Chapter 24
Chemistry of Coordination Compounds
• A central metal atom bonded to a group of molecules or ions is a metal complex.
• If it’s charged, it’s a complex ion.
• Compounds containing complexes are coordination compounds.
Complexes

• The molecules or ions coordinating to the metal are the ligands.
• They are usually anions or polar molecules.
• The must have lone pairs to interact with metal}

\[
\begin{align*}
:O-H & :N-H \\
H & H \\
:Cl^- & :C≡N^-
\end{align*}
\]
A chemical mystery:
Same metal, same ligands, different number of ions when dissolved

<table>
<thead>
<tr>
<th>Original Formulation</th>
<th>Color</th>
<th>Ions per Formula Unit</th>
<th>“Free” Cl⁻ Ions per Formula Unit</th>
<th>Modern Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₃•6 NH₃</td>
<td>Orange</td>
<td>4</td>
<td>3</td>
<td>[Co(NH₃)₆]Cl₃</td>
</tr>
<tr>
<td>CoCl₃•5 NH₃</td>
<td>Purple</td>
<td>3</td>
<td>2</td>
<td>[Co(NH₃)₅Cl]Cl₂</td>
</tr>
<tr>
<td>CoCl₃•4 NH₃</td>
<td>Green</td>
<td>2</td>
<td>1</td>
<td>trans-[Co(NH₃)₄Cl₂]Cl</td>
</tr>
<tr>
<td>CoCl₃•4 NH₃</td>
<td>Violet</td>
<td>2</td>
<td>1</td>
<td>cis-[Co(NH₃)₄Cl₂]Cl</td>
</tr>
</tbody>
</table>

- Many coordination compounds are brightly colored, but again, same metal, same ligands, different colors.
Werner’s Theory

Co(III) oxidation state
Coordination # is 6

- suggested in 1893 that metal ions have *primary* and *secondary* valences.
  - Primary valence equal the metal’s oxidation number
  - Secondary valence is the number of atoms directly bonded to the metal (coordination number)
Werner’s Theory

- The central metal and the ligands directly bonded to it make up the coordination sphere of the complex.
- In CoCl$_3$·6 NH$_3$, all six of the ligands are NH$_3$ and the 3 chloride ions are outside the coordination sphere.

<table>
<thead>
<tr>
<th>Original Formulation</th>
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<th>Ions per Formula Unit</th>
<th>“Free” Cl$^-$ Ions per Formula Unit</th>
<th>Modern Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl$_3$·6 NH$_3$</td>
<td>Orange</td>
<td>4</td>
<td>3</td>
<td>[Co(NH$_3$)$_6$]Cl$_3$</td>
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<tr>
<td>CoCl$_3$·5 NH$_3$</td>
<td>Purple</td>
<td>3</td>
<td>2</td>
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</tr>
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<td>CoCl$_3$·4 NH$_3$</td>
<td>Green</td>
<td>2</td>
<td>1</td>
<td>trans-[Co(NH$_3$)$_4$Cl$_2$]Cl</td>
</tr>
<tr>
<td>CoCl$_3$·4 NH$_3$</td>
<td>Violet</td>
<td>2</td>
<td>1</td>
<td>cis-[Co(NH$_3$)$_4$Cl$_2$]Cl</td>
</tr>
</tbody>
</table>
Werner’s Theory

In \( \text{CoCl}_3 \cdot 5 \text{NH}_3 \) the five \( \text{NH}_3 \) groups and one chlorine are bonded to the cobalt, and the other two chloride ions are outside the sphere.

