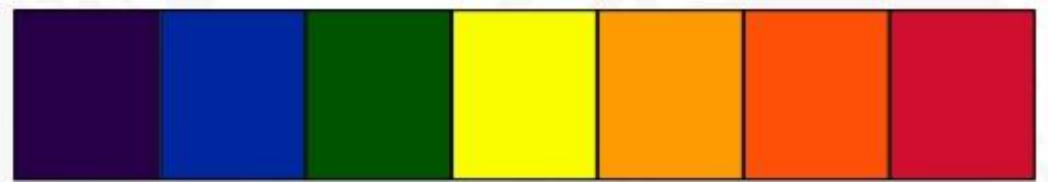
Crystal Field Theory



The relationship
between colors and
complex metal ions

By

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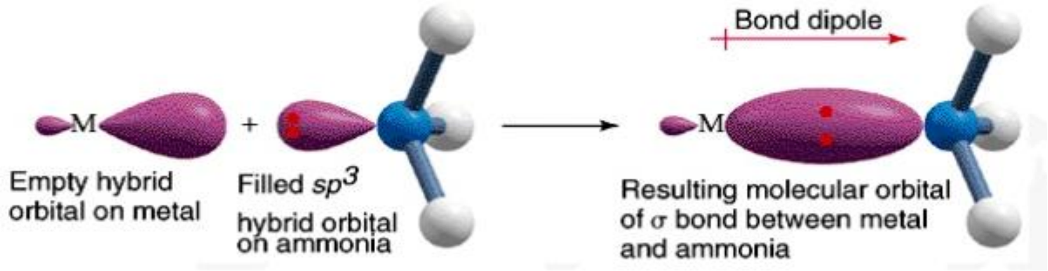
Origin & History:

- Advanced by Bethe and Van Velck and originally applied to explain the colour and magnetic properties of some ionic crystal.

- It is a hypothetical model where ligands are considered as point –ve charge (for negatively charged ligand) and dipoles (for neutral molecule) where as metals are considered as point +ve charge.

- Electric field generated by the ligands influences the distribution of electrons in the metal ions i.e. d-orbital splitting.

- \The bonding between the metal cation and the ligand is believed to be due to electrostatic attraction between the nucleus of the metal ion and the negative or partial negative charge invariably present on the ligands.



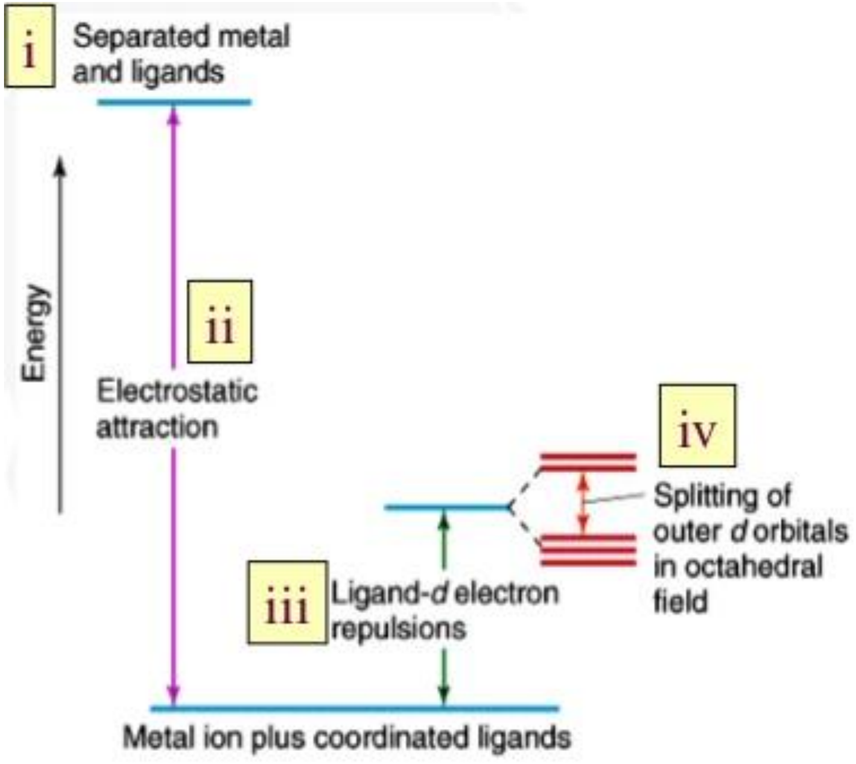
Metal-Ligand Bonding:

Energetics:

Electrostatic interaction between metal ion and donor atom of ligand:

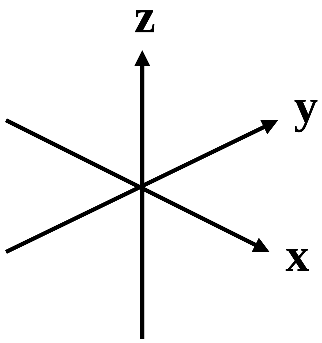
Steps involved are:

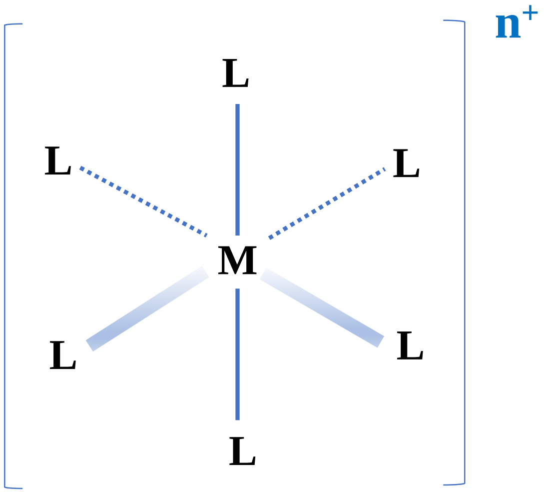
1) Metals and ligands orbitals initially have high energy when they are separated.
2) Metal –ligand orbitals get stabilized due to electrostatic interaction
3) Next destabilization happens due to ligand-d electron repulsion
4) Finally results splitting of metal 5, d-orbitals.
5) Depending upon the number (4 or 6) of attached ligand metal ion gives different geometry and consequently d-orbitals are not affected equally by the ligand field.

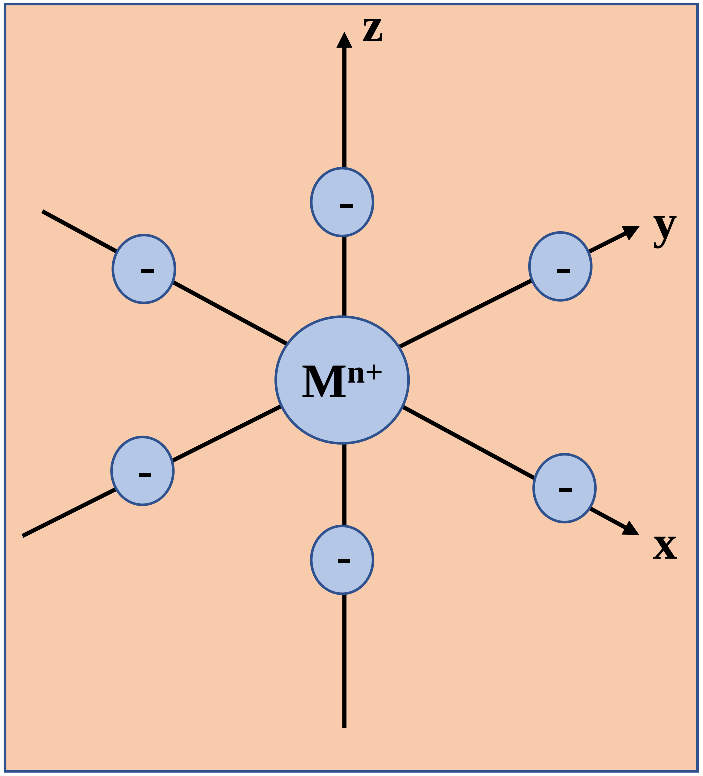


The Octahedral Crystal Field:

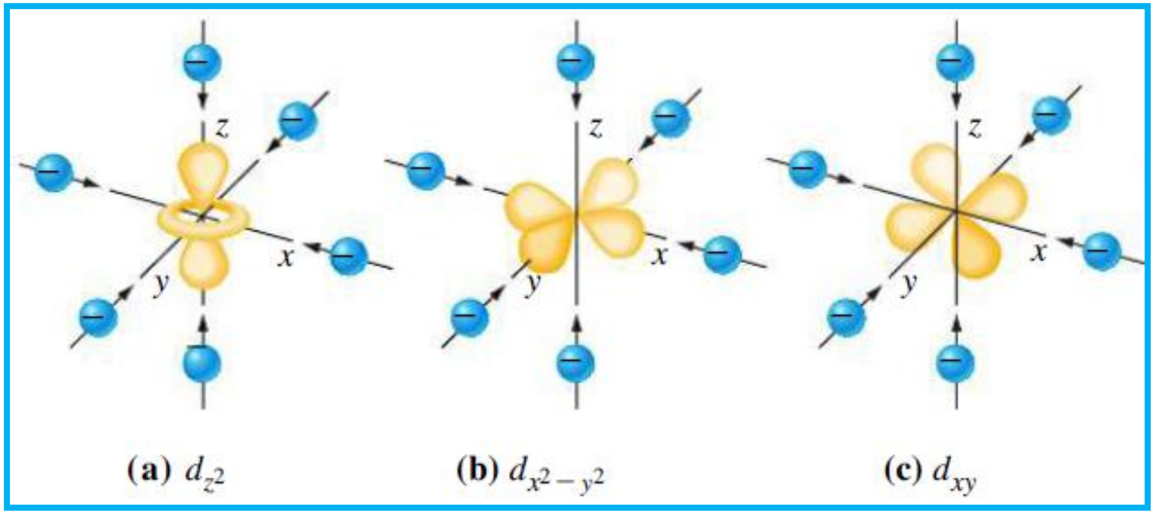
Consider metal ion, M^{m+}, lying at the centre of an octahedral set of point charges.



