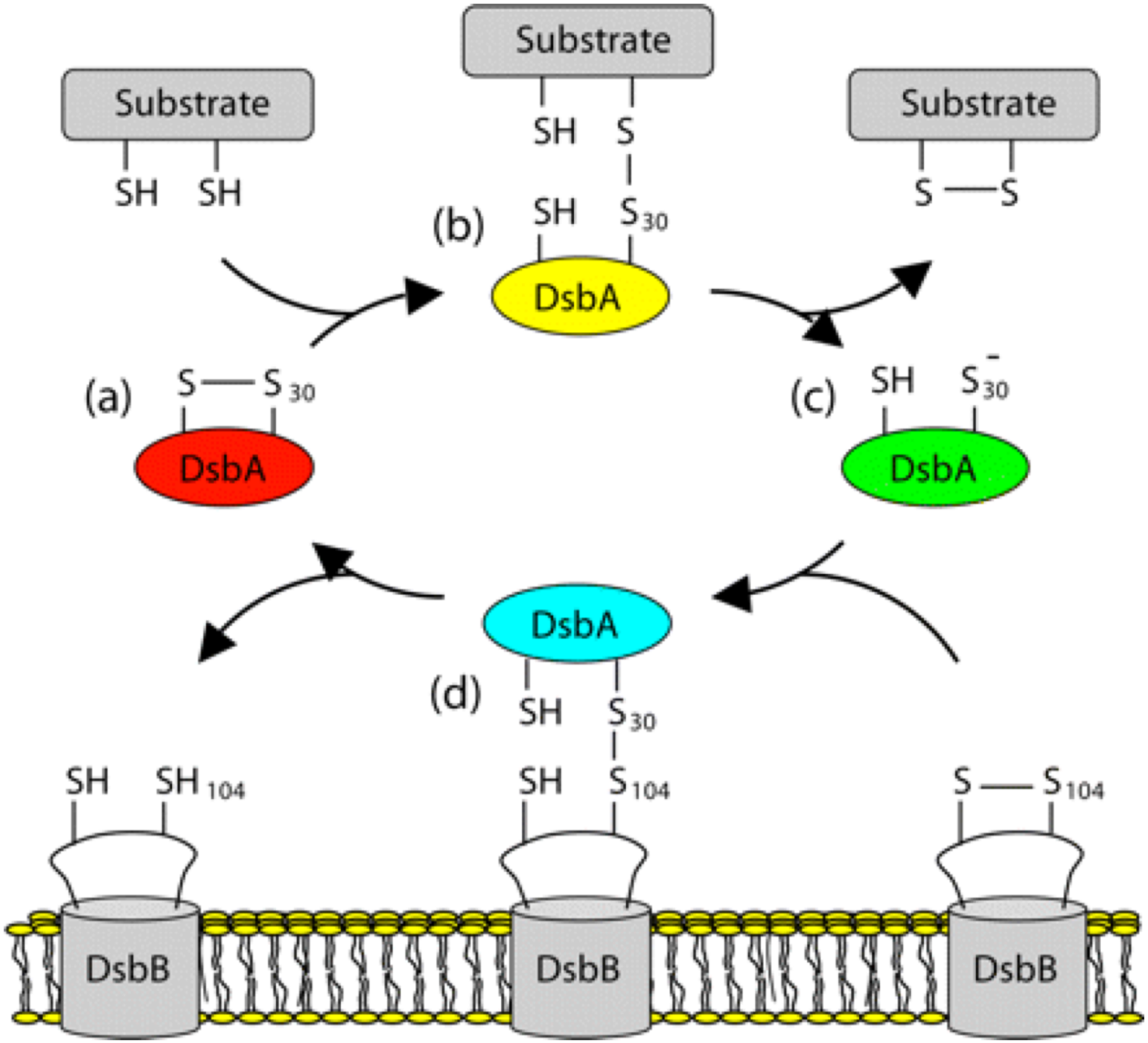
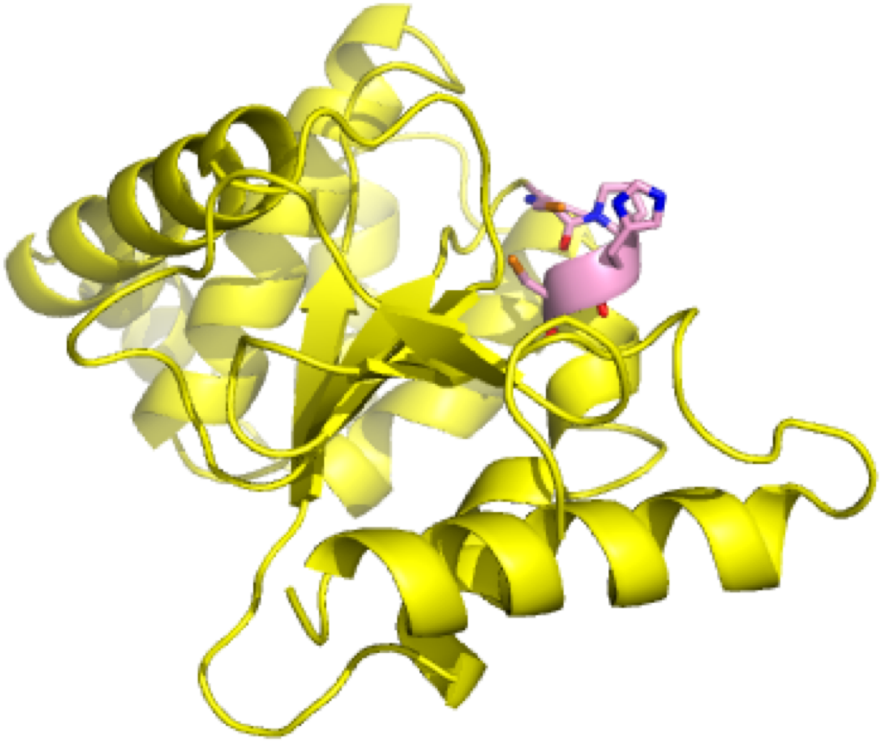

