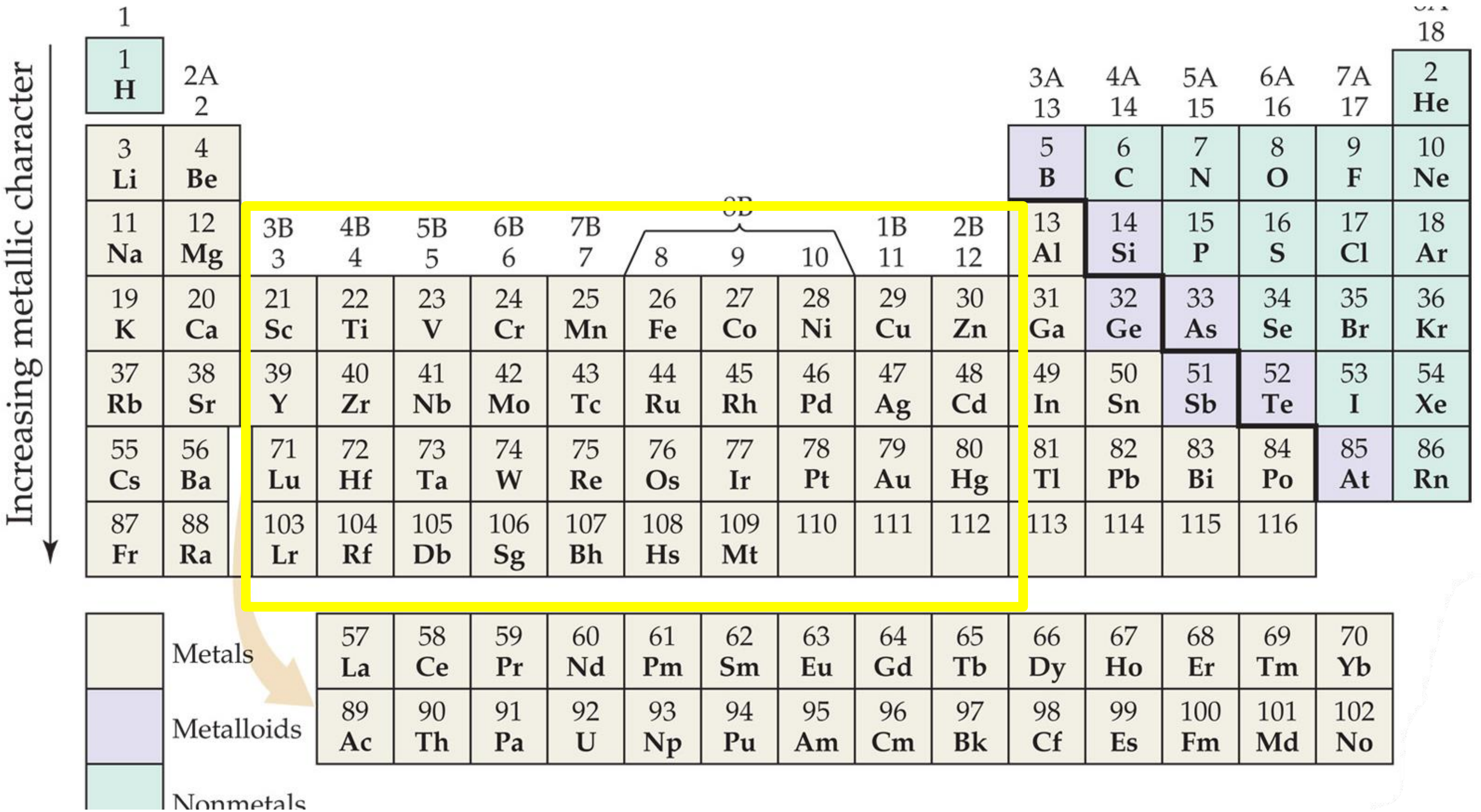
Chapter 23

Chemistry of Coordination Compounds

Coordination Compounds

- We’ve talked a lot about nonmetals.
- We’ve talked about ionic compounds
  - Alkali metals and alkali earth metals.
- How do we think about **transition metals** binding to other atoms?
- What do those d orbitals do?
- Does it matter? .

Transition metals



Increasing metallic character

1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8	9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114	115	116		
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	

Metals

Metalloids

Nonmetals

They don’t act like ”regular” metals

They sure don’t act like nonmetals

They make: **coordination compounds**

A chemical mystery:

Same metal, same ligands, but different behavior

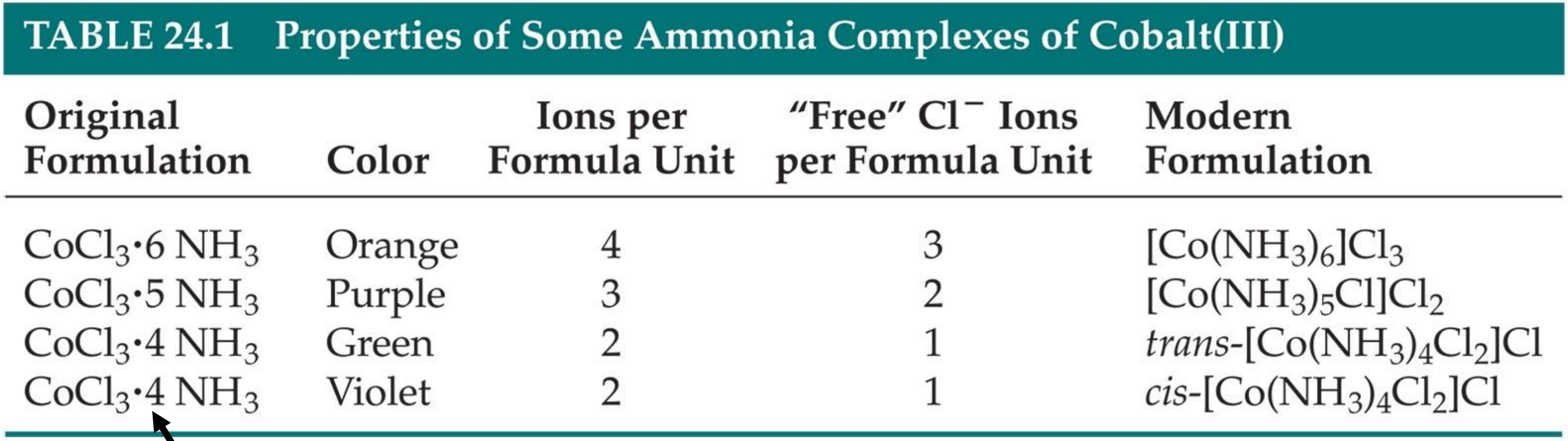


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

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*-$[Co(NH_3)_4Cl_2]Cl$

- Assumption: just ionic compounds with some ammonia loosely stuck on there, like sodium chloride.

A chemical mystery:

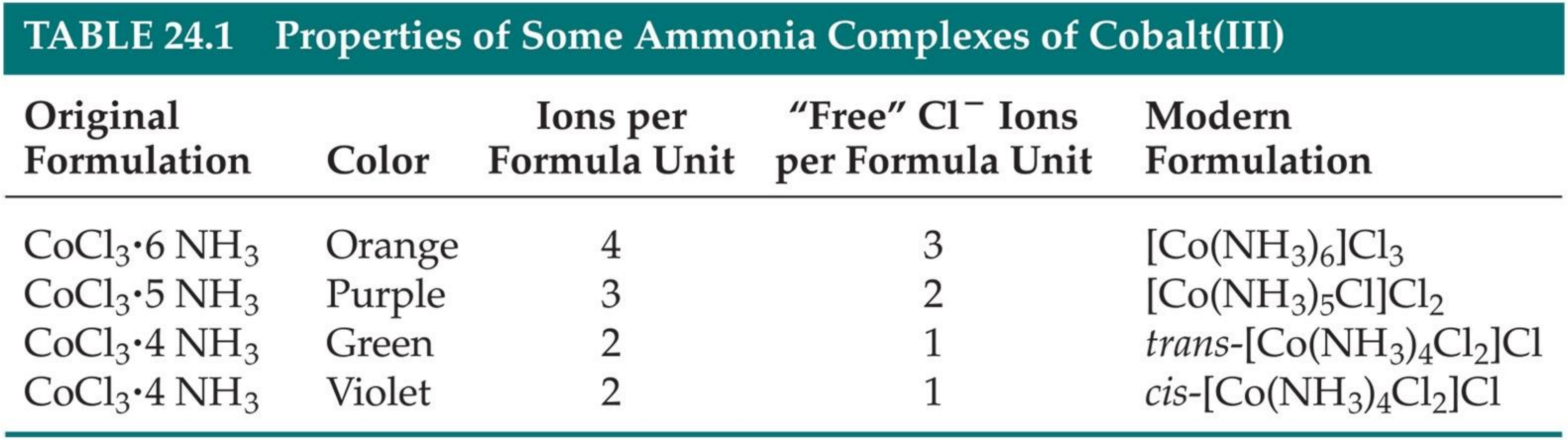


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

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*-$[Co(NH_3)_4Cl_2]Cl$

- NaCl. Let it sit out in the summer. What happens?
- It sucks up water, gets sticky, won't shake.

- $NaCl \cdot nH_2O$

A chemical mystery:

Same metal, same ligands, but different behavior

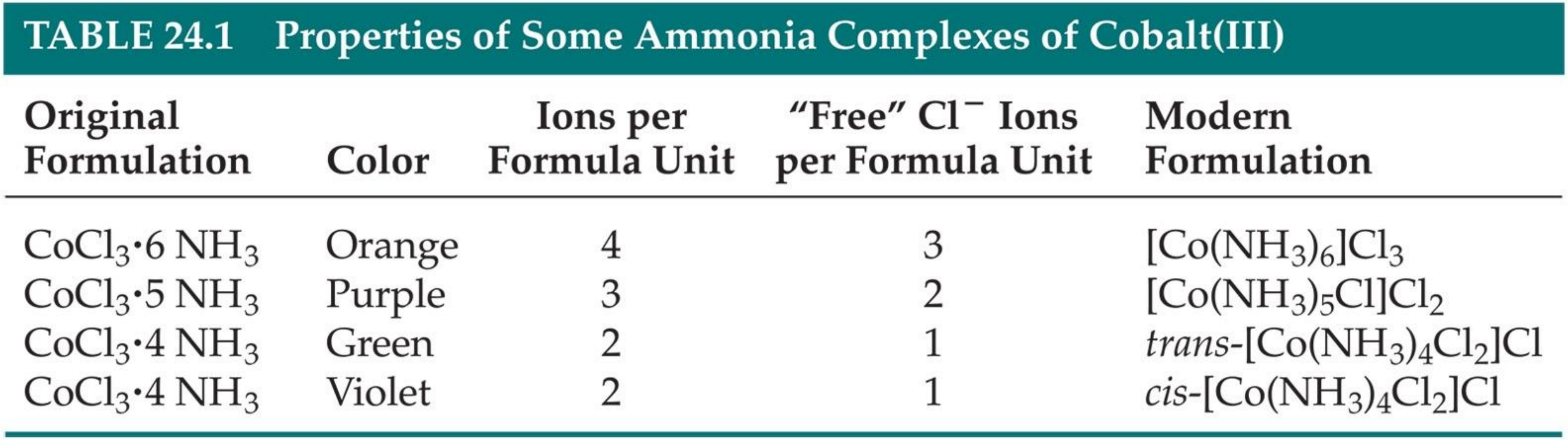


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

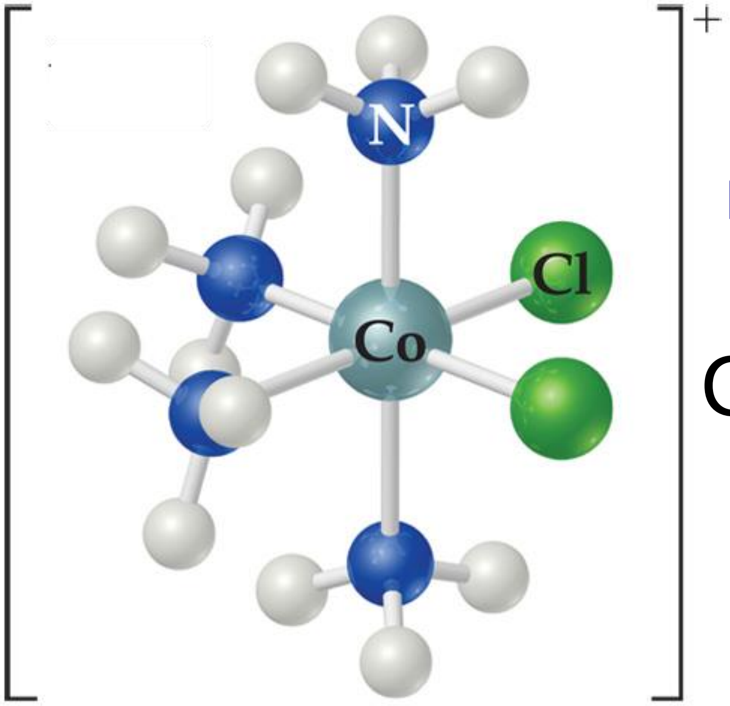
Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\ NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\ NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\ NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\ NH_3$	Violet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

- **Same ligands, but different stoichiometry**
- **Same ligands, different ionic species when dissolved in water.**
- **Many coordination compounds are brightly colored, but again, same metal, same ligands, different colors.**

Alfred Werner

Father of coordination chemistry

First inorganic chemist to win Nobel Prize



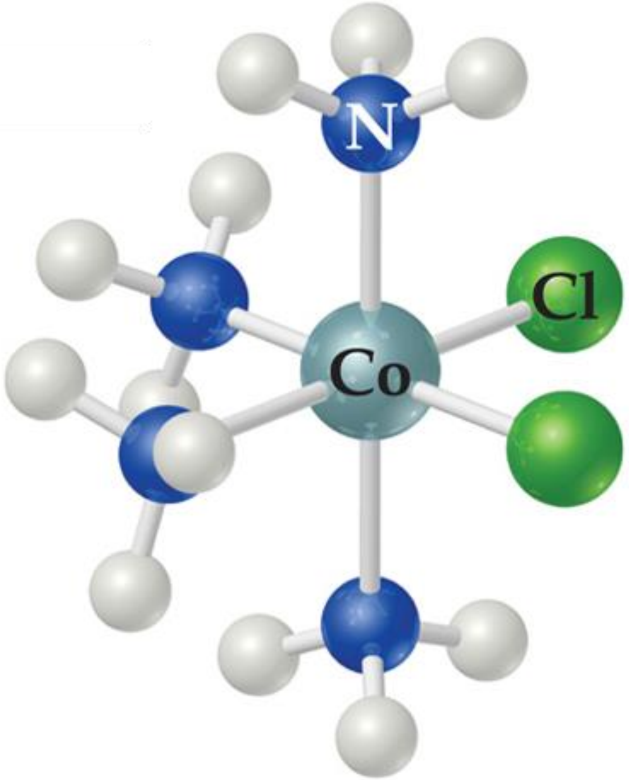
Cl-

Co(III) oxidation state

Coordination # is 6

- 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)**

Complexes



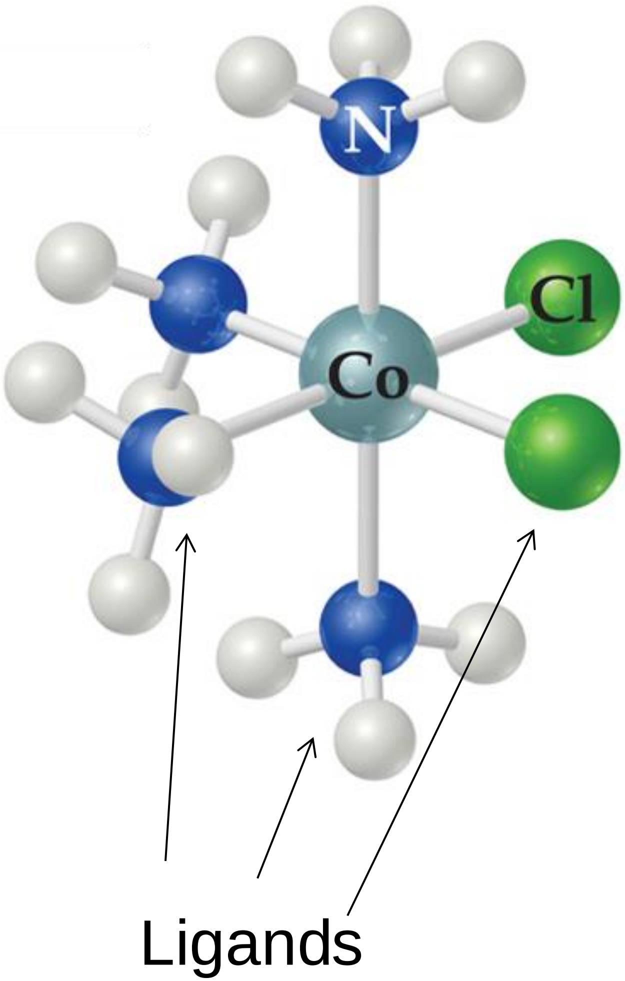
Is this an “ionic compound”

Does it dissociate in water?

No!

- 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.**

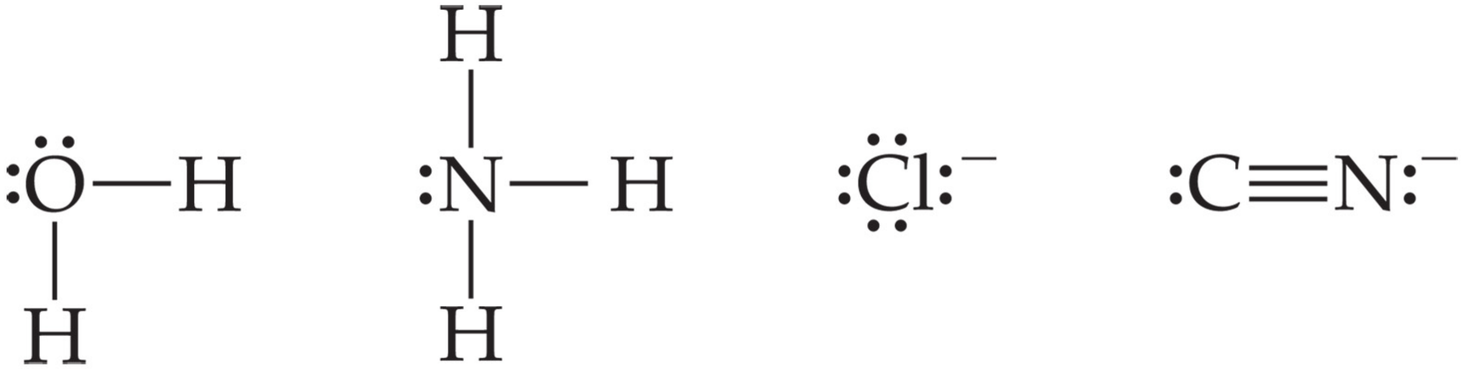
Complexes



- The molecules or ions coordinating to the metal are the **ligands.**
- **Ligands:**
  - can be anions or polar molecules.
  - 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.
- ***Anything with a lone pair can be a ligand.***



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. Act just like ions in ionic compound.**
- **Float away in water.**

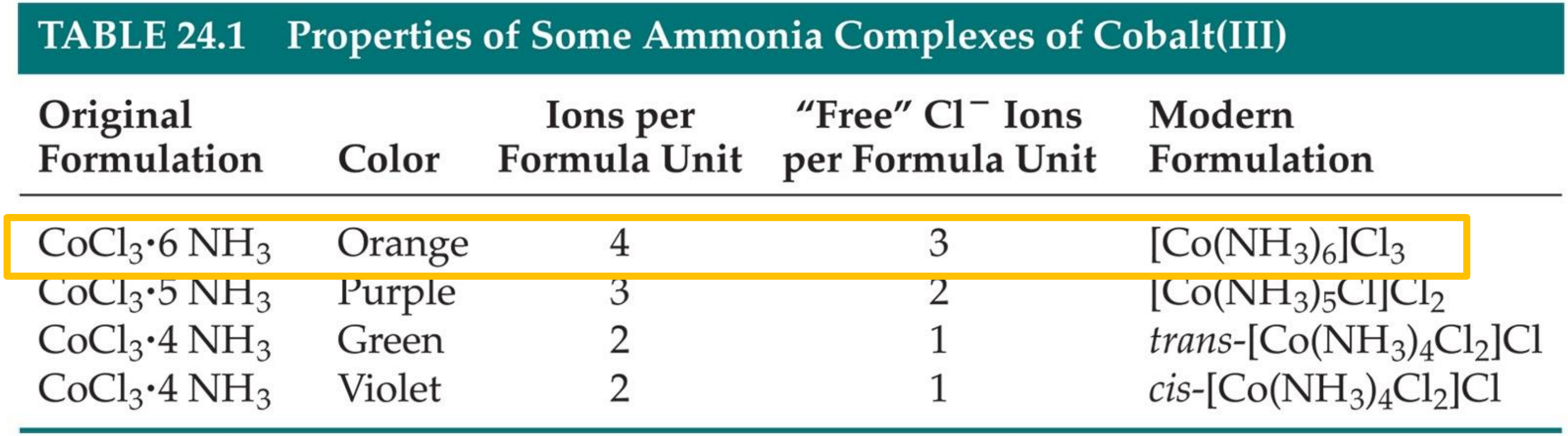


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

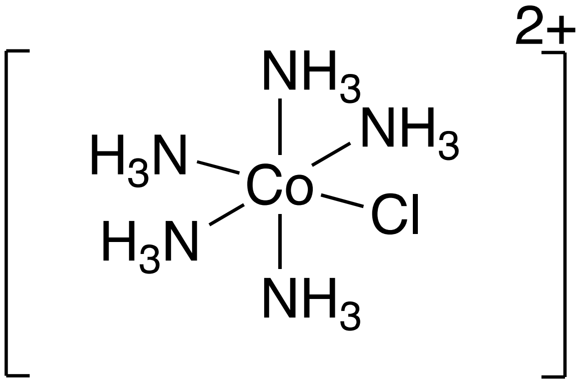
Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\ NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\ NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\ NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\ NH_3$	Violet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

Werner’s Theory

In $CoCl_3 \cdot 5\ NH_3$

five NH_3 groups and one chlorine are bonded to the cobalt,

the other two chloride ions are outside the sphere.



$2Cl^-$

Metal ion.
Like a polyatomic ion.
Like NH_4^+

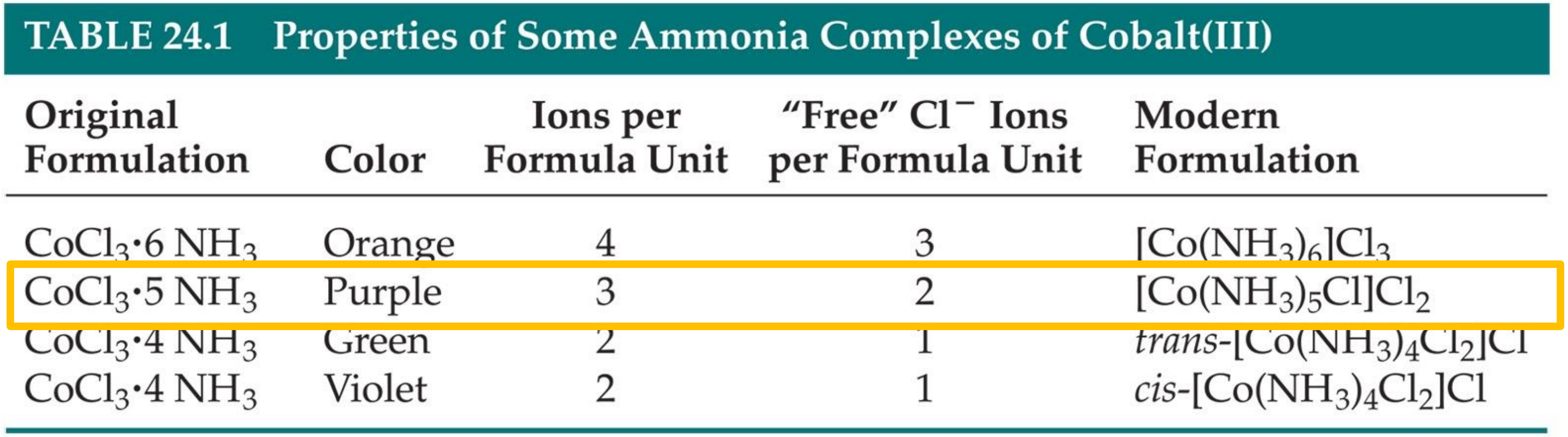


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

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*-$[Co(NH_3)_4Cl_2]Cl$

Werner's Theory

Given this insight:

Ligands **inside brackets**, part of ***coordination sphere, bonded directly to the metal.***

Those outside:

float away in water,

Loosely associated molecules (water, counterions)

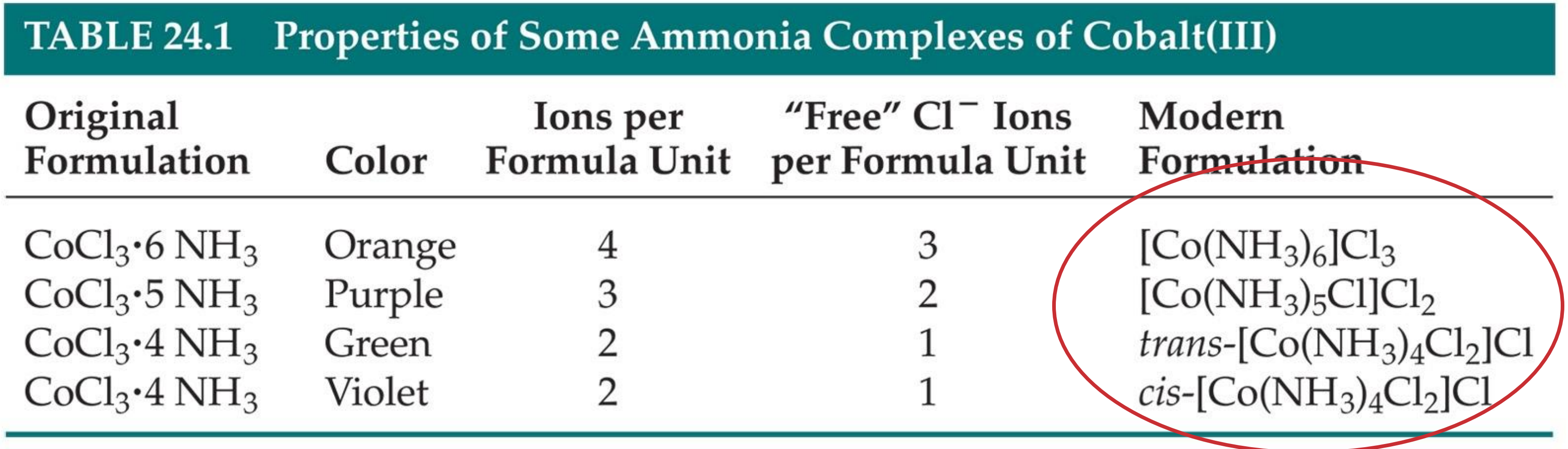


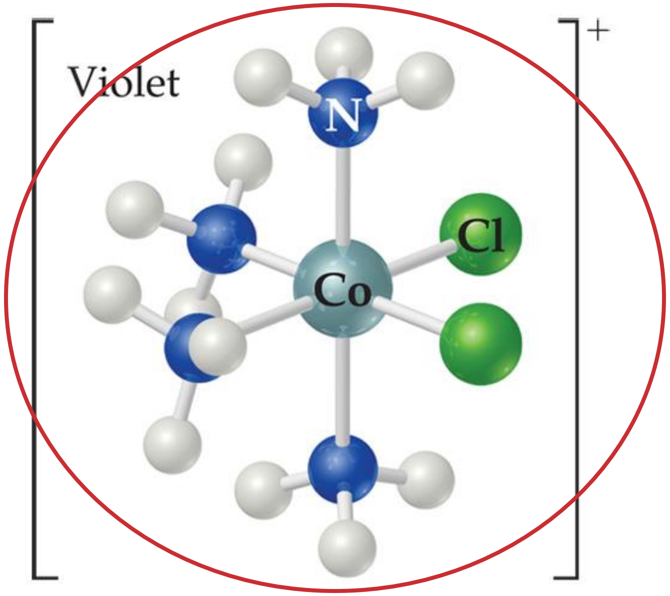
TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

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*-$[Co(NH_3)_4Cl_2]Cl$

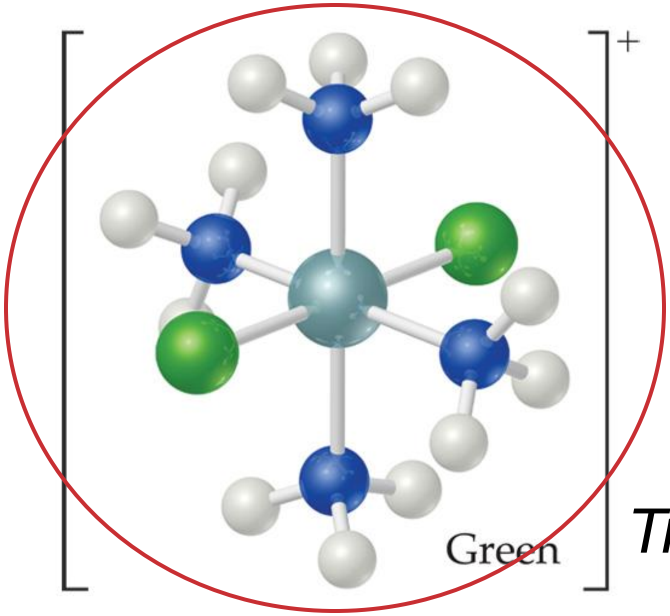
Werner’ s Theory

- The Compound $Pt(NH_3)_2Cl_2$ produces no ions when it dissolves in water. What is the coordination number for Pt?
- A. 1
- B. 2
- C. 3
- D. 4

Werner’ s Theory



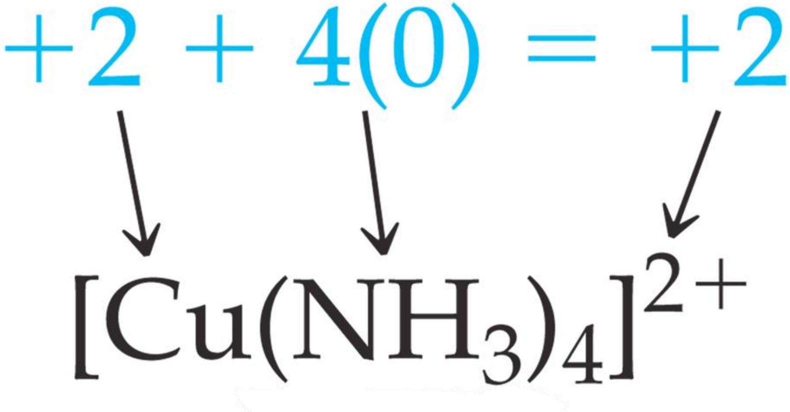
Cis



Trans

- A good theory must predict.
- Werner correctly predicts that there are two forms of $CoCl_3 \cdot 4\ NH_3$.
  - Correct formula:
  - $[Co(NH_3)_4Cl_2]Cl$.
  - Two ***stereoisomers***
  - Top, Cl’s next to each other
  - Bottom, Cl’s across from each other..

