STUDY MATERIAL

Lecture – 2

Name Of Teacher : Basudev Mandal

Discipline : B.SC (H)

Subject : Chemistry

Semester : VI

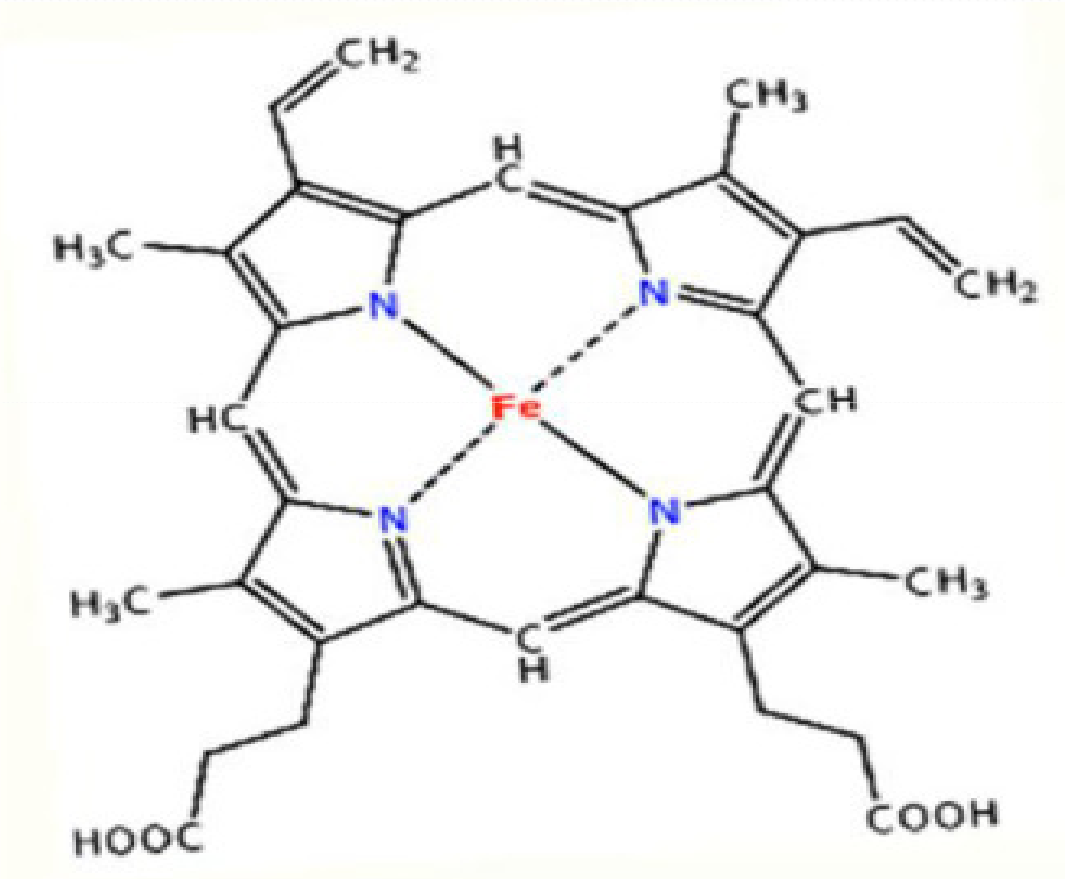
Course Code : CCT13

Topic : DIOXYGEN MANAGEMENT PROTEINS –Hb,Mb,Hr AND Hc

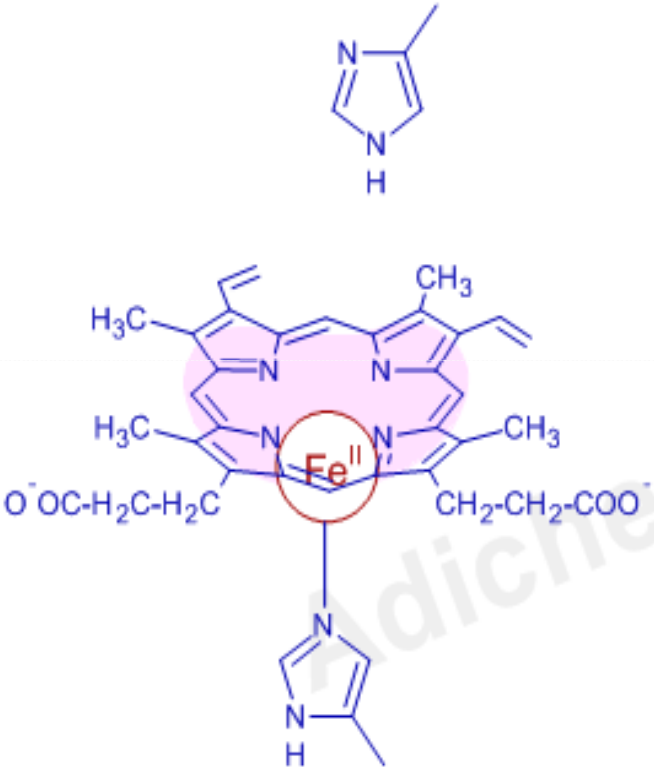
FEATURES OF OXYGEN CARRYING PROTEINS

Property	hemoglobin	hemerythrin	hemocyanin
