Problem Solutions

4.1 Hydrogen ions:
   (1) Arrhenius acid -- treats acids as substances that produce $\text{H}^+$ in solution
   (2) Brønsted-Lowry acid -- capable of transferring a proton ($\text{H}^+$)
   (3) Lewis acid -- $\text{H}^+$ is an electron pair acceptor

Hydroxide ions:
   (1) Arrhenius base -- treats bases as substances that produce $\text{OH}^-$ in solution
   (2) Brønsted-Lowry base -- capable of accepting a proton ($\text{H}^+$)
   (3) Lewis base -- $\text{OH}^-$ is an electron pair donor

4.2

4.3 The oxygen molecule has a number of lone pairs of electrons associated with it. One of these lone pairs can be donated to the central iron ion ($\text{Fe}^{2+}$) of the hemoglobin. The $\text{O}_2$, then, has served as an electron pair donor and is a Lewis base. The $\text{Fe}^{2+}$ is an electron pair acceptor and is a Lewis acid.

*4.4 This is an acid-base reaction under the Lewis system but not using the definitions of Arrhenius or Brønsted-Lowry.
4.5.  (a) Lewis base = hydroxide ion; Lewis acid = Zn$^{2+}$  
(b) Lewis base = water; Lewis acid = SO$_2$ (Sulfurous acid is often better described as SO$_2$·H$_2$O but also as OS(OH)$_2$, a form that would necessitate a rearrangement after the initial Lewis acid-base reaction.)  
(c) Lewis bases = two ammonias; Lewis acid = Ag$^+$

4.6.  
<table>
<thead>
<tr>
<th>Metal electrons</th>
<th>Ligand electrons</th>
<th>Total Electrons</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ir$^{3+}$ 74</td>
<td>6 Cl$^-$ 12</td>
<td>86</td>
<td>follows EAN</td>
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<tr>
<td>(b) Fe$^0$ 26</td>
<td>5 CO 10</td>
<td>36</td>
<td>follows EAN</td>
</tr>
<tr>
<td>(c) Cr$^0$ 24</td>
<td>6 CO 12</td>
<td>36</td>
<td>follows EAN</td>
</tr>
<tr>
<td>(d) Co$^{3+}$ 24</td>
<td>2 NH$_3$ 4</td>
<td>36</td>
<td>follows EAN</td>
</tr>
<tr>
<td></td>
<td>4 NO$_2^-$ 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) Ru$^{2+}$ 42</td>
<td>2 Cl$^-$ 4</td>
<td>52</td>
<td>does not follow EAN</td>
</tr>
<tr>
<td></td>
<td>3 PPh$_3$ 6</td>
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</table>

4.7.  
<table>
<thead>
<tr>
<th>Metal electrons</th>
<th>Ligand electrons</th>
<th>Total Electrons</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Cu$^{2+}$ 27</td>
<td>4 NH$_3$ 8</td>
<td>35</td>
<td>does not follow EAN</td>
</tr>
<tr>
<td>(b) Ag$^+$ 46</td>
<td>2 NH$_3$ 4</td>
<td>50</td>
<td>does not follow</td>
</tr>
<tr>
<td>(c) Fe$^{2+}$ 24</td>
<td>6 CN$^-$ 12</td>
<td>36</td>
<td>follows EAN</td>
</tr>
<tr>
<td>(d) Mo$^0$ 42</td>
<td>6 CO 12</td>
<td>54</td>
<td>follows EAN</td>
</tr>
<tr>
<td>(e) Fe$^{3+}$ 23</td>
<td>3C$_2$O$_4^{2-}$ 12</td>
<td>35</td>
<td>does not follow EAN</td>
</tr>
</tbody>
</table>

4.8. Coulomb's law says that the potential energy (PE) is equal to $Q_1Q_2/r$. If $r$ is infinite, then the PE is zero. But we also recognize that the proton and the electron are of opposite charges and, therefore, the net energy will be negative for finite values of $r$. When the proton and electron are merged to form a hydrogen atom, the distance $r$ between the two particles decreases and the value of $Q_1Q_2/r$ becomes more and more negative. As the energy of the proton-electron system becomes more negative, it follows that the system must be releasing energy to the environment.

