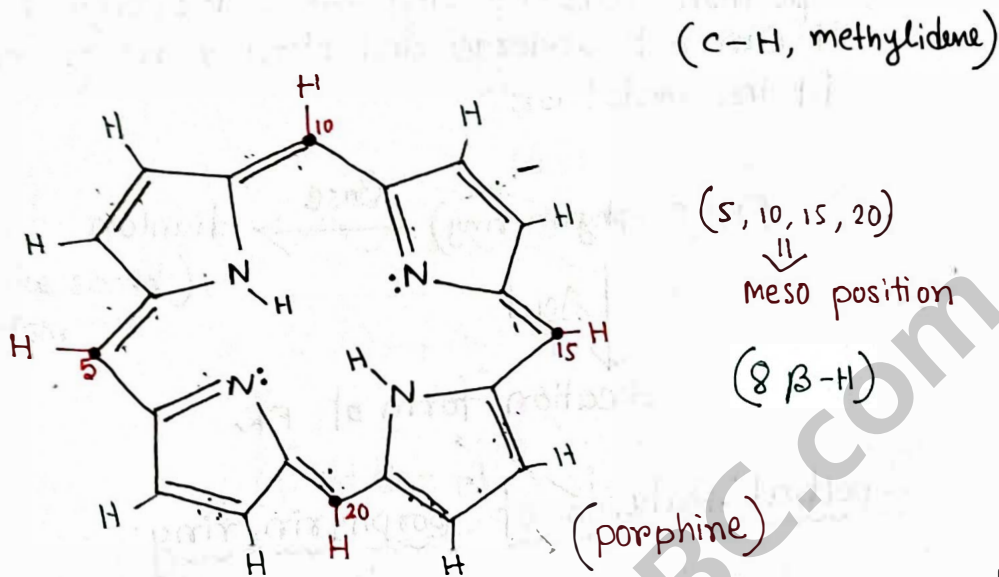


∴ Bio inorganic :-



Total π bonds \Rightarrow 18 \leftarrow \therefore macrocyclic system (only periphery boundary)

$4n+2 = 18$

$n = 4$ (aromatic system)

\Rightarrow rigid system than crown ether.

\Rightarrow macrocyclic rigid system.

\Rightarrow very selective for metal ions.

"Porphyrin rings are derivatives of porphine"

\Rightarrow porphyrin rings containing metal are called metalloporphyrins

e.g \Rightarrow Hemoglobin, Myoglobin.

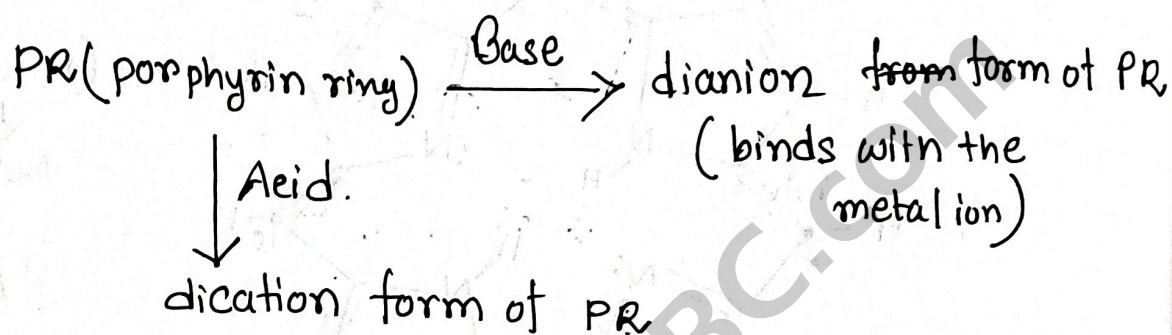
\Rightarrow Cavity is ideal for 3d TM Series.

Order: $Mn^{+2} < Fe^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$

$Zn < Fe^{+2} < Co^{+2} < Cu^{+2} < Ni^{+2}$ \rightarrow Square planar

\Rightarrow geometry: Square planar (4 pyrrole rings joined by methyldyne C-H)

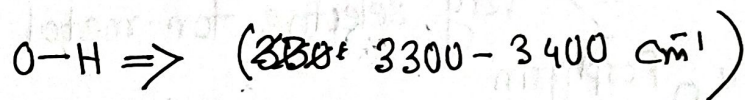
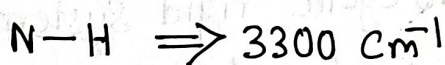
\Rightarrow If the metal size is higher, it will occupy position above the ring, since the ring is aromatic, it can not undergo distortion in its geometry to fit the metal ion.



Spectral features of porphyrin ring:

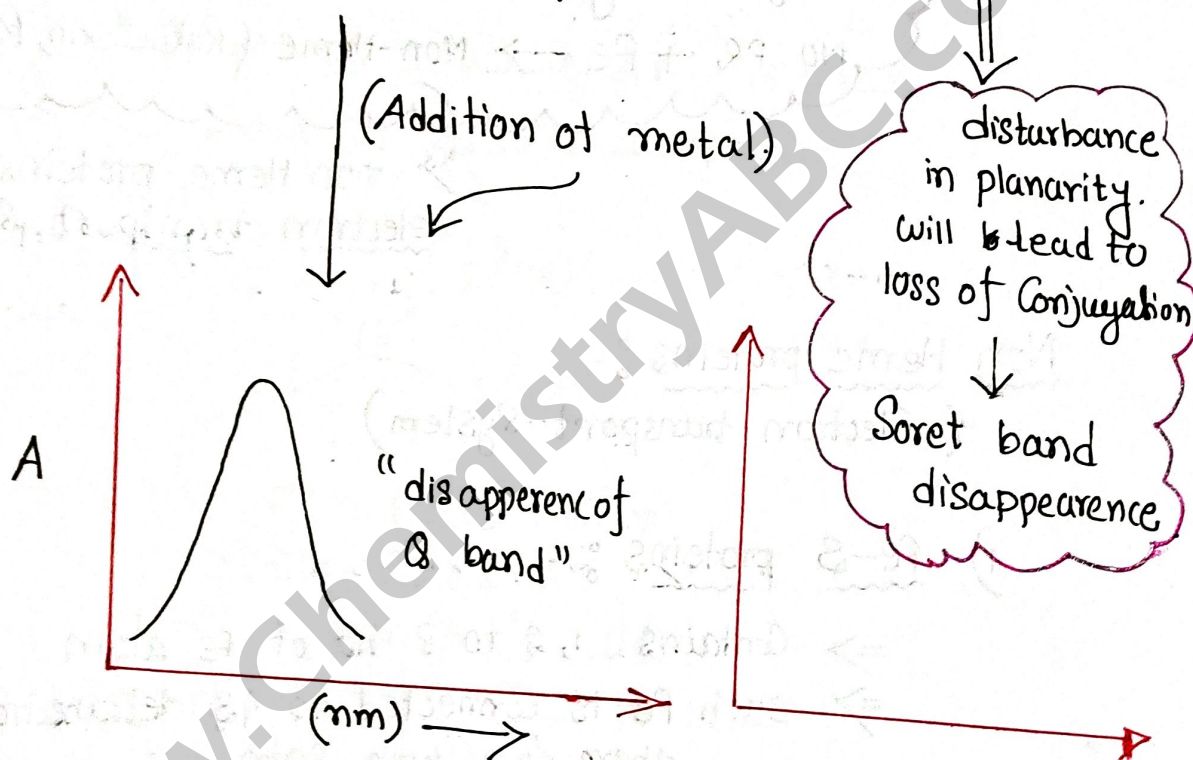
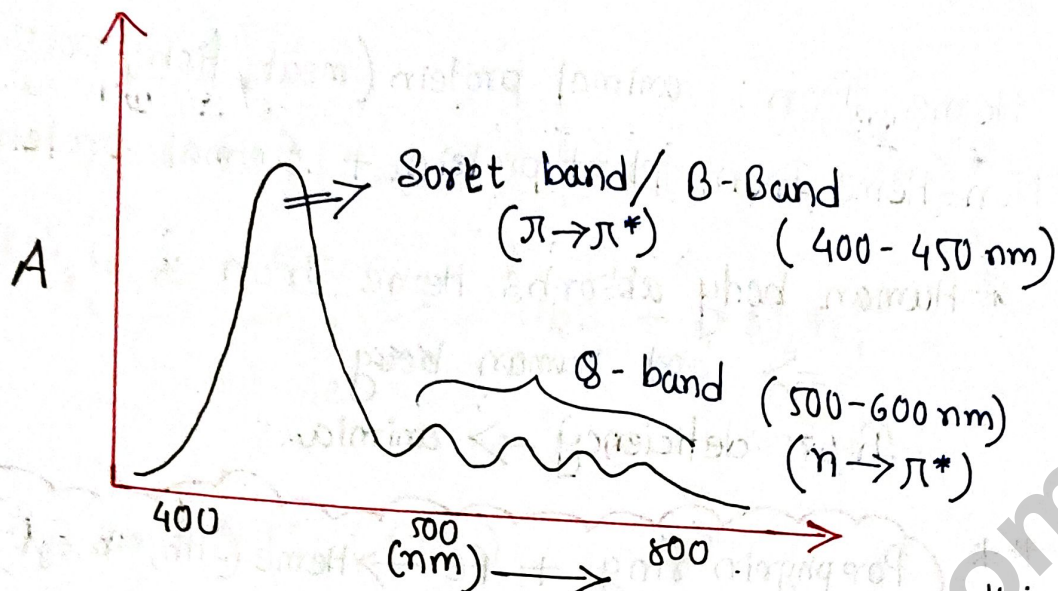
$^1\text{H-NMR}$:	4 meso-H		<u>Chemical shift</u>	← (diamagnetic current of aromatic ring)
	8 β -H		4	
	2 N-H		8	
			2	

IR : fundamental functional groups:



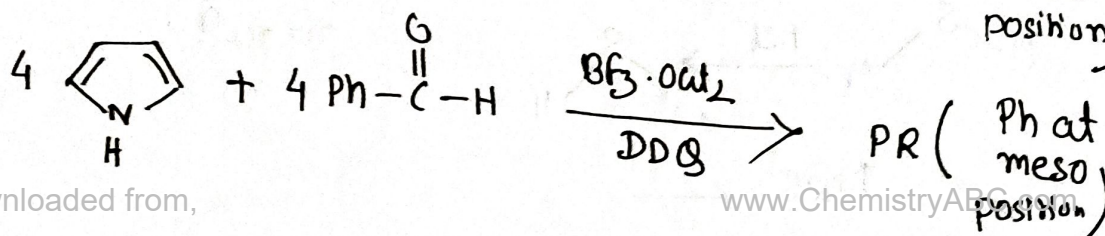
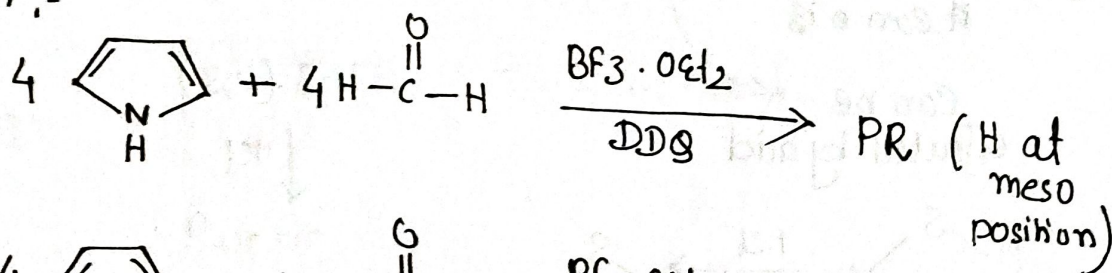
\Rightarrow IR data is not useful in case of porphyrin ring since, in case moisture gets trapped into it and extra peak of -OH will also be observed which will interfere with -N-H peak.

UV : (best way to characterise porphyrin system)



Colour of PR :- $\pi \rightarrow \pi^*$ intraligand charge transfer.
(the colour of PR changes with change in metal ion)

Preparation :-



● Heme Iron: animal protein (meat, fish, poultry)

Non-Heme Iron: plant protein + Animal protein

* Human body absorbs Heme iron *

⇒ and Human body
Iron deficiency ⇒ anemia.

** Porphyrin ring + Fe → Heme (Hb, Mb, cyt.)
No PR + Fe → Non-Heme (Rubredoxin, ferredoxin)

→ non Heme proteins are
electron transport system.

Non Heme proteins :-
(Electron transport System)

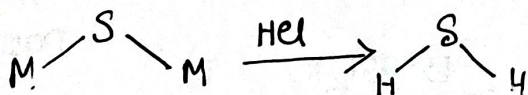
1) Fe-S proteins :-

⇒ Contains, 1, 2 to 8 no. of Fe atom.
⇒ each Fe is connected to 4S tetrahedral
there fore high spin.

