CHEMISTRY

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Last class…

- CFT – Octahedral complexes
- Spectrochemical series
- Charge on the central metal ion

In this class…

- Crystal Field Theory – continuation

$[Co(NH_3)_6]Cl_3$ CFSE and magnetic moment ?

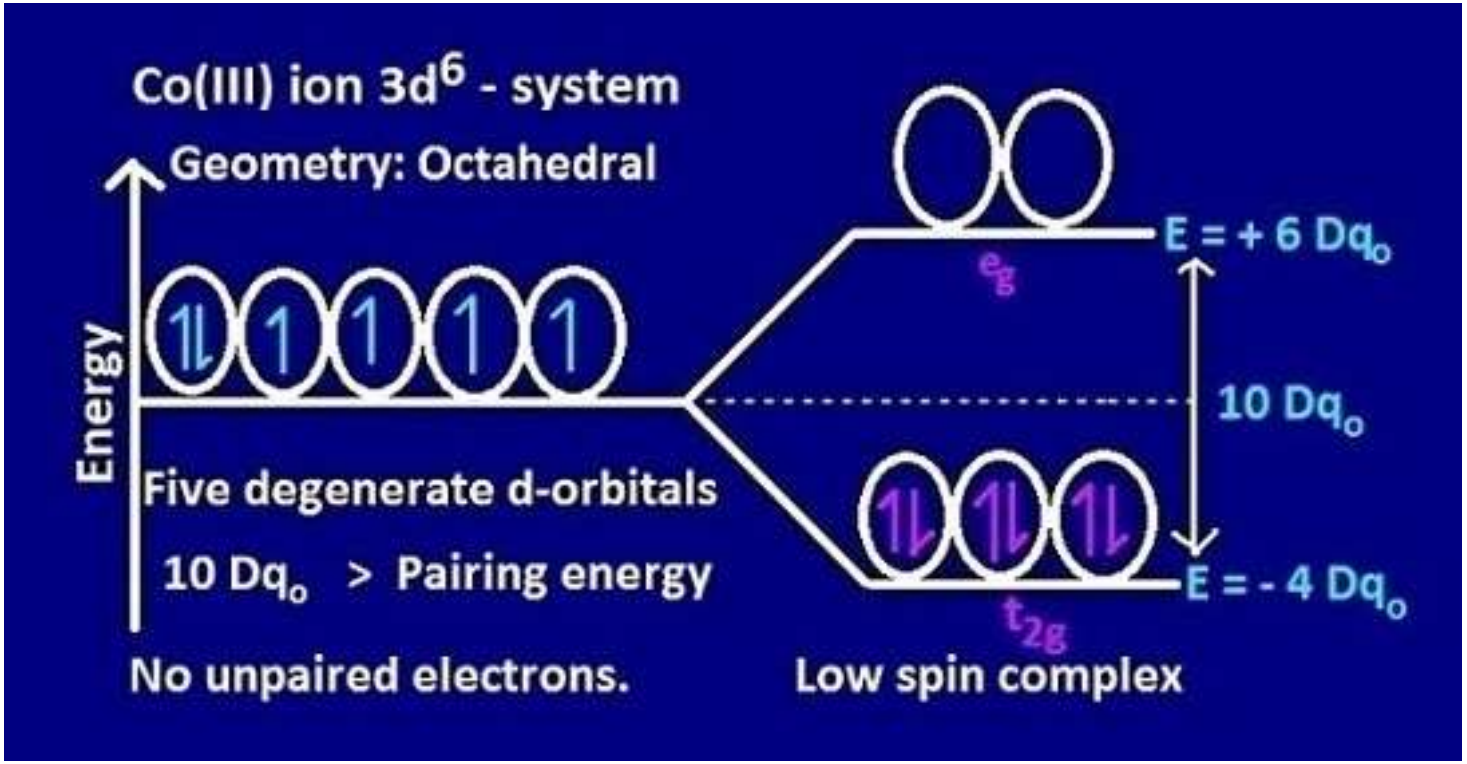
- Cobalt must be Co^{3+} because the charges (X+6(0)+3(-1)) must add up to the overall 0

