What is a transition metal?

“an element with valence d- or f-electrons”

ie. a d-block or f-block metal

d-block: transition elements

f-block: inner transition elements

Shapes of d-orbitals

What’s interesting about Transition Metal Complexes??

TABLE 20.1 Some Transition Metals Important to the U.S. Economy and Defense

<table>
<thead>
<tr>
<th>Metal</th>
<th>User</th>
<th>Percentage Imported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>Stainless steel (especially for parts exposed to corrosive gases and high temperatures)</td>
<td>91%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>High-temperature alloys in jet engines, magnets, electronics, steel bins</td>
<td>93%</td>
</tr>
<tr>
<td>Manganese</td>
<td>Steelmaking</td>
<td>97%</td>
</tr>
<tr>
<td>Platinum</td>
<td>Catalysts</td>
<td>97%</td>
</tr>
</tbody>
</table>
Oxidation State

When you lose the s electrons….
The d electrons become important.

How many d-electrons does the metal have?

<table>
<thead>
<tr>
<th>complex</th>
<th>O.S. of L</th>
<th>O.S. of M</th>
<th>no. d electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cr}_2\text{O}_7]^{2-}$</td>
<td>-2</td>
<td>+6</td>
<td>$d^0$</td>
</tr>
<tr>
<td>$[\text{MnO}_4]^{-}$</td>
<td>-2</td>
<td>+7</td>
<td>$d^3$</td>
</tr>
<tr>
<td>$[\text{Ag(NH}_3]_2]^{+}$</td>
<td>0</td>
<td>+1</td>
<td>$d^{10}$</td>
</tr>
<tr>
<td>$[\text{Ti(H}_2\text{O})_6]^{3+}$</td>
<td>0</td>
<td>+3</td>
<td>$d^1$</td>
</tr>
<tr>
<td>$[\text{Co(en)}_3]^{3+}$</td>
<td>0</td>
<td>+3</td>
<td>$d^6$</td>
</tr>
<tr>
<td>$[\text{PtCl}_2(\text{NH}_3)_2]^{-}$</td>
<td>-1, 0</td>
<td>+2</td>
<td>$d^2$</td>
</tr>
<tr>
<td>$[\text{V(CN)}_6]^{3-}$</td>
<td>-1</td>
<td>+2</td>
<td>$d^3$</td>
</tr>
<tr>
<td>$[\text{Fe(ox)}]^{3+}$</td>
<td>-2</td>
<td>+3</td>
<td>$d^5$</td>
</tr>
</tbody>
</table>

Alfred Werner - Nobel Prizewinner 1913

CoCl$_2$ . 6NH$_3$ yellow  + Ag$^+$ $\rightarrow$ 3 moles AgCl
CoCl$_2$ . 5NH$_3$ purple + Ag$^+$ $\rightarrow$ 2 moles AgCl
CoCl$_2$ . 4NH$_3$ green   + Ag$^+$ $\rightarrow$ 1 mole AgCl
CoCl$_2$ . 3NH$_3$         + Ag$^+$ $\rightarrow$ 0 moles AgCl
Werner’s conclusions
- The metal is in a particular oxidation state (primary valancy)
- The complex has a fixed coordination number (secondary valancy)
- The ligands are bound to the metal via a bond which resembles a covalent bond

What is a coordination complex?
- Central metal ion or atom surrounded by a set of ligands
- The ligand donates two electrons to the d-orbitals around the metal forming a dative or coordinate bond

Molecular model: The CO(NH₃)₆³⁺ ion

Common Coordination Numbers of Transition Metal Complexes

Common Coordination Geometries
- Linear
- Tetrahedral
- Square planar
- Octahedral

Coordination number 4
- Tetrahedral geometry
- Square planar geometry
Tetrahedral complexes

Favoured by steric requirements
large ligands e.g. Cl-, Br-, I-
small metal ions …with pseudo-noble gas configuration e.g. Zn^2+