⇒ Labile or Non labile Sulfur.

inorganic Sulfur
it can be

Can be effected by acid

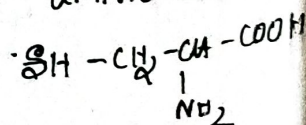


↑ IR S

organic Sulfur
M-S (cys)

cystein

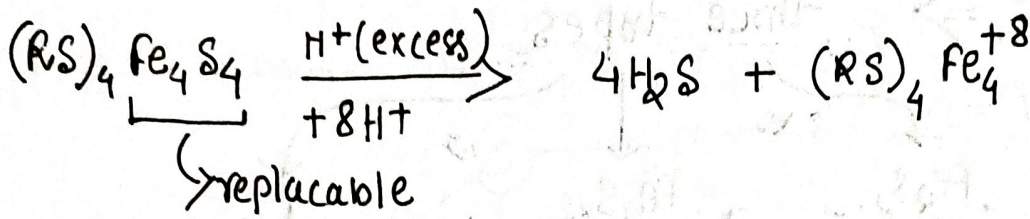
amino acid



M-S (cys)
↓ HCl
no. see?



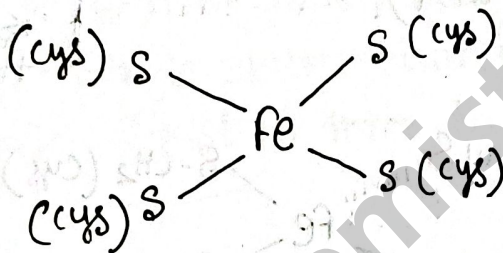
$n =$ no. of labile Sulfur.



① Rubredoxin :- $(Fe_1 S_0)$

$Fe_1 S_0 \Rightarrow$ no replacable Sulfur is present.

\Rightarrow Also known as bacterial rubredoxin.



\Rightarrow Zero labile Sulfur.

\Rightarrow one Fe atom.

\Rightarrow 4-non labile Sulfur.

\Rightarrow it is Coloured, due to LMCT.

\Rightarrow tetrahedral, high Spin.

\Rightarrow Rubredoxin

oxidised
(Fe(III))

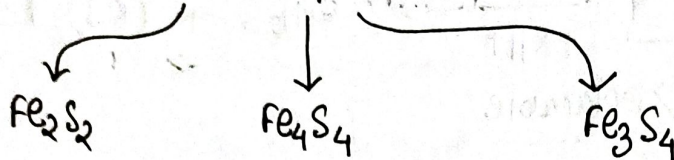
reduced
(Fe(II))

\Rightarrow it is single e^- transfer. agent.

② ferredoxin :-

⇒ Contain more than 1 Fe atoms.

⇒ three types



(i) Fe_2S_2 :-

⇒ also known as photosynthetic ferredoxin (it is present in plant).

⇒ Single e⁻ transfer agent.

⇒ Td (both unit).

[when two cysteine is replaced by two histidine, then it is RIESKE protein]



RIESKE

⇒ 2 Fe atoms

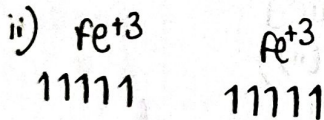
⇒ 2 labile sulfur.

⇒ 4 non labile sulfur.

⇒ Fe_2S_2 exist in two form.

oxidised

i) both are in +3



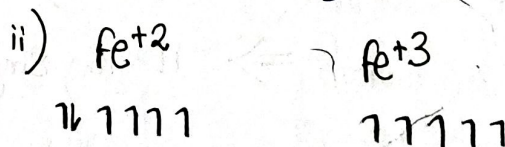
11 11 11 11 11
 (Antiferromagnetic Coupling)

⇒ Diamagnetic

⇒ ESR inactive.

reduced

i) 1 Fe is in +2
1 Fe is in +3



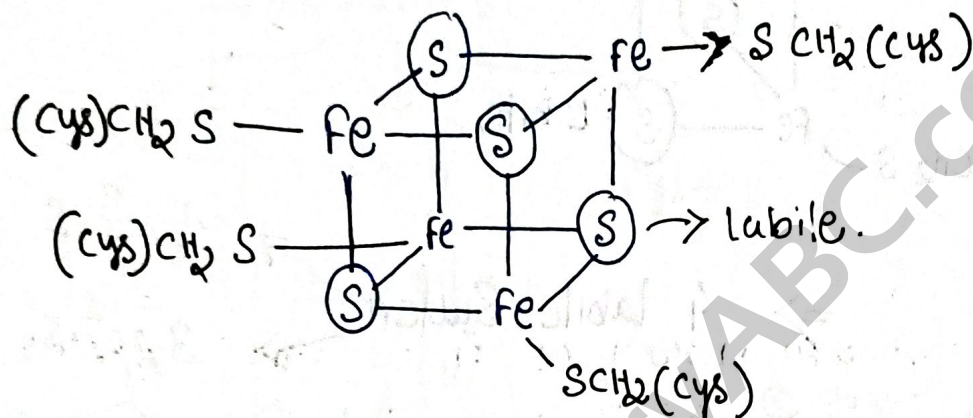
11 11 11 11 11 1
 (Antiferromagnetic Coupling)

⇒ paramagnetic

⇒ ESR active.

(ii) Fe₄S₄:

- ⇒ most Common and most Stable.
- ⇒ it is present in active site of Nitrogen fixation protein.
- ⇒ Cubane Structure.



- ⇒ 4 labile S
- ⇒ 4 Fe atom.
- ⇒ 4 non-labile Sulfur.
- ⇒ Single electron transfer agent.
- ⇒ Exist in three form.

↓
oxidised

Same as before

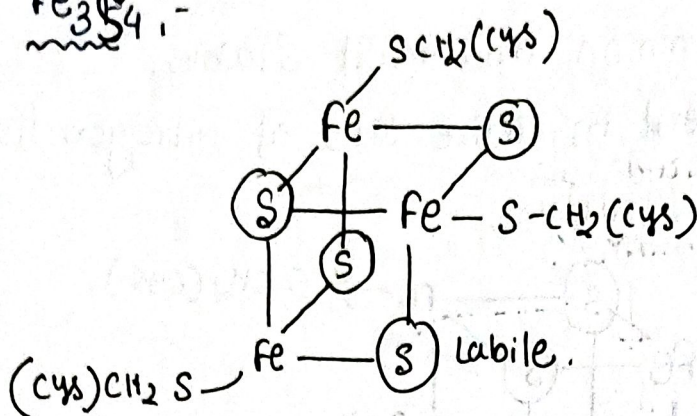
- i) $2\text{Fe} \Rightarrow +3(d^5)$
- $2\text{Fe} \Rightarrow +2(d^6)$
- ⇒ overall Spin = 0
- ⇒ Diamagnetic
- ⇒ ESR inactive

↓
Reduced

- i) $3\text{Fe} \Rightarrow +2$
- $1\text{Fe} \Rightarrow +3$
- ⇒ overall Spin $+\frac{1}{2}$
- ⇒ paramagnetic.
- ⇒ ESR active.

** $\text{d-Fe}_2\text{S}_2$ is dimer of Fe_4S_4
⇒ $1e^-$ transfer agent.

iii) Fe_3S_4 :-



\Rightarrow 4 labile Sulfur \rightarrow $1 \mu^3-S$
 \rightarrow $3 \mu^2-S$

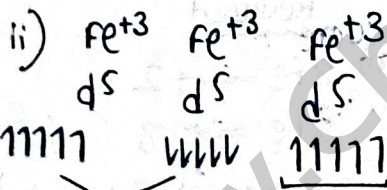
\Rightarrow 3 non labile Sulfur.

\Rightarrow 3 Fe atom.

\Rightarrow Exist in two form :-

Oxidised

i) All 3 Fe $\Rightarrow +3$



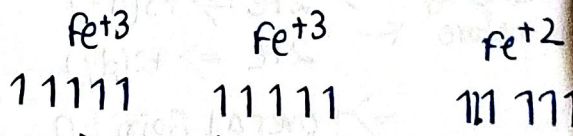
zero $S = \frac{5}{2}$

\Rightarrow overall Spin $\frac{5}{2}$

\Rightarrow paramagnetic
 \Rightarrow ESR active

Reduced

i) 1 Fe^{+2}
 2 Fe^{+3}



$S = 0$

\therefore overall Spin = 2

\Rightarrow paramagnetic
 \Rightarrow ESR active.

Note: All Ferradoxins are single e- transfer agent.

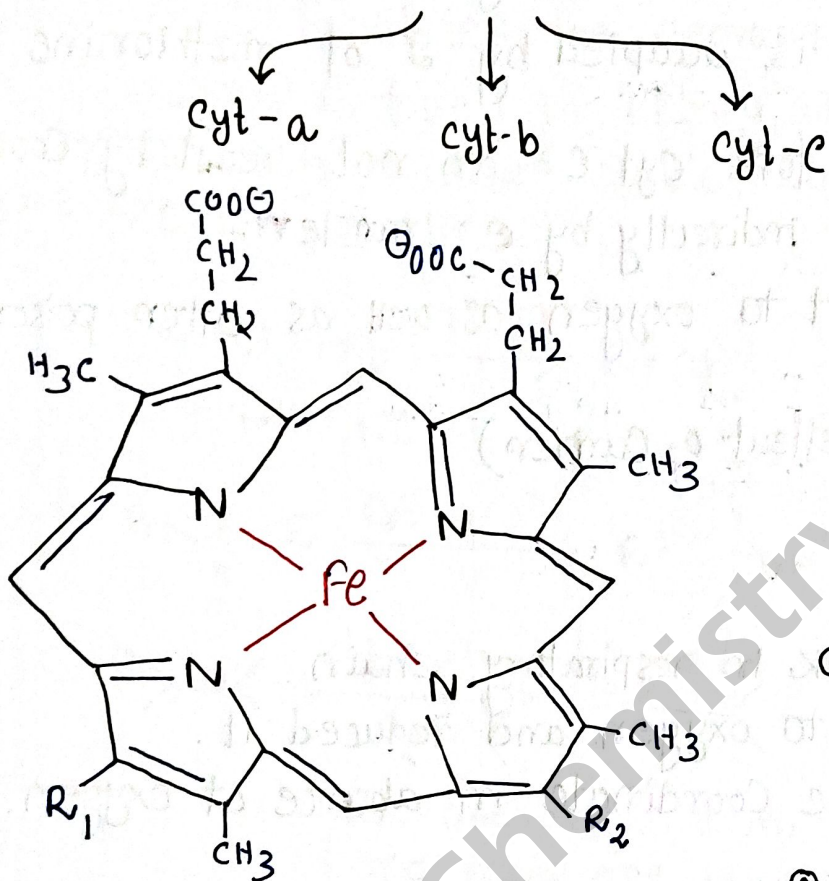
\Rightarrow only Fe_3S_4 ESR active in oxidised as well as reduced form.

Heme proteins :-

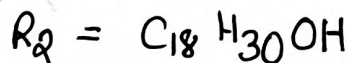
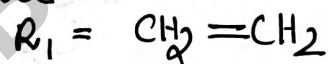
⊙ ~~cytochromes~~ Cytochromes
(PR + Fe)

⇒ plants and animals.

⇒ cytochromes

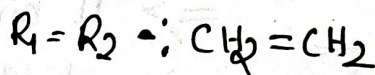


⊙ Heme A :-



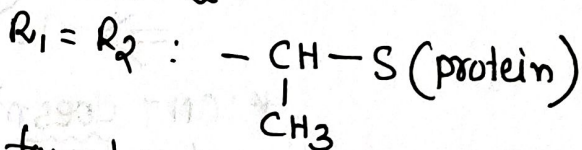
(found in cyt-a)

⊙ Heme B :-



(found in cyt-b, Hb, Mb)

⊙ Heme c :-



(found in cyt c)

⇒ oxidised form ⇒ Fe⁺³

Reduced form ⇒ Fe⁺²

∴ Reduction potential : cyt a > cyt-c > cyt-b
0.4v 0.26v 0.03v

∴ Order of e⁻ follow : b → c → a → O₂

⇒ the e⁻ follow system in respiratory chain from food.
⇒ "cyt a" binds to oxygen.

Cytochrome - C :-

- ⇒ 4 Coordination Sites are occupied by N atom of porphyrin ring.
- ⇒ 5th Site is occupied by N atom of Histidine.
- ⇒ 6th site is occupied by S of methionine.
- ⇒ ∴ there fore cyt-C Can not react by Coordination and it reacts indirectly by e⁻ transfer.
- ∴ it is inert to oxygen as well as other poison's like CO, CN⁻,
- ↳ (do effent O₂ Carrier)

Cytochrome - A :-

- ⇒ last link in respiratory chain.
- ⇒ it binds to oxygen and reduced it.
- ⇒ it is five Coordinate in absence of oxygen.