- d electron count : Co : electronic configuration is $3d^7 4s^2$

- d electron count Co^{3+} : $3d^6$

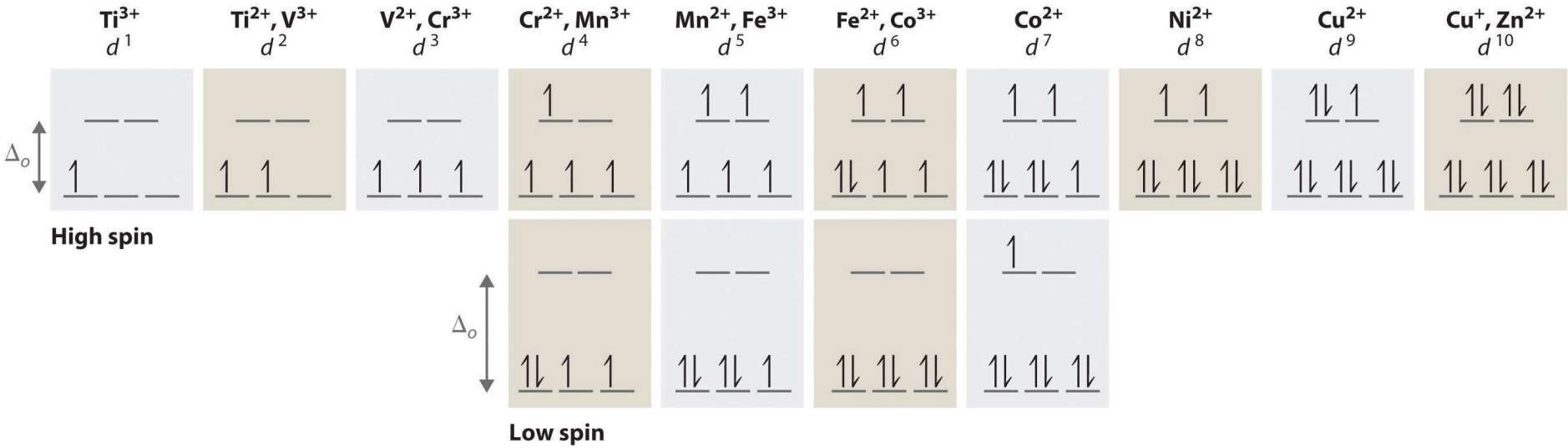
Element	Symbol	Z	Electronic configuration
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

$[Co(NH_3)_6]^{3+}$ magnetic moment ?

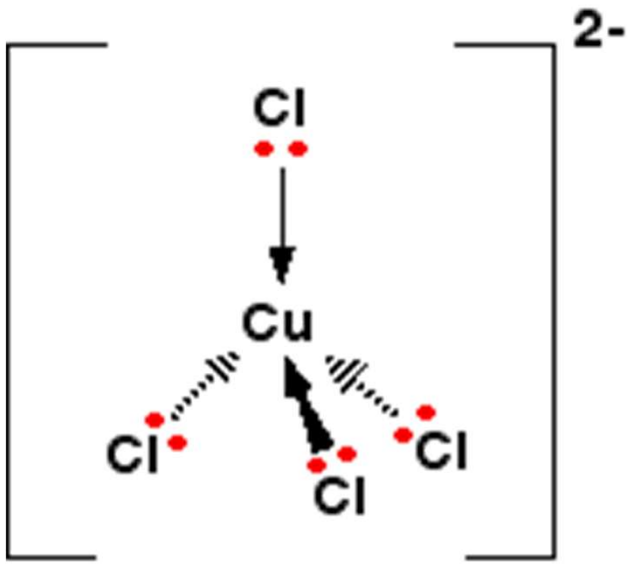


- 6 electrons are present in t_{2g} level and 0 electrons are present in e_g level.
- The crystal field stabilization energy of $[Co(NH_3)_6]Cl_3$ is **$CFSE = 6\times(-0.4\Delta_0)+0\times(0.6\Delta_o) = -2.4\Delta_0$**

