Coordination Compounds

Compounds containing Transition Metals

Coordination Compounds

Transition Metals

Sc → Cu 1st row
Y → Ag 2nd row
La → Au 3rd row

Properties of metals

Not as reactive as group 1 or 2
1s or 2s valence electrons
Highly colored compounds
High mp, bp, density
Hard, strong, conductors
Form complex ions
Many oxidation states
Catalytic activity

Trends

Down group:

- Same outer electron configuration
- Decrease in reactivity

Across period

- Increase in atomic no.
- Increase in atomic mass
- Increase in nuclear charge, I.E.
- Slight decrease in radii

Reaction with acid

Many react: Fe, Ni, Co → hydrogen

Some inert: Cr, Au, Pt

Electron configuration

$_{20}Ca: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

$= [Ar]4s^2 = 4s^2$

$_{21}Sc \rightarrow {}_{29}Cu$ e^- added to 3d subshell

$_{21}Sc: 4s^2\ 3d^1$ $_{22}Ti: 4s^2\ 3d^2$

Exception: $_{24}Cr: 4s^1\ 3d^5$

Ions

When metals lose elections to form (+) ions, electrons come from 4s before 3d

Co: $4s^2\ 3d^7$ → Co^{3+}: $3d^6$

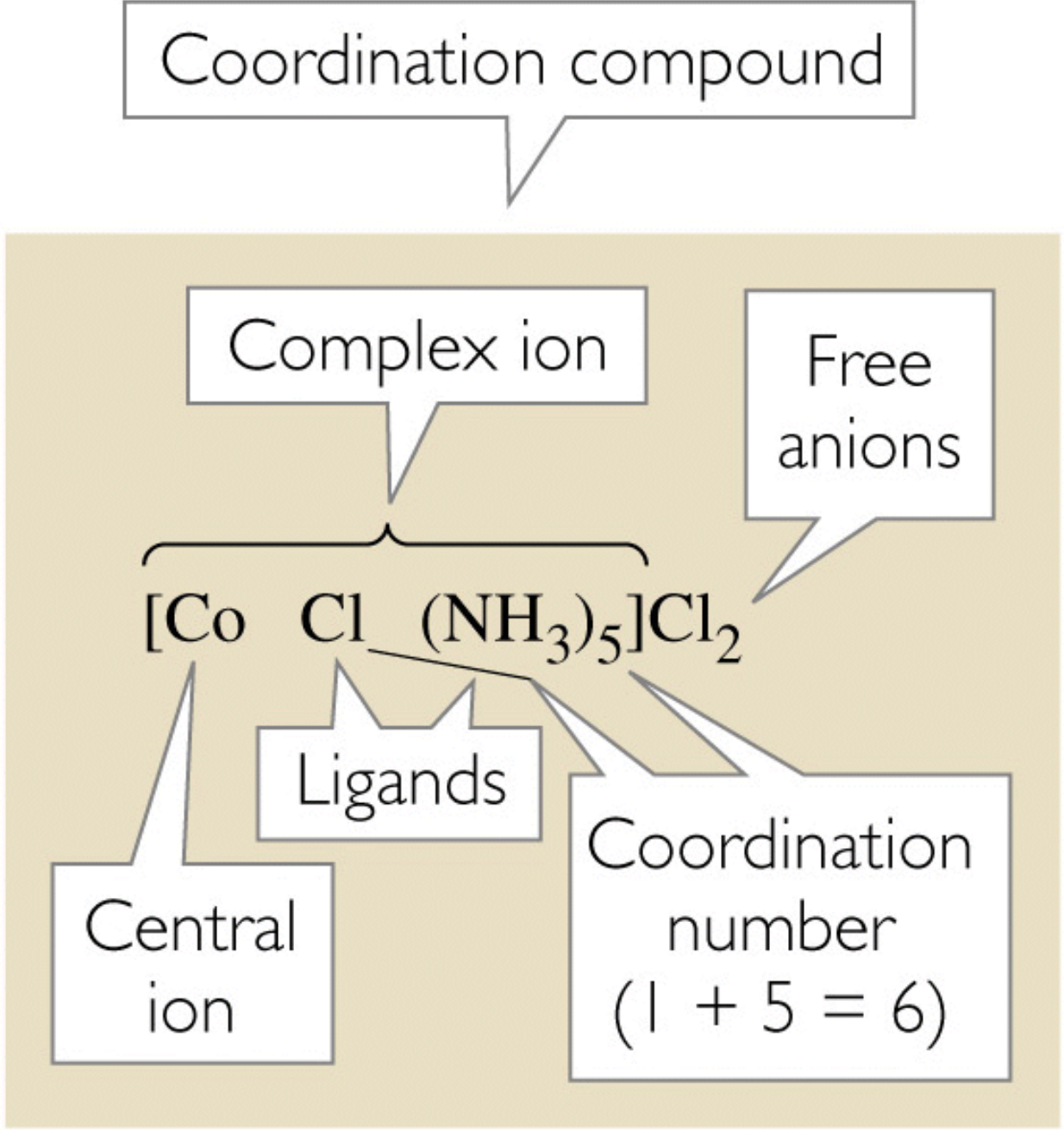
Oxidation states

Variable in compounds

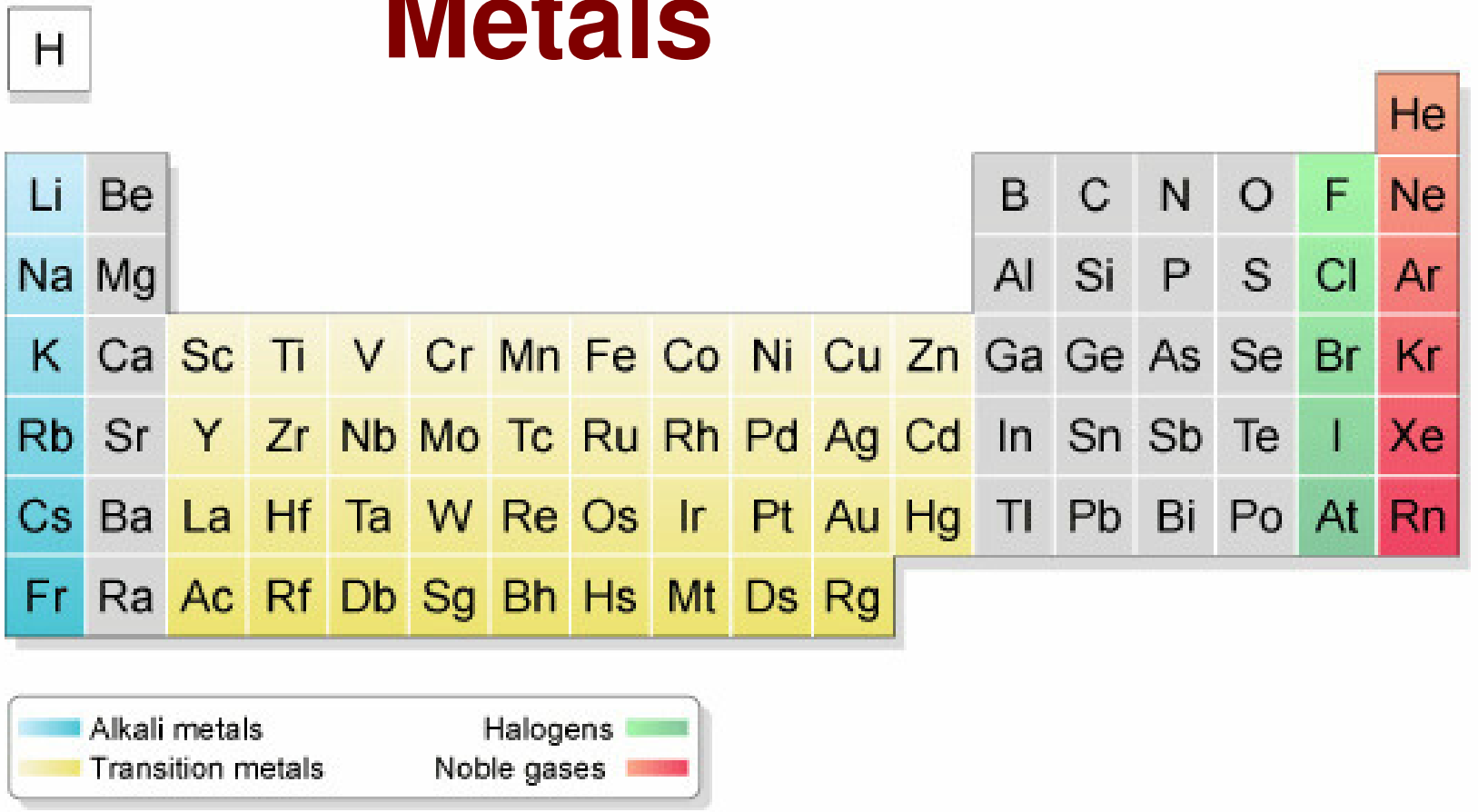
Mostly +2 or +3

Reaches max at center of series

High: VF_5 Mn_2O_7 CrO_3


Coordination compound
Complex ion
Free anions
[Co Cl (NH3)5]Cl2
Ligands
Central ion
Coordination number (1 + 5 = 6)

Transition Metals



Naming Compounds

Compounds may be:

Cation	Neutral	Anion
