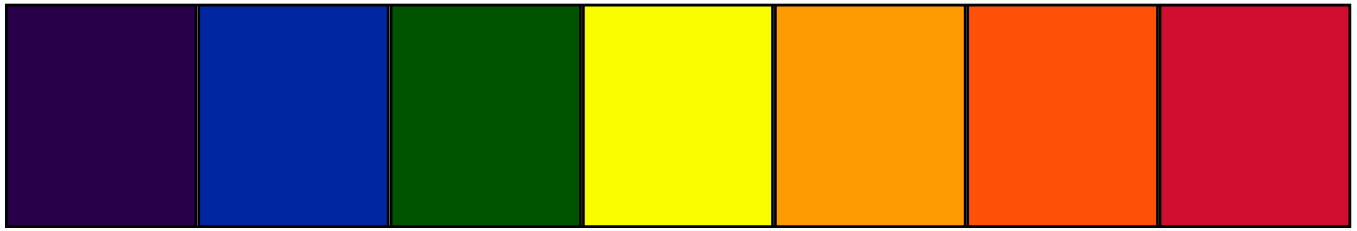
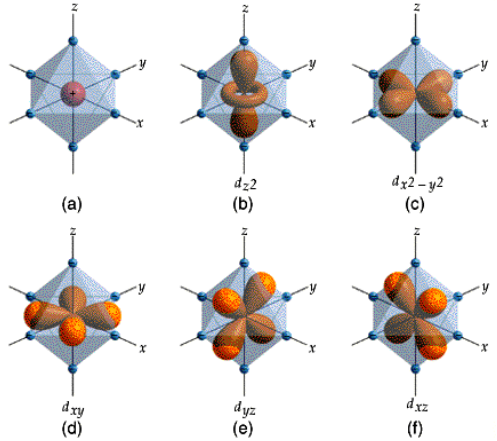
Understanding **Electronic Spectral Properties** trend

Crystal Field Theory



400 500 600 800

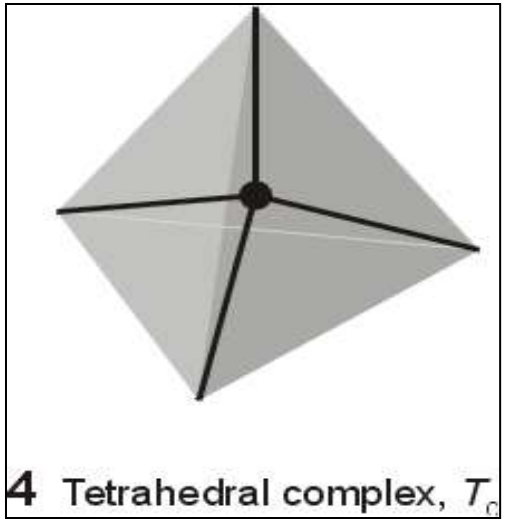
- **The relationship between colors and complex metal ions**



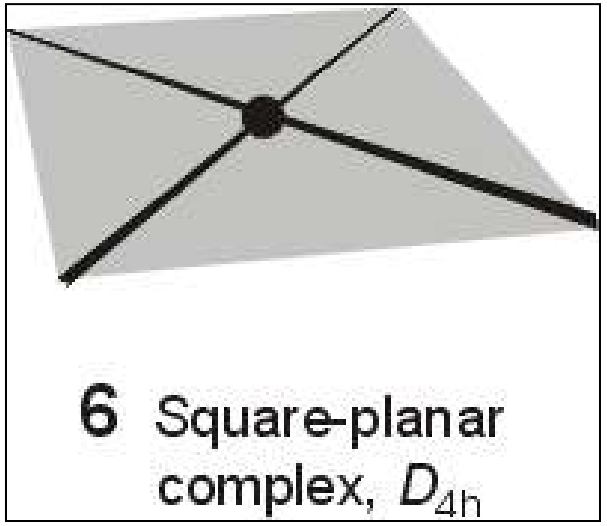
Crystal Field Model

- 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.