Cyanide poisoning:-

- ⇒ it occurs if CN⁻ binds cyt-a instead of O₂
- * CN⁻ doesn't bind to hemoglobin.
- ↳ binds to met-hemoglobin.

treatment of CN⁻ poisoning:

- ⇒ { Amyl nitrite injection
Sodium nitrite injection } used.
- (in our body amount of met-hemoglobin is very low) → used for the Conversion of Hemoglobin
- met-hemoglobin

↳ that's why Amyl nitrite

or, Sodium nitrite is used to increase met-hemoglobin in our body. and then CN⁻ binds with met-hemoglobin and it release from our body.

∴ " Amyl nitrite or Sodium nitrite, oxidised Hemoglobin to met-hemoglobin, met-Hemoglobin tightly bind to CN⁻ there fore it removes from system."

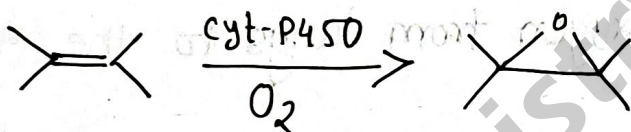
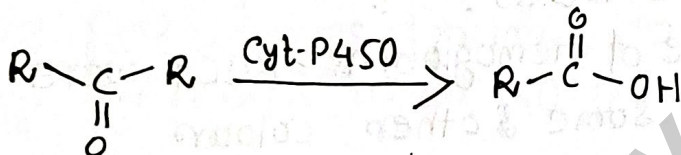
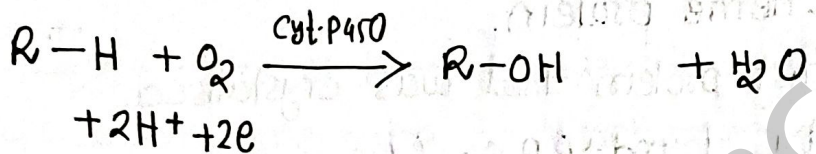
Cytochrome P-450

⇒ Cyt-P-450 are the group of Cyt, founds plants, animal and bacteria., It absorbs at 450 nm.

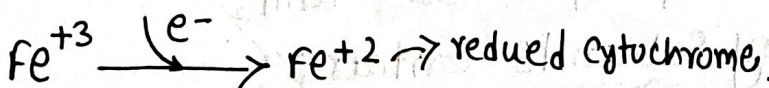
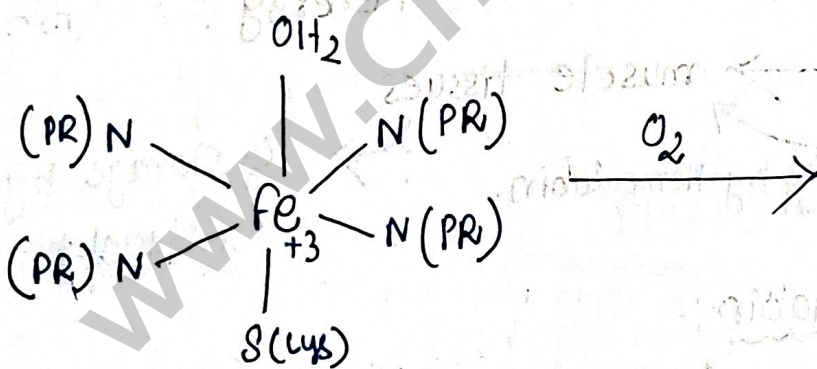
⇒ Soret band appears at 450 nm (due to $\pi \rightarrow \pi^*$)

⇒ facilitates the cleavage of O_2

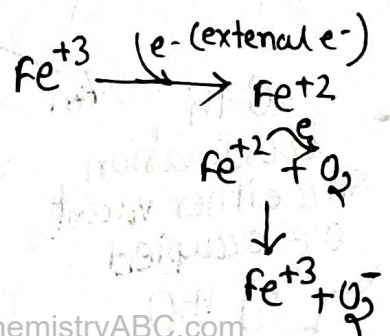
⇒ it is found in kidney where it oxidises insoluble hydrocarbon to water soluble, alcohols, epoxides, which can be excreted in urine.



Note: one oxygen atom is inserted to substrate. and other one is reduced to water.



when reduced cytochrome transfer e^- from metal atom Fe^{+2} to O_2 . it forms Superoxide ion. O_2^{\ominus} . (Stretching frequency decreases)



O₂ transport and storage :-

Heme protein

- Hemoglobin
- Myoglobin

Non-Heme protein

- Hemocyanin
- Hemerythrin

Hemoglobin :- (Hb)

- ⇒ Heme protein
- ⇒ first protein that was crystallised.
- ⇒ it is found RBCs.
- ⇒ in absence of Hemoglobins, RBCs were either colourless or of some other colour.
- ⇒ transport oxygen from lungs to the muscle tissues.

Respiration: O₂ inhale.



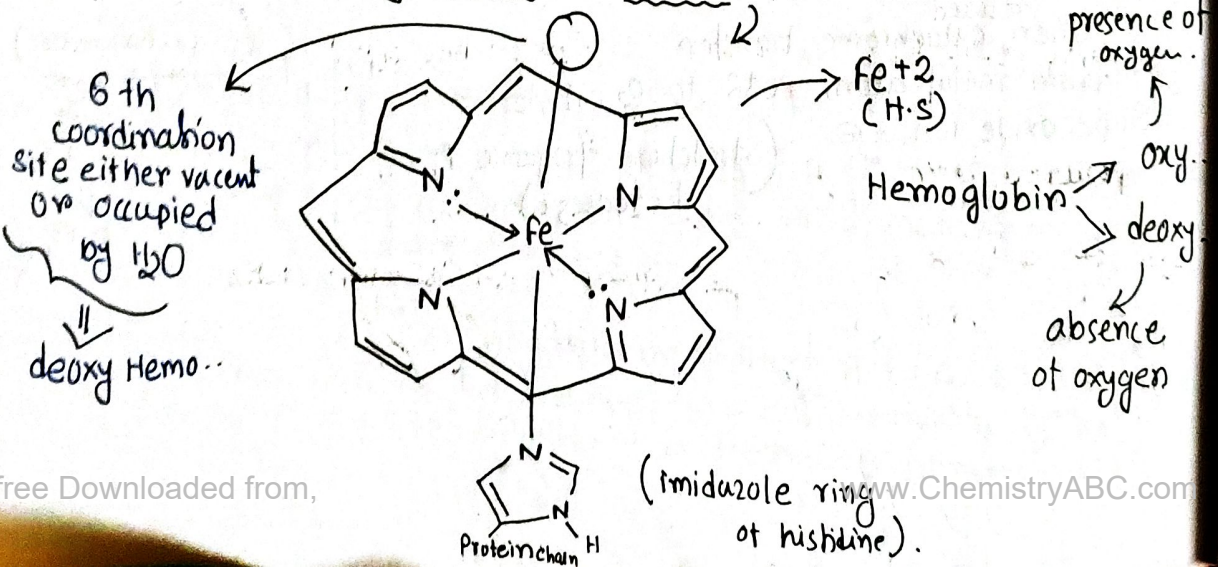
lungs → muscle tissues

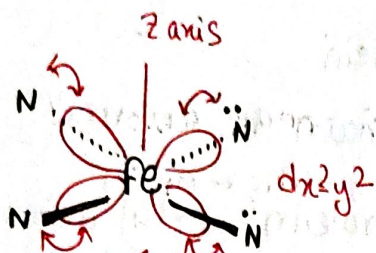
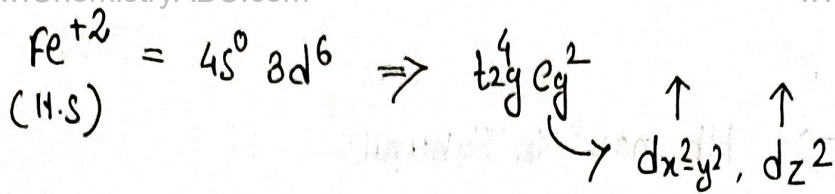
O₂ transport by Hemoglobin.

O₂ storage by (Myoglobin)

Structure of Hemoglobin :-

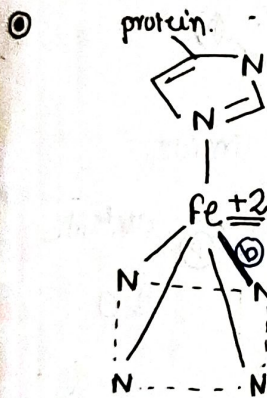
- ⇒ made up of 4 sub-units
- Every subunits contains :-



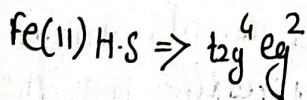


(repulsion between dx^2-y^2 orbital of metal and e-density on Nitrogen)

\Rightarrow the electron present in dx^2-y^2 orbital is repelled by lone pair of Nitrogen of porphyrin ring. therefore Fe^{+2} becomes too large to fit in the porphyrin cavity. and it is ^{present} about 40 pm out of the plane.



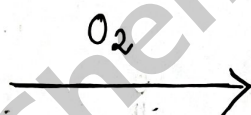
(Square-based pyramidal)
(deoxy-Hb)
{ Fe(II) }
H.S



\Rightarrow paramagnetic

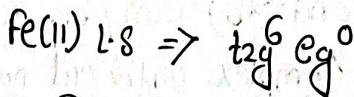
\Rightarrow Fe-N bond is larger than in oxy Hb

$b > a$



Fe(II) L.S
(maximum book - 2-
Fe(II), G_{1210}
फिरे फिरे रंग - 2-
Fe(III) (मभर G_{172})

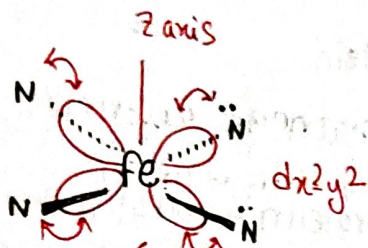
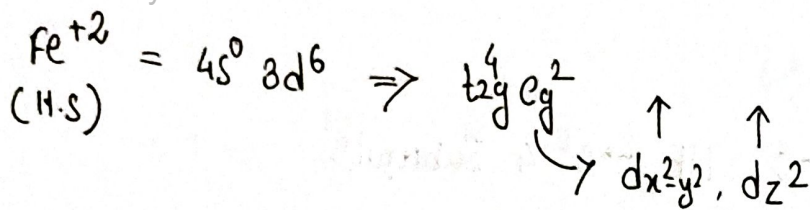
\therefore we consider Fe^{+2} in also oxy Hb (Fe(II) low spin)



\Rightarrow Diamagnetic.

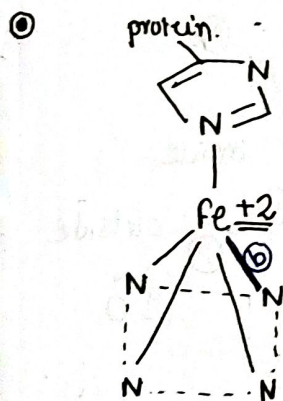
\Rightarrow Fe-N bond is comparatively small.

(In CSIR: Fe(III) high spin

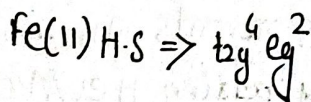


(repulsion between dx^2-y^2 orbital of metal and e-density on Nitrogen)

\Rightarrow the electron present in dx^2-y^2 orbital is repelled by lone pair of Nitrogen of porphyrin ring. therefore Fe^{+2} becomes too large to fit in the porphyrin cavity. and it is ^{present} about 40 pm out of the plane.

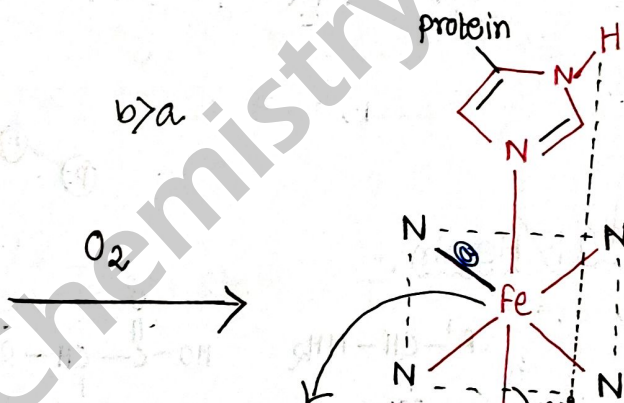


(Square-based pyramidal)
 (deoxy-Hb)
 $\{ Fe(II) \}$
 H.S



\Rightarrow paramagnetic

\Rightarrow Fe-N bond is larger than in oxyHb

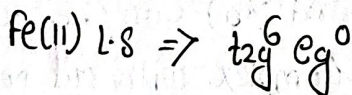


$Fe(II) L.S$
 (maximum, book - 2)
 $Fe(II), G_{1210}$
 $Fe(III) (M.B.U.F. G_{1212})$

octahedral.
 (oxy-Hb)

form of Super oxide
 $Fe^{II} (L.S)$
 Nadeem sir

\therefore we consider Fe^{+2} in also oxy Hb ($Fe(II) L.S$)



\Rightarrow Diamagnetic.

