Bioinorganic Chemistry

M.Sc. III SEM

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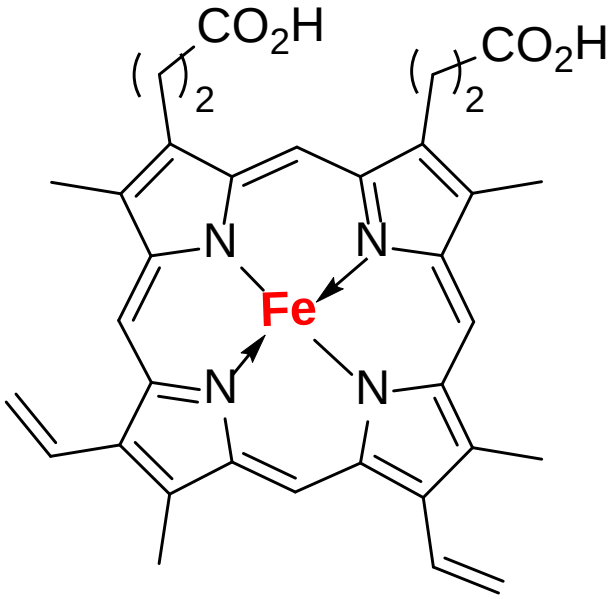
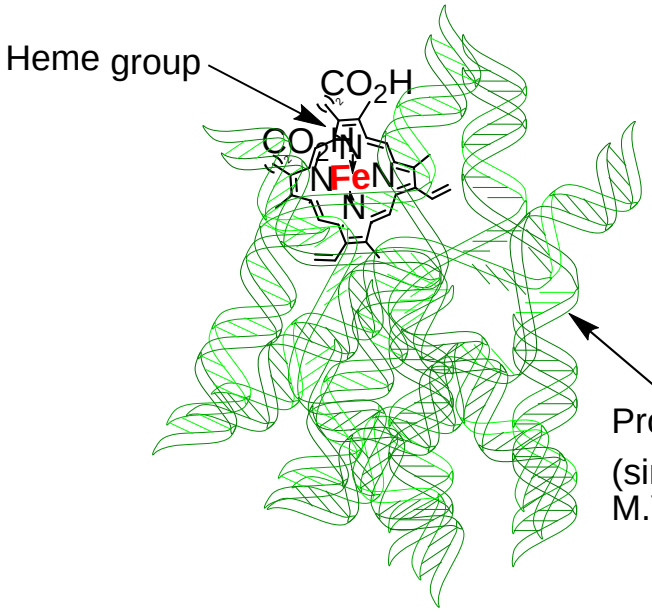
Myoglobin and Hemoglobin

