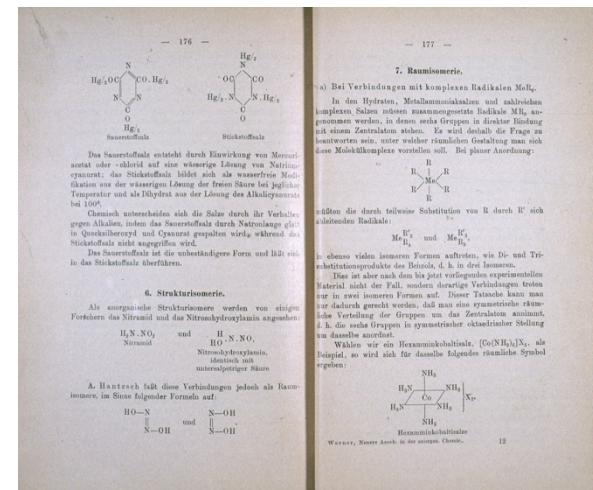
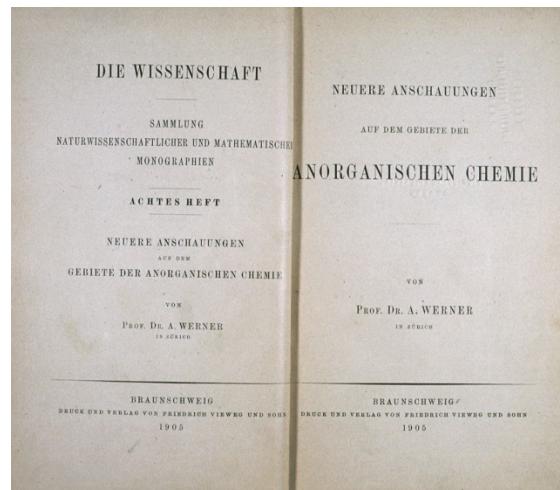


Alfred Werner: Structure of Coordination Complexes

- Rules governing the structure of organic compounds were available by 1880.
- No such understanding was developed for inorganic complexes until 1893 when Alfred Werner put forward his theory.



Alfred Werner
Structure of inorganic compounds
Chemistry Nobel Laureate



Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie. Braunschweig, 1905

Compounds of Transition Metals

- Scientists were perplexed by the nature of compounds made by transition metals.
- The interesting properties exhibited by such compounds such as color and magnetism provided impetus to understand their bonding.
- All precious/semi-precious stones owe their color to transition metals.



Corundum Mineral
 Al_2O_3



Ruby
 $\text{Cr} \rightarrow \text{Al}$



Amethyst
 $\text{Mn} \rightarrow \text{Al}$



Topaz
 $\text{Fe} \rightarrow \text{Al}$



Sapphire
 $\text{Ti} \& \text{Co} \rightarrow \text{Al}$



Beryl mineral,
 $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

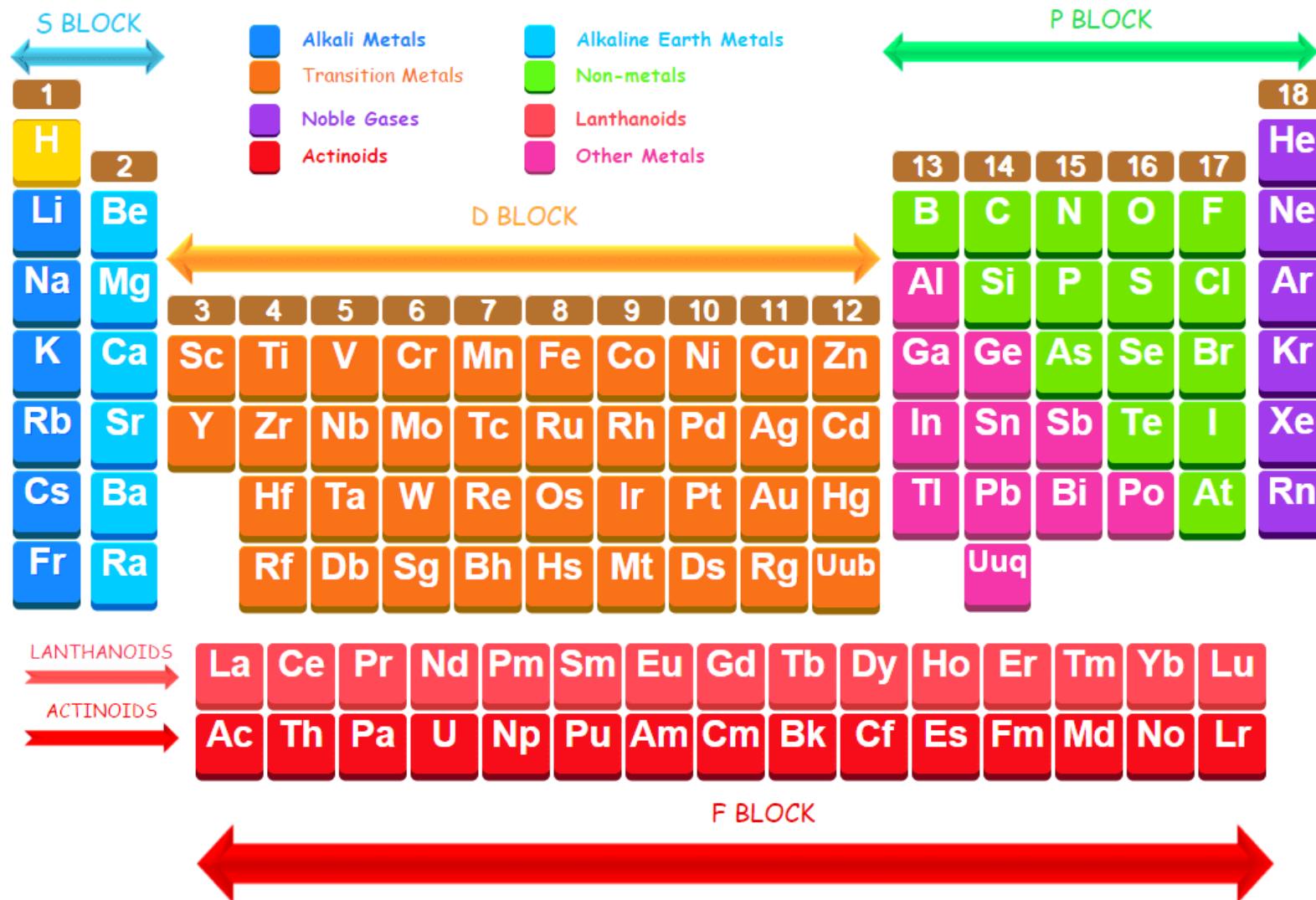


Aquamarine
 $\text{Fe} \rightarrow \text{Al}$



Emerald
 $\text{Cr} \rightarrow \text{Al}$

Coordination Compounds of the Transition Elements

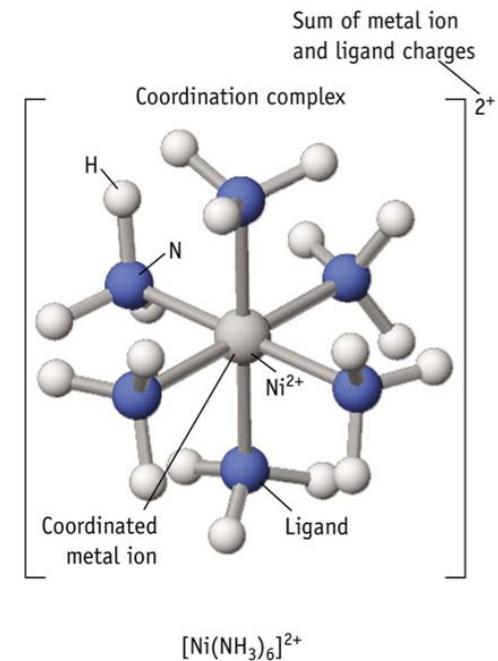
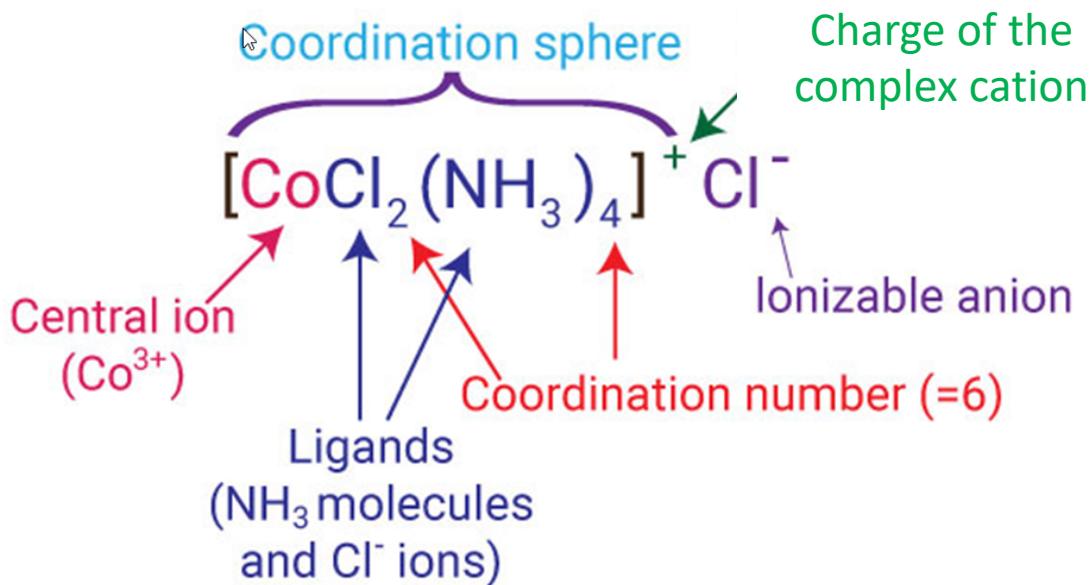


Components of a Coordination Compound

- A coordination compound contains at least one complex ion, which consists of a central metal cation bonded to “ligands”.
- Ligands can be neutral molecules or anions.
- A complex ion is associated with counterions of opposite charge.

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ — $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and two Cl^- ; Co is in +3 oxidation state

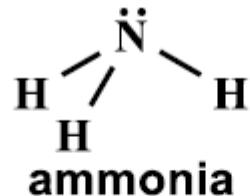
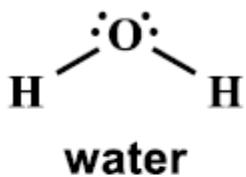
$\text{K}_3[\text{Fe}(\text{CN})_6]$ — $[\text{Fe}(\text{CN})_6]^{3-}$ and three K^+ ; Fe is in +3 oxidation state



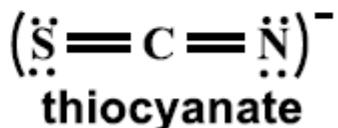
Ligands

- Molecules that bind to metal with donor atoms having lone pair of electrons.
- Types: Monodentate, polydentate, chelating ligands.
- Influence structures, chemical reactivity, and photophysical properties.

- Examples of monodentate ligands



carbon monoxide

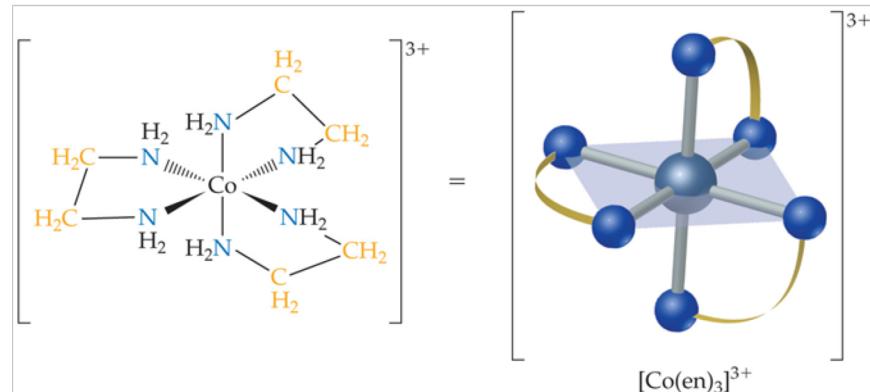
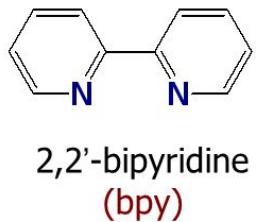
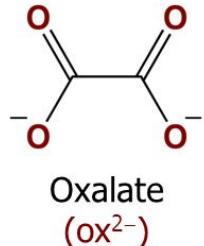
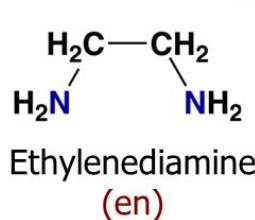


Ligand	Formula	Name
Fluoride ion	:F ⁻	Fluoro
Chloride ion	:Cl ⁻	Chloro
Nitrite ion	:NO ₂ ⁻	Nitro
	:ONO ⁻	Nitrito
Carbonate ion	:OCO ₂ ²⁻	Carbonato
Cyanide ion	:CN ⁻	Cyano
Thiocyanate ion	:SCN ⁻	Thiocyanato
	:NCS ⁻	Isothiocyanato
Hydride ion	:H ⁻	Hydrido
Oxide ion	:O ²⁻	Oxido
Hydroxide ion	:OH ⁻	Hydroxo
Water	:OH ₂	Aqua
Ammonia	:NH ₃	Ammine
Carbon monoxide	:CO	Carbonyl
Nitrogen monoxide	:NO	Nitrosyl

The ligating atom is indicated by a pair of red dots representing a lone pair of electrons. In the CO₃²⁻ ligand, either one or two of the oxygen atoms can donate a lone pair to the metal.

