Chapter 7 Solutions

1) RNA is stabilized by aquated magnesium ions, $[Mg(OH_2)_6]^{2+}$, not by naked ions. A complex with a size and coordination sphere similar to the magnesium complex, such as $[Co(NH_3)_6]^{3+}$, will also stabilize RNA. Conversely, Zn^{2+} stabilizes protein structures by binding directly to side chains or backbone functional groups. This requires the dehydration of $[Zn(OH_2)_6]^{2+}$, which is facilitated due to a ligand exchange rate of $2*10^7$ s^{-1}. Assuming (perhaps incorrectly) that the exchange rates for the hexaquacobalt(III) and hexammoniacobalt(III) are the same, $[Co(NH_3)_6]^{3+}$ is 13 orders of magnitude less labile than the aquated zinc. This complex will not serve as a substitute for zinc in the stabilization of protein structures.

2) Given $\Delta S = R*(-10.4 - 1.5*\ln[(i+1)(j+1)(k+1)]$, where R = 1.987 $cal*mol^{-1}*K^{-1}$, i = 2, j = 13, k =2

$\Delta S = 1.987\ cal*mol^{-1}*K^{-1} * [-10.4 - 1.5*\ln(3*14*3)] = -35.1\ cal*mol^{-1}*K^{-1}$

where

$\Delta G = -RT*\ln K = \Delta H - T\Delta S$

if we assume that there is no enthalpic change upon cross-link formation (not necessarily valid), we can set $\Delta H = 0$ and solve for K

$-RT*\ln K = -T\Delta S$, $R*\ln K = \Delta S$, $\ln K = \Delta S / R$, $K = \exp(\Delta S / R)$
$K = \exp(-35.1 / 1.987) = 2.13*10^{-8}$

3) Platination slightly unwinds DNA and induces a bend towards the major groove. DNA-binding proteins recognize structural features such as these. For a protein to recognize both platinated and cruciform DNA, the cruciform DNA must have structural motifs similar to the platinated DNA. Therefore, the activity of cisplatin must be due to some process which recognizes the structural change in the DNA, not the cisplatin itself.

4) Since metal-scavenging EDTA inhibits and additional zinc dramatically enhances the hormone-receptor interaction, the presence of zinc must be necessary for growth hormone to interact with the prolactin receptor. Mutation of His18, His21 or Glu17 in growth hormone to alanine weakens this interaction; mutation of His188 in the receptor produces the same effect. These results suggest that zinc binds to His18, His21 and Glu17 in growth hormone, and to His188 in the prolactin receptor.