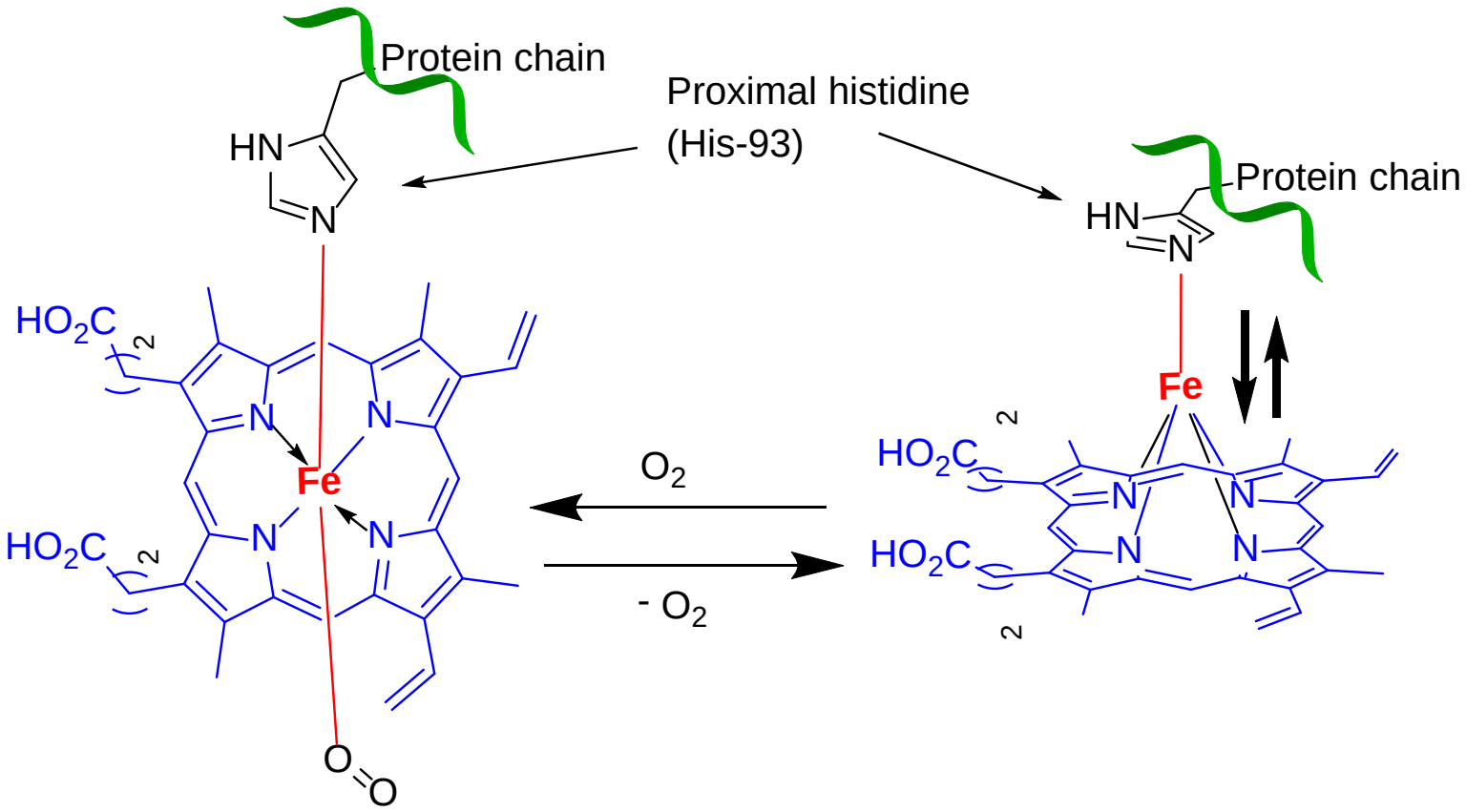


The heme group (heme b)



