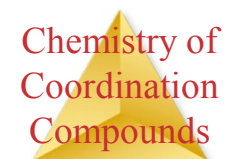


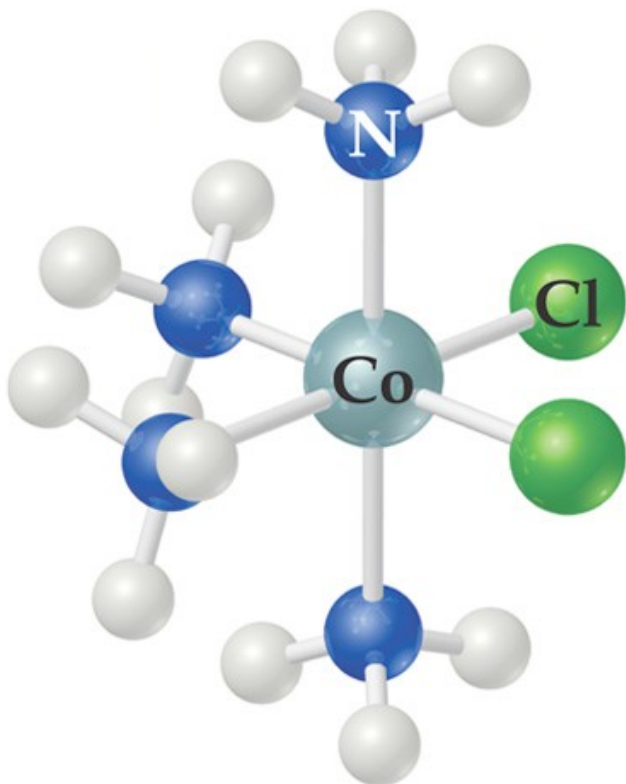


# Chemistry of Coordination Compounds

Represented by- Saurav K. Rawat  
M.Sc. (Chem.)  
(Physical Special)



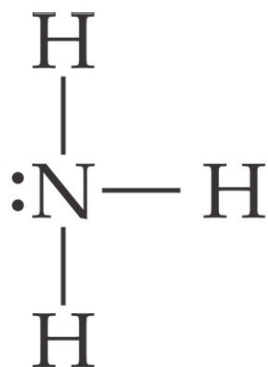
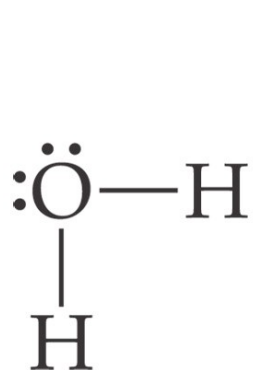
# Complexes



- A central metal atom bonded to a group of molecules or ions is a metal complex.
- If it's charged, it's a complex ion.
- Compounds containing complexes are coordination compounds.

# Complexes

- The molecules or ions coordinating to the metal are the **ligands**.
- They are usually anions or polar molecules.
- They must have lone pairs to interact with metal



# A chemical mystery:

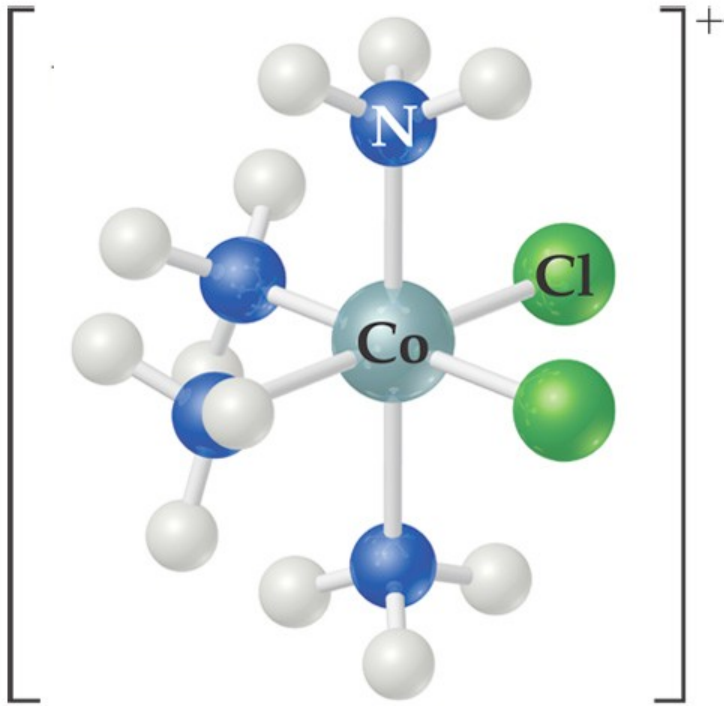
## Same metal, same ligands, different number of ions when dissolved

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

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

- Many coordination compounds are brightly colored, but again, same metal, same ligands, different colors.

# Werner's Theory



Co(III) oxidation state

Coordination # is 6

- suggested in 1893 that metal ions have **primary** and **secondary** valences.
  - Primary valence equal the metal's oxidation number
  - Secondary valence is the number of atoms directly bonded to the metal (coordination number)

# Werner's Theory

- The central metal and the ligands directly bonded to it make up the **coordination sphere** of the complex.
- In  $\text{CoCl}_3 \cdot 6 \text{NH}_3$ , all six of the ligands are  $\text{NH}_3$  and the 3 chloride ions are outside the coordination sphere.

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

Original Formulation	Color	Ions per Formula Unit	"Free" $\text{Cl}^-$ 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> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

# Werner's Theory

In  $\text{CoCl}_3 \cdot 5 \text{NH}_3$  the five  $\text{NH}_3$  groups and one chlorine are bonded to the cobalt, and the other two chloride ions are outside the sphere.

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

Original Formulation	Color	Ions per Formula Unit	"Free" $\text{Cl}^-$ 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> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

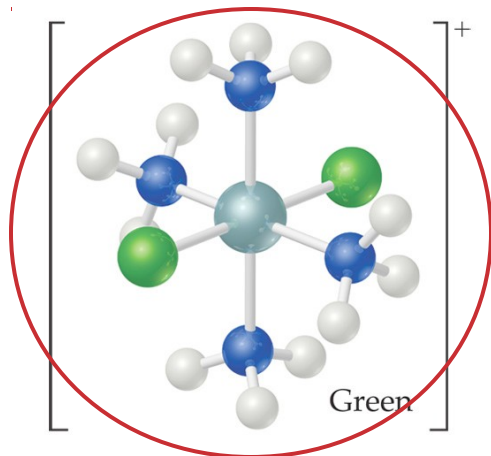
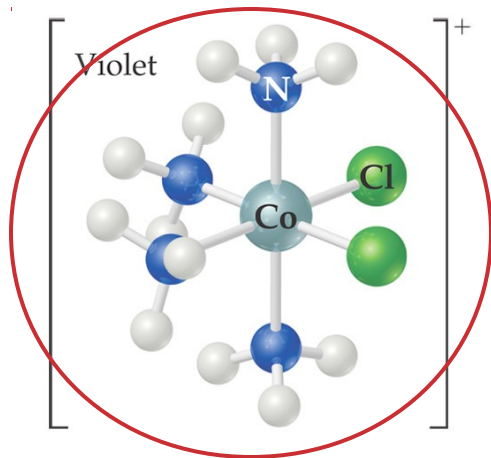
# Werner's Theory

Werner proposed putting all molecules and ions within the sphere in brackets and those “free” anions (that dissociate from the complex ion when dissolved in water) outside the brackets.

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

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

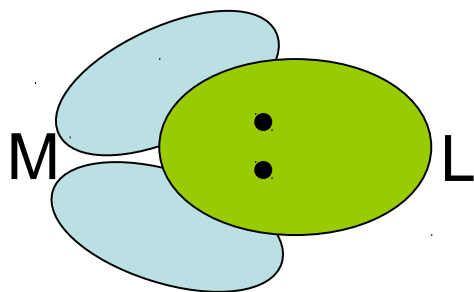
# Werner's Theory



- This approach correctly predicts there would be two forms of  $\text{CoCl}_3 \cdot 4 \text{NH}_3$ .
  - The formula would be written  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .
  - One of the two forms has the two chlorines next to each other.
  - The other has the chlorines opposite each other.

# What is Coordination?

- When an orbital from a ligand with lone pairs in it overlaps with an empty orbital from a metal

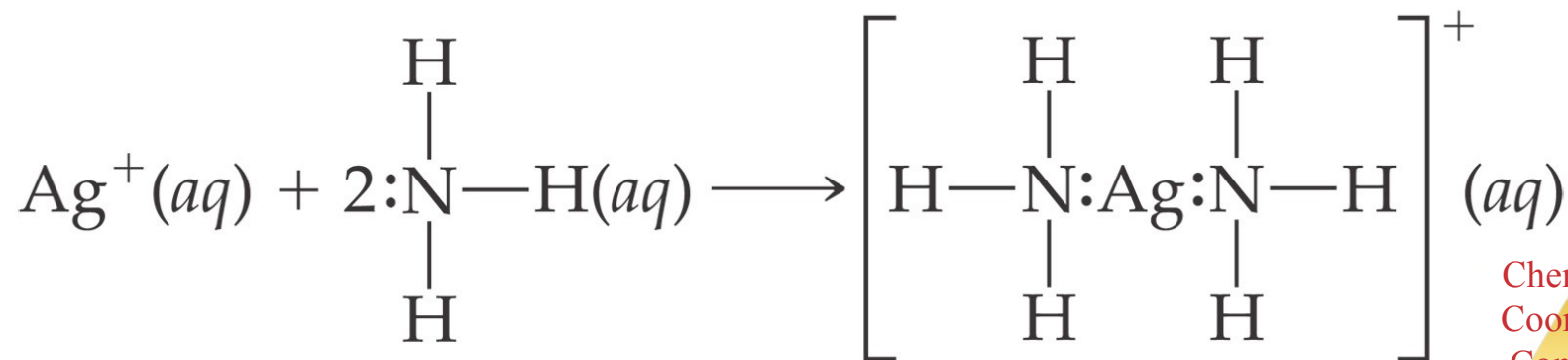


Sometimes called a  
coordinate covalent  
bond

So ligands *must* have lone pairs of electrons.

# Metal-Ligand Bond

- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have nonbonding electrons.
  - The metal (Lewis acid) has empty orbitals.

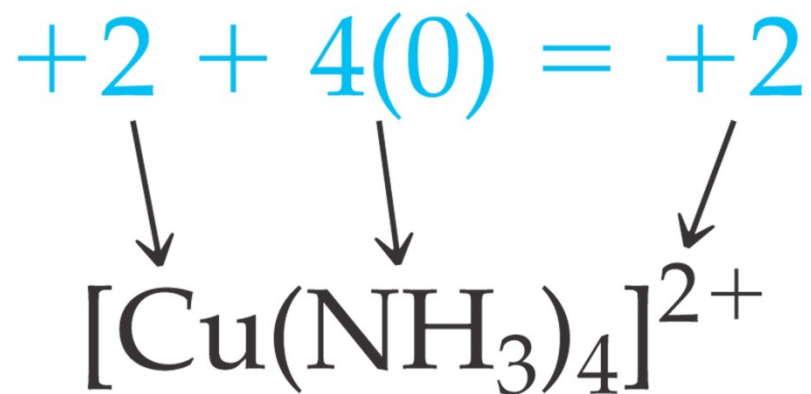


# Metal-Ligand Bond

The metal's coordination ligands and geometry can greatly alter its properties, such as color, or ease of oxidation.



# Oxidation Numbers



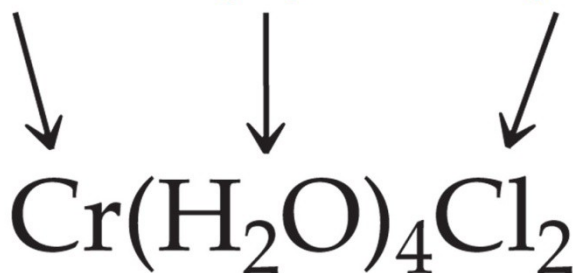
Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.

# Oxidation Numbers

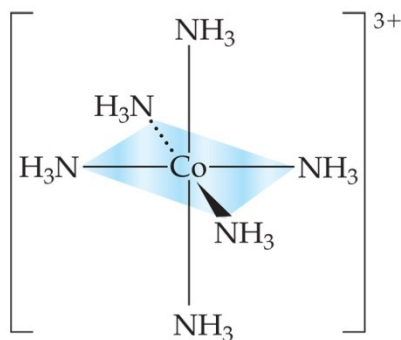
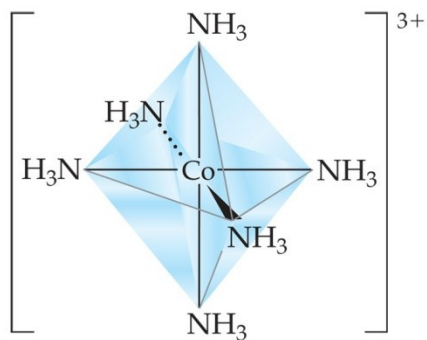
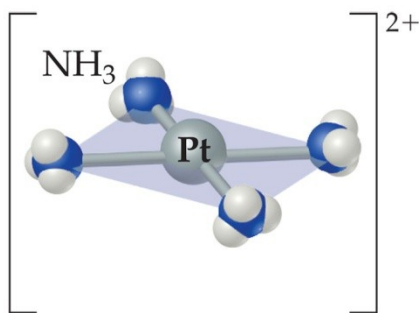
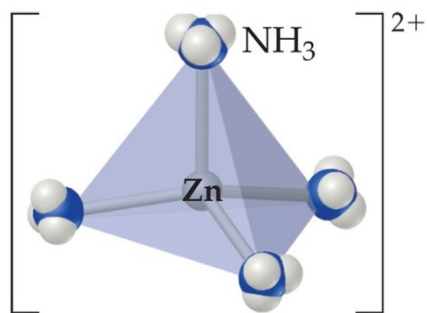
Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

**Example:  $\text{Cr(III)(H}_2\text{O)}_4\text{Cl}_2$**

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

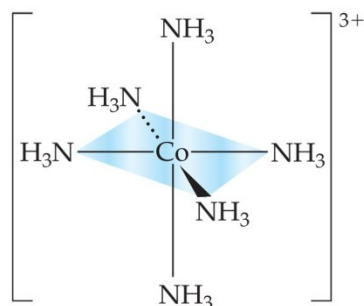
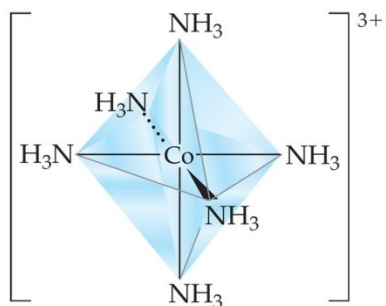
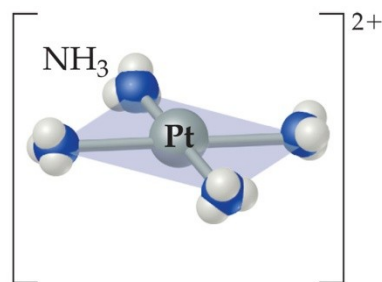
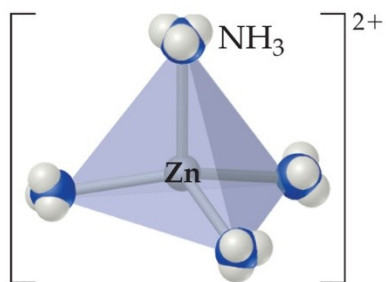


# Coordination Number



- The atom that supplies the lone pairs of electrons for the metal-ligand bond is the donor atom.
- The number of these atoms is the coordination number.

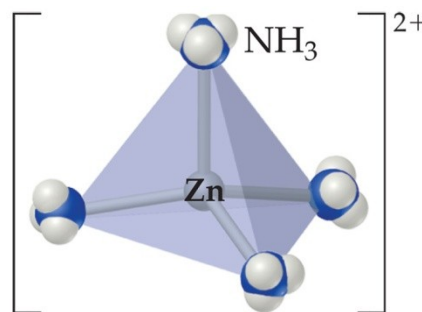
# Coordination Number



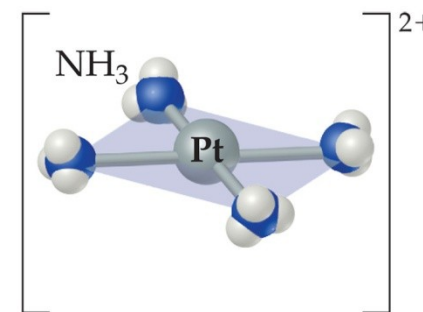
- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.

# Geometries

- There are two common geometries for metals with a coordination number of four:
  - Tetrahedral
  - Square planar



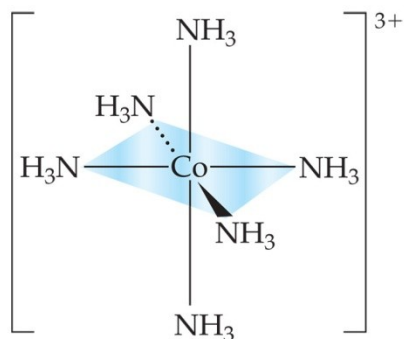
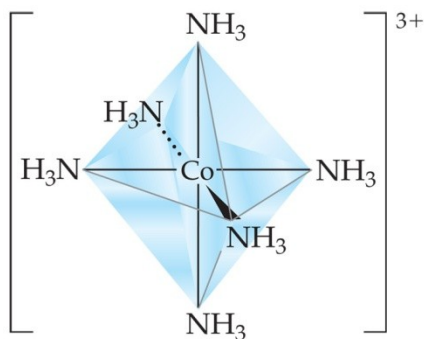
**Tetrahedral**



**Square planar**

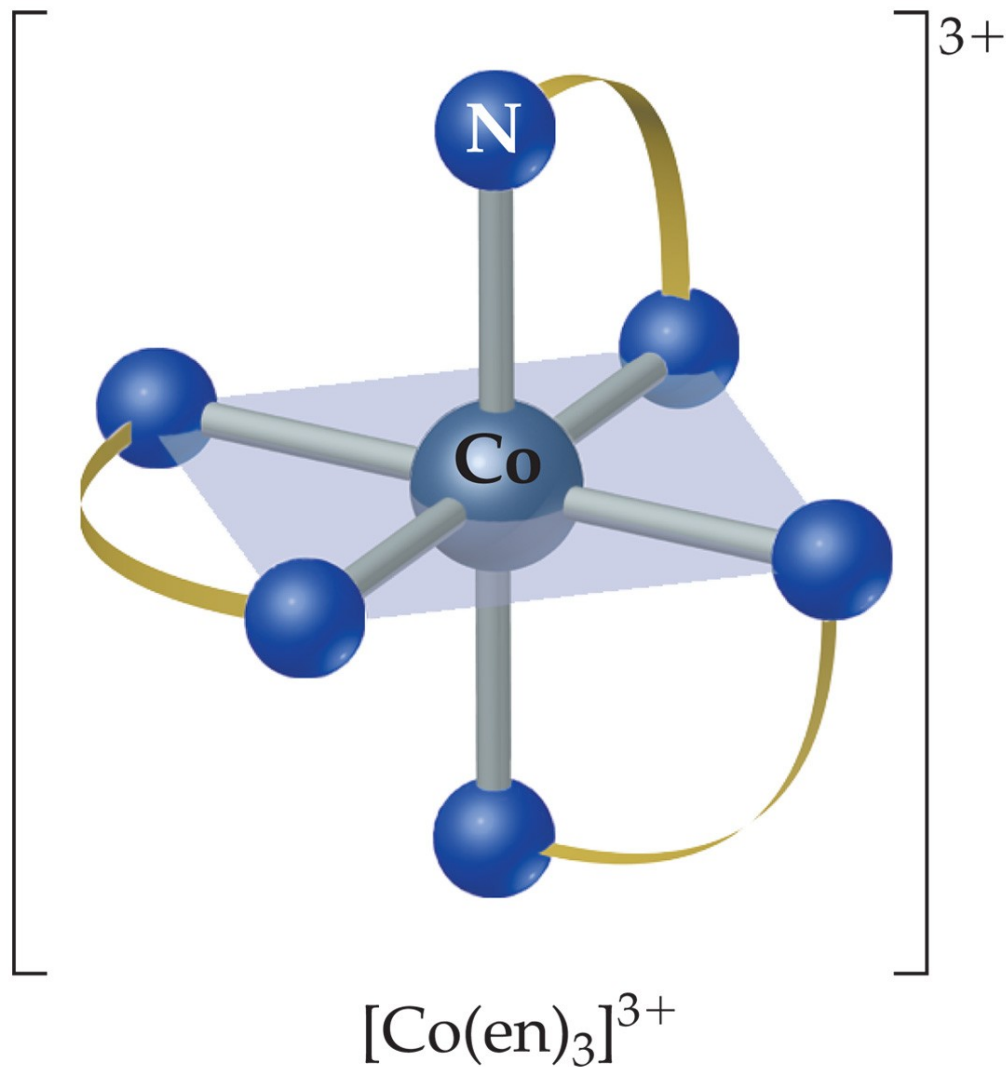
Why square planar? We'll get to that

# Geometries



By far the most-encountered geometry, when the coordination number is six, is octahedral.