Substrate
SH SH
(a)
S — S 30
DsbA
Substrate
SH S
(b)
SH S30
DsbA
Substrate
S — S
(c)
SH S30
DsbA
DsbA
(d)
SH S30
SH SH 104
SH S104
S — S104
DsbB
DsbB
DsbB

DsbA – Helix Dipole Influence Cys30 pK_a



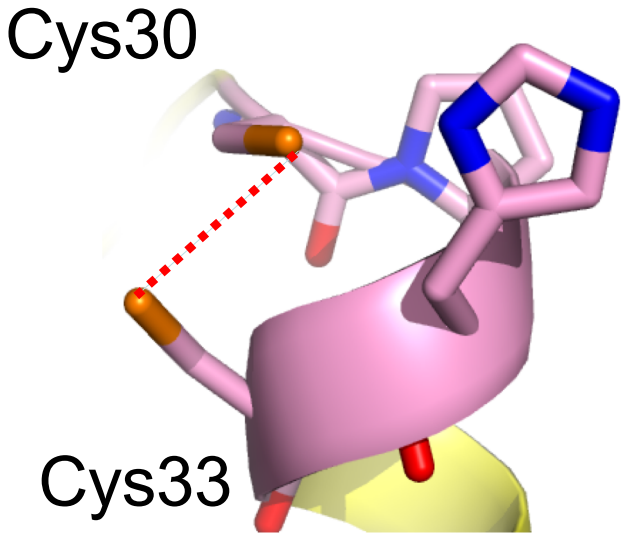
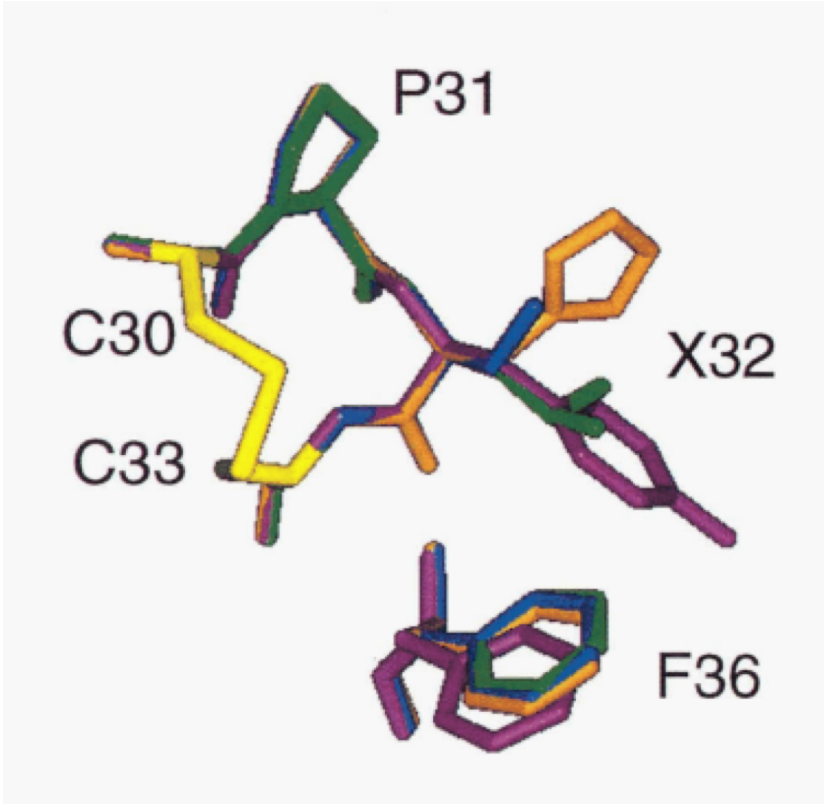


Table 3.3 Equilibrium constants and redox potentials for intramolecular disulfide bonds in proteins.[a,b]

	Protein	K_{ox}, M	$E^{o'}_{protein(ss)}$, V	*Reference*
	Wild Type DsbA			
1	(Cys30-Pro-His-Cys33)	8.1×10^{-5}	–0.120	16
		1.2×10^{-4}	–0.122	24
		1.31×10^{-4}	–0.125	22
2	DsbA(Gly-His)[c]	7.3×10^{-4}	–0.147	24
3	DsbA(Ala-Thr)[c]	1.4×10^{-3}	–0.156	24
4	DsbA(Pro-Tyr)[c]	1.8×10^{-3}	–0.159	24
5	DsbA(Gly-Pro)[c]	1.4×10^{-1}	–0.215	24
6	DsbA(Pro-Gly)[c]	5.9×10^{-4}	–0.145	24
7	DsbA(Ser-Val)[c]	9.0×10^{-4}	–0.150	27
8	DsbA(Ser-Phe)[c]	1.2×10^{-3}	–0.154	27
9	DsbA(Pro-Leu)[c]	1.6×10^{-3}	–0.158	27
10	DsbA(Leu-Thr)[c]	3.9×10^{-3}	–0.169	27
11	DsbA(Thr-Arg)[c]	6.8×10^{-3}	–0.176	27
12	DsbA(Pro-Pro)[c]	2.0×10^{-1}	–0.190	27
13	DsbA(F26L)	4.3×10^{-5}	–0.111	22
14	DsbB			
	(Cys41-Val-Leu-Cys44)	1.7×10^{-6}	–0.069	23
	(Cys104-Cys130)		–0.186	23
15	DsbC			
	(Cys98-Gly-Tyr-Cys101)	1.95×10^{-4}	–0.130	28
16	Wild Type Trx			
	(Cys32-Gly-Pro-Cys35)	11.3, 10	–0.271, –0.270	40,41
17	Trx(Ala-Thr)[c]	0.243	–0.222	40
18	Trx(Gly-His)[c]	0.228	–0.221	40
19	Trx(Pro-His)[c]	0.061	–0.204	40
20	Trx(Pro-Tyr)[c]	0.0273	–0.194	40
21	Grx1			
	(Cys-Pro-Tyr-Cys)		–0.233	15
22	Grx3			
	(Cys-Pro-Tyr-Cys)		–0.198	15

