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Topic: Bio-Chemistry

② Electron transport proteins:

Electron transport proteins are responsible for the transport of electrons from a biological redox couple having a lower standard redox potential to one having a higher standard redox potential. Standard redox potential of an electron transport protein should be intermediate between those of the electron acceptor and the electron donor couples. Electron transporting metalo proteins are mainly the Iron-sulphur proteins (e.g; ferredoxins) and the Iron(III) heme proteins (e.g; cytochromes). Both these groups operate through their Fe(III)-Fe(II) couples.

• Fe-sulphur proteins:

Iron-sulphur proteins function as electron carriers in biological redox reactions. e.g; photosynthesis, Nitrogen fixation and mitrocondrial respiration. These consist of non heme iron co-ordinated

by cysteine sulphur (–SH) and acid labile inorganic sulphide sulphur (S=). Different types of Iron-sulphur proteins are given below

① Rubridoxin

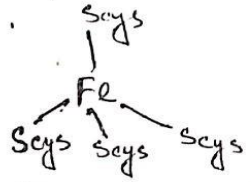


Fig: active site structure of Rubridoxin

Rubridoxin is the simplest of the Iron sulphur proteins. It contains one Fe and no acid labile sulphur (S=). Iron in Rubridoxin is co-ordinated by four cysteinyl sulphur atoms in a distorted tetrahedral geometry in which Iron-sulphur bonds are unusually short. It is a low molecular weight protein (6000) consisting of 53–54 amino acids

The oxidised form of the protein is red coloured, contains high spin Fe(III). The reduced form is colourless and contains Fe(II) in a high spin configuration. The distorted tetrahedral structure of Fe is responsible for the lower redox potential and rapid electron transfer properties of Rubridoxin. It is a single electron transport protein due to the following couple

$$\left[\overset{III}{Fe}(S\text{-}cys)_4\right]^{\ominus} + e \rightleftharpoons \left[\overset{II}{Fe}(S\text{-}cys)_4\right]^{=}$$

② Ferredoxins

(a) 2Fe-2S Ferredoxins

Fig:- Active site structure of 2Fe-2S protein

2Fe-2S Ferredoxins occur in the chloroplasts of many plants, in several bacteria, in Pig adrenal glands. These consist of a single peptide chain of 98-amino acids (Molecular weight 10,500). Its active site contains two Iron centres bridged by two acid labile sulphur ($-S^{=}$) and each Iron is bound to 4 cysteine sulphur atoms of the protein chain in such a manner that the indivisual $(cys-S)_2 Fe(S^{2-})_2$ units appear tetrahedral providing high spin configuration of Fe.

In the oxidised form, both the iron atoms are in Fe(III) state with high spin configurations yet the protein is diamagnetic due to antiferromagnetic coupling [Fe(III)....Fe(III)] 2Fe-2S Ferredoxins functions as one electron transport proteins

$$\left[(cys-S)_2 \overset{III}{Fe}(S^{2-})_2 \overset{III}{Fe}(S\text{-}cys)_2\right]^{2-} + e \rightleftharpoons \left[(cys-S)_2 \overset{III}{Fe}(S^{2-}) \overset{II}{Fe}(S\text{-}cys)_2\right]^{3-}$$

In the reduced form, a high spin Fe(II) and a high spin Fe(II) are antiferromagnetically coupled to give a net electron spin of $S = 1/2$ in the ground state. The electron transport occurs with very small energy transfers, as the redox potential of this protein is very low.

b) 4Fe-4S proteins

4Fe-4S proteins can undergo one electron redox reactions. Active sites of these proteins consist for four iron atoms, four acid labile sulphide sulphur (S^{2-}) and four cysteinyl sulphur atoms arranged in a cubic structure.

In the structure each iron is tetrahedrally coordinated by three acid labile sulphide sulphur and one cysteine

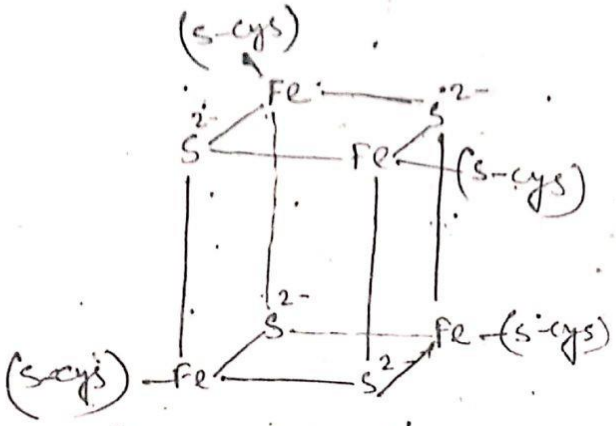


Fig:- active site structure of 4Fe-4S proteins.

sulphur (s-cys).

