Chapter 19

INTRODUCTION TO TRANSITION METAL COMPLEXES

Exercises

19.1  (a) Element belonging to the d-block, though usually Groups 3 and 12 are excluded.
      (b) Molecules or ions covalently bonded to a central metal ion.
      (c) Energy separation between different members of the metal’s d-orbital set when the metal ion is surrounded by a set of ligands.

19.3  The cyanide ligand stabilizes low oxidation states (in a similar manner to carbon monoxide) and also stabilizes normal oxidation states (as a pseudohalide ion).

19.5  \([\text{Pt(NH}_3\text{)}_4]^{2+}[\text{PtCl}_4]^{2-}\)

19.7  The geometric isomers are:

And for one of the geometric isomers, there are two optical (chiral) isomers.
19.9  (a) Ammonium pentachlorocuprate(II); (b) pentaammineaquacobalt(III) bromide; (c) potassium tetracarbonylchromate(-III); (d) potassium hexafluoronickelate(IV); (e) tetraamminecopper(II) perchlorate.

19.11  (a) [Mn(OH$_2$)$_6$](NO$_3$)$_2$.
(b) Pd[PdF$_6$].
(c) [CrCl$_2$(OH)$_2$]Cl·2 H$_2$O.
(d) K$_3$[Mo(CN)$_8$].

19.13  (a) The $d^6$ configuration in an octahedral field:

\[
\begin{array}{c}
1 \downarrow 1 \\
\text{high spin} \\
1 \downarrow 1 \downarrow \\
\text{low spin}
\end{array}
\]

(b) The $d^6$ configuration in a tetrahedral field:

\[
\begin{array}{c}
1 \downarrow 1 \\
\text{high spin} \\
1 \downarrow \\
\text{low spin}
\end{array}
\]

19.15  The largest value of $\Delta$ is for the cobalt(III) complex, the others being cobalt(II) because the splitting increases with increase in oxidation state. The smallest value is for cobalt(II) in a tetrahedral environment compared to the middle cobalt(II) in an octahedral environment because $\Delta_{\text{tet}}$ is only about four-ninths the value of $\Delta_{\text{oct}}$. 
19.17 (a) \([\text{ReF}_6]^2-\), because the heavier metal will have the greater crystal field splitting.
(b) \([\text{Fe(CN)}_6]^3-\), because the higher charge Fe(III) will have the greater crystal field splitting.

19.19 | Configuration | CFSE  \\---|----------------|
|\(d^0\) | \(-0.0 \Delta_{\text{tet}}\) \\
|\(d^1\) | \(-0.6 \Delta_{\text{tet}}\) \\
|\(d^2\) | \(-1.2 \Delta_{\text{tet}}\) \\
|\(d^3\) | \(-0.8 \Delta_{\text{tet}}\) \\
|\(d^4\) | \(-0.4 \Delta_{\text{tet}}\) \\
|\(d^5\) | \(-0.0 \Delta_{\text{tet}}\) \\
|\(d^6\) | \(-0.6 \Delta_{\text{tet}}\) \\
|\(d^7\) | \(-1.2 \Delta_{\text{tet}}\) \\
|\(d^8\) | \(-0.8 \Delta_{\text{tet}}\) \\
|\(d^9\) | \(-0.4 \Delta_{\text{tet}}\) \\
|\(d^{10}\) | \(-0.0 \Delta_{\text{tet}}\)

19.21 The optimum situation energetically is for the ion with the greater CFSE to occupy the octahedral sites. Thus the mixed metal oxide NiCr\(_2\)O\(_4\) will adopt the normal spinel structure, \((\text{Ni}^{2+})_4(\text{Cr}^{3+})_6\)O\(_4\), because the Cr\(^{3+}\) ion, having the higher oxidation state, will have a greater CFSE than that of the Ni\(^{2+}\) ion.

19.23 Balanced chemical equation:
\[
[\text{Ni(OH}_2)_6]^{2+}(aq) + 2 \text{det}(aq) \rightarrow [\text{Ni(det)}_2]^{2+}(aq) + 6 \text{H}_2\text{O}(l)
\]
The formation of this product will be favored as a result of the chelate effect—the increase in entropy from the increase in moles.

**Beyond the Basics**
19.25 The ligand tricyclohexylphosphine is probably too large for two of them to fit around an iron(III) in addition to the three chloro-ligands.

19.27 (a) \(M^{2+}\) should disproportionate as the sum of the potentials \((0.00 + 0.20)\) V is positive. The equation would be
\[
3 \ M^{2+}(aq) \rightarrow M(s) + 2 \ M^{3+}(aq)
\]
(b) $2 \text{M}^{2+}(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow 2 \text{M}^{3+}(aq) + \text{H}_2(g)$

To find the limit of spontaneity, we can set $E = 0$.

Because only the hydrogen-ion concentration varies, we can write a simplified Nernst equation:

$$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{1}{[\text{H}^+]^2} \right) = +0.20 \text{ V} - \frac{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}{2 \times (9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \ln \left( \frac{1}{[\text{H}^+]^2} \right)$$

$$[\text{H}^+] = 4.1 \times 10^{-4}$$

$pH = 3.38$

19.29 For zinc, with its filled $d^{10}$ orbitals, there is no crystal field stabilization energy; thus geometry is primarily determined by electron-pair repulsions.

For nickel, a square-planar geometry will maximize CFSE and it will enable some degree of $\pi$ bonding to occur between the part-empty $d$ orbitals of the nickel and the filled $d$ orbitals of the selenium.

19.31 (a) $[\text{Cr(OH}_2)_6]^{3+} \cdot 3\text{Cl}^-$, hexaaquachromium(III) chloride;
(b) $[\text{Cr(OH}_2)_5\text{Cl}]^{2+} \cdot 2\text{Cl}^-$, pentaaquachlorochromium(III) chloride;
(c) $[\text{Cr(OH}_2)_4\text{Cl}_2]^+ \cdot \text{Cl}^-$, tetraaquadichlorochromium(III) chloride.

19.33 Fluoride is a weaker field ligand than chloride. Thus the crystal-field splitting for the fluoro- compound will be less than that of the chloro- compound. To give a yellow-orange color, the chloro- compound must be absorbing in the blue (higher energy) portion of the spectrum. To give a blue color, the fluoro- compound must be absorbing in the red (lower energy) portion of the spectrum.