

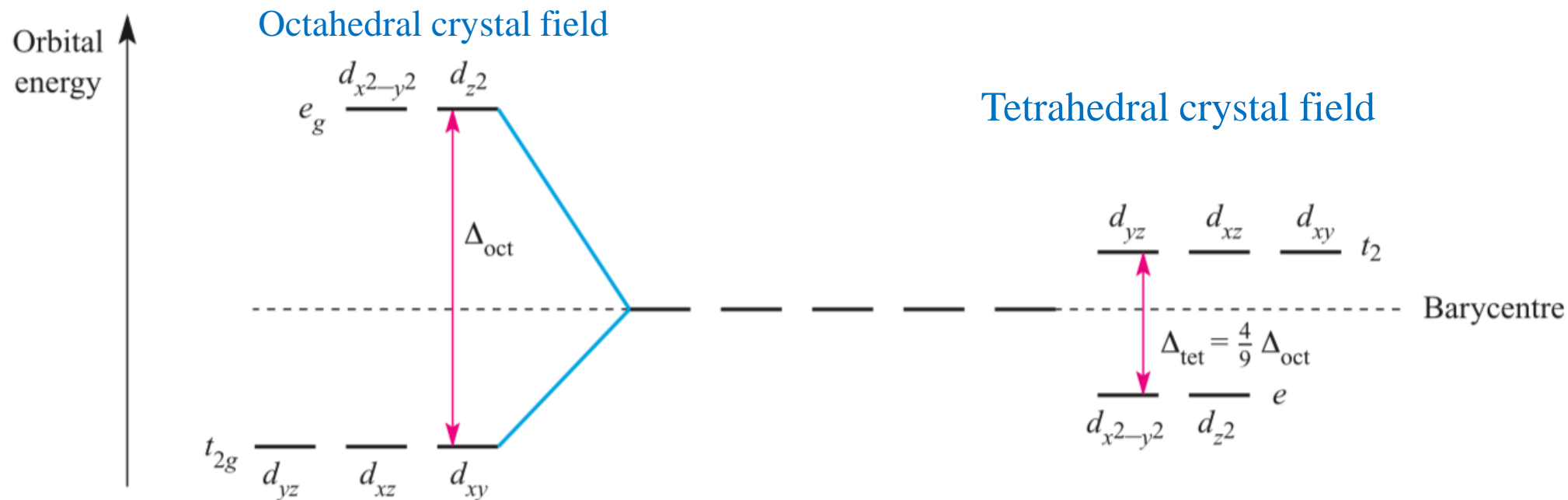
Inorganic chemistry

Lecture 2

Applications of crystal field theory

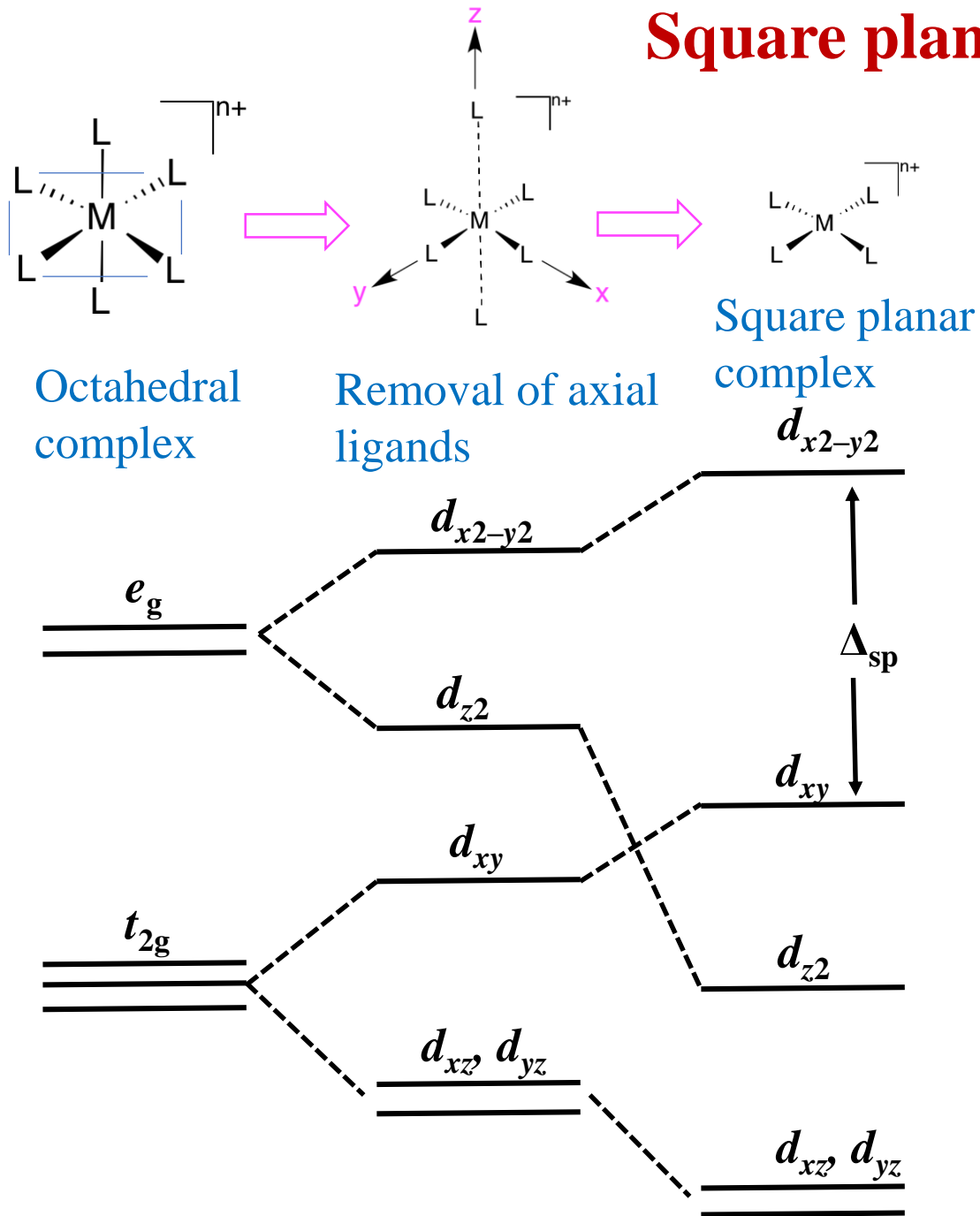
It tried to incorporate the writing in the pdf, but the file size became so high that it was not possible to incorporate it. Therefore, I request you to follow the lecture.

