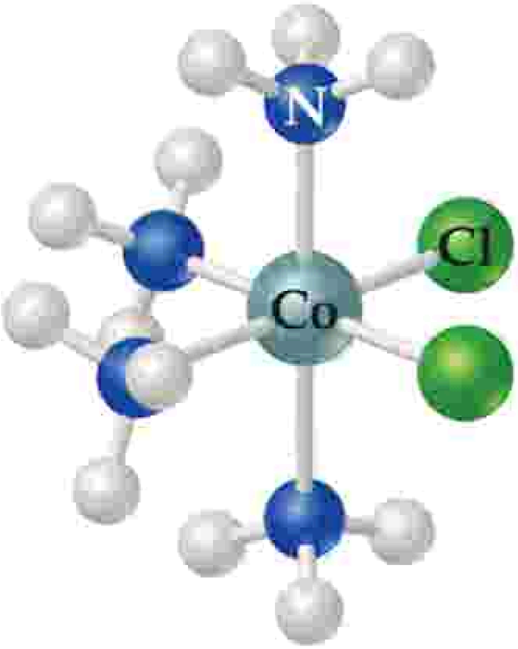
Chapter 24
Chemistry of Coordination Compounds

Coordination Compounds

- How do we think about transition metals binding to other atoms?
- What do those d orbitals do?

- We call them, **coordination compounds.**

Complexes

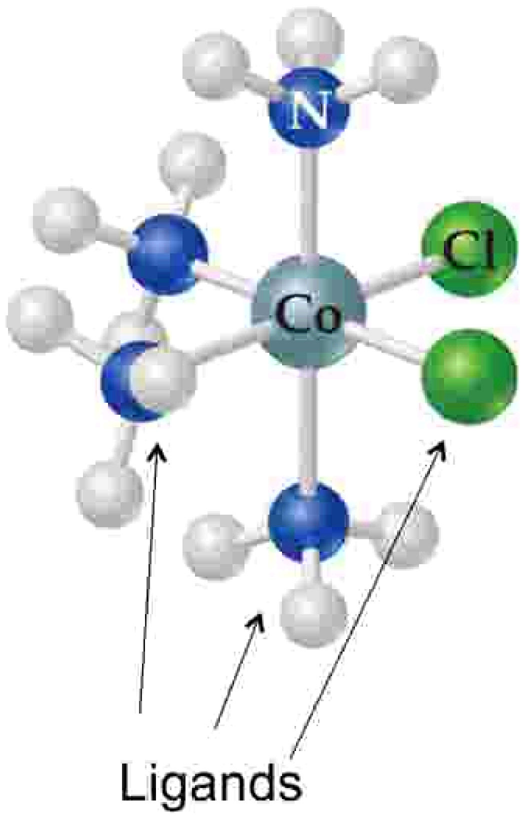


Question, is this an “ionic compound”

Does it dissociate in water?

- A central metal atom can bond to a group of molecules or ions: **metal complex.**
- If it’s charged: **complex ion.**
- Compounds containing complexes are **coordination compounds.**

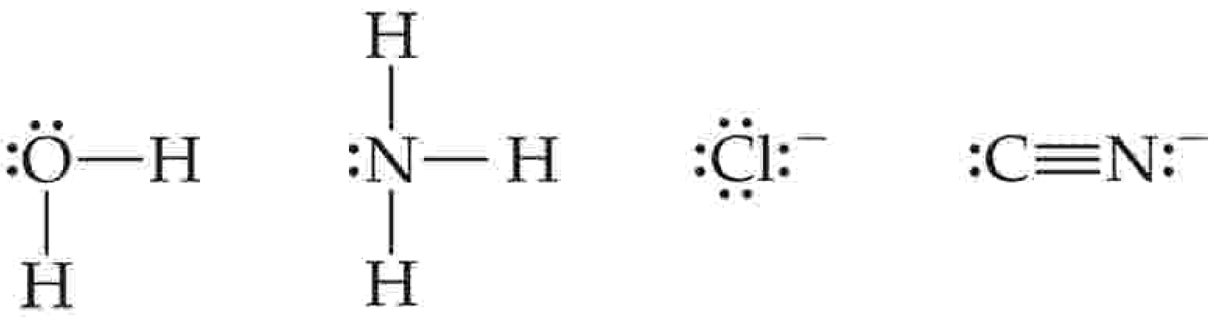
Complexes



- 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

Complexes

- Examples of some common ligands
- Note, all have lone pairs
- Some are charged, others are not.



A chemical mystery:

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

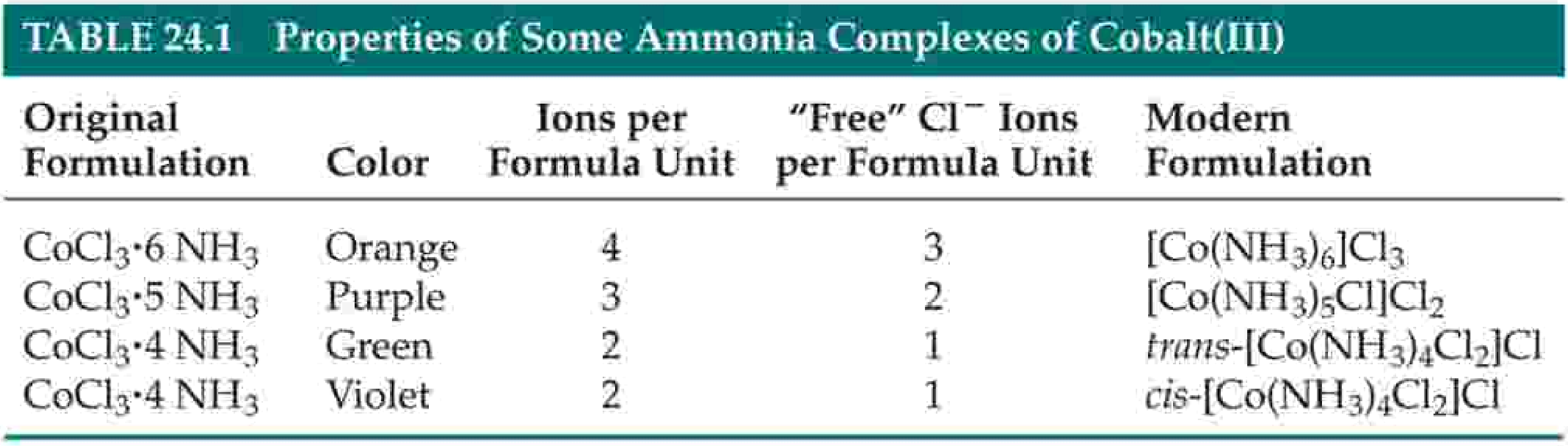
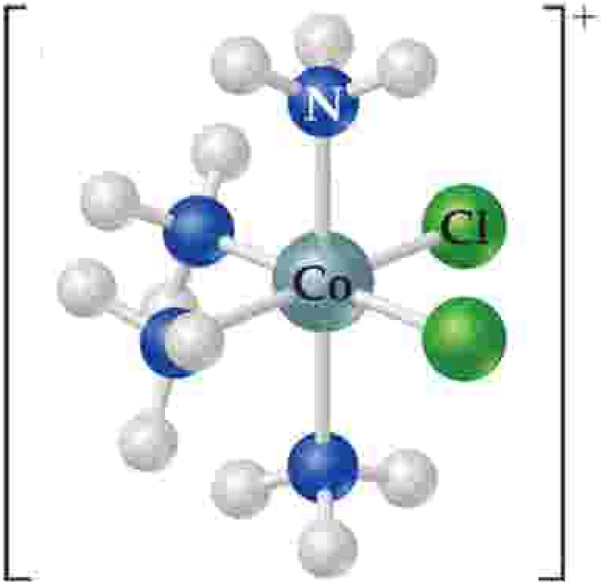


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\,NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\,NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\,NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\,NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

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

Werner's Theory



Co(III) oxidation state

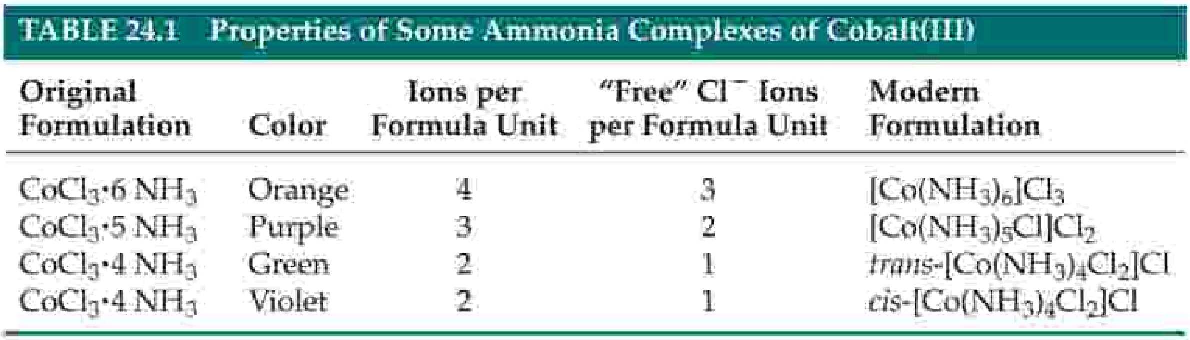
Coordination # is 6

Cl-

- suggested in 1893 that metal ions have ***primary*** and ***secondary*** valences.
  - Primary valence equals 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 $CoCl_3 \cdot 6\ NH_3$, all six of the ligands are NH_3 and the 3 chloride ions are outside the coordination sphere.



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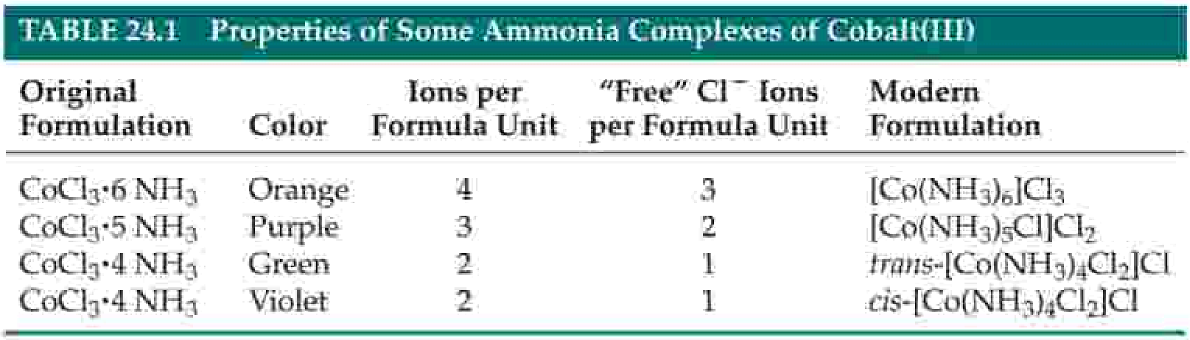
Werner’s Theory

In $CoCl_3 \cdot 5\ NH_3$ the five NH_3 groups and one chlorine are bonded to the cobalt, and the other two chloride ions are outside the sphere.



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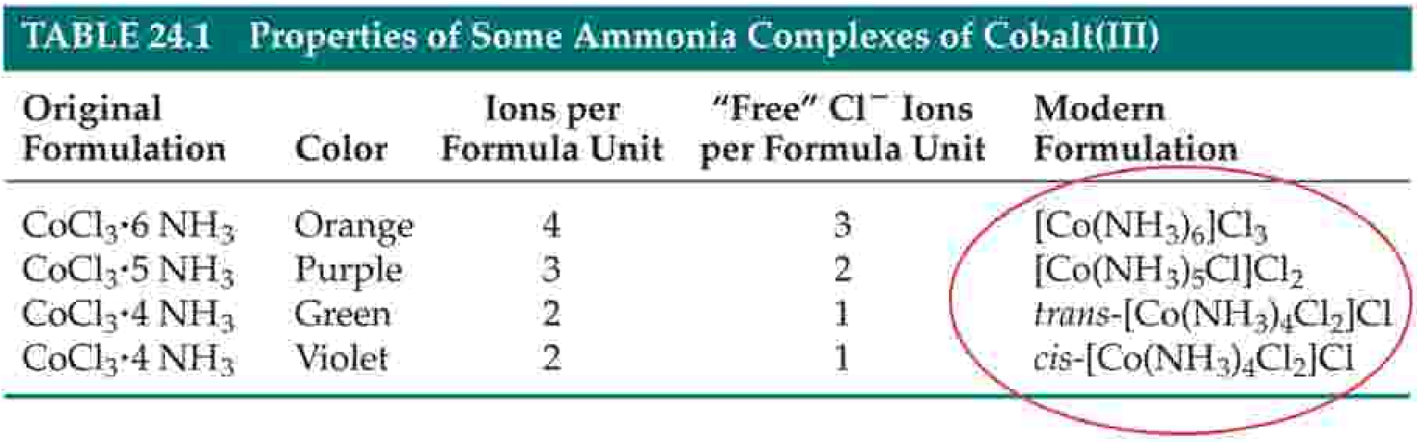
Werner's Theory

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.



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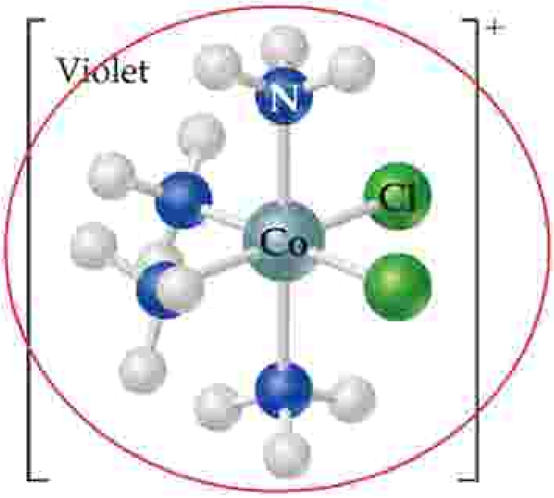
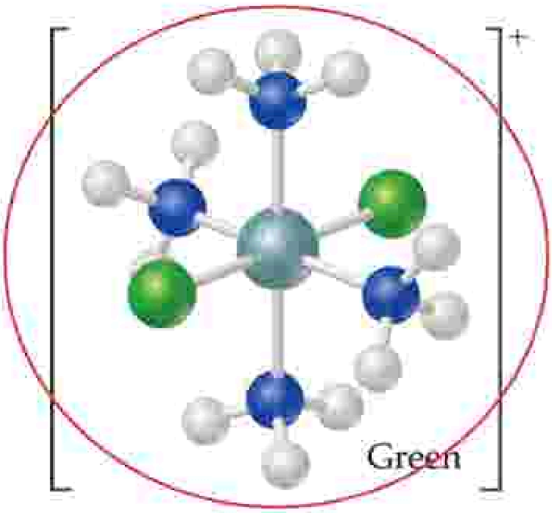
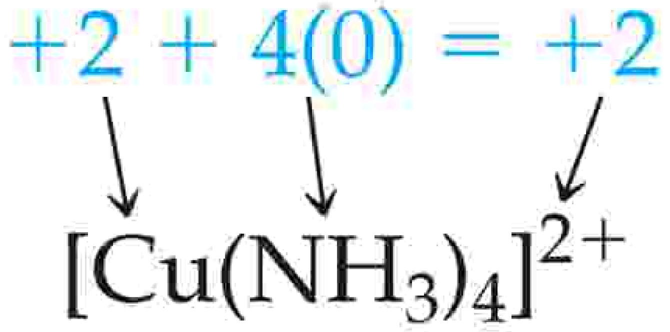
Werner's Theory





- This approach correctly predicts there would be two forms of $CoCl_3 \cdot 4\ NH_3$.
  - The formula would be written $[Co(NH_3)_4Cl_2]Cl$.
  - One of the two forms has the two chlorines next to each other.
  - The other has the chlorines opposite each other.

Oxidation Numbers



$$+2 + 4(0) = +2$$

$$[Cu(NH_3)_4]^{2+}$$

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.

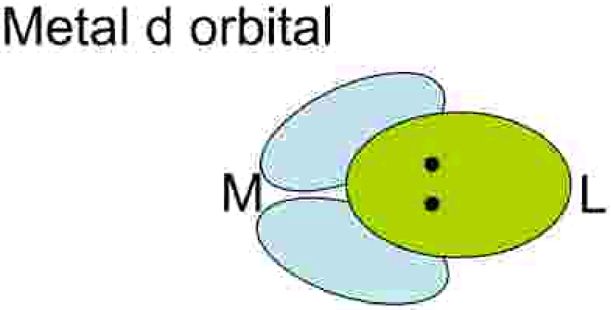
Example: $\mathrm{Cr(III)(H_2O)_4Cl_2}$

$$\underset{\downarrow}{+3} + \underset{\downarrow}{4(0)} + \underset{\downarrow}{2(-1)} = +1$$

$$\mathrm{Cr(H_2O)_4Cl_2^{+}}$$

What is Coordination?

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

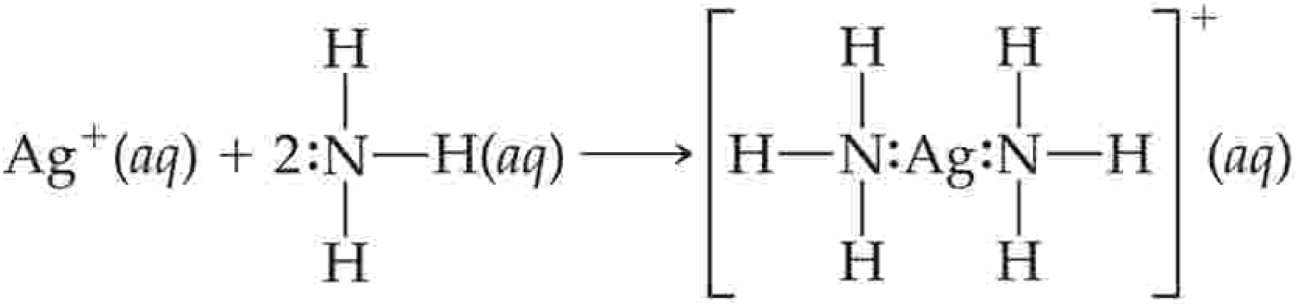


Sometimes called a coordinate covalent bond

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.



$$\mathrm{Ag}^{+}(aq) + 2{:}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}\mathrm{—H}(aq) \longrightarrow \left[\mathrm{H—}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}{:}\mathrm{Ag}{:}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}\mathrm{—H}\right]^{+}(aq)$$

What is Coordination?

So ligands *must* have lone pairs of electrons.

- **There are 3 ways of looking at bonding in coordination compounds:**
  - **Valence bond theory**
  - **Ligand Field Theory (adaptation of MO theory)**
  - **Crystal Field Theory (theory of pure electrostatic interactions**

Valence Bond theory

- Just like we learned before.
  - We mix the atomic orbitals on the metal before we bond the ligands:
- For Transition metals we have 9-14 valence orbitals
  - 1 ns
  - 5 (n-1)d
  - 3 np
  - 5 nd

Valence Bond theory

- Just like we learned before.
  - We mix the atomic orbitals on the metal before we bond the ligands:
- For Transition metals we have 14 valence orbitals
  - 1 ns
  - 5 (n-1)d
  - 3 np
  - 5 nd if needed.