4.9. Coulomb's law says that the potential energy (PE) is equal to $Q_1Q_2/r$. If $r$ is infinite, then the PE is zero. But we also recognize that the two electrons have the same charge and, therefore, the net energy will be positive for finite values of $r$. When the two electrons are placed side by side, the distance $r$ between the two particles decreases and the value of the potential energy ($= Q_1Q_2/r$) becomes more and more positive.

4.10. Note that both of these orbitals are located in xy plane. However, the lobes of the 3d$_{xy}$ point in between the axes whereas those of the 3d$_{x^2-y^2}$ point right along them. (The dashed lines are nodes.)
4.11. (nodes = dashed lines)

*4.12.

*4.13.

*4.14. All six of the dependent d orbitals have the same shape but different orientations in space. The 3d<sub>z</sub> orbital is a linear combination of the dependent 3d<sub>x^2-y^2</sub> and 3d<sub>x^2</sub> orbitals. Both of these latter orbitals look exactly like the other four dependent d orbitals but the 3d<sub>x^2-y^2</sub> points along the z and y axes while the 3d<sub>x^2</sub> points along the z and x axes. When these two orbitals are combined, the resulting 3d<sub>z</sub>
orbital has twice as much probability of finding an electron along the z axis as it does along either the x or the y axis.

4.15. The six independent orbitals are classified as dependent because any one of them can be written as a linear combination of the others. If one writes a linear combination of the 3d_{z^2} and 3d_{x^2-y^2} orbitals to make the 3d_{z^2} orbital, the resulting five orbitals are no longer dependent but independent.

4.16. Since each of the 3p orbitals points along a given x, y, or z Cartesian axis, each would be equally affected by the two ligands of the octahedral field it would encounter. Therefore, since each 3p orbital would be affected in the same way, these orbitals would remain degenerate in such a field.

*4.17.  
(a)

(b) The 3dxz orbital points in between the x and z axes and therefore avoids, to some extent, the ligands located on these axes. On the other hand the 3dz^2-x^2 orbital points directly along the x and z axes and therefore points directly at the ligands. Given these relative positions, it is not surprising that a d electron prefers not to occupy the 3dz^2-x^2 orbital. That is, the 3d z^2-x^2 orbital is of higher energy.

4.18. During stages I to III of the construction of an octahedral field about a metal ion, the system is becoming more and more ordered. (The twelve electrons, scattered originally an infinite distance from the metal, are brought in and organized to form the field.) A more ordered system is less random and therefore of lower entropy. It follows that entropy decreases during the construction of the field about the metal ion. If ΔS is negative for this process, ΔH must be negative in order to make ΔG negative. Recall that a reaction or process is spontaneous only if ΔG, which is equal to ΔH-TΔS, is negative.

*4.19. Given that the 3d_{x^2} orbital is a linear combination of the 3d_{x^2-y^2} and 3d_{x^2-y^2} orbitals which are identical in shape and relative orientation (that is, they all point directly at the ligands of the octahedral field) to the 3d_{x^2-y^2} orbital, all of these orbitals (including the 3d_{x^2} and 3d_{x^2-y^2}) should be degenerate in such a crystal field.

4.20. In a tetragonal compression along the z axis, any orbital with a z component will be destabilized. Since the ligands along the x and y axis move out slightly, any orbital with an x or y component will be stabilized.
4.21. (a) The $3d_z$ orbital will point directly at the two ligands along the z axis of the linear field. The $3d_{yz}$ and $3d_{xz}$ ligands point in between the z axis and either the y or the x axis and therefore are destabilized somewhat. The $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals, being fully in the xy plane do not point at the z axis ligands at all are the most stabilized.

