Chapter 23
Chemistry of Coordination Compounds
Coordination Compounds

• How do we think about transition metals binding to other atoms?
• What do those d orbitals do?

• We call them, coordination compounds.
Complexes

A central metal atom can bond to a group of molecules or ions: metal complex.

If it’s charged: complex ion.

Compounds containing complexes are coordination compounds.

Question, is this an “ionic compound”?

Does it dissociate in water?
Complexes

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

- Examples of some common ligands
- Note, all have lone pairs
- Some are charged, others are not.
A chemical mystery:
Same metal, same ligands, but different behavior

- Same ligands, but different stochiometry
- Same ligands, different ionic species when dissolved in water.
- Many coordination compounds are brightly colored, but again, same metal, same ligands, different colors.

**TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)**

<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><em>trans</em>-[Co(NH₃)₄Cl₂]Cl</td>
</tr>
<tr>
<td>CoCl₃•4 NH₃</td>
<td>Violet</td>
<td>2</td>
<td>1</td>
<td><em>cis</em>-[Co(NH₃)₄Cl₂]Cl</td>
</tr>
</tbody>
</table>
suggested in 1893 that metal ions have *primary* and *secondary* valences.

- Primary valence equals 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 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

<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>CoCl$_3$·6 NH$_3$</td>
<td>Orange</td>
<td>4</td>
<td>3</td>
<td>[Co(NH$_3$)$_6$]Cl$_3$</td>
</tr>
<tr>
<td>CoCl$_3$·5 NH$_3$</td>
<td>Purple</td>
<td>3</td>
<td>2</td>
<td>[Co(NH$_3$)$_5$Cl]Cl$_2$</td>
</tr>
<tr>
<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 CoCl$_3$ - 5 NH$_3$

five NH$_3$ groups and one chlorine are bonded to the cobalt,
the other two chloride ions are outside the sphere.

<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>CoCl$_3$·6 NH$_3$</td>
<td>Orange</td>
<td>4</td>
<td>3</td>
<td>[Co(NH$_3$)$_6$]Cl$_3$</td>
</tr>
<tr>
<td>CoCl$_3$·5 NH$_3$</td>
<td>Purple</td>
<td>3</td>
<td>2</td>
<td>[Co(NH$_3$)$_5$Cl]Cl$_2$</td>
</tr>
<tr>
<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

Given this insight:
Ligands inside brackets, part of coordination sphere, bonded directly to the metal. Those outside, float away in water, counterions.

<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>
Werner’s Theory

• A good theory must predict.
• Werner correctly predicts that there are two forms of CoCl$_3$·4 NH$_3$.
  ➢ Correct formula: [Co(NH$_3$)$_4$Cl$_2$]Cl.
  ➢ Two stereoisomers
  ➢ Top, Cl’s next to each other
  ➢ Bottom, Cl’s across from each other..
Oxidation Numbers

Key issue in metal complexes

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

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

Easily found using:

- Charge of the complex ion
- Charge of each of the ligands.
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: $\text{Cr(III)}(\text{H}_2\text{O})_4\text{Cl}_2$

$+3 + 4(0) + 2(-1) = +1$

$\text{Cr(H}_2\text{O})_4\text{Cl}_2^+$
Electron configuration of metals in complexes.

- Generally a transition metal has an electron configuration like this:
  - \([n \text{ noble gas}]ns^2(n-1)d^m\)

- Example:
  - V: \([\text{Ar}]4s^23d^3\)
  - Pt: \([\text{Xe}]6s^24f^{14}5d^8\)
Electron configuration of metals in complexes.

• But, when transition metals lose electrons to become cations. They lose the s electrons first:

• Example:

  ➢ V: [Ar]4s²3d³
    • V²⁺: [Ar]3d³
  ➢ Pt: [Xe]6s²4f¹⁴5d⁸ (we can drop the f’s, they don’t do anything)
    • Pt²⁺: [Xe]5d⁸
    • Pt³⁺: [Xe]5d⁷
What is Coordination?

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

Metal d orbital

Sometimes called a coordinate covalent bond

So ligands must have lone pairs of electrons.

Because metals don’t share no electrons!

