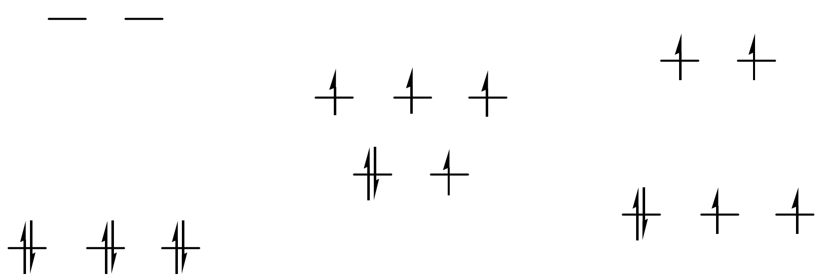
# Chapter 2 Solutions

1) a. $Fe^{3+}$, $d^5$
   b. $Co^{2+}$, $d^7$
   c. $Ca^{2+}$, $d^0$
   d. $Ru^{3+}$, $d^5$

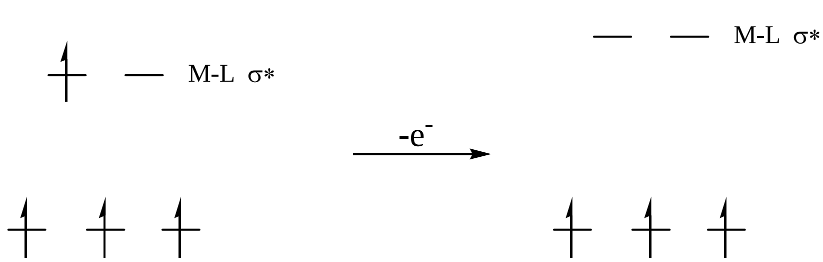
2) Hard metals prefer hard ligands and soft metals prefer soft ligands. Serine, threonine and tyrosine are hard ligands and would bind $UO_2^{2+}$, which is a hard ion. Cysteine and methionine are soft ligands and would bind $Hg^{2+}$, which is a soft ion. Glutamate, aspartate and histidine are intermediate ligands and could bind either a hard or a soft ion.

3)



$[Fe(CN)_6]^{4-}$ $[FeCl_4]^{2-}$ $[Fe(OH_2)_6]^{2+}$

4) $Cr^{2+}$ in an octahedral coordination environment has one electron in an orbital of metal-ligand antibonding character. Oxidation to $Cr^{3+}$ removes this electron. Thus, ligands bound to $Cr^{2+}$ are much more labile than those bound to $Cr^{3+}$. A potential mechanism for the reduction of the protein is as follows. Water readily dissociates from $[Cr(OH_2)_6]^{2+}$, allowing the complex to bind to the protein. The bound complex then reduces the protein, presumably via an inner-sphere mechanism, with chromium being oxidized from +2 to +3. With this change, the metal-protein bonds are strengthened due to the removal of the antibonding electron and the increased coulombic attraction (the metal becomes more positive and the protein becomes more negative).




$[Cr^{II}(OH_2)_6]^{2+}$ $[Cr^{III}L_n]^{m+}$

5) $Cu^{I}$ is $d^{10}$ and prefers a tetrahedral geometry; $Cu^{II}$ is $d^{9}$ and prefers a square-planar geometry. Ignoring electronic differences in the ligands, the complex that is easier to reduce will attain a tetrahedral geometry more readily. Reducing a complex from $Cu^{II}$ to $Cu^{I}$ will force one of the ligands to rotate out of plane to facilitate a tetrahedral geometry about the metal. The *tert*-butyl groups in the ligand for complex II are sterically more bulky than the methyl groups in the ligand for complex I. As a result, complex II will have a tetragonal geometry instead of square planar. This deviation towards a tetrahedral geometry will facilitate the reduction of complex II from $Cu^{II}$ to $Cu^{I}$, since the reorganization energy will be lower than for complex I. Thus, complex II will be easier to reduce than complex I.