Square planar geometry

Square planar complexes are formed by d^8 metal centres
i.e. group 10 Ni^{2+}, Pd^{2+}, Pt^{2+}
Au^{3+}

Summary

Rules for Naming Coordination Compounds:
• As with any ionic compound, the cation is named before the anion.
• In naming a complex ion, the ligands are named before the metal ion.
• In naming ligands, an -o is added to the root name of the anion. For example, the halides in ligands are called fluoro, chloro, bromo, and iodo.
• In naming a metal ion, the suffix -ide is added to the root name of the metal, except for tetrafluoride, tetra-iodide, etc.
• The prefixes mono-, di-, tri-, tetra-, etc. are used to denote the number of simple ligands. The prefixes bis-, tris-, tetra-,etc. are also used, especially for more complicated ligands or ones that already contain two, three, etc. of the same ligand.
• The coordination state of the central metal ion is designated by a Roman numeral in parentheses.
• When more than one type of ligand is present, the present ligands are named in alphabetical order. The prefixes do not affect the order.
• If the complex ion has a negative charge, the suffix -ide is added to the name of the metal. Sometimes the Latin name is used to identify the metal (see Table 20.15).

TABLE 20.15 Latin Names Used for Some Metal Ions in Anionic Complex Ions

<table>
<thead>
<tr>
<th>Metal</th>
<th>Anionic Complex Base Name</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>

These rules are applied in Example 20.1.

TABLE 20.14 Names of Some Common Unidentate Ligands

<table>
<thead>
<tr>
<th>Neutral Molecules</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqua</td>
<td>H_2O</td>
</tr>
<tr>
<td>Ammine</td>
<td>NH_3</td>
</tr>
<tr>
<td>Methylamine</td>
<td>CH_3NH_2</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>CO</td>
</tr>
<tr>
<td>Nitrosyl</td>
<td>NO</td>
</tr>
<tr>
<td>Fluoro</td>
<td>F^-</td>
</tr>
<tr>
<td>Chloro</td>
<td>Cl^-</td>
</tr>
<tr>
<td>Bromo</td>
<td>Br^-</td>
</tr>
<tr>
<td>Iodo</td>
<td>I^-</td>
</tr>
<tr>
<td>Hydroxo</td>
<td>OH^-</td>
</tr>
<tr>
<td>Cyano</td>
<td>CN^-</td>
</tr>
</tbody>
</table>
Nitrogen binding ligands

- **Ethylenediamine (en)**

- **Ammonia (ammine)**
Coordination of EDTA
Ethylenediamine tetraacetic acid

Coordination isomerism
Ligands are distributed differently between the two metal centres

\[[\text{Cu(NH}_3\text{)}_4][\text{PtCl}_4]\quad [\text{Pt(NH}_3\text{)}_4][\text{CuCl}_4]\quad \text{square planar}\]

\[[\text{Co(NH}_3\text{)}_4][\text{Cr(CN)}_6]\quad [\text{Cr(NH}_3\text{)}_4][\text{Co(CN)}_6]\quad \text{octahedral}\]

Classes of isomers

Coordination Isomerism
Exchange of a ligated anion with a counterion
\[\text{e.g. } [\text{Co(NH}_3\text{)}_5\text{Br}]\text{SO}_4 \quad [\text{Co(NH}_3\text{)}_5(\text{SO}_4)]\text{Br} \]

Coordination Isomerism (Ionisation isomerism)

Linkage isomerism
Ambidentate ligands which can bind through more than one different donor atom

\[\text{yellow} \quad \text{nitro-complex} \quad \text{red} \quad \text{nitrito-complex} \]

\[\text{Pd(NCS)}_2(\text{PPh}_3)_2 \quad \text{isocyanate} \quad [\text{Pd(SCN)}_2(\text{PPh}_3)_2] \quad \text{thiocyanate}\]
NO$_2$ bonding as a ligand to metal ion