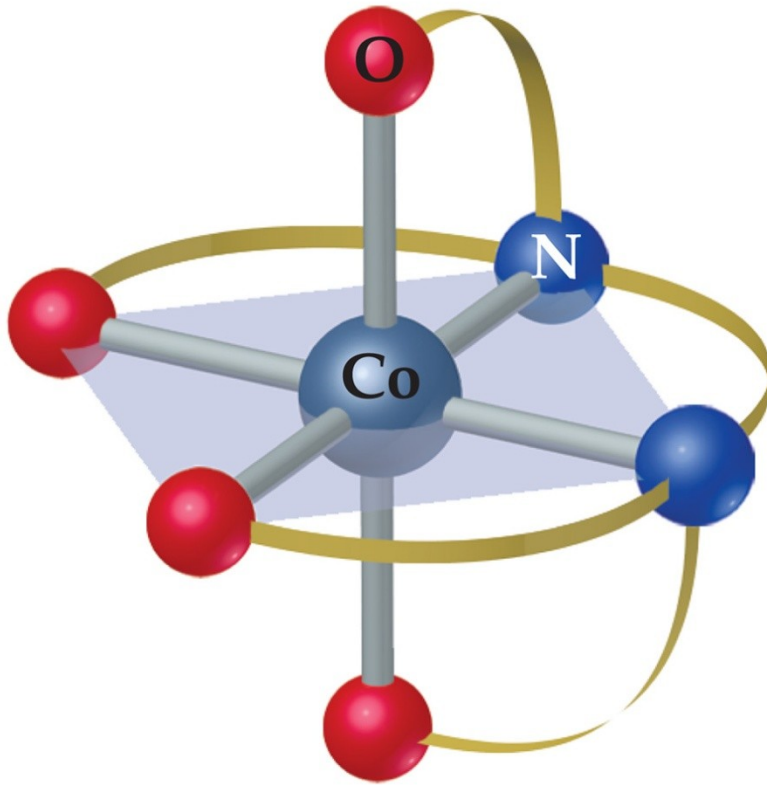
# Polydentate Ligands



- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylenediamine,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , represented here as en, each N is a donor atom.
- Therefore, en is bidentate.

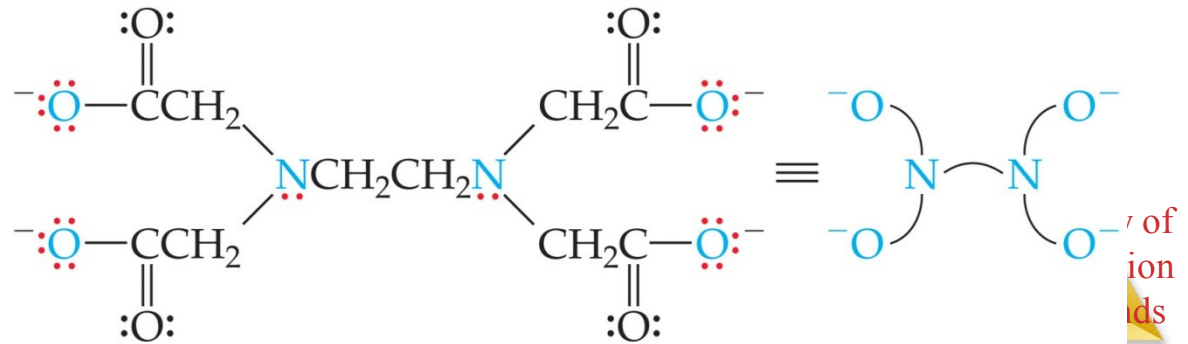
# Polydentate Ligands

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.



CoEDTA<sup>-</sup>

Wraps around the central atom like an octopus



[EDTA]<sup>4-</sup>

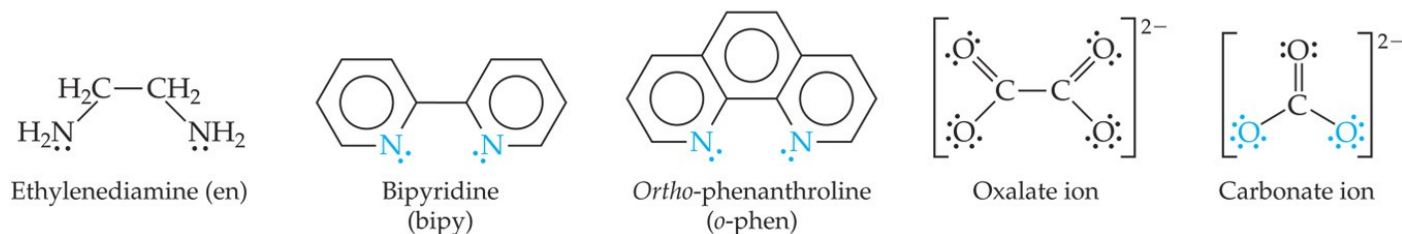
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# Polydentate Ligands

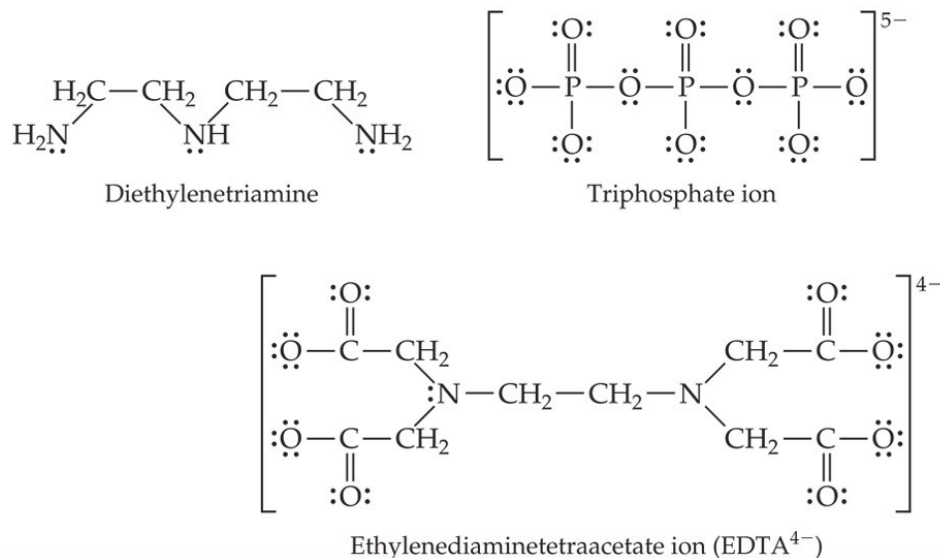
## Ligand Type Examples

Monodentate	$\text{H}_2\ddot{\text{O}}:$ Water	$:\ddot{\text{F}}:^-$ Fluoride ion	$[:\text{C}\equiv\text{N}:]^-$ Cyanide ion	$[\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion
	$:\text{NH}_3$ Ammonia	$:\ddot{\text{Cl}}:^-$ Chloride ion	$[\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ Thiocyanate ion or	$[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion or

## Bidentate

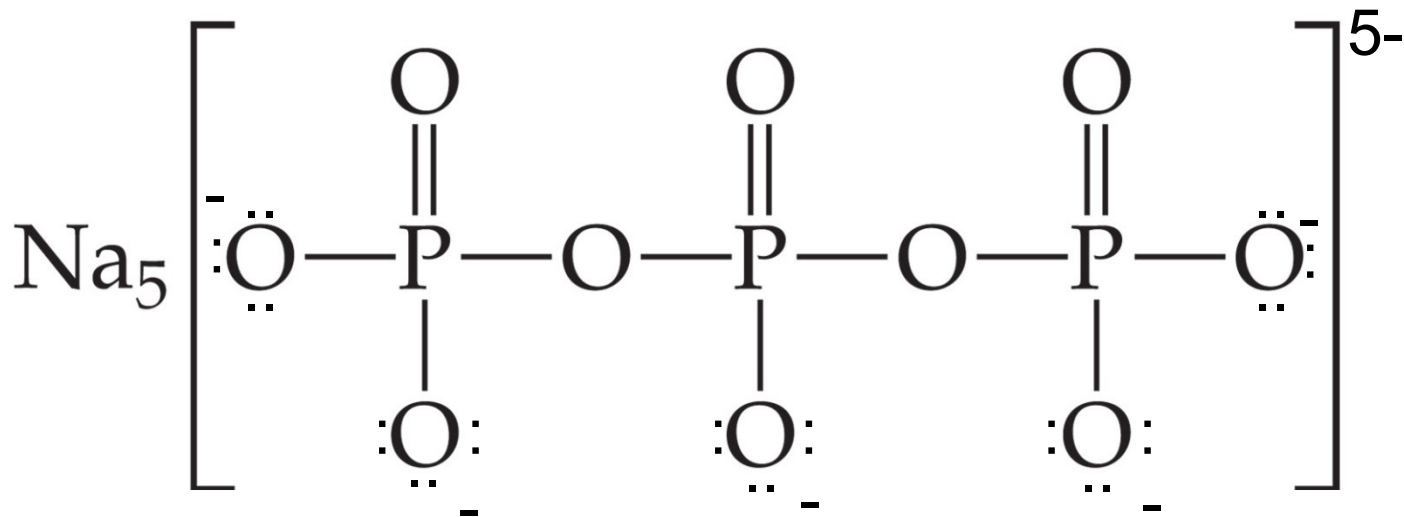


## Polydentate



Chelating agents generally form more stable complexes than do monodentate ligands.

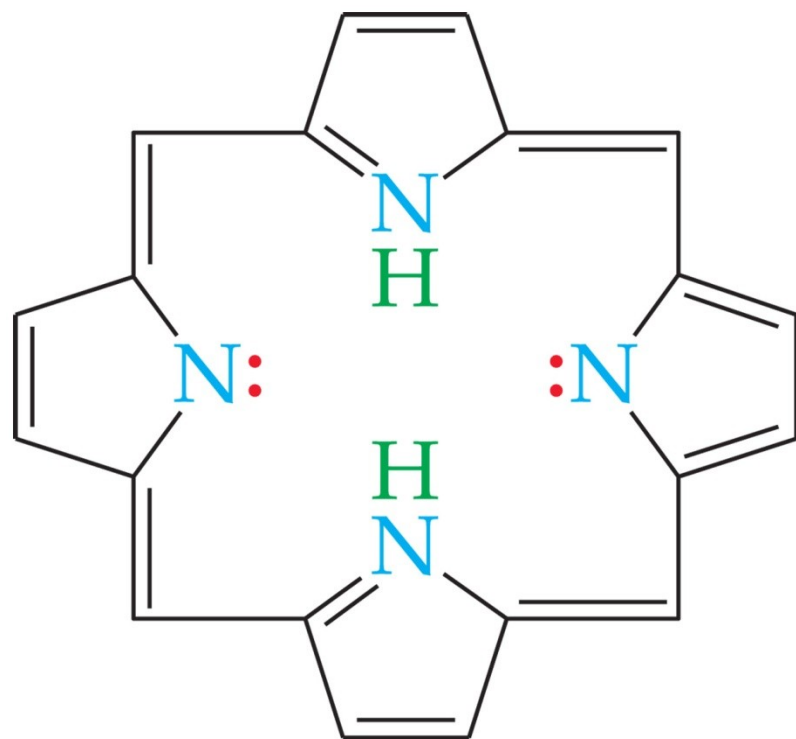
# Chelating Agents



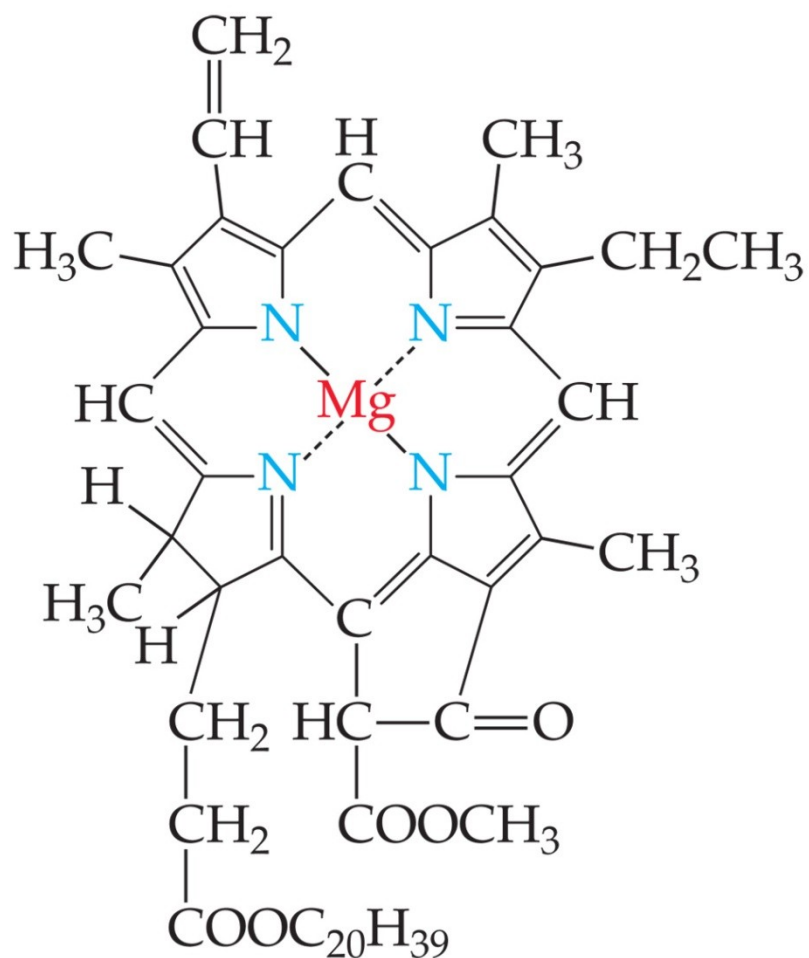
- Bind to metal ions removing them from solution.
- Phosphates are used to tie up  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in hard water to prevent them from interfering with detergents.

# Chelating Agents

- Porphyrins are complexes containing a form of the porphine molecule shown at right.
- Important biomolecules like heme and chlorophyll are porphyrins.



# Chelating Agents



Porphines (like chlorophyll *a*) are tetradentate ligands.

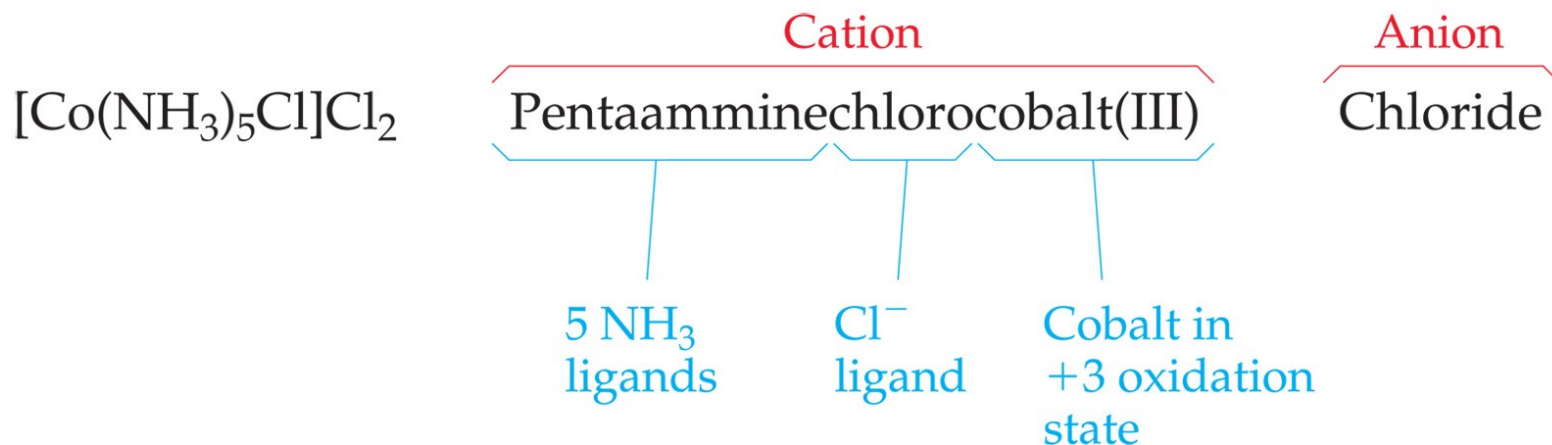
# Nomenclature of Coordination Compounds

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, $\text{N}_3^-$	Azido	Oxalate, $\text{C}_2\text{O}_4^{2-}$	Oxalato
Bromide, $\text{Br}^-$	Bromo	Oxide, $\text{O}^{2-}$	Oxo
Chloride, $\text{Cl}^-$	Chloro	Ammonia, $\text{NH}_3$	Ammine
Cyanide, $\text{CN}^-$	Cyano	Carbon monoxide, $\text{CO}$	Carbonyl
Fluoride, $\text{F}^-$	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, $\text{OH}^-$	Hydroxo	Pyridine, $\text{C}_5\text{H}_5\text{N}$	Pyridine
Carbonate, $\text{CO}_3^{2-}$	Carbonato	Water, $\text{H}_2\text{O}$	Aqua

- The basic protocol in coordination nomenclature is to name the ligands attached to the metal as prefixes before the metal name.
- Some common ligands and their names are listed above.

