Lecture 10 - Further Consequences of d-Orbital Splitting

- Four coordinate geometries - crystal field theory for tetrahedral and square planar complexes
- Factors determining the stability of a complex.
- Preferred geometries: octahedral site preference energy (OSPE).
- Preferred geometries: why square planar nickel and platinum?

1. Four Coordinate Geometries
   (i) Tetrahedral complexes

   d-Orbital splitting for tetrahedral coordination. A cube, an octahedron, and a tetrahedron are related geometrically. Octahedral coordination results when ligands are placed in the centers of cube faces. Tetrahedral coordination results when ligands are placed on alternate corners of a cube.
Now consider the effect of the ligands on the energies of the d-orbitals in tetrahedral coordination, with the $d_{yz}$ and $d_{xz}$ orbitals as examples. An electron in the $d_{yz}$ orbital can approach the ligand to within a distance of $a/2$, where $a$ is the cube edge length. However, an electron in $d_{xz}$ only approaches the ligands at a distance of $a/(2^{1/2})$, a distance 1.414 times as long as the distance in the $d_{yz}$ case. This means that the $d_{xz}$ orbital is lower in energy than the $d_{yz}$ orbital, exactly the opposite case as in octahedral coordination.

The $d_{yz}$ orbital in tetrahedral coordination. Electrons in this orbital can approach within a distance of $a/2$ to ligand electrons.

The $d_{xz}$ orbital in tetrahedral coordination: electrons in $d_{xz}$ are further from the ligands than electrons in $d_{yz}$.

The $d_{xy}$ and $d_{xz}$ orbitals behave the same way as $d_{yz}$, and $d_{x^2-y^2}$ behaves the same way as $d_{z^2}$. The resulting d-orbital splitting diagram for tetrahedral coordination is the inverse of the diagram for octahedral coordination, as shown below.

The energy difference between the $t_2$ and $e$ orbitals is called the tetrahedral splitting energy $\Delta_t$.

(Note that the orbitals are labelled $t_2$ and $e$, not $t_{2g}$ and $e_g$: $g$ refers to a geometry, such as octahedral, that has a center of symmetry. The tetrahedral geometry has no center of symmetry).
Crystal Field Stabilization Energy in Tetrahedral Complexes.

- The tetrahedral crystal field stabilization energy is calculated the same way as the octahedral crystal field stabilization energy.
- The magnitude of the tetrahedral splitting energy is only 4/9 of the octahedral splitting energy, or
  \[ \Delta_t = \frac{4}{9} \Delta_o. \]
- As a result of the relatively small size of the tetrahedral splitting energy, there are no low-spin tetrahedral (ML₄) complexes.
- It is always more energetically favorable to put an electron into a \( t_2 \) orbital rather than pair it in an \( e \) orbital.

Let’s calculate the crystal field stabilization energy for a tetrahedral cobalt(II) complex. Cobalt(II) is a \( d^7 \) ion.

- The electronic configurations of the free ion and the tetrahedral complex are shown below.

\[
\begin{align*}
\uparrow \uparrow \downarrow \downarrow & \quad \uparrow \uparrow \downarrow \downarrow \quad +\frac{2}{9} \Delta_t \\
\text{Co}^{2+} \text{free ion} & \quad \text{tetrahedral Co}^{2+}_{4-4} \\
\downarrow \downarrow & \quad \uparrow \uparrow \quad -\frac{3}{5} \Delta_t
\end{align*}
\]

\[
\text{CFSE} = (4 \text{ electrons})(3/5 \Delta_t) + (3 \text{ electrons})(2/5 \Delta_t) = -1.2 \Delta_t
\]
A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:

**Crystal Field Stabilization Energies for Tetrahedral Complexes of d¹ - d¹⁰ Ions**

<table>
<thead>
<tr>
<th># of d-electrons</th>
<th>Tetrahedral CFSE</th>
<th># of d-electrons</th>
<th>Tetrahedral CFSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.6 ( \Delta_t )</td>
<td>6</td>
<td>-0.6 ( \Delta_t )</td>
</tr>
<tr>
<td>2</td>
<td>-1.2 ( \Delta_t )</td>
<td>7</td>
<td>-1.2 ( \Delta_t )</td>
</tr>
<tr>
<td>3</td>
<td>-0.8 ( \Delta_t )</td>
<td>8</td>
<td>-0.8 ( \Delta_t )</td>
</tr>
<tr>
<td>4</td>
<td>-0.4 ( \Delta_t )</td>
<td>9</td>
<td>-0.4 ( \Delta_t )</td>
</tr>
<tr>
<td>5</td>
<td>zero</td>
<td>10</td>
<td>zero</td>
</tr>
</tbody>
</table>

(ii) **Square Planar Complexes**

*d-Orbital Splitting in Square Planar Coordination.*

- Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane. As the z-ligands move away, the ligands in the square plane move a little closer to the metal.
- The orbital splitting diagram for square planar coordination can thus be derived from the octahedral diagram.
As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy.