10 Octahedral complex, O_h



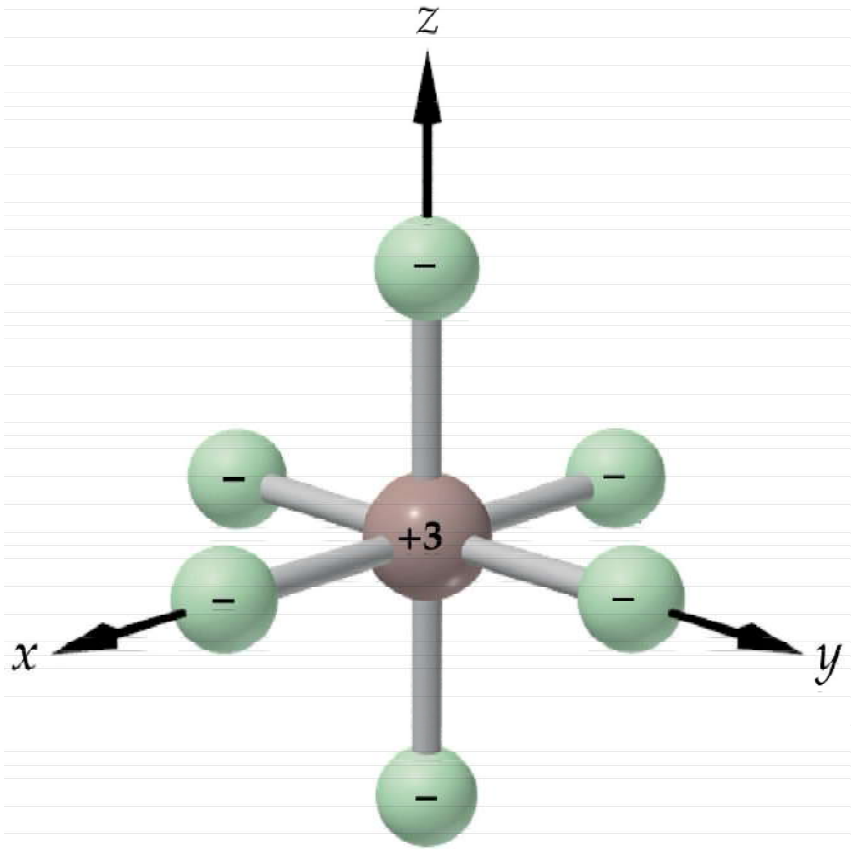
4 Tetrahedral complex, T_d



6 Square-planar complex, D_{4h}

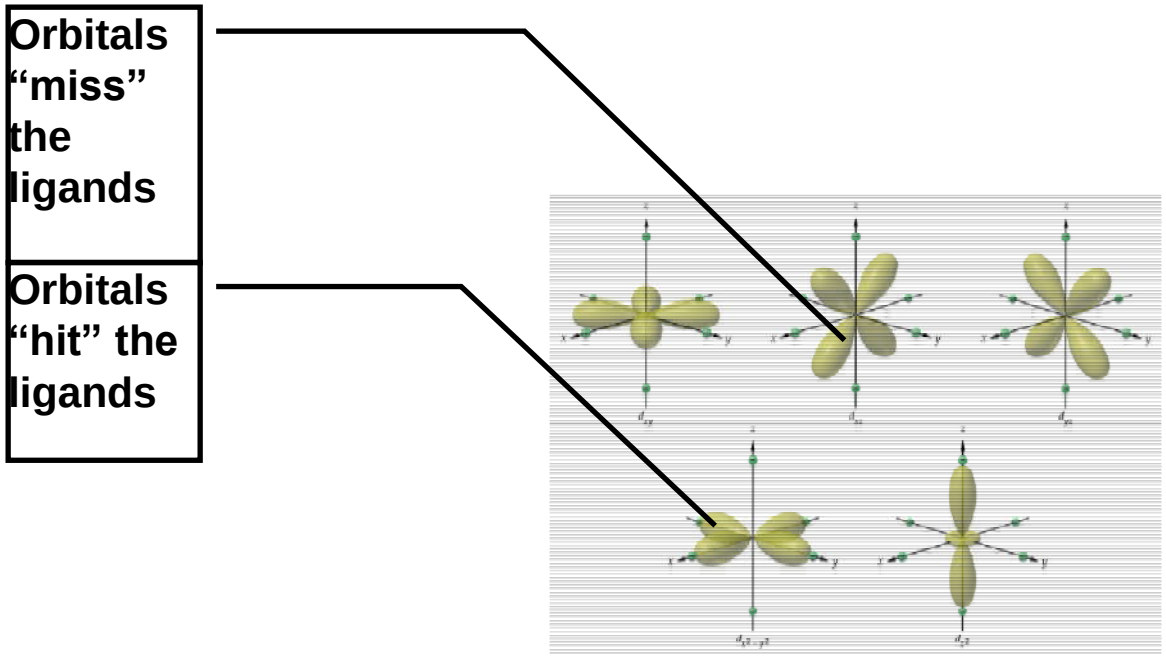
The crystal field theory

- The ligands are considered negative charges
- The central ion is a positive charge
- The effect of the electrostatic interactions on the energies of the d orbitals form the basis of the theory



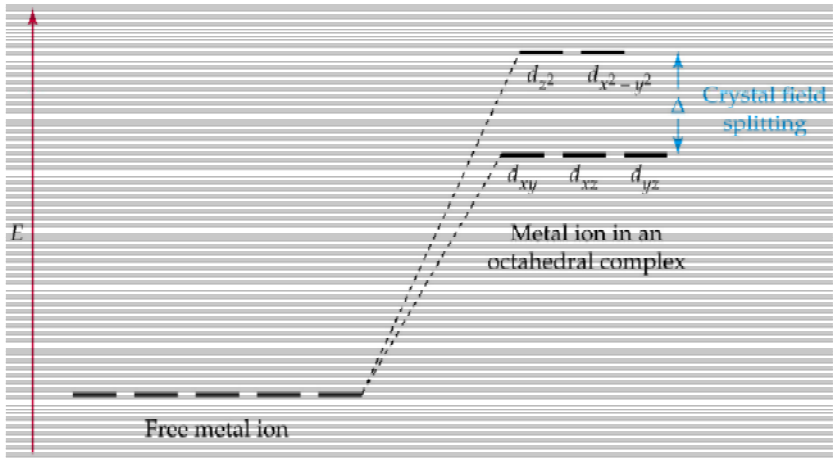
