Chapter 23: The Transition Elements and Their Coordination Compounds

23.1 An Overview of Transition Element Properties

23.2 The Inner Transition Elements

23.3 Highlights of Selected Transition Metals

23.4 Coordination Compounds

23.5 Theoretical Basis for the Bonding and Properties of Complexes
**Fig. 23.1**

The diagram illustrates the periodic table focusing on the *d* and *f* block elements. The transition elements are highlighted in blue, with the inner transition elements shaded in grey. The periodic table is organized by periods and groups, with elements classified according to their block assignment:

- **d Block Elements**: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
- **f Block Elements**: La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg
- **Inner Transition Elements**: Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
- **Periodic Table**: The full periodic table is shown, with elements arranged by atomic number, group, and period.

This visual representation provides a clear overview of the distribution of transition and inner transition elements within the periodic table.
# Orbital Occupancy of the Period 4 Metals–I

<table>
<thead>
<tr>
<th>Element</th>
<th>Partial Orbital Diagram</th>
<th>Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td><img src="image1" alt="Diagram" /></td>
<td>1</td>
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<tr>
<td>Ti</td>
<td><img src="image2" alt="Diagram" /></td>
<td>2</td>
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<tr>
<td>V</td>
<td><img src="image3" alt="Diagram" /></td>
<td>3</td>
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<td>Cr</td>
<td><img src="image4" alt="Diagram" /></td>
<td>6</td>
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<td>Mn</td>
<td><img src="image5" alt="Diagram" /></td>
<td>5</td>
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</table>

Table 23.1 (p. 1003)
## Orbital Occupancy of the Period 4 Metals–II

<table>
<thead>
<tr>
<th>Element</th>
<th>Partial Orbital Diagram</th>
<th>Unpaired Electrons</th>
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<tbody>
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<td>Fe</td>
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Table 23.1 (p. 1003)
Fig. 23.3

Horizontal Trends in Period 4 Elements

A. Atomic radius (pm) (Atomic size)

B. Electronegativity

C. First ionization energy (kJ/mol)

Fig. 23.3
Vertical Trends within the Transition Elements

Fig. 23.4
<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
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Table 23.2
(p. 1006)
# Standard Electrode Potentials of Period 4 M^{2+} Ions

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^0 ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ti}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Ti}(s) )</td>
<td>-1.63</td>
</tr>
<tr>
<td>( \text{V}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{V}(s) )</td>
<td>-1.19</td>
</tr>
<tr>
<td>( \text{Cr}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Cr}(s) )</td>
<td>-0.91</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Mn}(s) )</td>
<td>-1.18</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Fe}(s) )</td>
<td>-0.44</td>
</tr>
<tr>
<td>( \text{Co}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Co}(s) )</td>
<td>-0.28</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Ni}(s) )</td>
<td>-0.25</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Cu}(s) )</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} \text{(aq)} + 2 \text{e}^- \rightarrow \text{Zn}(s) )</td>
<td>-0.76</td>
</tr>
</tbody>
</table>

In general reducing strength decreases across the series.

The less negative the \( E^0 \) the less the reducing strength.

**Table 23.3 (p. 1007)**
Colors of Representative Compounds of the Period 4 Transition Metals

Fig. 23.6

a = Scandium oxide  
b = Titanium(IV) oxide  
c = Vanadyl sulfate dihydrate  
ed = Sodium chromate  
e = Manganese(II) chloride tetrahydrate  
f = Potassium ferricyanide  
g = Cobalt(II) chloride hexahydrate  
h = Nickel(II) nitrate hexahydrate  
i = Copper(II) sulfate pentahydrate  
j = Zinc sulfate heptahydrate
## Some Properties of Group 6B(6) Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Radius (pm)</th>
<th>IE₁ (kJ/mol)</th>
<th>$E^\circ (V)$ for $M^{3+}<em>{\text{(aq)}}/M</em>{\text{(s)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>128</td>
<td>653</td>
<td>-0.74</td>
</tr>
<tr>
<td>Mo</td>
<td>139</td>
<td>685</td>
<td>-0.20</td>
</tr>
<tr>
<td>W</td>
<td>139</td>
<td>770</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