\Rightarrow Fe-N bond is comparatively small.

(In CSIR: $Fe(III)$ high spin

Composition :-

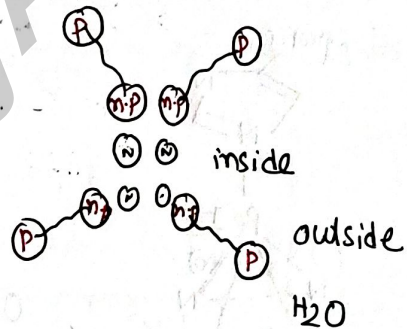
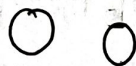
⇒ Hb has 4 Subunits
 Heme + globin ⇒ protein

one Heme with its protein chain is Subunit.

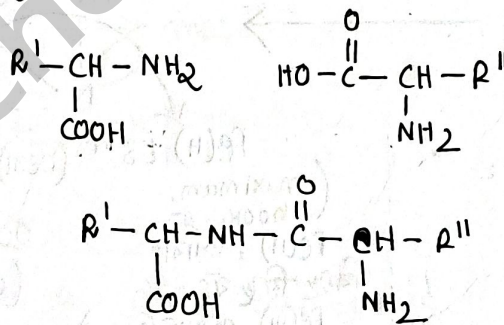
2 Subunit forms α protein → 141 amino acid

2 Subunit forms β protein → 146 A.A.

Imp ⇒ Each protein has polar and non polar groups.
 polar groups of each protein are on outside of the structure leaving a hydrophobic interior. therefore Heme gr is held in water resistance protein pocket.

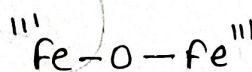


Hematin :-/ Hemin :-



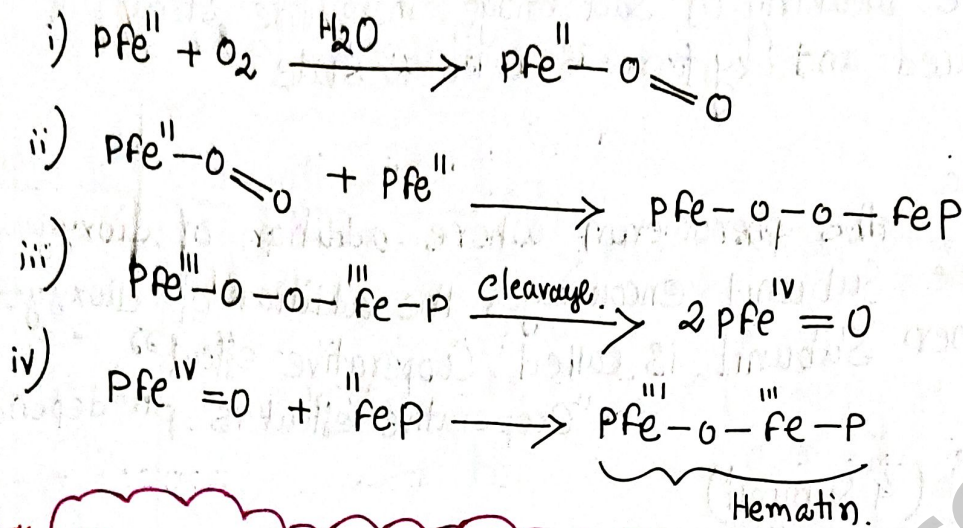
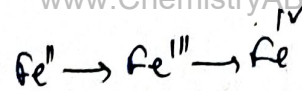
the polypeptide chain (which prevents the oxidation of Hb and Mb) can be removed. by adding HCl/Acetone the Fe-PR Complex. without polypeptide chain is oxidised to Fe³⁺ by oxygen molecule in aqueous solution. and is converted into stable μ-oxo dimer which is called Hematin.

Stable μ-oxo-dimer (Hematin)



↓
 unable to transport O₂

Mechanism :-



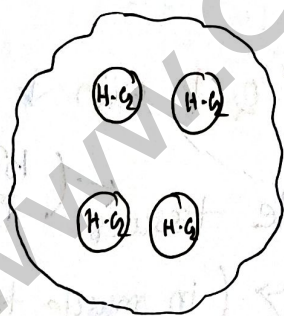
** Hb is a tetramer of Myoglobin.

Myoglobin :-

- ⇒ has only 1 heme group per molecule.
- ⇒ Stores O_2 in muscle tissues.
- ⇒ binds to O_2 more strongly than Hb

Cooperative effect :-

* Deoxy-Hb (Tensed state \equiv T-state)



⇒ protein chain.

⇒ the four subunit of Hb are linked with each other through salt bridge between four polypeptide chain. These bridges are formed by electrostatic interaction between NH_3^+ and COO^- group present on all four polypeptide chain. These salt bridges introduce strain into the molecule. therefore called T state.

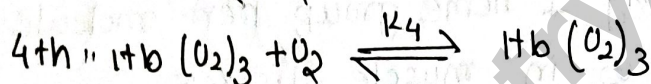
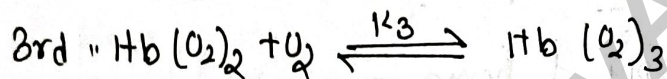
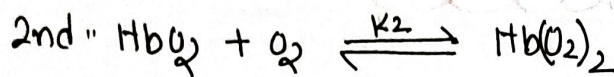
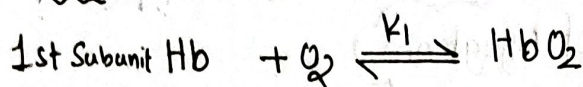
* oxy-Hb (Relaxed state \equiv R-state)

the movement of Fe atom and imidazole ring towards the Porphine plane results in

the breaking of salt bridge. therefore strain is reduced. and oxy form is called R state.

66 the phenomenon where addition of dioxygen to one subunit encourages the addition of dioxygen to other subunit is called Cooperative effect.
"Cooperative effect is pH dependt".

Hb (4 Subunit)

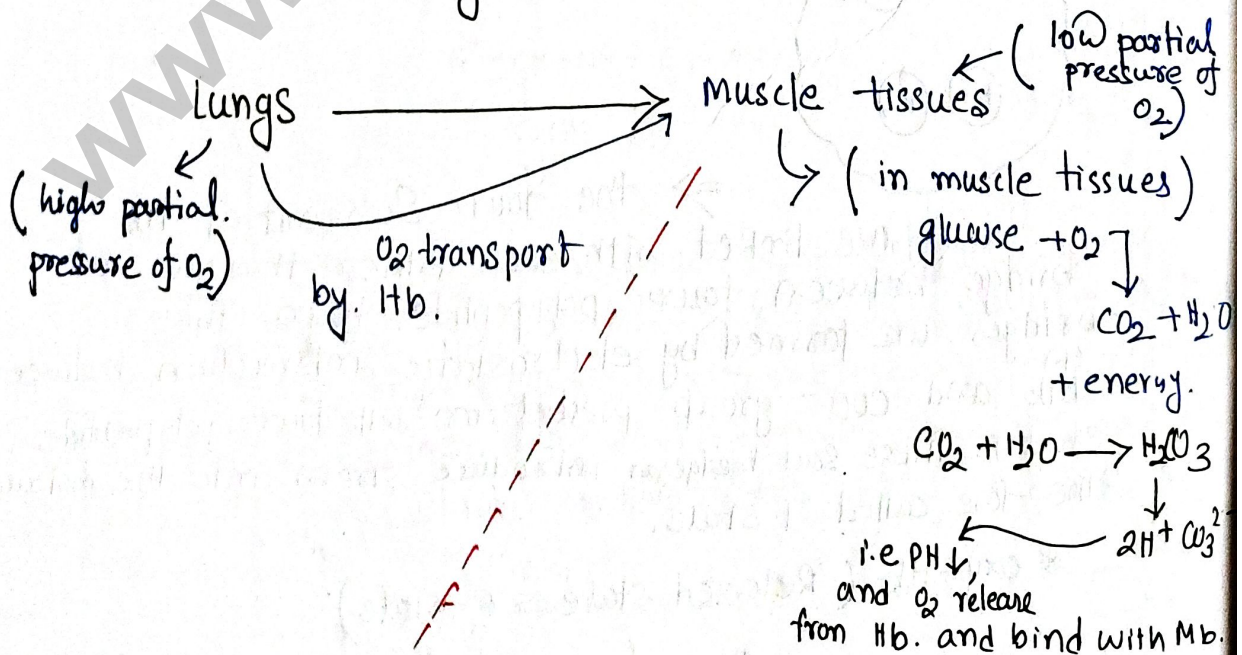


$$\therefore K_4 > K_3 > K_2 > K_1$$

↳ Binding of first O₂ is most difficult.

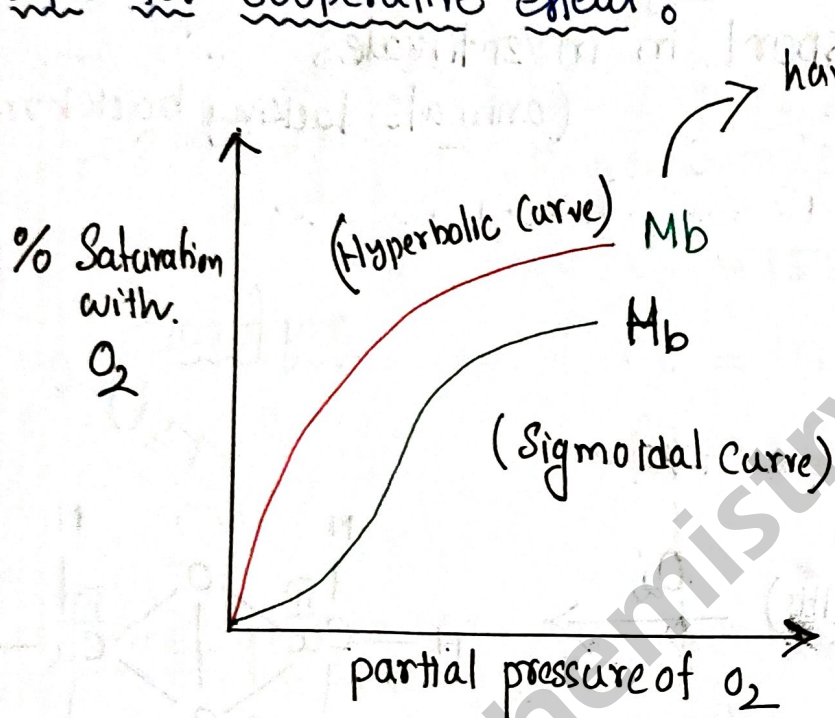
Bohr effect

The affinity of Hb towards O₂ ↓ with ↓ in pH.



Hb : pH dependt
Mb : pH independt

graph for cooperative effect :-



have no. Cooperative effect.
but only have only one unit.

(Affinity of Hb for O_2 \uparrow with \uparrow in partial pressure of O_2)

Hb : high affinity for O_2 at high partial pressure.

Mb : high affinity for O_2 at low partial pressure.

Poisoning effect to CO and CN^- :-

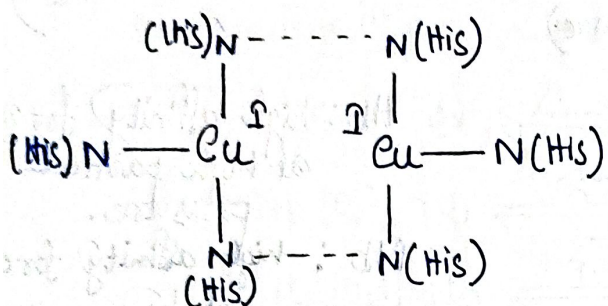
O_2 is neither soft nor strong ligand. therefore it can not coordinate to fairly soft Fe^{+2} ion. if strong like CO, CN^- ligands are present. therefore CO binds 200 times stronger than O_2 and hence stop the transport the oxygen.

(Asphyxia) \rightarrow Condⁿ where body is deprived of O_2 .