Why? Because they are cations.
The concept of a Lewis Acid

- This bond is formed between a Lewis acid and a Lewis base.
  - Lewis base: electron donor.
  - Lewis acid: electron acceptor.

\[
\begin{align*}
H^+ & + \cdot\cdot\cdot\Theta \quad \longrightarrow \quad H_2O \\
\text{Lewis acid} & \quad \text{Lewis Base} \\
\text{electron acceptor} & \quad \text{electron donor}
\end{align*}
\]
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.
  - The concept of a Lewis acid/base is very important!

\[
\text{Ag}^+ (aq) + 2: \text{N} \equiv \text{H}(aq) \rightarrow \left[ \begin{array}{c}
\text{H} \\
\text{N} \equiv \text{Ag} \equiv \text{N} \\
\text{H} \\
\end{array} \right]^+ (aq)
\]
What is Coordination?

So ligands *must* have lone pairs of electrons.

- There are 3 ways of looking at bonding in coordination compounds:
  - Valence bond theory
  - Ligand Field Theory (adaptation of MO theory)
  - Crystal Field Theory (theory of pure electrostatic interactions)
Valence Bond theory

• Just like we learned before.
  ➢ We mix the atomic orbitals on the metal before we bond the ligands:

• For Transition metals we have 9-14 valence orbitals
  ➢ 1 ns
  ➢ 5 (n-1)d
  ➢ 3 np
  ➢ 5 nd
Valence Bond theory

• Just like we learned before.
  ➢ We mix the atomic orbitals on the metal before we bond the ligands:

• For Transition metals we have 14 valence orbitals
  ➢ 1 ns
  ➢ 5 (n-1)d
  ➢ 3 np
  ➢ 5 nd if needed.
Valence Bond theory

• Example

• Co(NH$_3$)$_6^{3+}$
• Co electron configuration: 4s$^2$3d$^7$
• Co$^{3+}$ electron configuration: 4s$^0$3d$^6$
• Need six orbitals for six ligands so:
  ➢ Hybridize 1 4s, 3 4p and 2 3d to give:
     ➢ sp$^3$d$^2$ orbitals. *The 6 valence electrons of Co$^{3+}$ sit in the other 3 d orbitals.*
Valence Bond theory

• Example

• \( \text{Ni}(\text{NH}_3)_6^{2+} \)
• \( \text{Ni}^{2+} \) electron configuration (8 valence electrons):
  • \( 4s^23d^6 \) ----→ \( 4s^03d^8 \)
• Need six orbitals for six ligands but:
  – 4 3d orbitals are full, only 1 3d orbital left
  – Must hybridize 1 4s, 3 4p and 2 4d to give:
    – \( \text{sp}^3\text{d}^2 \) orbitals. The 8 electrons of \( \text{Ni}^{2+} \) sit in five 3d orbitals.
Ligand Field theory (MO theory for coordination compounds)

Example:

$\text{Ti}(\text{NH}_3)^{3+}$
Metal-Ligand Bond

The metal’s ligands and geometry greatly alter its properties, such as color, ease of oxidation, Magnetic properties Etc.
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

- Metal ions with $d^8$ configuration are often 4 coordinate.
- 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.
- 3 en’s give coordination number of six.
Polydentate Ligands

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.

Wraps around the central atom like an octopus
Polydentate Ligands

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 tetradeutate ligands.
Porphyrin Heme binds the oxygen in your blood

Part of Hemoglobin molecule
Hemoglobin tetramer has 4 hemes

Oxygen binding causes conformational change
Makes the other sites bind oxygen better
# 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>

- coordination complex nomenclature:
  - name the ligands as prefixes before the metal name.
Nomenclature of Coordination Compounds

- **Cation** appears first (as always)
- **Anion** is named last.
- Ligands are listed alphabetically before the metal. Prefixes ignored when alphabetizing.

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

- **Cation**: Pentaamminechlorocobalt(III)
- **Anion**: Chloride
  - 5 NH\(_3\) ligands
  - Cl\(^-\) ligand
  - Cobalt in +3 oxidation state
Nomenclature of Coordination Compounds

- Anionic ligands end in “o”;
- Neutral ligands are not changed.
- Prefixes = number of each ligand.
- If the name of the ligand itself has such a prefix, alternatives like \textit{bis}-, \textit{tris}-, etc., are used.

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

- \text{Pentaamminechlorocobalt(III)}
- \text{Cobalt in +3 oxidation state}
- \text{5 NH}_3 \text{ ligands}
- \text{Cl}^- \text{ ligand}
- \text{Anion Chloride}
Nomenclature of Coordination Compounds

- If complex is anion, its ending is changed to -ate.
- The oxidation number of the metal is given by a Roman numeral in parentheses after the metal.