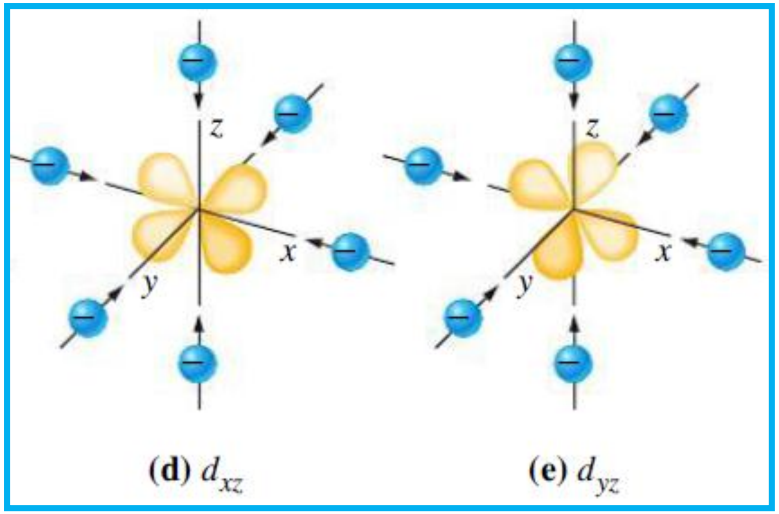




Approach of six ligands to a metal ion in Octahedral Field



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



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

Splitting of five d-orbitals in Octahedral Ligand Field:

- The electrostatic repulsion between the ligands and the electrons of the central metal atom or ion will be much greater when the electrons are housed in e_g set of orbitals (d_{x2-y2}- and d_{z2} orbitals) which are directly points towards the ligands.

- Electrons are housed in the t_{2g} set of orbitals (d_{xy}, d_{xz}, d_{yz} orbitals) experienced comparatively less repulsive interaction as they are directed in between the Cartesian coordinate axes.

- The energy difference between the e_g and t_{2g} set of orbitals is measured in terms of crystal field splitting parameter,Δ_o or 10 Dq.

$4(e_g \text{ electrons}) \times 0.6\,\Delta_o = 2.4\,\Delta_o$

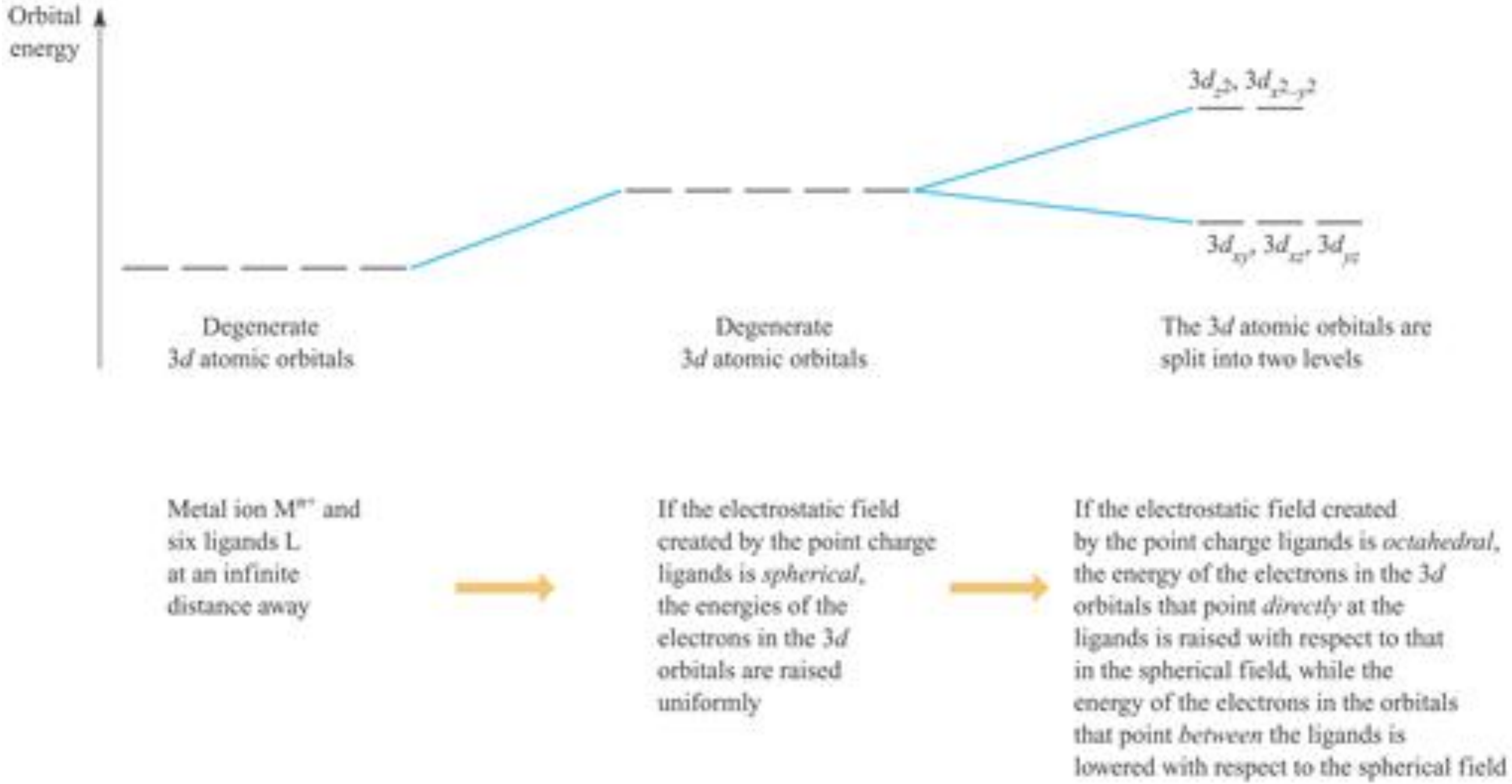
$6(t_{2g} \text{ electrons}) \times (-0.4)\,\Delta_o = -2.4\,\Delta_o$

……………………………………………………………………

Total Energy = 0,

- So total energy is conserved.

Energetics:



Metal ion M^{n+} and six ligands L at an infinite distance away

If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the 3*d* orbitals are raised uniformly

If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the 3*d* orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands is lowered with respect to the spherical field

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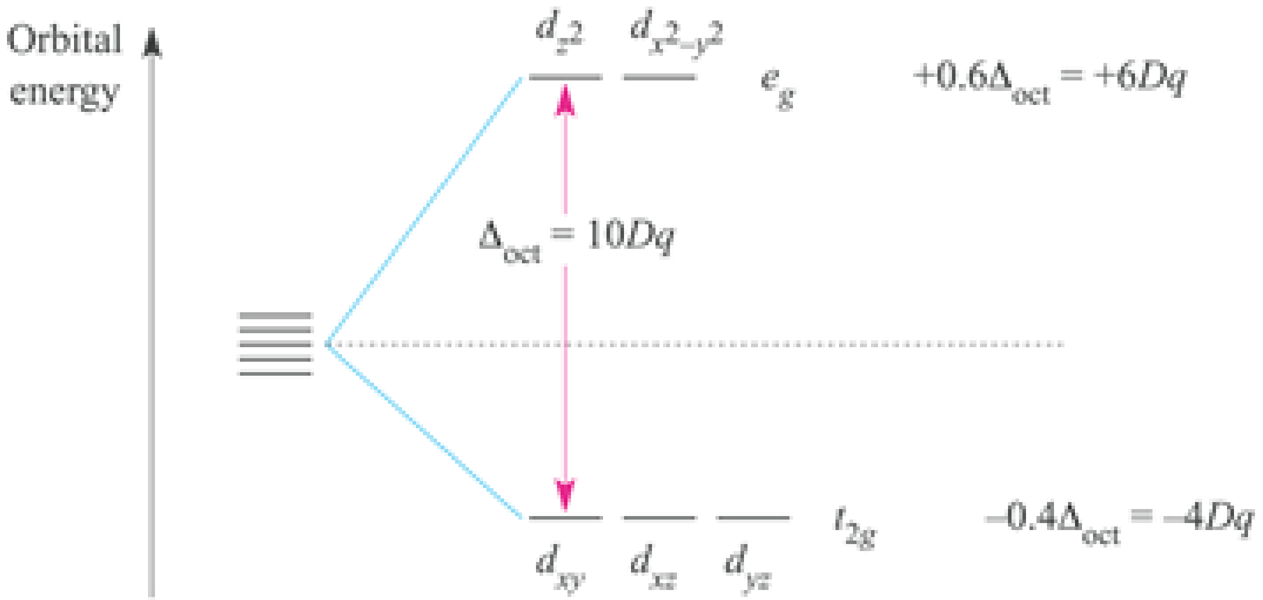


t_{2g} : d_{xy} , d_{yz} , d_{zx}

e_g : d_{z^2} , $d_{x^2-y^2}$

- For strong ligand field: crystal field splitting high; Δ(oct) > Pairing Energy (P); results low spin metal complexes
- For weak ligand field: crystal field splitting low; Δ(oct) < Pairing Energy (P); results high spin metal complexes

Factors Affecting the Magnitude of Δ

1. Higher oxidation states of the metal atom correspond to larger Δ.

   Δ =10,200 cm^{-1} for $[Co^{II}(NH_3)_6]^{2+}$ and 22,870 cm^{-1} for $[Co^{III}(NH_3)_6]^{3+}$
   Δ =32,200 cm^{-1} for $[Fe^{II}(CN)_6]^{4-}$ and 35,000 cm^{-1} for $[Fe^{III}(CN)_6]^{3-}$

