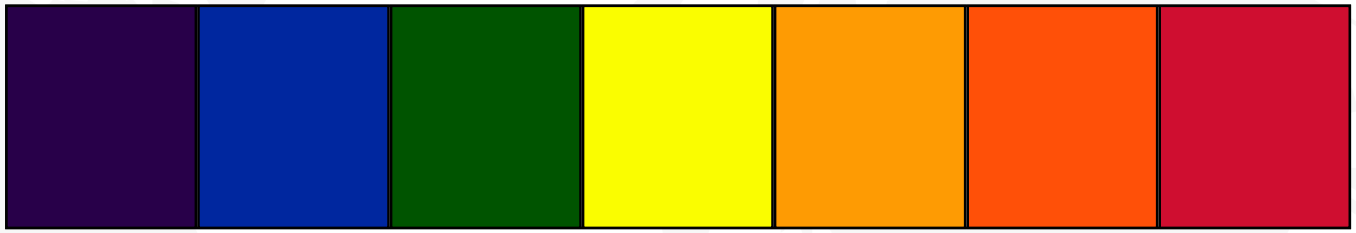
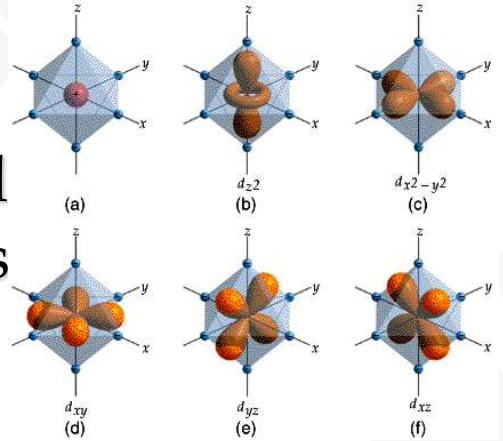
PRESENTATION
BY
Dr.V.A.Kalantre

Crystal Field Theory



400 500 600 800

The relationship between colors and complex metal ions



Transition Metal Gems

Gemstone owe their color from trace transition-metal ions

Corundum mineral, Al_2O_3: Colorless

- Cr → Al : Ruby
- Mn → Al: Amethyst
- Fe → Al: Topaz
- Ti &Co → Al: Sapphire

Beryl mineral, $Be_3Al_2Si_6O_{18}$: Colorless

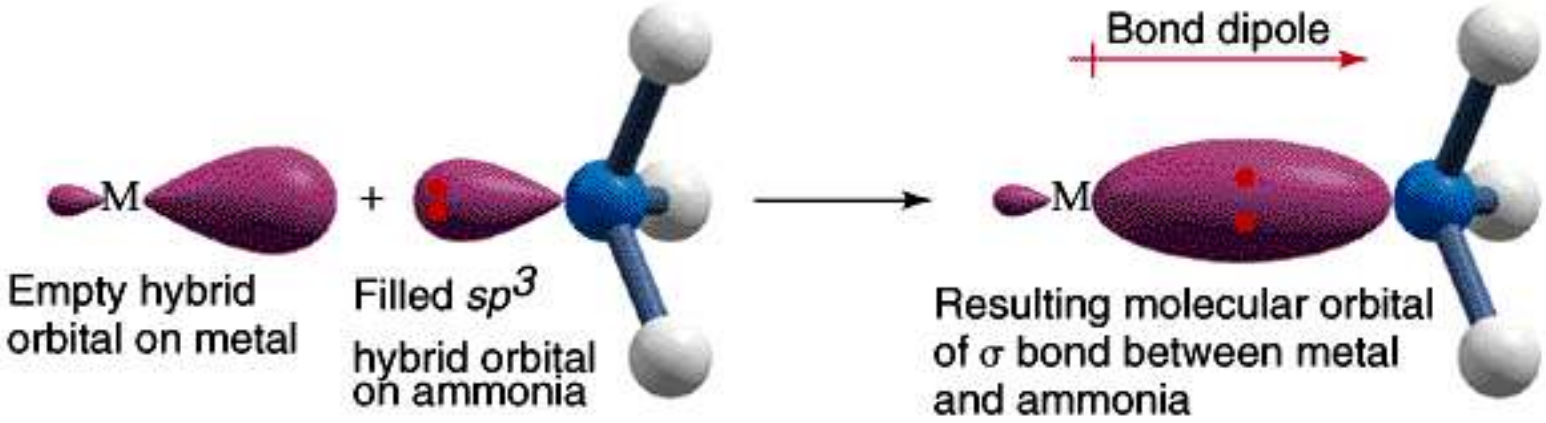
- Cr → Al : Emerald
- Fe → Al : Aquamarine

Crystal-Field Theory

Model explaining bonding for transition metal complexes

- Originally developed to explain properties for crystalline material
- Basic idea:

  Electrostatic interaction between lone-pair electrons result in coordination.



