Chapter 19: Phenomena

Phenomena: Transition metal complexes are often used in paints for coloration due to their wide range of colors. Using the data below identify any patterns in the colors of compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Compound</th>
<th>Color of Compound</th>
<th>Color Absorbed by Compound</th>
<th>Energy Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(H₂O)₆]Cl₃</td>
<td>Blue</td>
<td>Orange</td>
<td>184 kJ mol⁻¹</td>
</tr>
<tr>
<td>2</td>
<td>[Co(NH₃)₆]Cl₃</td>
<td>Yellow</td>
<td>Violet</td>
<td>266 kJ mol⁻¹</td>
</tr>
<tr>
<td>3</td>
<td>[Co(NH₃)₅(H₂O)]Cl₃</td>
<td>Red</td>
<td>Green</td>
<td>228 kJ mol⁻¹</td>
</tr>
<tr>
<td>4</td>
<td>[Co(H₂O)₆]Br₃</td>
<td>Blue</td>
<td>Orange</td>
<td>184 kJ mol⁻¹</td>
</tr>
<tr>
<td>5</td>
<td>[Ni(NH₃)₆]Cl₂</td>
<td>Blue</td>
<td>Orange</td>
<td>200 kJ mol⁻¹</td>
</tr>
<tr>
<td>6</td>
<td>[Ni(H₂O)₆]Cl₂</td>
<td>Green</td>
<td>Red</td>
<td>177 kJ mol⁻¹</td>
</tr>
<tr>
<td>7</td>
<td>[CoCl(NH₃)₅]Cl₂</td>
<td>Violet</td>
<td>Yellow</td>
<td>214 kJ mol⁻¹</td>
</tr>
<tr>
<td>8</td>
<td>[CoCl₂(NH₃)₄]Cl</td>
<td>Green</td>
<td>Red</td>
<td>172 kJ mol⁻¹</td>
</tr>
<tr>
<td>9</td>
<td>[Fe(H₂O)₆]Cl₂</td>
<td>Green</td>
<td>Red</td>
<td>173 kJ mol⁻¹</td>
</tr>
<tr>
<td>10</td>
<td>[Fe(H₂O)₆]Cl₃</td>
<td>Yellow</td>
<td>Violet</td>
<td>300 kJ mol⁻¹</td>
</tr>
</tbody>
</table>
Big Idea: The properties of d-block metals are governed by the availability of d-orbitals and their variable valence electrons. The physical properties of d-block complexes depend on the properties of the ligands bound to the metal.
Transition metals, are located in groups 3 through 11. They are called transition metals because they transition between the highly reactive s block metals and the much less reactive metals of group 12 and the p block.
### Chapter 19: Transition Metals and Coordination Chemistry

#### d-Block Elements and Their Compounds

<table>
<thead>
<tr>
<th></th>
<th>Scandium (Sc)</th>
<th>Titanium (Ti)</th>
<th>Vanadium (V)</th>
<th>Chromium (Cr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Facts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reacts vigorously with water</td>
<td></td>
<td>Resistant to corrosion (protective oxide skin)</td>
<td>Vanadium compounds come in a wide range of color due to its many oxidation states</td>
<td>Corrosion resistant</td>
</tr>
<tr>
<td>Requires strong reducing agent for extraction from its ores</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Uses</strong></td>
<td></td>
<td>Jet engines</td>
<td>Makes tough steel for automobile and truck springs</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Few uses</td>
<td></td>
<td>Dental applications</td>
<td>Glazes for ceramics</td>
<td>Chrome plating</td>
</tr>
<tr>
<td>Not essential to life</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Scandium, Sc; 3B(3)
- Titanium, Ti; 4B(4)
- Vanadium, V; 5B(5)
- Chromium, Cr; 6B(6)
### d-Block Elements and Their Compounds

<table>
<thead>
<tr>
<th></th>
<th>Manganese (Mn)</th>
<th>Iron (Fe)</th>
<th>Cobalt (Co)</th>
<th>Nickel (Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Facts</strong></td>
<td>Not as corrosion resistant as chromium but more corrosion resistant than iron</td>
<td>Most widely used d metal</td>
<td>Most abundant element on earth</td>
<td>70% of the western world's nickel comes from ore that was brought close to the earth surface nearly 2 billion year ago by the violent impact of a huge meteor</td>
</tr>
<tr>
<td><strong>Uses</strong></td>
<td>Alloying with steel</td>
<td>Main component in steel (next biggest component C up to 2.1%)</td>
<td>Alloying with steal</td>
<td>Used to make stainless steel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Essential to life</td>
<td>Used to make permanent magnets found in speakers</td>
<td>Nickel is alloyed with copper to make nickel coins</td>
</tr>
</tbody>
</table>

