Chapter 21
Transition Metals and Coordination Chemistry
Topics

- The transition metals: a survey
- The first-row transition metals
- Coordination compounds
- Isomerism
- Bonding in complex ions: the localized electron model
- The crystal field model
21.1 The transitions metals: a survey

General Properties

• In the main group elements chemistry changes markedly across a given period as the number of electrons changes
• Chemical similarities occur mainly within the vertical groups
• Transition metals show great similarities within a given period as well as within a given group.
• In transition elements the last electrons added for transition metals are inner electrons
  • \(d\) electrons for the d-block transition metals
  • and \(f\) electrons for the lanthanides and actinides
• The inner electrons cannot participate easily in bonding as can the valence s and p electrons
The Position of the Transition Elements on the Periodic
The Position of the Transition Elements on the Periodic Table

<table>
<thead>
<tr>
<th>d-block transition elements</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td>La*</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
<tr>
<td></td>
<td>Ac†</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Uun</td>
<td>Uuu</td>
<td>Uub</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>f-block transition elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Lanthanides</td>
</tr>
<tr>
<td>Ce</td>
</tr>
<tr>
<td>Th</td>
</tr>
<tr>
<td>†Actinides</td>
</tr>
<tr>
<td>Th</td>
</tr>
</tbody>
</table>

* Lanthanides
† Actinides
All Group A elements are known as main group elements or representative elements.
### Transition Metals

**Filling d-orbital shells**

<table>
<thead>
<tr>
<th>d-Block transition elements</th>
<th>3d</th>
<th>4d</th>
<th>5d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
</tr>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
</tr>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
</tr>
<tr>
<td>La*</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
</tr>
<tr>
<td>Ac†</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
</tr>
</tbody>
</table>

**Filling f-orbital shells**

<table>
<thead>
<tr>
<th>f-Block transition elements</th>
<th>*Lanthanides</th>
<th>†Actinides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>Pr</td>
</tr>
<tr>
<td></td>
<td>Th</td>
<td>Pa</td>
</tr>
</tbody>
</table>

* Lanthanides
† Actinides
Electron configuration of elements in the Periodic Table
Partial Electron Configurations of all elements
<table>
<thead>
<tr>
<th>Element</th>
<th>Partial Orbital Diagram</th>
<th>Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>4s: ↑↓ 3d: ↑</td>
<td>1</td>
</tr>
<tr>
<td>Ti</td>
<td>4s: ↑↓ 3d: ↑↑</td>
<td>2</td>
</tr>
<tr>
<td>V</td>
<td>4s: ↑↓ 3d: ↑↑↑↑</td>
<td>3</td>
</tr>
<tr>
<td>Cr</td>
<td>4s: ↑ 3d: ↑↑↑↑↑↑</td>
<td>6</td>
</tr>
<tr>
<td>Mn</td>
<td>4s: ↑↓ 3d: ↑↑↑↑↑↑</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>4s: ↑↓ 3d: ↑↑↑↑↑↑</td>
<td>4</td>
</tr>
<tr>
<td>Co</td>
<td>4s: ↑↓ 3d: ↑↑↑↑↑</td>
<td>3</td>
</tr>
<tr>
<td>Ni</td>
<td>4s: ↑↓ 3d: ↑↑↑↑↑↑↑</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>4s: ↑ 3d: ↑↑↑↑↑↑↑</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>4s: ↑↓ 3d: ↑↑↑↑↑↑↑↑↑</td>
<td>0</td>
</tr>
</tbody>
</table>
Electronic Configurations

- **d – block transition metals**
  - $ns^2 (n-1)d^x$ where $n = 4, 5, 6, 7$
  - (Hund’s Rule)
  - Ions lose $s$ electrons first.

- **f – block transition elements**
  - $ns^2 (n-1)d^{0,1} (n-2)f^x$ where $n = 6, 7$
  - Lanthanides & Actinides are even more similar than members of d – block.
General Properties of Transition metals

- Metallic luster
- high electrical and thermal conductivity
- Wide range of melting points (e.g. W at 3400°C, Hg is liquid at 25°C)
- Wide range of reactivity toward O$_2$
- Iron forms various oxides:
  - Fe$_2$O$_3$ - rust
  - Fe$_3$O$_4$
- Oxides of Cr, Co, and Ni protect the surface of the metal from further oxidation
- Very hard Coinage metals (Au, Ag, Pt, Pd) do not react readily with O$_2$
- They exist as more than one oxidation state: FeCl$_2$; FeCl$_3$
- They readily form ionic complexes

- Most compounds are colored
- Most compounds are paramagnetic (they contain unpaired electrons)
For Sc-Mn: the maximum possible oxidation state corresponds to the **loss of all 4s and 3d electrons**.

