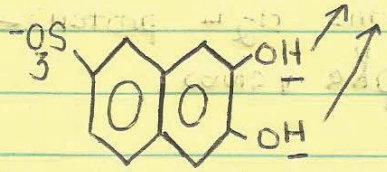
Bioinorganic Chemistry
Assignment 2 Answer Key

Aqueous speciation

1)



Dissociable protons

	log β	β
$L^{3-} + H^+ \rightleftarrows HL^{2-}$	12	10^{12}
$HL^{2-} \overset{K_a}{\rightleftarrows} L^{3-} + H^+$	-12	10^{-12}

Recall β values are K values for a net reaction.

Acid dissociation

$$pK_a = -\log K_a = -(-12) = 12$$

$HL^{3-} + H^+ \rightleftarrows H_2L^-$	8.09	$10^{8.09}$
$H_2L^- \rightleftarrows HL^{3-} + H^+$	-8.09	$10^{8.09}$

$$pK_a = -(-8.09) = 8.09$$

At micromolar concentrations and in the absence of Fe(III), you should see the following ligand speciation

H_2L^- Nearly 100% from pH 0 to 6.0
Decreases to 0% at pH ~ 9.5

HL^{2-} Increases from 0% @ pH ~ 6.0 to 95% @ pH 9.5

L^{3-} Starts to appear @ pH 9.5

In the presence of micromolar amounts of Fe(III)

H_2L^- is only ~65% present @ pH 2.0
L^{3-} is ~35% present @ this same pH and bound to Fe(III).

∴ Therefore even @ a low pH, the presence of Fe(III) facilitates dissociation of the H_2L^- protons + decreases their effective pKa values.

2. You MUST include the Fe(III) hydrolysis constants into the data file that I gave you.

M	L	H	log β
1	0	-1	-2.19
1	0	-2	-5.76
1	0	-3	-14.30
1	0	-4	-21.71 → I made a mistake in the notes
2	0	-2	-2.92
0	0	-1	-14.00
0	1	1	12
0	1	2	20.09
1	1	0	23.00
1	2	0	41.00
1	3	0	51.00

@ [M] = 0.02 ~~mM~~
[L] = 0.02 mM

At low pH, there is free Fe(III)
Between pH 2-4, there is dominantly the 110 species.
At higher pH, there is more Fe(III) hydrolysis species