Recap of last lecture



$$\Delta_t = \frac{4}{9} \Delta_o \approx \frac{1}{2} \Delta_o$$

Square planar crystal field

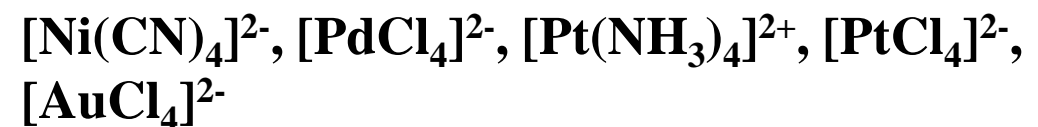


➤ Square planar is related to octahedral splitting: Removing the axial ligands of an octahedron to infinity results in a square plane

Some book has mentioned $\Delta_{sp} = 1.7\Delta_0$, it is relative term. You need to remember that $\Delta_{sp} > \Delta_0$ (that's all), value is not important

➤ It is observed that $\Delta_{sp} > \Delta_0$ for complexes of the same metal and ligands with the same M–L bond lengths.

Second and third row metal d^8 complexes (e.g. Pt(II), Pd(II), Rh(I), Ir(I)) are invariably square planar.



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
→ larger is the Δ

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

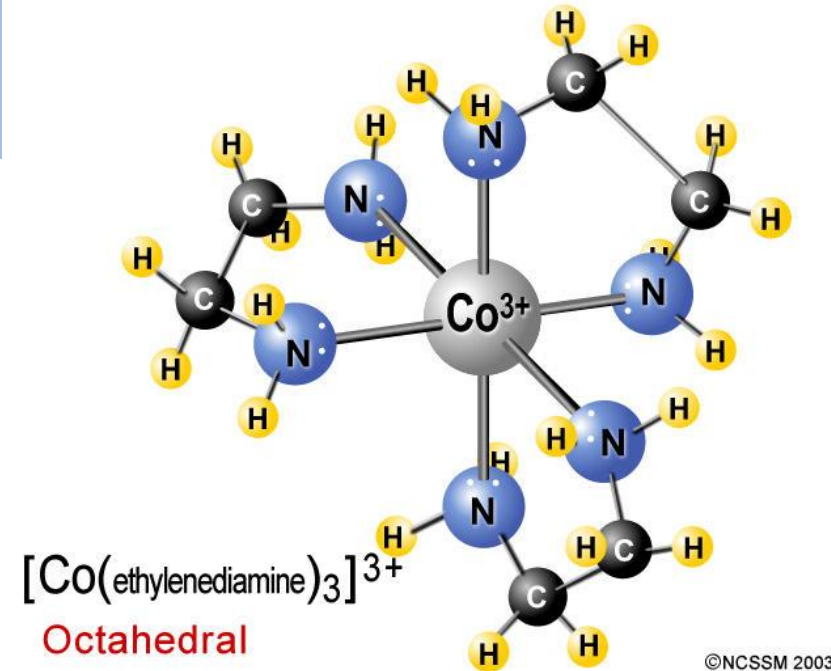
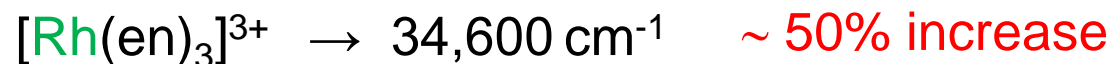
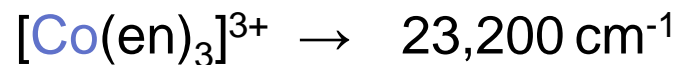
3. Number of ligands and shape of complex

(Octahedral, tetrahedral, square planar....)

4. Relative strength of the ligand (Spectrochemical Series)

Factors Affecting the Magnitude of Crystal Field Splitting Δ

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



Consequence:

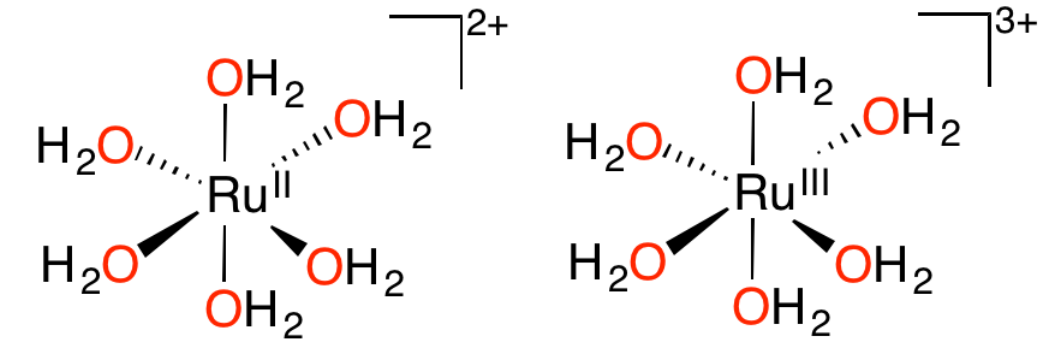
Second and third row transition metals will have greater tendency to form low spin complexes

Reason:

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

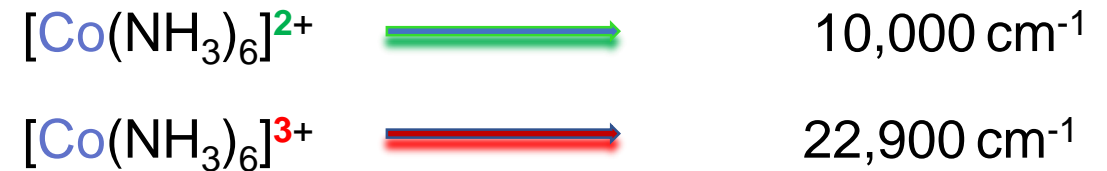
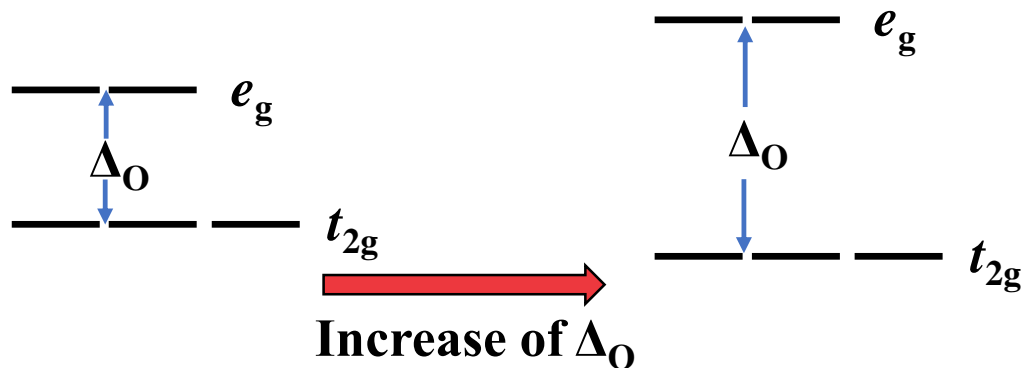
Factors governing the magnitude of Δ