Valence Bond theory

- Example

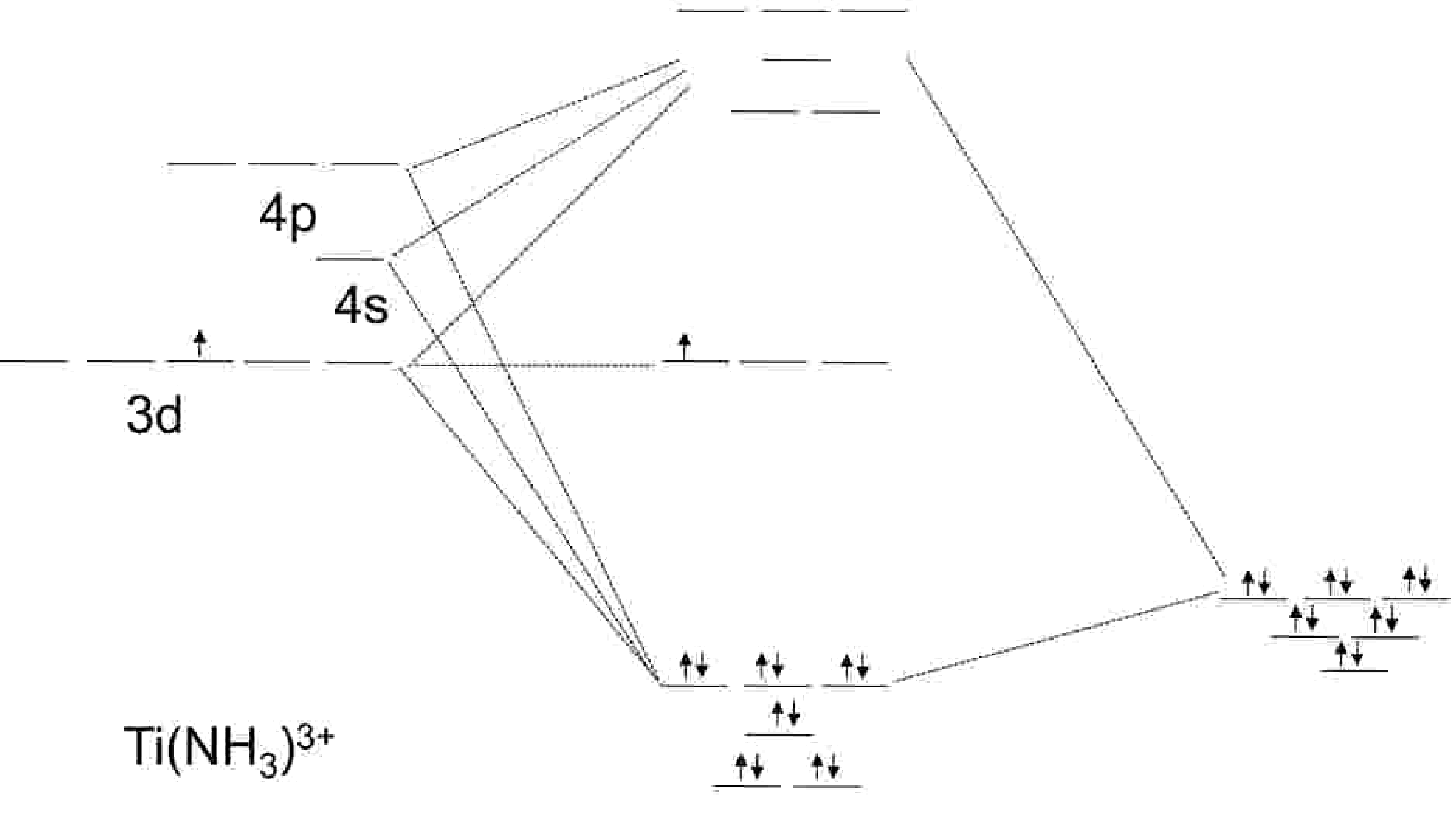
- $Co(NH_3)_6^{3+}$
- Co^{3+} electron configuration:
- $4s^2 3d^4$ ----→ $4s^0 3d^6$
- Need six orbitals for six ligands so:
  - ➢Hybridize 1 4s, 3 4p and 2 3d to give:
  - ➢Sp^3d^2 orbitals. The 6 electrons of Co^{+3} sit in the other 3 d orbitals.

Valence Bond theory

- Example

- $Ni(NH_3)_6^{2+}$
- Ni^{2+} electron configuration (8 electrons):
- $4s^2 3d^6$ ----→ $4s^0 3d^8$
- Need six orbitals for six ligands but:
  - ➢4 3d orbitals are full, only 1 3d orbital left
  - ➢Must hybridize 1 4s, 3 4p and 2 4d to give:
  - ➢sp^3d^2 orbitals. The 8 electrons of Ni^{2+} sit in five 3d orbitals.

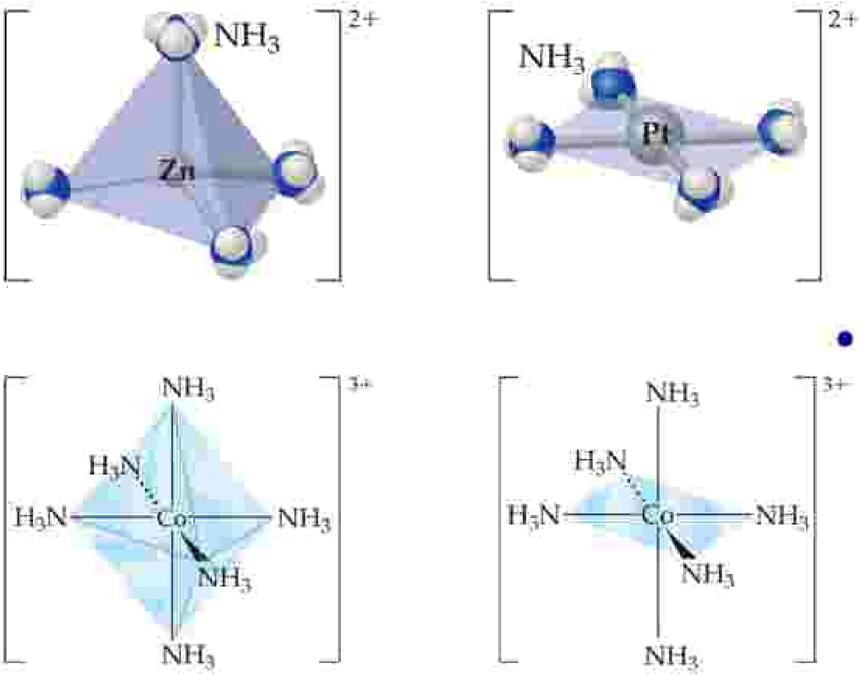
Ligand Field theory (MO theory for coordination compounds)



Metal-Ligand Bond

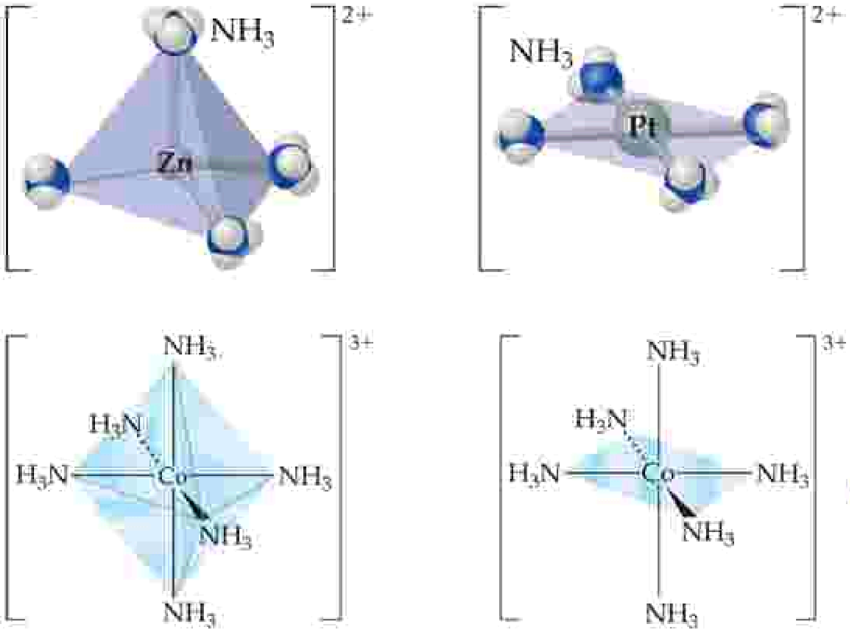
The metal's coordination ligands and geometry can greatly alter its properties, such as color, or ease of oxidation.

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.

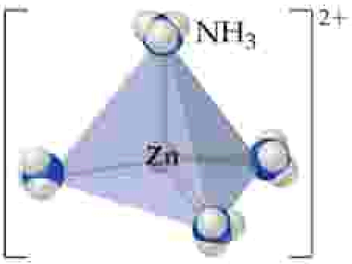
Coordination Number



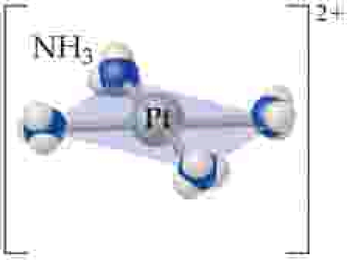
- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.

Geometries

- Metal ions with d^8 configuration are often 4 coordinate
- There are two common geometries for metals with a coordination number of four:
  - Tetrahedral
  - Square planar



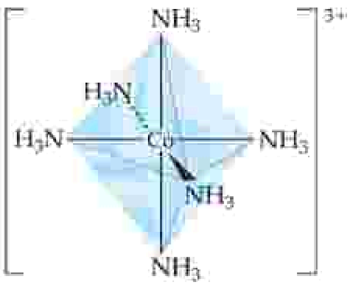
Tetrahedral

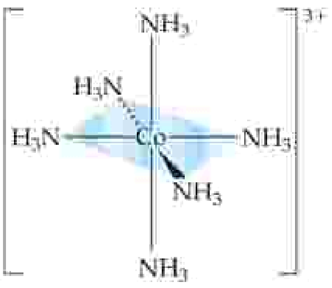


Square planar

Why square planar? We'll get to that

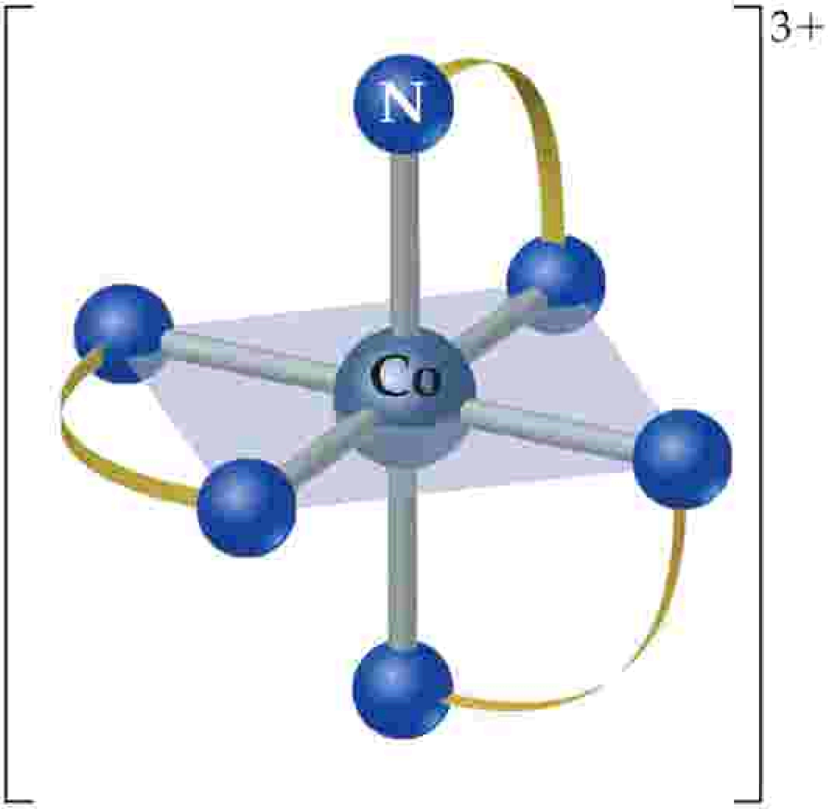
Geometries





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

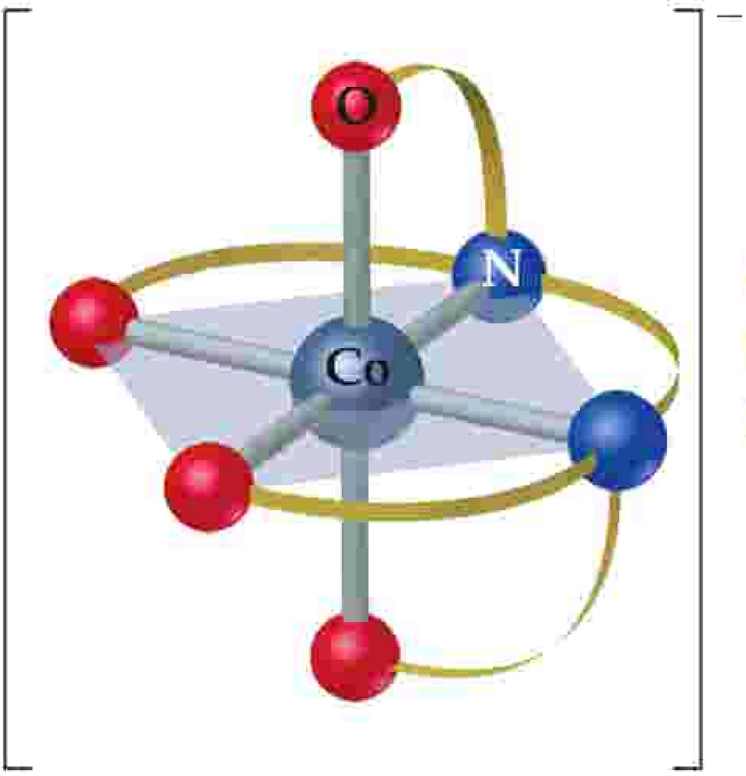
Polydentate Ligands



$[Co(en)_3]^{3+}$

- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylenediamine, $NH_2CH_2CH_2NH_2$, represented here as en, each N is a donor atom.
- Therefore, en is bidentate.

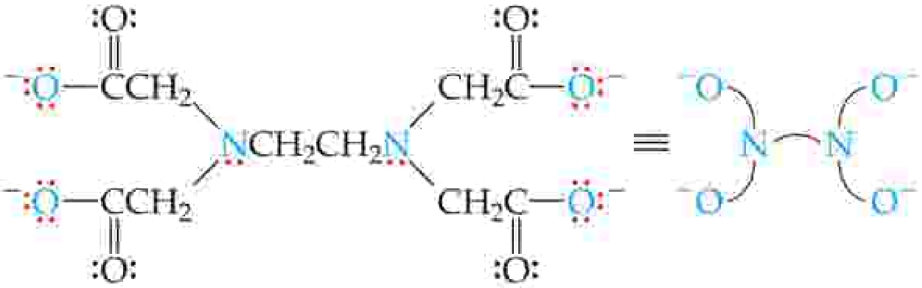
Polydentate Ligands



$CoEDTA^-$

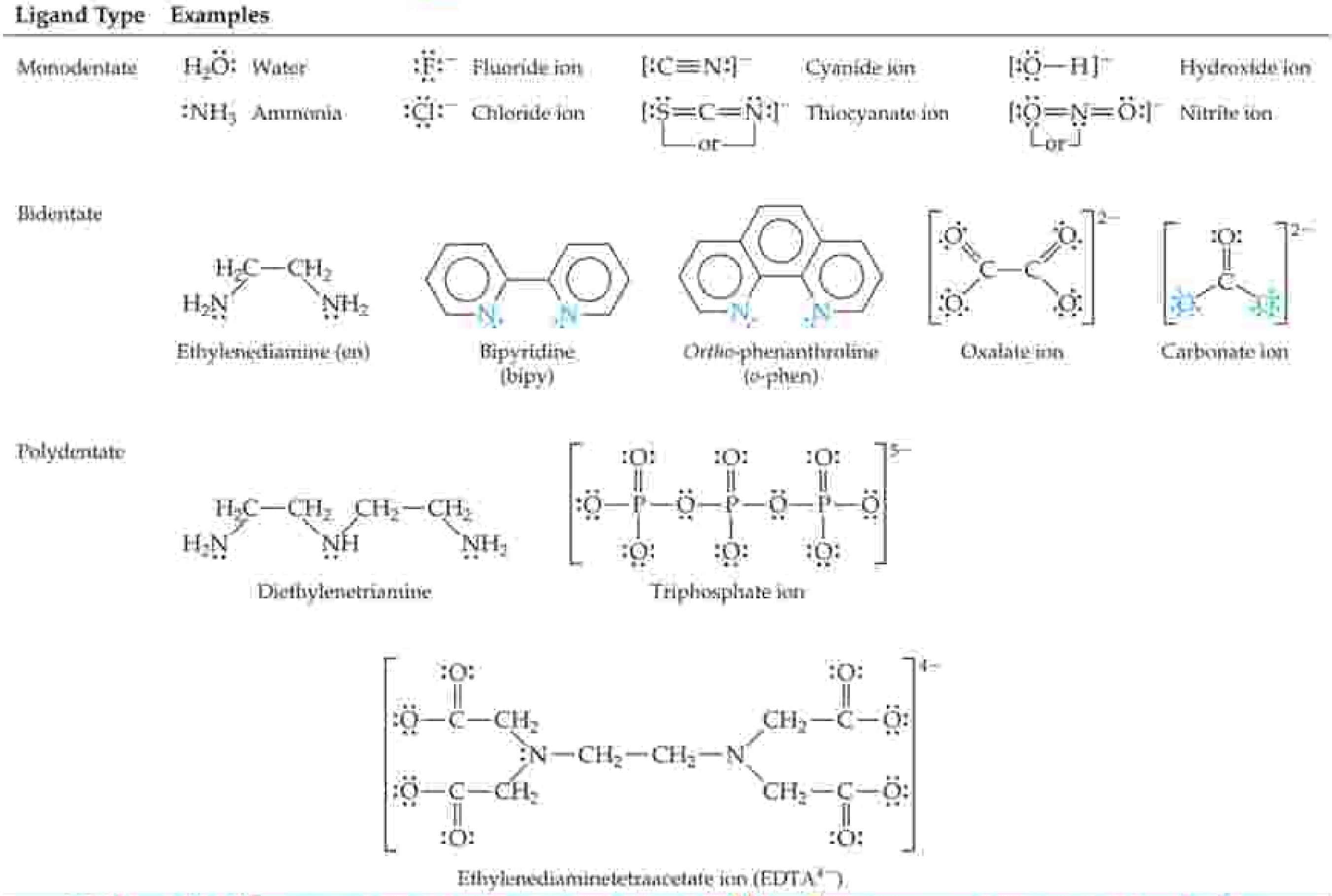
Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.