2. In groups, heavier analogues have larger Δ.

   For hexaammine complexes $[M^{III}(NH_3)_6]^{3+}$:
   Δ = 22,870 cm^{-1} (C o)
   34,100 cm^{-1} (Rh)
   41,200 cm^{-1} (Ir)

3. Geometry of the metal coordination unit affects Δ greatly.

   Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6:
   Δ = 10,200 cm^{-1} for $[Co^{II}(NH_3)_6]^{2+}$ 5,900 cm^{-1} for $[Co^{II}(NH_3)_4]^{2+}$

4. Nature of the ligands.

   For $[Co^{III}L_6]$ Δ in cm^{-1}: 13,100 (F^-); 20,760 (H_2O); 22,870 (NH_3),
   For $[Cr^{III}L_6]$, Δ in cm-1: 15,060 (F^-); 17,400 (H_2O); 26,600 (CN^-)

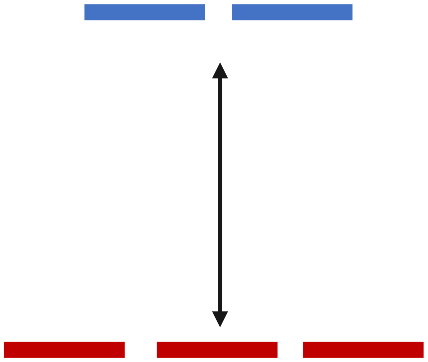
Electronic configuration of some n^{+} d^{n} metal cations in octahedral complexes

Complex	Valence electrons	Unpaired electrons	Electron configuration	Spin configuration
$Ti(H_2O)_6^{3+}$	$3d^{1}$	1	$(t_{2g})^{1}$	$(\uparrow)^{1}$
$Cr(H_2O)_6^{3+}$	$3d^{3}$	3	$(t_{2g})^{3}$	$(\uparrow\uparrow\uparrow)^{3}$
$Fe(H_2O)_6^{3+}$	$3d^{5}$	5	$(t_{2g})^{3}(e_g)^{2}$	$(\uparrow\uparrow\uparrow\ )^{\square}\square\uparrow\uparrow)^{\square}$
$Fe(CN)_6^{3-}$	$3d^{5}$	1	$(t_{2g})^{5}$	$(\uparrow\downarrow\uparrow\downarrow\uparrow)^{5}$
$Fe(H_2O)_6^{2+}$	$3d^{6}$	4	$(t_{2g})^{4}(e_g)^{2}$	$(\uparrow\downarrow\uparrow\uparrow)^{4}(\uparrow\uparrow)^{2}$
$Fe(CN)_6^{2-}$	$3d^{6}$	0	$(t_{2g})^{6}$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^{6}$
$Ni(H_2O)_6^{2+}$	$3d^{8}$	2	$(t_{2g})^{6}(e_g)^{2}$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^{6}(\uparrow\uparrow)^{2}$
$Cu(H_2O)_6^{2+}$	$3d^{9}$	1	$(t_{2g})^{6}(e_g)^{3}$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^{6}(\uparrow\downarrow\uparrow)^{3}$
$Zn(H_2O)_6^{2+}$	$3d^{10}$	0	$(t_{2g})^{6}(e_g)^{4}$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^{6}(\uparrow\downarrow\uparrow\downarrow)^{4}$

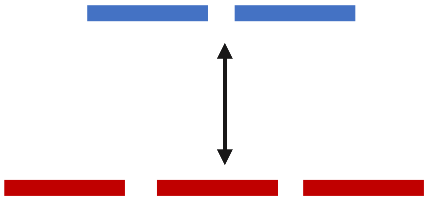
The Spectrochemical Series:

- The common ligands can be arranged in order of their increasing field strength (i.e., splitting power) in a series called the Spectrohemical Series.
- This order remains practically constant for different metals in the spectrochemical series.

I^- < Br^- < S^{2-}<Cl^-<NO_3^-<F^-<HO^-<EtOH<Oxalate< H_2O<EDTA<NH_3 & Py< ethlenediammine<dipyridine<O-phenanthroline<NO_2^-<CN^-<CO



Strong Field Ligand



Weak Field Ligand

- Ligand that give rise to high energy transition (such as CO) is referred to as a strong-field ligand; low energy transitions (such as Br-) referred to as weak-field ligand.

Distribution of Electrons in an Octahedral Complex

	High-spin	CFSE	Low-spin	CFSE
d^1	$t_{2g}^{1}\, e_g^{0}$	$-0.4\, \Delta\, o$	$t_{2g}^{1} e_g^{0}$	$-0.4\, \Delta\, o$
d^2	$t_{2g}^{2}\, e_g^{0}$	$-0.8\, \Delta\, o$	$t_{2g}^{2} e_g^{0}$	$-0.8\, \Delta\, o$
d^3	$t_{2g}^{3}\, e_g^{0}$	$-1.2\, \Delta\, o$	$t_{2g}^{3} e_g^{0}$	$-1.2\, \Delta\, o$
d^4	$t_{2g}^{3} e_g^{1}$	$-0.6\, \Delta\, o$	$t_{2g}^{4} e_g^{0}$	$-1.6\, \Delta\, o$
d^5	$t_{2g}^{3} e_g^{2}$	$0.0\, \Delta\, o$	$t_{2g}^{5} e_g^{0}$	$-2.0\, \Delta\, o$
d^6	$t_{2g}^{4} e_g^{2}$	$-0.4\, \Delta\, o$	$t_{2g}^{6} e_g^{0}$	$-2.4\, \Delta\, o$
d^7	$t_{2g}^{5} e_g^{2}$	$-0.8\, \Delta\, o$	$t_{2g}^{6} e_g^{1}$	$-1.8\, \Delta\, o$
d^8	$t_{2g}^{6} e_g^{2}$	$-1.2\, \Delta\, o$	$t_{2g}^{6} e_g^{2}$	$-1.2\, \Delta\, o$
d^9	$t_{2g}^{6} e_g^{3}$	$-0.6\, \Delta\, o$	$t_{2g}^{6} e_g^{3}$	$-0.6\, \Delta\, o$
d^{10}	$t_{2g}^{6} e_g^{4}$	$-0.0\, \Delta\, o$	$t_{2g}^{6} e_g^{4}$	$0.0\, \Delta\, o$

Net energy decrease is called crystal field stabilization energy (CFSE).

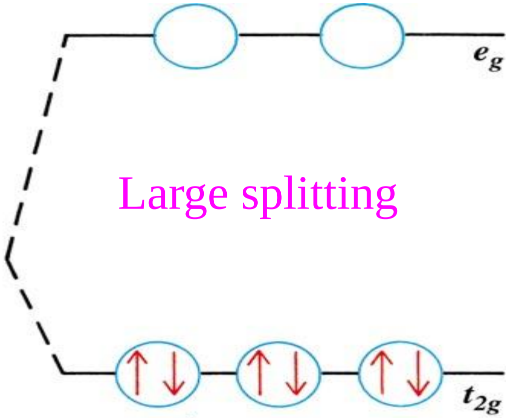
- There are two possibilities for metal ions having d^4-d^7 electronic configuration. Depending upon nature of the ligands and the metal ions they could be high-spin or low spin complexes. Weaker ligands tend to give high-spin complexes, whereas stronger ligands tend to give low-spin complexes.

- In all electronic configurations involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons (i.e. Pairing Energy, P).

Crystal Field Splitting of d orbitals: high spin and low spin situations for a d^6 metal

Ligand strength: (Weak) $I^- < F^- < H_2O < NH_3 < CN^-$ (Strong)

Case I: Low spin



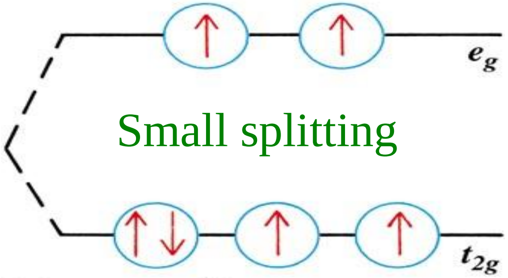
Large splitting

(a) $Fe(CN)_6^{4-}$ (low spin)

Net unpaired
spins = 0:
Diamagnetic

Energy gap larger than advantage due to Hund's rule

Case II: High spin



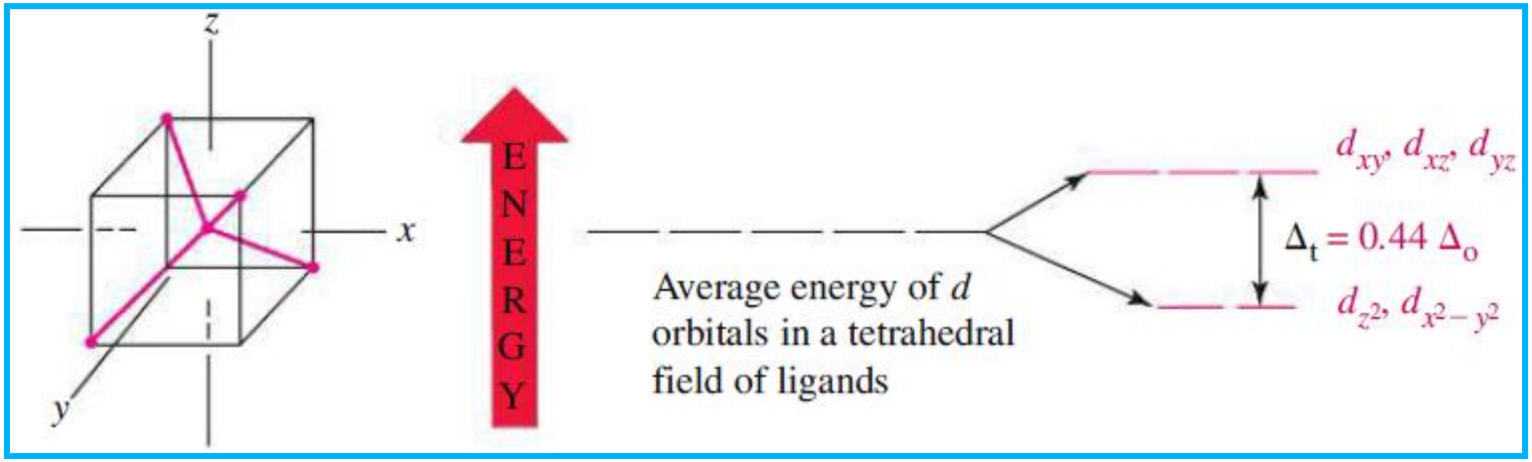
Small splitting

(b) $Fe(H_2O)_6^{2+}$ (high spin)

Net unpaired
spins = 4:
Strongly paramagnetic

Energy gap small;
Hund's rule applies

CF Splitting: Tetrahedral Field



- Suppose a tetrahedral molecule is present inside the cube and metal ion is seated at the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

- It has no center of symmetry. So there is no question of mentioning ‘g’ or ‘u’ terms.

