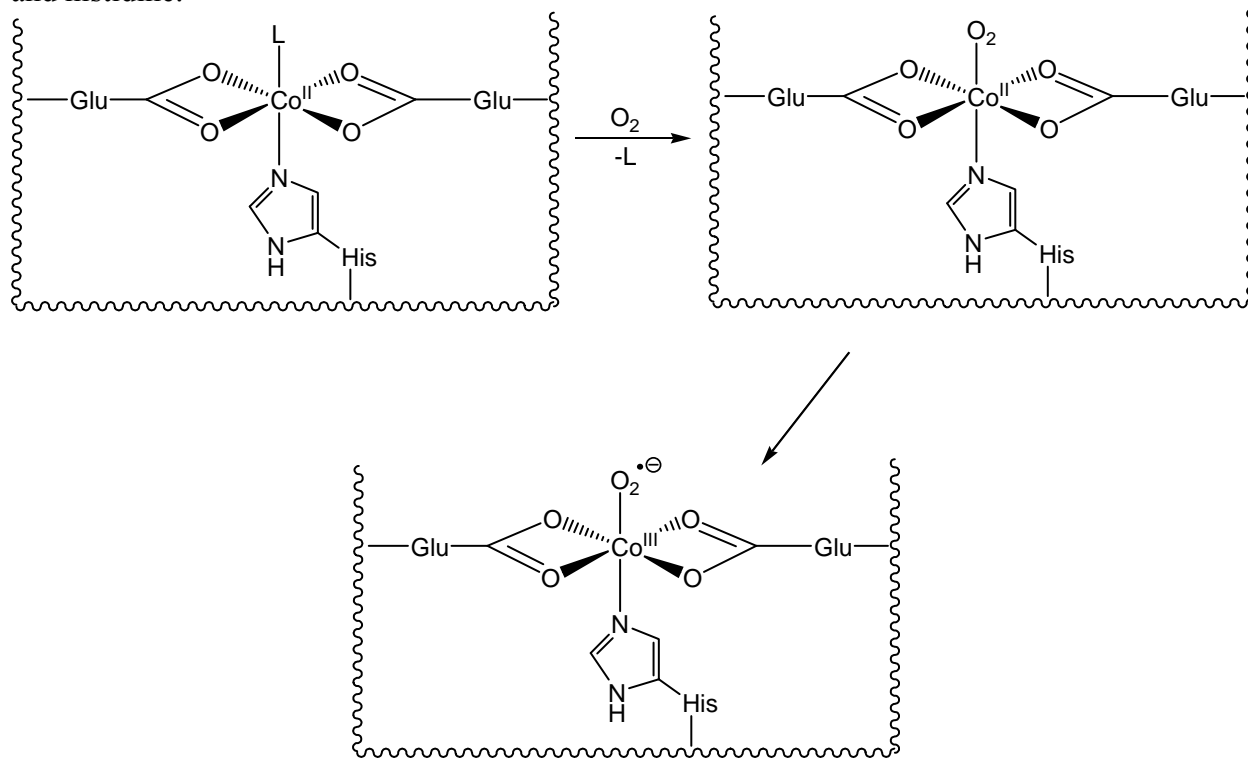


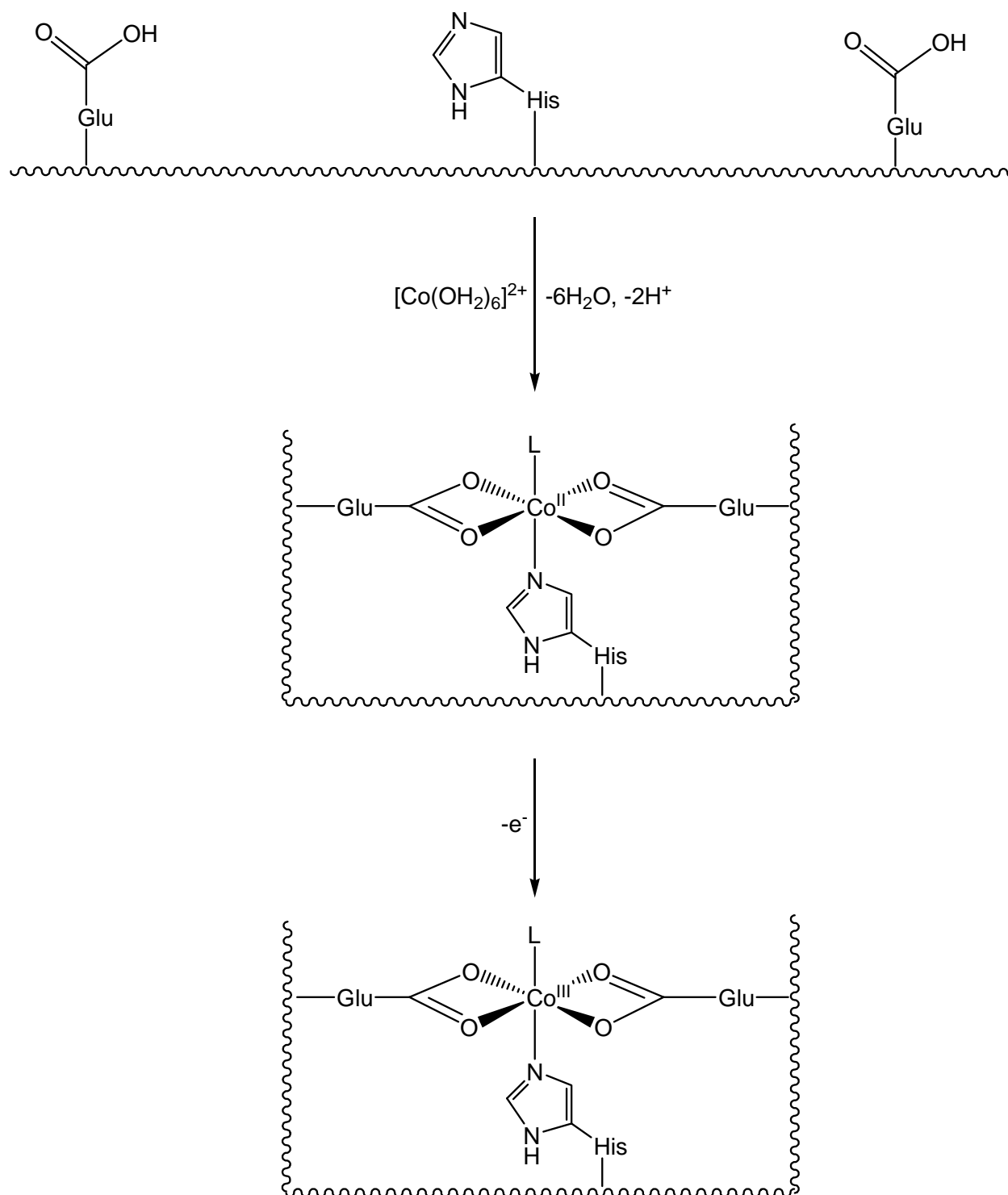
Chapter 8 Solutions

- 1) As a general strategy, the more labile Co^{2+} would be incorporated into a metalloprotein and subsequently be oxidized to the substitution inert Co^{3+} (see Supplemental 1).
- 2) Since reversible dioxygen binding would require the cobalt to toggle between 2+ and 3+, ligands which can bind both oxidation states should be employed, such as glutamate, aspartate and histidine.

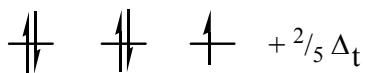
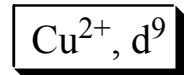


- 3) Ceruloplasmin catalyzes the reduction of O_2 to water, a four-electron process, while simultaneously oxidizing iron. As iron is oxidized from +2 to +3, it is loaded in to ferritin.
- 4) The rate constant for electron transfer between donor and acceptor in the absence of DNA will be different than in the presence of DNA. Presumably, the positively charged donor/acceptor complexes can associate with the negatively charged DNA. Consequently, electron transfer will take place through the polynucleotide rather than through solution. An experimenter could change the length of the DNA strand added or synthesize the DNA strand with the donor/acceptor pair covalently attached.