(b) To calculate the position of the barycenter, one assigns the position roughly between the first and second levels and uses the relationship that

$$E_{\text{stabilization}} = E_{\text{destabilization}}$$

$$2(0.74\Delta - x) = 2x + 1(0.91\Delta + x)$$

$$1.48\Delta - 2x = 3x + 0.91\Delta$$

$$0.57\Delta = 5x$$
\[ x = 0.11\Delta \]
4.22.  

\[ \Delta_o \]

\[ \text{barycenter} \]

\[ 0.656\Delta_o - x \]

\[ 0.086\Delta_o \]

\[ E_{\text{stabilization}} = E_{\text{destabilization}} \]

\[ 1(0.656\Delta_o - x) + 2[(0.656\Delta_o - x) + (0.086\Delta_o)] = x + (\Delta_o + x) \]

\[ 2.14\Delta_o - 3x = 2x + \Delta_o \]

\[ 1.14\Delta_o = 5x \]

\[ x = 0.228\Delta_o \text{ or } 0.23\Delta_o \]

4.23. By analogy to other fields, the crystal field splitting energy of the 3p orbitals in a square planar field can be labeled as \( \Delta_{sp} \). In order for the energy of stabilization to be equal to the energy of destabilization, the 3px and 3py orbitals (which point directly at the ligands in the xy plane) would have to be destabilized by \( \frac{1}{3}\Delta_{sp} \) while the 3pz orbital (which does not point at any ligand) would be stabilized by \( \frac{2}{3}\Delta_{sp} \).

4.24.  

Given that the barycenters of both the \( e_g \) and \( t_{2g} \) sets stay constant, there is no net gain or loss of energy when the \( t_{2g} \) set is split by the tetragonal elongation. In the \( e_g \) set, however, two electrons are stabilized by the indicated amount while only one electron is destabilized by that amount. The result is an additional energy of stabilization as indicated in the above figure.
4.25. (a) Since a cubic field is two tetrahedral fields superimposed upon each other (as shown in Figure 4.7), its crystal field splitting diagram is qualitatively the same as that for a tetrahedral field. (b) As shown in Figure 4.8, the 3d_{xy} orbital points towards four of the edges of the cube and therefore is closer to the ligands than the 3d_{x^2 - y^2} orbital that points towards the centers of four of the faces of the cube. It follows that the 3d_{xy} and similar orbitals are destabilized while the 3d_{x^2 - y^2} (and the similar 3d_{z^2}) orbital is stabilized.


*4.27. (a) Both the 3d_{x^2 - y^2} and 3d_{z^2} orbitals point directly at ligands and therefore are destabilized. (The 3d_{x^2 - y^2} points at four ligands and is more destabilized than the 3d_{z^2} which points at only one.) The 3d_{xy}, 3d_{yz}, and 3d_{xz} orbitals point in between the ligands and are stabilized. (The 3d_{yz} and 3d_{xz} orbitals have components along the z-axis, where there is only one ligand, and therefore are more stable than the 3d_{xy} orbital.)

\[
\begin{align*}
3d_{xy} & \quad 3d_{yz} & \quad 3d_{xz} \\
\Delta_c & \quad & \\
3d_{x^2 - y^2} & \quad 3d_{z^2} & \quad 3d_{2 - y^2}
\end{align*}
\]

\[
\begin{align*}
& \quad 2/5 \Delta_c \\
& \quad 3/5 \Delta_c \\
3d_{z^2} & \quad 3d_{x^2 - y^2}
\end{align*}
\]

(b) 
\[
E_{\text{stabilization}} = E_{\text{destabilization}}
\]

\[
2[(0.37 \Delta + (0.17 \Delta - x)) + (0.17 \Delta - x)] = x + (0.83 \Delta + x)
\]

\[
1.25 \Delta - 3x = 2x + 0.83 \Delta \\
0.42 \Delta = 5x \\
x = 0.084 \Delta
\]

Therefore, the barycenter sits about midway between the 3d_{z^2} and 3d_{xy} orbitals.
4.28. The 3d_{x^2-r^2} and 3d_{x^2-y^2} orbitals point directly at the ligands located along the z axis and therefore are the most destabilized. The 3dx and 3dx orbitals do have a z-component but do not point directly at the ligands. The 3dy and 3dy orbitals do not have a z-component and do not point directly at the ligands and therefore are stabilized the most.

