Significance of Δ_o and its physical measurement

Electronic spectrum of $[Ti(H_2O)_6]^{3+}$

$3d^1 4s^0$

e_g

t_{2g}

(a)

(b)

494 nm = 20,300 cm^{-1}

Light of 510 nm
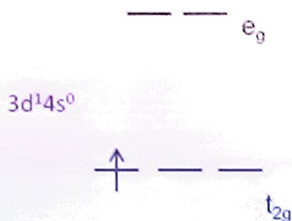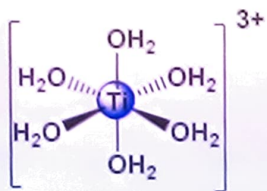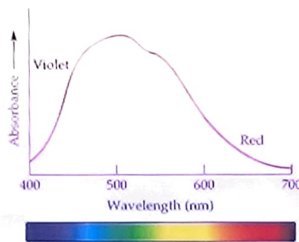
$t_{2g}{}^1 e_g{}^0$ $t_{2g}{}^0 e_g{}^1$
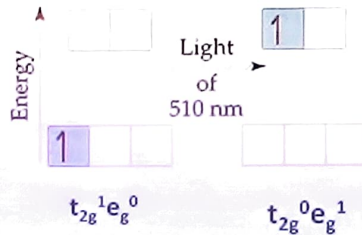
1 kj = 83.7 cm^{-1}

$[Ti(H_2O)_6]^{3+}$ Δ_o = 20,300 cm^{-1} = 243 kj/mol

Since an electron in the t_{2g} set is stabilized by -0.4 Δ_o 243 X -0.4 = -97 kj/mol

The complex is stabilized to the extent of 97 kj/mol compared to a hypothetical spherical field due to the splitting of the d orbitals; This extra stablization of the complex is called crystal field stabilization energy (CFSE)

Factors affecting the magnitude of crystal field splitting, Δ

1. Nature of metal ion (row to which it belongs)
   Going from the first row to second row there is an increase in Δ_o : Larger the metal $\rightarrow$ larger is the Δ

2. Oxidation state of the metal ion (higher the oxidation state more is the Δ_o

3. Number of ligands and shape of complex
   (Octahedral, tetrahedral, square planar....)

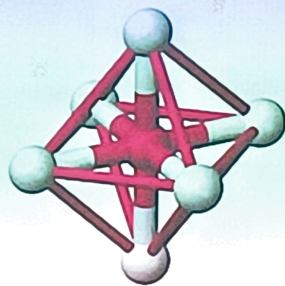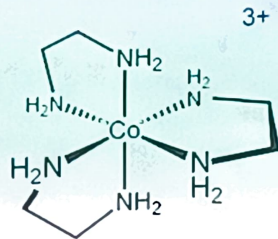4. Relative strength of the ligand (Spectrochemical Series)

1. Size of the metal ion / Row to which the metal ion belong: Larger the size (row to which it belongs) larger the Δ value

$[Co(en)_3]^{3+}$ $\longrightarrow$ 23,200 cm^{-1}

$[Rh(en)_3]^{3+}$ $\longrightarrow$ 34,600 cm^{-1} ~ 50% increase

$[Ir(en)_3]^{3+}$ $\longrightarrow$ 41,000 cm^{-1} ~ 25% increase

Δ_0 (cm^{-1})= 3d < 4d < 5d

- Second and third row transition metals will have greater tendency to form low spin complexes

- Around a large metal ion, a given set of ligands experience less steric crowding and therefore can approach closer to the metal ion. More closer- larger will be the splitting

Factors affecting the magnitude of crystal field splitting, Δ

2. Charge on the metal ion / Oxidation state of the metal ion: Greater the charge larger the Δ value

$[Co(NH_3)_6]^{2+}$ ———————   10,000 cm^{-1} $[Cr(H_2O)_6]^{2+}$ ——————— 14,000 cm^{-1}

$[Co(NH_3)_6]^{3+}$ ———————   22,900 cm^{-1} $[Cr(H_2O)_6]^{3+}$ ——————— 17,400 cm^{-1}