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<tr>
<th>Original Formulation</th>
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<th>Ions per Formula Unit</th>
<th>“Free” ( \text{Cl}^- ) Ions per Formula Unit</th>
<th>Modern Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CoCl}_3 \cdot 6 \text{NH}_3 )</td>
<td>Orange</td>
<td>4</td>
<td>3</td>
<td>( [\text{Co(NH}_3)_6] \text{Cl}_3 )</td>
</tr>
<tr>
<td>( \text{CoCl}_3 \cdot 5 \text{NH}_3 )</td>
<td>Purple</td>
<td>3</td>
<td>2</td>
<td>( [\text{Co(NH}_3)_5\text{Cl}] \text{Cl}_2 )</td>
</tr>
<tr>
<td>( \text{CoCl}_3 \cdot 4 \text{NH}_3 )</td>
<td>Green</td>
<td>2</td>
<td>1</td>
<td>( \text{trans-[Co(NH}_3)_4\text{Cl}_2]\text{Cl} )</td>
</tr>
<tr>
<td>( \text{CoCl}_3 \cdot 4 \text{NH}_3 )</td>
<td>Violet</td>
<td>2</td>
<td>1</td>
<td>( \text{cis-[Co(NH}_3)_4\text{Cl}_2]\text{Cl} )</td>
</tr>
</tbody>
</table>
Werner’s Theory

Werner proposed putting all molecules and ions within the sphere in brackets and those “free” anions (that dissociate from the complex ion when dissolved in water) outside the brackets.

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</tbody>
</table>
Werner’s Theory

- This approach correctly predicts there would be two forms of CoCl$_3$·4 NH$_3$.
  - The formula would be written [Co(NH$_3$)$_4$Cl$_2$]Cl.
  - One of the two forms has the two chlorines next to each other.
  - The other has the chlorines opposite each other.
What is Coordination?

- When an orbital from a ligand with lone pairs in it overlaps with an empty orbital from a metal

So ligands must have lone pairs of electrons.
Metal-Ligand Bond

- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have nonbonding electrons.
  - The metal (Lewis acid) has empty orbitals.

\[
\text{Ag}^+ (aq) + 2 \text{NH}_3 (aq) \rightarrow [\text{H} - \text{N} : \text{Ag} : \text{N} - \text{H}]^+ (aq)
\]
Metal-Ligand Bond

The metal’s coordination ligands and geometry can greatly alter its properties, such as color, or ease of oxidation.
Oxidation Numbers

Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.

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

\([\text{Cu(NH}_3\text{)}_4]^{2+}\]
Oxidation Numbers

Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

Example: \( \text{Cr(III)}(\text{H}_2\text{O})_4\text{Cl}_2 \)

\[ +3 + 4(0) + 2(-1) = +1 \]

\[ \text{Cr(H}_2\text{O})_4\text{Cl}_2 \]
Coordination Number

- The atom that supplies the lone pairs of electrons for the metal-ligand bond is the donor atom.
- The number of these atoms is the coordination number.
Coordination Number

- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.
Geometries

- There are two common geometries for metals with a coordination number of four:
  - Tetrahedral
  - Square planar

Why square planar? We’ll get to that
By far the most-encountered geometry, when the coordination number is six, is octahedral.
Polydentate Ligands

- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylenediamine, \( \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \), represented here as en, each N is a donor atom.
- Therefore, en is bidentate.
Polydentate Ligands

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms. Wraps around the central atom like an octopus.
Polydentate Ligands

<table>
<thead>
<tr>
<th>Ligand Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodentate</td>
<td>H₂O: Water</td>
</tr>
<tr>
<td></td>
<td>:NH₃: Ammonia</td>
</tr>
</tbody>
</table>

Bidentate

- Ethylenediamine (en)
- Bipyridine (bpy)
- Ortho-phenanthroline (o-phen)
- Oxalate ion
- Carbonate ion

Polydentate

- Diethylenetriamine
- Triphosphate ion
- Ethylenediaminetetraacetate ion (EDTA⁴⁻)

Chelating agents generally form more stable complexes than do monodentate ligands.
Chelating Agents

- Bind to metal ions removing them from solution.
- Phosphates are used to tie up Ca\(^{2+}\) and Mg\(^{2+}\) in hard water to prevent them from interfering with detergents.
Chelating Agents

- Porphyrins are complexes containing a form of the porphine molecule shown at right.
- Important biomolecules like heme and chlorophyll are porphyrins.
Chelating Agents

