A molecule’s color can depend on oxidation state or liganded state. Example: oscillating clock.

Consider the overall reaction:

\[ \text{IO}_3^- + 2 \text{H}_2\text{O}_2 + \text{CH}_3(\text{CO}_2\text{H})_2 + \text{H}^+ \rightarrow \text{ICH( CO}_2\text{H})_2 + 2 \text{O}_2 + 3 \text{H}_2\text{O} \]

The overall reaction can be broken into two components (1 and 2), the second of which can be further divided into components (a and b):

\[(1) \quad \text{IO}_3^- + 2 \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{HOI} + 2 \text{O}_2 + 2 \text{H}_2\text{O} \quad \text{what is happening to “I”?} \]

(Note that the HOI produced in the first reaction is a reactant in the second reaction.)

\[(2) \quad \text{HOI} + \text{CH}_3(\text{CO}_2\text{H})_2 \rightarrow \text{ICH( CO}_2\text{H})_2 + \text{H}_2\text{O} \]

\[(a) \quad \text{I}^- + \text{HOI} + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O} \quad \text{what is being oxidized and what is being reduced in this reaction?} \]

\[(b) \quad \text{I}_2\text{CH}_2(\text{CO}_2\text{H})_2 \rightarrow \text{ICH}_2(\text{CO}_2\text{H})_2 + \text{H}^+ + \text{I}^- \]

As this reaction proceeds, the color will oscillate from clear to amber to deep blue. Specifically, \( \text{I}^- \) is clear. The amber color is from \( \text{I}_2 \) formation. The deep blue color results from the \( \text{I}^- \) and \( \text{I}_2 \) binding to the starch present in the solution. Thus, the color of iodine depends on its oxidation state and its liganded state (whether or not it is bound to starch).

**Transition metal coordination complexes** can have beautiful colors. The color given off by a coordination complex depends on the nature of the transition metal and the nature of the ligands. Crystal field theory can be used to explain the observed colors of various coordination complexes.

**Spectrochemical Series** - relative abilities of common ligands to split the d-orbital energy levels.

**Strong field ligands** - produce large energy separations between d-orbitals

**Weak field ligands** - produce small energy separations between d-orbitals

\[ \text{I}^- < \text{Br}^- < \text{Cl}^- \quad < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} \quad < \text{NH}_3 < \text{CO} < \text{CN}^- \]

<table>
<thead>
<tr>
<th>weak field ligands</th>
<th>strong field ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_o ) small</td>
<td>( \Delta_o ) is large</td>
</tr>
</tbody>
</table>

High spin | Low spin
**Spectrochemical Series (Octahedral Example)**
Consider Fe$^{3+}$ in two different compounds: high spin $[\text{Fe(H}_2\text{O)}_6]^3+$ and low spin $[\text{Fe(CN)}_6]^3-$.

\[
\begin{align*}
\text{d count} &= ? \\
\begin{array}{c}
\text{d}_{x^2-y^2} \\
\text{d}_{z^2} \\
\hline
\text{d}_{xy} \quad \text{d}_{xz} \quad \text{d}_{yz}
\end{array} \\
\begin{array}{c}
\text{t}_{2g} \\
\text{e}_g \\
\hline
\text{t}_{2g} \\
\text{e}_g
\end{array} \\
\begin{array}{c}
\Delta_o \\
2\Delta_o
\end{array}
\end{align*}
\]

\[\begin{align*}
\text{high spin} \\
\text{Fe}^{3+} \text{ in } [\text{Fe(H}_2\text{O)}_6]^3+ \\
d^n \text{ electron configuration} = \\
\text{CFSE} =
\end{align*}\]

\[\begin{align*}
\text{low spin} \\
\text{Fe}^{3+} \text{ in } [\text{Fe(CN)}_6]^3- \\
d^n \text{ electron configuration} = \\
\text{CFSE} =
\end{align*}\]

**Light Absorbed by Octahedral Coordination Complexes**
A substance absorbs photons of light if the energies of the photons match the energies required to excite the electrons to higher energy levels.

\[
E_{\text{light}} = hv = \Delta_o
\]

- $E =$ energy of light absorbed
- $h =$ planck's constant
- $v =$ frequency
- $\Delta_o =$ octahedral crystal field splitting energy

If high frequency light is absorbed, the wavelength of the absorbed light is _______.

\[
c = \lambda v
\]

- $c =$ speed of light
- $\lambda =$ wavelength
- $v =$ frequency
Going back to our example: high spin \([\text{Fe}(\text{H}_2\text{O})_6]^{3+}\) and low spin \([\text{Fe}(\text{CN})_6]^{3-}\)
High spin \([\text{Fe}(\text{H}_2\text{O})_6]^{3+}\) has a crystal field splitting energy of 171 kJ/mol
Low spin \([\text{Fe}(\text{CN})_6]^{3-}\) has a crystal field splitting energy of 392 kJ/mol

Calculate the wavelength of light absorbed by both complexes.

