

Inorganic Chemistry (CY11001)

Bonding in coordination compounds: CFT

Books to Refer:

Inorganic Chemistry by Shriver & Atkins

Inorganic Chemistry by James E. Huheey

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Bonding in coordination compounds: CFT

- Introduction....1704 (PB)...1799 (CoCl₃.
*n*NH₃) by Tassaert)
- Jorgensen....
- Alfred Werner - 1893
- VBT : Pauling & Slater (1935)
- **To LEARN: Crystal Field Theory (CFT):
Hans Bethe**
- Modified CFT/ Ligand Field Theory / MOT
van Vleck (1935)

Nobel prize 1913



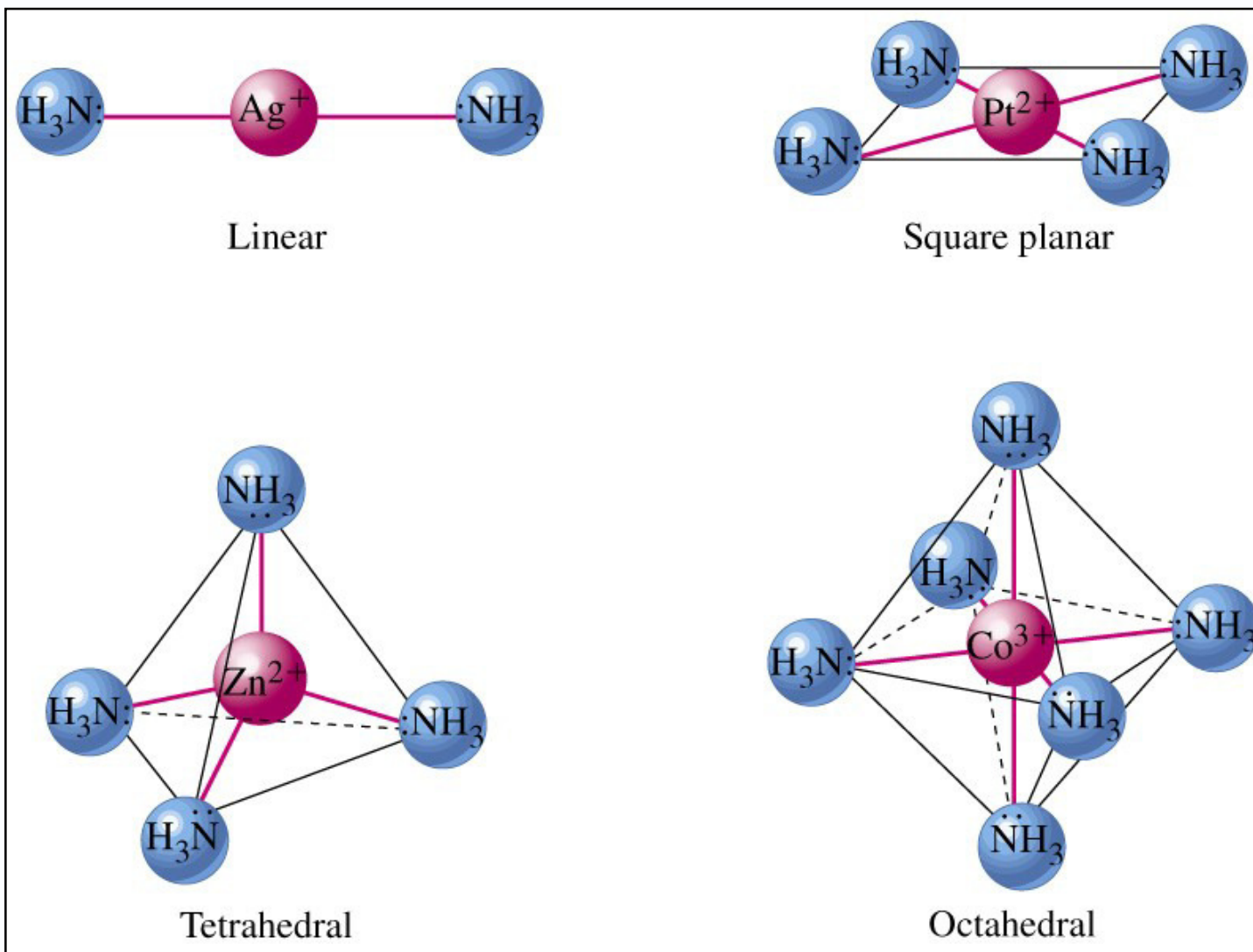




Gemstone owe their color from trace transition-metal ions

- Mineral of Al: Colorless
- Cr → Al : Ruby
- Fe → Al: Topaz
- Ti & Co → Al: Sapphire
- Cr → Al : Emerald
- Fe → Al : Aquamarine

How & Why?



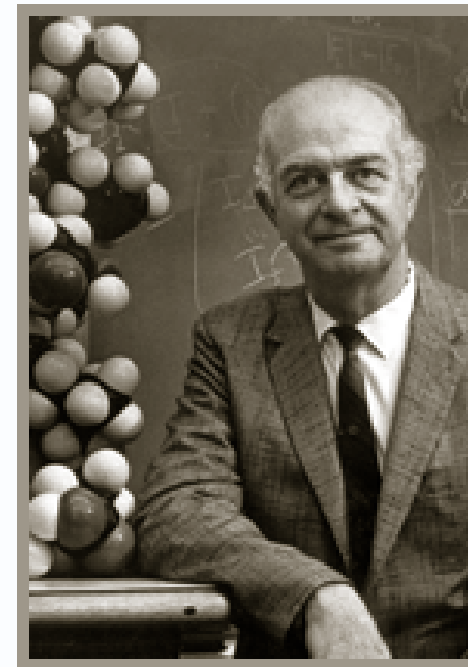
Werner's theory can't predict the geometry of the complex

Valance Bond Theory

Basic Principle

A covalent bond forms when the orbitals of two atoms overlap and are occupied by a pair of electrons that have the highest probability of being located between the nuclei.

covalent bond/ coordinate covalent bond



Linus Carl Pauling
(1901-1994)