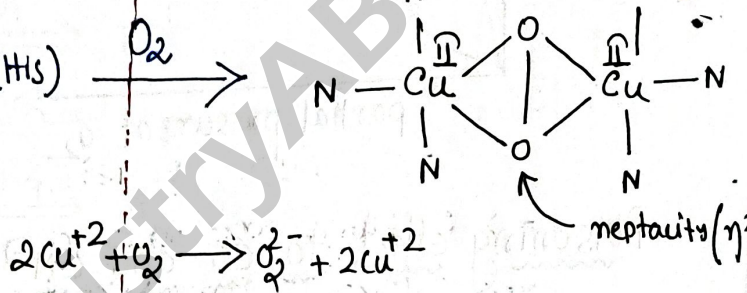
Hemocyanin: (means blue blood)

- ⇒ Non Heme protein.
- ⇒ Copper Containing protein.
- ⇒ O₂ transport in invertebrates (animals lacking backbone)
- ⇒

deoxy form



oxy form



- * Cu --- Cu ⇒ 354 nm
- * Colourless
Cu⁺: 3d¹⁰ → no transition
- * Diamagnetic, ESR inactive

- * Cu --- Cu ⇒ 360 nm.
- * Blue colour, due to LMCT
O₂²⁻ → Cu⁺²
- * diamagnetic:

Cu ⁺²	Cu ⁺²
↑ ↑ ↑ ↑ ↑	↑ ↑ ↑ ↑ ↑

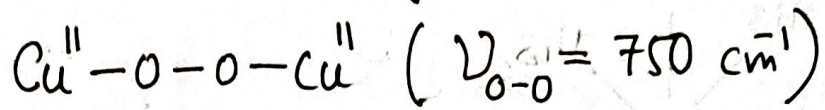
↓
antiferromagnetic Coupling
ESR inactive.

- O²⁻ ⇒ oxide.
- O₂⁻ ⇒ Super oxide
- O₂²⁻ ⇒ peroxide.

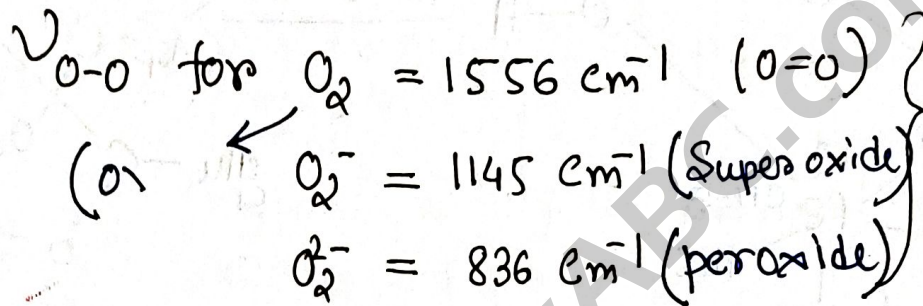
Cu⁺ ⇒ Cuprous
Cu⁺² ⇒ Cupric.

Spectral features :-

Raman Spectra shows Symmetric binding of O_2



\Rightarrow this value rules out the possibility of mononuclear peroxo Complex.



Hemerythrin :-

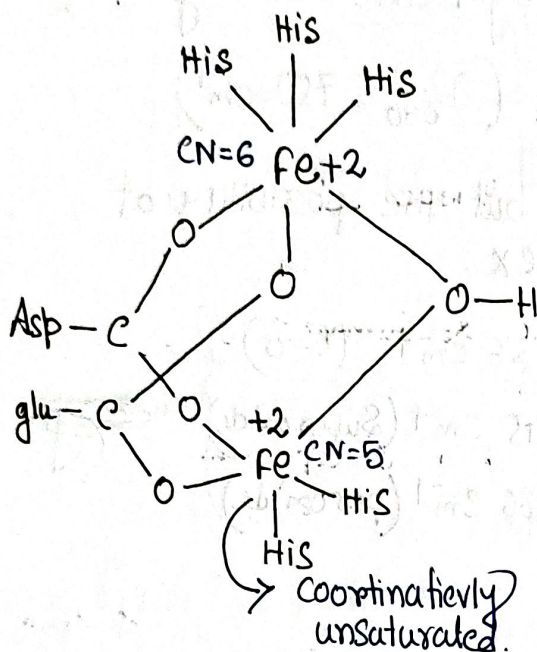
- \Rightarrow non-Heme protein
- \Rightarrow storage and transport of oxygen.
- \Rightarrow found in invertebrates.
- \Rightarrow Contains 8 Subunits.
- \Rightarrow each Subunit Contains 113 amino acid and $2Fe^{+2}$
- \Rightarrow it binds O_2 reversibly.
- \Rightarrow in muscle tissues, fewer Subunits (less than 8)
- \Rightarrow No cooperativity.

Structure :-

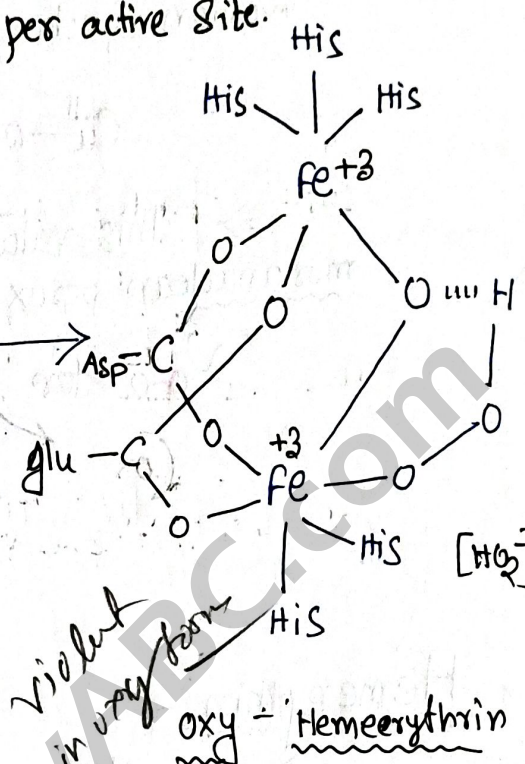
850 cm^{-1} \leftarrow $O-O$ in Hemerythrin.

Structure:-

there are two iron centers per active site.



deoxy-Hemoglobin
Hemeerythrin



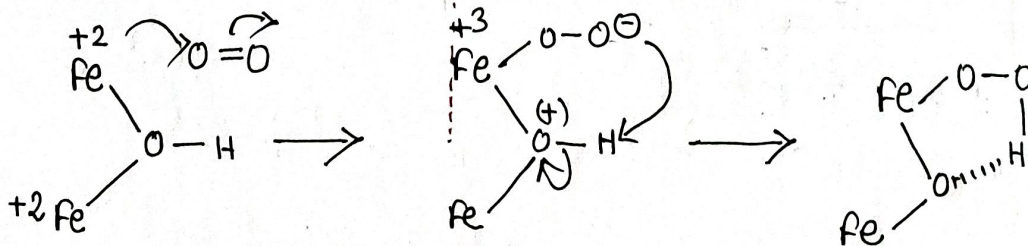
Violet in dry form
oxy-Hemerythrin



- * 2 Fe⁺²
- * High Spin Complex
- * 1 Fe has 5 C.N another has 6 C.N
- * Colourless

- * 2 Fe⁺³
- * Low Spin Complex.
- * Both Fe have CN=6
- * Coloured due to LMCT (violet)

Mechanism :-



⇒ Mosbauer Spectroscopy reveals that both the Fe⁺³ in the oxy form are present in different environment.

Vitamin B₁₂

deficiency = anemia.

⇒ diol. dehydrase reⁿ.

⇒ 1,2 Carbon shift in organic substrate.

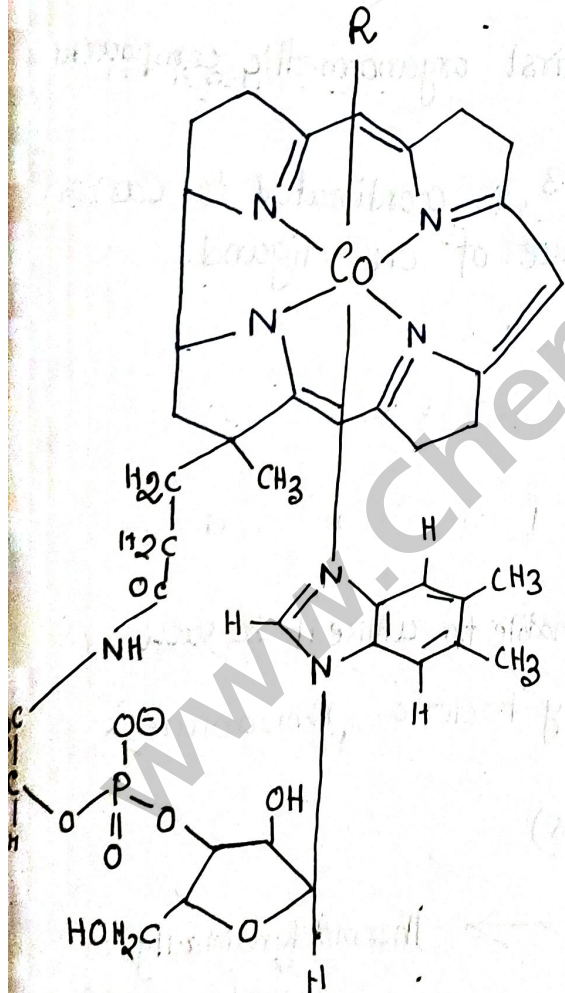
⇒ Conversion of ribonucleotide to deoxyribonucleotide.

Co⁺³ is coordinated to 4 N atoms of Corrin ring. (Corrin ring has 1 less =CH bridge between two pyrrol rings)

∴ there fore Corrin ring less symmetric and less unaturated than porphyrin ring.

∴ 5th Coordination Site is occupied by N atom of imidazole ring.

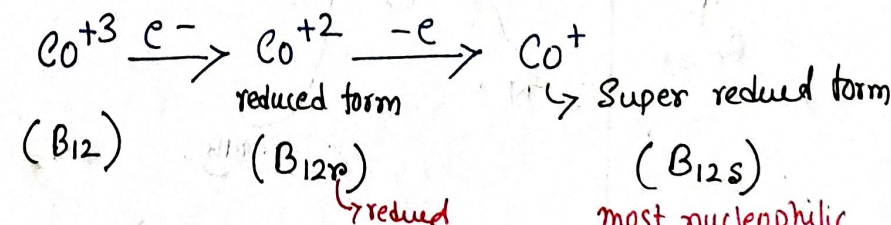
methylcobalamin
org. compound → ~~cyano~~ → cyanocobalamin
Coenzyme B₁₂



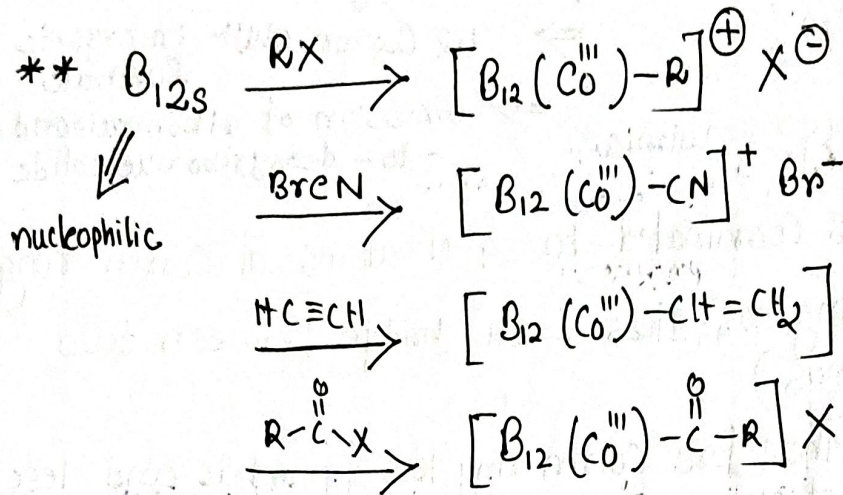
- ⇒ if R = CN[⊖] ⇒ vit B-12
- ⇒ if R = CH₃ ⇒ methylcobalamin.
- ⇒ if CN = 5 (i.e R is absent, the Cobalamin)
- ⇒ if R = 5'-deoxy adenosyl (adenocyl Cobalamin)

⇓
Coenzym B₁₂

- * geometry: octahedral
- * low spin ⇒ d⁶ ⇒ t_{2g}⁶ e_g⁰
- * Metal: Co⁺³
- * Diamagnetic.
- * ESR inactive.
- * Red in colour.
- * (π → π* transition)



most nucleophilic and easily undergo alkylation by oxidative addition.



\Rightarrow the reaction of ATP with Vit. B_{12} generates direct Co-C bond between Adenosyl and Cobalt. the resulting molecule is called vit B_{12} Coenzyme.

\Rightarrow Coenzyme B_{12} is the first organometallic compound in living system.

\Rightarrow In Coenzyme B_{12} Co^{+3} is coordinated to Carbon of adenosyl ligand in place of CN^{\ominus} ligand.