Wraps around the central atom like an octopus



$[EDTA]^{4-}$

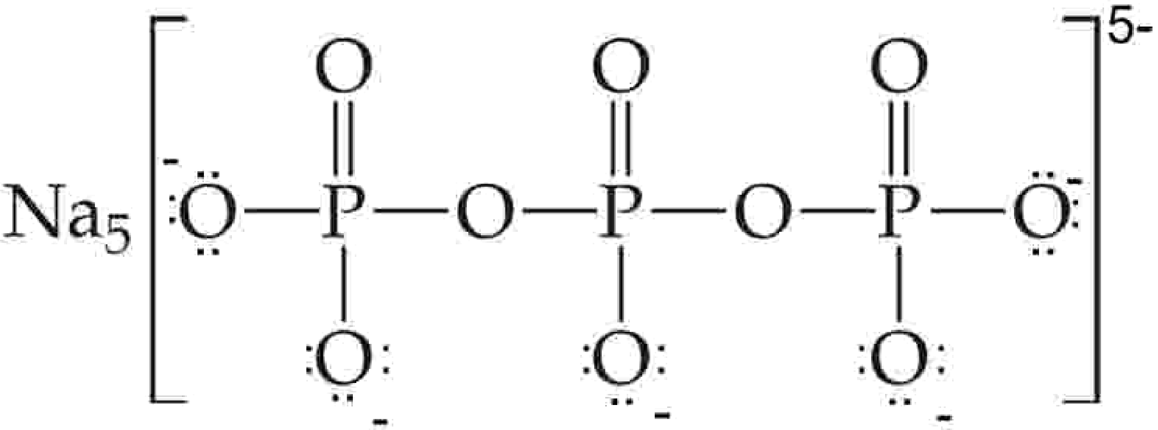
Polydentate Ligands



Ligand Type	Examples
Monodentate	$H_2\ddot{O}$: Water :NH_3 Ammonia :F:$^-$ Fluoride ion :Cl:$^-$ Chloride ion [:C≡N:]$^-$ Cyanide ion [:S=C=N:]$^-$ Thiocyanate ion (or) [:O—H]$^-$ Hydroxide ion [:O=N—O:]$^-$ Nitrite ion (or)
Bidentate	Ethylenediamine (en) Bipyridine (bipy) *Ortho*-phenanthroline (*o*-phen) Oxalate ion Carbonate ion
Polydentate	Diethylenetriamine Triphosphate ion Ethylenediaminetetraacetate ion ($EDTA^{4-}$)

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

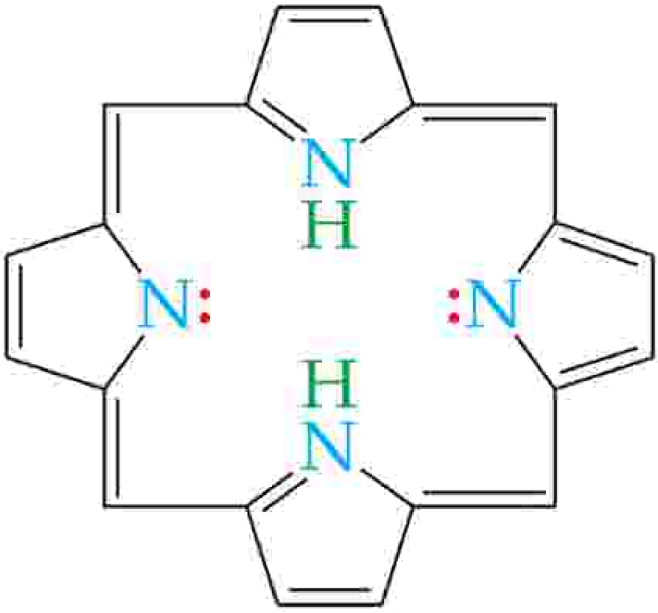
Chelating Agents



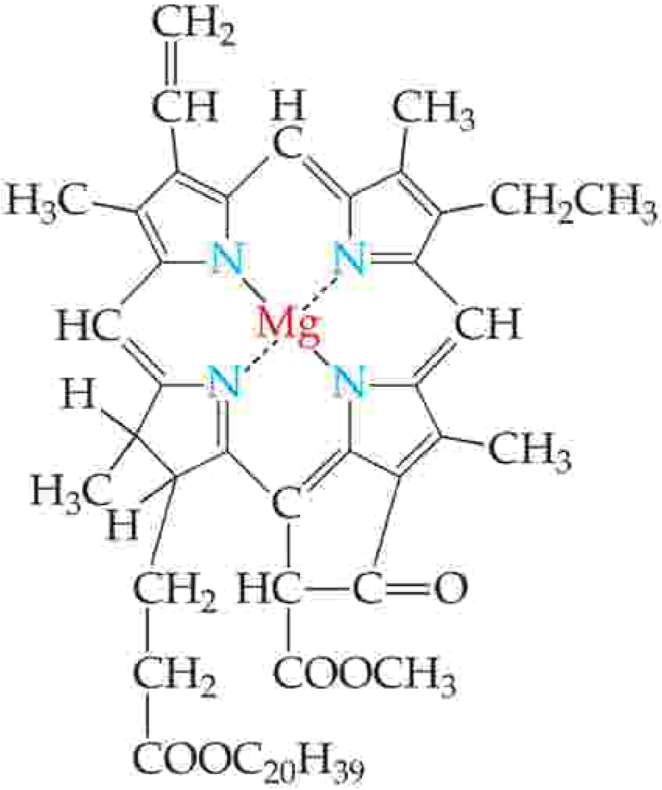
- Bind to metal ions removing them from solution.
- Phosphates are used to tie up Ca^{2+} and Mg^{2+} in hard water to prevent them from interfering with detergents.

Chelating Agents

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



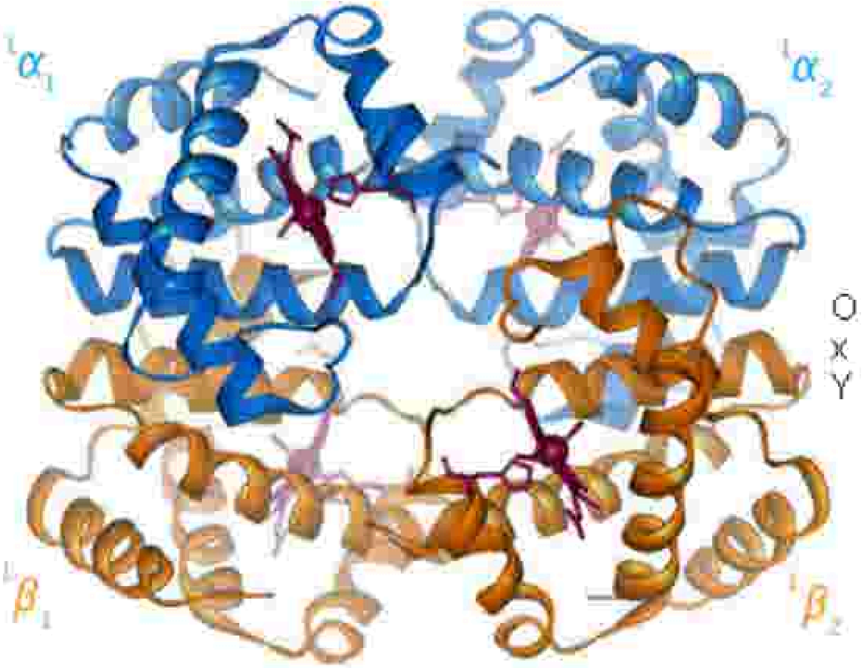
Chelating Agents



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

Porphyrin Heme binds the oxygen in your blood

Part of Hemoglobin molecule
Hemoglobin tetramer has 4 hemes



Oxygen binding causes conformational change
Makes the other sites bind oxygen better

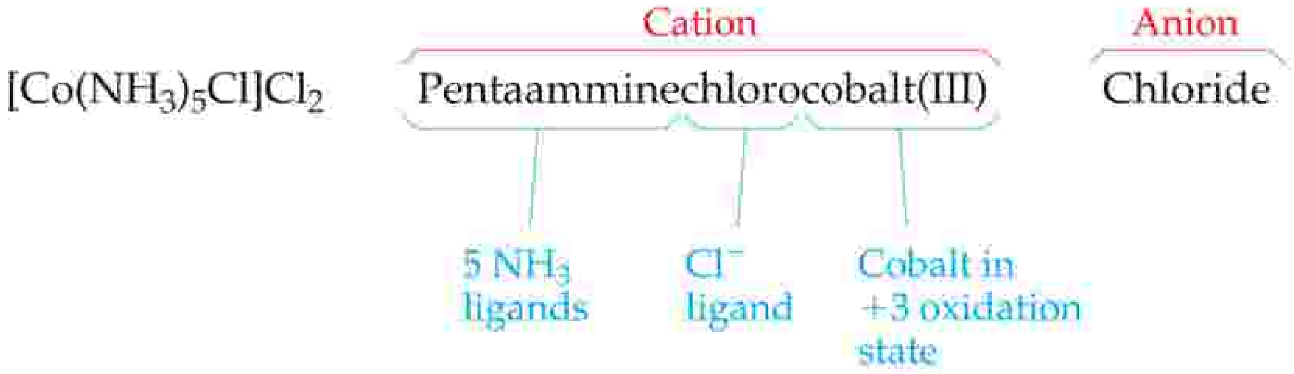
Nomenclature of Coordination Compounds

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-	Hydroxo	Pyridine, C_5H_5N	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

- coordination complex nomenclature:
  - name the ligands as prefixes before the metal name.

Nomenclature of Coordination Compounds

- **Cation** appears first (as always)
- **Anion** is named last.
- Ligands are listed alphabetically before the metal. Prefixes ignored when alphabetizing.



$[Co(NH_3)_5Cl]Cl_2$

Cation

Pentaamminechlorocobalt(III)

Anion

Chloride

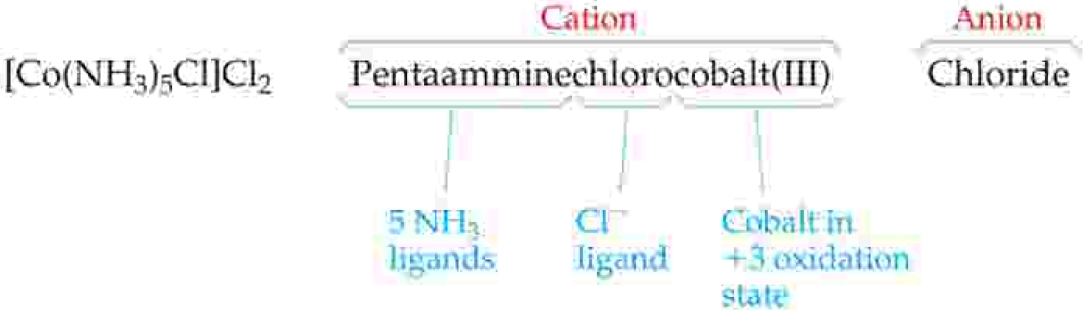
$5\ NH_3$ ligands

Cl^- ligand

Cobalt in +3 oxidation state

Nomenclature of Coordination Compounds

- Anionic ligands end in “o”;
- neutral ligands are not changed.
- Prefixes = number of each ligand.
- If the name of the ligand itself has such a prefix, alternatives like *bis*-, *tris*-, etc., are used.



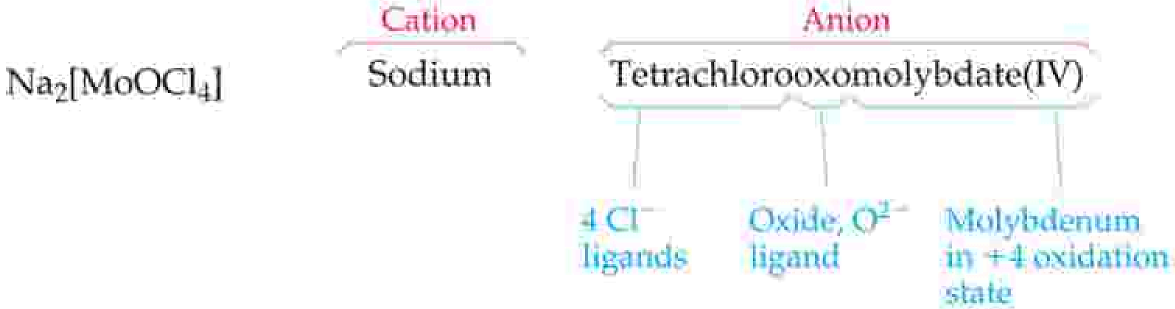
$[Co(NH_3)_5Cl]Cl_2$

Cation: Pentaamminechlorocobalt(III)

Anion: Chloride

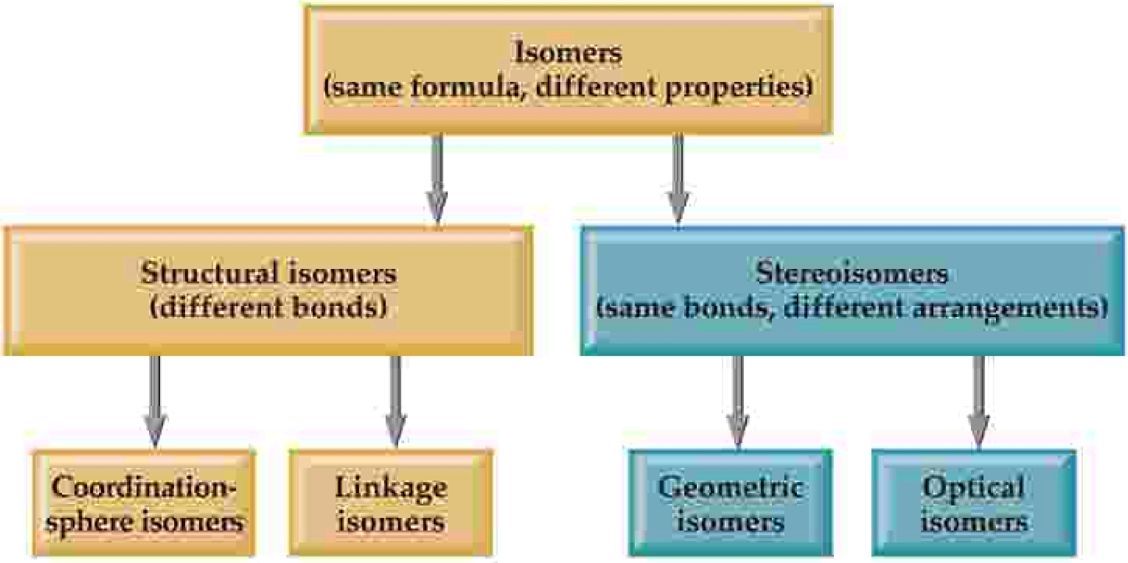
Nomenclature of Coordination Compounds

- If complex is anion, its ending is changed to *-ate*.
- The oxidation number of the metal is given by a Roman numeral in parentheses after the metal.



$Na_2[MoOCl_4]$

Isomers



Isomers
(same formula, different properties)

Structural isomers
(different bonds)

Stereoisomers
(same bonds, different arrangements)

Coordination-sphere isomers

Linkage isomers

Geometric isomers

Optical isomers

Isomers have the same molecular formula, but either:

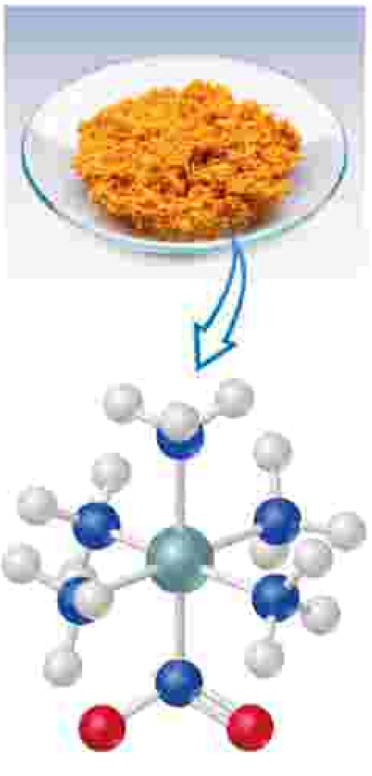
Their bonding is different (structural isomers) or

Their spatial arrangement is different (stereoisomers).

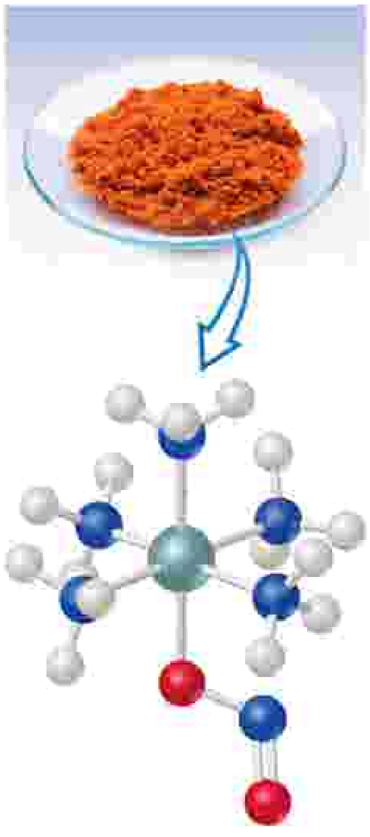
Structural Isomers

If a ligand (like the NO_2 group at the bottom of the complex) has more than one donor atom (*atom with lone pairs*) as the donor atom, linkage isomers are formed.

Is this a *structural* or *geometric* isomer?



Nitro isomer



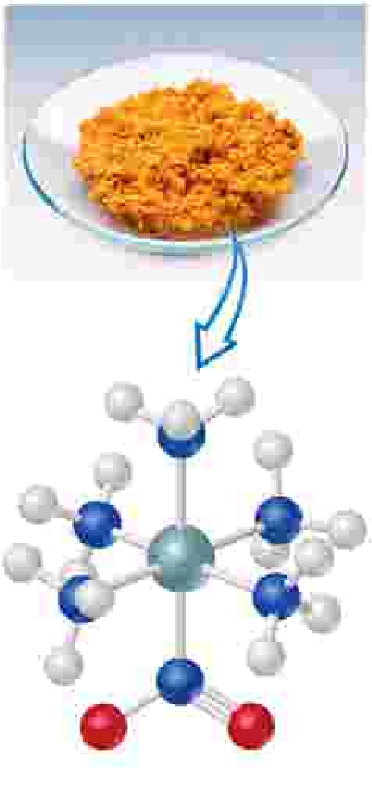
Nitrito isomer

Structural Isomers

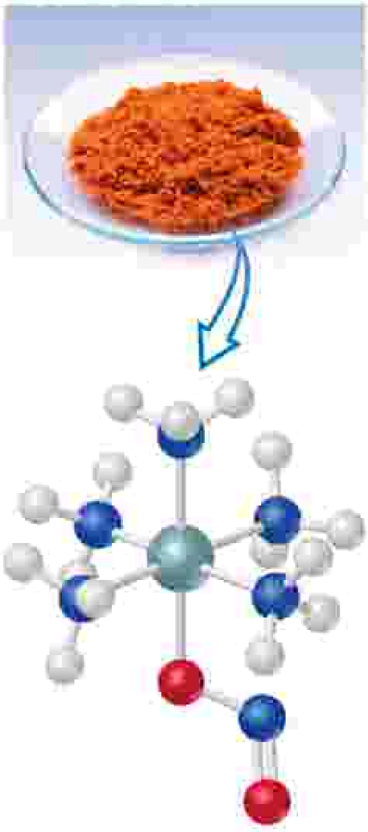
If a ligand (like the NO_2 group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, linkage isomers are formed.

Is this a *structural* or *geometric* isomer?

Structural,
bonding different



Nitro isomer

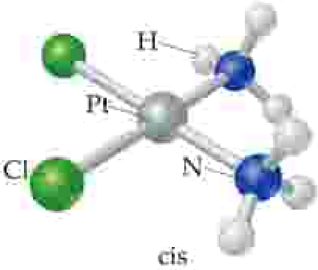


Nitrito isomer

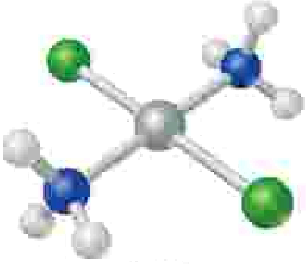
Structural Isomers

- Some isomers differ in what ligands are bonded to the metal (coordination sphere) and which are not.
- these are coordination-sphere isomers.
- Example:
- Three isomers of $CrCl_3(H_2O)_6$ are
  - ➢The violet $[Cr(H_2O)_6]Cl_3$,
  - ➢The green $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and
  - ➢The (also) green $[Cr(H_2O)_4Cl_2]Cl \cdot 2\ H_2O$.