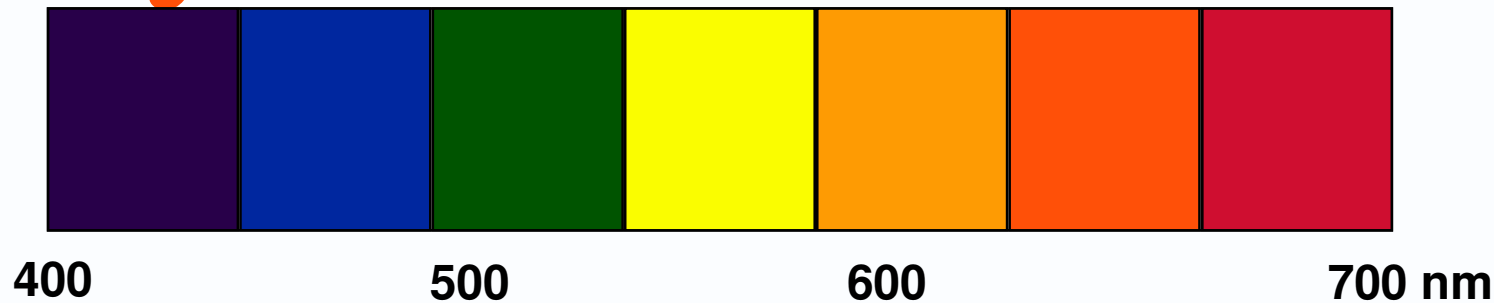
Nobel prizes: 1954, 1962

Limitations of VB theory

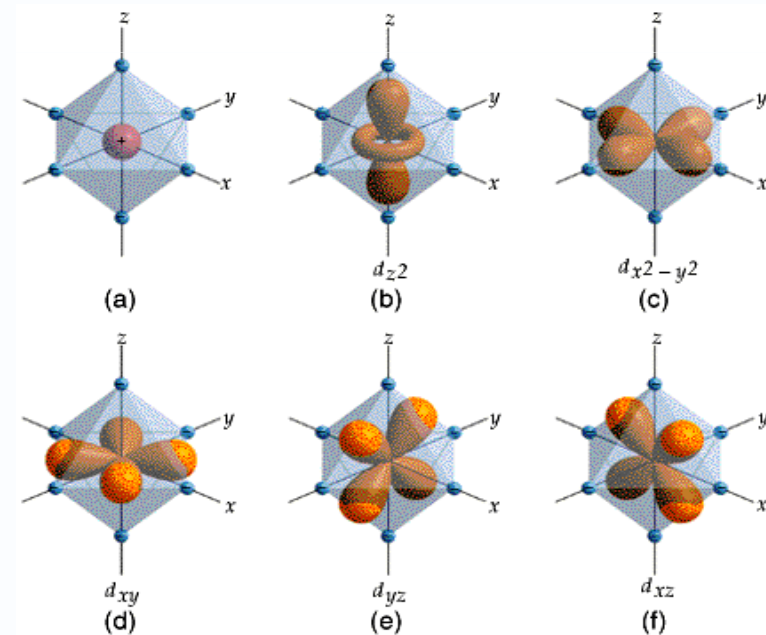
Cannot account for colour of complexes

Cannot account for spectrochemical series

Crystal Field Theory

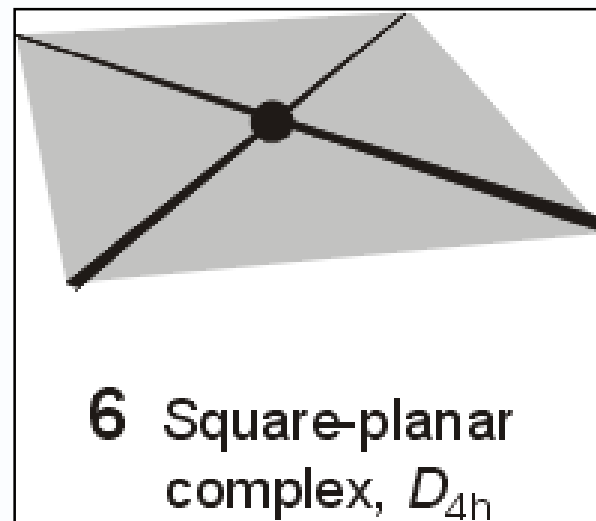
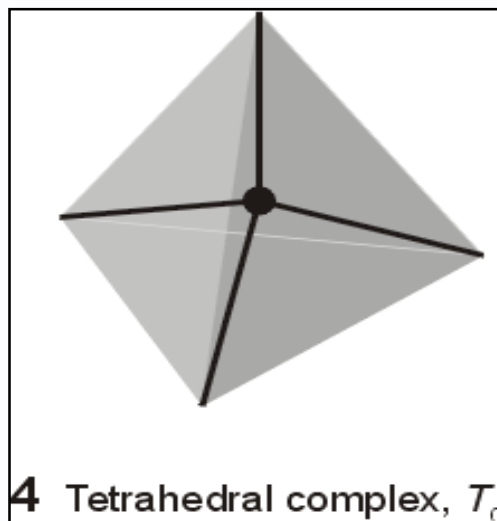
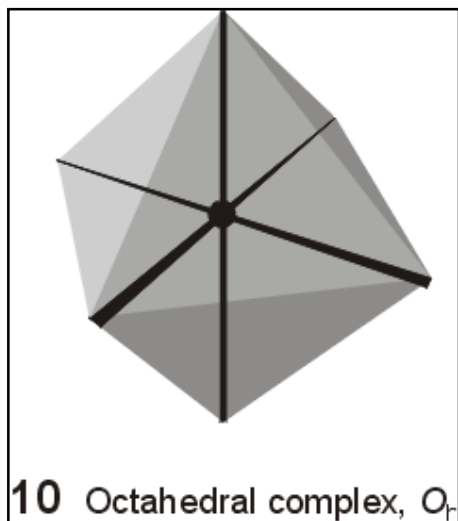


- The relationship between colors and complex metal ions



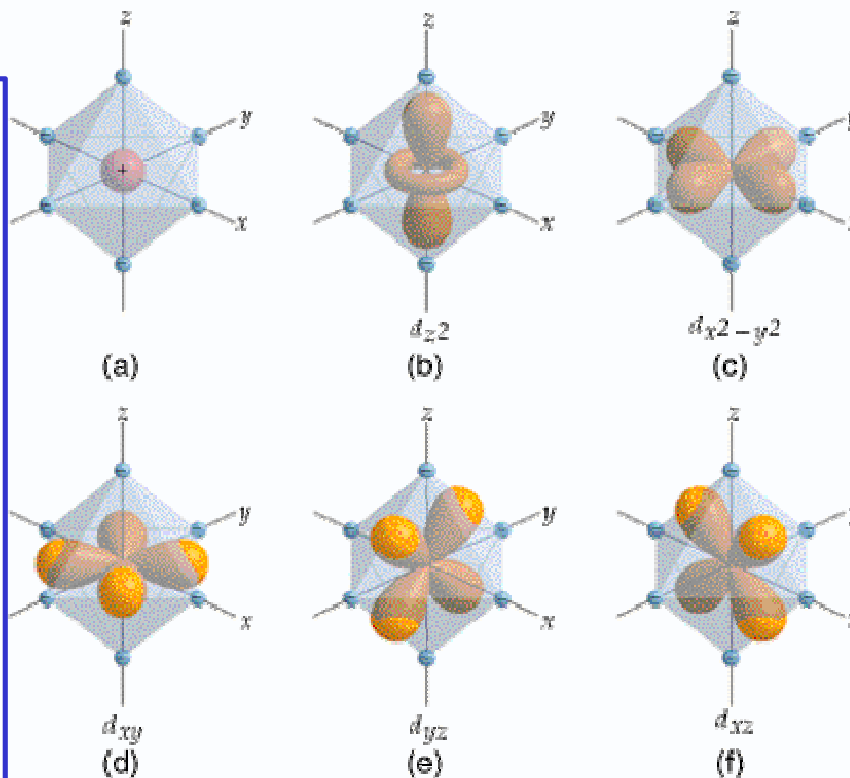
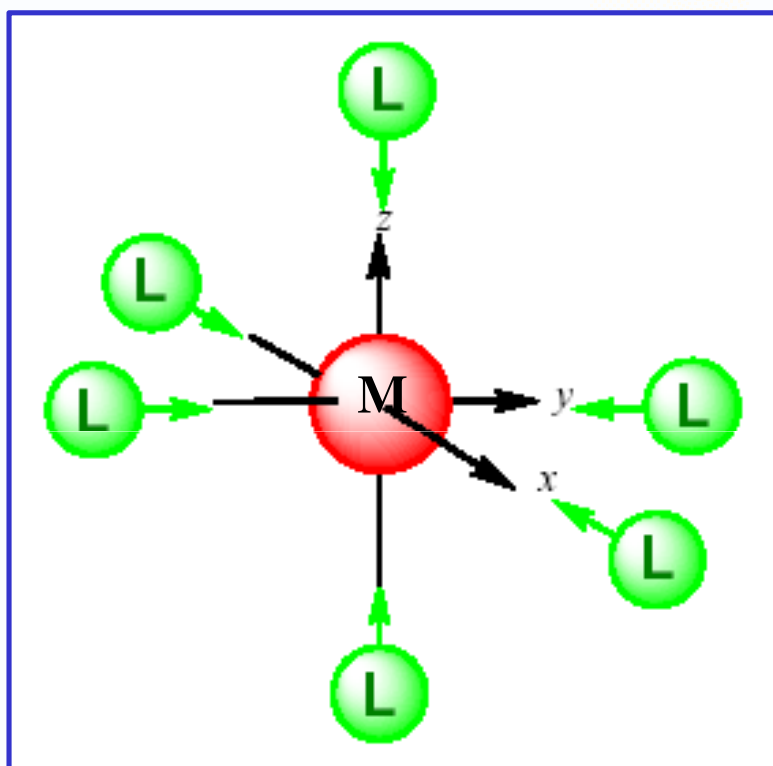
Crystal Field Model

- No orbital overlap, no existence of covalent bonding.
- A purely *ionic* model for transition metal complexes.
- Ligands are considered as point charge.
- Predicts the pattern of splitting of d-orbitals.
- Used to rationalize spectroscopic and magnetic properties.



