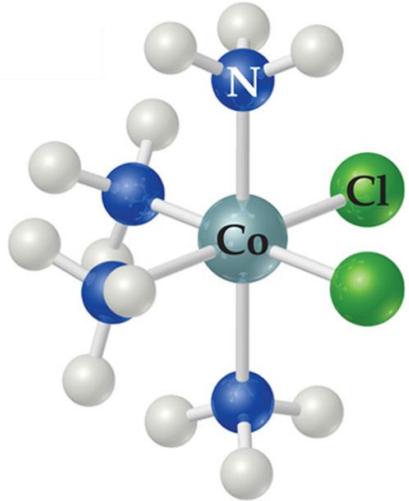


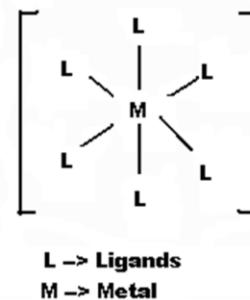
# Bonding in coordination compounds

Nobel prize 1913

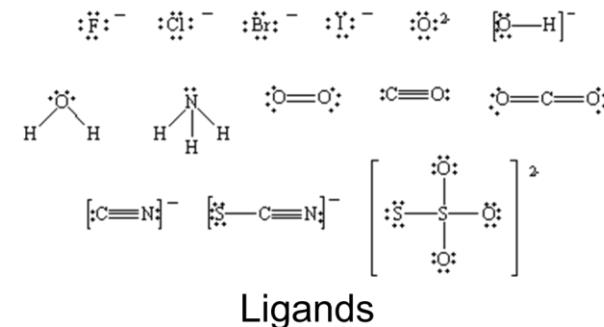


Central metal atom (or ion) bonded to one or more *ligands*.

Ligands:

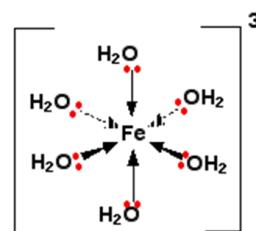


L → Ligands  
M → Metal

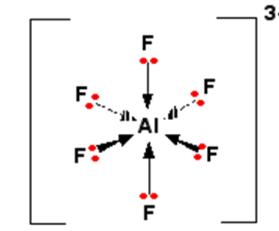


Ligands

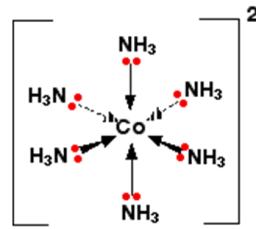
metal & ligand complexes as ions:



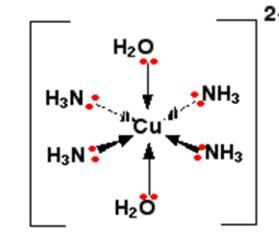
[Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>



[AlF<sub>6</sub>]<sup>3-</sup>



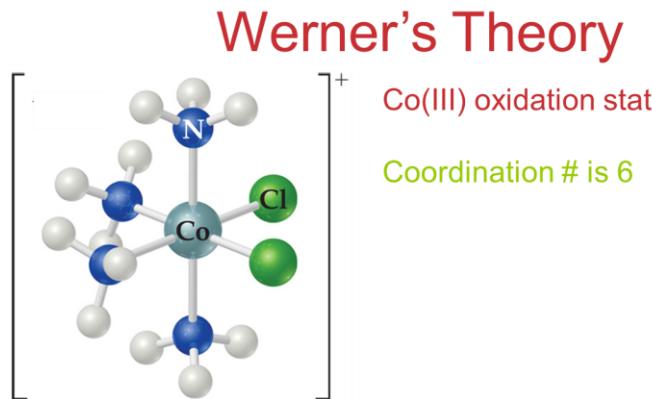
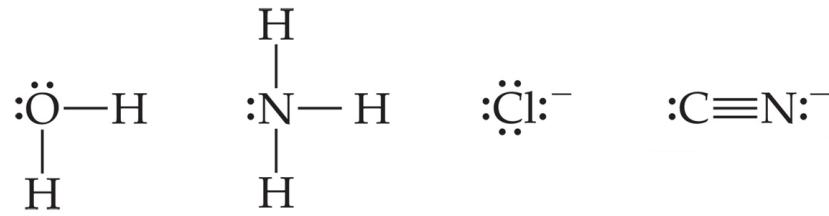
[Co(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>



[Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>

- 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.

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



- 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)

## A chemical mystery: Same metal, same ligands, different number of ions when dissolved

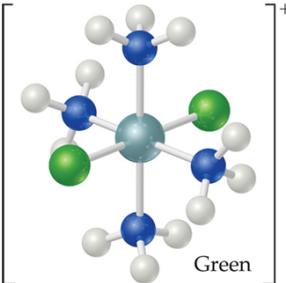
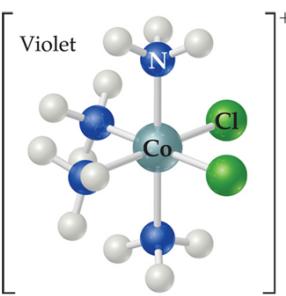
TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

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

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

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

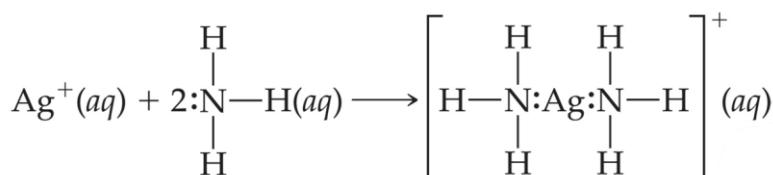
Werner proposed putting all molecules and ions within the sphere in brackets and those "free" anions (that dissociate from the complex ion when dissolved in water) outside the brackets.



- 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.

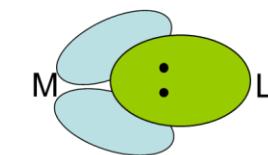
## Metal-Ligand Bond

- 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.



## 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



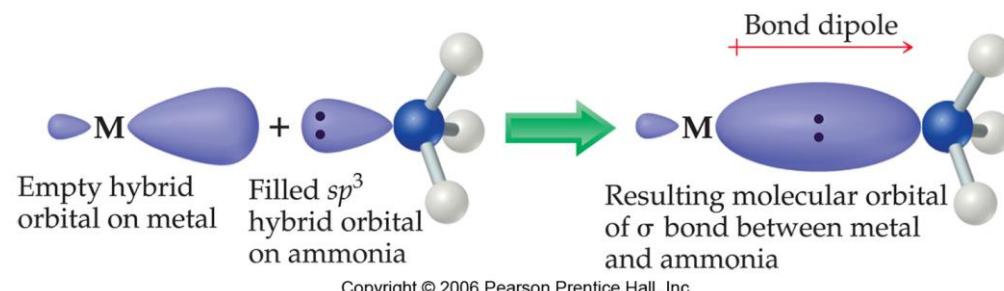
So ligands **must** have lone pairs of electrons.

Model of ligand/metal bonding.

Electron pair comes from ligand

Bond very polarized.

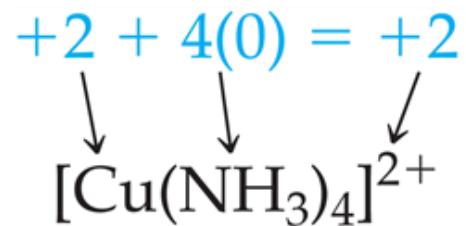
**Assumption:** interaction pure electrostatic.



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

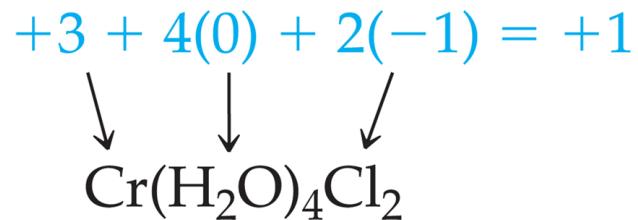
## Oxidation Numbers



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

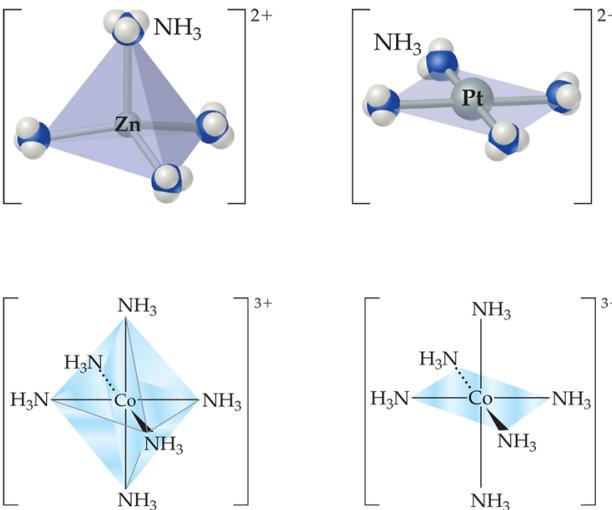
Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

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



## 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**.

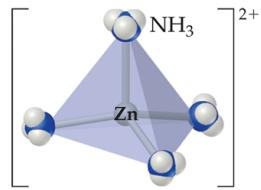


- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.

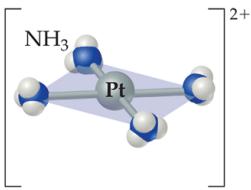
# Geometries

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

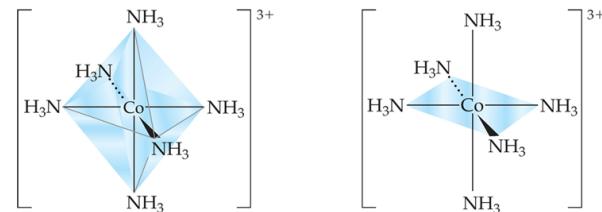
- Tetrahedral
- Square planar



Tetrahedral



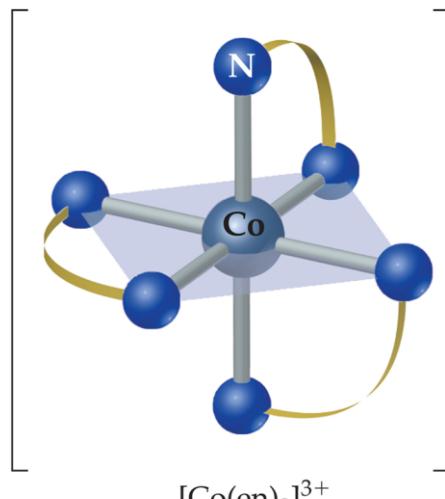
Square planar



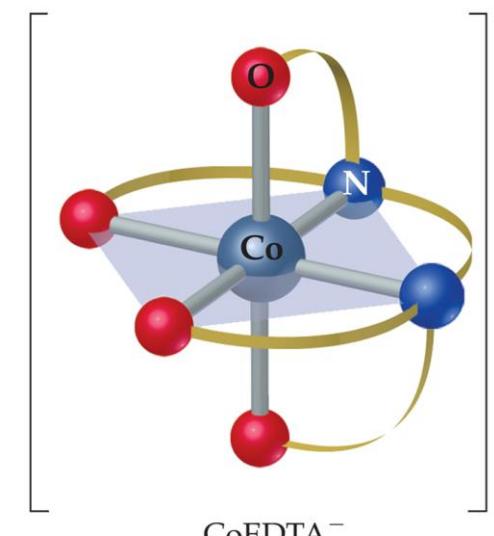
By far the most-encountered geometry, when the coordination number is six, is octahedral.

Why square planar? We'll get to that

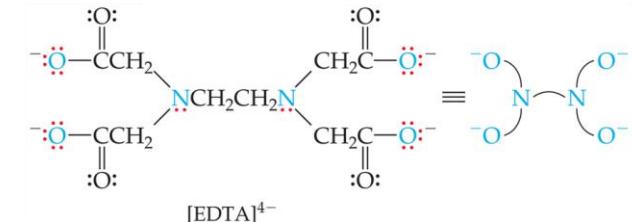
## Polydentate Ligands



- 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.