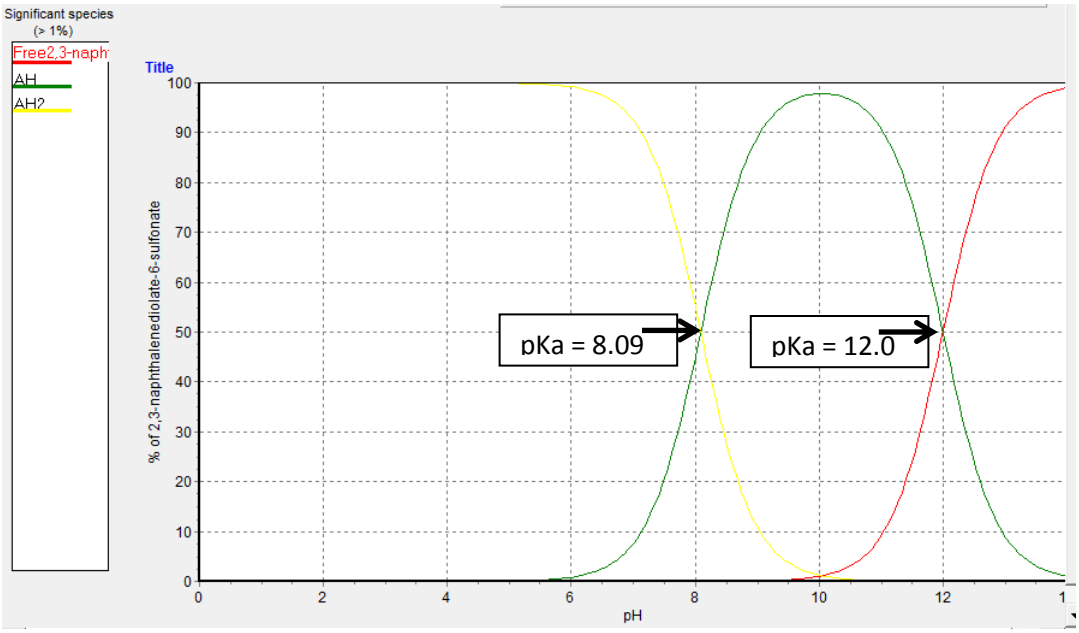
@ [M] = 0.02 mM
[L] = 0.04 mM

At low pH, there is free Fe(III)
Between pH 1-3, there is mostly the 110 species.
Between pH 4-9, there is " the 120 species.

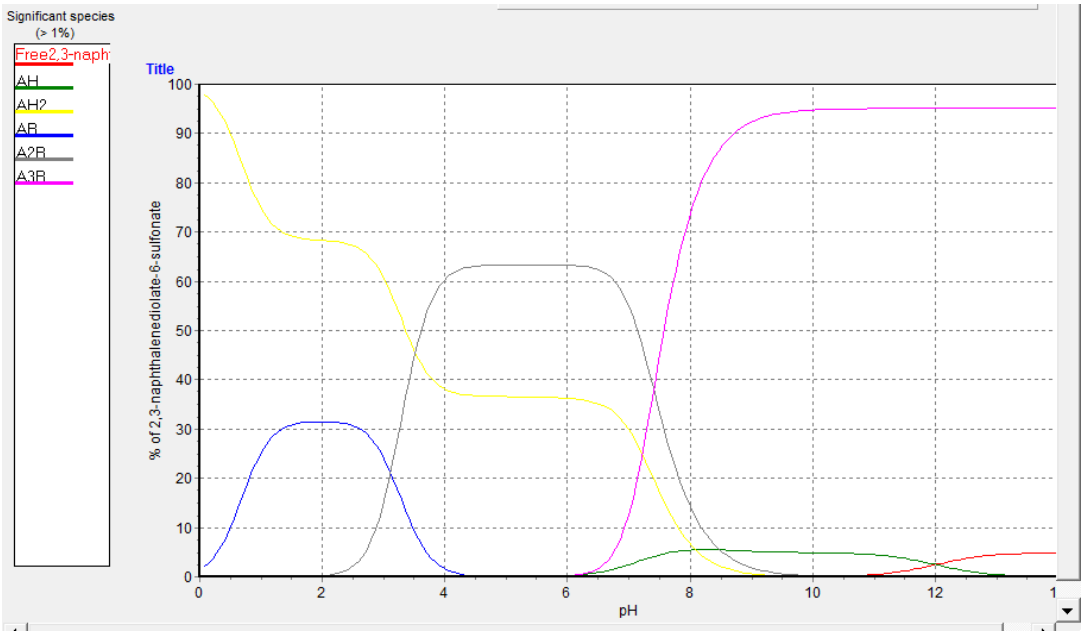
@ [M] = 0.02 mM
[L] = 0.06 mM
At low pH, there is free Fe(III)
Between pH 1-3, there is mostly the 110 species.
" pH 4-7, " " " " 120 "
" pH > 9.5, there " " " 130 "

1a. [Fe^{3+}] = 0.0 mM; [ligand] = 0.06 mM. Plotted for ligand's perspective.