Oxidation Numbers
Key issue in metal complexes



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

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

Easily found using:

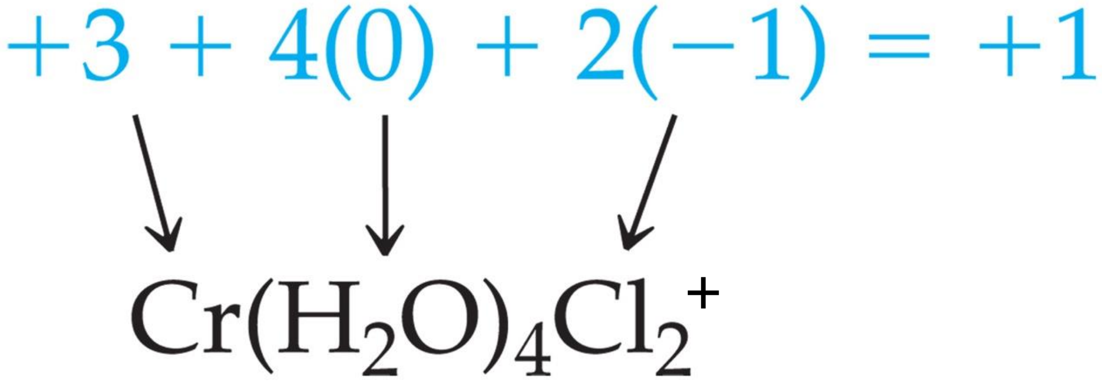
Charge of the complex ion

Charge of each of the ligands.

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



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

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

Oxidation Numbers

What is the oxidation number for Co in:

$Co(NH_3)_5Cl_3$?

A. 0

B. +1

C. +2

D. +3

E. +4

F. +5

Electron configuration of metals in complexes.

- Generally a transition metal has an electron configuration like this:
- [noble gas]$ns^2(n-1)d^m$
- Example:
- V: $[Ar]4s^2 3d^3$
- Pt: $[Xe]6s^2 4f^{14} 5d^8$

Electron configuration of metals in complexes.

- But, when transition metals lose electrons to become cations. *They lose the s electrons first*:
- Example:
  - ➢V: [Ar]$4s^2 3d^3$
    - V^{2+}: [Ar]$3d^3$
  - ➢Pt: [Xe]$6s^2 4f^{14} 5d^8$ **(Note: The f electrons aren't valence e^-)**
    - Pt^{2+}: [Xe]$5d^8$
    - Pt^{3+}: [Xe]$5d^7$

Electron configuration of metals in complexes.

- :
- What is the electron configuration for Co in:
- $[Co(NH_3)_6]Cl_3$?
  - A. $[Ar]4s^2 3d^7$
  - B. $[Ar]3d^7$
  - C. $[Ar]3d^6$
  - D. $[Ar]4s^2 3d^4$

Metal-Ligand Bond

The metal’s ligands and geometry greatly alter its properties, such as

color,

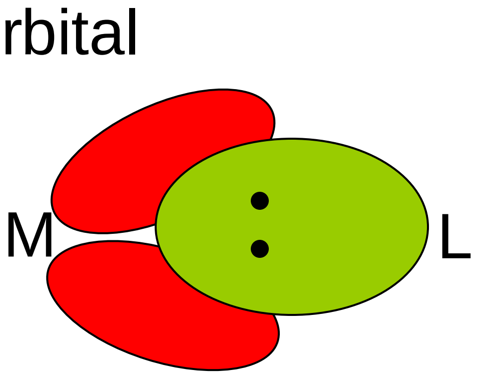
ease of oxidation.

Magnetic properties

Etc.

What is Coordination?

- **an orbital from a ligand with lone pairs**
- **overlaps with an *empty* orbital from a metal**



Sometimes called a coordinate covalent bond

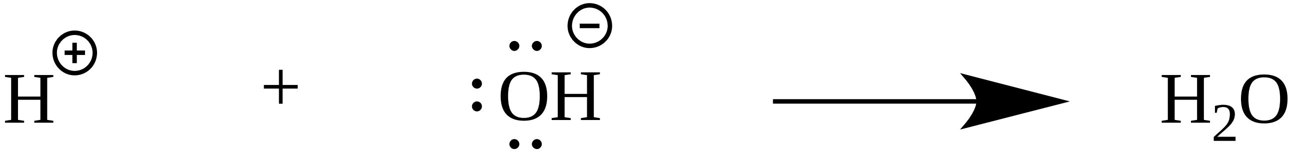
So ligands *must* have lone pairs of electrons.

Because metals *don’t share no electrons!*

Why? Because they are cations.

The concept of a Lewis Acid

- This bond is formed between a Lewis acid and a Lewis base.
  - Lewis base: electron *donor*.
  - Lewis acid: electron *acceptor*.

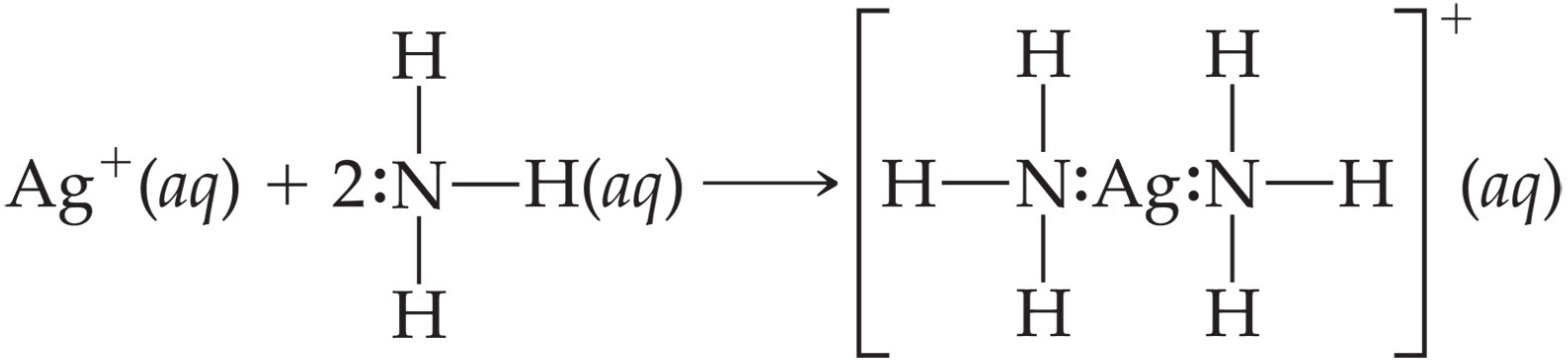


Lewis acid
electron
acceptor

Lewis Base
electron
donor

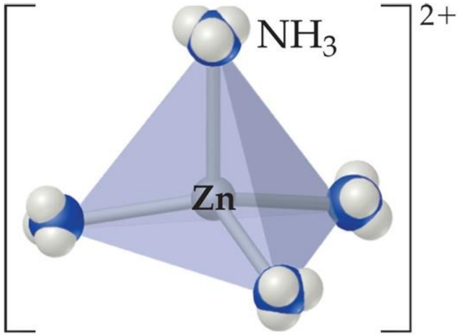
Metal-Ligand Bond

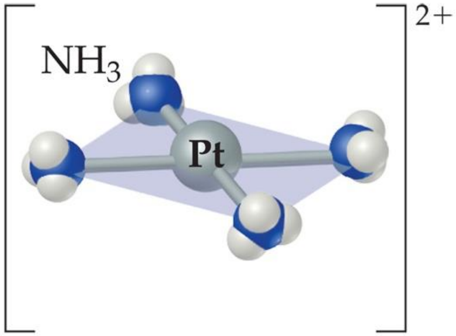
- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have lone pairs of electrons
  - The metal (Lewis acid) has empty orbitals.
  - **The concept of a Lewis acid/base is very important!**

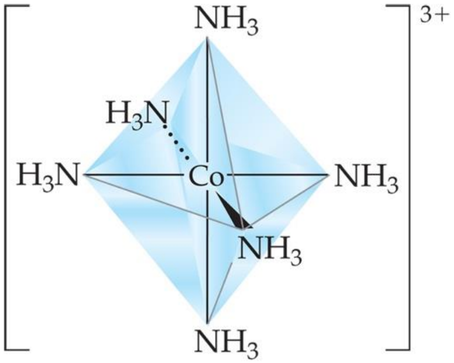


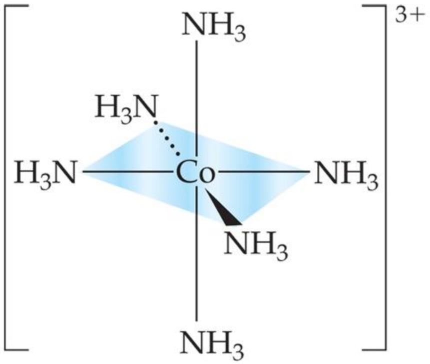
$$\mathrm{Ag}^{+}(aq) + 2{:}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}\!-\!\mathrm{H}(aq) \longrightarrow \left[\mathrm{H}\!-\!\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}{:}\mathrm{Ag}{:}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}\!-\!\mathrm{H}\right]^{+}(aq)$$

Coordination Number



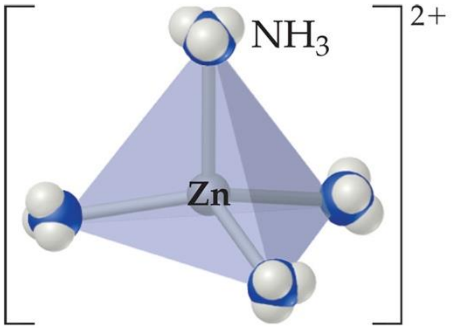


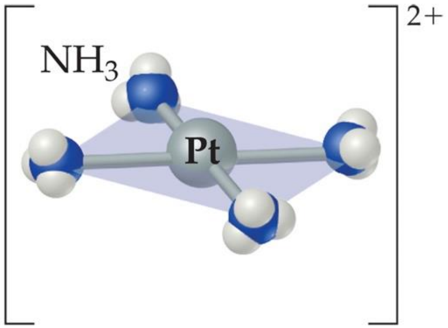


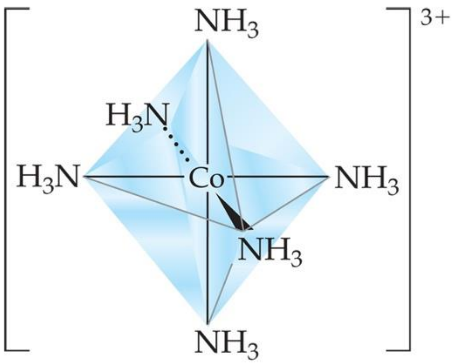


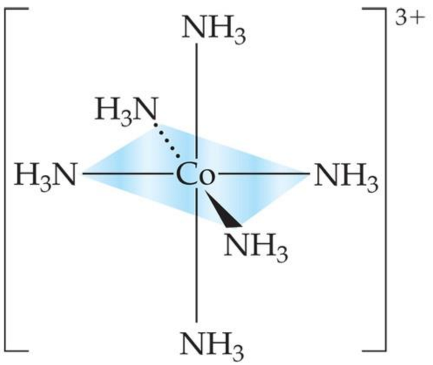
- The atom that supplies the lone pairs of electrons for the metal-ligand bond is the donor atom.
- The number of these atoms is the coordination number.

Coordination Number





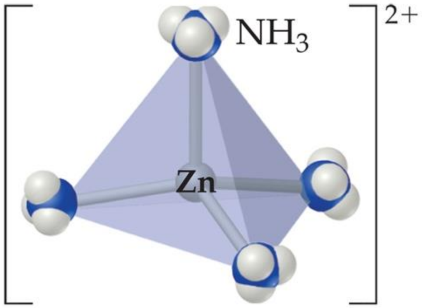




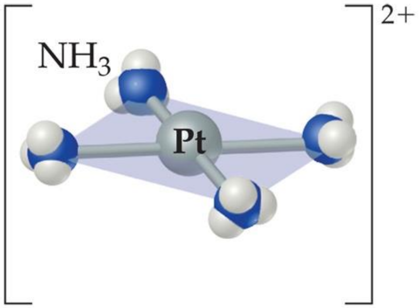
- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most common coordination numbers are 4 and 6.

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



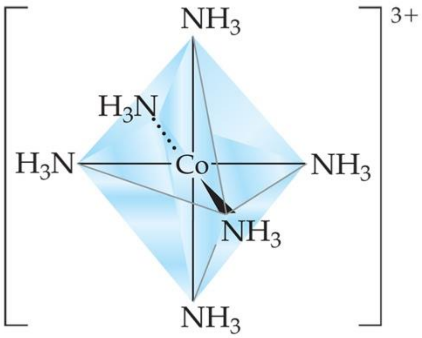
Tetrahedral

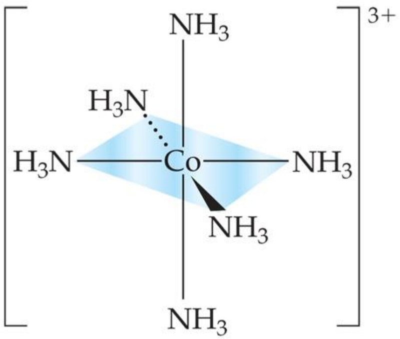


Square planar

Why square planar? We'll get to that

Geometries

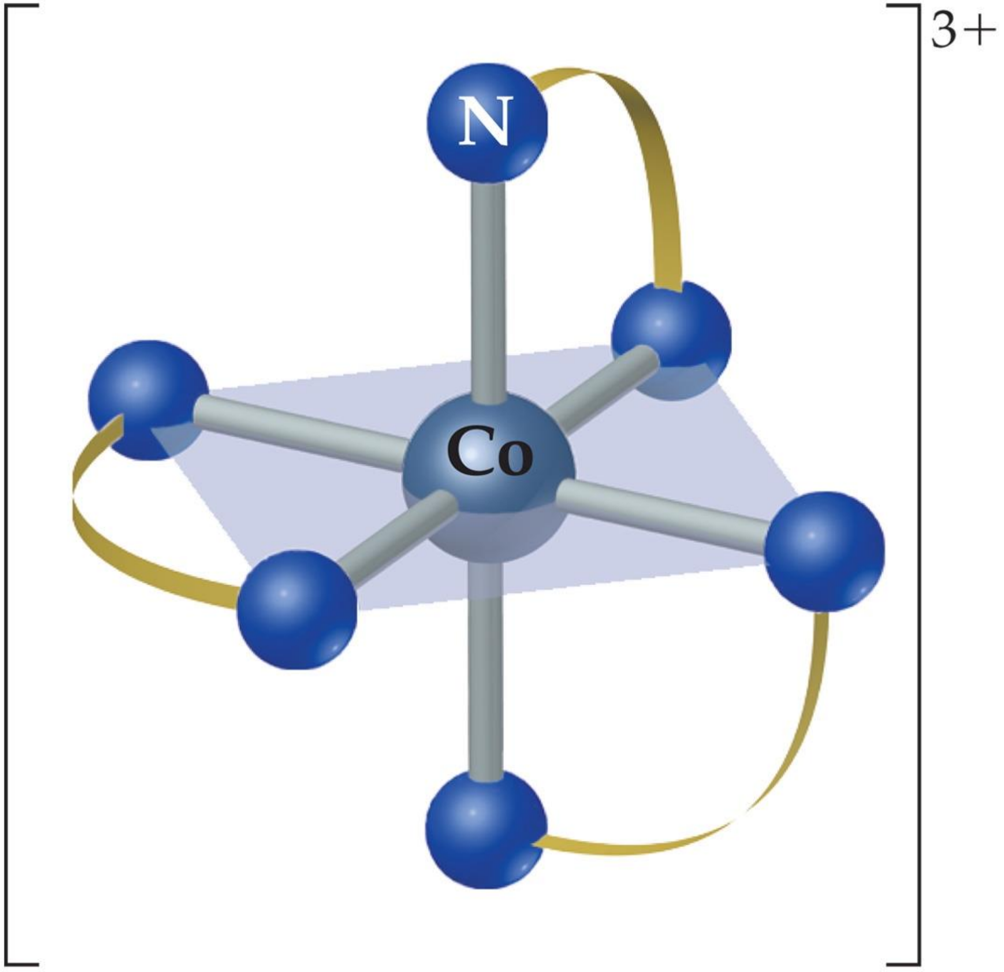




By far the most-encountered geometry, when the coordination number is six, is octahedral.

All six coordinate compounds will be octahedral in this class.

Polydentate Ligands

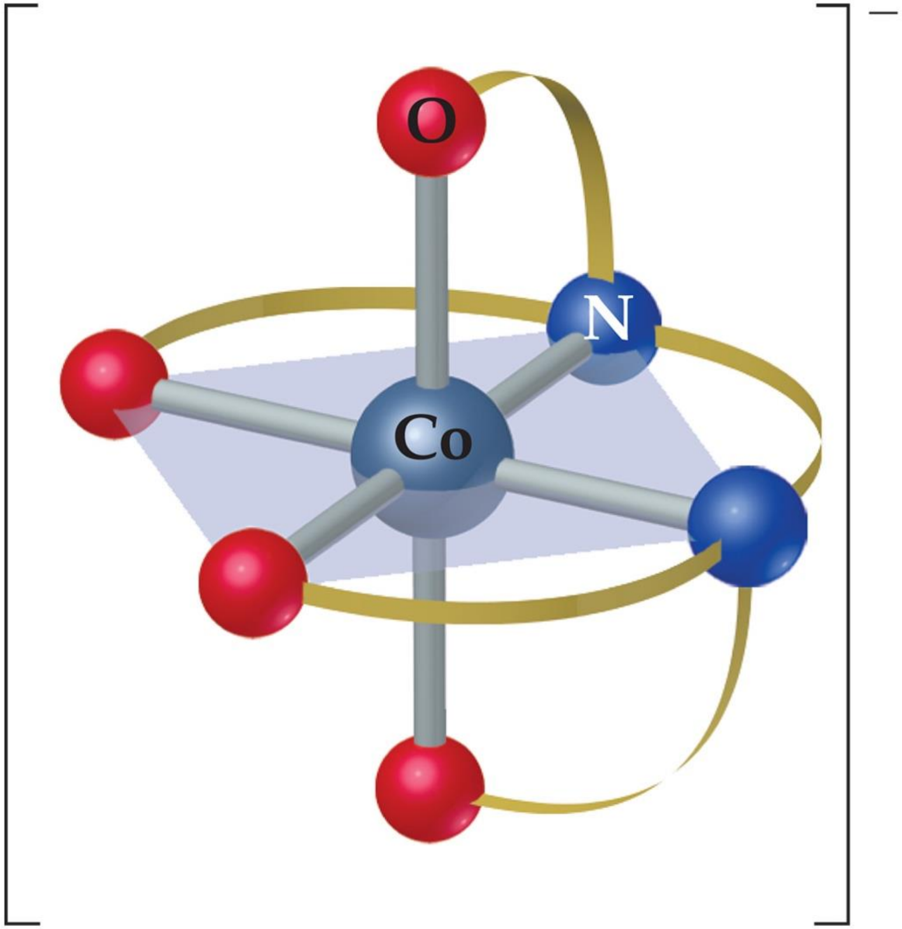


$[Co(en)_3]^{3+}$

- 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.
- 3 en's give coordination number of **six.**

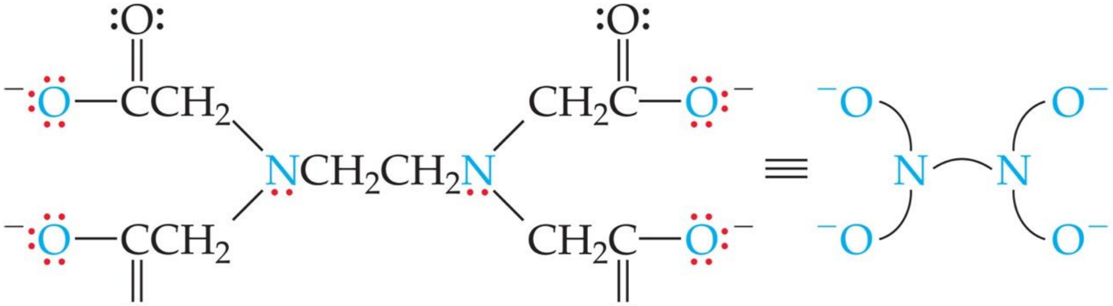
Polydentate Ligands

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has **six** donor atoms.



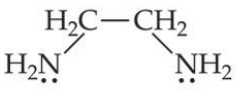
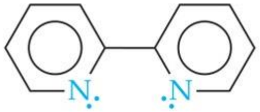
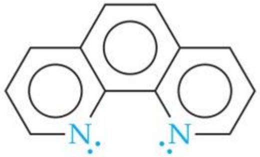
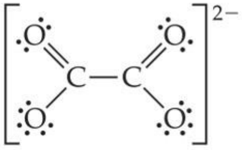
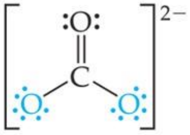
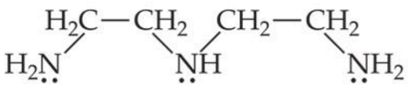
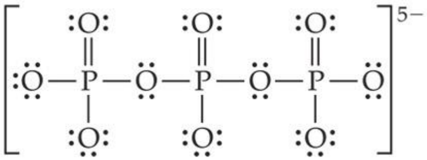
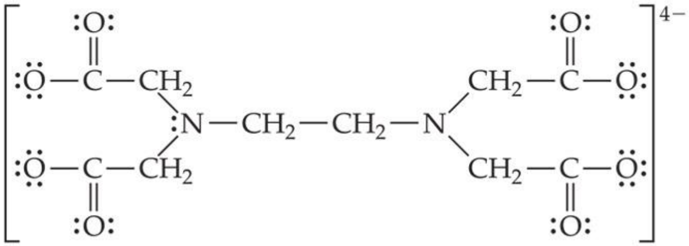
$CoEDTA^-$

Wraps around the central atom like an octopus



$[EDTA]^{4-}$

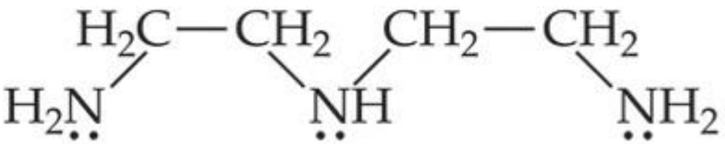
Polydentate Ligands

Ligand Type	**Examples**
Monodentate	$H_2\ddot{O}:$ Water $:NH_3$ Ammonia $:\ddot{F}:^-$ Fluoride ion $:\ddot{Cl}:^-$ Chloride ion $[:C\equiv N:]^-$ Cyanide ion $[:\underbrace{\ddot{S}=C=\ddot{N}}_{\text{or}}:]^-$ Thiocyanate ion $[:\ddot{O}-H]^-$ Hydroxide ion $[:\underbrace{\ddot{O}=\underset{..}{N}}_{\text{or}}=\ddot{O}:]^-$ Nitrite ion
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.

Polydentate Ligands

Polydentate



Diethylenetriamine

What’s the ***minimum*** number of diethylenetriamine ligands required to make an octahedral complex?