Metal ion	Fe^{II}	Fe^{II}	Cu^{I}
Number of subunits	4	8	10 – 100
M	65.000	108.000	450.000 – 10 000 000
M:O_2 ratio	1:1	2:1	2:1
Colour (deoxy)	purply-red	colourless	colourless
Colour (oxy)	bright red	violet-pink	blue
Metal bindig site	porphin	protein	protein

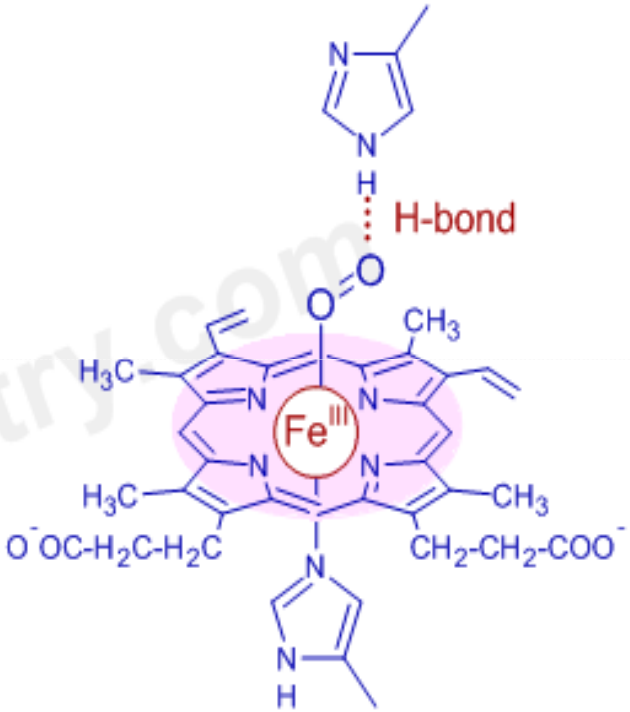
Fe (II) PROTOPORPHYRIN IX (PIX)



STRUCTURE OF HEMOGLOBIN (Hb)