Ligands

□ Examples of bidentate ligands

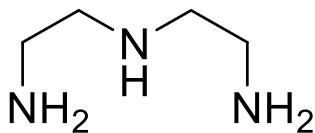
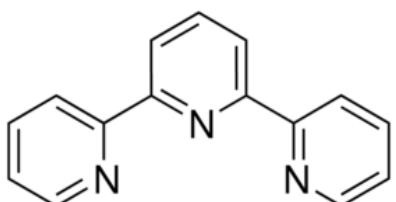


Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

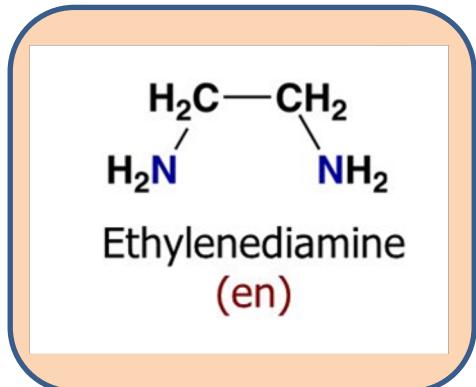
*Bidentate and polydentate ligands are also called **chelating agents**.*

□ Examples of tridentate ligands

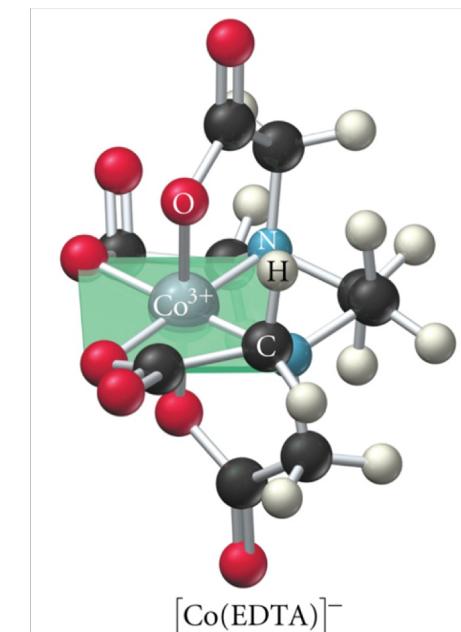
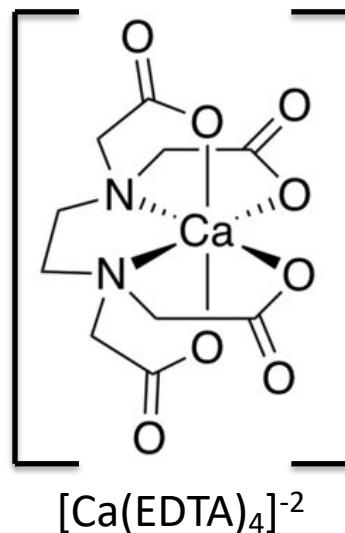
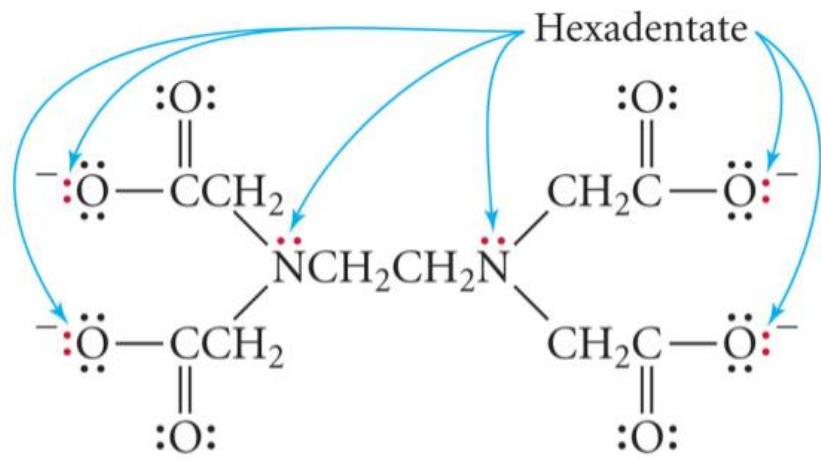
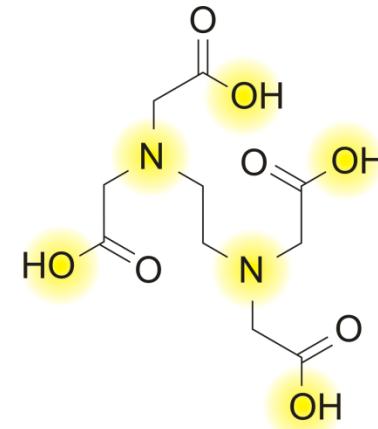


Ligands

- Polydentate ligand: EDTA (Ethylenediaminetetraacetic acid)

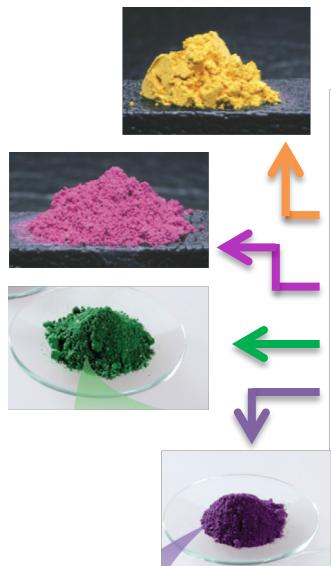


Replace the “H” atoms
on nitrogen by acetic acid



Werner's Theory

- The combination of CoCl_3 and NH_3 resulted in many compounds. Their nature was explained by Alfred Werner in 1893.
- The oxidation number of a metal is +3 in each compound. However, the number of atoms bonded to the metal is different. He called this the coordination number.



Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6 \text{ NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5 \text{ NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4 \text{ NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4 \text{ NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

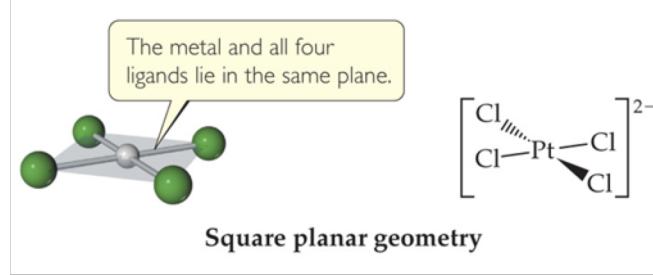
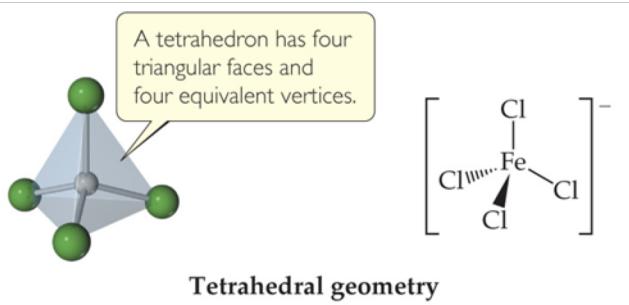
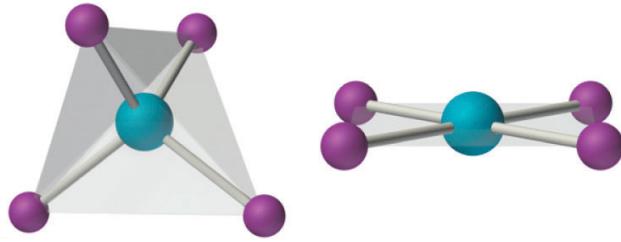
- The key to solving this problem is the number of ions produced in solution per formula unit: along with ONE cation, the rest would tell how many Cl^- ions are NOT connected directly to the metal.
- Precipitation of AgCl confirmed amount of free Cl^- .

Coordination Number and Geometry

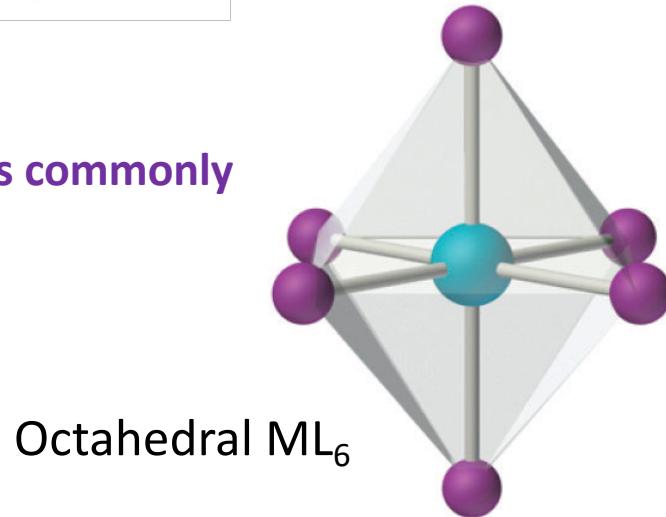
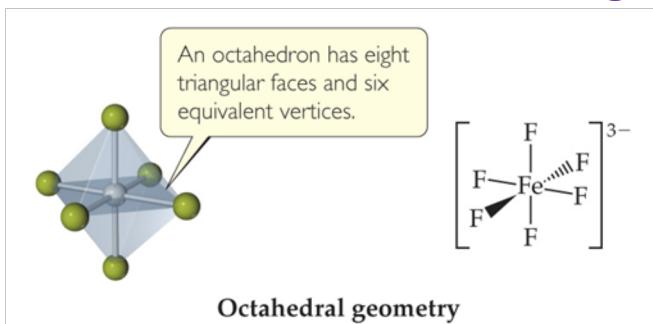
- For coordination number two, a linear geometry is observed



- For coordination number 4, both tetrahedral and square planar geometries are possible



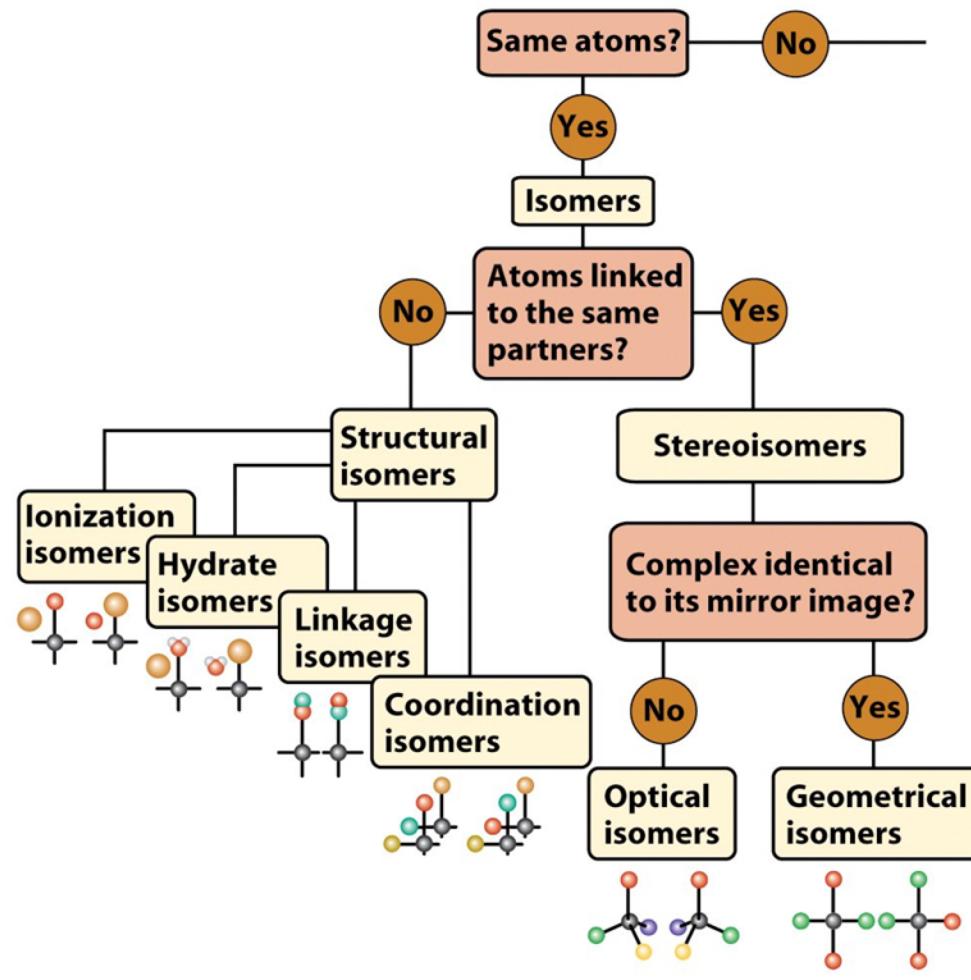
- For coordination number 6, octahedral geometry is commonly observed



Our discussion will focus mainly on coordination numbers 4 and 6

Isomerism

- ❑ Isomers: Same atomic composition, different bonding arrangements



Isomerism

□ Ionization Isomerism

Interchange of an anionic ligand within the coordination sphere with an anion outside the coordination sphere.



□ Coordination Isomerism

Found in compounds in which both cations and anions are complex ions, arise from interchange of ligands from the cationic part to the anionic part.



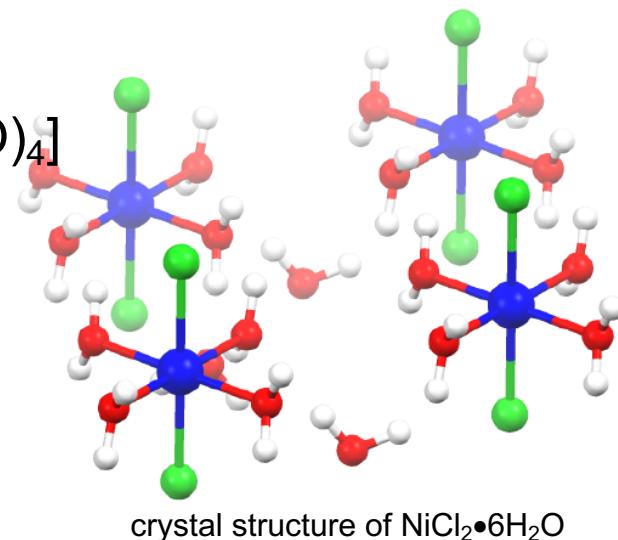
Isomerism

□ Hydrate Isomerism

Isomers differ in whether (or how many) water molecules are present inside or outside the coordination sphere. As an example, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ can be either of the three compounds below:



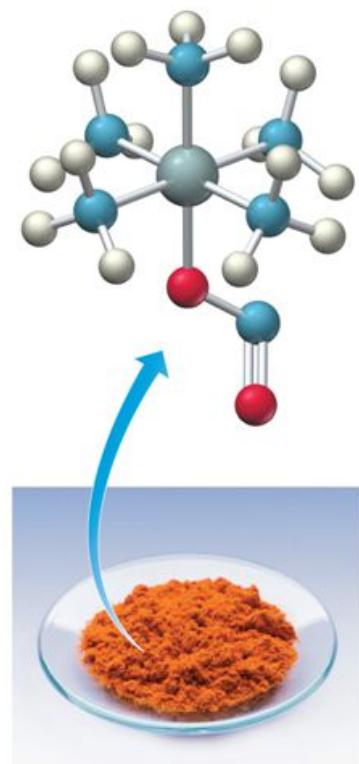
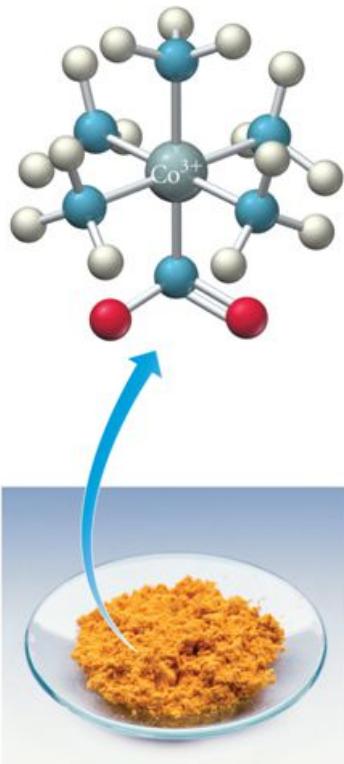
- The dot in the above formulas refers to water molecules that are not bound to the central metal, but are part of the lattice.
- $\text{NiCl}_2 \bullet 6\text{H}_2\text{O}$ consists of separated *trans*- $[\text{NiCl}_2(\text{H}_2\text{O})_4]$ molecules linked more weakly to adjacent water molecules. Only four of the six water molecules in the formula are bound to the nickel (II) cation, and the remaining two are waters of crystallization as the crystal structure resolves.