Relative positions of ligands and d orbitals

- d_{xy} etc interact least with the ligands
- d_{x2-y2} and d_{z2} interact most with the ligands in an octahedral field



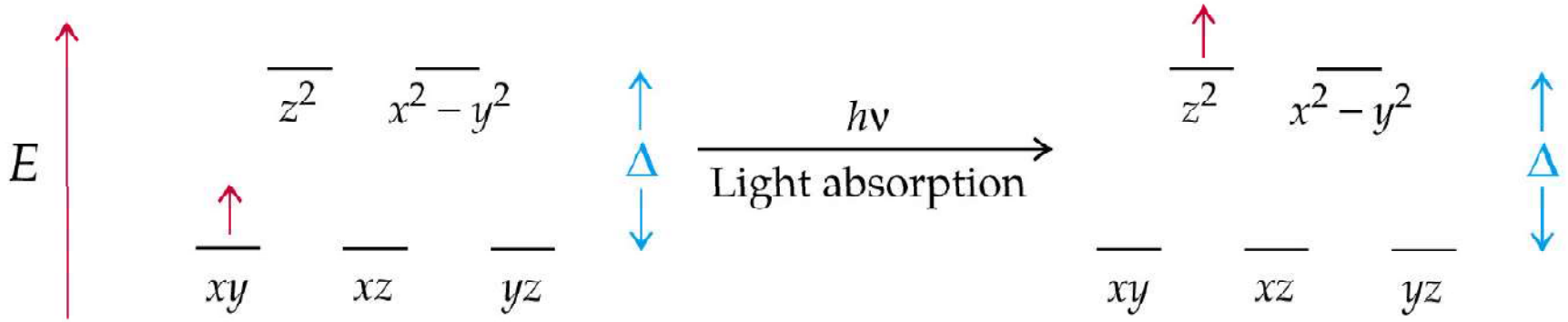
Crystal field splitting

- The orbitals that interact more strongly with the ligands are raised in energy (electrostatic repulsion) more than those that interact less strongly
- The result is a splitting of the levels

