



# CHEMISTRY

7<sup>th</sup> and 8<sup>th</sup> class Date : 23-09-2021

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## Last class...

- ☐ CFT - introduction

## In this class...



- ❑ Crystal Field Theory – continuation

## Transition metal complex



### Variation in colour & magnetic property (How to account ?)



## Orbitals and quantum numbers



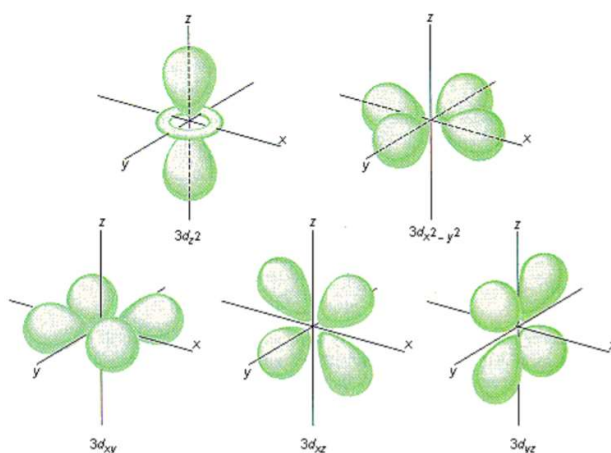
Name	Symbol	Allowed Values	Property
principal	$n$	positive integers (1, 2, 3,...)	orbital energy (size)
angular momentum	$l$	integers from 0 to $n-1$	orbital shape ( $l$ values of 0, 1, 2 and 3 correspond to $s$ , $p$ , $d$ and $f$ orbitals, respectively.)
magnetic	$m_l$	integers from $-l$ to 0 to $+l$	orbital orientation
spin	$m_s$	$+1/2$ or $-1/2$	direction of $e^-$ spin

Each electron in an atom has its own unique set of four (4) quantum numbers.

## Transition metal complex, d orbitals



### d orbitals



$d_{xy}$ : lobes lie in-between the x and the y axes.

$d_{xz}$ : lobes lie in-between the x and the z axes.

$d_{yz}$ : lobes lie in-between the y and the z axes.

$d_{x^2-y^2}$ : lobes lie on the x and y axes.

$d_{z^2}$ : there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

## Crystal field theory



- ❑ Crystal field theory, more specifically crystal field splitting, **uses the d-orbitals and their degeneracy to describe spectroscopic properties of transition metal complexes.**
- ❑ **Crystal field theory** is a model of the electronic structure of transition-metal complexes that considers how the energies of the d orbitals of a metal ion are affected by the electric field of the ligands
- ❑ *CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck (1930s)*

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## Salient features of CFT



- ❑ **Central metal cation is surrounded by ligands** which contain **one or more lone pairs of electrons**
- ❑ **The ionic ligands ( $F^-$ ,  $Cl^-$ ,  $CN^-$ ) are considered as negative point charges** (also called as point charges) and the **neutral ligands considered as point dipoles** or simple dipoles
- ❑ The **metal and ligand don't mix their orbitals or share electrons**, i.e., it does not consider any orbital overlap
- ❑ The **interaction between metal cation and ligand is purely electrostatic**, i.e., the metal – ligand bond is considered to be 100% ionic

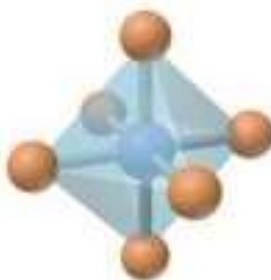
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Material Technology

## Octahedral complex



Coordination Number	Shape	Examples
6	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{V}(\text{CN})_6]^{4-}$ , $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ , $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{FeCl}_6]^{3-}$ , $[\text{Co}(\text{en})_3]^{3+}$



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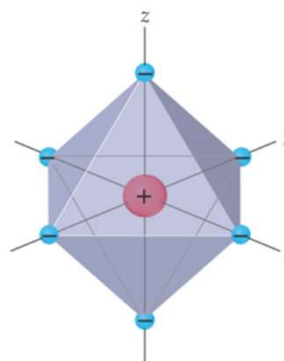
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## CFT as applied to octahedral complexes