Myoglobin

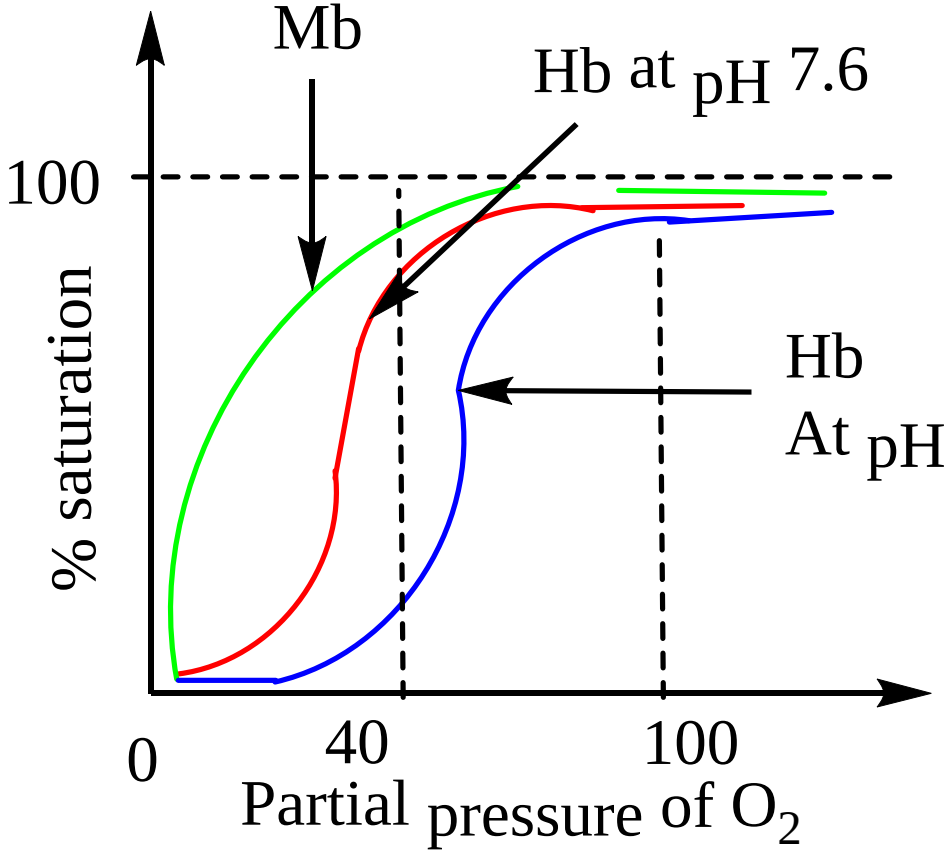
Myoglobin and Hemoglobin

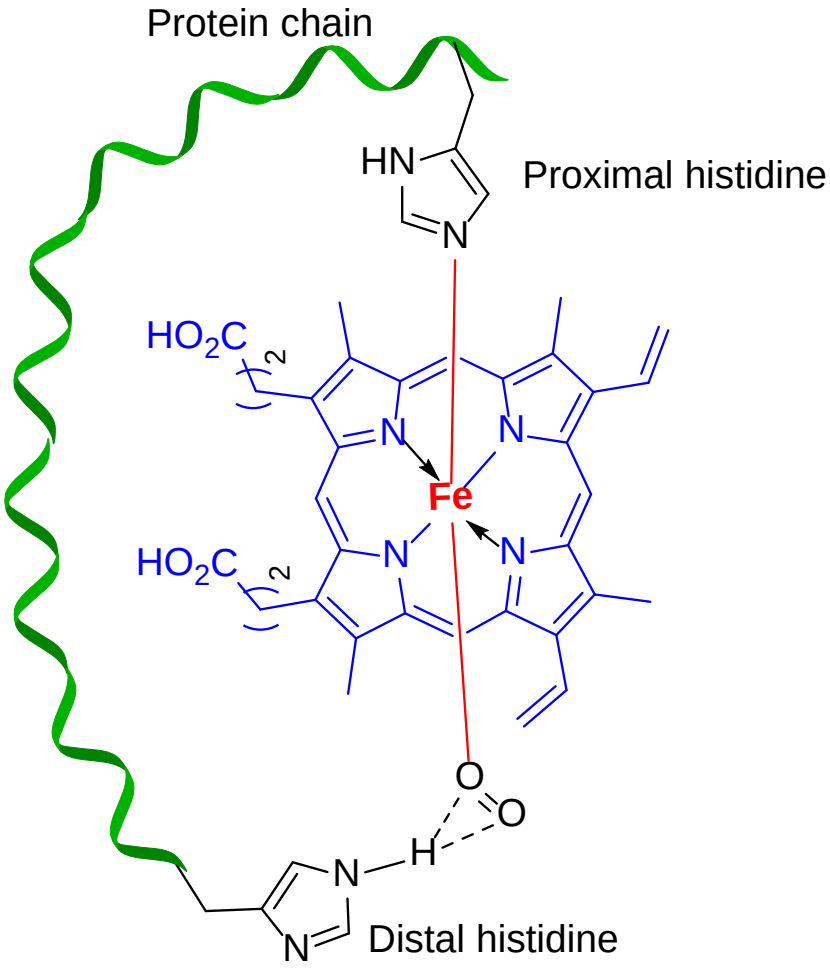


Oxymyoglobin/Oxyhemoglobin
Six coordinated iron atom,
Low spin, in the palne of heme
R-state

Deoxymyoglobin/deoxyhemoglobin
Five coordinated iron atom,
High spin, out of the palne of heme,
T-state