But beyond Mn, transition metal ions **do not achieve that high oxidation state**. 3d orbitals become of lower energy as **nuclear charge increases** and electrons become increasingly difficult to remove.
- **Oxidation States**: Most transition metal oxidation states are brightly colored.

- Manganese is shown left to right:
  - $\text{Mn}^{2+}$
  - $\text{Mn}^{3+}$
  - $\text{Mn}^{4+}$
  - $\text{Mn}^{6+}$
  - $\text{Mn}^{7+}$
Ionization energies

- Ionization energy increases gradually from left to right across the period.
- The **third** ionization energy (when electron is removed from 3d orbital) increases faster than the **1st ionization** energy as a result of a decrease in the energy of the 3d orbitals (increase in the stability) across the period.
Plots of the First (Red Dots) and Third (Blue Dots) Ionization Energies for the First-Row Transition Metals
Reduction potentials (ε°) for 1st-row transition metals in aqueous solutions:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Reduction Reaction</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Ti^{2+} + 2e^-</td>
<td>1.63</td>
</tr>
<tr>
<td>V</td>
<td>V^{2+} + 2e^-</td>
<td>1.20</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn^{2+} + 2e^-</td>
<td>1.18</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr^{2+} + 2e^-</td>
<td>0.91</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn^{2+} + 2e^-</td>
<td>0.76</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe^{2+} + 2e^-</td>
<td>0.44</td>
</tr>
<tr>
<td>Co</td>
<td>Co^{2+} + 2e^-</td>
<td>0.28</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni^{2+} + 2e^-</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu^{2+} + 2e^-</td>
<td>-0.34</td>
</tr>
</tbody>
</table>

Reducing ability generally decreases from left to right across the period. Only Cr and Zn do not follow this trend.
The 4d and 5d transition series

- There is a general although not regular decrease in size going from left to right in each series.
- There is a significant increase in radius in going from 3d to 5d.
- The 4d and 5d metals are remarkably similar in size.
Atomic Radii of the 3d, 4d, and 5d Transition Series
Lanthanide contraction

- Elements between La and Hf electrons are filling 4f orbitals
- 4f orbitals are buried in the interior of these atoms
- Additional electrons do not add to atomic size
- Increasing the nuclear charge caused the radii of lanthanide elements to decrease going from left to right;
- This lanthanide contraction just offsets the normal increase in size due to going from one n level to another
- Thus 4d and 5d elements have similar sizes
- 4d and 5d have similar chemistry in the vertical groups (Hf and Zr are similar)
21.2 The first raw transition metals

Electron Configurations For Potassium Through Krypton

<table>
<thead>
<tr>
<th>K</th>
<th>Ca</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
<th>Ge</th>
<th>As</th>
<th>Se</th>
<th>Br</th>
<th>Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>4s 1</td>
<td>4s 2</td>
<td>3d 1</td>
<td>3d 2</td>
<td>3d 3</td>
<td>4s 1 3d 5</td>
<td>3d 5</td>
<td>3d 6</td>
<td>3d 7</td>
<td>3d 8</td>
<td>4s 1 3d 10</td>
<td>3d 10</td>
<td>4p 1</td>
<td>4p 2</td>
<td>4p 3</td>
<td>4p 4</td>
<td>4p 5</td>
<td>4p 6</td>
</tr>
</tbody>
</table>
The first raw transition metals

Scandium, Sc

- It is a rare element, exists as 3+ oxidation state
- Most of its compounds are colorless and diamagnetic. Sc$^{3+}$ has no electrons in the 3d orbital (electrons responsible for both properties)
- It is not widely used. May be in some electronic devices
Titanium (0.6% by mass of Earth's crust)

- Titanium metal—characterized by low density, high strength, chemical inertness—used as a structural element in high-demand uses such as jet engines, high-performance bicycles, etc.

- Titanium ions—often found in +4 oxidation state (indicated as Ti$^{4+}$, or Ti(IV))

  \[
  \text{TiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{TiO}_2(\text{s}) + 2\text{HCl}(\text{g})
  \]

- In the +3 oxidation state, Titanium in Sapphire (Ti$^{3+}$:Al$_2$O$_3$) is one of the most important commercial laser materials
Manganese (Mn)
(Latin *magnes*, magnet, from magnetic properties of pyrolusite, MnO₂)

- Manganese minerals are widely distributed, primarily as oxides, silicates, and carbonates.

- Mn is the only transition metal that can exist in all oxidations states from +2 to +7

- A manganese catalyst in green plants is responsible for all of the oxygen in our environment, produced through photosynthesis.

- Mn is used to form many important alloys. In steel, Mn improves the rolling and forging qualities, strength, toughness, stiffness, and other properties.
Iron (Fe)

- The use of iron is prehistoric. Many important alloys are primarily iron, including alloys with carbon, Mn, Ni, Cr, etc.

- High abundance in the universe—found in the sun and many stars in considerable quantity. Iron is a principal component of one class of meteorites, the siderites.