[a] K_{ox} for reaction of the dithiol form of the protein with GSSG.
[b] Relative to $E^{o'}_{GSH} = -0.240$ V.
[c] The indicated dipeptide sequence was substituted for the dipeptide between the two active-site cysteines of wild-type DsbA or Trx.

X32	E°’ (V)	pK_a C30
His	-0.122	3.4
Leu	-0.158	4.4
Tyr	-0.159	3.8
Ser	-0.172	4.9



Protein Science (1997), 6: 1893-1900.

Table 1. Standard Reduction Potential of Dioxygen Species in Water, pH 7, 25 °C[3]

reaction	$E°$ (V) vs NHE[a]
$O_2 + e^- \rightarrow O_2^{\bullet -}$	−0.18[b]
$O_2^{\bullet -} + e^- + 2H^+ \rightarrow H_2O_2$	+0.91
$H_2O_2 + e^- + H^+ \rightarrow H_2O + OH^\bullet$	+0.39
$OH^\bullet + e^- + H^+ \rightarrow H_2O$	+2.31
$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$	+0.28[b]
$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$	+1.35
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$	+0.81[b]

[a]Normal hydrogen electrode = NHE. [b]The standard state used here is unit pressure.

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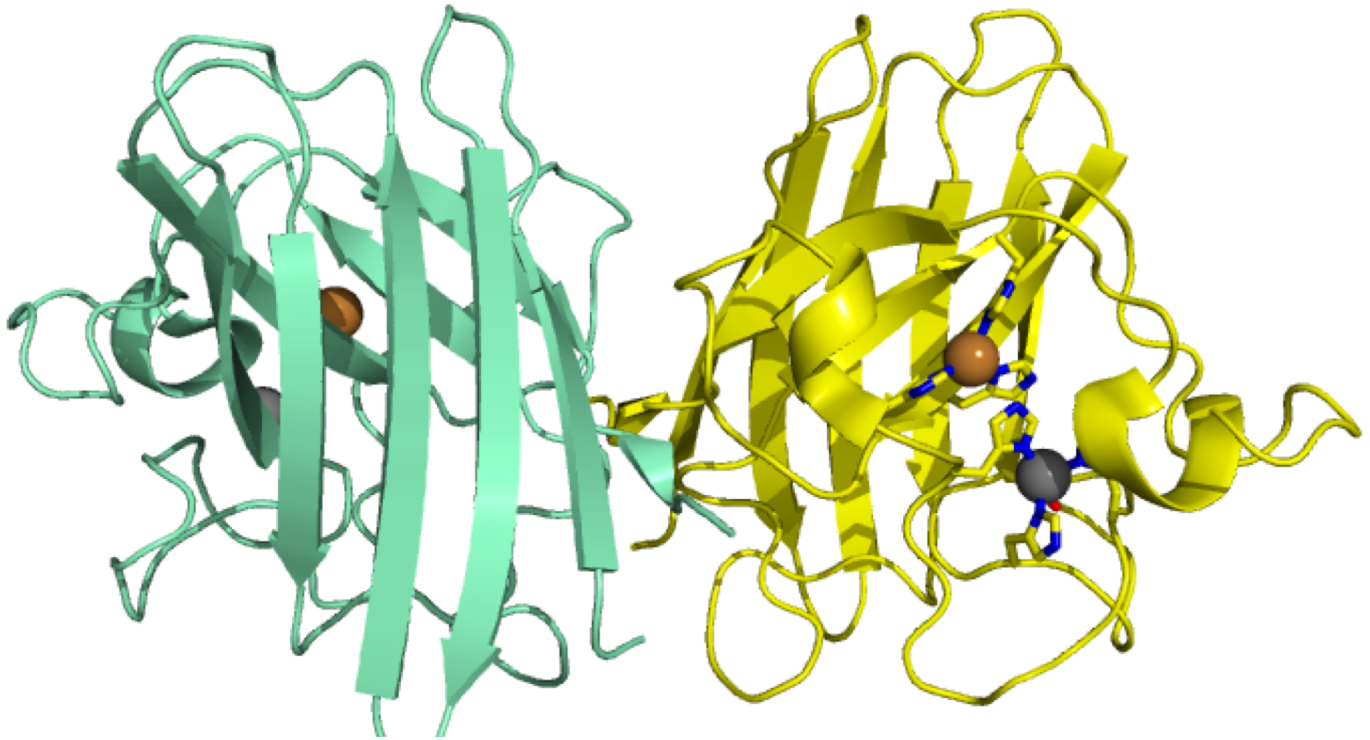
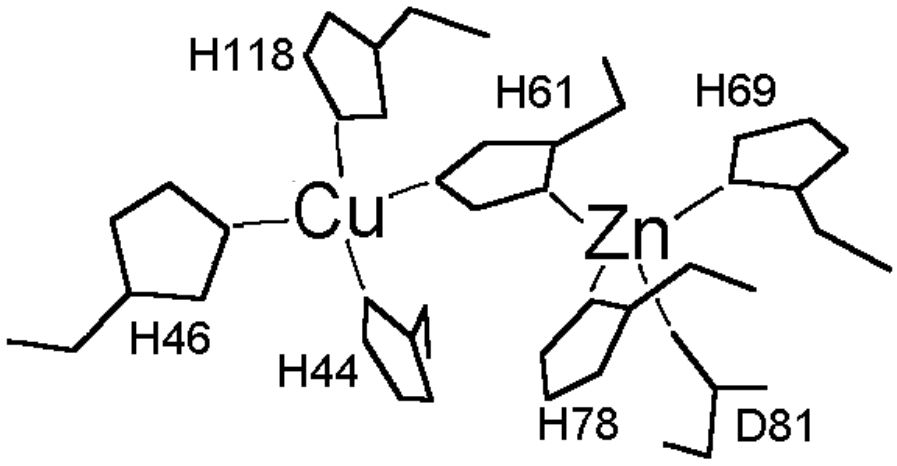
How to Catalyze Superoxide Disproportionation