Transport of dioxygen





O_2 binding curve for Hb and Mb

Transport of dioxygen

$$Hb + O_2 \overset{k_1}{\rightleftharpoons} HbO_2$$

$$HbO_2 + O_2 \overset{k_2}{\rightleftharpoons} Hb(O_2)_2$$

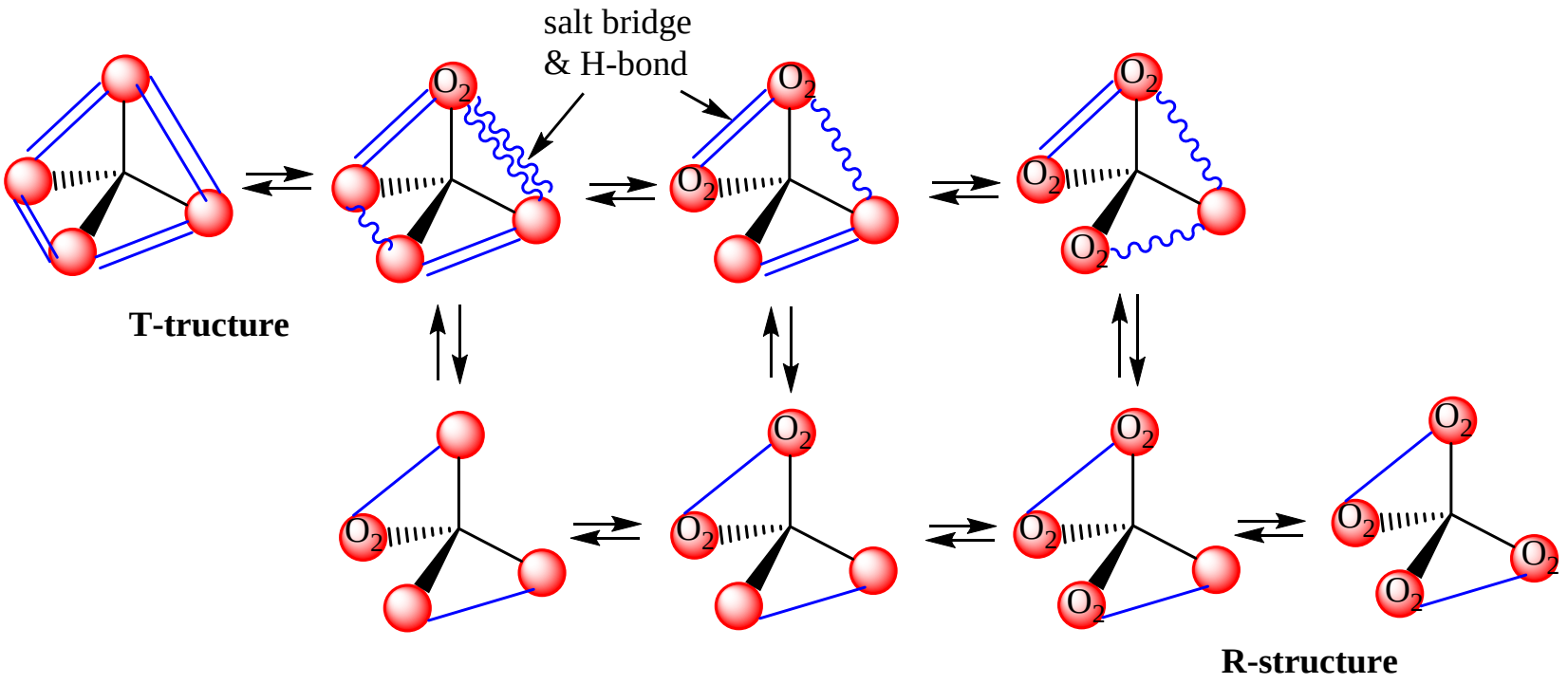
$$Hb(O_2)_2 + O_2 \overset{k_3}{\rightleftharpoons} Hb(O_2)_3$$

$$Hb(O_2)_3 + O_2 \overset{k_4}{\rightleftharpoons} Hb(O_2)_4$$

$$Hb + 4O_2 \overset{K}{\rightleftharpoons} Hb(O_2)_4$$

$k_1 < k_2 < k_3 < k_4$

$K = k_1 \times k_2 \times k_3 \times k_4$



Equilibrium between R and T structures of Hb

Irreversible oxidation of Hb

$Fe(II) + O_2 \rightleftharpoons Fe(III)\text{-}O_2^{1-}$

$Fe(III)\text{-}O_2^{1-} + Fe(II) \rightleftharpoons Fe(III)\text{-}O_2\text{-}Fe(III)$