A. 1

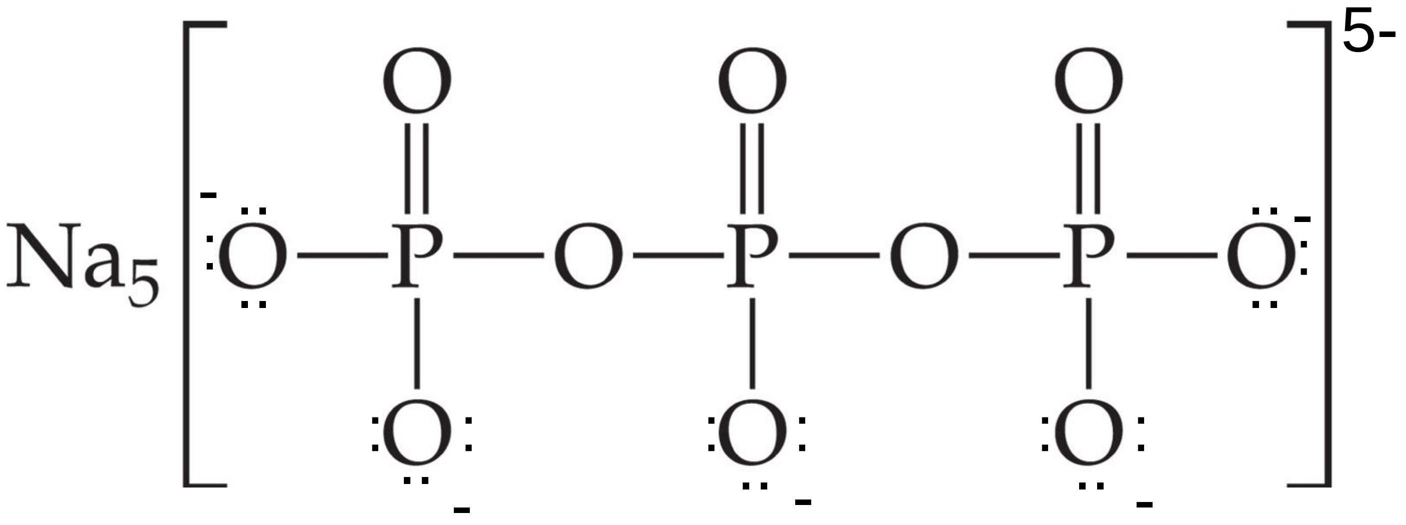
B. 2

C. 3

D. 4

E. 6

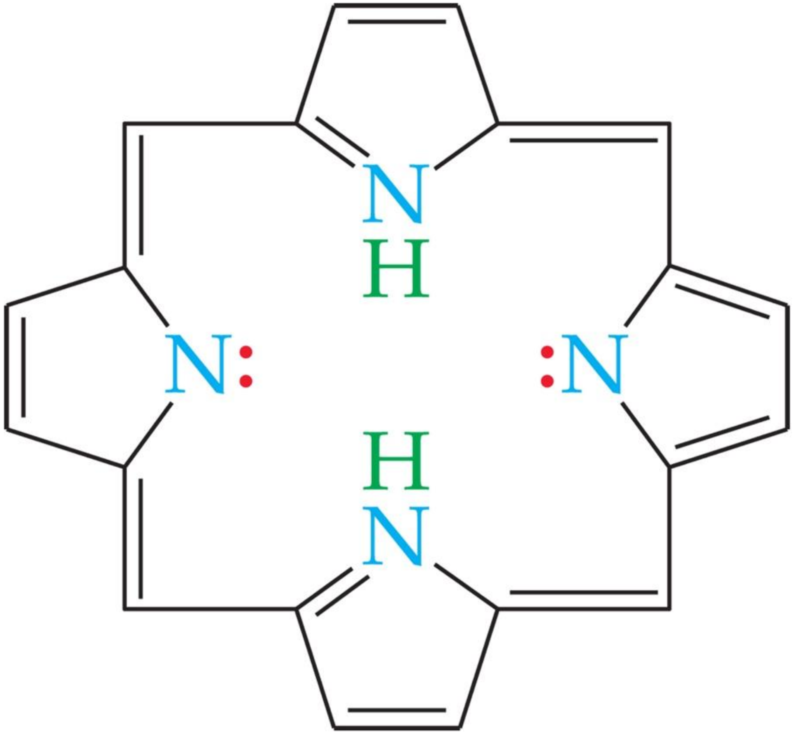
Chelating Agents



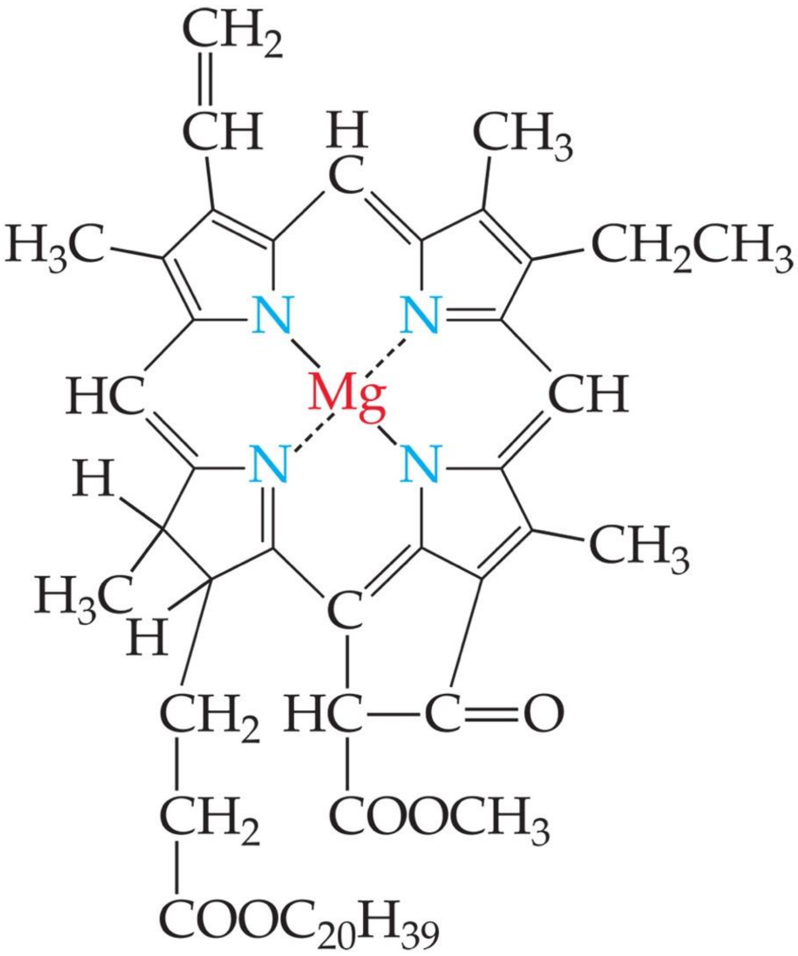
- Bind to metal ions removing them from solution.
- Phosphates are used to tie up Ca^{2+} and Mg^{2+} in hard water to prevent them from interfering with detergents.

Chelating Agents

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



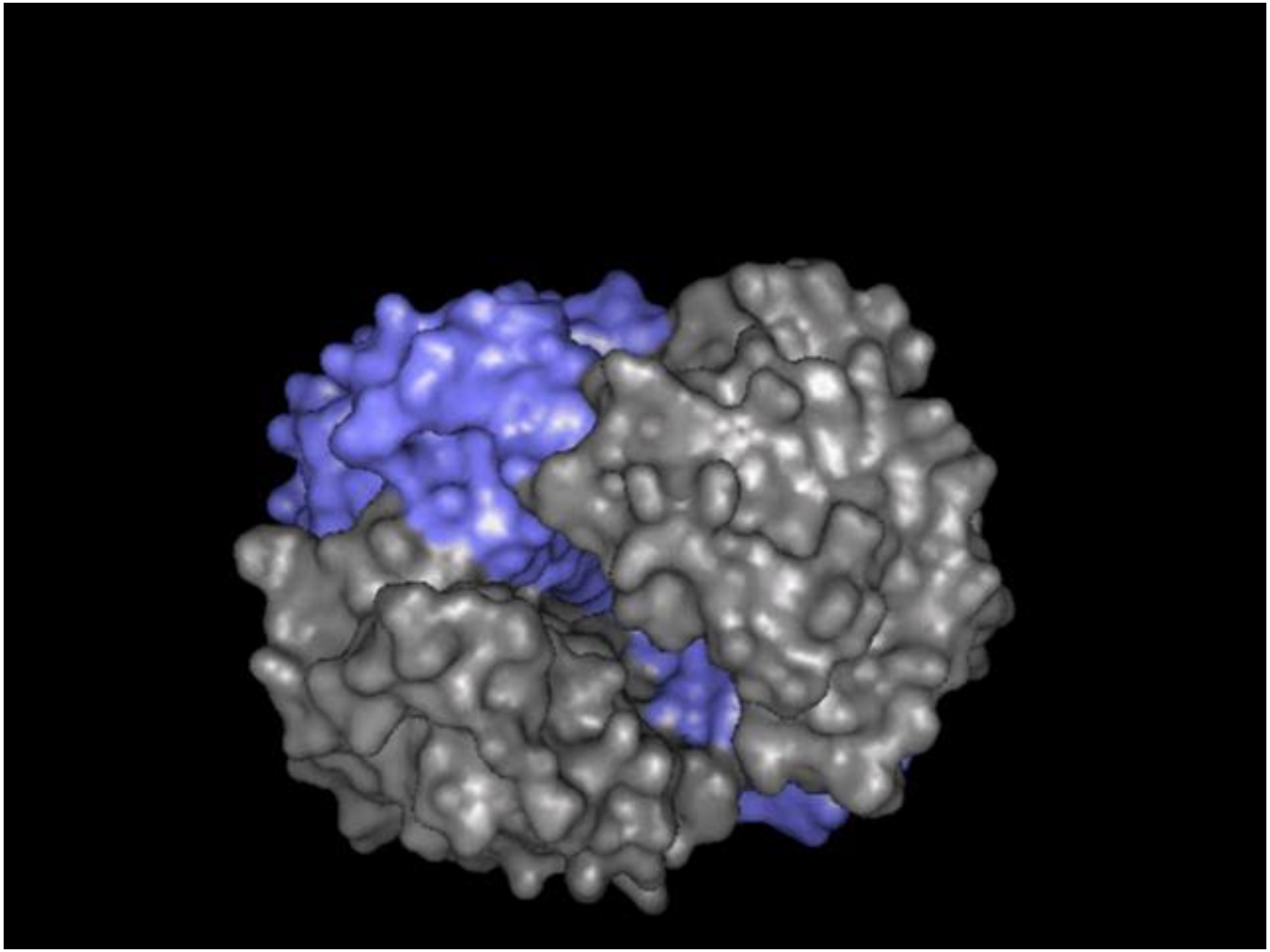
Chelating Agents



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

Porphyrin Heme binds the oxygen in your blood

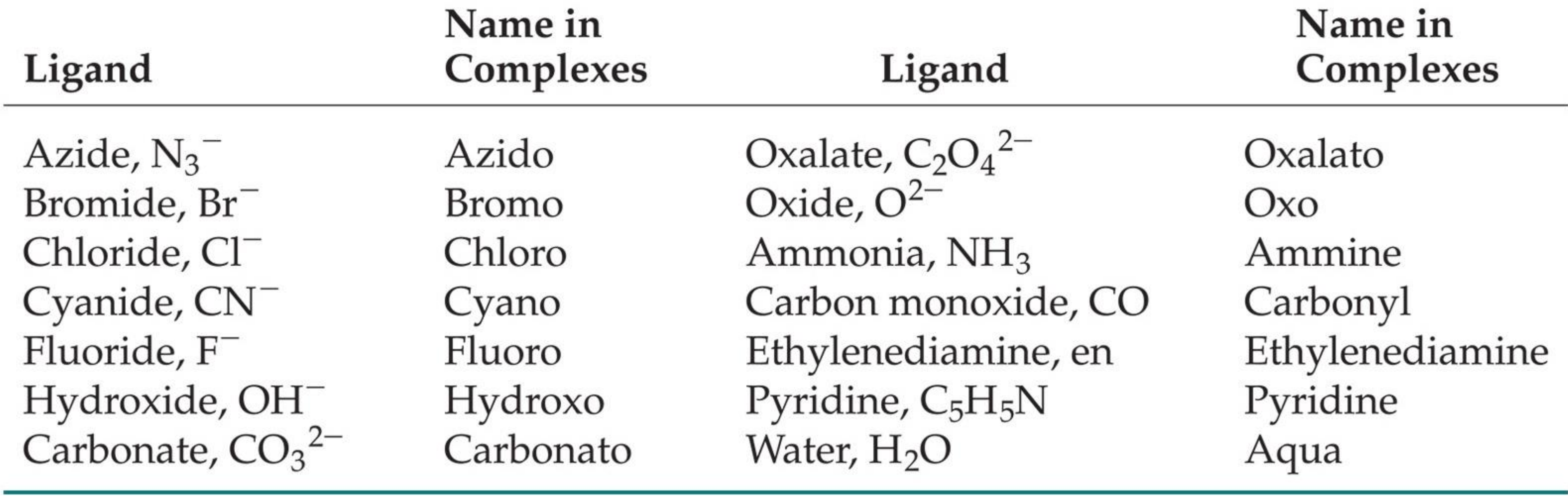
Hemoglobin tetramer has 4 hemes



Oxygen binding causes conformational change

Makes the other sites bind oxygen better

Nomenclature of Coordination Compounds

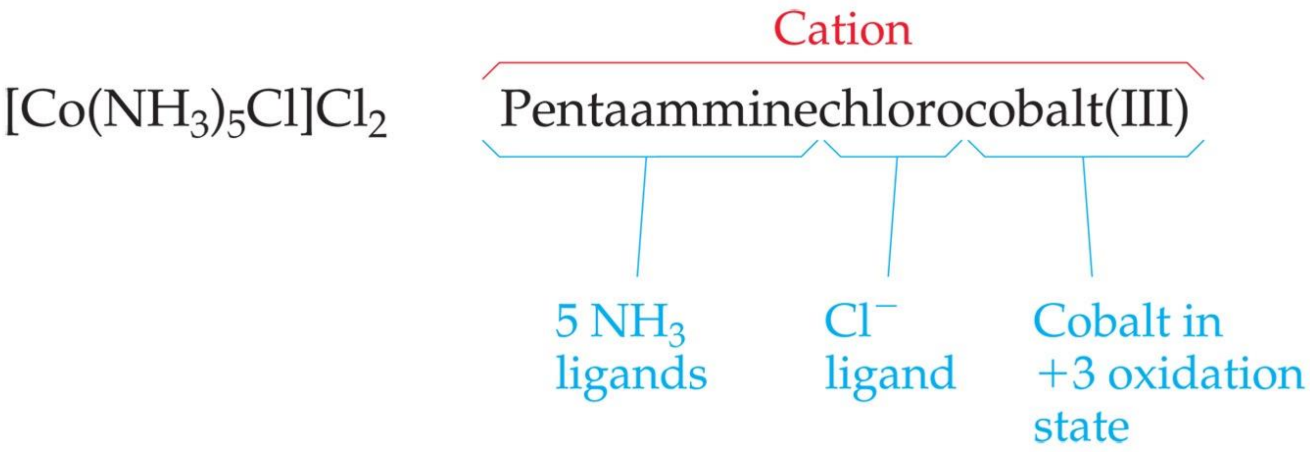


Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-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

- coordination complex nomenclature:
  - ➢ The ligands are prefixes (in front of metal name).
  - ➢ Note, all the anionic ligands end in "o"
  - ➢ Neutral ligands don't.

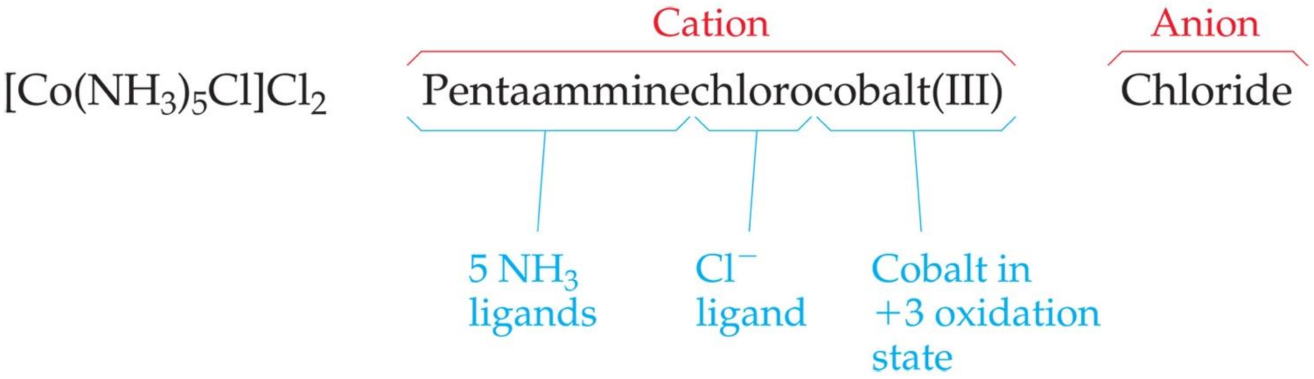
Nomenclature of Coordination Compounds

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



Nomenclature of Coordination Compounds

- Anionic ligands end in “o”;
- neutral ligands are not changed.
- Prefixes = number of each ligand.



$[Co(\textit{en})_3]Cl_3$. tris-ethylenediamineColbalt(III) chloride

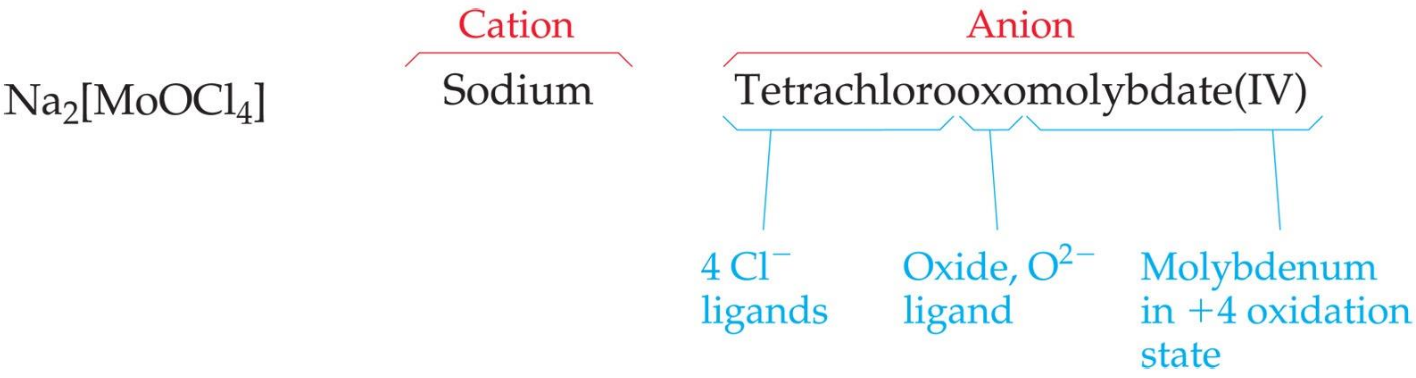
Nomenclature of Coordination Compounds

- 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(*en*)$_3$]Cl$_3$. tris-ethylenediamineCobalt(III) 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.



Nomenclature of Coordination Compounds

- Name the following metal complex:
- $[Co(en)(NH_3)Cl]Cl_2$

A. AminochloroethylenediamineColbalt(III) chloride

B. Amminechloroethylenediaminecobalt(III) chloride

C. Ammineethylenediaminechloridecobalt(III) chloro

D. Aminoethylenediaminochlorocobalt(III) chloride

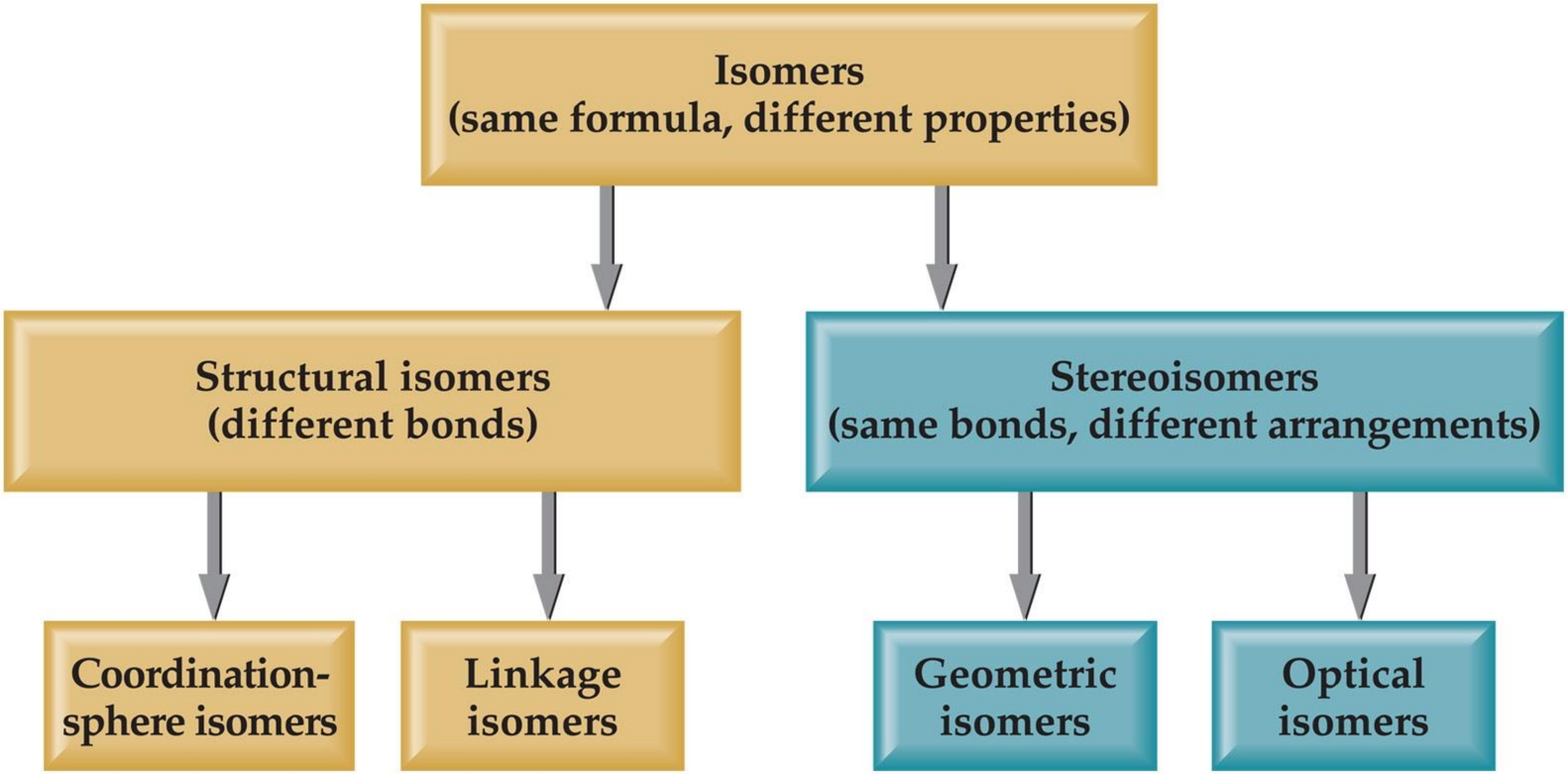
E. None of the above.

Nomenclature of Coordination Compounds

- Name the following metal complex:
- $[Co(en)(NH_3)Cl]Cl_2$

A. AminochloroethylenediamineColbalt(III) chloride
B. Amminechloroethylenediaminecobalt(III) chloride
C. Ammineethylenediaminechloridecobalt(III) chloro
D. Aminoethylenediaminochlorocobalt(III) chloride
E. None of the above.

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).

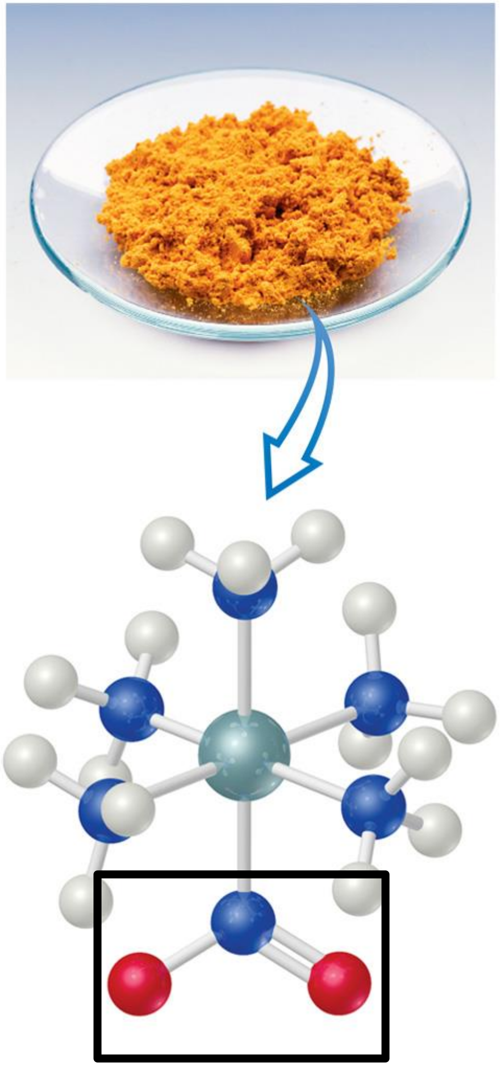
Isomers

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 possible.

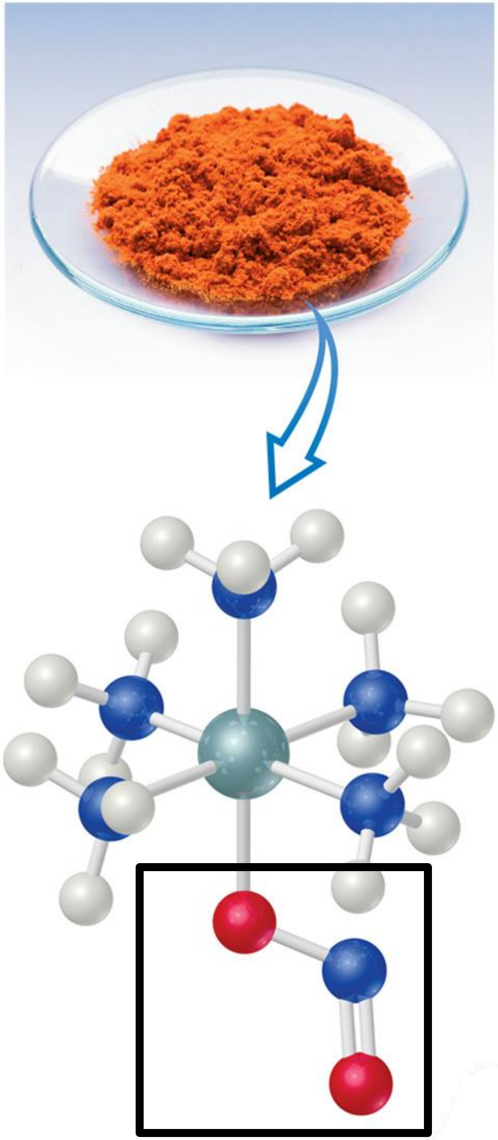
Is this isomer?

A. *structural*

B. *geometric*



Nitro isomer



Nitrito isomer

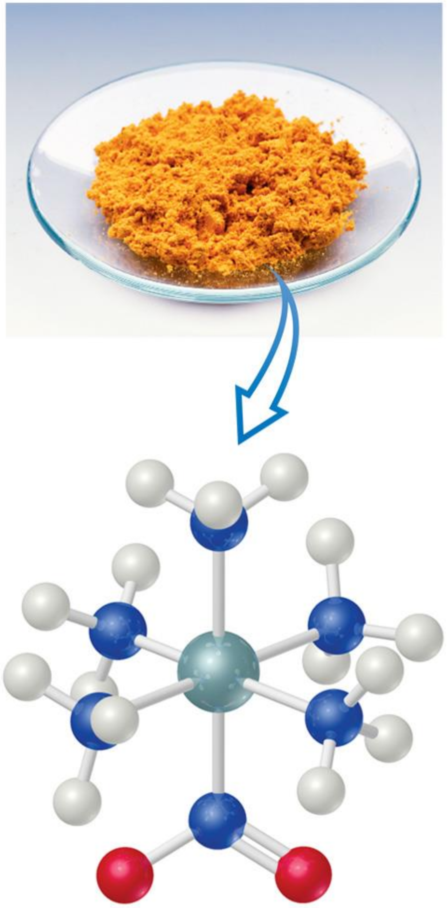
Structural Isomers

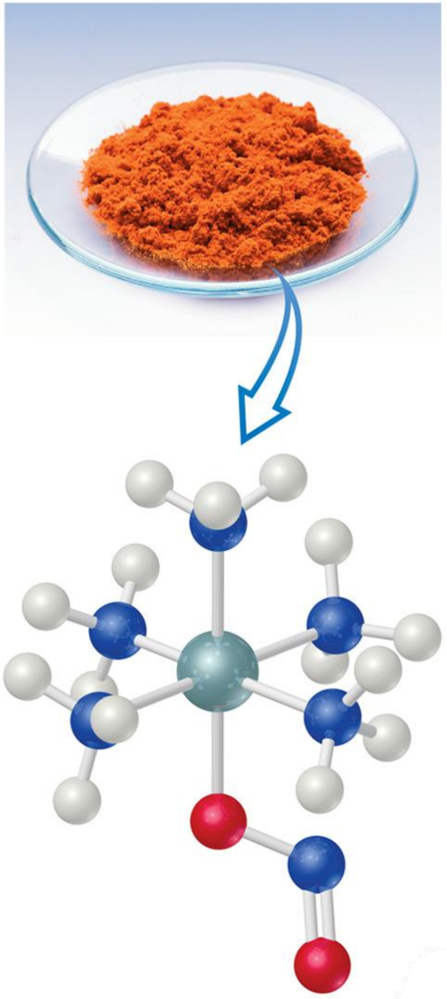
If a ligand (like the NO_2 group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, linkage isomers are formed.