- The core of the earth is thought to be ca. 90% iron. The most common iron ore in the Earth's crust is hematite ($\text{Fe}_2\text{O}_3$)

- Fe is a vital element for plant and animal life. For example, it is at the core of hemoglobin, the oxygen transporter in our blood.

- Iron is the cheapest, most abundant, useful, and important of all metals.
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Cobalt (Co)

(German Kobald, goblin or evil spirit. Greek cobalos, mine)

- Occurs in many minerals, often associated with Ni, Ag, Pb, Cu, and Fe ores
- Important metal for magnetic applications, including magnetic steels and magnetic shielding alloys.
- Cobalt salts have been used for centuries as color pigments (cobalt blues) in porcelain, glass, pottery, and enamels
Nickel (Ni)
(German, from kupfernickel, "Old Nick's copper" or Satan's copper)
- As a metal, it is chiefly valued for its alloys with Fe and Co
- Fine Ni powders used as catalysts for hydrogenation reactions
Copper (Cu)

(Latin cuprum, from the island of cyprus)

• Said to have been mined for > 5000 years
• Cu metal is highly conductive of heat and electricity
• Most important copper ores are sulfides, oxides, and carbonates
Zinc (Zn)

(German Zink, of obscure origin)

- Centuries before it was recognized as a distinct element, Zn ores were used for making brass

- ZnO is widely used in the manufacture of paints, cosmetics, pastics, storage batteries, and electrical equipment among others.

- ZnS (among the most abundant natural ores of Zn) is used as an important phosphor material in X-ray and TV screens, and in fluorescent lights
21.3 Coordination Compounds

- A coordination compound consists of a complex ion and counter ions (anions or cations as needed to produce a neutral compound).
- Often complex ions (both cation and anion)
- But neutral is possible if ligands exactly balance metal ion’s charge.
- \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl} ; [\text{Fe(en)}_2(\text{NO}_2)_2]\text{SO}_4\]
- \(\text{K}_3 [\text{Fe(CN)}_6]\)
- Often highly colored
  - Since MO energy separations match visible light photon energies, \(\therefore\) absorb visible light.
Werner’s Theory

- Metal ions have **primary** and **secondary** valences.
- The **primary** valence is the **oxidation number** of the metal.
- The **secondary** valence is the **number of atoms** directly bonded to the metal ion which is the **coordination number**.
- Square brackets are used to set off the coordination sphere from the rest of the compound.
- When a complex **dissolves**, the **coordination sphere remains intact**.
Composition of Complex Ions and Coordination Compounds

\[
\text{Cu}^{2+} (aq) + 4 \text{NH}_3 (aq) \rightarrow \text{Cu(NH}_3\text{)}^2_4 (aq)
\]

\[\text{Light Blue}\]

\[
\text{Cu}^{2+} + 4 : \text{N} - \text{H} \rightarrow \text{Cu}\]

\[\text{Covalent Bond}\]

\[\text{Coordinate Bond}\]

(Complex ion)
$[\text{Cu} \ (\text{NH}_3)_4]^2+ \quad \text{Charge of the complex ion}$

$\text{Central atom}$

$\text{Ligand group}$

$\text{(neutral molecule &/or -ve ion)}$

$\text{Coordination number}$

$[\text{Cu} \ (\text{NH}_3)_4^2+ \text{Cl}_2 : \text{Coordination Compound}]$
## Typical Coordination Numbers for Some Common Metal Ions

<table>
<thead>
<tr>
<th>$M^+$</th>
<th>Coordination Numbers</th>
<th>$M^{2+}$</th>
<th>Coordination Numbers</th>
<th>$M^{3+}$</th>
<th>Coordination Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^+$</td>
<td>2, 4</td>
<td>Mn$^{2+}$</td>
<td>4, 6</td>
<td>Sc$^{3+}$</td>
<td>6</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>2</td>
<td>Fe$^{2+}$</td>
<td>6</td>
<td>Cr$^{3+}$</td>
<td>6</td>
</tr>
<tr>
<td>Au$^+$</td>
<td>2, 4</td>
<td>Co$^{2+}$</td>
<td>4, 6</td>
<td>Co$^{3+}$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni$^{2+}$</td>
<td>4, 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu$^{2+}$</td>
<td>4, 6</td>
<td>Au$^{3+}$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn$^{2+}$</td>
<td>4, 6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Types of Complex Species

Coordination Compounds

Complex Species

- Complex Anion
  - $[\text{Pt} (\text{NH}_3) \text{Cl}_3]^{-}$
  - (Pt$^{2+}$)
- Neutral Complex
  - $[\text{Pt} (\text{NH}_3)_2 \text{Cl}_2]^0$
  - (Pt$^{2+}$)
- Complex Cation
  - $[\text{Pt} (\text{NH}_3)_4]^{2+}$
  - (Pt$^{2+}$)

Coordination Compounds
• **Charge of a complex** is the sum of the charges on central metal and ligands.

\[
[Cu(NH_3)_4]^{2+}
\]

\[+2 + 4 (0) = +2\]

1) What is the oxidation number for [Co(NH_3)_5Cl](NO_3)_2?