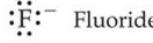
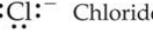
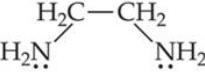
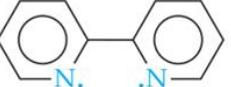
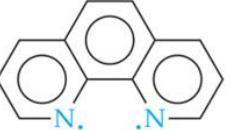
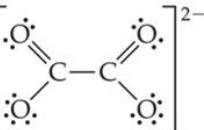
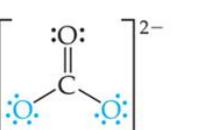
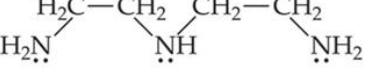
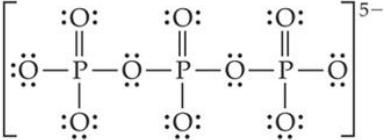
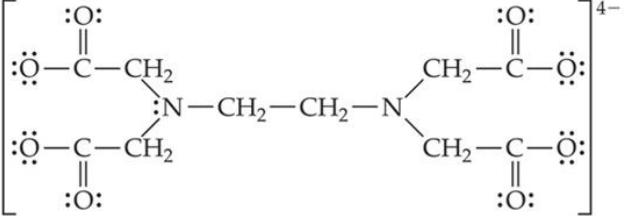


Wraps around the central atom like an octopus



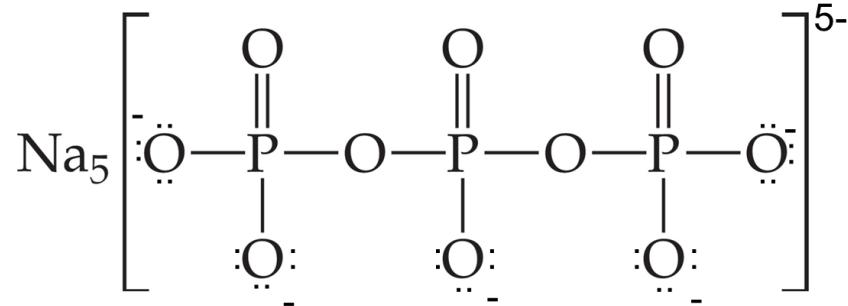
Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.

# Polydentate Ligands

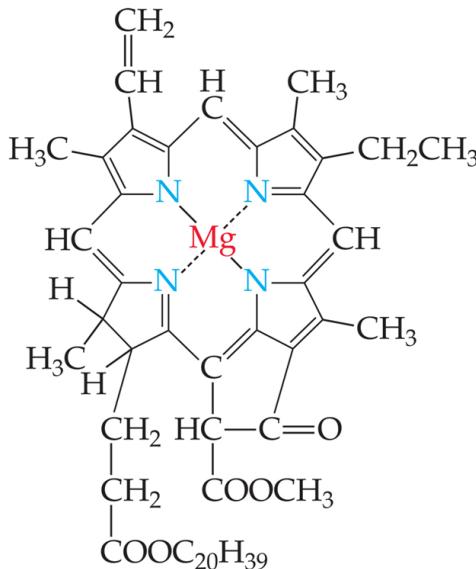
Ligand Type	Examples
Monodentate	$\text{H}_2\ddot{\text{O}}$ : Water $:\text{NH}_3$ : Ammonia
	 Fluoride ion  Chloride ion
	$[\text{:C}\equiv\text{N}:]^-$ Cyanide ion $[\text{:S}=\text{C}=\text{N}:]^-$ Thiocyanate ion
	$[\text{:}\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion $[\text{:}\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion
Bidentate	 Ethylenediamine (en)
	 Bipyridine (bipy)
	 Ortho-phenanthroline (o-phen)
	 Oxalate ion
	 Carbonate ion
Polydentate	 Diethylenetriamine
	 Triphosphate ion
	 Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ )

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

# Chelating Agents

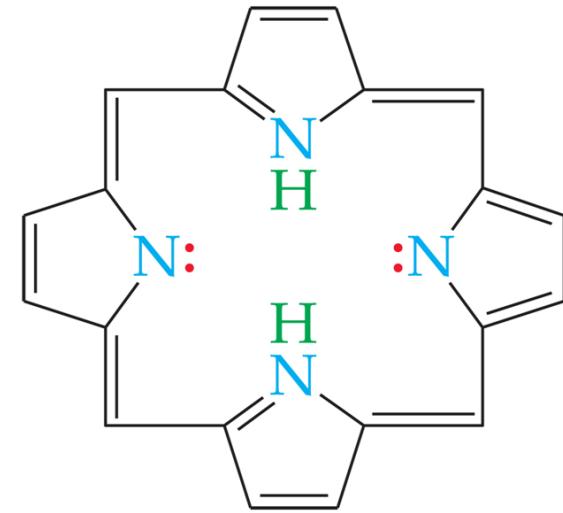


- Bind to metal ions removing them from solution.
- Phosphates are used to tie up  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in hard water to prevent them from interfering with detergents.



Porphines (like chlorophyll a) are tetradentate ligands.

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

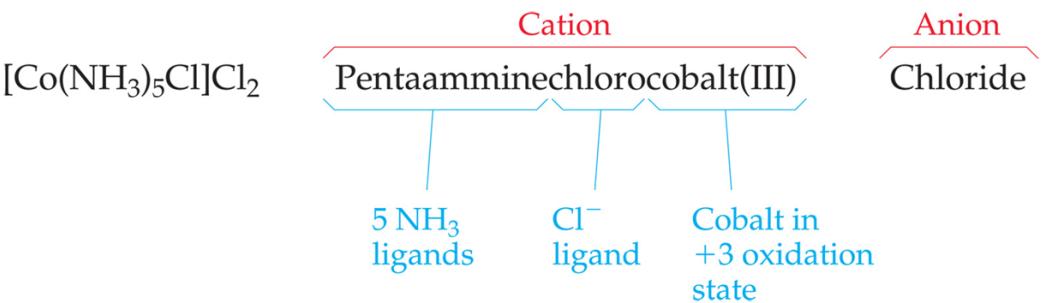


# Nomenclature of Coordination Compounds

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, 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

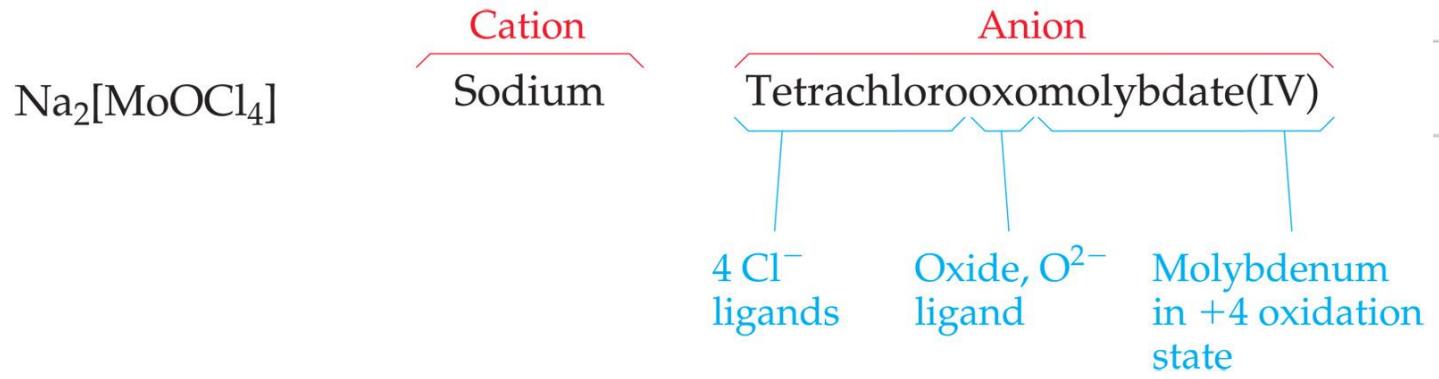
- The basic protocol in coordination nomenclature is to name the ligands attached to the metal as prefixes before the metal name.
- Some common ligands and their names are listed above.

- 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.



- 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.

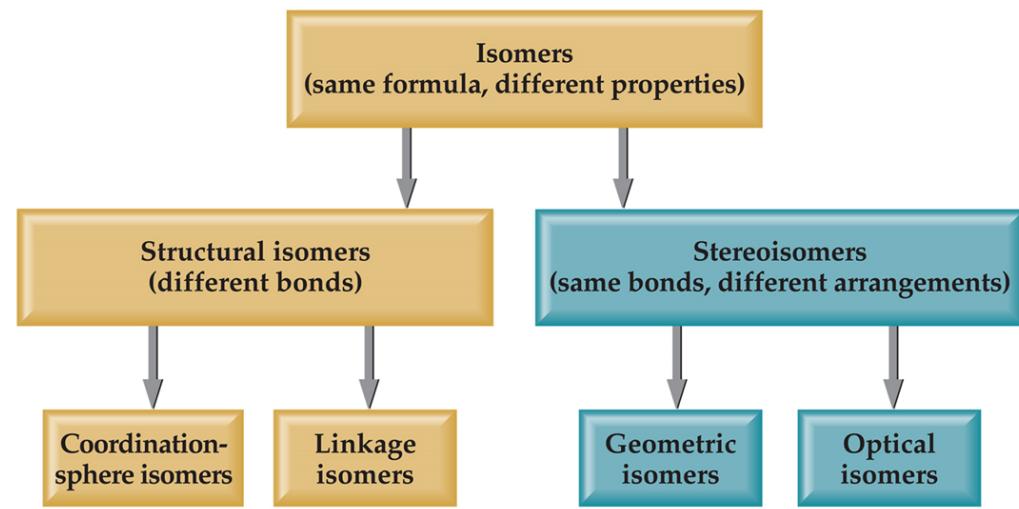
- If the complex is an anion, its ending is changed to *-ate*.
- The oxidation number of the metal is listed as a Roman numeral in parentheses immediately after the name of the metal.



<u>Complex</u>	<u>Name</u>
$[\text{Ni}(\text{CN})_4]^{2-}$	tetracyanonickelate(II) ion
$[\text{CoCl}_6]^{3-}$	hexachlorocobaltate(III) ion
$[\text{CoCl}_2(\text{NH}_3)_4]^+$	tetraaminedichlorocobalt(III) ion
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	sodium hexanitrocobaltate(III)
$[\text{CrCl}_2(\text{en})_2]_2\text{SO}_4$ dichlorobis(ethylenediamine)chromium(III) sulfate	

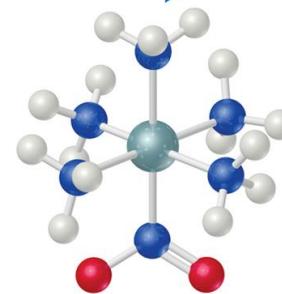
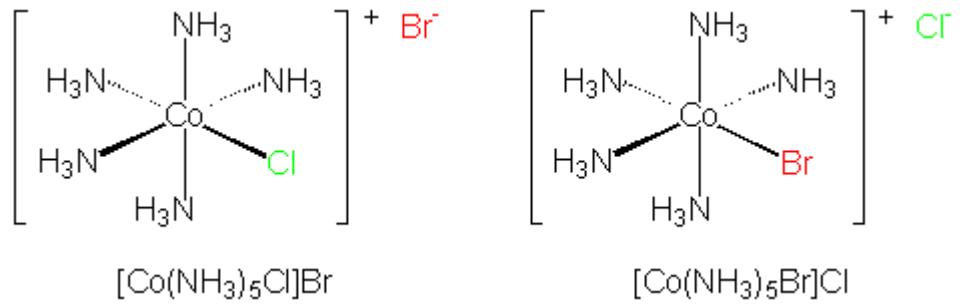
$[\text{CoCl}(\text{en})_2(\text{ONO})]^+$	Chloridobis-(ethylene-1,2-diamine)nitritocobalt(III) ion.
$[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel (0).
$\text{K}_4[\text{Ni}(\text{CN})_4]$	Potassium tetracyanonickelate(0).
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	Tetraaquachloridochromium(III) chloride.
$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	Triaminetrinitrocobalt(III)

1.  $[\text{CO}(\text{H}_2\text{O})_6]\text{Cl}_2$  ..... Hexaquacobalt (II) chloride
2.  $[\text{Ni}(\text{en})_3]\text{Cl}_3$  ..... Tris (ethane -1, 2-diamine) nickel (III) chloride
3.  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  ..... Hexaammine chromium (III) chloride
4.  $\text{K}_4[(\text{Fe}(\text{CN})_6)]$  ..... Potassium hexacyanoferrate(II)
5.  $\text{K}_3[(\text{Fe}(\text{CN})_6)]$  ..... Potassium hexacyanoferrate(III)
6.  $\text{K}[(\text{AgCl}_2)]$  ..... Potassium dicloridoargentate(I)
7.  $\text{Na}_3[\text{CrF}_6]$  ..... Sodium hexafluoridochromate(III)
8.  $[\text{Ni}(\text{CO})_4]$  ..... Tetracarbonylnickel(0)
9.  $[\text{Fe}(\text{CO})_5]$  ..... Pentacarbonyliron (0)
10.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  ..... Diamminedichloroplatinum(II)
11.  $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$  ..... Diamminesilver (I) dicyanoargentate(I)

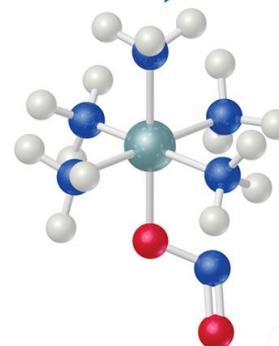


Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

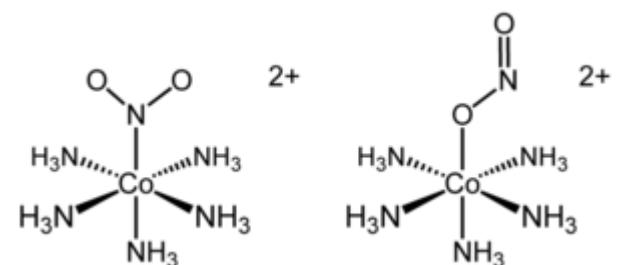
If a ligand (like the  $\text{NO}_2$  group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, **linkage isomers** are formed.