4.29.

$$E_{\text{stabilization}} = E_{\text{destabilization}}$$

$$2(0.19\Delta + x) + 2x = 0.79\Delta - x$$

$$0.38\Delta + 4x = 0.79\Delta - x$$

$$5x = 0.41\Delta$$

$$x = 0.082\Delta$$

4.30. Tetrahedral complexes are almost always high spin because $\Delta_t$ is about half the magnitude of $\Delta_o$ and almost always less than the pairing energy, P.

4.32. High- and low-spin tetrahedral complexes

- $d^3$: $e^3$ and $e^2t^1_2$
- $d^4$: $e^4$ and $e^2t^2_2$
- $d^5$: $e^4t^1_2$ and $e^2t^3_2$
- $d^6$: $e^4t^2_2$ and $e^3t^3_2$

4.33. Only $d^8$ would have high- and low-spin possibilities. $d^7$ would involve the sum of the top-most energy split and the middle-level split and so does not meet the condition set in the statement of the problem.
4.34. $d^5$ and $d^6$ could also have high- and low-spin possibilities but they do not satisfy the condition of the problem statement.

4.35. Cr$^{3+}$ 3; Co$^{2+}$ 7; Pd$^{4+}$ 6; Pt$^{2+}$ 8; Cu$^{2+}$ 9

4.36. (a) $d^4$, octahedral, low-spin (2) (d) $d^7$, octahedral, high-spin (3)
       (b) $d^6$, tetrahedral, high-spin (4) (e) $d^2$, cubic (2)
       (c) $d^9$, square planar (1) (f) $d^8$, octahedral with tetragonal elongation (2)

4.37. $d^3$ CFSE = $3(2/5 \Delta_o) = 6/5 \Delta_o$
       $d^8$ CFSE = $6(2/5 \Delta_o) - 2(3/5 \Delta_o) = 6/5 \Delta_o$

4.38. $d^5$ high-spin $3(2/5 \Delta_o) - 2(3/5 \Delta_o) = 0$
       low-spin $5(2/5 \Delta_o) - 2P = 2 \Delta_o - 2P$

       $d^6$ high-spin $4(2/5 \Delta_o) - 2(3/5 \Delta_o) = 2/5 \Delta_o$
       low-spin $6(2/5 \Delta_o) - 2P = 12/5 \Delta_o - 2P$

       $d^7$ high-spin $5(2/5 \Delta_o) - 2(3/5 \Delta_o) = 4/5 \Delta_o$
       low-spin $6(2/5 \Delta_o) - 1(3/5 \Delta_o) - P = 9/5 \Delta_o - P$

4.39. (a) $[\text{Fe(CN)}_6]^{4-}$ Fe$^{2+}$ $d^6$ low-spin: CFSE = $12/5 \Delta_o - 2P$
       (low-spin chosen because the cyanide ligand is so high in the spectrochemical series)

       (b) $[\text{Ru(NH}_3)_6]^{3+}$ Ru$^{3+}$ $d^5$ low-spin: CFSE = $2 \Delta_o - 2P$
       (low-spin because ammonia ligand is moderately high in the series and Ru$^{3+}$ is large and highly charged leading to a large crystal field splitting energy)

       (c) $[\text{Co(NH}_3)_6]^{3+}$ Co$^{3+}$ $d^6$ low-spin: CFSE = $12/5 \Delta_o - 2P$
       (low-spin because ammonia ligand is moderately high in the series and Co$^{3+}$ is highly charged leading to a moderately high crystal field splitting energy)