$[Co(NH_3)_4Cl_2]Br$	$[Ni(CO)_4]$	$K_3[Fe(CN)_6]$

Learn steps for naming

Naming Compounds

1. Name cation, then anion (unless neutral)
2. Name ligands first (alphabetical)

   name metal

   give metal oxidation state

Naming Compounds

Ligand Names: (table 20.3)

Br^-	bromo
CN^-	cyano
H_2O	aquo
NH_3	ammine
CO	carbonyl
$C_2O_4^{2-}$	oxalato

Naming Compounds

Indicate number of ligands by prefix:

di tri tetra penta hexa

prefix not included in alphabetical order

If ligand name has prefix use:
bis tris tetrakis
bis(ethylenediamine)

Naming Compounds

3. Metal oxidation state: iron(III)
4. Anionic complex: table 20.4
   add -ate ending to metal

cobaltate	ferrate
chromate	cuprate
titanate	aurate

5. Neutral complex: one word

Naming Compounds

$[Ag(NH_3)_2]Cl$

$[Ag(NH_3)_2]^+ Cl^-$

$[Ag^+(NH_3)^0{}_2]^+ Cl^-$

diamminesilver(I) chloride

Naming Compounds

$K_4[Fe(CN)_6]$

$K_4^{4+}[Fe(CN)_6]^{4-}$

$K_4^{4+}[Fe^{2+}(CN)^{6-}_6]^{4-}$

potassium hexacyanoferrate(II)

Naming Compounds

$[Co(NH_3)_4(H_2O)Cl]Cl_2$

$[Co(NH_3)_4(H_2O)Cl]^{2+}\ Cl_2^{2-}$

$[Co^{3+}(NH_3)^{0}{}_4(H_2O)^{0}\ Cl^{-}]^{2+}\ Cl_2^{2-}$

[cobalt(III) tetraammine aquo chloro] chloride

t aquochlorocobalt(III) chloride

Naming Compounds

$[Co(NH_3)_3Cl_3]$

triamminetrichlorocobalt(III)

Writing Formulas

diamminedibromoplatinum(IV) chloride

$$[Pt^{4+}(NH_3)_2Br_2]^{2+}\ Cl^-_2$$

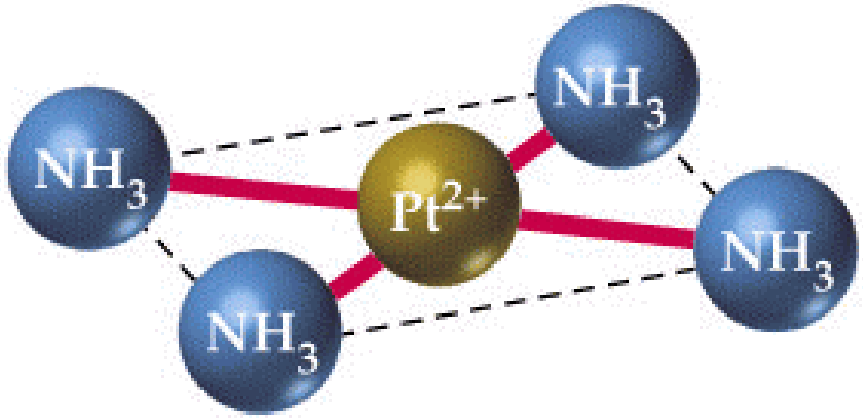
Writing Formulas

potassium hexacyanoaurate(III)