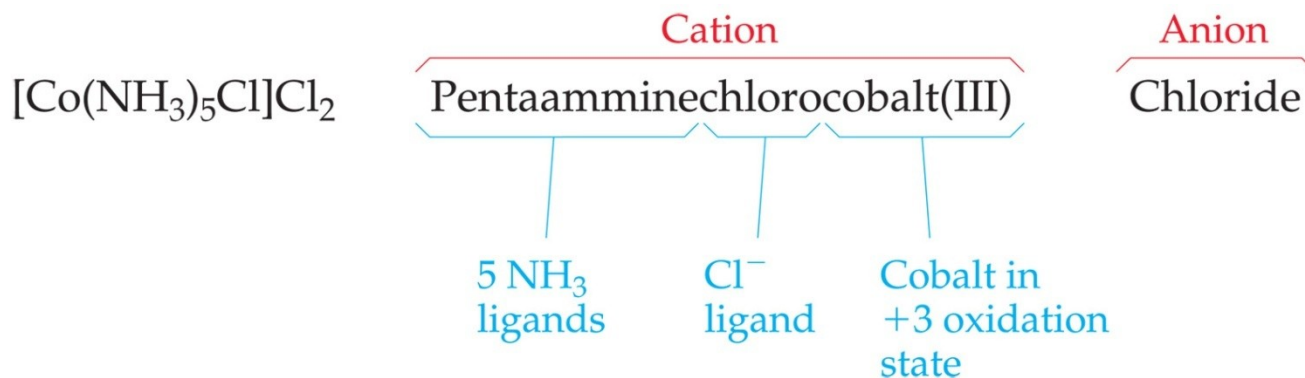
# Nomenclature of Coordination Compounds

- As always the name of the **cation** appears first; the **anion** is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.



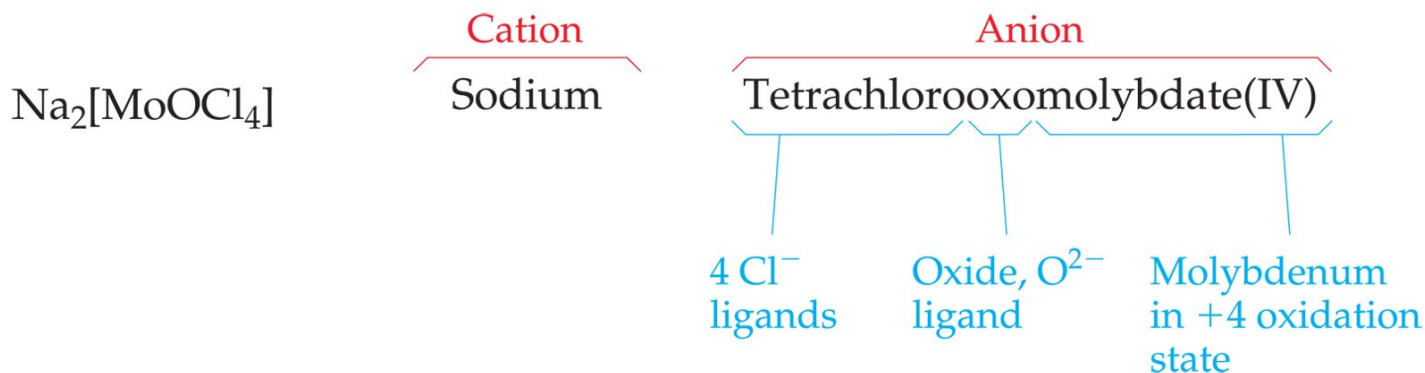
# Nomenclature of Coordination Compounds

- The names of anionic ligands end in “o”; the endings of the names of neutral ligands are not changed.
- Prefixes tell the number of a type of ligand in the complex. If the name of the ligand itself has such a prefix, alternatives like *bis-*, *tris-*, etc., are used.

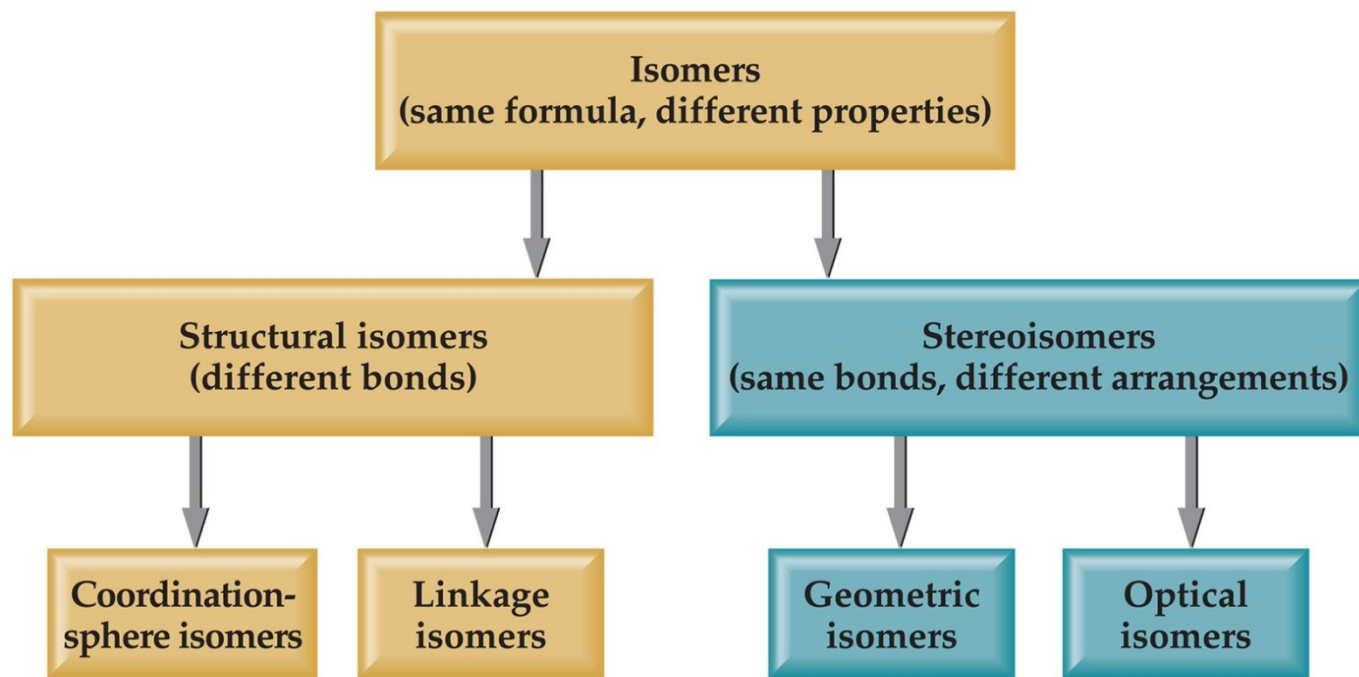


# Nomenclature of Coordination Compounds

- If the complex is an anion, its ending is changed to *-ate*.
- The oxidation number of the metal is listed as a Roman numeral in parentheses immediately after the name of the metal.



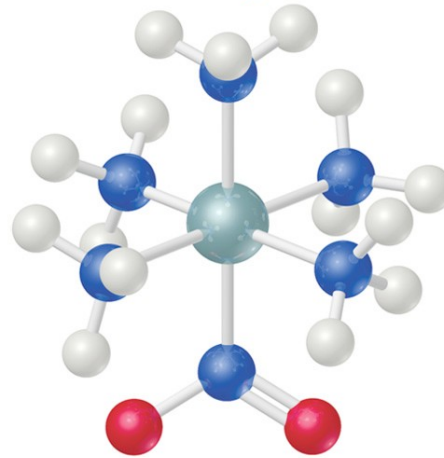
# Isomers



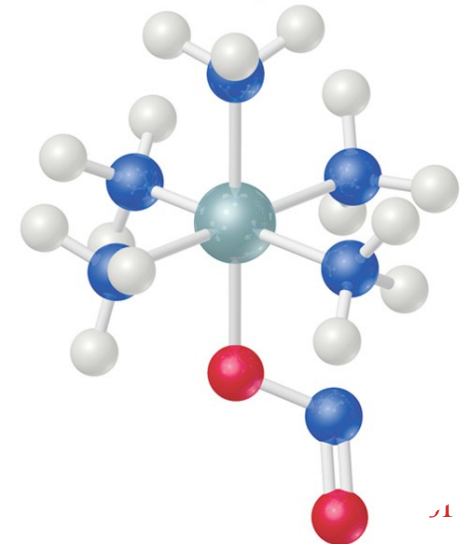
Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

# Structural Isomers

If a ligand (like the  $\text{NO}_2$  group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, linkage isomers are formed.



Nitro isomer

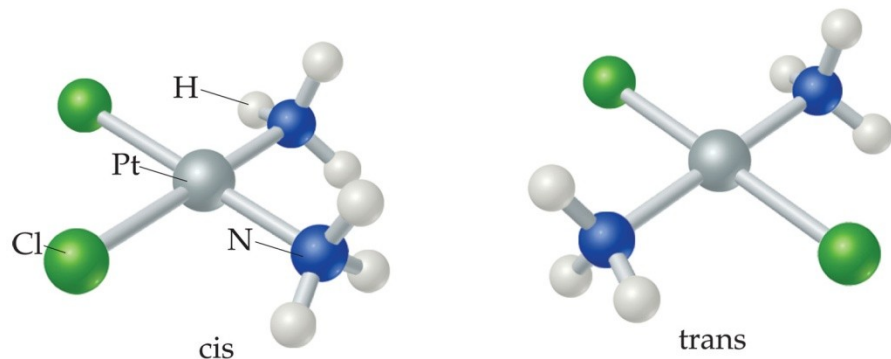


Nitrito isomer

# Structural Isomers

- Some isomers differ in what ligands are bonded to the metal and what is outside the coordination sphere; these are **coordination-sphere isomers**.
- Three isomers of  $\text{CrCl}_3(\text{H}_2\text{O})_6$  are
  - The violet  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,
  - The green  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , and
  - The (also) green  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$ .

# Geometric isomers



- With these **geometric isomers**, two chlorines and two NH<sub>3</sub> groups are bonded to the platinum metal, but are clearly different.

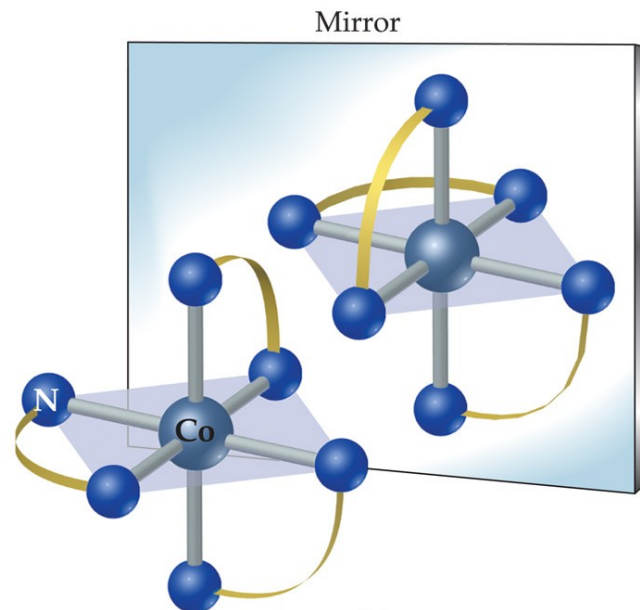
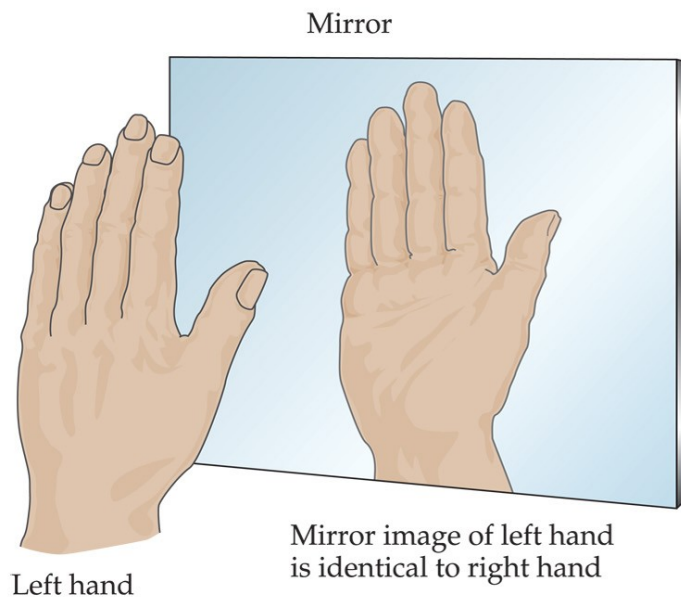
- *cis*-Isomers have like groups on the same side.
- *trans*-Isomers have like groups on opposite sides.

# of each atom the same

Bonding the same

Arrangement in space different

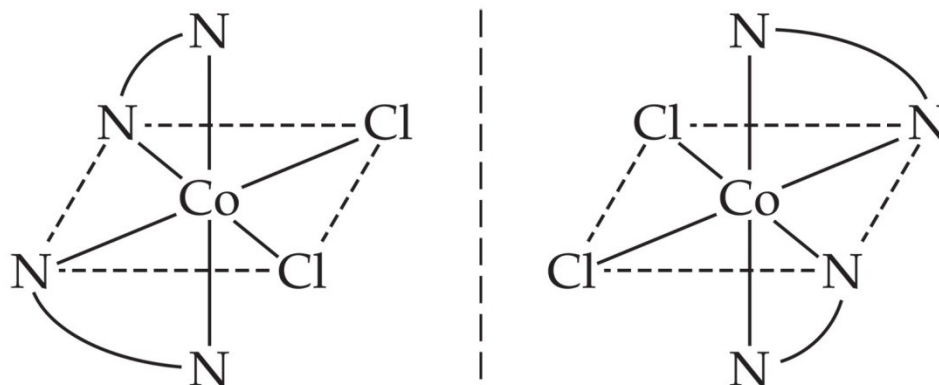
# Stereoisomers



- Other stereoisomers, called **optical isomers** or **enantiomers**, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