Porphines (like chlorophyll a) are tetradeprnate ligands.
Nomenclature of Coordination Compounds

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name in Complexes</th>
<th>Ligand</th>
<th>Name in Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azide, N$_3^-$</td>
<td>Azido</td>
<td>Oxalate, C$_2$O$_4^{2-}$</td>
<td>Oxalato</td>
</tr>
<tr>
<td>Bromide, Br$^-$</td>
<td>Bromo</td>
<td>Oxide, O$_2^-$</td>
<td>Oxo</td>
</tr>
<tr>
<td>Chloride, Cl$^-$</td>
<td>Chloro</td>
<td>Ammonia, NH$_3$</td>
<td>Ammine</td>
</tr>
<tr>
<td>Cyanide, CN$^-$</td>
<td>Cyano</td>
<td>Carbon monoxide, CO</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>Fluoride, F$^-$</td>
<td>Fluoro</td>
<td>Ethylenediamine, en</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>Hydroxide, OH$^-$</td>
<td>Hydroxo</td>
<td>Pyridine, C$_5$H$_5$N</td>
<td>Pyridine</td>
</tr>
<tr>
<td>Carbonate, CO$_3^{2-}$</td>
<td>Carbonato</td>
<td>Water, H$_2$O</td>
<td>Aqua</td>
</tr>
</tbody>
</table>

- The basic protocol in coordination nomenclature is to name the ligands attached to the metal as prefixes before the metal name.
- Some common ligands and their names are listed above.
Nomenclature of Coordination Compounds

• As always the name of the cation appears first; the anion is named last.
• Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.

[Co(NH₃)₅Cl]Cl₂

- 5 NH₃ ligands
- Cl⁻ ligand
- Cobalt in +3 oxidation state

Cation: Pentaamminechlorocobalt(III)
Anion: Chloride
Nomenclature of Coordination Compounds

- The names of anionic ligands end in “o”; the endings of the names of neutral ligands are not changed.
- Prefixes tell the number of a type of ligand in the complex. If the name of the ligand itself has such a prefix, alternatives like $\text{bis}$-, $\text{tris}$-, etc., are used.

\[
\text{[Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2
\]

- 5 $\text{NH}_3$ ligands
- Cl$^-$ ligand
- Cobalt in +3 oxidation state

Cation: Pentaamminechlorocobalt(III)
Anion: Chloride
Nomenclature of Coordination Compounds

- If the complex is an anion, its ending is changed to -ate.
- The oxidation number of the metal is listed as a Roman numeral in parentheses immediately after the name of the metal.

\[ \text{Na}_2[\text{MoOCl}_4] \]

- Cation: Sodium
- Anion: Tetrachlorooxo(molybdate)(IV)

4 Cl\(^-\) ligands
Oxide, O\(^2-\) ligand
Molybdenum in +4 oxidation state
Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).
Structural Isomers

If a ligand (like the NO$_2$ group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, **linkage isomers** are formed.
Structural Isomers

• Some isomers differ in what ligands are bonded to the metal and what is outside the coordination sphere; these are coordination-sphere isomers.

• Three isomers of $\text{CrCl}_3(\text{H}_2\text{O})_6$ are
  - The violet $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$,
  - The green $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and
  - The (also) green $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$. 
Geometric isomers

- With these geometric isomers, two chlorines and two \( \text{NH}_3 \) groups are bonded to the platinum metal, but are clearly different.

- **cis-Isomers** have like groups on the same side.
- **trans-Isomers** have like groups on opposite sides.

# of each atom the same  
Bonding the same  
Arrangement in space different
Other stereoisomers, called **optical isomers or enantiomers**, are mirror images of each other.

Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.
A molecule or ion that exists as a pair of enantiomers is said to be chiral.
Enantiomers

• Most of the physical properties of chiral molecules are the same, boiling point, freezing point, density, etc.