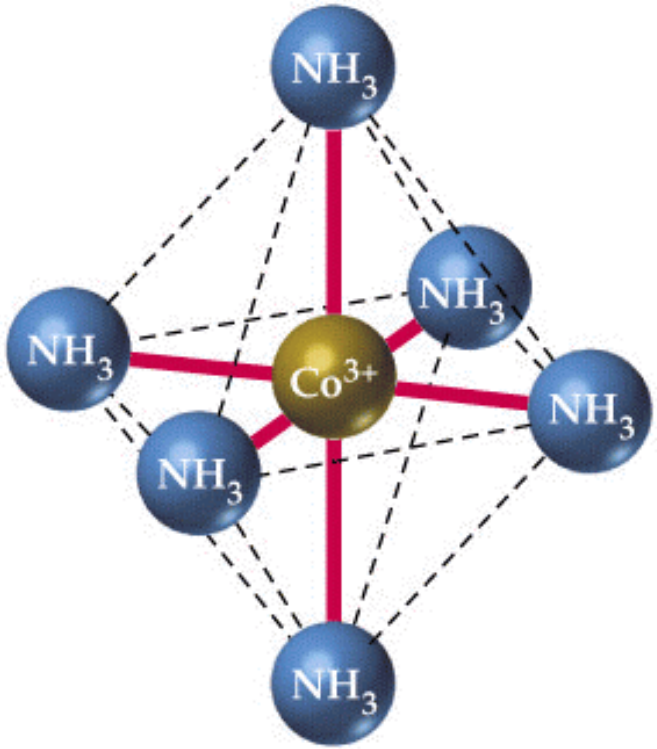
$K_3^+ [Au^{3+}(CN)_6]^{3-}$

$K_3[Au(CN)_6]$

Isomers

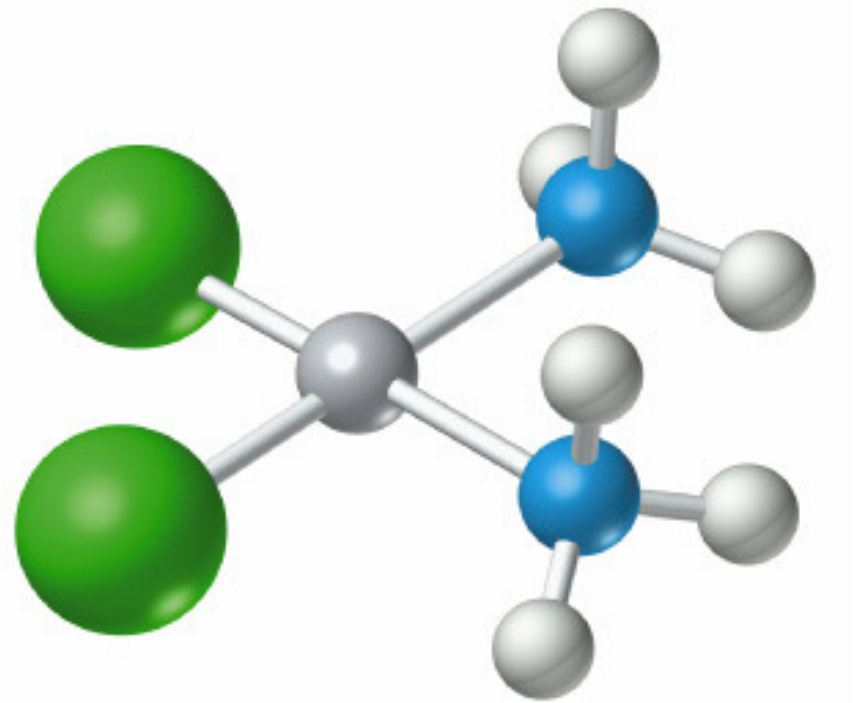


Square planar

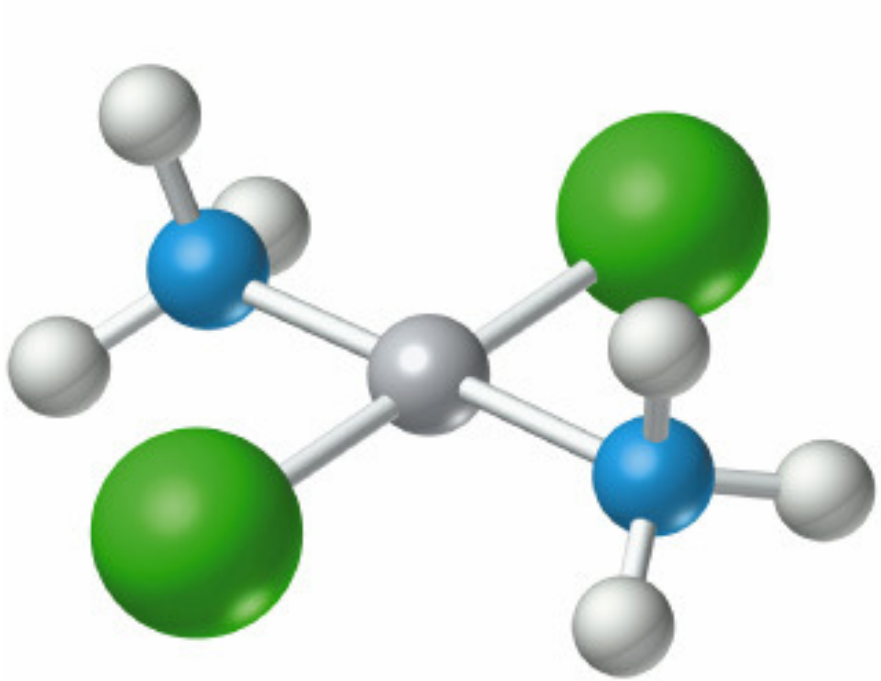


Octahedral

Isomers

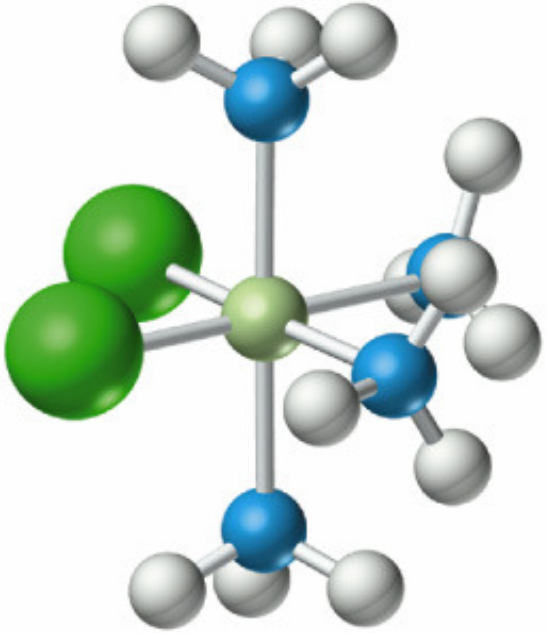


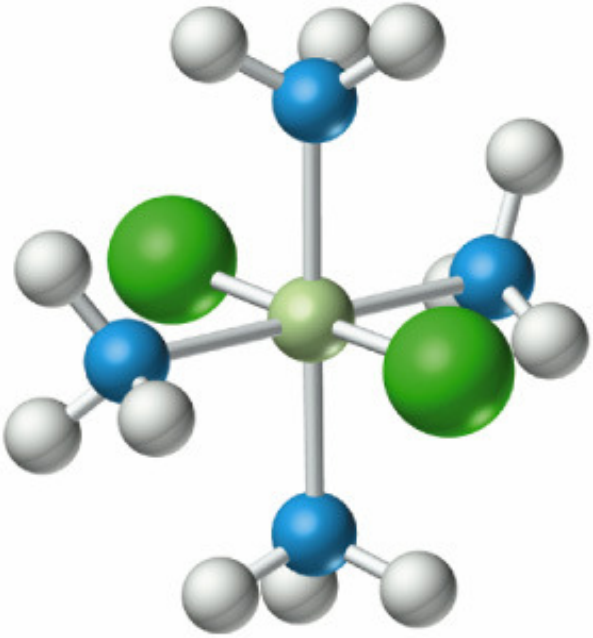
cis-$[PtCl_2(NH_3)_2]$

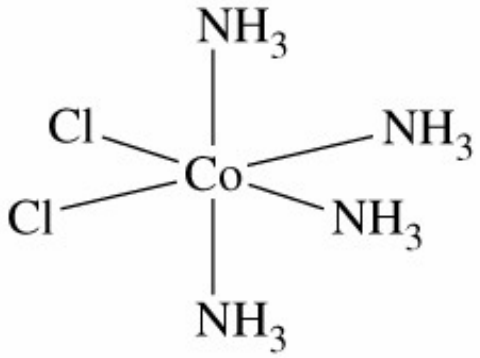


trans-$[PtCl_2(NH_3)_2]$

Isomers

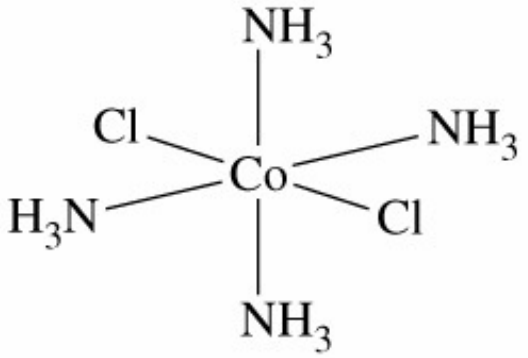






cis-$[CoCl_2(NH_3)_4]^+$

(purple)



trans-$[CoCl_2(NH_3)_4]^+$

(green)

Bonding

Bonding theory must explain

- Color
- Magnetism
- Isomerism
- Bond Strength

Bonding

Crystal Field Theory (CFT)

Color
Magnetism

What bonds ligand to metal?