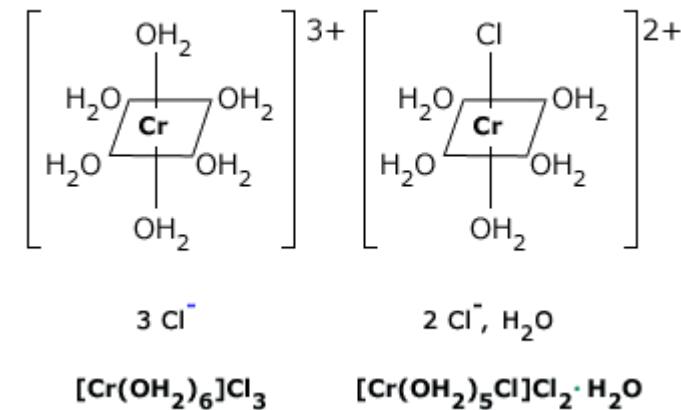
Nitro isomer



Nitrito isomer



- 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  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$ .

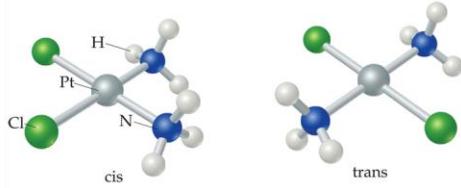


A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (Solvate Isomerism), which in the case of water is called Hydrate Isomerism. The best known example of this occurs for chromium chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) which may contain 4, 5, or 6 coordinated water molecules (assuming a coordination number of 6). The dot here is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula. Alfred Werner's coordination theory indicates that several of the water molecules are actually bonded directly (via coordinate covalent bonds) to the central chromium ion. In fact, there are several possible compounds that use the brackets to signify bonding in the complex and the dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

These isomers have very different chemical properties and on reaction with  $\text{AgNO}_3$  to test for  $\text{Cl}^-$  ions, would find 1, 2, and 3  $\text{Cl}^-$  ions in solution, respectively.

Upon crystallization from water, many compounds incorporate water molecules in their crystalline frameworks. These "waters of crystallization" refers to water that is found in the crystalline framework of a metal complex or a salt, which is not directly bonded to the metal cation. In the first two hydrate isomers, there are water molecules that are artifacts of the crystallization and occur inside crystals. These waters of crystallization contribute to the total weight of water in a substance and are mostly present in a definite (stoichiometric) ratio.

## Geometric isomers



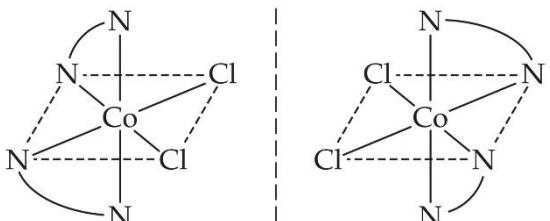
- With these geometric isomers, two chlorines and two  $\text{NH}_3$  groups are bonded to the platinum metal, but are clearly different.

➤ *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

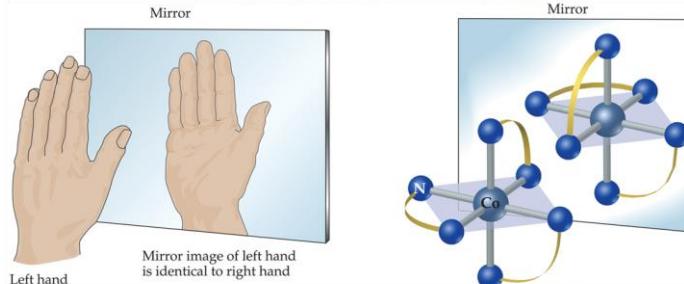
## Enantiomers

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

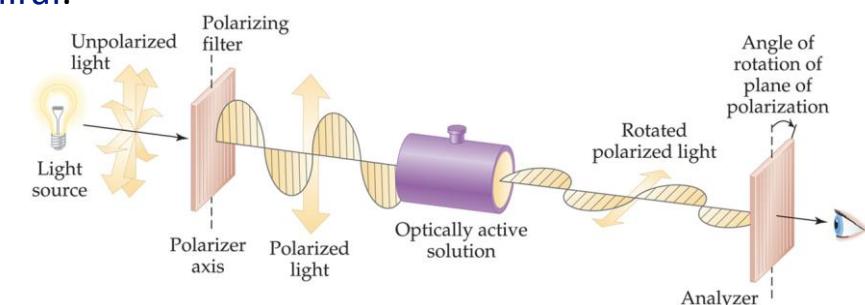


- Most of the physical properties of chiral molecules are the same, boiling point, freezing point, density, etc.
- One exception is the interaction of a chiral molecule with plane-polarized light.
- If one enantiomer of a chiral compound is placed in a polarimeter and polarized light is shone through 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.

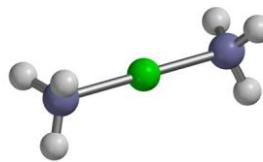
## Stereoisomers



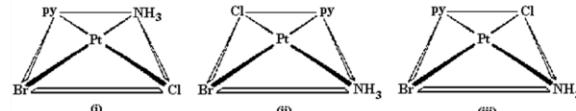
- Other stereoisomers, called **optical isomers** or **enantiomers**, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.



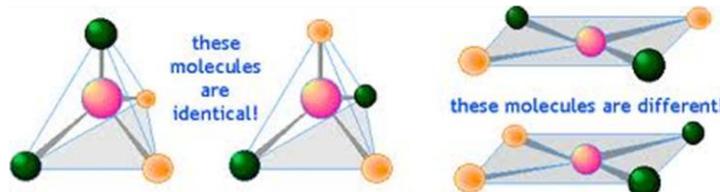
Anything that's **linear** is not chiral (achiral),  
i.e. mirror image is always same as original.



Anything that's **square planar** is not chiral  
(achiral),  
i.e. mirror image is always same as original.



Anything that's tetrahedral is chiral  
**only if all four groups are different.**



octahedral is chiral with **monodentate groups** only if:

- (a) all six groups are different (ABCDEF) or
- (b) two groups are the same and **cis** (AABCDE) or
- (c) three groups are the same and **fac**,  
i.e. none trans (AAABCD) or
- (d) there are two pairs of identical groups and both  
are **cis** (AABBCCD)

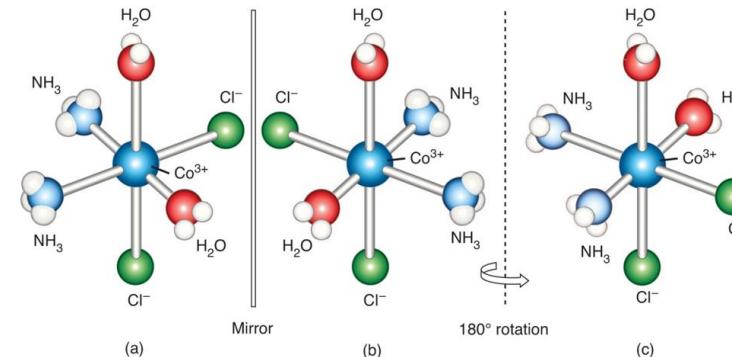


Figure 26.31 The all-*cis* form of the complex ion  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}]^{4+}$  is optically active. The structures shown in (a) and (b) are nonsuperimposable mirror images of each other. The structure shown in (c) is the same as that in (b) but rotated 180 degrees. Notice that structure (c) cannot be superimposed on (a).

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OR

some possibilities with **bidentate ligands**,  
*cis*-dichlorobisethylenediaminecobalt(III)

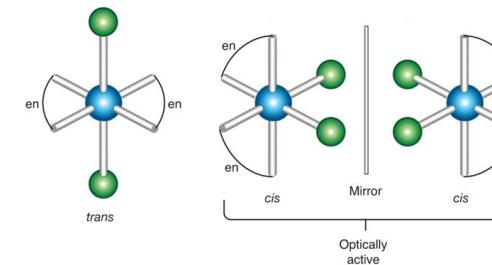


Figure 26.32 The complex ion  $[\text{CoCl}_2(\text{en})_2]^{+}$  can form a *trans* and a *cis* isomer. The *cis* form is chiral.

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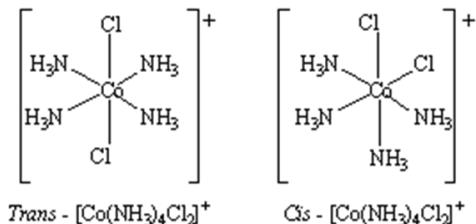
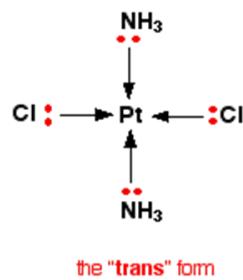
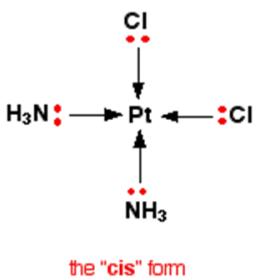
If any pair of identical groups is **trans**,  
there is no chirality!

any octahedral molecule with a mirror plane is achiral.  
(any single pair of identical **trans ligands**  
guarantees a mirror plane)

## Geometrical isomers of Complexes

Differ only in arrangement of ligands around metal ion.

Metal complexes that differ only in which ligands are **adjacent** to one another (**cis**)  
or  
**directly across** from one another (**trans**).



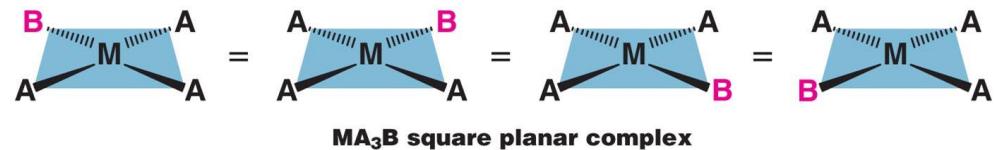
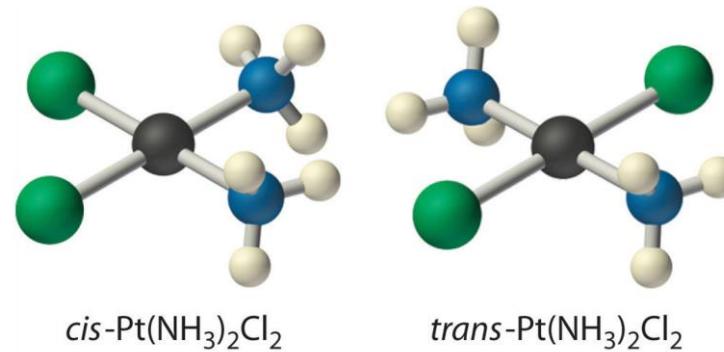
Geometrical isomers are most important for **square planar** & **octahedral complexes**.

### Square planar complexes:

all vertices of a square are **equivalent**, it does not matter which vertex is occupied by ligand B in a square planar **MA<sub>3</sub>B** complex.

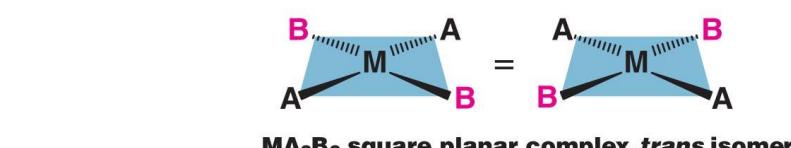
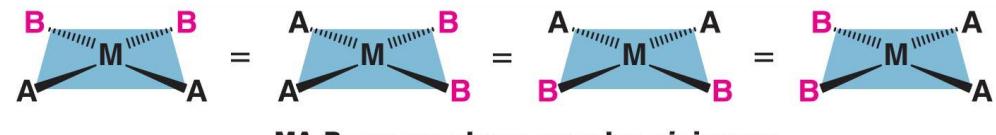
Only one geometrical isomer is possible

*Cis-platin* isomer fights cancer,  
*Trans-platin* doesn't



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Only one isomer when there's one B ligand.  
With **two**, there are other possible arrangements.