A: Ligand, B: Metal, H: Hydrogen



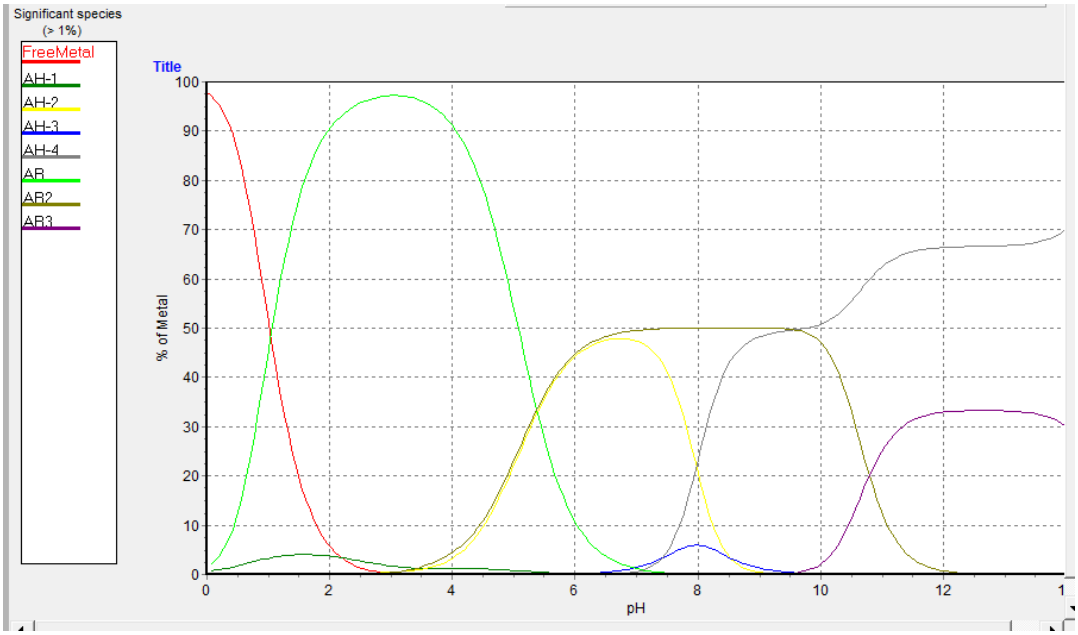
b. [Fe^{3+}] = 0.02 mM; [ligand] = 0.06 mM. Plotted for ligand's perspective.



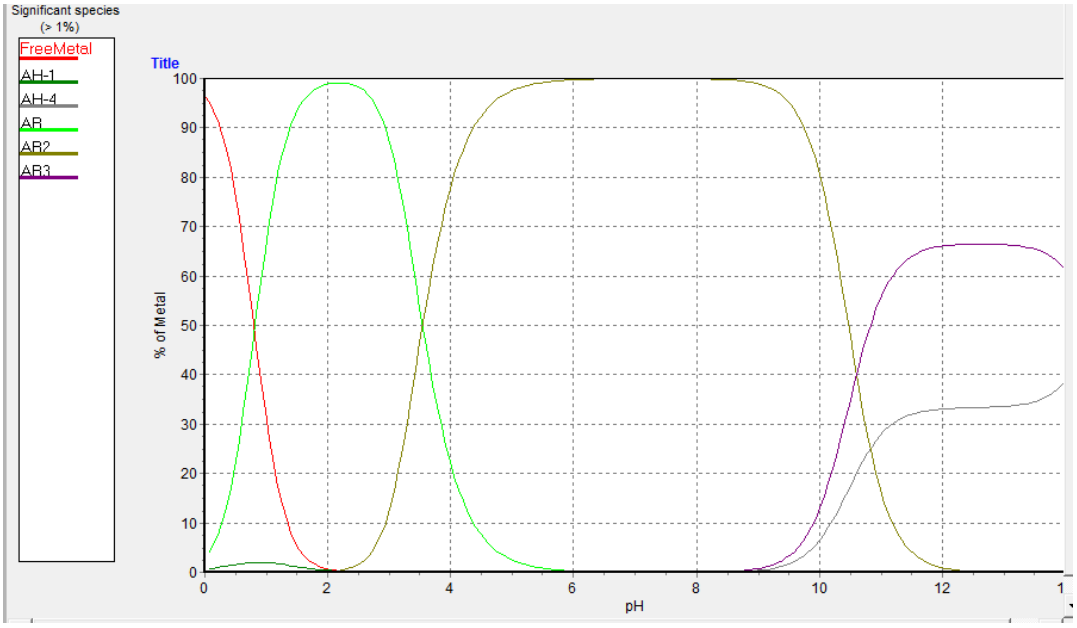
2. Plots for Fe^{3+} perspective.