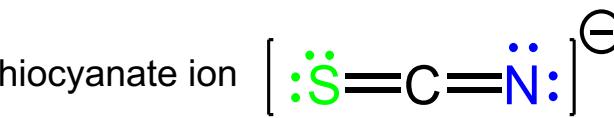
Isomerism

□ Linkage Isomerism

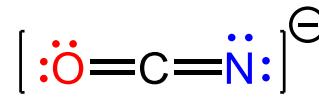
Occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN⁻/NCS⁻ and NO₂⁻/ONO⁻.



Thiocyanate ion

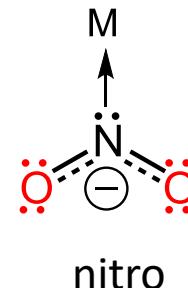


cyanate ion



Thiocyanato NCS:→
Isothiocyanato SCN:→

cyanato NCO:→
isocyanato OCN:→



nitrito

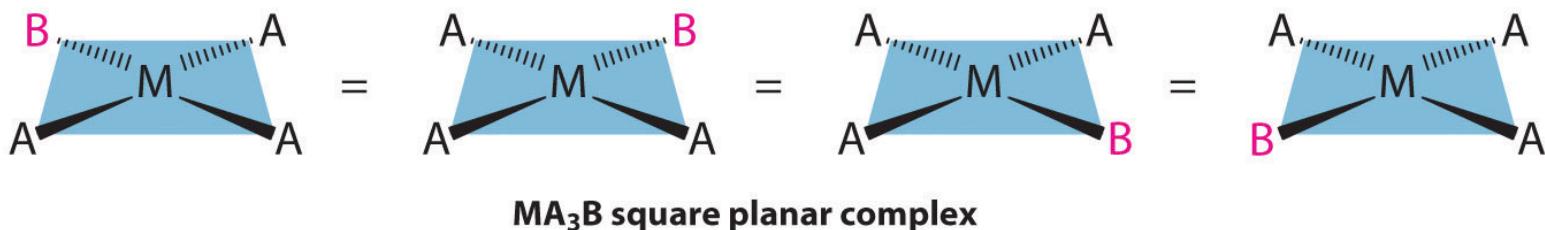
Stereoisomerism

□ Geometric Isomerism

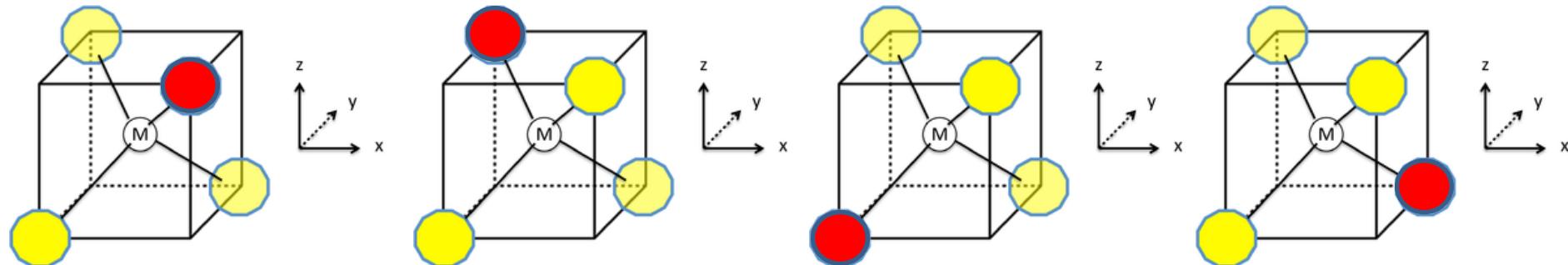
Metal binds to same ligands but with different spatial arrangement.
Interconversion not possible without breaking bonds.

MA₃B Case:

All the below structures are equivalent



□ For a tetrahedral complex, there are no geometric isomers (all 4 structures below are equivalent (same)).



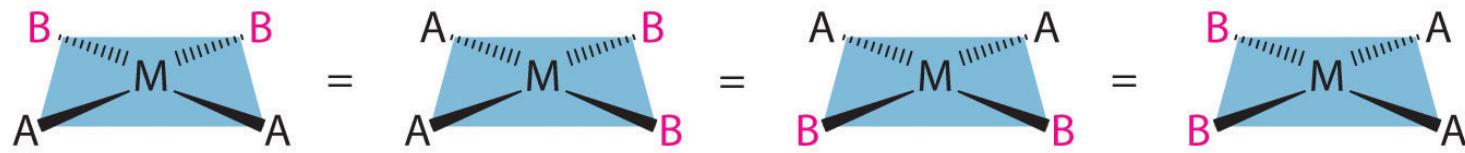
Stereoisomerism

□ Geometric Isomerism

Metal binds to same ligands but with different spacial arrangement.

Interconversion not possible without breaking bonds.

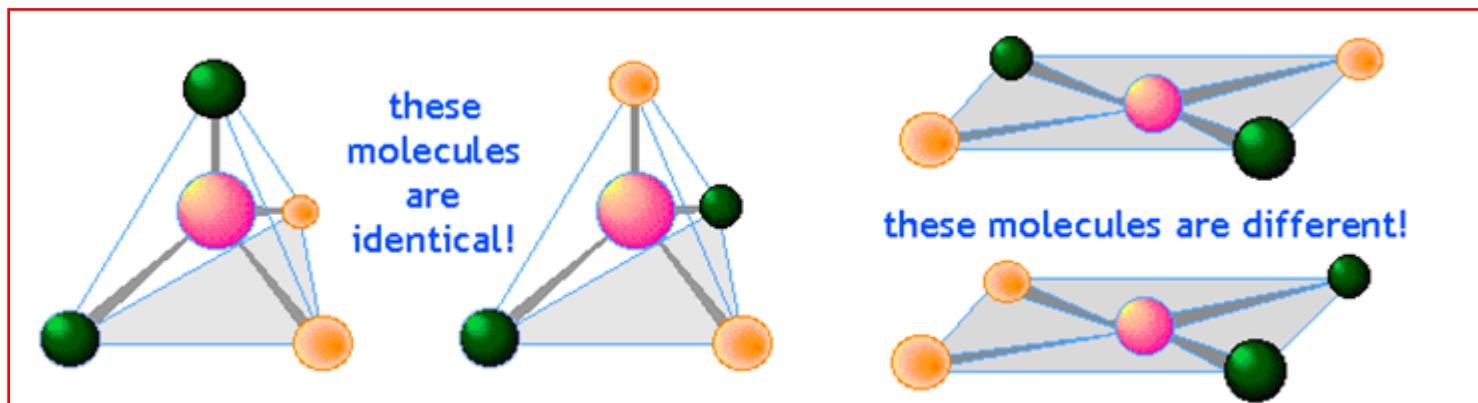
MA₂B₂ Case:



MA_2B_2 square planar complex, *cis* isomer

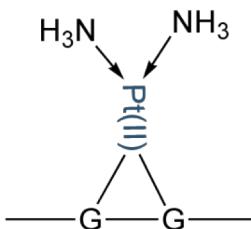
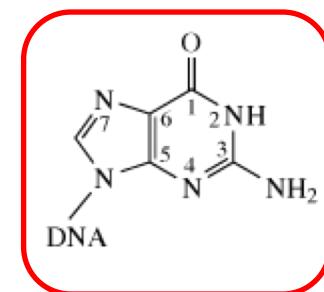
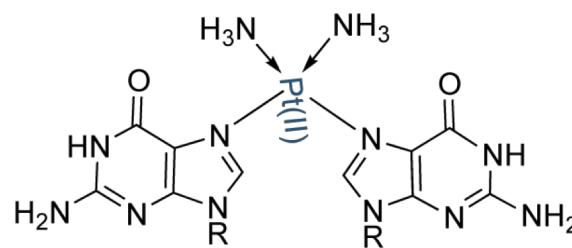
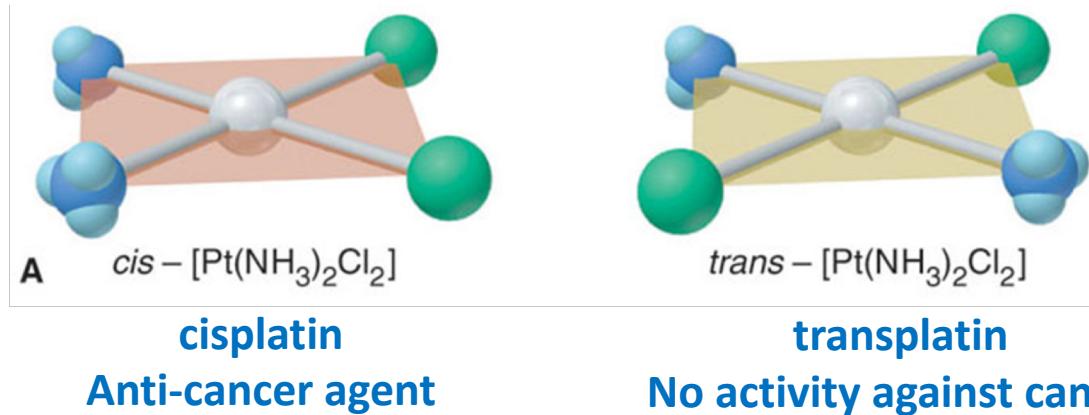


MA_2B_2 square planar complex, *trans* isomer

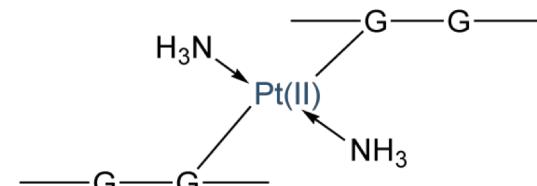


Stereoisomerism

□ Two geometric isomers can behave very differently



cisplatin forms intra-strand crosslinks:
poorly repaired

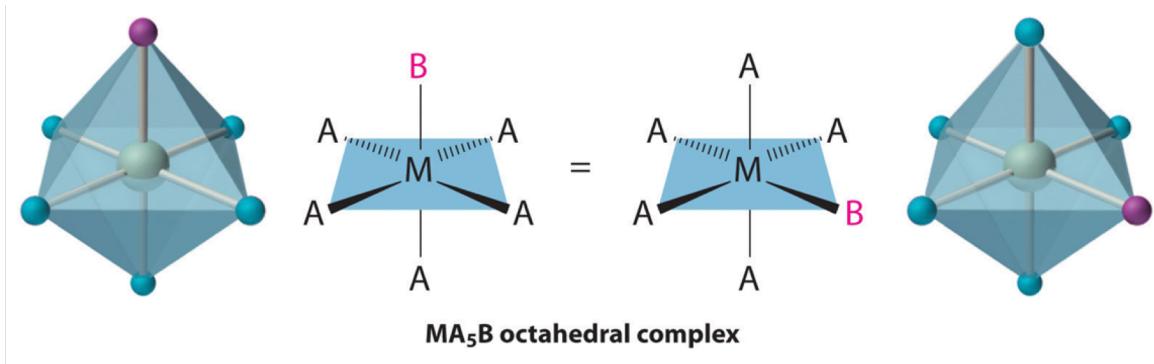


trans-platin forms inter-strand crosslinks:
repaired more efficiently

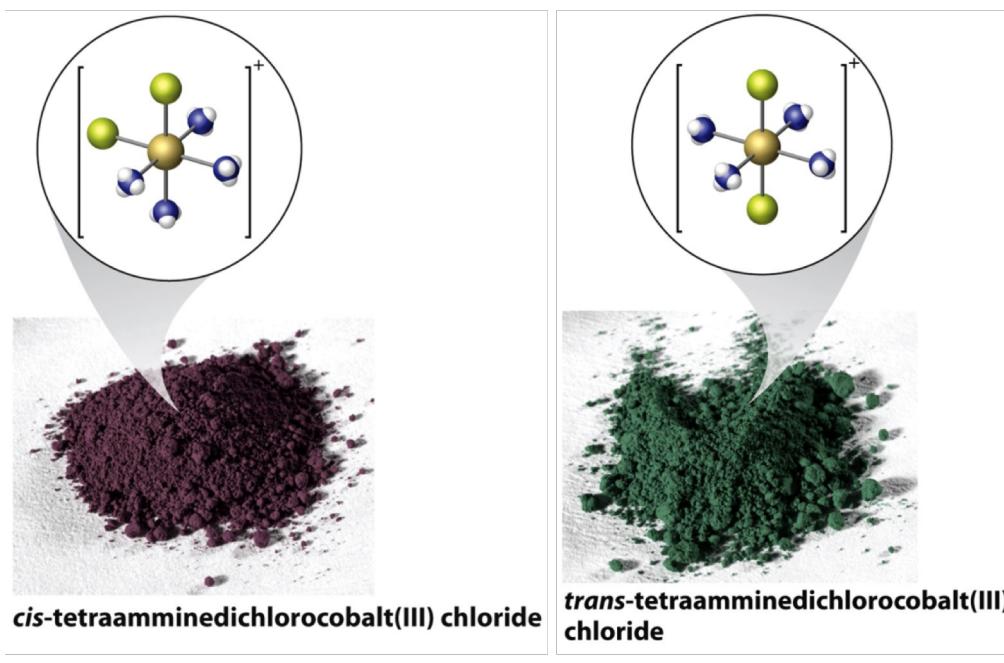
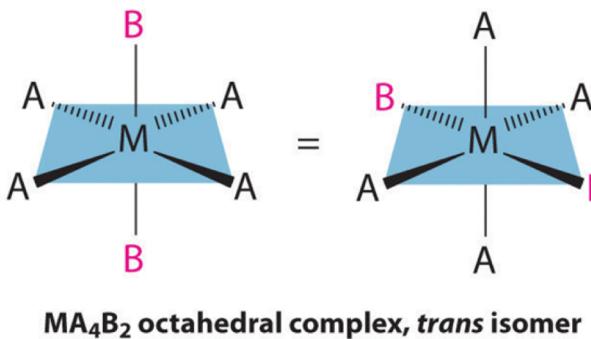
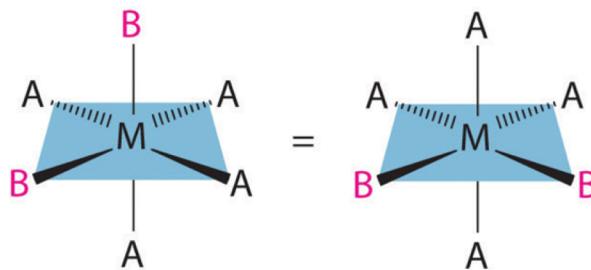
Stereoisomerism