Table 23.4 (p. 1008)
23.2 The Inner Transition Elements

14 lanthanides and 14 radioactive actinides

The lanthanides - Silvery, high melting metals. **Common oxidation state is +3**

Ground-state electronic configuration is [Xe] 6s^2 4f^x 5d^0

Exceptions: Ce [Xe] 6s^2 4f^1 5d^1 forms stable Ce^{4+} ion with f^0

Gd [Xe] 6s^2 4f^7 5d^1 forms stable Gd^{3+} ion with f^7

Lu [Xe] 6s^2 4f^{14} 5d^1 forms stable Lu^{3+} ion with f^{14}

Ionic bonding is more prevalent for the lower oxidation states. TiCl_2 ionic

Covalent bonding is more prevalent for the higher oxidation states. TiCl_4 molecular liquid

In higher oxidation states, the atoms have higher charge densities, so they polarize the electron clouds of the nonmetal ions more strongly and the bonding becomes more covalent
Chromium metal and Cr$^{2+}$ are reducing agents

\[4\text{Cr}^{2+}(\text{aq}) + \text{O}_2 + 4\text{H}^+(\text{aq}) \rightarrow 4\text{Cr}^{3+}(\text{aq}) + 2\text{H}_2\text{O(l)}\]

Chromium(VI) in acid solution are strong oxidizing agents.

\[4\text{Cr}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 4\text{Cr}^{3+}(\text{aq}) + 2\text{H}_2\text{O(l)} \quad E^0 = 1.33\text{V}\]

In basic solution, CrO$_4^{2-}$ ion is a weaker oxidizing agent.

\[\text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O(l)} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3(\text{s}) + 5\text{OH}^-(\text{aq}) \quad E^0=-0.13\text{V}\]
Concept of Valence-State Electronegativity

Why chromium form o xoanion and why the oxide acidity increases with oxidation state?

A metal in higher oxidation state is positively charged and attracts electrons - in effect its electronegativity increases. This effective electronegativity is called Valence-State Electronegativity.

<table>
<thead>
<tr>
<th>Substance</th>
<th>EN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium metal</td>
<td>1.6</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>1.7</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>2.3</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1.5</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>2.1</td>
</tr>
</tbody>
</table>

So Chromium(VI) forms covalently bound o xoanion of a relatively strong acid.
**Mn₂O₇** reacts with **H₂O** to form **HMnO₄**, a strong oxidizing agent.
Manganese metal is reactive

\[ \text{Mn(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \quad \text{E}^\circ = 1.18\text{V} \]

**All manganese species with oxidation states \( > +2 \) act as oxidizing agents.**

\[ \text{MnO}_4^- \text{(aq)} + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O(l)} \quad \text{E}^\circ = 1.68\text{V} \]

\[ \text{MnO}_4^- \text{(aq)} + 2\text{H}_2\text{O(l)} + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-\text{(aq)} \quad \text{E}^\circ = 0.59\text{V} \]

\[ \text{Mn}^{2+} \text{resists oxidation in air(} \text{unlike Cr}^{2+} \text{ and Fe}^{2+} \text{) because removing an electron from d}^5 \text{ configuration is difficult.} \]
Silver\([\text{Kr}]\ 5s^1\ 4d^{10}\) has the highest electrical conductivity of any element.

Important oxidation state is +1.

\[2\text{Al}(s) + 3\text{Ag}_2\text{S}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Al}(	ext{OH})_3(s) + 6\text{Ag}(s) + 3\text{H}_2\text{S}(g)\]

\[\text{EO} = 0.86\text{V}\]

The Black and white Photography

* Silver halides undergo a redox reaction when exposed to light

* Silver chloride, bromide and iodide are not water soluble.

* \(\text{Ag}^+\) is easily reduced: \(\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s); \text{EO} = 0.80\text{V}\)

* \(\text{Ag}^+\) forms several stable, water-soluble complex ions.
AgBr microcrystals dispersed in gelatin (light-sensitive emulsion) coated on a plastic support is the photographic film.