The oxidised form contains three high spin Fe(III) and one high spin Fe(II) and its paramagnetism is equivalent to one unpair electron due to anti ferromagnetic interaction. The reduced form contains two Fe(III) and two Fe(II) and is diamagnetic due to anti-ferromagnetic interaction. These protein function as one electron carriers;

$$[(\overset{III}{Fe})_3(\overset{II}{Fe})(S^{2-})_4(s\text{-}cys)_4]^{\ominus} + e \rightleftharpoons [(\overset{III}{Fe})_2(\overset{II}{Fe})_2(S^{2-})_4(s\text{-}cys)_4]^{2-}$$

(c) 8 Fe-8S proteins:

These type of ferredoxins function as electron carriers in the biological nitrogen fixation. These ferredoxins are small and consist of two 4Fe-4S clusters situated at 12Å apart. Each of which can undergo

one electron change. As a result the whole protein functions as a two electron carrier. The oxidised form contains equal number of Fe(III) and Fe(II) but shows lower magnetic moment due to antiferromagnetic coupling. Magnetic moment of the protein increases on reduction

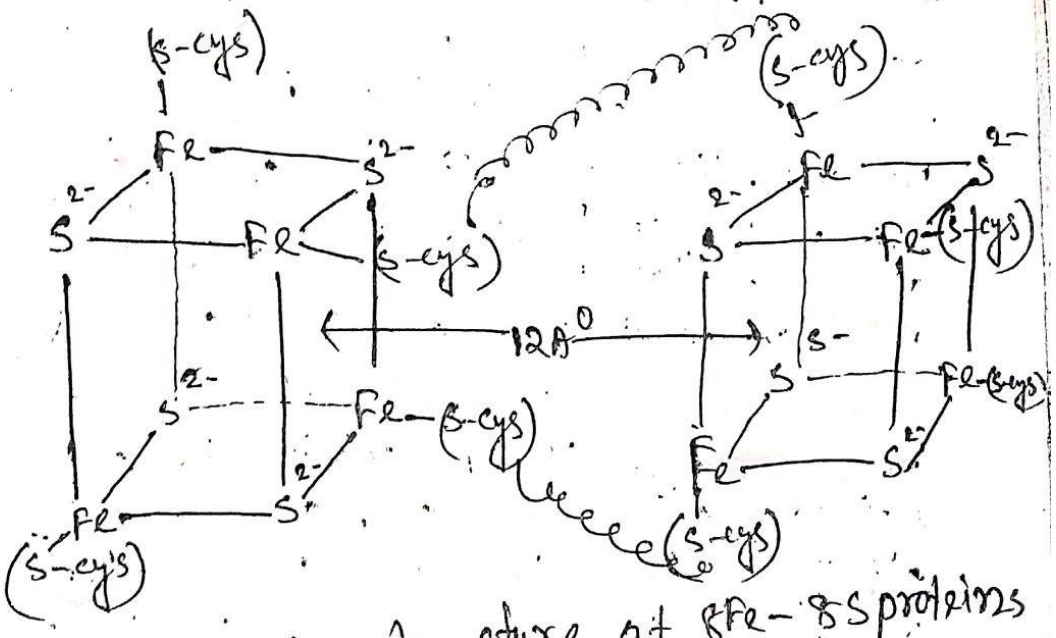


Fig:- Active site structure of 8Fe-8S proteins

$$2\times\left\{\left[(\overset{III}{Fe})_2(\overset{II}{Fe})_2(S^{2-})_4(S\text{-}cys)_4\right]^{2-}+e \rightleftharpoons \left[(\overset{III}{Fe})(\overset{II}{Fe})_3(S^{2-})_4(S\text{-}cys)_4\right]^{3-}\right\}$$

- $Na^+ - K^+$ (transporting) ATPase (Na^+ pump):