- The two ‘e’ (d_{x2-y2} and d_{z2}) orbitals point to the center of the face of the cube while the three ‘t_2’ (d_{xy}, d_{yz} and d_{zx}) orbitals point to the center of the edges of the cube.

- Thus, the t_2 orbitals are nearer to the direction of approach of the ligands than the e orbitals. (The ligands do not directly approach any of the metal d orbitals)

Continued……

❖ Tetrahedral complexes are high spin:

- There are only 4 ligands in the tetrahedral complex and hence the ligand field is roughly 2/3 of the octahedral field.

- The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly $2/3 \times 2/3 = 4/9$ of Δ_o.

- As a result, all tetrahedral complexes are high-spin since the Δ_t is normally smaller than the paring energy (P). Hence, low spin configurations are rarely observed. Usually, if a very strong field ligand is present, square planar geometry will be favored.

❖ When do we expect tetrahedral geometry?

- Small metal ions and large ligands (Cl^-, Br^- and I^-) because then ligand-ligand repulsions cancel the energy advantage of forming more metal-ligand bonds.

- Metal ions with zero CFSE (d^0, d^5, d^{10}) or small CFSE (d^2 and d^7).

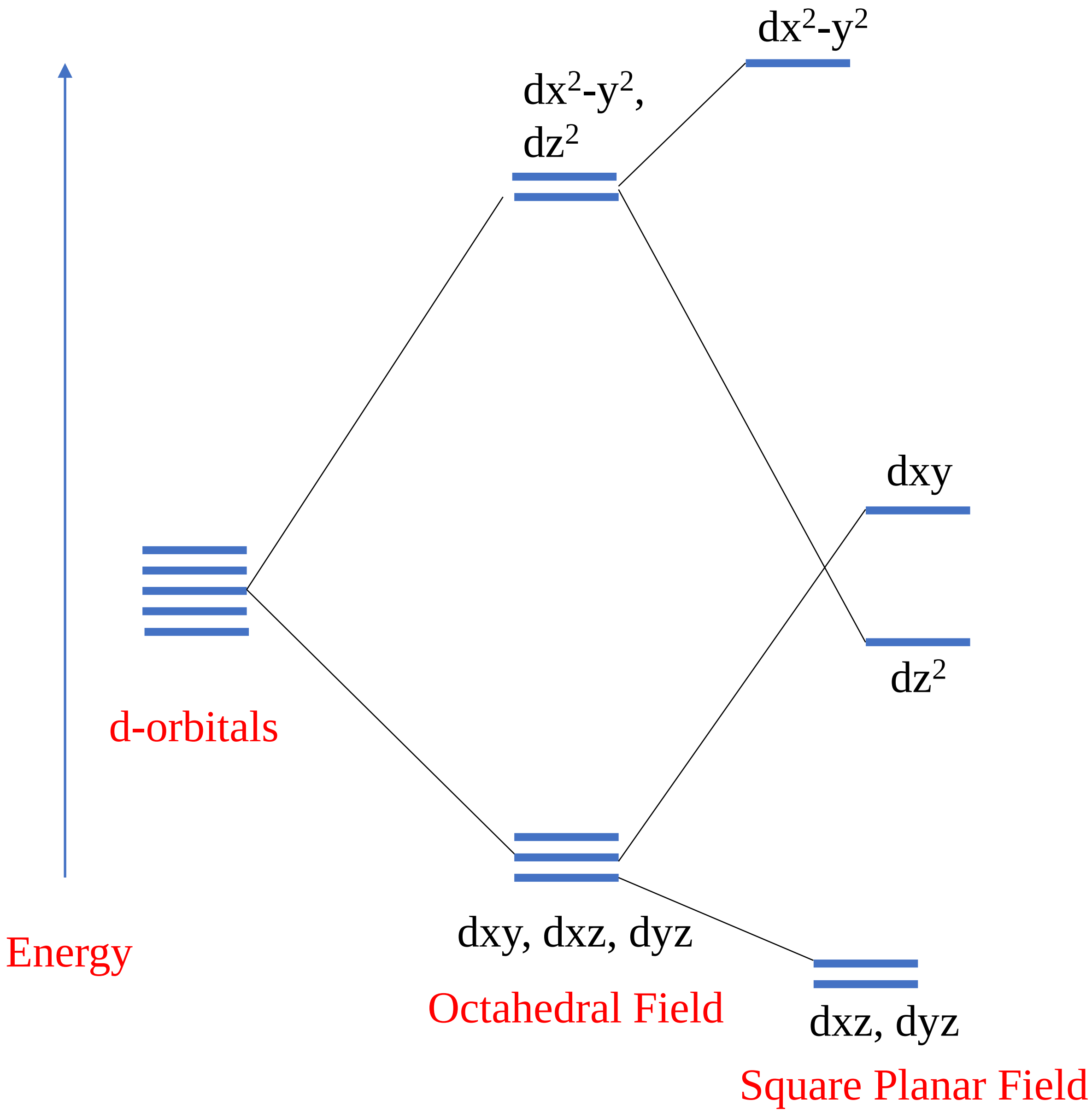
Examples: MnO_4^- (d^0), $FeCl_4^-$ (d^5, h.s.), $CoCl_4^{2-}$ (d^7, h.s.), $ZnCl_4^{2-}$ (d^{10})

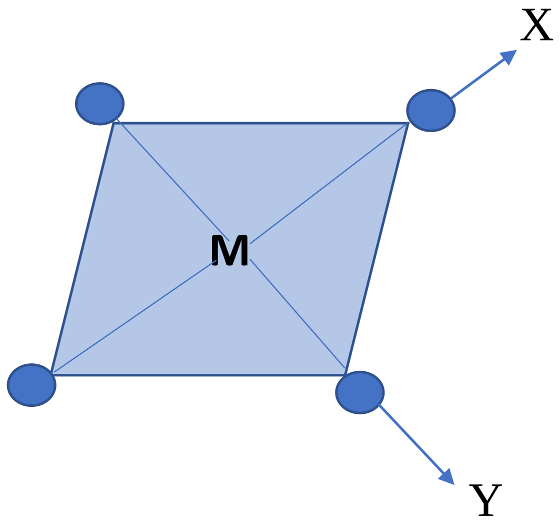
Distribution of Electrons in a Tetrahedral Complex

- Tetrahedral splitting is seldom large enough to result in pairing of the electrons. As a result, low-spin tetrahedral complexes are not common. A rare example is $Cr[N(SiMe_3)_2]_3[NO]$.

	Electronic configuration	CFSE
d^1	e^1t_2	-0.6 Δt
d^2	e^2t_2	-1.2 Δt
d^3	$e^2t_2^1$	-0.8 Δt
d^4	$e^2t_2^2$	-0.4 Δt
d^5	$e^2t_2^3$	0.0 Δt
d^6	$e^3t_2^3$	-0.6 Δt
d^7	$e^4t_2^3$	-1.2 Δt
d^8	$e^4t_2^4$	-0.8 Δt
d^9	$e^4t_2^5$	-0.4 Δt
d^{10}	$e^4t_2^6$	0.0 Δt

CF Splitting: Square Planar Field





- Ligands along the Z axis are removed from an octahedral complex to get a square planar complex.

When to Expect Square Planar Geometry .

