Coordination Chemistry III: Electronic Spectra

Most coordination compounds of transition metals have vivid colors

- Prussian blue
- Emeralds
  - Cr(III) in Be$_3$Al$_2$(SiO$_3$)$_6$
- Amethysts (iron and titanium in alumina)
- Rubies (chromium in alumina)
- Blood (red heme group)
Why are inorganic compounds colored?

- Most organic compounds are transparent in the visible region (thus they are white)
- Inorganic compounds owe their color to transitions between the d orbitals of the metals
- We need to look closely at the energies of these orbitals and the possible ways that electrons can be raised from lower to higher energy levels
Complementary colors

Cu^{2+}(d^9)

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<table>
<thead>
<tr>
<th>Wavelength Range (nm)</th>
<th>Wave Numbers (cm(^{-1}))</th>
<th>Color</th>
<th>Complementary Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 400</td>
<td>&gt; 25,000</td>
<td>Ultraviolet</td>
<td></td>
</tr>
<tr>
<td>400–450</td>
<td>22,000–25,000</td>
<td>Violet</td>
<td>Yellow</td>
</tr>
<tr>
<td>450–490</td>
<td>20,000–22,000</td>
<td>Blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490–550</td>
<td>18,000–20,000</td>
<td>Green</td>
<td>Red</td>
</tr>
<tr>
<td>550–580</td>
<td>17,000–18,000</td>
<td>Yellow</td>
<td>Violet</td>
</tr>
<tr>
<td>580–650</td>
<td>15,000–17,000</td>
<td>Orange</td>
<td>Blue</td>
</tr>
<tr>
<td>650–700</td>
<td>14,000–15,000</td>
<td>Red</td>
<td>Green</td>
</tr>
<tr>
<td>&gt; 700</td>
<td>&lt; 14,000</td>
<td>Infrared</td>
<td></td>
</tr>
</tbody>
</table>
Quantum numbers of multielectron atoms

- Consider carbon atoms (1s\(^2\) 2s\(^2\) 2p\(^2\)) – we would expect for the two p electrons to have the same energy.
- However, there are three major energy levels for the p\(^2\) electrons, differing in \(\Pi_c\) and \(\Pi_e\).

- The 2p electrons are not independent of each other; the orbital angular momenta (ml values) and the spin angular momenta (ms values) interact in a manner called LS coupling (Russell-Saunders coupling).
- The interactions produce atomic states called microstates that can be described by new quantum numbers:

\[
M_L = \Sigma m_l \quad \text{and} \quad M_S = \Sigma m_s
\]
Microstates for p\(^2\)

- One possible set of values for the two electrons in the p\(^2\) configuration would be
  
  First electron: \( m_l = +1 \) and \( m_s = +\frac{1}{2} \}
  
  Second electron: \( m_l = 0 \) and \( m_s = -\frac{1}{2} \}
  
  Notation: \( 1^+0^- \)

- We get a total of 15 microstates

\[\begin{array}{cccc}
  & M_s & M_L & \\
  & -1 & 0 & +1 \\
  +2 & 1^+ & 1^- & \\
  +1 & 1^- & 0^- & 1^+ & 0^- & 1^+ & 0^+
  \\
  0 & -1^- & 1^- & -1^- & 1^- & 0^+ & 0^- & 1^+ & 0^- & 1^+ & 0^+
  \\
  -1 & -1^- & 0^- & -1^- & 0^- & 1^+ & 0^- & 0^+
  \\
  -2 & & -1^+ & -1^- & & & &
\end{array}\]
Quantum numbers in multielectron atoms

- $L = \text{total orbital angular momentum quantum number}$
- $S = \text{total spin angular momentum quantum number}$

- $L$ and $S$ describe collection of microstates, whereas $M_L$ and $M_S$ describe the microstates themselves.
- $L$ and $S$ are the largest possible values for $M_L$ and $M_S$.
- The values of $S$ are used to calculate the spin multiplicity ($2S+1$).
- The ground term (lowest energy) will have the highest spin multiplicity. When two terms have the same multiplicity, the ground term will have the highest value of $L$. 
Spin-orbit coupling and Hund’s third law

- $J =$ total angular momentum quantum number
- $J$ can go from $L+S$, $L+S-1$, $L+S-2$, etc. to $|L-S|$
- For subshells that are less than half filled, the state with the lowest $J$ value will have the lowest energy. For subshells that are more than half filled, the state with the highest $J$ value will have the lowest energy