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

Structural,

bonding different


Nitro isomer

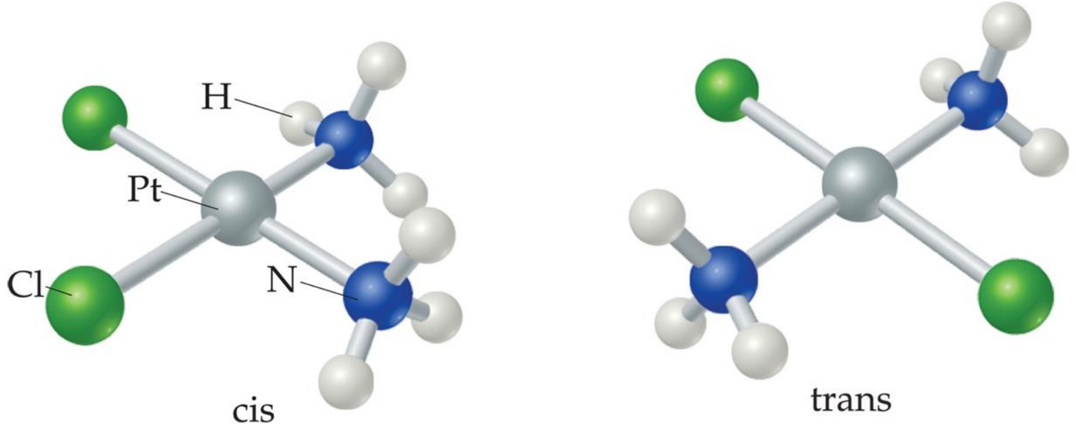

Nitrito isomer

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 $[Cr(H_2O)_5Cl]Cl_2 \cdot \mathbf{H_2O}$, and
  - ➢ The (also) green $[Cr(H_2O)_4Cl_2]Cl \cdot \mathbf{2\ H_2O}$.

Difference: Water directly coordinated, or loosely bound. (like wet salt)

Geometric isomers



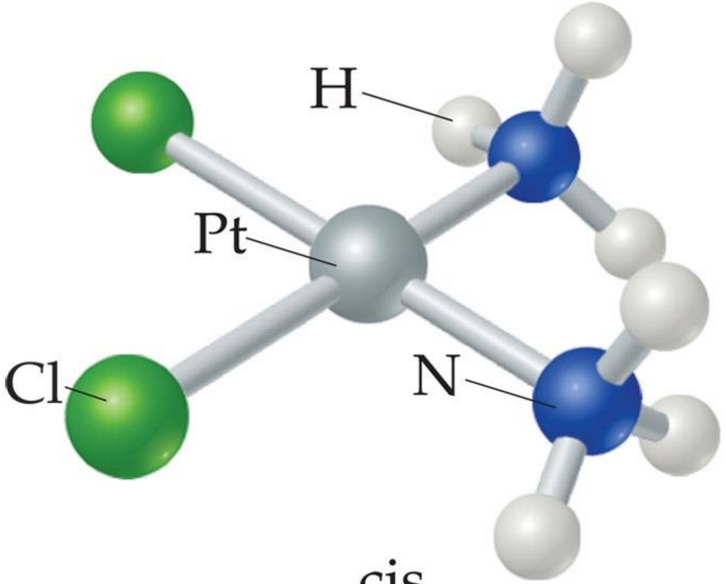
- $Pt(NH_3)_2Cl_2$

  Has two *geometric isomers*, two chlorines and two NH_3 groups are bonded to the platinum metal, but are clearly different.

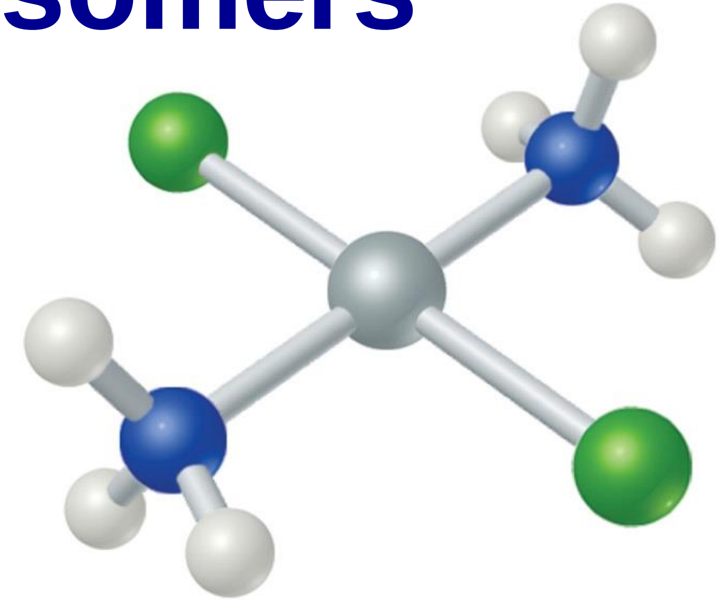
  - *cis*-Isomers have like groups on the same side.
  - *trans*-Isomers have like groups on opposite sides.

# 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

These include testicular cancer, ovarian cancer, cervical cancer, breast cancer, bladder cancer, head and neck cancer, esophageal cancer, lung cancer, mesothelioma, brain tumors and neuroblastoma.

This one doesn’t

Geometric isomers

How many isomers do the following molecules have?

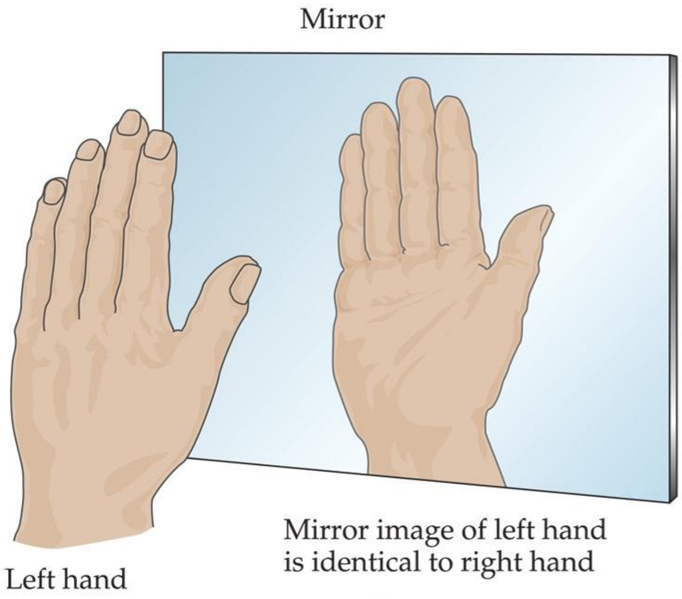
1. $Pt(NH_3)Cl_3$

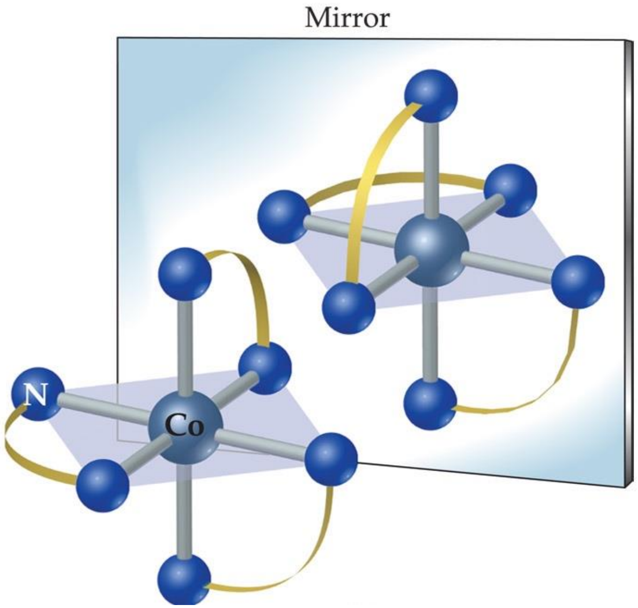
2. $[Co(NH_3)_3Cl_3]$

3. $[Co(NH_3)_2Cl_2(H_2O)_2]Cl$

A. 1
B. 2
C. 3
D. 4
E. More than 4

Stereoisomers

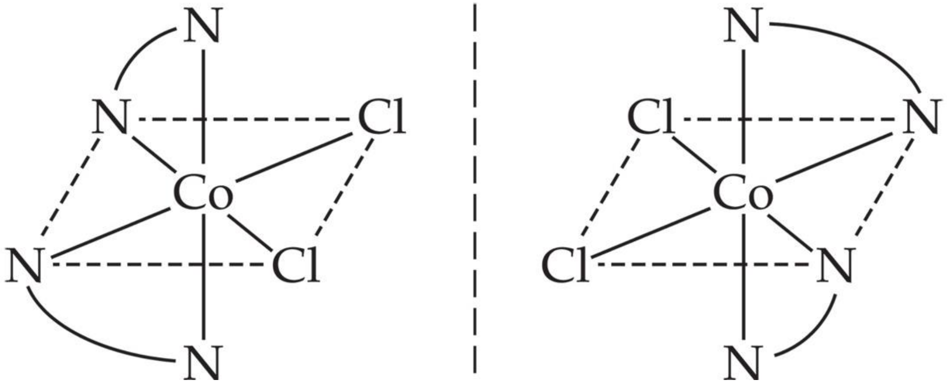




- Other stereoisomers, called optical isomers or enantiomers, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

Enantiomers

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

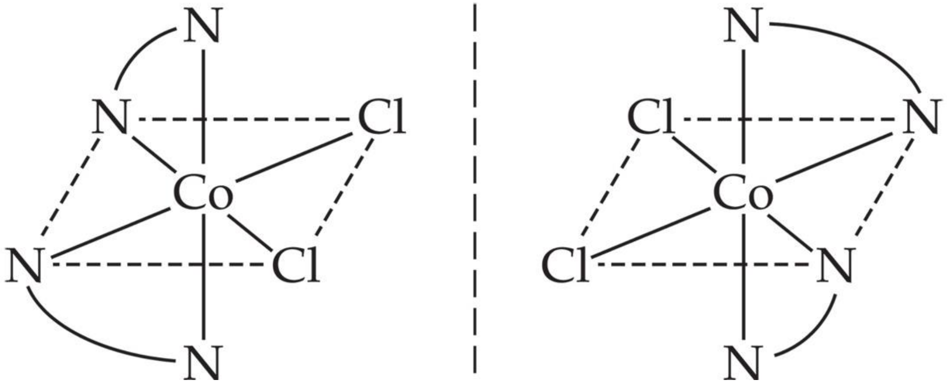


Enantiomers

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

But how do you tell if something is chiral?

Can you put a mirror through it and reflect itself.



Enantiomers

Which of the following molecules are chiral?

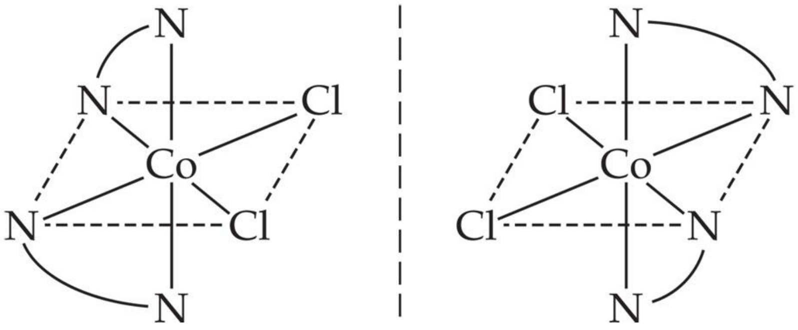
A. $[Pt(NH_3)_2Cl_2]$ (square planar)

B. $[Zn(NH_3)ClBr(H_2O)]$ (tetrahedral)

C. $[Co(NH_3)_4Cl_2]$

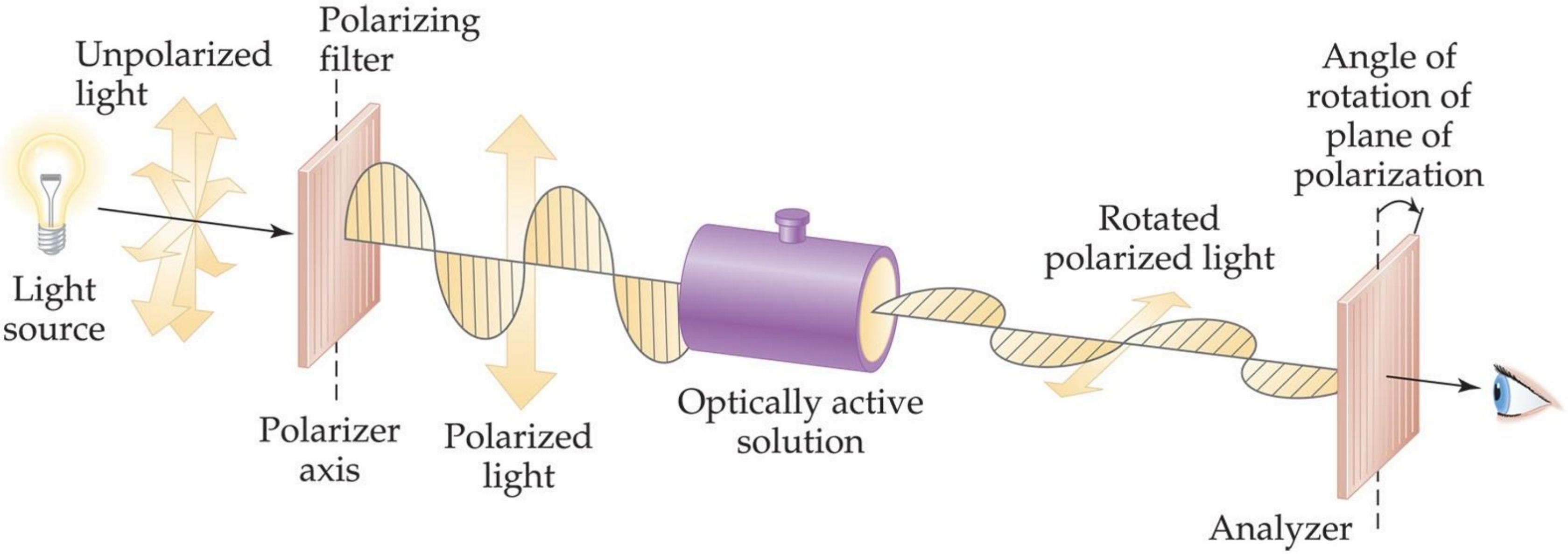
D. All of the above

E. B and C



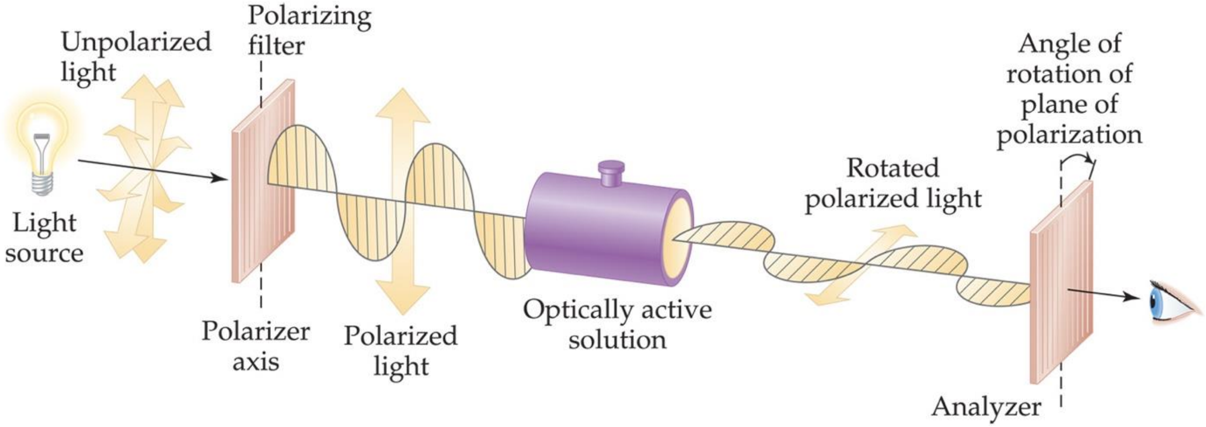
Enantiomers

- 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.



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 14 possible valence orbitals:
  - 1 ns
  - 3 np
  - 5 (n-1)d
  - 5 nd if needed.

Valence Bond theory

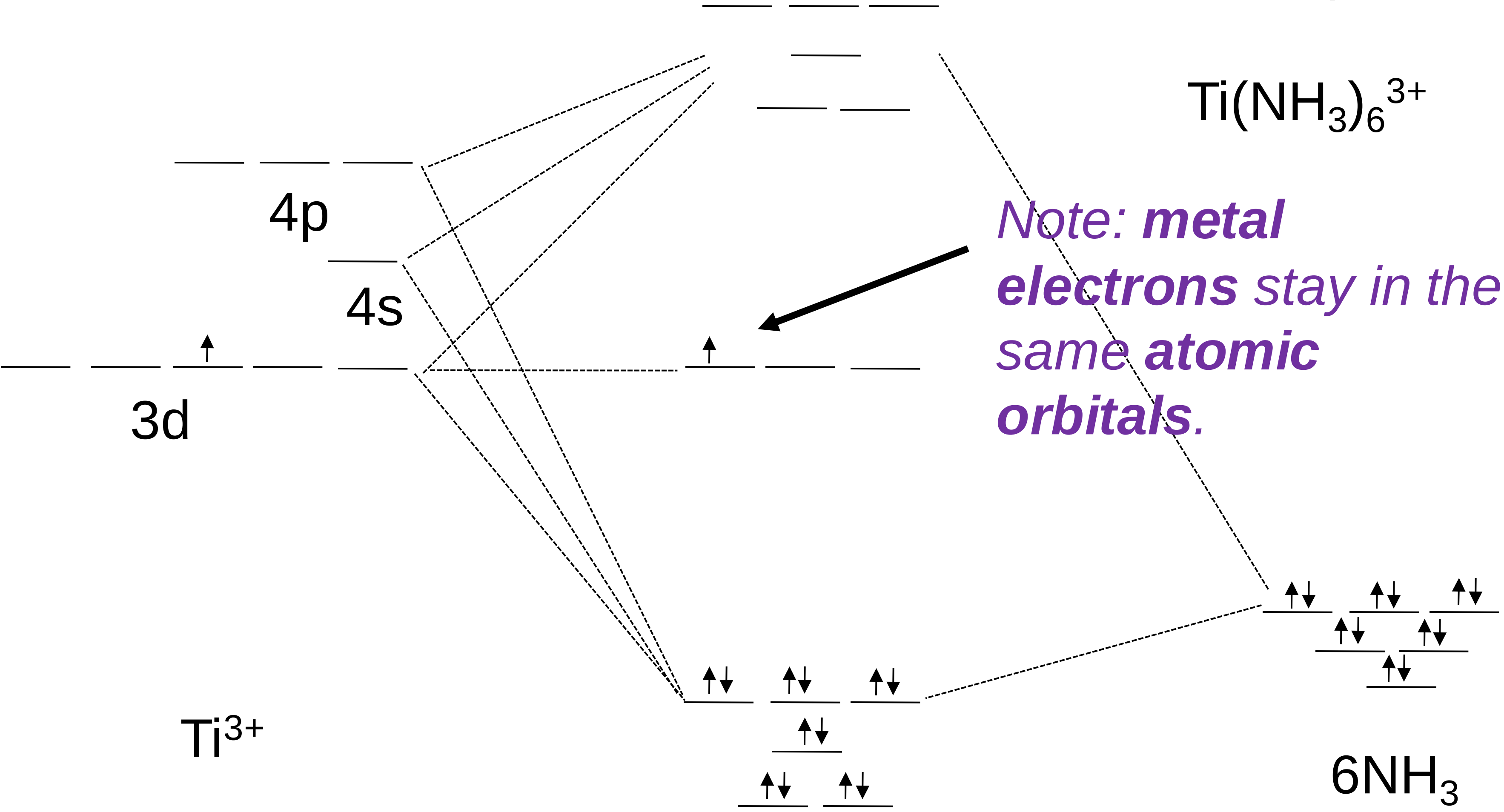
- Example

- $Co(NH_3)_6^{3+}$
- Co electron configuration: $4s^2 3d^7$
- Co^{3+} electron configuration: $4s^0 3d^6$
- Need six orbitals for six ligands so:
  - Hybridize 1 4s, 3 4p and 2 3d to give:
  - sp^3d^2 orbitals. ***The 6 valence electrons of*** Co^{+3} ***sit in the other 3 d orbitals.***

Ligand Field theory (MO theory for coordination compounds)

Example:

$Ti(NH_3)_6^{3+}$



*Note: **metal electrons** stay in the same **atomic orbitals**.*

Explaining the properties of transition metal coordination complexes

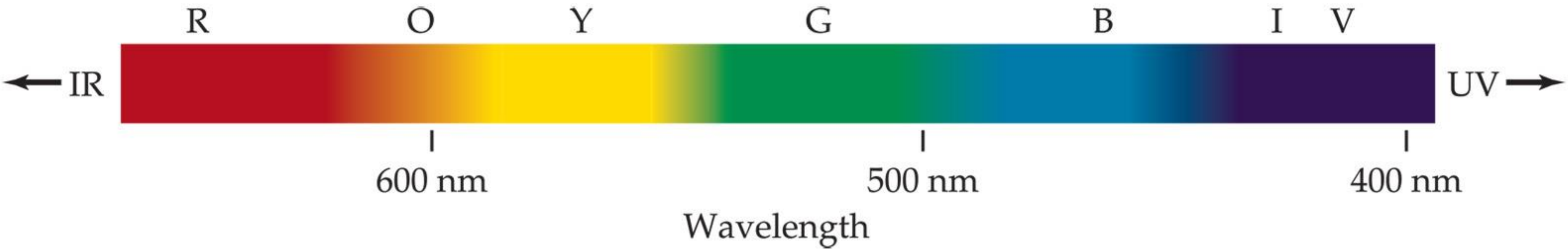
1. Magnetism
2. color

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 an 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.

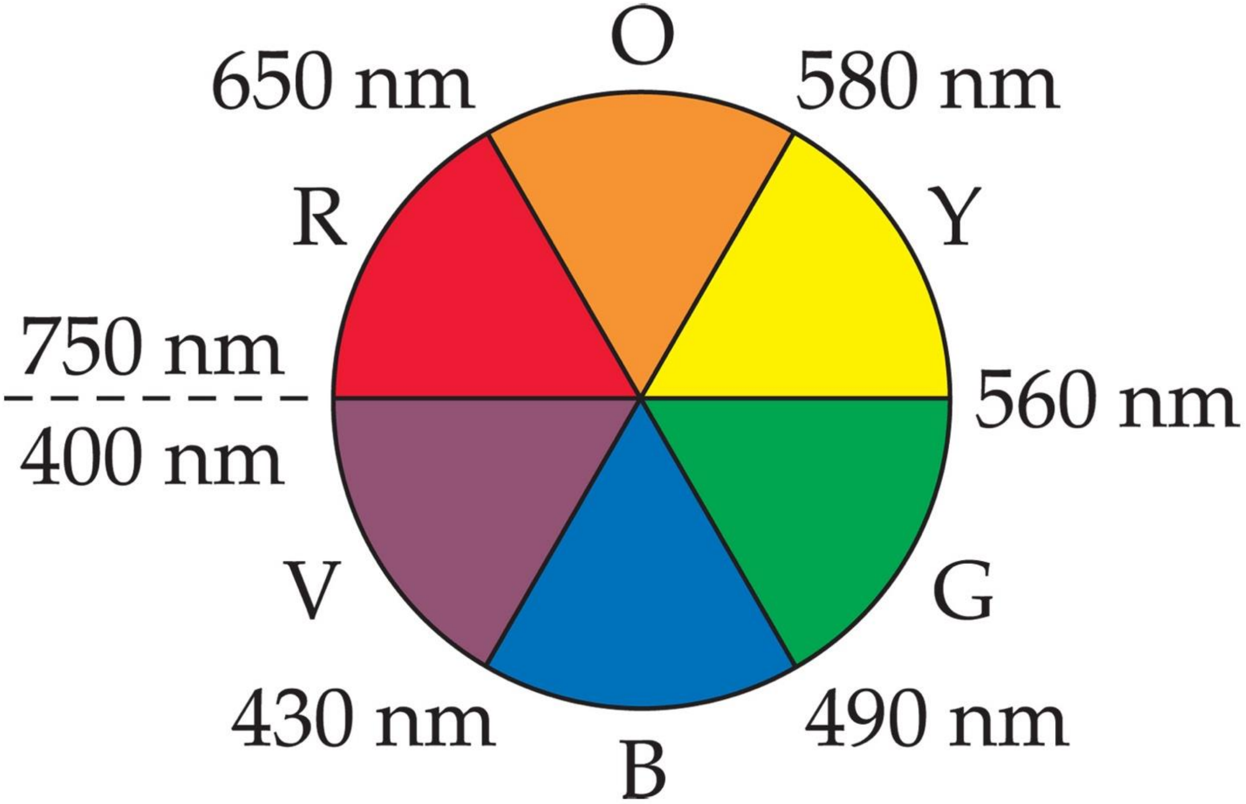
Why? *Your brain.*

Absorb **Orange**

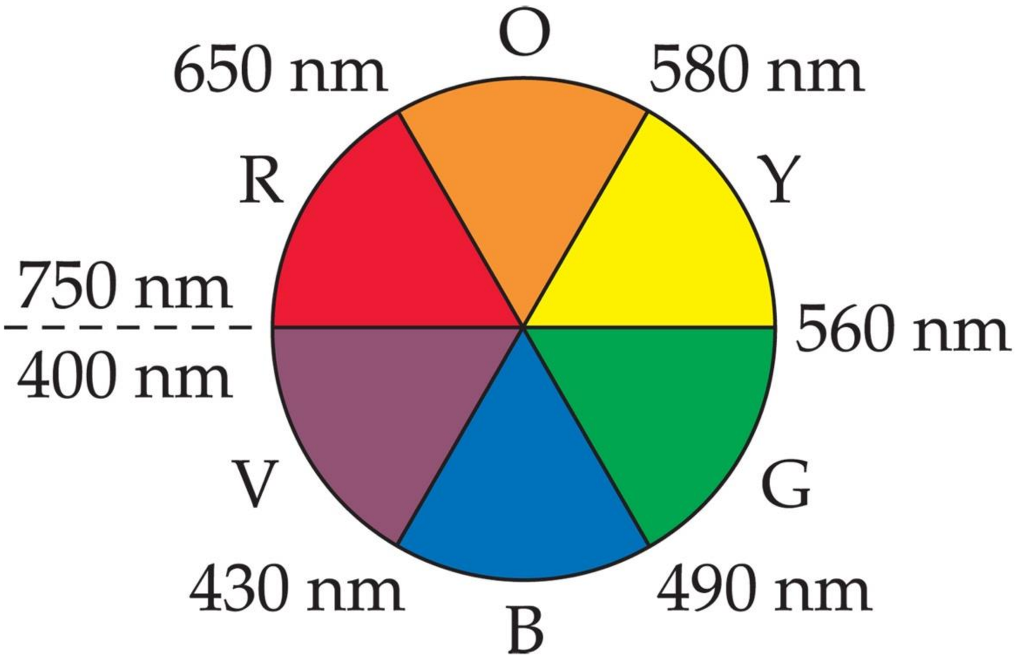
See **Blue**

Absorb **Red**

See **Green**



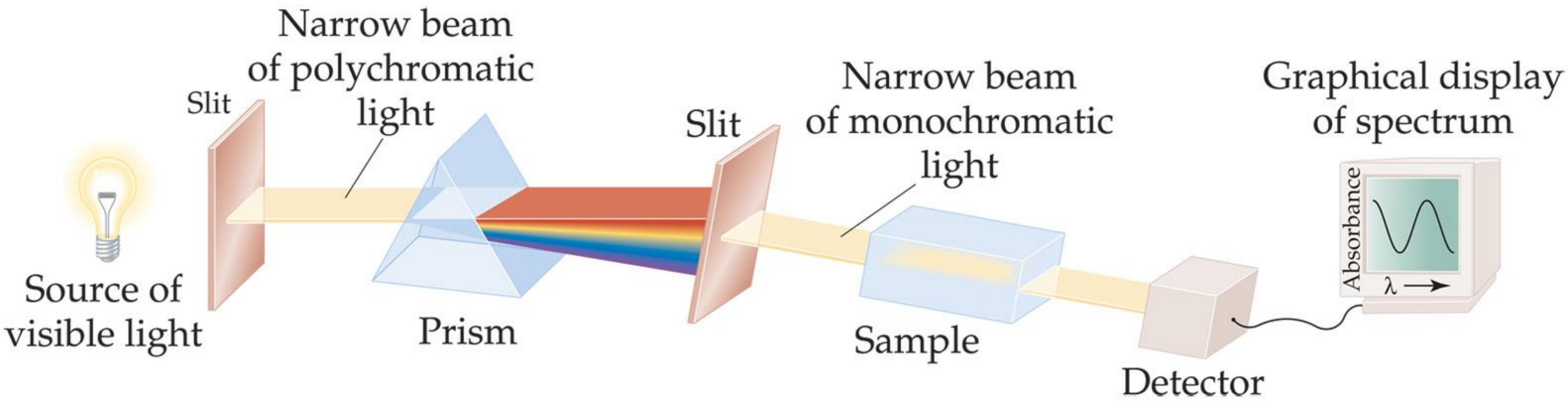
$[Ti(H_2O)_6]^{3+}$
Absorbs in green yellow.
Looks purple.