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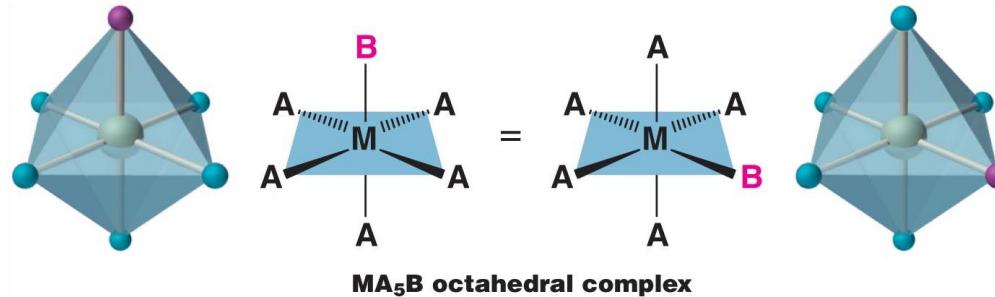
## Isomers of Metal Complexes

### Octahedral complexes:

Only one structure possible for octahedral complexes  
(if only one ligand is different from other five):

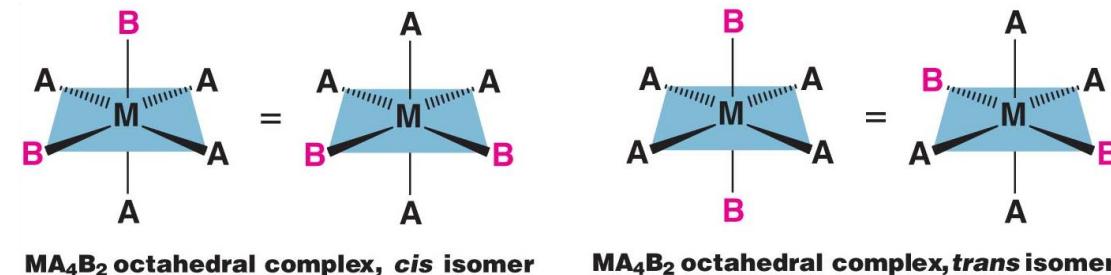


since all six vertices of an octahedron are equivalent.



If two ligands in an octahedral complex are different from other four ( $\text{MA}_4\text{B}_2$ ), two isomers are possible:

two B ligands can be \_\_\_\_\_.

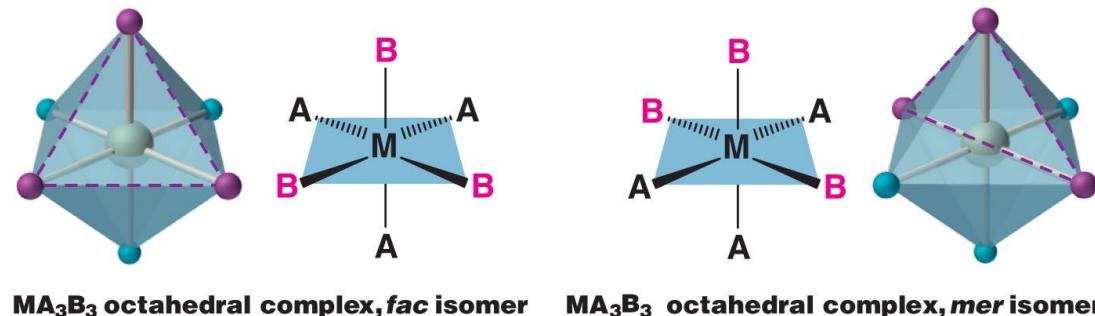


### Octahedral isomer complexes:

Replacing another A ligand by B gives an  $\text{MA}_3\text{B}_3$  complex for which there are two isomers:

**Fac:** 3 ligands of each kind occupy opposite triangular **faces** of the octahedron

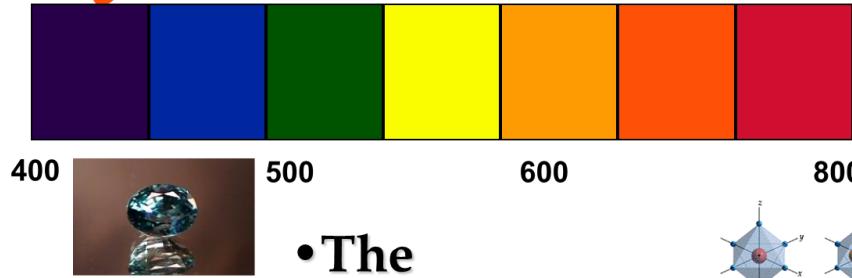
**Mer:** 3 ligands of each kind lie on the **meridian** (cut across flat mid-plane)



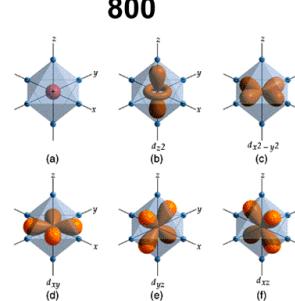
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(cut across flat mid-plane)

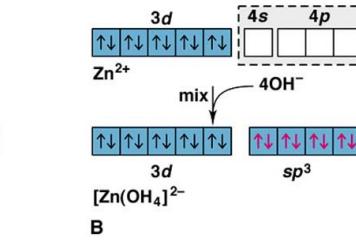
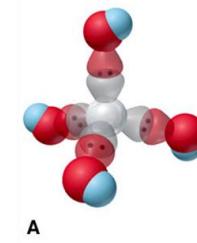
# Crystal Field Theory



- The relationship between colors and complex metal ions

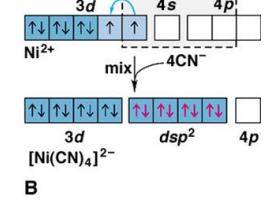
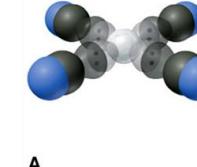


Tetrahedral e.g.  $[\text{Zn}(\text{OH})_4]^{2-}$



B

Square Planar e.g.  $[\text{Ni}(\text{CN})_4]^{2-}$



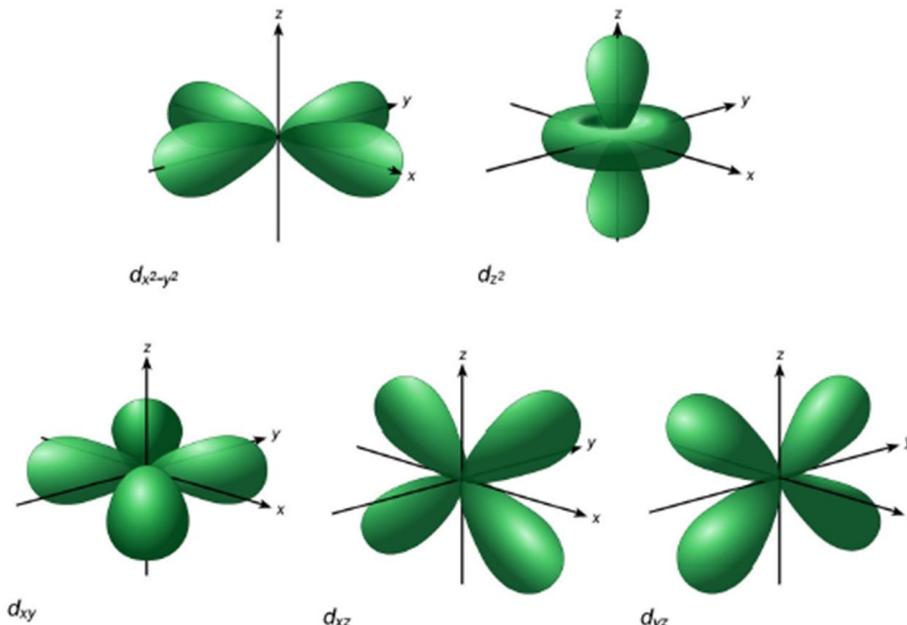
B

## Limitations of VB theory

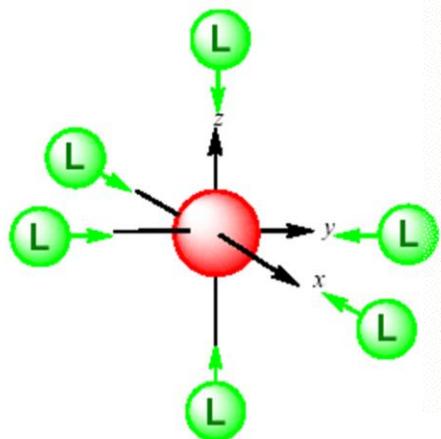
- Cannot account for colour of complexes
- May predict magnetism wrongly
- Cannot account for spectrochemical series

- A purely *ionic* model for transition metal complexes.
- Ligands are considered as point charge.
- Predicts the pattern of splitting of d-orbitals.
- Used to rationalize spectroscopic and magnetic properties.

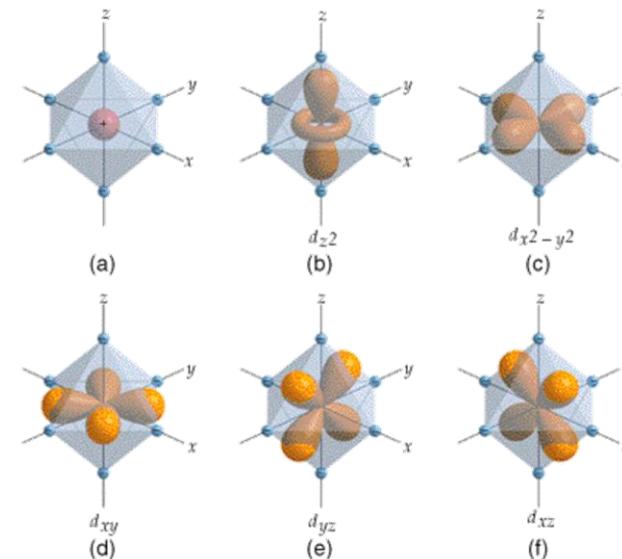
## d-orbitals: look attentively along the axis



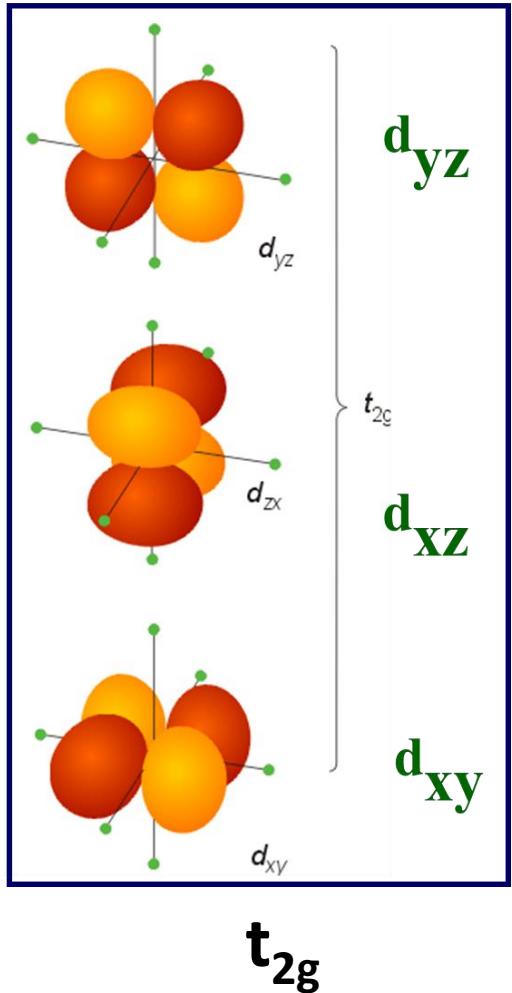
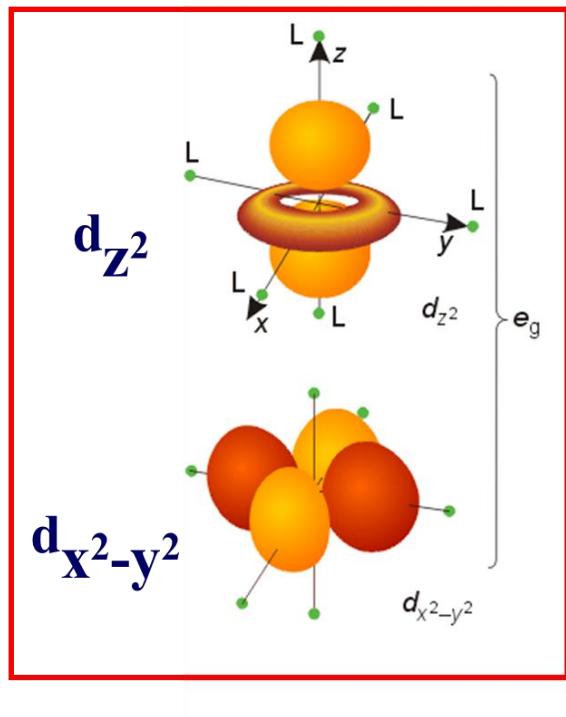
Octahedral Field