1. Exposing the film:

\[
\begin{align*}
\text{Br}^- & \xrightarrow{h\nu} \text{Br}^- + e^- \quad \text{oxidation} \\
\text{Ag}^+ + e^- & \rightarrow \text{Ag} \quad \text{reduction}
\end{align*}
\]

\[
\text{Ag}^+ + \text{Br}^- \xrightarrow{h\nu} \text{Ag} + \text{Br}
\]

The exposed crystals are called latent image.

2. Developing the image:

The latent image is developed into the actual image by reducing more of the silver ions in the crystal in a controlled manner using hydroquinone (\(\text{H}_2\text{C}_6\text{H}_4\text{O}_2;\text{H}_2\text{Q}\)) a weak reducing agent.

\[
2\text{Ag}^+(s) + \text{H}_2\text{Q}(aq) \rightarrow 2\text{Ag}(s) + \text{Q}(aq;\text{oxidised form}) + 2\text{H}^+(aq)
\]
The reaction rate depends on $H_2Q$ concentration, temperature and the time the emulsion is bathed in the solution.

3. Fixing the image: Stopping the reduction of $Ag^+$ by removing it by converting to a soluble complex ion with sodium thiosulfate solution (hypo)

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$$

4. Washing the negative: Water soluble ions are washed away in water producing the negative.

5. Printing: The image on the negative is projected onto print-paper coated with emulsion ($AgCl$ in gelatin) and exposed to light. The most light sensitive silver iodide is used in the emulsion for High speed film.
Mercury - The only liquid metal

1. Distorted crystal structure - each mercury atom is surrounded by 6 rather than 12 nearest neighbors.

2. A filled tightly held d subshell leaves only two 6s electrons for metallic bonding.

Interactions among mercury atoms are relatively few and relatively weak - result solid form breaks down at -38.9°C

Hg⁺  [Xe] 6s\(^1\)4f\(^{14}\)5d\(^{10}\)  

[Hg-Hg]\(^{2+}\) diatomic ion Hg\(_2\)^{2+}

Hg\(^{2+}\)  [Xe]4f\(^{14}\) 5d\(^{10}\)

Cd\(^{2+}\)  [Kr] 4d\(^{10}\)

Zn\(^{2+}\)  [Ar] 3d\(^{10}\)
Components of a Coordination Compound

A. $[\text{Co(NH}_3\text{)}_6]\text{Cl}_3(s) \xrightarrow{\text{H}_2\text{O}} [\text{Co(NH}_3\text{)}_6]^{3+}(aq) + 3\text{Cl}^-(aq)$

B. $[\text{Pt(NH}_3\text{)}_4]\text{Br}_2$
*Coordination number:* Number of ligand atoms bonded directly to the central metal ion and is specific for a given metal ion in a particular oxidation state and compound.

\[ \text{Co(NH}_3\text{)}_6\text{]}^{3+} \quad \text{CN is 6} \quad \text{Lone pairs from six ligands(NH}_3\text{) are bonded to the Co}^{3+} \text{ion.} \]

*Geometry:* The geometry (shape) of a complex ion depends on the coordination number and nature of the metal ion.

*Donor atoms per ligand:* The ligands of complex ions are molecules and anions with one or more donor atoms that each donate a lone pair of electrons to the metal ion to form a covalent bond.

Ligands are classified as unidentate, bidentate, polydentate depending on the number of donor atoms present.

Complex ion that contain the ligands is called a chelate.
# Numbers, Shapes

## Table 23.6 Coordination Numbers and Shapes of Some Complex Ions

<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\text{)}_2]^+), ([\text{AuCl}_2]^-)</td>
</tr>
<tr>
<td>4</td>
<td>Square planar</td>
<td>([\text{Ni(CN)}_4]^{2-}), [\text{PdCl}_4]^{2-}), ([\text{Pt(NH}_3\text{)}_4]^{2+}), ([\text{Cu(NH}_3\text{)}_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-}), ([\text{Cr(NH}_3\text{)}_4\text{Cl}_2]^+), ([\text{Mn(H}_2\text{O)}_6]^{2+}), ([\text{FeCl}_6]^{3-}), ([\text{Co(en)}_3]^{3+})</td>
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*most d\(^8\)*