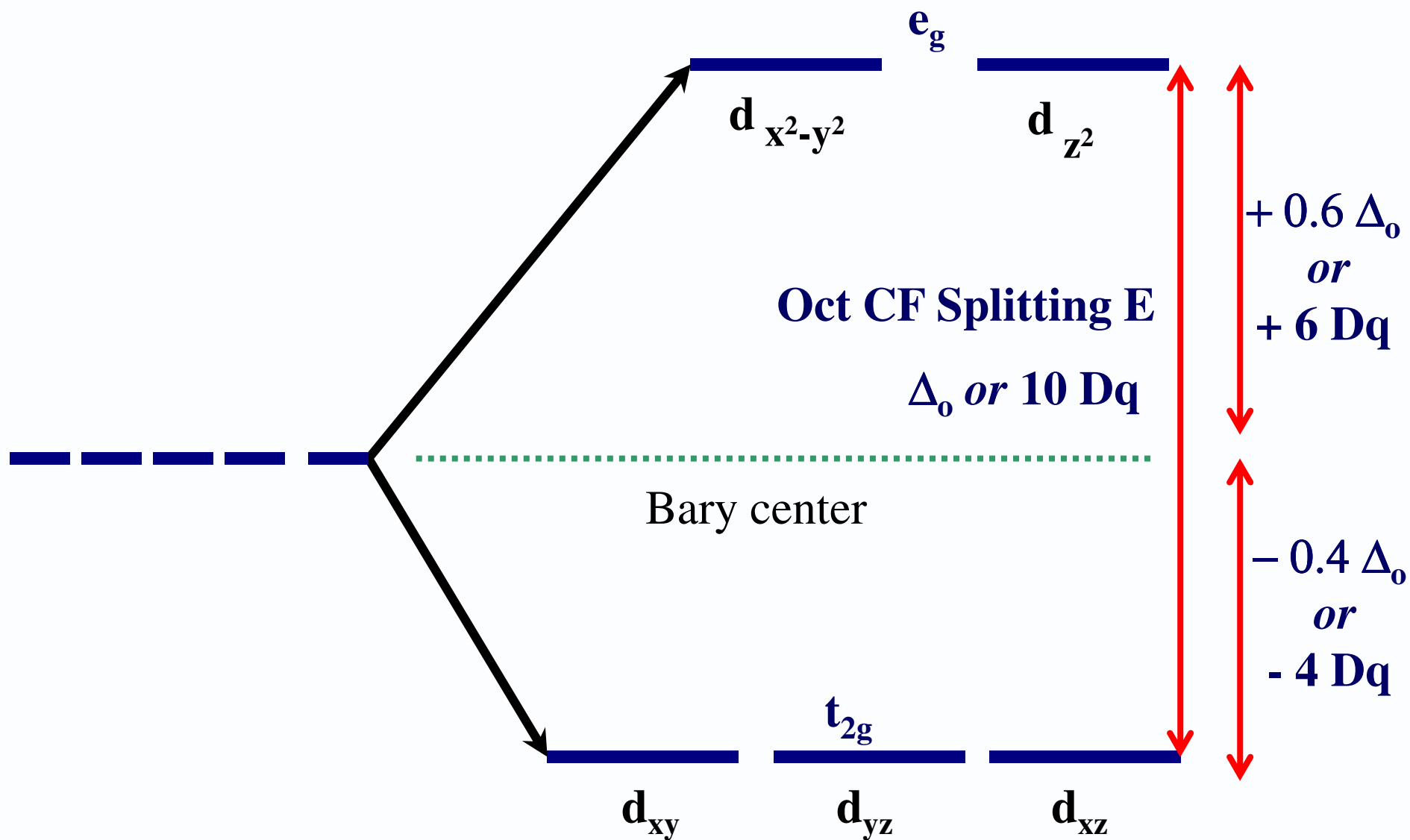
predicts the geometry of the complex

Octahedral Field



- The ligands are approaching along the axes
- The orbitals directed along the axes will experience more repulsive force
- Thus, $d_{x^2-y^2}$ & d_{z^2} will experience stronger repulsion than.....

Oct CF Splitting



Crystal Field Stabilization Energy

d^1, d^2, d^3 ...only one arrangement possible

$d^4 d^5 d^6 d^7$

- In weak/low field (HS): $\Delta_o < P$, $\Rightarrow t_{2g}^3 e_g^1$
- In strong/high field (LS) $\Delta_o > P$, $\Rightarrow t_{2g}^4$
- P: pairing energy

How about electronic arrangement d^8, d^9, d^{10} ?

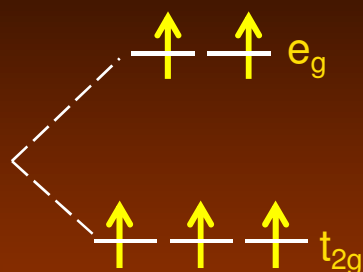
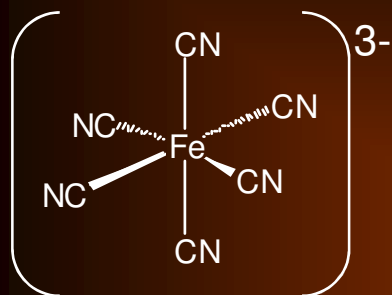
(Do It Yourself)

What is the crystal field stabilization energy (CFSE) of $[\text{Fe}(\text{CN})_6]^{3-}$?

C.N. = 6 \therefore O_h

Fe(III) \therefore d^5

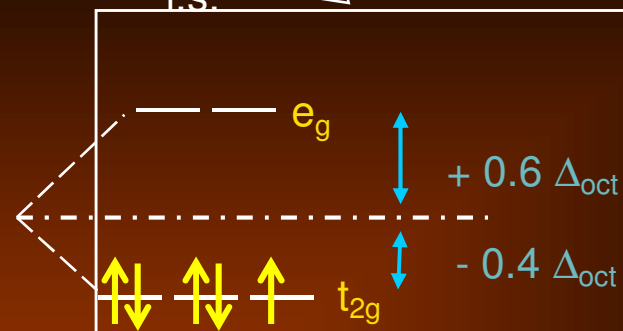
h.s.



$$\text{CFSE} = 3 \times -0.4 \Delta_o + 2 \times 0.6 \Delta_o = 0$$

l.s.

$\text{CN}^- = \text{s.f.l.}$



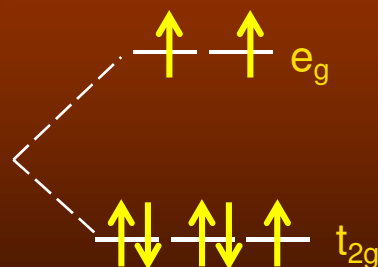
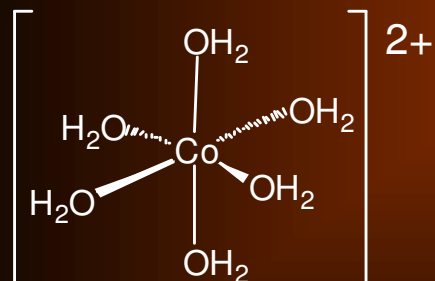
$$\text{CFSE} = 5 \times -0.4 \Delta_o + 2P = -2.0 \Delta_o + 2P$$

If the CFSE of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is $-0.8 \Delta_{\text{oct}}$, what spin state is it in?

C.N. = 6 \therefore O_h

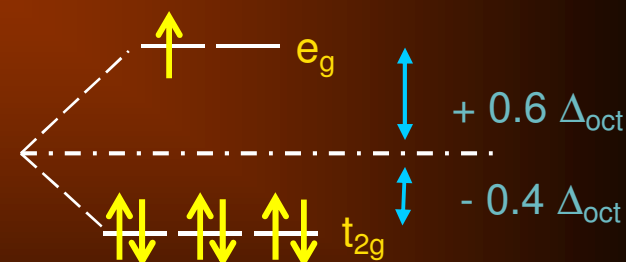
Co(II) \therefore d^7

h.s.



$$\text{CFSE} = (5 \times -0.4 \Delta_o) + (2 \times 0.6 \Delta_o) = -0.8 \Delta_o$$

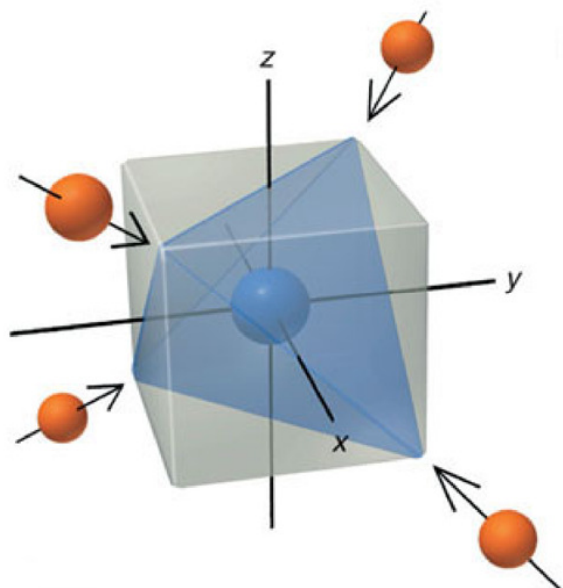
l.s.