□ Octahedral Complexes

MA₅B Case:



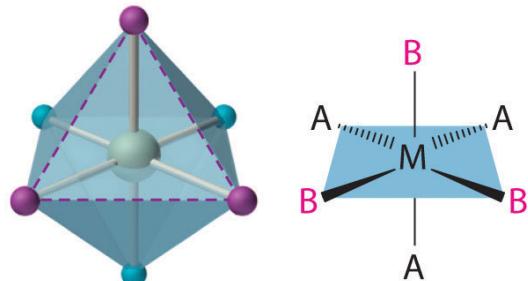
MA₄B₂ Case:



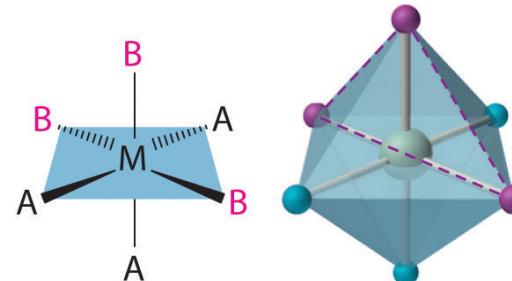
Stereoisomerism

□ Octahedral Complexes

MA₃B₃ Case: facial and meridional isomers

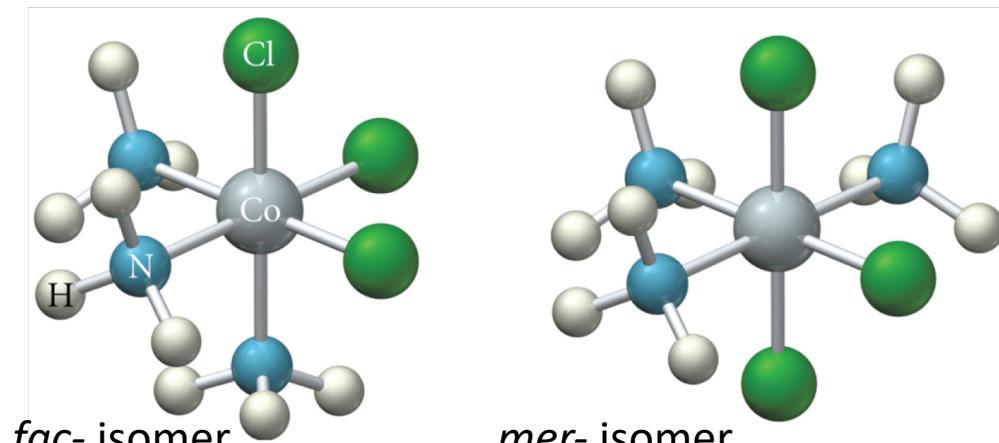


MA₃B₃ octahedral complex, *fac* isomer

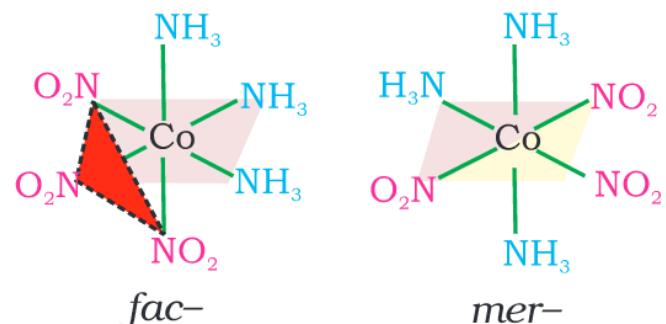


MA₃B₃ octahedral complex, *mer* isomer

- *fac*-isomers have 3 identical ligands on one triangular face
- *mer*-isomers have 3 identical ligands in a plane bisecting the molecule



[Co(NH₃)₃Cl₃]

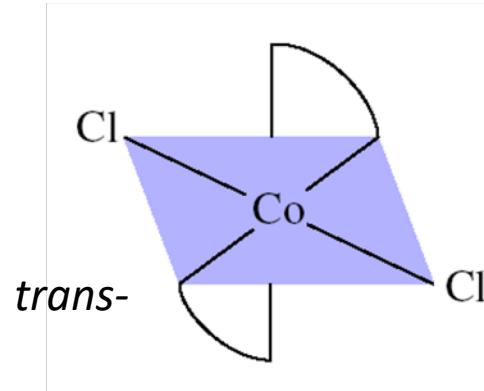
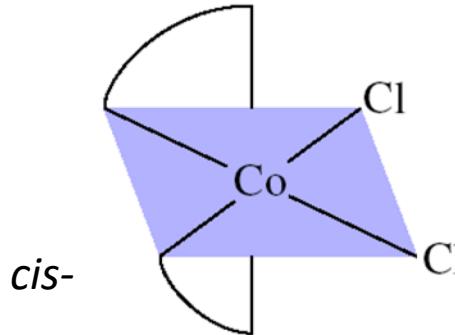


[Co(NH₃)₃(NO₂)₃]

Stereoisomerism

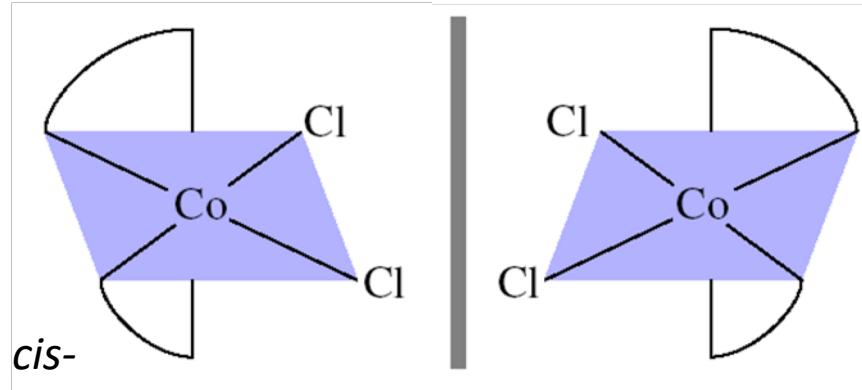
□ Octahedral Complexes

M(A-A)₂B₂ Case: [Co(en)₂Cl₂]⁺ has three stereoisomers

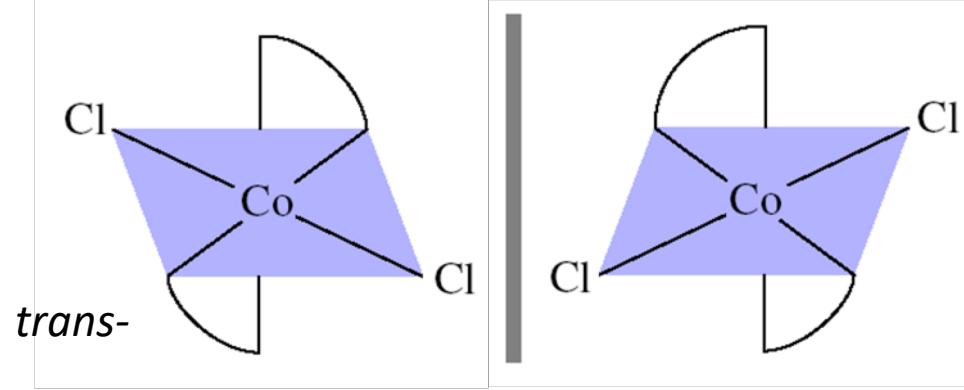


But...this situation is not so simple...

Mirror plane



Mirror plane



Non-superimposable mirror images

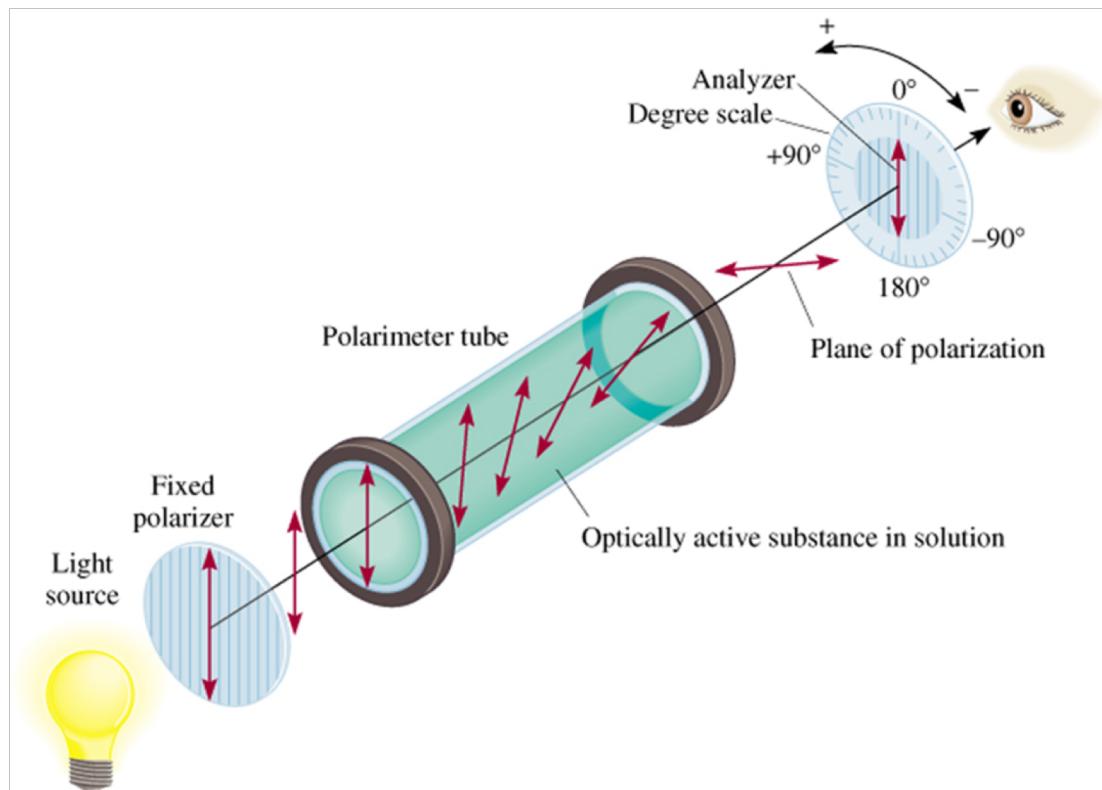
superimposable mirror images

□ The cis- form is an enantiomeric pair.

Stereoisomerism

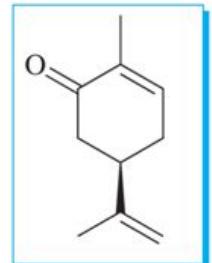
□ Optical Isomerism

- Optical isomers, or enantiomers, are mirror images of one another that don't superimpose on each other.
- They are said to be chiral.
- Their properties differ from each other only when in contact with other chiral substances.

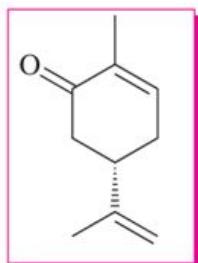


An Interesting Side-Note About Enantiomers

- How can we distinguish the following two enantiomers?



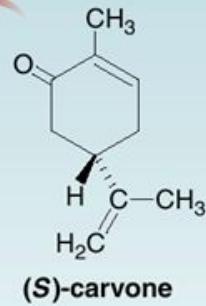
(R)-(-)-Carvone



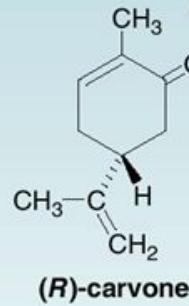
(S)-(+)-Carvone



caraway seeds



(S)-carvone



(R)-carvone

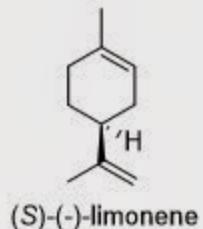


spearmint leaves

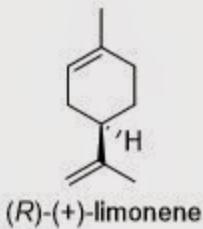
(S)-Carvone has the odor of caraway.

(R)-Carvone has the odor of spearmint.

- There are more such enantiomeric pairs!



(S)-(-)-limonene



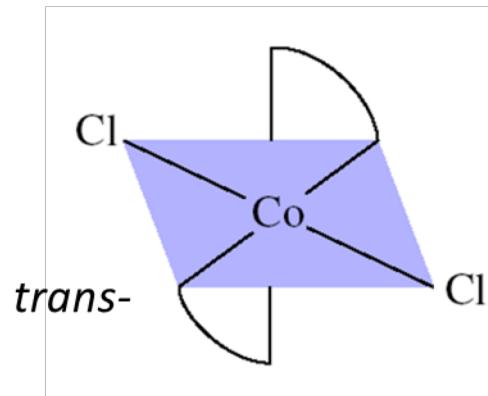
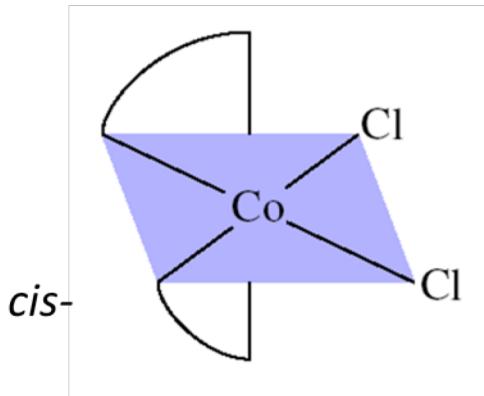
(R)-(+)-limonene



