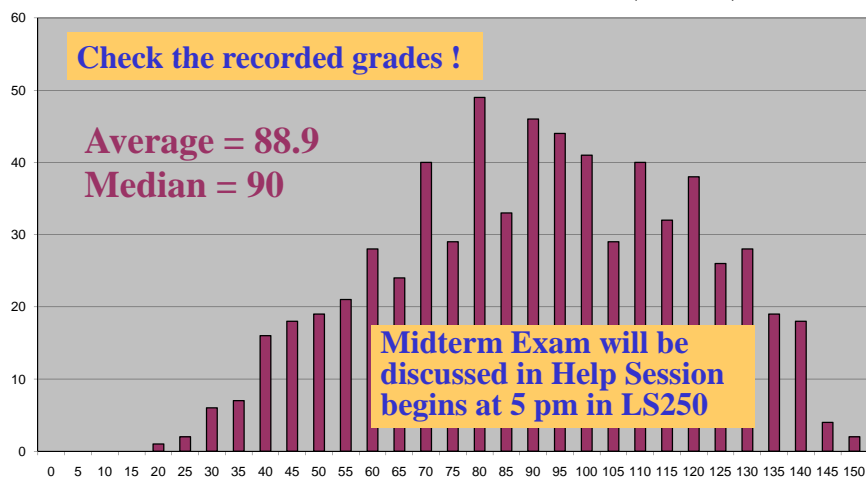


## Midterm Exam Grades

Chem151 Midterm Exam Grade Distribution (Fall 2009)



## Chem 151 Lecture 7

### Introduction to Coordination Chemistry

#### Exp 5

- Ligand Substitution of Fe(III), Cu(II) and Co(II) complexes
- Study of Absorption Spectrophotometry
- Naming Coordination compounds

#### Exp 6

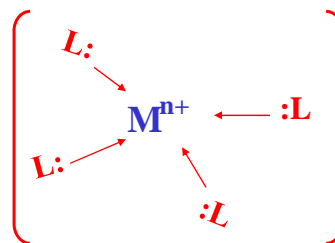
- Syntheses of coordination complexes of Co(III) and of Cu(II)
- Obtain Absorption Spectra of Co(III) & Cu(II) complexes
- Calculate percentage yield of the syntheses

## Complexes

Central metal (ion) surrounded by certain numbers of ligands

$M^{n+}$  is the central metal ion which has empty orbitals that can accept electron pairs.

**L** are the ligands. They can be anions or neutral molecules that contain at least one atom that is capable of donating a pair of electrons to the central metal to form a coordinate covalent bond.



(Dative bond)

A coordination complex can be a cation, an anion, or a neutral molecule

A coordination compound is a compound containing at least one complex (ion).

Complex cation + Simple anion       $[\text{Co}(\text{NH}_3)_6]\text{SO}_4$

Simple cation + Complex anion       $\text{K}_2[\text{CoCl}_4]$

Complex cation + Complex anion       $[\text{Co}(\text{NH}_3)_6][\text{CoCl}_4]$

A complex neutral molecule       $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

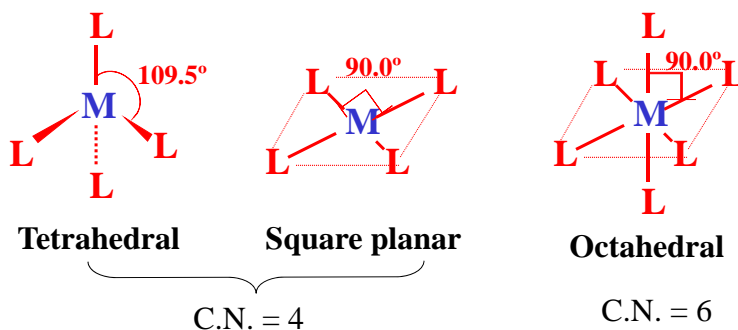
What is the oxidation number of the central metal in each complex?

The number of ligand sites around the central metal in a complex is called the **coordination number**.

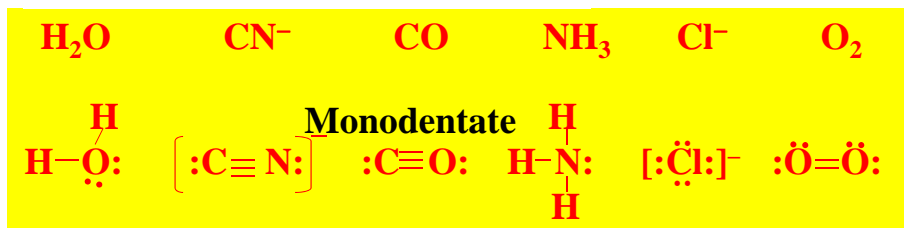
The C.N. of a complex ion depends on the nature of the central metal ion and the ligands: e.g., the C.N. of  $\text{Fe}^{3+}$  and is almost always 6; The C.N. of  $\text{Co}^{2+}$  can be 4 or 6.