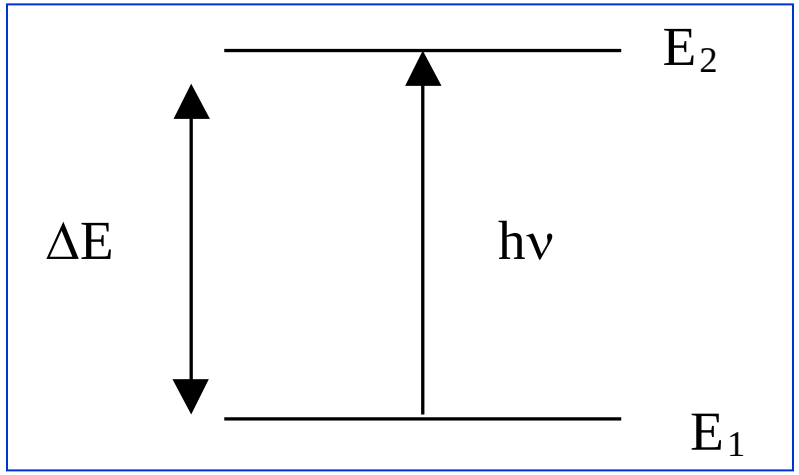


Splitting and spectroscopy

- Electrons in the incompletely filled d orbitals can be excited from lower occupied to higher unoccupied orbitals
- The frequency of the absorption is proportional to the crystal field splitting: $\Delta = h\upsilon = hc/\lambda$