$[Ru(H_2O)_6]^{2+}$ ———————   19,800 cm^{-1}
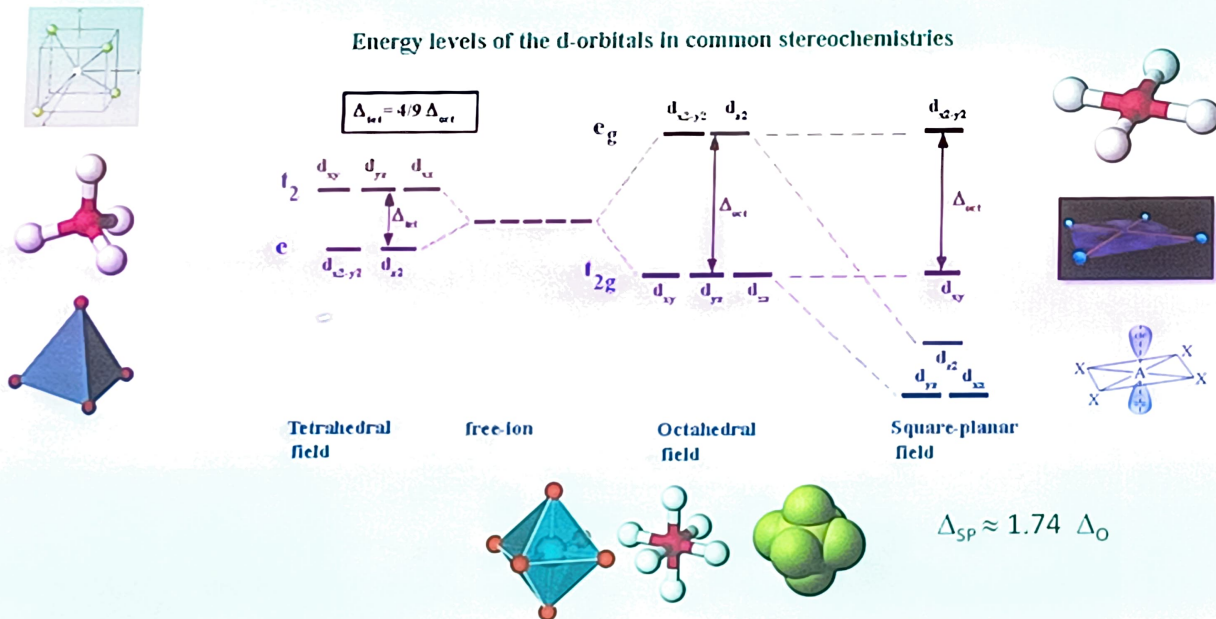
$[Ru(H_2O)_6]^{3+}$ ———————   28,600 cm^{-1}

- Higher the charge on the metal, the ligands are pulled in towards the metal more and therefore the ligands split the energies of the metal d orbitals to a greater extent

3. Number of ligands around the metal and shape of complex
   (Octahedral, tetrahedral, square planar....)

Energy levels of the d-orbitals in common stereochemistries

$$\Delta_{tet} = 4/9 \, \Delta_{oct}$$

t_2 : d_{xy} d_{yz} d_{xz}

Δ_{tet}

e : $d_{x^2-y^2}$ d_{z^2}

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

Δ_{oct}

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

$d_{x^2-y^2}$

Δ_{oct}

d_{xy}

d_{z^2}

d_{yz} d_{zx}

Tetrahedral field

free-ion

Octahedral field

Square-planar field

$$\Delta_{SP} \approx 1.74 \; \Delta_{O}$$
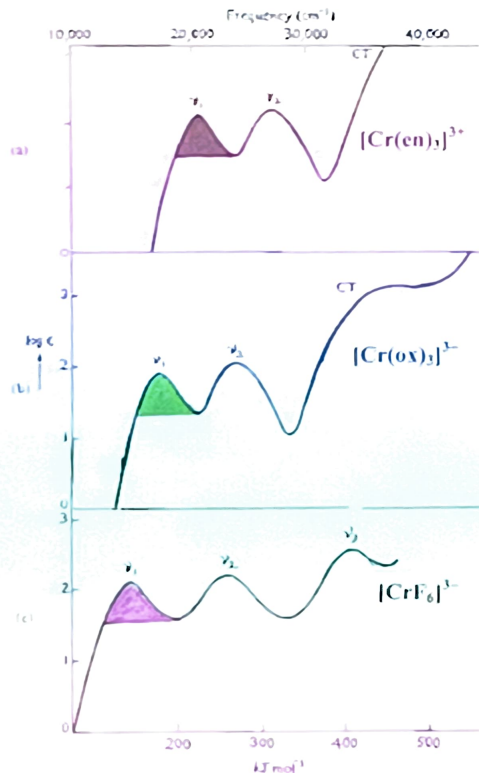
The effect of different ligands on the degree of Δ splitting is understood from the UV-Vis absorption spectra of complexes of the same metal-ion with different ligands