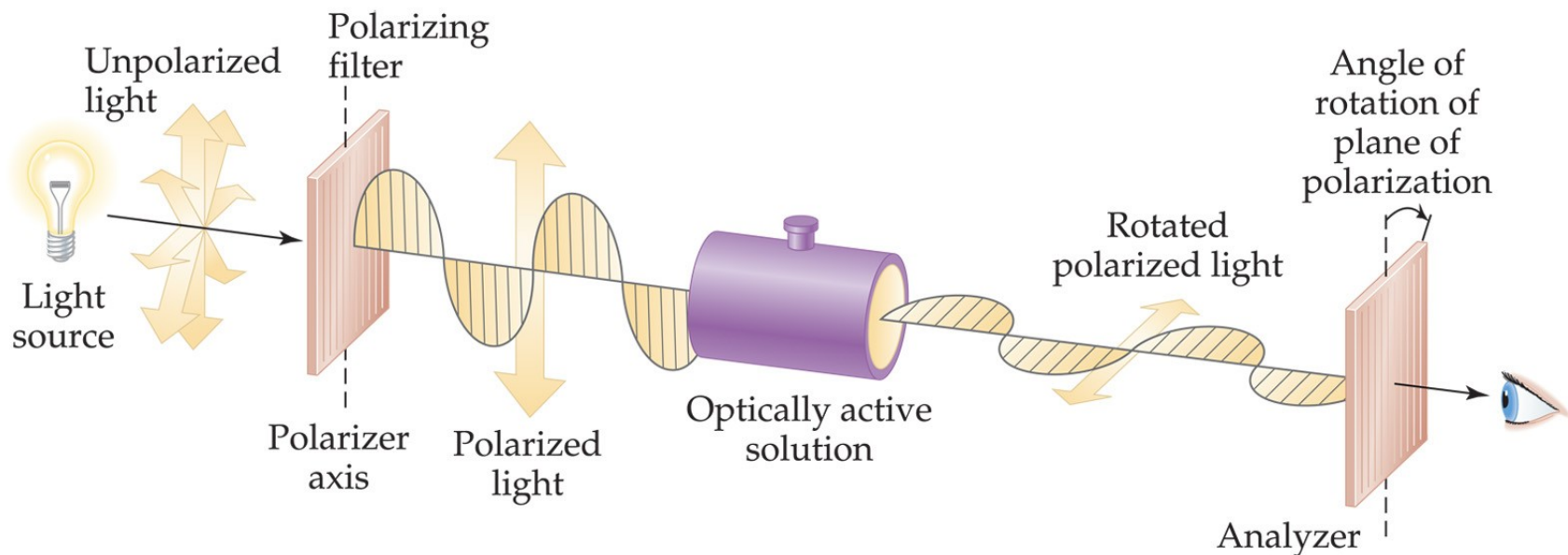
# Enantiomers

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



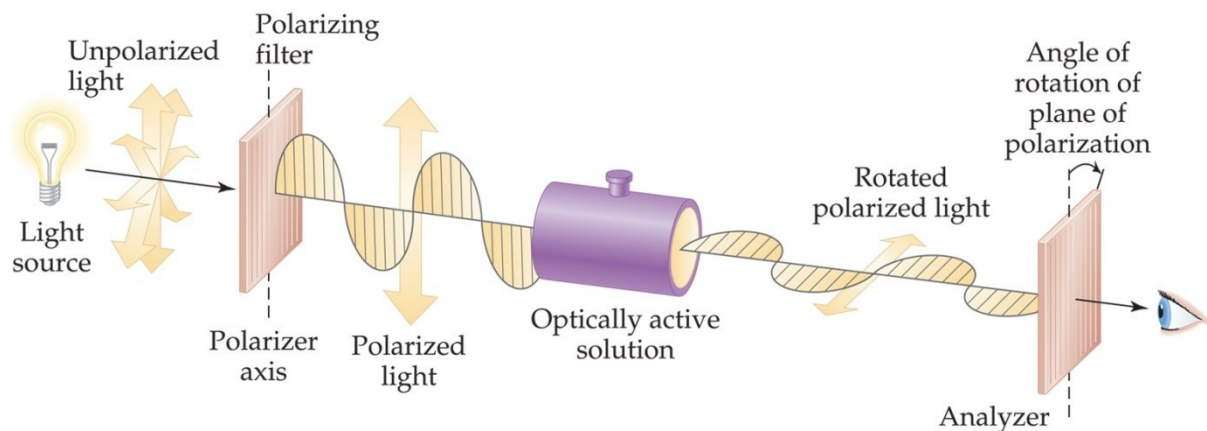
# Enantiomers

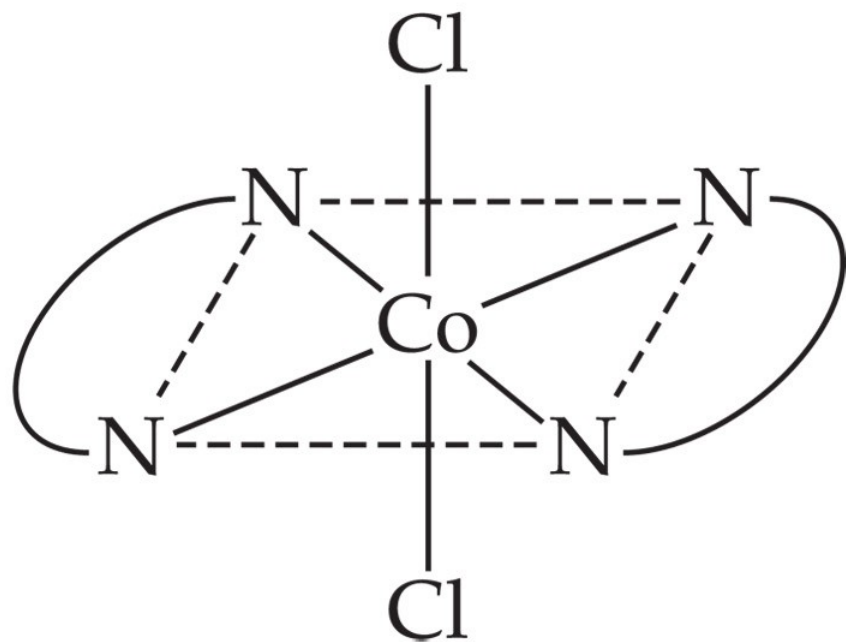
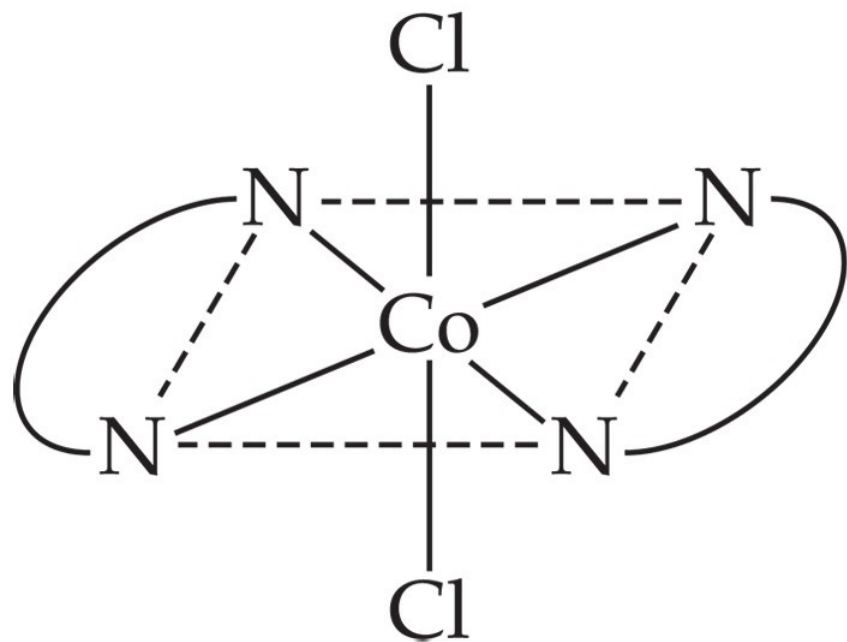
- Most of the physical properties of chiral molecules are the same, boiling point, freezing point, density, etc.
- One exception is the interaction of a chiral molecule with plane-polarized light.



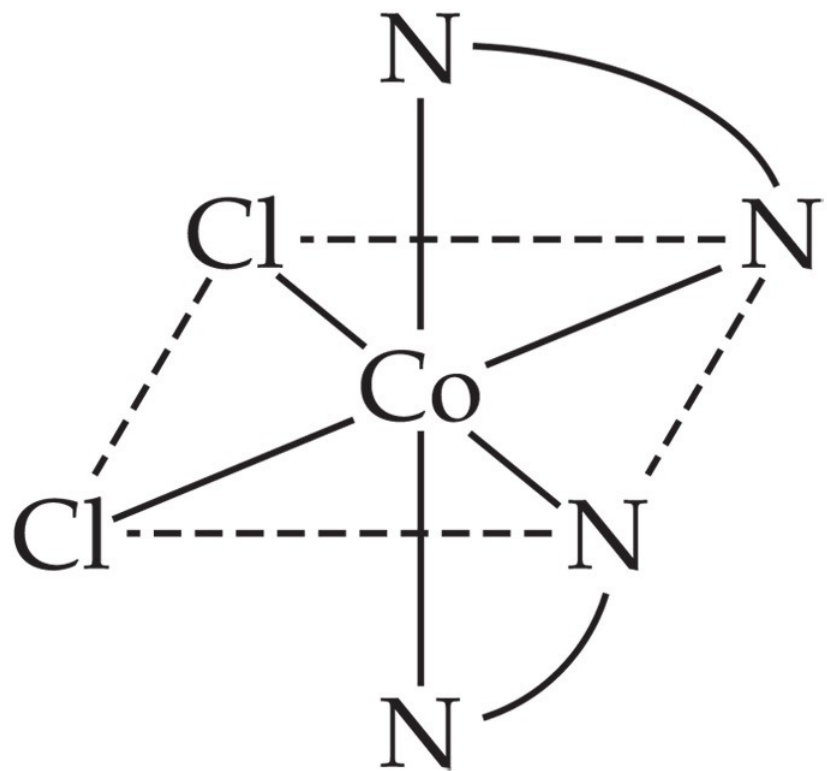
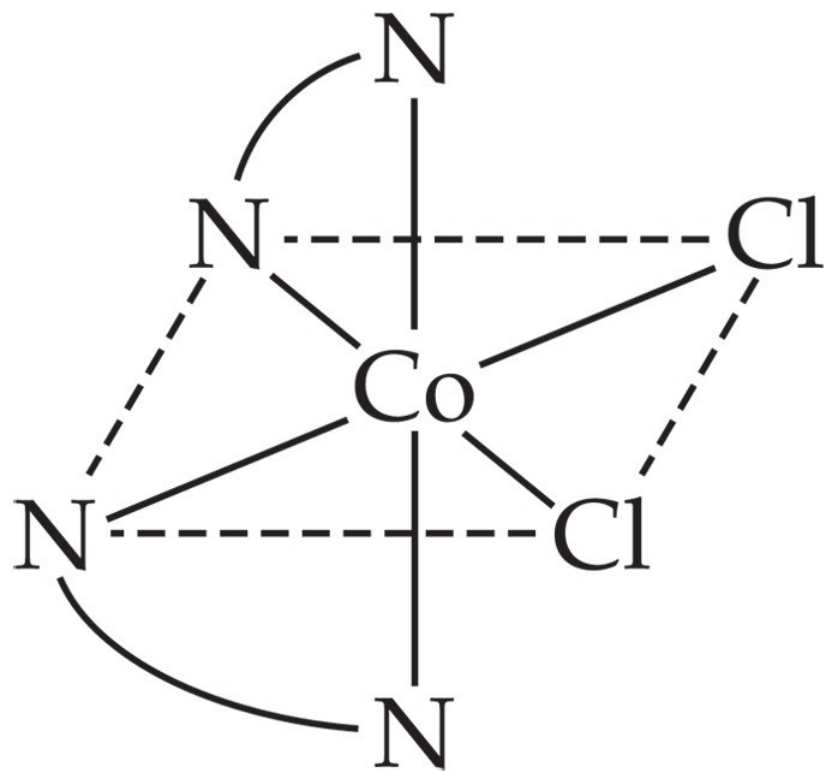
# Enantiomers

- If one enantiomer of a chiral compound is placed in a polarimeter and polarized light is shone through it, the plane of polarization of the light will rotate.
- If one enantiomer rotates the light  $32^\circ$  to the right, the other will rotate it  $32^\circ$  to the left.

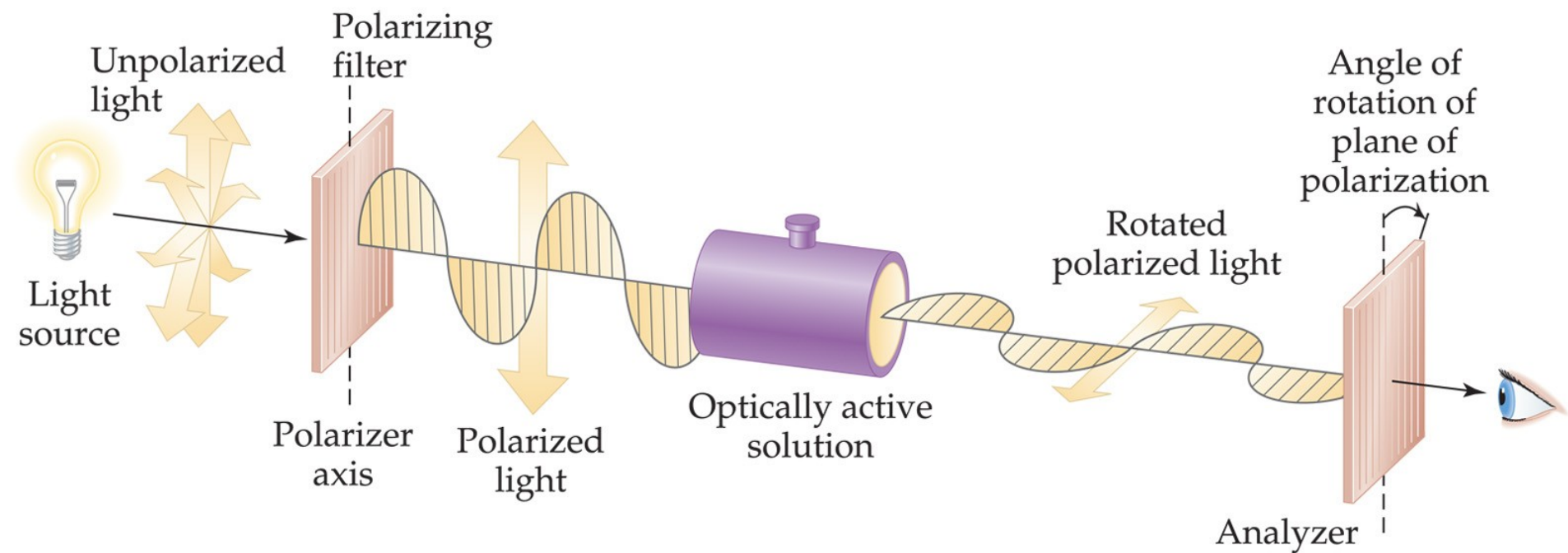




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# Explaining the properties of transition metal coordination complexes

1. Magnetism
2. color

# Metal complexes and color

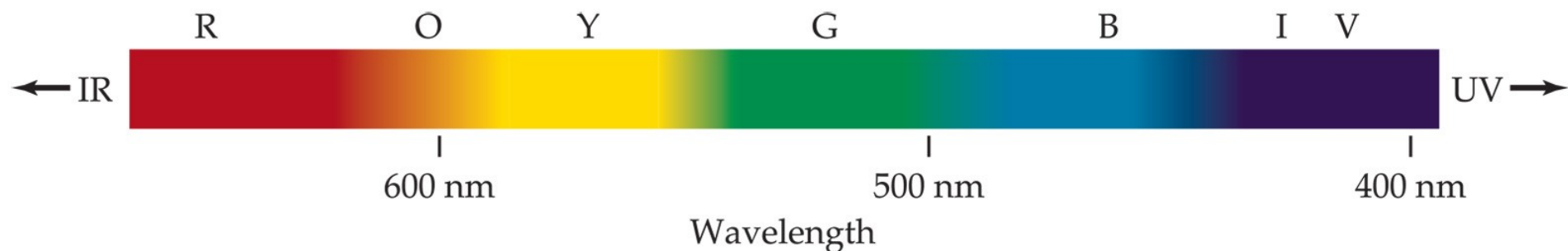
The ligands of a metal complex effect its color



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Addition of  $\text{NH}_3$  ligand to  $\text{Cu}(\text{H}_2\text{O})_4$  changes its color

# Why does anything have color?



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Light of different frequencies give different colors

We learned that elements can *emit* light of different frequency or color.

But these coordination complexes are not emitting light

They *absorb* light.

How does that give color?

Light can bounce off an object or get absorbed by object

No light absorbed, all reflected get **white** color  
All light absorbed, none reflected get **Black** color  
What if only one color is absorbed?

# Complimentary color wheel

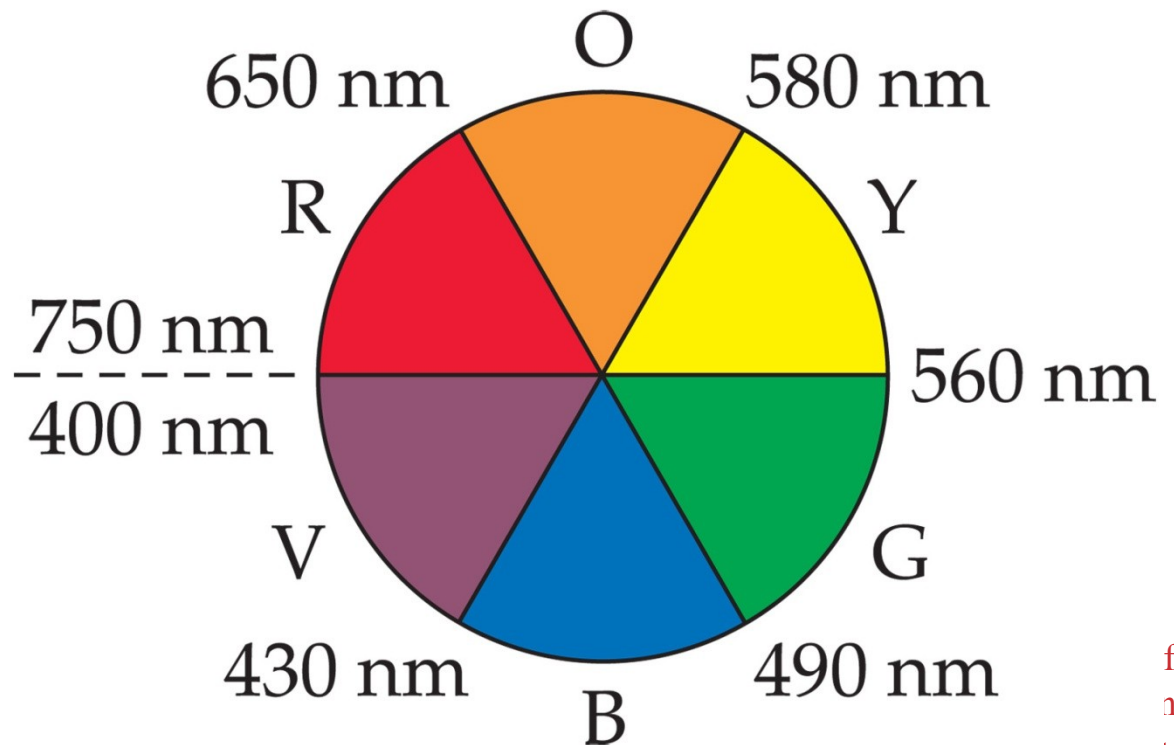
If one color absorbed, the color opposite is perceived.

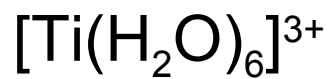
Absorb **Orange**

See **Blue**

Absorb **Red**

See **Green**



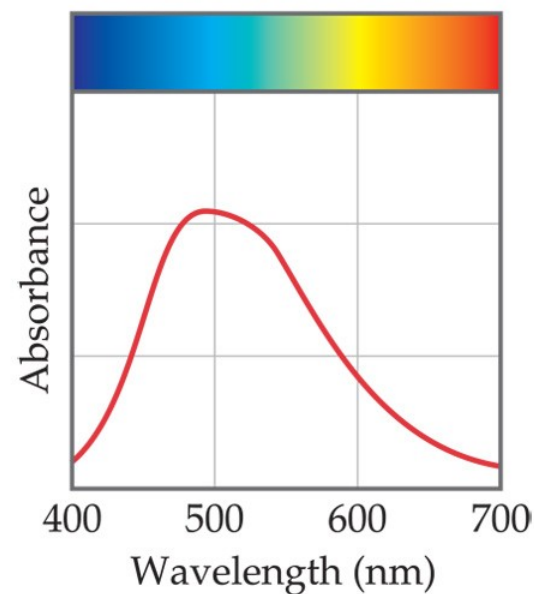


Absorbs in green yellow.

Looks purple.

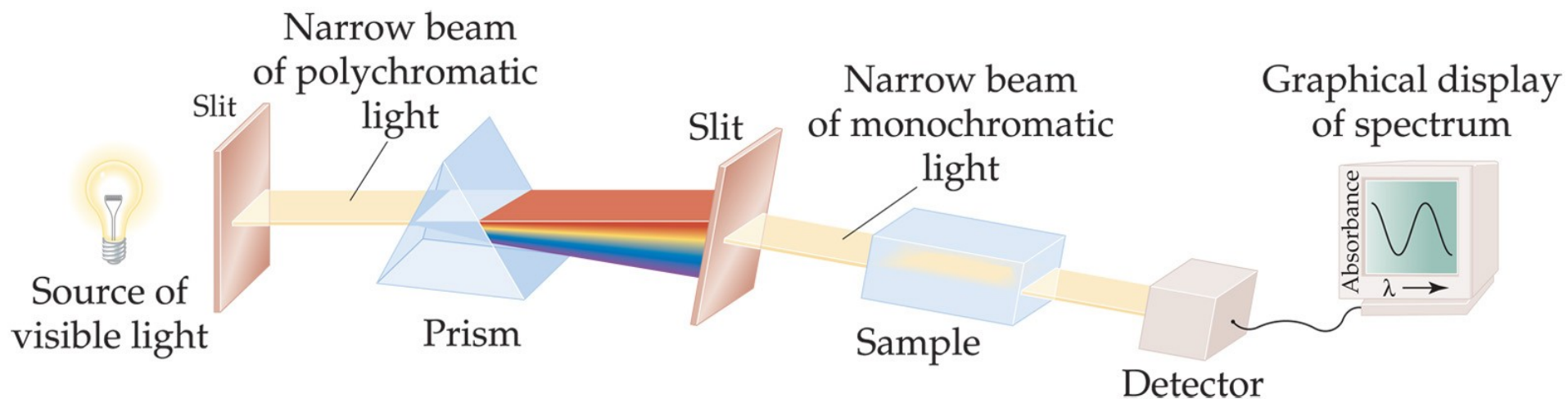


(a)



(b)

# A precise measurement of the absorption spectrum of Compounds is critical



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# Metal complexes and color

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

Why do different ligands change absorption?



