

CHEM 212  
Coordination Chemistry

Chapter 24

Why Study Descriptive Chemistry of  
Transition Metals

- ◆ Transition metals are found in nature
  - ▲ Rocks and minerals contain transition metals
  - ▲ The color of many gemstones is due to the presence of transition metal ions
    - \* Rubies are red due to Cr
    - \* Sapphires are blue due to presence of Fe and Ti
  - ▲ Many biomolecules contain transition metals that are involved in the functions of these biomolecules
    - \* Vitamin B12 contains Co
    - \* Hemoglobin, myoglobin, and cytochrome C contain Fe

Why Study Descriptive Chemistry of  
Transition Metals

- ◆ Transition metals and their compounds have many useful applications
  - ▲ Fe is used to make steel and stainless steel
  - ▲ Ti is used to make lightweight alloys
  - ▲ Transition metal compounds are used as pigments
    - \*  $\text{TiO}_2$  = white
    - \*  $\text{PbCrO}_4$  = yellow
    - \*  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (prussian blue) = blue
  - ▲ Transition metal compounds are used in many industrial processes

Why Study Descriptive Chemistry of  
Transition Metals

- ◆ To understand the uses and applications of transition metals and their compounds, we need to understand their chemistry.
- ◆ Our focus will be on the 4<sup>th</sup> period transition elements.

Periodic Table

d block transition elements

f block transition elements

Transition Metals

- ◆ General Properties
  - ▲ Have typical metallic properties
  - ▲ Not as reactive as Grp. IA, IIA metals
  - ▲ Have high MP's, high BP's, high density, and are hard and strong
  - ▲ Have 1 or 2 s electrons in valence shell
  - ▲ Differ in # d electrons in n-1 energy level
  - ▲ Exhibit multiple oxidation states

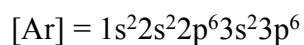
### d-Block Transition Elements

IIIB	IVB	VB	VIB	VIIIB	VIII B			IB	II B
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Most have partially occupied d subshells in common oxidation states

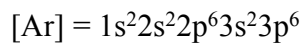
### Electronic Configurations

Element	Configuration
Sc	[Ar]3d <sup>1</sup> 4s <sup>2</sup>
Ti	[Ar]3d <sup>2</sup> 4s <sup>2</sup>
V	[Ar]3d <sup>3</sup> 4s <sup>2</sup>
Cr	[Ar]3d <sup>5</sup> 4s <sup>1</sup>
Mn	[Ar]3d <sup>5</sup> 4s <sup>2</sup>



### Electronic Configurations

Element	Configuration
Fe	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>
Co	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>
Ni	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>
Cu	[Ar]3d <sup>10</sup> 4s <sup>1</sup>
Zn	[Ar]3d <sup>10</sup> 4s <sup>2</sup>



### Transition Metals

- ◆ Characteristics due to d electrons:
  - ▲ Exhibit multiple oxidation states
  - ▲ Compounds typically have color
  - ▲ Exhibit interesting magnetic properties
    - \* paramagnetism
    - \* ferromagnetism

### Oxidation States of Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4		+4			
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

### Oxidation States of Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

37/01      37/01      37/01      37/01      37/01      37/01      37/01      37/01      37/01

loss of ns e's

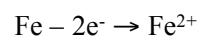
loss of ns and (n-1)d e's

### Electronic Configurations of Transition Metal Ions

- ◆ Electronic configuration of  $\text{Fe}^{2+}$

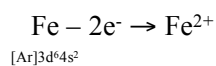
### Electronic Configurations of Transition Metal Ions

- ◆ Electronic configuration of  $\text{Fe}^{2+}$



### Electronic Configurations of Transition Metal Ions

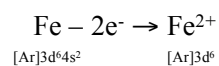
- ◆ Electronic configuration of  $\text{Fe}^{2+}$



valence ns e<sup>-</sup>'s removed  
first

### Electronic Configurations of Transition Metal Ions

- ◆ Electronic configuration of  $\text{Fe}^{2+}$



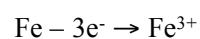
valence ns e<sup>-</sup>'s removed  
first

### Electronic Configurations of Transition Metal Ions

- ◆ Electronic configuration of  $\text{Fe}^{3+}$

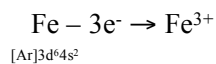
### Electronic Configurations of Transition Metal Ions

- ◆ Electronic configuration of  $\text{Fe}^{3+}$



### Electronic Configurations of Transition Metal Ions

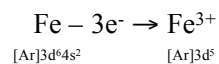
#### ◆ Electronic configuration of Fe<sup>3+</sup>



valence ns e<sup>-</sup>'s removed  
first, then n-1 d e<sup>-</sup>'s

### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of Fe<sup>3+</sup>



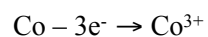
valence ns e<sup>-</sup>'s removed  
first, then n-1 d e<sup>-</sup>'s

### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of Co<sup>3+</sup>

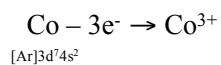
### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of Co<sup>3+</sup>



### Electronic Configurations of Transition Metal Ions

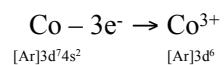
#### ◆ Electronic configuration of Co<sup>3+</sup>



valence ns e<sup>-</sup>'s removed  
first, then n-1 d e<sup>-</sup>'s

### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of Co<sup>3+</sup>



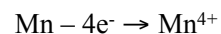
valence ns e<sup>-</sup>'s removed  
first, then n-1 d e<sup>-</sup>'s

### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of $\text{Mn}^{4+}$

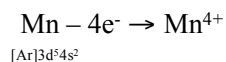
### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of $\text{Mn}^{4+}$



### Electronic Configurations of Transition Metal Ions

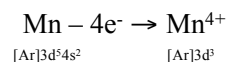
#### ◆ Electronic configuration of $\text{Mn}^{4+}$



valence ns e<sup>-</sup>'s removed  
first, then n-1 d e<sup>-</sup>'s

### Electronic Configurations of Transition Metal Ions

#### ◆ Electronic configuration of $\text{Mn}^{4+}$

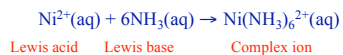


valence ns e<sup>-</sup>'s removed  
first, then n-1 d e<sup>-</sup>'s

### Coordination Chemistry

#### ◆ Transition metals act as Lewis acids

\* Form complexes/complex ions



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

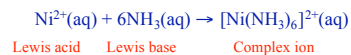
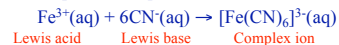
Lewis acid = metal = center of coordination

Lewis base = ligand = molecules/ions covalently bonded to metal in complex

### Coordination Chemistry

#### ◆ Transition metals act as Lewis acids

\* Form complexes/complex ions



Complex with a net charge = complex ion

Complexes have distinct properties

### Coordination Chemistry

- ◆ Coordination compound
  - ▲ Compound that contains 1 or more complexes
  - ▲ Example
    - \*  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
    - \*  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$
    - \*  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

### Coordination Chemistry

- ◆ Coordination sphere
  - ▲ Metal and ligands bound to it
- ◆ Coordination number
  - ▲ number of donor atoms bonded to the central metal atom or ion in the complex
    - \* Most common = 4, 6
    - \* Determined by ligands
      - Larger ligands and those that transfer substantial negative charge to metal favor lower coordination numbers