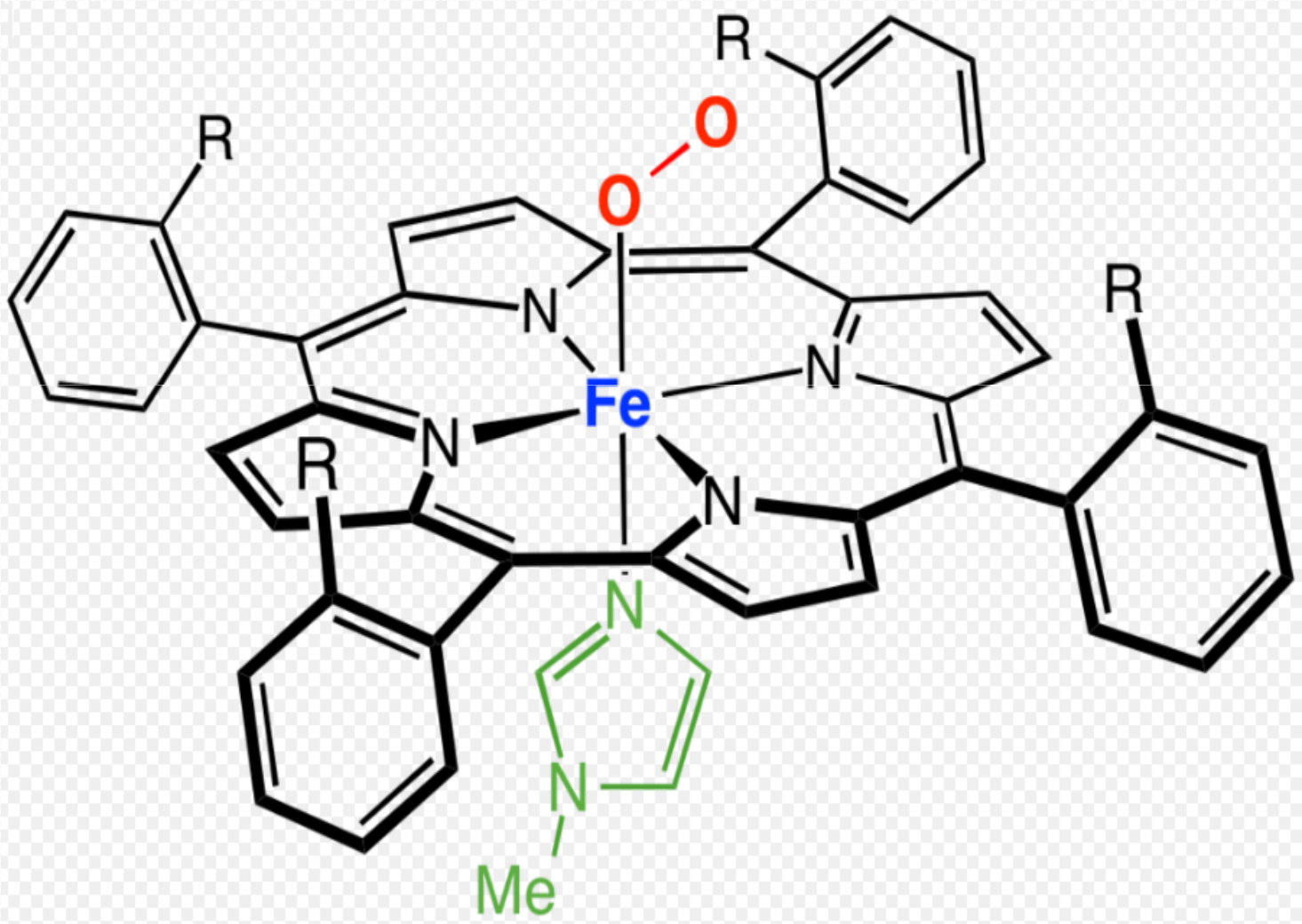


Deoxy Hb
Domed porphyrin
High spin Fe(II) - out of ring



Oxy Hb
Planar porphyrin
Fe ion moves into the ring
Bent O_2

STRUCTURE OF MYOGLOBIN (Mb)



STRUCTURAL FEATURES OF Hb/Mb

- The active sites of both Hb and Mb contain the heme group in which Iron (II) is equatorially coordinated by the pyrole N atoms of Pix.
- In de-oxy Hb/Mb, the fifth position is coordinated by N atoms of a globin chain.
- In de-oxy Hb/Mb, the sixth position is vacant but hydrophobically shielded by globin chain.Therefore only nonpolar neutral molecule such as O_2,CO etc can bind to the sixth position.

