M.SC Semester III
Core Course XI
Bio-InorganicChemistry

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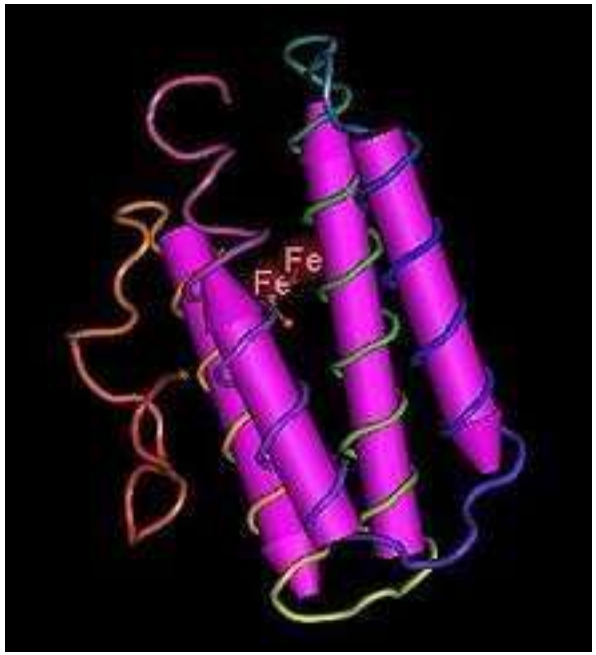
TOPIC:-Unit III Hemerthrine

Introduction

- Hemerythrine from geek words aiua (blood) and epuopoc (red), is an oligomeric protein responsible for oxygen transport in marine invertibrates phyla such as brachiopods and in a single annelid worm. Myohemerythrine is a monomeric oxygen binding protein found in the muscles of invertebrates.

Explanation

- In a great variety of worms the oxygen- carrying molecules are iron-bearing proteins , but they donot contain porphyrins. They are all presumably similar in chemical nature and are called hemerythrins. The mos studied one is that which is derived from saltwater worm Goldfingia gouldii. It has a molecular weight of 108,000 but consists of eight identical subunits. Each unit consists of two iron atoms.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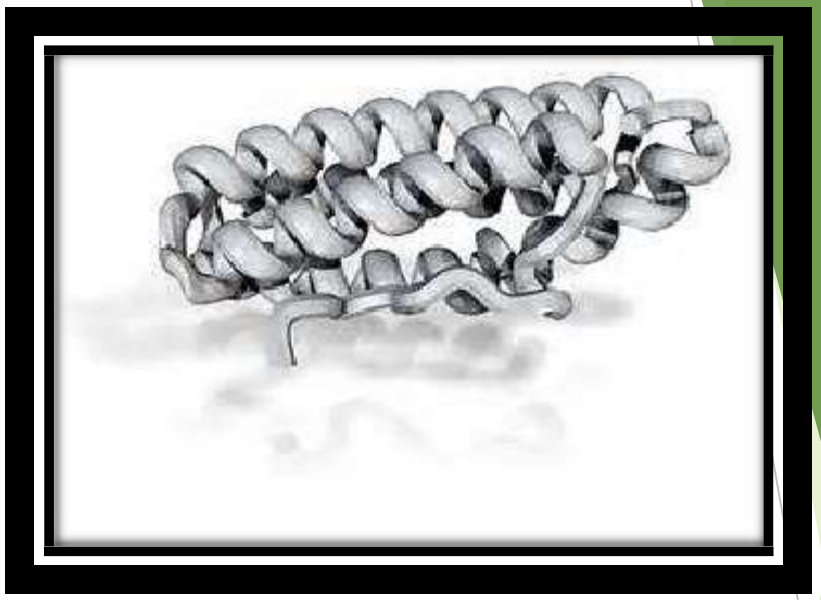

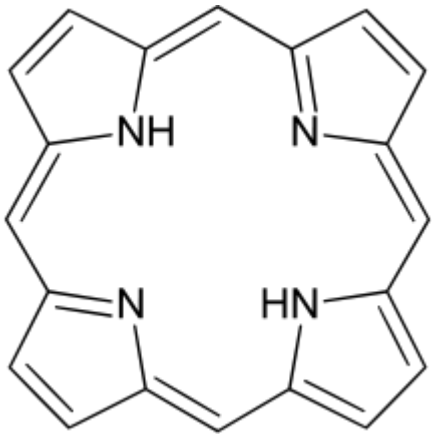
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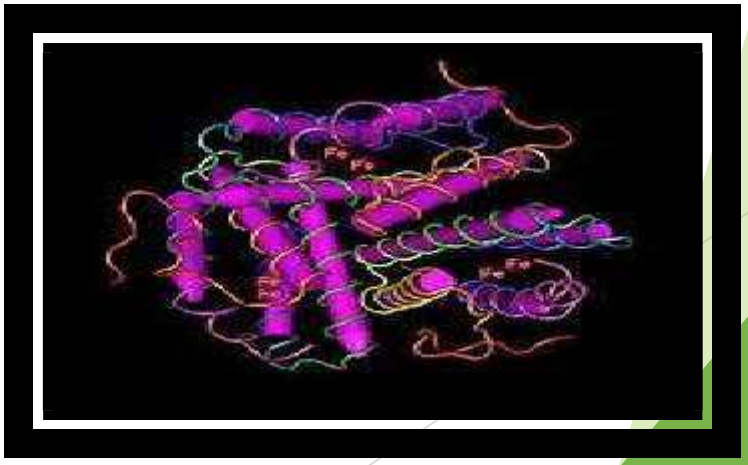


- Each subunit consists of 113 aminoacids arranged in four nearly parallel helical segments having 30 to 40 Angstrom lenth. The iron atoms are held within these 4 segments . The 2 iron atoms are close together. In the case of aquametherythrin , which contans two iron atoms (in +3 state)

Oxygen affinity

- The oxygen affinity of this particular hemerythrine is not ph sensitive , though others are. Hemerythrine bind oxygen 5 to 10 times more strongly than hemoglobin and myoglobin. Each subunits can bind one oxygen molecule, thus the ratio of iron to oxygen is 2:1 .