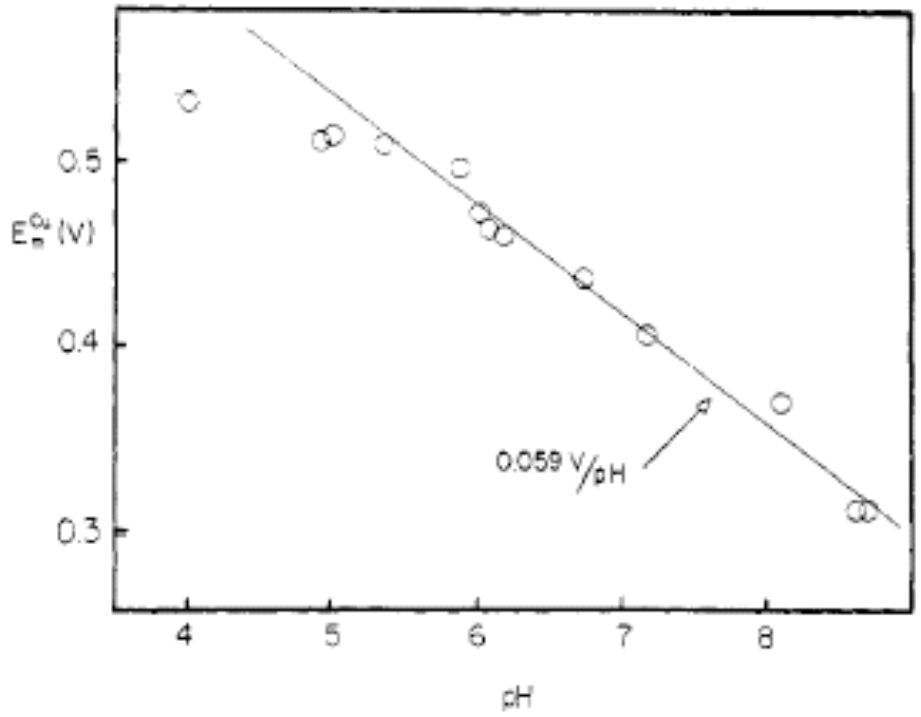
Ox + e^- → **Red**	$E_{red}^{\circ\prime} > -0.18$ V
$O_2^{\bullet-} \rightarrow O_2 + e^-$	$-E_{red}^{\circ\prime} = +0.18$ V
Ox + $O_2^{\bullet-}$ → **Red** + O_2	$E_{rxn}^{\circ\prime} > 0$ V
Red → **Ox** + e^-	$-E_{red}^{\circ\prime} > -0.91$ V
$O_2^{\bullet-} + 2\ H^+ + e^- \rightarrow H_2O_2$	$E_{red}^{\circ\prime} = +091$ V
Red + 2 H^+ + $O_2^{\bullet-}$ → **Ox** + H_2O_2	$E_{rxn}^{\circ\prime} > 0$ V