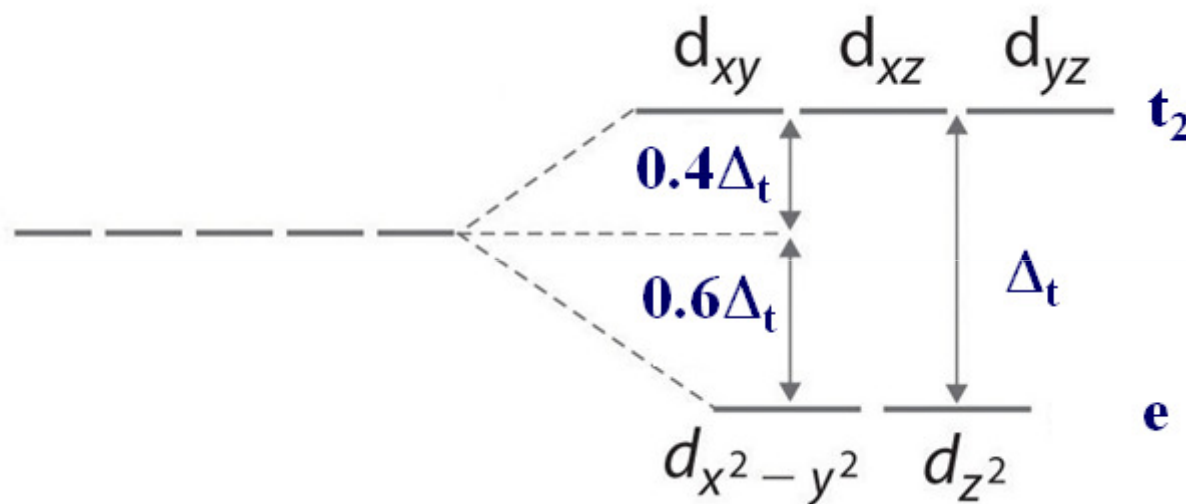
$$\text{CFSE} = (6 \times -0.4 \Delta_o) + (0.6 \Delta_o) + P = -1.8 \Delta_o + P$$

In Tetrahedral Field

- The directions x,y,z point to the face centres
- dx^2-y^2 & dz^2 point along x,y,z directions
- Others point in between x,y,z directions i.e. towards corners



approach through alternate corners of cube

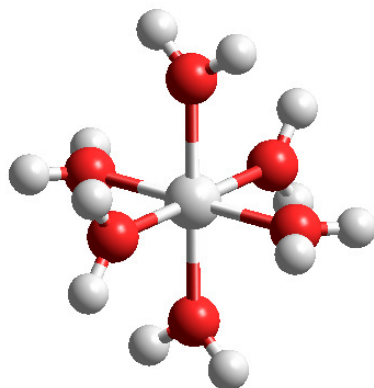


$$\Delta_t = 4/9\Delta_o$$

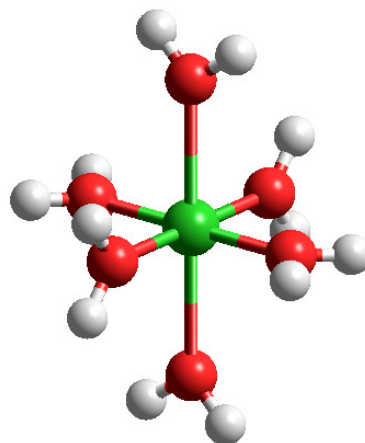
'g' is dropped as no center of symmetry for Td

Distortion in Octahedral Complex (Jahn-Teller Theorem)

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
(no J-T distortion)



Symmetrical or
Regular octahedron



$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
(J-T distortion)

distorted octahedron

1937: Hermann **J**ahn and Edward **T**eller

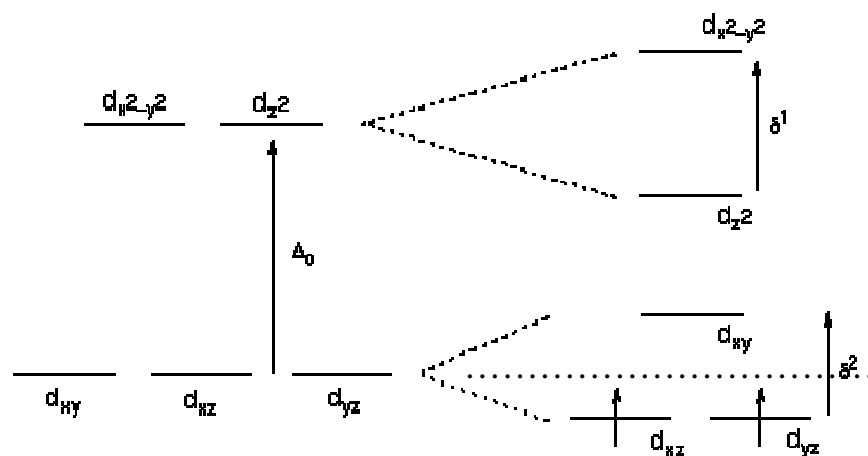
*In an electronically **degenerate state**, a nonlinear molecule undergoes distortion to remove the degeneracy by lowering the **symmetry** and thus by lowering the **energy**.*

Symmetrically occupied orbitals ———> non-degenerate state ———> NO J-T Distortion

Asymmetrically occupied orbitals ———> degenerate state ———> J-T Distortion

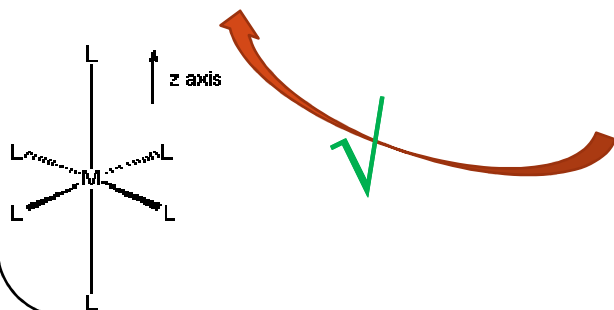
Type of Distortion

An octahedral complex with a d^2 electronic configuration:

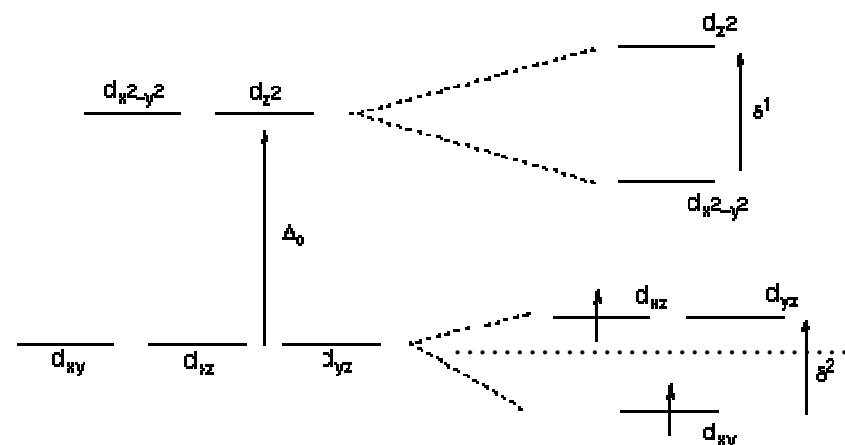


Elongation distortion/Z-out

we have gained $-2/3 \delta^2$ of additional stabilization energy

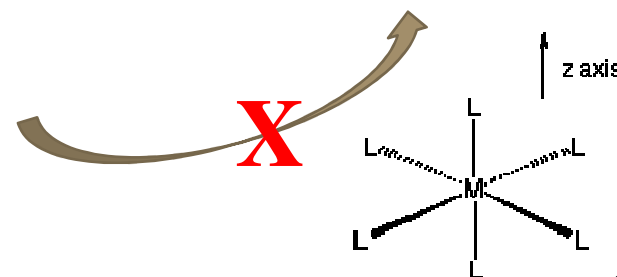


Did we remove degeneracy?



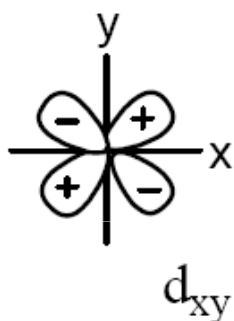
Flattening distortion/Z-in

we have gained $-1/3 \delta^2$ of additional stabilization energy

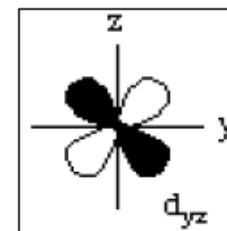
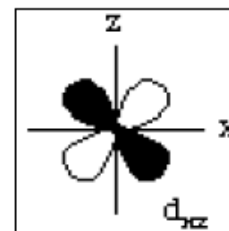
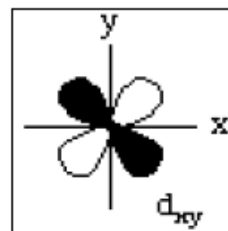


General Question: Can we tell how big a Jahn-Teller distortion will be?