Oxidation state of the metal ion. The magnitude of Δ increases with increasing ionic charge on the central metal ion. For a given ligand and a given metal, crystal-field splitting increases with increase in metal oxidation state.



$$\Delta_{\text{O}} = 19800 \text{ cm}^{-1}$$

$$\Delta_{\text{O}} = 28600 \text{ cm}^{-1}$$

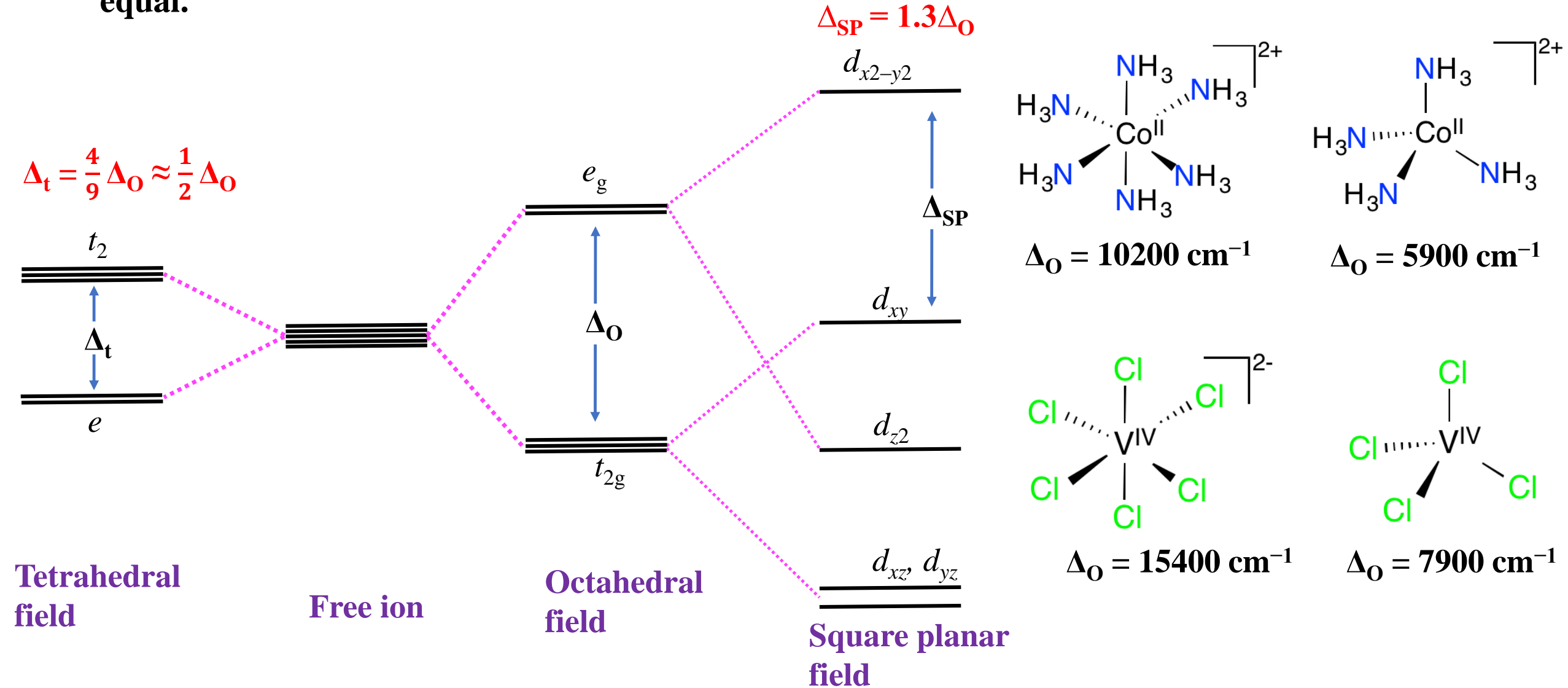


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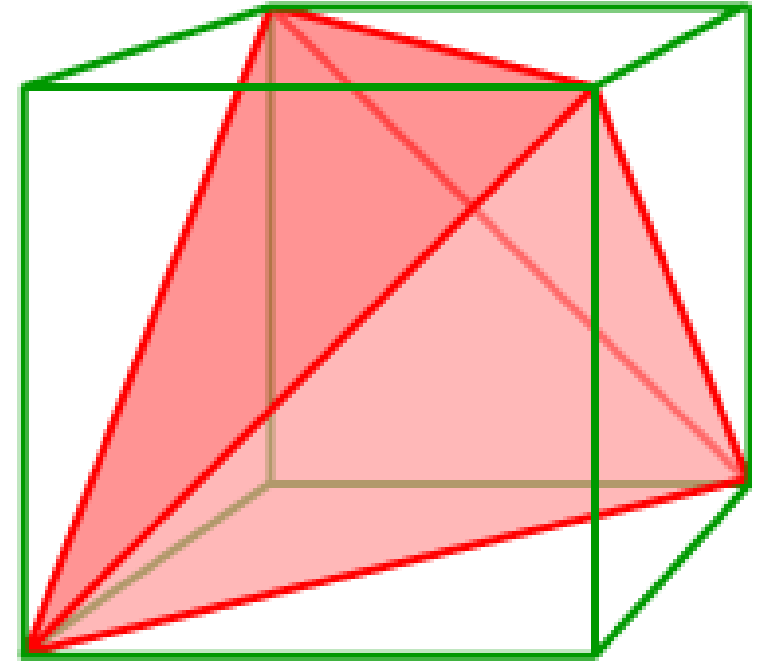
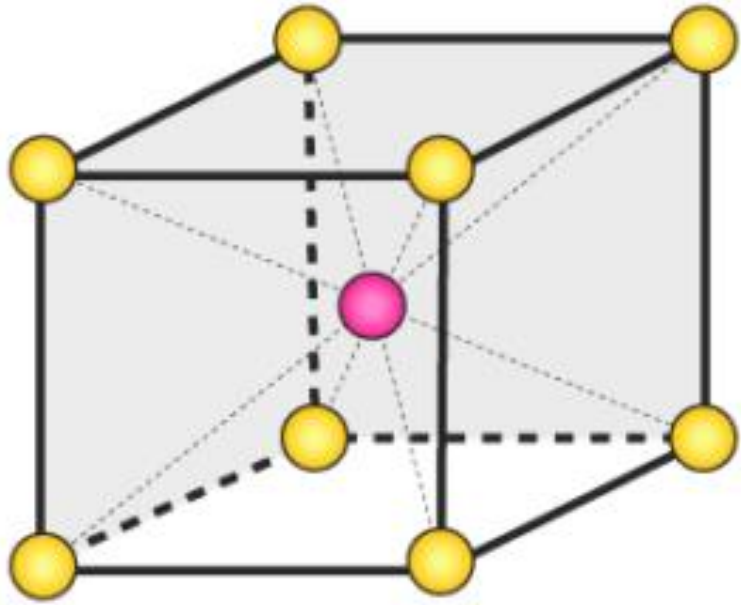
Higher the charge on the metal, the ligands are pulled in towards the metal more and therefore the ligands split the energies of the metal d orbitals to a greater extent