(a)

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?

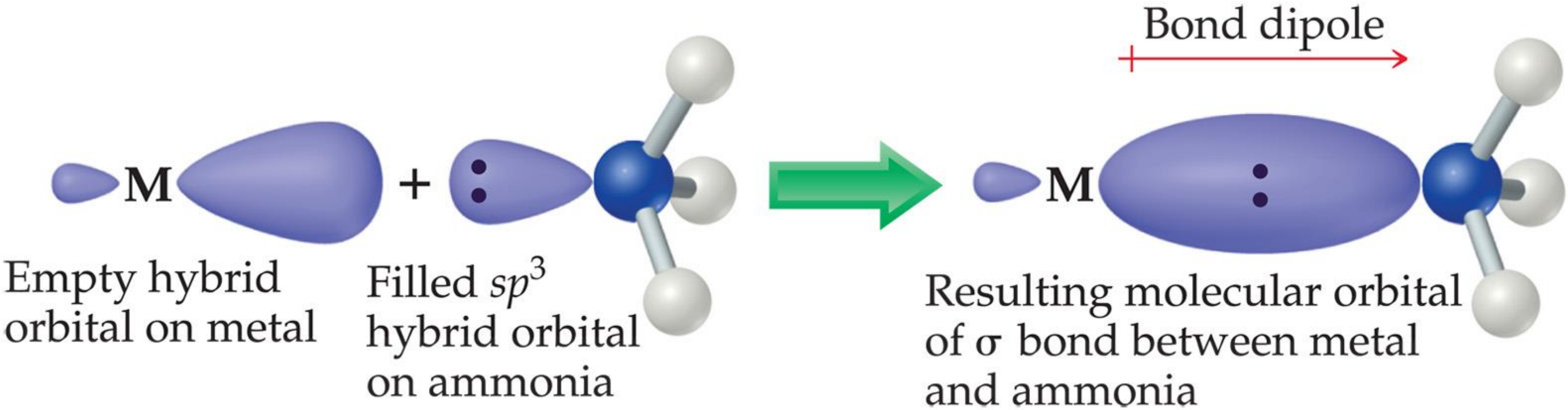
Crystal Field Theory

Model of ligand/metal bonding.

Electron pair comes from ligand

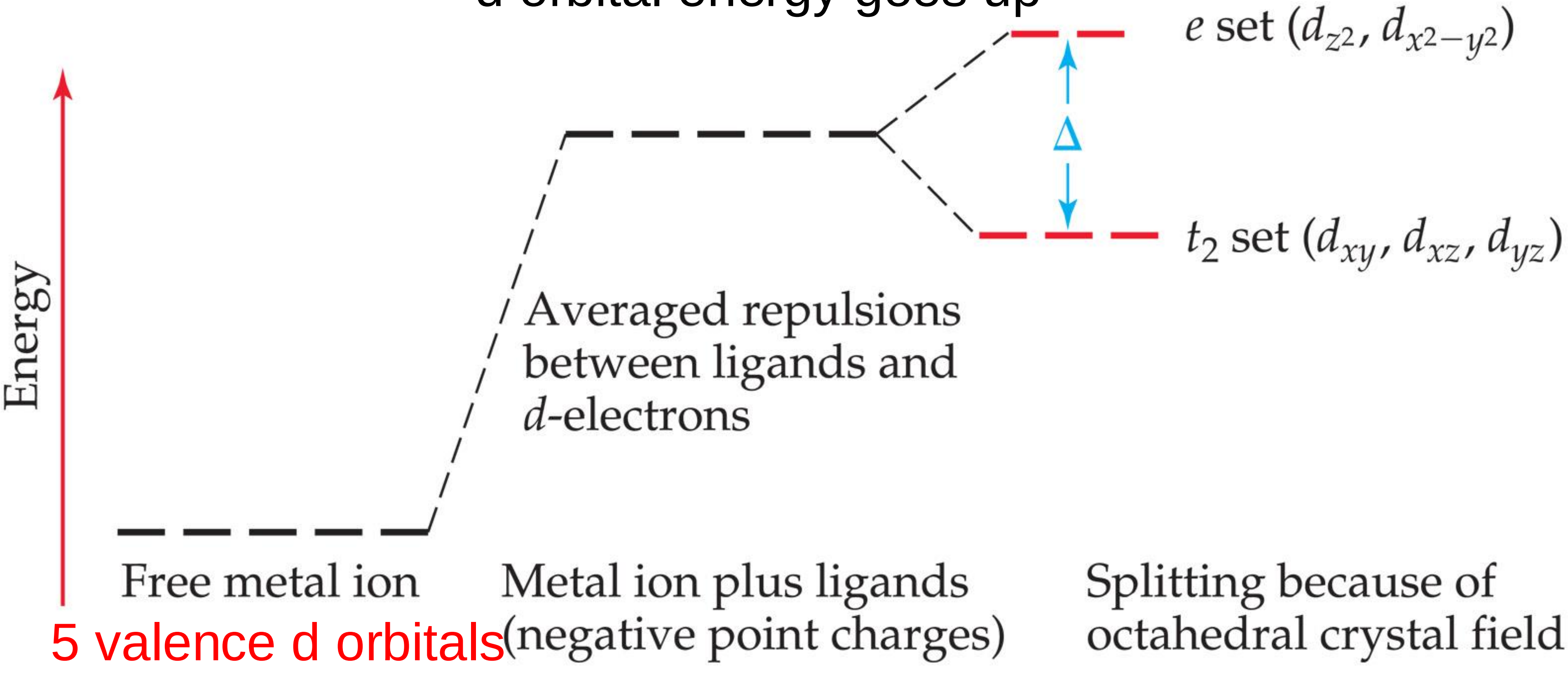
Bond very polarized.

Assumption: interaction pure electrostatic.



Now, think of point charges being attracted to the positively Charged metal. What happens to the d orbitals?

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



5 valence d orbitals

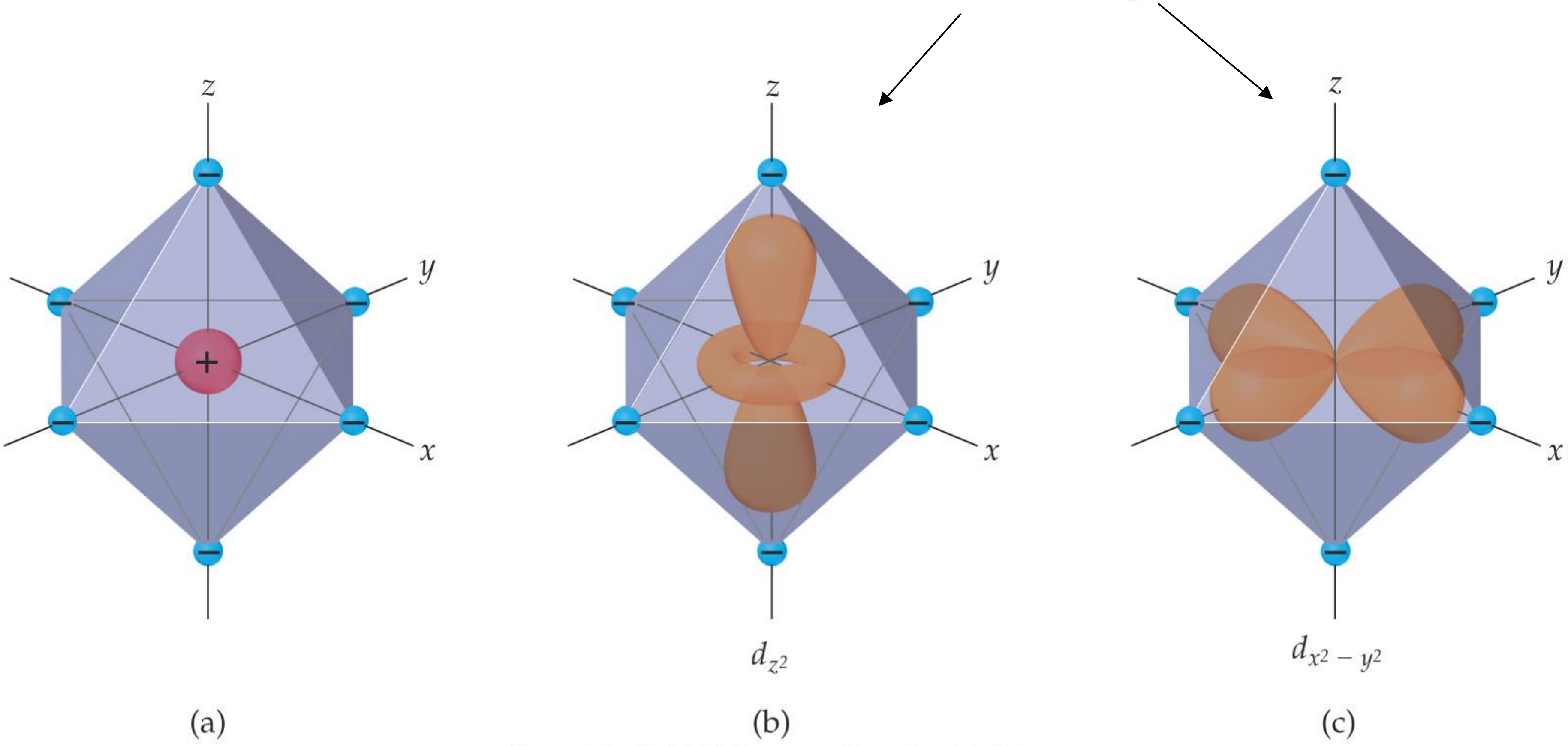
‘’Why this splitting?

Ligands will interact with some d orbitals more than others

Depends on relative orientation of orbital and ligand

Ligands point right at lobes

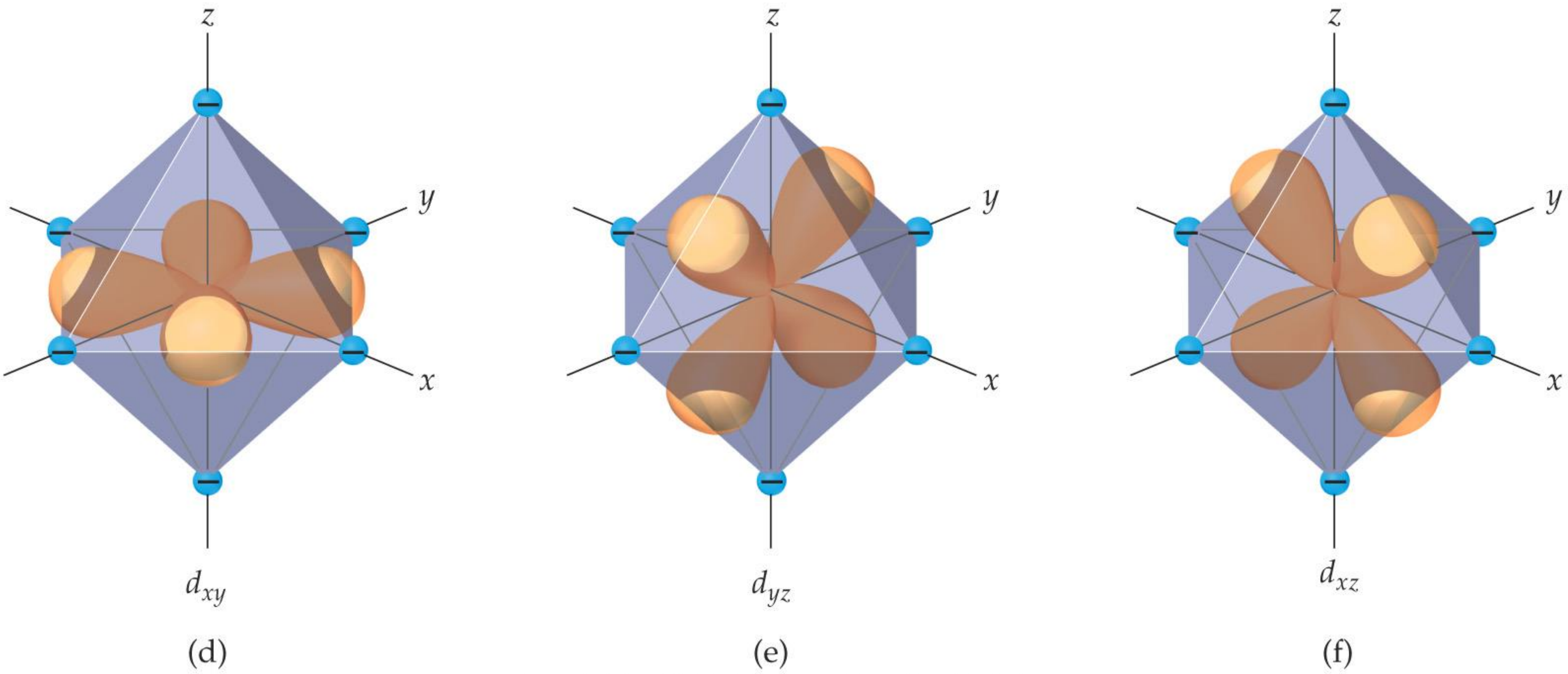
Orbitals are ***Higher in E.***



(a) (b) (c)

In these orbitals, the ligands are between the lobes

Interact less strongly, ***are lower in E.***

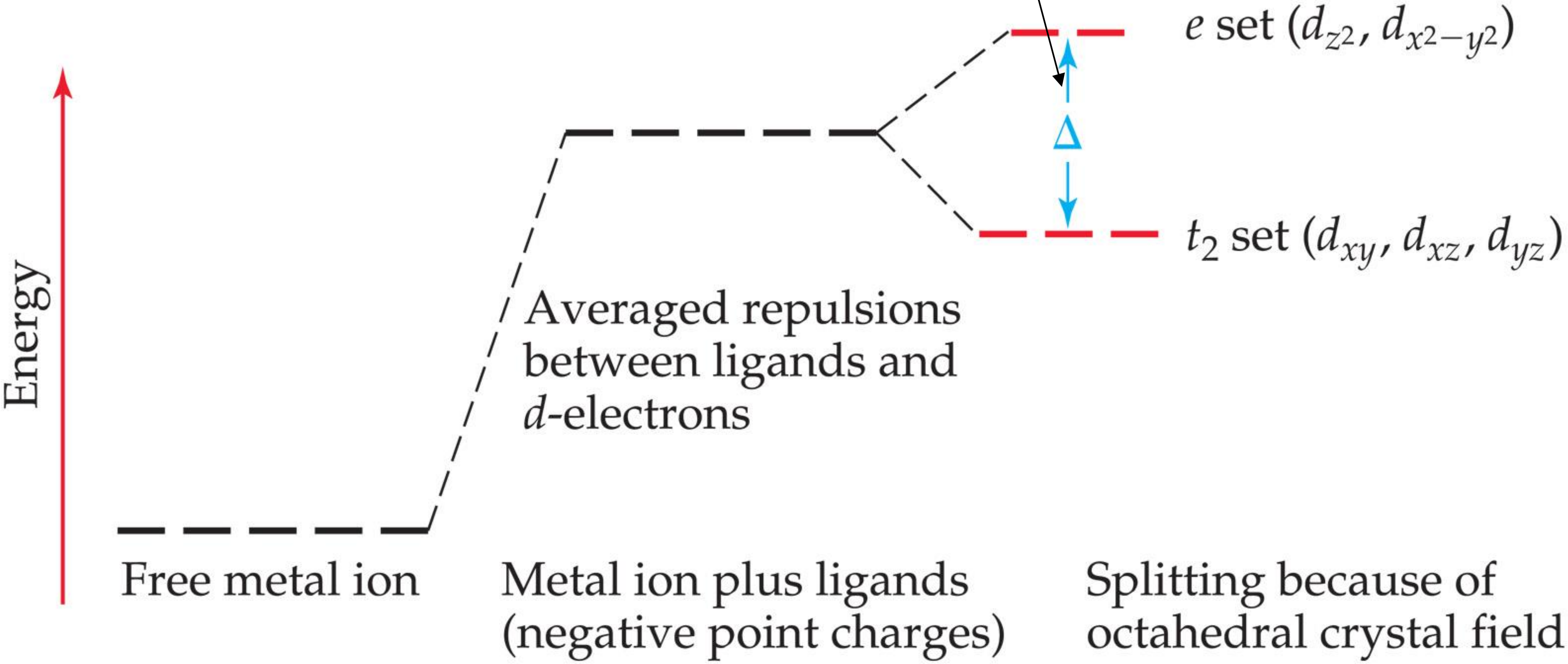


d_{xy} (d)

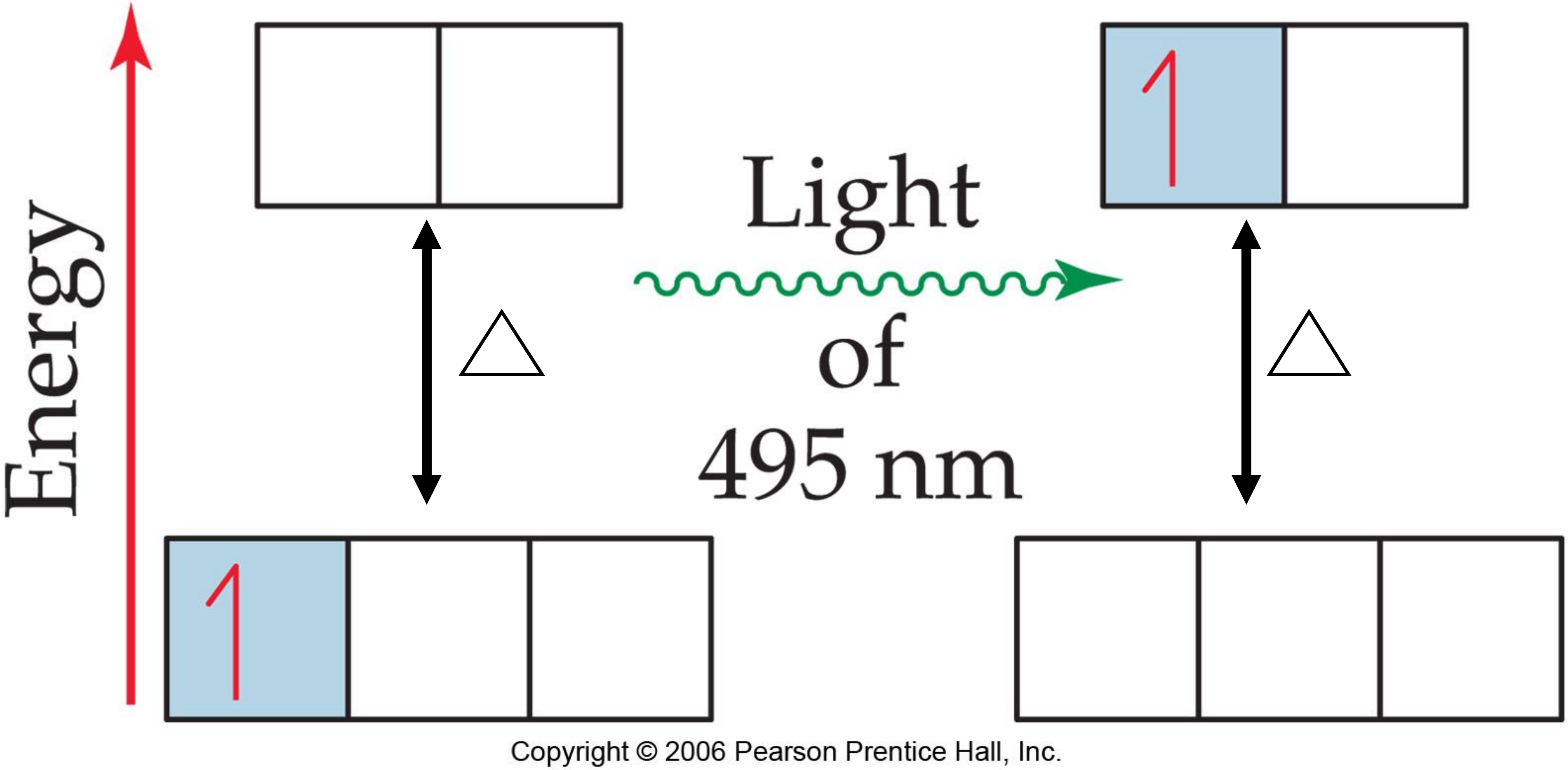
d_{yz} (e)

d_{xz} (f)

Splitting due to ligand/orbital orientation.



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

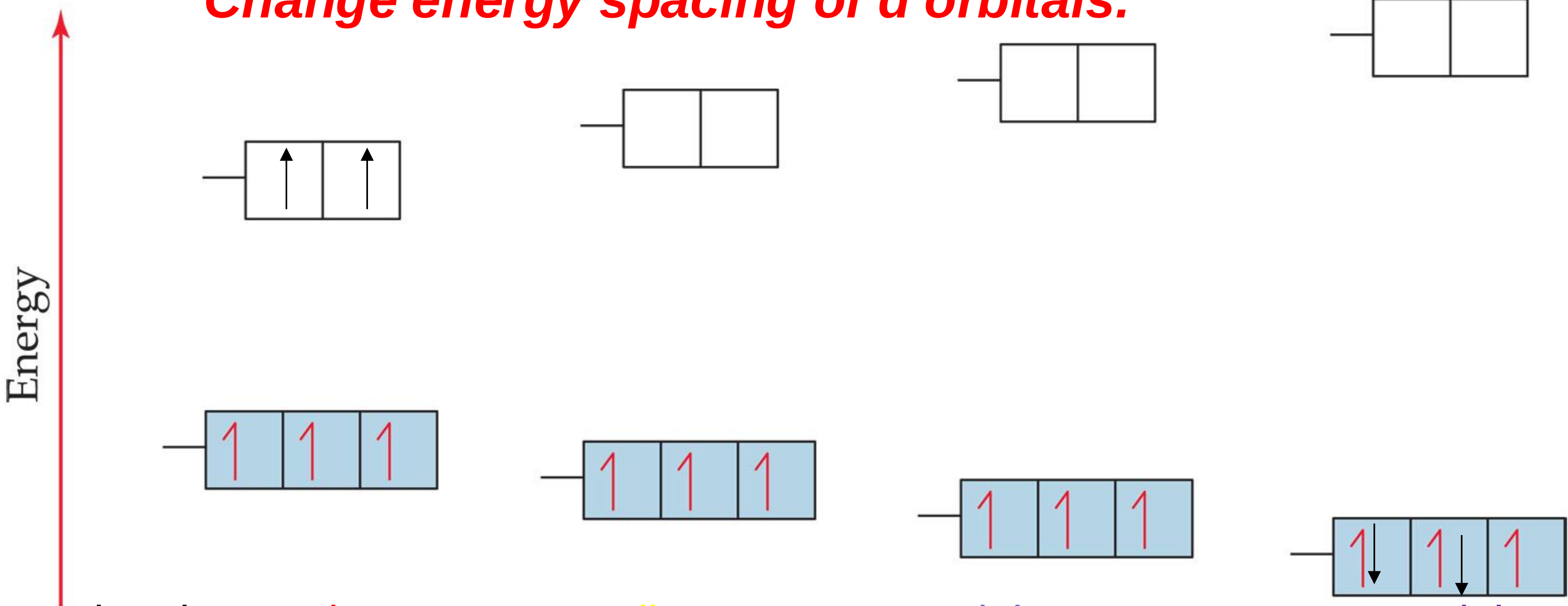


$\triangle = hc/\lambda \ = hc/495\ \text{nm}$

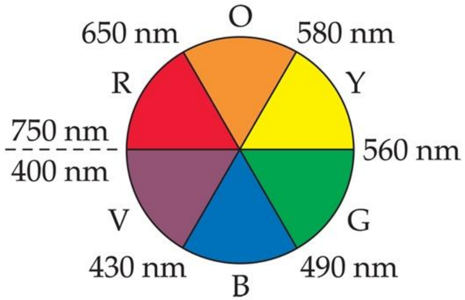
Different ligands

Interact with the d orbitals more strongly or weakly

Change energy spacing of d orbitals.



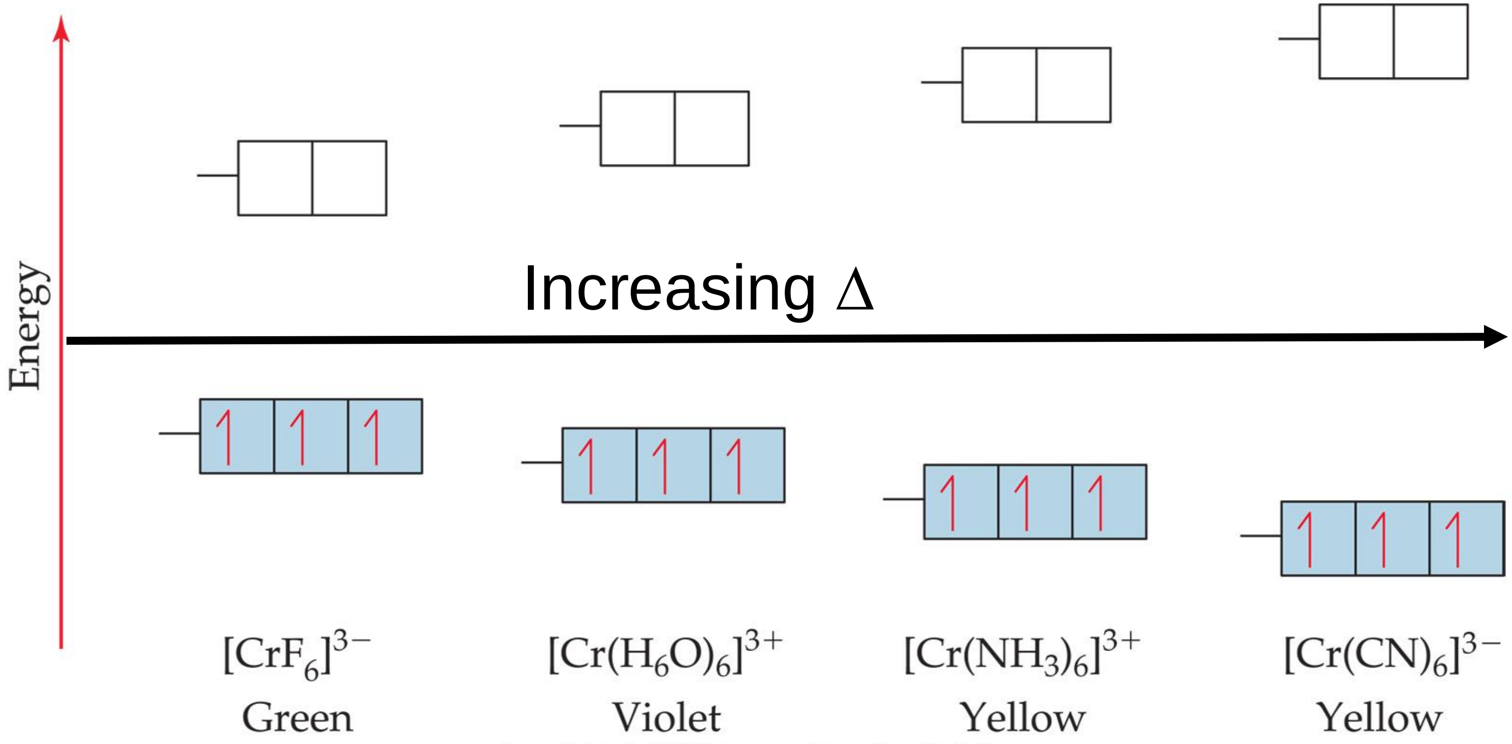
Absorbs:	red.	yellow	violet	more violet
	$[CrF_6]^{3-}$	$[Cr(H_6O)_6]^{3+}$	$[Cr(NH_3)_6]^{3+}$	$[Cr(CN)_6]^{3-}$
Color	Green	Violet	Yellow	Yellow



Spectrochemical series (strength of ligand interaction)

Low field Increasing Δ High field

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

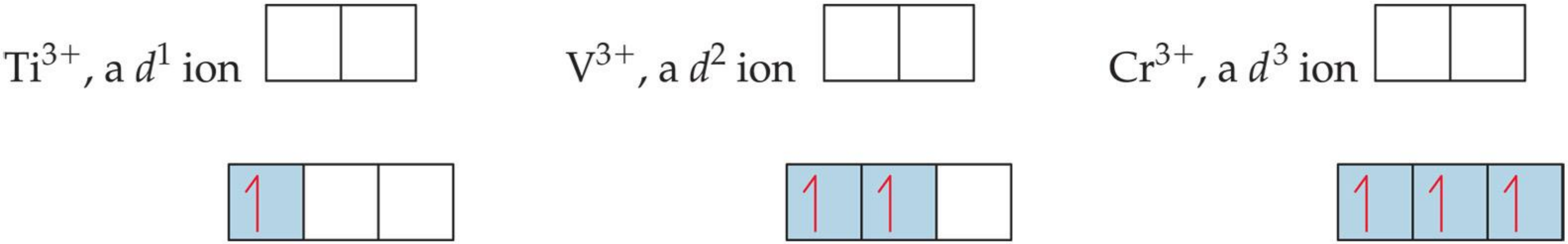


Copyright © 2006 Pearson Prentice Hall, Inc.