(a) 

(b) 

Classes of isomers

Isomers (same formula but different properties)

Structural isomers (different bonds)

Coordination isomerism

Linkage isomerism

Geometric (cis-trans) isomerism

Stereoisomers (same bonds, different spatial arrangements)

Optical isomerism

Geometrical isomerism

Square Planar Geometry

cis-[PtCl$_2$(NH$_3$)$_2$]

cis-platin

cis-diamminedichloroplatinum(II)  

trans-[PtCl$_2$(NH$_3$)$_2$]

trans-diamminedichloroplatinum(II)

cis = side by side  

Trans = across

Cis/trans isomers

(a) Cis

(b) Trans

Geometrical Isomerism

axial ligands

equatorial ligands

trans-[Co(NH$_3$)$_4$Cl$_2$]$^+$
green

cis-[Co(NH$_3$)$_4$Cl$_2$]$^+$
violet
Chloride ligands

Trans

Cis

Geometrical Isomerism

MERIDONAL

mer

mer-[Co(NH₃)₃(NO₂)₃]

Octahedral geometry

[ML₃X₃]

MERIDONAL

FACIAL

fac

fac-[Co(NH₃)₃(NO₂)₃]

How many distinct isomers are there in the figure?

trans-isomers

cis-isomers
Electromagnetic Radiation

Unpolarized light

Polarized light

Polarizing sun glasses reduce glare of polarized reflections from surfaces

When light is incident at the Brewster angle, the reflected light is linearly polarized because the reflection coefficient for the II component is zero.

Action of Polarized Sunglasses

Light Waves Vibrating Perpendicular to the Highway

Light Waves Vibrating Parallel to the Highway

Figure 4

Light Passing Through Crossed Polarizers

Polarizer 1 (Vertical)  Polarizer 2 (Horizontal)

Incident Beam (Unpolarized)  Vertically Polarized Light Wave
Optical Isomer and Interaction with Light
Enatiomers rotate the plane of polarized light.

Dextrorotatory - “d” isomer
Complex which rotates plane of polarized light to the right.
Levorotatory - “l” isomer
Complex which rotates plane of polarized light to the left.

Chiral molecules are optically active because effect on light

Presence of a mirror symmetry plane assures superimposable mirror image

Super Imposable and Non-Super Imposable Mirror Images

- Molecules/ions that have enantiomer are chiral
Isomers I and II

Trans/cis isomer—mirror images

Octahedral arrangement d-orbitals

Six Anions Interacting with the d-Orbitals of a Central Metal Ion

Energy of 3d orbitals
Paramagnetic Substances Are Drawn into a Magnetic Field on a Gouy Balance

Paramagnetic Substances Contain Unpaired Electron Spins

Strong/weak fields, d⁶ Configuration

Strong and Weak Fields, d⁴ Configuration

Gem Stones Such As Emerald Are Colored Due to Light Absorption by Metal Ions

Colour of transition metal complexes

Visible spectrum

<table>
<thead>
<tr>
<th>Colour of transition metal complexes</th>
<th>Visible spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruby</td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ with Cr³⁺ impurities</td>
<td></td>
</tr>
<tr>
<td>Sapphire</td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ with Fe³⁺ and Ti⁴⁺ impurities</td>
<td></td>
</tr>
<tr>
<td>Emerald</td>
<td></td>
</tr>
<tr>
<td>Beryl</td>
<td></td>
</tr>
<tr>
<td>AlSiO₃ containing Be with Cr³⁺ impurities</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Strong Field
Low Spin