![Manganese, Mn; 7B(7)](image1)
![Iron, Fe; 8B(8)](image2)
![Cobalt, Co; 8B(9)](image3)
![Nickel, Ni; 8B(10)](image4)
## d-Block Elements and Their Compounds

<table>
<thead>
<tr>
<th>Facts</th>
<th>Copper (Cu)</th>
<th>Zinc (Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• One of the coinage metals</td>
<td>• Corrosion resistant</td>
</tr>
<tr>
<td></td>
<td>• High conductivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Corrosion resistant</td>
<td></td>
</tr>
<tr>
<td>Uses</td>
<td>• Alloying: Brass (Cu + Zn) and Bronze (Cu and Sn)</td>
<td>• Used for galvanizing</td>
</tr>
<tr>
<td></td>
<td>• Used for electrical wires</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Used for water pipes</td>
<td></td>
</tr>
</tbody>
</table>
The shape of the $d$-orbitals affect the properties of transition metals. The $d$-orbital lobes are far apart and so only weakly repel each other. The $d$-orbitals have low electron density near the nucleus therefore are not very effective at shielding.
Most d-block metals have more than one oxidation state other than 0. Elements close to the center of the row have the widest range of oxidation numbers.

Orange boxes are common oxidation numbers.

Green boxes are other known states.
The ordering of the ns and (n-1)d energy level shifts once the (n-1)d orbitals contain e\(^-\) causing the (n-1)d e\(^-\) to be lower in energy than the ns electrons. Therefore, ns electrons are lost before (n-1)d electrons when forming transition metal ions. ns electrons are also lost before (n-2)f electrons.
Student Question

What is the correct electron configuration for Ir$^{3+}$?

a) $[\text{Xe}]4f^{13}5d^{7}$
b) $[\text{Xe}]6s^24f^{14}5d^{7}$
c) $[\text{Xe}]4f^{14}5d^{6}$
d) $[\text{Xe}]6s^24f^{14}5d^{4}$
e) None of the Above
Coordination Compounds

**Complex Ion**: A charged species consisting of a metal ion surrounded by ligands.

**Ligand**: A group attached to a central metal ion in a complex.

Central grey atom is transition metal. Colored atoms ligands.

Examples:

- $[\text{Fe(H}_2\text{O)}_6]^3+$
- $[\text{CoCl}_4]^{2-}$
- $[\text{NiBr}_4]^{2-}$
- $[\text{Ag(NH}_3)_2]^+$

**Note**: Complex ions are written inside brackets. If ligands are bound to a metal but the species formed is not an ion the system is still written in brackets ex: $[\text{Hg(CH}_3)_2]$.

**Note**: Complex ions do not dissociate in solution.
### Coordination Compounds

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>Aqua</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Ammine</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>Bromo</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Chloro</td>
</tr>
<tr>
<td>CN$^-$</td>
<td>Cyano</td>
</tr>
<tr>
<td>CO</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>NH$_2$CH$_2$CH$_2$NH$_2$</td>
<td>Ethylenediamine (en)</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>Hydroxo</td>
</tr>
<tr>
<td>I$^-$</td>
<td>Iodo</td>
</tr>
<tr>
<td>CH$_3$NH$_2$</td>
<td>Methylamine</td>
</tr>
<tr>
<td>NO$_2^-$ (N bonded to metal)</td>
<td>Nitro</td>
</tr>
<tr>
<td>ONO$^-$ (O bonded to metal)</td>
<td>Nitrito</td>
</tr>
<tr>
<td>NO</td>
<td>Nitrosyl</td>
</tr>
<tr>
<td>C$_2$O$_4^{2-}$</td>
<td>Oxalato (ox)</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>Sulfato</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>Thiocyanato</td>
</tr>
</tbody>
</table>

**Chelate:** A complex containing at least one polydentate ligand that forms a ring of atoms.

**Note:** Bidentate ligands form 2 bonds to the metal ion.
Coordination Compounds

- **Coordination Number**: The number of bonds formed between the metal ion and the ligands in a complex ion.