Structure of CuZnSOD



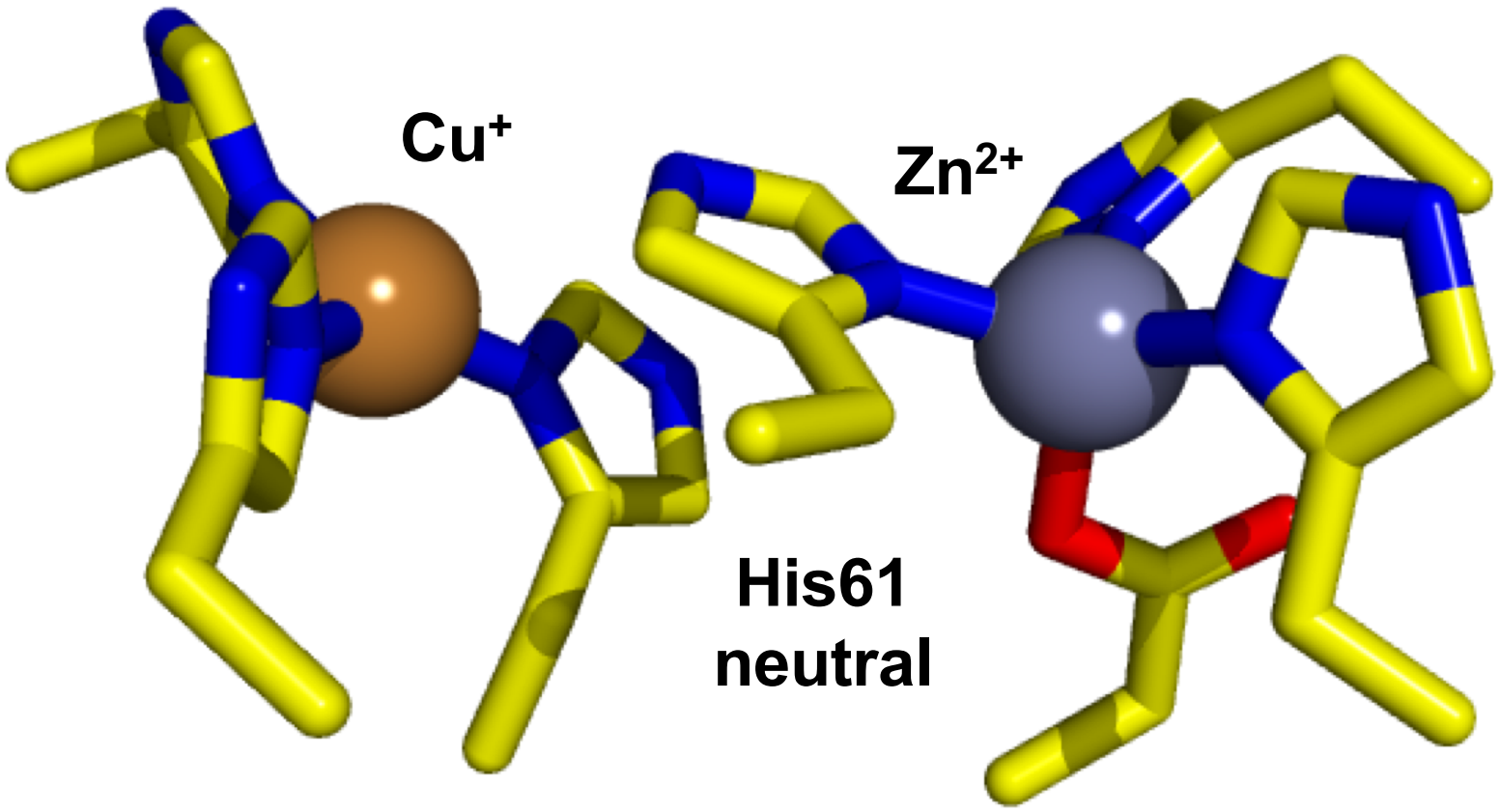


Reduction Potential Varies with pH

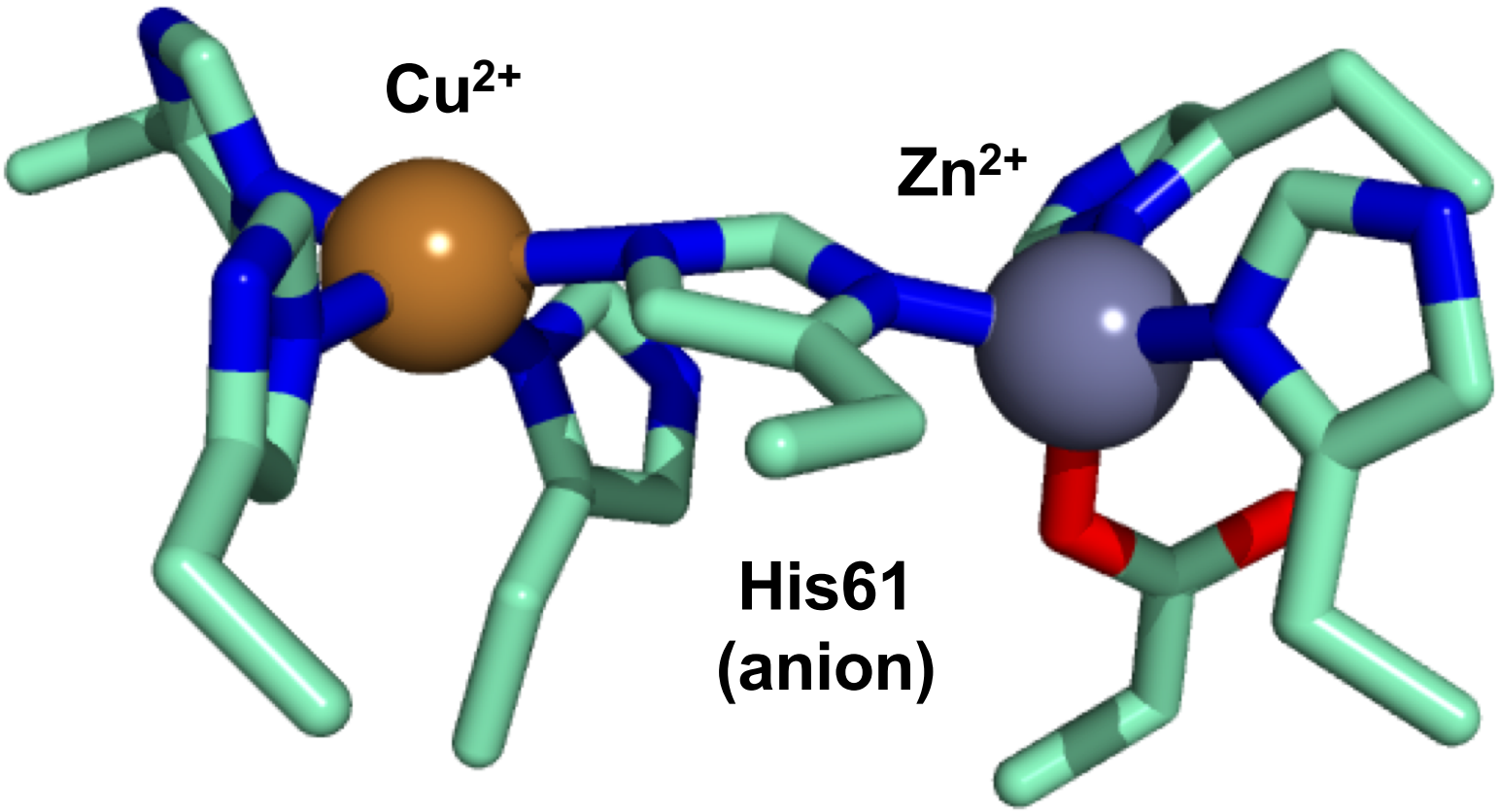


BIOCHEMISTRY, VOL. 12, NO. 24, 1973

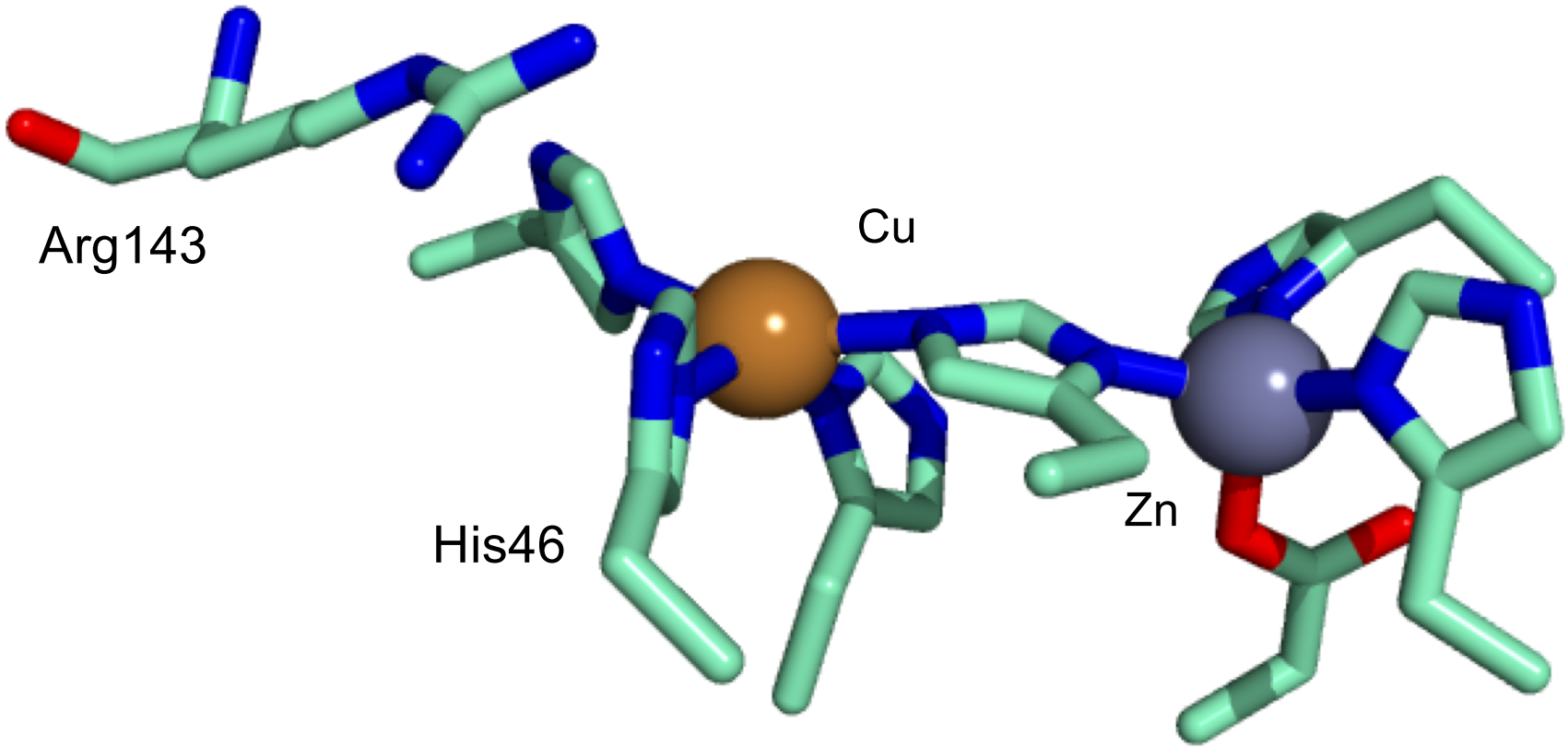
Reduction Changes Coordination