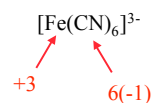
### Coordination Chemistry

Complex charge = sum of charges on the metal and the ligands



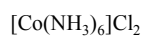
### Coordination Chemistry

Complex charge = sum of charges on the metal and the ligands



### Coordination Chemistry

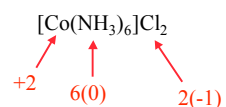
Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions



neutral compound

### Coordination Chemistry

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions



## Coordination Chemistry

### ◆ Ligands

▲ classified according to the number of donor atoms

▲ Examples

- \* monodentate = 1
- \* bidentate = 2
- \* tetradentate = 4
- \* hexadentate = 6
- \* polydentate = 2 or more donor atoms

## Coordination Chemistry

### ◆ Ligands

▲ classified according to the number of donor atoms

▲ Examples

- \* monodentate = 1
- \* bidentate = 2 ← chelating agents
- \* tetradentate = 4
- \* hexadentate = 6
- \* polydentate = 2 or more donor atoms

## Ligands

### ◆ Monodentate

▲ Examples:

- \*  $\text{H}_2\text{O}$ ,  $\text{CN}^-$ ,  $\text{NH}_3$ ,  $\text{NO}_2^-$ ,  $\text{SCN}^-$ ,  $\text{OH}^-$ ,  $\text{X}^-$  (halides),  $\text{CO}$ ,  $\text{O}^{2-}$

▲ Example Complexes

- \*  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- \*  $[\text{Fe}(\text{SCN})_6]^{3-}$

## Ligands

### ◆ Bidentate

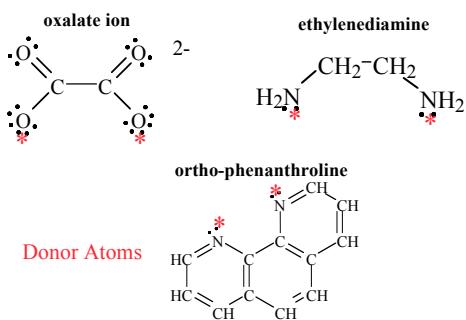
▲ Examples

- \* oxalate ion =  $\text{C}_2\text{O}_4^{2-}$
- \* ethylenediamine (en) =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
- \* ortho-phenanthroline (o-phen)

▲ Example Complexes

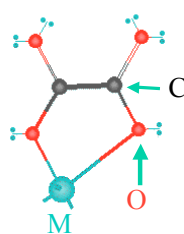
- \*  $[\text{Co}(\text{en})_3]^{3+}$
- \*  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$
- \*  $[\text{Fe}(\text{NH}_3)_4(\text{o-phen})]^{3+}$

## Ligands

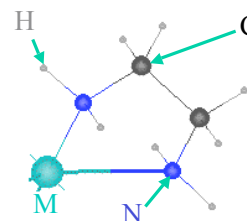


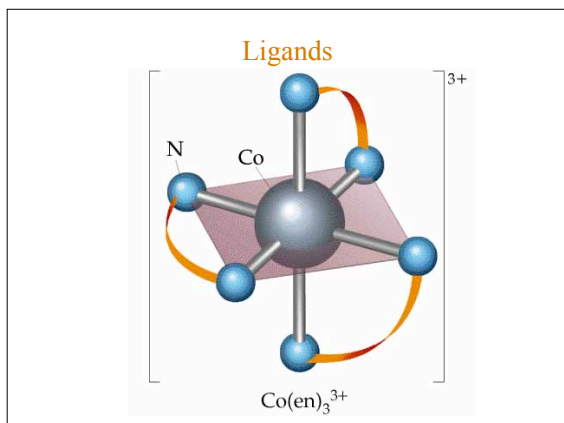
## Ligands

oxalate ion



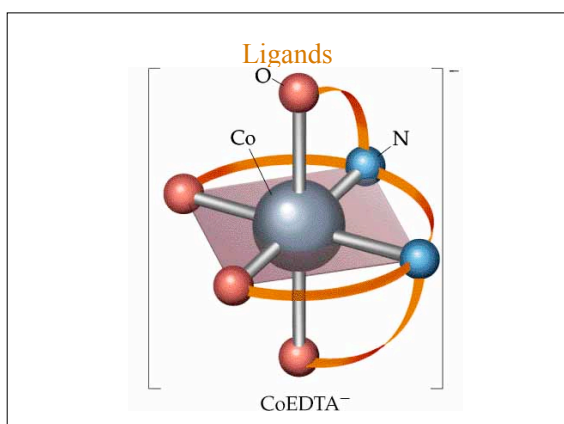
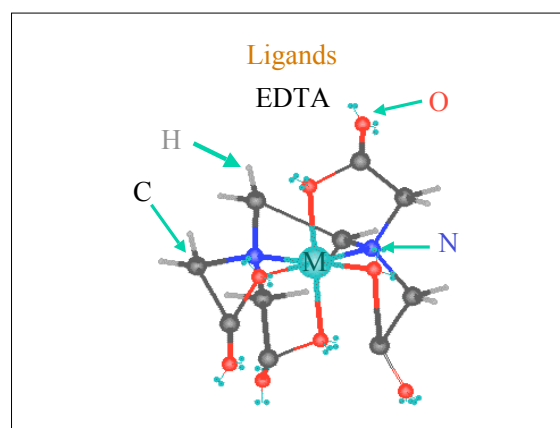
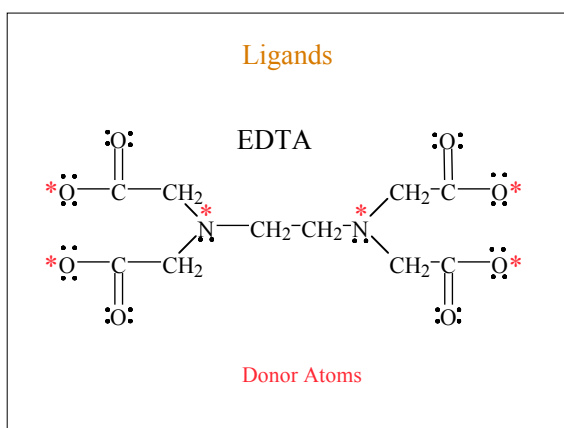
ethylenediamine





**Ligands**

- ◆ Hexadentate
  - ▲ ethylenediaminetetraacetate (EDTA) =  $(\text{O}_2\text{CCH}_2)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CO}_2)_2^{4-}$
  - ▲ Example Complexes
    - \*  $[\text{Fe}(\text{EDTA})]^{-1}$
    - \*  $[\text{Co}(\text{EDTA})]^{-1}$




**Common Geometries of Complexes**

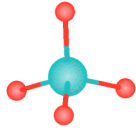

<u>Coordination Number</u>	<u>Geometry</u>
2	<p style="text-align: center;">Linear</p>



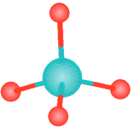

**Common Geometries of Complexes**

<u>Coordination Number</u>	<u>Geometry</u>
2	 <p style="text-align: center;">Linear</p>
<p>Example: <math>[\text{Ag}(\text{NH}_3)_2]^+</math></p>	

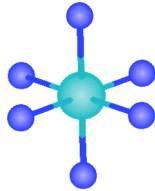
**Common Geometries of Complexes**

<u>Coordination Number</u>	<u>Geometry</u>
4	<p>tetrahedral (most common)</p> 
	<p>square planar (characteristic of metal ions with 8 d e<sup>-</sup>'s)</p> 