Energetics

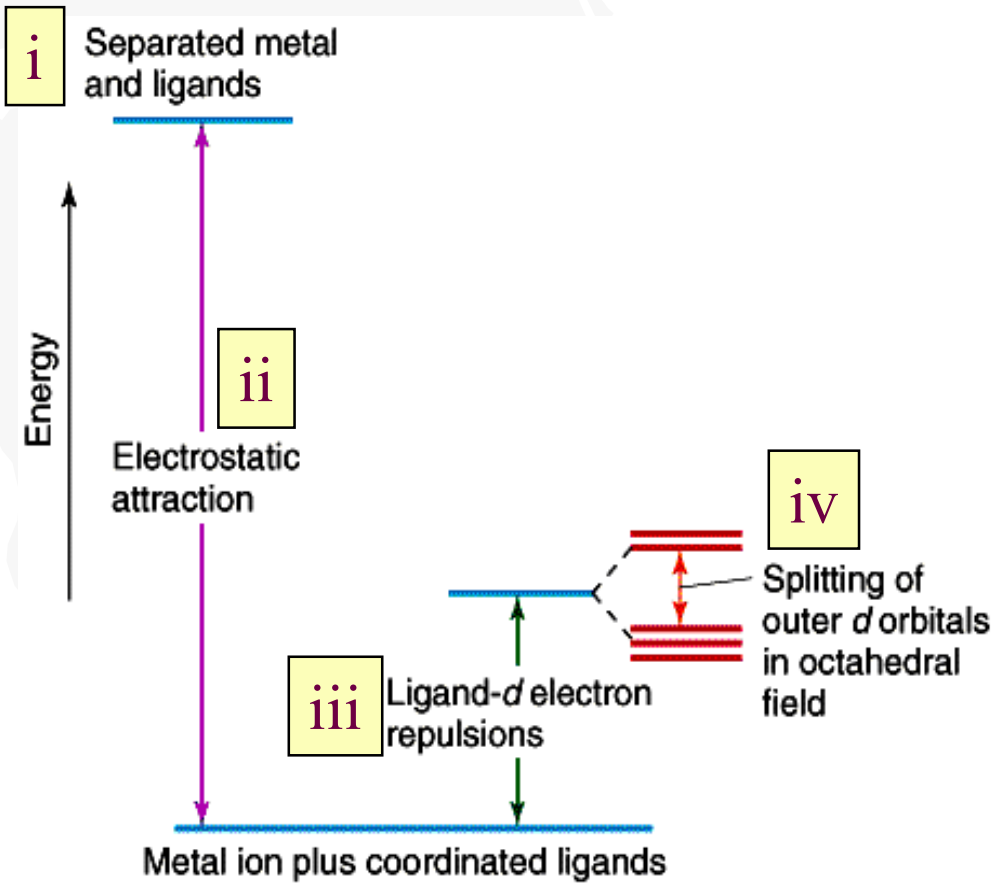
CFT - Electrostatic between metal ion and donor atom

i) Separate metal and ligand high energy

ii) Coordinated Metal - ligand stabilized

iii) Destabilization due to ligand -d electron repulsion

iv) Splitting due to octahedral field.

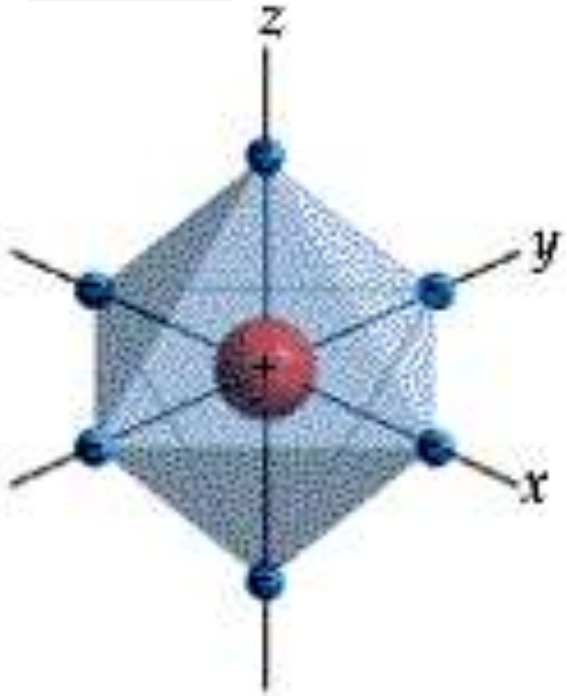


Ligand-Metal Interaction

Crystal Field Theory - Describes bonding in Metal Complexes

Basic Assumption in CFT:

Electrostatic interaction between ligand and metal



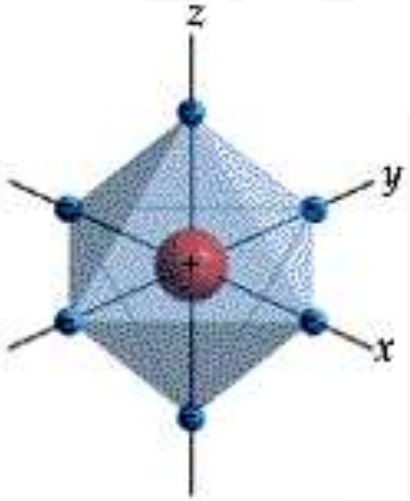
d-orbitals align along the octahedral axis will be affected the most.