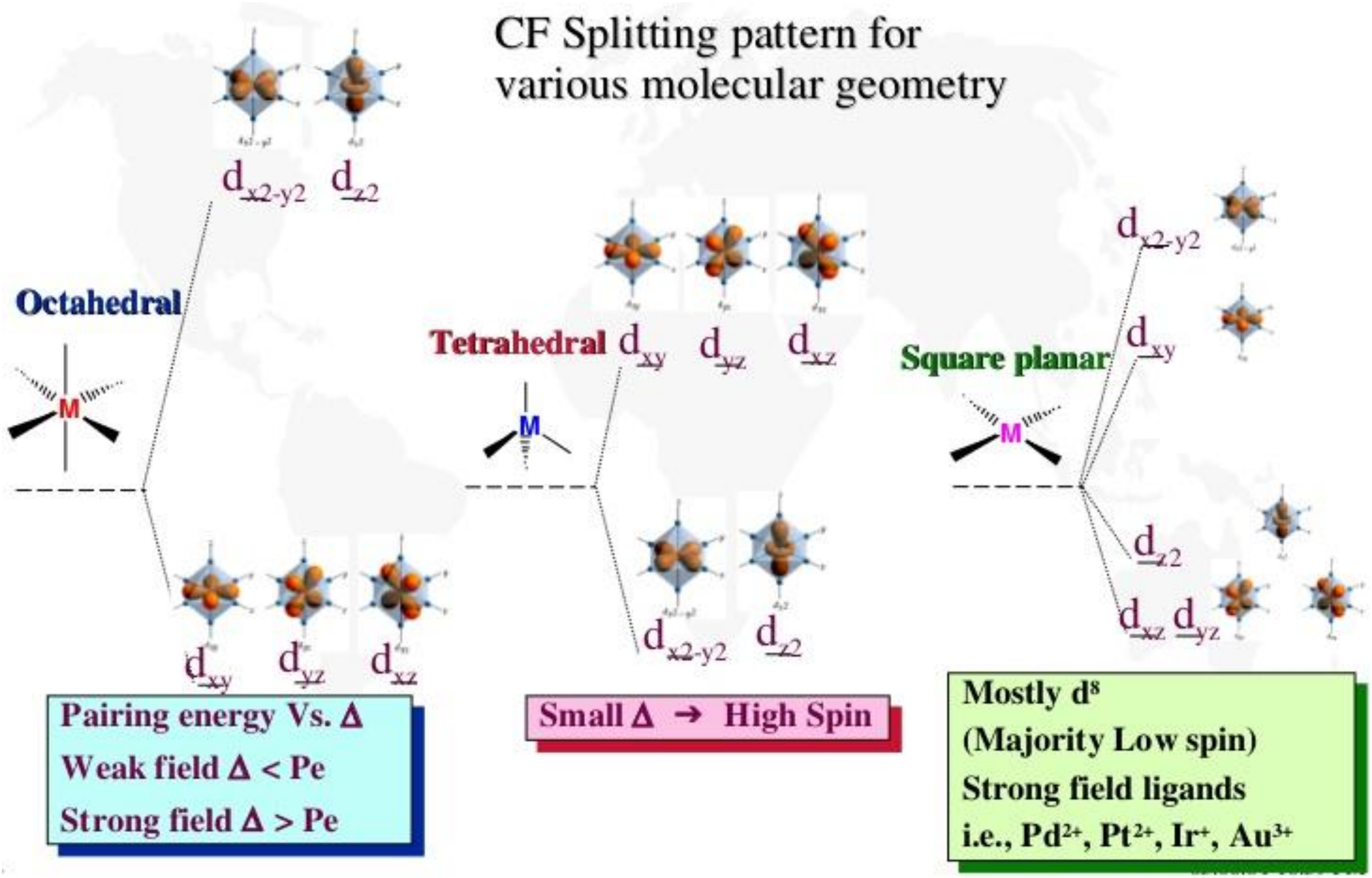
❖ In the case of d^8 metals and strong ligands:

Ni^{2+}, in the presence of strong field ligands such as CN^- forms a square planar complex.

❖ 2nd and 3rd row d^8 metals form square planar geometry irrespective of the nature of the ligand:

With Pd^{2+} (which already generates a strong field) even a weak field ligand such as Cl^- leads to the formation of a square planar complex, for example, $[PdCl_4]^{2-}$.

CF Splitting: Octahedral Vs. Tetrahedral Vs. Square Planar



CF Splitting pattern for various molecular geometry

Pairing energy Vs. Δ

Weak field Δ < Pe

Strong field Δ > Pe

Small Δ → High Spin

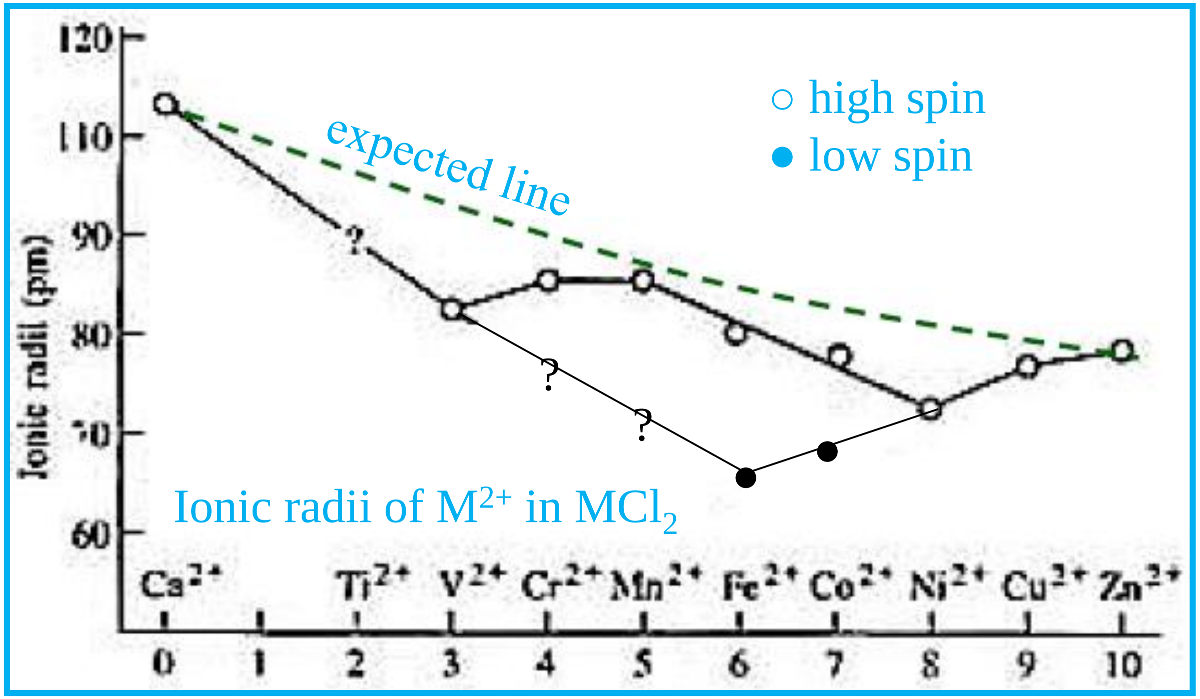
Mostly d^8

(Majority Low spin)

Strong field ligands

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

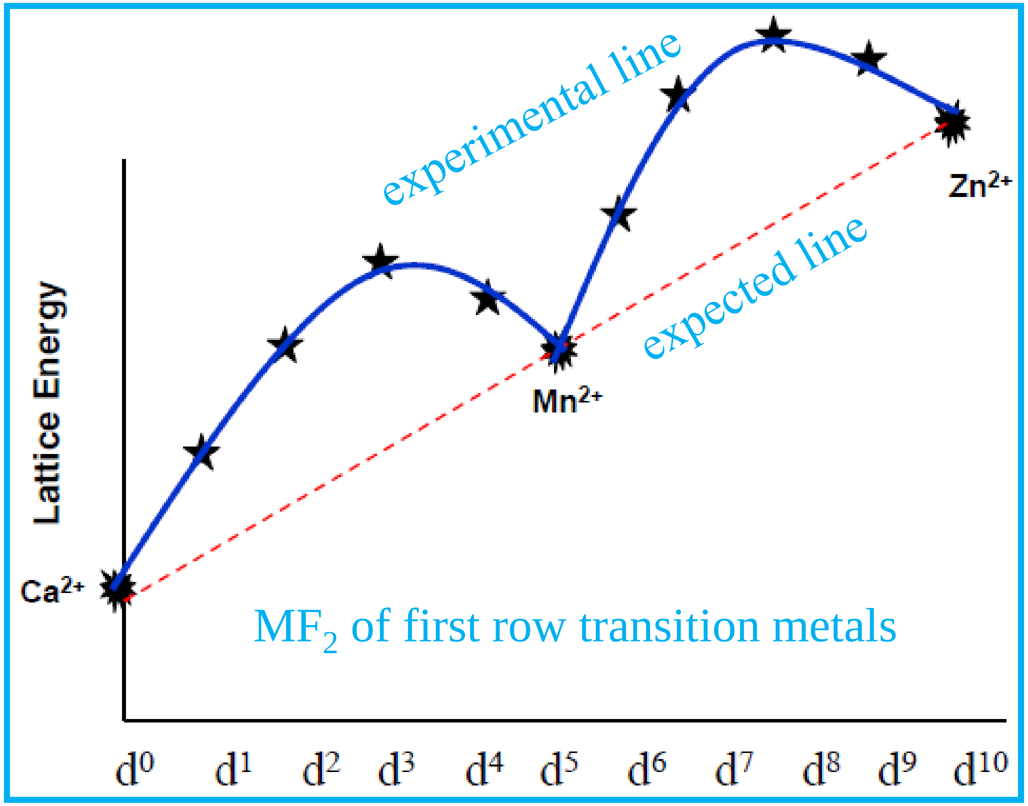
Applications of Crystal Field Theory: Ionic Radii



- For a given oxidation state, the ionic radius is expected to decrease continuously across a transition series. Deviations from the expected line can be attributed to different electronic configurations (resulting from crystal field splitting).

- For weak field case, ionic radius starts to increase with $t_{2g}^3e_g^1$ configuration as the electron in the e_g level experience repulsion with the ligands. For strong field case, ionic radius starts to increase with $t_{2g}^6e_g^1$ configuration.