The $d_{z^2}$ orbital falls the most, as its electrons are concentrated in lobes along the z-axis.

The $d_{xz}$ and $d_{yz}$ orbitals also drop in energy, but not as much.

Conversely, the $d_{x^2-y^2}$ and the $d_{xy}$ orbitals increase in energy. The splitting diagram for square planar complexes is more complex than for octahedral and tetrahedral complexes, and is shown below with the relative energies of each orbital.

Crystal Field Stabilization Energy in Square Planar Complexes.

Square planar coordination is rare except for $d^8$ metal ions. Among the $d^8$ metal ions exhibiting square planar coordination are nickel(II), palladium(II), platinum(II), rhodium(I), iridium(I), copper(III), silver(III), and gold(III). Copper(II) and silver(II), both $d^9$ ions, are occasionally found in square planar coordination.

All known square planar complexes of $d^8$ ions are diamagnetic, because the highest-energy orbital ($d_{x^2-y^2}$) is greatly destabilized, and pairing in the $d_{xy}$ orbital is more favorable than placing an unpaired electron in the $d_{x^2-y^2}$ orbital.
The crystal field stabilization energy for a diamagnetic square planar d\textsuperscript{8} metal complex is readily calculated by the usual method:

\[
\text{CFSE}_{\text{Square planar}} = 4 \text{ electrons} \times (-0.51 \text{ A}_e) + 2 \text{ electrons} \times (-0.43 \text{ A}_e) \\
+ 2 \text{ electrons} \times (0.14 \text{ A}_e) + P \\
- 2.44 \text{ A}_e + P
\]

The pairing energy correction is included because a free d\textsuperscript{8} ion has 2 unpaired electrons, but a square planar d\textsuperscript{8} complex has no unpaired electrons.

2. **Factors Determining the Stability of a Metal Complex**

   i. The number of ligand atoms coordinated to the metal (the coordination number). Other things being equal, the more ligands that are coordinated, the greater the bond energy. Thus 6-coordinate complexes are inherently more stable than 4-coordinate complexes, but not by the ratio of 6:4 because of the next factor.

   ii. **Bond energy for each M-L bond.** The greater the bond energy, the more stable the complex. This factor interacts with the first. Four-coordinate complexes have shorter bonds than six-coordinate complexes, and shorter bonds are stronger bonds. For a divalent ion such as Ni(II), the estimated bond energy for each Ni-OH\textsubscript{2} bond in [Ni(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+} is about 300 kJ/mol; for the tetraaquo complex. In either tetrahedral or square geometry it is about 350 kJ/mol. [Estimated from the hydration energy for the Ni(II) ion.]
iii. **Inherent nature of the ligand.** Chelating ligands are an example here; complexes of polydentate ligands are more stable than corresponding monodentate complexes (e.g. octahedral [Ni(en)$_3$]$_2^+$ is more stable than octahedral [Ni(NH$_3$)$_6$]$_2^+$).

*Due to the chelate effect* - Those that form 5 and 6-membered rings are more stable than monodentate ligands.

- This is an entropic effect. $\Delta S$ gets larger and more negative when you add monodentate ligands - why because it requires 6 separate collisions between metal and the ligands.
- $\Delta S$ is a measure of disorder, large and positive $\Delta S$ is favorable, negative $\Delta S$ is unfavorable.

\[ \Delta G = \Delta H - T \Delta S \]

the less negative $\Delta S$, the more negative the Gibbs free energy $\Delta G$, the more favorable (entropywise) the reaction.

iv. **The crystal field stabilization energy (CFSE).**

It is possible to calculate CFSE's in any geometry in terms of the octahedral splitting energy $\Delta o$; we've seen how to do it for three common geometries: octahedral, tetrahedral, and square planar. Clearly, the CFSE is important, and it depends on the number of d-electrons, and which orbitals they occupy.

However, it's not just the CFSE in terms of $\Delta o$ that we need, it's the value in kJ/mol, and that depends on the actual magnitude of $\Delta o$ for a given complex.

Remember that $\Delta o$ depends on the following factors:

i. **The specific metal ion.** Even if two metal ions have the same charge and the same ligands, and are in the same period of the periodic table, they can have different values of $\Delta o$.