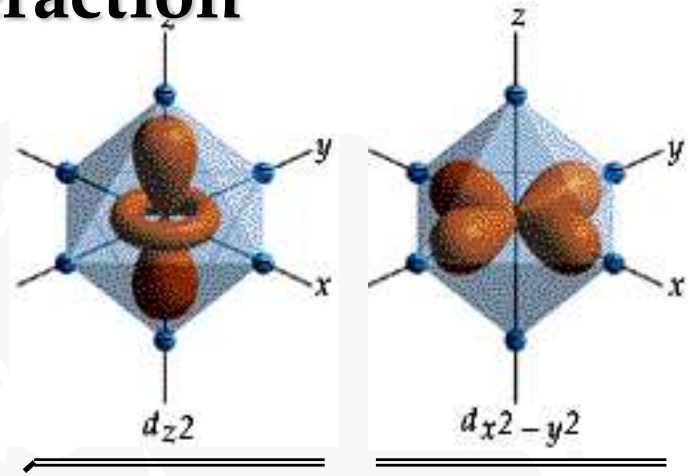
More directly the ligand attacks the metal orbital, the higher the the energy of the d-orbital.

In an octahedral field the degeneracy of the five d-orbitals is lifted

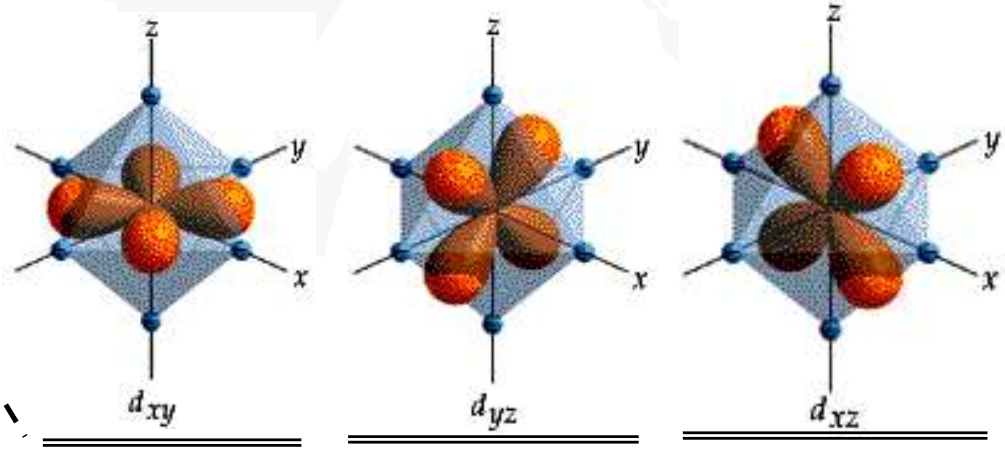
d-Orbitals and Ligand Interaction (Octahedral Field)

Ligands approach metal





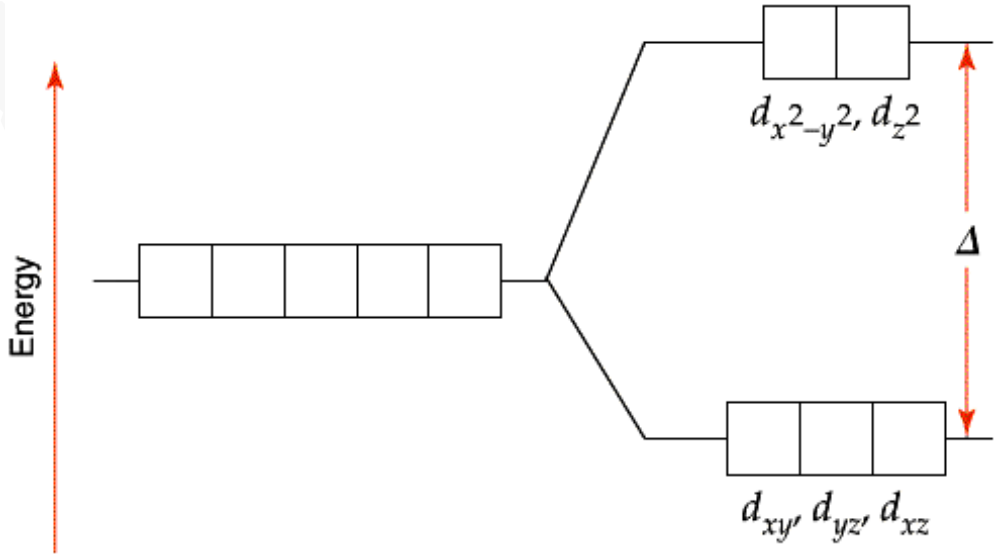
d-orbitals pointing directly at axis are affected most by electrostatic interaction



d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

Splitting of the d-Orbitals

Octahedral field Splitting Pattern:



The energy gap is referred to as Δ (10 Dq) , the crystal field splitting energy.

The d_{z2} and d_{x2-y2} orbitals lie on the same axes as negative charges.

Therefore, there is a large, unfavorable interaction between ligand (-) orbitals.

These orbitals form the degenerate high energy pair of energy levels.

The d_{xy} , d_{yx} and d_{xz} orbitals bisect the negative charges.

Therefore, there is a smaller repulsion between ligand & metal for these orbitals.

These orbitals form the degenerate low energy set of energy levels.