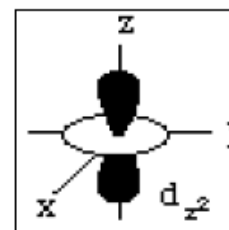
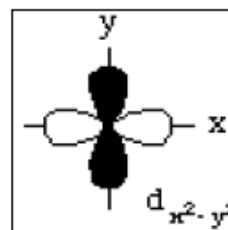
To an extent



The black and white lobes refer to the alternating sign of the wavefunction

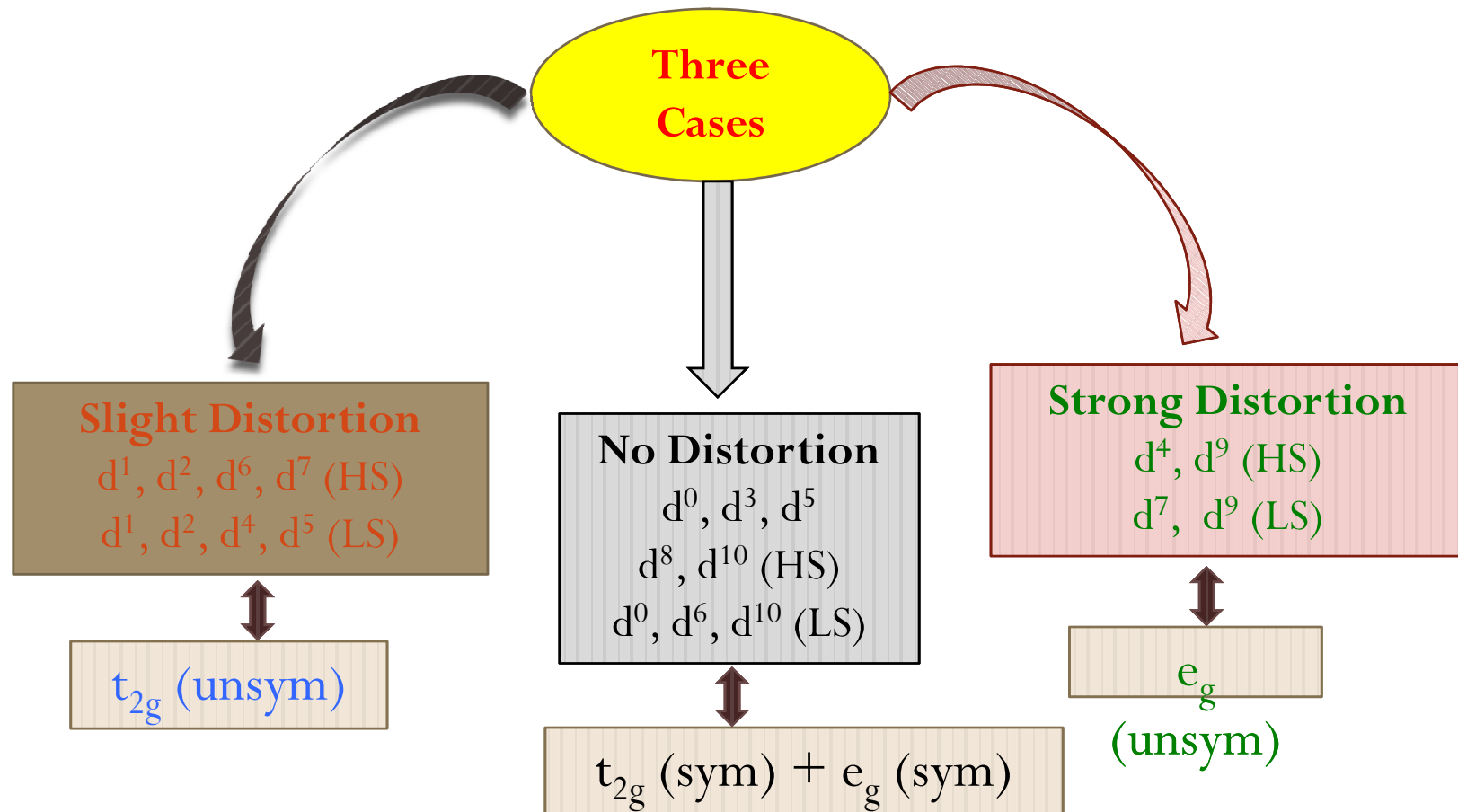


t_{2g}



e_g

Condition of Distortion:



Magnitude of Δ_0

Oxidation state of the metal ion



+2 to +3: 50%

+3 to +4: 30%

Nature of the metal ion

Down the group: 3d to 4d:: area of 4d > 3d:: hence higher repulsion



Nature of the ligand (weak vs strong field ligand)

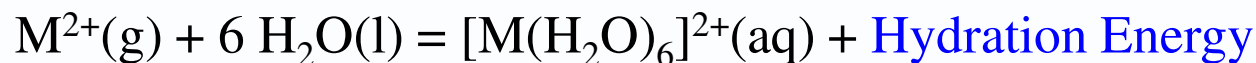
Expt determined series by Tsuchida in 1938:



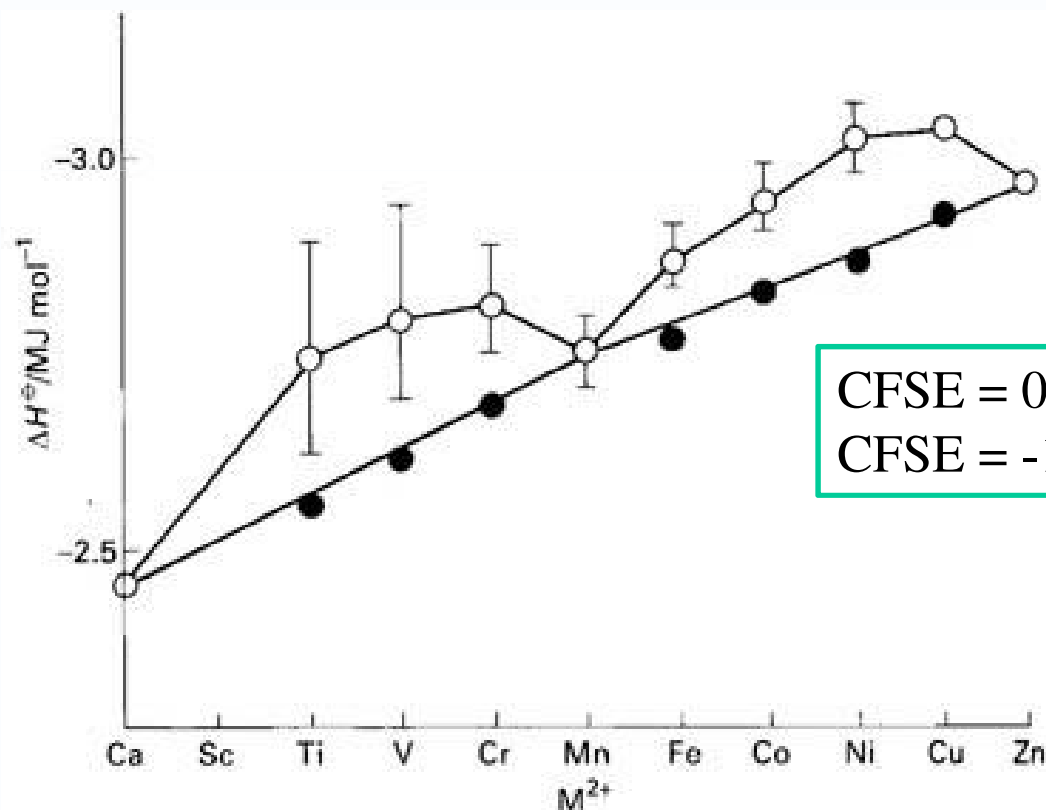
NH_3 is stronger than H_2O : couldn't be explained by CFT

Uses of CFSE Values

Hydration Enthalpy of M^{2+} ions (H_2O is weak field ligand, the complexes are high spin).