Geometric isomers



cis

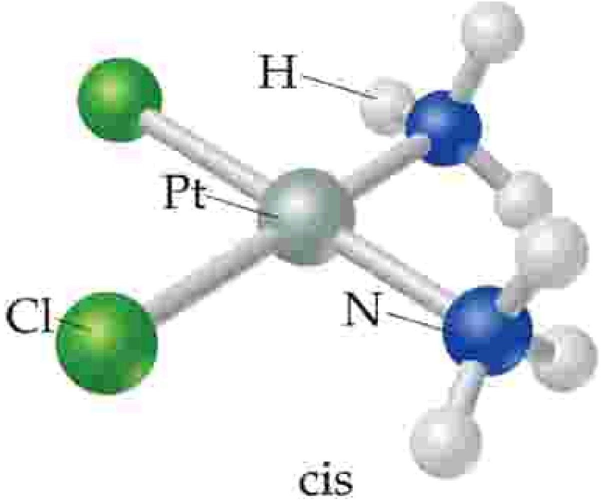


trans

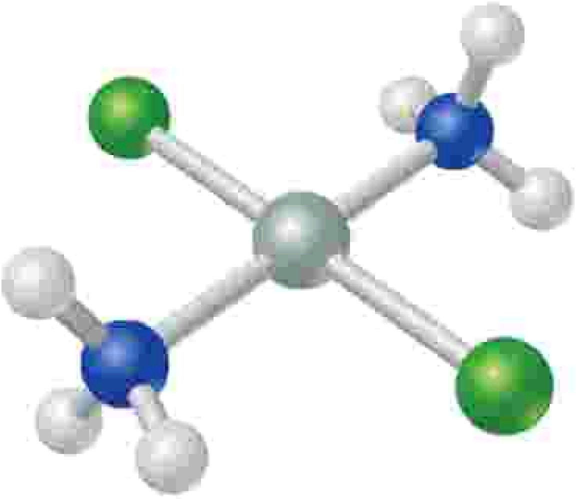
- $Pt(NH_3)_2Cl_2$
- Has two *geometric isomers*, two chlorines and two NH_3 groups are bonded to the platinum metal, but are clearly different.
  - ➢*cis*-Isomers have like groups on the same side.
  - ➢*trans*-Isomers have like groups on opposite sides.

# of each atom the same
Bonding the same
Arrangement in space different

Geometric isomers



cis

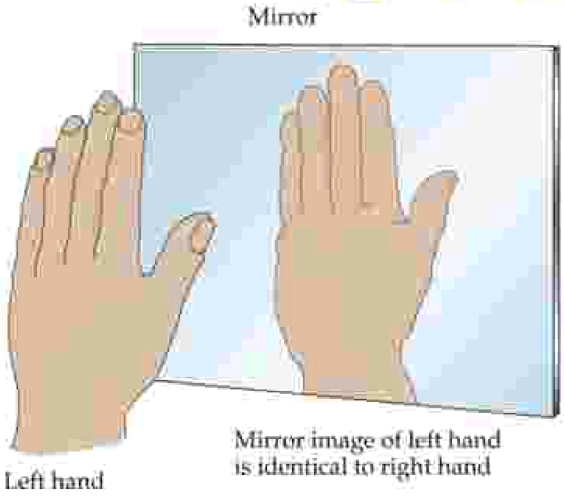


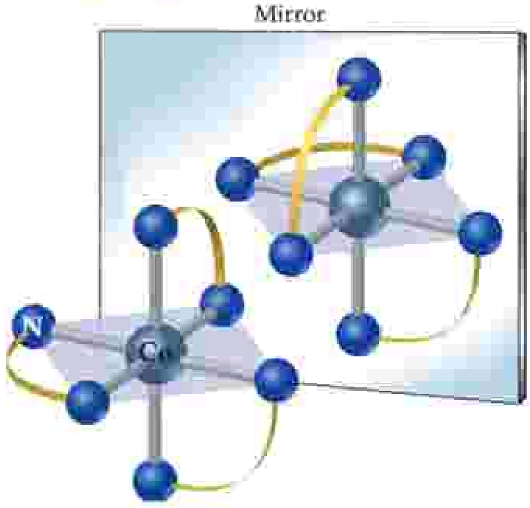
trans

This compound binds DNA
Kills rapidly dividing cancer cells

This one doesn’ t

Stereoisomers

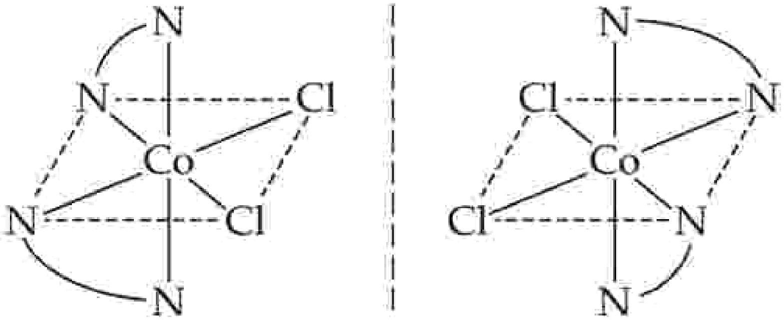




- Other stereoisomers, called optical isomers or enantiomers, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

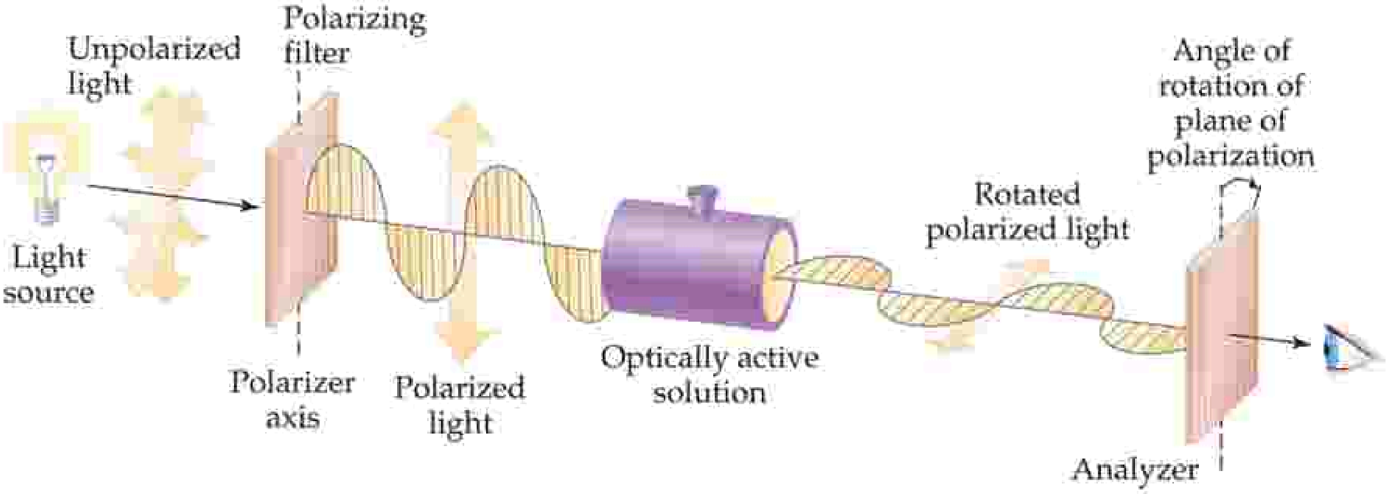
Enantiomers

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



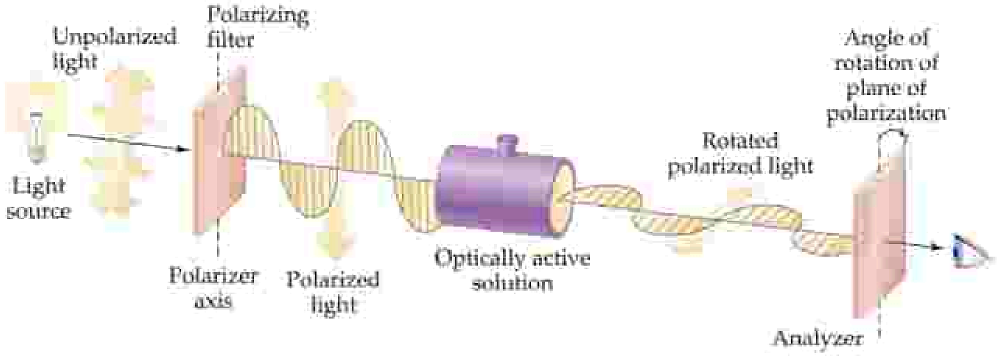
Enantiomers

- Physical properties of chiral molecules are identical (boiling point, freezing point, density, etc.)
- One exception:
  - interaction of a chiral molecule with plane-polarized light.



Enantiomers

- A chiral compound will rotate plane polarized light.
- If one enantiomer rotates the light 32° to the right, the other will rotate it 32° to the left.
- Generally, only when 2 chiral things interact is there a difference in properties.



Explaining the properties of transition metal coordination complexes

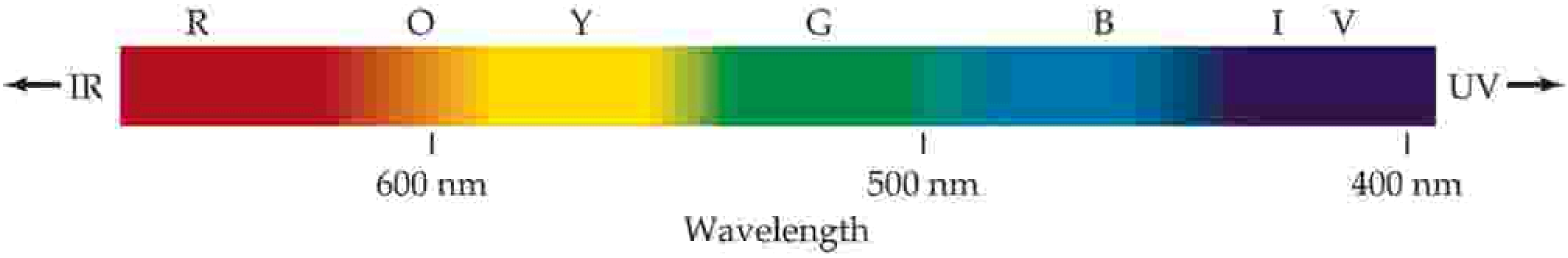
1. Magnetism
2. color

Metal complexes and color

The ligands of a metal complex effect its color

Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

Why does anything have color?



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

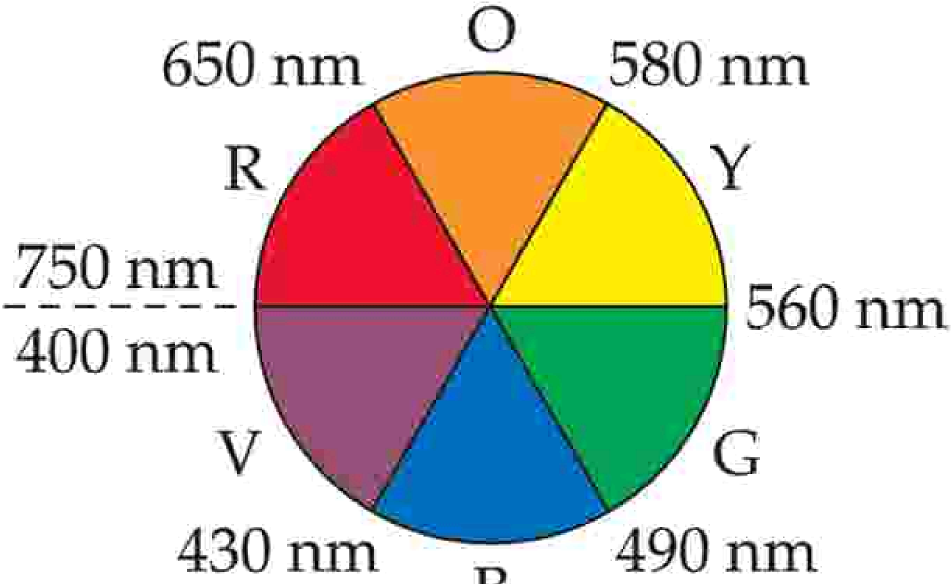
If one color absorbed, the color opposite is perceived.

Absorb **Orange**

See **Blue**

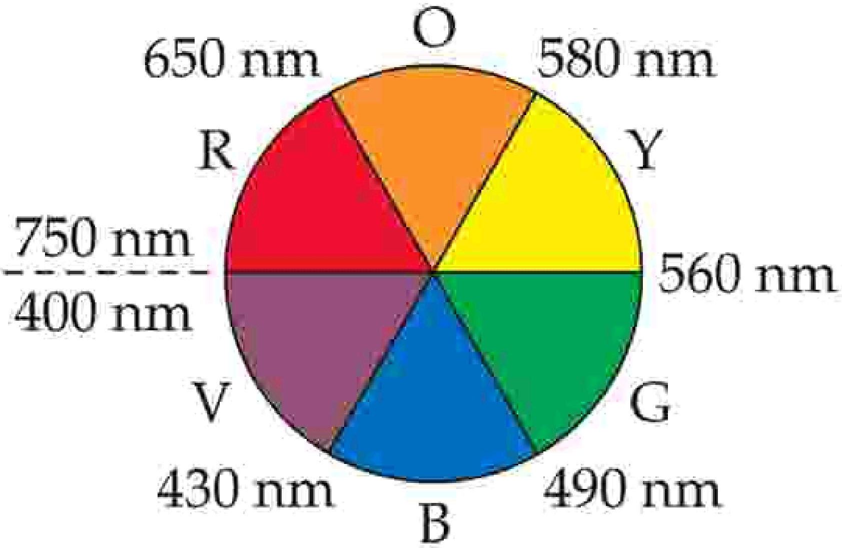
Absorb **Red**

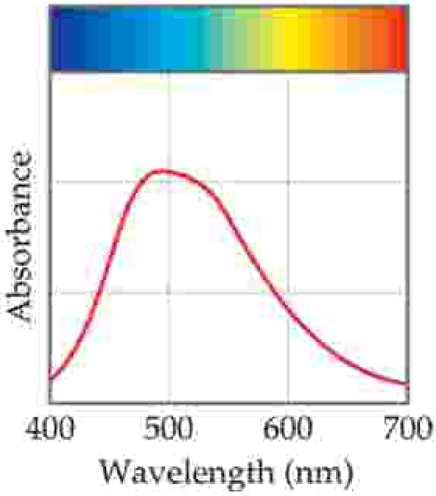
See **Green**



$[Ti(H_2O)_6]^{3+}$
Absorbs in green yellow.
Looks purple.

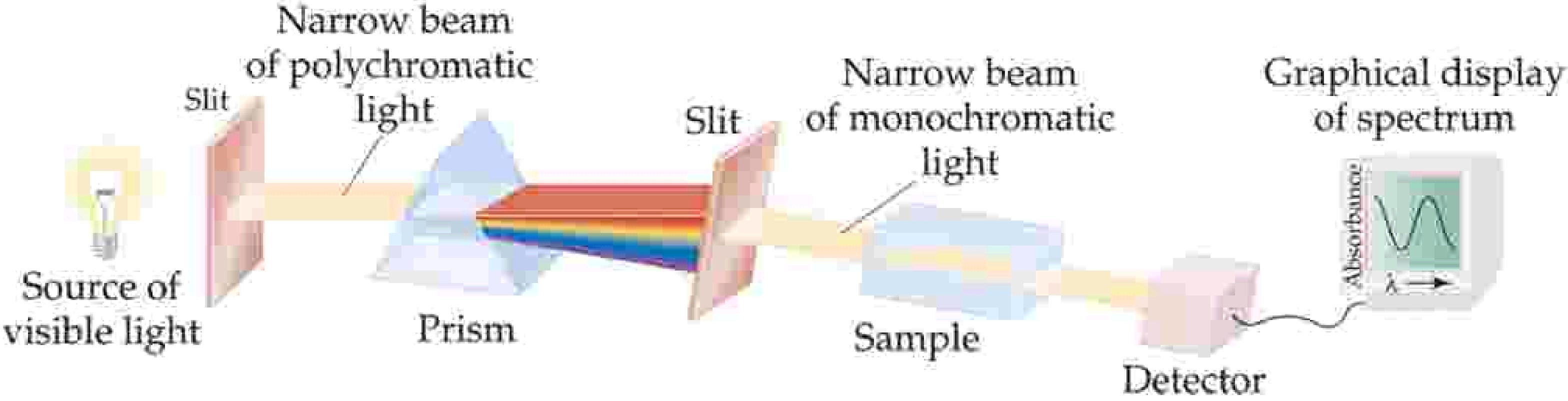
(a)





(b)

How is an absorption spectrum of a Compound measured? A spectrophotometer.



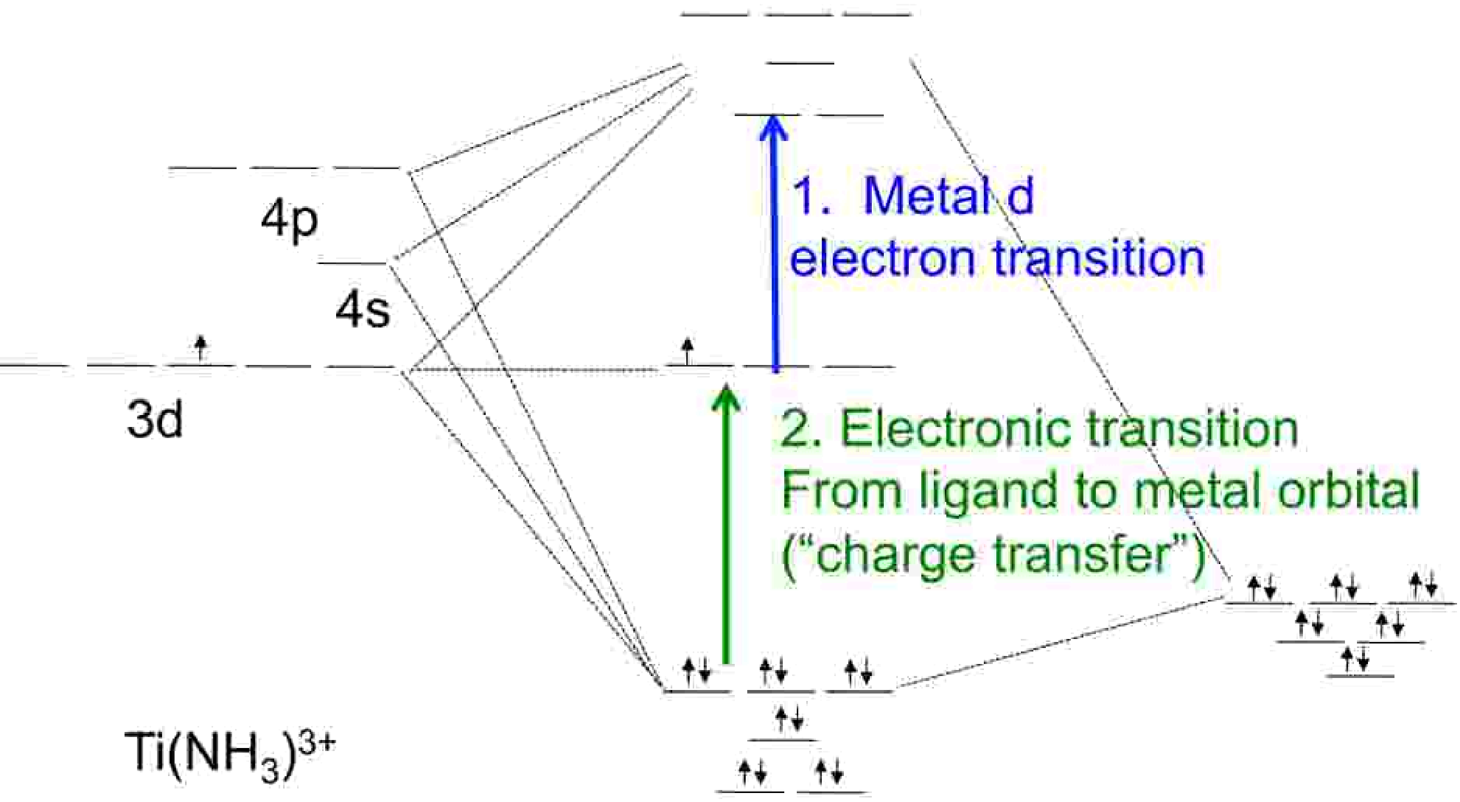
So color comes from:

Absorption (metal complexes)

Emission (element line spectra)

How is light absorbed in a metal complex?