2) A complex ion contains a Cr^{3+} bound to four H_2O molecules and two Cl^- ions. Write its formula.
Ligands

- A Ligand is a neutral molecule or ion having a lone electron pair that can be used to form a bond to a metal ion (Lewis base).

- Coordinate covalent bond: metal-ligand bond

- Monodentate ligand: one bond to metal ion

- Polydentate ligand: can form more than two bonds to a metal ion

- Chelating agent or chelate: Ligands have more than one atom with a lone electron pair
Ligands

- From Latin *ligare*, “to bind”
- Must be a Lewis base (e\(^{-}\) donor)
- Could, as does EDTA, have several Lewis base functionalities: *polydentate*!
- If monodentate, should be small enough to permit others to bind.
- Relative bonding strengths:

  \[
  \text{X}^- < \text{OH}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- \]

Chelate: polydentate
Ligands; Chelating Agents

Ligand: A Species (molecule or anion) with unshared pair(s) of electrons (Lewis Base)

Usually, the ligand contains an atom of: (C, N, O, S, F, Cl, Br, I)
Types of Ligands

1. Monodentate Ligands
   (Donate a single electron pair).

\[ \text{NH}_3, \text{OH}^-; [\text{OH}]^-; \text{F}, \text{Cl}, \text{Br}, \text{I}; \text{NO}_2^-, \text{CN}^-, \text{SCN}^- \]

Each ligand donates only one pair of e\textsuperscript{-}.
Multidentate Ligands (Chelating Agents)

Contain more than one atom of unshared pair of electrons, i.e., they donate more than one pair of e-

* Oxalate (bidentate)

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{O} \\
\end{array}
\]

\(\text{C}_2\text{O}_4^{2-}\)

* Ethylenediamine (bidentate)

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\end{array}
\]

\((\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2)\)
* Ethylenediaminetetraacetic acid (EDTA)

(hexadentate)
### TABLE 21.13 Some Common Ligands

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unidentate/monodentate</strong></td>
<td>$\text{H}_2\text{O}$, $\text{CN}^-$, $\text{SCN}^-$ (thiocyanate), $\text{X}^-$ (halides)</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}_3$, $\text{NO}_2^-$ (nitrite), $\text{OH}^-$</td>
</tr>
<tr>
<td><strong>Bidentate</strong></td>
<td>Oxalate ($\text{C}_2\text{O}_4^2-$)</td>
</tr>
<tr>
<td></td>
<td>Ethylenediamine (en) ($\text{H}_2\text{N}-(\text{CH}<em>2)</em>{\text{2}}-\text{NH}-(\text{CH}<em>2)</em>{\text{2}}-\text{NH}_2$)</td>
</tr>
<tr>
<td></td>
<td>Diethylenetriamine (dien) ($\text{H}_2\text{N}-(\text{CH}<em>2)</em>{\text{2}}-\text{NH}-(\text{CH}<em>2)</em>{\text{2}}-\text{NH}_2$)</td>
</tr>
<tr>
<td></td>
<td>Ethylenediaminetetraacetate (EDTA) ($\text{H}_2\text{N}-(\text{CH}<em>2)</em>{\text{2}}-\text{NH}-(\text{CH}<em>2)</em>{\text{2}}-\text{NH}_2$)</td>
</tr>
</tbody>
</table>

**Polydentate**

Six coordinating atoms
Bidentate and Monodentate Ligand
The Coordination of EDTA with a $2^+$ Metal Ion
Determining Oxidation Number and Coordination Number For a Complex

- **Charge on complex = charge on metal ion + Charges of ligands**

- **Example: [Rh(NH$_3$)$_5$Cl](NO$_3$)$_2$**

- **First determine the charge on the complex**

- **Since NO$_3^-$ is not a part of the complex, the charge on the complex is 2+**

- **2+ = x + -1 so x = +3; The coordination number is 6.**

- **Write the formula for a complex made from platinum(II) and two ammonia molecules and two bromide ions**