Absorption: Red. Yellow. Violet. More violet

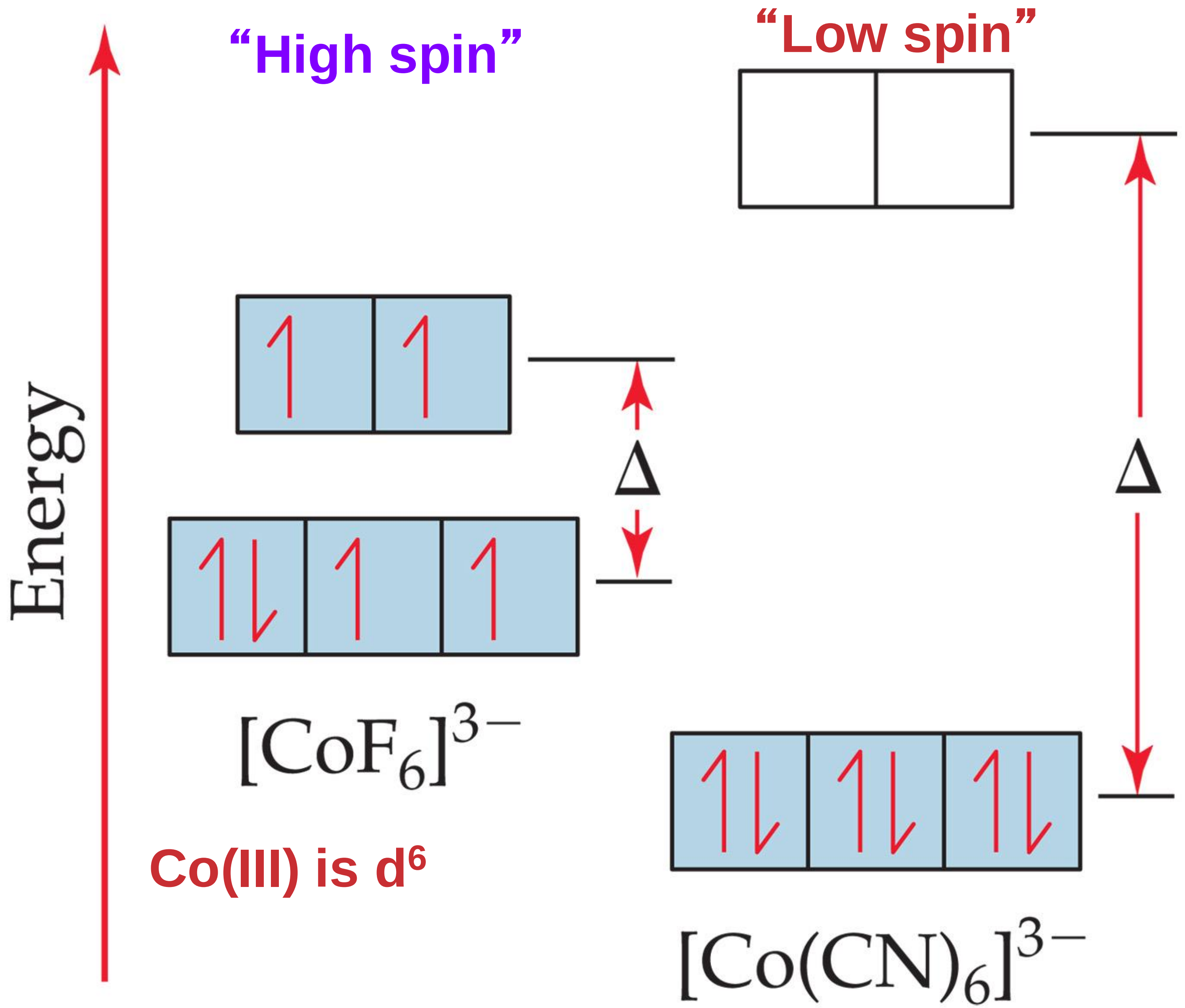
You do **NOT** have to memorize the spectrochemical series.

Electron configurations of some octahedral complexes



As Energy difference increases, electron configuration Changes.

Electrons will pair when d orbitals energy difference gets *larger.*

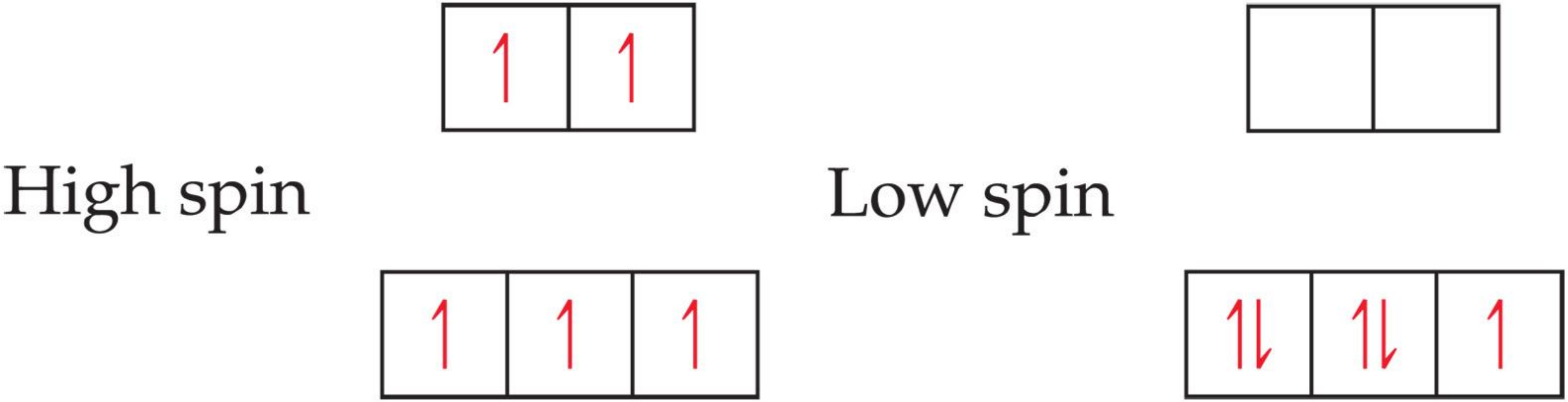


“High spin”

“Low spin”

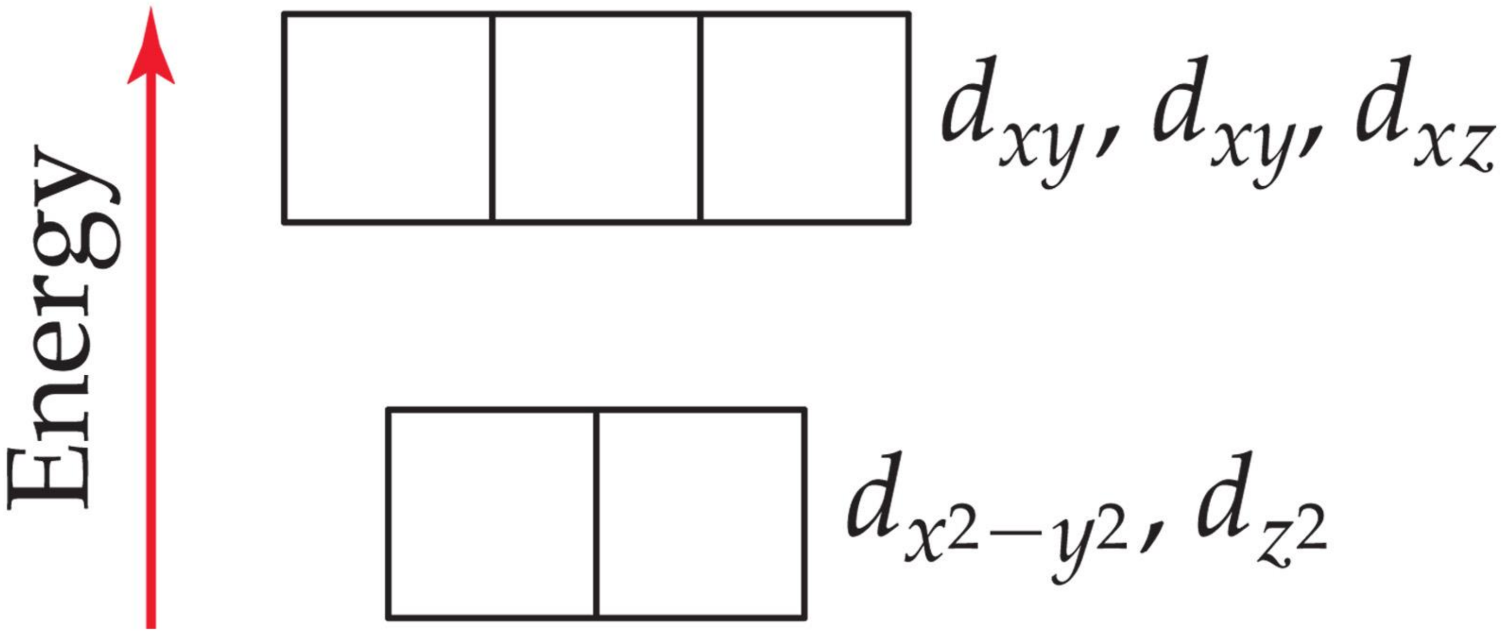
Co(III) is d^6

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



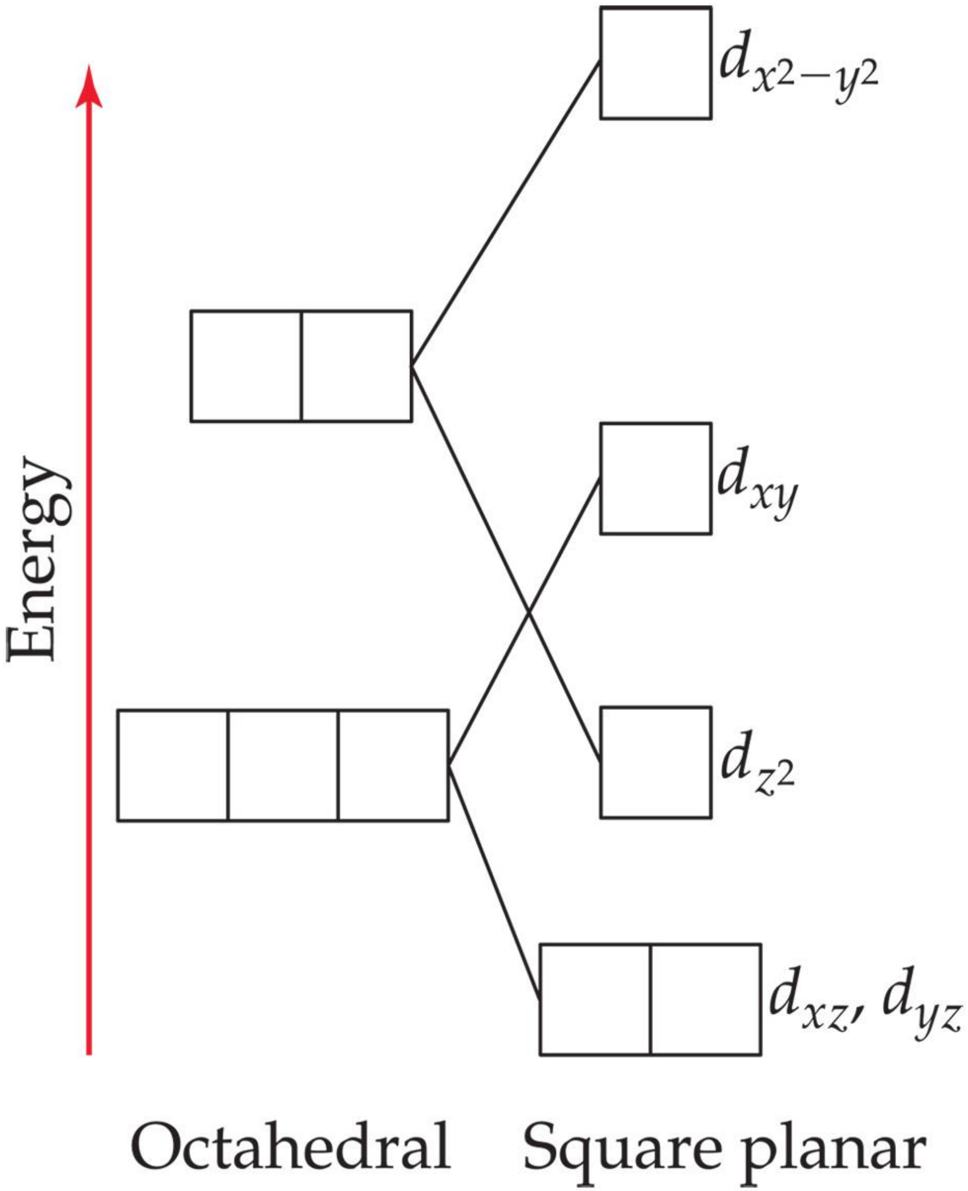
Tetrahedral Complexes

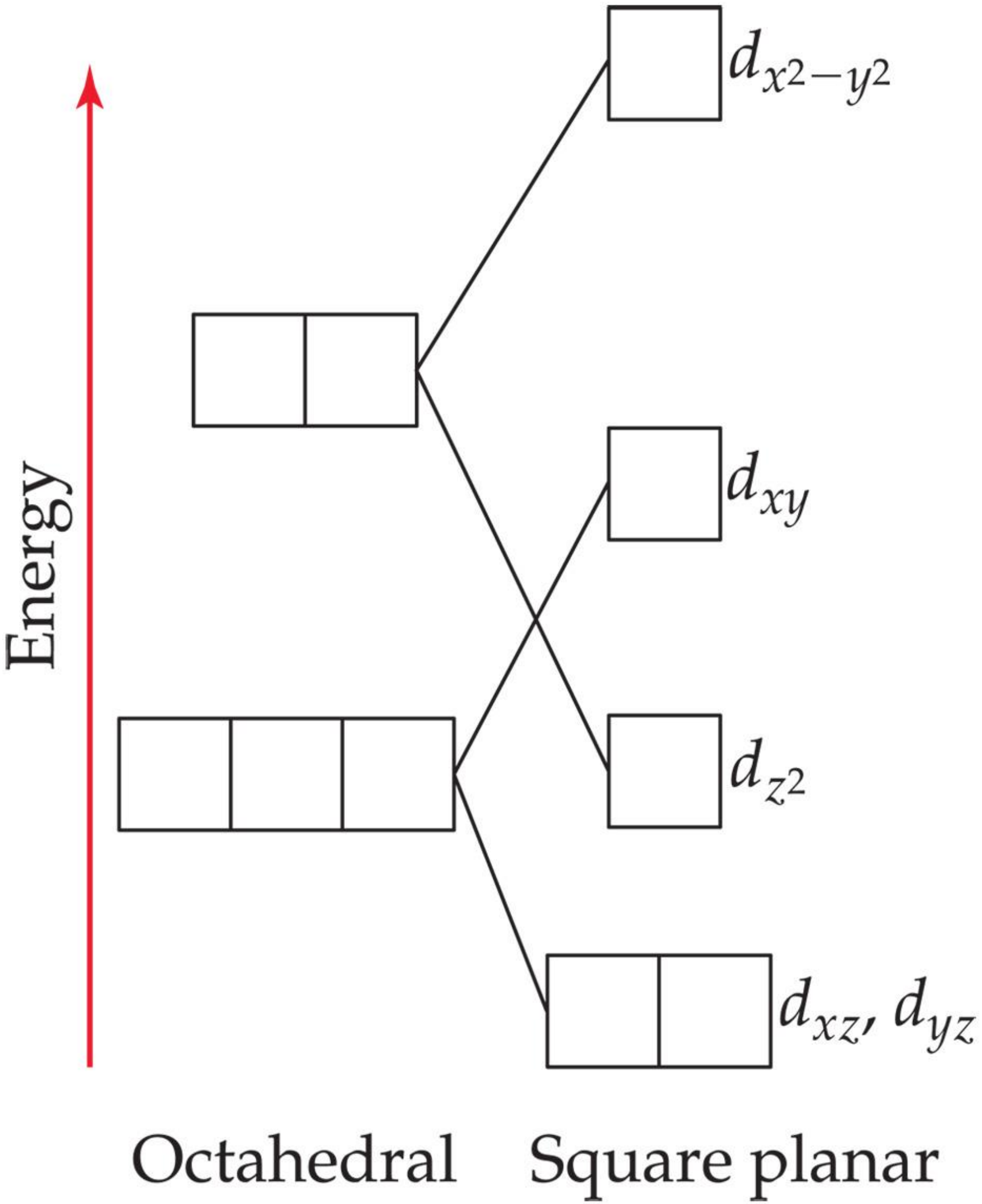
In tetrahedral complexes, orbitals are inverted.
Again because of orientation of orbitals and ligands.
Δ is always small, always high spin (less ligands)



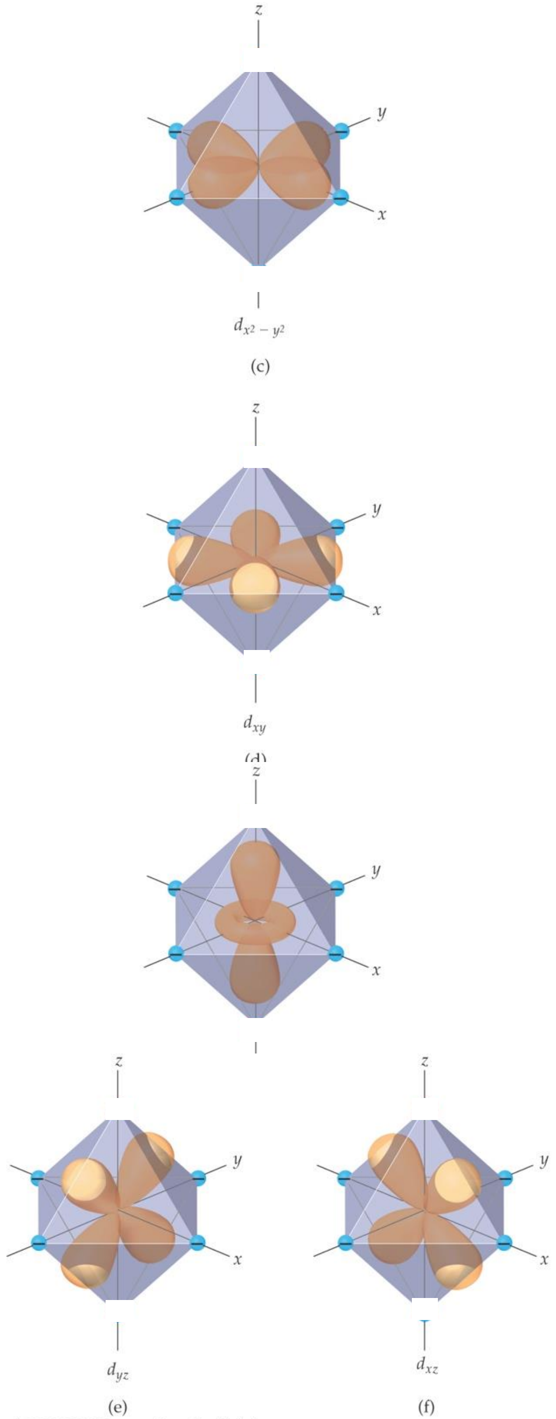
Copyright © 2006 Pearson Prentice Hall, Inc.

Square planar complexes are different still



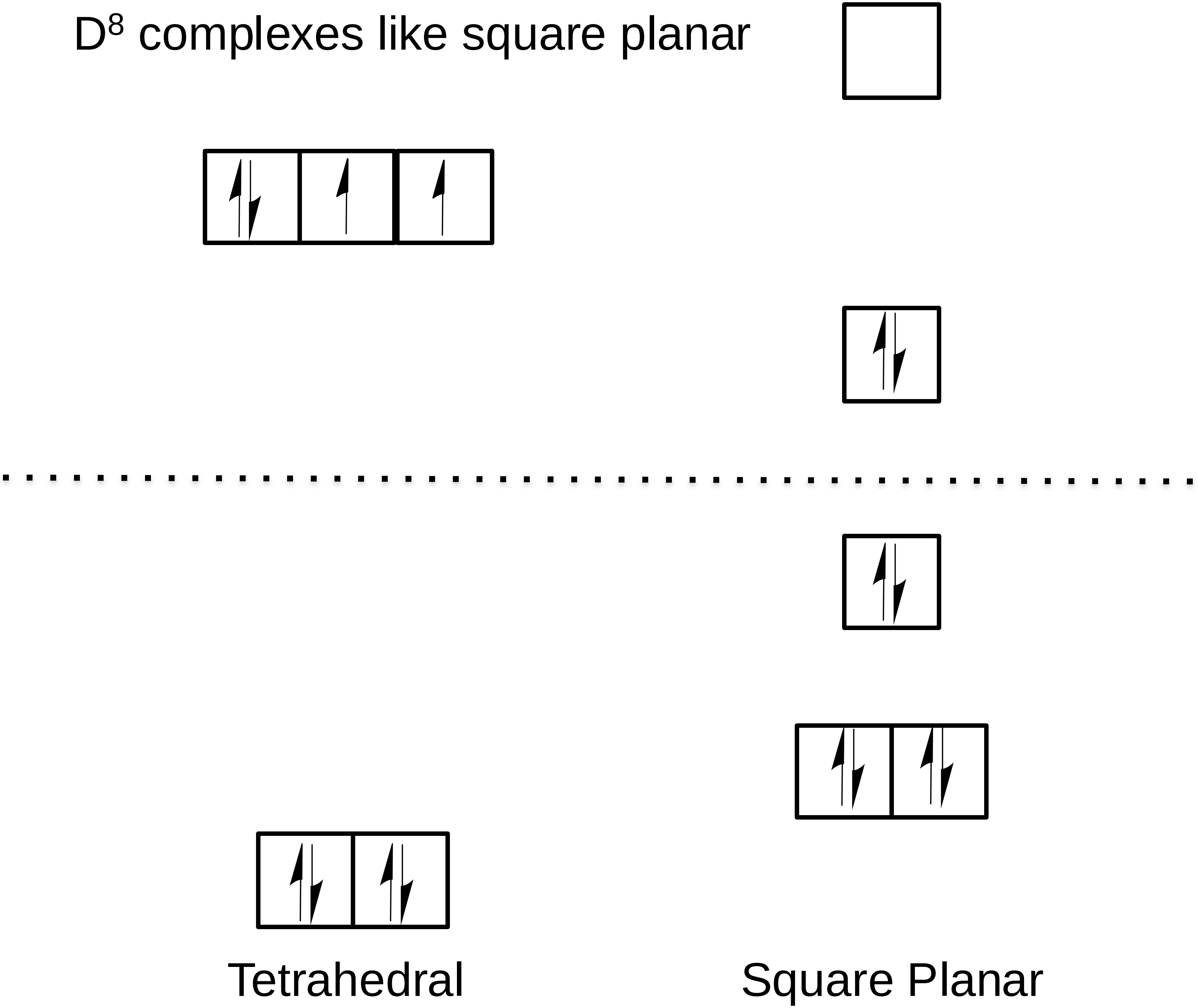


$d_{x^2-y^2}$
Energy
d_{xy}
d_{z^2}
d_{xz}, d_{yz}
Octahedral
Square planar



z
y
x
$d_{x^2-y^2}$
(c)
z
y
x
d_{xy}
(d)
z
y
x
z
y
x
d_{yz}
(e)
z
y
x
d_{xz}
(f)

D^8 complexes like square planar



Intense color can come from "**charge transfer**"
Ligand electrons jump to empty metal orbitals

$KMnO_4$

K_2CrO4

$KClO_4$

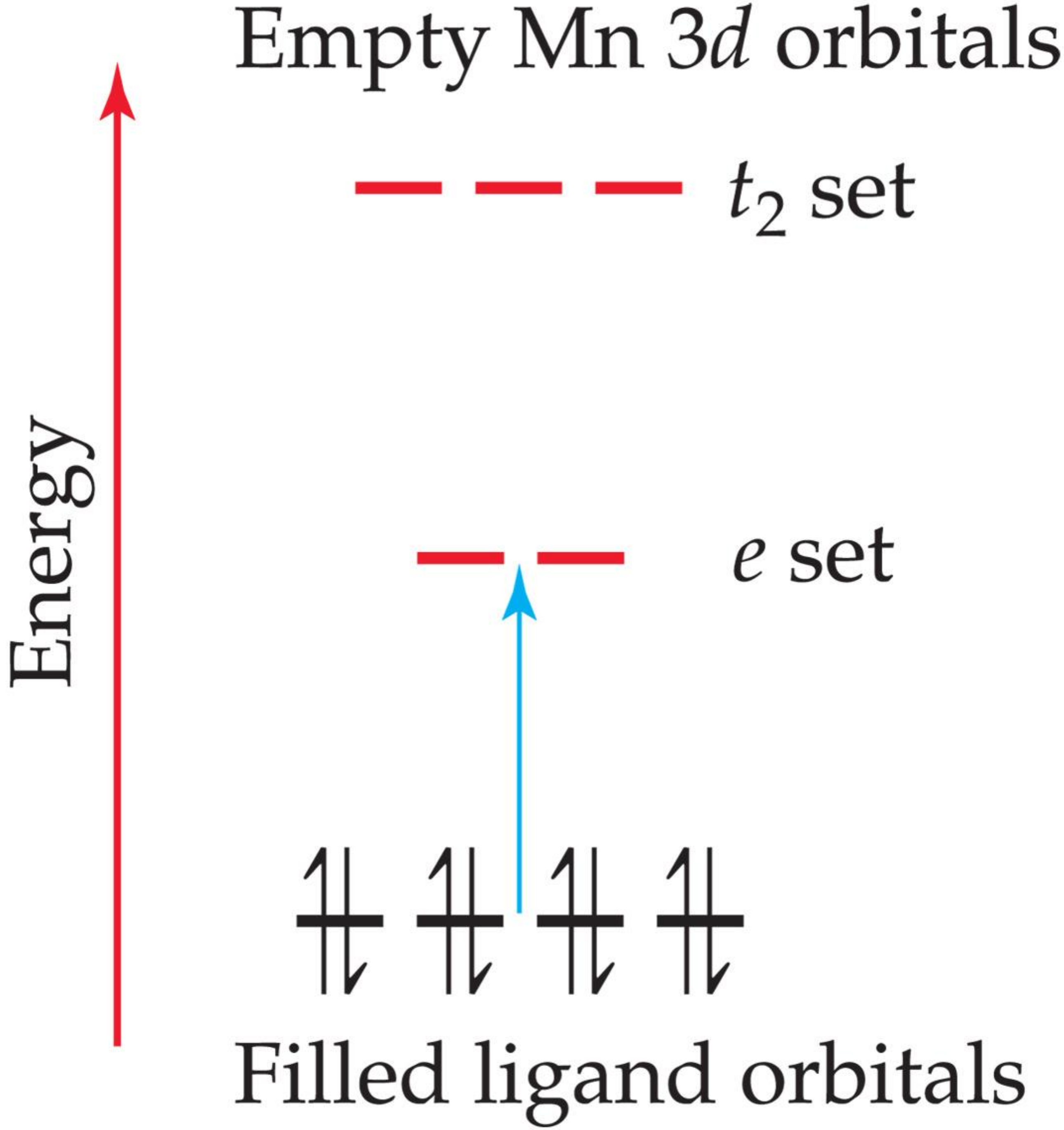
Mn^{+7}: $[Ar]4s^0 3d^0$

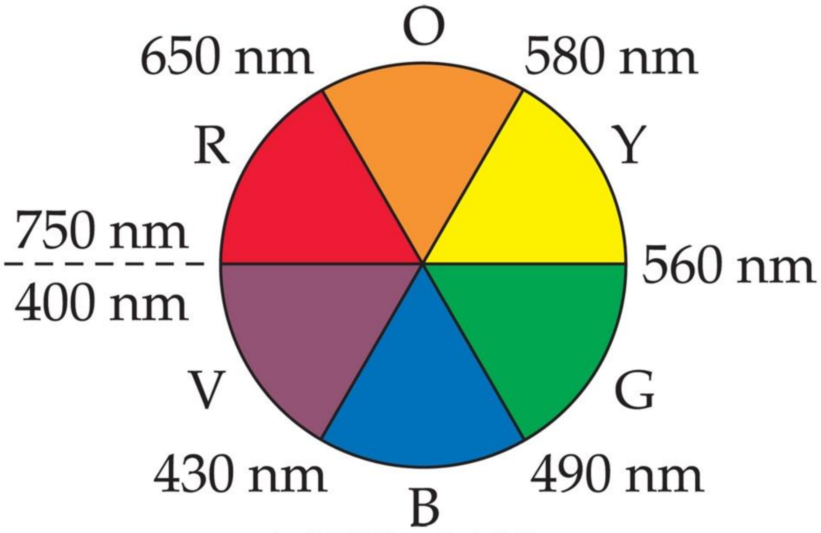
Cr^{+6}: $[Ar]4s^0 3d^0$

No d electrons.