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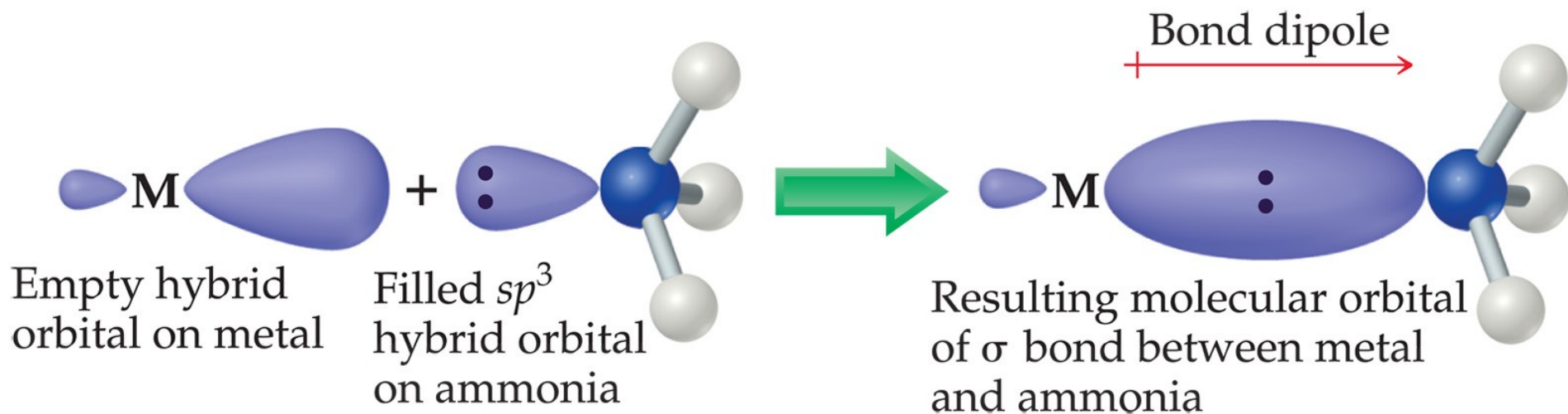
Addition of  $\text{NH}_3$  ligand to  $\text{Cu}(\text{H}_2\text{O})_4$  changes its color

Model of ligand/metal bonding.

Electron pair comes from ligand

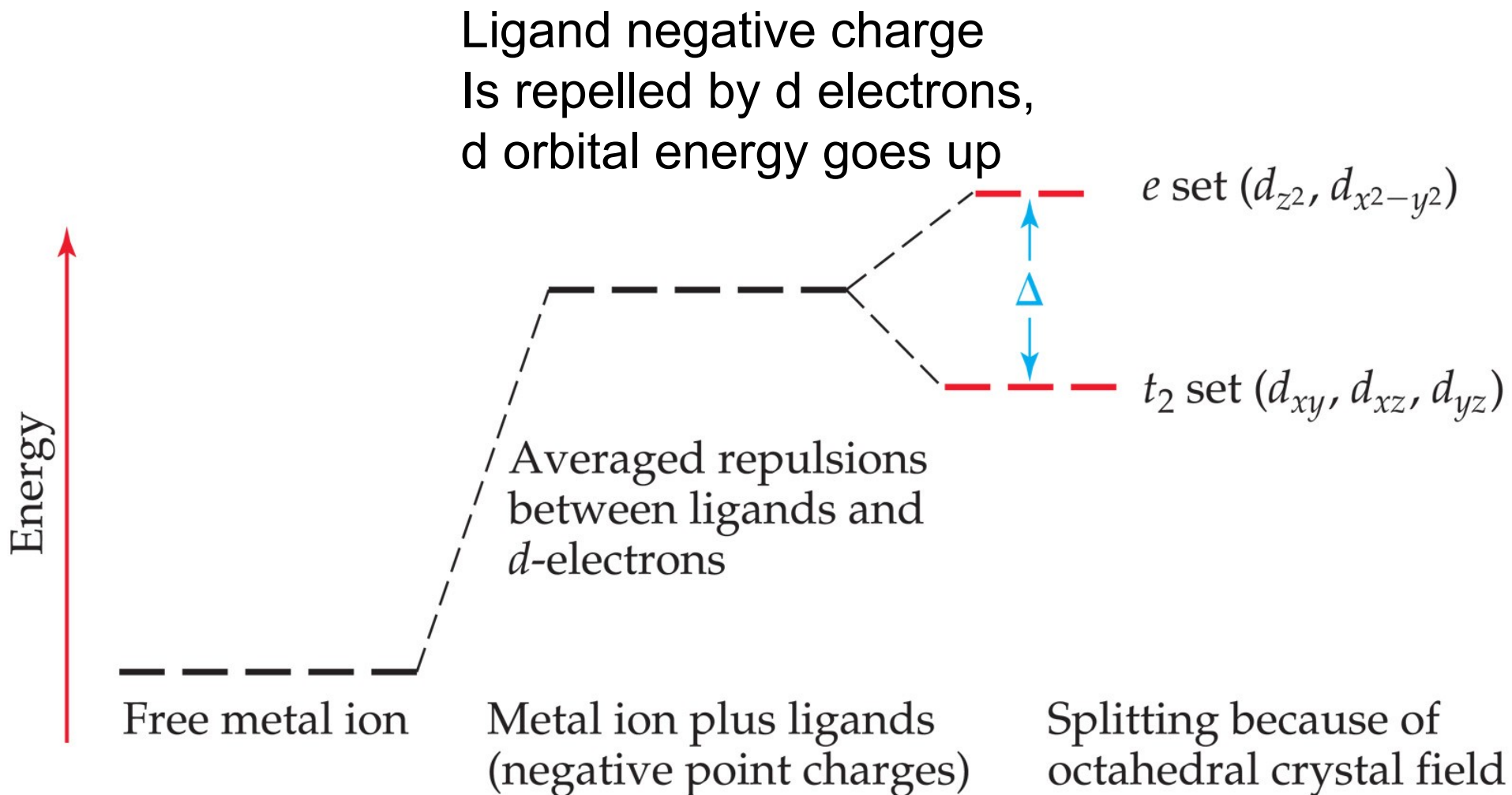
Bond very polarized.

**Assumption: interaction pure electrostatic.**



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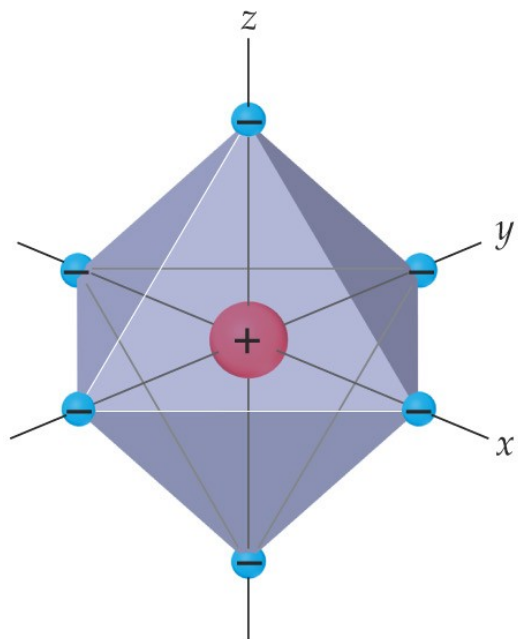
Now, think of point charges being attracted to metal nucleus  
Positive charge. What about electrons in d orbitals?



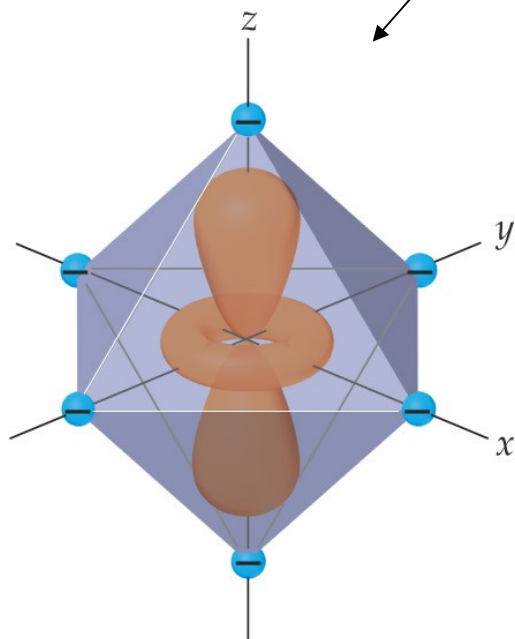
Ligands will interact with some d orbitals more than others

Depends on relative orientation of orbital and ligand

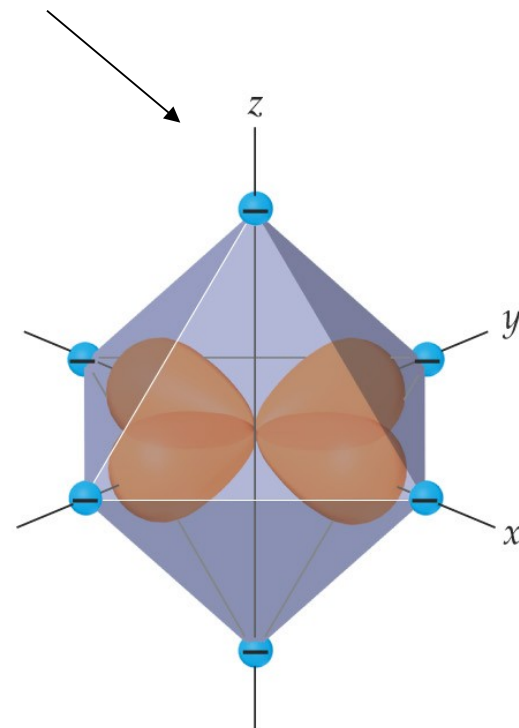
Ligands point right at lobes



(a)

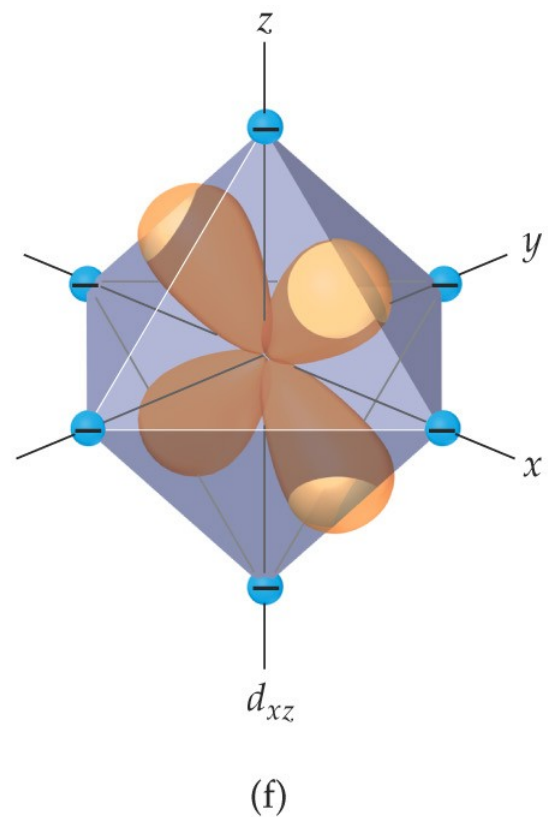
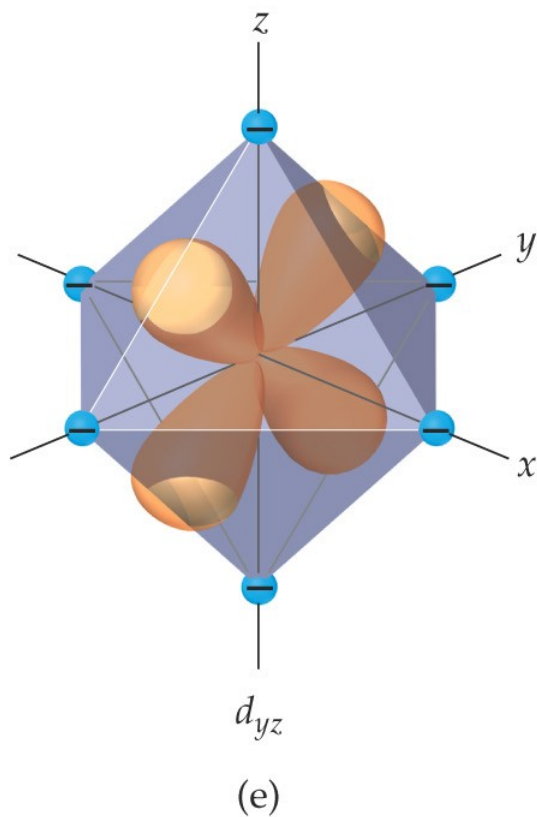
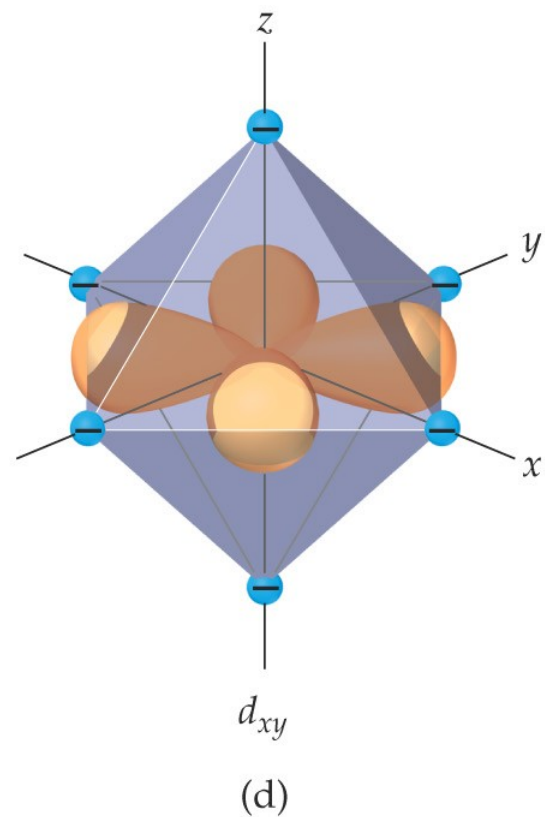


(b)

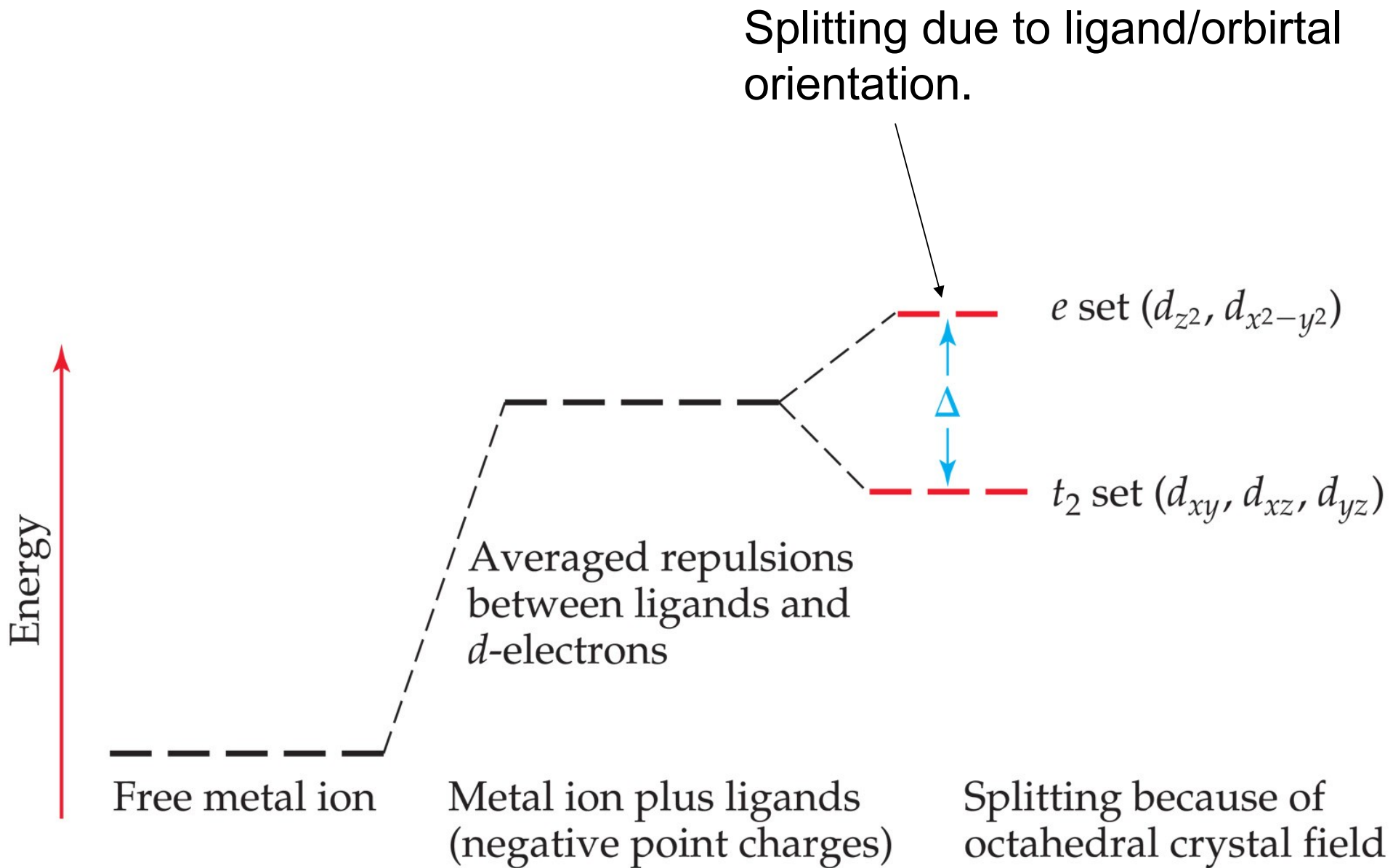


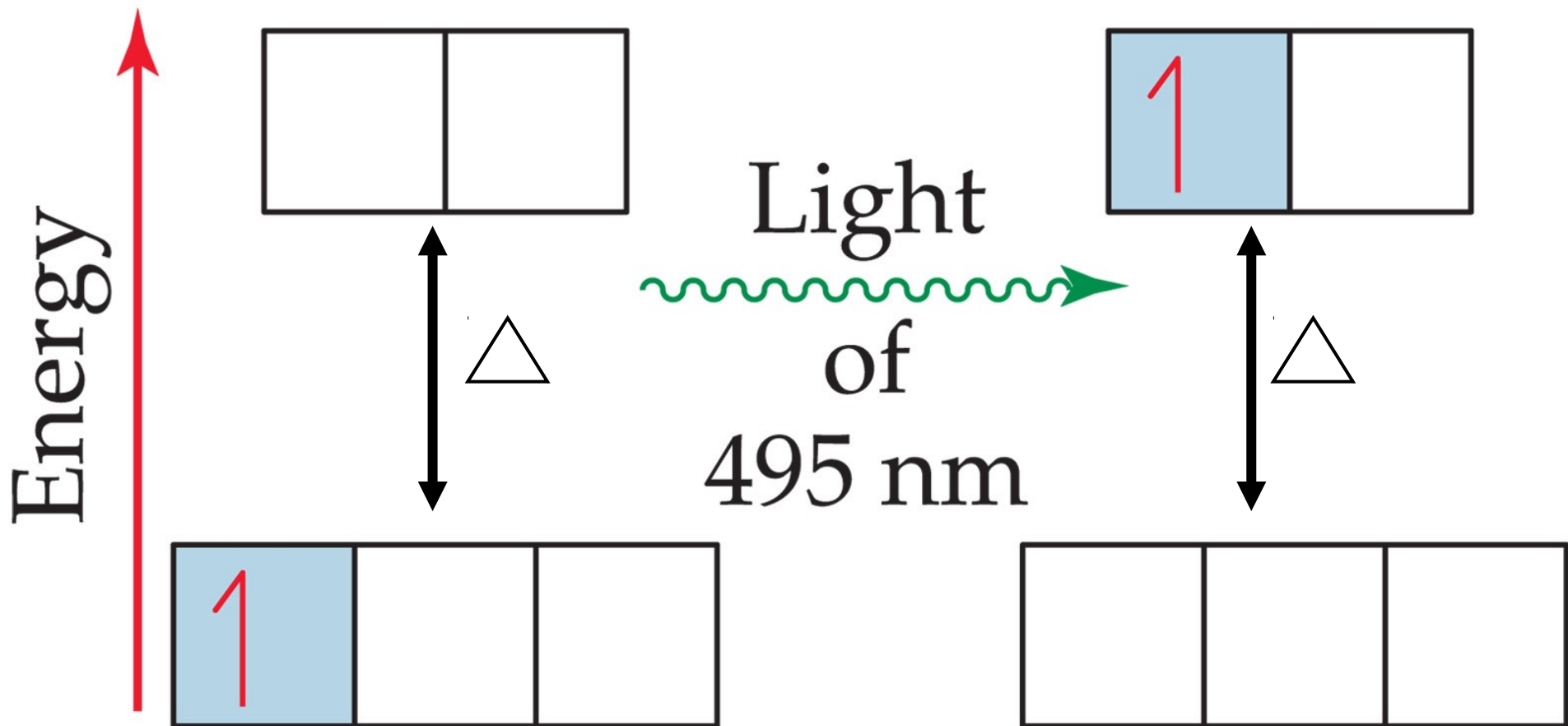
(c)