*most d\(^{10}\)*
# Ligands in Coordination Compounds

## Table 23.7 Some Common Ligands in Coordination Compounds

<table>
<thead>
<tr>
<th>Ligand Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unidentate</td>
<td>$\text{H}_2\text{O}$: water $\text{F}^-$: fluoride ion $\text{C}≡\text{N}^-$: cyanide ion $\text{Cl}^-$: chloride ion $\text{NH}_3$: ammonia $\text{S}=\text{C}=\text{N}^-$: thiocyanate $\text{O}^-$: hydroxide ion $\text{N}=\text{O}^-$: nitrite ion</td>
</tr>
<tr>
<td>Bidentate</td>
<td>$\text{H}_2\text{C}−\text{CH}_2$ ethylenediamine (en) $\text{O}_2\text{C}−\text{C}−\text{O}^2-$ oxalate ion</td>
</tr>
<tr>
<td>Polydentate</td>
<td>$\text{H}_2\text{N}−\text{CH}_2−\text{CH}_2−\text{CH}_2−\text{CH}_2−\text{NH}_2 \text{ diethylenetriamine}$ $\text{PO}_4\text{O}_3\text{O}^5-$ triphosphate ion $\text{N}−\text{CH}_2−\text{CH}_2−\text{CH}_2−\text{CH}_2−\text{CH}_2−\text{NH}_2 \text{ ethylenediaminetetraacetate (EDTA) ion}$</td>
</tr>
</tbody>
</table>

\[ \text{p. 1018} \]
Writing Formulas:
1. The cation is written before the anion.
2. The charge of the cation(s) is balanced by the charge of the anion(s)
3. In the complex ion, neutral ligands are written before anionic ligands, and the whole ion is placed in brackets.

The whole complex ion may be a cation or an anion

\[ \text{K}_2[\text{Co(NH}_3)_2\text{Cl}_4] \quad \text{complex ion is anion} \quad [\text{Co(NH}_3)_2\text{Cl}_4]^{2-} \]

Charge of the metal ion = charge of complex ion - total charge of ligands

\[ = (2^-) - [(2 \times 0) + (4 \times 1^-)] = 2^+ \]

\[ \text{[Co(NH}_3)_4\text{Cl}_2]\text{Cl} \quad \text{complex ion is cation} \quad [\text{Co(NH}_3)_4\text{Cl}_2]^+ \]

Charge of the metal ion = (1+) - [(4 \times 0) + (2 \times 1^-)] = 3+
Coordination compounds can have complex cation and complex anion

\[[\text{Co(NH}_3\text{)}_5\text{Br}]_2 \text{[Fe(CN)}_6\text{]}\] Complex cation is \[\text{[Co(NH}_3\text{)}_5\text{Br]}^{2+}\]

Charge on metal ion = \((2^+) - [(5 \times 0) - (1 \times 1^-)]\) = 3+

Complex cation is \([\text{Fe(CN)}_6]^{4-}\)

Charge on metal ion = \((4^-) - (6 \times 1^-)\) = 2+

Names of Coordination Compounds

1. The cation is named before the anion.

\[[\text{Co(NH}_3\text{)}_4\text{Cl}_2\text{]}\text{Cl}\] tetraamminedichloroecobalt(III) chloride

\[\text{K}_3[\text{Fe(CN)}_5\text{NO}]\] Potassiumpentacyanonitrosylferrate(II)

\[\text{Na}_3[\text{Fe(CN)}_6]\] sodium hexacyanoferrate(III)
2. Within the complex ion, the ligands are named, in alphabetical order before the metal ion

\[
[\text{Al(NH}_3\text{)}_2(\text{H}_2\text{O})_2\text{BrCl}]\text{NO}_3
\]

Diamminediaquabromochloroaluminium(III) nitrate

3. Neutral ligands generally have the molecule name (few exceptions) Anionic ligands drop the -ide and add -o after the root name.