Relatively high concentration of K^+ ion is required for several vital processes occuring in animal cells. K^+ ion keeps the ribosome in its most active conformation during protein bio-synthesis. A large number of enzymes require K^+ ion for showing their maximum activity. Na^+ and K^+ concentration gradients across the cell membrane maintain the membrane potential of excitable tissues, which transmit the impulses in the form of action potential. When the tissue is excited, an abrupt increase in the perme

permeability of the membrane to Na^+ and K^+ ion takes place, resulting in a transient viscous discharge or collapse of membrane potential. For these reasons most animal cells tend to maintain a relatively high and constant concentration intracellular K^+ ion. Na^+ ion inhibits many K^+ activated enzymes. The cells therefore, tend to maintain a must concentration intracellular K^+ ion. The extracellular fluids of mammels contents a relatively high concentration of Na^+ ion and a very low concentration of K^+ ion.

The high concentration of K^+ ion inside and the predominants of Na^+ ion outside the cells generate an electrical potential of about −16 milli volt. The energy required for maintaining such an electrical non-equilibriums situation is provided by the hydrolysis of appropriate number of ATP molecules, resulting from respiration. It involves a membrane bound enzymes Na^+–K^+ ATPase. This enzyme pumps K^+ ion in and Na^+ ion outside the cell by utilising ATP. The enzyme binds and releases Na^+ and K^+ ions at different stages in the reaction cycle. Conformational change of the enzyme during the transport process facilitate the uptake of a specific cation from one side of the membrane and is released to the other side.

For every molecule of ATP hydrolysis, three Na^+ ions are pumped out and two K^+ ions are pumped in. 100 ATP molecules can be hydrolysed by

each ATPase molecule. So the whole process becomes.

$$3Na^+\text{-in} + 2K^+\text{-out} + ATP + H_2O \xrightleftharpoons{Na^+K^+ ATPase} 3Na^+\text{-out} + 2K^+\text{-in} + ADP + P_i$$

[P_i = Inorganic phosphate].

* • **Cytochromes:**

Cytochromes are a group of Fe(III) heme proteins that functions as electron carriers in ~~mytocondri~~ mitochondrial oxidation, photosynthesis etc. They are classified as a, b, c etc. on the basis of their absorption spectra.

Cytochrome-a, b, c also differ in their porphyrin substitution and in Fe co-ordination. The heme group of cytochrome-b has the proto porphyrin-IX (P-IX) structure and is not covalently linked with the protein part. The cytochrome-a heme has a formyl group (—CHO) at position-8 of the porphyrin ring and a long hydrocarbon chain ($C_{17}H_{29}O$) at position-2. cytochrome-c has the same group as cytochrome-b's but the vinyl group at 2 and 4 positions are condensed with —SH groups. As a result the heme group is co-valently linked with the protein chain to the cysteine residues at positions 13 and 17 of the protein.

Fe in cytochromes is equatorially co-ordinated by the four pyrrolnitrogen atom of the porphyrin ring system. 5th and 6th positions of iron are axially co-ordinated by different groups of the protein

chain. In cytochrome-a, 5th and 6th ligands are histidine imidazole nitrogen atom.