- What is the coordination number for:

<table>
<thead>
<tr>
<th>Shape</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
</tr>
<tr>
<td>Square Planar</td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td></td>
</tr>
</tbody>
</table>
Determine the coordination number and oxidation number, respectively, of the transition metal ion $[\text{CrBr}_2(\text{en})_2]^+$?

a) 4, 3
b) 4, 2
c) 6, 3
d) 6, 2
e) None of the Above
Coordination Compound: A compound composed of a complex ion and counter ion sufficient to give no net charge.

Counter Ion: Anions or cations that balance the charge on the complex ion in a coordination complex.

Example: $K_3[Fe(CN)_6]$
- $K^+$ counter ion
- $[Fe(CN)_6]^{3-}$ complex ion

Note: Counter ions can dissociate in water (ionically bonded) while complex ions can not dissociate in water (covalently bonded).
Coordination Compounds

**Student Question**

How many of the following coordination compounds will form a precipitate when treated with an aqueous solution of AgNO$_3$?

- $[\text{CrCl}_3(\text{NH}_3)_3]$  
- $[\text{CrCl(NH}_3)_5](\text{OH})_2$  
- $[\text{Cr(NH}_3)_6]\text{Cl}_3$  
- $\text{Na}_3[\text{Cr(CN)}_6]$  

a) 0  
b) 1  
c) 2  
d) 3  
e) 4
Naming Coordination Complexes

1. Cations (positively charged) are named before the anions (negatively charged).
2. Name the ligands first and then the metal atom or ion. When writing the chemical formula of complex ions the metal comes first.
3. Most neutral ligands have the same name as the molecule.

Example: \( \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \) (ethylenediamine)

Exceptions: \( \text{H}_2\text{O} \) aqua \hspace{1cm} \( \text{NH}_3 \) ammine
\( \text{CO} \) carbonyl \hspace{1cm} \( \text{NO} \) nitrosyl

4. Anionic ligand (- charged) end in \(-\text{o}\);
   -ide (such as chloride) change to \(-\text{o} \) (chloro)
   -ate (such as sulfate) change to \(-\text{ato} \) (sulfato)
   -ite (such as nitrite) change to \(-\text{ito} \) (nitrito)
Naming Coordination Complexes (Continued)

5. Greek prefixes indicate the number of each type of ligands in the complex.

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-</td>
<td>tri-</td>
<td>tetra-</td>
<td>penta-</td>
<td>hexa-</td>
</tr>
</tbody>
</table>

**Note:** If the ligand already contains a Greek prefix (ethylenediamine) or if it is polydentate (able to attach at more than one binding site) then use the following prefixes instead. In addition, the name of the ligand is put in parenthesis.

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>bis-</td>
<td>tris-</td>
<td>tetrakis-</td>
</tr>
</tbody>
</table>

6. The oxidation state of the central metal ion is designated by a Roman numeral in parentheses.
7. When more than one ligand is present, the ligands are named in alphabetical order (not including Greek prefixes).

8. If the complex has an overall negative charge (the suffix –ate is added to the stem of the metal’s name).

   a. If the symbol of the metal originates from Latin and it has an overall negative charge the Latin name is used for the metal.

Examples:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Anionic Base Name</th>
<th>Metal</th>
<th>Anionic Base Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Ferrate</td>
<td>Silver</td>
<td>Argentate</td>
</tr>
<tr>
<td>Copper</td>
<td>Cuprate</td>
<td>Gold</td>
<td>Aurate</td>
</tr>
<tr>
<td>Lead</td>
<td>Plumbate</td>
<td>Tin</td>
<td>Stannate</td>
</tr>
</tbody>
</table>
**Coordination Compounds**

**Name The Compound:**  
\([\text{Ag(NH}_3\text{)}_2][\text{Ag(CN)}_2]\)

Cation: \([\text{Ag(NH}_3\text{)}_2]^?\)  
Anion: \([\text{Ag(CN)}_2]^?\)

**Determine Possible Ions**

Possible Ag ions: \(\text{Ag}^+, \text{Ag}^{2+}, \text{and} \text{Ag}^{3+}\)

\[x(\text{charge on Ag}_{cat}) = -(-2(\text{from CN}^-) + y(\text{charge on Ag}_{an})\]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(x = -(-2 + 1))</td>
</tr>
<tr>
<td>2</td>
<td>(x = -(-2 + 2))</td>
</tr>
<tr>
<td>3</td>
<td>(x = -(-2 + 3))</td>
</tr>
</tbody>
</table>
Coordination Compounds