Factors governing the magnitude of Δ

- **Number and geometry of the ligands.** The point-charge model predicts that Δ for a tetrahedral complex will be only about 50% as large as for an octahedral complex, all other factors being equal.



Factors governing the magnitude of Δ : *Number and geometry of the ligands*



- Similar to tetrahedral complex, none of the metal d orbitals points exactly at the ligands, but the d_{xy} , d_{yz} and d_{xz} orbitals come nearer to doing so than the d_{z^2} and $d_{x^2-y^2}$ orbitals.

Tetrahedron is related to cube in splitting of energy levels $\Delta_t = \frac{1}{2} \Delta_c$
Same arrangement of orbitals

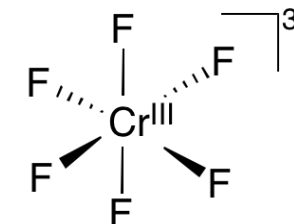
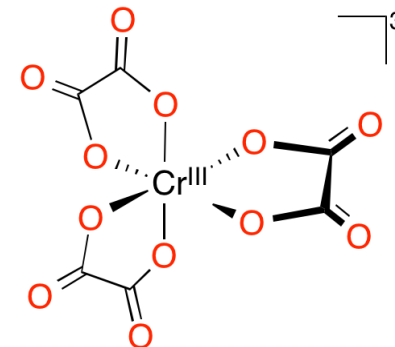
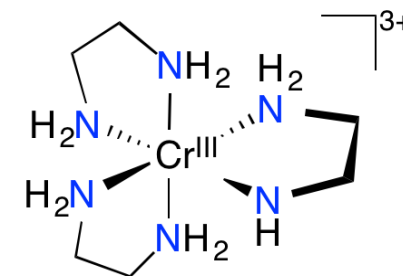
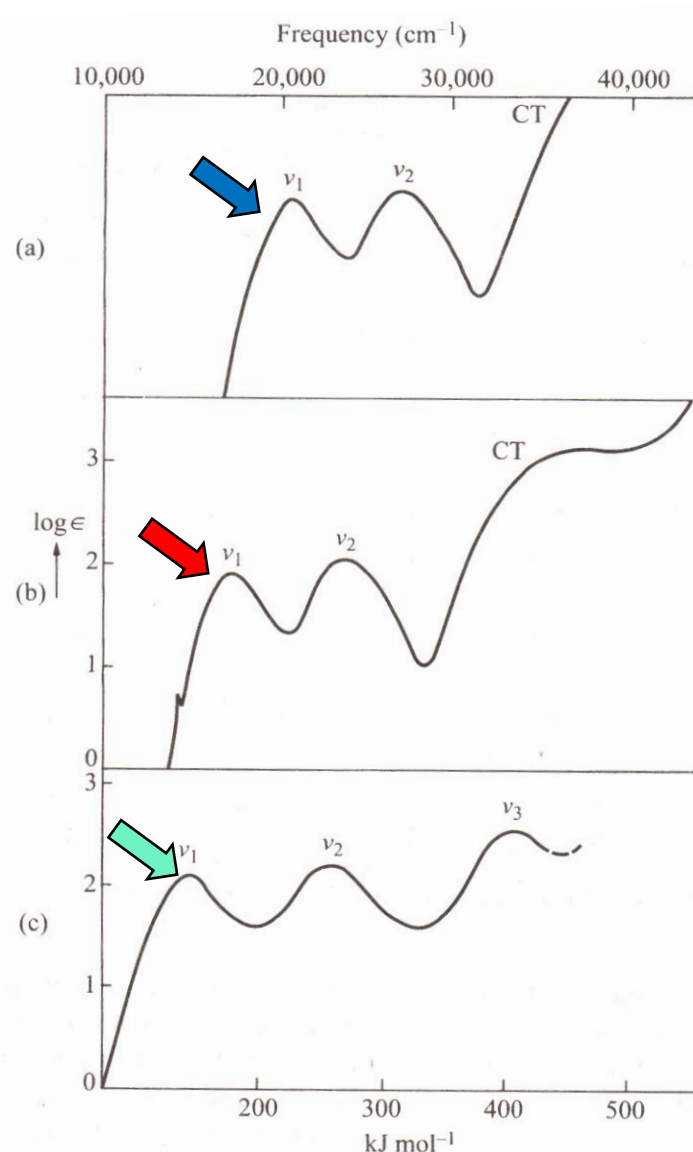
Factors governing the magnitude of Δ

➤ **Nature of the ligands.** The crystal field splitting parameter, Δ , varies systematically with the identity of the ligand. A ligand that gives rise to a large Δ value (such as CN^-) is referred to as a strong-field ligand, whereas one that gives rise to a smaller Δ value (such as Br^-) is referred to as a weak-field ligand.

➤ Three $d-d$ transitions are predicted for each of the Cr(III) complexes; where ν_1 correspond to Δ_o .