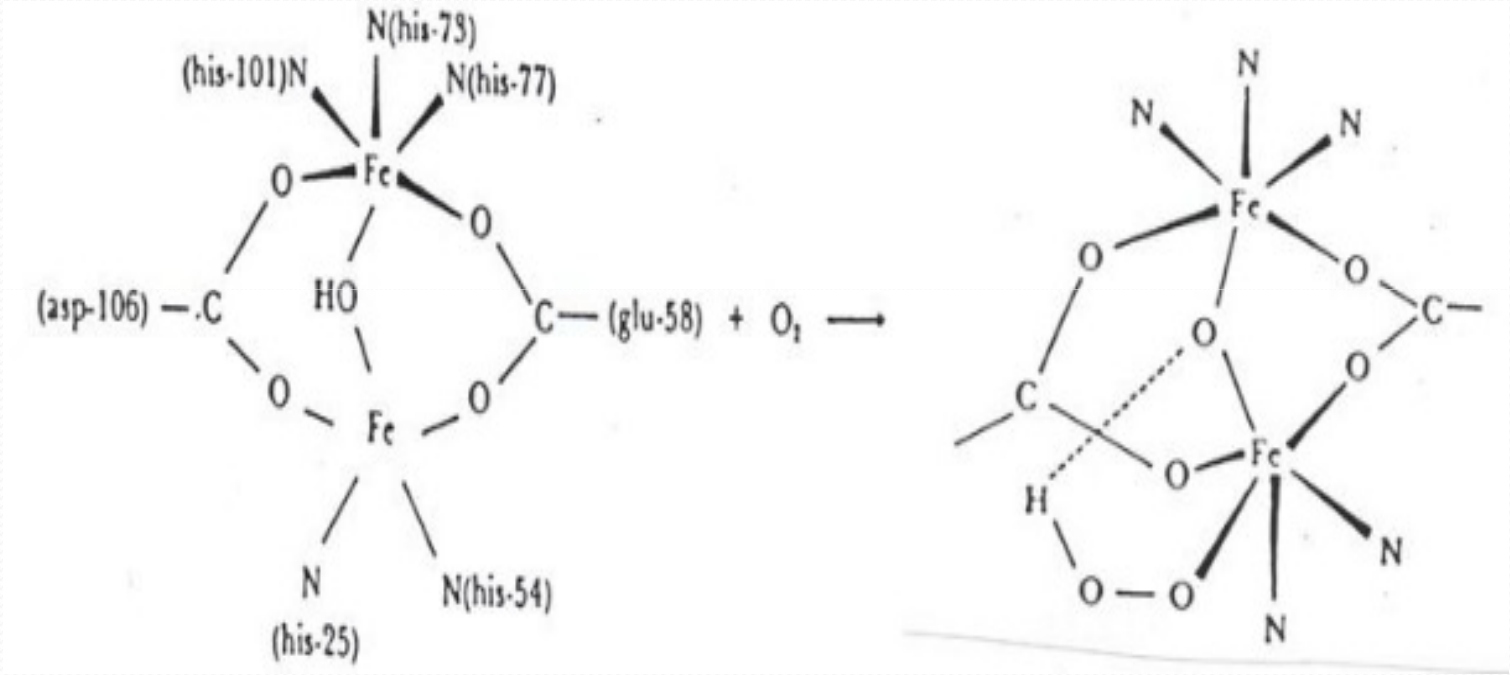
STRUCTURAL FEATURES OF Hb/Mb

- Penta coordinated Fe(II) deoxy Hb/Mb has a square pyramidal geometry and Fe (II) is situated about 0.40 Å out of porphyrin ring plane and upon binding with O2 moves within 0.12 Å of the plane results oxy Hb/Mb with octahedral geometry and High Spin Fe (II) (r=0.92 Å) is converted to Low Spin Fe (III) (0.75 Å) and fits into porphyrin cavity.This brings about a conformational change through the rupture of –COO- ------ NH3+– salt bridge interactions.Then the constrained Hb tetramer relaxes by exposing the sixth position of the remaining heme groups to oxygenation.This phenomenon is known as co-operative interaction.

STRUCTURAL FEATURES OF Hb/Mb

- Hb and Mb are paramagnetic in deoxyform and purple color.
- Hb and Mb are diamagnetic in oxyform due to antiferromagnetic coupling.
- In oxy Hb /Mb,Fe is in Fe(III) L.S and O2 is in superoxide O_2^- state.
- The intense red color of oxyHb/Mb is due to LMCT (superoxide O_2^- to Fe (III) π- π^*) transition.
- Proximal histidine residue binds to the fifth coordination site.
- Distal histidine residue resides in the region of sixth coordination site and stabilises oxy Hb/Mb through H-bonding with superoxide $O_2^{-\cdot}$

STRUCTURE OF HEMERYTHRIN (Hr)