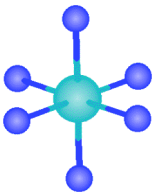
**Common Geometries of Complexes**

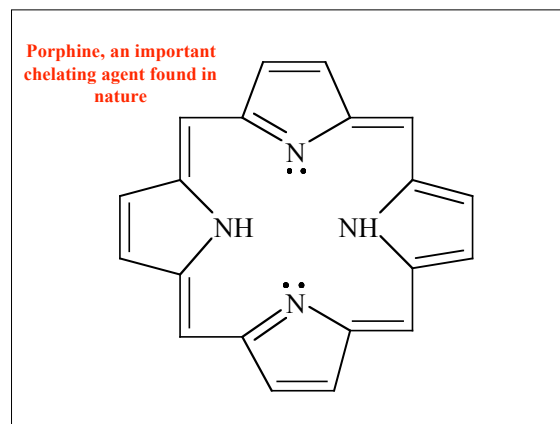
<u>Coordination Number</u>	<u>Geometry</u>
4	<p>tetrahedral</p> 
<p>Examples: <math>[\text{Zn}(\text{NH}_3)_4]^{2+}</math>, <math>[\text{FeCl}_4]^-</math></p>	
	<p>square planar</p> 
<p>Example: <math>[\text{Ni}(\text{CN})_4]^{2-}</math></p>	

**Common Geometries of Complexes**

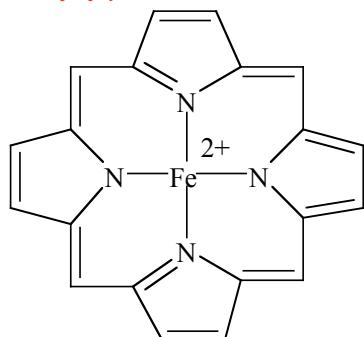
<u>Coordination Number</u>	<u>Geometry</u>
6	 <p style="text-align: center;">octahedral</p>

**Common Geometries of Complexes**

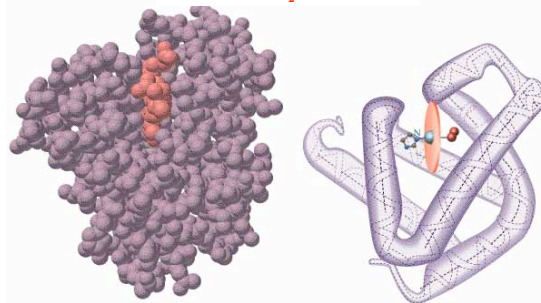
<u>Coordination Number</u>	<u>Geometry</u>
6	 <p style="text-align: center;">octahedral</p>
<p>Examples: <math>[\text{Co}(\text{CN})_6]^{3-}</math>, <math>[\text{Fe}(\text{en})_3]^{3+}</math></p>	



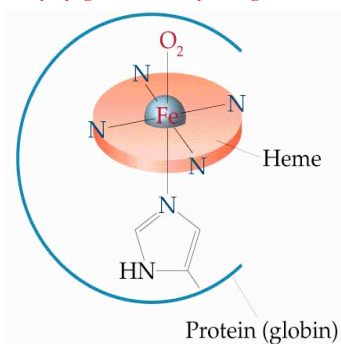
### Metalloporphyrin



### Myoglobin, a protein that stores O<sub>2</sub> in cells

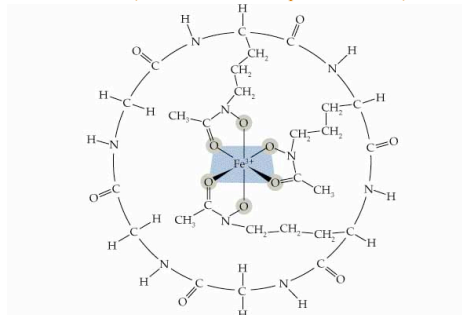


### Coordination Environment of Fe<sup>2+</sup> in Oxymyoglobin and Oxyhemoglobin



### Ferrichrome (Involved in Fe transport in bacteria)

FG24\_014.JPG



### Nomenclature of Coordination Compounds: IUPAC Rules

- ◆ The cation is named before the anion
- ◆ When naming a complex:
  - ▲ Ligands are named first
    - \* alphabetical order
  - ▲ Metal atom/ion is named last
    - \* oxidation state given in Roman numerals follows in parentheses
  - ▲ Use no spaces in complex name

### Nomenclature: IUPAC Rules

- ◆ The names of anionic ligands end with the suffix -o
  - ▲ -ide suffix changed to -o
  - ▲ -ite suffix changed to -ito
  - ▲ -ate suffix changed to -ato

### Nomenclature: IUPAC Rules

Ligand	Name
bromide, Br <sup>-</sup>	bromo
chloride, Cl <sup>-</sup>	chloro
cyanide, CN <sup>-</sup>	cyano
hydroxide, OH <sup>-</sup>	hydroxo
oxide, O <sup>2-</sup>	oxo
fluoride, F <sup>-</sup>	fluoro

### Nomenclature: IUPAC Rules

Ligand	Name
carbonate, CO <sub>3</sub> <sup>2-</sup>	carbonato
oxalate, C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	oxalato
sulfate, SO <sub>4</sub> <sup>2-</sup>	sulfato
thiocyanate, SCN <sup>-</sup>	thiocyanato
thiosulfate, S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	thiosulfato
Sulfite, SO <sub>3</sub> <sup>2-</sup>	sulfito

### Nomenclature: IUPAC Rules

- ◆ Neutral ligands are referred to by the usual name for the molecule

- ▲ Example

- \* ethylenediamine

- ▲ Exceptions

- \* water, H<sub>2</sub>O = aqua

- \* ammonia, NH<sub>3</sub> = ammine

- \* carbon monoxide, CO = carbonyl

### Nomenclature: IUPAC Rules

- ◆ Greek prefixes are used to indicate the number of each type of ligand when more than one is present in the complex

- ▲ di-, 2; tri-, 3; tetra-, 4; penta-, 5; hexa-, 6

- ◆ If the ligand name already contains a Greek prefix, use alternate prefixes:

- ▲ bis-, 2; tris-, 3; tetrakis-, 4; pentakis-, 5; hexakis-, 6

- ▲ The name of the ligand is placed in parentheses

### Nomenclature: IUPAC Rules

- ◆ If a complex is an anion, its name ends with the -ate

- ▲ appended to name of the metal

### Nomenclature: IUPAC Rules

Transition Metal	Name if in Cationic Complex	Name if in Anionic Complex
Sc	Scandium	Scandate
Ti	titanium	titanate
V	vanadium	vanadate
Cr	chromium	chromate
Mn	manganese	manganate
Fe	iron	ferrate
Co	cobalt	cobaltate
Ni	nickel	nickelate
Cu	Copper	cuprate
Zn	Zinc	zincate

## Isomerism

- ◆ Isomers
  - ▲ compounds that have the same composition but a different arrangement of atoms
- ◆ Major Types
  - ▲ structural isomers
  - ▲ stereoisomers

## Structural Isomers

- ◆ Structural Isomers
  - ▲ isomers that have different bonds

## Structural Isomers

- ◆ Coordination-sphere isomers
  - ▲ differ in a ligand bonded to the metal in the complex, as opposed to being outside the coordination-sphere

## Coordination-Sphere Isomers

- ◆ Example  
[Co(NH<sub>3</sub>)<sub>5</sub>Cl]Br vs. [Co(NH<sub>3</sub>)<sub>5</sub>Br]Cl