The origin of the color of the transition metal compounds

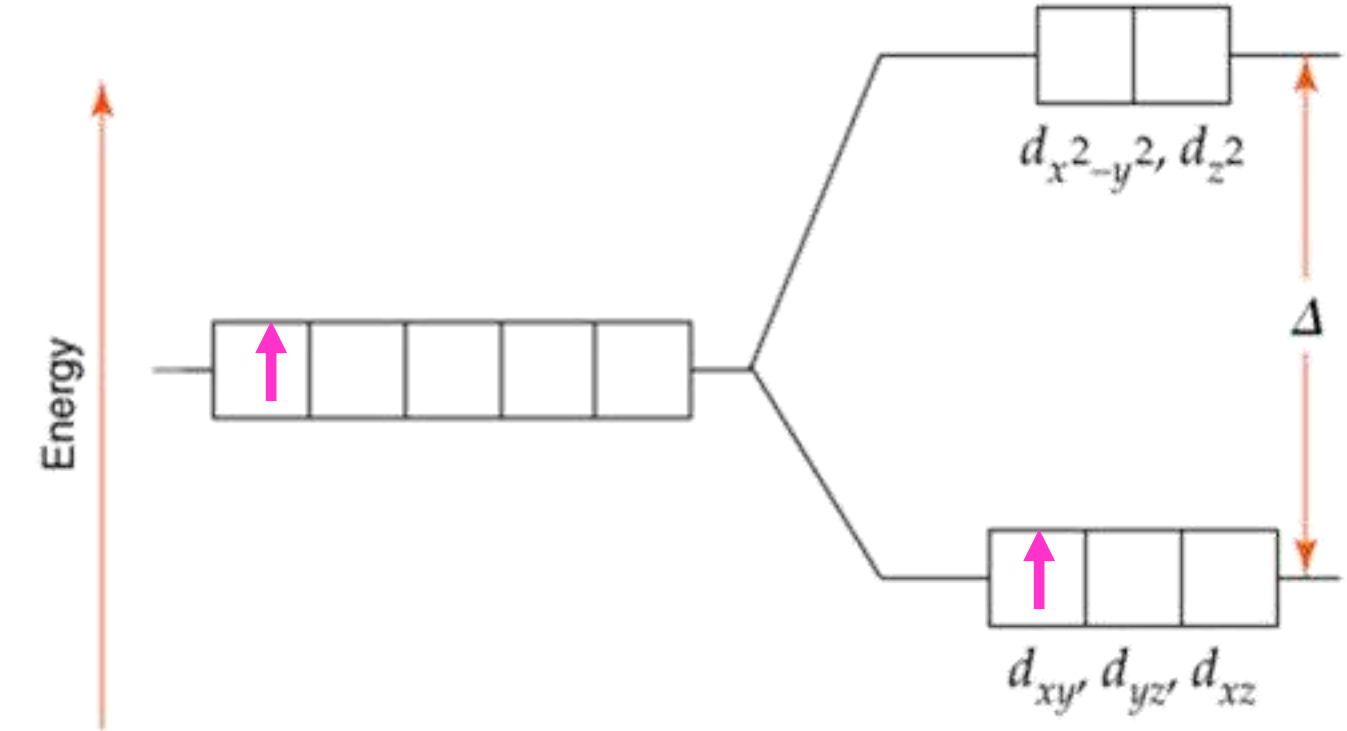


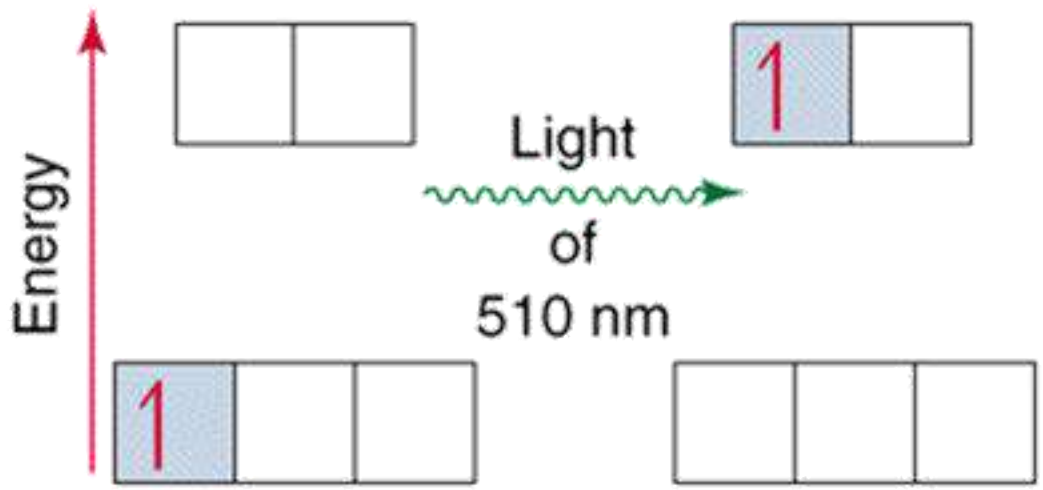
$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_o, therefore the colour

Electronic absorption spectra

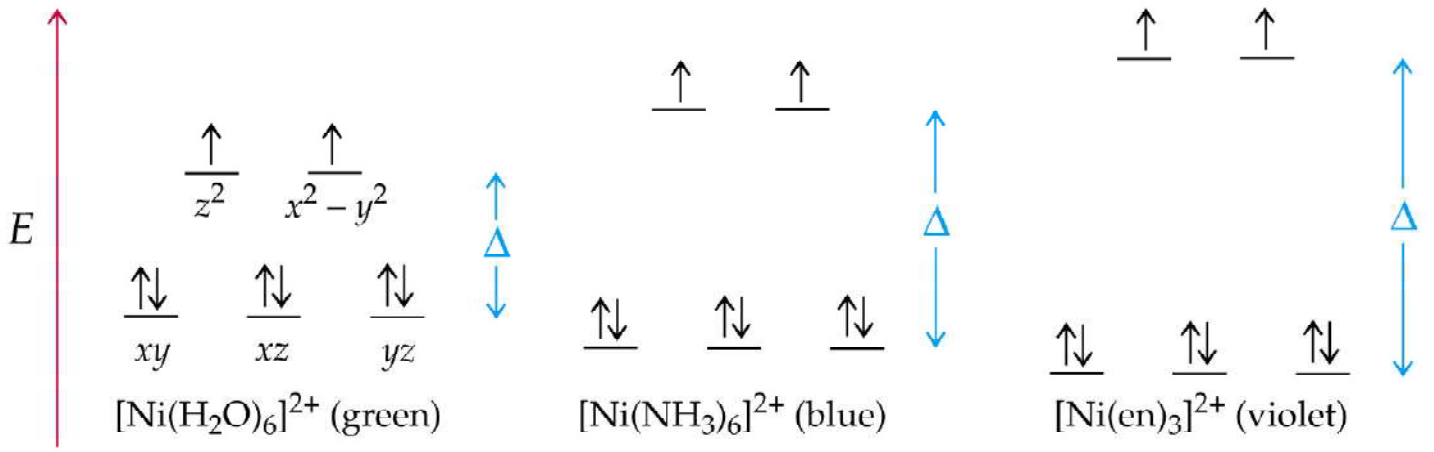
- Selection rules
  - Transitions that occur without change in number of unpaired electrons (spin multiplicity) are allowed
  - Transitions that involve a change in the number of unpaired spins are "forbidden" and are therefore of low intensity.
    - > solutions of high-spin d^5, e.g., Mn(II), complexes are lightly colored
- Absorption bands are broad because metal-ligand bonds are constantly changing distance (vibration) and since electronic transitions occur faster than atomic motions this means that there are effectively many values of Δ_o.
- d^1 and d^9, and high-spin d^4 and d^6 ions have only one spin-allowed transition; high-spin d^2, d^3, d^7 and d^8 have three spin-allowed transitions


