Chemistry 1000 Lecture 26: Crystal field theory

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November 6, 2018
The d orbitals

$3d_{x^2-y^2}$

$3d_{z^2}$

$3d_{xy}$

$3d_{xz}$

$3d_{yz}$
In an isolated atom or ion, the d orbitals are all degenerate, i.e. they have identical orbital energies.

When we add ligands however, the spherical symmetry of the atom is broken, and the d orbitals end up having different energies.

The qualitative appearance of the energy level diagram depends on the structure of the complex (octahedral vs square planar vs. . . ).

The relative size of the energy level separation depends on the ligand, i.e. some ligands reproducibly create larger separations than others.
In an octahedral complex, the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals point directly at some of the ligands while the $d_{xy}$, $d_{xz}$ and $d_{yz}$ do not.

This enhances the repulsion between electrons in a metal $d_{x^2-y^2}$ or $d_{z^2}$ orbital and the donated electron pair from the ligand, raising the energy of these metal orbitals relative to the other three. Thus:

\[ \Delta = \text{crystal-field splitting} \]
**Note:** Sometimes we write $\Delta_o$ instead of $\Delta$ to differentiate the crystal-field splitting in an octahedral field from the splitting in a field of some other symmetry (e.g. $\Delta_t$ for tetrahedral).
At first, just follow Hund’s rule, e.g. for a d\(^3\) configuration,

\[
\begin{align*}
\downarrow & \quad \downarrow & \quad \downarrow \\
\text{d}_{z^2} & \quad \text{d}_{x^2-y^2} & \\
\text{d}_{xy} & \quad \text{d}_{xz} & \quad \text{d}_{yz}
\end{align*}
\]

\(P = \) pairing energy = extra electron-electron repulsion energy required to put a second electron into a d orbital + loss of favorable spin alignment
For $d^4$, two possibilities:

- $P < \Delta$
  - $d_{z^2}$, $d_{x^2-y^2}$
  - $d_{xy}$, $d_{xz}$, $d_{yz}$
  - low spin

- $P > \Delta$
  - $d_{z^2}$, $d_{x^2-y^2}$
  - $d_{xy}$, $d_{xz}$, $d_{yz}$
  - high spin

Experimentally, we can tell these apart using the paramagnetic effect, which should be twice as large for the high-spin $d^4$ than for the low-spin $d^4$ configuration.
We can order ligands by the size of $\Delta$ they produce.

$\Rightarrow$ spectrochemical series

- A ligand that produces a large $\Delta$ is a strong-field ligand.
- A ligand that produces a small $\Delta$ is a weak-field ligand.

(strong) $\text{CO} \approx \text{CN}^- > \text{phen} > \text{en} > \text{NH}_3 > \text{EDTA}^{4-} > \text{H}_2\text{O} > \text{ox}^{2-} \approx \text{O}^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$(weak)
Example: Iron(II) complexes

- Electronic configuration of Fe\(^{2+}\): [Ar]3d\(^6\)
- \([\text{Fe(H}_2\text{O)}_6]\)^\(^{2+}\) is high spin:

  \[
  \begin{array}{c}
  \uparrow \\
  \downarrow \\
  d_{z^2} \\
  \uparrow \\
  \\
  \uparrow \\
  \downarrow \\
  \downarrow \\
  d_{x^2-y^2} \\
  \downarrow \\
  \downarrow \\
  \downarrow \\
  d_{xy} \\
  \downarrow \\
  \downarrow \\
  \downarrow \\
  d_{xz} \\
  \downarrow \\
  \downarrow \\
  \downarrow \\
  d_{yz} \\
  \end{array}
  \]

- From the spectrochemical series, we know that all the ligands after \(\text{H}_2\text{O}\) in octahedral complexes with Fe\(^{2+}\) will also produce high-spin complexes, e.g. \([\text{Fe(OH)}_6]\)^\(^{4-}\) is high spin.

  \[(\text{strong}) \quad \text{CO} \approx \text{CN}^- > \text{phen} > \text{en} > \text{NH}_3 > \text{EDTA}^{4-} > \text{H}_2\text{O} > \text{ox}^{2-} \approx \text{O}^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- \quad (\text{weak}) \]

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Example: Iron(II) complexes (continued)

- \([\text{Fe(CN)}_6]^{4-}\) is low spin:

\[
\begin{array}{c|c|c|c}
\text{d}_z^2 & \text{d}_{x^2-y^2} \\
\hline \\
\text{d}_{xy} & \text{d}_{xz} & \text{d}_{yz} \\
\end{array}
\]

- Somewhere between CN\(^-\) and H\(_2\)O, we switch from low to high spin.

(strong) CO \(\approx\) CN\(^-\) > phen > en > NH\(_3\) > EDTA\(^{4-}\) > H\(_2\)O >
\(\text{ox}^{2-}\) \(\approx\) O\(^2-\) > OH\(^-\) > F\(^-\) > Cl\(^-\) > Br\(^-\) > I\(^-\) (weak)
Typically in the transition metals, $\Delta$ is in the range of energies of visible photons.

Absorption:

$$2x^2 - y^2 + \hbar \nu \rightarrow 2x^2 - y^2$$

Colored compounds absorb light in the visible range. The absorbed light is subtracted from the incident light:

White light     Absorption spectrum     Transmitted light
Example: copper sulfate

\[ \text{CuSO}_4 \cdot 5 \text{H}_2\text{O} \]

\[ \text{CuSO}_4 \text{ solution vs blank} \]
Example: copper sulfate

Visible spectrum

CuSO$_4$ in water

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.00</td>
</tr>
<tr>
<td>500</td>
<td>0.00</td>
</tr>
<tr>
<td>600</td>
<td>0.15</td>
</tr>
</tbody>
</table>

- violet
- blue
- green
- yellow
- orange
- red
The color wheel

- Colors in opposite sectors are complementary.
- Example: a material that absorbs strongly in the red will appear green.
Simple single-beam absorption spectrometer

source → monochromator → sample → detector
Dual-beam absorption spectrometer
Example: Cobalt(III) complexes

- The $[\text{Co(H}_2\text{O)}_6]^{3+}$ ion is green. From the color wheel, this corresponds to absorption in the red.

- The $[\text{Co(NH}_3)_6]^{3+}$ ion is yellow-orange. It absorbs in the blue-violet.

- The $[\text{Co(CN)}_6]^{3-}$ ion is pale yellow. It absorbs mostly in the ultraviolet, with an absorption tail in the violet.

- Note that these results are consistent with the spectrochemical series: The d level splitting is ordered $\text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$.
Examples: Colorless ions

- Titanium(IV) ion $\rightarrow d^0$ configuration

- Zinc(II) ion $\rightarrow d^{10}$ configuration