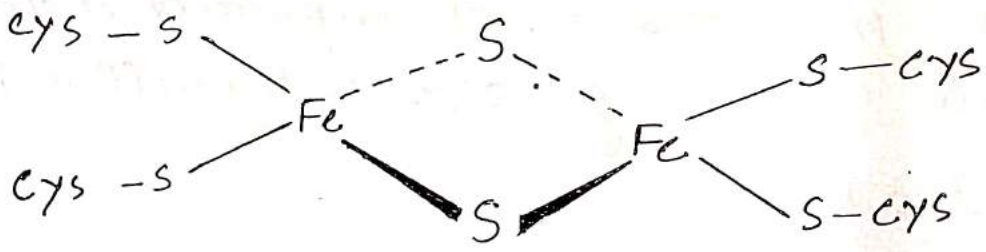
FERREDOXINS

[2Fe-2S] cluster

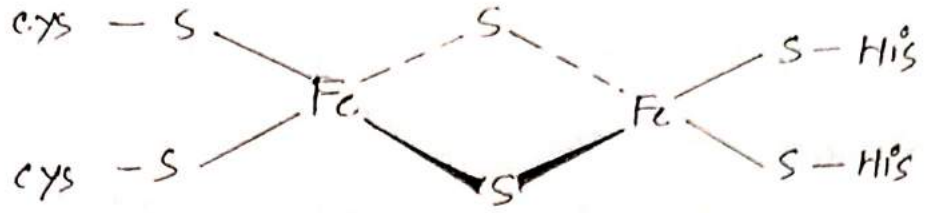
The simplest polymetallic system, the $[Fe_2S_2]$ cluster is continued by two iron ions bridged by two sulfide ions and coordinated by four cysteinyl ligands or by two cysteins and two histidine (in Rieske protein). The oxidised protein contains two Fe^{3+} ions, whereas the reduced proteins contain one Fe^{3+} and one Fe^{2+} ion. The species exist in two oxidation state $(Fe^{III})_2$ and Fe^{III} Fe^{II}.



$$[Fe^{III}Fe^{III}]^{2+} \underset{}{\overset{e^-}{\rightleftharpoons}} [Fe^{III}Fe^{II}]^{+}$$

$S = 0$ $\qquad$ $S = 1/2$

$E_0 \sim -150$ to -400 mV



$$Fe^{III}S_2Fe^{II}]^{2+} + e^- \rightleftharpoons Fe^{III}S_2Fe^{II}]^{+}$$

$S = 0$ $\qquad$ $S = 1/2$

$E_0 \sim -100$ to $+400$ mV

The structure of 2Fe–2S reveals a tetrahedron of 3 ligands surrounding each Fe atom. The two tetrahedra share an edge defined by two bridging sulfide ions and the core structure is designated $Fe_2(\mu_2\text{-}S)_2$. Several kind of spectroscopic evidence indicate that in the reduced 2Fe-2S$]^+$ cluster, the added electron is localized one one iron atom, so that one Fe^{II} and one Fe^{III} atom are present. In 2Fe–2S$]^{2+}$ clusters, the Fe–Fe distance is 2.72 A° and the clusters is diamagnetic.

Generally ferredoxin from spinach act as electron acceptor. But 2Fe–2S protein from Pseudomonas putida, named as Putidaredoxin act as donors to P–450 camphor monoxygenase system and Adrenodoxin act as electron donors to P-450 monoxygenase system that carries out 11 β – hydroxylation of steroids.