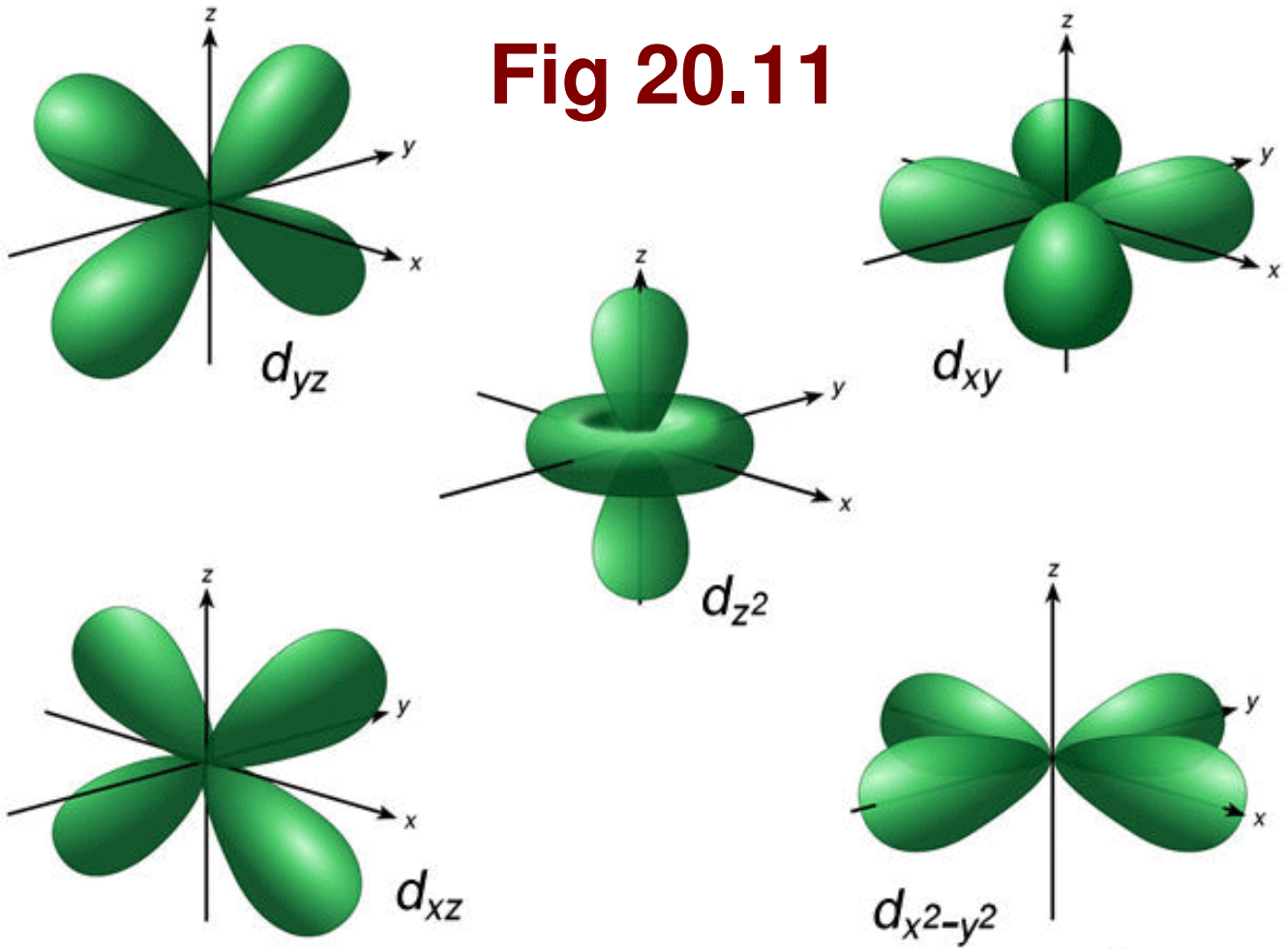
Crystal Field Theory

1. (+) metal ↔ (-) ligand
   ⇒ attraction
2. metal d e^- ↔ ligand lone pairs
   ⇒ repulsion