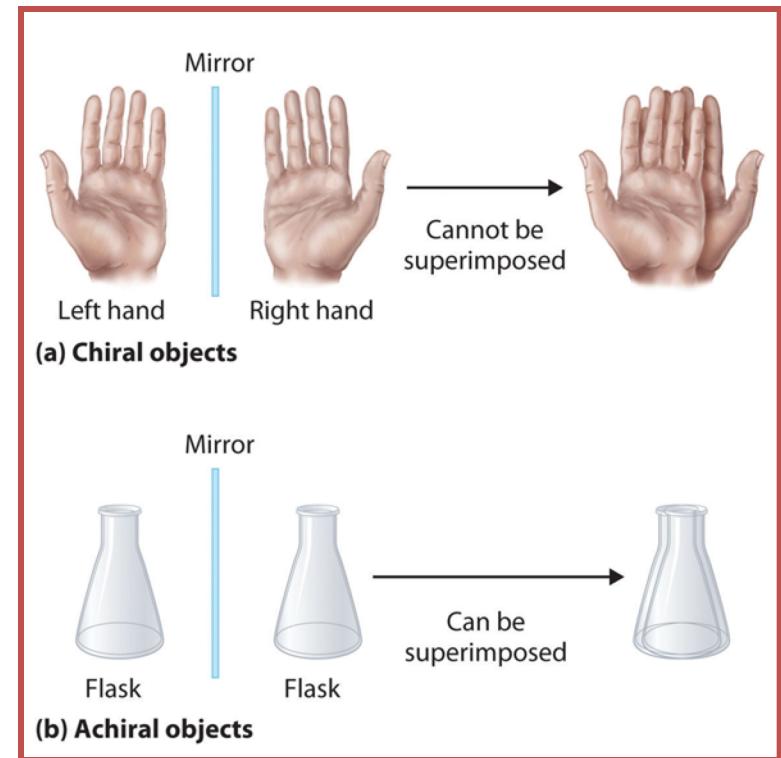
Stereoisomerism

□ Optical Isomerism

- *Do we need to draw mirror images every time we want to think about enantiomers?*
- *Enantiomers do not have a plane of symmetry*
- *Any molecule which possesses a plane of symmetry is superimposable on its mirror image*

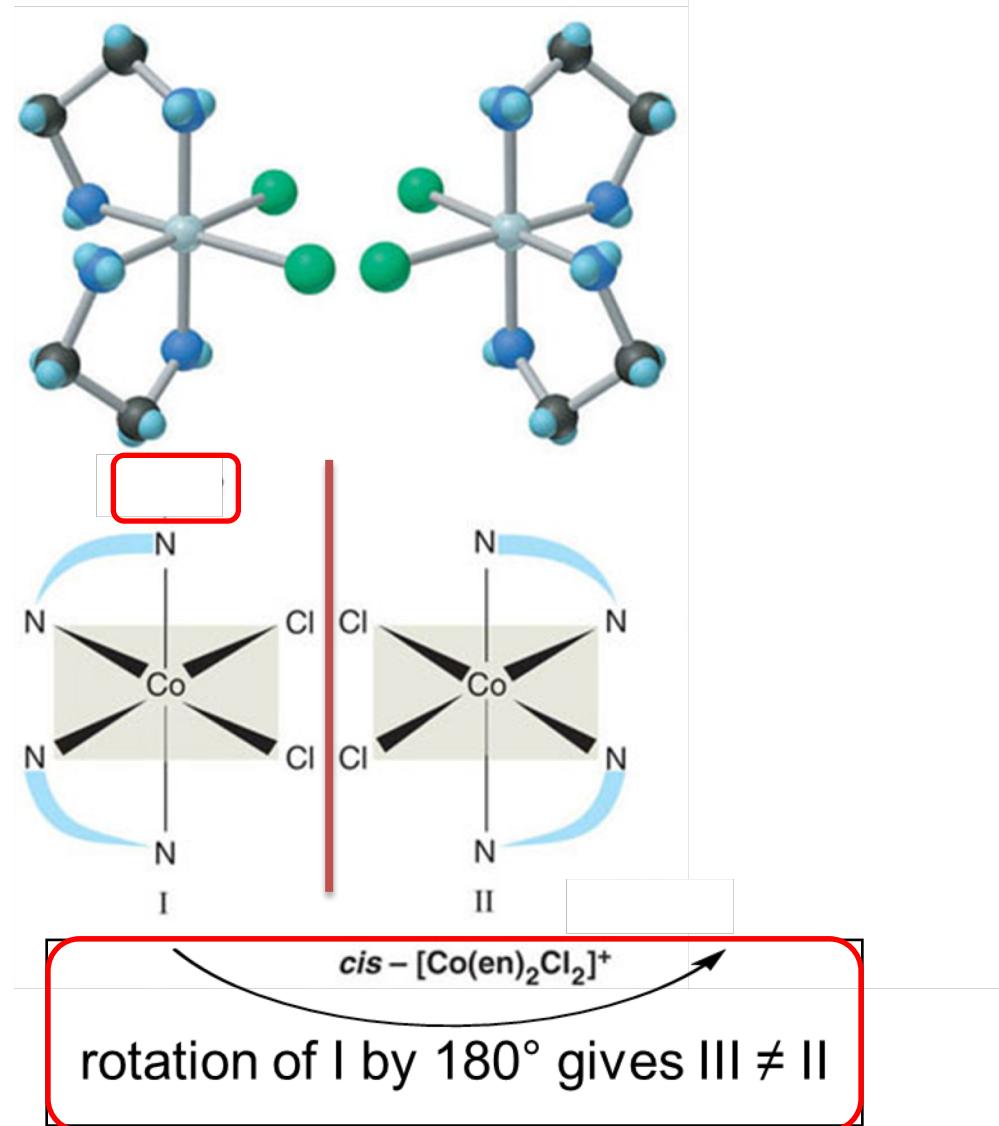
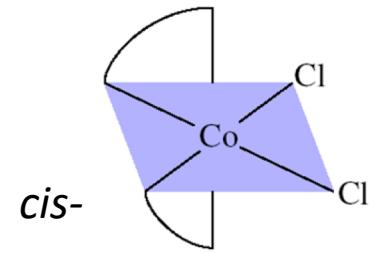


- *The trans- isomer indeed has a plane of symmetry*



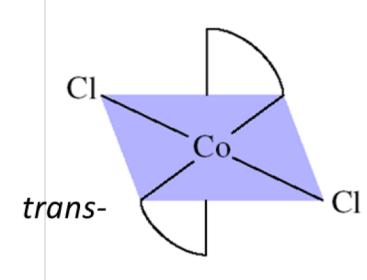
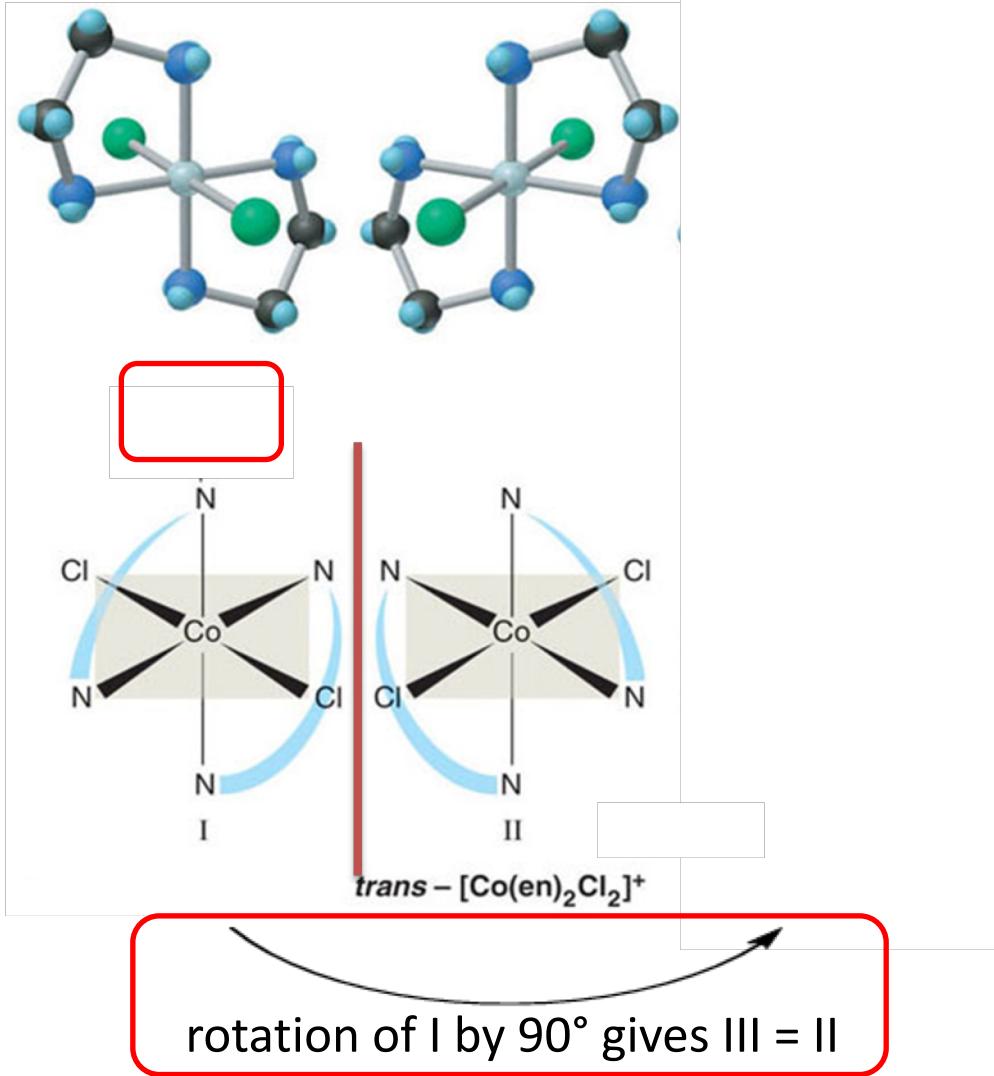
Stereoisomerism

□ Optical Isomerism



Stereoisomerism

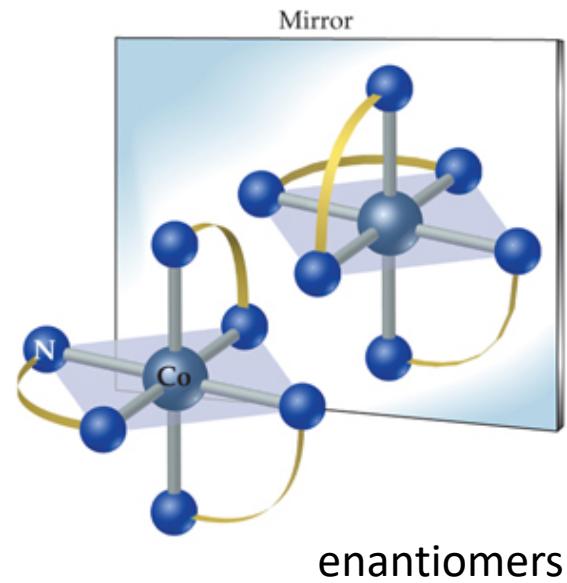
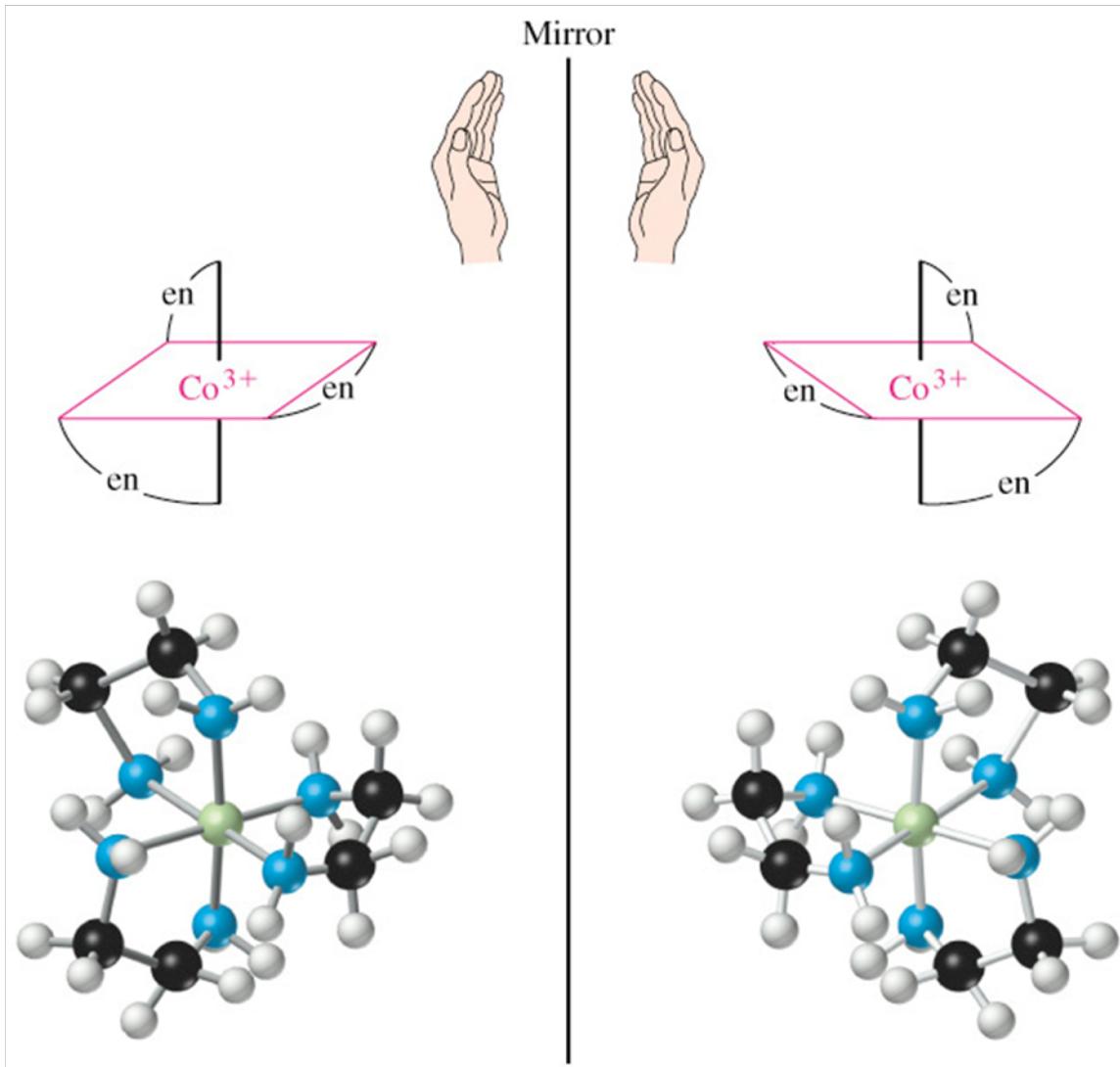
□ Optical Isomerism