<table>
<thead>
<tr>
<th>Metal Complex</th>
<th>$\Delta o$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(H$_2$O)$_6$]$^{3+}$</td>
<td>166</td>
</tr>
<tr>
<td>[Mn(H$_2$O)$_6$]$^{2+}$</td>
<td>93</td>
</tr>
<tr>
<td>[Fe(H$_2$O)$_6$]$^{3+}$</td>
<td>124</td>
</tr>
<tr>
<td>[Ni(H$_2$O)$_6$]$^{2+}$</td>
<td>111</td>
</tr>
</tbody>
</table>

But there are other, more subtle examples. For example, complexes of NH$_3$ are more stable than complexes of N-bonded NCS$^-$ and certain metal ions prefer specific donor atoms over others, which we will learn more about later on in the course when we study Hard-Soft Acid-Base Theory.
ii. The charge on the metal ion. We’ve seen in a previous lecture that the charge on the metal ion affects the value of \( \Delta_o \) for a given set of ligands. 

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \Delta_o ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{Co(NH}_3\text{)}_6]^{2+}</td>
<td>121</td>
</tr>
<tr>
<td>[\text{Co(NH}_3\text{)}_6]^{3+}</td>
<td>274</td>
</tr>
</tbody>
</table>

iii. The period number of the metal ion for metals in the same group. We’ve also seen that the octahedral splitting increases by about 50% on going from the 4th period to the 5th, and by another 25% on going from the 5th period to the 6th.

iv. The nature of the ligand. This is just a restatement of the spectrochemical series, that ligands can be arranged in order of their ability to split the d-orbitals.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \Delta_o ), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{CrCl}_6]^{3-}</td>
<td>158</td>
</tr>
<tr>
<td>[\text{Cr(H}_2\text{O)}_6]^{3+}</td>
<td>208</td>
</tr>
<tr>
<td>[\text{Cr(NH}_3\text{)}_6]^{3+}</td>
<td>257</td>
</tr>
<tr>
<td>[\text{Cr(en)}_6]^{3+}</td>
<td>262</td>
</tr>
<tr>
<td>[\text{Cr(CN)}_6]^{3+}</td>
<td>318</td>
</tr>
</tbody>
</table>

3. Preferred Geometries:

The preference for octahedral coordination over tetrahedral coordination and the Octahedral Site Preference Energy (OSPE)

In a previous lecture, we raised several questions that we wanted a bonding theory to explain. One of them had to do with the pronounced preference of some metal ions for a specific coordination number and geometry. For example:

a) \text{Cr}^{3+}, \text{Co}^{3+}, \text{and Pt}^{4+} were cited as ions that are found almost exclusively in octahedral coordination.

b) On the other hand, \text{Pt}^{2+} was stated to be an ion that occurred only in square planar coordination. Other ions that occur only in square planar coordination include \text{Au}^{3+}, \text{Rh}^{3+}, \text{and Ir}^{3+}.

c) A few metal ions (high-spin \text{Fe}^{3+}, high-spin \text{Mn}^{2+}, and \text{Zn}^{2+} among them) seem to have a fair proportion of tetrahedral complexes in addition to octahedral complexes, but no square planar complexes.

Let’s begin by looking at the electronic configurations of the ions just mentioned...
### Metal ions and geometries

<table>
<thead>
<tr>
<th>Metal ions and geometries</th>
<th># of d-electrons</th>
<th>d-orbital diagram</th>
<th>CFSE (neglect P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr^{3+} (octahedral)</td>
<td>3</td>
<td>$t_{2g}^3$</td>
<td>-1.2 $\Delta_o$</td>
</tr>
<tr>
<td>low-spin Fe^{3+}, Co^{3+}, Pt^{4+} (octahedral)</td>
<td>6</td>
<td>$t_{2g}^5$</td>
<td>-2.4 $\Delta_o$</td>
</tr>
<tr>
<td>Pt^{2+}, Au^{3+}, Rh^{+} (square)</td>
<td>8</td>
<td>$d_{xz}^2d_{yz}^2d_{xy}^2d_{yz}^2$</td>
<td>-2.44 $\Delta_o$</td>
</tr>
<tr>
<td>high-spin Fe^{3+}, Mn^{2+} (octahedral/tetrahedral)</td>
<td>5</td>
<td>$t_{2g}^2e_{g}^2$ (oct); $e_{g}^2t_{2g}^2$ (tet)</td>
<td>zero whether octahedral or tetrahedral</td>
</tr>
<tr>
<td>Zn^{2+} (octahedral)</td>
<td>10</td>
<td>$t_{2g}^9e_{g}^4$ (oct); $e_{g}^2t_{2g}^6$ (tet)</td>
<td>zero whether octahedral or tetrahedral</td>
</tr>
</tbody>
</table>

There is a correlation between electronic configuration and preferred geometries. Ions from different groups and different periods in the periodic table have similar properties based on the number of d-electrons and the crystal field stabilization energies.