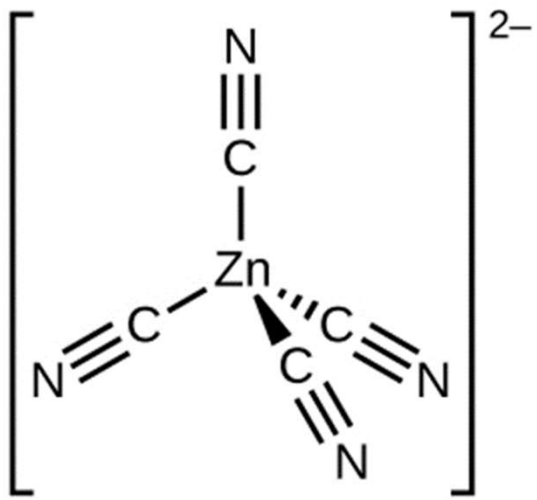
Summary, Octahedral, 3d elements, CFT

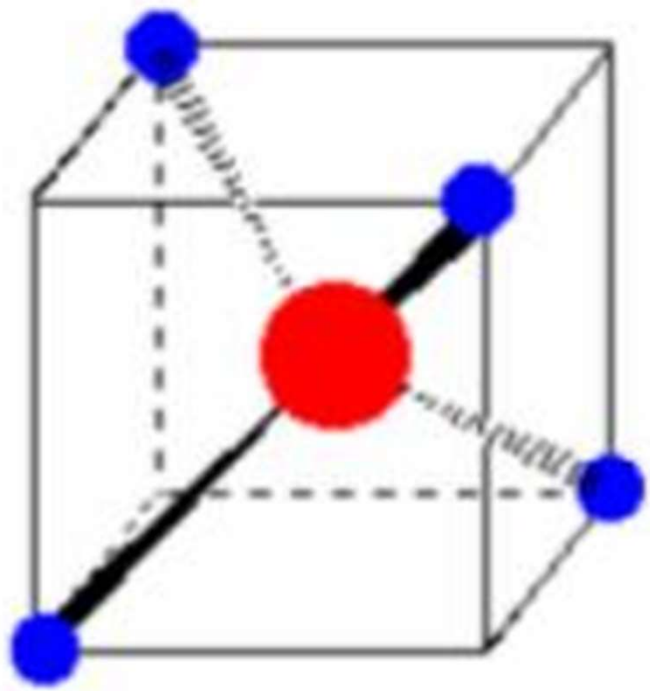


CFT as applied to tetrahedral complexes



$[CuCl_4]^{2-}$



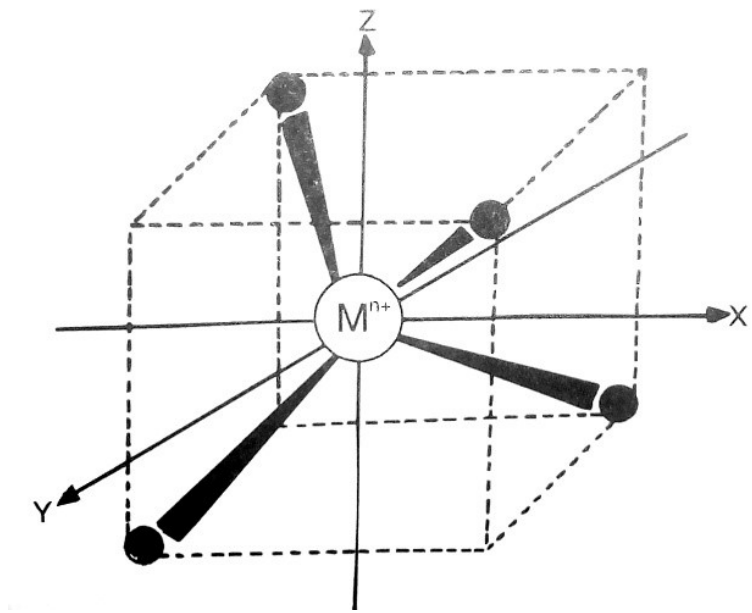


Tetrahedral complex in a cube. Ligands are on alternate corners of the cube.

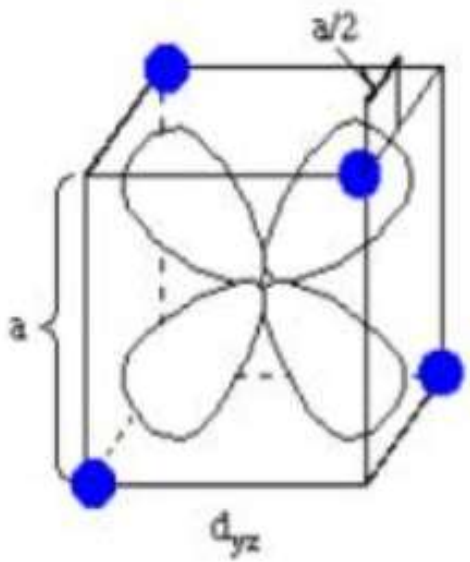
CFT as applied to tetrahedral complexes
Crystal field splitting of d-orbitals in tetrahedral complexes

- In case of free metal ion, all the five d-orbitals are degenerate, i.e., these have the same energy.

