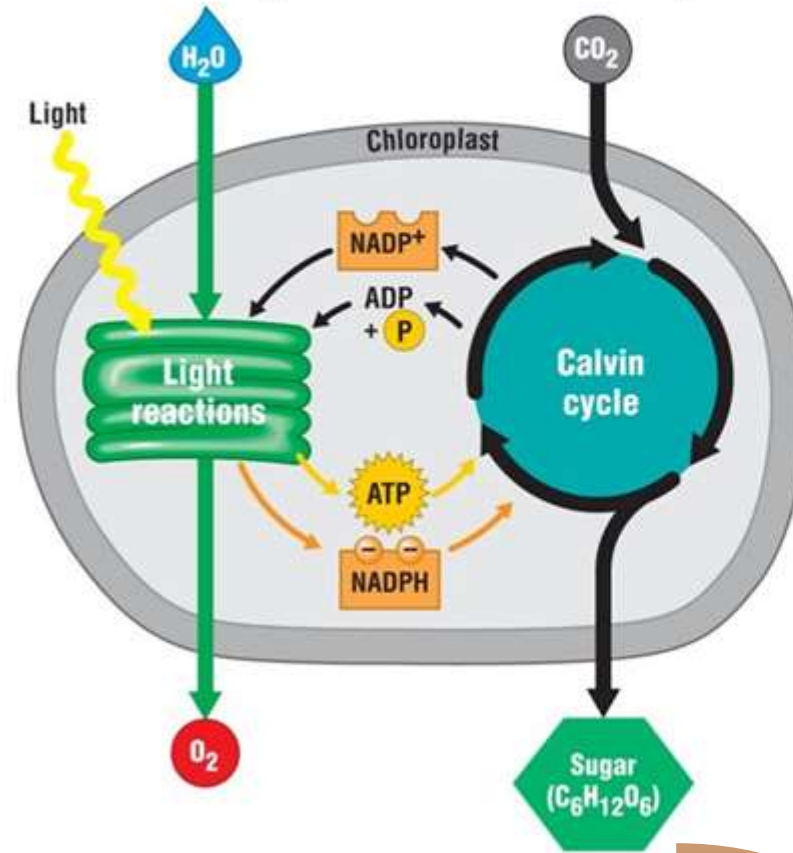


Two types of photosystems cooperate in the light reactions

A Photosynthesis Road Map



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

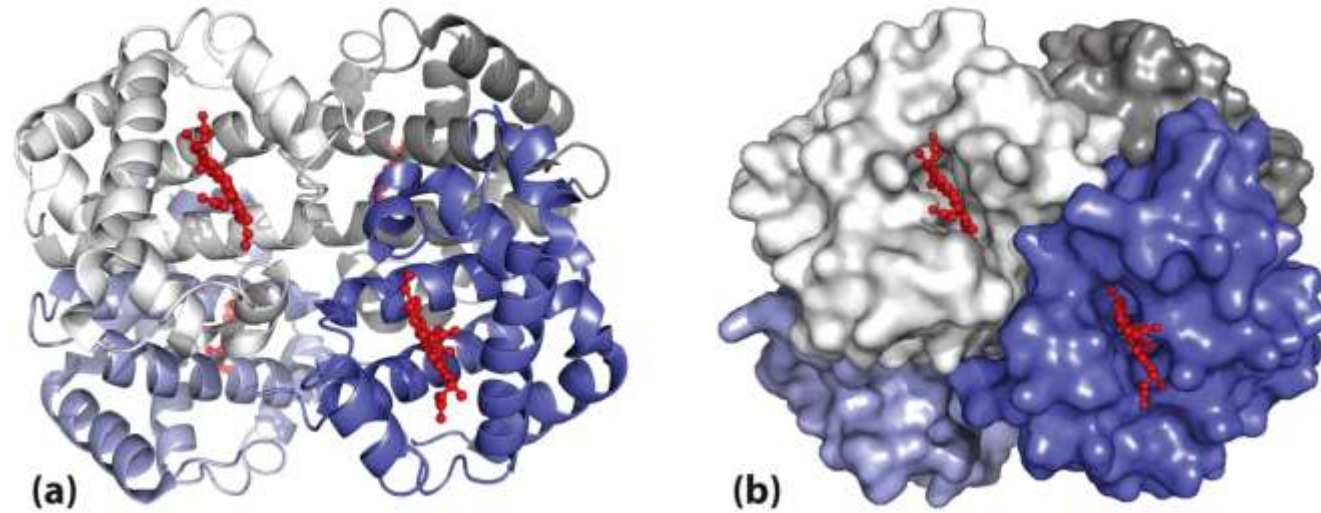
- Cellular respiration
- Cellulose
- Starch
- Other organic compounds