Complexes of different C.N. take different geometries.

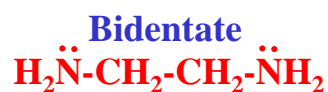
### Common Geometry of Complexes



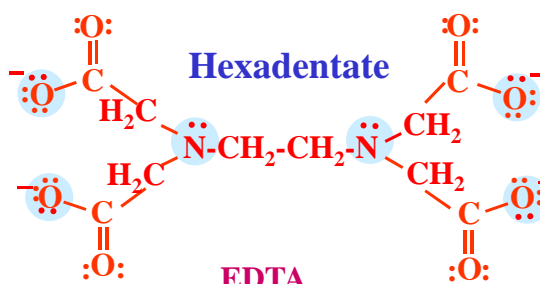
### Some Common Ligands:



### Polydentate Ligands:



Ethylenediamine

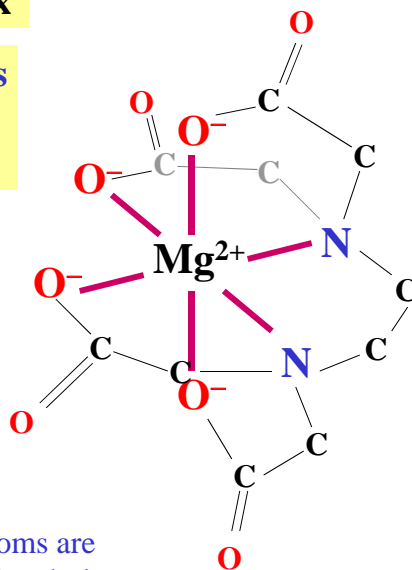


EDTA

Ethylenediaminetetraacetate

A  $\text{Mg}^{2+}$ -EDTA complex

A polydentate ligand is also called a



The H atoms are omitted for clarity

## Reactions Involving Coordination Compounds

When you add a reagent capable of acting as a ligand to a ppt. and the ppt. re-dissolves, the metal in the ppt. probably reacts with the reagent and turns into a complex ion.

## Ligand Substitution Reactions

The general format of ligand substitution reactions:



etc.

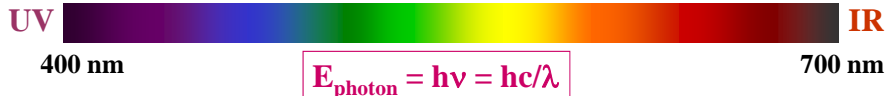
Ligands that have greater affinity to the central metal can substitute ligands having weaker affinity to the central metal.

A complex is said to be **labile** if it undergoes ligand substitution rapidly. It is said to be **inert (non-labile)** if the ligand substitution proceeds slowly or not at all.

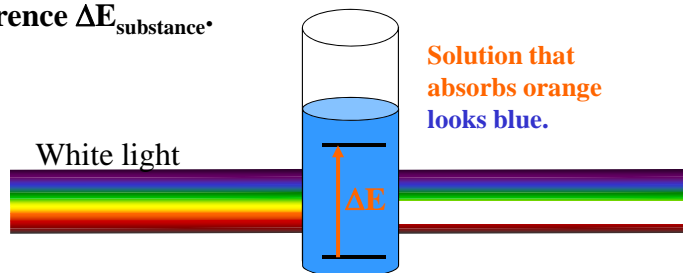
**Water is a common (but very weak) ligand of many metal ions.**

## Why are things colored?

White light is combination of many colors of light.

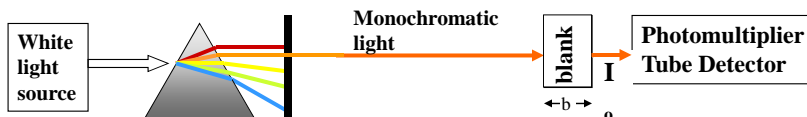


A substance absorbs energy (photons) and goes from its ground electronic state to an excited electronic state with energy gap difference  $\Delta E_{\text{substance}}$



The color we see is the **complementary color** of the light absorbed.

A **Spectrophotometer** can measure how much light is being absorbed/ transmitted.