- **[Pt(NH$_3$)$_2$Br$_2$]; Charge of complex = 2+ + (2)(1-) = 0**

- **The coordination number is 4**
<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Shape</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>$[\text{CuCl}_2]^-$, $[\text{Ag(NH}_3)_2]^+$, $[\text{AuCl}_2]^-$</td>
</tr>
<tr>
<td>4</td>
<td>Square planar</td>
<td>$[\text{Ni(CN)}_4]^{2-}$, $[\text{PdCl}_4]^{2-}$,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[\text{Pt(NH}_3)_4]^{2+}$, $[\text{Cu(NH}_3)_4]^{2+}$</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>$[\text{Cu(CN)}_4]^{3-}$, $[\text{Zn(NH}_3)_4]^{2+}$,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>$[\text{Ti(H}_2\text{O)}_6]^{3+}$, $[\text{V(CN)}_6]^{4-}$,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[\text{Cr(NH}_3)_4\text{Cl}_2]^+$, $[\text{Mn(H}_2\text{O)}_6]^{2+}$,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[\text{FeCl}_6]^{3-}$, $[\text{Co(en)}_3]^{3+}$</td>
</tr>
</tbody>
</table>
Writing the formulas of complexes

- List central atom first followed by ligands, may be enclosed by brackets with the charge shown outside.

\[
\text{[CrCl}_6\text{]}^{3-}
\] or \[
\text{CrCl}_6^{3-}
\]
• For more than one kind of ligands, ligands are listed in alphabetical order

• \([\text{Cr} \text{ Br}_2 (\text{en})_2 ] \text{Br}\)

• \([\text{Cr(H}_2\text{O})_4\text{Cl}_2]\text{Cl}\)
Naming Coordination Compounds

- Name the cation before the anion (end all anions with *ate*).
- Name the ligands before the metal within the complex.
- Ligands are named in alphabetical order (excluding prefixes used to designate the number of ligands).
- Anionic ligands end in the letter _o_.
- Special names are used for some ligands.
  - Water (*aqua*)
  - NH₃ (*ammine*)
  - CO (*carbonyl*)
- Prefixes are used to designate number of ligands
  - (di, tri, tetra, penta, hexa)
- For multiple polydentate ligands use (bis, tris, tetrakis, pentakis and hexakis)
Nomenclature of coordination compounds
Naming Anionic ligands

- Anions that electrically balance cationic coordination complexes can also be present as ligands in that complex!

- So they need different names that identify when they’re being used as ligands:

<table>
<thead>
<tr>
<th>Species</th>
<th>Cl⁻</th>
<th>NO₂⁻</th>
<th>CN⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>As ion:</td>
<td>chloride</td>
<td>nitrite</td>
<td>cyanide</td>
</tr>
<tr>
<td>As ligand:</td>
<td>chloro</td>
<td>nitro</td>
<td>cyano</td>
</tr>
</tbody>
</table>
- The suffix –ide is replaced by –O
- The suffix –ate or –ite is replaced by –ato
- Cl: chloro
- OH: hydroxo
- CN: cyano
- SO₄: sulfato
- NO₃: nitrato
- NO₂: nitro
- ONO: nitrito
- SCN: thiocyanato
- C₂O₄: oxalato
- CO₃: carbonato
Naming Neutral Molecules (ligands)

- The names of neutral molecules are not changed: ethylene diamine

\[ \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2 \]

- Some molecular ligands get new names

<table>
<thead>
<tr>
<th>Species</th>
<th>H$_2$O</th>
<th>NH$_3$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal:</td>
<td>water</td>
<td>ammonia</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>As ligand:</td>
<td>aqua</td>
<td>ammine</td>
<td>carbonyl</td>
</tr>
</tbody>
</table>
Name the following compound:

- \([ \text{Cr Br}_2 (\text{en})_2 ] \text{ Br}\)

  - Anion, bromide, is named \textit{last}
  - chromium(III) is named \textit{next-to-last}
  - Ligands named 1\textsuperscript{st} in alphabetical order:
    - Number of a ligands is shown as Greek prefix:
      - dibromo ... 
    - Unless it already uses “di” then use “bis”
      - Dibromobis(ethylenediammine) ...

- \textbf{Dibromobis(ethylenediammine)chromium(III) bromide}
Naming cationic complexes

1. Ligands → Central atom

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

* Hexaaquachromium(III) ion

* Oxidation state of the Central atom is indicated by Roman numeral

* The number of each kind of ligand is indicated by a Greek prefix

- di- tri- tetra- penta- hexa- hepta- octa- nona- deca-

- 2 3 4 5 6 7 8 9 10
* In case of more than one ligand, the ligands are listed in alphabetical order:

\[
[\text{Co} (\text{NH}_3)_4 \text{Cl}_2]^+ : \text{tetraammin dichlorocobalt(III)} \quad \text{im}
\]

\[
[\text{Zn} (\text{H}_2\text{O})_3 \text{OH}]^+ : \text{triaqua hydroxozinc(II)} \quad \text{im}
\]

* Ignore prefixes

* Ignore distinction between anionic & neutral ligands
* In case of more than one ligand, the ligands are listed in alphabetical order:

\[ [\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+ : \text{tetraamminedichlorocobalt(III)} \]

\[ [\text{Zn(H}_2\text{O)}_3\text{OH}]^+ : \text{triaquahydroxozinc(II)} \]