Magnitude of CF Splitting (Δ or 10Dq)

Color of the Complex depends on magnitude of Δ

1. **Metal: Larger metal → larger Δ**

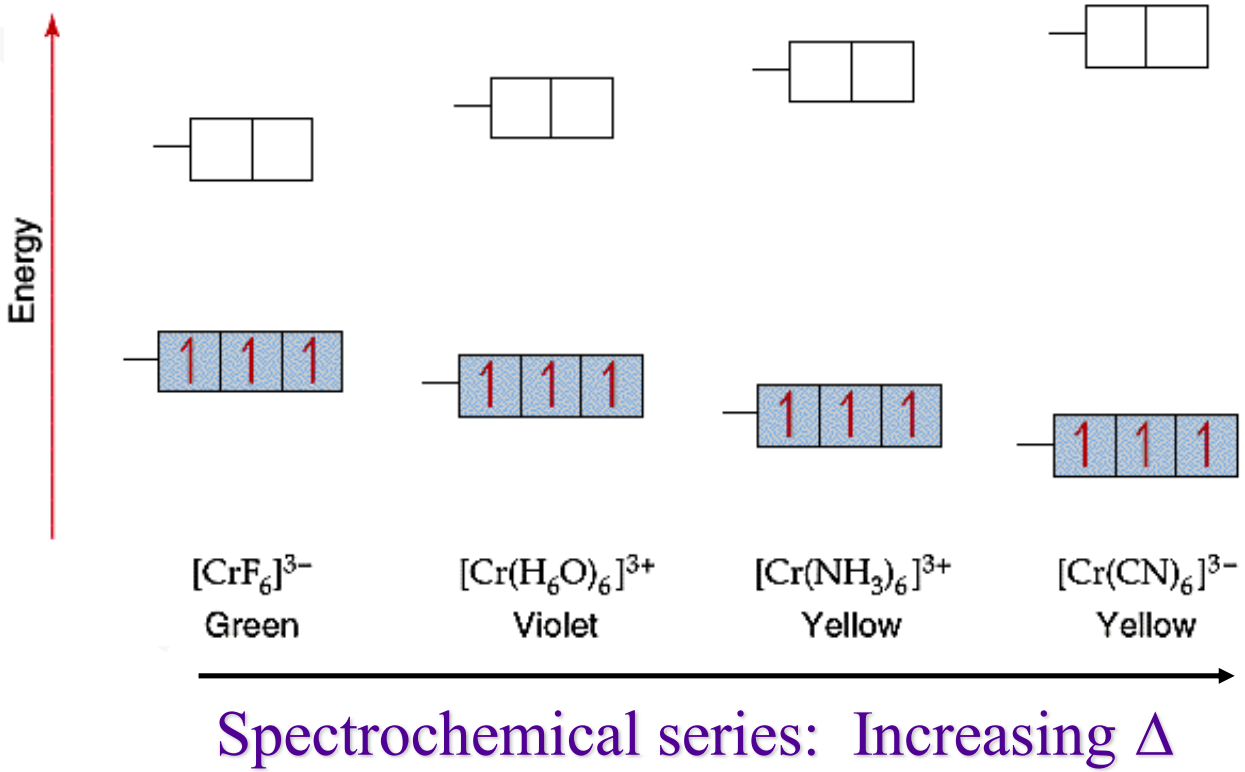
   Higher Oxidation State → larger Δ

2. **Ligand: Spectrochemical series**

   $Cl^- < F^- < H_2O < NH_3 < en < NO_2^- <$ (N-bonded) $< CN^-$

   Weak field Ligand: Low electrostatic interaction: small CF splitting.

   High field Ligand: High electrostatic interaction: large CF splitting.



Electron Configuration in Octahedral Field

Electron configuration of metal ion:

s-electrons are lost first.

Ti^{3+} is a d^1, V^{3+} is d^2 , and Cr^{3+} is d^3

Hund's rule:

First three electrons are in separate d orbitals with their spins parallel.

Fourth e- has choice:

Higher orbital if Δ is small; High spin

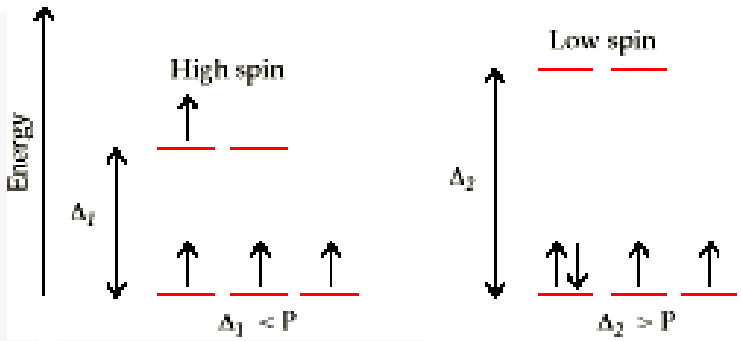
Lower orbital if Δ is large: Low spin.