• One exception is the interaction of a chiral molecule with plane-polarized light.
Enantiomers

- If one enantiomer of a chiral compound is placed in a polarimeter and polarized light is shone through it, the plane of polarization of the light will rotate.
- If one enantiomer rotates the light $32^\circ$ to the right, the other will rotate it $32^\circ$ to the left.
Chemistry of Coordination Compounds

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Explaining the properties of transition metal coordination complexes

1. Magnetism
2. Color
Metal complexes and color

The ligands of a metal complex effect its color

Addition of NH$_3$ ligand to Cu(H$_2$O)$_4$ changes its color
Why does anything have color?

Light of different frequencies give different colors

We learned that elements can emit light of different frequency or color.

But these coordination complexes are not emitting light

They absorb light.

How does that give color?
Light can bounce off an object or get absorbed by object

No light absorbed, all reflected get white color
All light absorbed, none reflected get Black color
What if only one color is absorbed?
Complimentary color wheel

If one color absorbed, the color opposite is perceived.

Absorb **Orange**
See **Blue**
Absorb **Red**
See **Green**
[Ti(H₂O)₆]³⁺
Absorbs in green yellow.
Looks purple.
A precise measurement of the absorption spectrum of Compounds is critical.
Metal complexes and color

But why do different ligands on same metal give different colors?
Why do different ligands change absorption?

Addition of $\text{NH}_3$ ligand to $\text{Cu(H}_2\text{O)}_4$ changes its color
Model of ligand/metal bonding.
Electron pair comes from ligand
Bond very polarized.

Assumption: interaction pure electrostatic.
Now, think of point charges being attracted to metal nucleus Positive charge. What about electrons in d orbitals?

Ligand negative charge Is repelled by d electrons, d orbital energy goes up

Energy

<table>
<thead>
<tr>
<th>Free metal ion</th>
<th>Metal ion plus ligands (negative point charges)</th>
<th>Splitting because of octahedral crystal field</th>
</tr>
</thead>
</table>

$e$ set $(d_{z^2}, d_{x^2-y^2})$

$t_2$ set $(d_{xy}, d_{xz}, d_{yz})$

Averaged repulsions between ligands and $d$-electrons

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Ligands will interact with some d orbitals more than others.

Depends on relative orientation of orbital and ligand.

Ligands point right at lobes.
In these orbitals, the ligands are between the lobes, and they interact less strongly.

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Splitting due to ligand/orbital orientation.

\[ \begin{align*}
& e \text{ set } (d_{z^2}, d_{x^2-y^2}) \\
& t_2 \text{ set } (d_{xy}, d_{xz}, d_{yz})
\end{align*} \]

Averaged repulsions between ligands and \( d \)-electrons

Free metal ion

Metal ion plus ligands (negative point charges)

Splitting because of octahedral crystal field

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Chemistry of Coordination Compounds

Light of 495 nm

\[ \triangle = 495 \text{ nm} \]

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Different ligands interact more or less, change E spacing Of D orbitals.

- [CrF₆]³⁻ Green
- [Cr(H₂O)₆]³⁺ Violet
- [Cr(NH₃)₆]³⁺ Yellow
- [Cr(CN)₆]³⁻ Yellow

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Spectrochemical series (strength of ligand interaction)

Increasing $\Delta$

$\text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^-$
Electron configurations of some octahedral complexes

$\text{Ti}^{3+}$, a $d^1$ ion  

$\text{V}^{3+}$, a $d^2$ ion  

$\text{Cr}^{3+}$, a $d^3$ ion
As Energy difference increases, electron configuration changes.

Co(III) is d^6

[CoF_6]^{3-} → [Co(CN)_6]^{3-}

“High spin”

“Low spin”
High spin

Low spin

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Tetrahedral Complexes

In tetrahedral complexes, orbitals are inverted. Again because of orientation of orbitals and ligands

$\Delta$ is always small, always low spin (less ligands)
Square planar complexes are different still.
Chemistry of Coordination Compounds

Tetrahedral

- $d_{x^2-y^2}$
- $d_{xy}$
- $d_{yz}$
- $d_{xz}$

Square planar

- $d_{x^2-y^2}$
- $d_{z^2}$
- $d_{xy}$
- $d_{yz}$
Intense color can come from “charge transfer”
Ligand electrons jump to metal orbitals

\[
\text{KMnO}_4 \quad \text{KCrO}_4 \quad \text{KClO}_4
\]

No d orbitals in Cl, orbitals higher in energy
Empty Mn 3d orbitals

\[ t_2 \] set

\[ e \] set

Filled ligand orbitals

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Chemistry of Coordination Compounds
Exam 4, MO theory and coordination compounds Chapter 9, end and Chapter 24.