1. **The octahedral site preference energy (OSPE) for Co(III) and other low-spin d^6 ions is very large.**

   The CFSE can be calculated for octahedral and tetrahedral cobalt(III) complexes as shown in the Figure below. The octahedral complex is much more stabilized by the d-orbital splittings than the tetrahedral complex.

   ![Diagram of d-orbital splittings](image)

   - Octahedral Co^{3+}L₆:
     - CFSE = -2.4 $\Delta_o$
     - Difference = -2.13 $\Delta_o$
     - Octahedral complex better stabilized by CFSE

   - Tetrahedral Co^{III}L₄:
     - CFSE = -0.6 $\Delta_o$
     - Difference = -0.27 $\Delta_o$
The difference between the crystal field stabilization energies for an octahedral complex and a complex in another geometry (tetrahedral in this case) is called the octahedral site preference energy.

The actual magnitude of the difference above, $\Delta_o$, is several hundred kilojoules since the octahedral splitting energy varies from about 60 kJ for the weakest ligands to more than 300 kJ for the strongest.

Thus, not only is octahedral coordination for Co(III) favored by the larger number of bonds compared to tetrahedral complexes, but also by the CFSE.

2. The octahedral site preference energy (compared to tetrahedral coordination) is also very large for Cr(III) and other d^3 ions, and for low-spin complexes of d^4, d^5, and d^7 ions.

The graph below gives the OSPE in terms of $\Delta_o$ for every d-electronic configuration. Again, octahedral coordination is not only favored by the greater number of bonds compared to tetrahedral, but also by the greater crystal field stabilization energy for octahedral d^3 and low-spin d^4, d^5, and d^7 complexes. It is not surprising that there are so many octahedral complexes for these ions.
3. Some metal ions have no electronic preference for octahedral coordination over tetrahedral coordination.

- For high-spin d⁵ complexes, d⁰ complexes, and d¹⁰ complexes, there is no difference in the crystal field stabilization energies in octahedral and tetrahedral geometries; they are zero in both geometries.

- The OSPE is small even for d¹, d², and high-spin d⁶ and d⁷ ions. Ions with these d-electron configurations are the most likely to be associated with tetrahedral complexes, as factors other than electronic structure determine the preferred geometry.

- Among the d⁰ ions are Ti(IV), V(V), and Mo(VI); the most common d⁵ ions are Mn(II) and Fe(III); and Zn(II), Cd(II), Hg(II), Cu(I), Ag(I), and Au(I) are the most common d¹⁰ ions. Many tetrahedral complexes are known for these ions.

3. Nickel(II) vs. platinum(II): why is Pt²⁺ found only in square planar coordination but Ni²⁺ is found in several geometries?

- Let’s consider a single example. Nickel forms the octahedral hexaammine complex, 
  \[\text{[Ni(NH₃)₆]}^{2+}\] , but platinum forms the square planar tetraammine complex
  \[\text{[Pt(NH₃)₄]}^{2+}\] . Both metal ions have 8 d-electrons. We can calculate a preference energy for octahedral over square planar coordination, just as we did for octahedral over tetrahedral. We will neglect the pairing energy for this calculation.

\[
\begin{align*}
\text{CFSE}^{\text{oct}} & = -1.2 \Delta_o \\
\text{CFSE}^{\text{sq-pl}} & = -2.44 \Delta_o
\end{align*}
\]
Notice that in this case, the crystal field stabilization (in terms of $\Delta_o$) is much greater for square planar coordination than for octahedral coordination! In fact, the preference energy (compared to octahedral coordination) for square planar coordination of a $d^8$ metal ion is $-1.24 \Delta_o$.

However, let’s use the following values and determine the absolute values for the square planar preference in kJ/mol.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(NH}_3)_x]^{2+}$</td>
<td>132</td>
</tr>
<tr>
<td>$[\text{Pt(NH}_3)_x]^{2+}$</td>
<td>359</td>
</tr>
</tbody>
</table>

Preference for square planar coordination by $[\text{Ni(NH}_3)_x]^{2+}$ = $-1.24 (132 \text{ kJ/mol}) = -164 \text{ kJ/mol}$

Preference for square planar coordination by $[\text{Pt(NH}_3)_x]^{2+}$ = $-1.24 (359 \text{ kJ/mol}) = -445 \text{ kJ/mol}$

Thus square planar $[\text{Pt(NH}_3)_x]^{2+}$ is stabilized by nearly 300 kJ/mol more than the corresponding nickel complex. This greater energy difference is enough to make up for the loss in bond energy suffered as an octahedral platinum(II) complex is transformed to a square planar complex, but is not usually enough to favor square planar complexes for nickel.

So why does nickel form square planar complexes at all? Actually, there are many fewer square planar complexes than there are octahedral ones. The ones that are square planar tend to be found with stronger-field ligands, i.e. those that are capable of giving high values for the octahedral splitting energy $\Delta_o$. 