## Coordination-Sphere Isomers

- ◆ Example  
[Co(NH<sub>3</sub>)<sub>5</sub>Cl]Br vs. [Co(NH<sub>3</sub>)<sub>5</sub>Br]Cl
- ◆ Consider ionization in water  
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br} \rightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]^+ + \text{Br}^-$   
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl} \rightarrow [\text{Co}(\text{NH}_3)_5\text{Br}]^+ + \text{Cl}^-$

## Coordination-Sphere Isomers

- ◆ Example  
[Co(NH<sub>3</sub>)<sub>5</sub>Cl]Br vs. [Co(NH<sub>3</sub>)<sub>5</sub>Br]Cl
- ◆ Consider precipitation  
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{NO}_3(\text{aq}) + \text{AgBr}(\text{s})$   
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow [\text{Co}(\text{NH}_3)_5\text{Br}]\text{NO}_3(\text{aq}) + \text{AgCl}(\text{aq})$

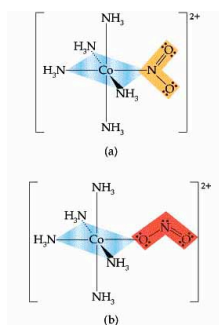
### Structural Isomers

- ◆ Linkage isomers
  - ▲ differ in the atom of a ligand bonded to the metal in the complex

### Linkage Isomers

- ◆ Example
  - ▲  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  vs.  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$

### Linkage Isomers



### Linkage Isomers

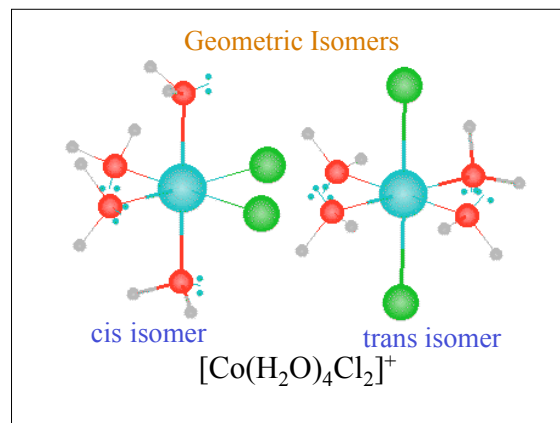
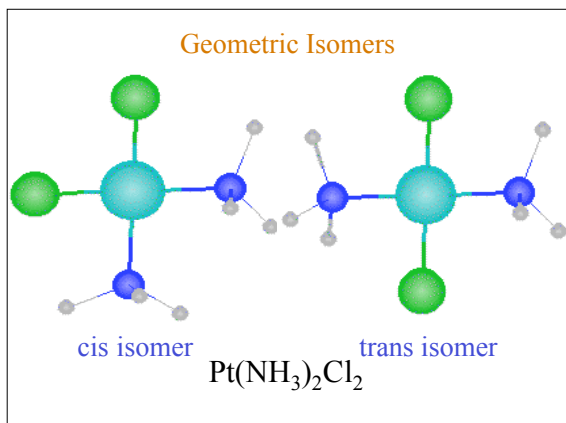
- ◆ Example
  - ▲  $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$  vs.  $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$
  - \* Co-SCN vs. Co-NCS

### Stereoisomers

- ◆ Stereoisomers
  - ▲ Isomers that have the same bonds, but different spatial arrangements

### Stereoisomers

- ◆ Geometric isomers
  - ▲ Differ in the spatial arrangements of the ligands

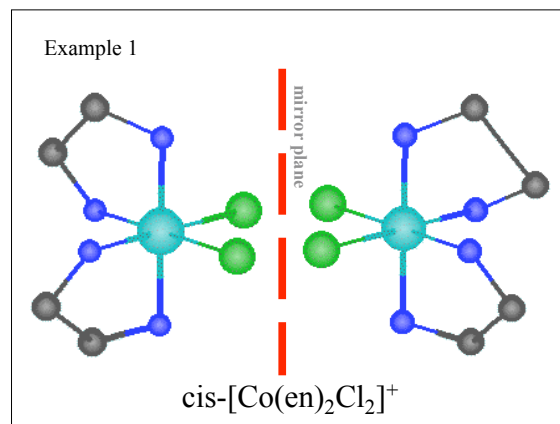
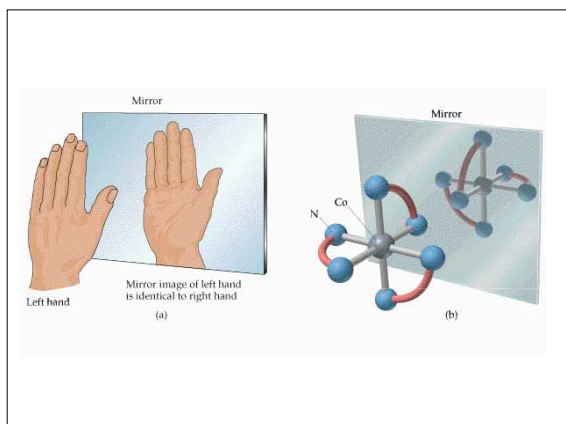