In these orbitals, the ligands are between the lobes  
Interact less strongly



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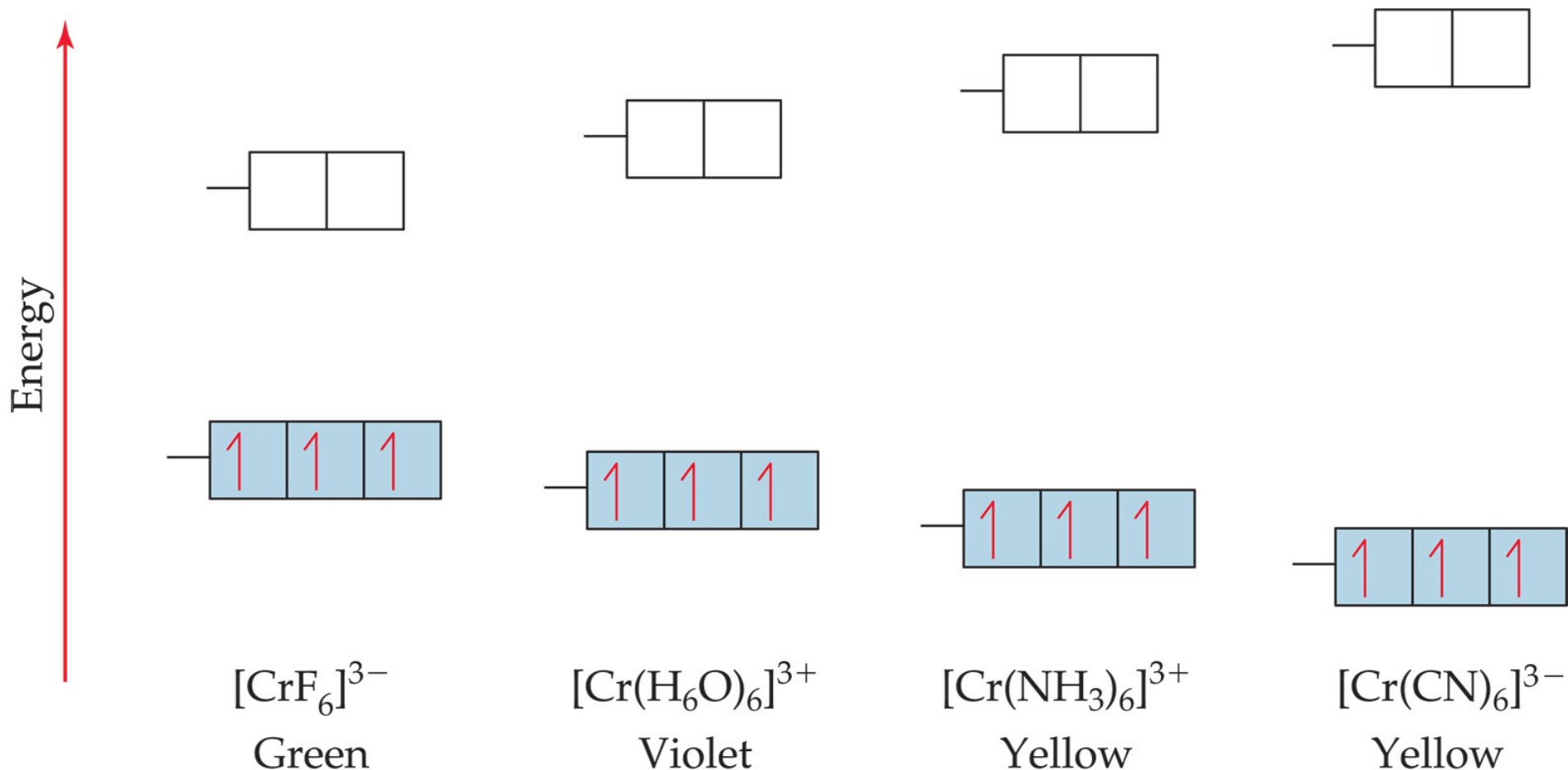




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$$\Delta = 495 \text{ nm}$$

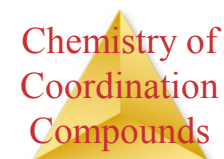
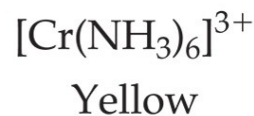
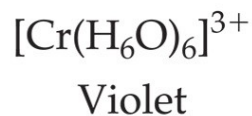
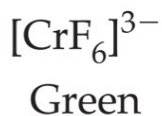
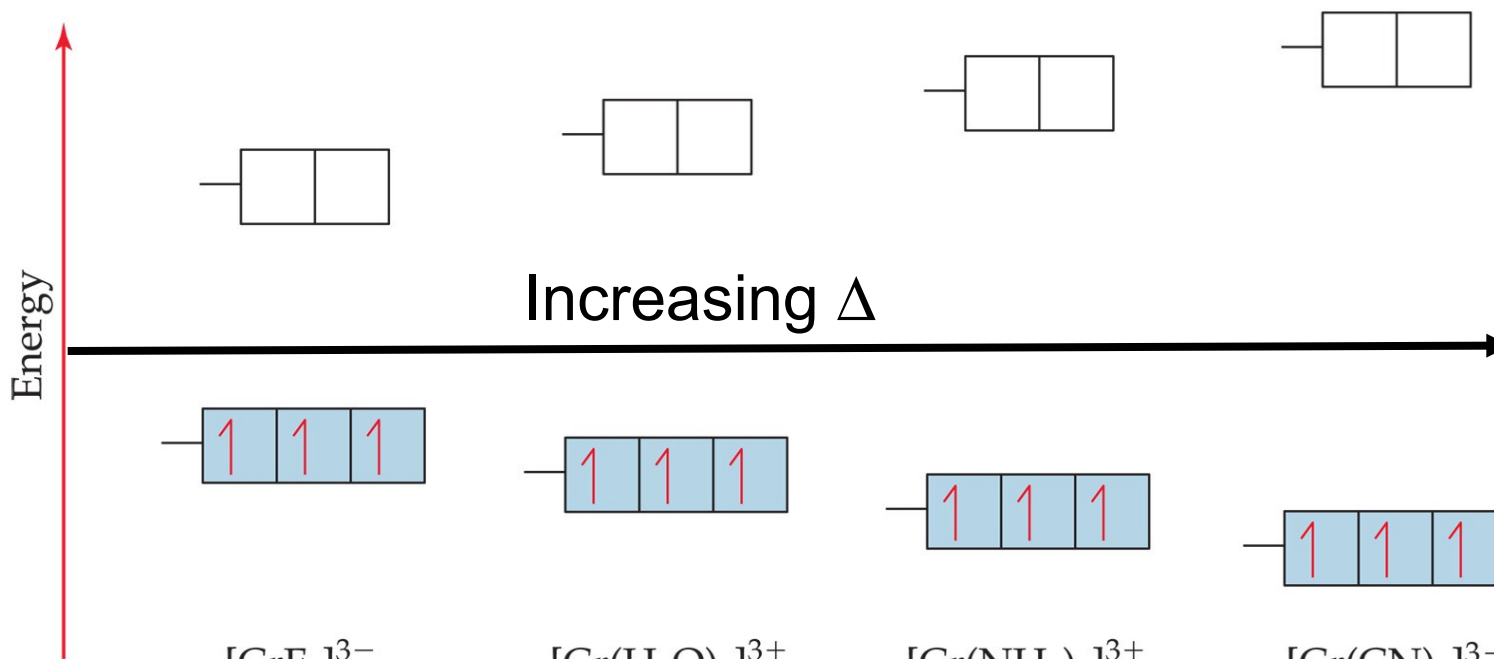
Different ligands interact more or less, change E spacing  
Of D orbitals.



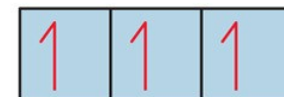
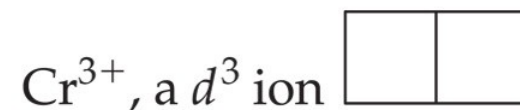
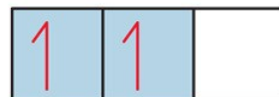
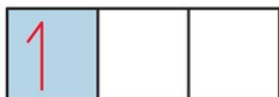
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# Spectrochemical series (strength of ligand interaction)

Increasing  $\Delta$

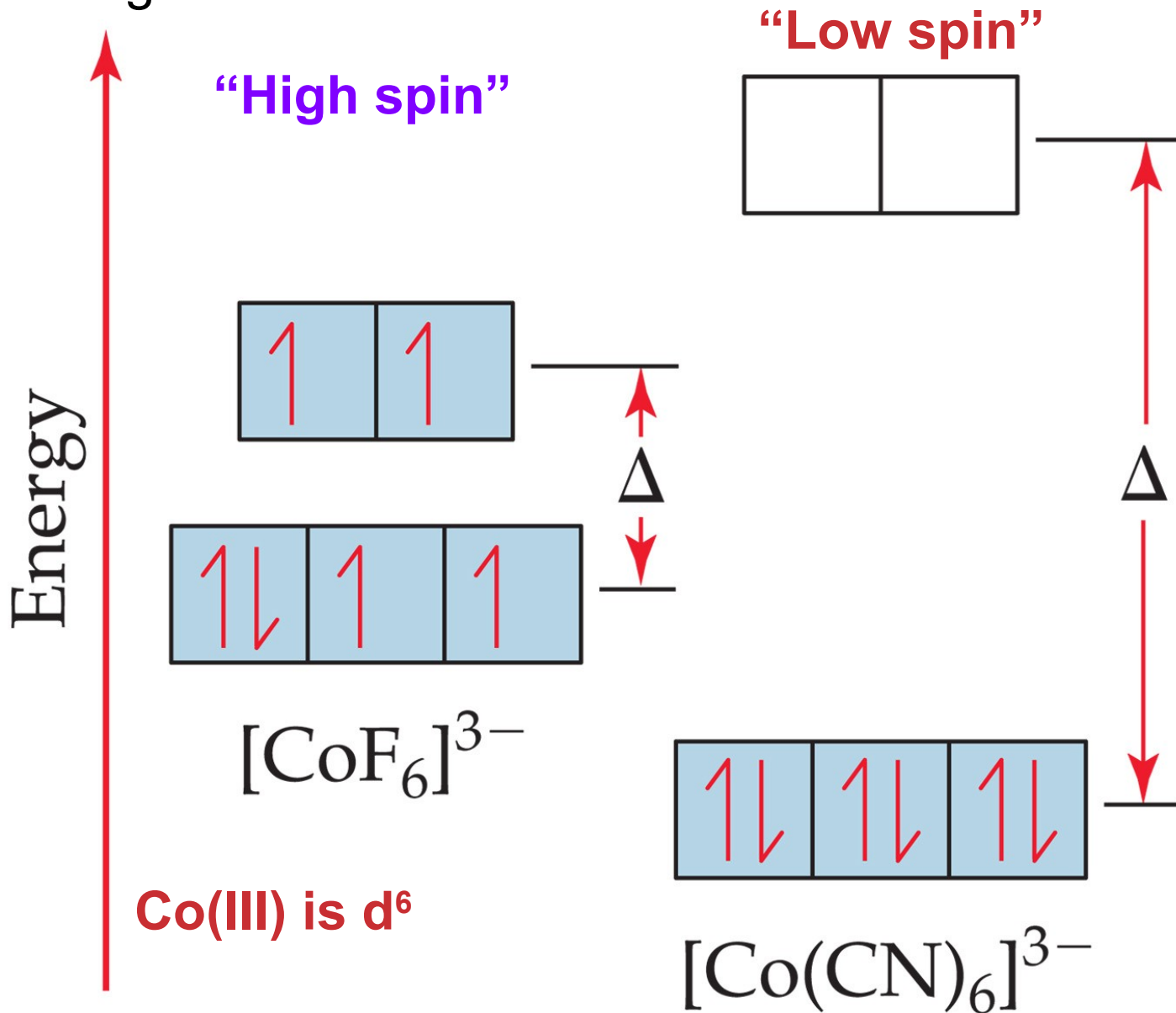


# Electron configurations of some octahedral complexes



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As Energy difference increases, electron configuration changes





High spin

Low spin

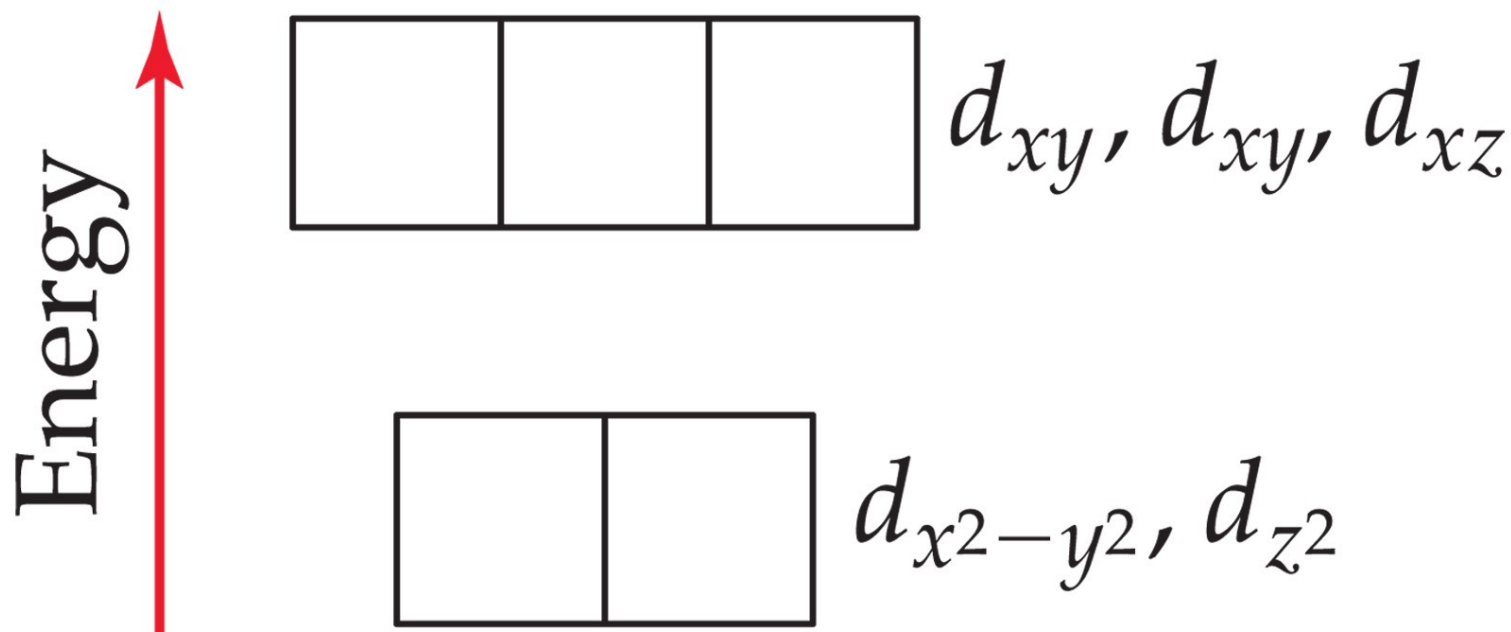


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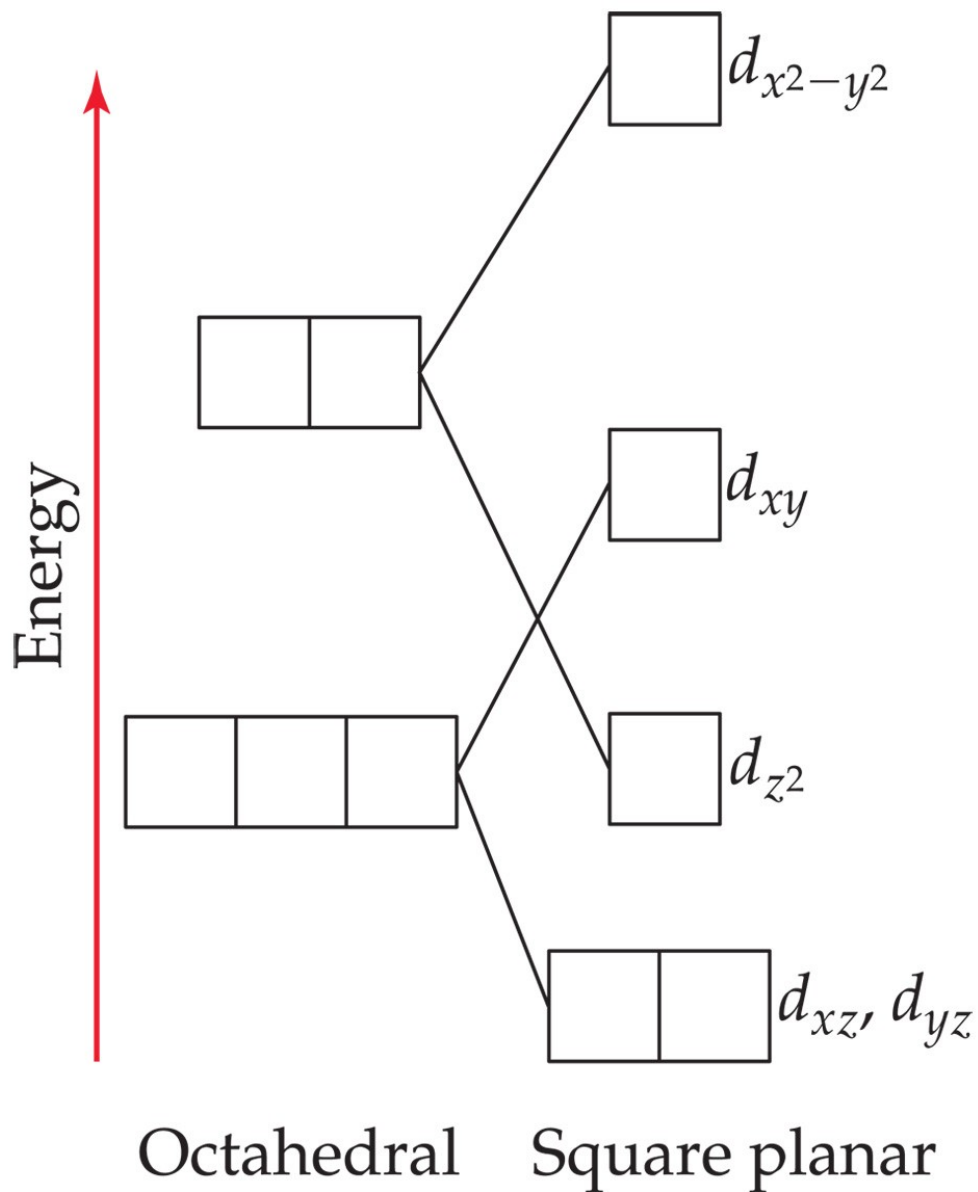
# Tetrahedral Complexes