$Fe(III)\text{-}O_2\text{-}Fe(III) \rightarrow 2Fe(IV)=O$

$Fe(IV)=O + Fe(II) \rightarrow Fe(III)\text{-}O\text{-}Fe(III)$

Hematin

Oxidation of iron as monomer

$Fe(III)\text{-}O_2^{1-} \rightleftharpoons Fe(III) + \dot{O}_2^{-}$

$Fe(III) + Cl^- \rightleftharpoons Fe(III)\text{-}Cl^-$

In lungs $Hb + O_2 \rightarrow Hb(O_2)_4$

In tissue $Hb(O_2)_4 + 4Mb \rightarrow 4MbO_2 + Hb$

Transport of CO_2

1) $Hb\text{—}NH_2 + CO_2 \rightleftharpoons Hb\text{—}NH\text{–}CO_2^- + H^+$

2) $CO_2 + H_2O \xrightleftharpoons{\text{carbonic anhydrase}} H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

Hemerythrin

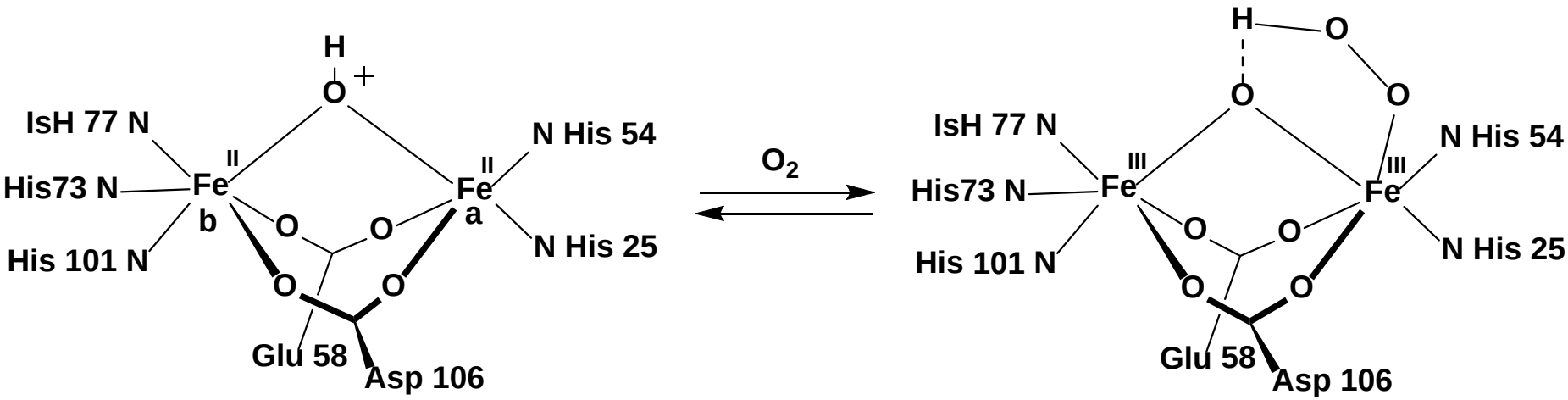
- Hemerythrin is an **Oligomeric Protein** and is a **nonheme** iron protein. Hemerythrin may be Monomeric, Trimeric and Octameric.

- Found in cells or "corpuscles" in the blood rather than free floating.

- Major role is oxygen transfer and storage.

- Dioxygen binding pigment found in Marine Invertibrates. Like – Pyla, Crabes.