MO theory: Rules:

• 1. The number of MO’s equals the # of Atomic orbitals
• 2. The overlap of two atomic orbitals gives two molecular orbitals, 1 bonding, one antibonding
• 3. Atomic orbitals combine with other atomic orbitals of similar energy.
• 4. Degree of overlap matters. More overlap means bonding orbital goes lower in E, antibonding orbital goes higher in E.
• 5. Each MO gets two electrons
• 6. Orbitals of the same energy get filled 1 electron at a time until they are filled.
Difference between pi and sigma orbitals

(a) “End-on” overlap of p orbitals forms \( \sigma \) and \( \sigma^* \) MOs.

(b) “Sideways” overlap of p orbitals forms two sets of \( \pi \) and \( \pi^* \) MOs.

End on

Side to side.
A typical MO diagram, like the one below. For 2p and 2s atomic orbital mixing.
Oxygen $O_2$ is paramagnetic, why?
Show me why.

<table>
<thead>
<tr>
<th></th>
<th>Large $2s-2p$ interaction</th>
<th>Small $2s-2p$ interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{B}_2$</td>
<td>$\text{C}_2$</td>
</tr>
<tr>
<td>$\sigma_{2p}^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi_{2p}^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{2p}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi_{2p}$</td>
<td>$\uparrow \uparrow$</td>
<td>$\uparrow \uparrow$</td>
</tr>
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<tr>
<td>$\sigma_{2s}$</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
</tr>
</tbody>
</table>

| Bond order                    | 1                  | 2                  | 3                  | 2                  | 1                  | 0                  |
| Bond enthalpy (kJ/mol)        | 290                | 620                | 941                | 495                | 155                | —                  |
| Bond length (Å)               | 1.59               | 1.31               | 1.10               | 1.21               | 1.43               | —                  |
| Magnetic behavior             | Paramagnetic       | Diamagnetic        | Diamagnetic        | Paramagnetic       | Diamagnetic        | —                  |
Exam 4 Chapter 24.

Concentrate on the homeworks and the quiz!

Terms:
1. Coordination sphere
2. Ligand
3. Coordination compound
4. Metal complex
5. Complex ion
6. Coordination
7. Coordination number

Same ligands different properties?
Figuring oxidation number on metal
Polydentate ligands (what are they)?

Isomers.

structural isomers (formula same, bonds differ)

geometric isomers (formula AND bonds same, structure differs)

Stereoisomers:

Chirality, handedness,
Chemistry of Coordination Compounds

Isomers (same formula, different properties)

Structural isomers (different bonds)
- Coordination-sphere isomers
- Linkage isomers

Stereoisomers (same bonds, different arrangements)
- Geometric isomers
- Optical isomers

Nitro isomer

Nitrito isomer
Stereoisomers
Explaining the properties of metal complexes

Magnetism and color

How does seeing color work?

Absorb **Orange**
See **Blue**
Absorb **Red**
See **Green**
Different ligands on same metal give different colors

Addition of \( \text{NH}_3 \) ligand to \( \text{Cu(H}_2\text{O)}_4 \) changes its color
Splitting of d orbitals in an octahedral ligand field

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

\[ d_{xy} \quad d_{yz} \quad d_{xz} \]
Spectrochemical series (strength of ligand interaction)

Increasing $\Delta$

$\text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^-$

Know low spin versus high spin
There is also splitting from tetrahedral and square planar. Know they are different, don’t remember exactly what they are like.