Coordination Complexes

The chemical, spectroscopic and magnetic properties of a transition metal compound can be related to the $d$ electron configuration at the metal center. There are three common coordination geometries that are most often considered, octahedral, tetrahedral and square planar. The orbital splitting diagrams for each are shown below.

Octahedron

- $e\uparrow$  
  - Low spin if $\Delta_o$ is large
  - High spin if $\Delta_o$ small

Tetrahedron

- $t\uparrow$  
  - Always high spin. $\Delta_t$ is always small

Square planar

- $x^2-y^2\uparrow$  
  - Always low spin. $\Delta_{sp}$ is always large
  - Square planar only found for $d^8$

Both the metal and the ligands determine the degree of splitting in a given complex. Metals with high charge are more likely to be low spin with large $d$ splittings. The ligands can be arranged in a series called the spectrochemical series. At one end of the series the “strong field” ligands usually give large $d$ splittings and low spin complexes, at the other end of the series, the “weak field” ligands tend to give smaller $d$ splittings and high spin complexes.

**Spectrochemical Series**

CO, CN$^-$ > NO$_2^-$ > en > H$_2$O > OH$^-$ > F$^-$ > Cl$^-$ > Br$^-$ > I$^-$

*Strong Field*  

*Weak Field*
**Example:** The ions [Co(NH$_3$)$_6$]$^{3+}$ and [CoF$_6$]$^{3-}$ have different magnetic properties, one is paramagnetic and one is diamagnetic. Draw d orbital splitting diagrams, show the electron occupancies and explain the magnetic behavior.

**Answer:**

<table>
<thead>
<tr>
<th></th>
<th>d orbital splitting</th>
<th>Electron occupancies</th>
<th>Magnetic Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td><img src="image" alt="d orbital splitting" /></td>
<td>All e$^-$ paired</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>[CoF$_6$]$^{3-}$</td>
<td><img src="image" alt="d orbital splitting" /></td>
<td>4 unpaired e$^-$</td>
<td>Paramagnetic</td>
</tr>
</tbody>
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The NH$_3$ complex is more likely to be low spin since NH$_3$ is higher in the spectrochemical series than is F$^-$.  

1. Draw d orbital splitting diagrams, show the electron occupancies, and indicate the number of unpaired electrons for each of the following. If the spin state is not given then make a prediction based upon the spectrochemical series.

   a. [Cr(NH$_3$)$_6$]$^{3+}$
   b. [Fe(H$_2$O)$_6$]$^{3+}$ (high spin)
   c. [Co(H$_2$O)$_6$]$^{2+}$
   d. [Fe(CN)$_6$]$^{3-}$
   e. [Mo(CO)$_6$]
   f. [FeCl$_4$]$^{2-}$
   g. [CoCl$_4$]$^{2-}$
   h. [PtCl$_4$]$^{2-}$ (low spin)

2. The ions [NiCl$_4$]$^{2-}$ and [Ni(CN)$_4$]$^{2-}$ have different magnetic properties, one is paramagnetic and one is diamagnetic. They also have different geometries, one is square planar and one is tetrahedral. Draw d orbital splitting diagrams, show the electron occupancies and explain the magnetic and structural behavior.

3. The [Co(NH$_3$)$_6$]$^{3+}$ ion is very stable and undergoes substitution reactions very slowly. It is said to be inert. In contrast the [Co(NH$_3$)$_6$]$^{2+}$ ion it is not very stable, it undergoes substitution reactions very rapidly and it is readily oxidized to the +3 ion. Draw d orbital splitting diagrams for each ion and explain the contrasting chemistry.