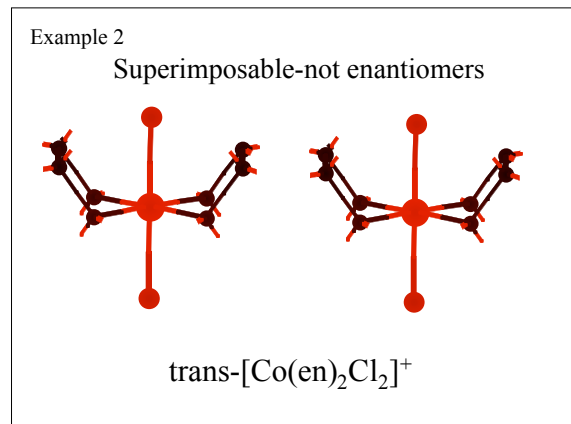
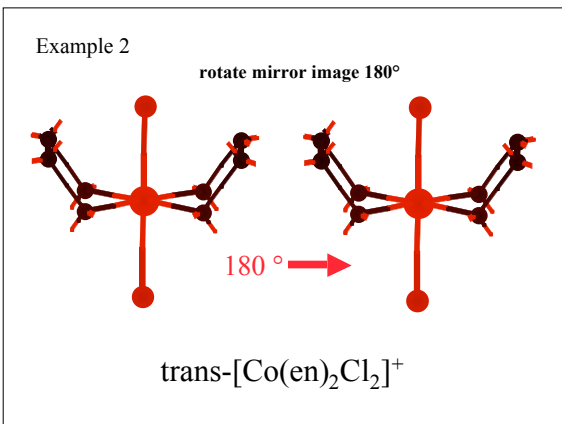
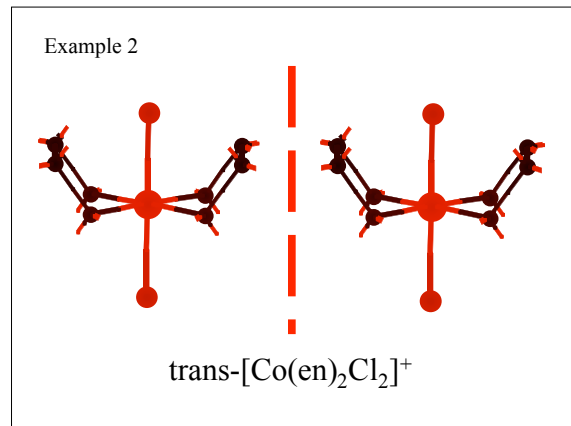
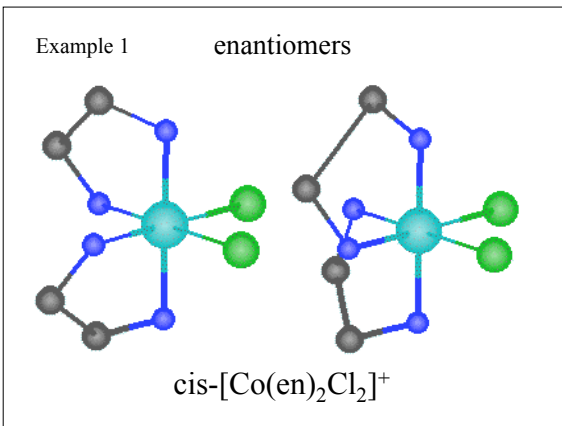
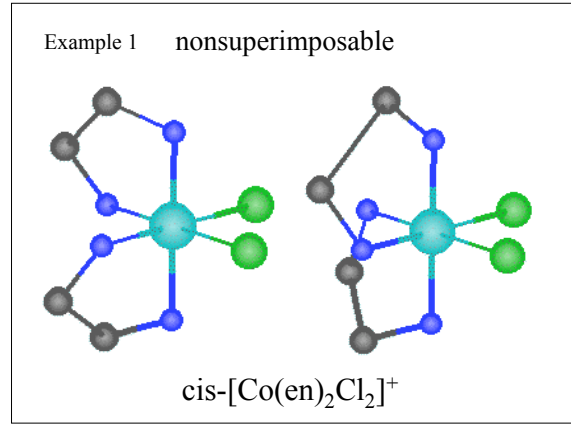
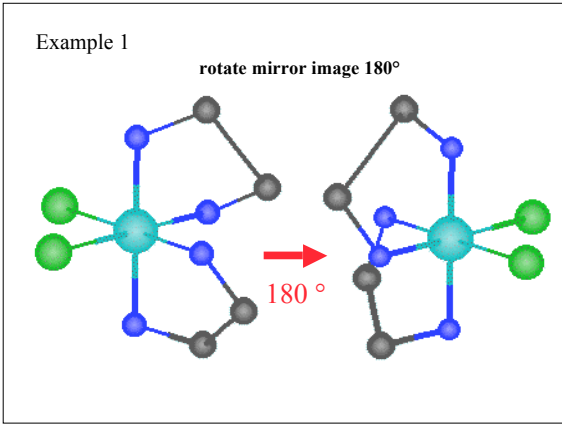
**Stereoisomers**

- ◆ Geometric isomers
  - ▲ Differ in the spatial arrangements of the ligands
  - ▲ Have different chemical/physical properties
    - \* different colors, melting points, polarities, solubilities, reactivities, etc.

**Stereoisomers**

- ◆ Optical isomers
  - ▲ isomers that are nonsuperimposable mirror images
    - \* said to be “chiral” (handed)
    - \* referred to as enantiomers
  - ▲ A substance is “chiral” if it does not have a “plane of symmetry”



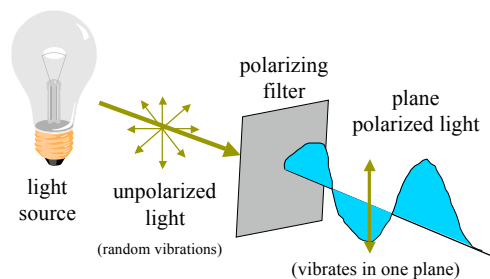


## Properties of Optical Isomers

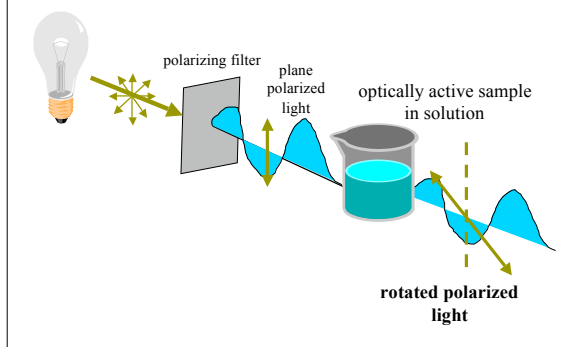
### ◆ Enantiomers

- ▲ possess many identical properties
  - \* solubility, melting point, boiling point, color, chemical reactivity (with nonchiral reagents)
- ▲ different in:
  - \* interactions with plane polarized light

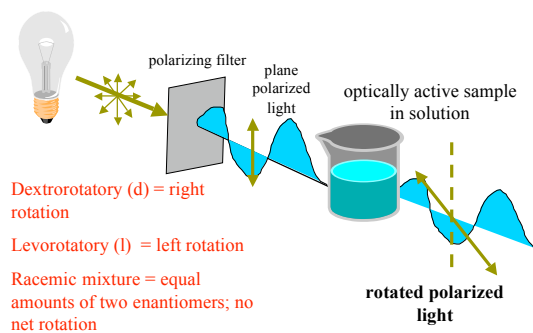
## Optical Isomers



## Optical Isomers



## Optical Isomers



## Properties of Optical Isomers

### ◆ Enantiomers

- ▲ possess many identical properties
    - \* solubility, melting point, boiling point, color, chemical reactivity (with nonchiral reagents)
  - ▲ different in:
    - \* interactions with plane polarized light
    - \* reactivity with "chiral" reagents
- Example
- $$d\text{-C}_4\text{H}_4\text{O}_6^{2-}(\text{aq}) + d, l\text{-}[\text{Co}(\text{en})_3]\text{Cl}_3(\text{aq}) \rightarrow d\text{-}[\text{Co}(\text{en})_3](d\text{-C}_4\text{H}_4\text{O}_6^{2-})\text{Cl}(\text{s}) + l\text{-}[\text{Co}(\text{en})_3]\text{Cl}_3(\text{aq}) + 2\text{Cl}^-(\text{aq})$$

## Properties of Transition Metal Complexes

### ◆ Properties of transition metal complexes:

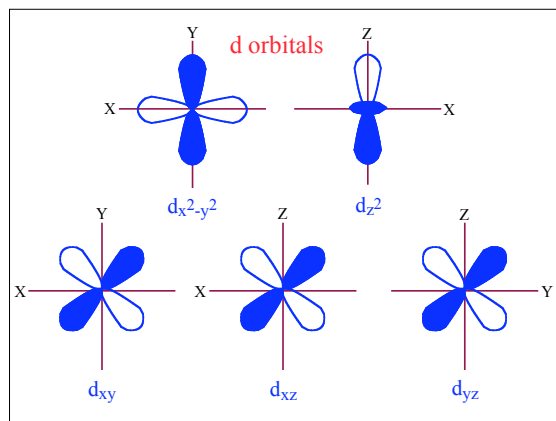
- ▲ usually have color
  - \* dependent upon ligand(s) and metal ion
- ▲ many are paramagnetic
  - \* due to unpaired d electrons
  - \* degree of paramagnetism dependent on ligand(s)
    - $[\text{Fe}(\text{CN})_6]^{3-}$  has 1 unpaired d electron
    - $[\text{FeF}_6]^{3-}$  has 5 unpaired d electrons



