

Why Study Transition Metals

- Transition metals found in nature
 Rocks and minerals contain transition metals
- *Red rubies (Cr), blue sapphires (Fe and Ti)
- Many biomolecules contain transition metals * Vitamin B12 (Co), Hemoglobin, myoglobin, and cytochrome C (all Fe)
- Transition metals used in industry
- ▲ Material science (steel, alloys)
- Transition metal compounds are used as pigments
 *TiO₂ (white), PbCrO₄ (yellow), Fe₄[Fe(CN)₆]₃ (Prussian blue)

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Periodic Table



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d-Block Transition Elements

IIIB	IVB	VB	VIB	VIIB	/		\backslash	IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg

Most have partially occupied d subshells in common oxidation states

Transition Metals

- General Properties
- ▲ Have typical metallic properties (malleable, etc.)
- ▲Not as reactive as alkali and alkaline earth metals
- Have high melting points, high boiling points, high density
- A Have 1 or 2 s electrons in valence shell
- ▲ Differ in # d electrons in n-1 energy level
- ▲ Exhibit multiple oxidation states
- ▲Both paramagnetic and diamagnetic ions exist
- ▲ Most ions deeply colored (crystal field theory)

Electronic Configurations

Element	<u>Configuration</u>		
Sc	$[Ar]3d^{1}4s^{2}$		
Ti	$[Ar]3d^24s^2$		
V	$[Ar]3d^34s^2$		
Cr	[Ar]3d ⁵ 4s ¹		
Mn	[Ar]3d ⁵ 4s ²		
Fe	$[Ar]3d^{6}4s^{2}$		
Ni	$[Ar]3d^84s^2$		
Cu	[Ar]3d ¹⁰ 4s ¹		
Zn	$[Ar]3d^{10}4s^2$		

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Electronic Configurations of Transition Metal Ions

Electronic configuration of Fe ions:

 $Fe - 2e^{-} \rightarrow Fe^{2+}$

valence *ns* electrons removed first, then *n-1 d* electrons

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Coordination Chemistry

Transition metals act as Lewis acids and form complexes or complex ions with Lewis bases or ligands

 $\begin{array}{c} Fe^{3+}(aq) + 6 \ CN^{-}(aq) \rightarrow Fe(CN)_{6}^{3-}(aq) \\ Lewis \ acid \qquad Lewis \ base \qquad Complex \ ion \end{array}$

 $\label{eq:Ni2+} \begin{array}{ll} Ni^{2+}(aq) + 6 \ NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}(aq) \\ \\ \mbox{Lewis acid} & \mbox{Lewis base} & \mbox{Complex ion} \end{array}$

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = **metal** = center of coordination Lewis base = **ligand** = molecules/ions covalently bonded to metal in complex

Oxidation States of Transition Elements



Paramagnetism and Diamagnetism							
Paramagnetic s diamagnetic	pecies l species	ave unpaired have all paire	electrons whi d electrons	le			
Paramagnetic sp magnetic field on the number	ecies ar ls; the n r of unp	e attracted or agnitude of t aired electron	repulsed by he effect depe is	nds			
Examples:							
Paramagnetic	Cr	[Ar] 🚹 🕇	1 1 1 3 d	↑ 4s			
Diamagnetic	Pd	[Kr] ↑↓ ↑	↓↑↓↑↓				

4 d

5s

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Coordination Chemistry

A coordination compound has one or more complexes. Examples: $[Co(NH_3)_6]Cl_3$, $[Cu(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_2Cl_2]$ The coordination number is the number of donor atoms bonded to the central metal atom or ion in the complex. Example: $[Co(NH_3)_6]^{3+}$ coordination number = 6 Example: $[PtCl_4]^{2+}$ coordination number = 4 Most common = 6, 4 and 2 Coordination number determined by ligands





Coordination Chemistry



Monodentate Ligands

- Monodentate ligands possess only one accessible donor group.
- H₂O is a good example since *all* metal ions exist as *aqua* complexes in water

Monodentate Ligand Examples:

▲ H₂O, CN-, NH₃, NO₂⁻, SCN-, OH-, X- (halides), CO, O²⁻

Example Complexes: [Co(NH₃)₆]³⁺

▲[Fe(SCN)₆]³⁻

Bidentate Ligands

Bidentate Ligands have "two teeth", able to bond with metal at two separate places

Bidentate Examples:

- ★ oxalate ion = $C_2O_4^{2-1}$
- ★ ethylenediamine (en) = $NH_2CH_2CH_2NH_2$
- ★ ortho-phenanthroline (o-phen)

Example Complexes:

- ▲ [Co(en)₃]³⁺
- \checkmark [Cr(C₂O₄)₃]³⁻
- ▲ [Fe(NH₃)₄(o-phen)]³⁺



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Bidentate Ligands







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Bidentate Ligands







EDTA

A commonly used *polydentate* ligand Forms 1:1 complexes with most metals except Group IA Forms stable, water soluble complexes High formation constants A *primary standard* material

See the movie "Blade" (!)