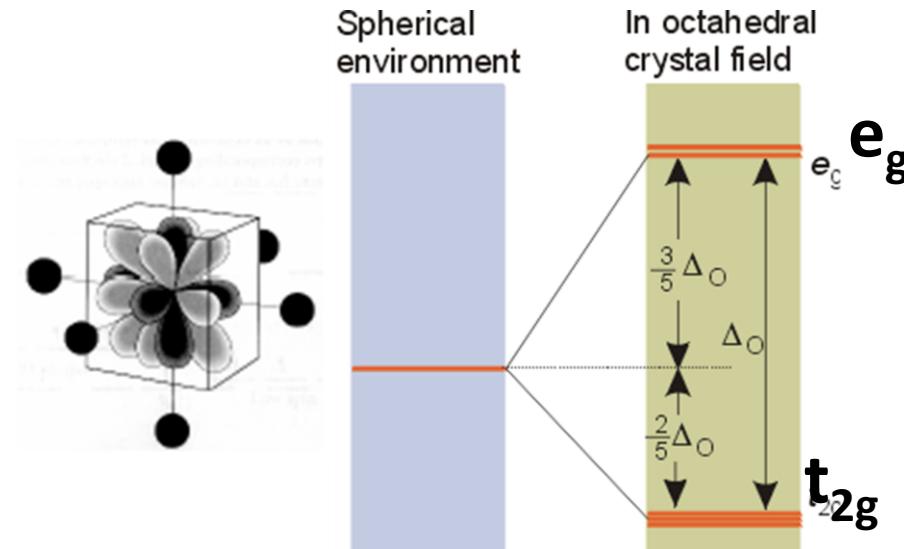
- We assume an octahedral array of negative charges placed around the metal ion (which is positive).
- The ligand and orbitals lie on the same axes as negative charges.
  - Therefore, there is a large, unfavorable interaction between ligand (-) and these orbitals.
  - These orbitals form the degenerate high energy pair of energy levels.
- The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals bisect the negative charges.
  - Therefore, there is a smaller repulsion between ligand and metal for these orbitals.
  - These orbitals form the degenerate low energy set of energy levels.



## In Octahedral Field

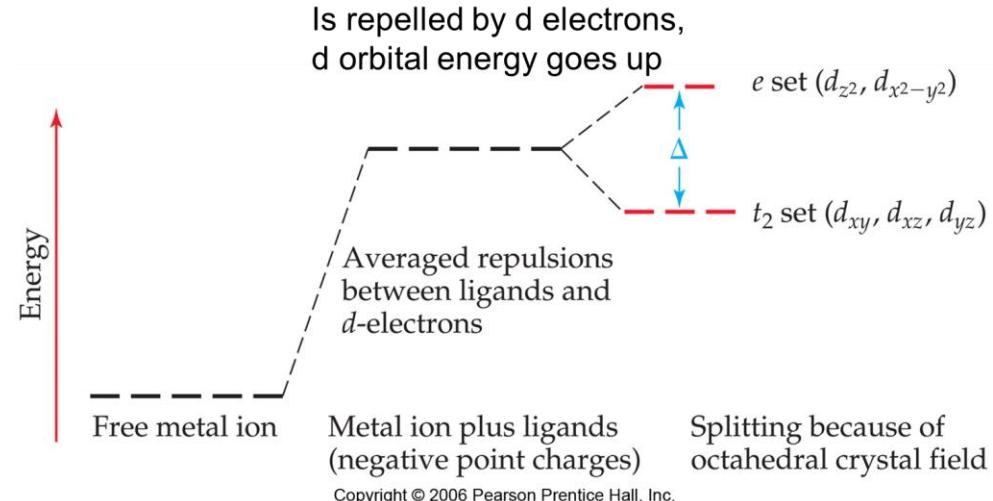


△ = crystal field splitting energy

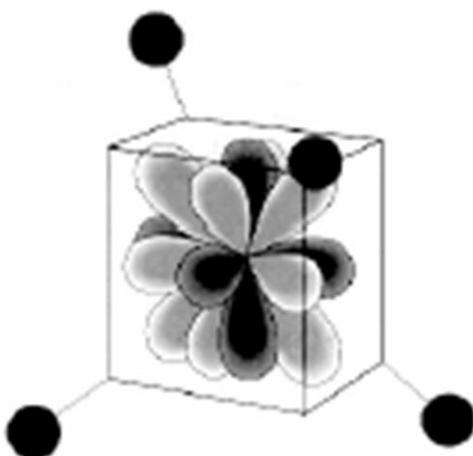
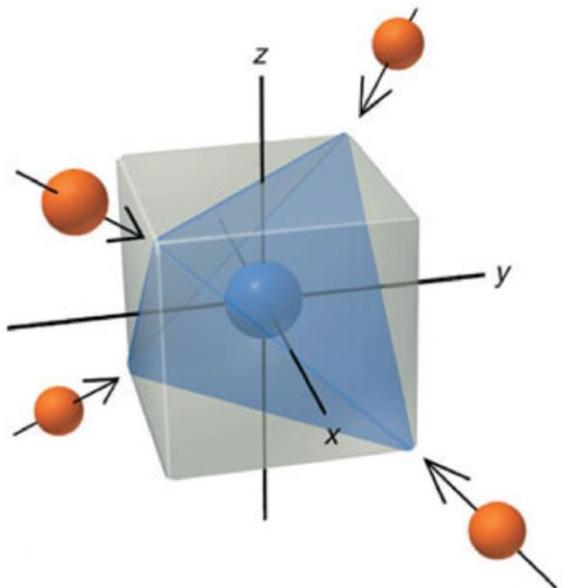
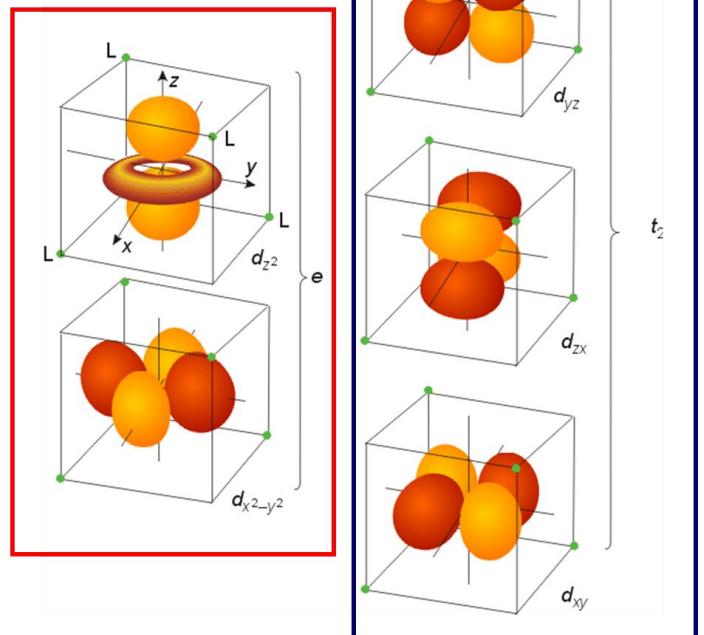


Now, think of point charges being attracted to metal nucleus  
Positive charge. What about electrons in d orbitals?

In octahedral complex A1g,T1u,Eg and T2g.  
1 and 2 show multiplicity. g is gerade and u is a ungerad. A is singly degenerate, E is doubly degenerate, T is triple degenerate



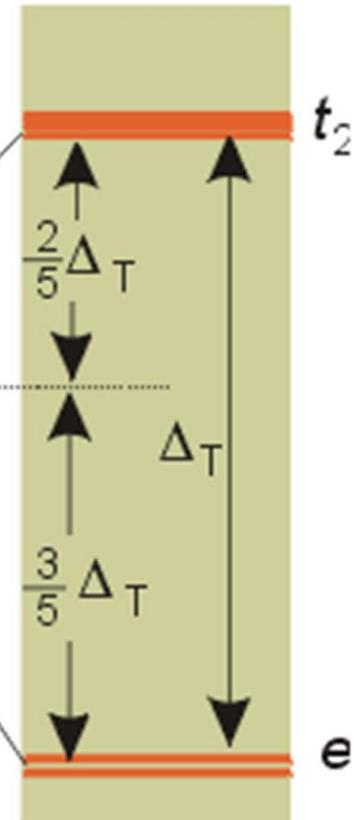
## In Tetrahedral Field



## Spherical environment



## In tetrahedral crystal field



## Factors That Affect the Magnitude of $\Delta_o$

magnitude of  $\Delta_0$  dictates whether a complex with 4, 5, 6, or 7 d e's is high spin or low spin:

1. **Large** values of  $\Delta_o$  yield a **low-spin** complex
  2. **Small** values of  $\Delta_o \rightarrow$  a **high-spin** complex

## Nature of the ligands

1. **Strong-field** ligands interact strongly with  $d$  orbitals of metal ions and give a **large**  $\Delta_o$ .
  2. **Weak-field** ligands interact more weakly and give a **smaller**  $\Delta_o$ .

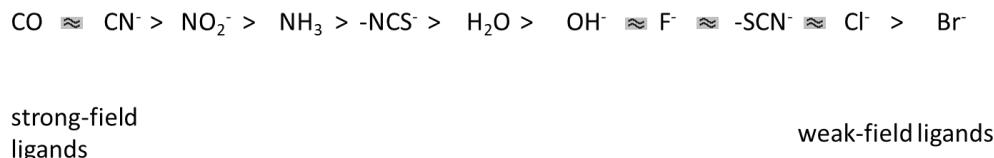
compound that has unpaired electrons in its splitting diagram will be paramagnetic and will be attracted by magnetic fields, while a compound that lacks unpaired electrons in its splitting diagram will be diamagnetic and will be weakly repelled by a magnetic field

## Nature of the ligands

experimentally observed order of the crystal field splitting energies produced by different ligands is called:  
the **spectrochemical series**

## **The Spectrochemical Series**

When geometry & **the metal** are held constant, splitting of  $d$  orbitals decreases in the following order:



## Strong Field Ligands:

(strongest)  $\text{CN}^-$ ,  $\text{CO} > \text{NO}_2^- > \text{en} > \text{NH}_3$

# Weak Field Ligands:

$$\text{H}_2\text{O} > \text{ox} > \text{OH}^- > \text{F}^- > \text{SCN}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- \text{ (weakest)}$$

# Crystal Field Splitting Energy (CFSE)

- In Octahedral field, configuration is:  $t_{2g}^x e_g^y$
- Net energy of the configuration relative to the average energy of the orbitals is:

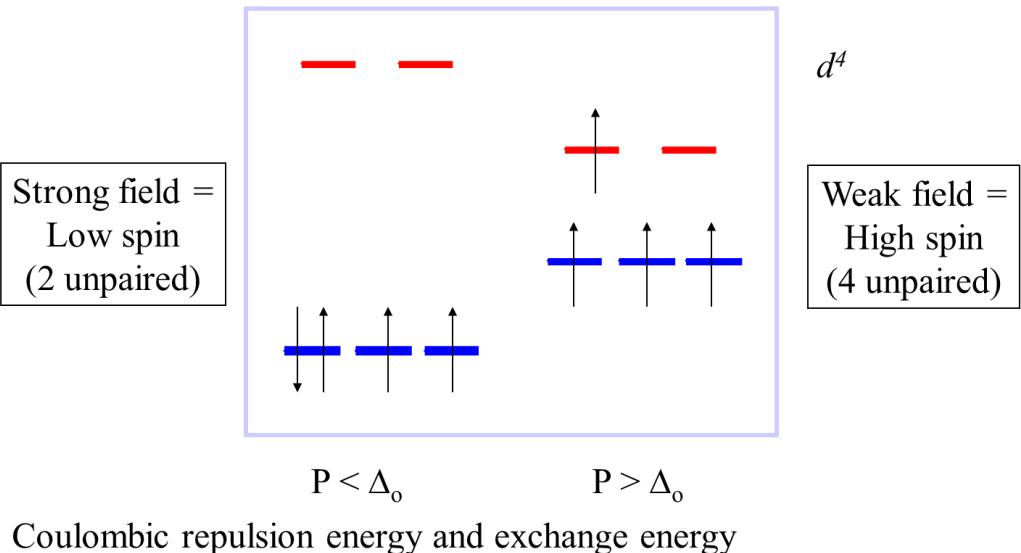
$$= (-0.4x + 0.6y)\Delta_o$$

$$\Delta_o = 10 \text{ Dq}$$

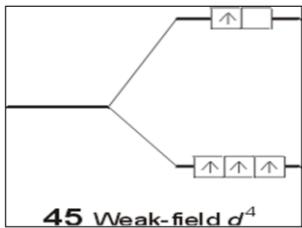
**BEYOND  $d^3$**

- In weak field:  $\Delta_o < P$ ,  $\Rightarrow t_{2g}^3 e_g^1$
- In strong field  $\Delta_o > P$ ,  $\Rightarrow t_{2g}^4$
- P - paring energy

When the 4<sup>th</sup> electron is assigned it will either go into the higher energy  $e_g$  orbital at an energy cost of  $\Delta_o$  or be paired at an energy cost of P, the pairing energy.