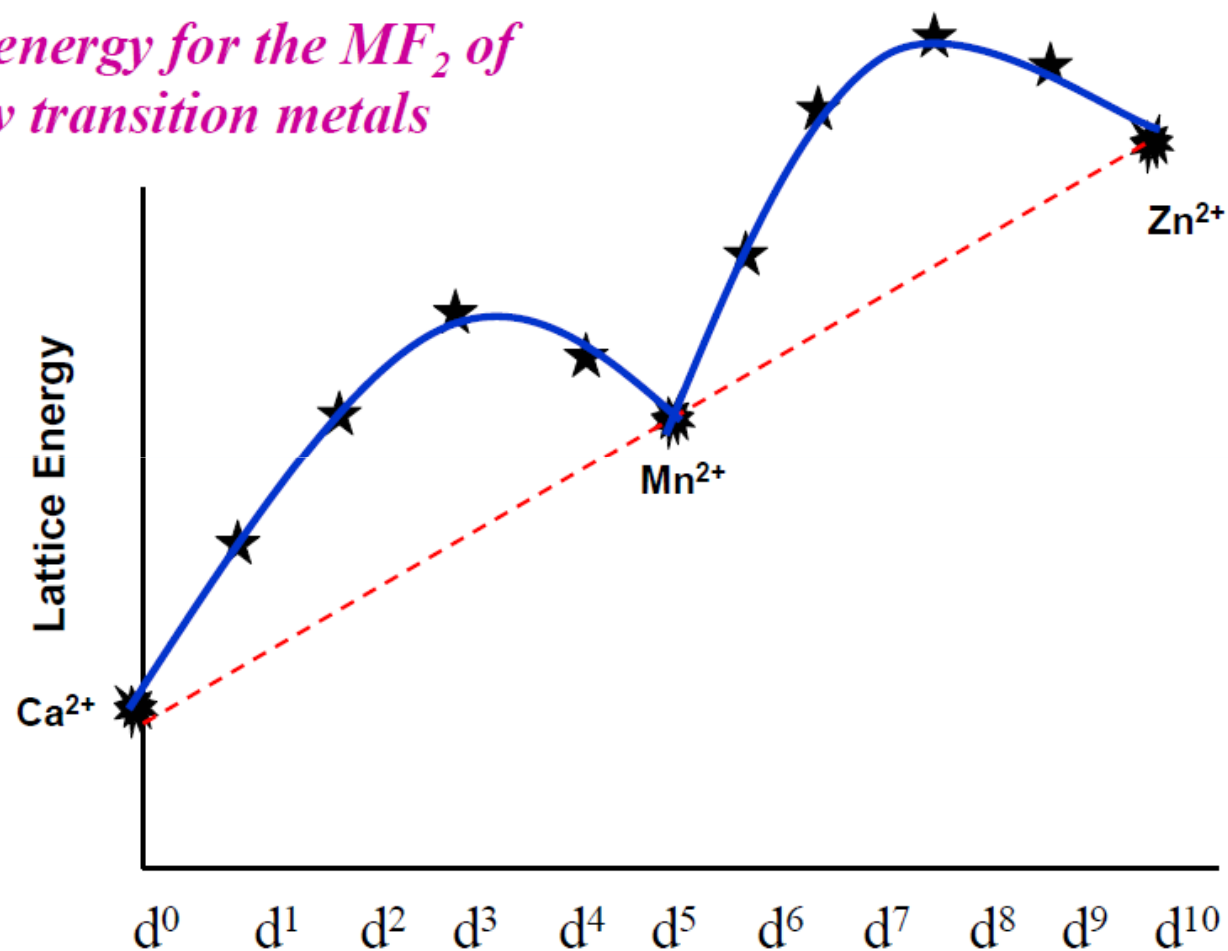


Plotting the enthalpy across the first transition series



Applications of CFT

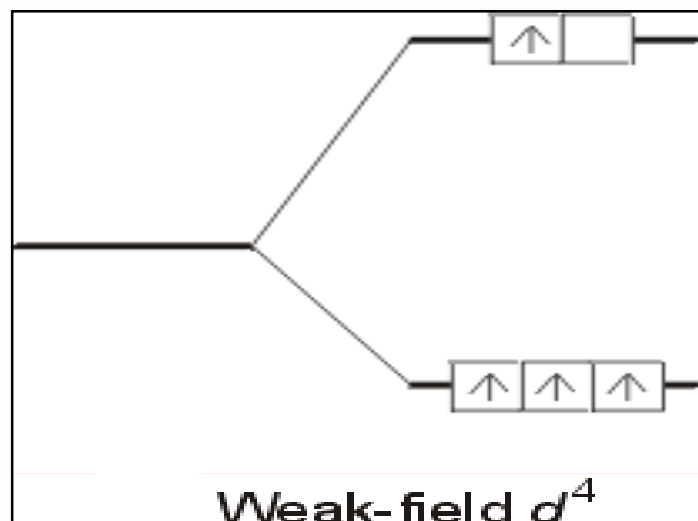
Lattice energy for the MF_2 of first row transition metals



F = weak field ligand

E required to break the crystals into its constituents ions or molecules

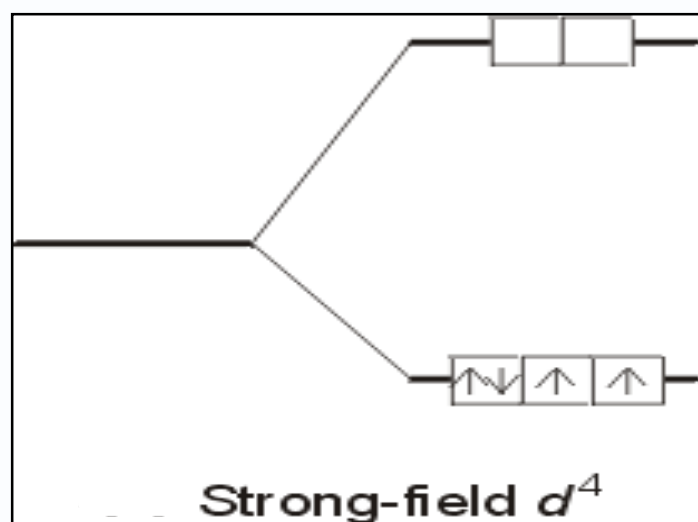
Ground-state Electronic Configuration, Magnetic Properties and Colour



Weak Field Complex

the total spin is $4 \times \frac{1}{2} = 2$

High Spin Complex

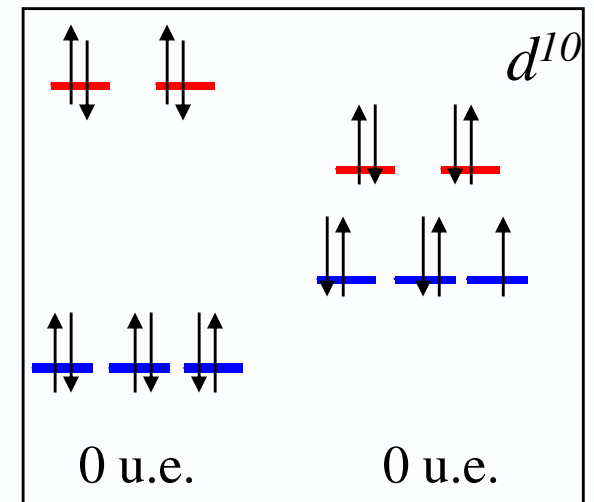
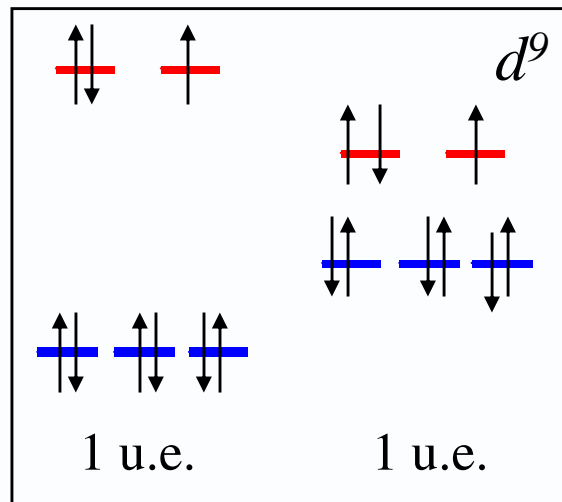
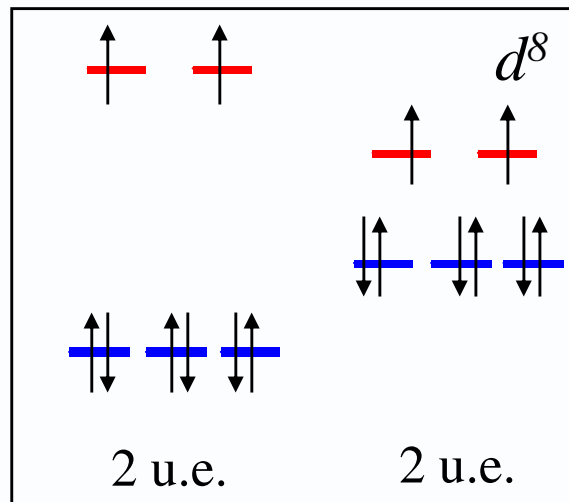
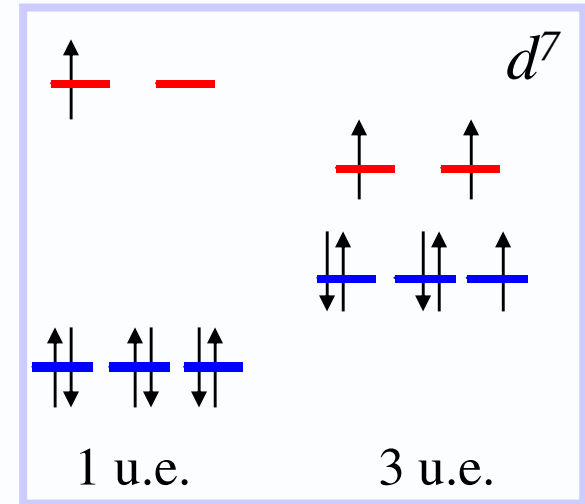
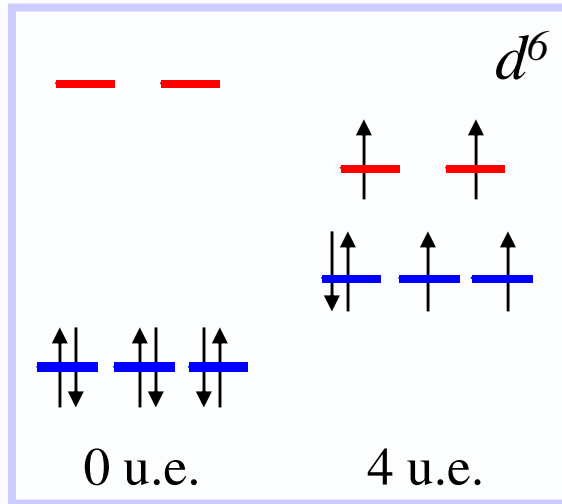
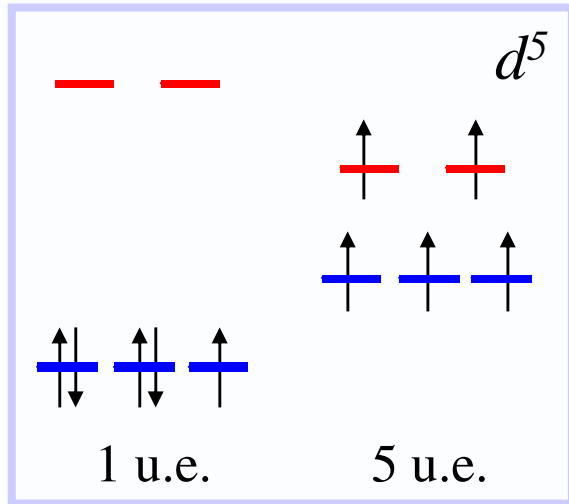