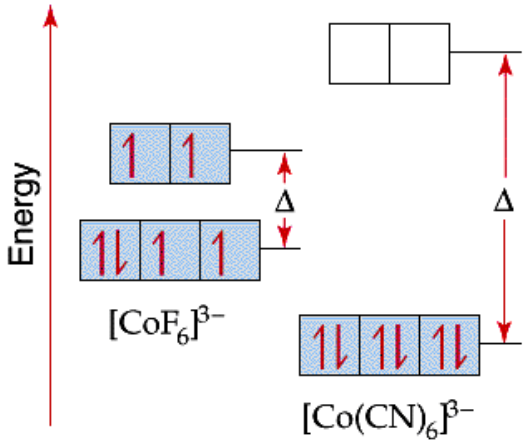
Weak field ligands

Small Δ , High spin complex

Strong field Ligands

Large Δ , Low spin complex

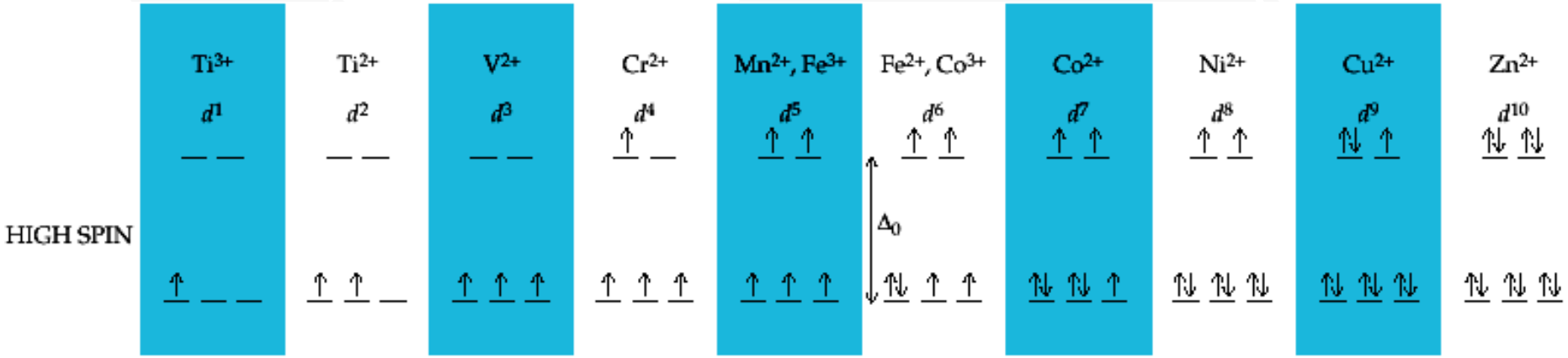


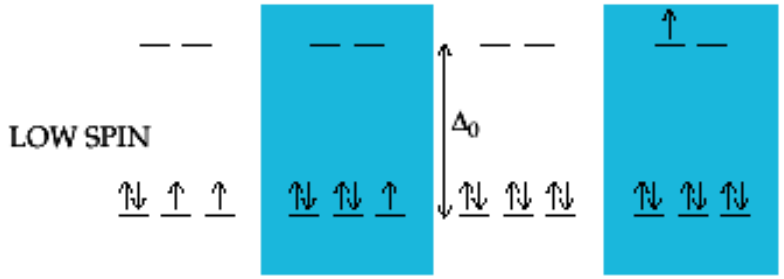


High Spin Vs. Low Spin (d^1 to d^{10})

Electron Configuration for Octahedral complexes of metal ion having d^1 to d^{10} configuration $[M(H_2O)_6]^{+n}$.

Only the d^4 through d^7 cases have both high-spin and low spin configuration.





Electron configurations for octahedral complexes of metal ions having from d^1 to d^{10} configurations. Only the d^4 through d^7 cases have both high-spin and low-spin configurations.

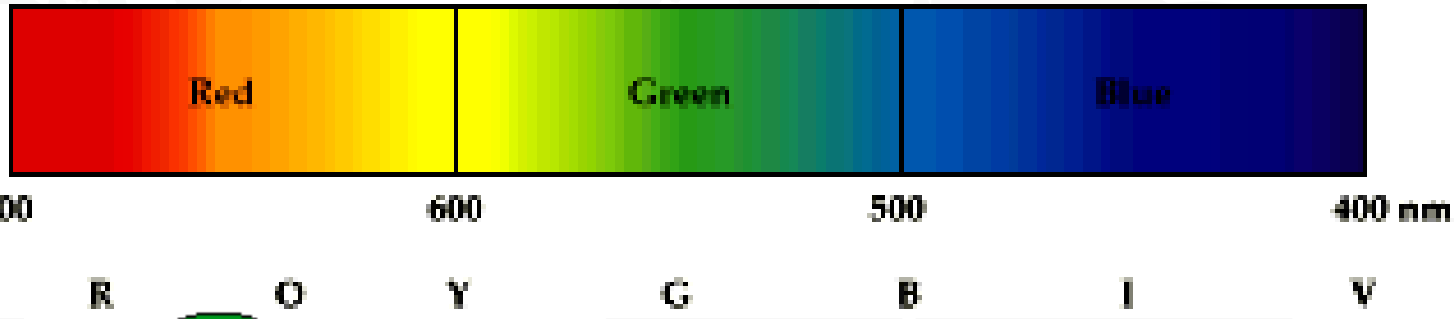
Color Absorption of Co^{3+} Complexes

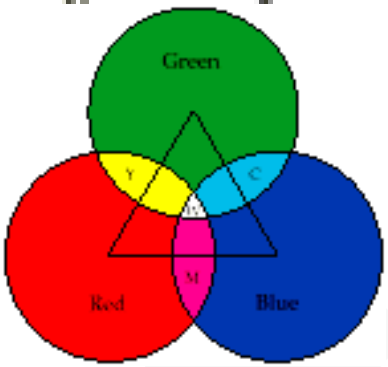
The Colors of Some Complexes of the Co^{3+} Ion