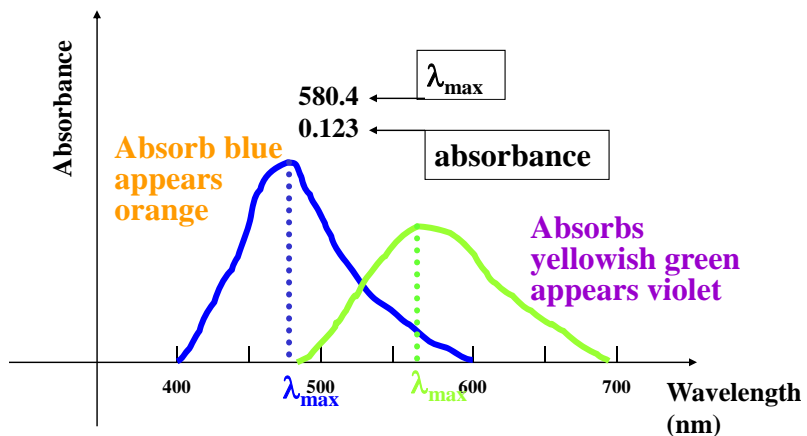
Absorbance = the amount of light absorbed by the sample

Absorbance  $\propto$  concentration of the light absorbing substance

Plotting the absorbance as a function of wavelengths gives an absorption spectrum.

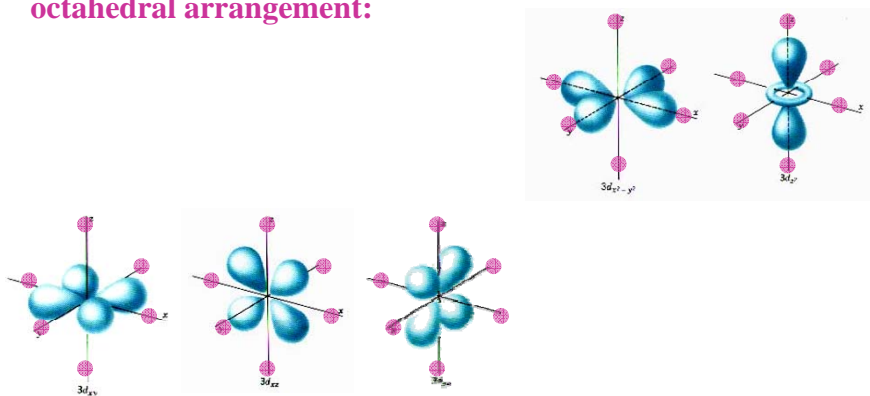
## Absorption Spectra of Complexes

Read Appendix V in your lab manual to learn the operation of the Genesys 5 Spectrophotometer. Be sure to set the peak label function ON to obtain  $\lambda_{\max}$ .



## Ligands interact with the d-orbitals of the central metal

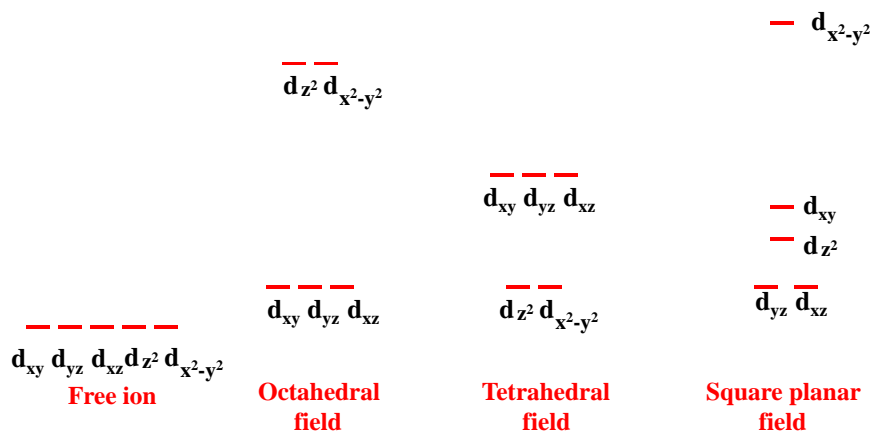
When the central metal is surrounded by six ligands in an octahedral arrangement:



The presence of ligands causes the d-orbitals to split in energy.

## Splitting of d-orbitals of the central metal in complexes

Splitting of d-orbitals of the central metal allows a complex to absorb electromagnetic wave within the visible spectrum. Thus, many complexes have color.



## A Quick Summary

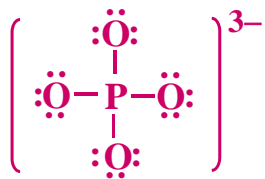
1. What makes a Coordination Complex/ Coordination Cpd?  
Central metal (that has empty orbitals)  
Ligands (ions/molecules containing lone pair electrons)
2. Common Coordination Numbers and the corresponding geometry of a complex
3. Common Reaction of Coordination Complexes (Complex formation and Ligand substitutions)
4. Why things have color? (we see the complimentary color of what a substance absorbs)
5. Many complexes are colorful because of the splitting of the d-orbitals in the central metal (causing it to absorb visible light.)