a. [Fe^{3+}] = 0.02 mM; [ligand] = 0.02 mM

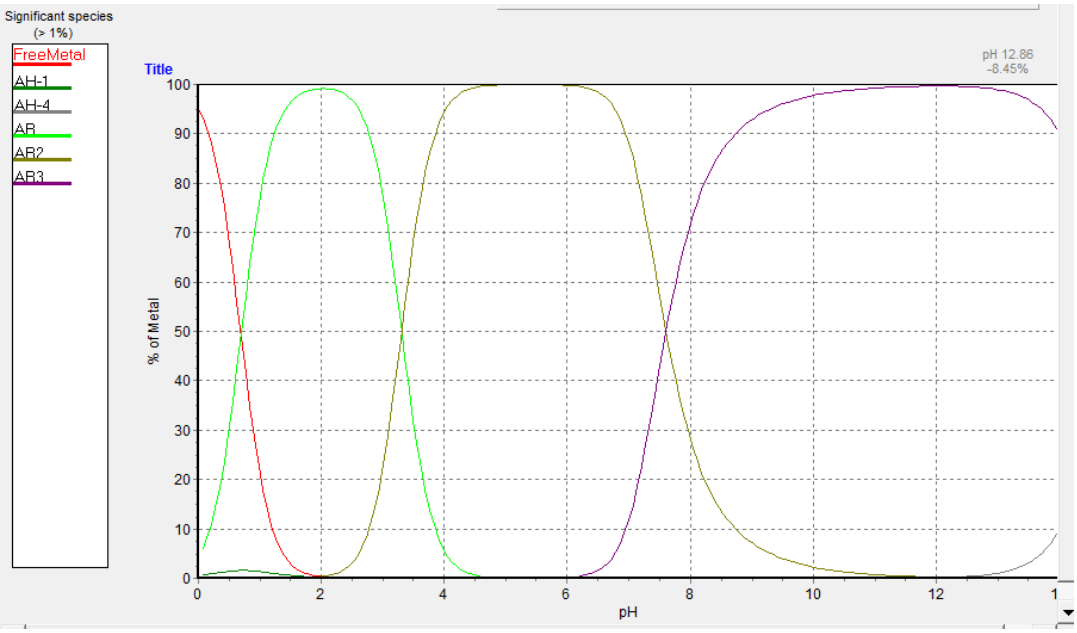
H-1, -2, -3, -4 are hydrolysis species



b. [Fe^{3+}] = 0.02 mM; [ligand] = 0.04 mM



c. [Fe^{3+}] = 0.02 mM; [ligand] = 0.06 mM



3. a. $Fe^{3+} + 3\,H_2L^- \rightleftarrows FeL_3^{6-} + 6H^+$

	$\log \beta$
$Fe^{3+} + 3\,L^{3-} \rightleftarrows FeL_3^{6-}$	51.0
$+\ 3(H_2L^- \rightleftarrows 3\times(L^{3-} + 2H^+))$	$3(-20.09)$
$Fe^{3+} + 3H_2L^- \rightleftarrows FeL_3^{6-} + 6H^+$	-9.27

$\beta = 10^{-9.27}$

$$\beta = \frac{[FeL_3^{6-}][H^+]^6}{[Fe^{3+}][H_2L^-]^3} \qquad \frac{\beta}{[H^+]^6} = \frac{[FeL_3^{6-}]}{[Fe^{3+}][H_2L^-]^3}$$