Ligand Field theory: 2 possibilities



1. Metal d electron transition

2. Electronic transition From ligand to metal orbital ("charge transfer")

Metal complexes and color

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

Why do different ligands change absorption?

Metal complexes and color

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

Why do different ligands change absorption?

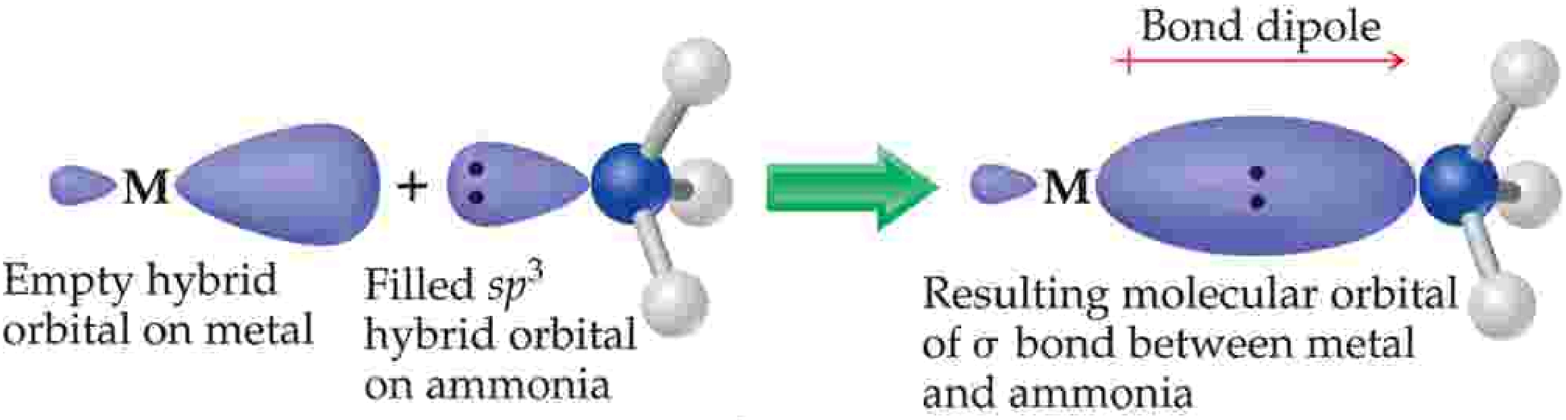
Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

Model of ligand/metal bonding.

Electron pair comes from ligand

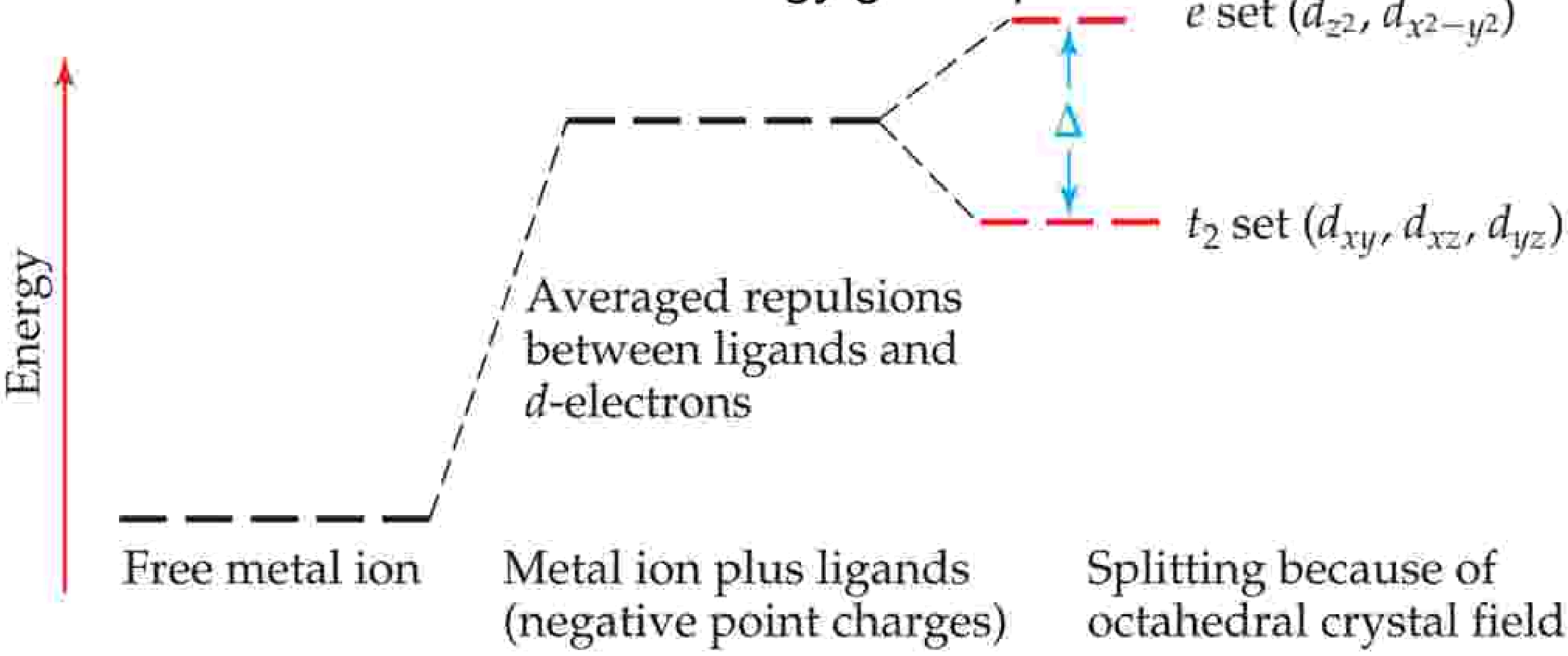
Bond very polarized.

Assumption: interaction pure electrostatic.



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

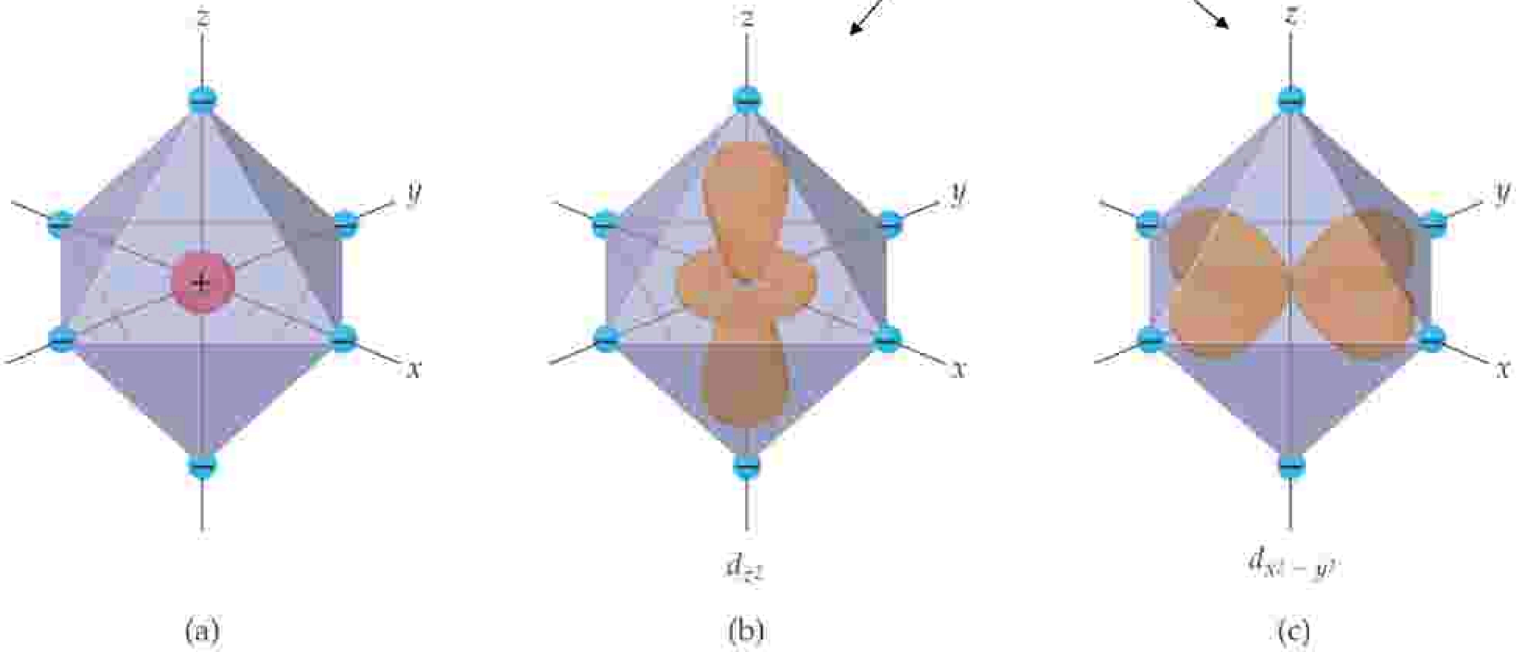
Ligand negative charge
Is repelled by d electrons,
d orbital energy goes up



Ligands will interact with some d orbitals more than others

Depends on relative orientation of orbital and ligand

Ligands point right at lobes



(a)

d_{z^2}

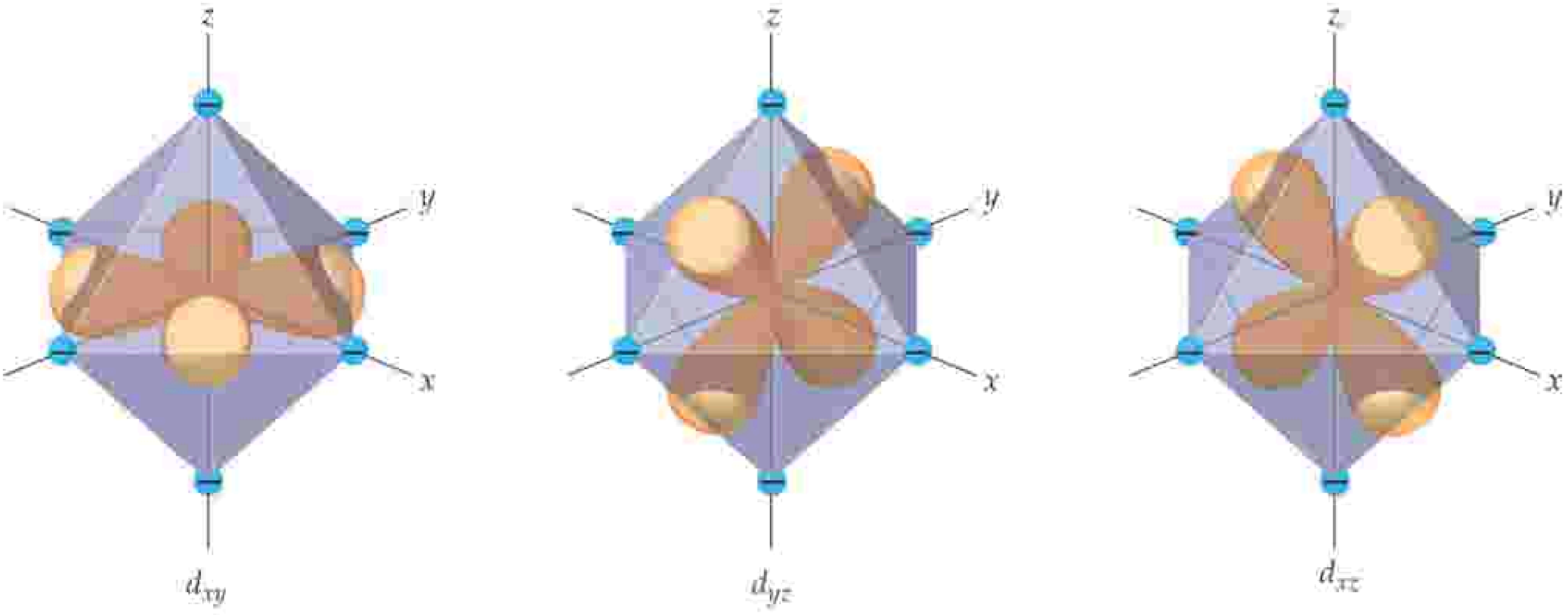
(b)

$d_{x^2-y^2}$

(c)

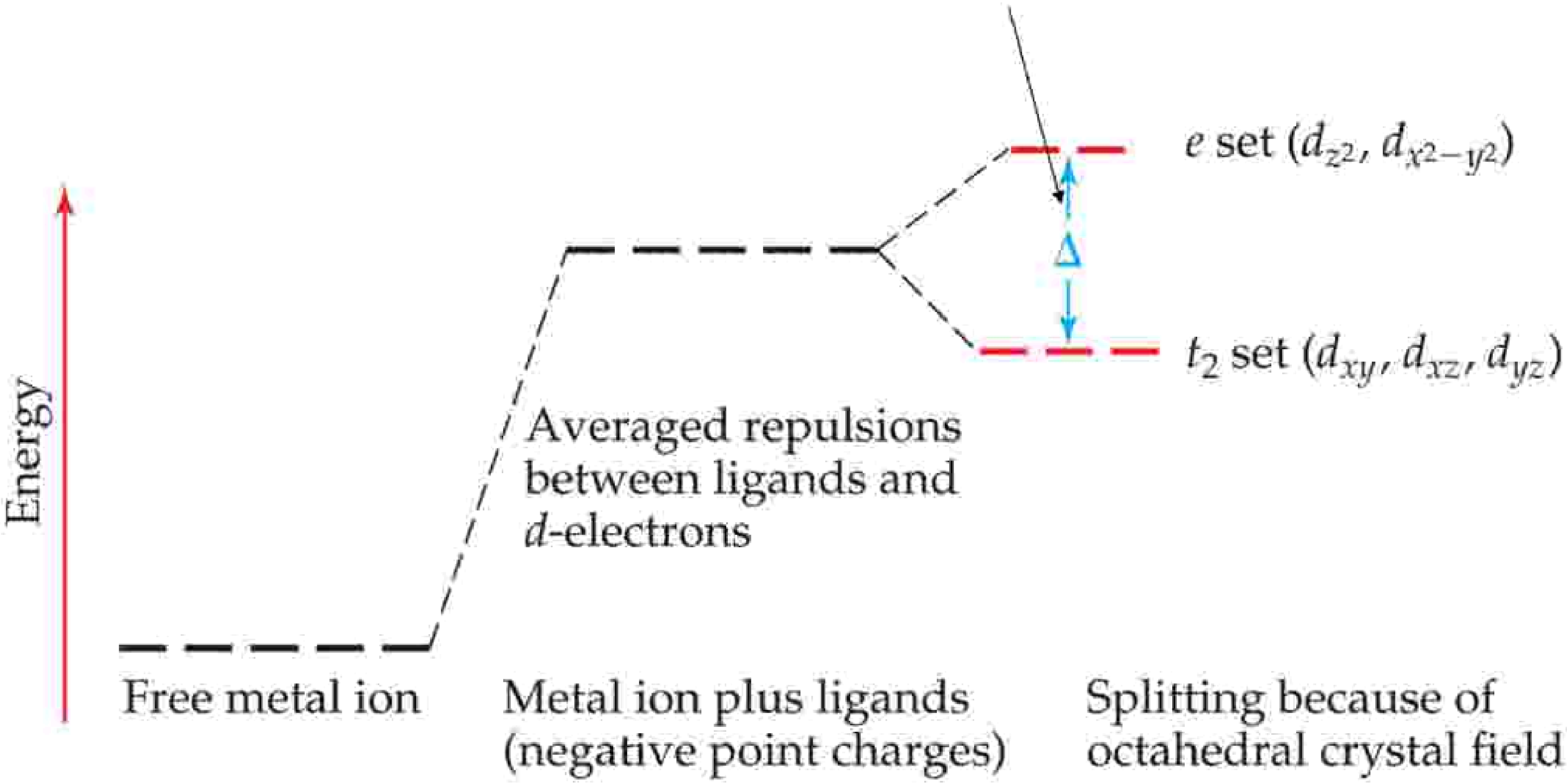
In these orbitals, the ligands are between the lobes

Interact less strongly

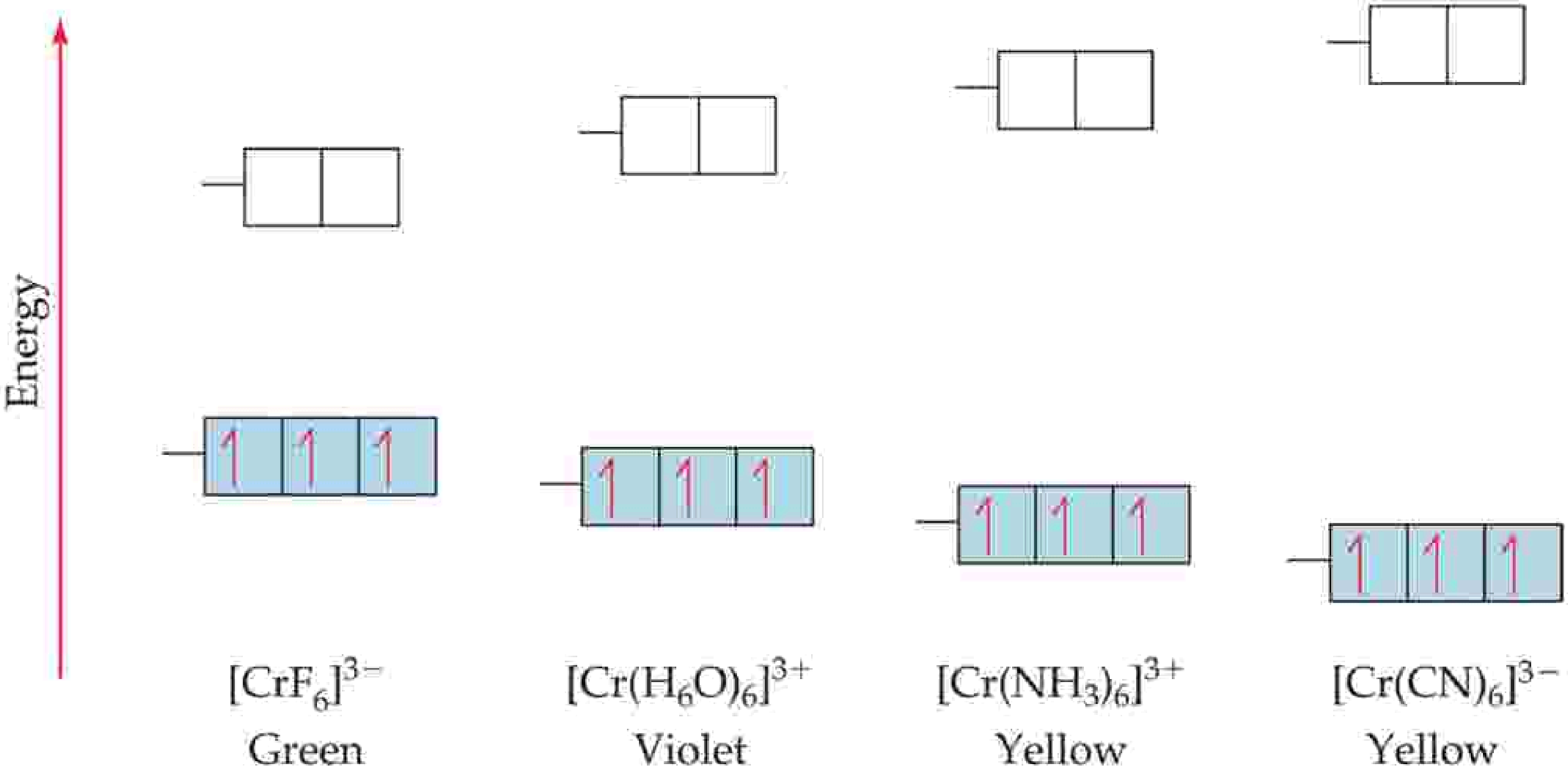


d_{xy} (d) d_{yz} (e) d_{xz} (f)