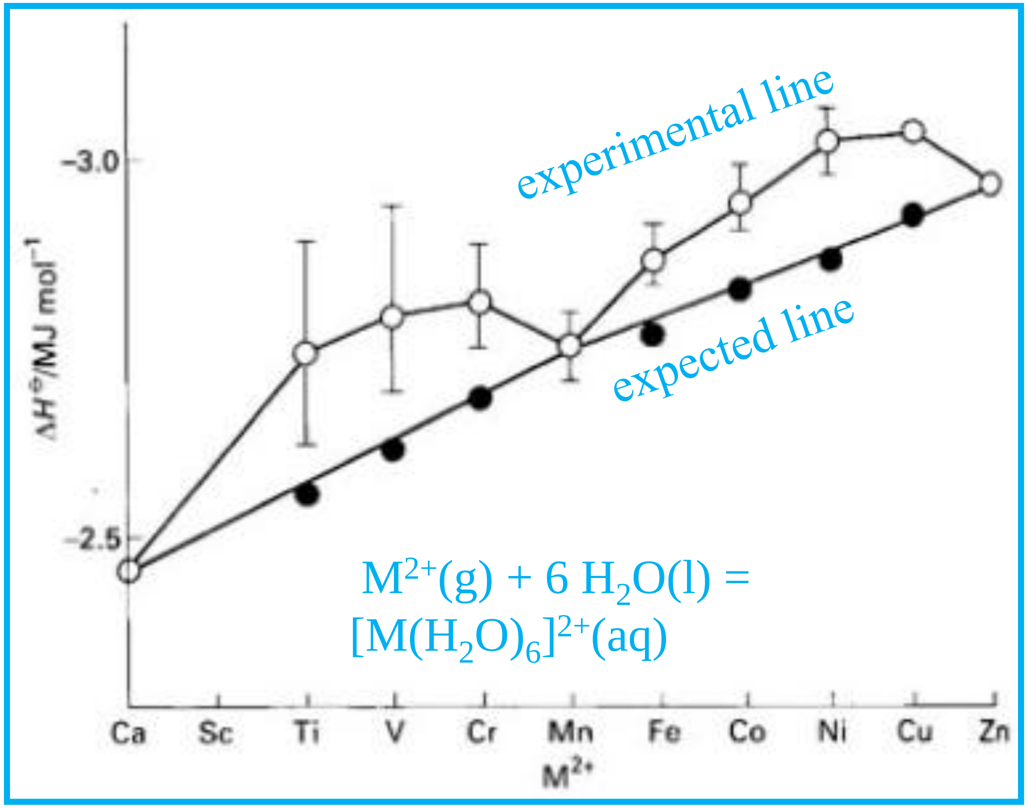
Applications of Crystal Field Theory: Lattice Energy



- The lattice energy is expected to increase continuously across the transition series as the ionic radii of the metals decrease (lattice energy is proportional to $1/(r^+ + r^-)$). Deviations from expected line can be attributed to CFSE.

- Ca^{2+}, Mn^{2+} and Zn^{2+} have d^0, d^5 and d^{10}, thus CFSE is 0. They follow the expected line. Other metal ions deviate from the expected line due to extra CFSE. CFSE increases from d^1 to d^3, decreases again to d^5, then rises to d^8.

Applications of Crystal Field Theory: Enthalpy of Hydration/Formation



$M^{2+}(g) + 6\ H_2O(l) = [M(H_2O)_6]^{2+}(aq)$

❖ Stronger electrostatic attraction energy between ions and water dipoles increases hydration enthalpy (ΔH). ΔH is proportional to the charge but inversely proportional to the radius of the ion. ΔH should increase (become more negative) continuously across transition series due to decrease in ionic radii. But, experimental ΔH values show characteristic double-humped shape.

❖ The trend for hydration enthalpies corresponds with the one for the ionic radii.

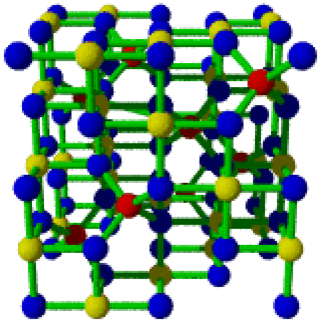
Applications of Crystal Field Theory: Geometry of Spinel

- The spinel is a **MIXED METAL OXIDE** with a general formula $(A^{2+})(2B^{3+})(O^{2-})_{4.}$ 'A' is a bivalent Gr II or a bivalent transition metal and 'B' is a trivalent Gr III metal or a trivalent transition metal.

- Close packing of oxide ion (weak field ligand) provides a cubic lattice containing both tetrahedral and octahedral holes.

- In normal spinel B(III) ion occupy octahedral holes whereas in case of inverted spinel A(II) ion occupy the octahedral holes and half of the B(III) ion occupy the tetrahedral holes.

- The difference in CFSE for a d^n system in octahedral and tetrahedral geometry is called Octahedral Site Stabilization Energy (OSSE).



So

How does CFT help us understand this structure?

Spinel structures and CFT

Normal Spinal Structure.

Spinel: $MgAl_2O_4$

Both Mg(II) and Al(III) are d^0 system. So there will be no spatial preference on CFSE ground.

So, M^{2+} ion occupy tetrahedral holes and M^{3+} ion occupy octahedral holes.

Inverse Spinal Structure.

Example: Magnetite: $(Fe^{3+})_T(Fe^{2+},Fe^{3+})_O(O^{2-})_4$

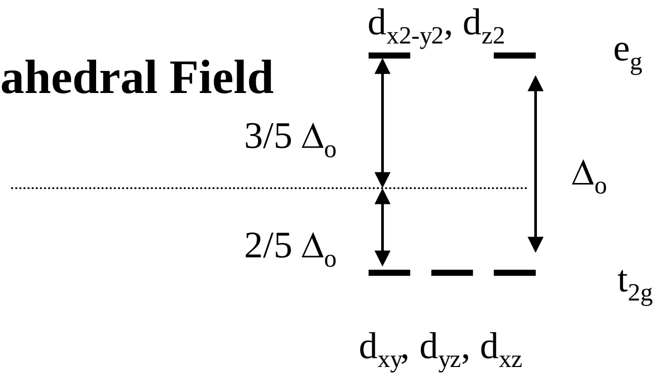
Fe_3O_4 $(Fe^{2+}, 2Fe^{3+}, 2O^{2-})$

Note the O^{2-} is a weak field ligand. (Fe is H.S.)

What are the electron configurations of the Fe ions?

$Fe^{3+}$is d^5 and Fe^{2+} is d^6.

Octahedral Field



d_{x2-y2}, d_{z2}

e_g

3/5 Δ_o

Δ_o

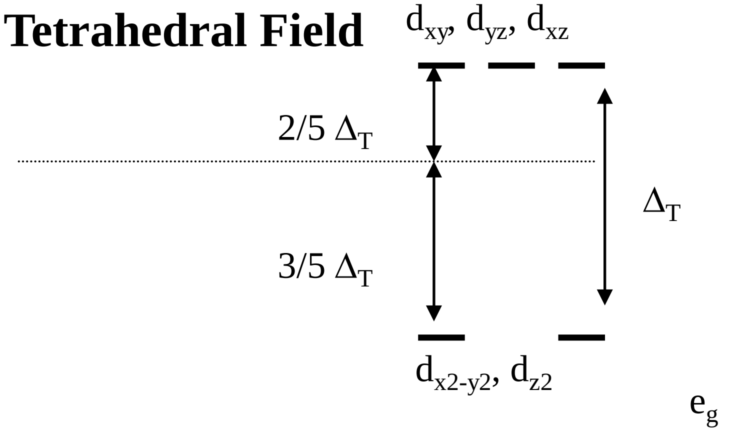
2/5 Δ_o

t_{2g}

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

OR

Tetrahedral Field



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

2/5 Δ_T

Δ_T

3/5 Δ_T

d_{x2-y2}, d_{z2}

e_g

Fe (II): CFSE(Oh)=-4 Dq

Fe(III): CFSE (Oh) = 0 Dq

Inverse Spinal

Mn_3O_4 Spinel Structure:

Mn(II) d^5 system CFSE = 0 for both Oh and Td field under weak field.
Mn (III) d^4 system CFSE = -0.6 Dq (Oh) and -0.4 Δt.

Inverted Spinel Structure

Co_3O_4 Spinel Structure:

Co(II) d^7 system CFSE = -0.8 Δo (Oh) and -1.2 Δt (Td)
Co(III) d^6 system CFSE = -0.4 Dq (Oh) and -0.6 Δt. (Td)
CFSE (d^6, low spin) = -24 Dq

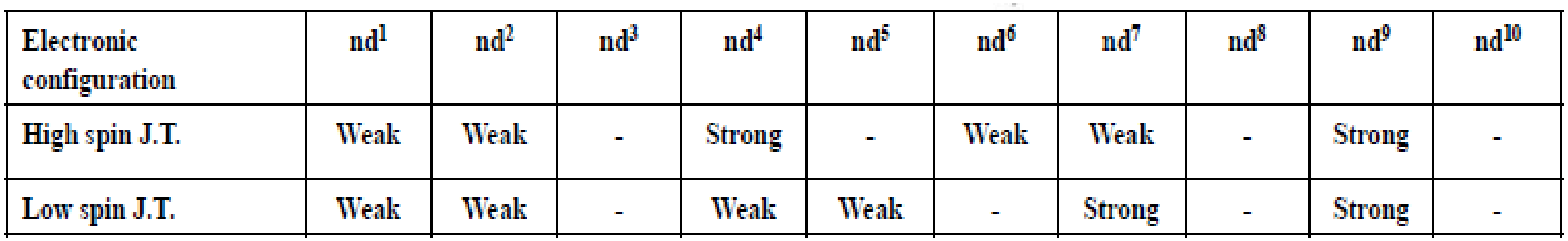
- Because of very high CFSE of d^6 system in low spin situation, instead of having high spin environment provided by oxide ions Co(III) adopts low spin and occupy octahedral holes Spinel Structure.

Result : Normal Spinel Structure.

Jahn-Teller Effect & CFT

- **Theorem:** In a nonlinear molecule, if degenerate orbitals are asymmetrically occupied, a distortion will occur to remove the degeneracy by lowering the symmetry and thus by lowering the energy.

- The theorem predicts which configurations will show distortions.



Electronic configuration	nd^1	nd^2	nd^3	nd^4	nd^5	nd^6	nd^7	nd^8	nd^9	nd^{10}
High spin J.T.	Weak	Weak	-	Strong	-	Weak	Weak	-	Strong	-
Low spin J.T.	Weak	Weak	-	Weak	Weak	-	Strong	-	Strong	-

- Octahedral complexes that are susceptible to Jahn-Teller distortions have degeneracy either in t_{2g} or e_g set of orbitals. The effect is most pronounced when degeneracy occurs in the e_g than the t_{2g} set of orbitals, because e_g orbitals are pointing directly at the ligands. Hence, complexes with e_g^1 or e_g^3 configurations (high spin d^4, low spin d^7 and d^9) will show significant distortions.