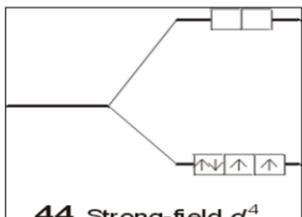


## Ground-state Electronic Configuration, Magnetic Properties and Colour



$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$

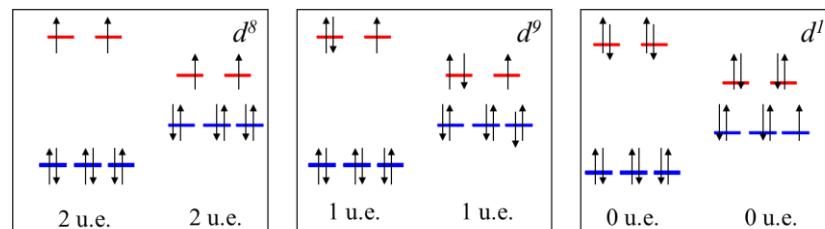
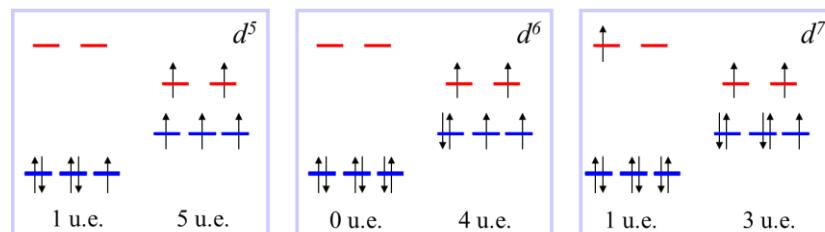
**Weak Field Complex**  
the total spin is  $4 \times \frac{1}{2} = 2$   
**High Spin Complex**



$[\text{Mn}(\text{CN})_6]^{3-}$

**Strong field Complex**  
total spin is  $2 \times \frac{1}{2} = 1$   
**Low Spin Complex**

Placing electrons in d orbitals



What is the CFSE of  $[\text{Fe}(\text{CN})_6]^{3-}$ ?

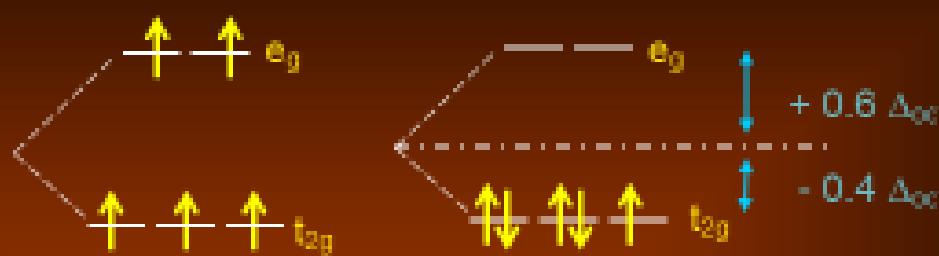
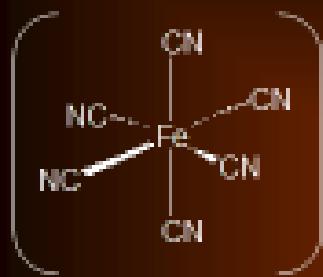
C.N. = 6 ::  $\text{O}_h$

$\text{Fe(III)} \therefore d^5$

h.s.

l.s.

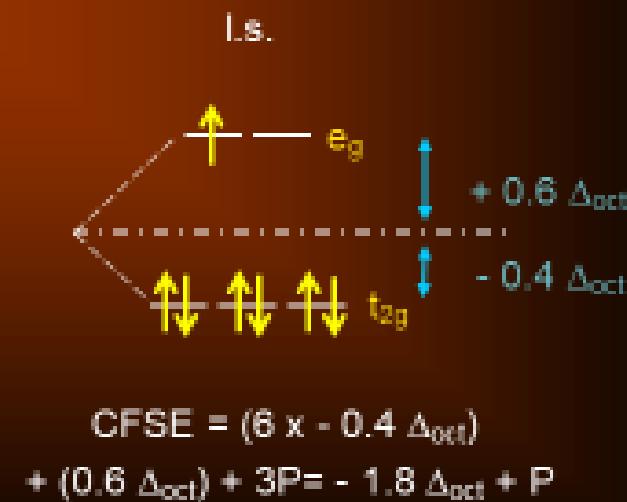
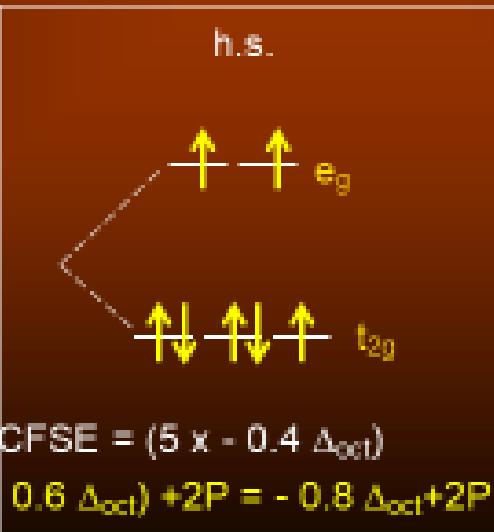
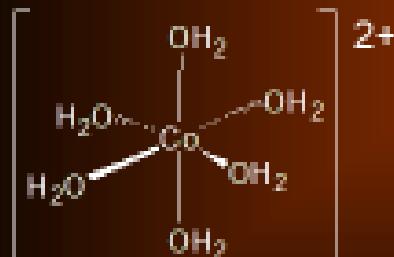
$\text{CN}^- = \text{s.f.l.}$

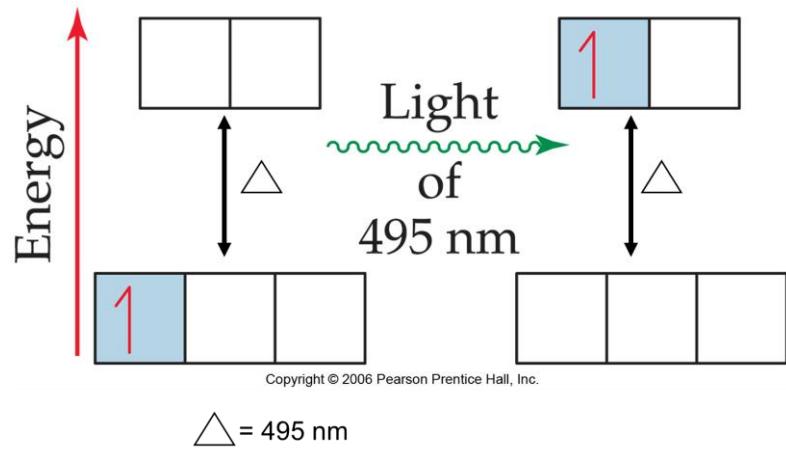


$$\text{CFSE} = 5 \times -0.4 \Delta_{\text{oct}} + 2P = -2.0 \Delta_{\text{oct}} + 2P$$

If the CFSE of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is  $-0.8 \Delta_{\text{oct}}$ , what spin state is it in?

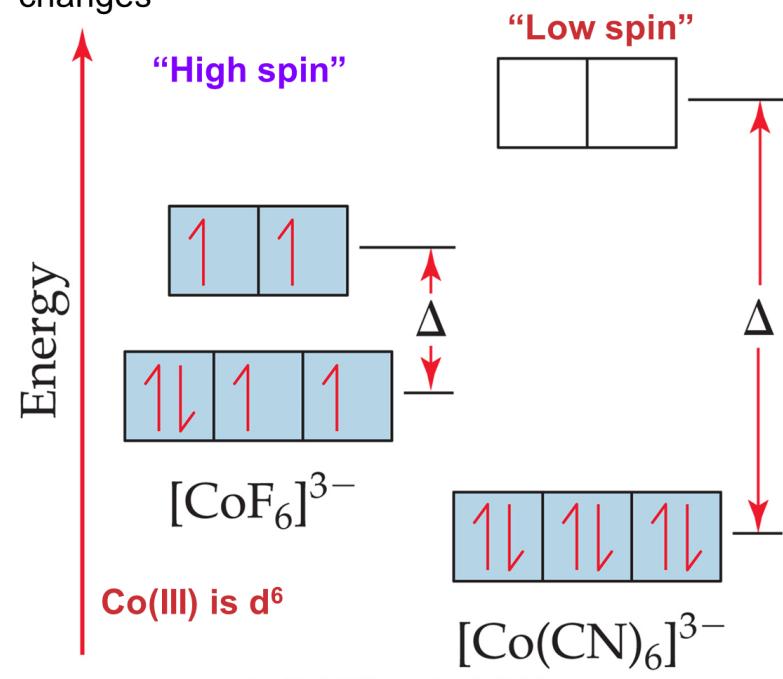
C.N. = 6 ::  $\text{O}_h$      $\text{Co(II)} \therefore d^7$



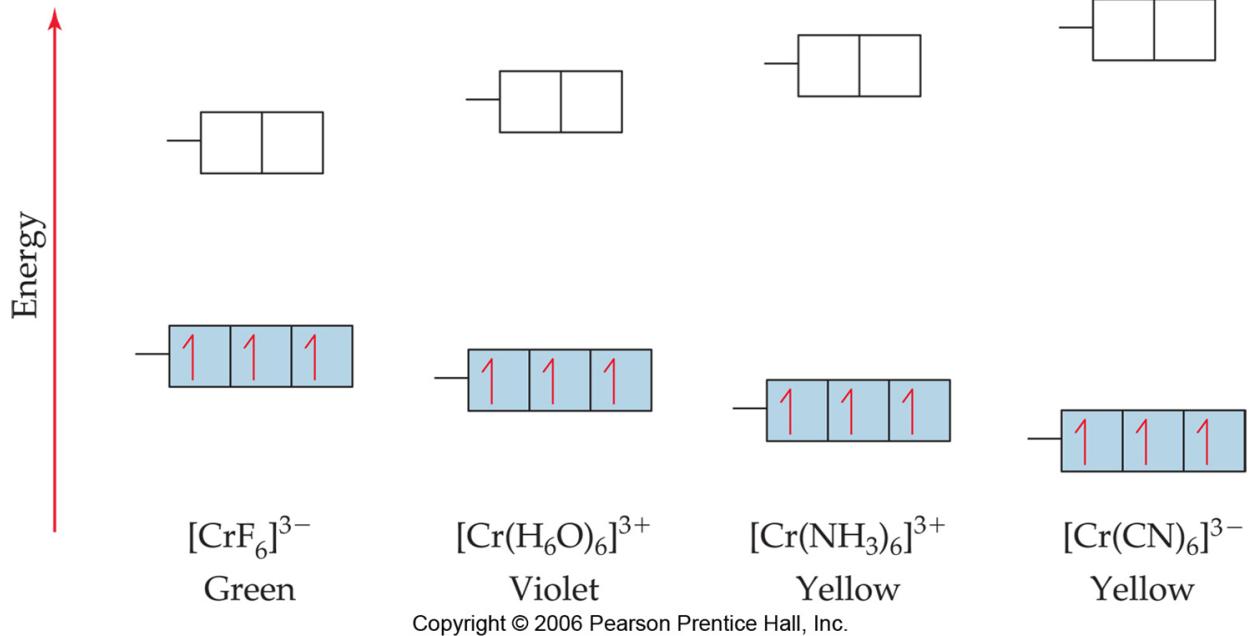


$$\Delta = 495 \text{ nm}$$

As Energy difference increases, electron configuration changes



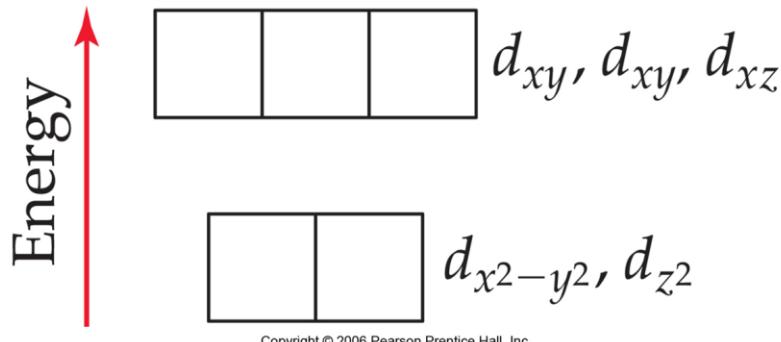
Different ligands interact more or less, change E spacing Of D orbitals.