➤ There is an increase in the frequency of the ν_1 (Δ_o) absorption band as the ligands on Cr^{3+} is changed from

$\text{F} \rightarrow \text{O based} \rightarrow \text{N based}$ ligands

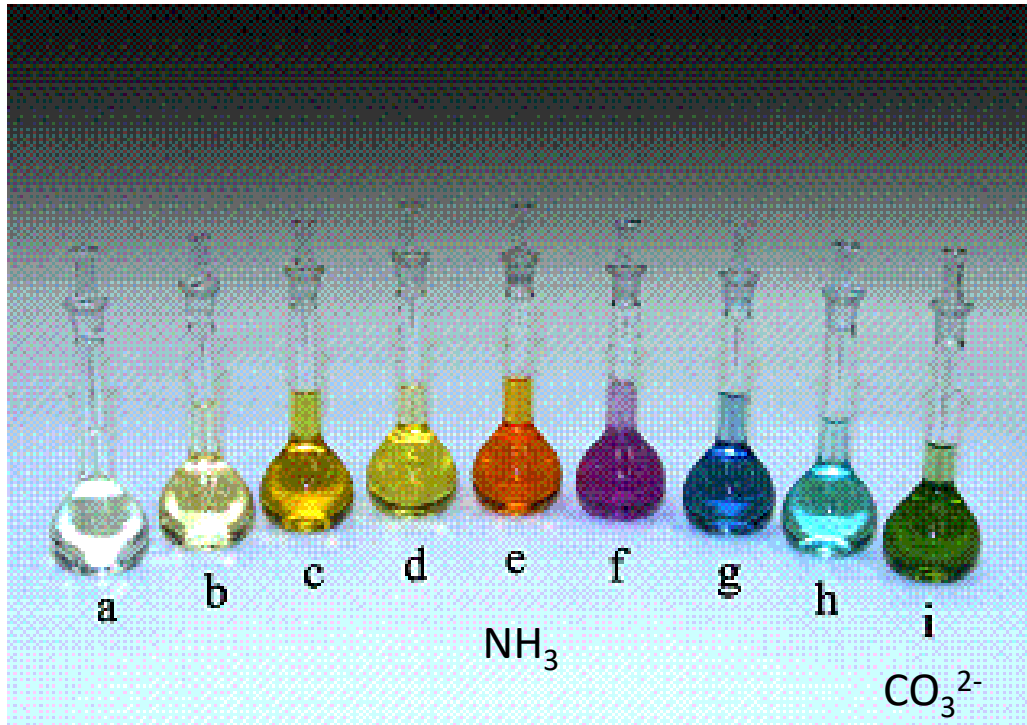


Spectra of three chromium(III) complexes: (a) Cr(en)_3^{3+} ; (b) $[\text{Cr(ox)}_3]^{3-}$; $[\text{CrF}_6]^{3-}$; ν_1 corresponds to Δ_o ; CT = charge transfer band.

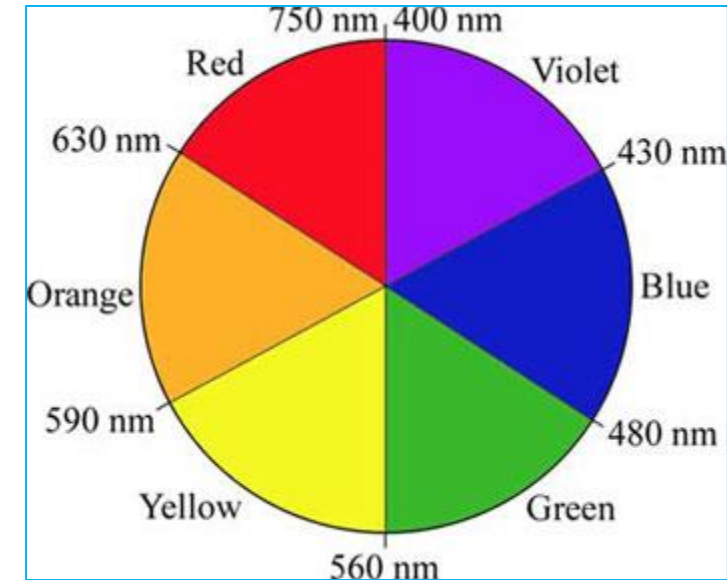
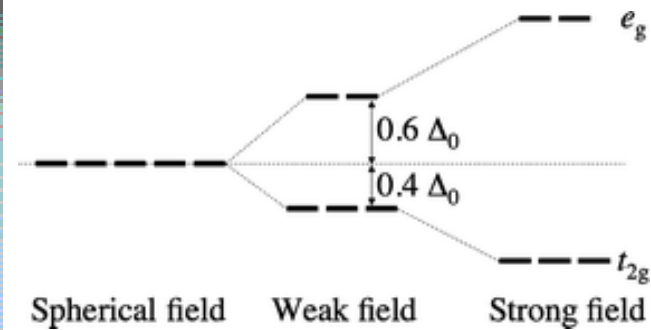
The Spectrochemical series

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{Ox} < \text{ONO}^- < \text{H}_2\text{O}$ Weak field $< \text{NCS}^- < \text{edta}^{4-} < \text{NH}_3 \sim \text{Py} < \text{en} < \text{bipy} < \text{Phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- \sim \text{CO}$ Strong field