4.40. (a) $[\text{Fe(H}_2\text{O})_6]^{3+}$ Fe$^{3+}$ $d^5$ water is midway in the spectrochemical series while Fe$^{3+}$ is fairly small with a large charge; therefore pick weak-field high-spin case:
       CFSE = $3(2/5 \Delta_o) - 2(3/5 \Delta_o) = 0$
(b) $[\text{PtCl}_6]^{2-}$  
$\text{Pt}^{4+}$  
$d^6$  
while chloride is low in the spectrochemical series, 
Pt$^{4+}$ is large and highly charged, therefore pick strong field, low-spin case:
\[
\text{CFSE} = 6(2/5 \Delta_o) - 2P = 12/5 \Delta_o - 2P
\]
(c) $[\text{Cr(NH}_3)_6]^{3+}$  
$\text{Cr}^{3+}$  
$d^3$  
CFSE = $3(2/5 \Delta_o) = 6/5 \Delta_o$

*4.41.

\[
\begin{align*}
\text{d}^8 \text{ octahedral} & \quad \text{CFSE} = 6(0.40\Delta_o) - 2(0.60\Delta_o) = 1.2 \Delta_o \\
\text{d}^8 \text{ square planar} & \quad \text{CFSE} = 4(0.428\Delta_o + 0.086\Delta_o) + 2(0.428\Delta_o) - 1(0.228\Delta_o) - 1(0.228\Delta_o + \Delta_o) = 1.456 \Delta_o
\end{align*}
\]

Therefore, the square planar configuration is of lower energy and is favored. The stronger the field ($\Delta_o$), the more favorable the square planar configuration becomes.

4.42.

\[
\begin{align*}
\text{low-spin case:} & \quad \text{CFSE} = 4(0.19\Delta + 0.082\Delta) + 2(0.082\Delta) - P = 1.25\Delta - P \\
\text{high-spin case:} & \quad \text{CFSE} = 3(0.19\Delta + 0.082\Delta) + 2(0.082\Delta) - 0.71\Delta = 0.27\Delta
\end{align*}
\]

The low-spin case will be favored as long as $0.98\Delta$ is greater than $P$. 
4.43.

\[ \text{CFSE} = 4(0.63\Delta) - 2(0.11\Delta) - 1(0.91\Delta + 0.11\Delta) \]

\[ = 1.28\Delta \]

*4.44.

\[ \text{octahedral} \]

\[ \text{CFSE} = 6(0.40\Delta) - 2P \]

\[ = 2.40\Delta - 2P \]

\[ \text{square pyramidal} \]

\[ \text{CFSE} = 4(0.37\Delta + 0.086\Delta) + 2(0.086\Delta) \]

\[ = 2.00\Delta - 2P \]

Since 0.40\Delta of CFSE is lost upon going to the square pyramidal complex, the substitution is probably slow.

4.45. In a tetragonal compression, the ligands located along the z axis move toward the metal ion. This movement results in more steric hindrance about the metal and causes the ligands located in the xy plane to move away from the metal center.

4.46. These are moderately high values of \( \Delta_o \). Even though the halides are fairly low in the spectrochemical series, the Pt\(^{4+}\) is a large, highly charged metal and causes a large crystal field splitting energy.

4.47. In \([\text{Ru(NH}_3\text{)}_6]^{2+}\), the Ru\(^{2+}\) is a moderately charged, large metal cation and the ammonia ligand is moderately high in the spectrochemical series. This set of conditions would probably result in a fairly large crystal field splitting energy and a strong-field low-spin state.

4.49. $\Delta$(Rh$^{3+}$) > $\Delta$(Co$^{3+}$) > $\Delta$(Co$^{2+}$)

(a) The larger Rh$^{3+}$ allows for the fluoride ligands to approach more closely to the d orbitals without steric hindrance.
(b) The more highly charged Co$^{3+}$ draws the ligands in more closely and thereby splits the d orbitals more than the Co$^{2+}$.