EDTA (Ethylenediamine tetraacetic acid) will adapt its coordination number to bond with the metal



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EDTA

Formation constants (K_f) for some metal - EDTA complexes.

lon	log K	lon	log K	lon	log K
Fe ³⁺	25.1	Pb ²⁺	18.0	La ³⁺	15.4
Th4+	23.2	Cd^{2+}	16.5	Mn ²⁺	14.0
Cr ³⁺	23.0	Zn ²⁺	16.5	Ca ²⁺	10.7
Bi ³⁺	22.8	Co ²⁺	16.3	Mg ²⁺	8.7
Cu ²⁺	18.8	Al ³⁺	16.1	Sr ²⁺	8.6
Ni ²⁺	18.6	Ce ³⁺	16.0	Ba ²⁺	7.8

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Nomenclature of Coordination

- The cation is named before the anion. When naming a complex:
- Cations named first, then anions. Anion metal gets *-ate* ending
- Ligands are named *first* in alphabetical order. Most ligands have *-o* ending; multiple ligands use Greek prefixes
- Metal atom/ion is named last with the oxidation state in Roman numerals.
- Use no spaces in complex name
- ◆ See <u>Coordination Compounds Handout</u>

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Nomenclature: IUPAC Rules

- Neutral ligands are referred to by their usual name with these exceptions:
- ★ water, $H_2O = aqua$
- \checkmark ammonia, NH₃ = **ammine**
- ▲ carbon monoxide, CO = carbonyl
- ▲ hydroxide, OH- = **hydroxo**
- If the ligand name already contains a Greek prefix, use alternate prefixes for multiple occurrences:
 - ▲bis-, 2; tris-, 3; tetrakis-, 4; pentakis-, 5; hexakis-, 6
- ▲ The name of the ligand is placed in parentheses; i.e. bis(ethylenediamine)

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Nomenclature: IUPAC Rules

[CoCl(NH₃)₅]Cl₂ pentaamminechlorocobalt(III) chloride

 $K_2[Cd(CN)_4]$ Potassium tetracyanocadmate(II) NiCl₂(en)₂ Dichlorobis(ethylenediamine)nickel(II) CrCl₃(C₄H₈O)₃ (C₄H₈O = tetrahydrofuran) Trichlorotris(tetrahydrofuran)chromium(III)





the first of a series of platinum coordination complexbased anti-cancer drugs (Platinol-AQ)

Isomerism

Isomers are compounds that have the same composition but a different arrangement of atoms in space

Important in inorganic and organic chemistry Major Types include:

- ▲ coordination sphere isomers
- ▲ linkage isomers
- ▲ geometric isomers (*cis, trans, mer, fac*)
- ▲ stereoisomers

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Coordination Sphere Isomers

Coordination sphere isomers differ if a ligand is bonded to the metal in the *complex*, as opposed to being outside the coordination sphere (ionic bonding). Different reactivities!

Consider [Co(NH₃)₅Cl]Br vs. [Co(NH₃)₅Br]Cl

 $[Co(NH_3)_5Cl]Br \rightarrow [Co(NH_3)_5Cl]^+ + Br^ [\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{Br}]\mathrm{Cl} \to [\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{Br}]^+ + \mathrm{Cl}^-$

With AgNO3:

 $[\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{Cl}]\mathrm{Br}(\mathrm{aq}) + \mathrm{AgNO}_3(\mathrm{aq}) \rightarrow$ $[Co(NH_3)_5Cl]NO_3(aq) + \frac{AgBr(s)}{2}$ $[\mathrm{Co(NH_3)_5Br}]\mathrm{Cl}(\mathrm{aq}) + \mathrm{AgNO_3(aq)} \rightarrow$ [Co(NH₃)₅Br]NO₃(aq) + AgCl(s)



(yellow color) b: pentaamminenitritocobalt(III) (red color)



Geometric Isomers

- Geometric isomers have same types and number of atoms, but they differ in the spatial arrangements of the ligands
- Inorganic complexes exhibit cis and trans isomerism in square planar and octahedral complexes, as well as mer and fac isomers in octahedral complexes
- Geometric isomers lead to different colors, melting points, boiling points, reactivities, solubilities, etc.