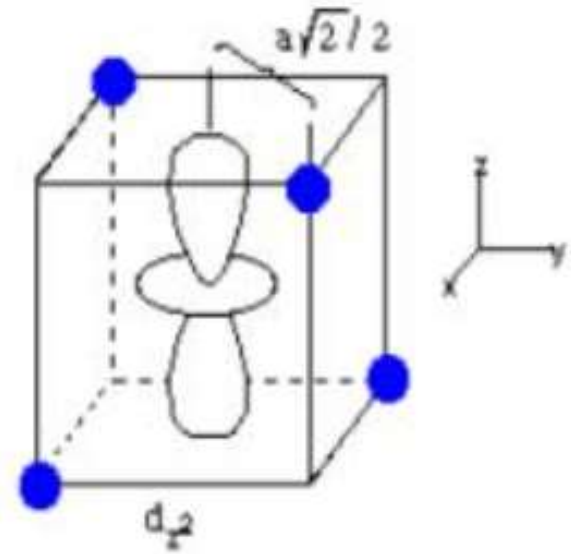
- In $[ML_4]^{n+}$, the central metal cation is surrounded tetrahedrally by four ligands. A tetrahedron may be supposed to have been formed from a cube.



- The **center of the cube** is the central of tetrahedron at which is **placed the central metal ion**. **Four alternate corners of the cube** are **the four corners of the tetrahedron** at which the **four ligands are placed**.



The d_{yz} orbital in tetrahedral coordination. Electrons in this orbital can approach within a distance of a/2 to ligand electrons.



The d_{z2} orbital in tetrahedral coordination: electrons in d_{z2} are further from the ligands than electrons in d_{yz}.

