Chapter 17 - Metals and Coordination Chemistry
Advanced Concepts
Chapter 17

17.8  Crystal Field Theory
**Bonding in Coordination Compounds (Valence Bond Theory)**

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Hybridization</th>
<th>Bonding Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>$sp$</td>
<td><img src="image" alt="Linear_Bonding" /></td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>$sp^3$</td>
<td><img src="image" alt="Tetrahedral_Bonding" /></td>
</tr>
<tr>
<td>Square planar</td>
<td>$dsp^2$</td>
<td><img src="image" alt="Square_planar_Bonding" /></td>
</tr>
<tr>
<td>Octahedral</td>
<td>$d^2sp^3$</td>
<td><img src="image" alt="Octahedral_Bonding" /></td>
</tr>
</tbody>
</table>

*Bonding takes place when the filled atomic orbital on the ligand overlaps an empty atomic orbital on the metal ion. Explains geometries well, but doesn't explain color or magnetic properties*
Bonding in Coordination Compounds
Crystal Field Theory

Bonds form due to the attraction of the electrons on the ligand for the charge on the metal cation.

Electrons on the ligands repel electrons in the unhybridized d orbitals of the metal ion.

The result:
The energies of orbitals the d sublevel are split.

The difference in energy depends the complex and kinds of ligands.
Crystal Field Theory

Crystal field splitting:
Separation of a set of d orbitals into subsets with different energies as a result of interactions between electrons in those orbitals with lone pairs of electrons in ligands.

Crystal field splitting energy:
The difference in energy between subsets of d orbitals split by interactions in a crystal field.
Ligands overlap with orbital lobes, resulting in strong repulsions.

Splitting of d Orbital Energies due to Ligands in a Octahedral Complex.

Ligands are between orbital lobes, resulting in weak repulsions.
Splitting of d Orbital Energies due to Ligands in a Octahedral Complex
If the distribution of the point charges is spherical then all $d$ orbitals will be affected in the same manner. All of the $d$ orbitals will rise in energy. In an octahedral arrangement, the point charges approach the metal atom along the Cartesian $x$, $y$ and $z$ axes. Thus, the orbitals that lie along these axes ($d_{z^2}$ and $d_{x^2-y^2}$) should rise in energy by a greater amount compared to the orbitals that do not lie exactly along the $x$, $y$ and $z$ axes ($d_{xy}$, $d_{yz}$, $d_{xz}$). The $d$ orbitals in the presence of an octahedral field can be described by the following energy diagram:
$d$ Orbitals in an Octahedral Field of Ligands

A

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

C $d_{z^2}$

D $d_{xy}$

E $d_{xz}$

F $d_{yz}$
Complex Ion Color and Crystal Field Strength

The colors of complex ions are due to electronic transitions between the split d sublevel orbitals.

The wavelength of maximum absorbance can be used to determine the size of the energy gap between the split d sublevel orbitals.

\[ E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = \Delta \]
Complex Ion Color and Crystal Field Strength

The strength of the crystal field depends in large part on the ligands:

**strong field ligands** include: CN$^-$ > NO$_2^-$ > en > NH$_3$

**weak field ligands** include: H$_2$O > OH$^-$ > F$^-$ > Cl$^-$ > Br$^-$ > I$^-$

Crystal field strength increases as the charge on the metal cation increases.
Splitting of d Orbital Energies due to Ligands in a Octahedral Complex
Tetrahedral Geometry and Crystal Field Splitting

Square Planar Geometry and Crystal Field Splitting
Square planar crystal field splitting. The d orbitals of a transition metal ion in a square planar field are split into several energy levels, depending on how close the orbital lobes are to the ligand electrons located at the four corners of the square. The \( d_{x^2-y^2} \) orbital is raised the most in energy because its lobes are directed right at the four corners of the square.
Square Planar Field Splitting

- $d_{x^2-y^2}$
- $d_{xy}$
- $d_{z^2}$
- $d_{xz}$, $d_{yz}$

Square planar field splitting energies

Free atom or ion
In a tetrahedral complex ion, such as $\text{Zn(NH}_3\text{)}_4^{2+}$, the $d$ orbitals of the metal ion undergo tetrahedral crystal field splitting. (b) The lobes of the higher-energy orbitals – $d_{xy}$, $d_{xz}$, and $d_{yz}$ – are closer to the ligands at the four corners of the tetrahedron than the lobes of the lower-energy orbitals are.
Tetrahedral Field Splitting

$\Delta_t$

$d$ orbitals in a free atom or ion

$d_{xy}$ $d_{yz}$ $d_{xz}$

$d_{x^2-y^2}$ $d_{z^2}$
Applications of Crystal Field Theory

Superconductors

Modification of Magnetic Properties
17.10 Isomerism in Coordination Compounds
Stereochemistry - Review of Isomerism

Isomers

- Structural Isomers
- Stereoisomers

  - Cis-trans Isomers
  - Isomers with chiral centers
Stereoisomers

**geometric isomers** are stereoisomers that differ in the spatial orientation of ligands.

**optical isomers** are stereoisomers that are nonsuperimposable mirror images of each other.
Stereoisomers of Complex Ions

Cis/Trans Isomerism in Square planar Complexes

$\text{cis}$-diamminedichloro-platinum(II)  $\text{trans}$-diamminedichloro-platinum(II)

$\text{Pt(NH}_3)_2\text{Cl}_2$
Octahedral Geometric Isomers

[Co(NH₃)₄Cl₂]Cl

cis

trans
Fac-Mer Isomerism in Octahedral Complexes
Stereochemistry - Examples of Enantiomers

L-carvone

D-carvone

(spearmint)

(caraway seeds)
Isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$

Cis

Trans
Complex Ion Enantiomers

Enantiomers
nonsuperimposable mirror images; chiral

optical isomers are stereoisomers that are nonsuperimposable mirror images of each other
**Complex Ion Enantiomers**

**Enantiomers**

*nonsuperimposable mirror images; chiral*

\[ [\text{Co(en)}_3]^3+ \]
Applications of Coordination Compounds

extraction of metals from ores

use of chelating agents in heavy metal poisoning

chemical analysis

commercial coloring agents

drug molecules

biomolecules
  porphyrin ring
  cytochrome C
  hemoglobin
  chlorophyll
  carbonic anhydrase