4.50. $[\text{Re(CN)}_6]^{3-}$ contains Re$^{3+}$ ($d^4$) in a strong-field low-spin configuration and therefore should have two unpaired electrons ($t_{2g}^4$). $[\text{MnCl}_6]^{4-}$ contains Mn$^{2+}$ ($d^5$) in a weak-field high-spin configuration and therefore should have five unpaired electrons ($t_{2g}^3 e_g^2$).

4.51. Phosphines have d orbitals with which to form $\pi$-interactions with a transition metal whereas ammines do not. Phosphines are able to accept $\pi$-electron density from filled metal d orbitals and thereby increase both the partial positive and partial negative charges on the metal and ligands, respectively. The resulting enhanced electrostatic M-L interaction increases the split between the sets of metal d orbitals in phosphine complexes. Phosphines, therefore, are generally stronger-field ligands than ammines.

4.52. Using only electrostatic arguments, the F$^-$ ligand is a small charged ion and therefore should be able to get close to and effectively split the d orbitals of a transition metal atom or ion. The P(C$_6$H$_5$)$_3$ ligand, on the other hand, is neutral and much larger and therefore should not be able to get as close to or effectively split the d orbitals of a given metal. (It is $\pi$-interactions that make the fluoride a weak-field ligand and triphenyl phosphine strong-field.)

*4.53. Trifluorophosphine would be the stronger ligand, that is, it would be higher in the spectrochemical series. Sterically, PF$_3$ is much smaller and compact than the bulky PPh$_3$. Therefore, the PF$_3$ will get closer to the metal and more significantly influence the relative energies of the d-orbitals. Electronically, the high electronegativity of the fluorine atoms in PF$_3$ will help draw electron density toward the ligand. This extra electron-withdrawing power will make the $\pi$-back bonding stronger in the M-PF$_3$ bond than in the M-PPh$_3$ bond. The empty 3d orbital of the phosphorus is capable of accepting electron density back from a filled $t_{2g}$ type orbital. The presence of the three electron-withdrawing fluorine atoms enhances this effect. As a result the M-PF$_3$ bond will be more polar and the splitting of the d orbitals more enhanced.

4.54. Organic sulfides, R$_2$S, should be relatively high in the spectrochemical series because, like the phosphines, they are capable of accepting $\pi$-electron density from filled metal d orbitals. This interaction increases both the partial positive and partial negative charges on the metal and ligands, respectively. The resulting enhanced electrostatic M-L interaction increases the split between the sets of metal d orbitals in these complexes.

4.55. $d^6$ octahedral: strong-field: $t_{2g}^6$, $n = 0$, $\mu_S = 0$
weak-field: $t_{2g}^4 e_g^2$, $n = 4$, $\mu_S = \sqrt{(4)(4+2)} = 4.90$ BM

$d^6$ tetrahedral: strong-field: $e_t^4 t_2^2$, $n = 2$, $\mu_S = \sqrt{(4)(2+2)} = 2.83$ BM
weak-field: $e_t^3 t_2^3$, $n = 4$, $\mu_S = 4.90$ BM
4.56. Na$_2$[Ni(CN)$_4$]·3H$_2$O involves Ni$^{2+}$, a d$^8$ metal ion. If the complex anion were tetrahedral it would have an electronic configuration of e$^4$t$^2$ with two unpaired electrons. If it were square planar it would be as shown at right with no unpaired electrons. Since the compound is diamagnetic, it must be square planar. The complex is strong-field low-spin because the cyanide ligands are so high in the spectrochemical series.

4.57.  