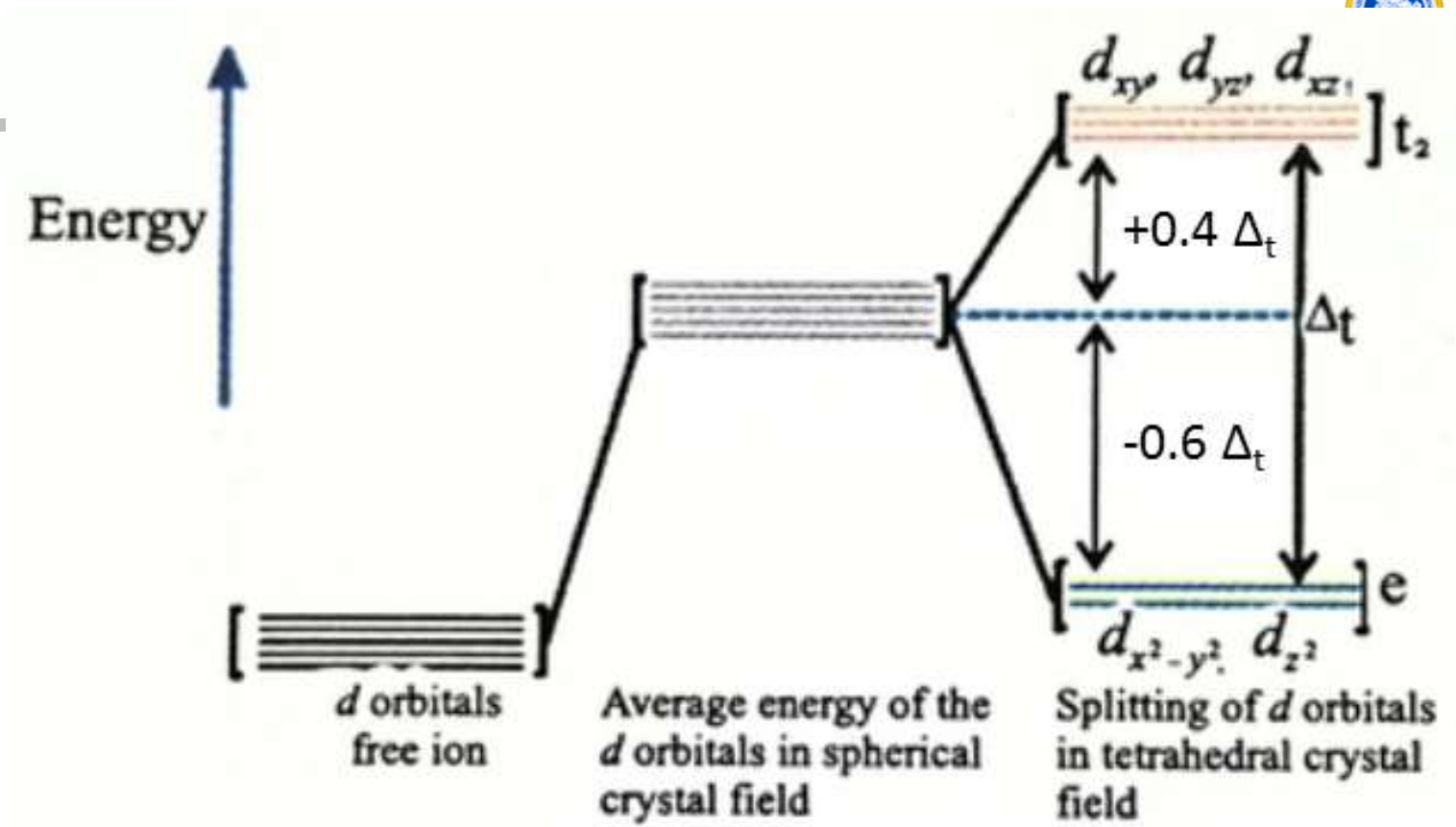
where a is the cube edge length

- Four ligands are **lying between the three axes viz., x, y and z axes** which pass through the center of the six faces of the cube and thus go through the center of the cube.

- Since the lobes of the ***t_2 orbitals (d_{xy}, d_{yz} and d_{xz}) are lying between the axes, ie., are lying closely in the path of the ligands***, these orbitals **experience greater force of repulsion** than those in ***e orbitals (d_{z^2} and $d_{x^2-y^2}$) whose lobes are lying along the axes***, ***ie., are lying between the ligands.***

- Thus the t_2 orbitals are **nearer to the direction of approach of the ligands than the e orbitals**. Hence, t_2 orbitals have higher energy compared to e-orbitals. So **the energy of t_2 orbitals is increased while that of e is decreased.**

- The d-orbitals are now split into two levels viz., **higher energy t_2 level and lower energy e level** which **is the reverse that seen for t_{2g} and e_g sets in octahedral complexes.**