- Many microorganisms and most animals obtain energy by respiration, the oxidation of organic or inorganic molecules by Oxygen.
- Oxygen is such a powerful oxidant that the oxidation reactions used to obtain metabolic energy.
- In higher-level organisms, the respiratory apparatus is located in internal compartments called mitochondria, which are the power plants of a cell.
- Oxygen must therefore be transported not only to a cell but also to the proper compartment within a cell.
- A transport system is available to provide an adequate supply of oxygen for the interior cells of an organisms.
- Three different chemical solutions to the problem of oxygen transport have developed independently in the course of evolution

Protein	Source	M per Subunit	M per O ₂ Bound	Color (deoxy form)	Color (oxy form)
hemoglobin	mammals, birds, fish, reptiles, some insects	1 Fe	1 Fe	red-purple	red
hemerythrin	marine worms	2 Fe	2 Fe	colorless	red
hemocyanin	mollusks, crustaceans, spiders	2 Cu	2 Cu	colorless	blue

Quaternary Structure of Hemoglobin

- **Hemoglobin** (M_r 64,500) contains **four polypeptide chains** with one **heme prosthetic group each**, in which the iron atoms are in the **ferrous (Fe^{2+}) state** (Fig).
- *The protein portion, globin, consists of **two α chains (141 residues each)** and **two β chains (146 residues each)**.*
- *The **subunits of hemoglobin are arranged in symmetric pairs**, each **pair having one α and one β subunit**.*
- *Hemoglobin can therefore be described either as a tetramer or as a dimer of $\alpha\beta$ protomers.*
- *A related protein called myoglobin temporarily store oxygen in the tissues.*
- *Myoglobin is a relatively small protein that contains 153 amino acids.*



Hemoglobin Hb

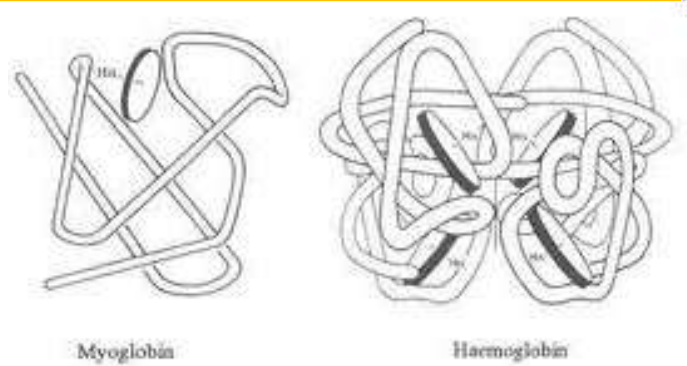
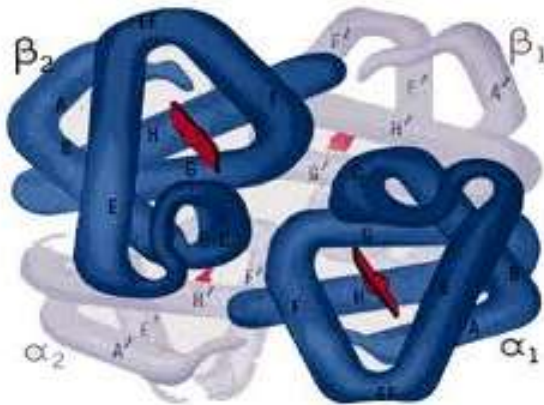