Halides ; sulfur donors < Oxygen donors < Nitrogen donors < CN^- , CO

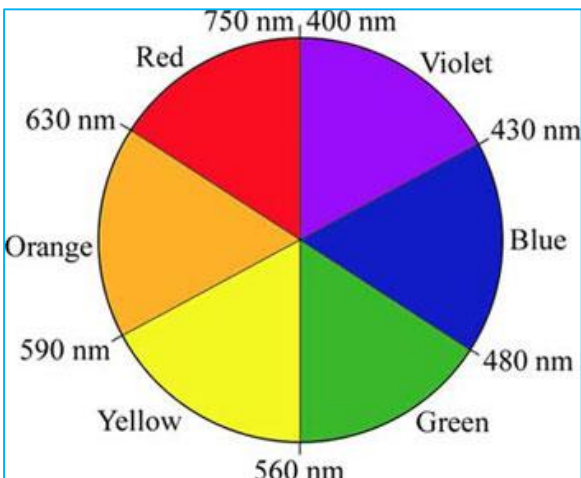
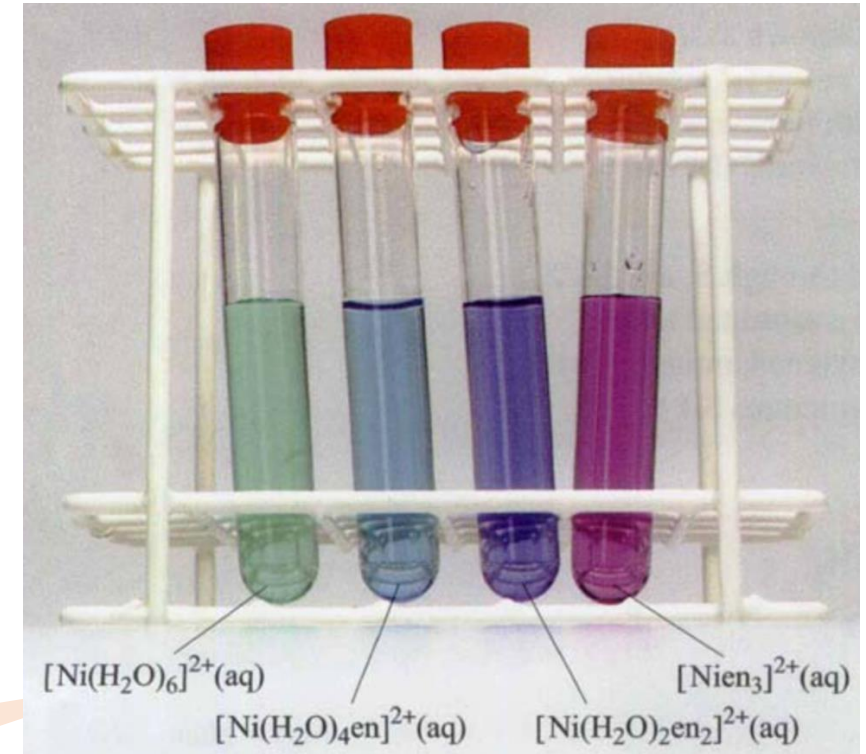
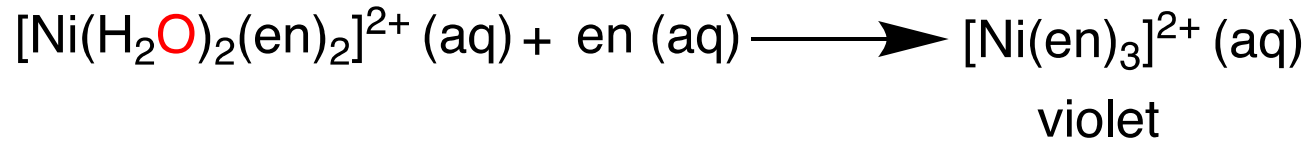
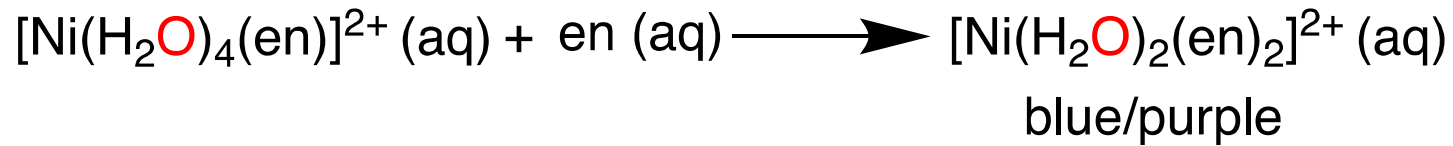
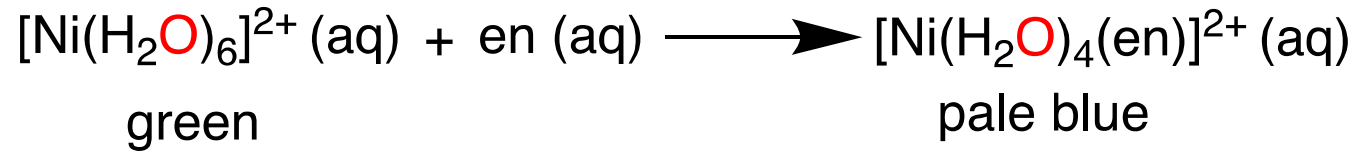


The spectrochemical series was first proposed in 1938 based on the results of absorption spectra of cobalt complexes



COBALT(III) complexes of (a) CN^- , (b) NO_2^- , (c) phen, (d) en, (e) NH_3 , (f) gly, (g) H_2O , (h) ox^{2-} , (i) CO_3^{2-}

When ethylenediamine (en) is slowly added to an aqueous solution of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, The solution colour changes from green to blue to purple to violet. Explain the observation?



As the number of 'en' ligand increases around Ni^{2+} , value of Δ_o increases simultaneously. The value of λ_{max} also changes simultaneously.

Aqueous solutions of complexes of Ni(II) with an increasing number of 'en' ligands.

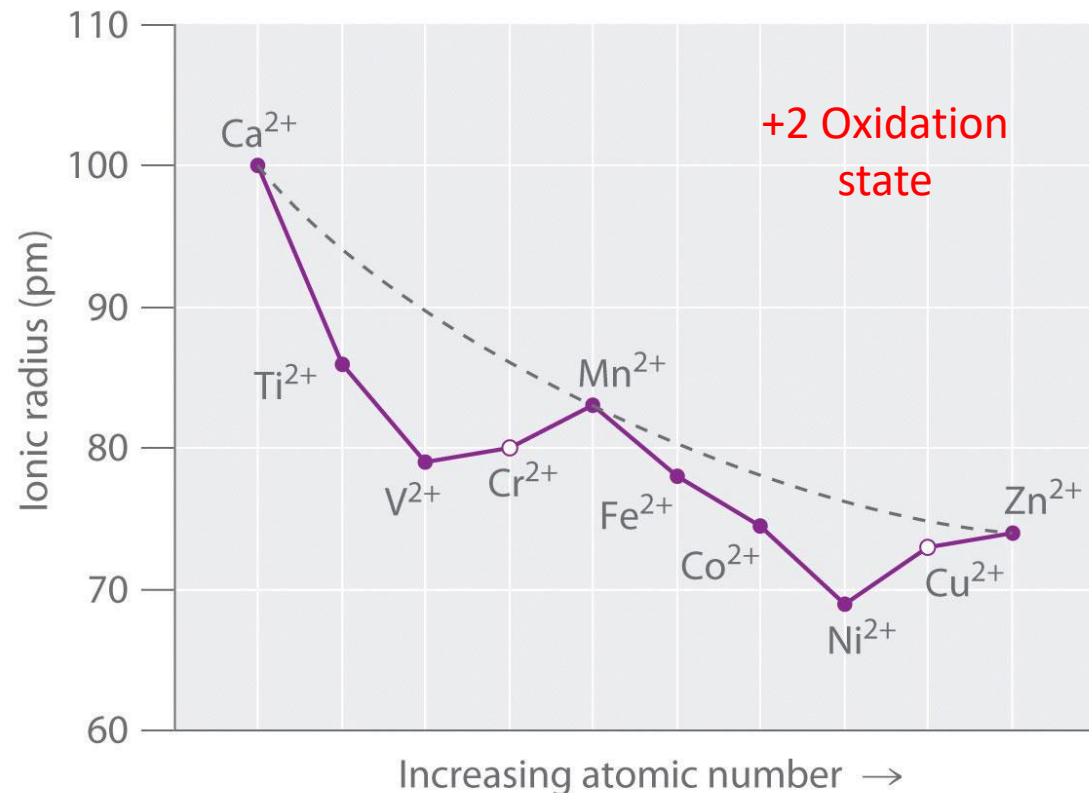
Crystal Field theory are useful in interpreting several behavior of transition metals complexes:

