Coordination Chemistry: Bonding Theories

Crystal Field Theory

Chapter 20
Review of the Previous Lecture

1. We discussed different types of isomerism in coordination chemistry
   - **Structural or constitutional isomers**-Bonds not between the same atoms
   - **Stereo or configurational isomers**-Bonds between the same atoms

2. We then focused on the relationship between coordination number and structures in coordination compounds

3. We discussed the factors that favor low and high coordination numbers
1. Chemistry of the d-orbitals

For transition metals in row n of the periodic table, we consider the effect of ligand interactions with the n-1 d-orbitals.

- If in n = 4, then we focus on the five 3d orbitals.
- If in n = 5, then we focus on the five 4d orbitals.
2. Crystal Field Theory

- A purely electrostatic consideration
  - Ligand electrons create an electric field around the metal center
  - Ligands are point charges and we do not take their orbitals into consideration
  - No metal-ligand covalent interactions
3. Energy of the d-orbitals

The energy of the five d orbitals of the transition metals is equal in the absence of ligands.
3. Energy of the d-orbitals

A spherical distribution of ligand electrons equally destabilizes the energy of the d orbital electrons.
3. Energy of the d-orbitals

Degenerate 3d atomic orbitals

The 3d atomic orbitals are split into two levels
3. Energy of the d-orbitals

In an octahedral coordination environment:

- The axial ligands interact directly with the two lobes of the $d_{z^2}$ orbital while the equatorial ligands interact with the torsoid lobe.
- The equatorial ligands interact directly with the four lobes of the $d_{x^2-y^2}$ orbital.
- The $d_{z^2}$ and $d_{x^2-y^2}$ orbitals are destabilized whereas the $d_{xy}$, $d_{xz}$, and $d_{yz}$ are stabilized.
4. The Octahedral Crystal Field

Octahedral coordination environment:
- Point Group: $O_h$
- $d_{z^2}$ and $d_{x^2-y^2}$ orbitals: $e_g$ symmetry
- $d_{xy}$, $d_{xz}$, and $d_{yz}$: $t_{2g}$ symmetry
<table>
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<tr>
<th>(O_h)</th>
<th>E</th>
<th>8 C₃</th>
<th>6 C₂</th>
<th>6 C₄</th>
<th>3 C₂ (= C₂⁺)</th>
<th>i</th>
<th>6 S₄</th>
<th>8 S₆</th>
<th>3 σ₁</th>
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- \(x^2 + y^2 + z^2\)
- \((2z^2 - x^2 - y^2, x^2 - y^2)\)
- \((R_x, R_y, R_z)\)
- \((xz, yz, xy)\)
- \((x, y, z)\)
4. The Octahedral Crystal Field

Octahedral coordination environment:
- Point Group: $O_h$
- $d_{z^2}$ and $d_{x^2-y^2}$ orbitals: $e_g$ symmetry
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A. The Magnitude of $\Delta_{\text{oct}}$

Determined by the strength of the crystal field:
- Weak field
- Strong field

$\Delta_{\text{oct}}$ (weak field) < $\Delta_{\text{oct}}$ (strong field)

\[ \text{d}^5 \text{ electron configuration: } \]  
\[ \text{e}^- \text{ prefer to go into higher energy orbitals than pair} \]

Gaseous ion

Weak field (high-spin) complex  
e.g. $[\text{Fe(OH}_2)_6]^{3+}$

Strong field (low-spin) complex  
e.g. $[\text{Fe(CN)}_6]^{3-}$
B. Crystal Field Stabilization Energy (CFSE)

Consider a d\(^1\) electron configuration:

i.e. \([\text{Ti(H}_2\text{O)}_6]^{3+} \rightarrow \text{Ti}^{3+}\)

Ground State

- The single electron will be in less energetic ground state.
**B. Crystal Field Stabilization Energy (CFSE)**

Calculate the magnitude by which the single electron is stabilized.

\[
\text{CFSE} = -[(\# \text{ electrons in } t_{2g}) \times 0.4\Delta_{oct}] + [(\# \text{ electrons in } e_g) \times 0.6\Delta_{oct}]
\]

\[
= -[1 \times 0.4\Delta_{oct}] + [0] = -0.4\Delta_{oct} \text{ Relative to the Bary center}
\]
C. CFSE and High vs Low Spin