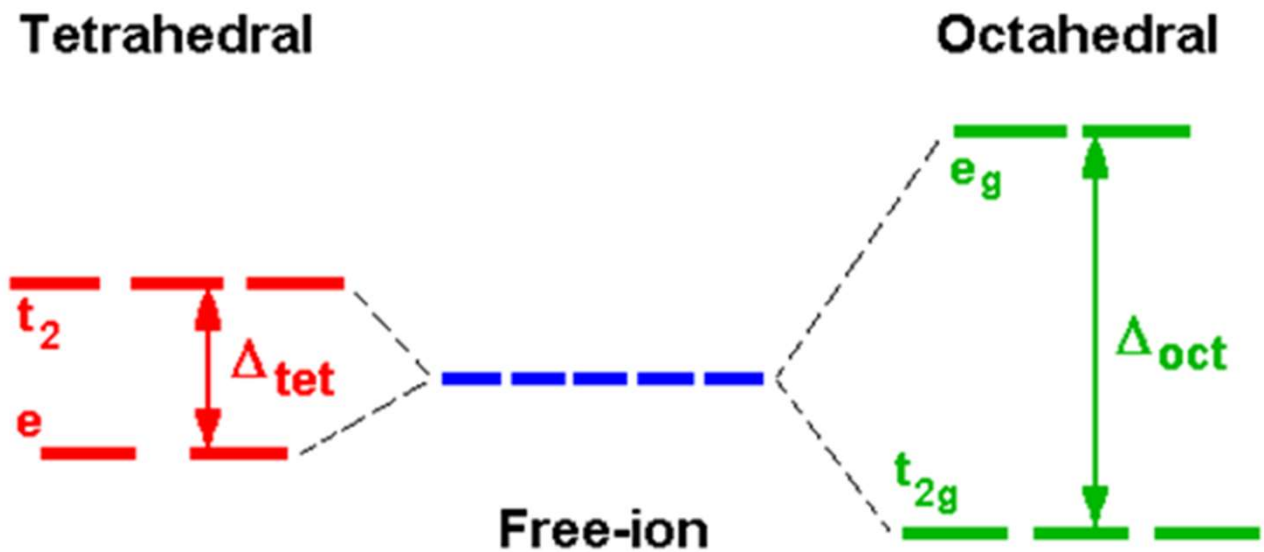


- The energy gap between t_2 and e sets is denoted by Δ_t. It has been shown that $\Delta_t < \Delta_o$, t_2 orbitals are now closest to the ligands and not point directly at the ligands. ***<u>In octahedral complex, there is a ligand along the axis and in tetrahedral complex no ligand lies directly along any axis.</u>***

- There are only **4 ligands** in the tetrahedral complex while in an octahedral complex there are **6 ligands**, **So $\Delta_t < \Delta_o$. 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 Δt is roughly 2/3 x 2/3 = 4/9 of Δo.**

- ***Δ_t = 4/9 Δo = 0.44 Δo (approx. 0.45 Δo)***



- The energy of t_2 orbitals is raised 0.4 Δ_t while the energy of e orbitals is lowered 0.6 Δ_t

- ***In case of tetrahedral complex, since $\Delta_t < P$, the electrons tend to remain unpaired and hence only high spin tetrahedral complexes are known.***

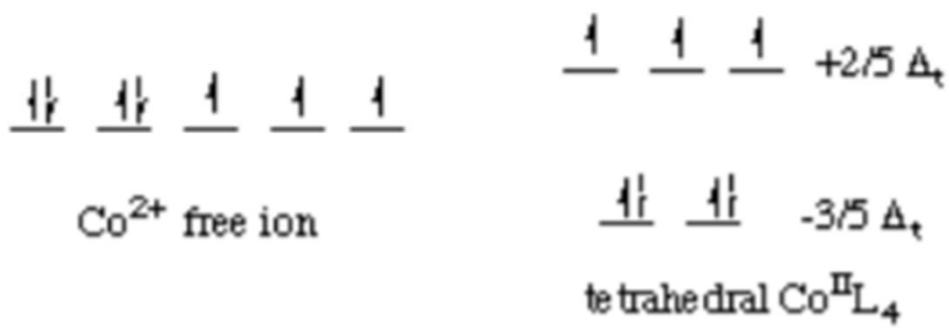
Filling up t_2 and e orbitals with electrons in high spin tetrahedral complexes

- The filling of t_2 and e orbitals **takes place according to Hund's rule,** i.e., electrons pair up only when each of the five d-orbitals is at least singly filled.

- The pairing of electrons will start from e orbitals, since these orbitals have less energy than t_2 orbitals.

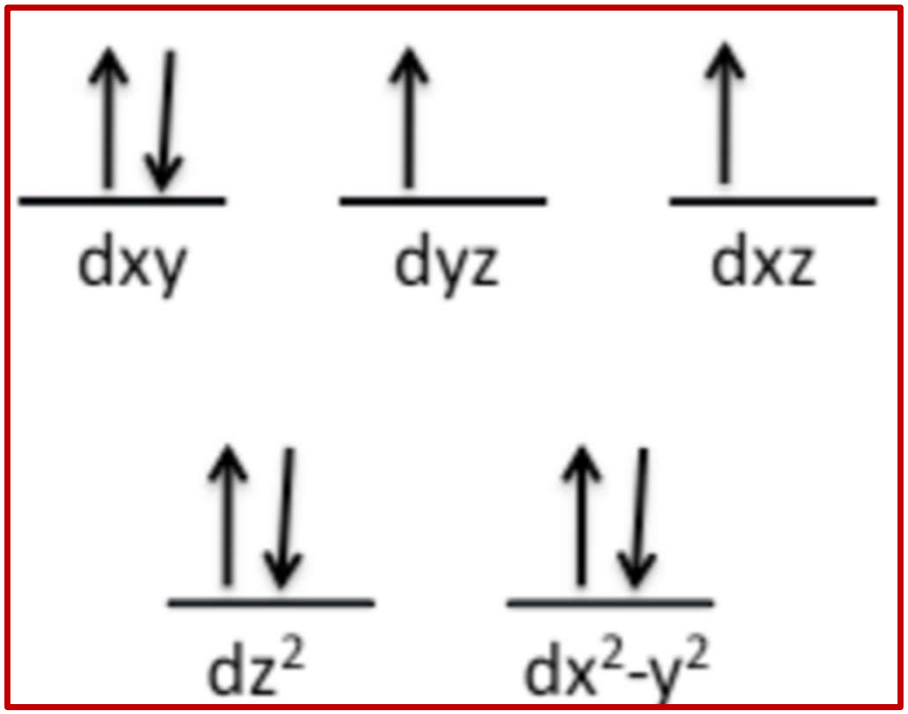
- Let's calculate the crystal field stabilization energy for a tetrahedral cobalt(II) complex. Cobalt(II) is a d^7 ion.