<table>
<thead>
<tr>
<th>µ$^{exptl}$ (BM)</th>
<th># of unpaired electrons</th>
<th>$\text{M}^{n+}$</th>
<th>d$^m$ config.</th>
<th>elect. spin state</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(CN)$_6$]$^{4-}$</td>
<td>1.8</td>
<td>1</td>
<td>Mn$^{2+}$ d$^5$</td>
<td>t$_{2g}^5$</td>
</tr>
<tr>
<td>[Mn(CN)$_6$]$^{3-}$</td>
<td>3.2</td>
<td>2</td>
<td>Mn$^{3+}$ d$^4$</td>
<td>t$_{2g}^4$</td>
</tr>
<tr>
<td>[Mn(NCS)$_6$]$^{4-}$</td>
<td>6.1</td>
<td>5</td>
<td>Mn$^{2+}$ d$^5$</td>
<td>t$_{2g}^4$ e$^2$_g</td>
</tr>
<tr>
<td>[Mn(acac)$_3$]</td>
<td>5.0</td>
<td>4</td>
<td>Mn$^{3+}$ d$^4$</td>
<td>t$_{2g}^3$ e$^1$_g</td>
</tr>
</tbody>
</table>

4.58. CFS$E = 4(0.37\Delta + 0.086\Delta) + 0.086\Delta - 0.084\Delta - P$

(Note: as stated in the problem hint, the basic splitting diagram is given in Problem 4.27. The actual splits among various sets of d orbitals were also shown in Problem 4.44.)

4.59. [CoI$_6$]$^{3-}$ Co$^{3+}$ d$^6$ high-spin t$_{2g}^4$ e$_g^2$ n = 4 $\mu_S = \sqrt{(4)(6)} = 4.90$ BM

4.60. A magnetic moment of 2.96 BM indicates two unpaired electrons while diamagnetism indicates none. To have the possibility of both 2 and zero unpaired electrons, all the complexes must involve a square planar crystal field about the metal ions. (A tetrahedral d$^8$ field must always have two unpaired electrons.) The nickel complex must be weak-field high-spin while the analogous palladium compound is strong-field high-spin. The possible structures of the palladium compound are shown below.
4.61. For the [RuF₆]⁴⁻ ion, \( \mu = 2.84 \chi^{1/2} = 2.84[(1.01 \times 10^{-2})(298)]^{1/2} = 4.93 \text{ BM} \) which is consistent with 4 unpaired electrons. For the [Ru(PR₃)₆]²⁺ ion, \( \chi_M = 0 \) indicates that \( \mu = 0 \) and therefore there are no unpaired electrons. Four unpaired electrons are consistent with a d⁶ ion in a weak field while zero unpaired electrons correspond to a d⁶ ion in a strong field.

*4.62. Cyanide is a very strong-field ligand while water is about in the middle of the spectrochemical series. Adopting the rather simplistic view of the origin of the colors of coordination compounds, one can postulate that the cyano complexes tend to absorb light in the higher frequency visible range (for example, blue, indigo, and violet) and therefore transmit or reflect the lower frequencies such as the yellows while the aqua complexes absorb at the lower visible frequencies (for example, red, orange, yellow) and transmit or reflect the higher frequencies such as the blues and greens.

4.63. Yes, it would be surprising if all the compounds involving these complex ions were to be the same color. Given the spectrum (pun intended) of crystal field splitting abilities of the ligands involved, these complexes should absorb at a variety of wavelengths and therefore be of various colors.

*4.64. The hexaammine, tris(ethylenediamine), and hexanitro Co³⁺(d⁶) complexes with zero magnetic moments correspond to strong-field low-spin (t₂g⁶) configurations. They have relatively large \( \Delta_o \)'s and therefore absorb at higher frequencies. The fluoro/aqua complexes have nonzero magnetic moments and correspond to weak-field high-spin complexes (t₂g⁴e₉). They have relatively small \( \Delta_o \)'s and therefore absorb at lower frequencies. The first group may appear orange-yellow because they absorb the higher frequencies (for example, blue, indigo, and violet) and transmit or reflect the lower ones, for example, the oranges and yellows. The second group may appear blue because they absorb the lower frequencies (for example, red, orange, and yellow) and transmit or reflect the higher ones, for example, the blues.

