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

Question, is this an "ionic compound"

Does it dissociate in water?

- 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.

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

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

Original	Color	Ions per	"Free" Cl [–] Ions	Modern
Formulation		Formula Unit	per Formula Unit	Formulation
CoCl ₃ ·6 NH ₃	Orange	4	3	[Co(NH ₃) ₆]Cl ₃
CoCl ₃ ·5 NH ₃	Purple	3	2	[Co(NH ₃) ₅ Cl]Cl ₂
CoCl ₃ ·4 NH ₃	Green	2	1	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂]Cl
CoCl ₃ ·4 NH ₃	Violet	2	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂]Cl

- 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.



Alfred Werner

Father of coordination chemistry
 First inorganic chemist to win Nobel
 Prize
 Co(III) oxidation state
 CI-

Coordination # is 6

- 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 CoCl₃ · 6 NH₃, all six of the ligands are NH₃ and the 3 chloride ions are outside the coordination sphere.

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CoCl ₃ •4 NH ₃	Violet	2	1	<i>cis-</i> [Co(NH ₃) ₄ Cl ₂]Cl

Werner's Theory

In $CoCl_3 \cdot 5 NH_3$

five NH₃ groups and one chlorine are bonded to the cobalt,

the other two chloride ions are outside the sphere.

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CoCl ₃ •4 NH ₃	Violet	2	1	<i>cis-</i> [Co(NH ₃) ₄ Cl ₂]Cl

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

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Werner's Theory

- A good theory must predict.
- Werner correctly predicts that there are two forms of $CoCl_3 \cdot 4 NH_3$.
 - Correct formula:
 - \succ [Co(NH₃)₄Cl₂]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

 $\int \int \int /$ [Cu(NH₃)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: Cr(III)(H₂O)₄Cl₂

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

 $\downarrow \qquad \downarrow \qquad /$
 $Cr(H_2O)_4Cl_2^+$

Electron configuration of metals in complexes.

- Generally a transition metal has an electron configuration like this:
- [n noble gas]ns²(n-1)d^m
- Example:
- V: [Ar]4s²3d³
- Pt: [Xe]6s²4f¹⁴5d⁸

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
 - $ightarrow Pt: [Xe]6s^24f^{14}5d^8$ (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*.



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!



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

• 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

• 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.

- Example
- $Co(NH_3)_6^{3+}$
- Co electron configuration: 4s²3d⁷
- Co³⁺ electron configuration: 4s⁰3d⁶
- Need six orbitals for six ligands so:
 ➢ Hybridize 1 4s, 3 4p and 2 3d to give:
 ➢ sp³d² orbitals. The 6 valence electrons of Co⁺³ sit in the other 3 d orbitals.

• Example

- $Ni(NH_3)_6^{2+}$
- Ni²⁺ electron configuration (8 valence electrons):
- $4s^23d^6 \rightarrow 4s^03d^8$
- 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:
 ▶ sp³d² orbitals. The 8 electrons of Ni²⁺ sit in five 3d orbitals.



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 d⁸ configuration are often 4 coordinate
- There are two common geometries for metals with a coordination number of four:
 - > Tetrahedral
 - Square planar





Tetrahedral

Square planar

Why square planar? We'll get to that

Geometries

3 +



By far the mostencountered 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, NH₂CH₂CH₂NH₂, represented here as en, each N is a donor atom.
- Therefore, en is bidentate.
- 3 en's give coordination number of **six**.



[EDTA]⁴⁻

Polydentate Ligands



complexes than do monodentate ligands.

Chelating Agents



- Bind to metal ions removing them from solution.
- Phosphates are used to tie up Ca²⁺ and Mg²⁺ 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.



Chelatíng Agents



Porphines (like chlorophyll *a*) are tetradentate 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 Coordínation Compounds

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N ₃ ⁻	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br ⁻	Bromo	Oxide, O ^{2–}	Oxo
Chloride, Cl ⁻	Chloro	Ammonia, NH ₃	Ammine
Cyanide, CN ⁻	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F ⁻	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH ⁻	Hydroxo	Pyridine, C ₅ H ₅ N	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

coordination complex nomenclature:

 \succ name the ligands as prefixes before the metal name.

Nomenclature of Coordínation Compounds

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



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 *bis*-, *tris*-, etc., are used.



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.



Isomers



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?