## Crystal Field Theory

### ◆ Crystal Field Theory

- ▲ Model for bonding in transition metal complexes
  - \* Accounts for observed properties of transition metal complexes
- ▲ Focuses on d-orbitals
- ▲ Ligands = point negative charges
- ▲ Assumes ionic bonding
  - \* electrostatic interactions



## Crystal Field Theory

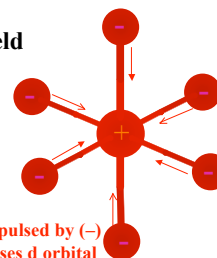
### ◆ Electrostatic Interactions

- ▲ (+) metal ion attracted to (-) ligands (anion or dipole)
  - \* provides stability
- ▲ lone pair  $e^-$ 's on ligands repulsed by  $e^-$ 's in metal d orbitals
  - \* interaction called crystal field
  - \* influences d orbital energies
    - not all d orbitals influenced the same way

## Crystal Field Theory

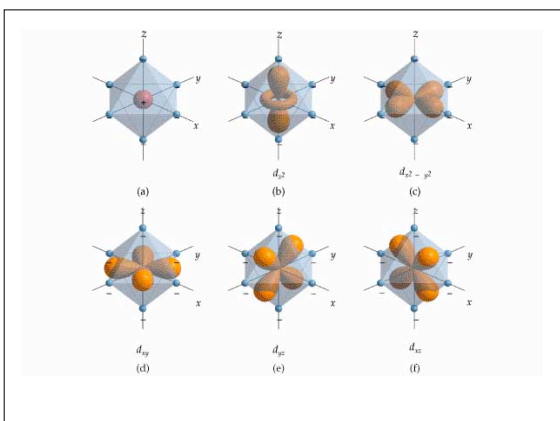
### Octahedral Crystal Field

(-) Ligands attracted to (+) metal ion; provides stability

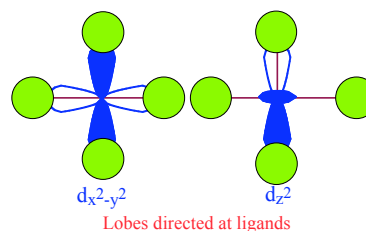


d orbital  $e^-$ 's repulsed by (-) ligands; increases d orbital potential energy

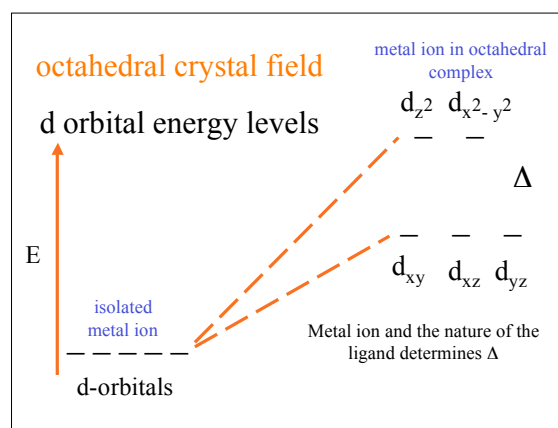
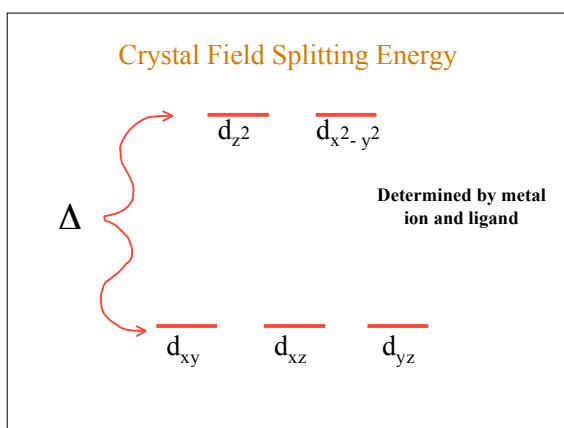
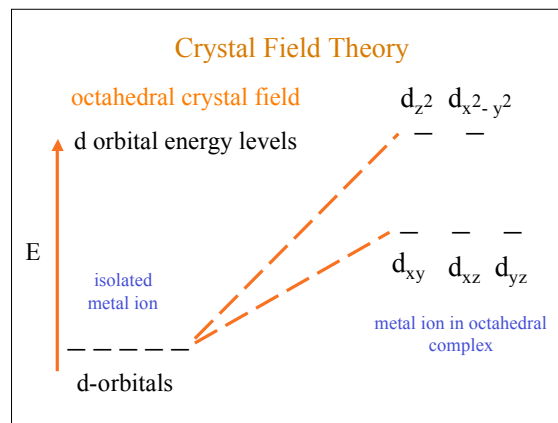
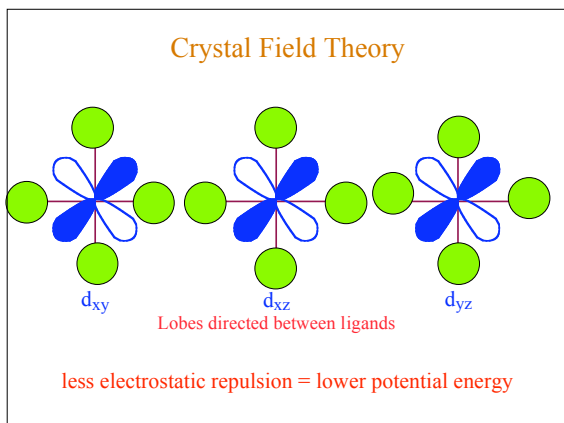
ligands approach along x, y, z axes



## Crystal Field Theory



greater electrostatic repulsion = higher potential energy



- ### Properties of Transition Metal Complexes
- ◆ Properties of transition metal complexes:
    - ▲ usually have color
      - \* dependent upon ligand(s) and metal ion
    - ▲ many are paramagnetic
      - \* due to unpaired d electrons
      - \* degree of paramagnetism dependent on ligand(s)
        - $[\text{Fe}(\text{CN})_6]^{3-}$  has 1 unpaired d electron
        - $[\text{FeF}_6]^{3-}$  has 5 unpaired d electrons

- ### Crystal Field Theory
- ◆ Crystal Field Theory
    - ▲ Can be used to account for
      - \* Colors of transition metal complexes
        - A complex must have partially filled d subshell on metal to exhibit color
        - A complex with 0 or 10 d e's is colorless
      - \* Magnetic properties of transition metal complexes
        - Many are paramagnetic
        - # of unpaired electrons depends on the ligand

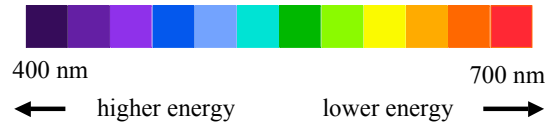
### Colors of Transition Metal Complexes

- ◆ Compounds/complexes that have color:
  - ▲ absorb specific wavelengths of visible light (400 –700 nm)
  - \* wavelengths not absorbed are transmitted

### Visible Spectrum

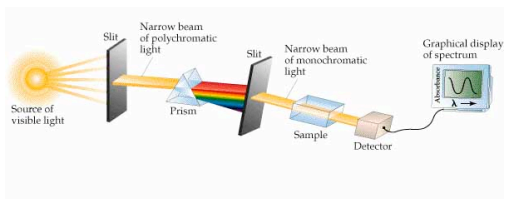
wavelength, nm

(Each wavelength corresponds to a different color)