Isomers
Same Number and Type of Atoms

Structural Isomers
- Different Bonds
- Different Chemical Formulas
- Different Name

Stereoisomers
- Same Bonds
- Different Orientations
- Same Chemical Formulas
- Different Name

Linkage Isomers
Coordination Isomers
Geometric Isomers
Optical Isomers
Coordination Compounds

Types of Structural Isomers:

- **Linkage Isomers:** Isomers in which atoms or groups of atoms can assume different position around a rigid bond.

  Example: \([\text{CoCl(NO}_2\text{)(NH}_3\text{)}_4]^+\) and \([\text{CoCl(ONO)(NH}_3\text{)}_4]^+\) (bonding atom written first)

- **Coordination Isomers:** Isomers that differ by the exchange of one or more ligands between cationic complex and an anionic complex.

  Example: \([\text{Cr(NH}_3\text{)}_6][\text{Fe(CN)}_6]\) and \([\text{Fe(NH}_3\text{)}_6][\text{Cr(CN)}_6]\)
Types of Stereoisomers:

- **Geometric Isomers**: Isomers in which atoms or groups of atoms can assume different positions around a rigid bond.

  - **Cis**: Ligands are on the same side.
  - **Trans**: Ligands are on the opposite side.

**Note**: Geometric Isomers are also sometimes referred to as cis-trans isomers.
How many geometric isomers of the square planar complex \([\text{PtBrCl(NH}_3\text{)(H}_2\text{O)})]\) are possible?

a) 1  
b) 2  
c) 3  
d) 4  
e) None of the Above
Coordination Compounds

Types of Stereoisomers: (Continued)

- **Optical Isomers**: Isomers in which one molecule is the mirror image of the other molecule.

- **Chiral Complex**: A complex that is not identical with its mirror image.

- **Achiral Complex**: A complex that is identical to its mirror image.

- **Enantiomers**: A chiral complex and its mirror image.

**Note**: If the mirror image is identical to the starting configuration, they are not considered optical isomers.

**Note**: If something is chiral it will have an optical isomer.

**Note**: If something is achiral it will not have an optical isomer.
Student Question

How many complex species will exhibit optical isomerism?

\[\mathrm{[CoCl_4(en)]}^-\quad \text{trans-[CrBrCl(en)_2]^+}\]

\[\text{cis-[CoCl}_2(\text{NH}_3)_4]^+\quad \text{cis-[CrBr}_2(\text{ox})_2]^-
\]

\[\text{cis-[CoCl}_3(\text{NH}_3)_3]\]

a) 0  
b) 1  
c) 2  
d) 3  
e) 4
In crystal field theory one assumes that the ligands can be represented by negative point charges and that the metal is a positive point charge located at the center of the system. One then examines how these negative point charges interact with the $d$ orbitals.

Which orbitals are lower in energy?

$e_g$-orbitals

$t_{2g}$-orbitals

Energy
Crystal Field Theory

Tetrahedral Complexes:

- **$t_{2g}$-orbitals**
  - $d_{x^2-y^2}$
  - $d_{xy}$
  - $d_{xz}$
  - $d_{yz}$

- **$e_g$-orbitals**
  - $d_{z^2}$

Which orbitals are lower in energy?
## Crystal Field Theory

### Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>~ Wavelength</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>800-620 nm</td>
<td>Red</td>
</tr>
<tr>
<td>620-580 nm</td>
<td>Orange</td>
</tr>
<tr>
<td>580-560 nm</td>
<td>Yellow</td>
</tr>
<tr>
<td>560-490 nm</td>
<td>Green</td>
</tr>
<tr>
<td>490-430 nm</td>
<td>Blue</td>
</tr>
<tr>
<td>420-400 nm</td>
<td>Violet</td>
</tr>
</tbody>
</table>

### Determining Color Absorbed

<table>
<thead>
<tr>
<th>Observed</th>
<th>Adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Green</td>
</tr>
<tr>
<td>Orange</td>
<td>Blue</td>
</tr>
<tr>
<td>Yellow</td>
<td>Violet</td>
</tr>
<tr>
<td>Green</td>
<td>Red</td>
</tr>
<tr>
<td>Blue</td>
<td>Orange</td>
</tr>
<tr>
<td>Violet</td>
<td>Yellow</td>
</tr>
</tbody>
</table>
Student Question