* Ignore prefixes
* Ignore distinction between anionic & neutral ligands
Anionic Complexes

Complexes that are anions are named with the suffix, \(-\text{ate}\), after the name of the central metal atom.

\[ \text{Zn(OH)}_4^{2-} \]

\textit{tetrahydroxozincate} (II)

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

\textit{hexacyanoferrate} (III)
When the symbol of element is derived from the Latin name, -ate, is added to this name

CuCl₄²⁻: tetrachlorocuprate(II)
PbBr₃(H₂O)₆⁺: triaquabromoplumbate(II)
- When the complex has a negative charge overall (i.e. is an anion), -ate is added to the metal name.
- Also, the Latin names are used.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Name of Metal in Anionic Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Aluminate</td>
</tr>
<tr>
<td>Chromium</td>
<td>Chromate</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Cobaltate</td>
</tr>
<tr>
<td>Copper</td>
<td>Cuprate</td>
</tr>
<tr>
<td>Gold</td>
<td>Aurate</td>
</tr>
<tr>
<td>Iron</td>
<td>Ferrate</td>
</tr>
<tr>
<td>Lead</td>
<td>Plumbate</td>
</tr>
<tr>
<td>Manganese</td>
<td>Manganate</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Molybdate</td>
</tr>
<tr>
<td>Nickel</td>
<td>Nickelate</td>
</tr>
<tr>
<td>Silver</td>
<td>Argentate</td>
</tr>
<tr>
<td>Tin</td>
<td>Stannate</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Tungstate</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zincate</td>
</tr>
</tbody>
</table>
Numbers for Ligands Containing Greek prefixes

e.g. ethylenediamine

The number is indicated by the prefixes:

- bis-
- tris-
- tetrakis-

(twice) (thrice) (four times)

\[ \text{Cu(en)}_2^{2+} : \text{bis(ethylenediamine)Copper(II)} \]

\[ \text{Cr(en)}_3^{3+} : \text{tris(ethylenediamine)Chromium(III)} \]
Names of Coordination Compounds

(Compounds Containing Complex Ions)

Name of Cation → Name of Anion

\[[\text{Cu} (\text{NH}_3)_4]\text{Cl}_2\]: tetraamminecopper(II) chloride

\[[\text{Fe} (\text{en})_3]\text{PO}_4\]: tris(ethylenediamine)iron(III) phosphate

\(K_3[\text{Fe} (\text{en})_6]\): potassium hexacyanoferrate(III)

\[[\text{Co} (\text{en})_3](\text{NO}_3)_3\]: tris(ethylenediamine)cobalt(III) nitrate
Name the following compound:

- $\text{Na}_2 \left[ \text{PbI}_4 \right]$
- Sodium tetraiodoplumbate(II)
  - While lead(II) is the source, the Latin root is used for the complex with “ate” denoting anion.
- $\text{Li} \left[ \text{AgCl}_2 \right]$, lithium dichloroargentate
21.4 Isomerism

- Isomers are compounds with the same chemical formula but different structures.
- Having different structures, they will have defacement physical and chemical properties.
Some Classes of Isomers in coordination compounds

Isomers
(same formula but different properties)

- Structural isomers
  (different bonds)

- Stereoisomers
  (same bonds, different spatial arrangements)

  - Geometric (cis-trans) isomerism
  - Optical isomerism

- Coordination isomerism
- Linkage isomerism
Structural isomerism

- Isomers contain the same atoms but one or more bonds differ.

- Two types:

1. Coordination isomerism

   The composition of the complex ion varies

   \[ \text{[Cr(NH}_3\text{)}_5\text{SO}_4\text{]}\text{Br} : \text{[Cr(NH}_3\text{)}_5\text{Br}]\text{SO}_4 \]
Coordination isomers

- \([ \text{Pb} \ (\text{en})_2 \text{Cl}_2 \ ] \ \text{Br}_2\)
- bis(ethylenediammine)dichlorolead(IV) bromide
  - Only 1 of 3 possible coordination isomers
  - The other 2 are
    - \([ \text{Pb} \ \text{Br} \ (\text{en})_2 \text{Cl} \ ] \ \text{Br} \ \text{Cl}\)
- bromobis(ethylenediammine)chlorolead(IV)bromide chloride
  - \([ \text{Pb} \ \text{Br}_2 \ (\text{en})_2 \ ] \ \text{Cl}_2\)
- dibromobis(ethylenediammine)lead(IV) chloride
Linkage isomerism

- The composition of the complex ion is the same, but the point of attachment of at least one of the ligands differs.