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Properties of Optical Isomers

- Optical isomers or enantiomers possess many identical properties
- Enantiomers have similar solubilities, melting points, boiling points, colors, chemical reactivity (with nonchiral reagents)
- Enantiomers differ in their interactions with plane polarized light and other chiral reagents



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Optical Isomers



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Properties of Optical Isomers

Differences in enantiomer reactivity with other chiral reagents can lead to separation methods

Example:

 $\begin{array}{l} d\text{-}C_4H_4O_6^{2\text{-}}(\text{aq}) + d, l\text{-}[\text{Co}(\text{en})_3]\text{Cl}_3(\text{aq}) \rightarrow \\ chiral \ reagent \qquad racemic \ mixture \\ d\text{-}[\text{Co}(\text{en})_3](d\text{-}C_4H_4O_6^{2\text{-}})\text{Cl}(\text{s}) + \end{array}$

solid d enantiomer

l-[Co(en)₃]Cl₃(aq) +2Cl-(aq)

aqueous l enantiomer

Very complex procedures, but important (Ritalin, Thalidomide, etc.)

Crystal Field Theory

- **Crystal Field Theory** is a model for bonding in transition metal complexes
- Accounts for color and magnetism of complexes quite well
- Focuses on d-orbitals of metals. Ligands are considered to be point negative charges
- Assumes ionic bonding (no covalent bonding)
- As in organic chemistry, **molecular orbital theory** is better but much more complex

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Crystal Field Theory

- *Electrostatic attractions* between the positive metal ion and the negative ligands bond them together, *lowering* the energy of the whole system
- The lone pair e's on ligands repulsed by e's in metal d orbitals; this interaction is called the crystal field
- The repulsion influences d orbital energies, but not all d orbitals influenced the same way

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Crystal Field Splitting Energy







- Crystal Field Theory can be used to account for the colors of complexes as well as magnetic properties
- A complex *must* have a partially filled metallic d subshell to exhibit color; i.e. a complex with d⁰ or d¹⁰ is colorless
- Amount of paramagnetism depends on ligands; i.e. [FeF₆]³- has five unpaired electrons while [Fe(CN)₆]³- has only one

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590

Yellow

560

The color observed in a compound/complex is actually the

complementary color of the color absorbed

480

Green

- Absorption of UV-visible radiation by compound or complex occurs *only* if the radiation has the energy needed to raise an e- from its ground state (highest occupied orbital or HOMO) to an excited state (usually the lowest unoccupied orbital or LUMO)
- The light energy *absorbed* = energy difference between the ground state and excited state, or

$$\Delta \mathbf{E} = \mathbf{E}_{\text{LUMO}} - \mathbf{E}_{\text{HOMO}} = \mathbf{h}\mathbf{v} = \mathbf{h}\mathbf{c}/\lambda_{\text{max}}$$



...so observed color of

complex is navy blue.

The color observed in a compound/complex is actually the

complementary color of the color absorbed

[Cu(NH₃)₄]²⁺:

absorbs yellow,

orange, and red...

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- The **magnitude** of \triangle depends on the **ligand field** (i.e. *types of ligands*) and the **metal**, and \triangle determines the **color** of the complex
- Different complexes exhibit different colors due to the magnitude of Δ
- larger Δ = higher energy light absorbed, shorter wavelengths
- smaller Δ = lower energy light absorbed, longer wavelengths









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Paramagnetism of Transition Metal Complexes

Many complexes / compounds are paramagnetic due to unpaired d electrons

The degree of paramagnetism dependent on ligands ("ligand field")

Example with Fe^{3+} *:*

[Fe(CN)₆]³⁻ has 1 unpaired d electron

[FeF₆]³⁻ has 5 unpaired d electrons

Crystal Field Theory answers this discrepancy

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Electronic Configurations of Transition Metal Complexes

Filling electron shells via CH 221:

- lowest energy vacant orbitals are occupied first
- electrons fill degenerate orbitals singly until no longer possible (Hund's rule), then pair (Pauli Exclusion)