Therefore MUST be charge transfer transition

No d orbitals in Cl, orbitals higher
In energy


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

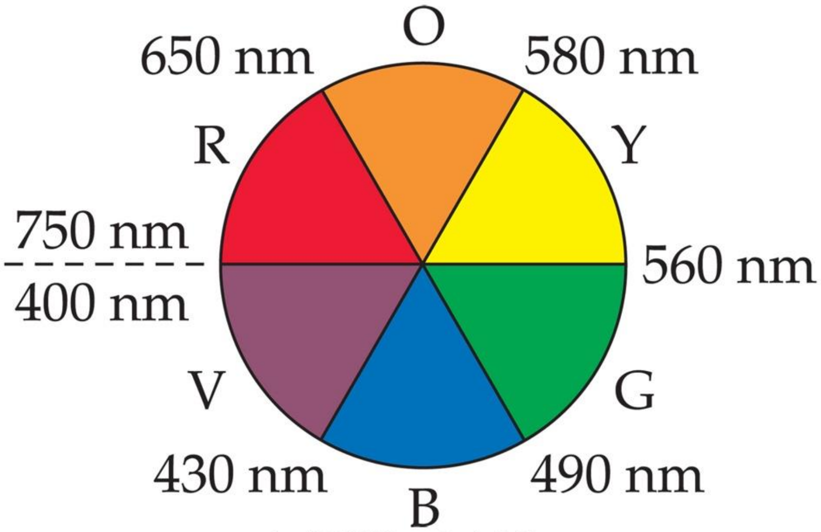


If a complex absorbs light at 610 nm, what color would you expect the complex to be?

A. Red
B. Orange
C. Yellow
D. Green
E. Blue

If a complex absorbs light at 610 nm, what color would you expect the complex to be?

BLUE



Are the following complexes diamagnetic or paramagnetic?

$[ZnCl_4]^{2-}$ (tetrahedral)

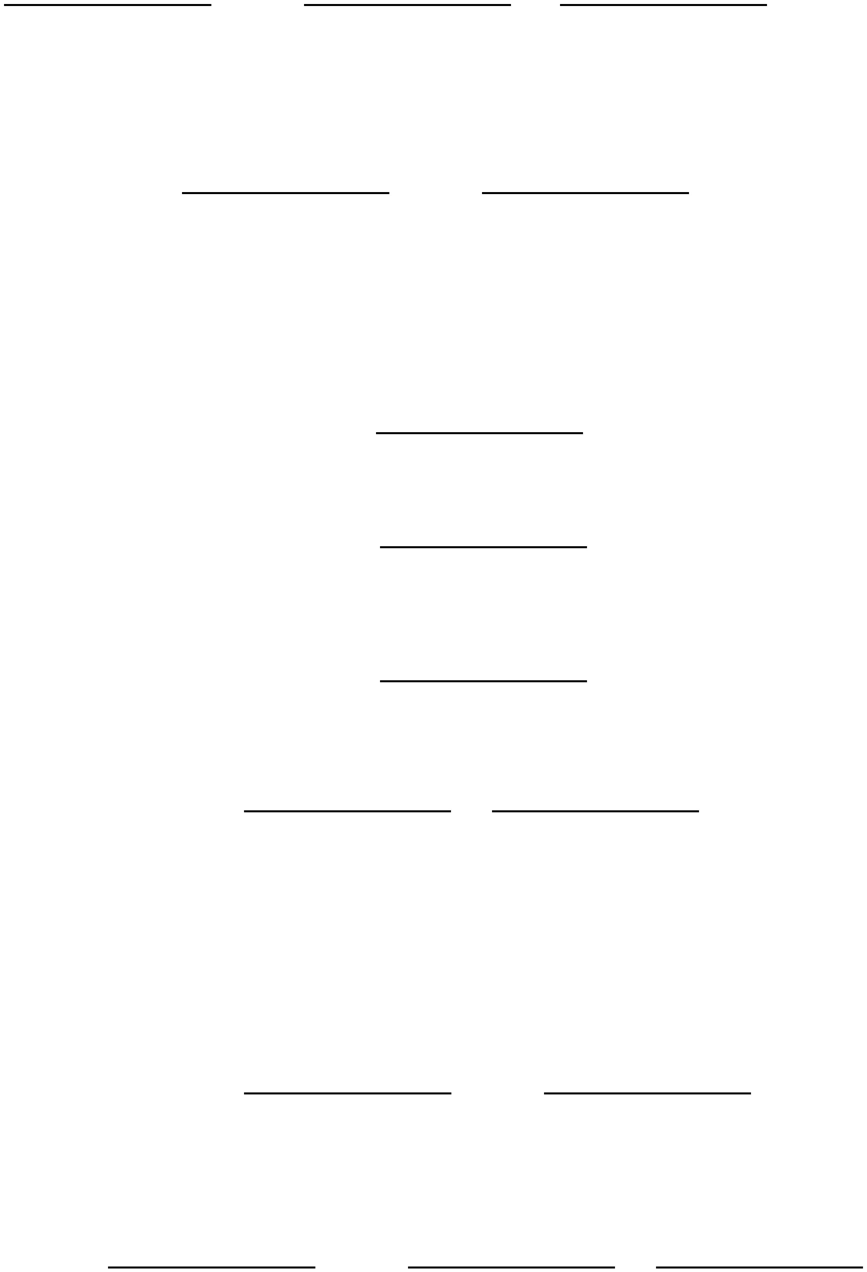
A. Paramagnetic
B. Diamagnetic

$[Pd(NH_3)_2Cl_2]$ (square planar)

A. Paramagnetic
B. Diamagnetic

$[V(H_2O)_6]Cl_3$

A. Paramagnetic
B. Diamagnetic

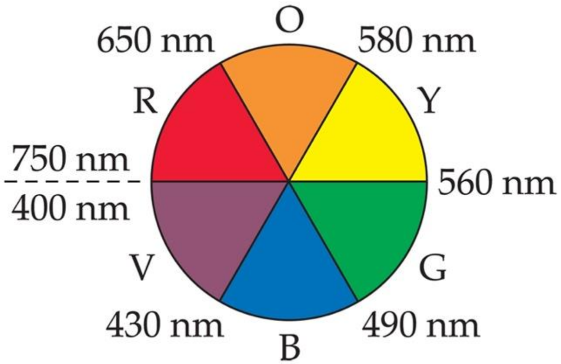


Are the following complexes diamagnetic or paramagnetic?

$[ZnCl_4]^{2-}$	Diamagnetic. (d^{10})
$[Pd(NH_3)_2Cl_2]$	Paramagnetic (d^8)
$[V(H_2O)_6]Cl_3$	Paramagnetic (d^3)

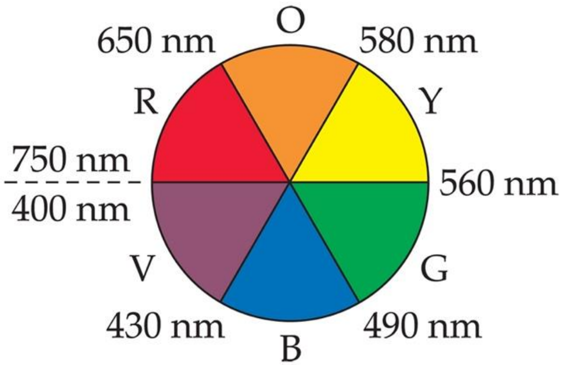
The color and absorption wavelength maximum is:

$Ni(H_2O)_6$	???	green
$Ni(NH_3)_6$	570	????
$Ni(en)_3$	???	red
$Ni(bipy)_3$	520	???



The color and absorption wavelength maximum is:

$Ni(H_2O)_6$	???	green
$Ni(NH_3)_6$	570	????
$Ni(en)_3$	???	red
$Ni(bipy)_3$	520	???



Copyright © 2006 Pearson Prentice Hall, Inc.

A. 410 nm
B. 460 nm
C. 520 nm
D. 570 nm
E. 610 nm

A. Red
B. Orange
C. Yellow
D. Green
E. Blue

If a complex absorbs light at 610 nm, what color would you expect the complex to be?

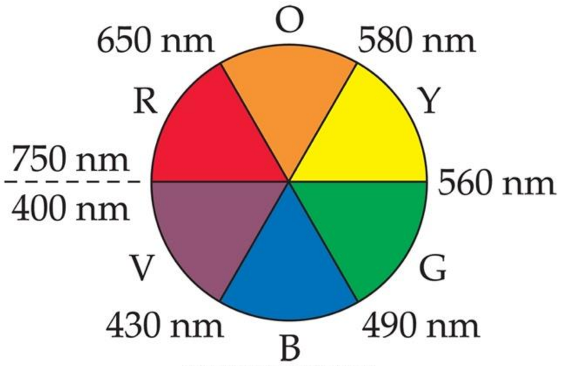
Are the following complexes diamagnetic or paramagnetic?

$[ZnCl_4]^{2-}$	Diamagnetic. (d^{10})
$[Pd(NH_3)_2Cl_2]$	Paramagnetic (d^8)
$[V(H_2O)_6]Cl_3$	Paramagnetic (d^3)

The color and absorption wavelength maximum is:

$Ni(H_2O)_6$	720	green
$Ni(NH_3)_6$	570	purple
$Ni(en)_3$	545	red
$Ni(bipy)_3$	520	Red

Where in the spectrochemical Series?



Copyright © 2006 Pearson Prentice Hall, Inc.

Exam 4 Topics

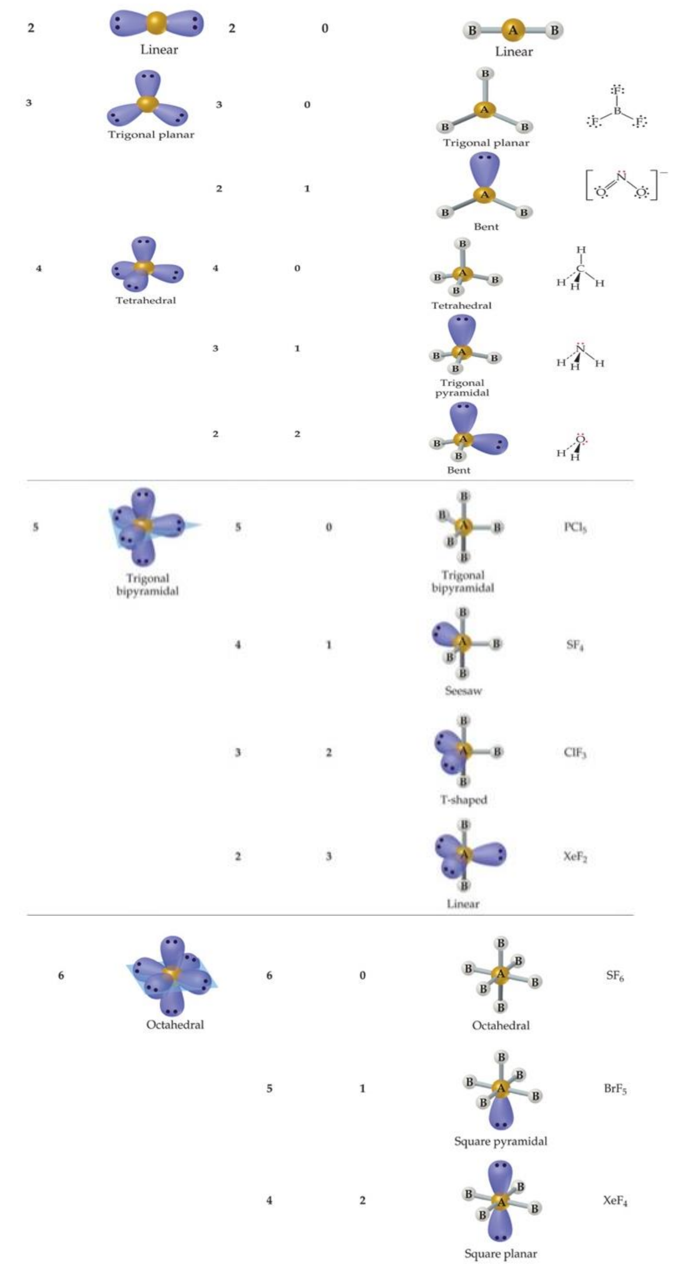
1. VSEPR
   1. What’s the geometery?
   2. What’s the shape?
   3. Is it polar?
2. Valence bond theory (hybridization)
3. Molecular orbital theory
4. Chapter 23, coordination chemistry

VSEPR:

First you have to make the Lewis structure
Count the number of things.
Match it to the geometry
Notice the lone pairs to get the shape.

Valence bond theory:

1. Hybridization
2. Double bonds due to overlap of atomic p orbitals (pi bonds)
3. Concept of delocalization what orbitals are overlaping in a delocalized system?



things	geometry			shape	
2	Linear	2	0	Linear	
3	Trigonal planar	3	0	Trigonal planar	
		2	1	Bent	
4	Tetrahedral	4	0	Tetrahedral	
		3	1	Trigonal pyramidal	
		2	2	Bent	
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2
6	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4

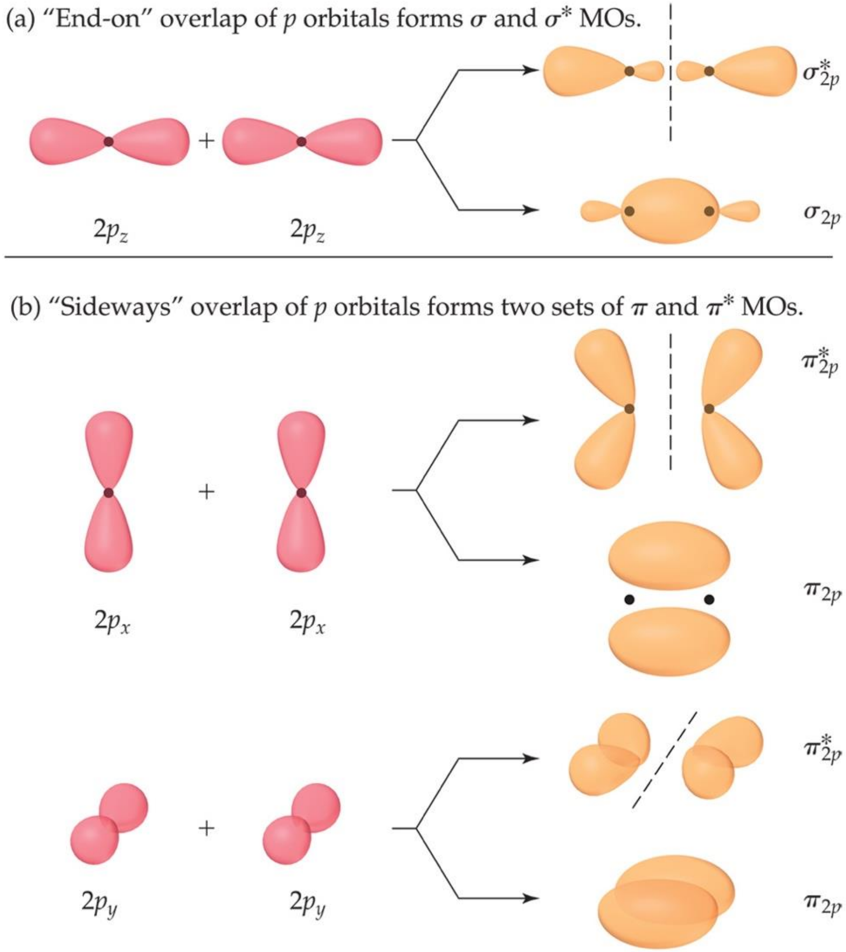
What is the shape of ClO_3^-

A. Trigonal planar
B. Tetrahedral
C. Trigonal pyramid
D. T-shaped
E. Seesaw

Exam 4,
Chapter 9,
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.

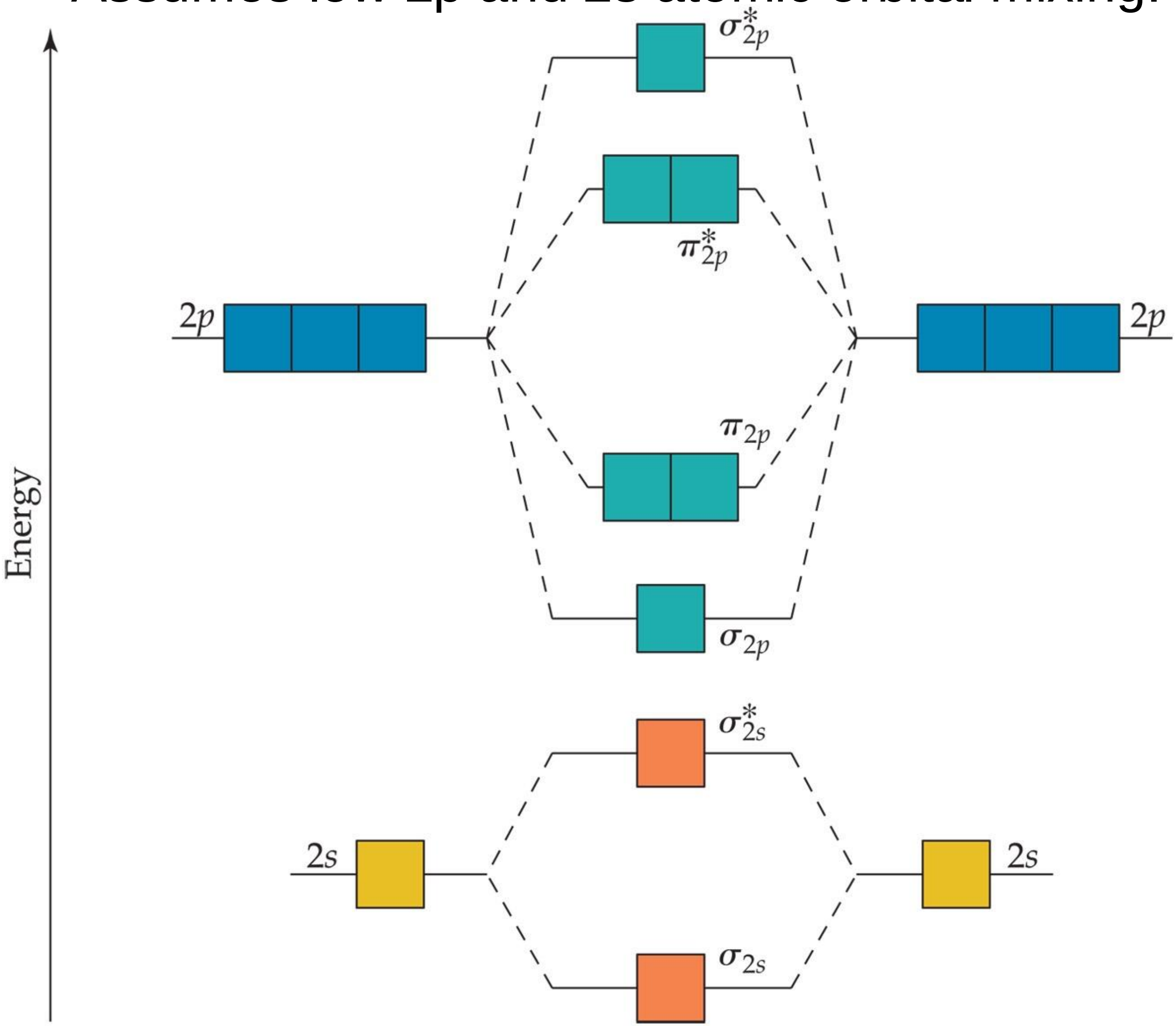
Difference between pi and sigma orbitals



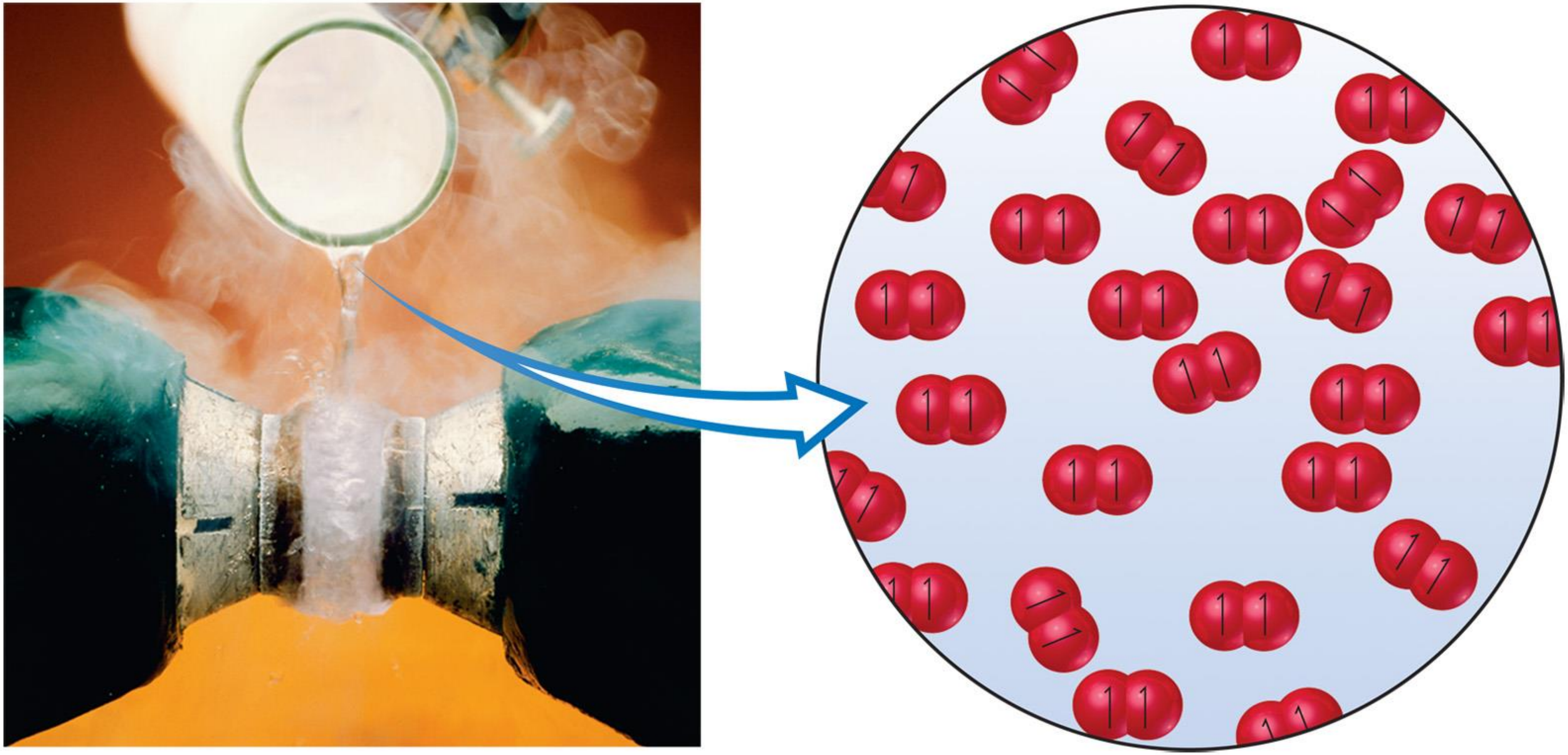
End on

Side to side.

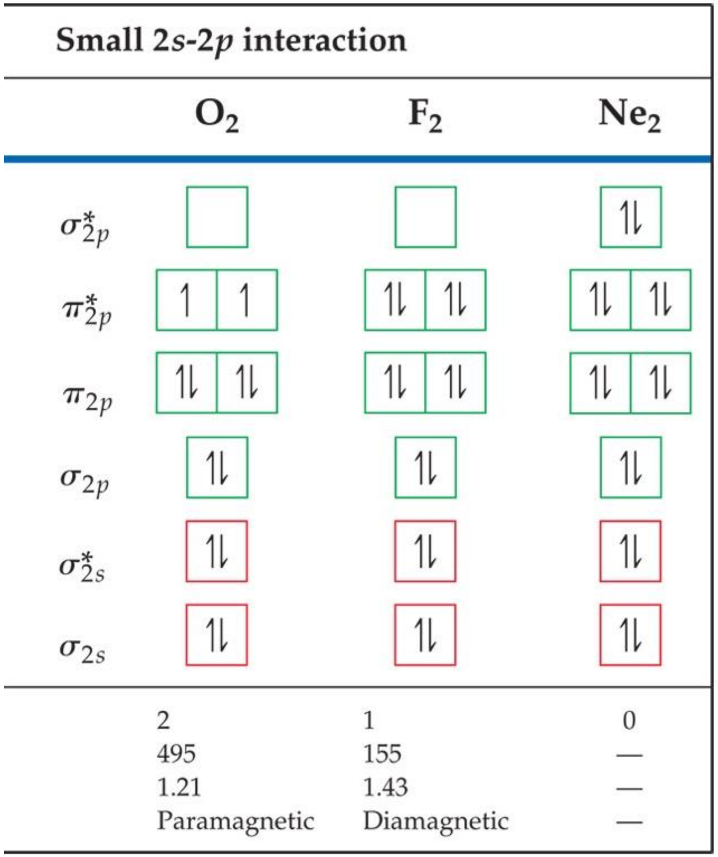
A typical MO diagram, like the one below. Assumes low 2p and 2s atomic orbital mixing.



Oxygen O_2 is Paramagnetic, why?