Energy
$d_{x^2-y^2}, d_{z^2}$
Δ
d_{xy}, d_{yz}, d_{xz}


Energy
Light
of
510 nm
1
1

Coat of many colours

- Transition metal ions exhibit colours that vary strongly with the type of ligand used and also colours demarcate due to different energy of involved d orbitals
- Spectrochemical series orders the ligands according to the degree of crystal field splitting achieved



The color of coordination compound

- Many of the colors of octahedral transition-metal compounds arise from the excitation of an electron from an occupied lower energy orbital to an empty higher energy orbital.

- The frequency (v) of light that is capable of inducing such a transition is related to the energy difference between the two states, which is the crystal-field splitting energy.

$$h\nu = \Delta$$

Spectrochemical series of ligands

- Weak field

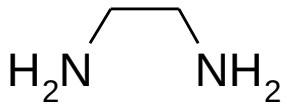
$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < CN^-$$

- Strong field

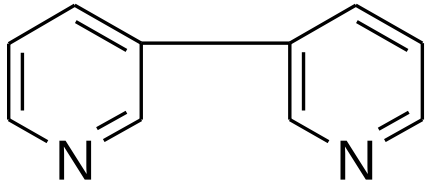
- When the d orbitals are empty (d^0) or full (d^{10}), the complexes are colourless – no d – d transitions
- The theory successfully accounts for observed optical and magnetic properties

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

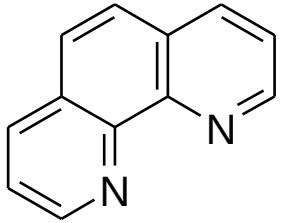
Weak Field $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$ **Strong Field**