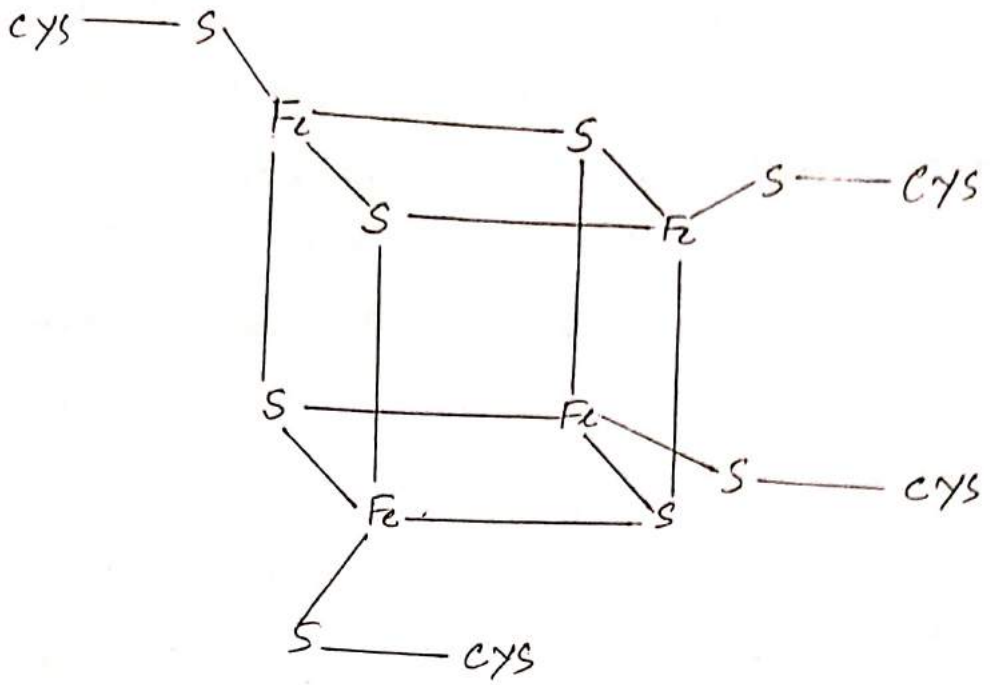
The binuclear iron cluster is found in a largely hydrophobic region of the protein but is within 5 Å of the protein surface. The sulfur atoms both inorganic and cysteinyl are H-bonded to six peptide NH group and one serine -OH group which presumably stabilize the iron sulfur cluster. Fe_2-S_2 unit- Pa. 11-KDa. protein is bound by cys-41, cys-46, cys-49, and cys-79.

The weakness of sulfur ligand field caused the iron atoms to be high spin. In all ferric oxidized state, the two Fe^{3+} sites are antiferromagnetically couple ie the spin fixed d³ on the two iron atoms are oppositely aligned. such that their pairing produces an effective S=0, diamagnetic ground state. In reduced form, a single unpaired electron is present, because $S = 5/2$ for Fe^{3+} and $S=2$ for Fe^{2+} sites are antiferromagnetically coupled, leaving one net unpair spin and $S = 1/2$ ground state and these circumstance allows for their magnetic coupling

4Fe-4S clusters:

→ four iron and four sulfide ions placed at the vertices of a cubane type structure. The Fe centers are typically tetracoordinated by cysteinyl ligands. The $[Fe_4S_4]$ proteins may be subdivided into low potential (bacterial type) and high potential (HiPIP) ferredoxin.

In HiPIP, the cluster shuttle between $[2Fe^{3+}, 2Fe^{2+}]$ $(Fe_4S_4^{2+})$ and $[3Fe^{3+}, Fe^{2+}]$ $(Fe_4S_4^{3+})$. and in bacterial ferredoxins, the pair of oxidation states are $[Fe^{3+}, 3Fe^{2+}]$ $(Fe_4S_4^{+})$ and $[2Fe^{3+}, 2Fe^{2+}]$ $(Fe_4S_4^{2+})$. The two families of 4Fe-4S cluster share the $Fe_4S_4^{2+}$ oxidation state. The diff. in the redox couples is attributed to the degree of hydrogen bonding, which strongly modifies the basicity of the cysteinyl ligands. It is crucial to note that, in sharp contrast to the Fe_2S_2 and Fe_3S_4 sites, the oxidation states are not localized in the Fe_4S_4 cluster. In each most cases, each Fe atom behaves as if it had the same average oxidation level as the other Fe atom in the cluster.



fig!— Fe_4S_4 - cubane like structure

The Redox - reaction is

$$Fe_4S_4]^{3+} + e^- \rightleftharpoons Fe_4S_4]^{2+} + e^- \rightleftharpoons Fe_4S_4]^{+}$$

$S = 1/2$ $\qquad$ $S = 0$ $\qquad$ $S = 1/2$

$E^\circ \sim +100$ to $+400$ mV

-300 to -700 mV

The $Fe_4S_4]^{3+} \rightleftharpoons Fe_4S_4]^{2+}$ for HiPIP

and $Fe_4S_4]^{2+} \rightleftharpoons Fe_4S_4]^{+}$ for Low potential

The structure for both oxidised and reduced HiPIP reveals that the Fe_4S_4 clusters remain intact during redox interconversion.

The binding of a given cluster by cystein residues from different portions of a polypeptide

chain apparently helps stabilize the tertiary str of the protein and brings the two cysteines into relating close proximity.