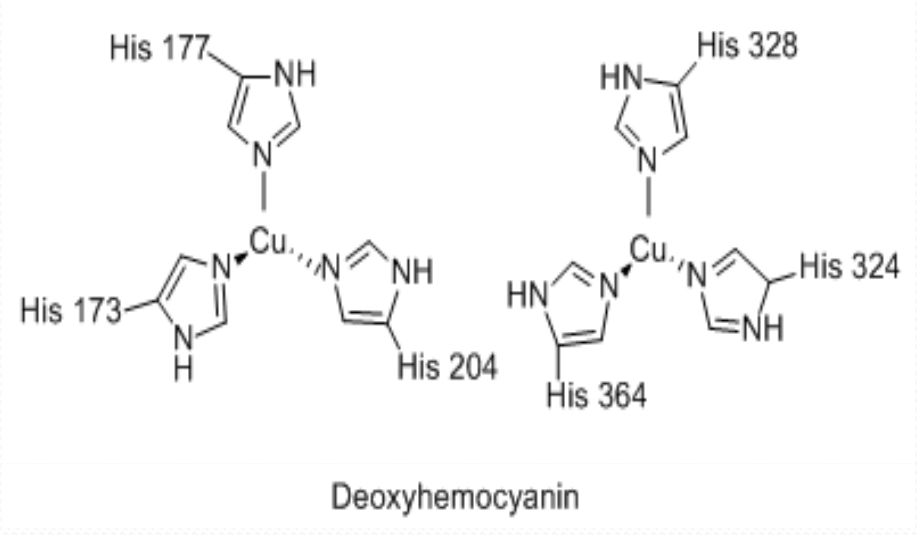
FUNCTION AND STRUCTURAL FEATURES OF HEMERYTHRIN (Hr)

- Hr is a non heme Iron containing O_2 storage protein.
- Two Fe (II) are in H.S
- Two Fe (II) bridged by one –OH group, two oxygen atoms of carboxylate site of glutamate protein and two oxygen atoms of carboxylate site of aspertate protein.
- One Fe (II) is coordinated with two N-histidine .
- Other Fe (II) is coordinated with three N- histidine.
- Two Fe (II) are non-equivalent.

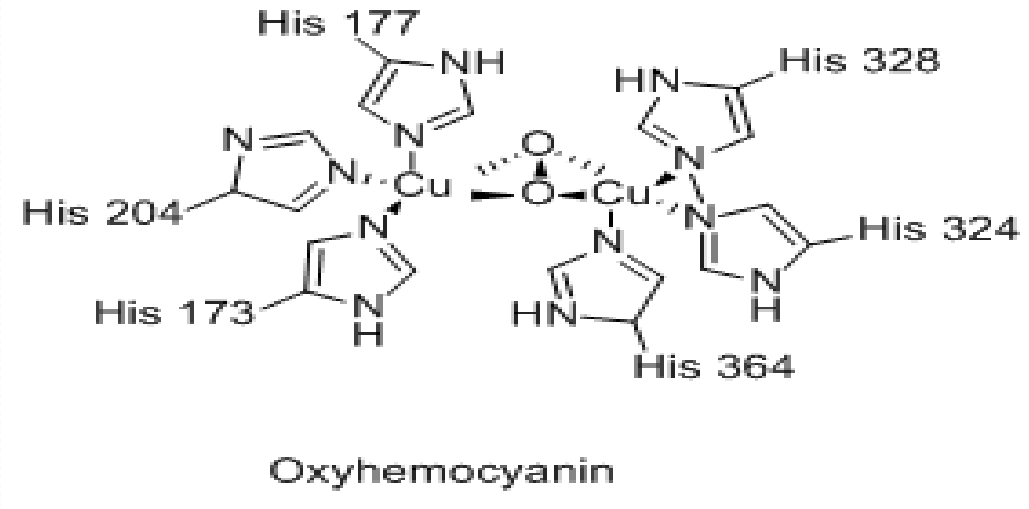
FUNCTION AND STRUCTURAL FEATURES OF HEMERYTHRIN (Hr)

- Each Fe (II) transfers one electron to O_2 giving peroxide O_2^{2-} and itself oxidised to Fe (III).
- Two Fe (III) undergo reduction to two Fe(II) and the μ-OXO group protonated to μ-OH group.
- Deoxy Hr is paramagnetic and colorless.
- Oxy Hr is diamagnetic due to antiferromagnetic coupling and violet-pink color for LMCT transition.

STRUCTURE OF HEMOCYANIN (Hc)



Deoxyhemocyanin



Oxyhemocyanin

FUNCTION AND STRUCTURAL FEATURES OF HEMOCYANIN (Hc)

- Hc is a non heme Copper containing O_2 transport protein.
- Each Fe (II) transfers one electron to O_2 giving peroxide O_2^{2-} and itself oxidised to Fe (III).
- Deoxy Hc is diamagnetic and colorless (as Cu(I) is in d^{10}).
- Oxy Hc is diamagnetic due to antiferromagnetic coupling (although Cu (II) is in d^9 containing one unpaired electron) and blue color due to LMCT (peroxide O_2^{2-} to Cu (II) π- π^*) transition.