Strong field Complex

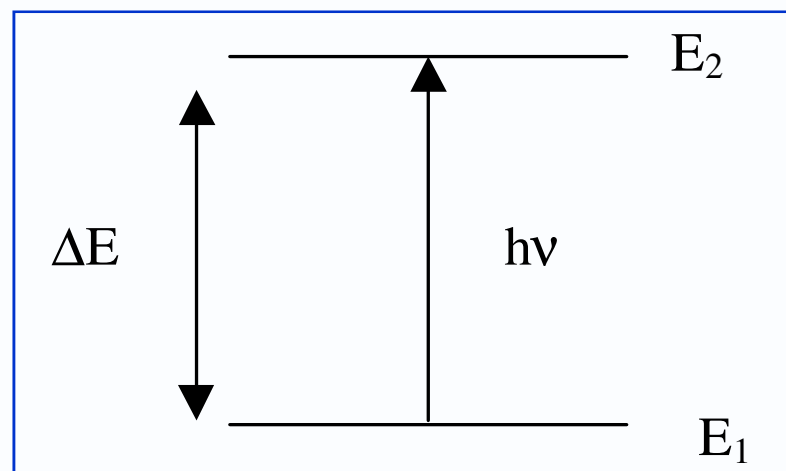
total spin is $2 \times \frac{1}{2} = 1$

Low Spin Complex

Placing electrons in d orbitals



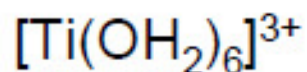
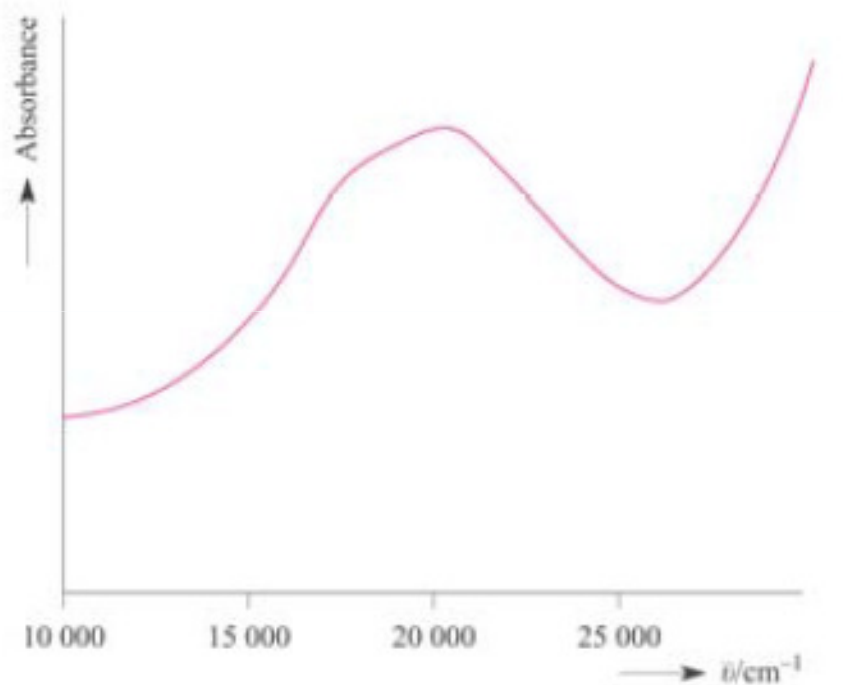
The origin of the color of the transition metal compounds



$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_o , therefore the colour

The optical absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



purple

Assigned transition:



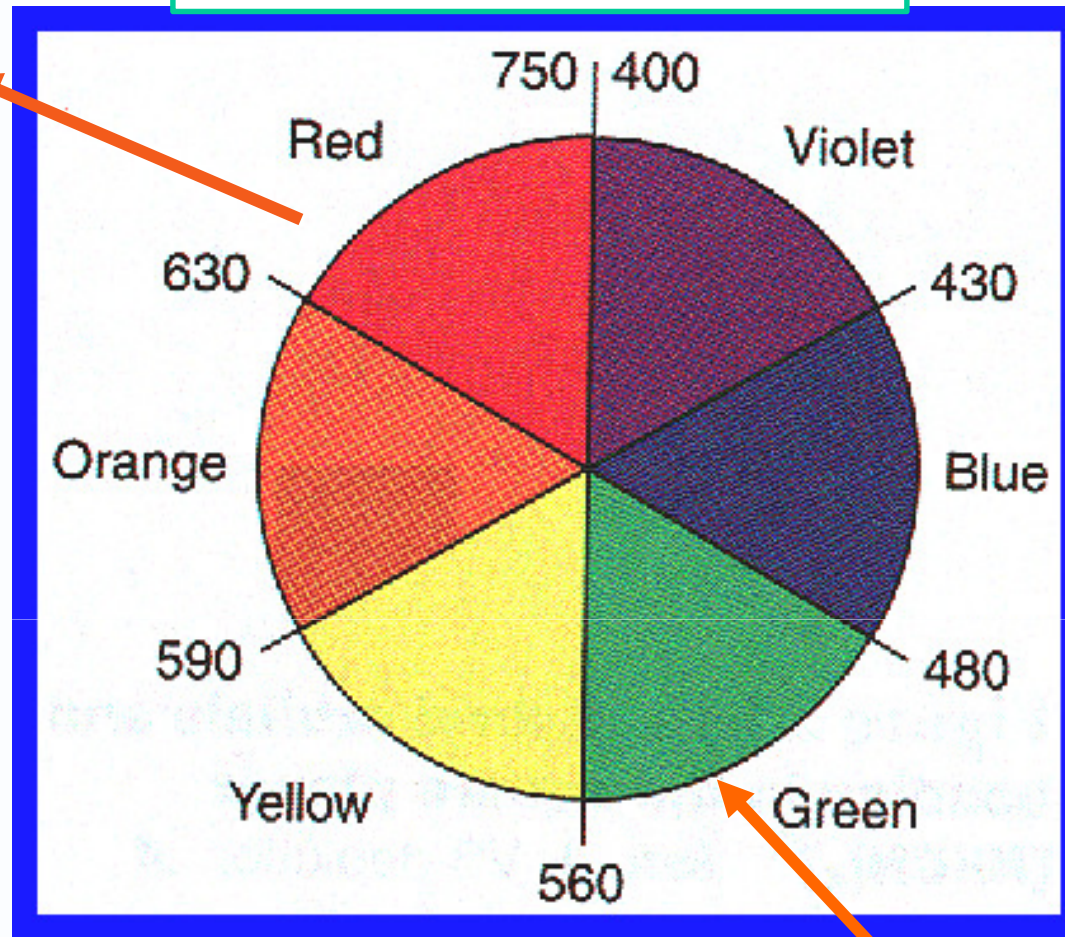
**This corresponds to
the energy gap**

$$\Delta_o = 243 \text{ kJ mol}^{-1}$$

490 nm

complementary color chart

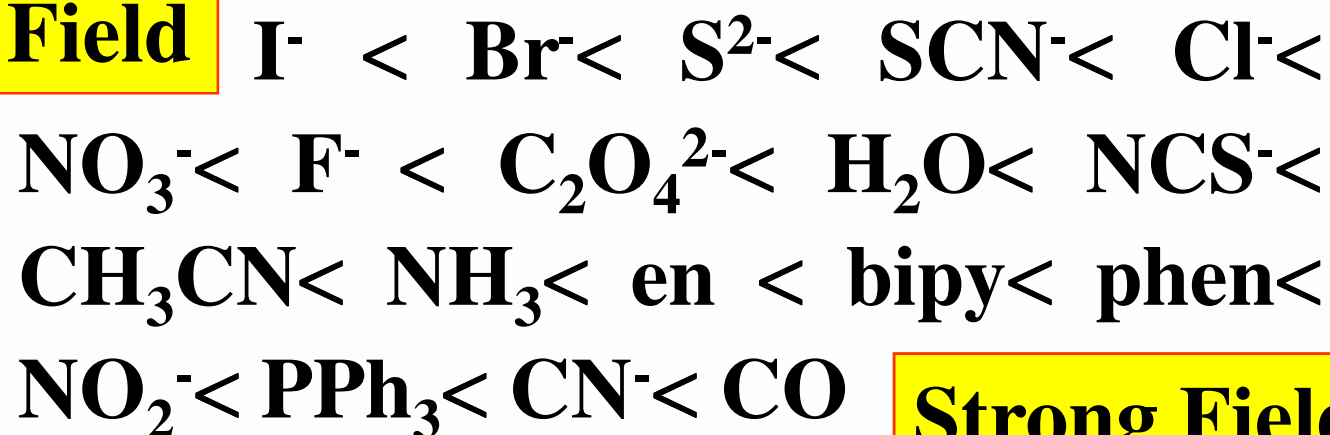
observed
color



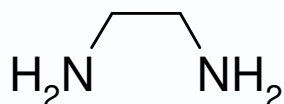
absorbed
color

- **Spectrochemical Series: An order of ligand field strength based on experiment:**