1. Ionic radii of transition metal ions in a complex
2. Enthalpy of hydration of transition metal ions
3. Site preference of Spinel and Inverse Spinel

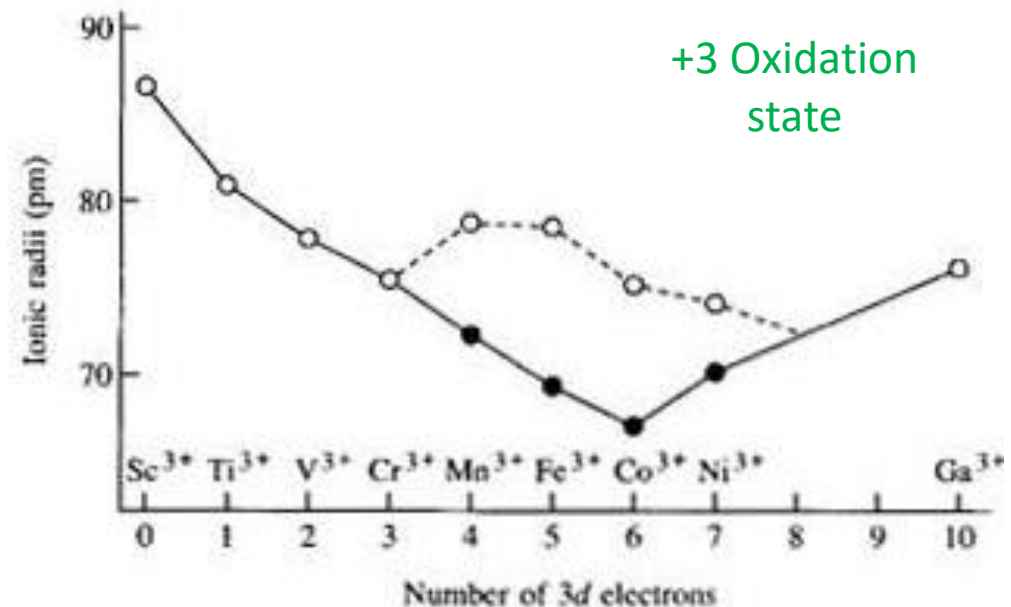
Ionic radii of transition metal ions in the presence of weak field and strong field ligands

One can expect decrease the ionic radii of the M^{2+} ions smoothly from Ca^{2+} to Zn^{2+} due to the increase in nuclear charge

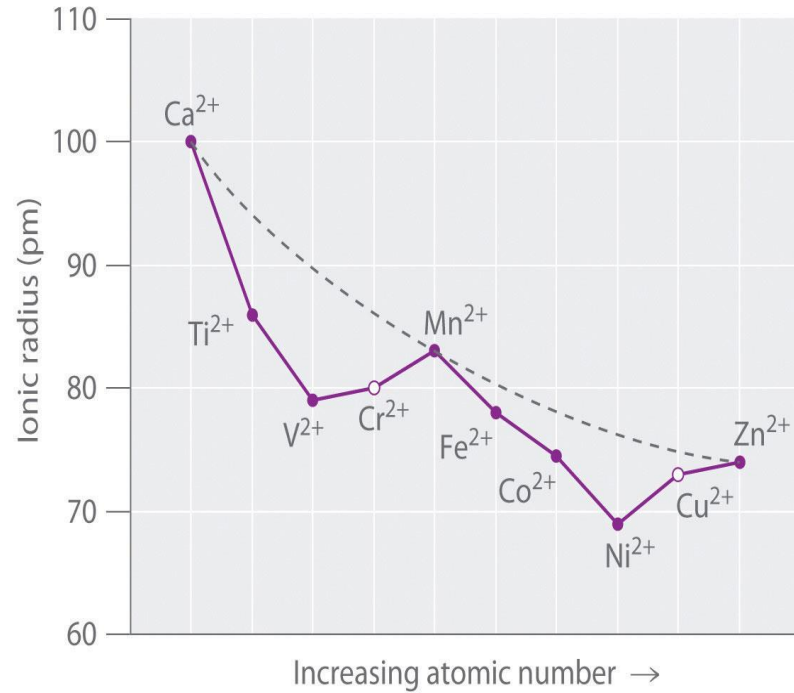
But the plot shown below (left) for weak field ligands indicate that the expected regular decrease is absent expect for Ca^{2+} , Mn^{2+} and Zn^{2+}



For strong field ligands like CN^- a different trend in variation is observed with a steady decrease till d^6 (t_{2g}^6) (tutorial question) 😊



Ionic radii of transition metal ions in the presence of weak field and strong field ligands



Why does the ionic radii decrease and then increase??

Ti^{2+} (d^2) electron occupy only t_{2g}

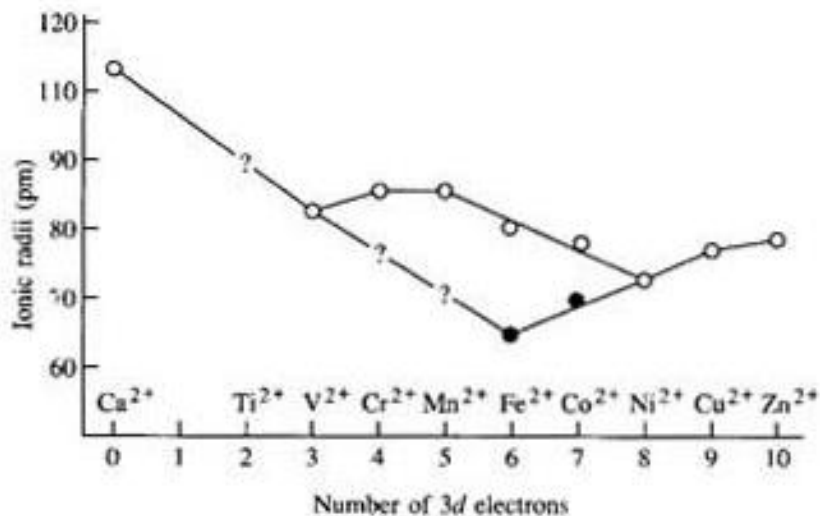
V^{2+} (d^3) electrons occupy only t_{2g}

Cr^{2+} (d^4 HS) electrons start occupying the e_g orbitals

As the e_g orbitals point directly towards the ligands, the repulsion between the metal electrons and ligand electrons will be higher than normal leading to the eventual increase in the ionic radius.

In the case of strong field ligand such as cyanide there will be a steady decrease in ionic radii till t_{2g}^6 is reached.