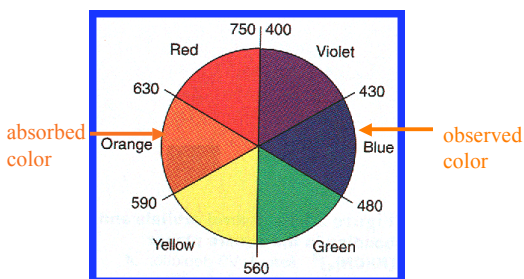
White = all the colors (wavelengths)

### Visible Spectrum



### Colors of Transition Metal Complexes

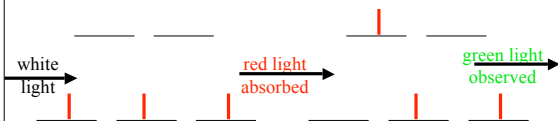
- ◆ Compounds/complexes that have color:
  - ▲ absorb specific wavelengths of visible light (400 –700 nm)
  - \* wavelengths not absorbed are transmitted
  - \* color observed = complementary color of color absorbed



### Colors of Transition Metal Complexes

- ◆ Absorption of UV-visible radiation by atom, ion, or molecule:
  - ▲ Occurs only if radiation has the energy needed to raise an  $e^-$  from its ground state to an excited state
    - \* i.e., from lower to higher energy orbital
    - \* light energy absorbed = energy difference between the ground state and excited state
    - \* “electron jumping”

### Colors of Transition Metal Complexes



For transition metal complexes,  $\Delta$  corresponds to energies of visible light.

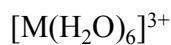
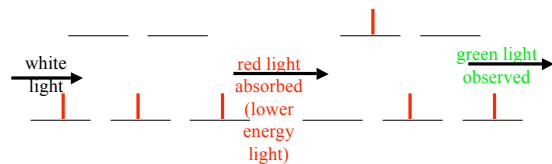
Absorption raises an electron from the lower d subshell to the higher d subshell.

### Colors of Transition Metal Complexes

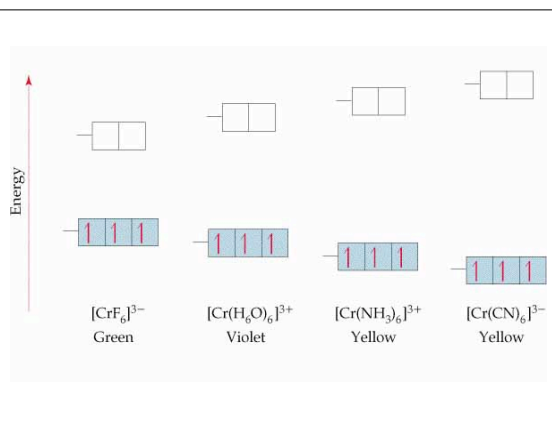
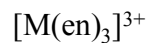
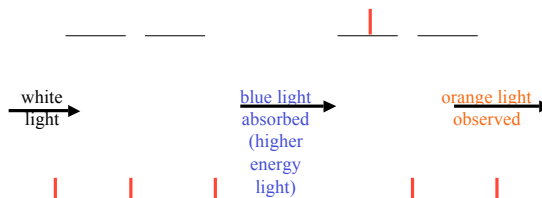
◆ Different complexes exhibit different colors because:

- ▲ color of light absorbed depends on  $\Delta$ 
  - \* larger  $\Delta$  = higher energy light absorbed
    - Shorter wavelengths
  - \* smaller  $\Delta$  = lower energy light absorbed
    - Longer wavelengths
- ▲ magnitude of  $\Delta$  depends on:
  - \* ligand(s)
  - \* metal

### Colors of Transition Metal Complexes



### Colors of Transition Metal Complexes



### Colors of Transition Metal Complexes

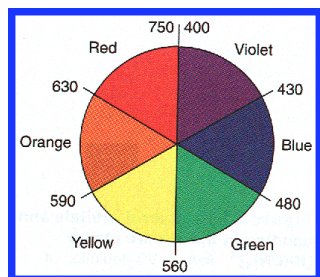
#### Spectrochemical Series

Smallest  $\Delta$   $\xrightarrow{\Delta \text{ increases}}$  Largest  $\Delta$



weak field

strong field



### Properties of Transition Metal Complexes

#### ◆ Properties of transition metal complexes:

- ▲ usually have color
  - \* dependent upon ligand(s) and metal ion
- ▲ many are paramagnetic
  - \* due to unpaired d electrons
  - \* degree of paramagnetism dependent on ligand(s)
    - $[\text{Fe}(\text{CN})_6]^{3-}$  has 1 unpaired d electron
    - $[\text{FeF}_6]^{3-}$  has 5 unpaired d electrons

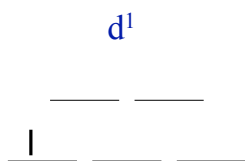
### Electronic Configurations of Transition Metal Complexes

- ◆ Expected orbital filling tendencies for  $e^-$ 's:
  - ▲ occupy a set of equal energy orbitals one at a time with spins parallel (Hund's rule)
    - \* minimizes repulsions
  - ▲ occupy lowest energy vacant orbitals first
- ◆ These are not always followed by transition metal complexes.

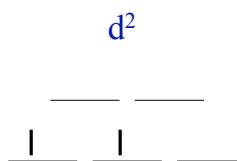
### Electronic Configurations of Transition Metal Complexes

- ◆ d orbital occupancy depends on  $\Delta$  and pairing energy, P
  - ▲  $e^-$ 's assume the electron configuration with the lowest possible energy cost
  - ▲ If  $\Delta > P$  ( $\Delta$  large; strong field ligand)
    - \*  $e^-$ 's pair up in lower energy d subshell first
  - ▲ If  $\Delta < P$  ( $\Delta$  small; weak field ligand)
    - \*  $e^-$ 's spread out among all d orbitals before any pair up

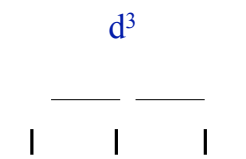
### d-orbital energy level diagrams octahedral complex



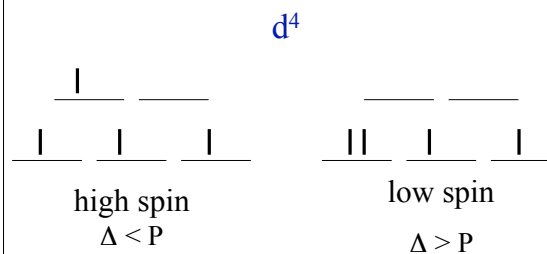
### d-orbital energy level diagrams octahedral complex



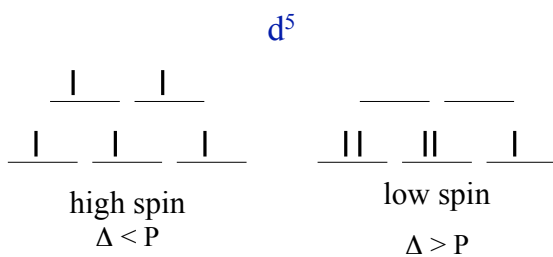
d-orbital energy level diagrams  
octahedral complex



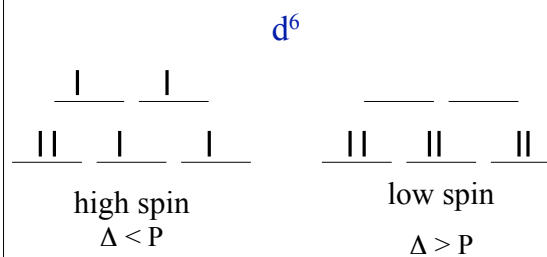
d-orbital energy level diagrams  
octahedral complex