- The electronic configurations of the free ion and the tetrahedral complex are shown below.



$$\text{CFSE} = (4\ \text{electrons})(-3/5\ \Delta_t) + (3\ \text{electrons})(2/5\ \Delta_t)$$
$$= -1.2\ \Delta_t$$

$[Ni(Br)_4]^{2-}$, CFSE, spin & magnetism?



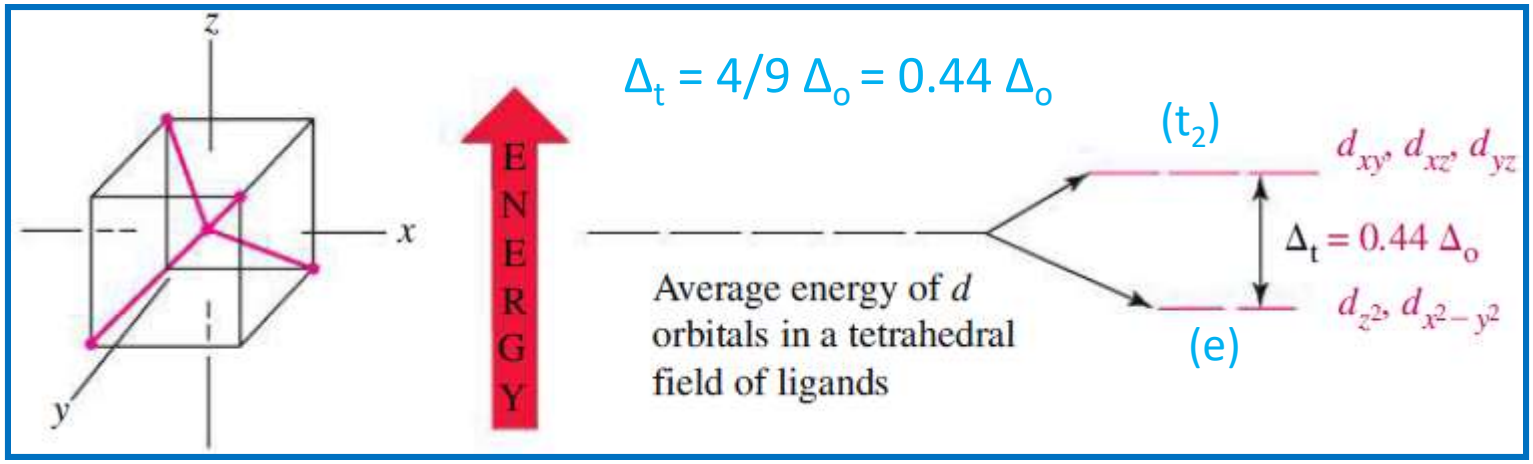
- **$e^4t_2^4$**
- **-4/5 Δt**
- **Unpaired electrons : 2**

$$\mu_{so} = \sqrt{n(n+2)}$$

$$\mu_{so} = \sqrt{4S(S+1)}$$

- **Paramagnetic**
- **Magnetic moment : 2.83 BM**

Crystal Field Theory: Summary, Tetrahedral Complexes



- Imagine a tetrahedral molecule inside a cube with **metal ions in the center** of the cube. The **ligands occupy the four alternate corners of the cube** leaving the rest four corners empty.

- The **two 'e' (d_{x2-y2} and d_z^2) 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)**

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.