Nitrogen fixation

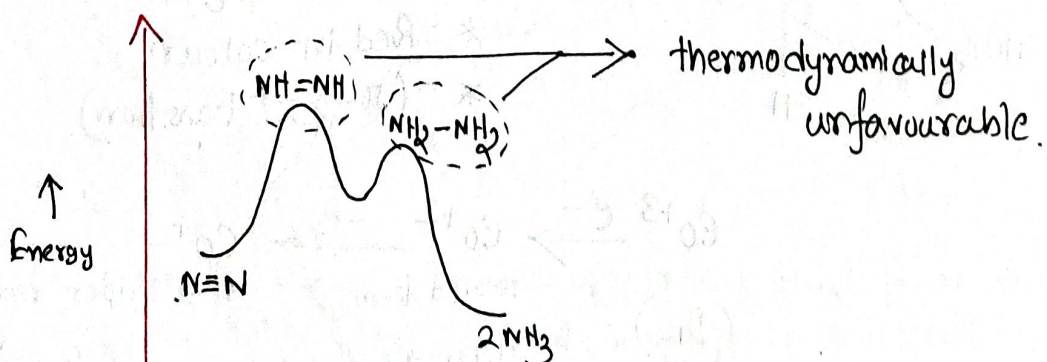


elemental form

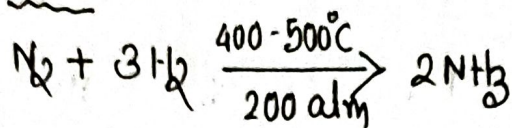
\hookrightarrow all forms of life are unable to utilise it as such.

\rightarrow Biological process (By bacteria, Rhizobium)

\rightarrow Industrial process
(Haber's process)



Industrial process:-



expensive.

Biological enzyme :

→ Nitrogenase enzyme. is required to Convert N_2 to NH_3 .

Nitrogenase enzyme generally three types.

→ Vanadium N.E.

→ Iron. N.E

→ Mo. N.E ⇒ most effective.

Nitrogenase enzyme are Composed of two metallo-proteins.

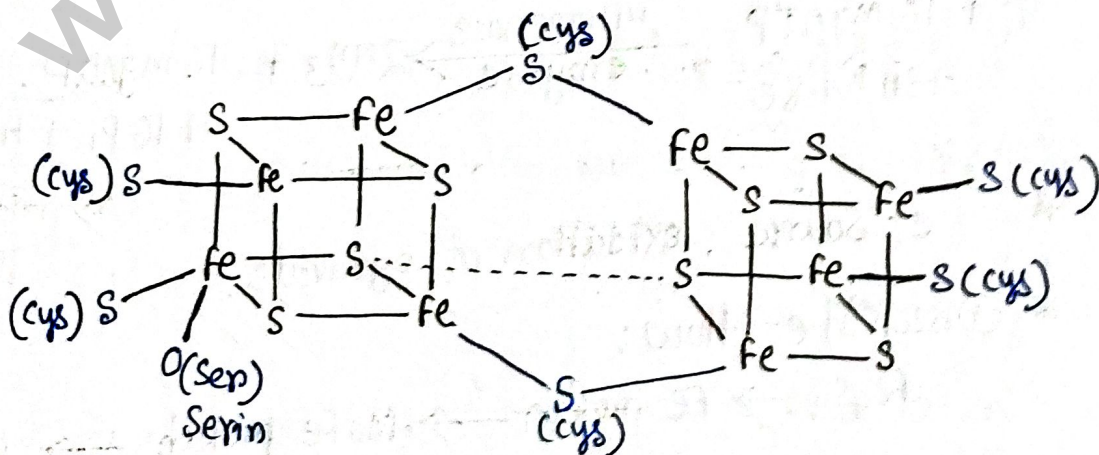
i) Fe protein.

ii) MFe protein as cofactors } *remu.*
(M = Mo, V, Fe)

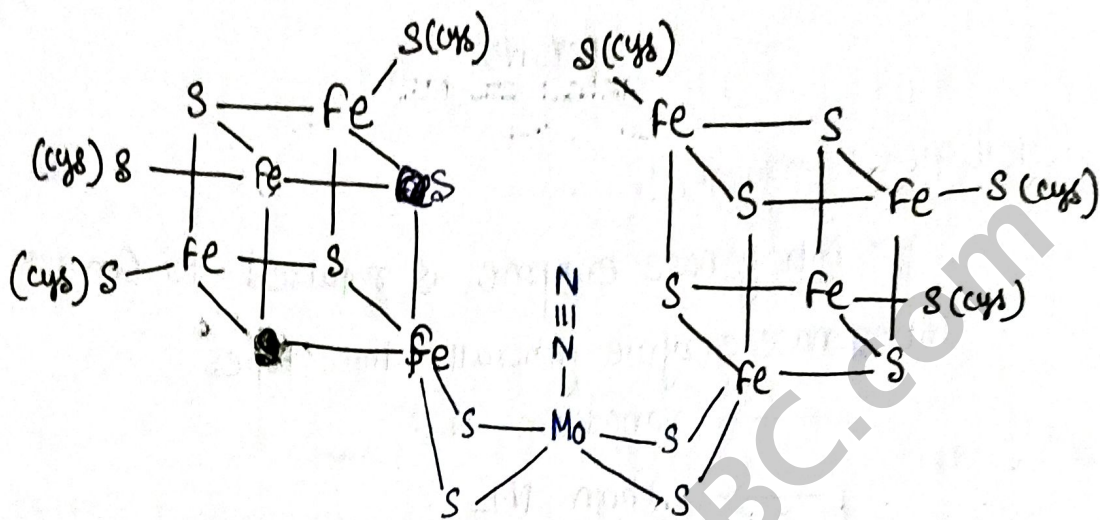
Mo ⇒ active site of nitrogenase.

Mo Nitrogenase enzyme :-

① Fe protein :



② Mofe protein :

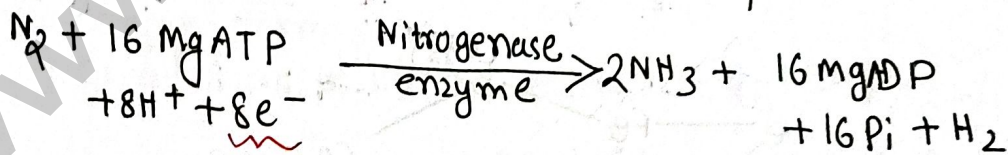


∴ $\angle N \equiv N$ (Mofe protein) < $\angle N \equiv N$ (free)
 ↳ due to back bonding.
 $\{ Mo \rightarrow \pi^*(N_2) \}$



Actual biological rean \Rightarrow requires $8e^-$

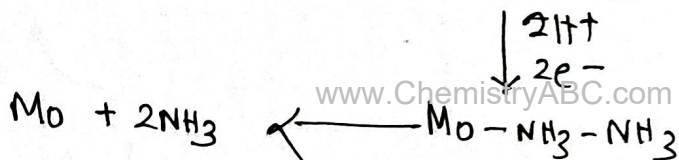
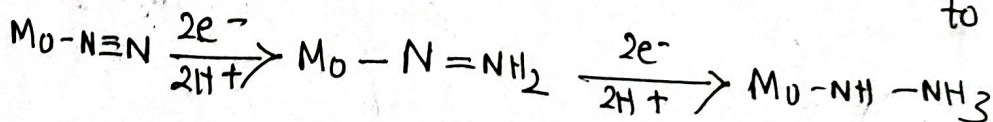
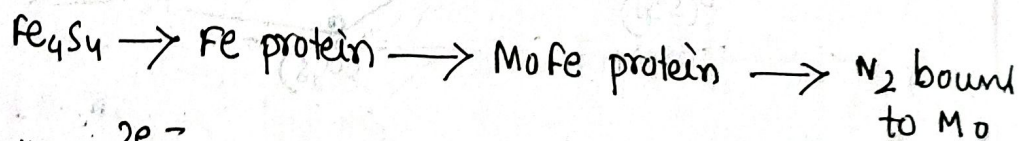
∴ 1 mol of H_2 is produced.



* e- source : oxidation of pyruvate.

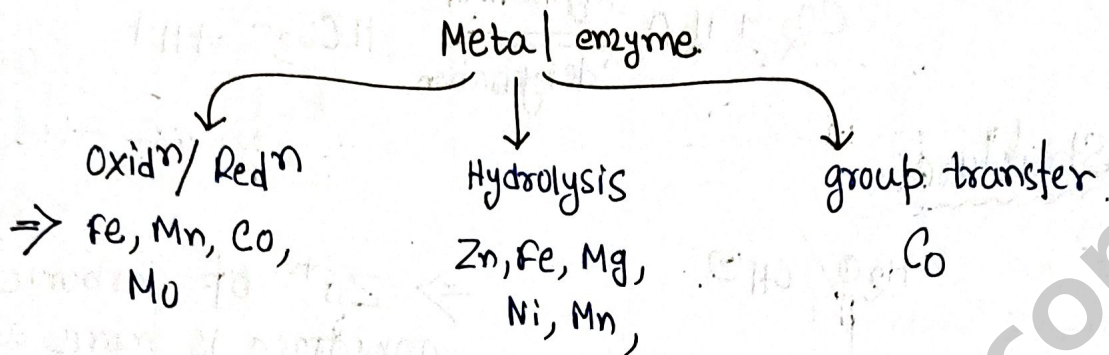
↳ inorganic phosphate.

* Direction of e- flow :



Metalloenzyme :-

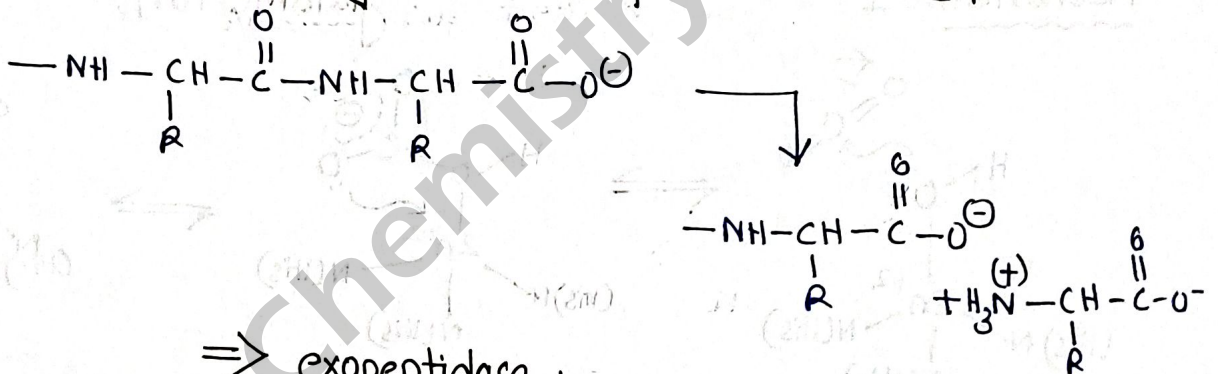
Metalloenzyme is an enzymatic protein in which a metal ion is embedded in the cavity of the enzyme.



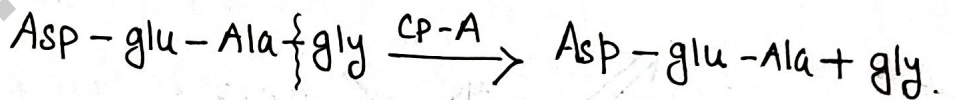
Zn metallo enzyme :-

1) Carboxy peptidase :-

=> Hydration of peptide bond.



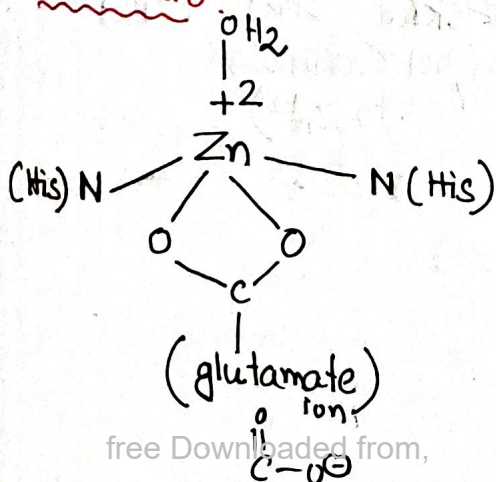
=> exopeptidase :-



=> cleaves from c-terminal.

=> cleaves one amino acid at one time.

