1. a. Outline the preparation of the cis and the trans isomers of $[\text{Pt(NH}_3\text{)}(\text{NO}_2\text{)Cl}_2]^-$ given that the substituent trans effects are in the order of $\text{NO}_2^- > \text{Cl}^- > \text{NH}_3$.

b. Why is the trans effect of amines such as $\text{NH}_3$ so weak, while that of phosphines is strong?

\[
\begin{align*}
\text{trans isomer} & \\
\left[ \text{Cl}_2\text{PtCl}_2 \right]^2- & \xrightarrow{\text{NO}_2^-} \left[ \text{Cl}\text{PtNO}_2\text{Cl} \right]^2- \xrightarrow{\text{NH}_3} \left[ \text{Cl}\text{PtNH}_3\text{Cl} \right] \xrightarrow{\text{NO}_2^-} \left[ \text{Cl}\text{PtNO}_2\text{Cl} \right] \\
\text{cis isomer} & \\
\left[ \text{Cl}_2\text{PtCl}_2 \right]^2- & \xrightarrow{\text{NH}_3} \left[ \text{Cl}\text{PtNH}_3\text{Cl} \right] \xrightarrow{\text{NO}_2^-} \left[ \text{Cl}\text{PtNO}_2\text{Cl} \right] \xrightarrow{\text{NH}_3} \left[ \text{Cl}\text{PtNH}_3\text{Cl} \right] \\
\end{align*}
\]

b) Phosphines can back bond using the empty d-orbitals on P, thus stabilizes the trigonal bipyramidal transition state in which the phosphine and the entering group are both in an equatorial positions — the orientation required for substitution trans to P. $\text{NH}_3$ can not do this since it has no orbitals capable of π bonding.

2. $\text{MnO}_4^-$ is intensely purple, $\text{MnCl}_4^{2-}$ is a moderately colored green yellow, while aqueous $\text{Mn}^{2+}$ is a very light pink, almost colorless.

a. Show the electrons in the orbitals for each.

b. What is the ground state electronic state in each case?

c. Explain why these three compounds are so different in their appearance.

For $\text{MnO}_4^-$, electronic transitions are charge transfer transitions from low-lying filled ligand orbitals to empty d orbitals. No selection rules are broken, so transitions are very intense.

For $\text{MnCl}_4^{2-}$, d-d transitions are spin forbidden, so transitions are weak.

For aqueous $\text{Mn}^{2+}$, d-d transitions are spin forbidden and they are forbidden due to symmetry (9~79), i.e., they are extremely weak.
3. [Co(en)$_2$Cl]$^+$ is relatively stable in neutral aqueous solution, but reacts almost instantaneously at pH > 7 to yield [Co(en)$_2$(OH)Cl]$^+$, where en is the bidentate ligand ethylenediammine.
   a. Suggest a mechanism at pH > 7. 
   b. What is the rate determining step? Is this associative or dissociative in nature?
   c. Why is this reaction so much faster than the reaction at neutral pH. Be specific.

   a) \[ \text{Rbs dissociative} \quad \text{[Co(NH$_2$CH$_2$CH$_2$NH)Cl]$_2$} \rightarrow \text{[Co(en)\textit{NH$_2$CH$_2$CH$_2$NH\textit{Cl]}^+ + Cl}^- \]
   \[ \text{[Co(en)\textit{NH$_2$CH$_2$CH$_2$NH\textit{Cl]}^+ + H}_2\text{O} \rightarrow \text{[Co(en)\textit{NH$_2$CH$_2$CH$_2$NH\textit{Cl} (H}_2\text{O))]^+} \]
   \[ \text{[Co(en)\textit{NH$_2$CH$_2$CH$_2$NH\textit{Cl} (H}_2\text{O))]^+} \rightarrow \text{[Co(en)$_2$ Cl(OH)]^+} \]

   c) The dissociation is from a neutral complex rather than a positively charged complex, i.e. the dissociation is faster.

4. Consider the following reaction:

   \[ [\text{Co(NH$_3$)$_3$X}]^{2+} + [\text{Cr(H$_2$O)$_6$}]^{2+} \rightarrow [\text{Cr(H$_2$O)$_5$X}]^{2+} + [\text{Co(H$_2$O)$_6$}]^{2+} + 5\text{NH}_4^+ \]

   a. If X is N$_3^-$, what mechanism would you expect is most likely for the electron transfer reaction? Why?
   b. Using V$^{2+}$ as the reductant rather than Cr$^{2+}$ significantly slows the reaction. Why?

   a) The outer sphere mechanism is always possible. However, with X = N$_3^-$, the two minimum requirements for an inner sphere mechanism are present —
   1) There is a ligand (N$_3^-$) that can simultaneously bond to both metals and hence as a bridge;
   2) There is a labile reductant (Cr(H$_2$O)$_6^{2+}$) that can readily lose a ligand, making room for the bridging ligand.
In this case, the electron will be transferred from the 5$^*$ orbit on Cr$^+$ to a 5$^*$ orbital on Co, the most favorable transfer for an inner sphere mechanism. All of these suggest this reaction likely proceeds via an inner-sphere mechanism.

   b) [V(H$_2$O)$_6$]$^{2+}$ is substitutionally much more inert than [Cr(H$_2$O)$_6$]$^{2+}$, making the dissociation of [V(H$_2$O)$_6$]$^{2+}$ the rate-determining step.