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

- **Cation**: Sodium
- **Anion**: Tetrachlorooxomolybdate(IV)
  - 4 Cl\(^-\) ligands
  - Oxide, O\(^{2-}\) ligand
  - Molybdenum in +4 oxidation state
Isomers have the same molecular formula, but either:

- Their bonding is different (structural isomers) or
- Their spatial arrangement is different (stereoisomers).
Structural Isomers

If a ligand (like the NO₂ group at the bottom of the complex) has more than one donor atom (atom with lone pairs) as the donor atom, linkage isomers are formed.

Is this a structural or geometric isomer?
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.

Is this a **structural** or **geometric** isomer?

**Structural,**

**bonding different**
Structural Isomers

• Some isomers differ in what ligands are bonded to the metal (coordination sphere) and which are not.
• these are coordination-sphere isomers.
• Example:
• Three isomers of CrCl$_3$(H$_2$O)$_6$ are
  ➢ The violet [Cr(H$_2$O)$_6$]Cl$_3$,
  ➢ The green [Cr(H$_2$O)$_5$Cl]Cl$_2$·H$_2$O, and
  ➢ The (also) green [Cr(H$_2$O)$_4$Cl$_2$]Cl·2H$_2$O.
Geometric isomers

- **Pt(NH$_3$)$_2$Cl$_2$**
  - Has two geometric isomers, two chlorines and two 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
This compound binds DNA. Kills rapidly dividing cancer cells. These include testicular cancer, ovarian cancer, cervical cancer, breast cancer, bladder cancer, head and neck cancer, esophageal cancer, lung cancer, mesothelioma, brain tumors and neuroblastoma.
Stereoisomers

- 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.
**Enantiomers**

A molecule or ion that exists as a pair of enantiomers is said to be chiral.
Enantiomers

- Physical properties of chiral molecules are identical (boiling point, freezing point, density, etc.)

- One exception:
  - Interaction of a chiral molecule with plane-polarized light.
**Enantiomers**

- A chiral compound will rotate plane polarized light.
- If one enantiomer rotates the light $32^\circ$ to the right, the other will rotate it $32^\circ$ to the left.
- Generally, only when 2 chiral things interact is there a difference in properties.
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 an object.

No light absorbed, all reflected get white color.
All light absorbed, none reflected get black color.
What if only one color is absorbed?
If one color absorbed, the color opposite is perceived.

Absorb Orange
See Blue
Absorb Red
See Green
$[\text{Ti(H}_2\text{O)}_6]^3+$
Absorbs in green yellow.
Looks purple.
How is an absorption spectrum of a Compound measured?

A spectrophotometer.
So color comes from:

Absorption (metal complexes)

Emission (element line spectra)

How is light absorbed in a metal complex?
Ligand Field theory: 2 possibilities

Ti(NH$_3$)$_6^{3+}$

1. Metal d electron transition
2. Electronic transition From ligand to metal orbital ("charge transfer")
Metal complexes and color

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

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

Assumption: interaction pure electrostatic.

Crystal Field Theory
Now, think of point charges being attracted to the positively Charged metal. What happens to the d orbitals?

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

- **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

Free metal ion  Metal ion plus ligands (negative point charges)  Splitting because of octahedral crystal field
Ligands will interact with some d orbitals more than others. Depends on relative orientation of orbital and ligand.

Ligands point right at lobes. Orbitals go higher in E.
In these orbitals, the ligands are between the lobes. Interact less strongly, *go lower in E.*
Splitting due to ligand/orbital orientation.

Averaged repulsions between ligands and d-electrons

Free metal ion  Metal ion plus ligands (negative point charges)  Splitting because of octahedral crystal field

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

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

Copyright © 2006 Pearson Prentice Hall, Inc.
Absorption of light promotes an electron to a higher in E_d orbital. $\Delta$ is E of the photon that can be absorbed.

$\Delta = 495 \text{ nm}$
Different ligands interact more or less,
Change energy spacing of d orbitals.

[CrF₆]³⁻  Green
[Cr(H₂O)₆]³⁺  Violet
[Cr(NH₃)₆]³⁺  Yellow
[Cr(CN)₆]³⁻  Yellow
**Spectrochemical series** (strength of ligand interaction)

Cl\(^-\) < F\(^-\) < H\(_2\)O < NH\(_3\) < en < NO\(_2\)\(^-\) < CN\(^-\)

Increasing \(\Delta\)
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

Copyright © 2006 Pearson Prentice Hall, Inc.
As energy difference increases, electron configuration changes. Hund’s rule breaks down because d orbitals are not degenerate.