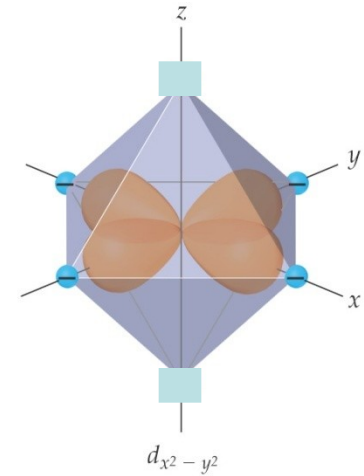
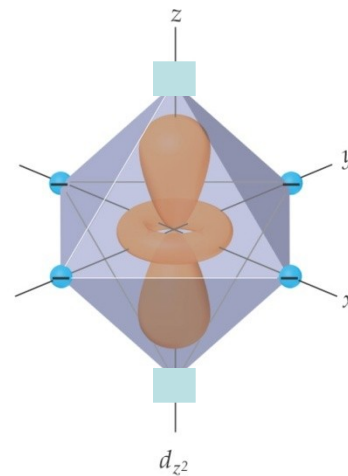
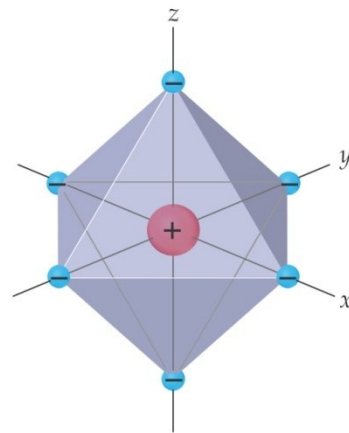
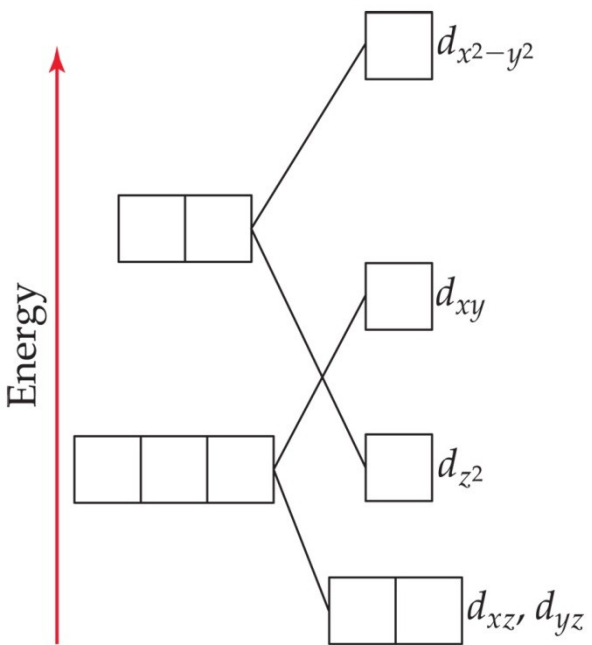
In tetrahedral complexes, orbitals are inverted.  
Again because of orientation of orbitals and ligands

**$\Delta$  is always small, always low spin (less ligands)**



# Square planar complexes are different still

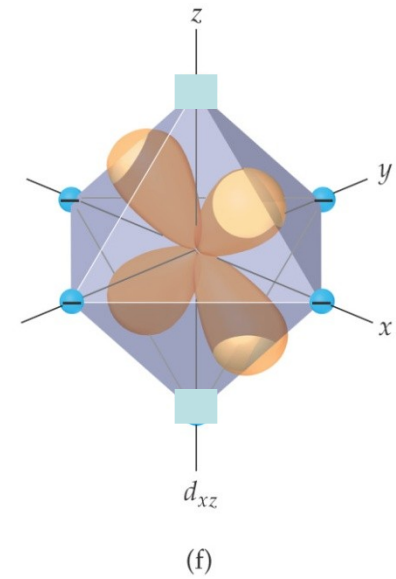
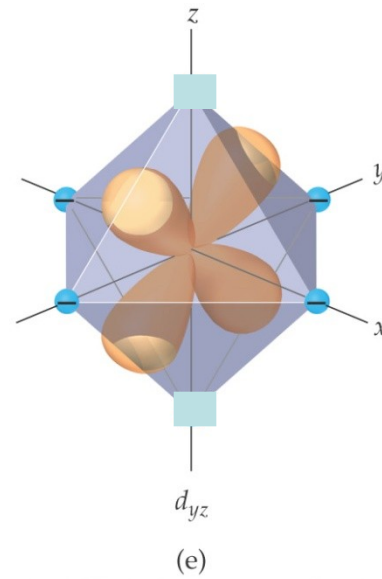
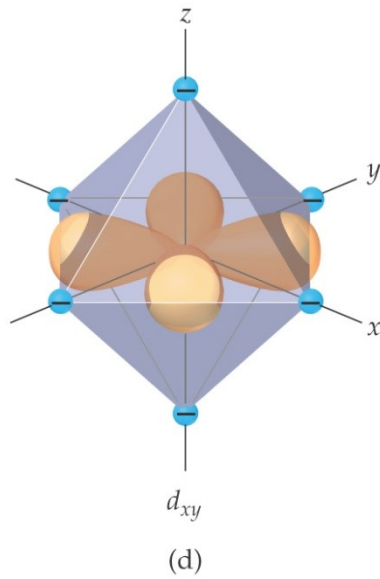




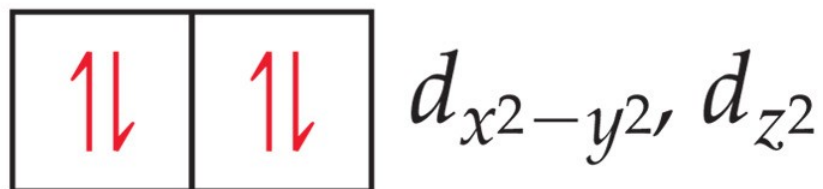
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### Octahedral Square planar

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Tetrahedral

Square planar

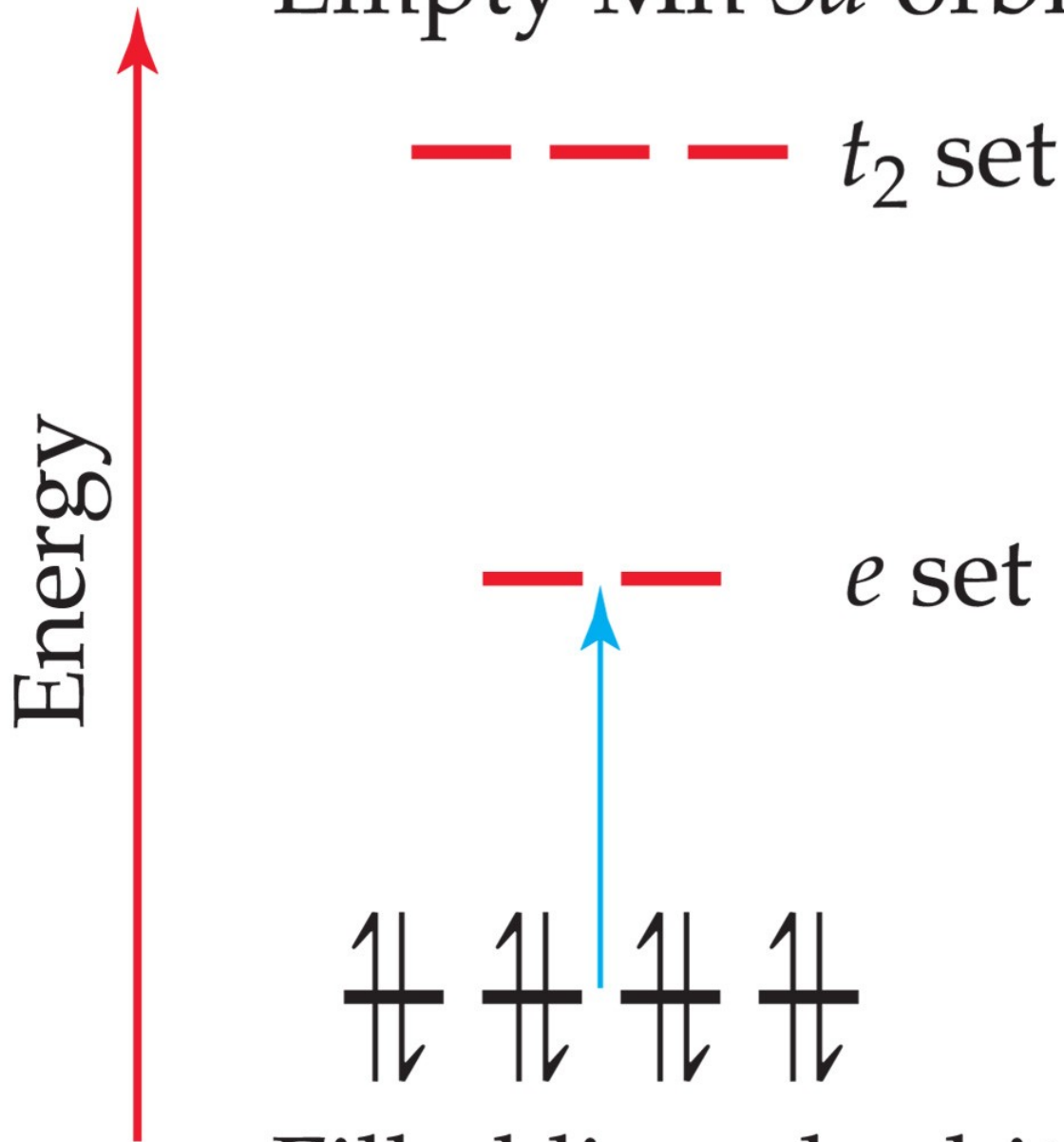
Intense color can come from “charge transfer”  
Ligand electrons jump to metal orbitals



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No d orbitals in  
Cl, orbitals higher  
In energy

# Empty Mn 3d orbitals



Filled ligand orbitals

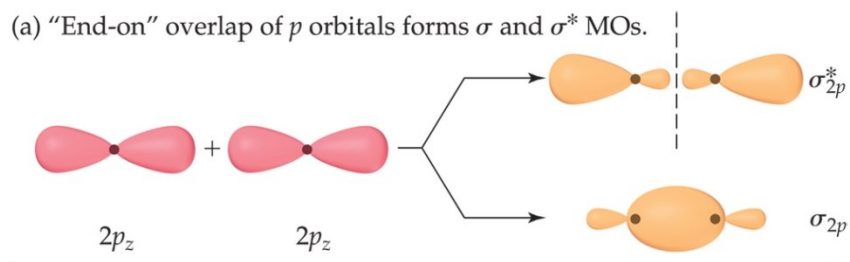
# MO theory for coordination compounds

## MO theory: Rules:

- 1. The number of MO's equals the # of Atomic orbitals
- 2. The overlap of two atomic orbitals gives two molecular orbitals, 1 bonding, one antibonding
- 3. Atomic orbitals combine with other atomic orbitals of *similar energy*.
- 4. Degree of overlap matters. More overlap means bonding orbital goes *lower* in E, antibonding orbital goes *higher* in E.
- 5. Each MO gets two electrons
- 6. Orbitals of the *same energy* get filled 1 electron at a time until they are filled.

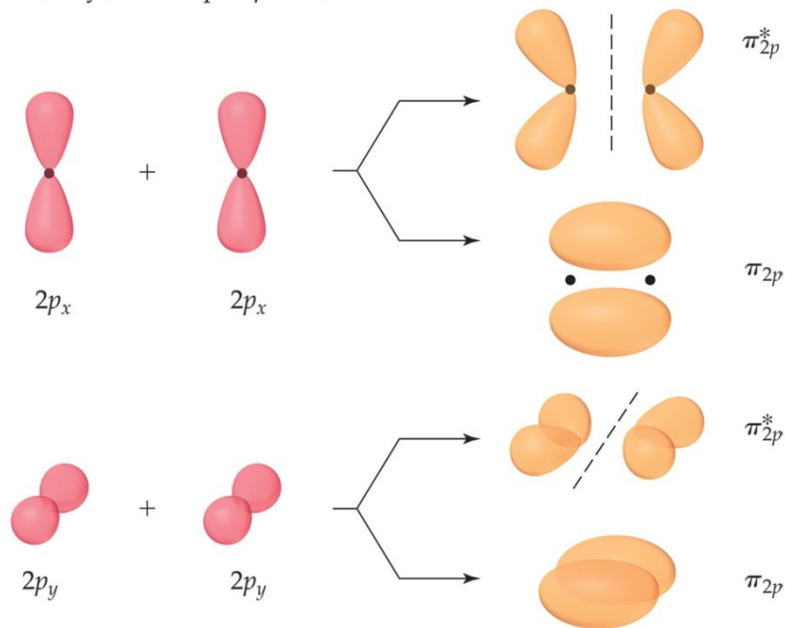
# Difference between pi and sigma orbitals

(a) "End-on" overlap of  $p$  orbitals forms  $\sigma$  and  $\sigma^*$  MOs.



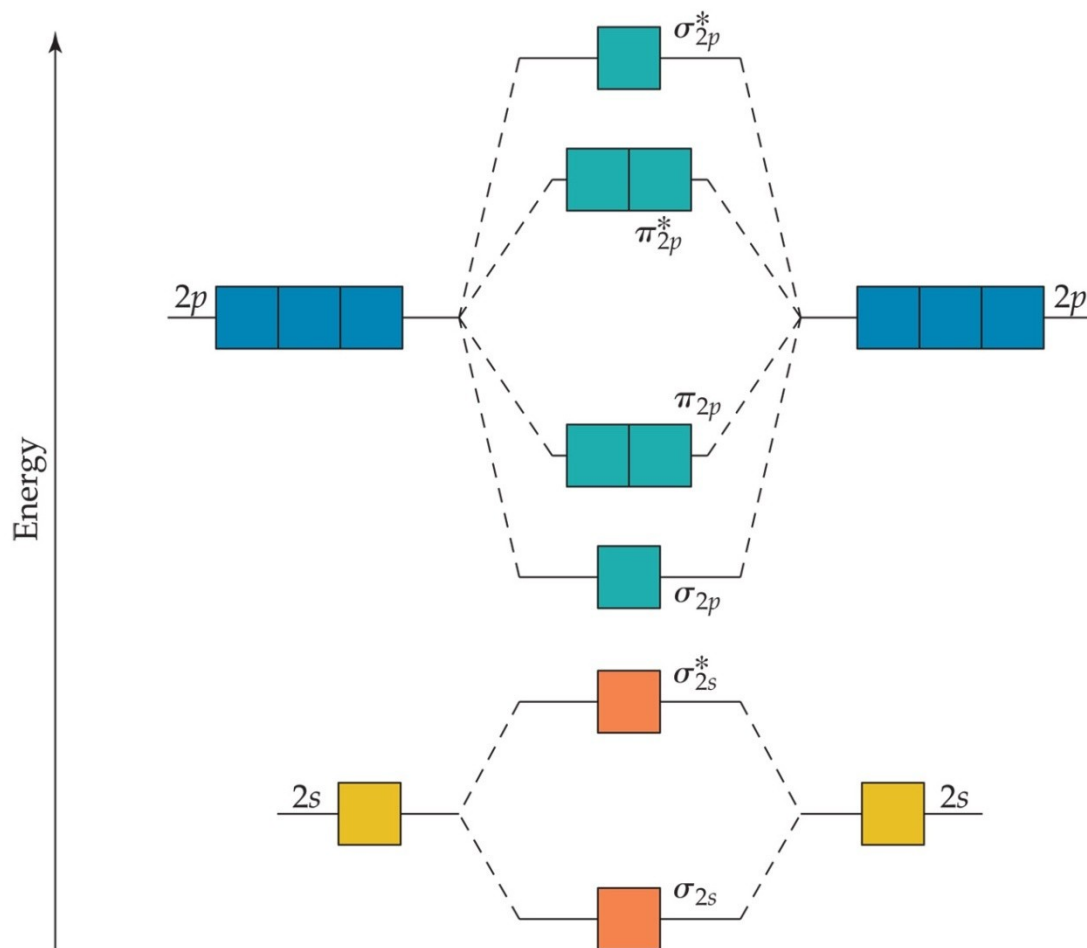
End on

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

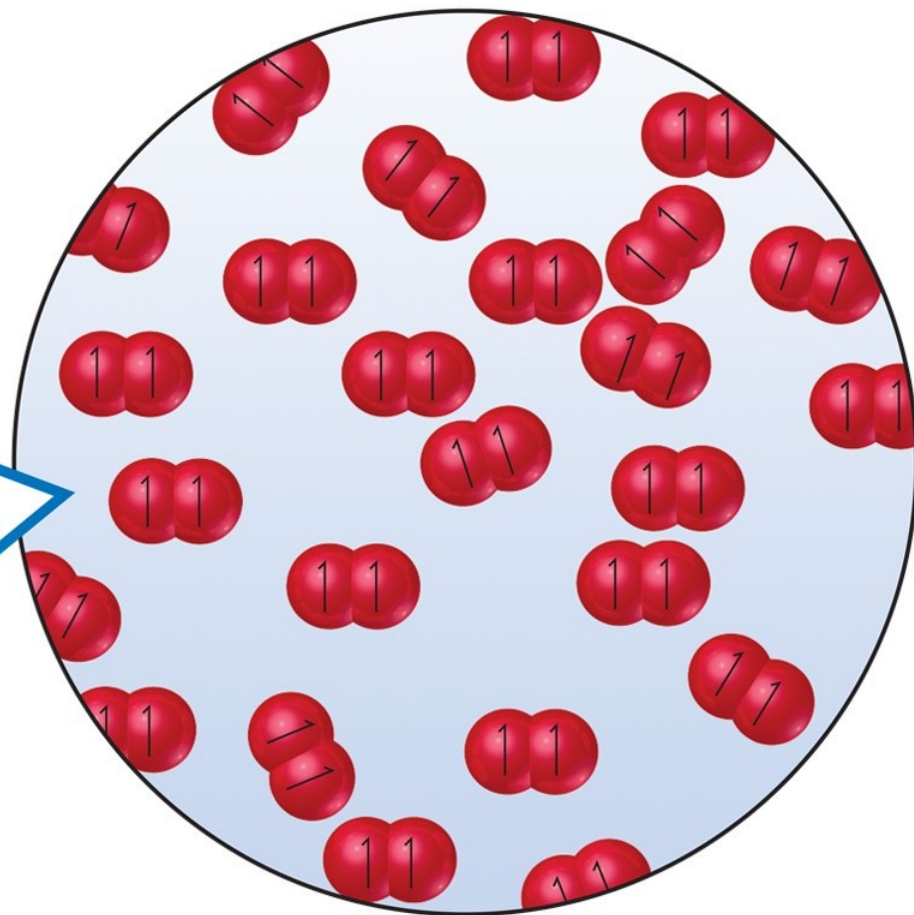


Side to side.