Figure 3 Myoglobin versus haemoglobin

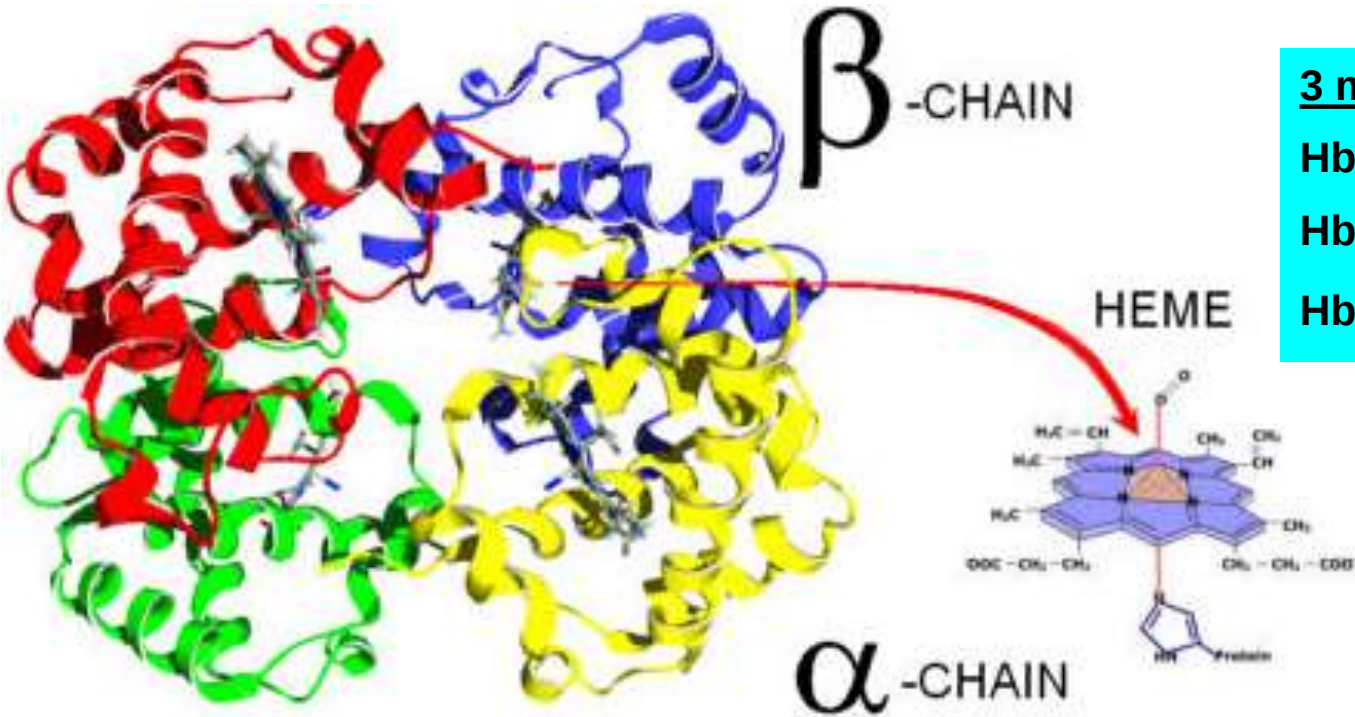
Property	Hemoglobin	Myoglobin
metal	Fe	Fe
M ⁿ⁺ ox state for deoxy	II	II
Metal:O ₂	Fe:O ₂	Fe:O ₂
Color deoxy	red-purple	red-purple
Color oxy	red	red
Metal coor motif	porphyrin	porphyrin
Molecular weight (Da)	65,000	16,700
# of subunits	4	1