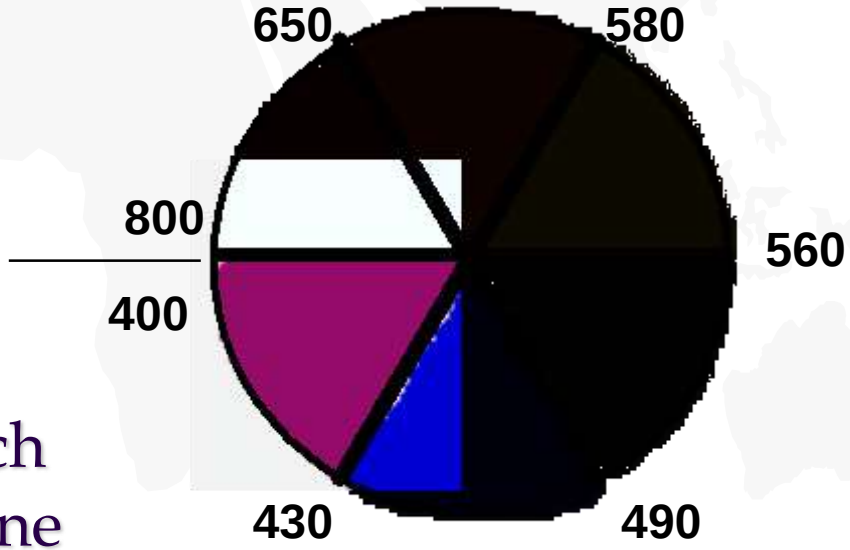
Complex Ion	Wavelength of light absorbed	Color of Light Absorbed	Color of Complex
$[CoF_6]^{3+}$	700 (nm)	Red	Green
$[Co(C_2O_4)_3]^{3+}$	600, 420	Yellow, violet	Dark green
$[Co(H_2O)_6]^{3+}$	600, 400	Yellow, violet	Blue-green
$[Co(NH_3)_6]^{3+}$	475, 340	Blue, violet	Yellow-orange
$[Co(en)_3]^{3+}$	470, 340	Blue, ultraviolet	Yellow-orange
$[Co(CN)_6]^{3+}$	310	Ultraviolet	Pale Yellow

The complex with fluoride ion, $[CoF_6]^{3+}$, is high spin and has one absorption band. The other complexes are low spin and have two absorption bands. In all but one case, one of these absorptionsis in the visible region of the spectrum. The wavelengths refer to the center of that absorption band.

Colors & How We Perceive it



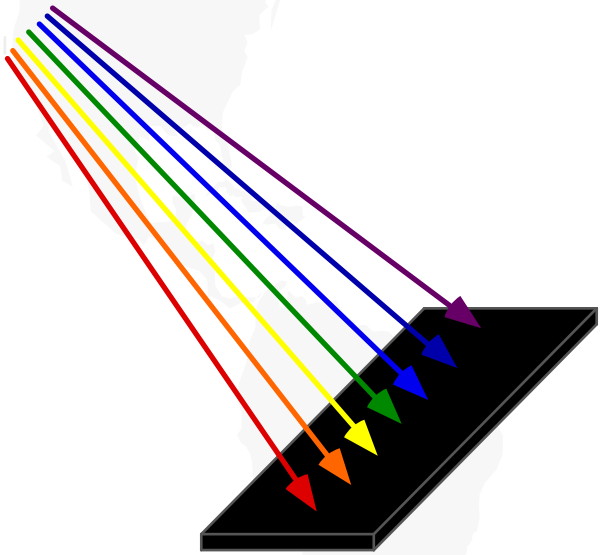




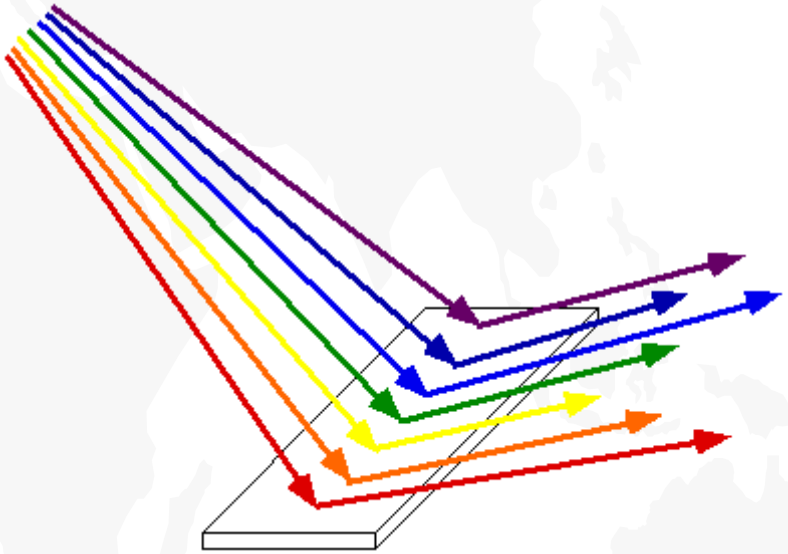
Artist color wheel showing the colors which are complementary to one another and the wavelength range of each color.

Black & White

When a sample absorbs light, what we see is the sum of the remaining colors that strikes our eyes.