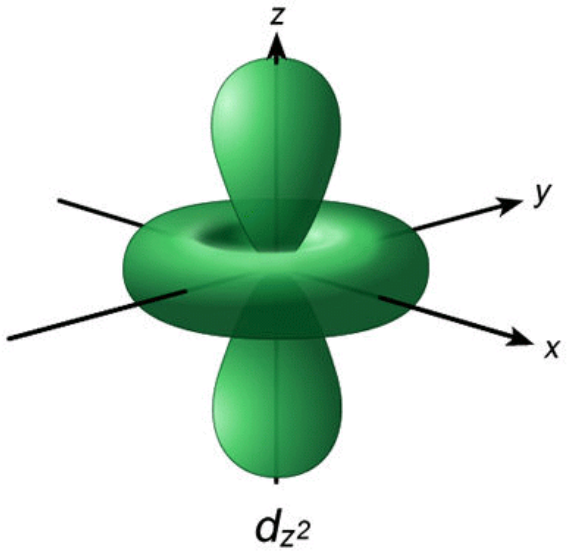
Know shapes of d-orbitals Fig 20.11

Crystal Field Theory

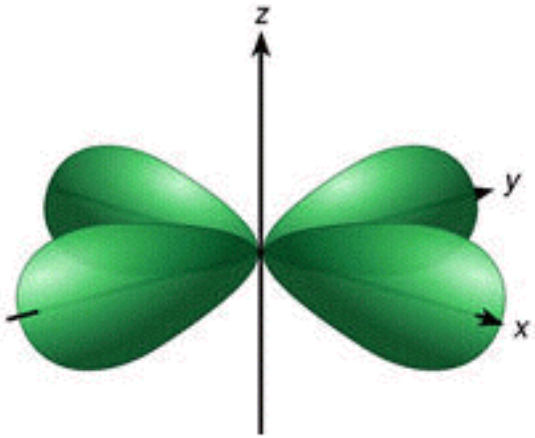
Fig 20.11



Crystal Field Theory



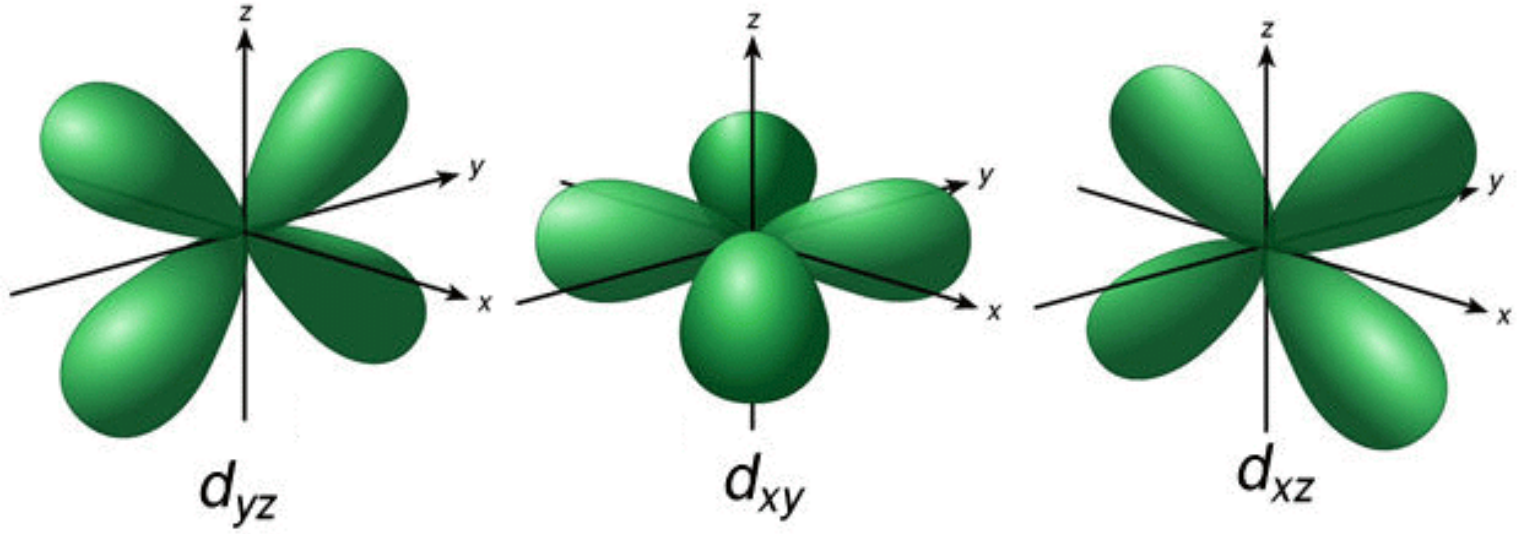
d_{z^2}



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

Lobes point along axes

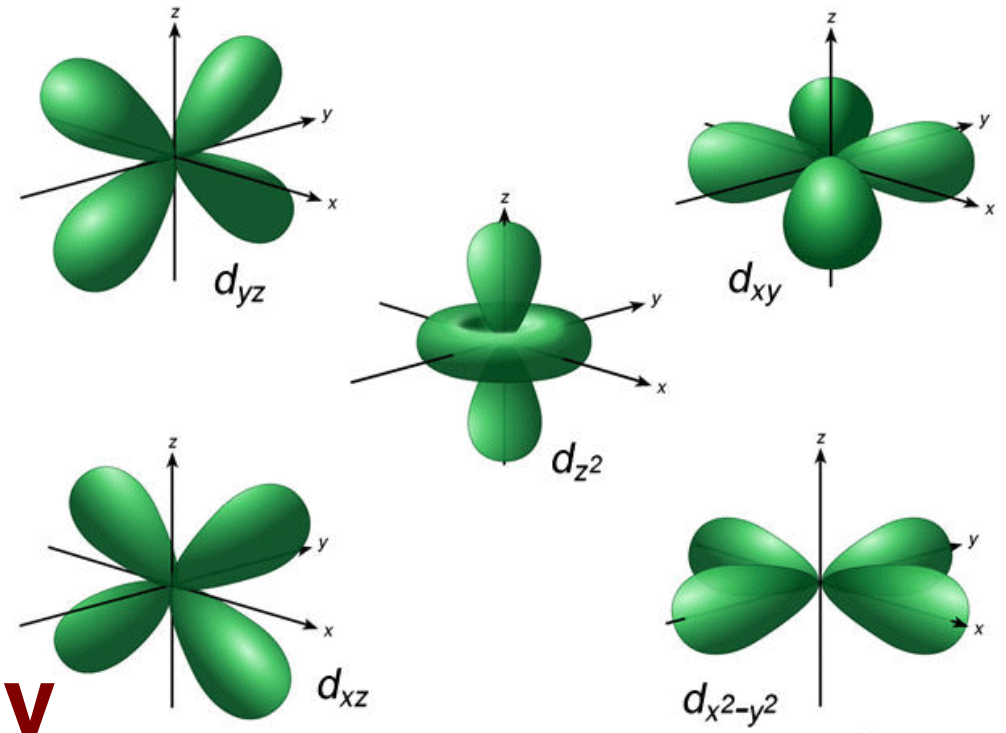
Crystal Field Theory



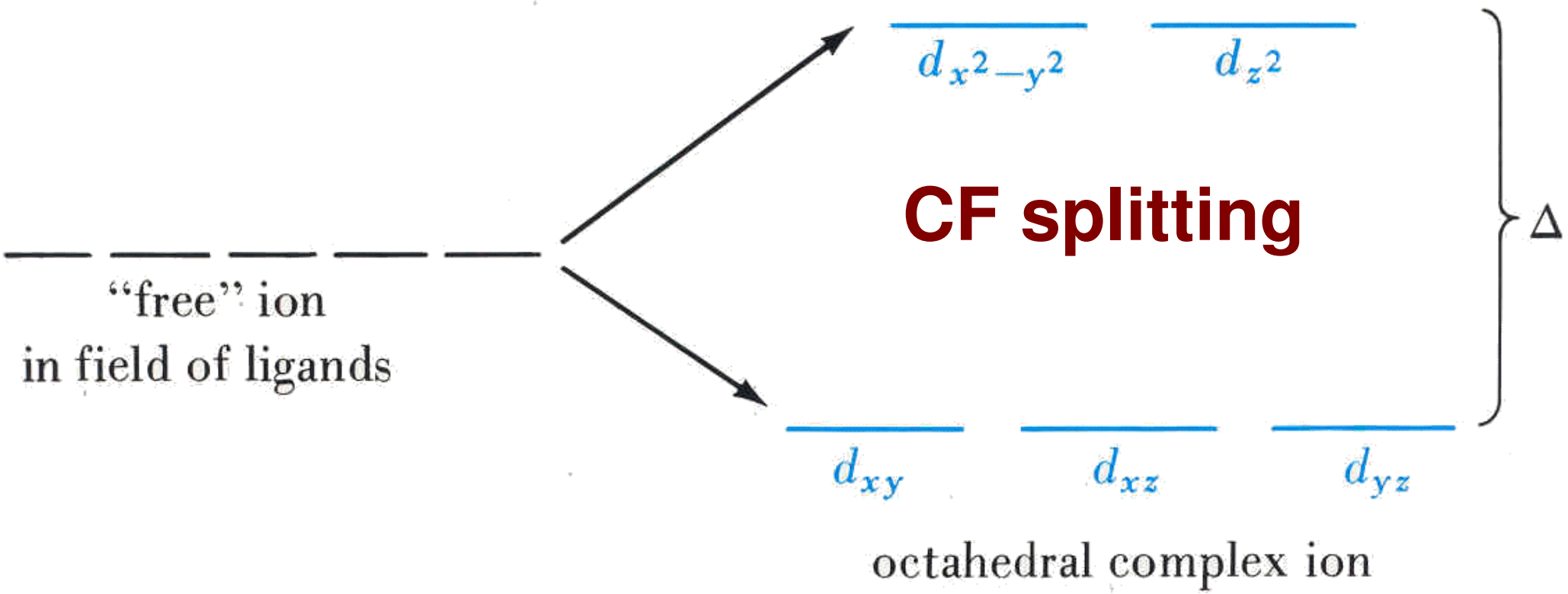
Lobes point between axes

Crystal Field Theory

- Ligands approach along axes
- Repels d-electrons
- All orbitals go up in energy
- Orbitals along axes go up more in energy