- \([\text{Co(NH}_3\text{)}_4(\text{NO}_2\text{)}\text{Cl}]\text{Cl}\)
  Tetraamminechloronitrocoaltar(III) chloride

- \([\text{Co(NH}_3\text{)}_4(\text{ONO})\text{Cl}]\text{Cl}\)
  Tetraamminechloronitritocobalt(III) chloride
Nitro, $\text{NO}_2^-$

Yellow

Nitrito, $\text{NO}_2^-$
Stereoisomerism

- Steroisomers have the same bonds but different spatial arrangements of the atoms. Two types:

  1. **Geometrical** isomerism or cis-trans isomerism
     
     It occurs when atoms or group of atoms can assume different positions around a rigid ring or bond

  2. **Optical** isomerism
     
     Isomers have opposite effects on plane-polarized light
Geometric Isomerisms

The structures differ only in the spatial arrangement of ligands about the central metal atom.

1. Tetrahedral Geometries

All positions are equivalent

**No Geometric isomerism**
2. Square Planar Geometries

* Ma₂b₂

Cis

Cl ─ Pt ─ NH₃

(polar)

trans

Cl ─ Pt ─ NH₃

NH₃ ─ Cl

(nonnopolar)

Ma₂b₂

MA₂BC

Adjacent Corners

(opposite Corners)
Cis-Yellow

Trans-Pale yellow
\[
\text{cis: } \text{MA}_2 \text{b c}
\]

\[
\text{trans: } \text{M c}
\]
Octahedral Geometry

Positions 1 4 2
1 4 3
1 4 4
or 1 4 5

are cis to each other

Positions 1 4 6 are trans to each other
Trans isomer

Cis isomer

Keep the ligand with smaller number in the same location each time
Optical isomerism

- Isomers have opposite effects on plane polarized light.
- Optical activity is exhibited by molecules that have superimposable mirror images.
- Your hands are nonsuperimposable mirror images.
- The two hands are related like an object and its mirror image; one cannot be turned to make it identical to the other.
- Many molecules show this feature, such as the.
- Objects that nonsuperimposable mirror images are said to be chiral (from the Greek word meaning "hand").
Unpolarized light consists of waves vibrating in many different planes.

- When light is emitted from a source, the oscillating electric fields of the photons in the beam are oriented randomly.
- If the light is passed through a polarizer, only the photons with electric fields oscillating in a single plane remain, constituting plane polarized light.
The rotation of the plane of polarized light by an optically active substance

Solutions of certain compounds could rotate the plane of polarization of light
A human hand exhibits a nonsuperimposable mirror image both with palms down.

Left and right hands are mirror images of each other.

Palm is facing you

Palm is facing the mirror
Isomers I and II of Co(en)$_3^{3+}$ are mirror images, that cannot be superimposed (Nonsuperimposable)
The Optical Isomers of Co(en)$_2$Cl$_2^+$

- The isomers above are nonsuperimposable mirror images called **enantiomers**.
- They rotate plane-polarized light in opposite directions and are thus optical isomers.
The isomer that rotates the plane of light to the right is said to be dextrorotatory, designated by $d$.

The isomer that rotates the plane of light to the left is levorotatory $l$.

Equal mixture of the $d$ and $l$ forms in solution, called a racemic mixture.

Racemic mixture does not rotate the plane of the polarized light at all because the two opposite effects cancel each other.
Enantiomers

• Objects that have nonsuperimposable mirror image (two hands) are said to be chiral (from Greek cheir: hand)
• An object or compound is **achiral** if it has a symmetry plane cutting through the middle
1. The VSEPR (Valence Shell Electron Pair Repulsion) can be used to account for bonding in complex ions but generally it does not work for predicting structure of complex ions.

- We can safely assume that a complex ion with a coordination number of 6 will have an octahedral arrangement of ligands, and complexes with two ligands will be linear.
- On the other hand, complex ions with a coordination number of 4 can be either tetrahedral or square planar.

2. The interaction between a metal ion and a ligand can be viewed as a Lewis acid-base reaction with the ligand donating a lone pair of electrons to an empty orbital of the metal ion to form a coordinate covalent bond:
Bonding in complexes

- Valence bond theory predicts metal complexes arise from **overlap of filled ligand orbitals and vacant metal orbitals**
- Resulting bond is a coordinate covalent bond
A Set of $d^2sp^3$ hybrid orbitals on $\text{Co}^{3+}$ can accept an electron pair from each of six $\text{NH}_3$ ligands to form the $\text{Co(NH}_3)_6^{3+}$ ion.
The hybrid orbitals required for tetrahedral, square planar and linear complex ions

- CoCl$_4^{2-}$
- Ni(CN)$_4^{2-}$
- Ag(NH$_3$)$_2^+$
Although the localized electron model can account in a general way for metal ligand bonds, it is rarely used today because it cannot readily account for important properties of complex ions such as magnetism and color.
21.6 Crystal Field Model

- The main reason the localized electron model cannot fully account for the properties of complex ions is that it gives no information about how the energies of the d orbitals are affected by complex ion formation.