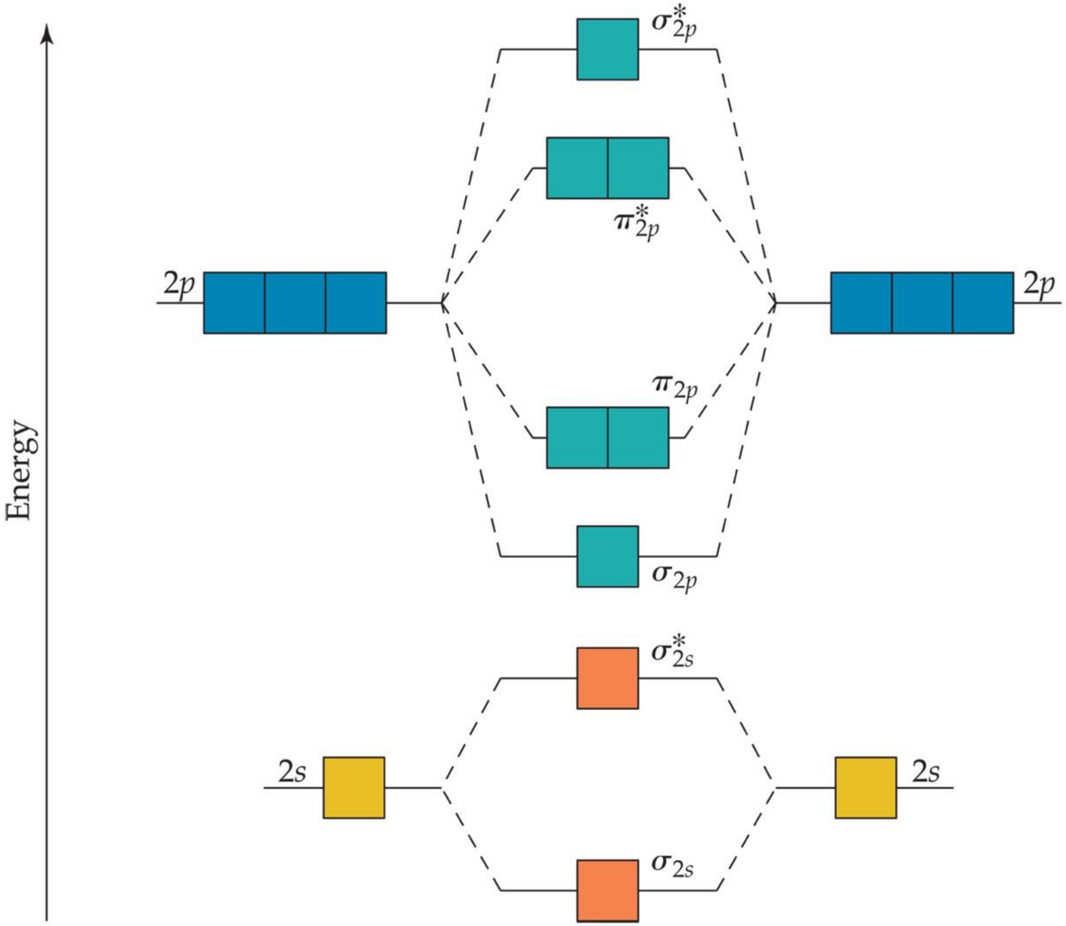


Show me why.



Small 2*s*-2*p* interaction

	O_2	**F_2**	**Ne_2**
σ^*_{2p}	☐	☐	↑↓
π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓
	2	1	0
	495	155	—
	1.21	1.43	—
	Paramagnetic	Diamagnetic	—



What is the bond order of BO^-

A. 1
B. 1.5
C. 12
D. 2.5
E. 3

Is BO^- paramagnetic?

A. Yes
B. No

Polydentate ligands

(what are they)?

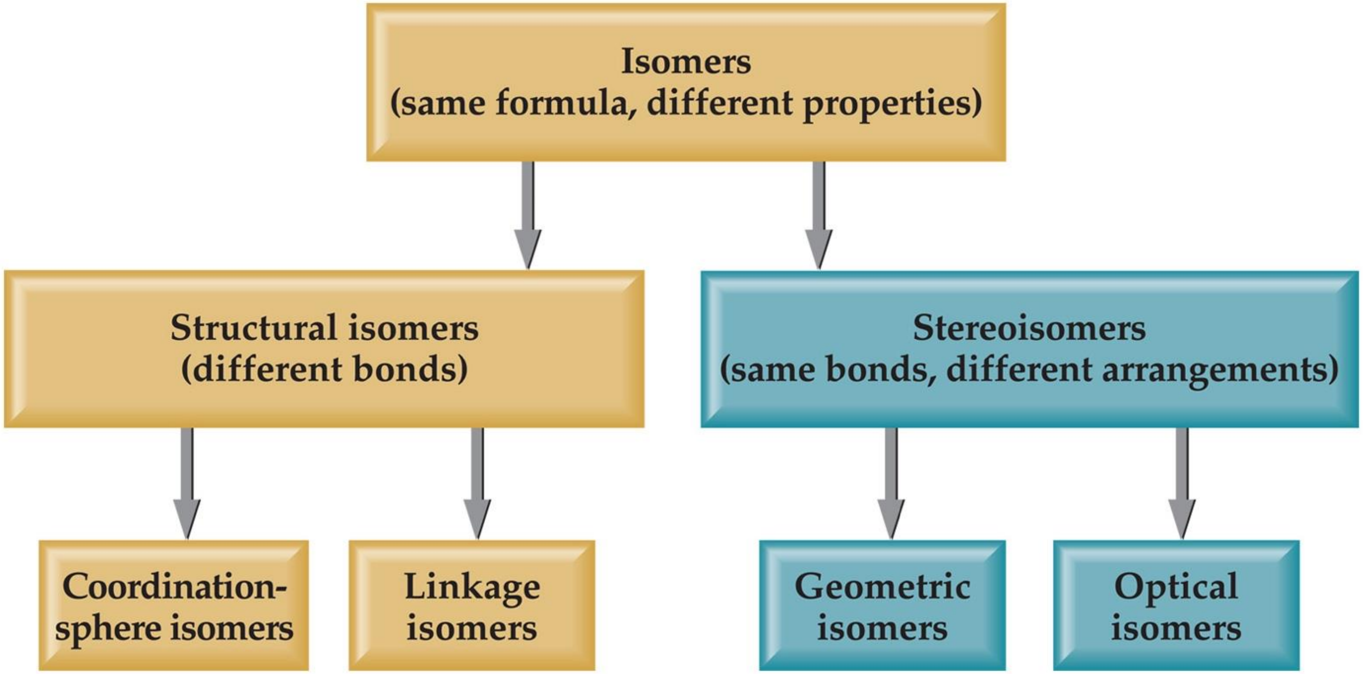
Only ethylene diamine will be used (en)

NH_2-CH_2-CH_2NH_2

Isomers.

structural isomers (formula same, bonds differ)

geometric isomers (formula AND bonds same, structure differs)



Isomers
(same formula, different properties)

Structural isomers
(different bonds)

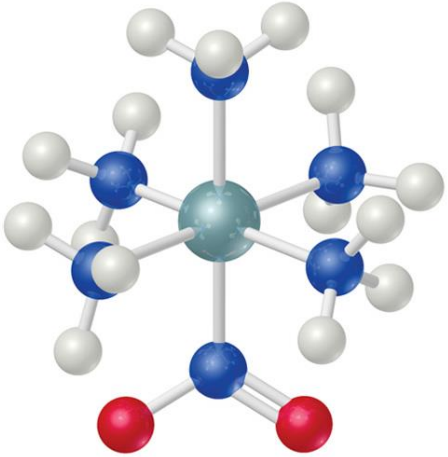
Stereoisomers
(same bonds, different arrangements)

Coordination-sphere isomers

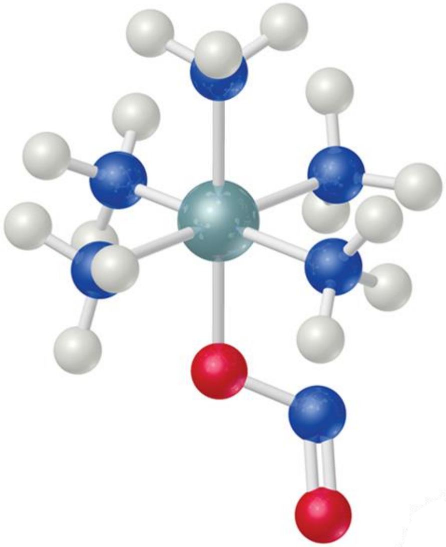
Linkage isomers

Geometric isomers

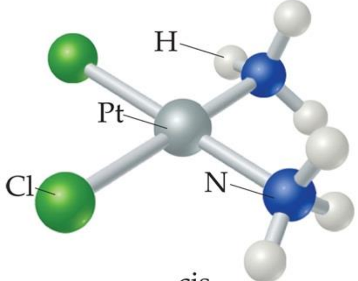
Optical isomers



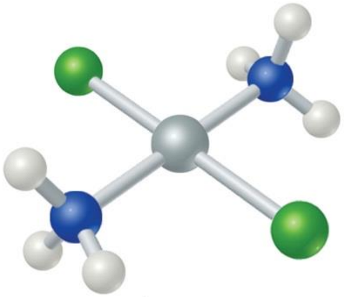
Nitro isomer



Nitrito isomer



cis



trans

Explaining the properties of metal complexes

Magnetism and color

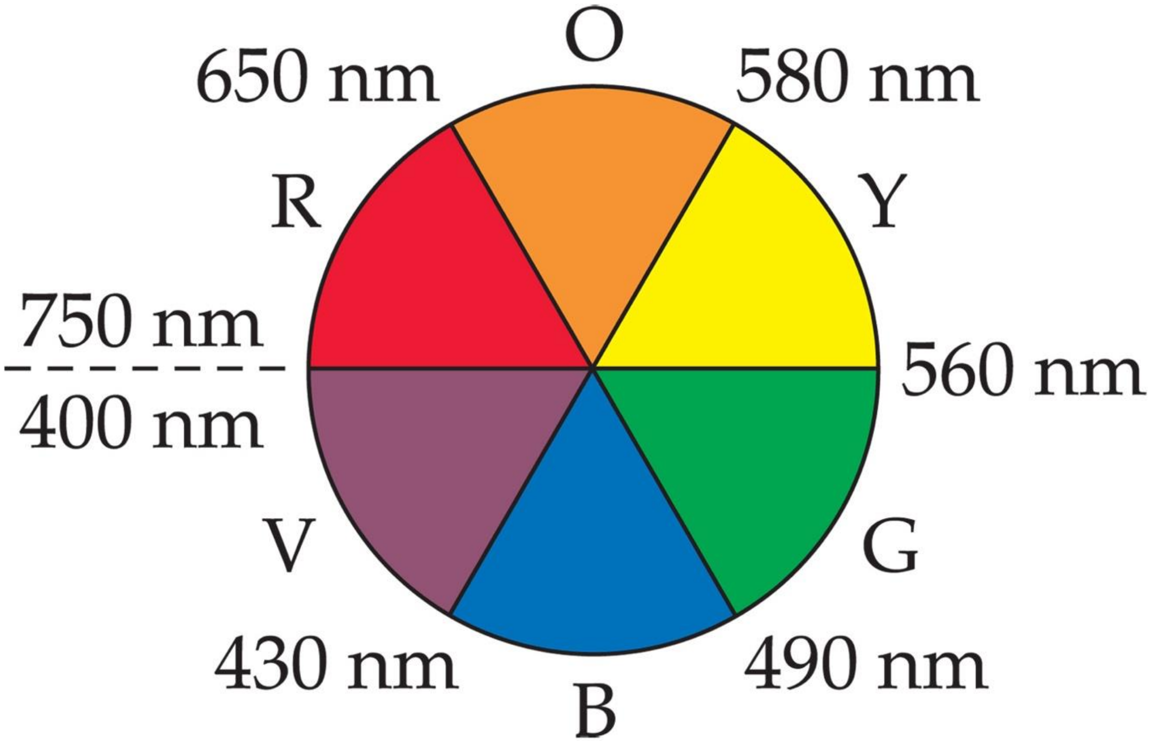
How does seeing color work?

Absorb **Orange**

See **Blue**

Absorb **Red**

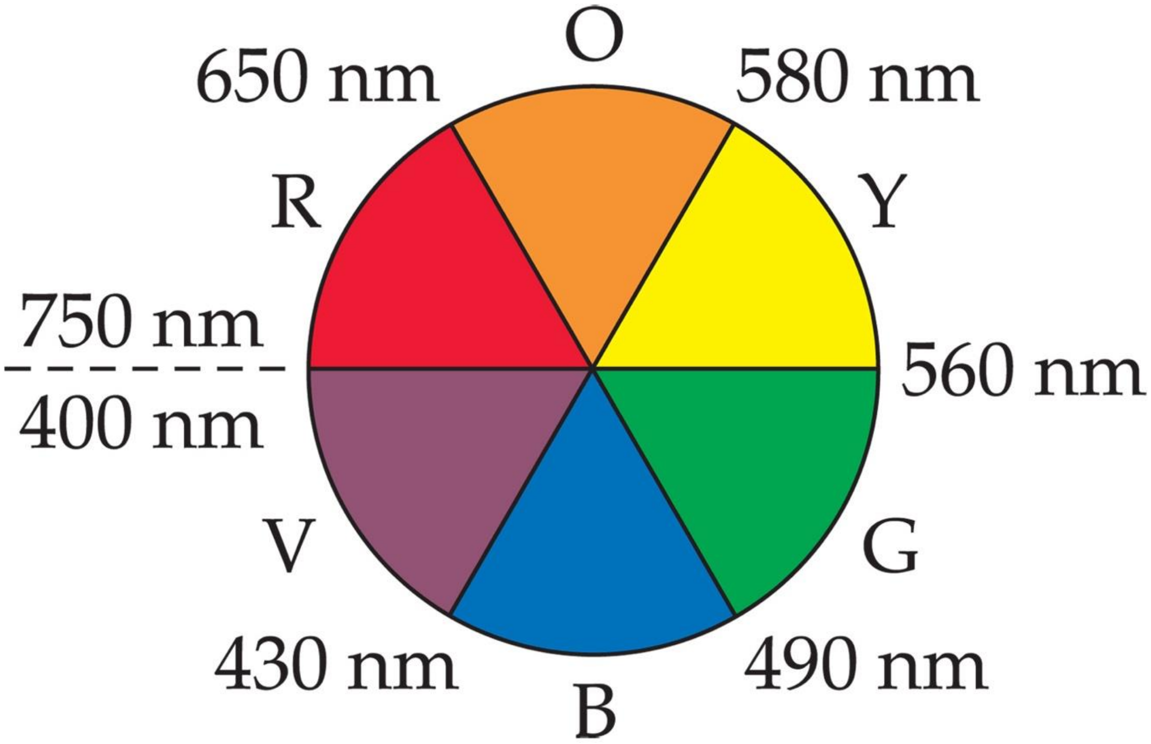
See **Green**



Explaining the properties of metal complexes

What color will a complex that absorbs 700 nm likely be?

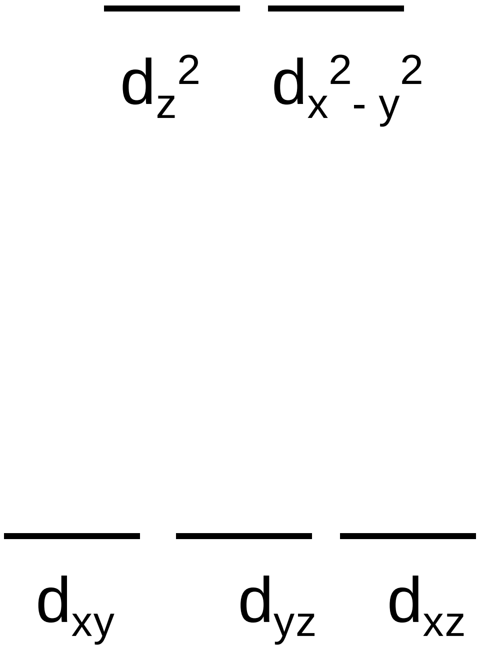
A. Red
B. Orange
C. Yellow
D. Green
E. Violet



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



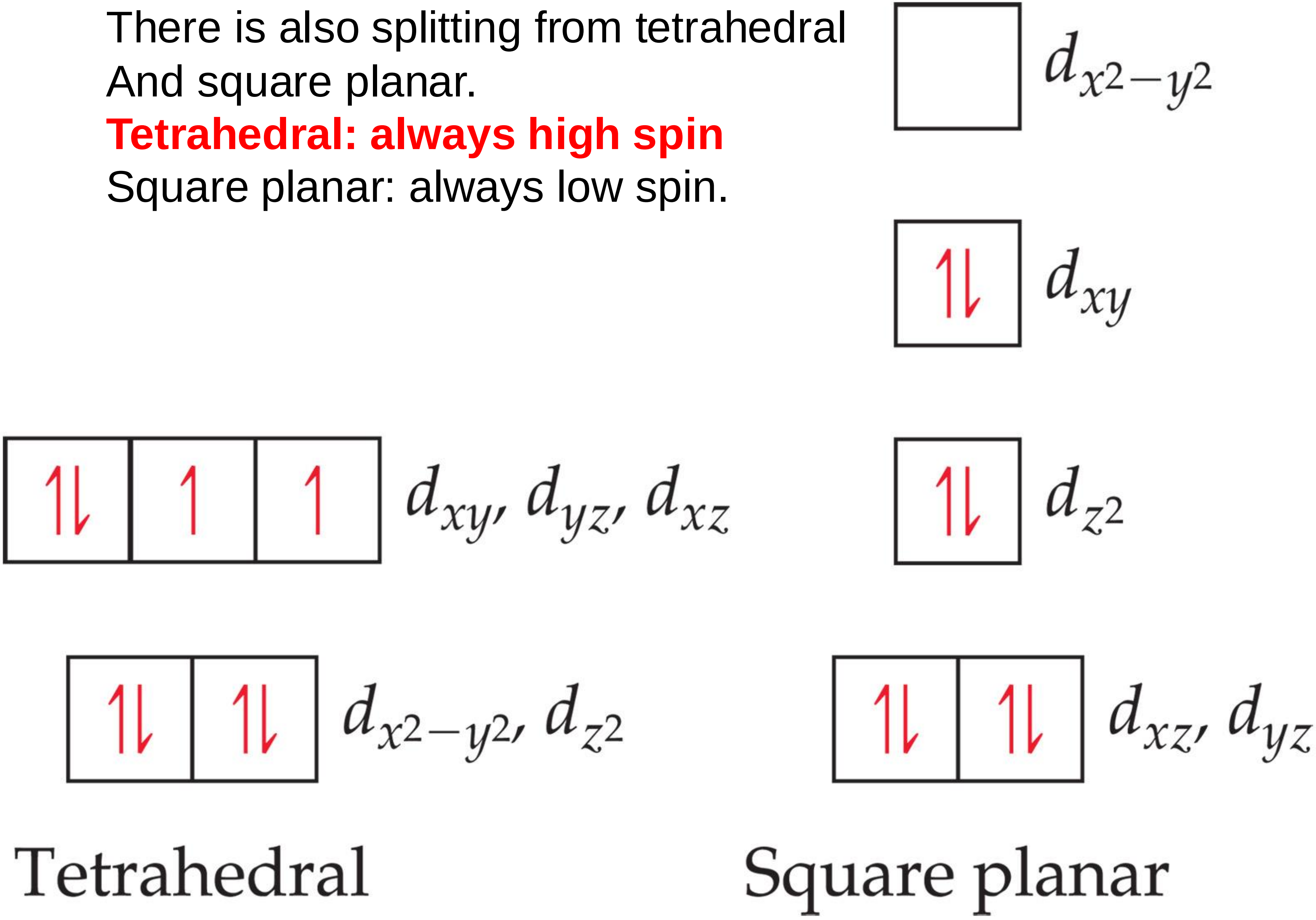
d_{z^2} $d_{x^2-y^2}$

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

There is also splitting from tetrahedral
And square planar.

Tetrahedral: always high spin

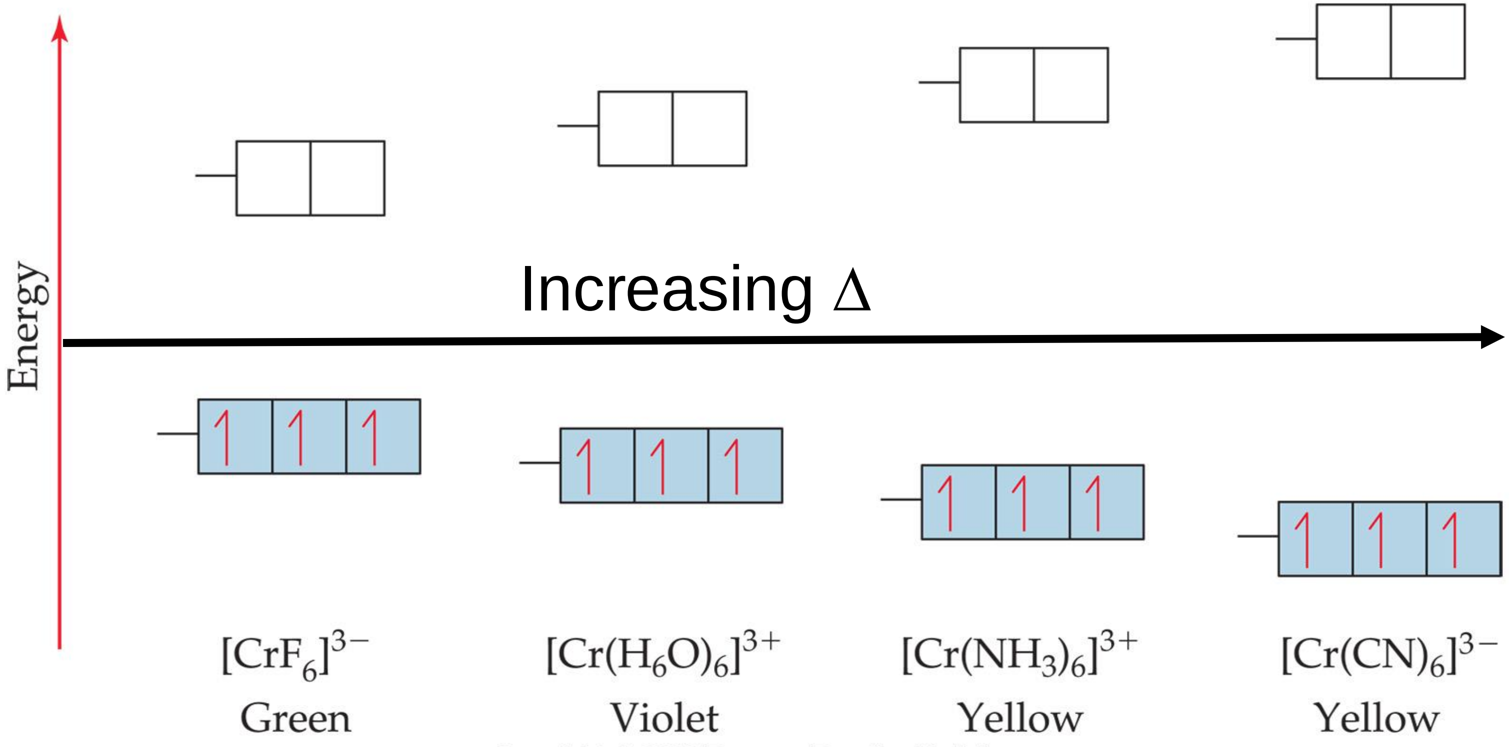
Square planar: always low spin.



Spectrochemical series (strength of ligand interaction)

Increasing Δ

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



Increasing Δ

$[CrF_6]^{3-}$ Green

$[Cr(H_2O)_6]^{3+}$ Violet

$[Cr(NH_3)_6]^{3+}$ Yellow

$[Cr(CN)_6]^{3-}$ Yellow

Know low spin versus high spin

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

$$\xrightarrow{\text{Increasing } \Delta}$$

Which of the following complexes is most likely to be high spin?

A. $[CoCl_6]^{3-}$

B. $[Co(H_2O)_4en]^{3+}$

C. $[Co(CN)_6]^{3-}$

The compound (written incorrectly) $CoCl_3 \cdot en_3$ would likely produce how many ions in solution?

A. 1

B. 2

C. 3

D. 4

E. 5

Exam 4 Chapter 23.

Concentrate on the homeworks and practice exam!

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

Exam breakdown:

VSEPR	IIII
Valence bond/hybridization:	IIIIII
Bond angles	IIII
Polarity	IIII
MO theory:	II
Color wheel, metal complex	III
Electron configuration of metal complexes:	IIIII
Oxidation state/coordination number:	III

Isomers:

Exam breakdown:

VSEPR	III
Valence bond/hybridization:	II
MO theory:	I
Color wheel, metal complex	III
Electron configuration of metal complexes:	IIII
Oxidation state/coordination number:	II
Charge transfer:	I
Isomers:	I
Organic	I

The FINAL

The best preparation:

1. **The four exams**.
    1. The plan is about 32-40 questions…
        1. 8-10 questions will be taken from each of the four previous exams.
2. It will start at **12:45 pm on Tuesday, December 12.**
3. It must end at 2:30 pm.
4. It will be in room **138** live, in person.

Topics:

Chapter 1.

Dimensional analysis (at least 1 problem)

significant figures

The FINAL

Chapter 2.

History of atomic structure

dalton

- cathode ray tubes
- **rutherford gold foil experiment**
- **Miliken's oil drop experiment**
- **atomic numbers, mass, isotopes**
- average at. weights
- **The periodic table**
    - **groups, periods, etc.**
- **molecular and empirical formulas**
- ions, ionic compounds
- naming inorganic compounds

The FINAL

Chapter 2.

naming binary molecular compounds

(nitrogen triodide)

atomic structure,

protons, neutrons, electrons

Chapter 3.

stoichiometry calculations

dealing with chemical reactions

limiting reagent

calculate empirical formula

Bring your calculator!!!!!!!

The FINAL

Chapter 4, aqueous reactions, solution stoichiometry

- strong and weak electrolytes
- the strong acids and the strong bases
- **Know your anions and cations.**
- precipitation reactions
- acid/base reactions
- **Redox, oxidation numbers, redox reactions**.
- **the activity series**
- solution stoichiometry
- titrations

The FINAL

Chapter 5, thermochemistry

- Kinetic and potential energy
- what is work versus heat?
- ΔH and ΔE
- what is a state function?
- pV work
- **calorimetry**
- Hess' s law, **enthalpies of formation**

The FINAL

Chapter 6, electronic structure of atoms

- wave and particle nature of light
- black body radiation, quantization of energy
- photons
- The photoelectric effect
- Line spectra & the bohr model
- Quantum mechanics
    - **atomic numbers**
    - **atomic orbitals**
    - electron spin
    - **electron configuration**
    - The periodic table explained

The FINAL

Chapter 7, Periodic properties of the elements

effective nuclear charge
sizes of atoms
sizes of ions
ionization energies
electron affinities

group trends for:
alkali metals
alkaline earth metals
oxygen group, halogens, noble gases

The FINAL

Chapter 8, chemical bonding

- ionic bonding
- metal bonding
- covalent bonding
- bond polarity
- **electronegativity**
- **Lewis structures**
- **multiple bonds**
- **resonance structures**
- **octet rule and exceptions**
- bond enthalpy and bond length

The FINAL

Chapter 9, **VSEPR,**
valence bond and
molecular orbital theory
self explanatory.

Chapter 23. Coordination Chemistry

tell me oxidation state of metal
Tell me coordination number
Be able to recognize complexes by name
be able to name them.
Crystal Field Theory.

The exam, the lowdown:

- questions from the previous 4 exams.
  - Exam 1:
  - Exam 2:
  - Exam 3:
  - Exam 4:

Valence Bond theory

- Example

- $Ni(NH_3)_6^{2+}$
- Ni^{2+} electron configuration (8 valence electrons):
- $4s^2 3d^8$ ----→ $4s^0 3d^8$
- Need six orbitals for six ligands but:
  - *All five 3d orbitals contain electrons*, can't use em.
  - 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.
  - ***The electrons of the metal stay in the atomic orbitals they were in before bonding, always.***