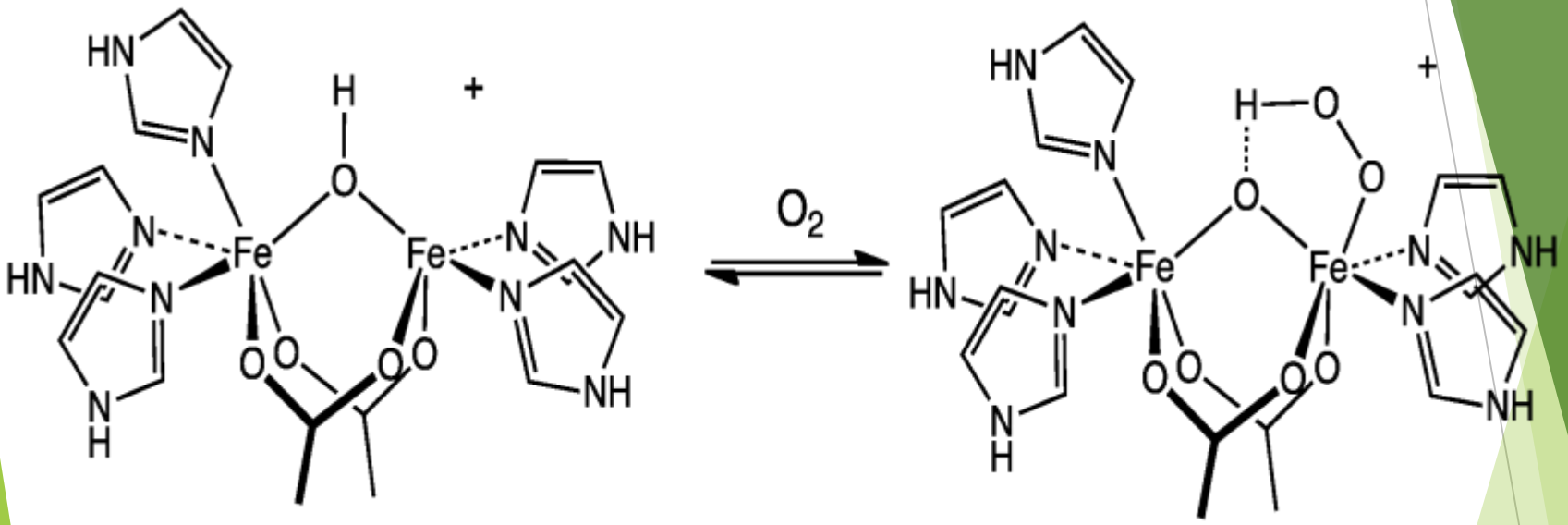
Colours

The deoxygenated substance is colourless while the oxygenated one is viole-pink.

Oxygen binding mechanism

The mechanism of dioxygen binding is unusual. Most O2 carriers operate via formation of dioxygen complexes, but hemerythrin holds the O2 as a hydroperoxide. The site that binds O2 consists of a pair of iron centres. The iron atoms are bound to the protein through the carboxylate side chains of a glutamate and aspartates as well as through five histidine residues.

The uptake of O2 by hemerythrin is accompanied by two-electron oxidation of the diferrous centre to produce a hydroperoxide (OOH−) complex. The binding of O2 is roughly described in this diagram: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NH

Deoxyhemerythrin contains two high-spin ferrous ions bridged by hydroxyl group (A). One iron is hexacoordinate and another is pentacoordinate. A hydroxyl group serves as a bridging ligand but also functions as a proton donor to the O2 substrate. This proton-transfer result in the formation of a single oxygen atom bridge in oxy- and methemerythrin. O2 binds to the pentacoordinate Fe^{2+} centre at the vacant coordination site (B). Then electrons are transferred from the ferrous ions to generate the binuclear ferric (Fe^{3+},Fe^{3+}) centre with bound peroxide

Quaternary structure and cooperativity

- Hemerythrin typically exists as a homooctamer or heterooctamer composed of α- and ß-type subunits of 13-14 kDa each, although some species have dimeric, trimeric and tetrameric hemerythrins. Each subunit has a four-α-helix fold binding a binuclear iron centre. Because of its size hemerythrin is usually found in cells or "corpuscles" in the blood rather than free floating.

- Unlike hemoglobin, most hemerythrins lack cooperative binding to oxygen, making it roughly 1/4 as efficient as hemoglobin. In some brachiopods though, hemerythrin shows cooperative binding of O2. Cooperative binding is achieved by interactions between subunits: the oxygenation of one subunit increases the affinity of a second unit for oxygen.

- Hemerythrin affinity for carbon monoxide (CO) is actually lower than its affinity for O2, unlike hemoglobin which has a very high affinity for CO. Hemerythrin's low affinity for CO poisoning reflects the role of hydrogen-bonding in the binding of O2, a pathway mode that is incompatible with CO complexes which usually do not engage in hydrogen bonding.