Stereoisomerism

□ Octahedral Complexes

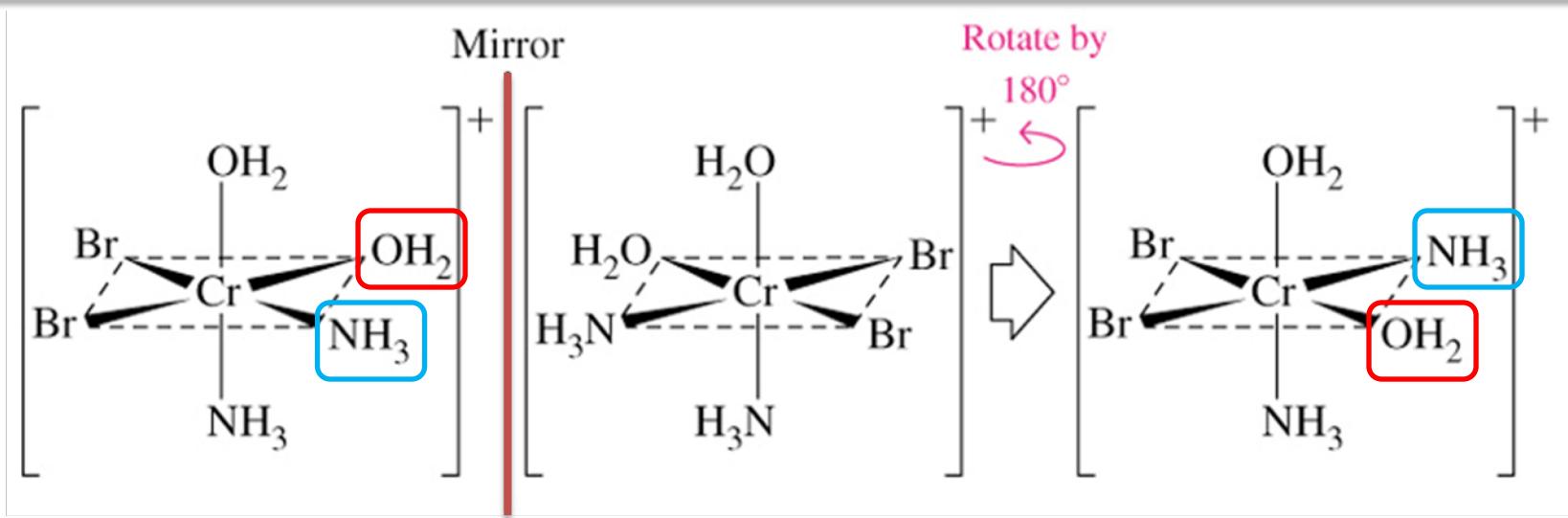
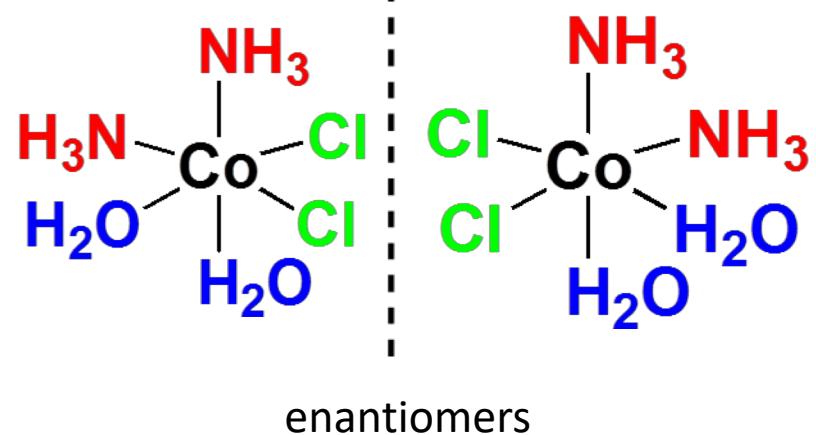
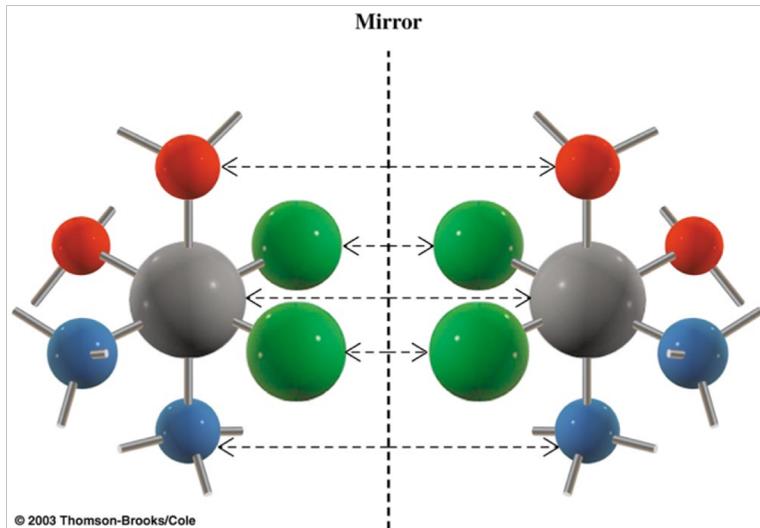
M(A-A)₃Case: [Co(en)₃]³⁺



Stereoisomerism

□ Octahedral Complexes

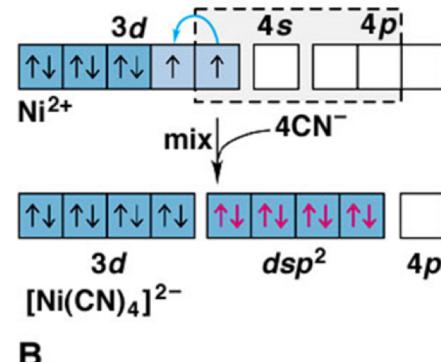
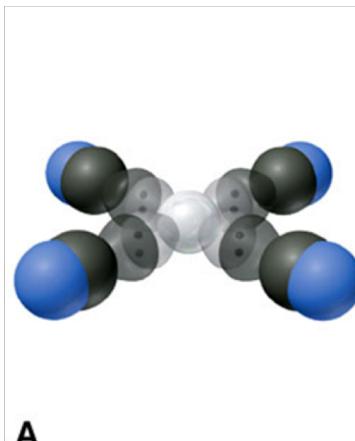
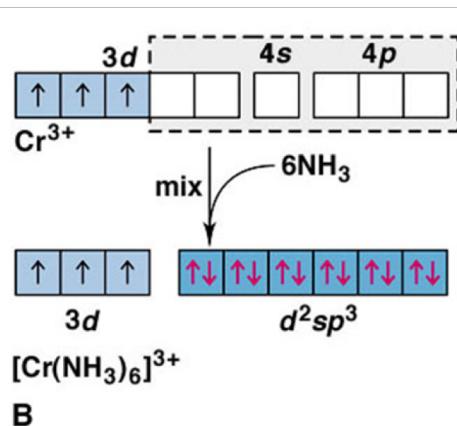
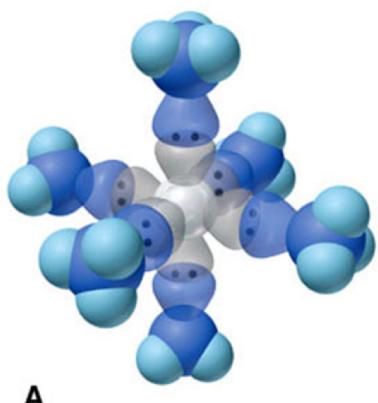
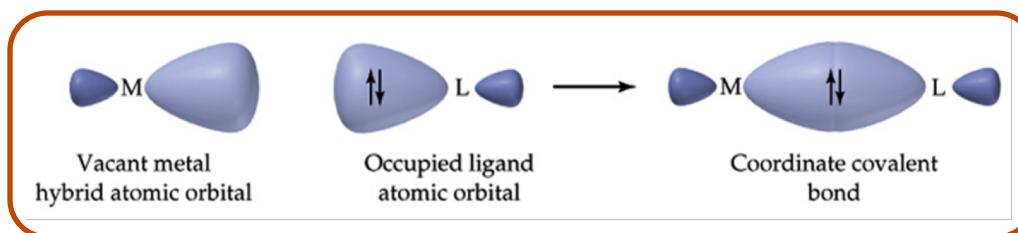
MA₂B₂C₂Case: (there are other geometric isomers as well; work it out)



Bonding in Coordination Compounds

□ Valence Bond Theory

- Proposed by Linus Pauling (Nobel Prize 1954) for nature of chemical bonds and elucidation of structure of complex systems.
- The model utilizes hybridization of metal valence orbitals to account for the observed structures and magnetic properties of complexes. $(n-1)d$, ns and np undergo hybridization to give hybridized orbitals. An empty hybrid orbital on the metal center can accept a pair of electrons from a ligand to form a σ -bond.



Valence Bond Theory: Limitations

$[\text{PtCl}_4]^{2-}$ which is diamagnetic – d^8 square planar



$[\text{NiCl}_4]^{2-}$ which is paramagnetic – d^8 tetrahedral



□ Limitations of Valence Bond Theory

- Electronic and spectroscopic properties (color) of coordination complexes is not explained.
- Quantitative interpretation of magnetic data is possible.
- Whether a complex of coordination number four is square planar or tetrahedral cannot be exactly predicted.
- Effect of ligands of different donor ability is neglected or high-spin and low-spin complexes cannot be distinguished.

Crystal Field Theory (CFT)

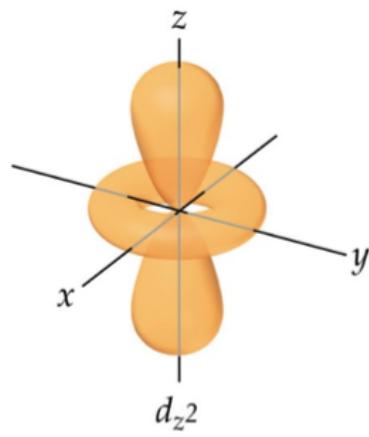
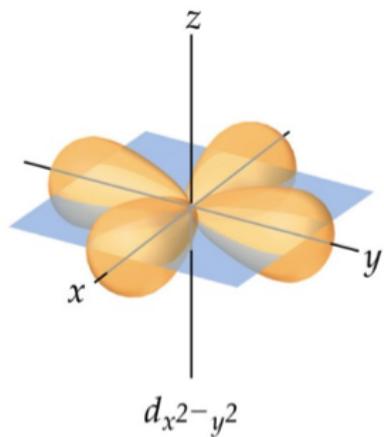
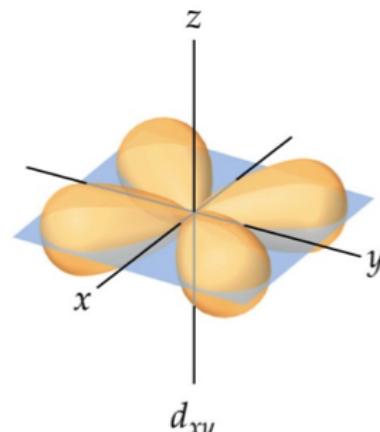
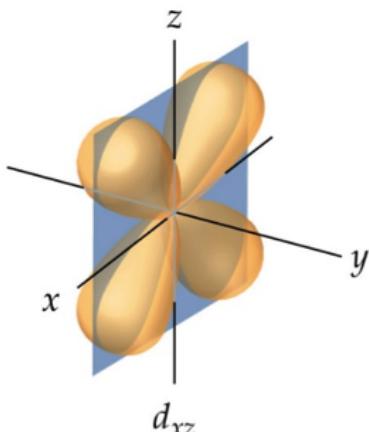
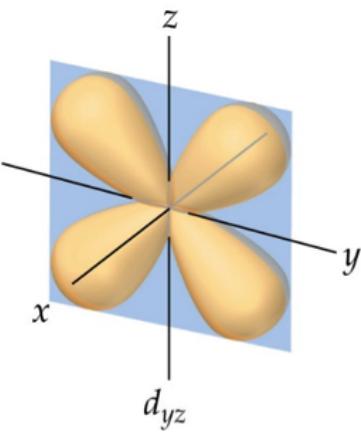
□ Assumptions/Features of CFT

- The interaction between the metal ion and the ligand is assumed to be purely electrostatic (ionic) in nature.
- The ligands are treated as point charges.
- Examines the energetics (splitting) of d -orbitals in certain geometries.

□ Nature of Interaction between Metal and Ligand

- The approaching ligand is considered to be a point charge repelled by the electrons in a metal's d -orbitals.
- Therefore, the d orbitals on a metal in a complex would not remain degenerate.
- Those that point toward ligands would be higher in energy than those that do not.

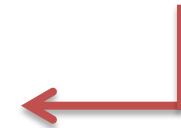
d-Orbitals



These three atomic orbitals point ***in between the axes***

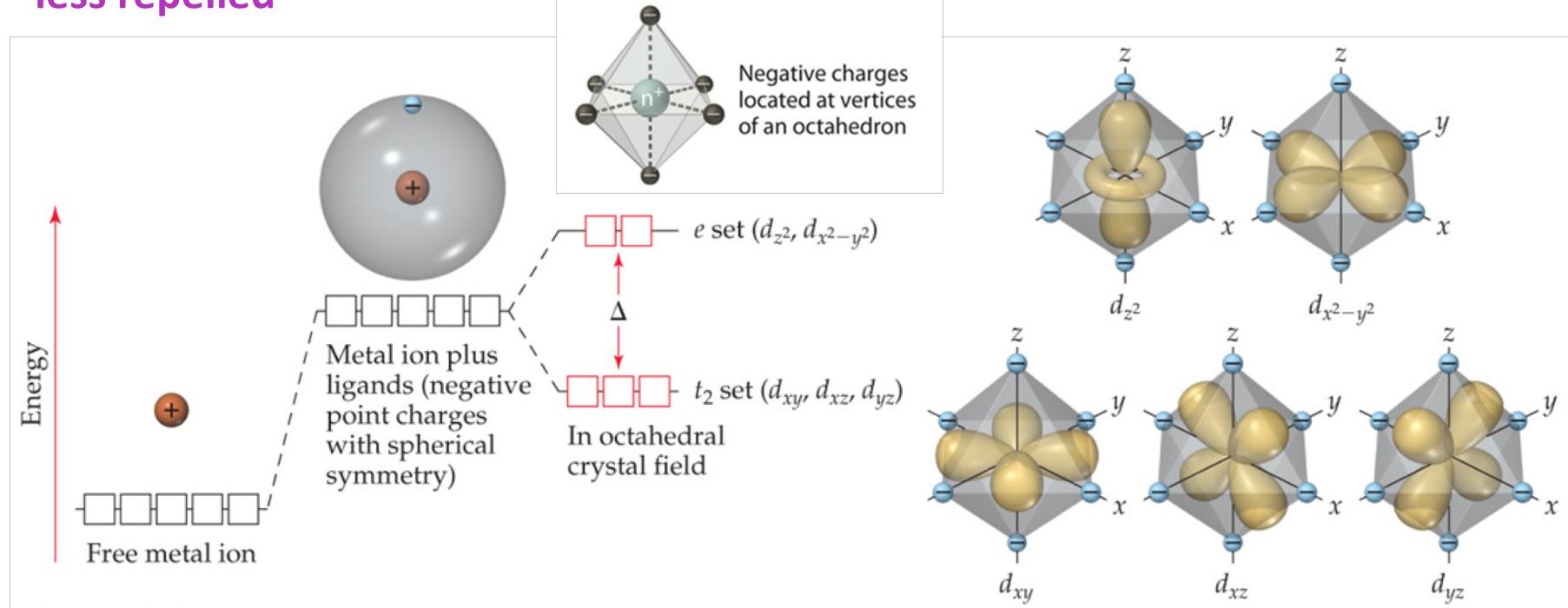
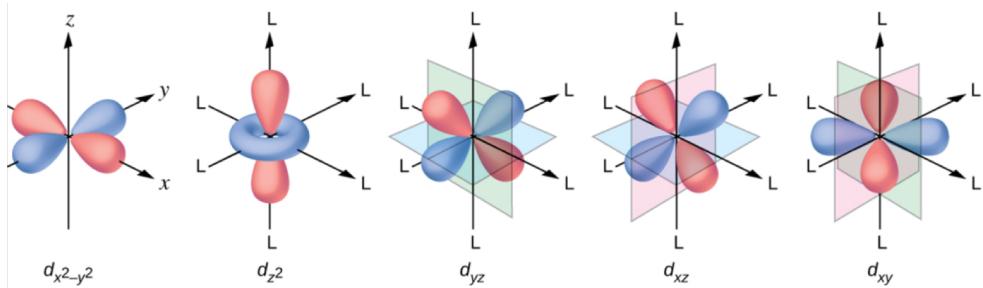