## Tetrahedral Complexes

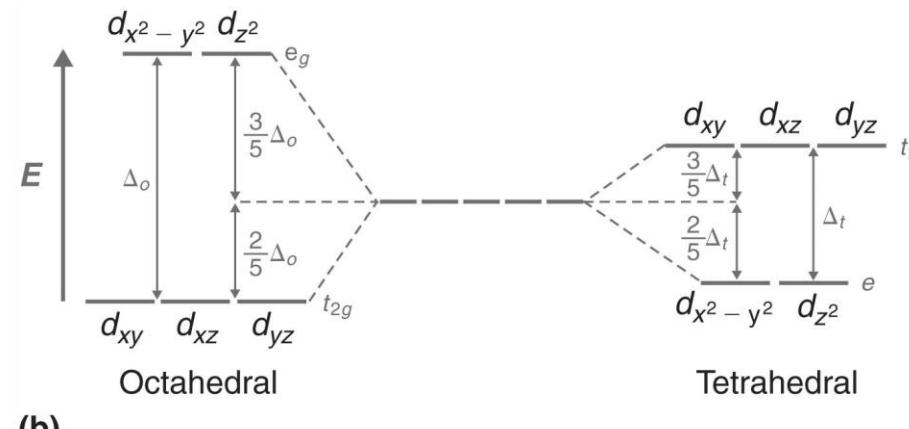
In tetrahedral complexes, orbitals are inverted.  
Again because of orientation of orbitals and ligands

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



## tetrahedral crystal field:

the splitting observed in a tetrahedral crystal field is opposite of splitting in octahedral complex.

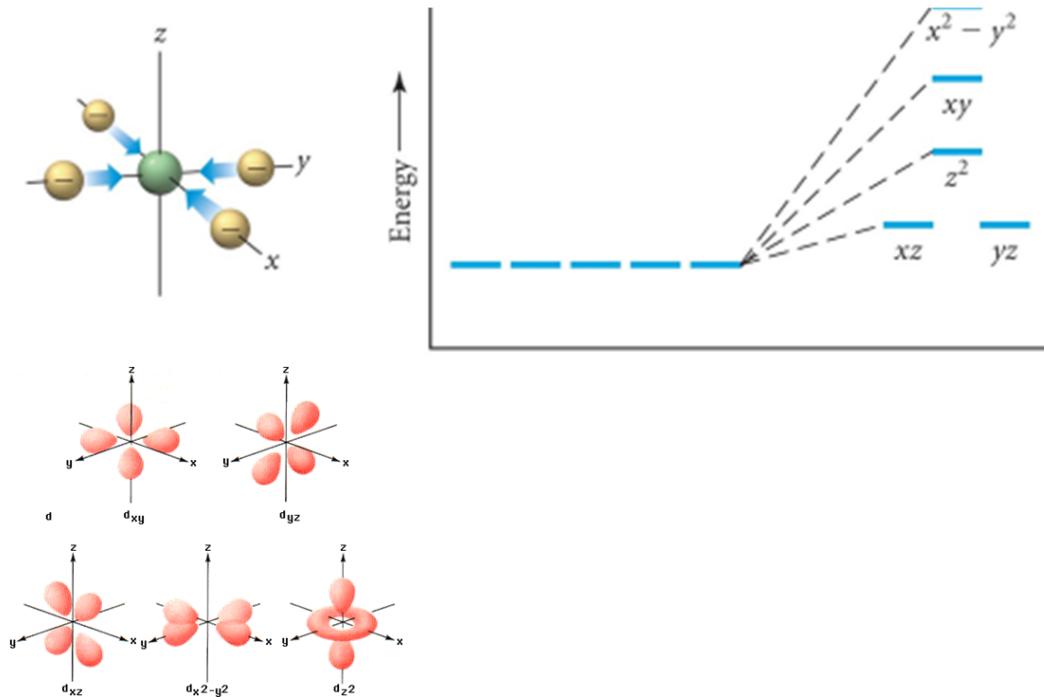


## Tetrahedral Complexes

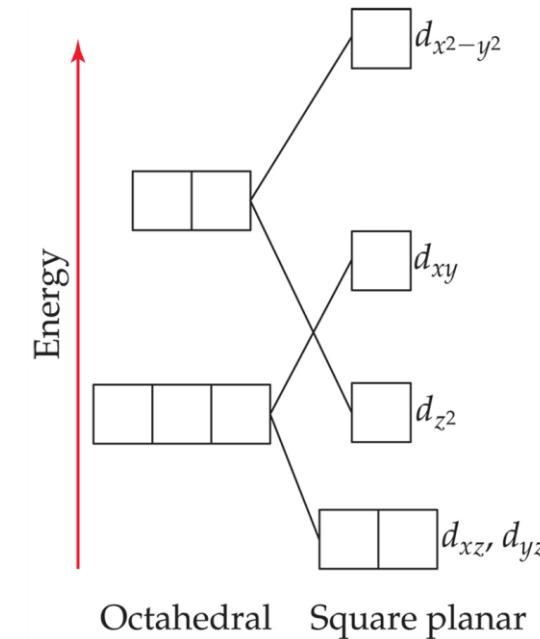
Splitting of energies of orbitals in tetrahedral complex,  $\Delta_o$ , is **smaller than** in an octahedral complex for two reasons:

1.  $d$  orbitals interact less strongly with ligands in a **tetrahedral arrangement**.
2. Only **four** negative charges rather than six, which decreases electrostatic interactions

With **square planar splittings**,  
 energy level for the  $x^2-y^2$  orbital is very high  
 so this is an especially good geometry  
 for d<sup>8</sup> complexes, e.g. Pt(II), Ni(II), Pd(II), Au(III)



Square planar complexes are different still



Octahedral      Square planar

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## Factors That Affect the Magnitude of $\Delta_o$

### Charge on the metal ion

Increasing charge on a metal ion has 2 effects:

1. Radius of metal ion *decreases*
2. **Neg charged ligands** are more strongly attracted to it.

Both factors **decrease** metal-ligand distance, which causes (-) charged ligands to interact more strongly with the *d* orbitals.

magnitude of  $\Delta_o$  increases as **charge on metal ion** increases

### Principal quantum # of the metal

For a **series of complexes** of metals from **same group** in periodic table with **same charge** and **same ligands**:

magnitude of  $\Delta_o$  increases with increasing quantum #:

### Principal quantum # of the metal

$$\Delta_o (3d) \ll \Delta_o (4d) < \Delta_o (5d)$$

Increase in  $\Delta_o$  w/ increasing principal quantum # is due to: **larger radius of valence orbitals** going down a column.

Repulsive **ligand-ligand** interactions are important for *smaller* metal ions, which results in shorter M-L distances and stronger ***d*-orbital-ligand** interactions

# 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

## Complimentary color wheel

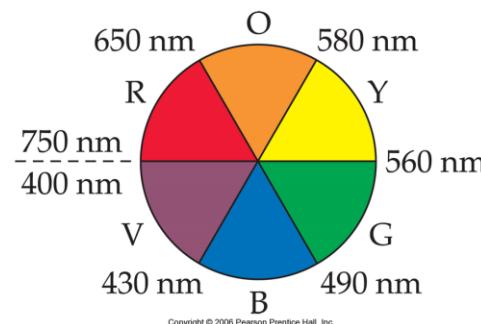
If one color absorbed, the color opposite is perceived.

Absorb Orange

See Blue

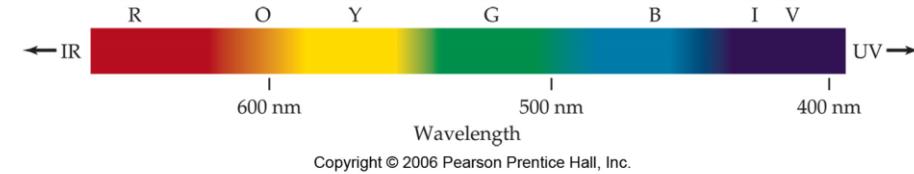
Absorb Red

See Green



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## 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.

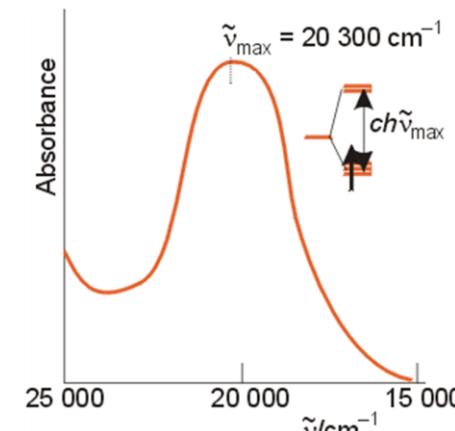
How does that give color?

No light absorbed, all reflected get white color

All light absorbed, none reflected get Black color

What if only one color is absorbed?

## The optical absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Assigned transition:

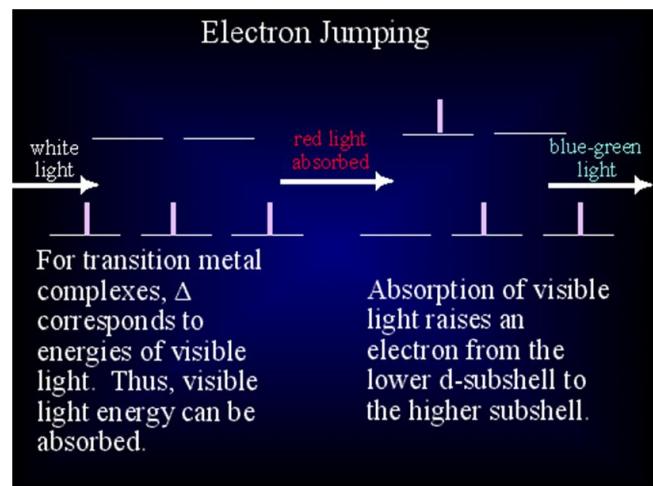


This corresponds to  
the energy gap

$$\Delta_O = 243 \text{ kJ mol}^{-1}$$

## Colors of Transition-Metal Complexes

Striking colors exhibited by transition-metal complexes are caused by the excitation of an e<sup>-</sup> from a lower-lying *d* orbital to a higher-energy *d* orbital, which is called a ***d-d transition***



The energy of a photon of light is inversely proportional to its wavelength

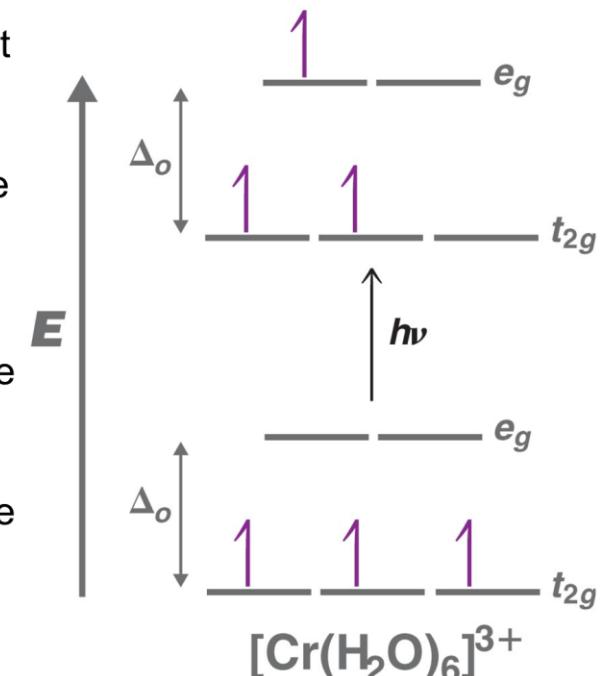
$$E = \frac{hc}{\lambda} = h\nu$$

For a photon to affect the ***d-d transition***,

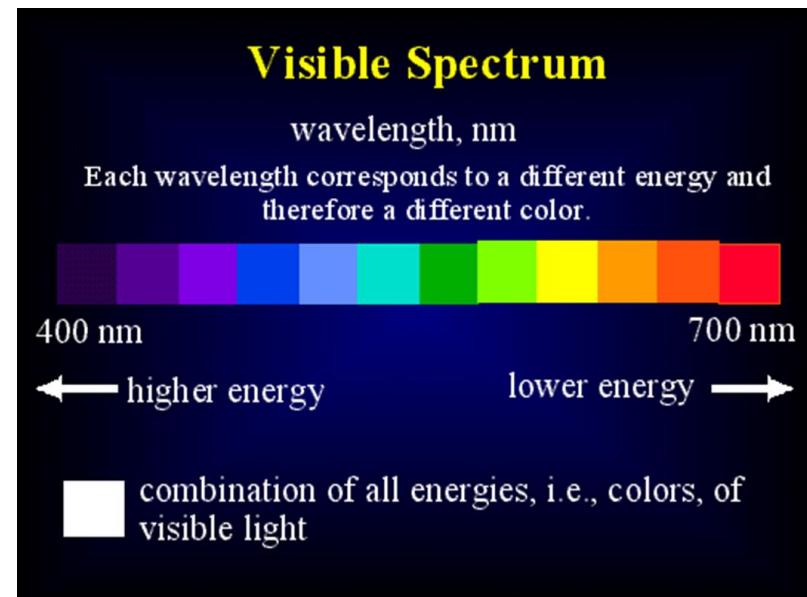
its E must be = to the difference in E btwn the two *d* orbitals,

which depends on the magnitude of  $\Delta_o$

which depends on the structure of the complex.