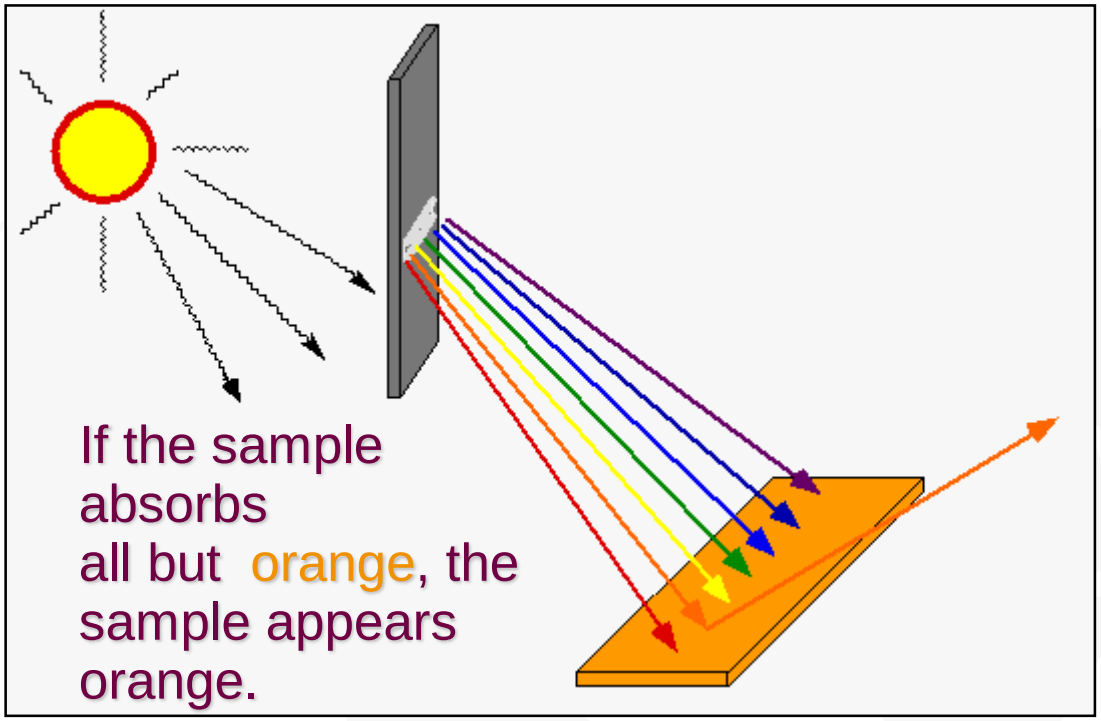


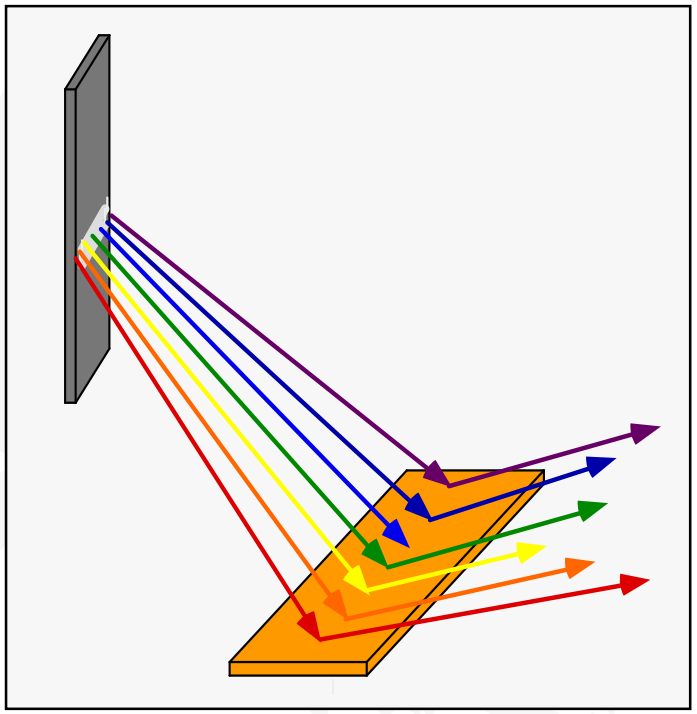
If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample. Consequently, it appears black.



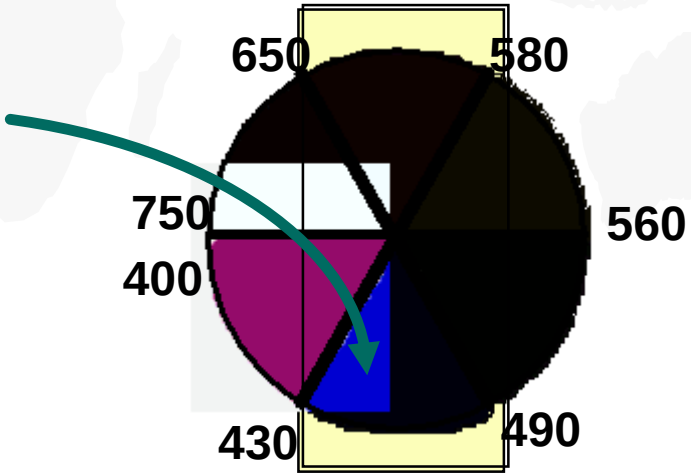
If the sample absorbs no visible light, it is white or colorless.