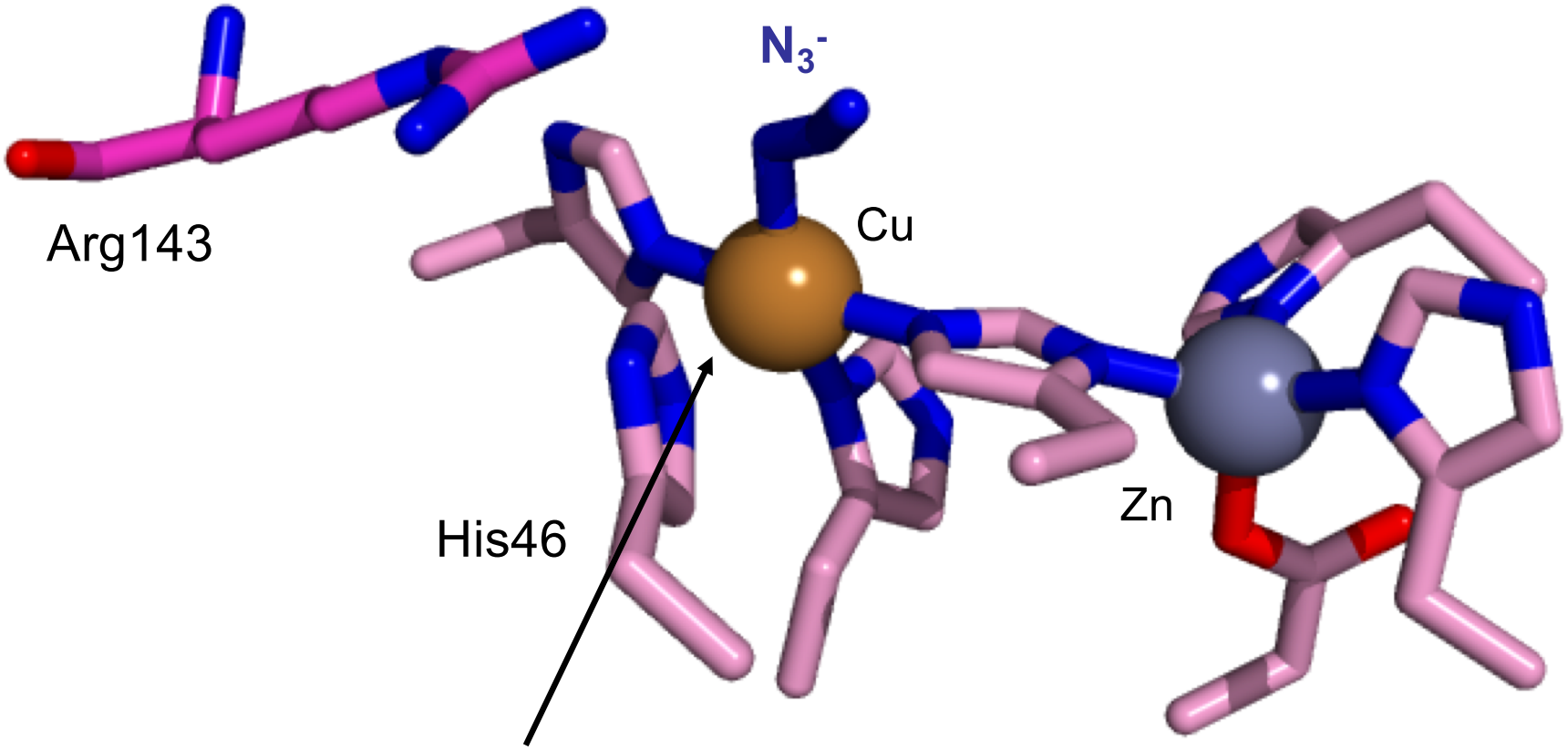
Reduction Changes Coordination

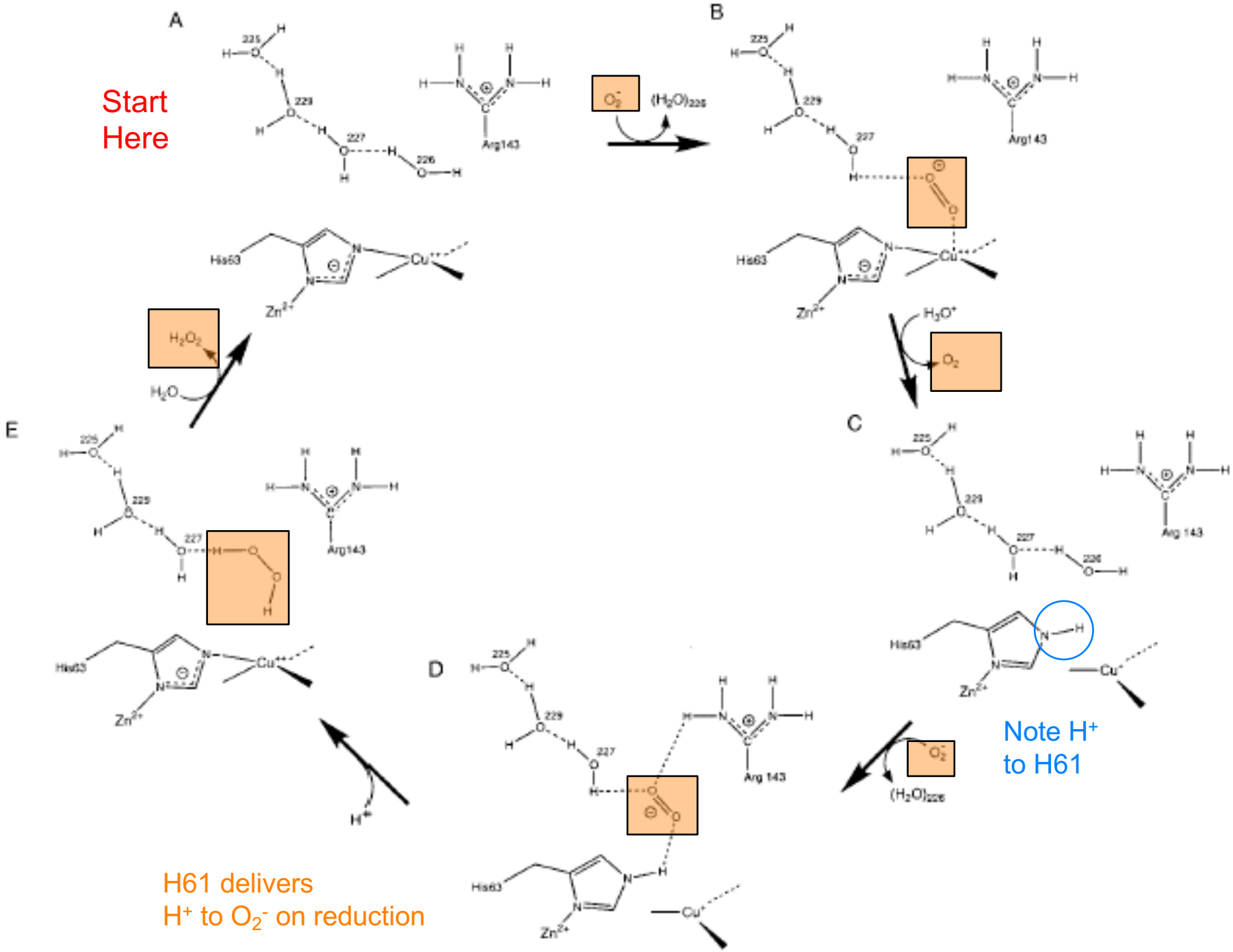


Azide Complex with CuZnSOD



Azide Complex with CuZnSOD

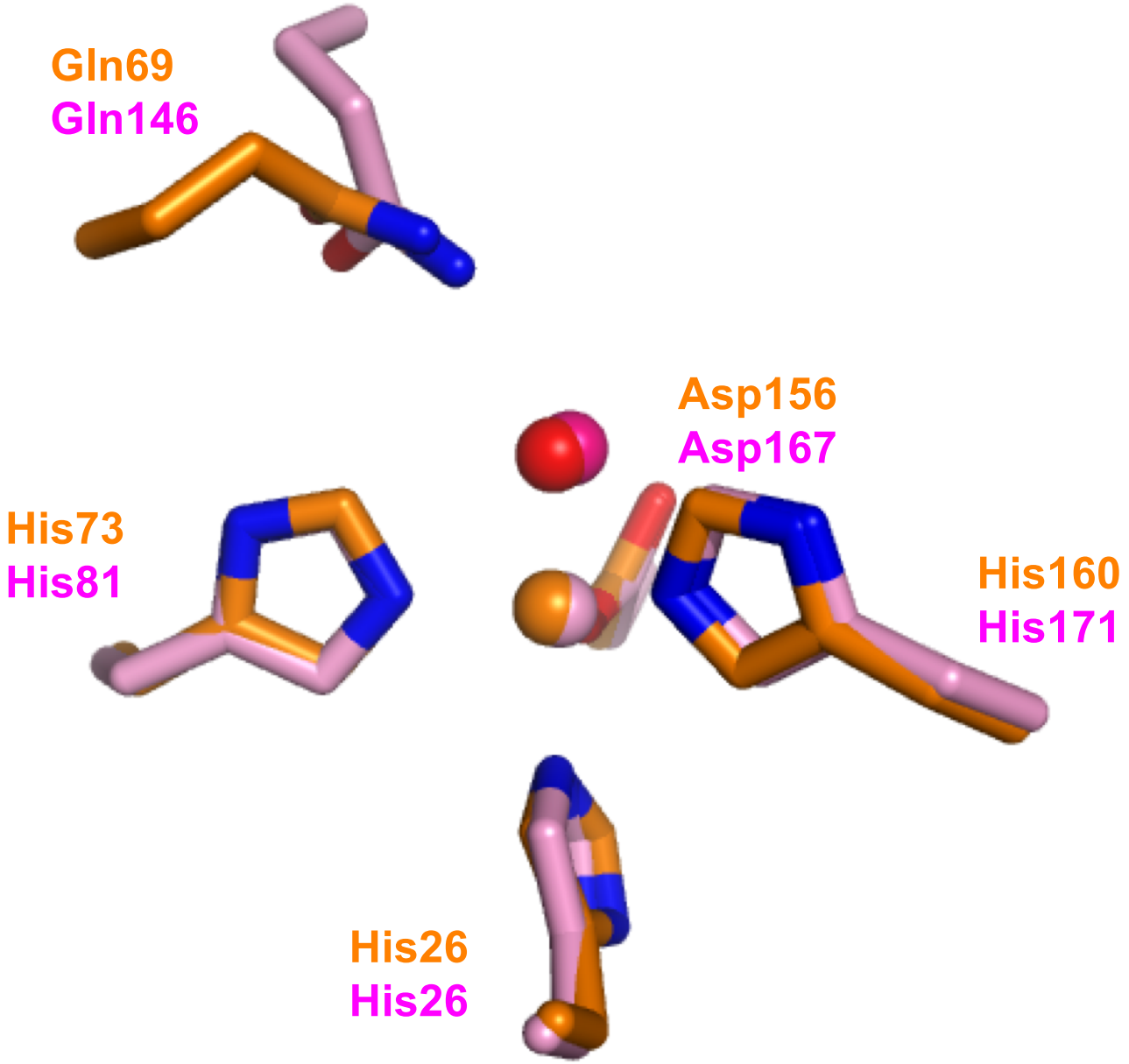



A
Start Here
B
C
D
E
Arg143
His63
Cu
Zn2+
H2O2
H2O
O2-
(H2O)226
H3O+
O2
H+
Note H+ to H61
H61 delivers H+ to O2- on reduction

Some reduction potentials

Half –reaction	**E° (V)**
$Fe(phen)_3^{3+} + e^- \rightarrow Fe(phen)_3^{2+}$	1.06
$Fe(H_2O)_6^{3+} + e^- \rightarrow Fe(H_2O)_6^{2+}$	0.77
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	0.36
$Fe(EDTA)^- + e^- \rightarrow Fe(EDTA)^{2-}$	0.10
$Fe(C_2O_4)_3^{3-} + e^- \rightarrow Fe(C_2O_4)_2^{2-} + C_2O_4^{2-}$	~0

Fe vs. Mn SOD


Gln69
Gln146
Asp156
Asp167
His73
His81
His160
His171
His26
His26

FeSOD Mechanism