Co(III) is d^6

[CoF_6]^{3-}

“High spin”

[Co(CN)_6]^{3-}

“Low spin”
The 2 choices for a $d^5$ metal, high spin (more unpaired electrons) or low spin (more paired electrons)
In tetrahedral complexes, orbitals are inverted. Again because of orientation of orbitals and ligands. Δ is always small, always high spin (less ligands)

\[ d_{xy}, d_{xy}, d_{xz} \]

\[ d_{x^2-y^2}, d_{z^2} \]
Square planar complexes are different still

Octahedral  Square planar
D₈ complexes like square planar

Tetrahedral

Square Planar
Intense color can come from “charge transfer”
Ligand electrons jump to empty metal orbitals

KMnO₄
K₂CrO₄
KClO₄

No d orbitals in Cl, orbitals higher in energy
Exam 4 Topics

1. Valence bond theory
2. Molecular orbital theory
3. Chapter 24, coordination chemistry
4. Chapter 25, Organic (a little)

Valence bond theory:
1. Hybridization (mostly covered in last exam)
2. Double bonds due to overlap of atomic p orbitals (pi bonds)
3. Concept of delocalization what orbitals are overlapping in a delocalized system?
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.

$$2p_z + 2p_z \rightarrow \sigma_{2p}^\sigma$$

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

$$2p_x + 2p_x \rightarrow \pi_{2p}^\pi$$

End on

Side to side.
A typical MO diagram, like the one below. For 2p and 2s atomic orbital mixing.
Oxygen $\text{O}_2$ is Paramagnetic, why?
Show me why.

<table>
<thead>
<tr>
<th>Large 2s-2p interaction</th>
<th>Small 2s-2p interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B₂</strong></td>
<td><strong>O₂</strong></td>
</tr>
<tr>
<td><strong>C₂</strong></td>
<td><strong>F₂</strong></td>
</tr>
<tr>
<td><strong>N₂</strong></td>
<td><strong>Ne₂</strong></td>
</tr>
<tr>
<td>( \sigma_{2p}^* )</td>
<td>( \sigma_{2p}^* )</td>
</tr>
<tr>
<td>( \pi_{2p} )</td>
<td>( \pi_{2p} )</td>
</tr>
<tr>
<td>( \sigma_{2p} )</td>
<td>( \sigma_{2p} )</td>
</tr>
<tr>
<td>( \pi_{2p} )</td>
<td>( \pi_{2p} )</td>
</tr>
<tr>
<td>( \sigma_{2s}^* )</td>
<td>( \sigma_{2s}^* )</td>
</tr>
<tr>
<td>( \sigma_{2s} )</td>
<td>( \sigma_{2s} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond order</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond enthalpy (kJ/mol)</td>
<td>290</td>
<td>620</td>
<td>941</td>
<td>495</td>
<td>155</td>
<td>—</td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>1.59</td>
<td>1.31</td>
<td>1.10</td>
<td>1.21</td>
<td>1.43</td>
<td>—</td>
</tr>
<tr>
<td>Magnetic behavior</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
<td>Diamagnetic</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
<td>—</td>
</tr>
</tbody>
</table>
Exam 4 Chapter 23.

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)?

Only ethylene diamine will be used (en)

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

Isomers.

- structural isomers (formula same, bonds differ)
- geometric isomers (formula AND bonds same, structure differs)

Stereoisomers:

- Chirality, handedness,
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
Explaining the properties of metal complexes

Magnetism and color

How does seeing color work?

Absorb **Orange**

See **Blue**

Absorb **Red**

See **Green**
Addition of NH$_3$ ligand to Cu(H$_2$O)$_4$ changes its color.
Splitting of d orbitals in an octahedral ligand field

- $d_{z^2}$
- $d_{x^2-y^2}$
- $d_{xy}$
- $d_{yz}$
- $d_{xz}$
Spectrochemical series (strength of ligand interaction)

Cl\(^-\) < F\(^-\) < H\(_2\)O < NH\(_3\) < en < NO\(_2\)\(^-\) < CN\(^-\)

Increasing \(\Delta\)

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

Tetrahedral

Square planar