$\uparrow \quad d_{xy} \quad d_{xz} \quad d_{yz}$

Strong magnetic field

Low-spin complex
$[\text{CoF}_6]^{3-}$
$\Delta < \epsilon$

Weak Field, High Spin

$\uparrow \quad d_{xy} \quad d_{xz} \quad d_{yz}$

Weak magnetic field

High-spin complex
$[\text{Co(NH}_3)_6]^{3+}$
$\Delta > \epsilon$

Both Paramagnetic
Different Number of Unpaired Electron Spins

$\uparrow \quad d_{xy} \quad d_{xz} \quad d_{yz}$

$\uparrow \quad d_{xy} \quad d_{xz} \quad d_{yz}$

$\uparrow \quad d_{xy} \quad d_{xz} \quad d_{yz}$

$\uparrow \quad d_{xy} \quad d_{xz} \quad d_{yz}$

Visible spectrum

<table>
<thead>
<tr>
<th>Colour of transition metal complexes</th>
<th>Visible spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruby</td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ with Cr³⁺ impurities</td>
<td></td>
</tr>
<tr>
<td>Sapphire</td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ with Fe³⁺ and Ti⁴⁺ impurities</td>
<td></td>
</tr>
<tr>
<td>Emerald</td>
<td></td>
</tr>
<tr>
<td>Beryl</td>
<td></td>
</tr>
<tr>
<td>AlSiO₃ containing Be with Cr³⁺ impurities</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Your Eyes See the Color that is **NOT** Absorbed

![Color Wheel Diagram]

Subtraction of Light by Absorption Leads to Color you See

![Diagram of Absorption and Emission]

Hexaquotitanium (III) Solutions Appear Violet Due to Absorption of Yellow and Green Light

![Image of Hexaquotitanium (III) Solution]

A Violet Colored Filter Absorbs Yellow-Green Light

![Diagram of Absorption by a Violet Filter]

Ti(H₂O)₆³⁺ - how many d electrons?

![Diagram of Energy Levels for Ti(H₂O)₆³⁺]

Ti(H₂O)₆³⁺ Absorbs Light Due to an Electron Transition from a t₂g d-orbital to an e₉ d-orbital

![Diagram of Electron Transition]

If a substance absorbs here...

...it appears as this color...

Ti (III): 3d⁰ configuration
Correlation of High and Low Spin Complexes With Spectrochemical Series

The Colors of Transition Metal Complexes can be Correlated with the Ligands They Bind
These Complexes All Contain Co (III) and 5 NH$_3$

Co (III): 3d$^6$ or 3d$^4$t$_{2g}^2$

Absorption:
- $t_{2g}^6 \rightarrow t_{2g}^5t_{eg}^1$
- $t_{2g}^4t_{eg}^2 \rightarrow t_{2g}^3t_{eg}^3$

The Splitting of d-Orbitals Depends on the Ligands Bonded to Ni (II) in It’s Octahedral Complexes

**TABLE 20.17** Several Octahedral Complexes of Cr$^{3+}$ and Their Colors

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(H$_2$O)$_6$]Cl$_3$</td>
<td>Violet</td>
</tr>
<tr>
<td>[Cr(H$_2$O)$_5$Cl]Cl$_2$</td>
<td>Blue-green</td>
</tr>
<tr>
<td>[Cr(H$_2$O)$_4$Cl$_2$]Cl</td>
<td>Green</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_6$]Cl$_3$</td>
<td>Yellow</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_5$Cl]Cl$_2$</td>
<td>Purple</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_4$Cl$_2$]Cl</td>
<td>Violet</td>
</tr>
</tbody>
</table>

The Splitting of d-Orbitals Depends on the Ligands Bonded to Ni (II) in It’s Octahedral Complexes

**Figure 20.28:** Crystal field diagrams for octahedral and tetrahedral complexes

**Figure 20.33:** The heme complex in which an Fe$^{2+}$ ion is coordinated to four nitrogen atoms of a planar porphyrin ligand.
Figure 20.34: Chlorophyll is a porphyrin complex

Figure 20.35: Representation of the myoglobin molecule

Figure 20.36: Representation of the hemoglobin structure

Figure 20.37: Normal red blood cell (right) and a sickle cell, both magnified 18,000 times.

Source: Visuals Unlimited