Nitrito isomer

Structural Isomers

If a ligand (like the NO₂ 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





Nitrito isomer

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 CrCl₃(H₂O)₆ are
 The violet [Cr(H₂O)₆]Cl₃,
 The green [Cr(H₂O)₅Cl]Cl₂ ⋅ H₂O, and
 The (also) green [Cr(H₂O)₄Cl₂]Cl ⋅ 2 H₂O.

Geometríc isomers



Pt(NH₃)₂Cl₂ Has two *geometric isomers*, two chlorines and two NH₃ 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

Geometríc isomers



This compound binds DNA Kills rapidly dividing cancer

cells These include <u>testicular</u> <u>cancer</u>, <u>ovarian cancer</u>, <u>cervical</u> <u>cancer</u>, <u>breast cancer</u>, <u>bladder</u> <u>cancer</u>, <u>head and neck</u> <u>cancer</u>, <u>esophageal</u> <u>cancer</u>, <u>lung</u> <u>cancer</u>, <u>mesothelioma</u>, <u>brain</u> tumors and neuroblastoma.



This one doesn't

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.

Enantíomers

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



Enantíomers

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

interaction of a chiral molecule with planepolarized light.



Enantíomers

- A chiral compound will rotate plane polarized light.
- If one enantiomer rotates the light 32° to the right, the other will rotate it 32° 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



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Addition of NH₃ ligand to Cu(H₂O)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?

Complimentary color wheel

If one color absorbed, the color opposite is perceived.



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$[Ti(H_2O)_6]^{3+}$ Absorbs in green yellow. Looks purple.





(a)

0

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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?



Metal complexes and color

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



Addition of NH₃ ligand to Cu(H₂O)₄ changes its color

Crystal Field Theory

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 the positively Charged metal. What happens to the d orbitals?



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*.





Absorption of light promotes an electron to a higher in E d orbital. Δ is E of the photon that can be absorbed.



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Different ligands interact more or less, Change energy spacing of d orbitals.



Spectrochemical series (strength of ligand interaction)



Electron configurations of some octahedral complexes



As Energy difference increases, electron configuration Changes. Hund's rule breaks down because d orbitals are not degenerate



The 2 choices for a d⁵ metal, high spin (more unpaired electrons) or low spin (more paired electrons)



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Tetrahedral Complexes

In tetrahedral complexes, orbitals are inverted. Again because of orientation of orbitals and ligands. Δ is always small, always high spin (less ligands)



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Square planar complexes are different still





D⁸ complexes like square planar













Tetrahedral

Square Planar

Intense color can come from "charge transfer" Ligand electrons jump to empty metal orbitals

KMnO₄







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KCIO₄



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 overlaping 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



(b) "Sideways" overlap of *p* orbitals forms two sets of π and π^* MOs.



End on

Side to side.

A typical MO diagram, like the one below. For 2p and 2s atomic orbital mixing.



Oxygen O₂ is Paramagnetic, why?



Show me why.

	Large 2 <i>s</i> -2 <i>p</i> interaction				Small 2 <i>s</i> -2 <i>p</i> interaction			
		B ₂	C ₂	N ₂		O ₂	F ₂	Ne ₂
	σ_{2p}^{*}				σ_{2p}^{*}			11
	π_{2p}^*				π_{2p}^{*}	1 1	11 11	11 11
	σ_{2p}			11	π_{2p}	11 11	11 11	11 11
	π_{2p}	1 1	11 11	11 11	σ_{2p}	11	11	11
	σ^*_{2s}	11	11	11	σ^*_{2s}	11	11	11
	σ_{2s}	11	11	11	σ_{2s}	11	11	11
Bond order Bond enthalpy (kJ/n Bond length (Å) Magnetic behavior	nol)	1 290 1.59 Paramagnetic	2 620 1.31 Diamagnetic	3 941 1.10 Diamagnetic		2 495 1.21 Paramagnetic	1 155 1.43 Diamagnetic	0

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) NH_2 - CH_2 - CH_2NH_2

Isomers.

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

Stereoisomers:

Chirality, handedness,



Stereoisomers



Explaining the properties of metal complexes

Magnetism and color

How does seeing color work?



Different ligands on same metal give different colors



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Addition of NH₃ ligand to Cu(H₂O)₄ changes its color

Splitting of d orbitals in an octahedral ligand field



Spectrochemical series (strength of ligand interaction)



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 planer looks like.





$$1 \quad 1 \quad 1 \quad d_{xy}, d_{yz}, d_{xz} \qquad 1 \quad d_{z^2}$$

$$1 d_{x^2-y^2}, d_{z^2}$$

Tetrahedral

Square planar

 $| 1 | 1 | d_{xz}, d_{yz}$