$pH = 7.4 = -\log[H^+]$

$[H^+] = 10^{-7.4}$

$$\frac{10^{-9.27}}{(10^{-7.4})^6} = 10^{35.13} = 1.35\times10^{35}$$

$+\beta$; $-\Delta G$ Thermodynamically favorable

b. $Fe^{3+} + 4OH^- \rightleftarrows Fe(OH)_4^-$

	$\log \beta$
$Fe^{3+} + 4H_2O \rightleftarrows Fe(OH)_4^- + 4H^+$	-21.71
$+\ 4(OH^- + H^+) \rightleftarrows 4H_2O$	$4\times(14)$
$Fe^{3+} + 4OH^- \rightleftarrows Fe(OH)_4^-$	34.29

$\beta = 10^{34.29}$

$$\beta = \frac{[Fe(OH)_4^-]}{[Fe^{3+}][OH^-]^4}$$

$pK_w = pH + pOH$

$14 = 7.4 + pOH$

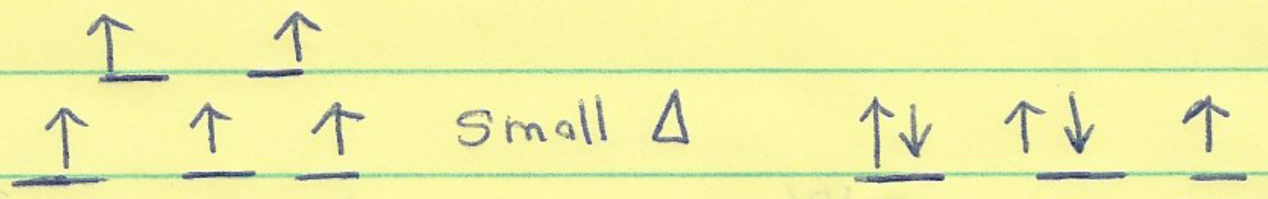
$6.6 = pOH = -\log[OH^-]$

$[OH^-] = 10^{-6.6}$

$$\beta\times[OH^-]^4 = \frac{[Fe(OH)_4^-]}{[Fe^{3+}]} = 10^{34.29}\times(10^{-6.6})^4 = \cancel{4.90\times10^{27}}\ 7.76\times10^{7}$$

$+\beta$; $-\Delta G$ Thermodynamically favorable

4. If neutral,
Mn: $4s^2 3d^5$



5 unpaired e^- | 1 unpaired e^-

⇒ The magnetic moment data does not support this.