### Characters of Fe(III) Complexes

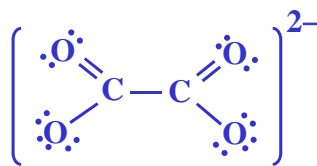
Most of the complexes of Fe(III) are 6-coordinated. A few tetrahedral complexes such as  $\text{FeCl}_4^-$ .

$\text{Fe}(\text{H}_2\text{O})_6^{3+}$  slightly hydrolyzes in water  $\text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+} + \text{H}^+$

$\text{Fe}^{3+}$  has great affinity for ligands that coordinates by oxygen, such as phosphate, oxalate, and EDTA.



Phosphate,  $\text{PO}_4^{3-}$

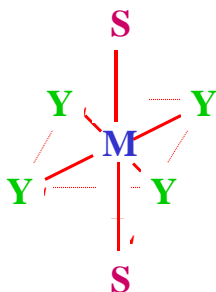


Oxalate,  $\text{C}_2\text{O}_4^{2-}$

### Characters of Cu(II) Complexes

Most of the complexes of Cu(II) are octahedral with a elongated axis.

The two farther ligand sites are usually occupied by solvent molecules.



Only 4 ligands are displaced in ligand substitution reactions.

## Characters of Co(II) Complexes

Co(II) complexes are very labile (undergo ligand substitution readily).

Co(II) forms tetrahedral complexes and octahedral complexes

Absorbs orange,  
a longer  $\lambda_{\max}$ .

Absorbs green,  
a shorter  $\lambda_{\max}$ .

Stable at high temperature

Stable at low temperature

Co(III) complexes are inert and mostly 6 coordinated. (Exp 6)

## Naming of Coordination Compounds

If the ligand is a simple anion, whose name typically ends with -ide, the 'ide' is changed to 'o'.

Cl<sup>-</sup> chloride → chloro  
O<sup>2-</sup> oxide → oxo  
OH<sup>-</sup> hydroxide → hydroxo  
CN<sup>-</sup> cyanide → cyano

If the ligand is a polyatomic anion, whose name typically ends with -ite or -ate, the final 'e' is changed to 'o'.

SO<sub>4</sub><sup>2-</sup> sulfate → sulfato  
SO<sub>3</sub><sup>2-</sup> sulfite → sulfito  
NO<sub>3</sub><sup>-</sup> nitrate → nitrato

If the ligand is a neutral molecule, the common name of the molecule is used.

exceptions:  
water → aqua  
ammonia → ammine  
carbon monoxide → carbonyl

The number of each kind of ligands is designated by the prefix: di, tri, ...etc. For polydentate ligands the prefix: bis, tris, tetrakis, etc. are used.

## Naming of Complex ions

- 1) Name the ligands first, in alphabetical order, followed by the name of the central metal.

e.g., diaquadichloroplatinum (IV)  $\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_2^{2+}$   
Triamminechlorocobalt (II)  $\text{Co}(\text{NH}_3)_3\text{Cl}^+$

- 2) If the complex ion is an anion, the name of the metal ends with the suffix -ate.

Platinum → Platinate  
Zinc → Zincate  
Nickel → Nickelate

Iron → Ferrate    Copper → Cuprate  
Lead → Plumbate    Tin → Stannate  
Silver → Argentate    Gold → Aurate

e.g., tetrachloroplatinate (II)  $\text{PtCl}_4^{2-}$   
amminetrichlorocobaltate (II)  $\text{Co}(\text{NH}_3)_3\text{Cl}_3^-$

- 3) The oxidation number of the metal is given as a Roman numeral in parentheses following the name of the metal.

## Naming of Coordination Compounds

Name the cation first, then, the anion.

When the coordination compound is a neutral complex, it is named like a complex cation.

$[\text{Co}(\text{NH}_3)_3\text{Cl}]_2\text{SO}_4$     Triamminechlorocobalt(II) sulfate

$\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2]$     Potassium bis(oxalato)cobaltate(II)

$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$     Diamminedichloroplatinum(II)

Ammonium tetrachlorocuprate(II)     $(\text{NH}_4)_2[\text{CuCl}_4]$

Dioxovanadium(V) nitrate     $[\text{VO}_2]\text{NO}_3$

Tollens reagent  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$     Diamminesilver(I) hydroxide

More in Prelab Practice 5 and Drilling Question #6