These rules help minimize repulsions between electrons. These rules work well for *gas-phase transition metal ions*, but they are not always followed by *transition metal complexes in a ligand field*

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Electronic Configurations of Transition Metal Complexes

For complexes in a ligand field, d orbital occupancy depends on \triangle and *pairing energy*, P

- Electrons assume the configuration with the lowest possible energy "cost"
- If △ > P (△ large; strong field ligand), e's pair up in lower energy d subshell first, referred to as a low spin complex
- If △ ≤ P (△ small; weak field ligand), e's spread out among all d orbitals before any pair up, referred to as a high spin complex



d-orbital energy level diagrams octahedral complex

d^1



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d-orbital energy level diagrams octahedral complex

d³



d-orbital energy level diagrams octahedral complex

 d^2









Electronic Configurations of Transition Metal Complexes

To determine which d-orbital energy level diagram to use on a complex or compound:

- \checkmark determine the oxidation # of the metal
- \checkmark determine the # of d e-'s
- ▲ determine if ligand is weak field or strong field
- ▲ draw energy level diagram

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Example with Co(NH₃)₆³⁺

- The absorbance spectrum of $Co(NH_3)_6^{3+}$ is shown to the right.
 - 400 500 600 700 Wavelength (nm)
- What is the name of the complex?
 What is the coordination number?
- 3. How many d electrons does the complex possess?
- 4. Will this be a high spin or low spin complex?
- 5. Is the compound paramagnetic?
- 6. What is the value of Δ for this complex?
- o. what is the value of Δ for this complex?
- What will be the observed color of the complex? What color is absorbed?

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Example with Co(NH₃)₆³⁺

What is the name of the complex?
 Each ammonia is neutral; hence, this is a cobalt(III) complex

Ammonia is named "ammine"; hence, Name = hexaamminecobalt(III) ion

- 2. What is the coordination number?
 - There are six monodentate ammonia ligands around the cobalt(III) ion; hence, this is a six coordinate compound, or the coordination number = 6

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Example with Co(NH₃)₆³⁺

3. How many d electrons does the complex possess?

Cobalt(III) ions have the electron configuration: [Ar]3d⁶ (two 4s and 1 3d electron removed) This complex has six d electrons (d⁶)

- Will this be a high spin or low spin complex? To answer this, we need to look at the spectrochemical series.
 - NH_3 is considered a strong field ligand, which implies that Δ , the splitting energy, will be greater than the electron pairing energy (P).

The octahedral $\rm NH_3$ ligand field makes this a low spin complex



- 5. Is the compound paramagnetic?
 - This is a d⁶ low spin complex in an octahedral field. Three degenerate d orbitals are filled first, followed by the remaining two orbitals.

Since each orbital holds two electrons, the three lower orbitals are full and the complex is diamagnetic





d-orbital energy level diagrams for

tetrahedral complexes









End of Chapter 19

See:

* <u>Chapter Nineteen Study Guide</u>

**Important Equations (following this slide)*

*End of Chapter Problems (following this slide)

End of Chapter Problems: Test Yourself

 Give the electron configuration for the Cr³⁺ ion. Is it paramagnetic or diamagnetic?
 Which of the following ligands is expected to be monodentate and which might be polydentate? a. CH₃NH₂ b. CH₂CN c. en d. Br⁻¹ e. phen
 Give the oxidation number of the metal ion in [Mn(NH₂)₈]SO₄

Give the oxidation number of the metal ion in Cr(en)₂Cl₂

Write the formula for potassium tetrachloroplatinate(II) Write the formula for tetraamminediaquairon(II)

Name the following: [Ni(C₂O₄)₂(H₂O)₂]²⁻ Name the following: Pt(NH₃)₂(C₂O₄)

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Important Equations, Constants, and Handouts

from this Chapter:

 The primary focus of this chapter is to introduce you to coordination compound nomenclature (with a little review of metals, electron configurations, etc. as well from CH 221 and CH 222)

Handouts:

<u>Coordination Compounds Handout</u>

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4. 5. 6. 7. 8.

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End of Chapter Problems: Answers

- [Ar]3d³, paramagnetic
 a, b, d. monodentate c, e: polydentate (bidentate)
 +2
 +2
 K₂[PtCl₄]
 [Fe(NH₃)₄(H₂O)₂]²⁺
 diaquabis(oxalato)nickelate(II) ion
 diammineoxalatoplatinum(II)