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



# Oxygen $O_2$ is Paramagnetic, why?



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# Show me why.

	Large 2s-2p interaction			Small 2s-2p interaction		
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
$\sigma_{2p}^*$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox" value="1↓"/>
$\pi_{2p}^*$	<input type="checkbox" value="1"/> <input type="checkbox"/>	<input type="checkbox" value="1"/> <input type="checkbox"/>	<input type="checkbox" value="1"/> <input type="checkbox" value="1"/>	<input type="checkbox" value="1"/> <input type="checkbox" value="1"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>
$\sigma_{2p}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>
$\pi_{2p}$	<input type="checkbox" value="1"/> <input type="checkbox" value="1"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/> <input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>
$\sigma_{2s}^*$	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>
$\sigma_{2s}$	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>	<input type="checkbox" value="1↓"/>
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

# For exam concentrate on these topics more

Concentrate on the homeworks and the quiz!

Terms:

1. Coordination sphere
2. Ligand
3. Coordination compound
4. Metal complex
5. Complex ion
6. Coordination
7. Coordination number

Same ligands different properties?

Figuring oxidation number on metal

Polydentate ligands (what are they)?

Isomers.

structural isomers (formula same, bonds differ)

geometric isomers (formula AND bonds same,  
structure differs)

Stereoisomers:

Chirality, handedness,

**Isomers**  
(same formula, different properties)

**Structural isomers**  
(different bonds)

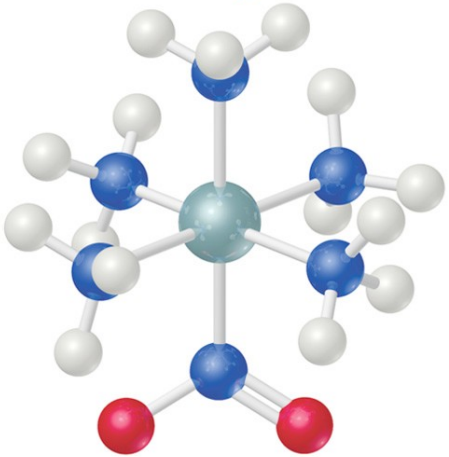
**Stereoisomers**  
(same bonds, different arrangements)

**Coordination-  
sphere isomers**

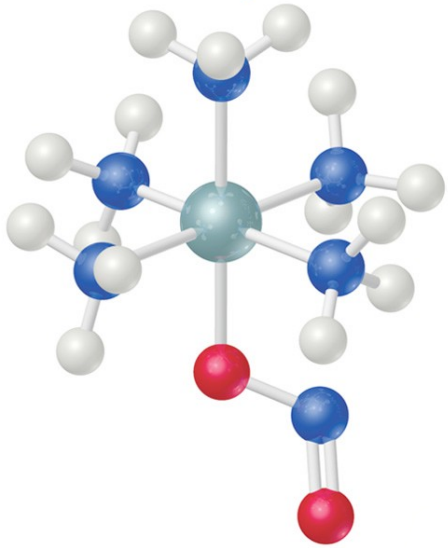
**Linkage  
isomers**

**Geometric  
isomers**

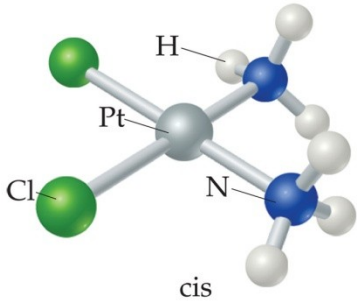
**Optical  
isomers**



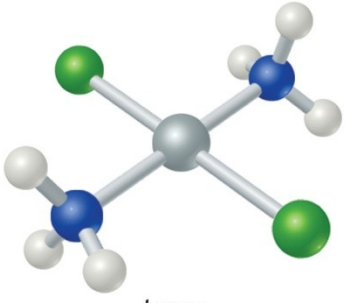
Nitro isomer



Nitrito isomer

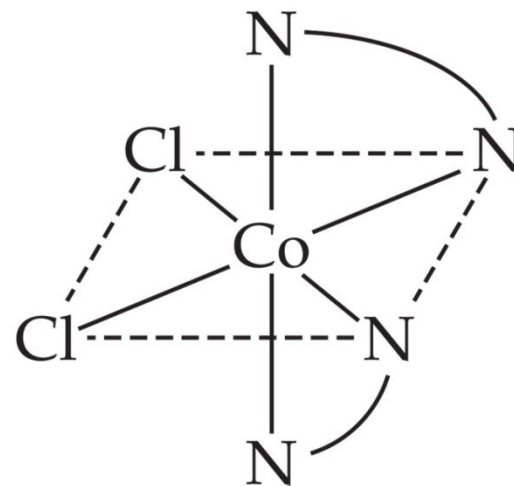
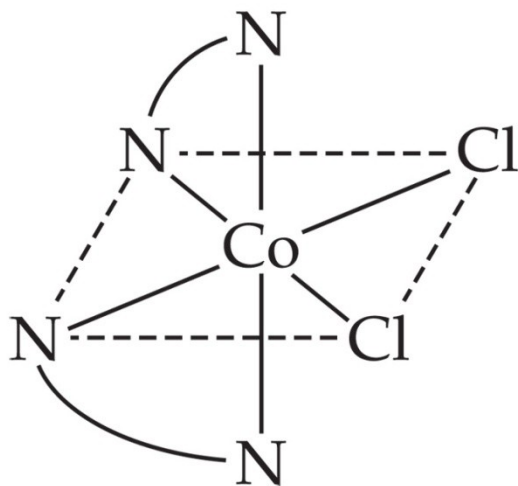
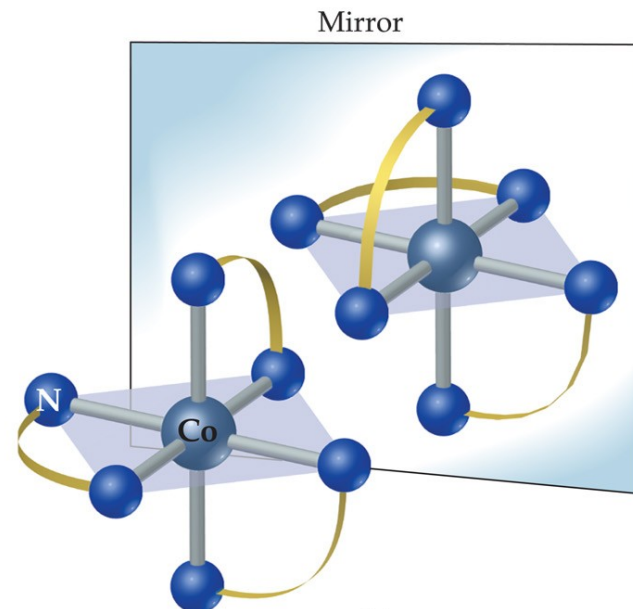
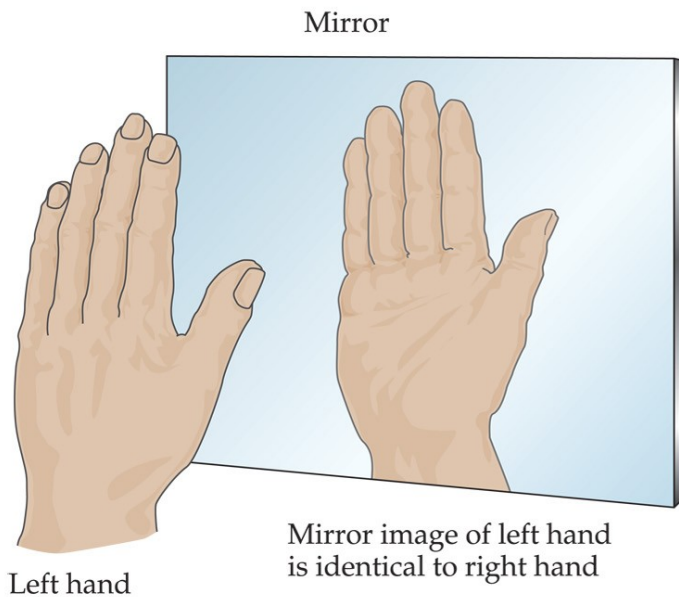


cis



trans

# Stereoisomers



# Explaining the properties of metal complexes

Magnetism and color

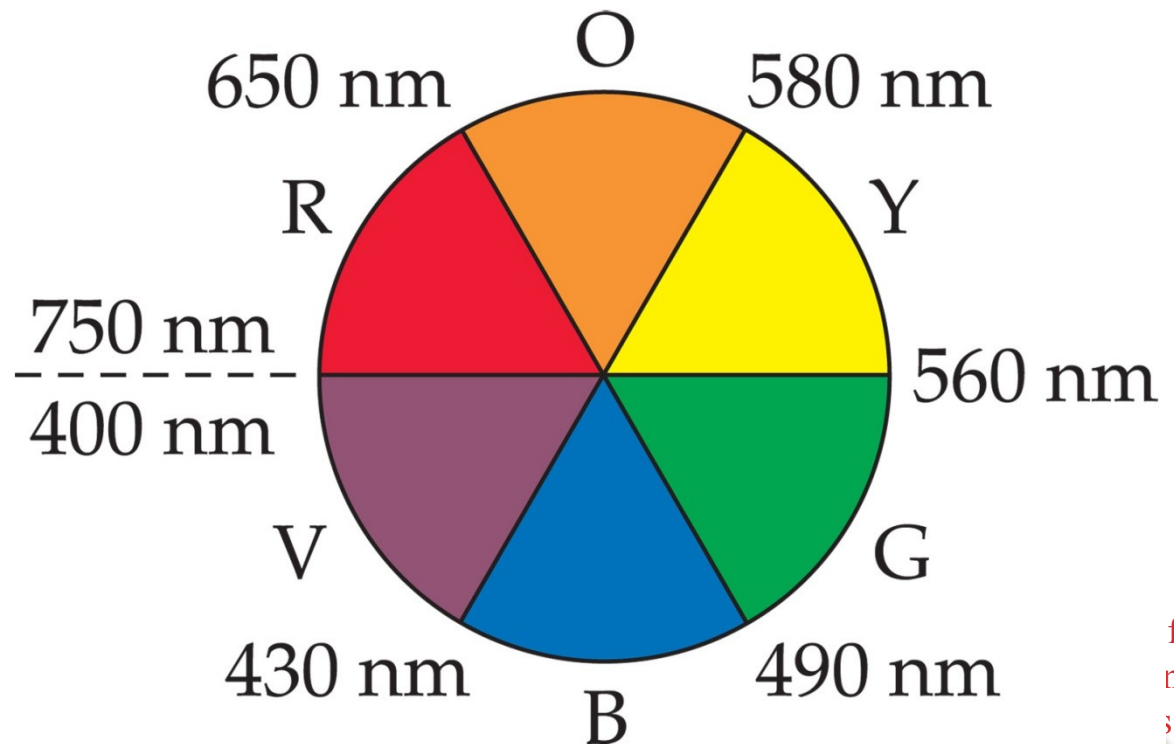
How does seeing color work?

Absorb **Orange**

See **Blue**

Absorb **Red**

See **Green**



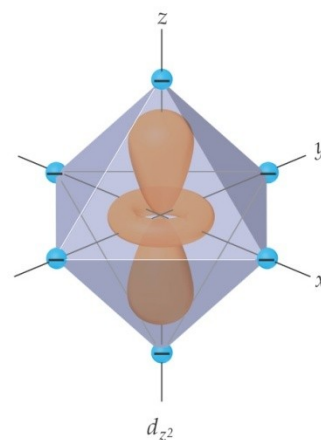
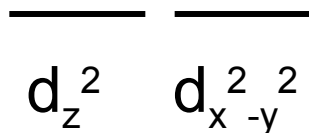
Different ligands on same metal give different colors



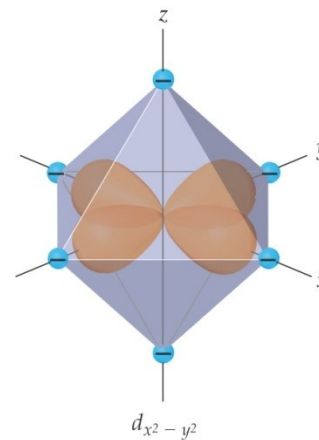
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**Addition of  $\text{NH}_3$  ligand to  $\text{Cu}(\text{H}_2\text{O})_4$  changes its color**

# Splitting of d orbitals in an octahedral ligand field

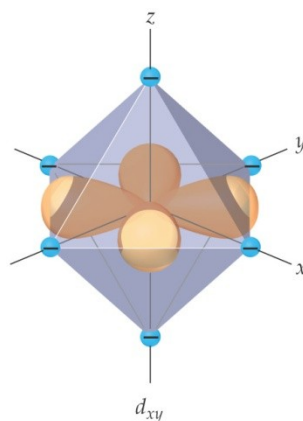
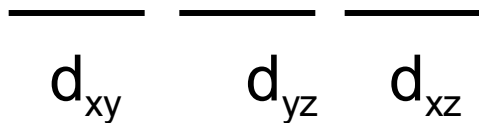


(b)

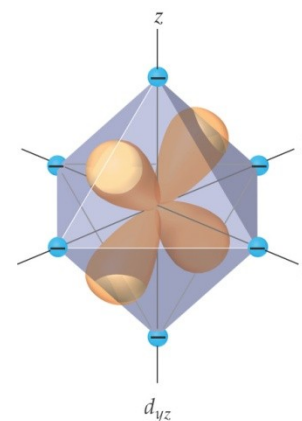


(c)

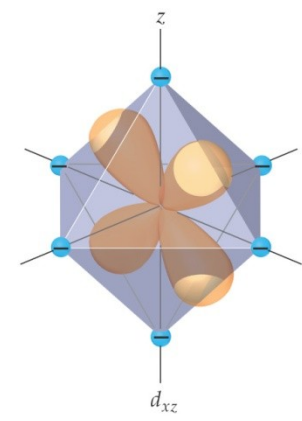
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(d)



(e)

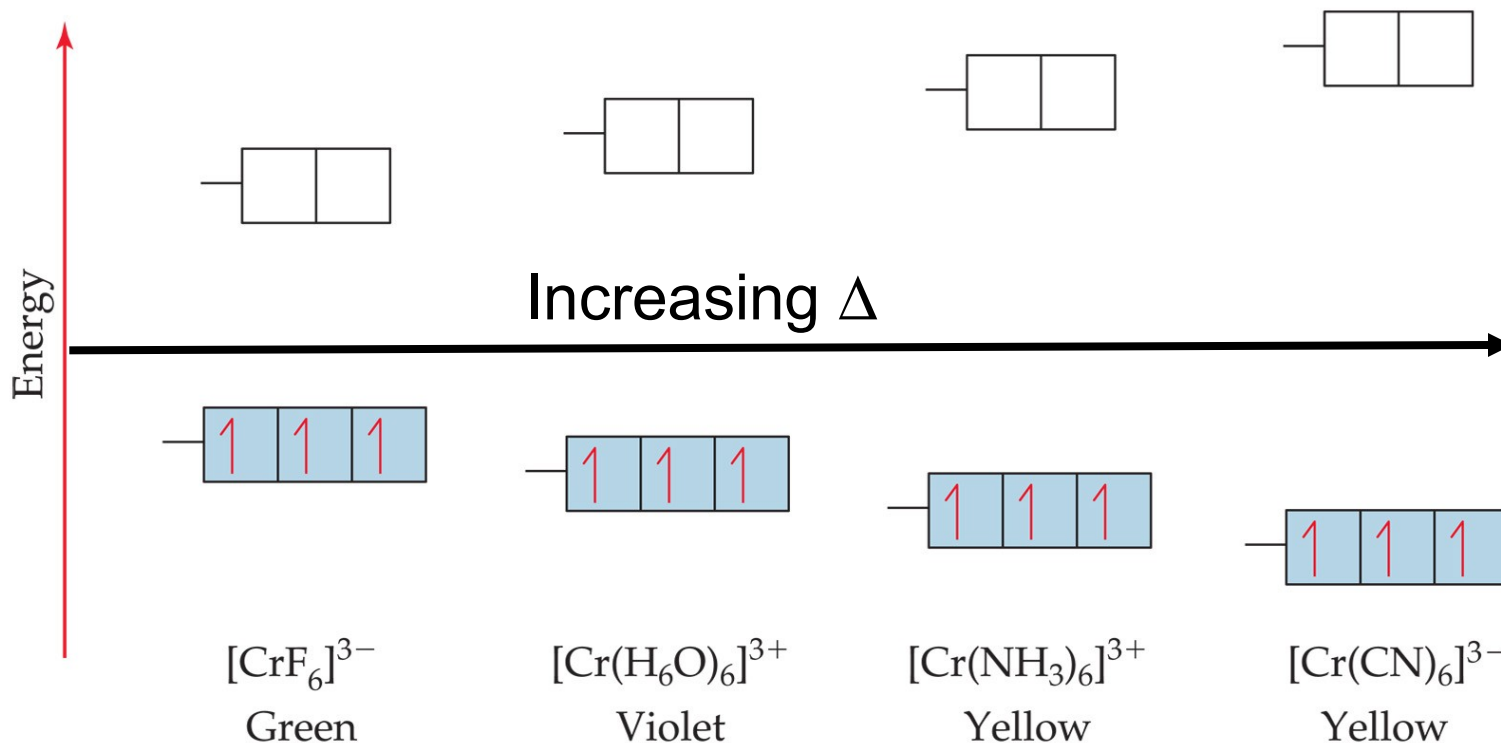


(f)

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# Spectrochemical series (strength of ligand interaction)

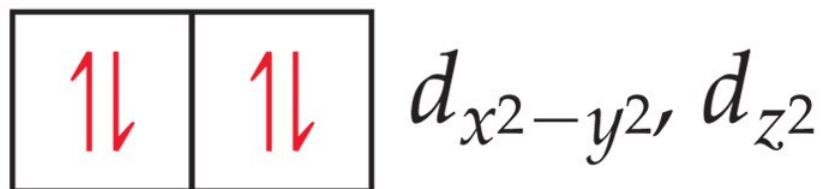
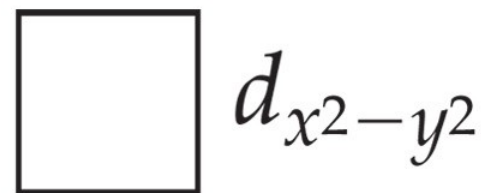
Increasing  $\Delta$



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Know low spin versus high spin

There is also splitting from tetrahedral  
 And square planar. Know they are  
 different, don't remember exactly what  
 they are like.



Tetrahedral

Square planar



*Rawat's Creation-*  
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[rwtdgreat@yahoo.co.uk](mailto:rwtdgreat@yahoo.co.uk)

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**@RawatDAgreatt**

**+919808050301**

**+919958249693**

Thank You!  
😊