Oxygen binding in hemerythrin



Deoxyhemerythrin

Fe_a^{2+} is 5-coordinate
Fe_b^{2+} is 6-coordinate
Ions are weakly coupled via tha bridging ligand
Colourless

Oxyhemerythrin

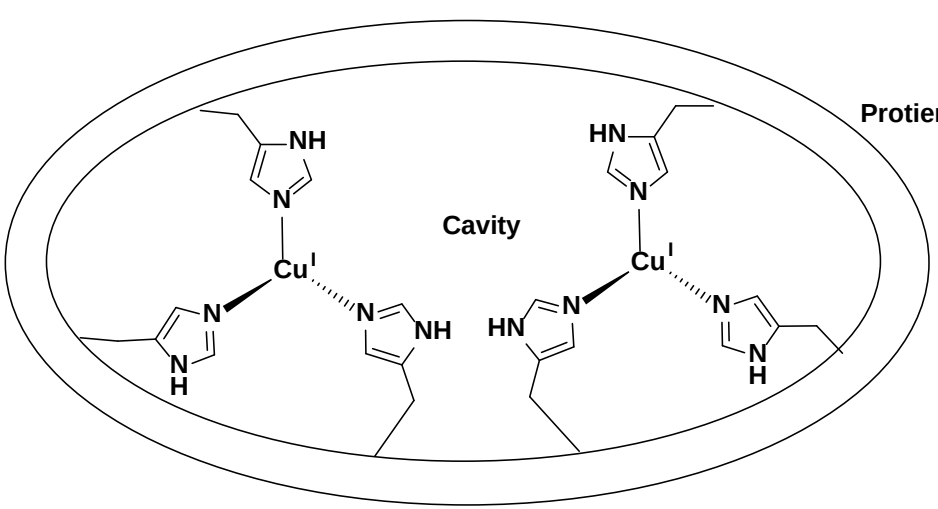
Both Fe^{3+} are 6-coordinate
Ions are strongly coupled via the bridging ligand
Violet – purple colour

Oxygen binding in hemerythrin

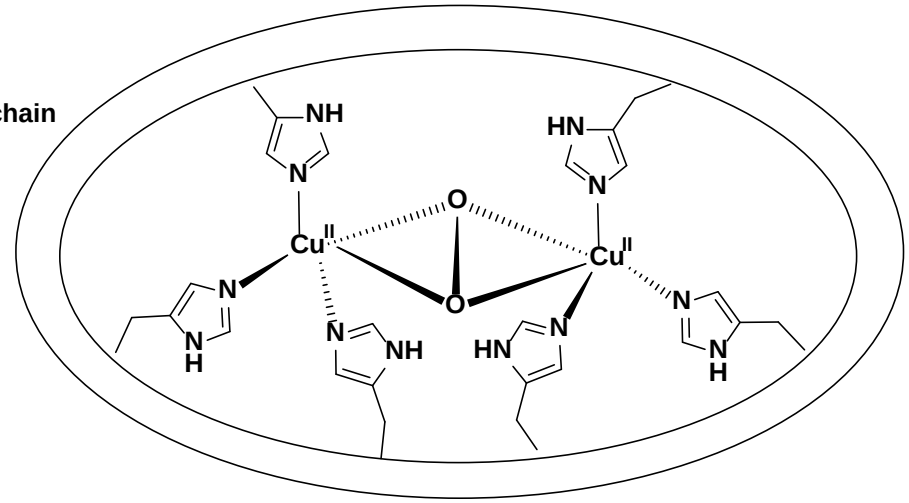
- Hemerythrin holds the O_2 as a hydroperoxide
- Colorless when deoxygenated, but turn a violet-pink in the oxygenated state
- Iron atoms are bound to the protein through the carboxylate side chains of a glutamate and aspartates as well as through five histidine residues.
- In oxy form peroxide bond (O-O single bond) is present and Raman stretching of it is 845 cm^{-1}

Hemocyanin

- Found in some Mollusca and Arthropoda species
- Deoxy form is colourless and oxy form is blue
- The oxygen binding center consists of two copper atoms, which exhibits +1 oxidation state in deoxyform and +2 oxidation state in oxyform
- Hemocyanin binds dioxygen in peroxide form and each oxygen is bonded with both copper centres



Deoxyhemocyanin



Oxyhemocyanin