There is an increase in the frequency of the υ_1 (Δ_o) absorption band as the ligands on Cr^{3+} is changed from F $\rightarrow$ O based $\rightarrow$ N based ligands

1. For Mn^{2+} ion, $P = 28,000$ cm^{-1} Δ_o value for $[Mn(CN)_6]^{3+}$ ion is 38,500 cm^{-1}. Does this complex has high spin on low spin configuration? Also write the configuration.

2. Calculate CFSE values in terms of Δ_o and P f on HS and LS octahedral complexes of Fe(II) and Co(II)? Predict whether the complexes are paramagnetic or diamagnetic.

3. Determine CFSE of a d^6 octahedral complex having $\Delta_o = 25000$ cm^{-1} and $P = 15000$ cm^{-1}.

4. The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single d electron. To excite this electron from the ground state t2g orbital to the eg orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δoct and occurs at 499 nm. Calculate the value of Δoct in Joules and predict what color the solution will appear.

5. Which ligand generates a stronger magnetic complex ion when bound to Fe^{2+} : EDTA or CN– ?

6. ZnI$_4$ have eight valence electrons. If it is found to be diamagnetic, then does it occupy a tetrahedral or square plan geometry?

1. Spectral Properties (colors and their origin)
   - d-d, LMCT and MLCT Transitions

2. Magnetic Properties
   - Due to the presence of unpaired electrons in the $(n-1)d$-orbitals, most of the transition metals ions and their compounds are paramagnetic i.e. they are attracted by the magnetic field.

   - As the number of unpaired electrons increases from 1 to 5, the magnetic moment and hence paramagnetic character also increase.

   - Those transition elements which have paired electrons are diamagnetic i.e. they are repelled by the magnetic field.

   - Metals like Co and Ni possess high paramagnetism where they obtain permanent magnetic moment and are referred as ferromagnetic.

- Magnetism is caused by moving charged electrical particles (Faraday, 1830s). These particles can be the current of electrons through an electric wire, or the movement of charged particles (protons and electrons) within an atom. These charged particles move much like planets in a solar system:

  ✓ *nucleus spin* around its own axis, causing a **very weak** magnetic field.
  ✓ *electrons orbit* around the nucleus, causing a **weak** magnetic field.
  ✓ *electrons spin* around their own axis, causing a **significant** magnetic field.
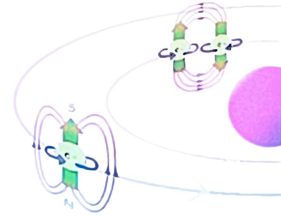
- **Spinning electrons generate the bulk of the magnetism in an atom.**

  Within each orbit, electrons with opposite spins pair together, resulting in no net magnetic field. Therefore, **only unpaired electrons** lead to magnetic moment

The **spin-only** formula (μ_s)

$$\mu_s = \sqrt{n(n+2)}$$

- The **spin-only** formula (μ_s) applies reasonably well to metal ions from the first row of transition metals: (units = $\mu_{B,}$ Bohr-magnetons)

Metal ion	d^n configuration	μ_s(calculated)	μ_{eff} (observed)
Ca^{2+}, Sc^{3+}	d^0	0	0
Ti^{3+}	d^1	1.73	1.7-1.8
V^{3+}	d^2	2.83	2.8-3.1
V^{2+}, Cr^{3+}	d^3	3.87	3.7-3.9
Cr^{2+}, Mn^{3+}	d^4	4.90	4.8-4.9
Mn^{2+}, Fe^{3+}	d^5	5.92	5.7-6.0
Fe^{2+}, Co^{3+}	d^6	4.90	5.0-5.6
Co^{2+}	d^7	3.87	4.3-5.2
Ni^{2+}	d^8	2.83	2.9-3.9
Cu^{2+}	d^9	1.73	1.9-2.1
Zn^{2+}, Ga^{3+}	d^{10}	0	0