**High spin \([\text{Fe}(\text{H}_2\text{O})_6]^{3+}\)**

\[
\lambda = \frac{c}{v} \text{ and } v = \frac{\Delta_o}{h}
\]

so \[\lambda = \frac{hc}{\Delta_o} = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.997 \times 10^8 \text{ m/s})}{(171 \text{ kJ/mol}) \times (1000 \text{ J/kJ}) \times (1 \text{ mol/6.022 x 10}^{23})} = 7.00 \times 10^{-7} \text{ m or 700. nm}
\]

\([\text{Fe}(\text{H}_2\text{O})_6]^{3+}\) absorbs red light

**Low spin \([\text{Fe}(\text{CN})_6]^{3-}\)**

\[
\lambda = \frac{hc}{\Delta_o} = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.997 \times 10^8 \text{ m/s})}{(392 \text{ kJ/mol}) \times (1000 \text{ J/kJ}) \times (1 \text{ mol/6.022 x 10}^{23})} = 3.05 \times 10^{-7} \text{ m or 305. nm}
\]

\([\text{Fe}(\text{CN})_6]^{3-}\) absorbs violet light

**Example: Explain the different colors of \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\) and \([\text{Cr}(\text{NH}_3)_6]^{3+}\)?**

oxidation number of Cr?

d count?

CN?

Type of Ligand?

Octahedral Crystal Field Splitting Diagrams:

\[\text{Cr}^{3+} \text{ in } [\text{Cr}(\text{H}_2\text{O})_6]^{3+}\]

\[\text{Cr}^{3+} \text{ in } [\text{Cr}(\text{NH}_3)_6]^{3+}\]
H$_2$O is a weak to intermediate field ligand ($\Delta_o$ is smaller)

NH$_3$ is a stronger field ligand ($\Delta_o$ is larger)

<table>
<thead>
<tr>
<th>$\Delta_o$</th>
<th>E</th>
<th>hv</th>
</tr>
</thead>
<tbody>
<tr>
<td>smaller $\Delta_o$</td>
<td>lower E</td>
<td>frequency absorbed</td>
</tr>
<tr>
<td>larger $\Delta_o$</td>
<td>higher E</td>
<td>frequency absorbed</td>
</tr>
</tbody>
</table>

c/v = $\lambda$.

Color of transmitted light is complementary to the color of absorbed light. Violet is complementary to yellow; blue is complementary to orange; green is complementary to red.

Transmitted light has a ______ wavelength  
[Cr(H$_2$O)$_6$]$^{3+}$ is violet (400-430nm)

Transmitted light has a ______ wavelength  
[Cr(NH$_3$)$_6$]$^{3+}$ is yellow (560-580nm)

Estimate crystal field splitting energy in kJ/mol

Example [CrCl$_6$]$^{3-}$ wavelength of most intensely absorbed light is 740 nm

predicted color:

frequency of light absorbed is c/$\lambda$ = (2.997 x 10$^8$ m/s)/(740 x 10$^{-9}$ m) = 4.05 x 10$^{14}$ s$^{-1}$
crystal field splitting energy $\Delta_o$ is hv = (6.626 x 10$^{-34}$ J s)(4.05 x 10$^{14}$ s$^{-1}$) = 2.68 x 10$^{-19}$ J

(2.68 x 10$^{-19}$ J) x (1 kJ/1000 J) x (6.022 x 10$^{23}$ mol$^{-1}$) = 160 kJ/mol

Which coordination complexes are colorless?

All d-orbitals are ________. No d-d transitions in the visible range possible.

Examples. Zn$^{2+}$ and Cd$^{2+}$
Color in Octahedral Coordination Complexes Summary

<table>
<thead>
<tr>
<th>Ligands</th>
<th>I⁻ &lt; Br⁻ &lt; Cl⁻</th>
<th>&lt;F⁻ &lt; OH⁻ &lt; H₂O</th>
<th>&lt;NH₃ &lt; CO &lt; CN⁻</th>
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</tr>
<tr>
<td>High spin</td>
<td>Low spin</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Absorb**
- low energy photons
- low frequency (ν)
- long wavelength (λ)
- (yellow/orange/red end of spectra)

**Complexes**
- high energy photons
- high frequency (ν)
- short wavelength (λ)
- (violet/blue/green end of spectra)

**Transmit**
- Complementary to absorbed
- (violet/blue/green end of spectra)
- (yellow/orange/red end of spectra)

Violet is complementary to yellow; orange is complementary to blue; red is complementary to green.

Cobalt containing coordination complexes display a wide variety of colors
Which vitamin contains cobalt?