- α 141 Amino acid
- β 146 Amino acid
- Mb 153 Amino acid



Four units of Hb

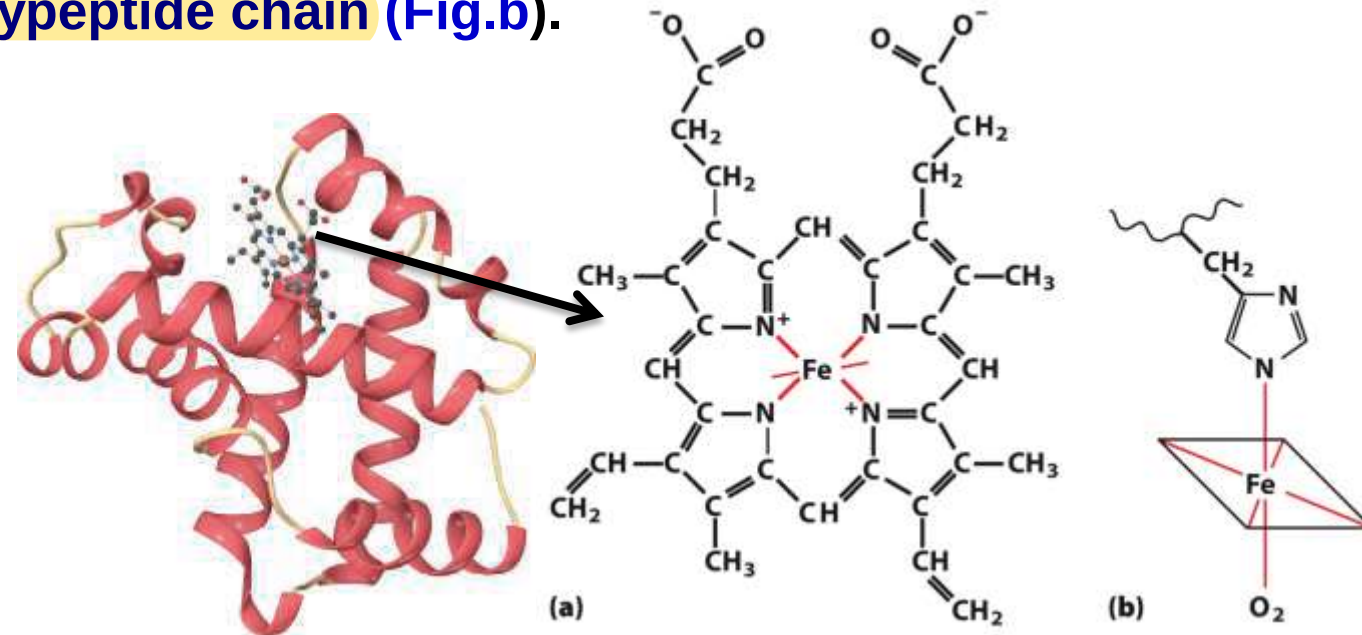
Hb is not an exact tetramer of Mb



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

The Heme Group of Myoglobin

- A heme group is present in myoglobin, hemoglobin, cytochromes, and many other proteins. Heme consists of a complex organic ring structure, protoporphyrin, which binds an iron atom in its ferrous (Fe^{2+}) state (Fig.a).
- The iron atom has six coordination positions, four of which are in the plane of the protoporphyrin and bonded to it, and two of which are perpendicular to the ring.
- In myoglobin and hemoglobin one of the perpendicular coordination positions is bound to a nitrogen atom of a His residue in the polypeptide chain (Fig.b).
- The sixth coordination position is open and serves as the binding site for an O_2 molecule.
- It is important that the myoglobin heme group is largely sequestered away from the solvent.
- The iron of free heme in solution is readily oxidized to the ferric (Fe^{3+}) state, which does not bind O_2 .

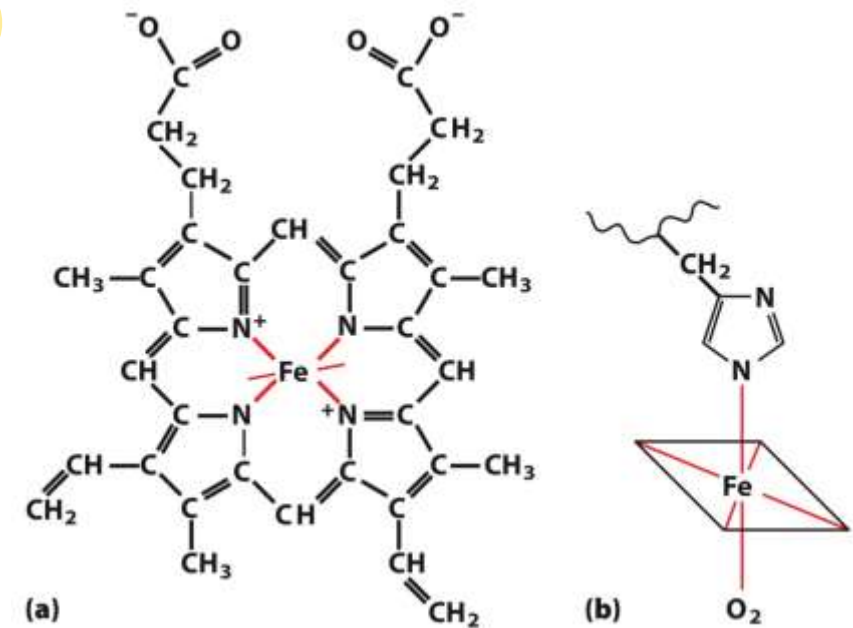


❖ Each of the subunit polypeptides contains a heme group—an iron atom at the center of a porphyrin ring—which reversibly binds a single O_2 molecule in the ferrous state (Fe^{2+}).