Bromochlorodediaquadiamminialuminium(III) nitrate

4. A numerical prefix denotes the number of a particular ligand.

For the ligands such as ethylenediamine which already has the prefix, use bis(2), tris(3) or tetrakis(4) to indicate the number of ligands, followed by the ligand name in parentheses.

\[
[\text{Cr(en)}_3](\text{ClO}_4)_3
\]

Trisethylenediamminechromium(III) perchlorate
# Names of Some Neutral and Anionic Ligands

<table>
<thead>
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<th>Name</th>
<th>Formula</th>
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<td><strong>A. Neutral</strong></td>
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<td>Aqua</td>
<td>$\text{H}_2\text{O}$</td>
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<td>Ammine</td>
<td>$\text{NH}_3$</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>$\text{CO}$</td>
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<td>Nitrosyl</td>
<td>$\text{NO}$</td>
</tr>
<tr>
<td><strong>B. Anionic</strong></td>
<td></td>
</tr>
<tr>
<td>Fluoro</td>
<td>$\text{F}^-$</td>
</tr>
<tr>
<td>Chloro</td>
<td>$\text{Cl}^-$</td>
</tr>
<tr>
<td>Bromo</td>
<td>$\text{Br}^-$</td>
</tr>
<tr>
<td>Iodo</td>
<td>$\text{I}^-$</td>
</tr>
<tr>
<td>Hydroxo</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>Cyano</td>
<td>$\text{CN}^-$</td>
</tr>
</tbody>
</table>

Table 23.8 (p. 1019)
## Names of Some Metal Ions in Complex Anions

<table>
<thead>
<tr>
<th>Metal</th>
<th>Name in Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Ferrate</td>
</tr>
<tr>
<td>Copper</td>
<td>Cuprate</td>
</tr>
<tr>
<td>Lead</td>
<td>Plumbate</td>
</tr>
<tr>
<td>Silver</td>
<td>Argentate</td>
</tr>
<tr>
<td>Gold</td>
<td>Aurate</td>
</tr>
<tr>
<td>Tin</td>
<td>Stannate</td>
</tr>
</tbody>
</table>

Table 23.9 (p. 1019)
5. The oxidation state of the central metal ion is given be a Roman numerical (in parentheses) only if the metal ion can have more than one state.

6. If the complex ion is an anion, we drop the ending of the metal name and add “-ate”

K[Pt(NH$_3$)$_5$Cl$_5$] Potassium amminepentachloroplatinate(IV)

[Cr(NH$_3$)$_6$][Cr(CN)$_6$] 
Hexaamminechromium(III) hexacyanochromate(III)

[Co(NH$_3$)$_5$Br]$_2$ [Fe(CN)$_6$] 
Pentaamminebromocobalt(III) hexacyanoferrate(IV)
### Some Coordination Compounds of Cobalt Studied by Werner

<table>
<thead>
<tr>
<th>Traditional Formula</th>
<th>Werner’s Data*</th>
<th>Modern Formula</th>
<th>Charge of Complex Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Ions</td>
<td>Free Cl⁻</td>
<td></td>
</tr>
<tr>
<td>CoCl₃ • 6 NH₃</td>
<td>4</td>
<td>3</td>
<td>[Co(NH₃)₆]Cl₃</td>
</tr>
<tr>
<td>CoCl₃ • 5 NH₃</td>
<td>3</td>
<td>2</td>
<td>[Co(NH₃)₅Cl]Cl₂</td>
</tr>
<tr>
<td>CoCl₃ • 4 NH₃</td>
<td>2</td>
<td>1</td>
<td>[Co(NH₃)₄Cl₂]Cl</td>
</tr>
<tr>
<td>CoCl₃ • 3 NH₃</td>
<td>0</td>
<td>0</td>
<td>[Co(NH₃)₃Cl₃]</td>
</tr>
</tbody>
</table>

Table 23.10 (p. 1020)
**Isomers**: Substances with the same chemical formula but different properties.
1. Coordination Isomers: Composition of the complex ion changes but not that of the compound

\[
\text{[Pt(NH}_3\text{)}_4\text{Cl}_2\text{]}(\text{NO}_2\text{)}_2 \quad \text{[Pt(NH}_3\text{)}_4(\text{NO}_2\text{)}_2\text{]}\text{Cl}_2
\]

ligand \quad \text{counter ion}

\[
\text{[Cr(NH}_3\text{)}_6\text{]}\text{[Co(CN)_6]} \quad \text{[Co (NH}_3\text{)}_6\text{]}\text{[Cr(CN)_6]}
\]