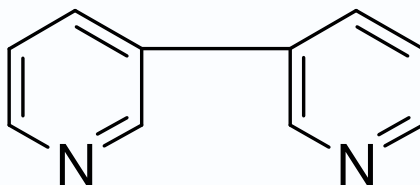
Weak Field



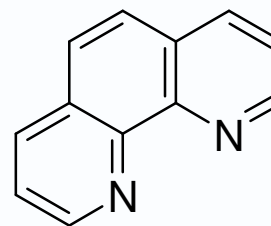
Strong Field



Ethylenediamine (en)



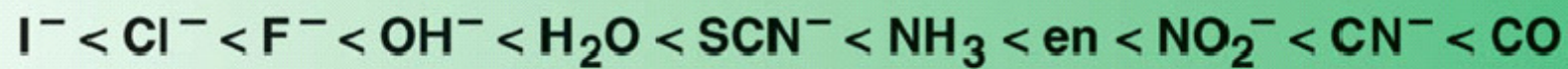
2,2'-bipyridine (bipy)



1.10 - phenanthroline (phen)

Spectrochemical Series

Or more simply :
 $X < O < N < C$



WEAKER FIELD

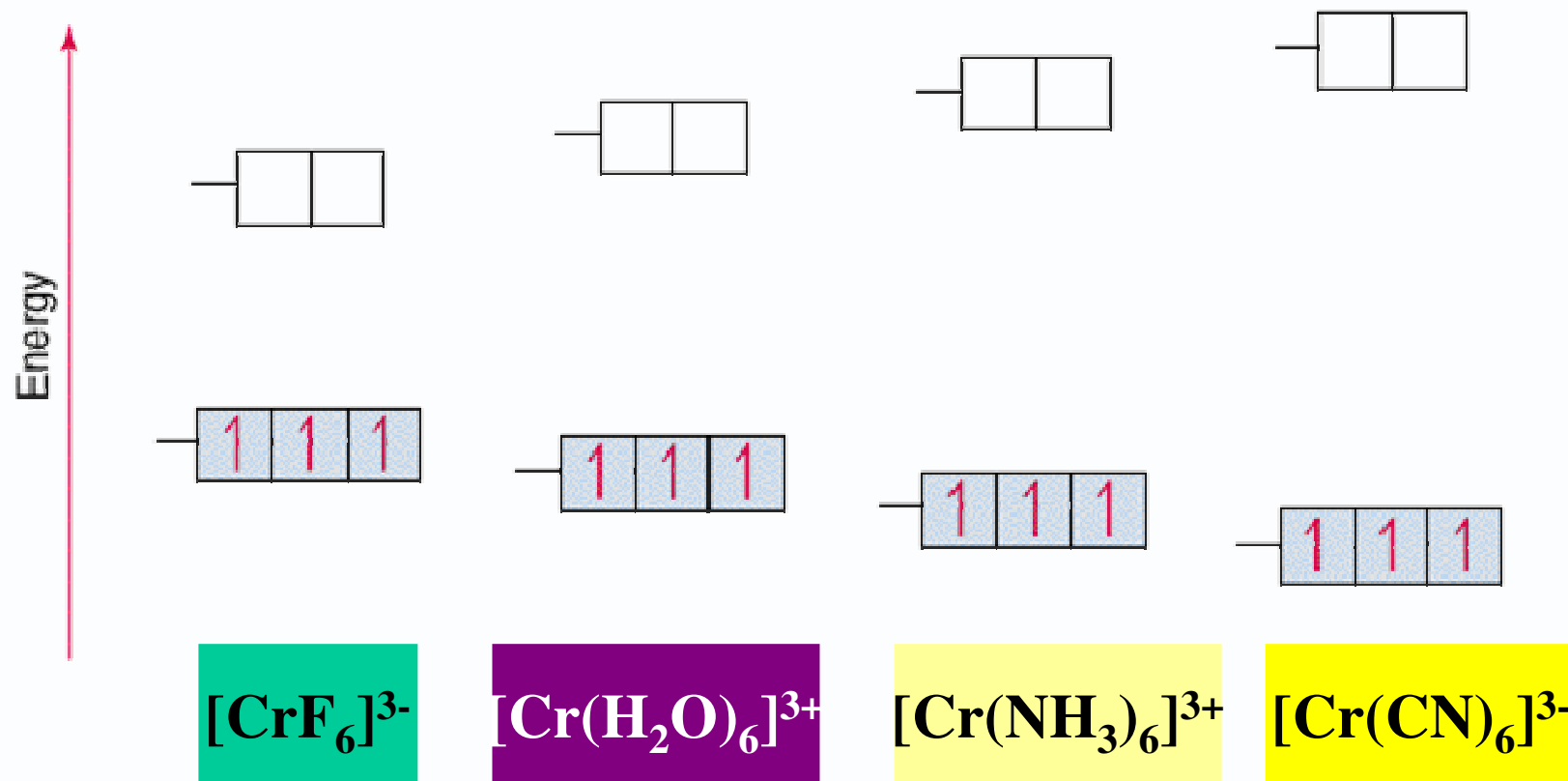
STRONGER FIELD

SMALLER Δ

LARGER Δ

LONGER λ

SHORTER λ



As Cr^{3+} goes from being attached to a weak field ligand to a strong field ligand, Δ increases and the color of the complex changes from green to yellow.

Colourless?

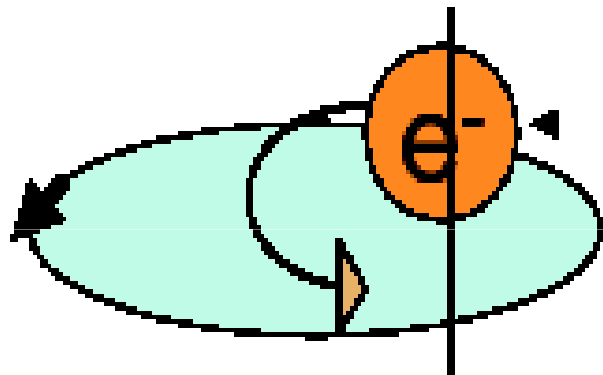
- For example, although scandium is a member of the d block, its ion (Sc^{3+}) hasn't got any d electrons left to move around.
- In the zinc case, the 3d level is completely full - there aren't any gaps to promote an electron in to. Zinc complexes are also colourless.

Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



**Orbital motion of e generates
current and magnetic field**

**Spin motion of e about its own
Axis also generates a magnetic field**

n = no. of unpaired electrons; spin quantum number S

$$\mu = \{n(n+2)\}^{1/2} \mu_B$$

$$\mu \text{ (spin only)} = 2\{S(S+1)\}^{1/2}$$

Ion	n	S	μ/μ_B Calculate d	Experimental
Ti³⁺	1	1/2	1.73	1.7 – 1.8
V³⁺	2	1	2.83	2.7 – 2.9
Cr³⁺	3	3/2	3.87	3.8
Mn³⁺	4	2	4.90	4.8 – 4.9
Fe³⁺	5	5/2	5.92	5.3

**Similar Calculation can be done
for Low-spin Complex**

orbital contribution is ignored

Limitations of CFT

- **Considers Ligand as Point charge/dipole only**
- **Does not take into account of the overlap of ligand and metal orbitals and can't explain partial covalent character of M-L bond**
- **too much emphasis on metal d orbital but ignore s & p orbitals as well as ligand pi orbitals**
- **Can't explain the relative position of ligand in spectrochemical series which is expt determined (OH^- is weaker than H_2O)**

Consequence

e.g. Fails to explain why CO is stronger ligand than CN^- in complexes having metal in low oxidation state (will be discussed in Organometallics)