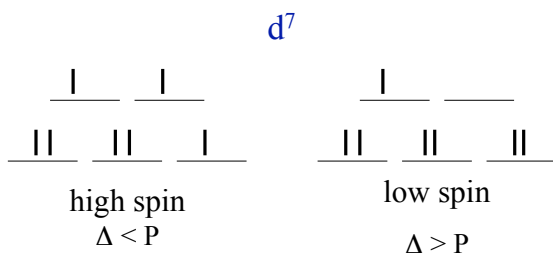
d-orbital energy level diagrams  
octahedral complex



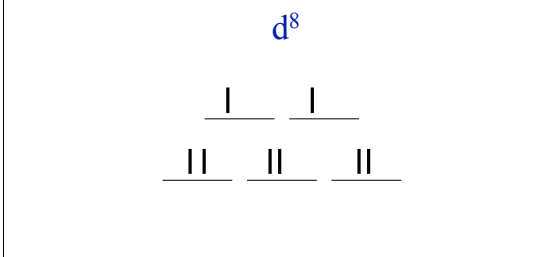
d-orbital energy level diagrams  
octahedral complex



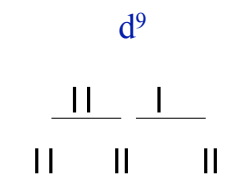
d-orbital energy level diagrams  
octahedral complex



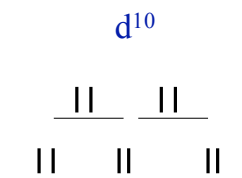
d-orbital energy level diagrams  
octahedral complex



d-orbital energy level diagrams  
octahedral complex



d-orbital energy level diagrams  
octahedral complex



Electronic Configurations of Transition Metal  
Complexes

◆ Determining d-orbital energy level diagrams:

- ▲ determine oxidation # of the metal
- ▲ determine # of d e<sup>-</sup>s
- ▲ determine if ligand is weak field or strong field
- ▲ draw energy level diagram

Colors of Transition Metal Complexes

Spectrochemical Series

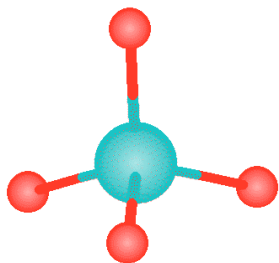
Smallest  $\Delta$  →  $\Delta$  increases → Largest  $\Delta$

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < CN^-$

weak field

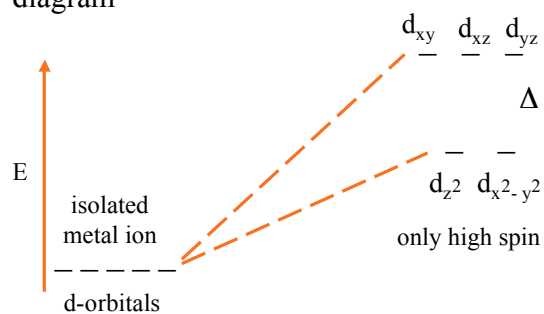
strong field

d-orbital energy level diagrams  
tetrahedral complex

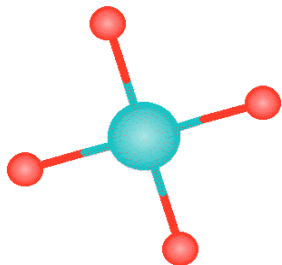


d-orbital energy level  
diagram

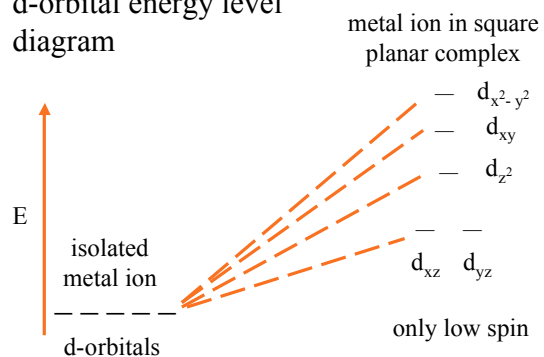
metal ion in  
tetrahedral complex



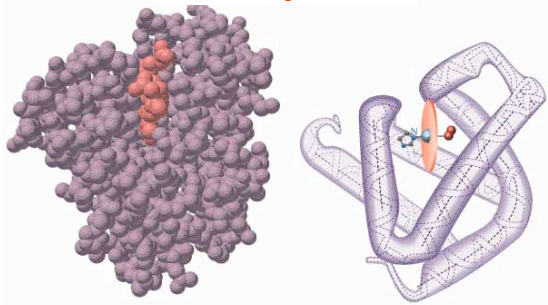
d-orbital energy level diagrams  
square planar complex



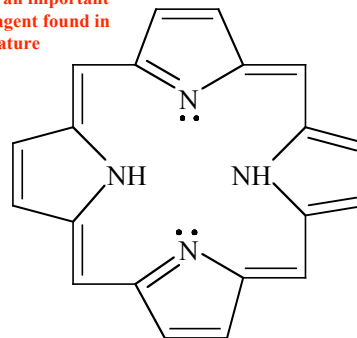
d-orbital energy level  
diagram



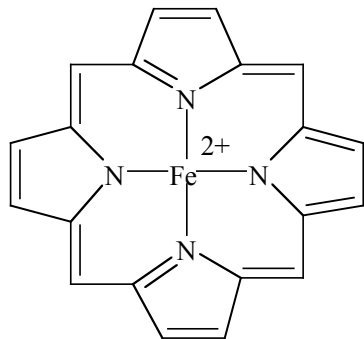
Myoglobin, a protein that stores  $O_2$  in cells



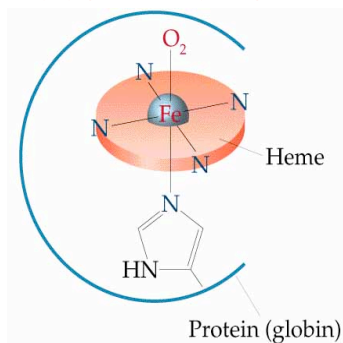
Porphine, an important chelating agent found in nature



Metalloporphyrin

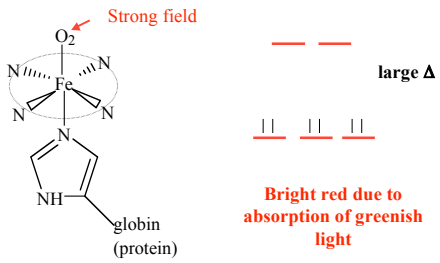


Coordination Environment of  $Fe^{2+}$  in Oxy-myoglobin and Oxyhemoglobin

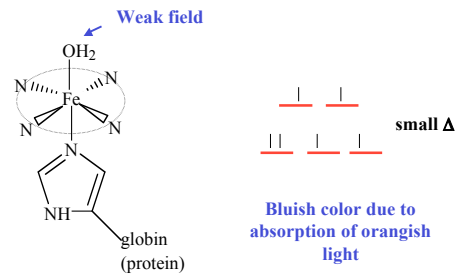




### Arterial Blood



### Venous Blood



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<http://strangematter.sci.waikato.ac.nz/>

End of Presentation