- This is critical because, the color and magnetism of complex ions result from changes in the energies of the metal ion d orbitals caused by the metal-ligand interactions.

- The crystal field model focuses on the energies of the d orbitals.

- In its simplest form, the crystal field model assumes that the ligands can be approximated by negative point charges and that metal-ligand bonding is entirely ionic.
Crystal Field Model, continued

- When ligands surround the metal cation, they change the energy of the d orbitals, splitting them into multiple energies. (originally the 5 d orbitals are said to be degenerate: have similar energies)

- There is tetrahedral splitting, square planar splitting and octahedral splitting.

- The resulting energy differences allow electrons to jump between d orbitals causing visible light absorption.
Octahedral arrangement of point charge ligands and the orientation of the 3d orbitals

- Two of the orbitals, \(d_{z^2}\) and \(d_{x^2-y^2}\), point their lobes directly at the point-charge ligands.

- Three of the orbitals, \(d_{xy}\), \(d_{yz}\), and \(d_{xz}\), point their lobes between the point charges.

Why and How?
Ligands create an electric field around the central ion that causes changes in the relative energies of the d-orbitals.

The **difference in the approach of ligand molecules towards the orbitals** of the central metal ion would split the d-orbitals into two groups of different energies.

Because the negative point-charge ligands repel negatively charged electrons, the electrons will first fill the d-orbitals farthest from the ligands to minimize repulsions.

That is the $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals are at a lower energy in the octahedral complex than are the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals.

The negative point-charge ligands increase the energies of all the d orbitals. However, the orbitals that point at the ligands are raised in energy more than those that point between the ligands.
$d$ orbitals of the free metal ion

$\Delta = \text{crystal field splitting energy}

\begin{align*}
&d_{xy} \quad d_{xz} \quad d_{yz} \\
&e_{g} \quad d_{z^2} \quad d_{x^2-y^2} \\
&t_{2g}
\end{align*}$

$d$ orbitals of the metal ion in an octahedral field of ligands
Possible electron arrangements in the split 3d orbitals in an octahedral complex of Co\(^{3+}\), (electron configuration 3d\(^6\)) in a strong field (large \(\Delta\) value),

- The electrons fill the t\(_{2g}\) set first, giving a diamagnetic complex.

(b) In a weak field (small \(\Delta\) value), the electrons occupy all five orbitals before any pairing occurs.

\[ \text{Co} : 4s^2\ 3d^7 \quad \text{Co}^{3+} : 3d^6 \]
The size of $\Delta$ depends on:

1. the **nature of the ligand** - "spectrochemical series" --

   $\Delta$ decreases as shown below
   
   \[
   \text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > I^- 
   \]
   "strong field ligands"    "weak field ligands"

   Large $\Delta$

   small $\Delta$

2. the **oxidation state** of the metal

   $\Delta$ is greater for $M^{3+}$ than for $M^{2+}$

3. the **row** of the metal in the periodic table

   for a given ligand and oxidation state of the metal,
   $\Delta$ increases going down in a group
   
   e.g., $\Delta$ is greater in $\text{Ru(NH}_3)_6^{3+}$ than in $\text{Fe(NH}_3)_6^{3+}$

   $\Delta$ decreases
   - $\lambda$ of light increase (more colored)
   - Tendency to form high spin complexes

$\text{SC}^{3+}: 18[\text{Ar}]$    No $d$-electrons
$\text{Zn}^{2+}: 18[\text{Ar}]3d^{10}$    No electron movement
$d$ Orbital Splitting Diagrams for Octahedral Complexes

Minimum Number of unpaired $e^-$

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

Small $\Delta$  "high spin"

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

$Fe(H_2O)_6^{2+}$

Large $\Delta$  "low spin"

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

$Fe(CN)_6^{4-}$
- CN\(^-\) is a stronger field ligand than is H\(_2\)O which leads to a greater \(\Delta\) value (i.e., a greater d orbital splitting)

- Fe(H\(_2\)O)\(_6\)\(^{2+}\) "high spin" complex paramagnetic (4 unpaired electrons)

- Fe(CN)\(_6\)\(^{4-}\) "low spin" complex diamagnetic (no unpaired electrons)

- the CN\(^-\) complex with the larger \(\Delta\) value absorbs light of higher energy (i.e., higher frequency but shorter wavelength)
Other coordination geometries

The crystal field diagrams for octahedral and tetrahedral complexes
The relative energies of the sets of $d$ orbitals are reversed.

For a given type of ligand, the splitting is much larger for the octahedral complex because in this arrangement the $dx^2$ and $d_{x^2-y^2}$ point their lobes directly at the point charges and are thus relatively high in energy.
d-orbital splitting diagram for square planar complexes

- The crystal field diagram for a square planar complex oriented in the xy plane with ligands along the x and y axes
The crystal field diagram for a linear complex where the ligands lie along the z axis.