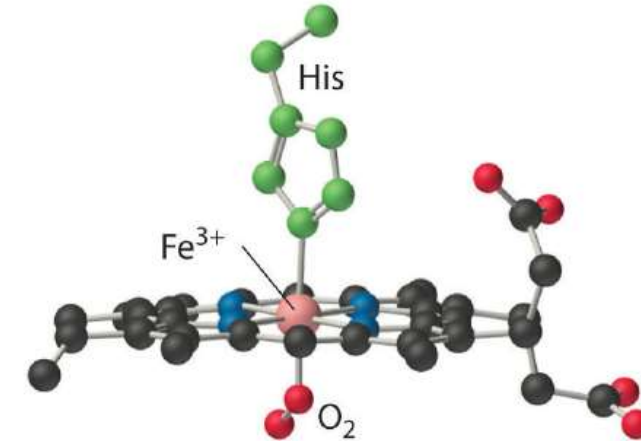
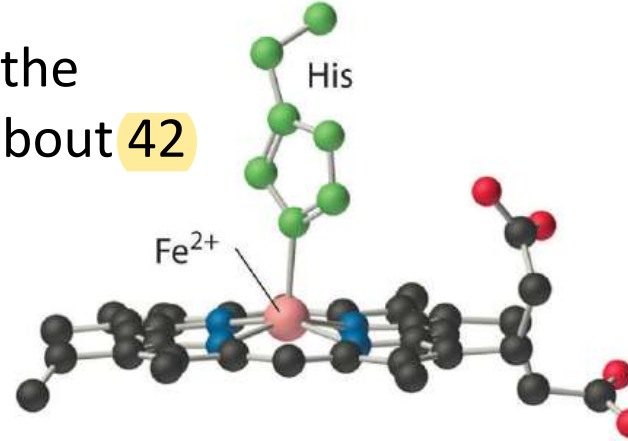
❖ Whereas free heme binds O_2 irreversibly and is converted to the ferric state (Fe^{3+}) in the process, Hb can reversibly bind O_2 because the valence state of the iron atom is protected by encapsulating the heme in the globin protein fold

❖ Each tetrameric ($\alpha_2\beta_2$) Hb can therefore reversibly bind four O_2 molecules.

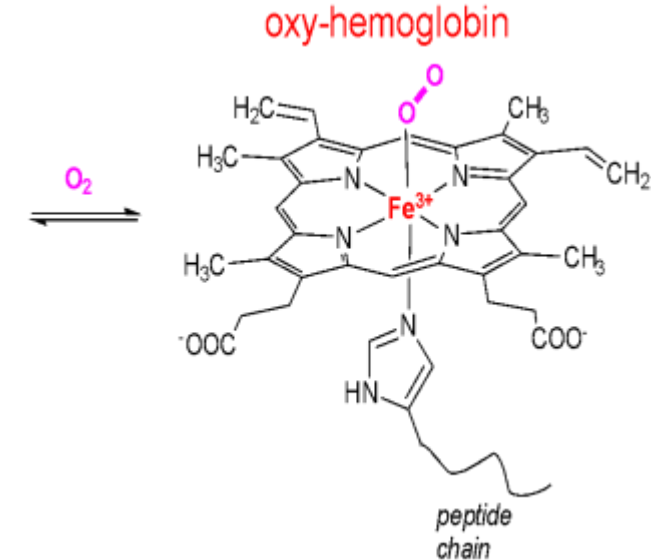
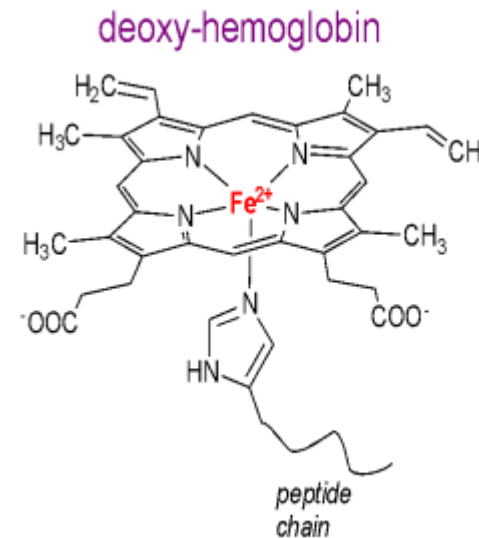
❖ Oxygenation changes the electronic state of the Fe^{2+} heme iron, which is why the color of blood changes from the dark, purplish hue characteristic of venous blood to the brilliant scarlet of arterial blood.