- 5) The metal is in a tetrahedral coordination environment, but upon protein unfolding, the metal is released into solution presumably to form the octahedral aqua complex (see Supplemental 2). Remember that $\Delta_t = \frac{4}{9} \Delta_o$. The change in LFSE for copper(II) going from a tetrahedral to octahedral geometry is half as exergonic as the same transformation for nickel(II). Thus, twice as much energy (such as heat) must be added to unfold a protein with copper(II) bound compared to a protein with nickel(II) bound.

Supplemental 1:

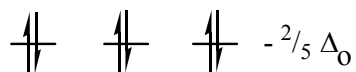
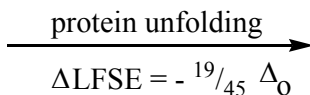


Supplemental 2:



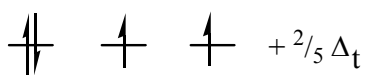
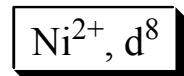
T_d

$$\begin{aligned} \text{LFSE} &= [4*(-^{3/5}) + 5*(+^{2/5})] \Delta_t \\ &= -^{2/5} \Delta_t \\ &= -^{8/45} \Delta_o \end{aligned}$$



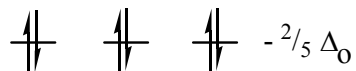
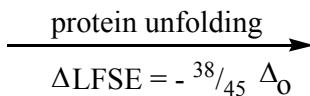
O_h

$$\begin{aligned} \text{LFSE} &= [6*(-^{2/5}) + 3*(+^{3/5})] \Delta_o \\ &= -^{3/5} \Delta_o \\ &= -^{27/45} \Delta_o \end{aligned}$$



T_d

$$\begin{aligned} \text{LFSE} &= [4*(-^{3/5}) + 4*(+^{2/5})] \Delta_t \\ &= -^{4/5} \Delta_t \\ &= -^{16/45} \Delta_o \end{aligned}$$



O_h

$$\begin{aligned} \text{LFSE} &= [6*(-^{2/5}) + 2*(+^{3/5})] \Delta_o \\ &= -^{6/5} \Delta_o \\ &= -^{54/45} \Delta_o \end{aligned}$$