$4.90 = \sqrt{n(n+2)}$

$4.90^2 = n(n+2)$

$0 = n^2 + 2n - 24.01$

$n = \frac{-2 \pm \sqrt{4 - 4(1)(-24.01)}}{2}$

$n = \frac{-2+10}{2} = 4$

for $[Mn(H_2O)_6]$

$2.83 = \sqrt{n(n+2)}$

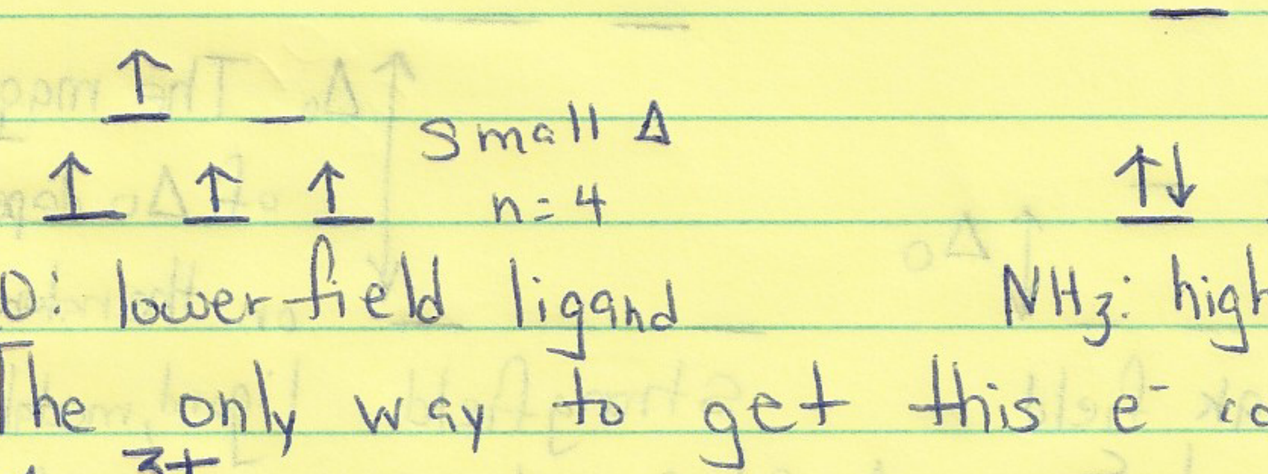
$0 = n^2 + 2n - 8$

$n = \frac{-2 \pm \sqrt{4 - 4(1)(-8)}}{2}$

$= -2 \pm \sqrt{4+32}$

$= -\frac{2+6}{2} = 2$

for $[Mn(NH_3)_6]$



H_2O: lower field ligand

NH_3: higher field ligand

The only way to get this e^- configuration is if Mn^{3+}

5 a. The en ligand decreases the $E^{0'}$ of Cu^{2+} meaning that it makes the thermodynamically favorable reduction, an unfavorable process. Therefore it would be harder to reduce Cu^{2+}.

b.

O_2 reduction $E'^0(V)$ values higher than Cu^{2+} + Cyt a_3

c. Higher values than $E'^0(V) = -0.114$

Ubiquinone, cyt b_6, cyt c_1, cyt c, cyt a, cyt a_3, O_2

$E'^0(V)$

d. $NAD^+ + H^+ + 2e^- \rightarrow NADH \quad -0.320$

$2[Cu(en)_2]^+ \rightarrow 2[Cu(en)_2]^{2+} + 2e^- \quad (\underline{0.114}) \times 2$

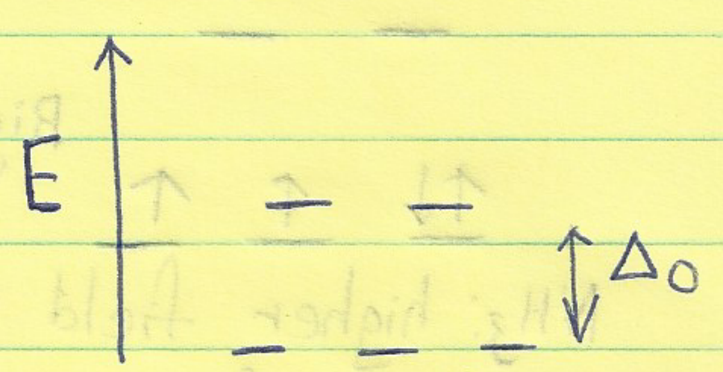
$-0.\cancel{206}092$

$\Delta G^\circ = -nFE^\circ$

$+ \quad -$

$\therefore$ Not favorable

6.

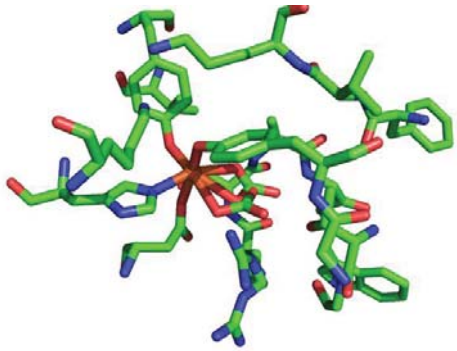


Δ_o The magnitude of Δ_o depends on the nature of ligand, metal, and geometry.