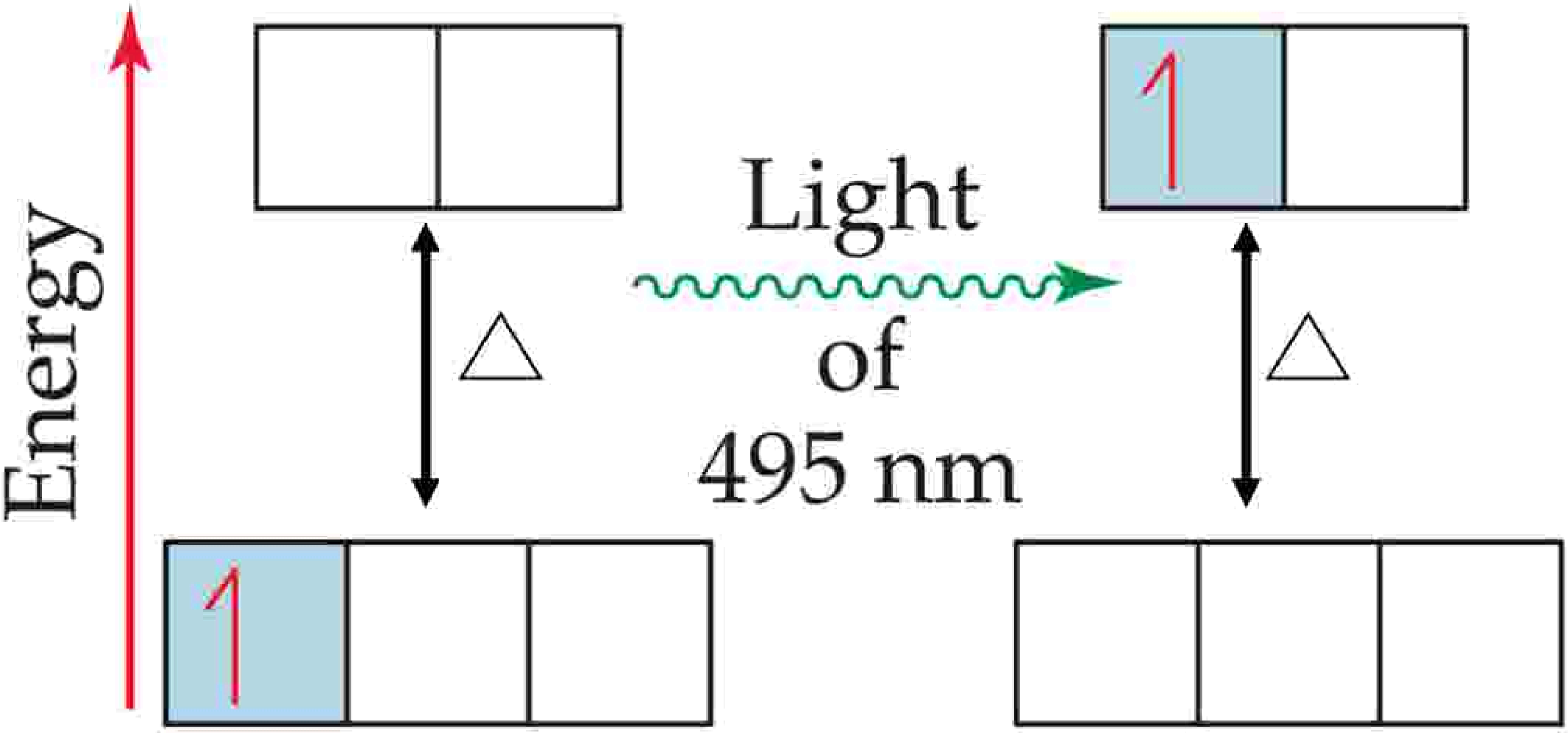
Splitting due to ligand/orbirtal orientation.



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



Absorption of light promotes an electron to a higher in E d orbital. Δ is E of the photon that can be absorbed.

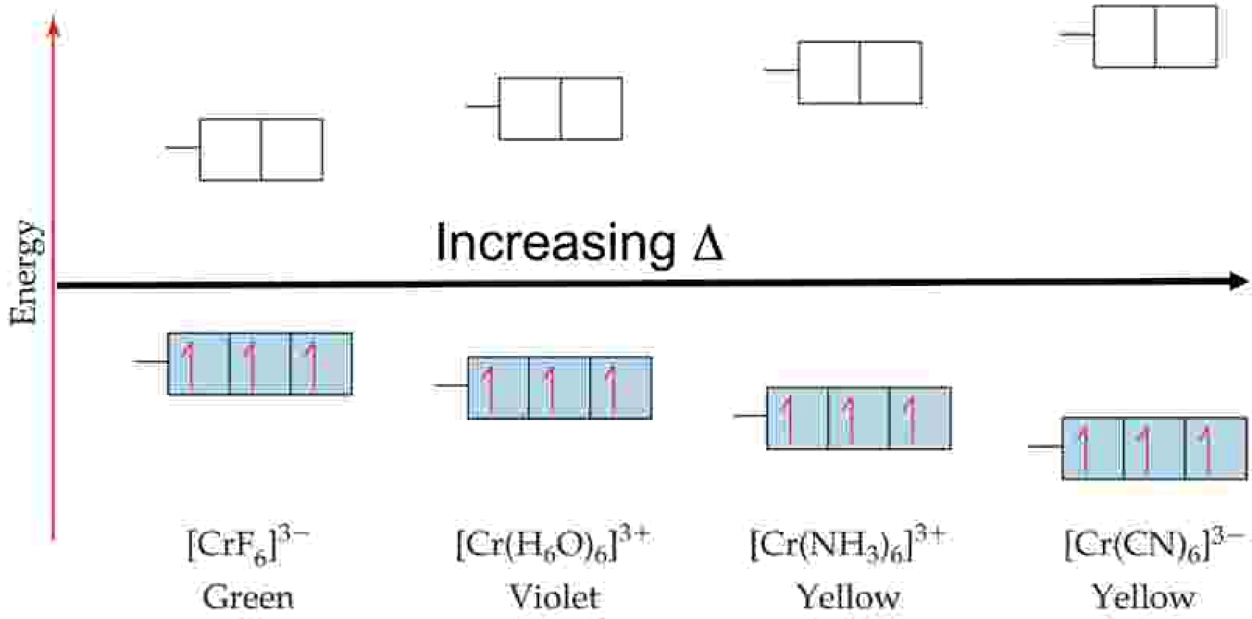


△ = 495 nm

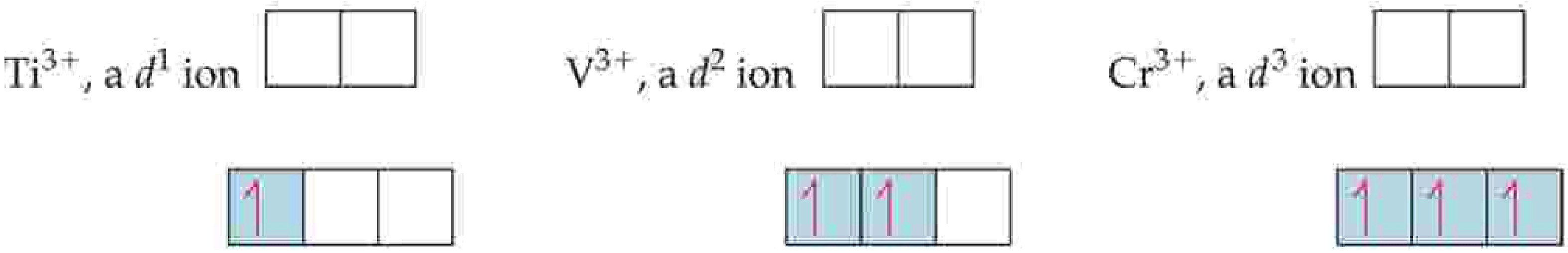
Spectrochemical series (strength of ligand interaction)

Low field Increasing Δ High field

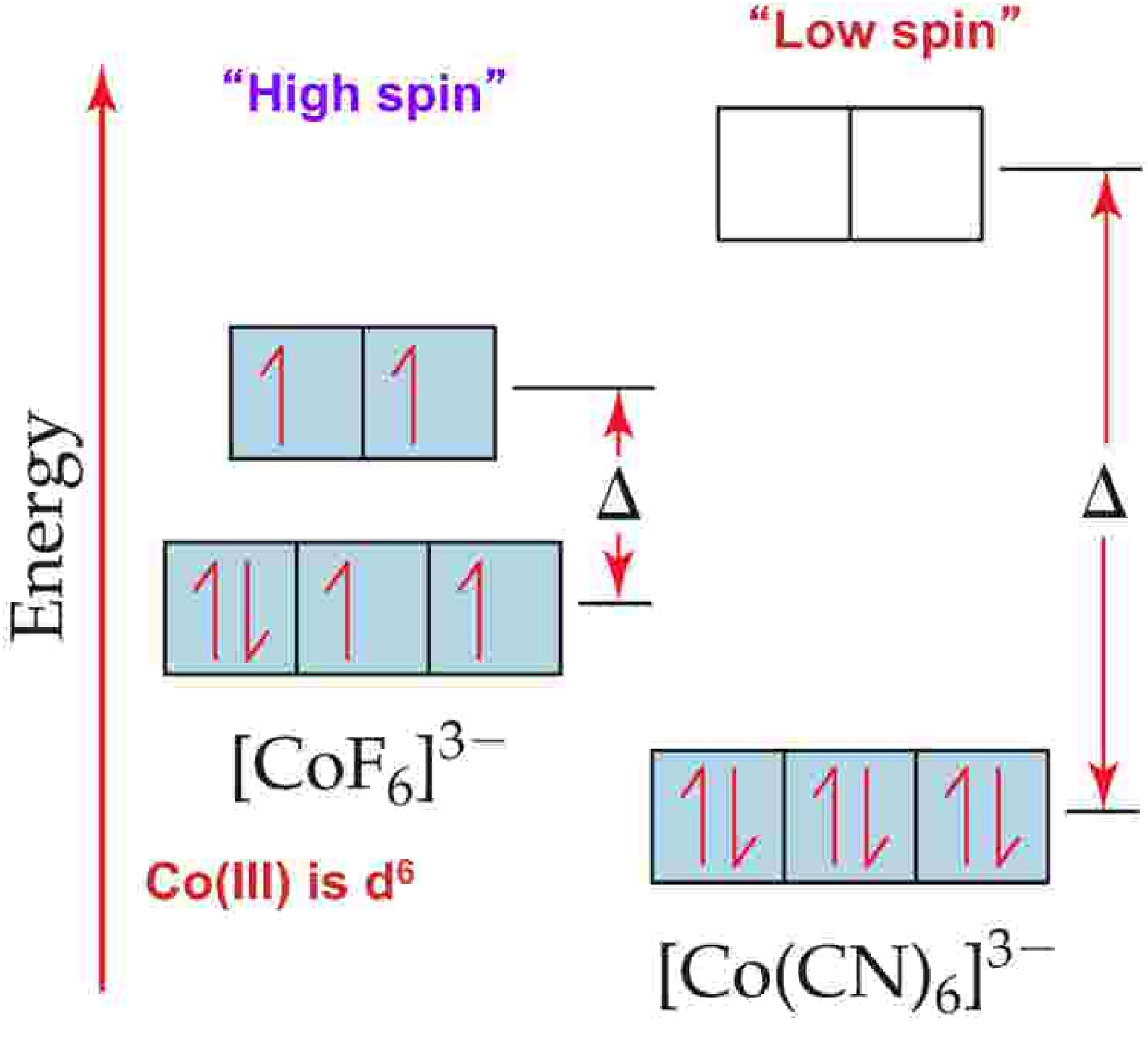
$Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^-$



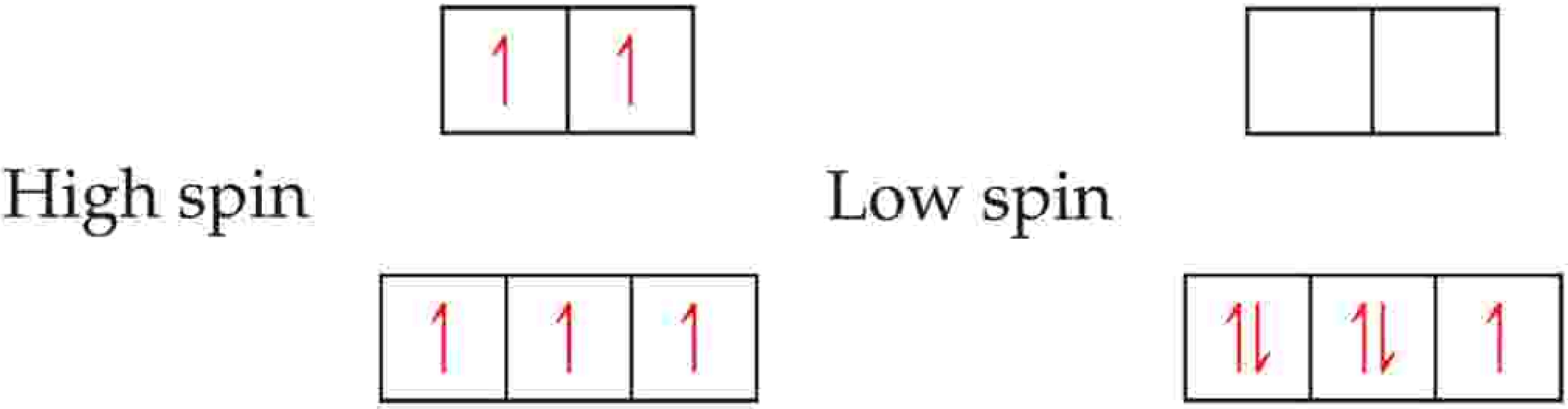
Electron configurations of some octahedral complexes



As Energy difference increases, electron configuration
Changes. Huhn' s rule breaks down because d orbitals are not degenerate

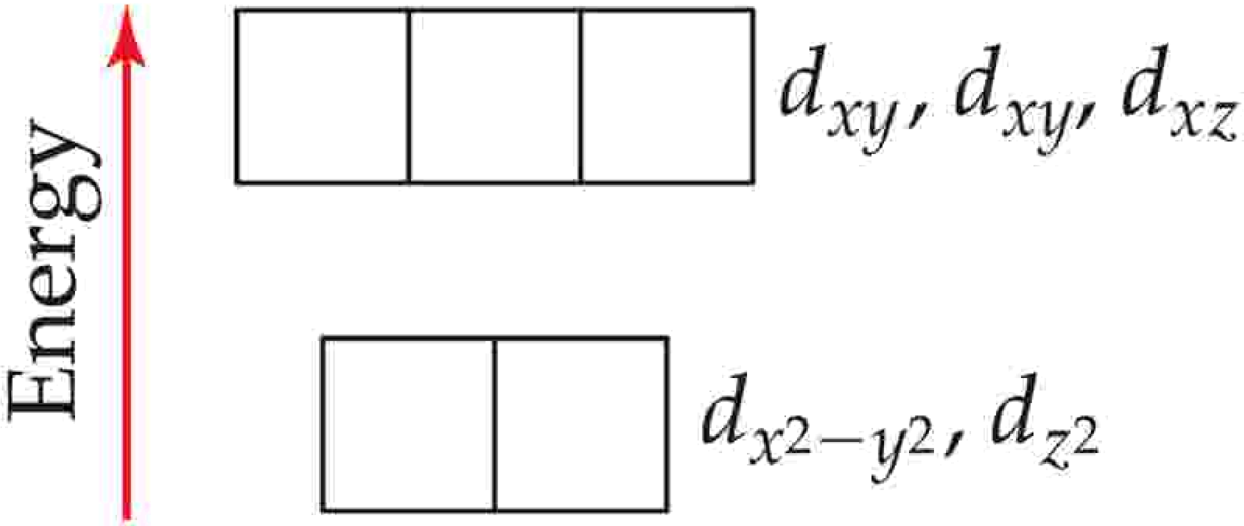


The 2 choices for a d^5 metal, high spin (more unpaired electrons) or low spint (more paired electrons)

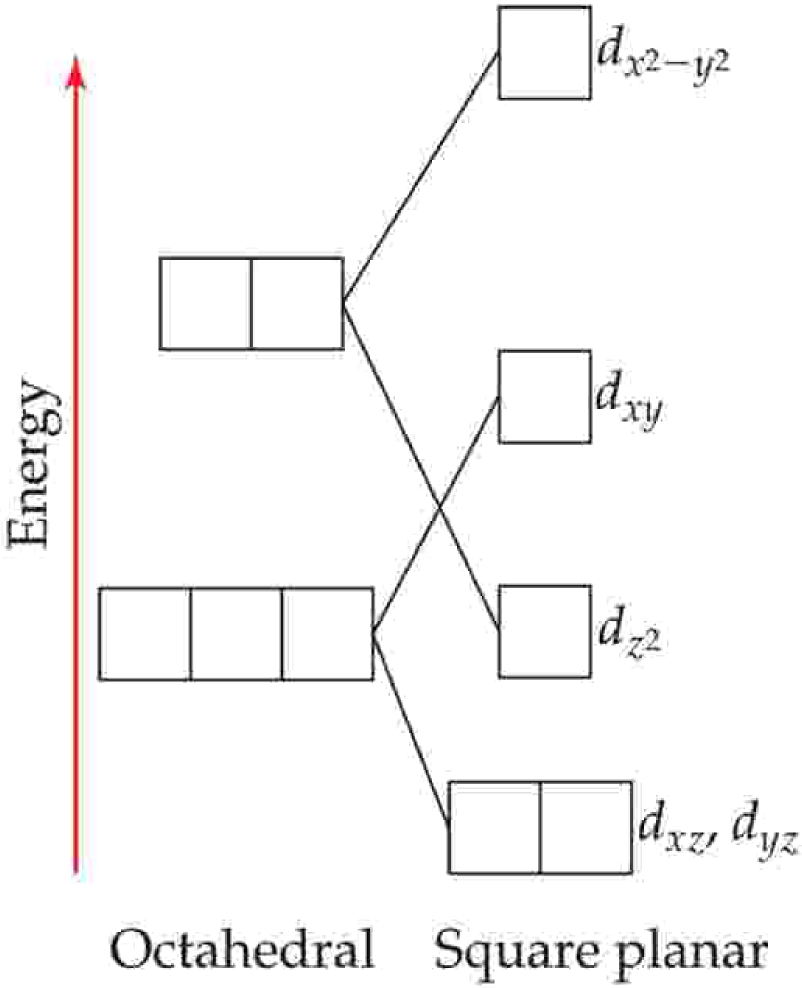


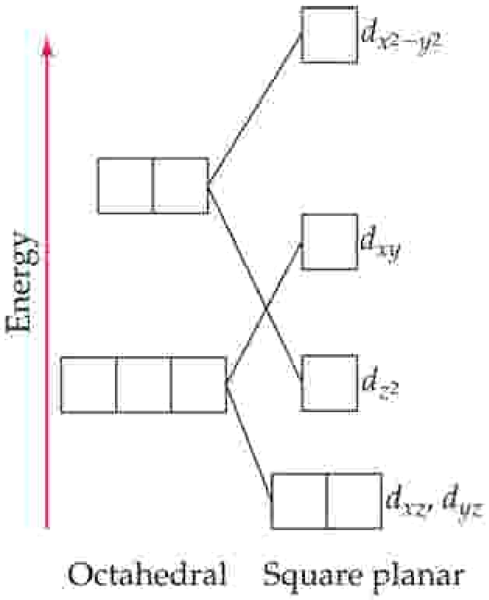
Tetrahedral Complexes

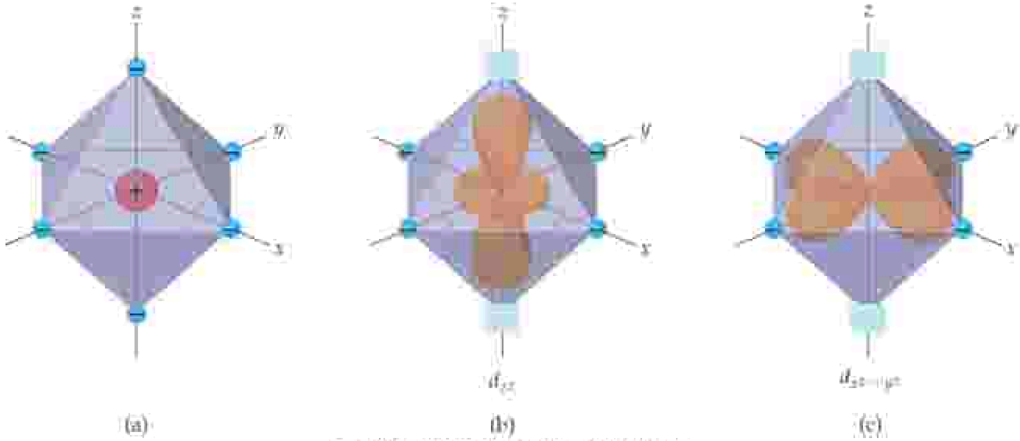
In tetrahedral complexes, orbitals are inverted.
Again because of orientation of orbitals and ligands.
Δ is always small, always high spin (less ligands)