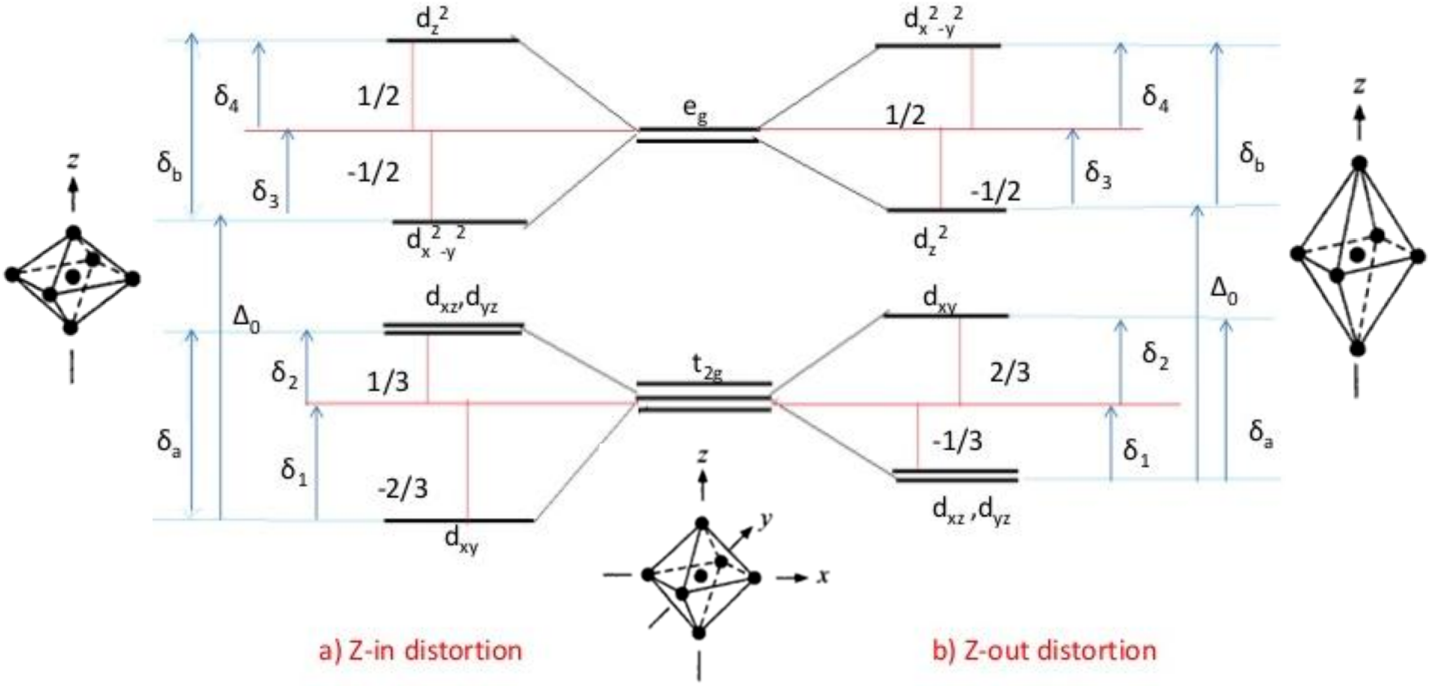
Types of Jahn-Teller Distortions

- **Axial Elongation (z-out distortion):** Occurs when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z-component, while the orbitals without a z-component are destabilized (higher in energy).

- **Axial Compression (z-in distortion):** Occurs when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals without a z-component, while the orbitals with a z-component are destabilized (higher in energy).

- The theorem can not predict the type of distortion occurs (z-out vs. z-in). However, because axial elongation weakens two bonds but equatorial elongation weakens four, axial elongation (z-out) is more common than axial compression (z-in).

Jahn-Teller Effect: Energy Level Splitting Patterns



$$\boxed{(n\times\delta_1)+(n\times\delta_2)+(n\times\delta_3)+(n\times\delta_4)}$$

- It is not possible to predict the magnitude of these splittings because the extent of distortions can not be predicted. However, we can say that the splitting of the e_g orbitals will be significantly larger than that of the t_{2g} orbitals because t_{2g} orbitals in an octahedral complex do not point directly at the ligands.

- Since none of the d orbitals in a tetrahedral complex point directly at the ligands, the distortion is too small and thus it is not measurable.

Jahn-Teller Effect: Explanation

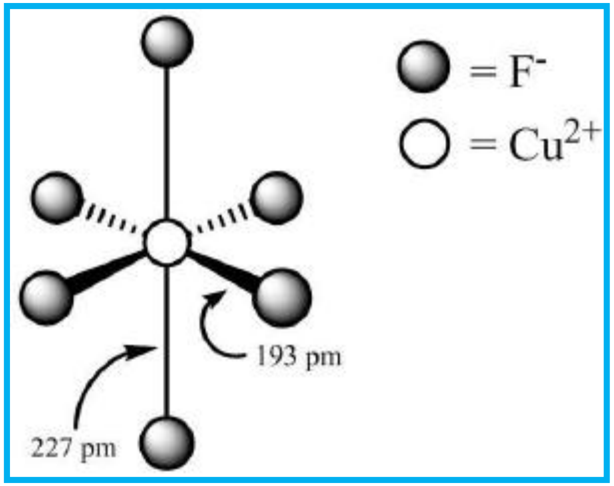
- If one or three electrons occupy the e_g orbitals (as in high-spin d^4, low-spin d^7 and d^9 complexes) a tetragonal distortion may be energetically advantageous.

- For example, in a high spin d^4 ion ($t_{2g}^3e_g^1$), if the last electron occupies d_{z2} orbital, most of the electron density will be concentrated between the cation and the two ligands on the z axis. Thus, there will be greater electrostatic repulsion associated with these ligands than with the other four ligands and the complex suffers elongation. Conversely, if the last electron occupies d_{x2-y2} orbital, elongation will occur along x and y axes. Similar situations will arise for a low spin d^7 ion ($t_{2g}^6e_g^1$).

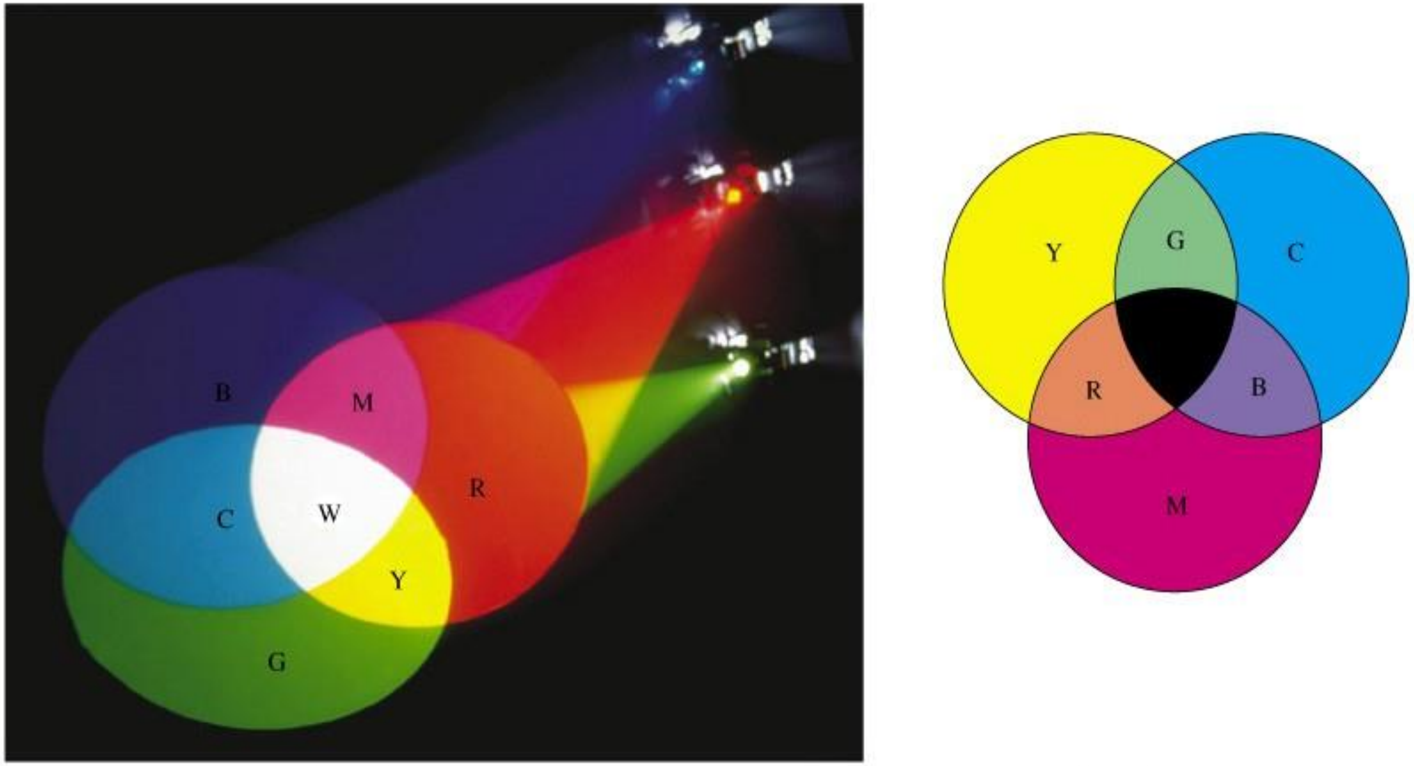
- Another example: for the d^9 configuration, two orbitals in the e_g set are occupied by one and two electrons, respectively. If two electrons occupies d_{z2} orbital and the third electron occupies d_{x2-y2} orbital, most of the electron density will be concentrated between the cation and the two ligands on the z axis. Thus, there will be greater electrostatic repulsion associated with these ligands than with the other four ligands and the complex suffers elongation. Conversely, if two electrons occupies d_{x2-y2} orbital and the third electron occupies d_{z2} orbital, elongation will occur along x and y axes.