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S_0$</td>
<td>21648.8</td>
</tr>
<tr>
<td>$^1D_2$</td>
<td>10193.7</td>
</tr>
<tr>
<td>$^3P_2$</td>
<td>43.5</td>
</tr>
<tr>
<td>$^3P_1$</td>
<td>16.4</td>
</tr>
<tr>
<td>$^3P_0$</td>
<td>0</td>
</tr>
</tbody>
</table>

LS coupling only

Spin–orbit coupling (exaggerated scale for $^3P$)
Electronic spectra of coordination compounds

- Selection rules govern the relative intensities of absorption bands; based on symmetry and spin multiplicity two of these rules can be stated as follows:
  - Transition between states of the same parity (g → g or u → u) are forbidden – Laporte selection rule
  - Transition between states of different spin multiplicity are forbidden (an example would be \(^4A_2 \rightarrow ^2A_2\))
- These rules would seem to rule out most electronic transitions for transition metal complexes, yet most of these complexes are vividly colored
Mechanisms by which selection rules are “relaxed”

- Vibrations can temporarily change the symmetry of a complex, a phenomenon called vibronic coupling
  - d-d transitions occur with $\varepsilon$ ranging $10-50 \text{M}^{-1}\text{cm}^{-1}$
- Tetrahedral complexes often absorb more strongly than octahedral complexes of the same metal in the same oxidation state. Metal-ligand bonding can be described as a combination of sp$^3$ and sd$^3$ orbitals – mixing of p orbital character (u) with the d-orbital character allows for relaxing the Laporte selection rule
- Spin-orbit coupling provides a mechanism of relaxing the spin rule – this is more important in the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ transition series
- **Correlation diagrams** make use of two extremes:
  - Free ions (no ligand field) – spectroscopic terms in the absence of any interactions with the ligands
  - Strong ligand field – the possible configurations in the presence of a strong ligand field (ligand field so strong that it overrides the effects of LS coupling)
  - In actual coordination compounds, the situation is intermediate between these two extremes
Correlation diagram for $d^2$ configuration

- All terms can be broken down to irreducible representations and they must match (far left with far right).
- Ground terms and states of the same spin multiplicity as the ground term are shown as heavy lines.
- Lines that connect states of the same symmetry designation do not cross.
Tanabe-Sugano diagrams are special correlation diagrams that are particularly useful in the interpretation of electronic spectra of coordination compounds.

- The lowest-energy state is plotted along the horizontal axis.
- The vertical distance above this axis is a measure of the energy of the excited state above the ground state.
- **Tanabe-Sugano diagrams** also show excited states.
- The most important excited states are those of the same spin multiplicity as the ground state.
- In the $d^2$ Tanabe-Sugano diagram shown in the right, these states are shown with the corresponding symmetry label.
- $B$ is the Racah parameter, a measure of the repulsion between terms of the same multiplicity.
Spin-allowed transitions for a $d^2$ configuration

$\nu_1: ^3T_{1g} (F) \rightarrow ^3T_{2g}$
$\nu_2: ^3T_{1g} (F) \rightarrow ^3T_{1g} (P)$
$\nu_3: ^3T_{1g} (I) \rightarrow ^2A_{2g}$
When the configuration is $d^4-d^7$, two possibilities exist: high spin and low spin.

A vertical line divides the diagram: the left side is for the high spin (weak field) complexes and the right side is for the low spin (strong field).
Janh-Teller distortions and their effect on spectra

- $d^1$ and $d^9$ configurations should have only a single transition band
- But JT distortions splits the energy levels and more bands (similar in energy) can be observed
Determining $\Delta_0$ from spectra

- The absorption spectra can be used to calculate $\Delta_0$
- Sometimes the spectra have overlapping bands, which make this more difficult (a mathematical approach is needed to reduce the bands to its individual components)
- The position of the absorption maxima can be used with a reasonable accuracy
Tetrahedral complexes

- Tetrahedral complexes have typically stronger absorption bands than octahedral complexes as a consequence of the Laporte rule.
- The hole formalism is used to compare the configurations of tetrahedral and octahedral complexes (we can use the correlation diagram for d^1 in O_h as the correlation diagram for d^9 in T_d).

\[ \begin{align*}
\text{Octahedral} & : t_{2g} \quad e_g \\
\text{Tetrahedral} & : t_{2g} \quad e_g
\end{align*} \]
Charge-transfer spectra

- Charge-transfer bands can be very intense (50,000 M\(^{-1}\)cm\(^{-1}\))
- CTTM or LMCT bands result when electrons are excited from the ligand to the metal orbitals – metal reduction takes place
Charge-transfer spectra

- Charge-transfer bands can be very intense (50,000 M\(^{-1}\)cm\(^{-1}\))
- CTTL or MLCT bands result when electrons are excited from the metal typically to ligand \(\pi^*\) orbitals – metal oxidation takes place