Absorption and Reflection



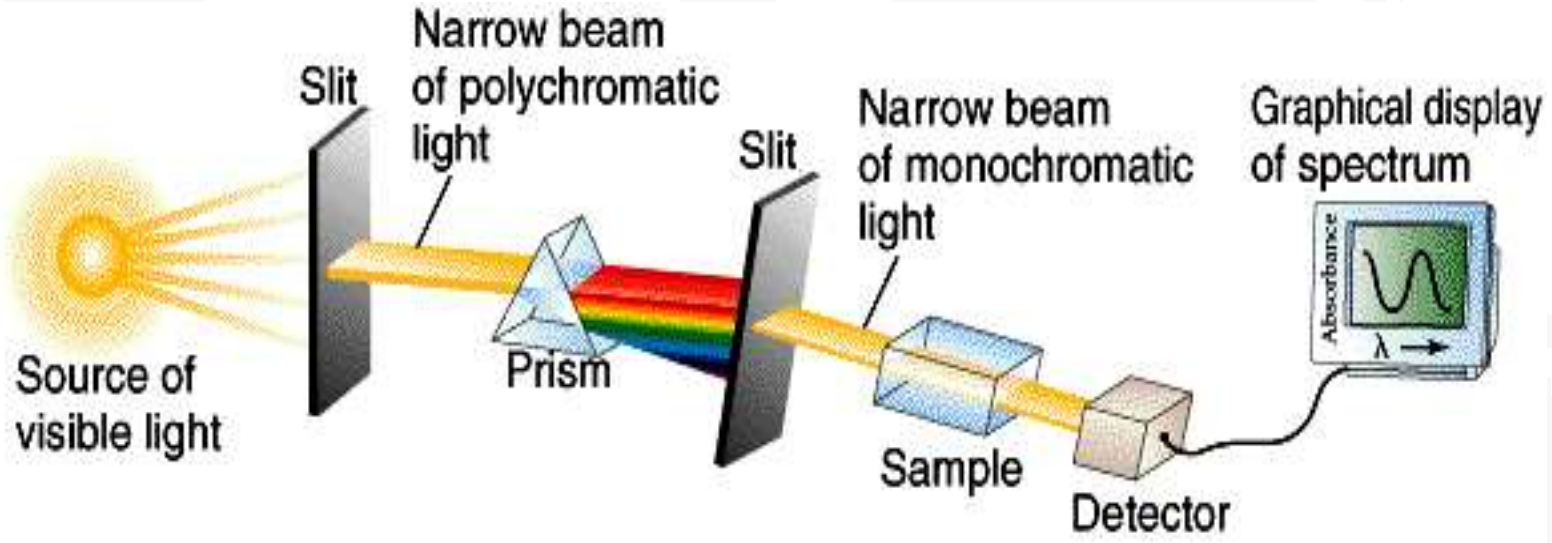


Further, we also perceive orange color when visible light of all colors except blue strikes our eyes. In a complementary fashion, if the sample absorbed only orange, it would appear blue; blue and orange are said to be complementary colors.



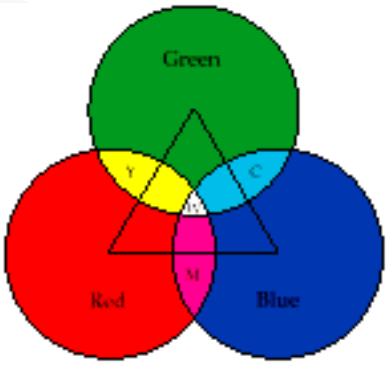
Light absorption Properties of Metal Complexes

Recording the absorption Spectrum



Complex Influence on Color

Compounds of Transition metal complexes solution.



$[Fe(H_2O)_6]^{3+}$ $[Ni(H_2O)_6]^{2+}$ $[Zn(H_2O)_6]^{2+}$

$[Co(H_2O)_6]^{2+}$ $[Cu(H_2O)_6]^{2+}$

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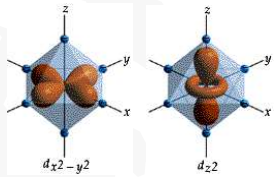
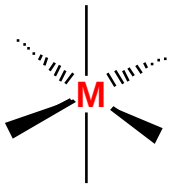
Octahedral, Tetrahedral & Square Planar

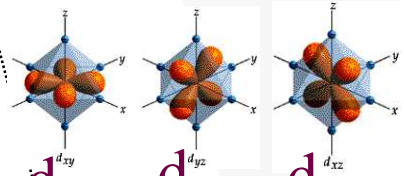
CF Splitting pattern for various molecular geometry



d_{x2-y2} d_{z2}

Octahedral





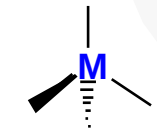
d_{xy} d_{yz} d_{xz}

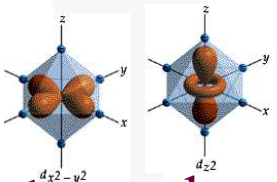
Pairing energy Vs. Δ

Weak field Δ < Pe

Strong field Δ > Pe

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





d_{x2-y2} d_{z2}

Small Δ → High Spin

Square planar

d_{x2-y2} d_{xy} d_{z2} d_{xz} d_{yz}

Mostly d^8

(Majority Low spin)

Strong field ligands

i.e., Pd^{2+}, Pt^{2+}, Ir^{+}, Au^{3+}

Summary

Crystal Field Theory provides a basis for explaining many features of transition-metal complexes. Examples include why transition metal complexes are highly colored, and why some are paramagnetic while others are diamagnetic. The spectrochemical series for ligands explains nicely the origin of color and magnetism for these compounds. There is evidence to suggest that the metal-ligand bond has covalent character which explains why these complexes are very stable. Molecular Orbital Theory can also be used to describe the bonding scheme in these complexes. A more in depth analysis is required however.