Structure

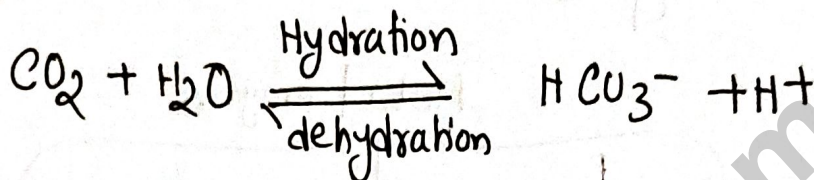


CN: 5

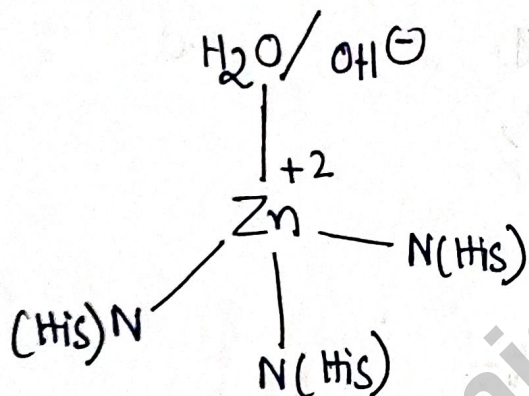
=> water attached to Zn⁺² is the nucleophile of the reaction.

2) Carbonic Anhydrase:

Catalyses the reversible hydration of CO_2

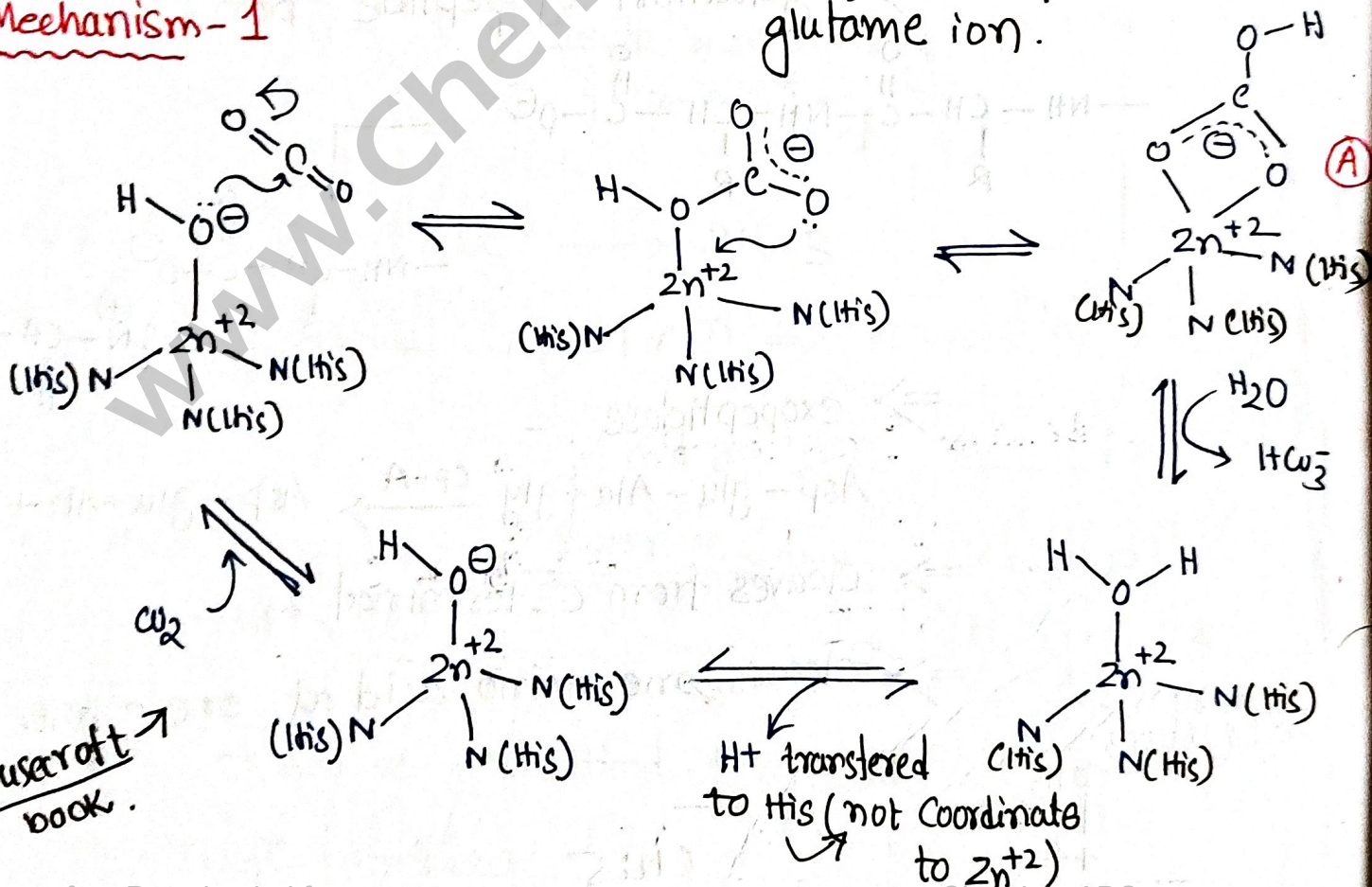


Structure:



$\Rightarrow \text{Zn}^{+2}$ of Carbonic anhydrase is more acidic than Carboxy peptidase. due to presence of a less basic or neutral nitrogen (Histidine residue) in comparison to glutamate ion.

Mechanism-1

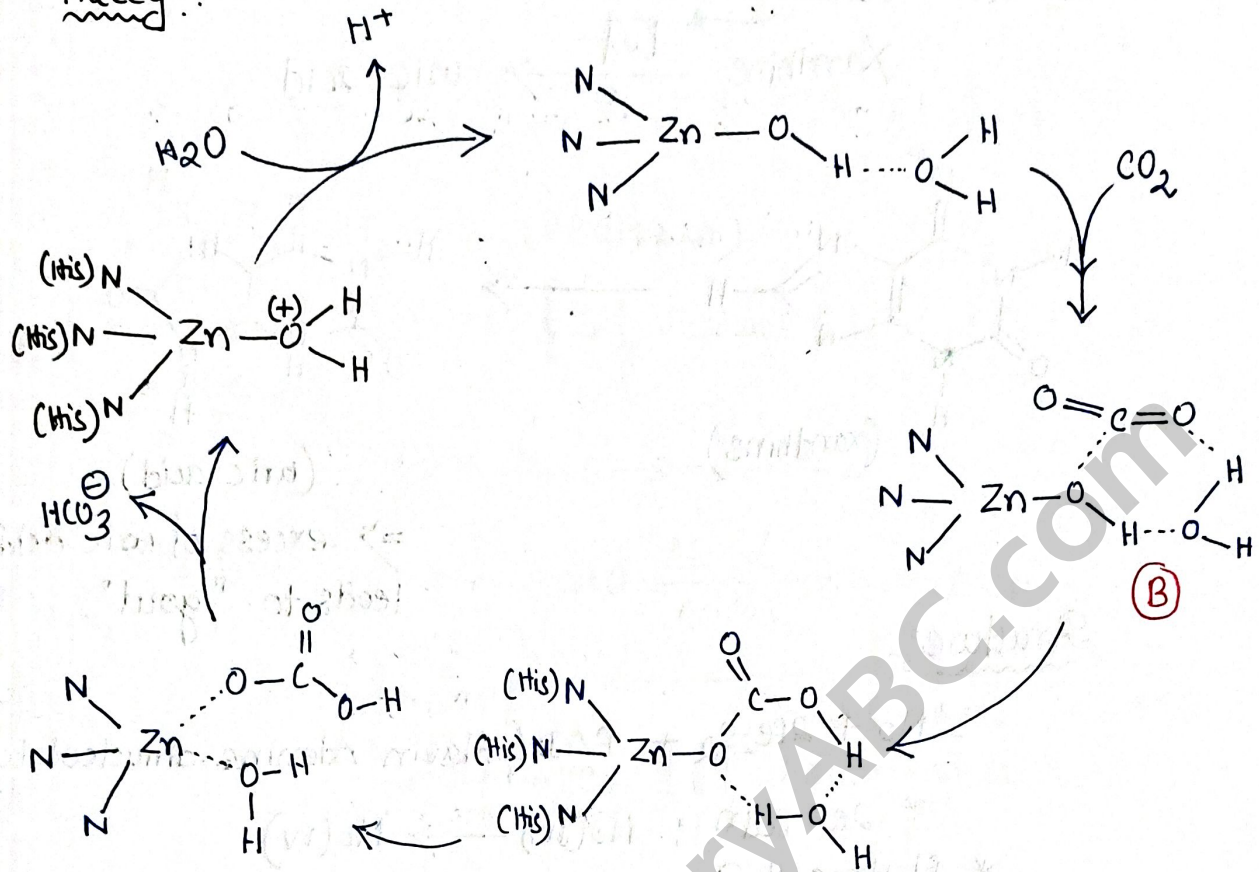


Houserott book.

Mechanism - 2

most useful mechn then

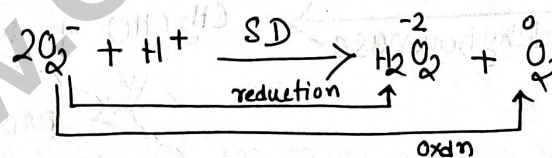
Huey:



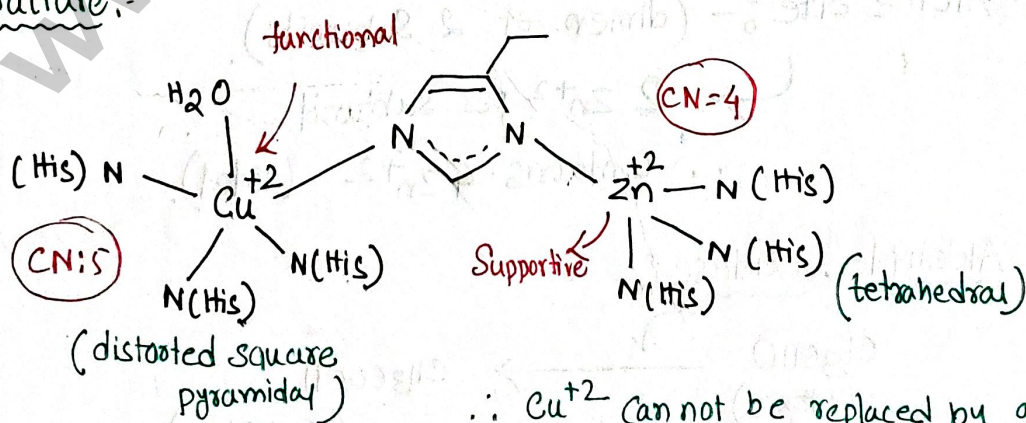
⇒ Difference in Str. (A) and Str. (B)

3. Superoxide Dismutase :-

Dismutase : disproportionation rexn



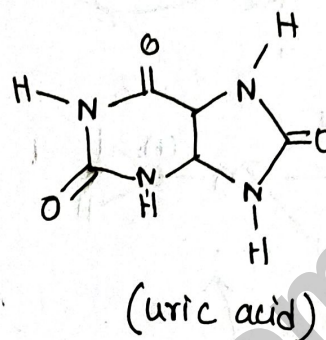
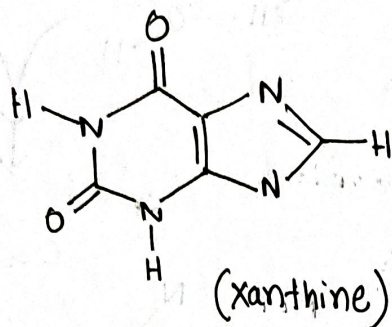
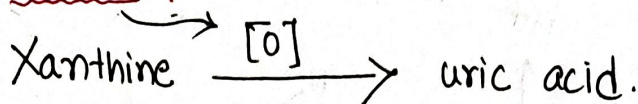
Structure:



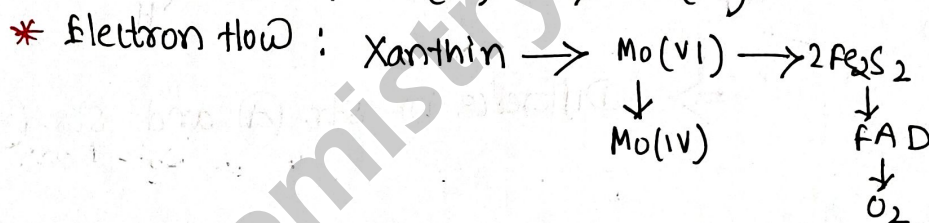
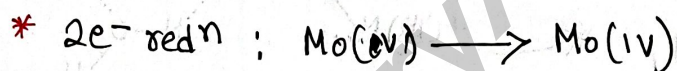
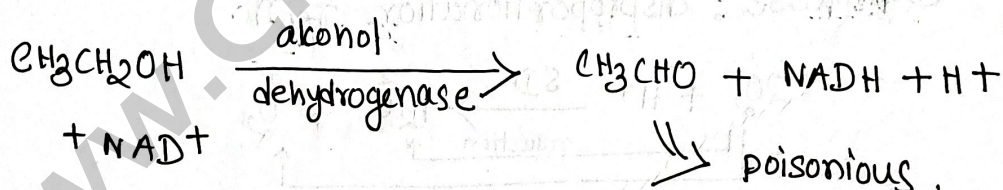
∴ Cu²⁺ cannot be replaced by another metal of +2 o.s. bcz it is function.

but Zn²⁺ Can be replaced by other divalent metal ion

ex: Cd²⁺/Co²⁺ (with retention of activity)

4. Xanthine Oxidase :-

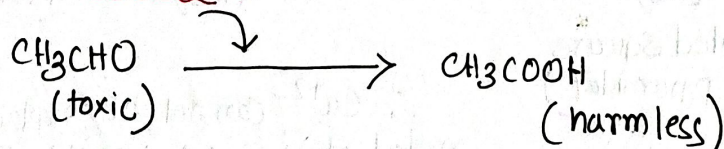
⇒ excess of uric acid leads to "gout".