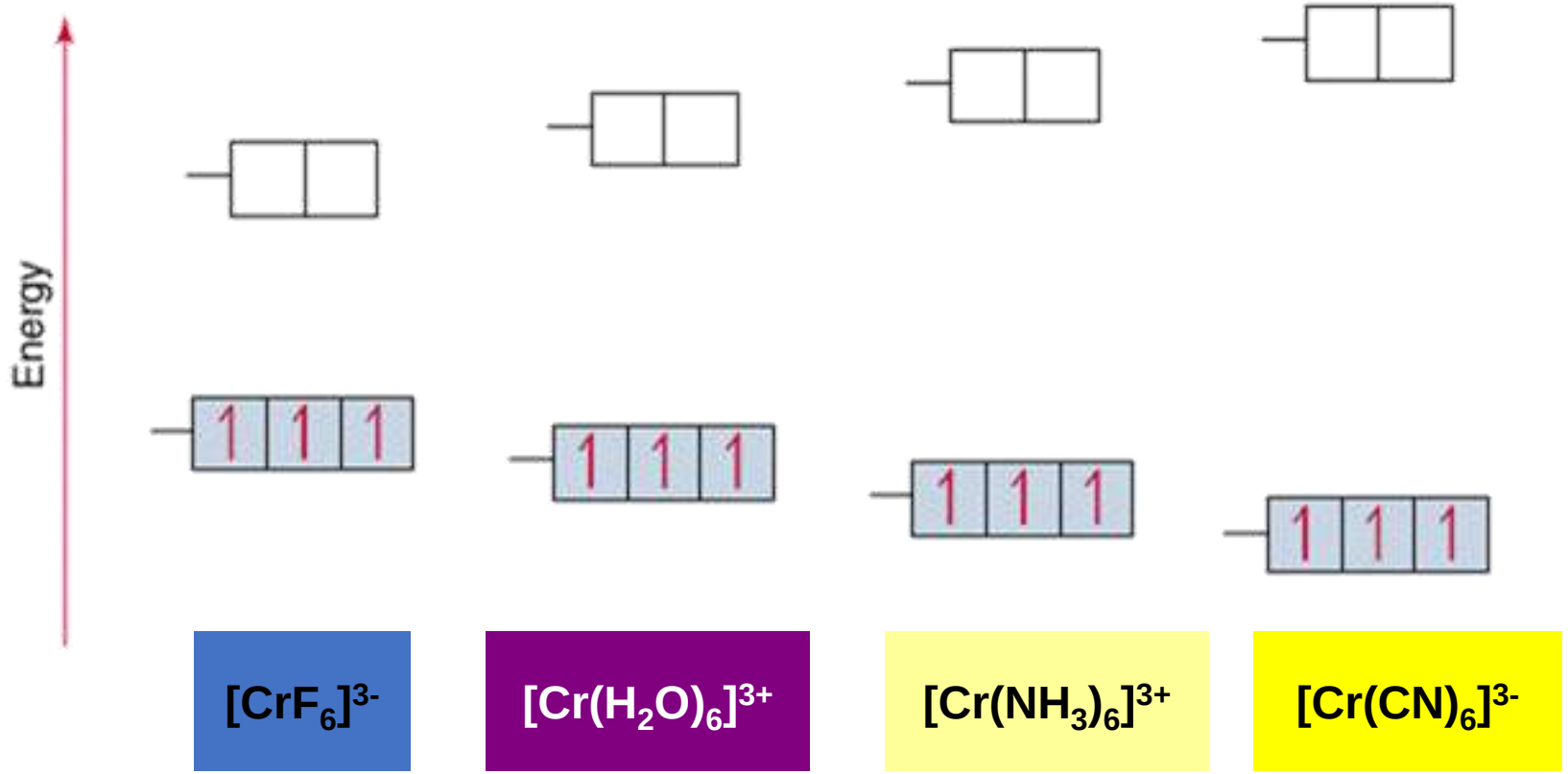
Ethylenediamine (en)



2,2'-bipyridine (bipy)



1.10 - penanthroline (phen)

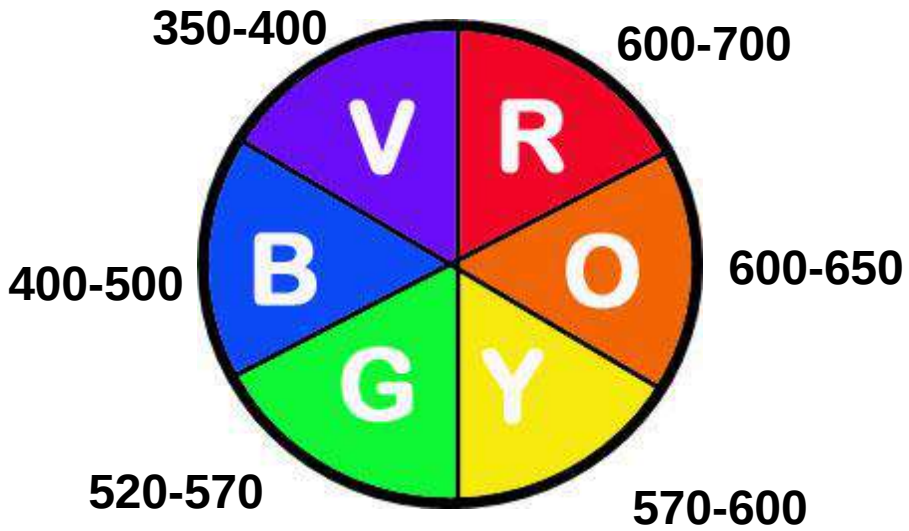


As Cr^{3+} goes from being attached to a weak field ligand to a strong field ligand, Δ increases and the color of the complex changes from green to yellow.