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

KMnO<sub>4</sub>



KCrO<sub>4</sub>



KClO<sub>4</sub>



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No d orbitals in  
Cl, orbitals higher  
in energy

Empty Mn 3d orbitals

— — —  $t_2$  set

— —  $e$  set

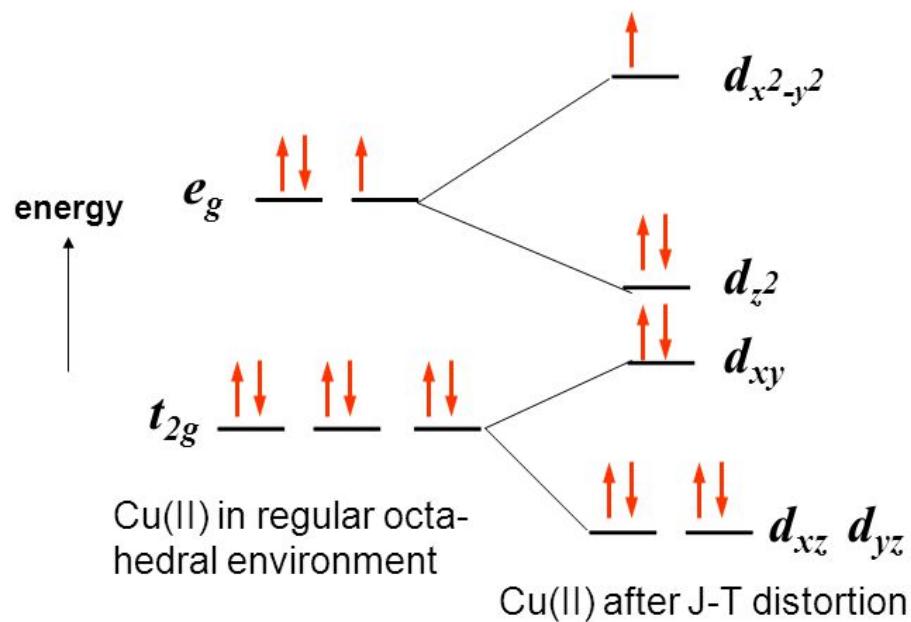


Filled ligand orbitals

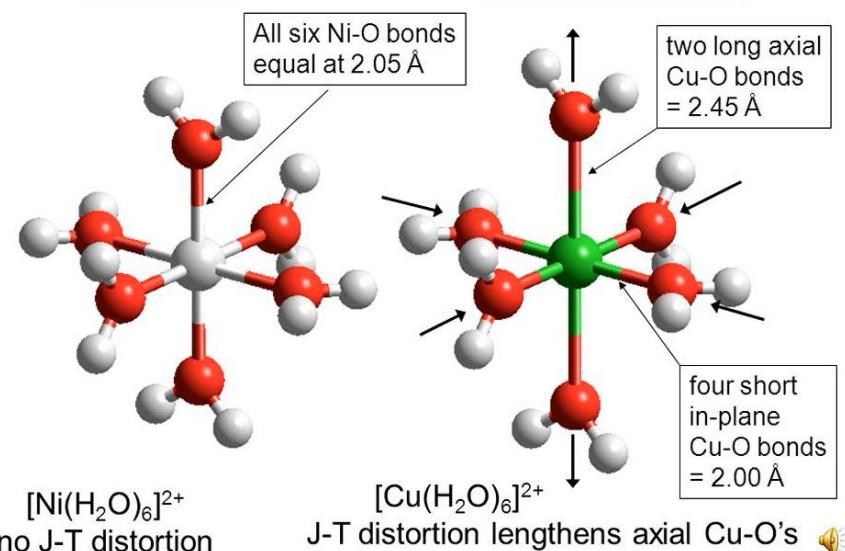
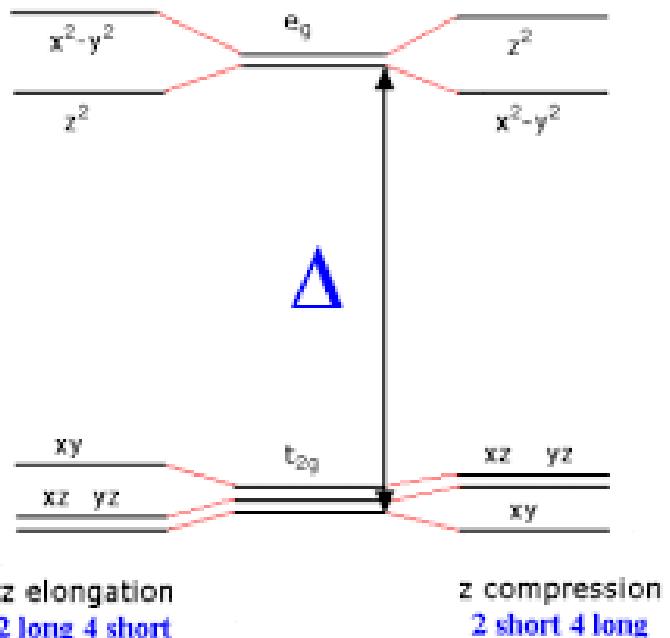
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## Splitting of the d-subshell by Jahn-Teller distortion

The CF view of the splitting of the d-orbitals is that those aligned with the two more distant donor atoms along the z-coordinate experience less repulsion and so drop in energy ( $d_{xz}$ ,  $d_{yz}$ , and  $d_z^2$ ), while those closer to the in-plane donor atoms



( $d_{xy}$ ,  $d_{x^2-y^2}$ ) rise in energy. An MO view of the splitting is that the  $d_{x^2-y^2}$  in particular overlaps more strongly with the ligand donor orbitals, and so is raised in energy. Note that all d-orbitals with a 'z' in the subscript drop in energy.

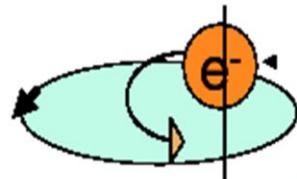


## Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

$n$  = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2} \mu_B$$

Ion	n	S	$\mu/\mu_B$ Calculate d	Experimental
Ti <sup>3+</sup>	1	1/2	1.73	1.7 – 1.8
V <sup>3+</sup>	2	1	2.83	2.7 – 2.9
Cr <sup>3+</sup>	3	3/2	3.87	3.8
Mn <sup>3+</sup>	4	2	4.90	4.8 – 4.9
Fe <sup>3+</sup>	5	5/2	5.92	5.3

Similar Calculation can be done for Low-spin Complex

- The magnetic moment  $\mu$  of a complex with total spin quantum number S is:

- $\mu = 2\{S(S+1)\}^{1/2} \mu_B$  ( $\mu_B$  is the Bohr magneton)
- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$
- Since each unpaired electron has a spin  $1/2$ ,
- $S = (1/2)n$ , where n = no. of unpaired electrons
- $\mu = \{n(n+2)\}^{1/2} \mu_B$
- In d<sup>4</sup>, d<sup>5</sup>, d<sup>6</sup>, and d<sup>7</sup> octahedral complexes, magnetic measurements can very easily predict weak versus strong field.
- Tetrahedral complexes - only high spin complexes result, for  $\Delta_t \ll \Delta_O$ .

## Limitations of CFT

**Considers Ligand as Point charge/dipole only**

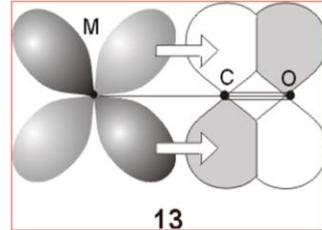
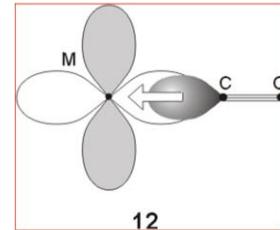
**Does not take into account of the overlap of ligand and metal orbitals**

## Consequence

e.g. Fails to explain why CO is stronger ligand than CN<sup>-</sup> in complexes having metal in low oxidation state

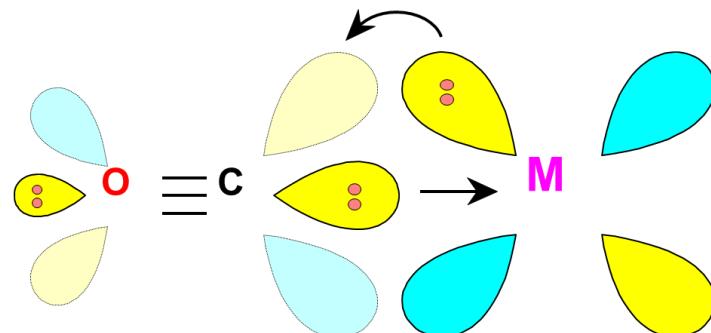
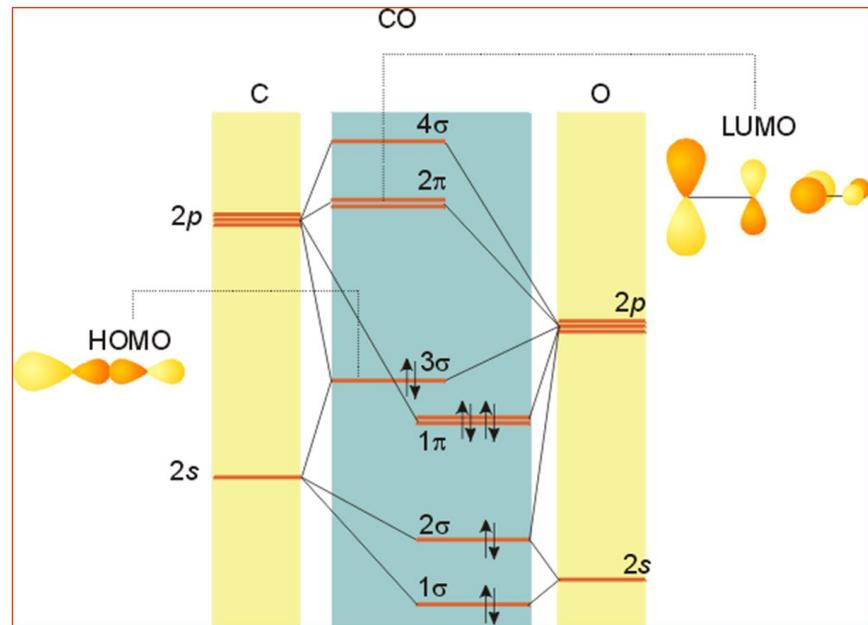
## Metals in Low Oxidation States

- In low oxidation states, the electron density on the metal ion is very high.**
- To stabilize low oxidation states, we require ligands, which **can simultaneously bind the metal center and also withdraw electron density from it.**



Ni(CO)<sub>4</sub>, [Fe(CO)<sub>5</sub>], [Cr(CO)<sub>6</sub>], [Mn<sub>2</sub>(CO)<sub>10</sub>], [Co<sub>2</sub>(CO)<sub>8</sub>], Na<sub>2</sub>[Fe(CO)<sub>4</sub>], Na[Mn(CO)<sub>5</sub>]

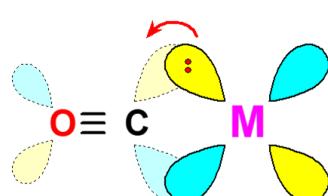
## Stabilizing Low Oxidation State: CO Can Do the Job



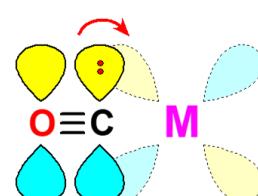
**σ orbital serves as a very weak donor to a metal atom**



CO-M sigma bond



M to CO pi backbonding



CO to M pi bonding  
(rare)