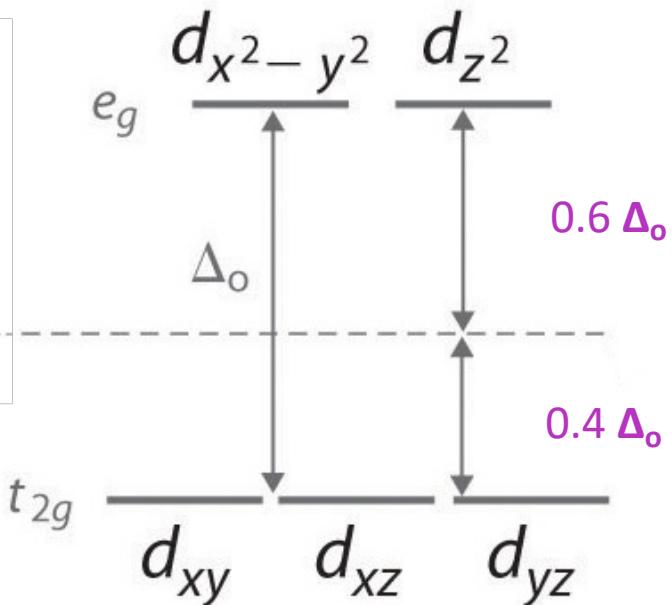
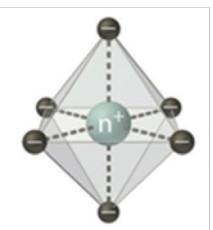
These two atomic orbitals point ***along the axes***



Metal Ion in an Octahedral Field

- The corners of octahedron are assumed to be placed on the axes.
- The ligands approach along the axes and occupy the corners
- Electrons in the d orbitals lying along the axes are repelled the most, while those lying in between the axes are less repelled



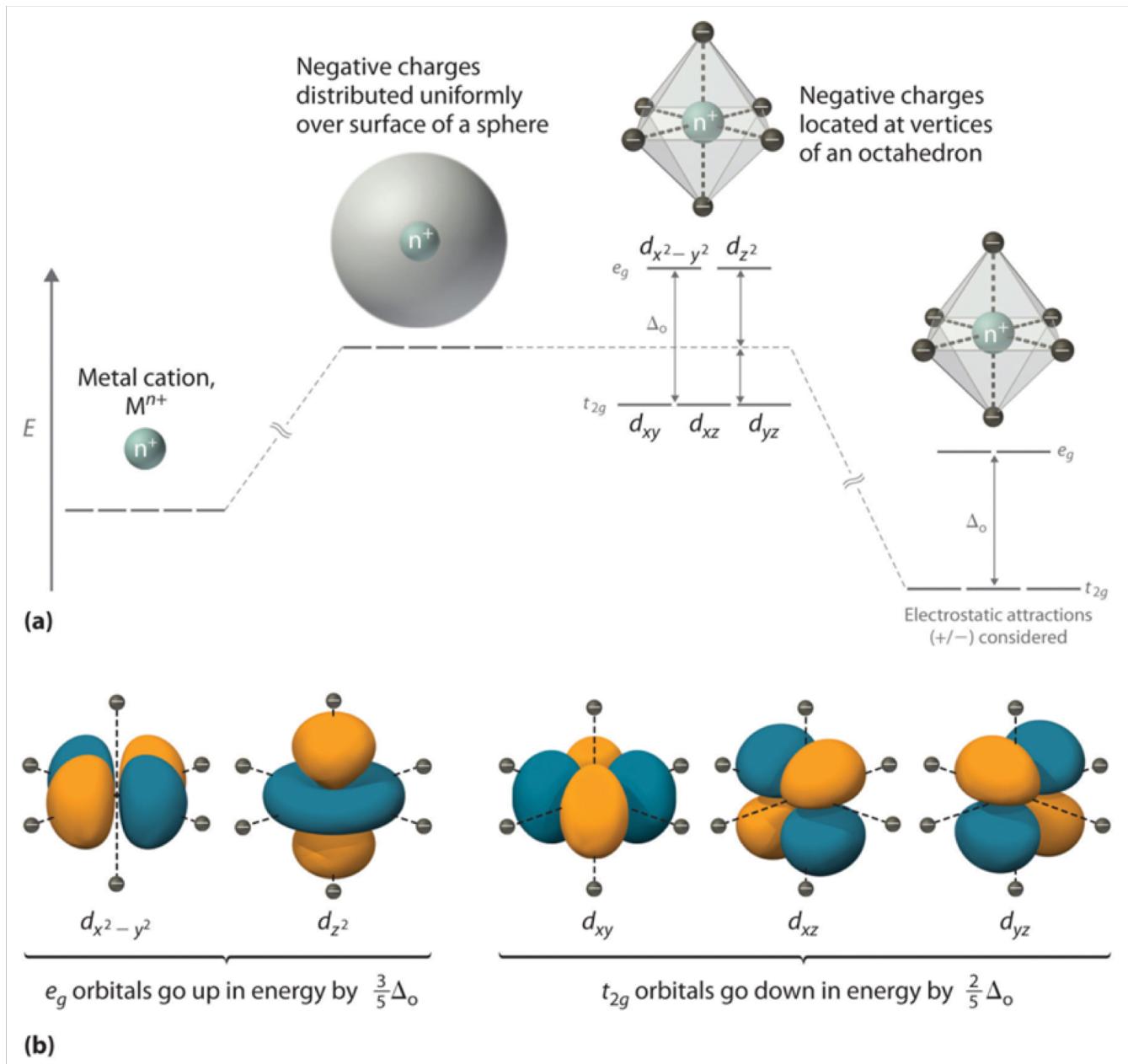


t_{2g} : triply degenerate set of orbitals
 e_g : doubly degenerate set of orbitals
 g = gerade; symmetric with respect to center of inversion
 u = ungerade; antisymmetric w.r.t. center of inversion

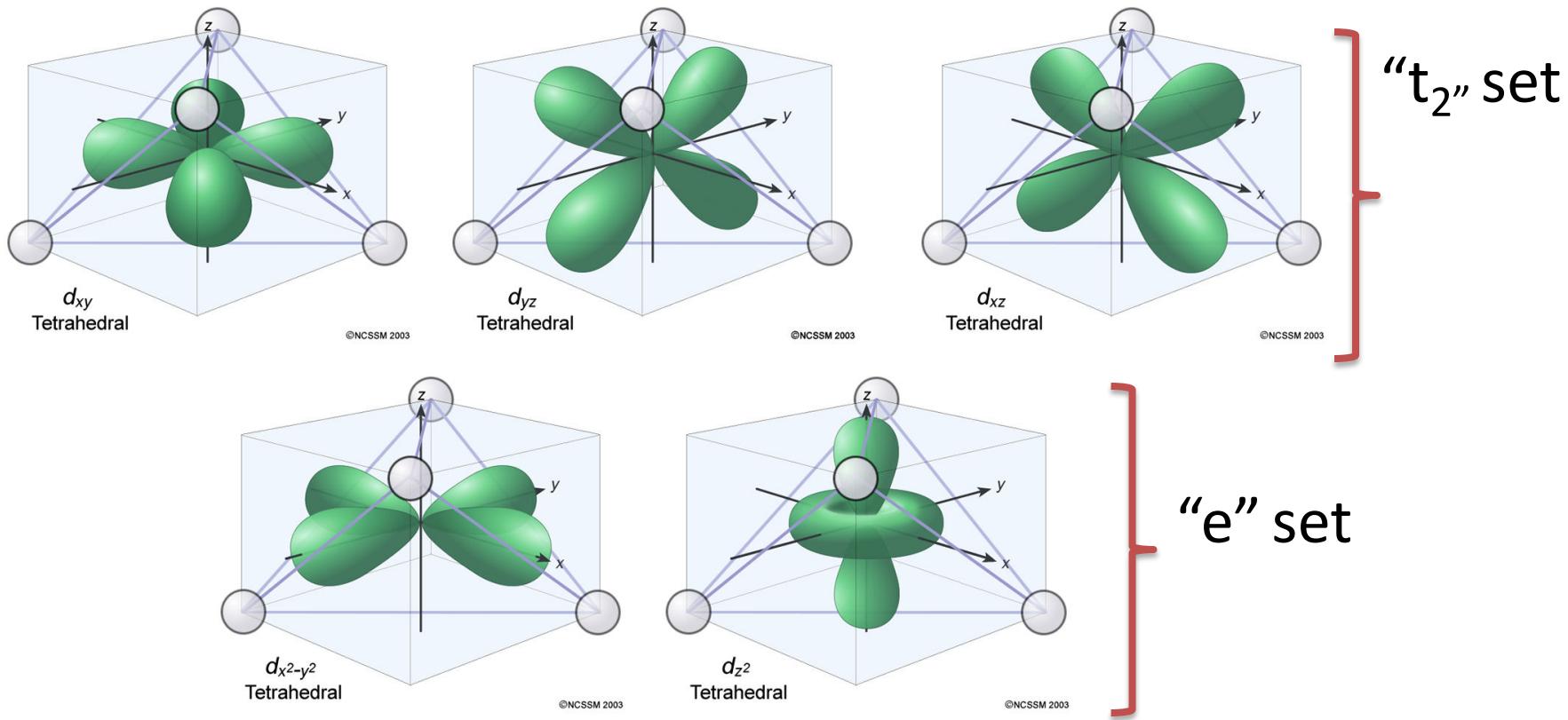
Barycenter

- Δ_o = crystal field splitting parameter; The energy separation between the two levels is denoted by Δ_o or 10 Dq.
- The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$) are labeled as e_g and the lower energy set is labeled as t_{2g} . These notations are based on the symmetry of the orbitals.
- To maintain the average energy, the e_g orbitals need to be destabilized by $0.6 \Delta_o$ (6 Dq) and the t_{2g} orbitals to be stabilized to the extent of $0.4 \Delta_o$ (4 Dq)

The Complete Picture

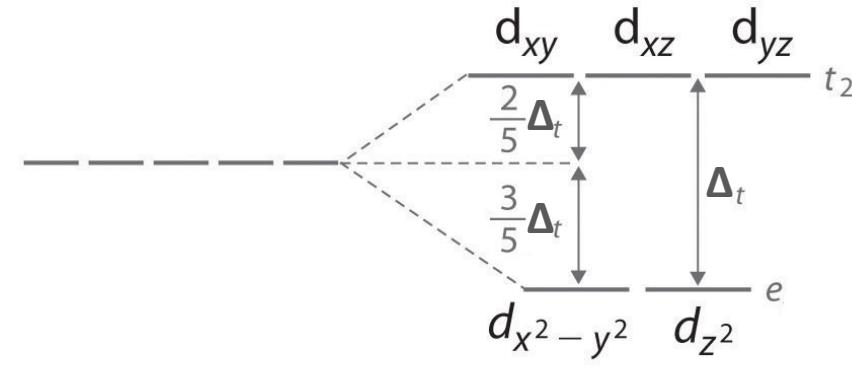
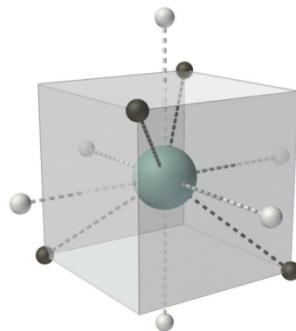
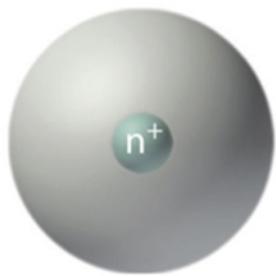


Tetrahedral Field



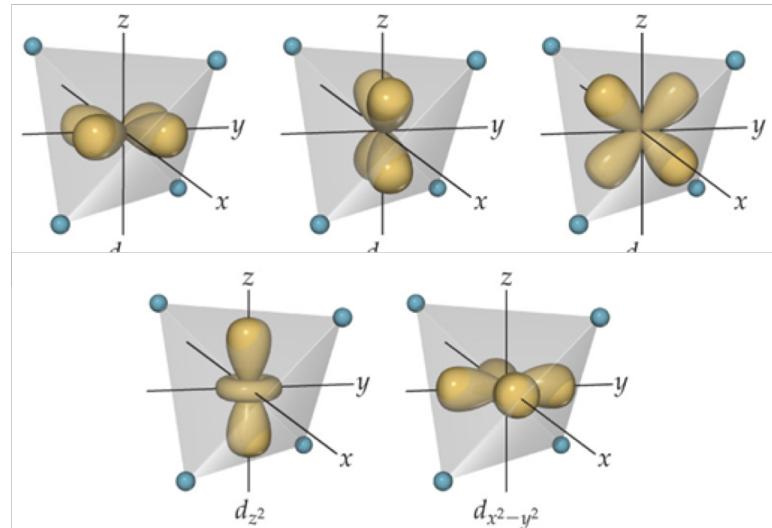
- ❑ No orbitals directly pointing toward the ligands.
- ❑ The e orbitals point between the two ligands present at opposite corners of a cube (thereby being less effected than the t_2 orbitals).
- ❑ The t_2 orbitals lie half an edge of the cube from ligand and point more directly toward ligands (destabilized).