2. Linkage isomers: Composition of the complex ion remains the same but the attachment of the ligand donor atom changes

\[
\text{[O = N - O]}^- \quad \text{[O = C = N]}^- \quad \text{S = C = N}^- \quad \text{N - C = N}^- \quad \text{S = C = N}^- \quad \text{S = C = N}^-
\]

Nitrito, ONO: \rightarrow \quad \text{isothiocyanato, SCN: } \rightarrow

Nitro, O\text{_2}N: \rightarrow \quad \text{thiocyanato, NCS: } \rightarrow
**Geometric (cis-trans) Isomerism**

**Diastereomers**

A  \( \text{cis} - [\text{Pt(NH}_3\text{)}_2\text{Cl}_2] \)  \( \text{trans} - [\text{Pt(NH}_3\text{)}_2\text{Cl}_2] \)

B  \( \text{cis} - [\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+ \)  \( \text{trans} - [\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+ \)
Optical Isomerism in an Octahedral Complex Ion

Fig. 23.12

enantiomers

No optical isomers

$cis - [Co(en)_{2}Cl_{2}]^{+}$

$trans - [Co(en)_{2}Cl_{2}]^{+}$
Hybrid Orbitals and Bonding in the Octahedral \([\text{Cr(NH}_3\text{)}_6]^3+\) Ion

Valence bond theory: The ligand (Lewis base) donates the electron pair and the metal ion (Lewis acid) accepts it to form one of the covalent bonds of the complex ion (Lewis adduct). One atom in the bond contribute both electrons, is called coordinate covalent bond.
Hybrid Orbitals and Bonding in the Square Planar \([\text{Ni(CN)}_4]^2-\) Ion

Fig. 23.14
Hybrid Orbitals and Bonding in the Tetrahedral $\text{[Zn(OH)}_4]^2-$ ion

Fig. 23.15
## Relation Between Absorbed and Observed Colors

<table>
<thead>
<tr>
<th>Absorbed Color</th>
<th>λ (nm)</th>
<th>Observed Color</th>
<th>λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>400</td>
<td>Green-yellow</td>
<td>560</td>
</tr>
<tr>
<td>Blue</td>
<td>450</td>
<td>Yellow</td>
<td>600</td>
</tr>
<tr>
<td>Green</td>
<td>490</td>
<td>Red</td>
<td>620</td>
</tr>
<tr>
<td>Yellow-green</td>
<td>570</td>
<td>Violet</td>
<td>410</td>
</tr>
<tr>
<td>Yellow</td>
<td>580</td>
<td>Dark blue</td>
<td>430</td>
</tr>
<tr>
<td>Orange</td>
<td>600</td>
<td>Blue</td>
<td>450</td>
</tr>
<tr>
<td>Red</td>
<td>650</td>
<td>Green</td>
<td>520</td>
</tr>
</tbody>
</table>

Table 23.11 (p. 1027)
Fig. 23.17

$d$ 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 $d_{yz}$
Splitting of $d$-Orbital Energies by an Octahedral Field of Ligands

3$d$ orbitals in free ion

Average of 3$d$ orbitals in octahedral ligand field

3$d$ orbital splitting in octahedral ligand field

Fig. 23.18
Effect of the Ligand on Splitting Energy

Weak-field ligands

\[ \text{[Cr(H}_2\text{O)}_6]}^{2+} \]

Strong-field ligands

\[ \text{[Cr(CN)}_6]\text{]}^{4-} \]

Fig. 23.19
The Color of $[\text{Ti(H}_2\text{O)}_6]^{3+}$

$\Delta E_{\text{electron}} = E_{\text{photon}} = h\nu = hc / \lambda$

Fig. 23.20
Fig. 23.21

Effects of Metal Oxidation State and of Ligand on Color

\[ \text{[V(H}_2\text{O)}_6]^{2+} \]