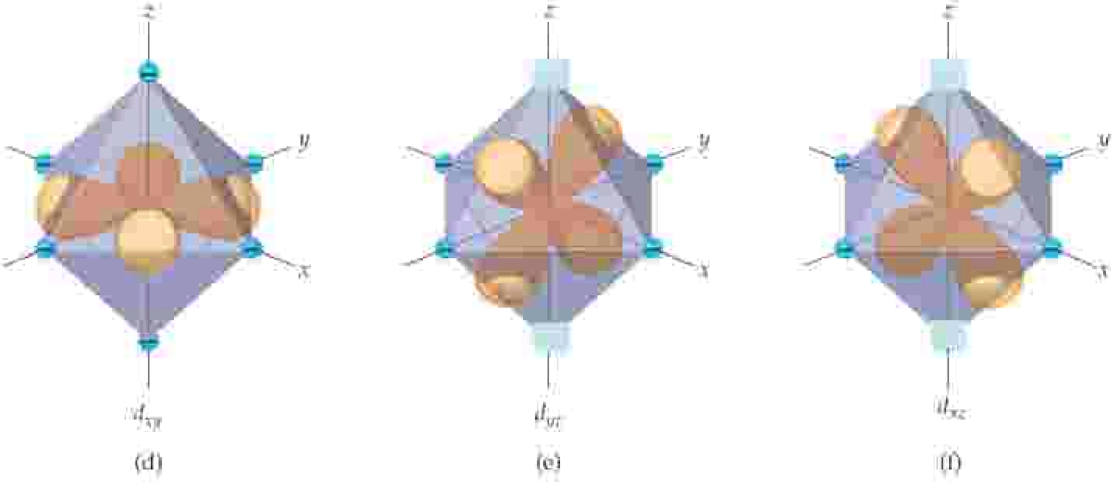


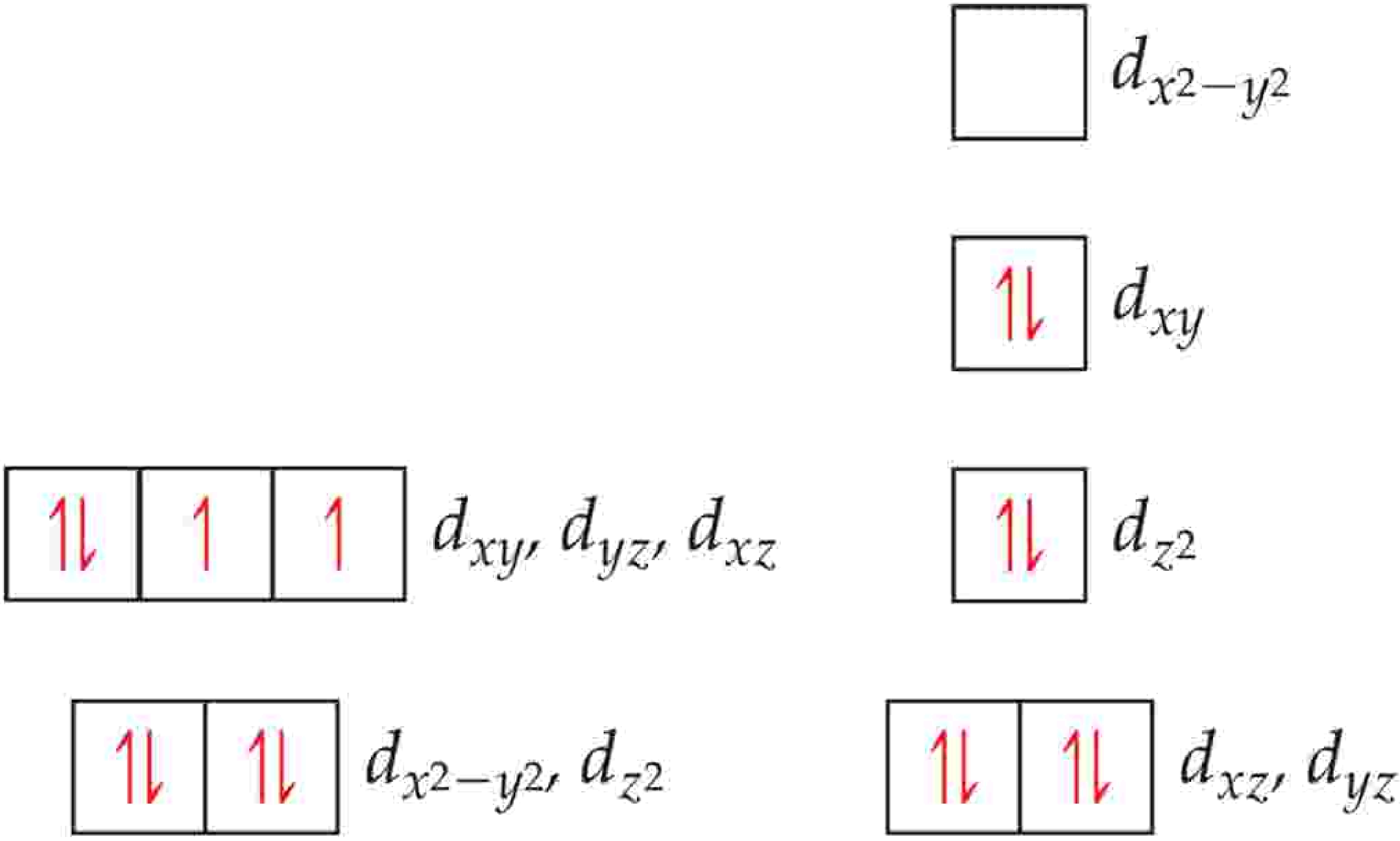
Square planar complexes are different still




Energy
$d_{x^2-y^2}$
d_{xy}
d_{z^2}
d_{xz}, d_{yz}
Octahedral
Square planar


z
y
x
+
d_{z^2}
$d_{x^2-y^2}$
(a)
(b)
(c)


z
y
x
d_{xy}
d_{yz}
d_{xz}
(d)
(e)
(f)



Tetrahedral

Square planar

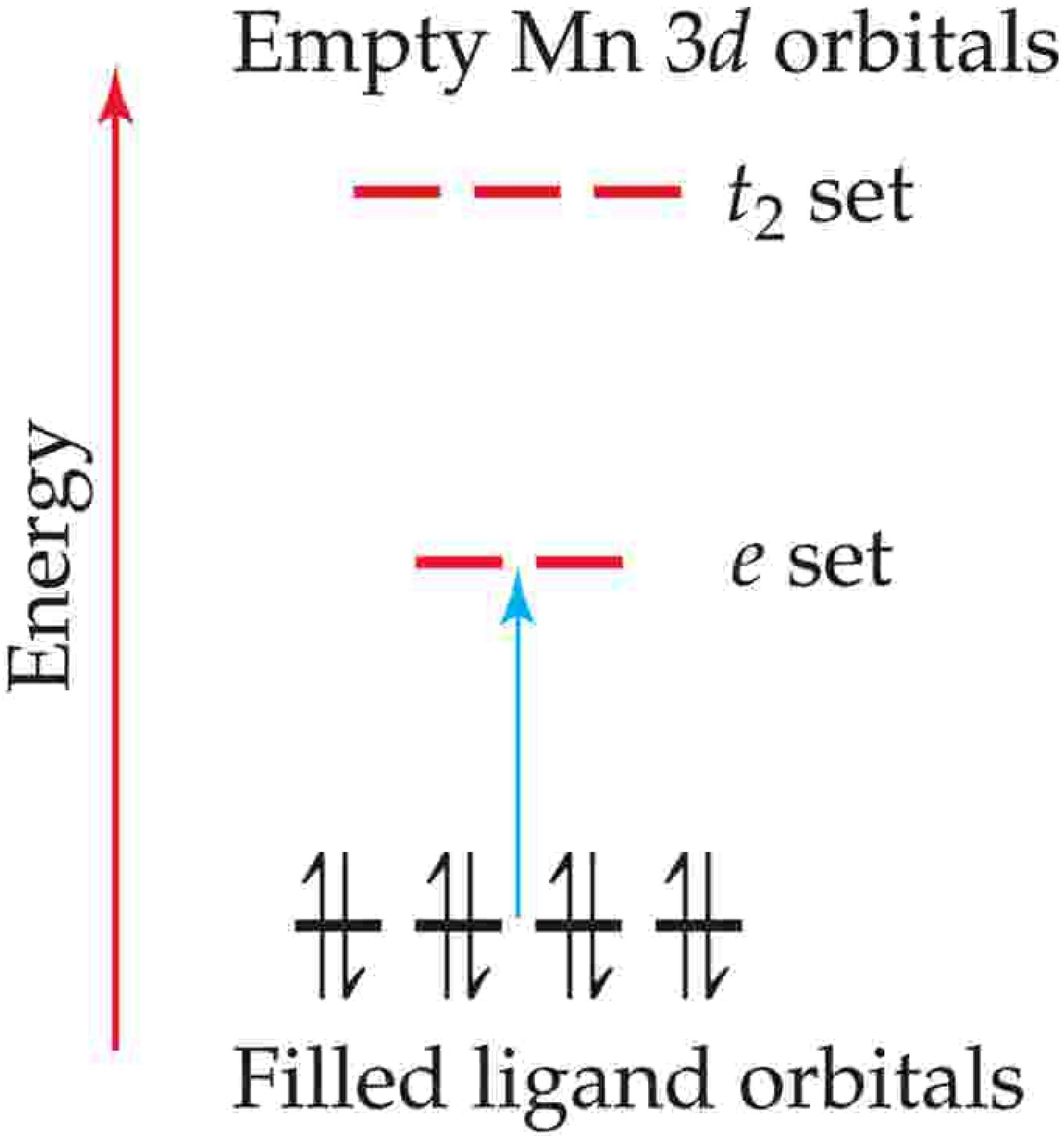
Intense color can come from “charge transfer”
Ligand electrons jump to empty metal orbitals

$KMnO_4$

K_2CrO4

$KClO_4$

No d orbitals in
Cl, orbitals higher
In energy


Empty Mn 3*d* orbitals
t_2 set
e set
Energy
Filled ligand orbitals

Exam 4 Topics

1. Valence bond theory
2. Molecular orbital theory
3. Chapter 24, coordination chemistry
4. Chapter 25, Organic (a little)

Valence bond theory:
1.Hybridization (mostly covered in last exam)
2.Double bonds due to overlap of atomic p orbitals (pi bonds)
3.Concept of delocalization what orbitals are overlaping in a delocalized system?

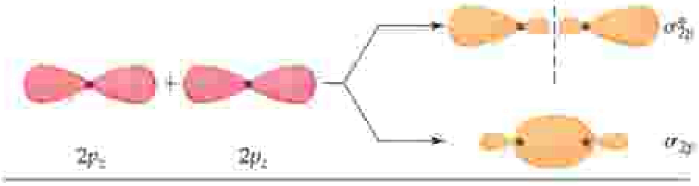
Exam 4, MO theory and coordination compounds Chapter 9, end and Chapter 24.

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.

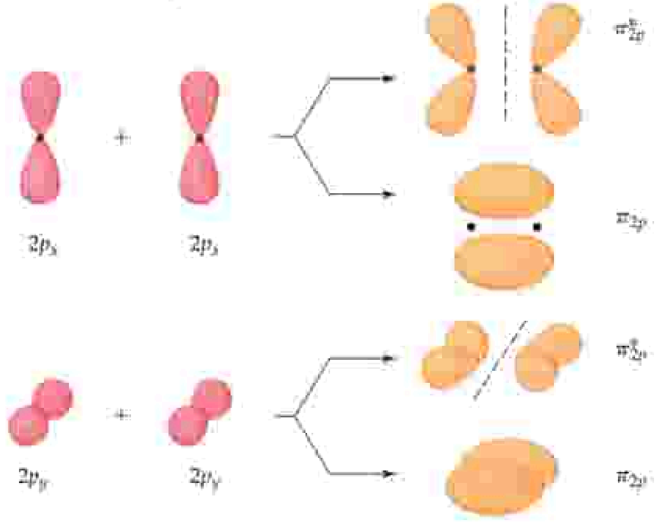
Difference between pi and sigma orbitals

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



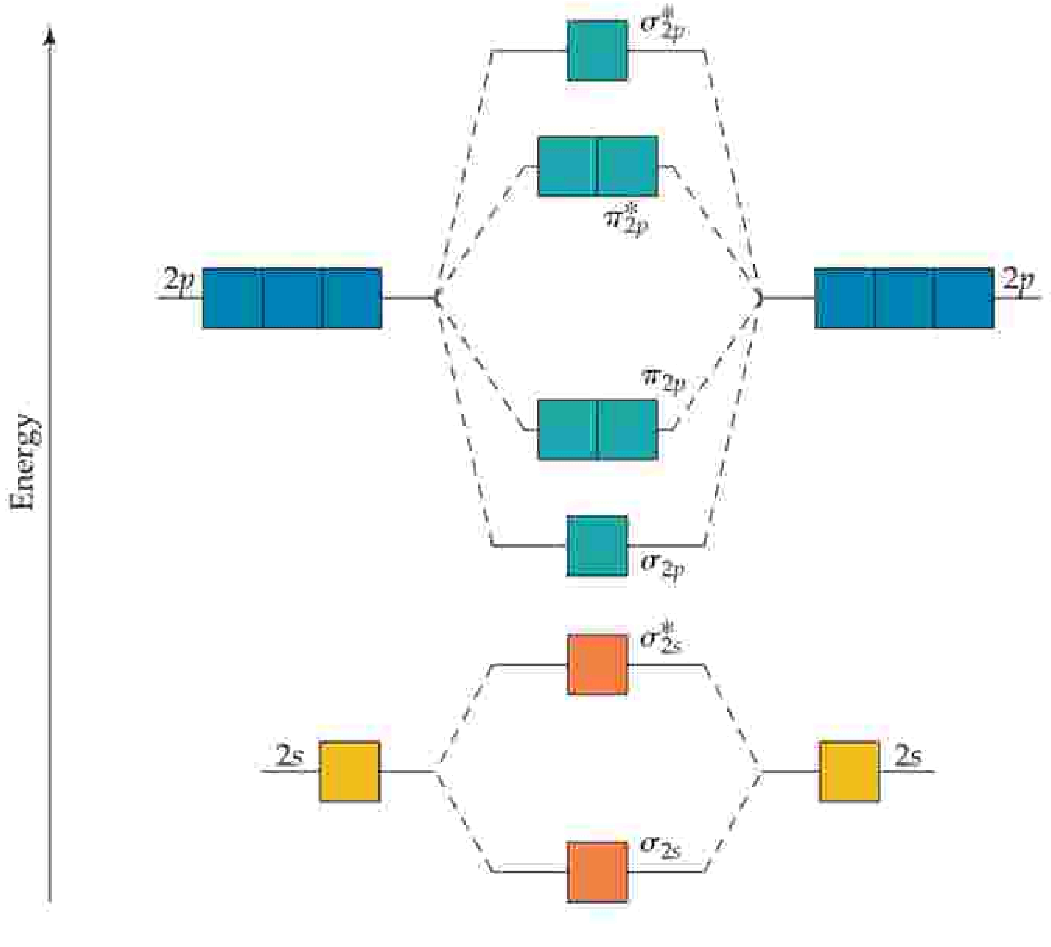
End on

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

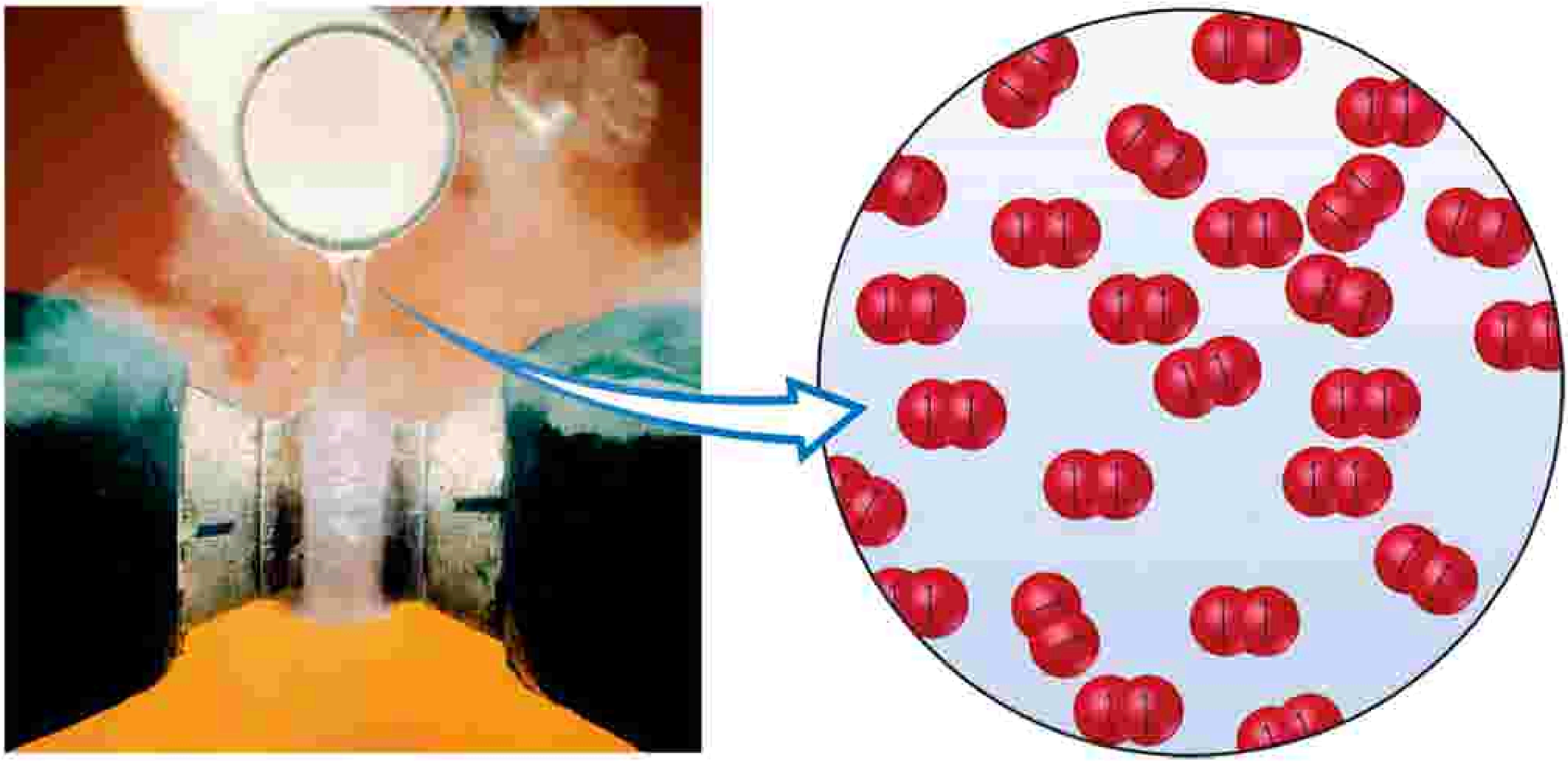


Side to side.