Tetrahedral Field



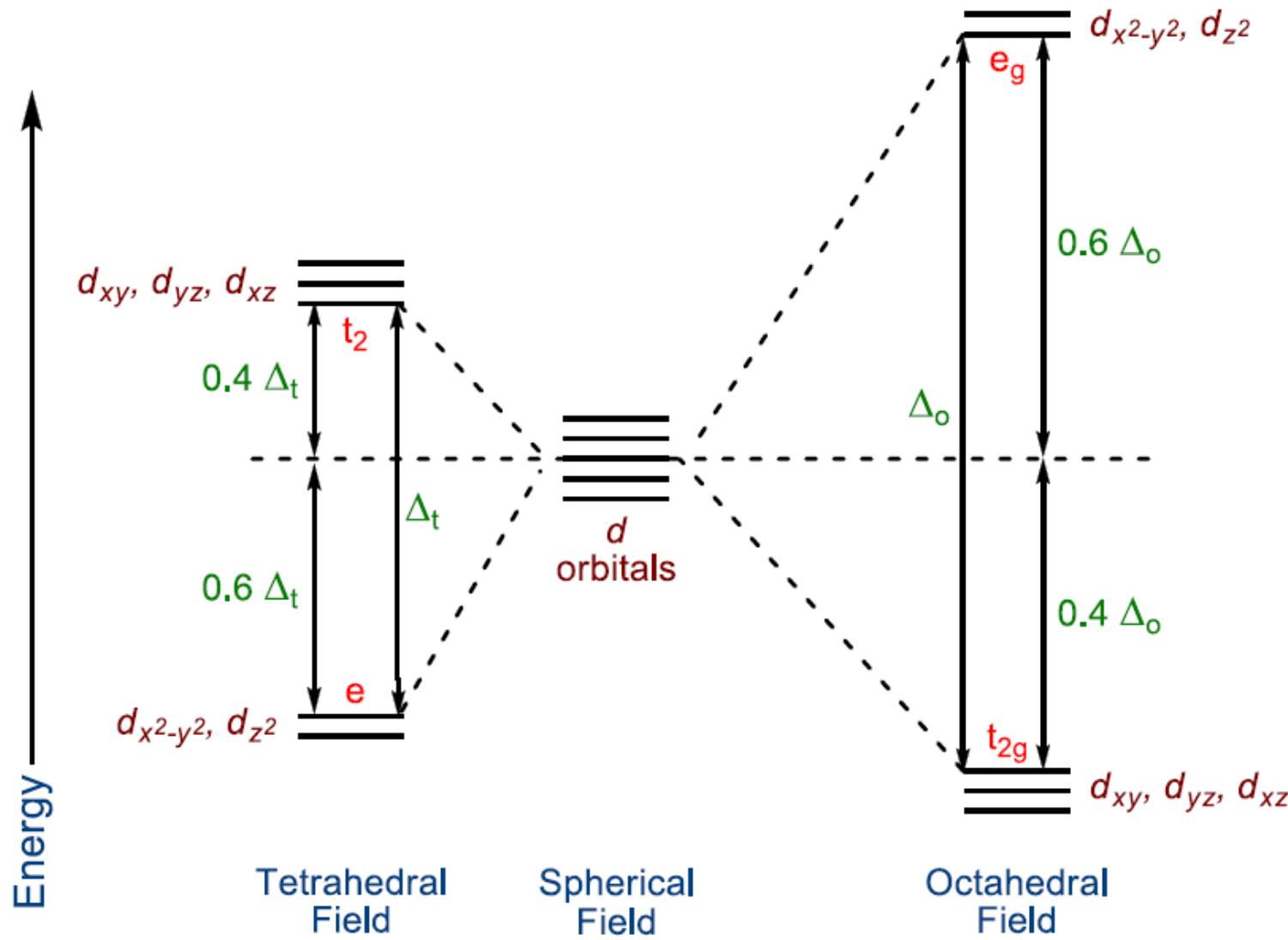
Spherical field

tetrahedral field

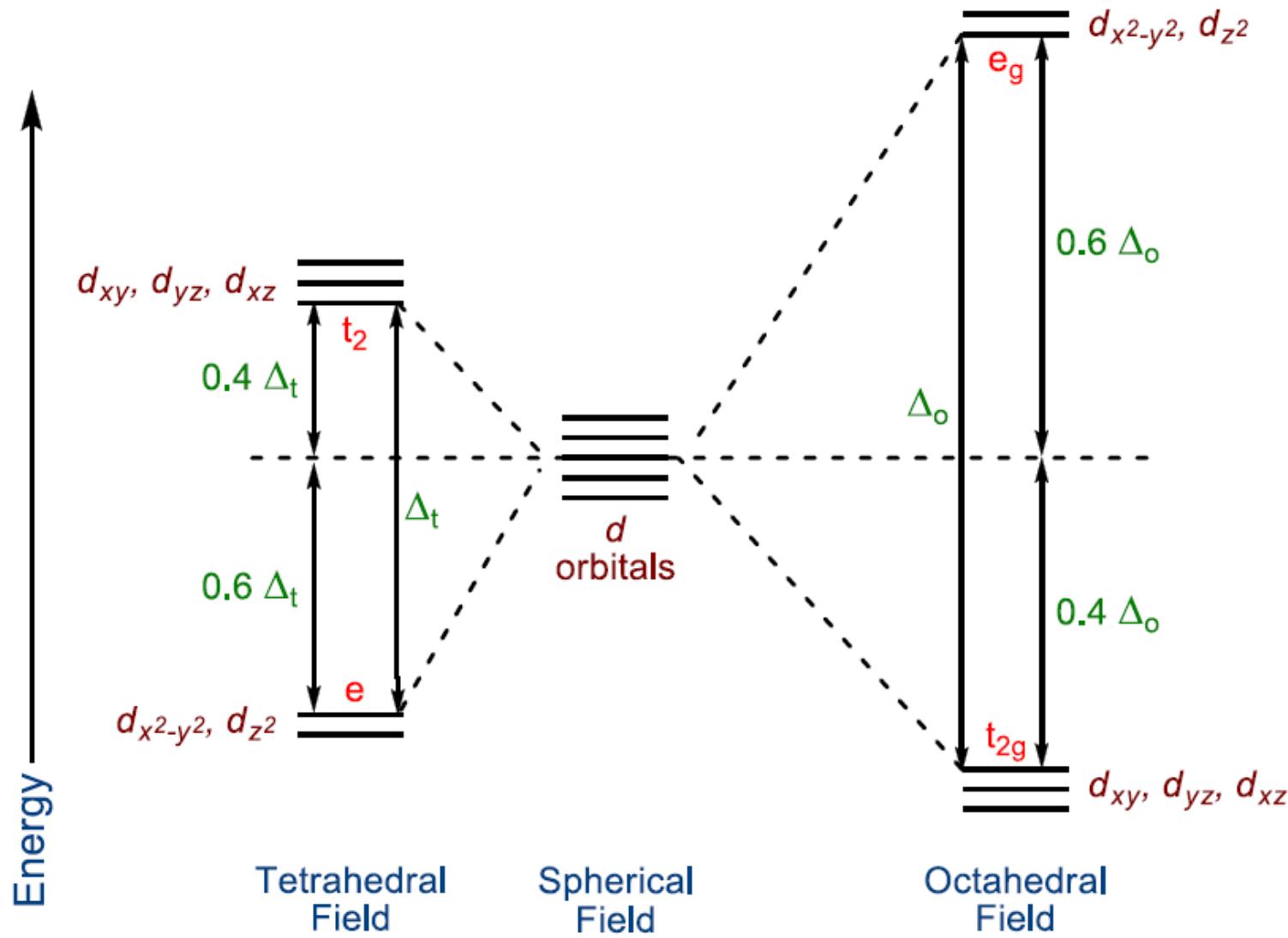


- The crystal field splitting in the tetrahedral field is intrinsically smaller than in the octahedral field. For most purposes the relationship may be represented as $\Delta_t = 4/9 \Delta_o$

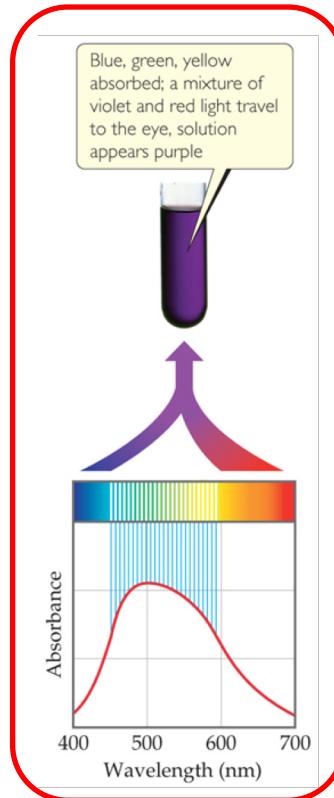
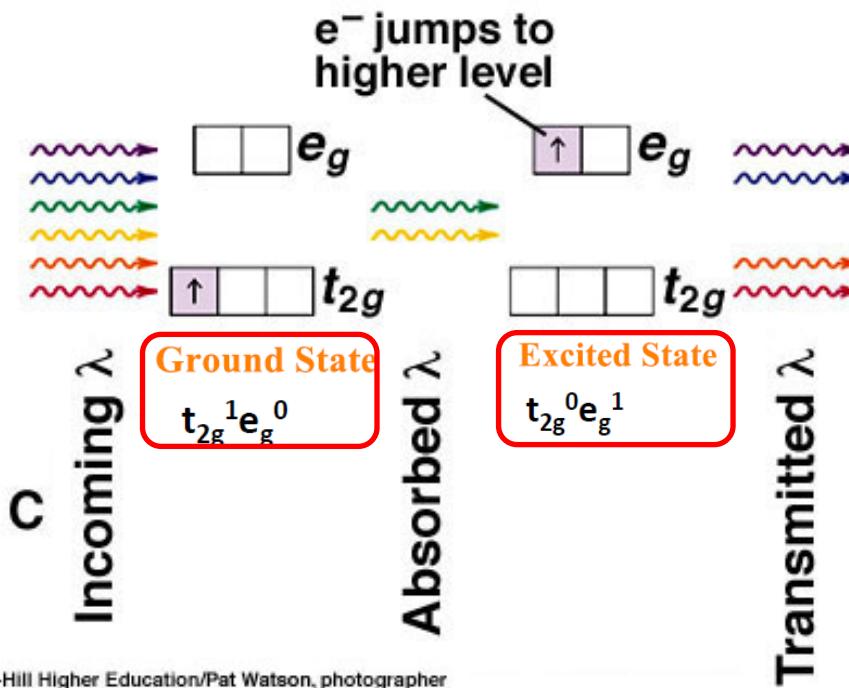
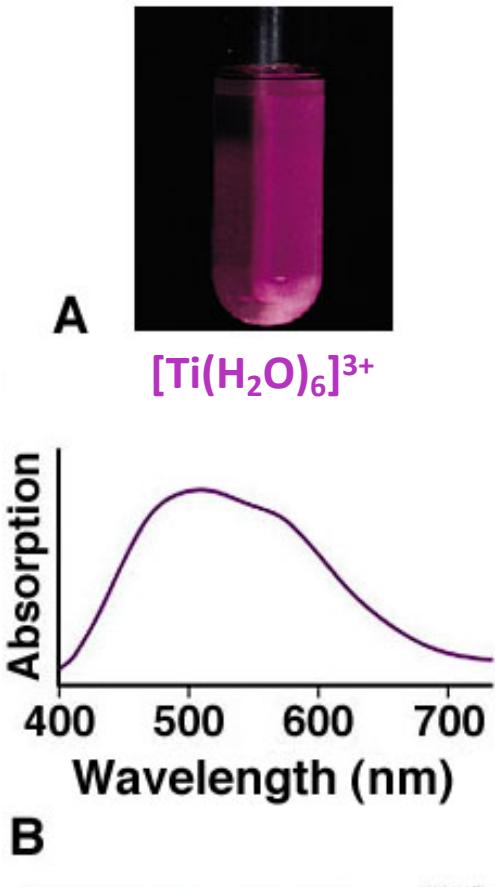
Comparison of Octahedral and Tetrahedral Fields



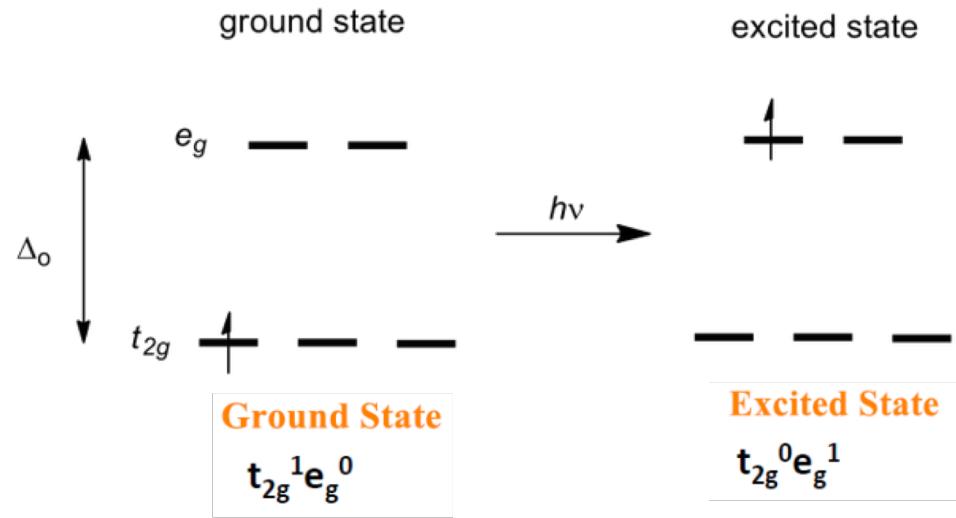
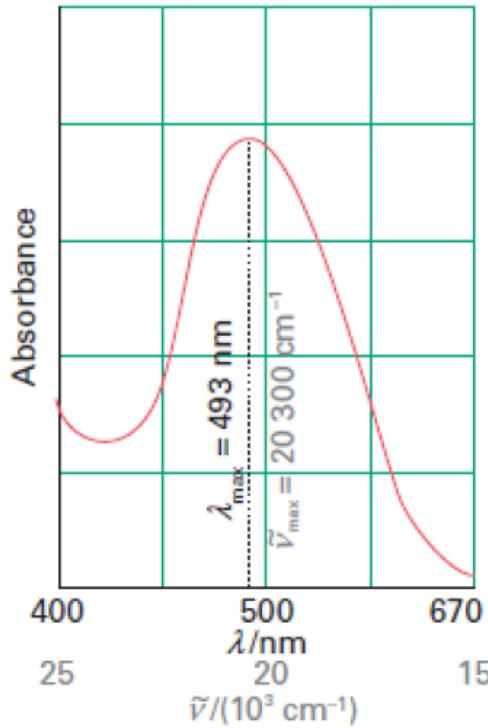
Comparison of Octahedral and Tetrahedral Fields



Determination of Δ



Determination of Δ



$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is a d^1 complex. The single electron in the t_{2g} orbitals absorb energy in the form of light and gets promoted to the e_g orbitals to show it's purple color.

For $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, this corresponds to 493 nm ($\Delta_0 = 20,300 \text{ cm}^{-1} = 243 \text{ kJ/mol}$).

For $t_{2g}^1 e_g^0$ configuration:

stabilization energy = $243 \times 0.4 = 97 \text{ kJ/mol}$,

this extra stabilization due to the splitting of d -orbitals called crystal field stabilization energy (CFSE).