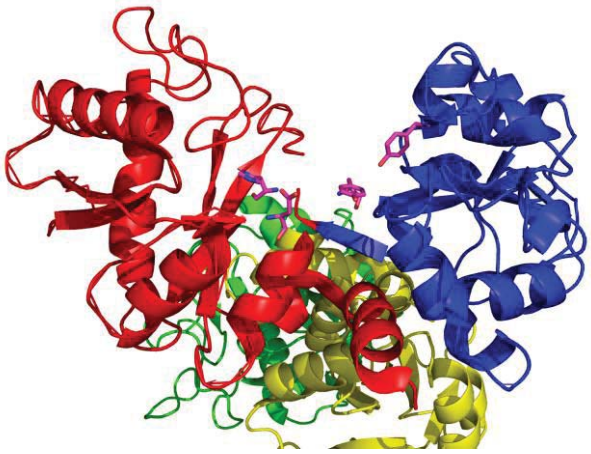
$\underline{\Delta_o} = E = h\nu = h\frac{c}{\lambda}$ $\quad A = \epsilon b c$; ϵ depends on population of excited e^-

Pymol:

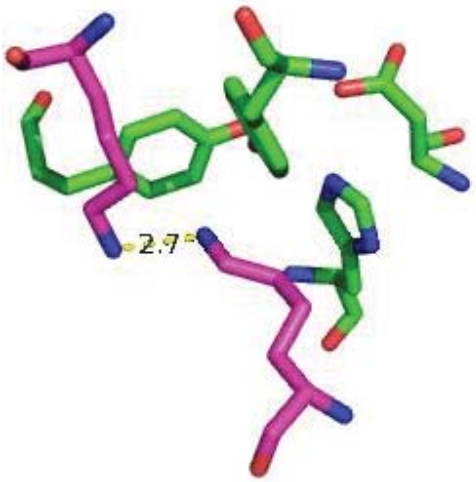
1. The metal binding site residues and nearby amino acids.



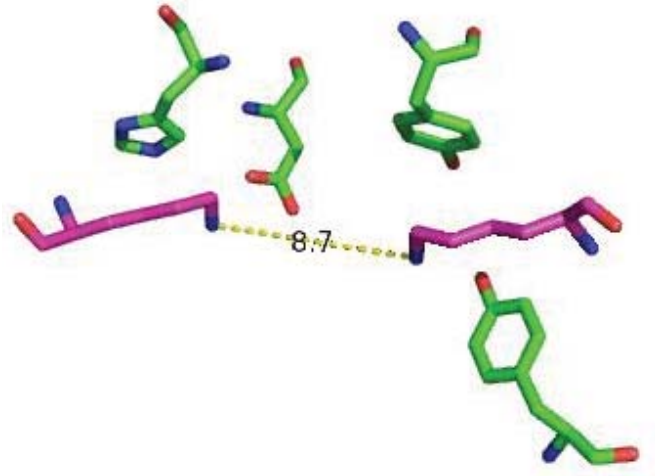
2. In this problem, we are exclusively focusing on the N-domain metal binding site, which typically binds Fe(III) at Asp63 and His249 of the N1 subdomain and at Tyr95 and Tyr188 of the N2 subdomain with the help of a carbonate synergistic anion. Metal binding brings the two subdomains close to one another and a hydrophobic box consisting of His249, Tyr95, and Tyr188 forms, which helps to bring Lys206 and Lys296 very close to one another. This results in deprotonation of one of the Lys due to the hydrophobic box favoring a chemical environment that is lower in charge. The Lys residues share the one remaining proton via a hydrogen bond.



1N84: In this structure, the Fe(III) is bound to all four protein residues at the binding site and carbonate. The two Lys residues come into very close and engage in a H-bond, which explains the very small distance between them. The domain is in a closed conformation.



2HAV: This is a structure where Fe(III) is not bound and so the two Lys residues are far apart and do not H-bond. The domain is in an open conformation.



3QYT- Fe(III), in this structure, is bound to only the tyrosine residues of the binding site and carbonate. A sulfate anion is also bound to the Fe(III), which inhibits the His and Asp from binding to the metal center. The sulfate anion must take up a significant amount of space and affect the electrostatics of the binding site to keep the two Lys residues even further away from one another than even in the apo form of the domain. An interesting thing is that this domain is in an open conformation but not as open as the apo form.