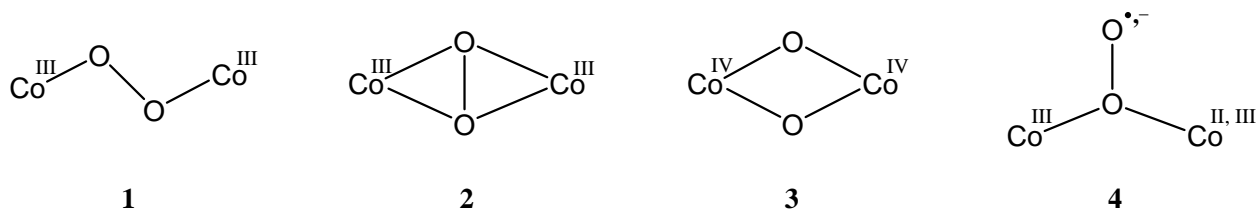# Chapter 11 Solutions

1) The O_2 ligand in $[(NC)_5Co-O_2-Co(CN)_5]^{6-}$ can adopt one of the following binding modes:

In modes **1** and **2**, the complex would be Co^{III}_2, whereas mode **3** would be Co^{IV}_2. Binding mode **4** could be either Co^{III}_2 or $Co^{II}Co^{III}$, depending on whether the terminal oxygen is an anion or radical anion, respectively. Given that there are 5 cyano ligands on each metal, the dicobalt(III) in binding mode **2** will probably not be able to reduce the dioxygen all the way to the bridging oxo in **3**. Also, octahedral Co(III) is an 18-electron species, so the 7-coordinate binding mode **2** will not be favored. Given the simplicity of the ligands bound to cobalt, and lack of asymmetry, binding mode **4** can be ruled out. Thus, $[(NC)_5Co-O_2-Co(CN)_5]^{6-}$ will have binding mode **1**, which formally contains a dicobalt(III) center. Note that cyano ligands are strong field. While the precursor complex $[Co(CN)_5]^{3-}$ will be low-spin d^7 and paramagnetic, the product will contain two low-spin d^6 metals and will be diamagnetic. To determine the binding mode of the O_2 ligand, an experimenter should use vibrational spectroscopy (IR and Raman).

2) Cytochromes P450 effect the activation of dioxygen by reduction. These enzymes catalyze the oxidation of alkanes to alcohols with concomitant production of water. Considering the oxidation states of the atoms involved in the reaction:
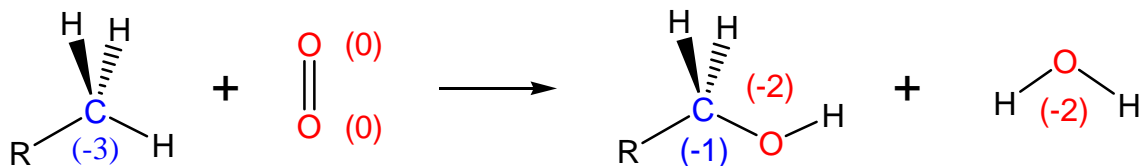
The oxygen atoms are reduced from an oxidation state of 0 to –2, consuming four electrons in the process. The carbon atom in the alkane is oxidized from –3 to –1, which releases two electrons. Thus, this reaction consumes a net two electrons. Since the iron is the catalytic site, it cannot have a net change in oxidation state. NADH is a hydride donor, but "H^-" could also be "$H^+ + 2e^-$". Essentially, NADH yields $NAD^+ + H^+ + 2e^-$ and completes the catalytic cycle.

3) For example, the reduction of $(CH_3)_2SO$ to $S(CH_3)_2$ occurs at +160 mV. However, the reduction of $(CH_3)_2SO_2$ to $(CH_3)_2SO$ occurs at –240 mV. An enzyme which can reduce a sulfoxide to a sulfide may not be able to reduce a sulfone to a sulfoxide, due to the difference in reduction potentials.

4) In addition to the native Cu_2Zn_2SOD (where each active site contains one zinc and one copper), an experimenter can obtain Cu_2Cu_2SOD or Zn_2Zn_2SOD. Since copper-only superoxide dismutases are known, one would expect Cu_2Cu_2SOD to be active. However, all known superoxide dismutases contain redox-active metals and this mechanism is a redox process. These considerations suggest that Zn_2Zn_2SOD will not be active. Zn_2Zn_2SOD has two d^{10} Zn^{2+} ions and will be diamagnetic (S=0). Cu_2Cu_2SOD can either have Cu^I_2 or Cu^ICu^{II} in each active site. The dicopper(I) active site contains two d^{10} metals and will be diamagnetic (S=0). The mixed-valent Cu^ICu^{II} active site will contain one d^{10} and one d^9 metal and will be paramagnetic $(S=^1/_2)$.