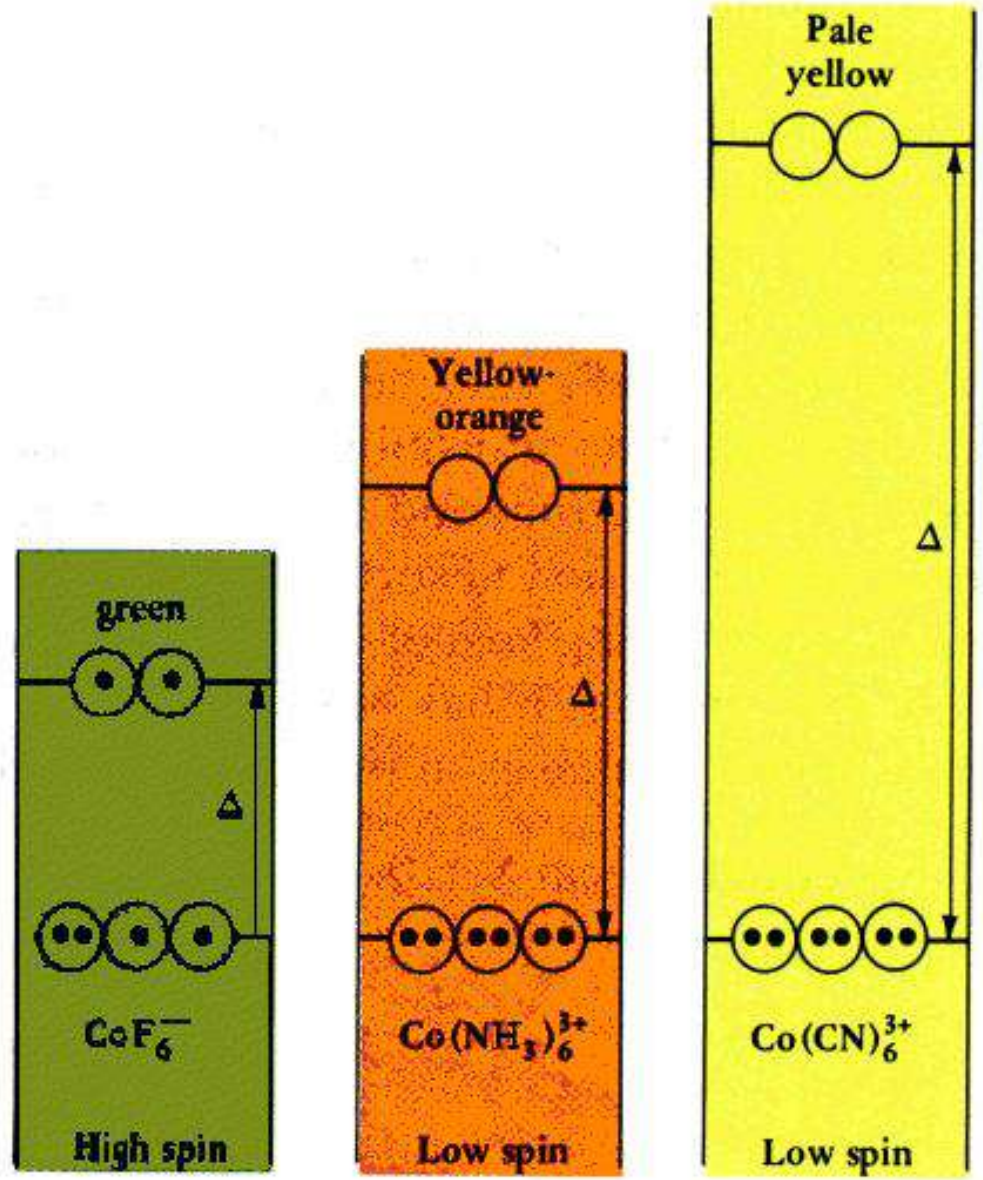
Let's Look at 4 Co^{3+} complexes:

	Config.	Color of Complex	Absorbs
$[Co(NH_3)_6]^{3+}$	d^6		
$[Co(NH_3)_5(OH_2)]^{3+}$	d^6		
$[Co(NH_3)_5Br]^{2+}$	d^6		
$[Co(NH_3)_5Cl]^{2+}$	d^6		

Greater Splitting



Values are in nm


green
Δ
CoF_6^{3-}
High spin
Yellow-orange
Δ
$Co(NH_3)_6^{3+}$
Low spin
Pale yellow
Δ
$Co(CN)_6^{3+}$
Low spin

- Greater is Δ, more energy is required to cause the d-d transition. For 4d-series elements, increasing Δ value in octahedral field is: $Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+}$ etc