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

\[ \text{[Cr(NH}_3)_6]^{3+} \]

\[ \text{[Cr(NH}_3)_5\text{Cl}]^{2+} \]
The Spectrochemical Series

I⁻ < Cl⁻ < F⁻ < OH⁻ < H₂O < SCN⁻ < NH₃ < en < NO₂⁻ < CN⁻ < CO

WEAKER FIELD  ---  STRONGER FIELD

SMALLER Δ  ---  LARGER Δ

LONGER λ  ---  SHORTER λ

Fig. 23.22
Final Exam

May 3    Wednesday    11 am to 2 pm

ROOM                  117    SR1

Chapter 21.7 and Chapter 23

Material from Exam 1, Exam 2, and Exam 3
Magnetic Properties of Transition Metal Complexes

Hund’s rule: Electrons occupy orbitals one at a time as long as orbitals of equal energy are available.

When all lower energy orbitals are half-filled, the next electron can

1. Enter a half-filled and pair up by overcoming a repulsive pairing energy ($E_{\text{pairing}}$) or

2. Enter an empty, higher energy orbital by overcoming the crystal field splitting energy ($\Delta$)

The relative sizes of $E_{\text{pairing}}$ and $\Delta$ determine the occupancy of the d-orbitals

- $E_{\text{pairing}} > \Delta$ high-spin weak field ligand
- $E_{\text{pairing}} < \Delta$ low-spin strong field ligand
High-spin and low-spin complex ions of Mn$^{2+}$

No field
Maximum number of unpaired electrons

Weak-field ligand
High-spin complex
$E_{\text{pairing}} > \Delta$

Strong-field ligand
Low-spin complex
$E_{\text{pairing}} < \Delta$

$\text{Hexaaquamanganese(II) chloride}$
$[\text{Mn(H}_2\text{O)}_6\text{]}\text{Cl}_2$

$\text{Potassium hexacyanomanganate(II)}$
$K_4[\text{Mn(CN)}_6]^{4-}$
$d^1$, $d^2$, and $d^3$ ions always form high-spin complexes. Low energy $t_{2g}$ orbitals only are available.

For $d^4$, $d^5$, $d^6$ and $d^7$ metal ions High-spin and Low-spin Complexes option available. $t_{2g}$ and $e_g$ are filled up

$d^8$ and $d^9$ ions - always form high-spin complexes. High energy $e_g$ orbitals only are available
Splitting of $d$-orbital Energies by a Tetrahedral Field and a Square Planar Field.

Fig. 23.25
## Some Transition Metal Trace Elements in Humans

<table>
<thead>
<tr>
<th>Element</th>
<th>Biomolecule Containing Element</th>
<th>Function of Biomolecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>Protein (?)</td>
<td>Redox couple in fat metabolism (?)</td>
</tr>
<tr>
<td>Chromium</td>
<td>Glucose tolerance factor</td>
<td>Glucose utilization</td>
</tr>
<tr>
<td>Manganese</td>
<td>Isocitrate dehydrogenase</td>
<td>Cell respiration</td>
</tr>
<tr>
<td>Iron</td>
<td>Hemoglobin and myoglobin</td>
<td>Oxygen transport</td>
</tr>
<tr>
<td></td>
<td>Cytochrome c,</td>
<td>Cell respiration; ATP form.</td>
</tr>
<tr>
<td></td>
<td>Catalase</td>
<td>Decomposition of H$_2$O$_2$</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Cobalamin (vitamin B$_{12}$)</td>
<td>Development of red blood cells</td>
</tr>
<tr>
<td>Copper</td>
<td>Ceruloplasmin</td>
<td>Hemoglobin synthesis</td>
</tr>
<tr>
<td></td>
<td>Cytochrome oxidase</td>
<td>Cell respiration; ATP syn.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Carbonic anhydrase</td>
<td>Elimination of CO$_2$</td>
</tr>
<tr>
<td></td>
<td>Carboxypeptidase A</td>
<td>Protein digestion</td>
</tr>
<tr>
<td></td>
<td>Alcohol dehydrogenase</td>
<td>Metabolism of ethanol</td>
</tr>
</tbody>
</table>

Table 23A (p. 1032)
Hemoglobin and the Octahedral Complex in Heme

Fig. 23.A (p. 1033)
The Tetrahedral Zn$^{2+}$ Complex in Carbonic Anhydrase

Fig. 23.B (p. 1033)