4.65. (a) \([\text{Ni(H}_2\text{O)}_2\text{(en)}_2] \rightleftharpoons \text{heat} \rightarrow [\text{Ni(en)}_2] + 2\text{H}_2\text{O}\)
(b) The [Ni(en)₂] could be either tetrahedral or square planar in nature. As shown below, only the square planar splitting could support the presence of a diamagnetic compound.
4.66. The two chloride counterions have replaced the water ligands that have been driven off by heating. The coordination sphere of the nickel(II) is still octahedral and the complex still diamagnetic. Chloride is lower in the spectrochemical series than water so the complex should absorb at a lower frequency. A logical scenario for the change in color is given below but we have to remember that we are making some rather large oversimplifications when we account for the color changes in this way.

![Diagram](image)

*4.67. When the two water ligands are driven off by heating, the nickel changes from an octahedral to a square planar environment. We know that \([\text{Ni(deen)}_2]\text{Br}_2\) must be square planar because the alternative coordination sphere, tetrahedral, cannot yield a diamagnetic species for the product. One way to rationalize the color change in this reaction is shown below. When the waters are driven off, there is more room for the somewhat bulky deen bidentates to get closer to the nickel therefore increasing the magnitude of the splitting between the uppermost two d-orbitals. As shown, this could result in the observed change of color. Again, we must be wary of such an oversimplification but, in any case, it is logical that the color should change in a fairly radical manner.

![Diagram](image)

*4.68. From the information given in problems 4.66 and 4.67, it appears that the water ligands are driven off by heating in both cases. In the chloride complex (Problem 4.66), the chloride counteranions come in to replace the waters. In the bromide complex (Problem 4.67), however, the bulkier bromides evidently cannot get in so the product stays as a square planar complex.

*4.69. The octahedral \([\text{Ni(H}_2\text{O)}_6]^{2-}\) has a \(t_{2g}^6e_g^2\) configuration corresponding to two unpaired electrons. The \([\text{Ni(CN)}_4]^{2-}\) must be a strong-field, square planar complex in order to be diamagnetic.
It must absorb at considerably higher frequencies (most likely into the ultraviolet) than the hexaaqua complex and therefore transmits or reflects all the visible frequencies and appears colorless.

4.70. To isolate the effect of a series of ligands on the crystal field splitting energies, one would ideally choose a given metal ion which always assumes a given coordination geometry. For example, one might choose compounds containing cobalt(III), octahedral coordination spheres. Using a series of ligands about the cobalt(III) and measuring the frequencies at which these compounds absorb light, one could construct at least a part of the spectrochemical series. Some complications could arise, however. One might have to use several different metals in order to include as many ligands as possible. You could have sets of cobalt and chromium octahedral compounds and perhaps several tetrahedral or square planar sets of the same or different metals as well. Within a given set, a portion of the spectrochemical series could be developed. Putting all the sets together would generate a rather complete listing of ligands in order of their increasing ability to split d orbitals.

4.71. To picture the bonding in coordination compounds as strictly ionic is, at first thought, rather unrealistic. However, this theory does a surprisingly good job at accounting for the existence and high stability of these compounds as well as their magnetic characteristics and colors. The experimental evidence for the theory, as covered in this chapter, comes from two major types of studies: magnetic measurements and absorption spectroscopy. Magnetic measurements generate values for the molar magnetic susceptibilities of a series of coordination compounds. Molar susceptibilities, in turn, generate molecular-level magnetic moments that can be related to the number of unpaired electrons and electronic configurations of a complex. These results are explained quite adequately by the crystal field theory. Absorption spectroscopy gives information on the frequencies of light absorbed by coordination compounds. These frequencies vary in ways (depending on the size and charge of the metal and ligands) that can be explained in many cases by the ionic crystal field theory.