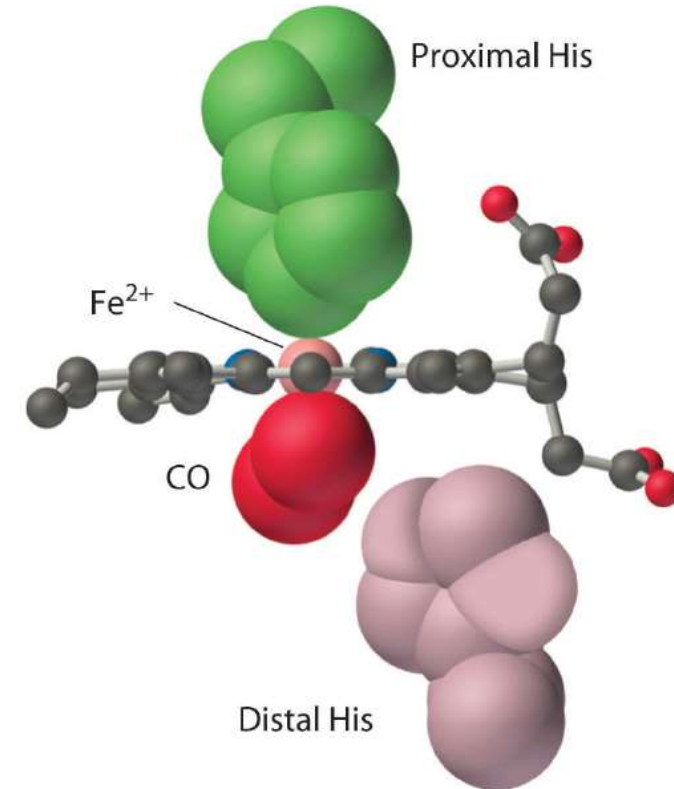
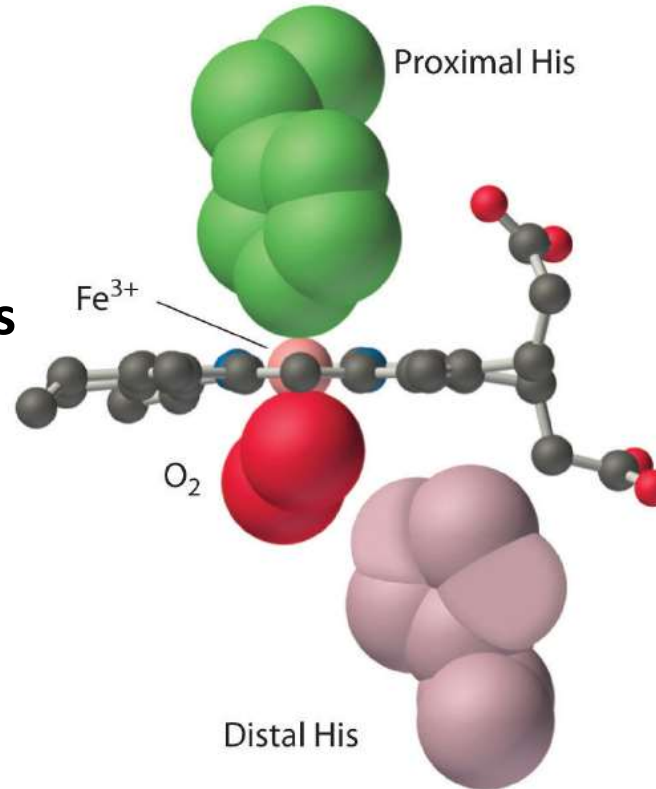
- In the ferrous form (deoxyhemoglobin), the iron is five-coordinate and high spin.
- Because high-spin Fe is too large to fit into the “hole” in the center of the porphyrin, it is about 42 pm above the plane of the porphyrin.



- When Oxygen binds to deoxymyoglobin to form oxymyoglobin, the iron is converted from five-coordinate (high spin) to six-coordinate (low spin; Figure).
- Because low-spin Fe^{3+} is smaller than high-spin Fe^{2+} , the iron atom moves into the plane of the porphyrin ring to form an octahedral complex.