Jahn-Teller Effect: Experimental Evidences

- **X-ray Crystallography:** In X-ray crystal structures, octahedral complexes having large distortions show different axial and equatorial bond lengths. For CuF_2, two axial bonds are elongated and four shorter equatorial bonds are the same length with each other.



The Origin of Colour : ABSORPTION

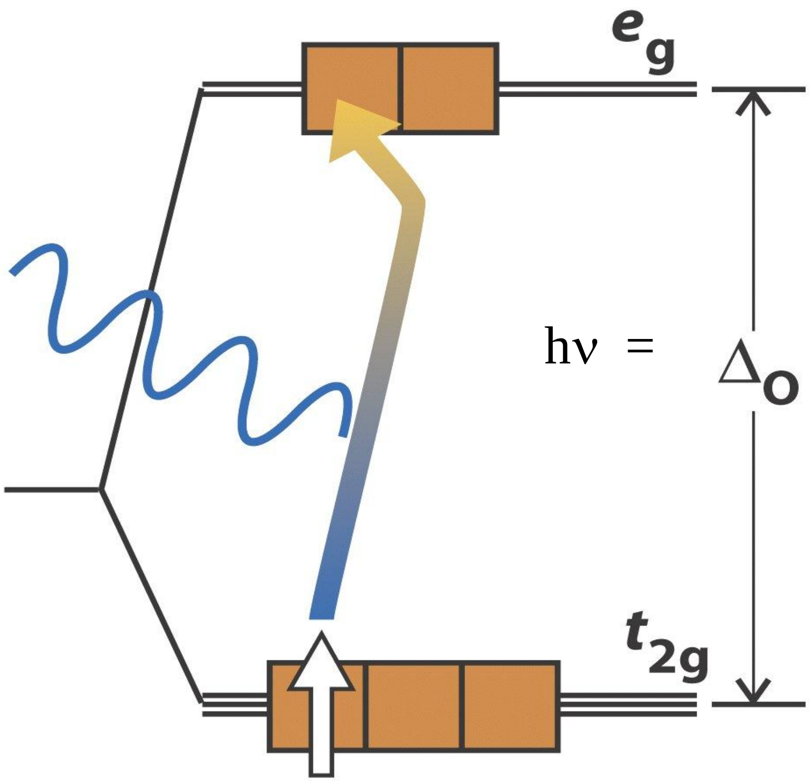


(a) Additive color mixing

(b) Subtractive color mixing

Artists wheel showing the colours which are complementary to one another.

Continued……..



Electron jumps from a t_{2g} to an e_g orbital due to absorption of a photon.

Condition of absorption:

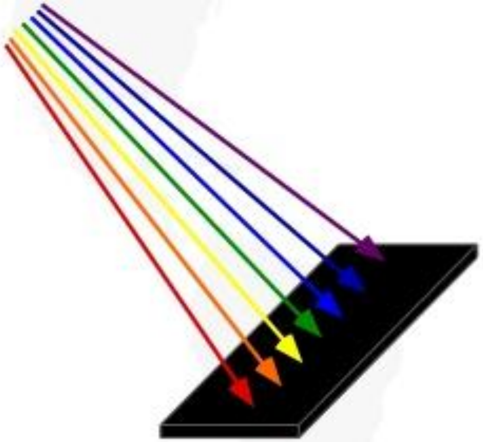
Δ_0, (the crystal field splitting parameter) equals the energy of a photon:

$\Delta_0 = h\nu = \Delta E$

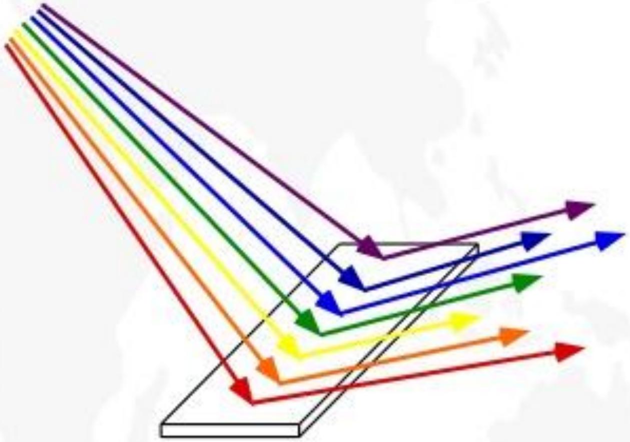
As Δ_0, varies, hν will also vary and consequently the color of the metal complexes will also change.

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.

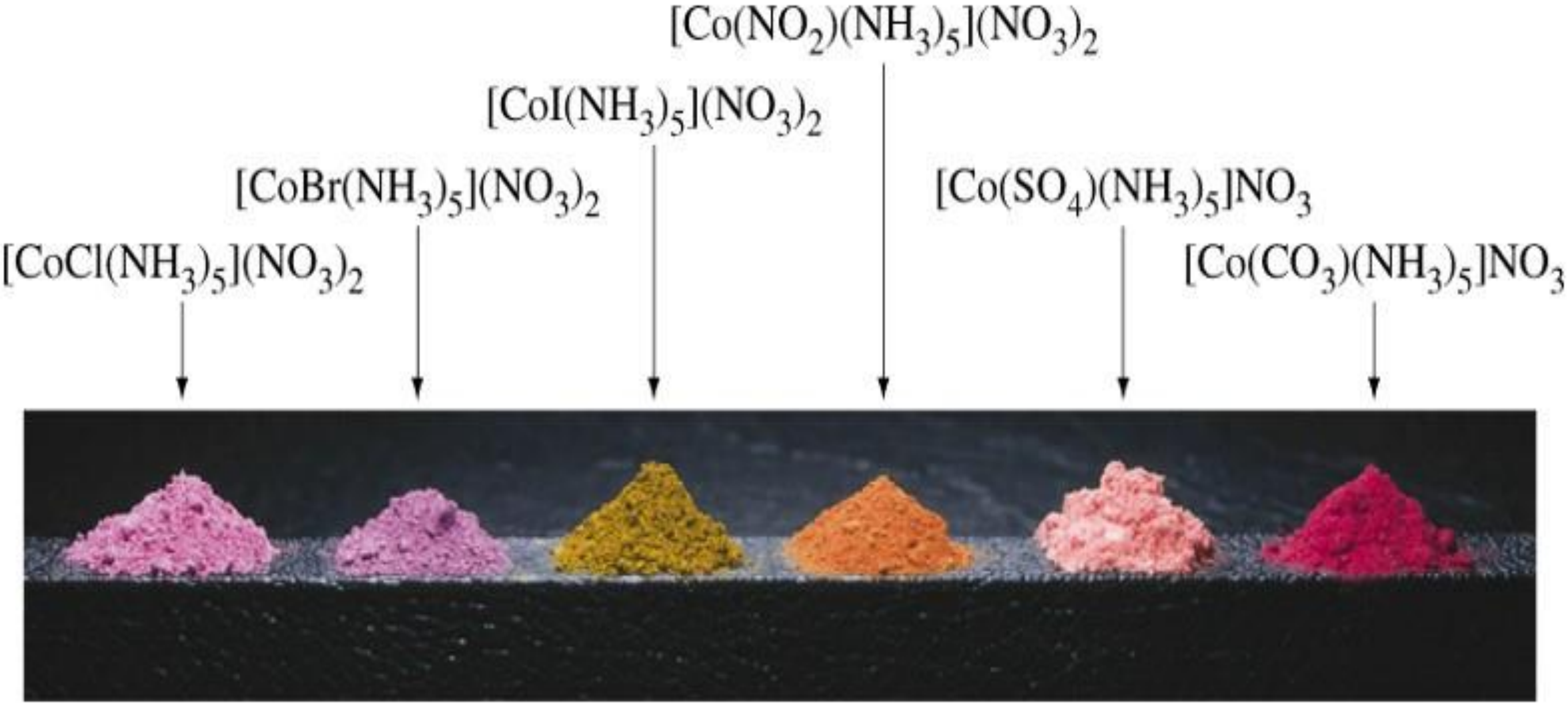


If the sample absorbs no visible light, it is white or colorless.

Range of Colour:

The colour of the complexes depends on the following factors:

- Charge on the metal ion
- Ligand



Measurement of Magnetic Moment:

The spin-only magnetic moment, μ, of a complex with total spin quantum number is given by:

$$\mu = \sqrt{S(S+1)}\,\mu_B$$

μ_B = Bohr magneton

Used to determine the number of unpaired spins in a complex, hence identify its ground-state configuration.

Compounds are classified as diamagnetic if they are repelled by a magnetic field and paramagnetic if they are accepted by a magnetic field.

CALCULATED SPIN-ONLY MAGNETIC MOMENTS

ION	N	S	μ/μ_B CALC.	EXPT.
Ti^{3+}	1	½	1.73	1.7-1.8
V^{3+}	2	1	2.83	2.7-2.9
Cr^{3+}	3	1½	3.87	3.8
Mn^{3+}	4	2	4.90	4.8-4.9
Fe^{3+}	5	2½	5.92	5.9

Examples:

The magnetic moment of a certain Co(II) complex is 4.0 μB . What is its *d*- electron configuration?

Solution:

A Co(II) complex is d^{7}.

Two possible configurations: $t_{2g}^{5}e_{g}^{2}$ (high-spin, S = 1½) with 3 unpaired electrons or $t_{2g}^{6}e_{g}^{1}$ (Low-spin, S = ½) with 1 unpaired electron.

The spin-only magnetic moments are 3.87 μ_B and 1.73 μ_B.

Therefore, the only consistent assignment is the high-spin configuration $t_{2g}^{5}e_{g}^{2}$.

Exercise:

The magnetic moment of the complex $[Mn(NCS)_6]^{4-}$ is 6.06 μB. What is its electron configuration?

Summary:

- Crystal field Theory provides a basis for explaining many properties of metal complexes like:
  i) colour of the metal complexes
  and ii) magnetic properties.

- Spectrochemical Series also provides a good explanation of the origin of colour.

THANK YOU