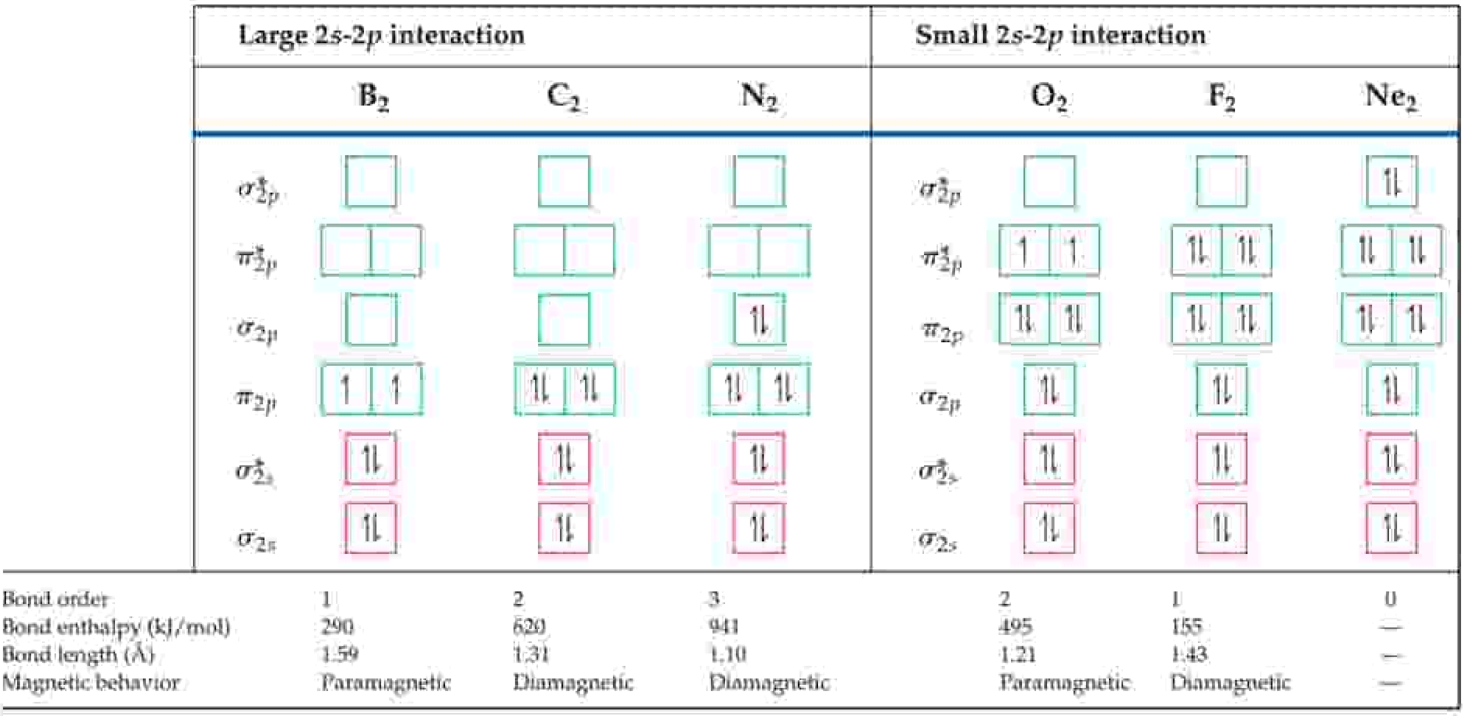
A typical MO diagram, like the one below. For 2p and 2s atomic orbital mixing.



Oxygen O_2 is Paramagnetic, why?



Show me why.



	Large 2s-2p interaction				Small 2s-2p interaction		
	B_2	C_2	N_2		O_2	F_2	Ne_2
σ^*_{2p}	☐	☐	☐	σ^*_{2p}	☐	☐	↑↓
π^*_{2p}	☐ ☐	☐ ☐	☐ ☐	π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	☐	☐	↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
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	—

Exam 4 Chapter 24.

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

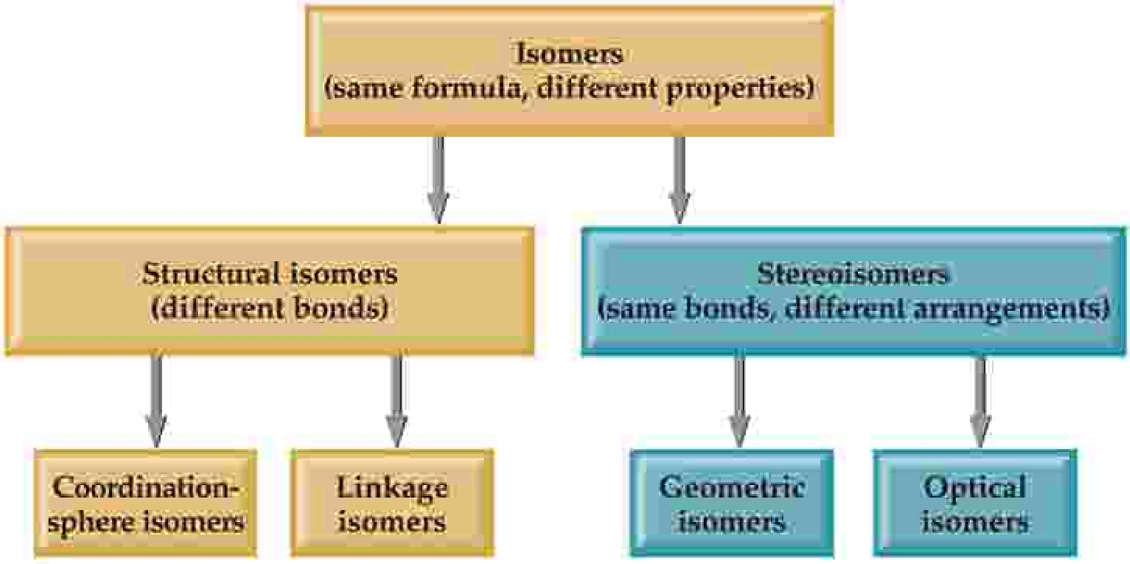
Polydentate ligands (what are they)?

Only ethylene diamine will be used (en)

NH_2-CH_2-CH_2NH_2

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)

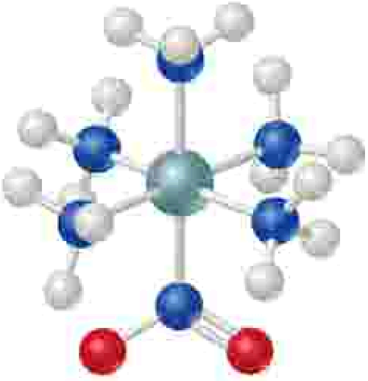
Stereoisomers
(same bonds, different arrangements)

Coordination-sphere isomers

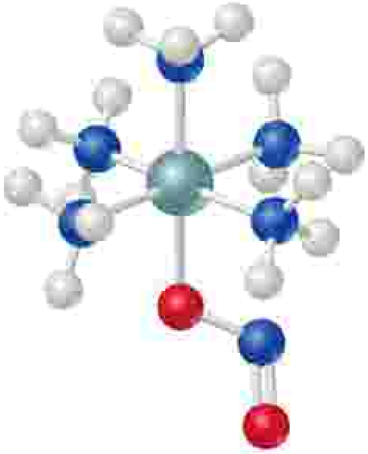
Linkage isomers

Geometric isomers

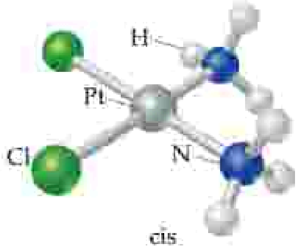
Optical isomers



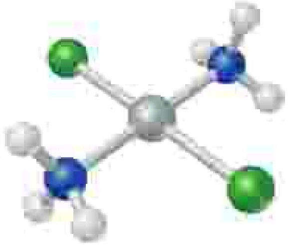
Nitro isomer



Nitrito isomer

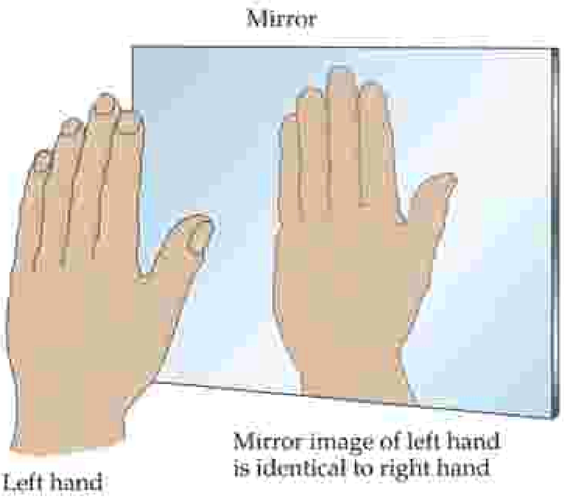


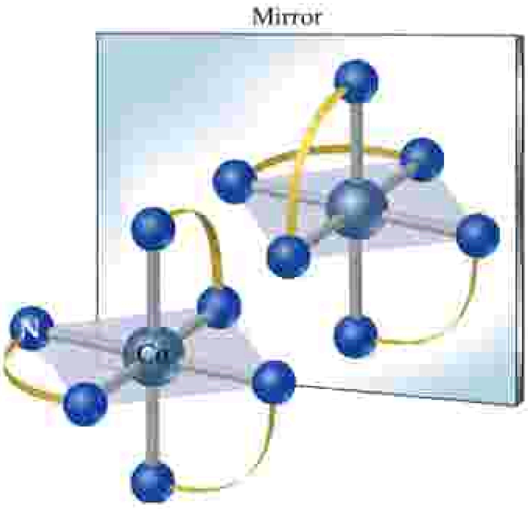
cis

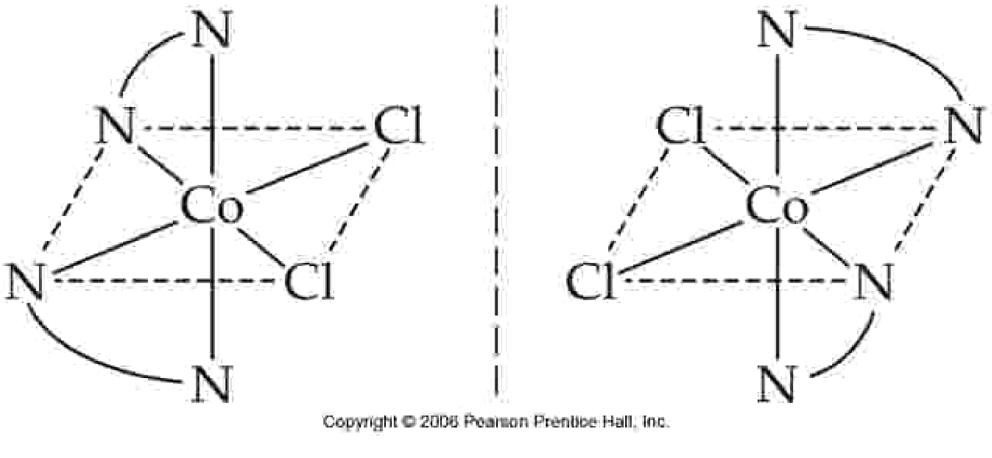


trans

Stereoisomers







Explaining the properties of metal complexes

Magnetism and color

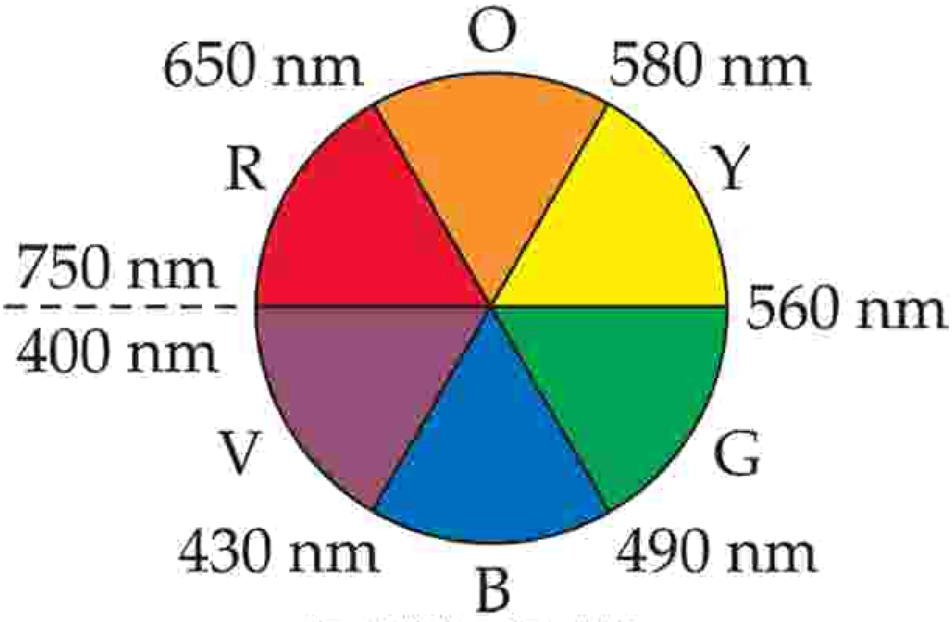
How does seeing color work?

Absorb **Orange**

See **Blue**

Absorb **Red**

See **Green**

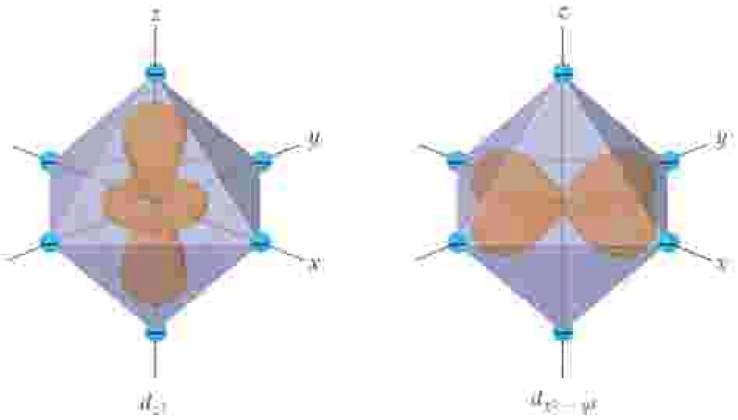


Different ligands on same metal give different colors

Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

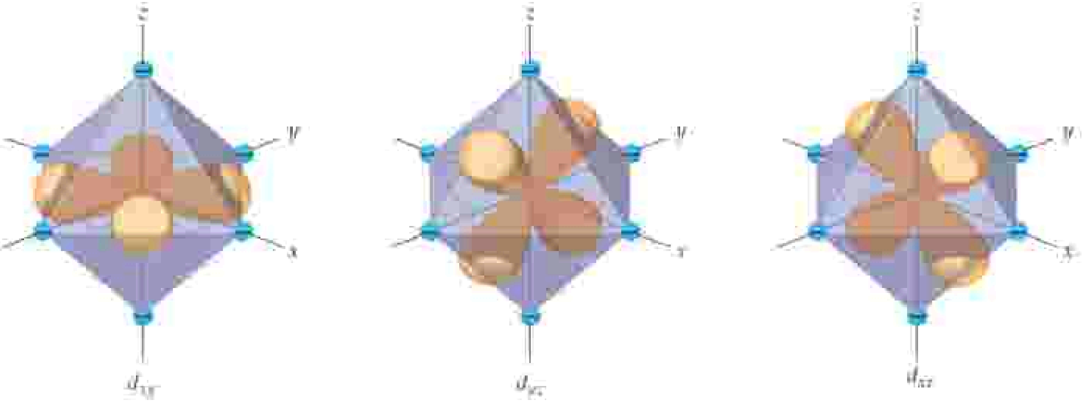
Splitting of d orbitals in an octahedral ligand field

d_{z^2} $d_{x^2-y^2}$



(b) (c)

d_{xy} d_{yz} d_{xz}

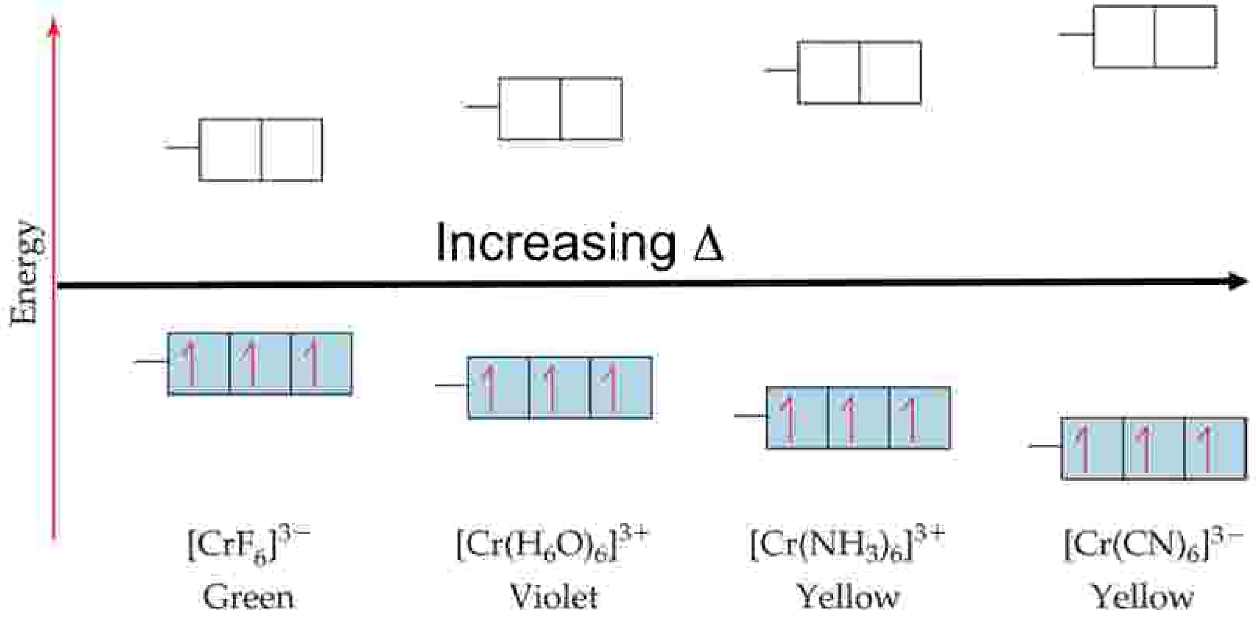


(d) (e) (f)

Spectrochemical series (strength of ligand interaction)

Increasing Δ

$Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^-$



Know low spin versus high spin

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