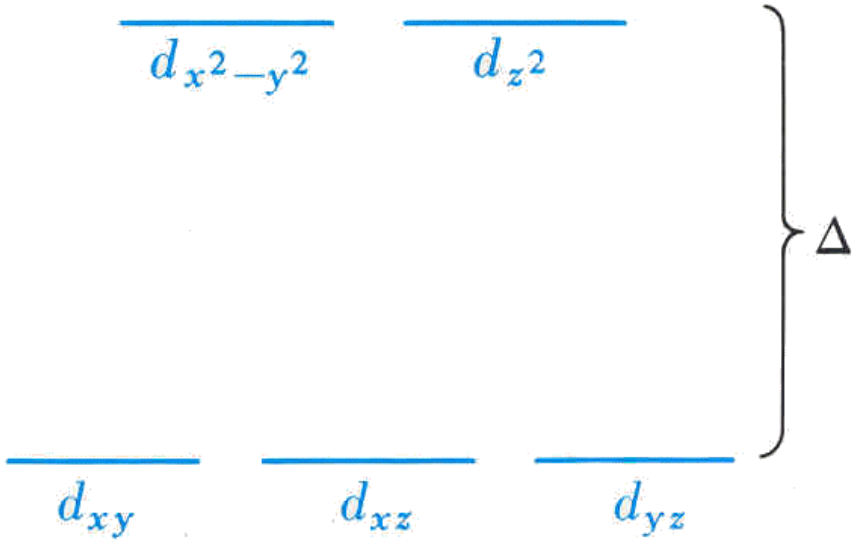


Crystal Field Theory



Δ is energy difference

Crystal Field Theory

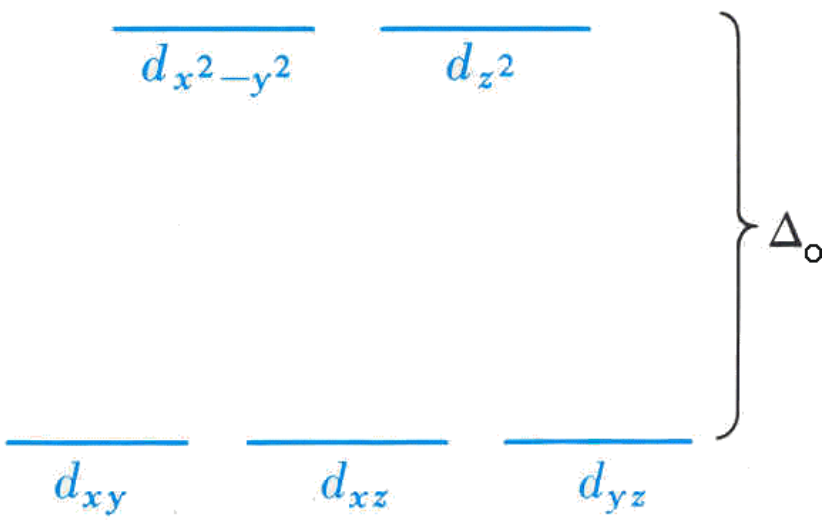


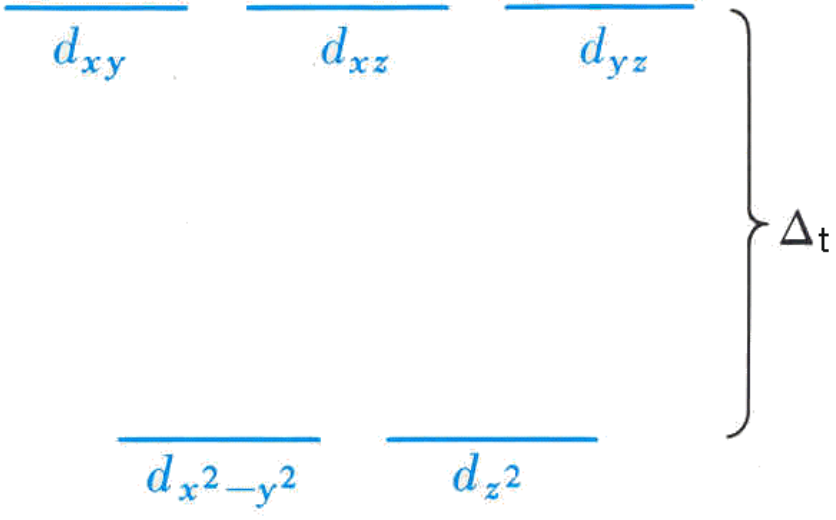
What determines if Δ is large or small?

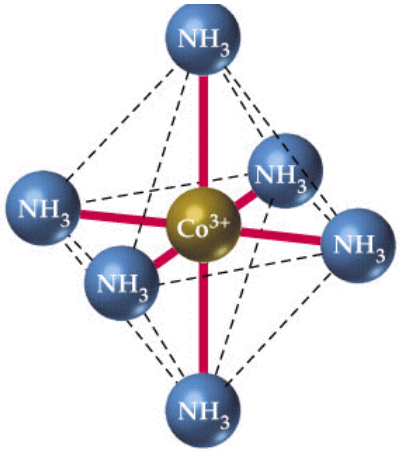
Metals
Ligands
Structure

Size of Δ determines color and magnetism

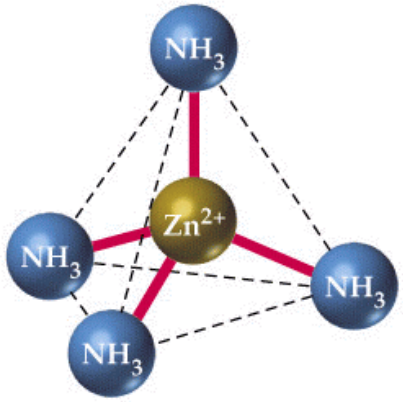
Crystal Field Theory







Octahedral



Tetrahedral

		d_{xy} d_{xz} d_{yz} d_{z^2} $d_{x^2-y^2}$	d_{z^2} $d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}	$d_{x^2-y^2}$ d_{xy} d_{z^2} d_{xz} d_{yz}
	Fig 20.18		Fig 20.12	Fig 20.19
d-orbital energies in "free" metal atom or ion	Average energy of *d* orbitals in the presence of ligands	**(a)** *d* orbitals in tetrahedral complex	**(b)** *d* orbitals in octahedral complex	**(c)** *d* orbitals in square planar complex

Crystal Field Theory

For a given metal and ligand:

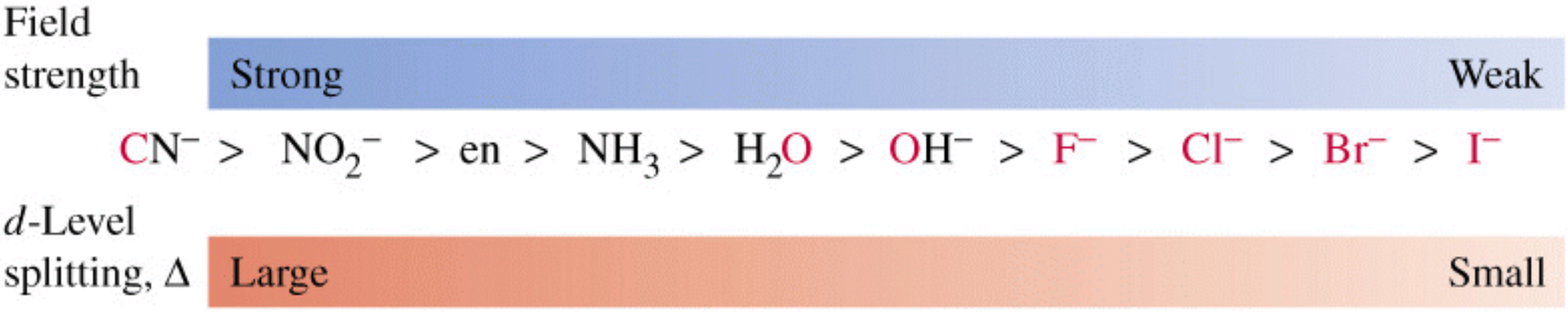
$\Delta_o > \Delta_t$

Δ increases with increasing oxidation number

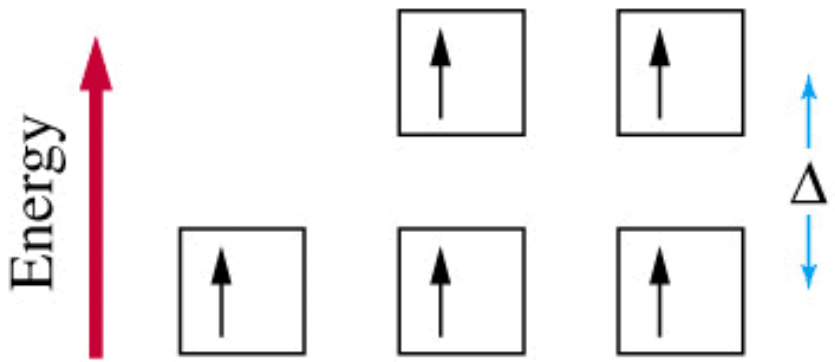
Crystal Field Theory

For a given metal & oxidation state:

Ligands ordered in spectrochemical series



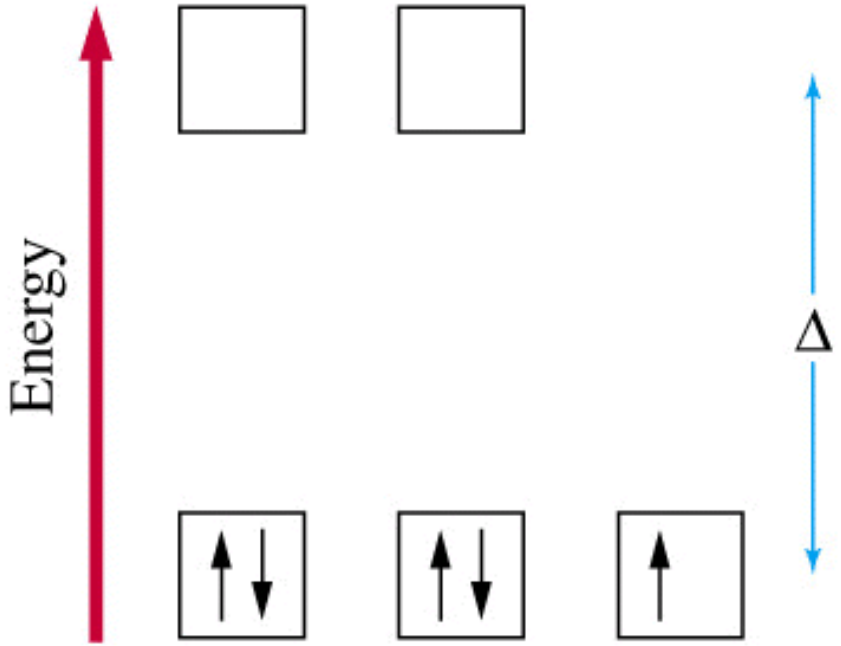
Ligands determine magnetic properties & Δ



Fe^{3+} in $[Fe(H_2O)_6]^{3+}$

A "high spin" complex

Lots of unpaired e$^-$



Fe^{3+} in $[Fe(CN)_6]^{3-}$

A "low spin" complex

Few unpaired e$^-$

Counting d-electrons

$_{21}Sc \rightarrow {}_{29}Cu$ Electrons added to 3d subshell

$_{21}Sc \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

$_{21}Sc \rightarrow [Ar]4s^2 3d^1$ $_{22}Ti \rightarrow [Ar]4s^2 3d^2$

Exceptions $_{24}Cr \rightarrow [Ar]4s^1 3d^5$

Counting d-electrons

When metals lose electrons to form ions, electrons come from 4s first

$_{22}Ti \rightarrow [Ar]4s^2 3d^2$ $\qquad$ $_{22}Ti^{2+} \rightarrow [Ar]3d^2$

Ti^{2+}: d^2

Counting d-electrons

When metals lose electrons to form ions, electrons come from 4s first

$_{27}Co \rightarrow [Ar]4s^2 3d^7$ $\quad$ $_{27}Co^{3+} \rightarrow [Ar]3d^6$

Co^{3+}: d^6

Magnetic Properties

Odd number of d e^-: paramagnetic

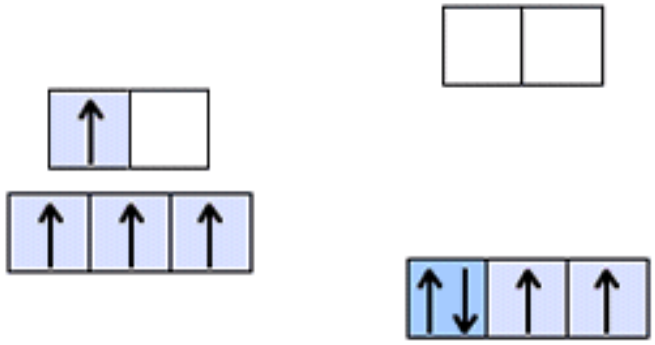
Even number of d e^-: diamagnetic

Hund's Rule
Electrons will arrange themselves in the same sublevel with the maximum number of unpaired electrons