Crystal Field Theory

Put the ligand in order from smallest crystal field splitting to largest:

a) en < NH₃ < H₂O
b) NH₃ < en < H₂O
c) en < H₂O < NH₃
d) H₂O < NH₃ < en
e) None of the above

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed Color</th>
<th>Absorbed Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H₂O + NiSO₄ → [Ni(H₂O)₆]²⁺ + SO₄²⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(H₂O)₆]²⁺ + 6NH₃ → [Ni(NH₃)₆]²⁺ + 6H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(NH₃)₆]²⁺ + 3en → [Ni(en)₃]²⁺ + 6NH₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Different ligands affect the $d$ orbitals of a given metal ion to different degrees and thus produce different values of the ligand field splitting. The spectrochemical series arranges ligands according to the relative magnitudes of the ligand field splitting that they produce.
Student Question

Predict the number of unpaired electrons of an octahedral $d^7$ complex with a strong field ligands and weak field ligands respectively.

a) 1, 3
b) 3, 1
c) None of the above
In crystal field theory one assumes that the ligands can be represented by negative point charges and that the metal is a positive point charge located at the center of the system. One then examines how these negative point charges interact with the $d$ orbitals.

Octahedral Complexes:

- $e_g$-orbitals
- $t_{2g}$-orbitals

Which orbitals are lower in energy?

Energy
Ligand Field Theory

- **Which orbitals are considered?**
  
  6 orbitals (1 orbital from each of the 6 ligands) come from the ligands. 9 orbitals (1 s orbital, 3 p orbitals, and 5 d orbital) come from the d-metal. Giving a total of 15 molecular orbitals.

- **Where do the electrons come that fill the molecular orbitals?**
  
  The electrons from the ligands (12 e⁻) fill up all of the bonding \( t_{2g} \) orbitals, leaving the electrons from the metal to fill the nonbonding and antibonding orbitals.
If the $t_{2g}$ orbital is closer in energy to the $\pi$ bonding orbital, the two orbitals will interact and the electron in the filled $\pi$ orbitals will enter the lower energy molecular orbital therefore the electrons in the $d$-metal will have to occupy the higher energy molecular orbital which will decrease the octahedral field splitting. This is what happens for weak field ligands.
If however the $t_{2g}$ orbitals are closer in energy to the $\pi$ antibonding orbital when the two orbitals interact, there are no electrons from the ligand to go into the lower energy molecular orbital. Therefore the electrons in the metal can enter the lower energy orbital and the octahedral field splitting will increase. This is what happens for strong field ligands.
Big Idea: The properties of d-block metals are governed by the availability of d-orbitals and their variable valence. The physical properties of d-block complexes depends on the properties of the ligands bound to the metal.

The d-Block Elements and Their Compounds

- Know that the shape of the d-orbital and the number of d electrons affects the physical properties of transition metals
  - Know the shape of d-orbitals
  - Be able to write out the electron configuration for transition metals and their ions (6,7)
Take Away From Chapter 19

- **Coordination Compounds** (16)
  - Be able to determine the coordination number of coordination compounds
  - Be able to determine the number of bonding sites on a ligand (32)
  - Be able to name coordination compounds (22,23,24,25,26)
  - Know that only counter ions dissociate not ligands when put into solution
    - Be able to determine the coordination compound from experimental data (27,71)
  - Be able to recognize different types of isomers (31,40)
    - Structural (37)
      - Linkage (39)
    - Coordination
    - Stereoisomers (42)
      - Geometric (33,34)
      - Optical

Numbers correspond to end of chapter questions.
Take Away From Chapter 19

- **Crystal Field Theory**
  - Know octahedral and tetrahedral $d$-orbital splitting \((46)\)
  - Know the effects of strong and weak field ligands \((45,51,53)\)
    - High Spin (weak field)
    - Low Spin (strong field)
  - Be able to predict magnetic properties \((52,56)\)
    - Diamagnetic (pair e$^-$)
    - Paramagnetic (unpaired e$^-$)
  - Be able to determine $d$-orbital splitting \((50,57)\)
    - $\Delta = \frac{hc}{\lambda}$

- **Ligand Field Theory**

Numbers correspond to end of chapter questions.