Structure :-5. Alcohol Dehydrogenase :-

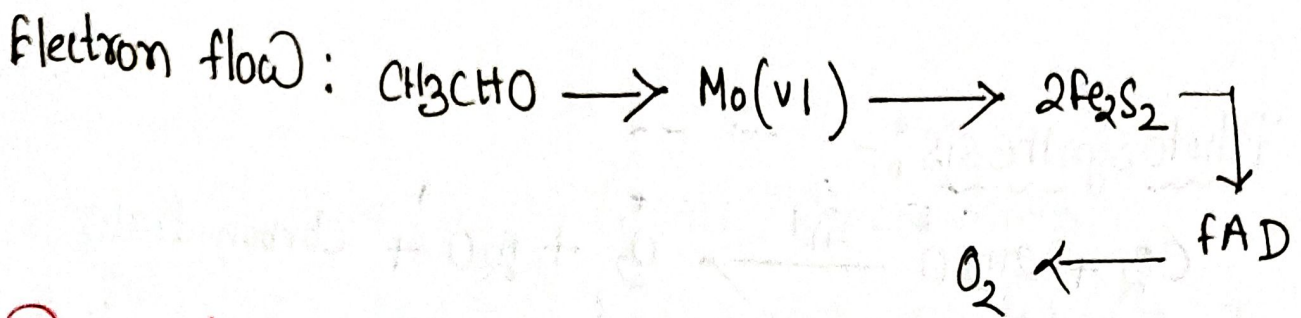
Active Site :- (dimer of 2 subunits).

↳ 2 Zn^{+2} per subunit.

∴ Contains 4 Zn^{+2} (total).

6. Aldehyde Oxidase :-

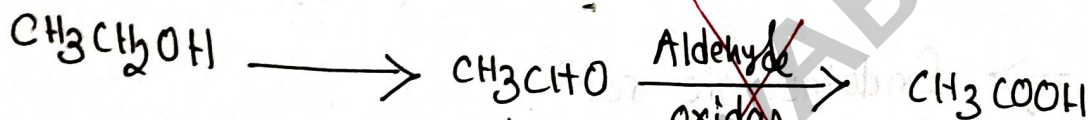
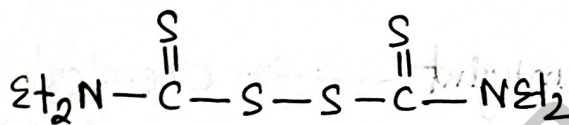
Active site : $1\text{Mo} + 2\text{Fe}_2\text{S}_2 + \text{FAD}$



Drug Antabuse :- (Disulfiram)

=> used for treat alcoholism.

Structure :-



Smelly

∴ discourage alcoholism.

↳ this process will not occur in presence of Disulfiram.

Iron storage and transport :-

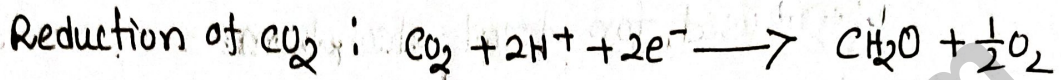
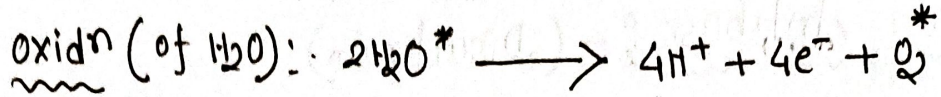
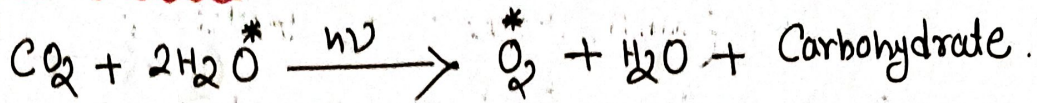
Transferrin :- protein that binds to Fe^{+3} (and not to Fe^{+2})

ferritin :- binds to iron in Fe^{+2} oxidation state.
(storage) ↳ storage of iron (Fe^{+2})

Siderophores :-

Fe^{+3} transport in most of the microorganism.

Photosynthesis :-



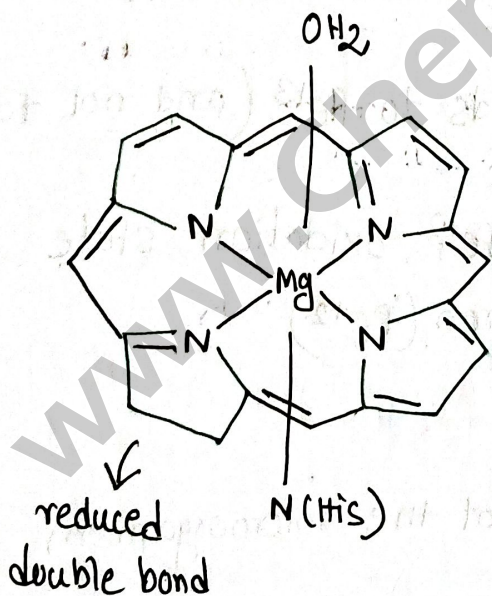
Sunlight \longrightarrow Chemical energy (ATP)

\Rightarrow Endothermic reⁿ.

Chlorophyll: (light harvesting system)

\longrightarrow Mg⁺²

\longrightarrow chlorin ring.



total double bonds = 10

A porphyrin ring with one double bond reduced is called "chlorin".

porphyrin Hb	corrin vit B-12	chlorin. chlorophyll.
-----------------	--------------------	--------------------------

Conjugation : porphyrin > chlorin > corrin

Double bonds : 11 > 10 > 6

Blue Copper protein :-

e.g: plastocyanin, Azurin, Ceruloplasmin

The Copper centre of BCP can be divided into 3 main type.

① Type-1: Cu is in trigonal planer or flat trigonal pyramidal.

⇒ 2N of Histidine, 1S of Cys ligand.

⇒ used for e⁻ transport.

⇒ Colour: Intensed blue colour due to LMCT (cys(S) → Cu²⁺)

⇒ FSR active.

② Type-2: Cu is in Square planer (or pyramidal) coordination environment.

⇒ 3N of histidines and additional O or N functional amino acids.

⇒ are functional units in oxidase, reductase, and dismutase.

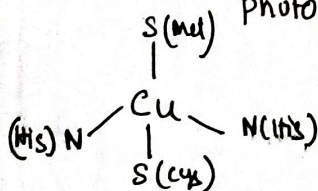
③ Type-3 :- O₂ transport.
Hemocyanine.

plastocyanin :-

⇒ found in green plants

⇒ It contains 1 Cu per molecule

⇒ involved in e⁻ transfer in photosynthesis.

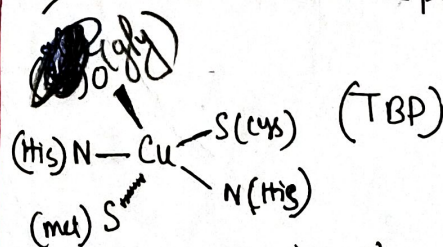


distorted
td (in
both reduced or
oxidised form)

Azurin

⇒ found in bacteria.

⇒ It contains 1 Cu per molecule.



⇒ in plane bonds are shorter than above or below the plane bonds.

Metal Complexes in medicine :-

① cis-platine (Anti cancer drug)

$\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (inhibits rapid division of tumor cells)

Pt binds to N-7 atoms of a pair of adjacent guanine bases of a fast growing tumor.

\therefore DNA structure distorted \therefore stops cell division

② Wilson Disease:

\Rightarrow excess of Cu in body, due to low level of Copper storage protein i.e ceruloplasmin.

Drug: D-pancillamine.

③ Arthritis:

\Rightarrow treatment: Complexes of Au(I)

④ Hypercalcemia:-

rapid loss of Calcium from the bones of cancer patients.

\Rightarrow GaNO_3

⑤ MRI (Magnetic resonance imaging)

ions used: Gd(III) , Fe(III) , Mn(II)

28/1/2021

The Sodium - Potassium Pump and Na⁺ - K⁺ ATP-ASE :-

higher Conc K⁺ inside cell
higher ~~lower~~ Conc Na⁺ inside cell
outside

K⁺ ion required for glucose metabolism.
protein biosynthesis
activation of some enzyme.

∴ The enzyme contains tetramer (α₂β₂)

Mg²⁺; Catalysis in ATP hydrolysis and
structure forming effect.

3Na⁺ : inside cell → outside cell.

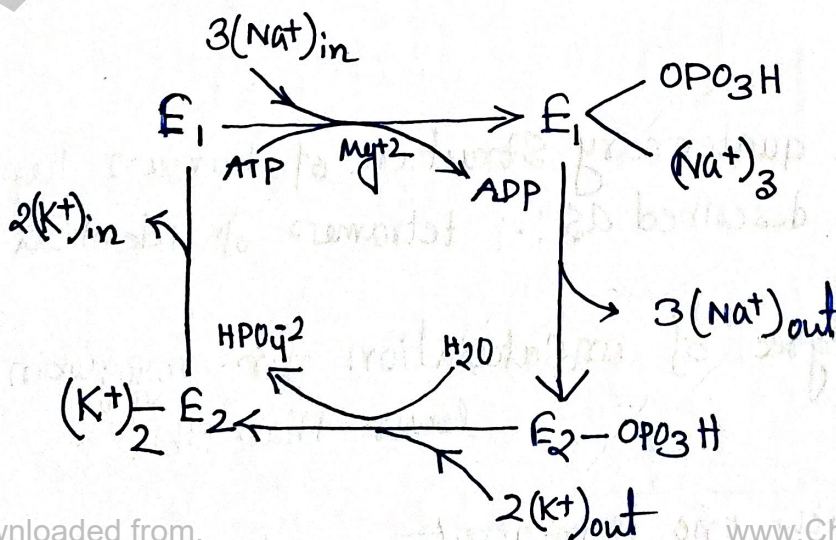
2K⁺ : outside → inside cell.

Conformation change: E₁ → E₂

Reversion:

E₁ ∴ stabilised by phosphorylation.

E₂ ∴ stabilised by dephosphorylation.



protein	O.S	function	Heme(H) Non Heme(NH)
Hemoglobin	Fe ^{II}	oxygen transport	H
myoglobin	Fe ^{II}	oxygen transport	H
cytochromes	Fe ^{II}	electron transfer	H
ferredoxin	Fe ^{II} , Fe ^{III}	Electron transfer	NH
Rubredoxin	Fe ^{III}	Electron transfer	NH
ferritin	Fe ^{II}	storage of iron	NH
transferrin	Fe ^{III}	Scavenging of iron	NH
Hemerythrin	Fe ^{II}	oxygen transport	NH
Fe-Mo protein	F	Nitrogen function of bacteria	NH
Catalase	Fe ^{III}	decomposition of H_2O_2	H
Peroxidase	Fe ^{III}	decomposition of H_2O_2	H
iron transport			
Siderophores			

Co : (Coenzyme B₁₂) ⇒ methylation of organic compound.

Cu : (Amine oxidase, Ceruloplasmin, Hemocyanin) ⇒ oxidation of amine to aldehyde.
 ↓
 oxygen carrier
 transport of Fe from ferritin to transferrin, Cu storage and transport.

Mn : (Arginase) : Electron transfer.

Mg, Mn : (Aminopeptidase) : Catalyzes the cleavage of amino acid.

Cu, Zn, Mo (Superoxide dismutase) ⇒ Dismutation of O₂⁻ into O₂ and H₂O₂

Mg, Cu, Zn ⇒ (Removal of phosphate group from substrate)
 (phosphatases)

Ni : (urease) : Hydrolysis of urea into CO₂ and NH₃.