The same trend is observed also for M^{3+} transition metal complexes

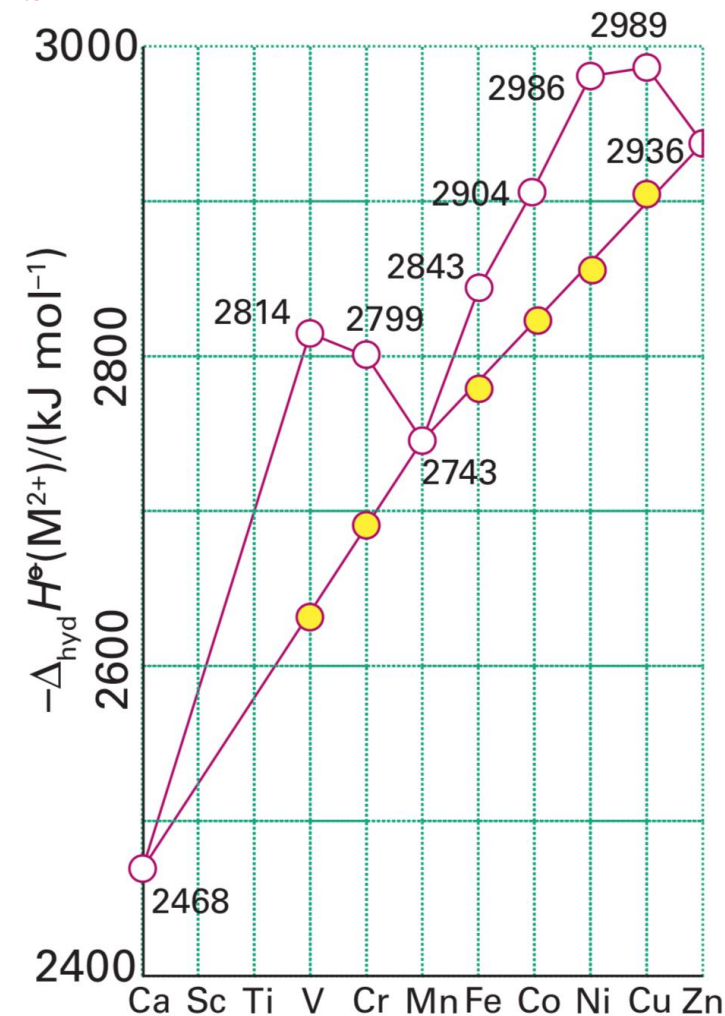


Hydration energy of transition metal ions

It is the heat exchange involved when 1 mole of gaseous ions become hydrated $M_{(g)}^{2+} + \text{excess } H_2O \rightarrow [M(H_2O)_6]^{2+}$; In other words, the amount of energy released when a mole of the ion dissolves in a large amount of water forming an infinite dilute solution in the process.

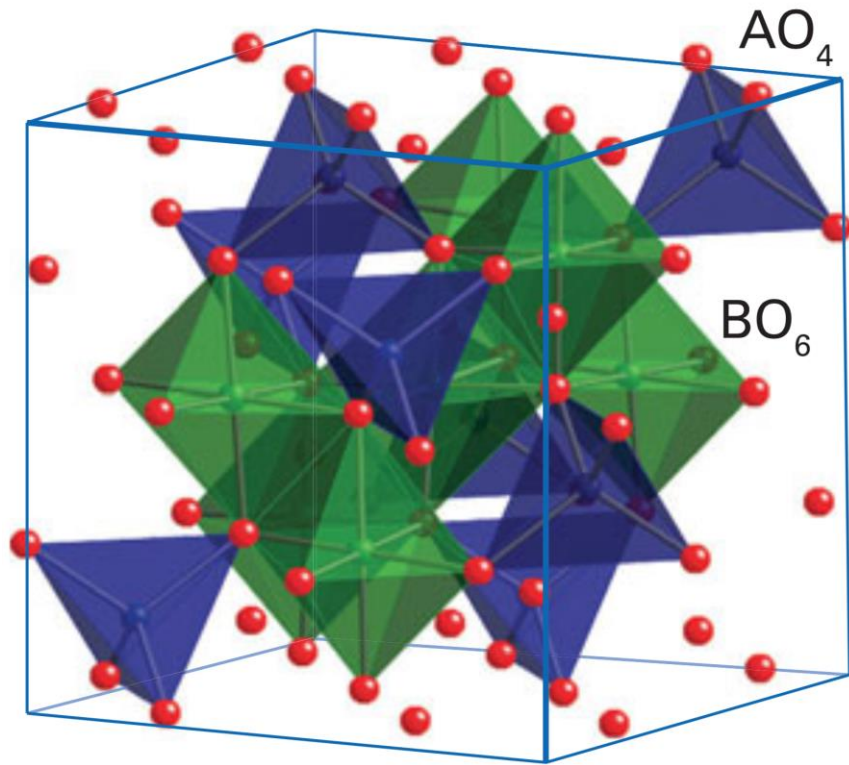
Higher the charge on the ions and smaller the size, more exothermic will be the hydration energy. So it is expected to increase smoothly on going from left to right of the transition metals

The heats of hydration show two “humps” consistent with the expected CFSE for the metal ions. For d^0 , d^5 , and d^{10} there is no additional stabilization of the aqua complex since these cases have no ligand field stabilization



The hydration enthalpy of M^{2+} ions of the first row of the d-block. The straight line shows the trend when the CFSE has been subtracted from the observed values.

Site preference of Spinel and Inverse Spinel



A segment of the spinel (AB_2O_4) unit cell showing the tetrahedral environment of A ions and the octahedral environments of B ions.

Spinel are a class of crystalline solids of the general formula AB_2O_4 ($A^{II}B^{III}_2O_4$) where

A = main group
(Group IIA) or
transition metal
ion in the +2
oxidation state

B = main group
(Group IIIA) or
transition metal
ion in the +3
oxidation state

The weak field oxide ions provide a cubic close-packed lattice. In one unit cell of AB_2O_4 there are 8 tetrahedral and 4 octahedral holes

Normal Spinel: A^{2+} ions
occupy $1/8^{\text{th}}$ of the Td holes
 B^{3+} ions occupy $1/2$ of the
octahedral holes

Eg. $MgAl_2O_4$
 Mg^{2+} Tetrahedral
 Al^{3+} octahedral

Inverse Spinel: The +2 ion
and one of the +3 ions
exchange positions i.e. Td
holes: +3 , Oh holes: both +2
and +3 ions

Eg. Fe_3O_4 (Magnetite)
 Fe^{3+} Tetrahedral
 Fe^{2+}, Fe^{3+} octahedral