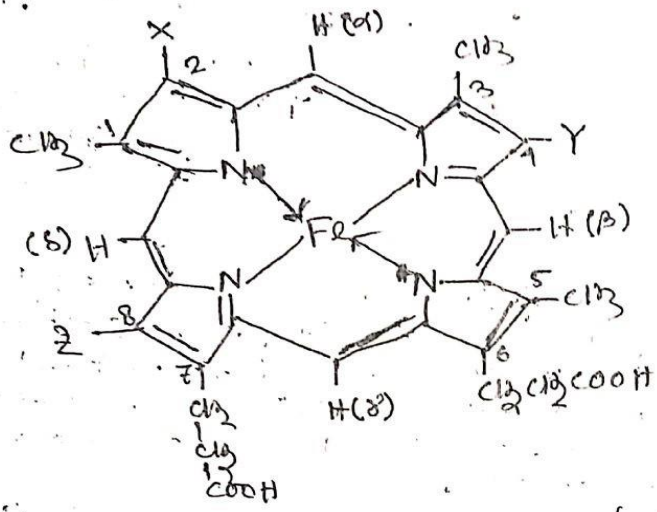
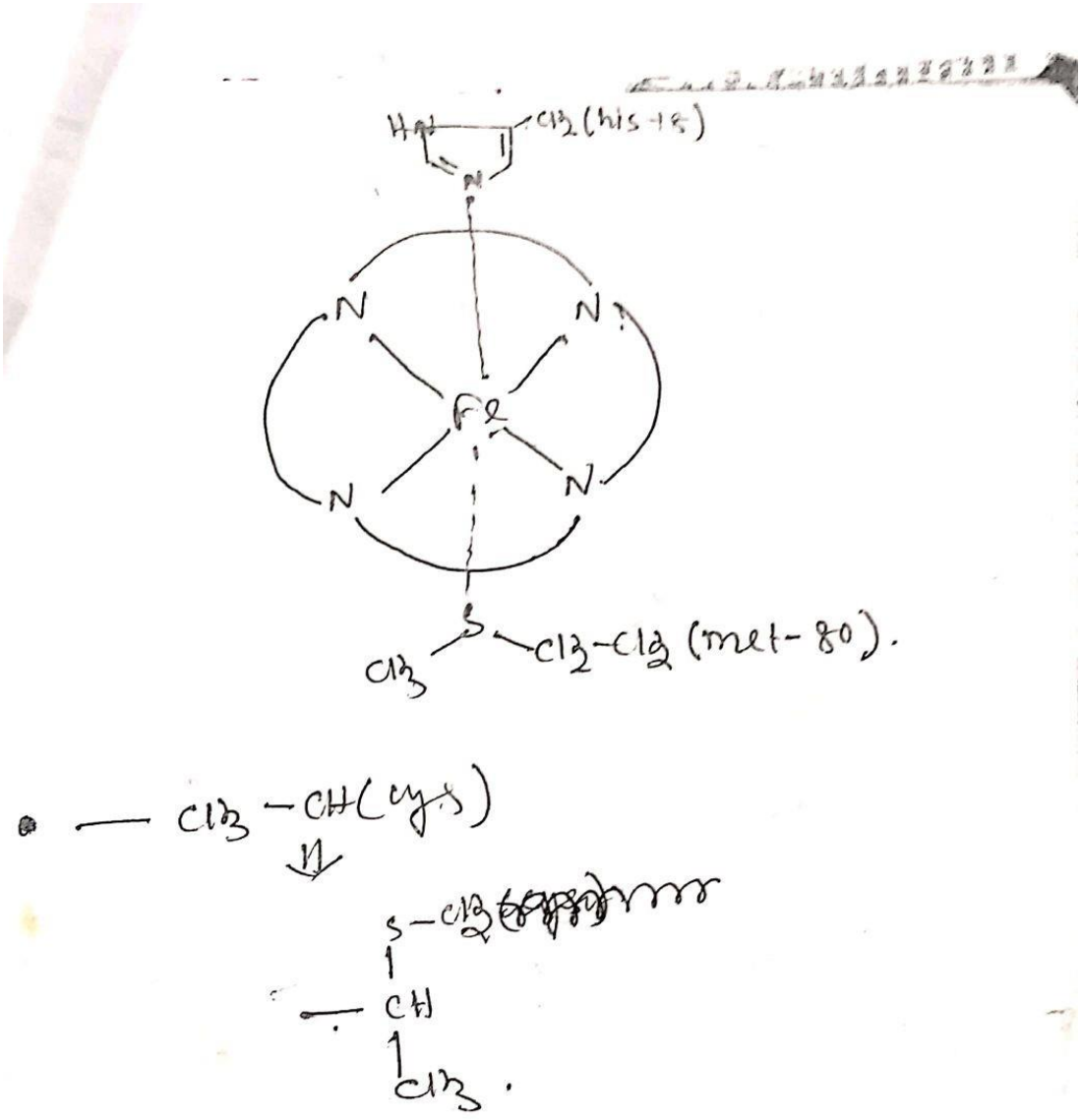


Fig:- Active site structures of cytochromes-a, b and c.

Porphyrin position	heme-a	heme-b	heme-c &
X	$C_{17}H_{29}O$	$-CH=CH_2$	H_3C-CH(cys)
Y	$-CH=CH_2$	$-CH=CH_2$	H_3C-CH(cys)
Z	$-CHO$	$-CH_3$	$-CH_3$

cytochrome-c has a polypeptide chain of 104 amino acid residues. The fifth position of Fe in cytochrome-c is co-ordinated by the imidazole nitrogen atom of the histedine-18 and the sixth position by the thio-ether sulphur atom of the methionine-80.

$$Fe^{III} + e^- \rightleftharpoons Fe^{II}$$



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