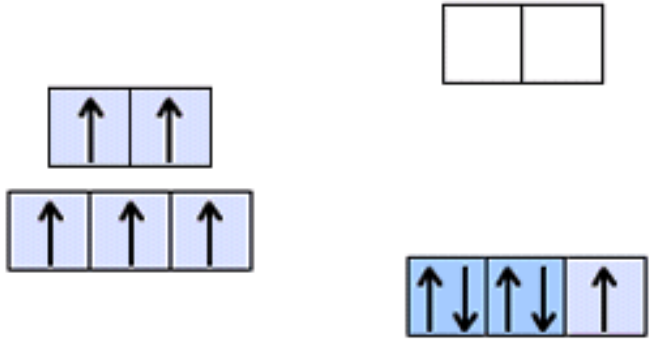
High spin:
weak-field ligand

Low spin:
strong-field ligand

d^4



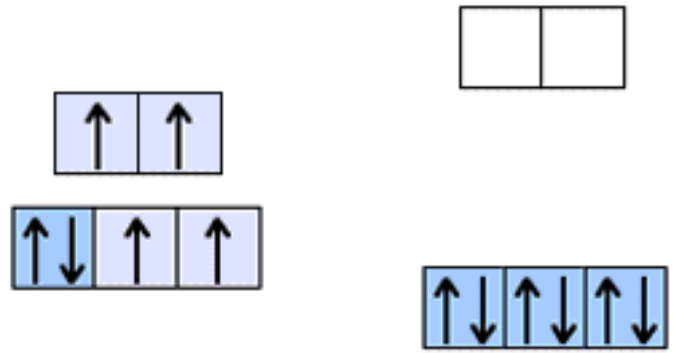
d^5



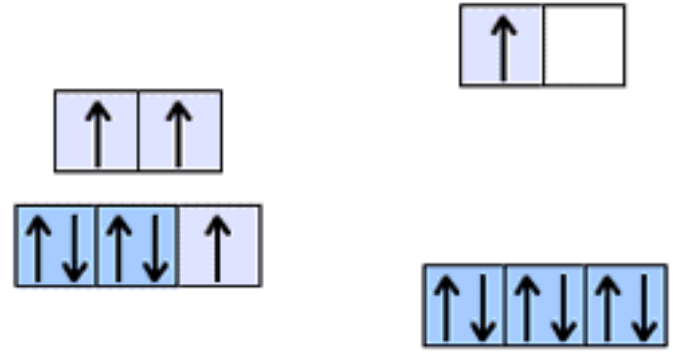
High spin:
weak-field ligand

Low spin:
strong-field ligand

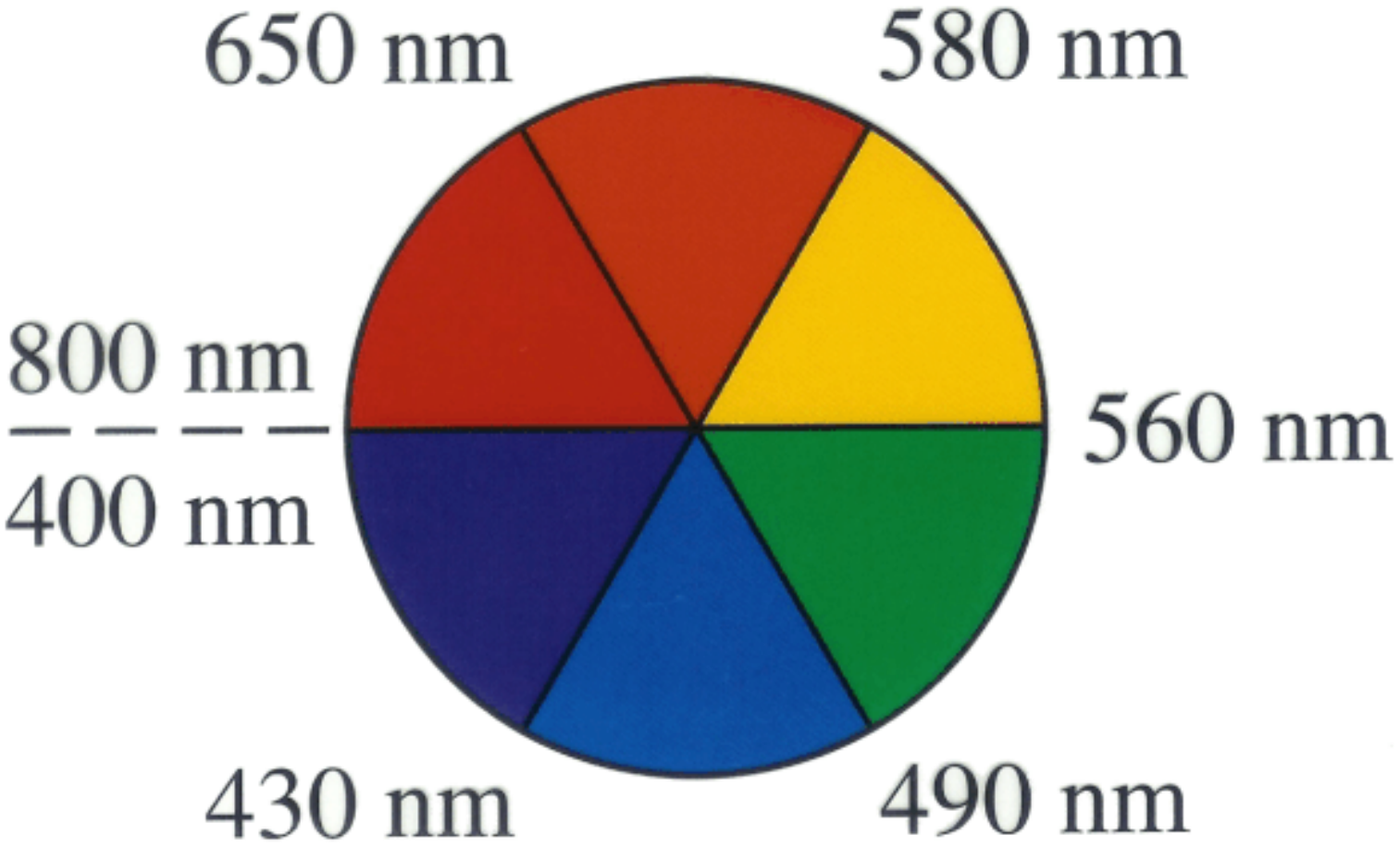
d^6



d^7



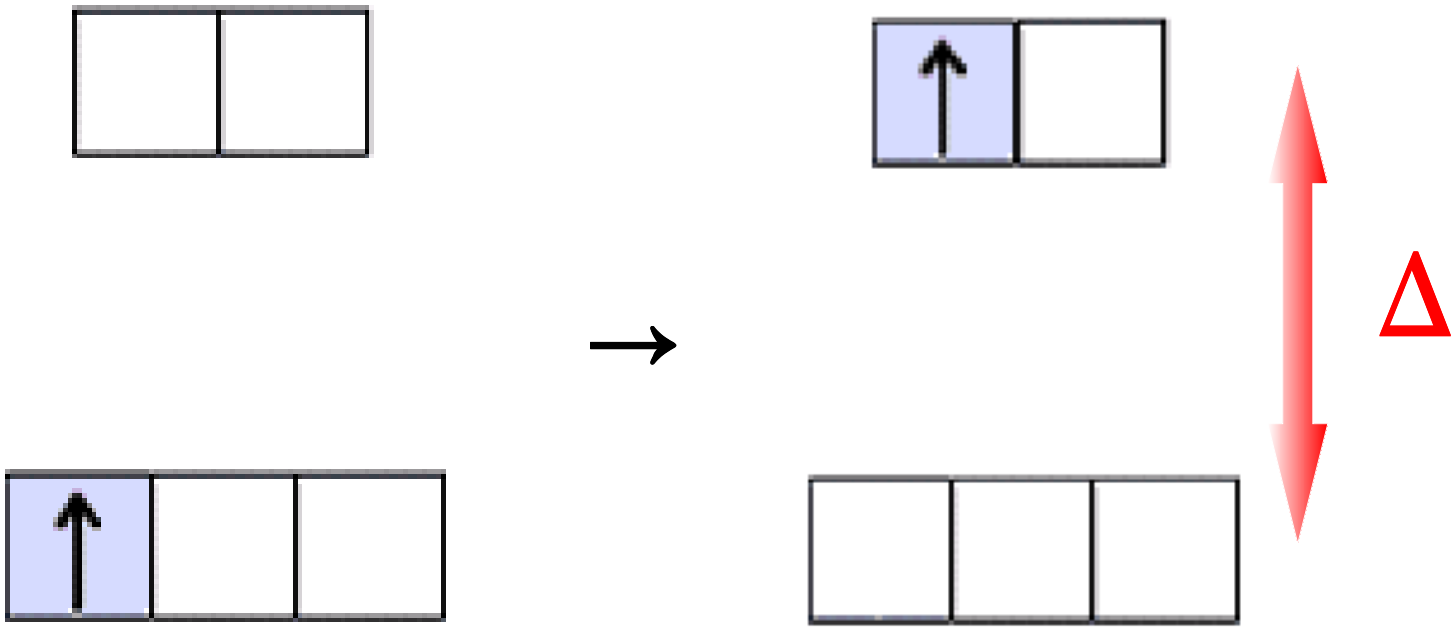
Color Wheel



Calculating Δ

$[Ti(H_2O)_6]^{3+}$ $Ti^{3+} \rightarrow [Ar]3d^1$

Absorbed light → electron to jump



Calculating Δ

$[Ti(H_2O)_6]^{3+}$ is a violet compound

Absorbs yellow light: λ = 550 nm

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

Calculating Δ

$[Ti(H_2O)_6]^{3+}$ is a violet compound

Absorbs yellow light: λ = 550 nm

$$\Delta = \frac{(6.63 \times 10^{-34}\ Js) \times (3 \times 10^{8}\ m/s)}{550 \times 10^{-9}\ m}$$

Calculating Δ

$[Ti(H_2O)_6]^{3+}$ is a violet compound

Absorbs yellow light: λ = 550 nm

$$\Delta = \frac{(6.63 \times 10^{-34}\ Js) \times (3 \times 10^{8}\ m/s)}{550 \times 10^{-9}\ m}$$

$$\Delta = 3.6 \times 10^{-19}\ J$$

White compounds

When Δ very large (>800 nm) or very small (<200 nm) falls outside of visible region

When have no d electrons Mn^{7+} or too many Zn^{2+}