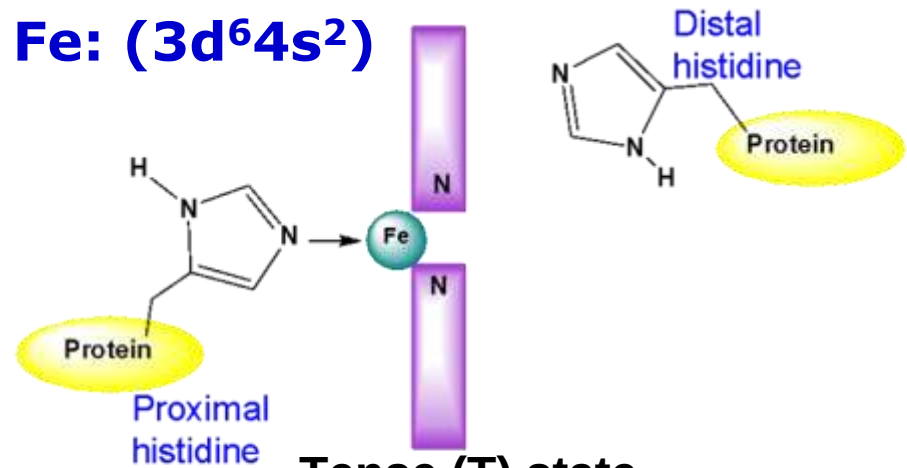


- The Fe–O₂ unit is bent, with an Fe–O–O angle of about 130°. Distal histidine in hemoglobin makes O₂ to bind in a bent fashion
- In the living system binding affinity for oxygen is reduced considerably in presence of CO.
- An isolated heme binds CO 25000 times as strongly as O₂ in solution.
- But, The affinity of CO for deoxyhemoglobin is only about 200 times greater than that of O₂, which suggests that something in the protein is decreasing its affinity for CO by a factor of about 100.
- For CO to bind strongly, it has to bind linearly which is made difficult by distal histidine.



- **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.
- The imidazole group of the distal histidine is located precisely where the oxygen atom of bound CO would be if the Fe–C–O unit were linear.
- Consequently, CO cannot bind to the heme in a linear fashion; instead, it is forced to bind in a bent mode that is similar to the preferred structure for the Fe–O unit.
- This results in a significant decrease in the affinity of the heme for CO, while leaving the O_2 affinity unchanged.
- **Thus the primary function of the distal histidine appears to be to decrease the CO affinity of hemoglobin and myoglobin to avoid self-poisoning by CO.**

Fe: ($3d^6 4s^2$)

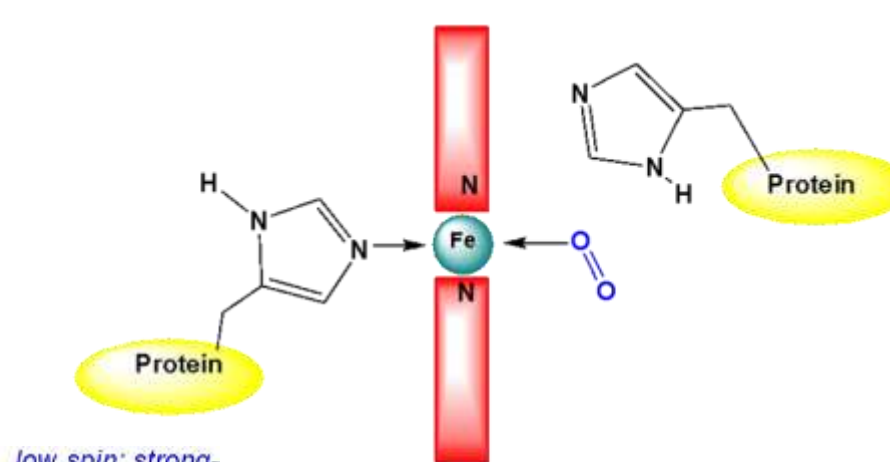


Tense (T) state

$Fe^{2+} t_{2g}^4 e_g^2$, High spin, radius 92 pm

Paramagnetic

Fe 42 pm outside porphyrin plane



Relaxed (R) state

$Fe^{3+} t_{2g}^5 e_g^0$, Low spin, radius 75 pm

Diamagnetic

Fe fits inside the porphyrin plane

- The electronic configuration of iron differs among the various hemoglobin species and is primarily responsible for their overall Magnetic properties.
- The valence state – ferrous (Fe^{2+}) or ferric (Fe^{3+}) – is irrelevant; **what matters is the number of unpaired electrons in the entire molecule.**