Consider a d⁴ electron configuration (Cr²⁺):

- Depending on the field, pairing may be invoked

\[ \Delta_{\text{oct}} < p \] (pairing energy)

Weak Field, High spin

\[ \Delta_{\text{oct}} > p \]

Strong Field, Low spin

**t²g**

\[ \uparrow \uparrow \uparrow \uparrow \]

\[ \downarrow \downarrow \uparrow \uparrow \]

\[ \Delta_{\text{oct}} < p \] (pairing energy)

Weak Field, High spin

\[ \Delta_{\text{oct}} > p \]

Strong Field, Low spin

\[ \text{CFSE} = -[3 \times 0.4 \Delta_{\text{oct}}] + [1 \times 0.6 \Delta_{\text{oct}}] = -0.6 \Delta_{\text{oct}} \]

\[ \text{CFSE} = -[4 \times 0.4 \Delta_{\text{oct}}] = -1.6 \Delta_{\text{oct}} + 1p \]
I. What determines $p$?

i. Inherent coulombic repulsion $\downarrow$ with $\uparrow n$
   
   • The more diffuse the orbital, the more able to have two electrons

ii. Loss of exchange energy as $e^{-}$ pair
II. What determines $\Delta$?

i. Oxidation state of the metal ion
   - $\uparrow \Delta$ with $\uparrow$ ionic charge

ii. Nature of M
   3d $<$ 4d $<$ 5d
   
   Really big $\Delta$, normally low spin (As you go down the periodic table, $\uparrow \Delta$)

iii. Number and geometry of ligands
   $\Delta_{\text{tetrahedral}}$ only $\sim$50% of $\Delta_{\text{octahedral}}$
II. What determines $\Delta$?

iv. Nature of ligands
   - Spectrochemical series (partial)


YOU CAN NOT UNDERSTAND THIS TREND WITH CRYSTAL FIELD THEORY
5. Octahedral Geometry Distortions

Tetragonal distortions known as the Jahn-Teller Effect

\[ \begin{align*}
D_{4h} & \quad \text{Z-in} \quad \text{O}_h \\
D_{4h} & \quad \text{Z-out}
\end{align*} \]
Jahn-Teller Effect

The theorem states that degenerate orbitals cannot be unequally occupied.

- The molecule distorts by lowering its symmetry to remove the degeneracy
- Quite common for octahedral complexes of $d^9$ ($Cu^{2+}$) and high-spin $d^4$ ions
- For $Cu^{2+}$ complexes, a Z-out ligand arrangement is common.
5. Octahedral Geometry Distortions

What about a d\(^1\) electron configuration?

\[ d_{z^2} \quad d_{x^2 - y^2} \]

\[ d_{xz} \quad d_{yz} \]

YES!!!
Degeneracy Removed

\[ d_{xy} \]

No

\[ d_{xy} \quad d_{xz} \quad d_{yz} \]

Degeneracy Removed

\[ d_{xy} \]

No

\[ d_{xz} \quad d_{yz} \]
6. The Tetrahedral Crystal Field

Tetrahedral coordination environment:
- Point Group: $T_d$
- $d_{z^2}$ and $d_{x^2-y^2}$ orbitals: e symmetry; these orbitals are not in direct contact with the ligands
- $d_{xy}$, $d_{xz}$, and $d_{yz}$: t$_2$ symmetry; these orbitals are in semi contact with the ligands
6. The Tetrahedral Crystal Field

Mostly high spin for these types of complexes.

\[ \Delta_{\text{tet}} < \rho \]
7. The Square Planar Crystal Field

Square planar coordination environment:

- Point Group: $d_{4h}$
- $d^8$ is diamagnetic vs paramagnetic for tetrahedral
8. Crystal Field Splitting Diagrams for Common Geometric Fields

- Energy $\Delta_{oct}$
- $d_z^2$
- $d_{xy}$
- $d_{xz}$
- $d_{yz}$

- Square planar
- Trigonal bipyramidal
- Square pyramidal
- Octahedral
- Pentagonal bipyramidal
- Square antiprismatic
- Tetrahedral