### Crystal field splitting of d-orbitals in octahedral complexes



- ❑ In  $[\text{ML}_6]^{n+}$ , the **central metal cation is placed at the center of the octahedron** and is surrounded by **six ligands which reside at the six corners of the octahedron** as shown in figure.
- ❑ The three axes, viz x-, y- and z-axes which point along the corners have also been shown
- ❑ In case of **free metal ion, all the five d-orbitals are degenerate**, i.e., these have the same energy.
- ❑ The **ligands on each of the three axes are allowed to approach towards the metal cation from both the ends of axes.**

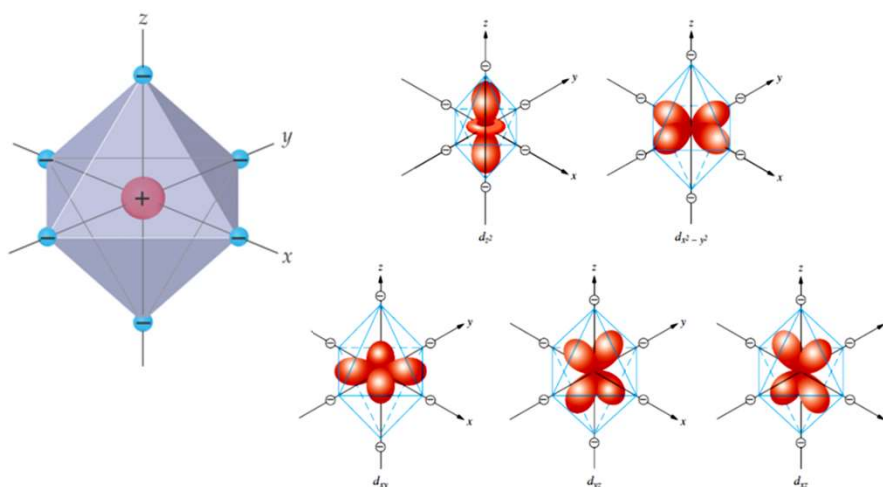


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## The five *d* orbitals and ligands



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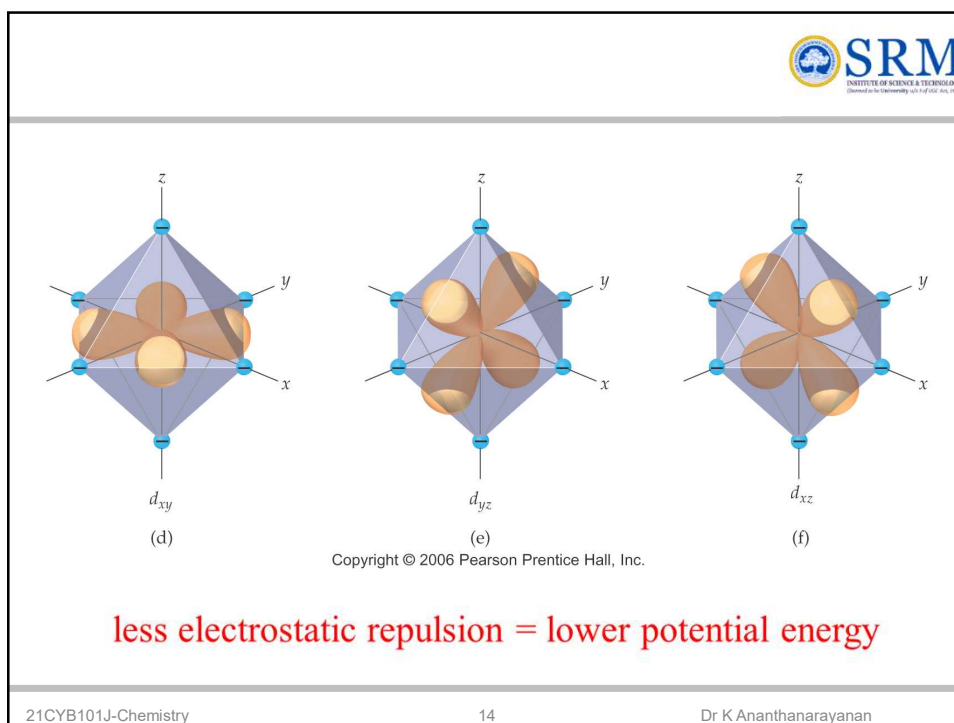
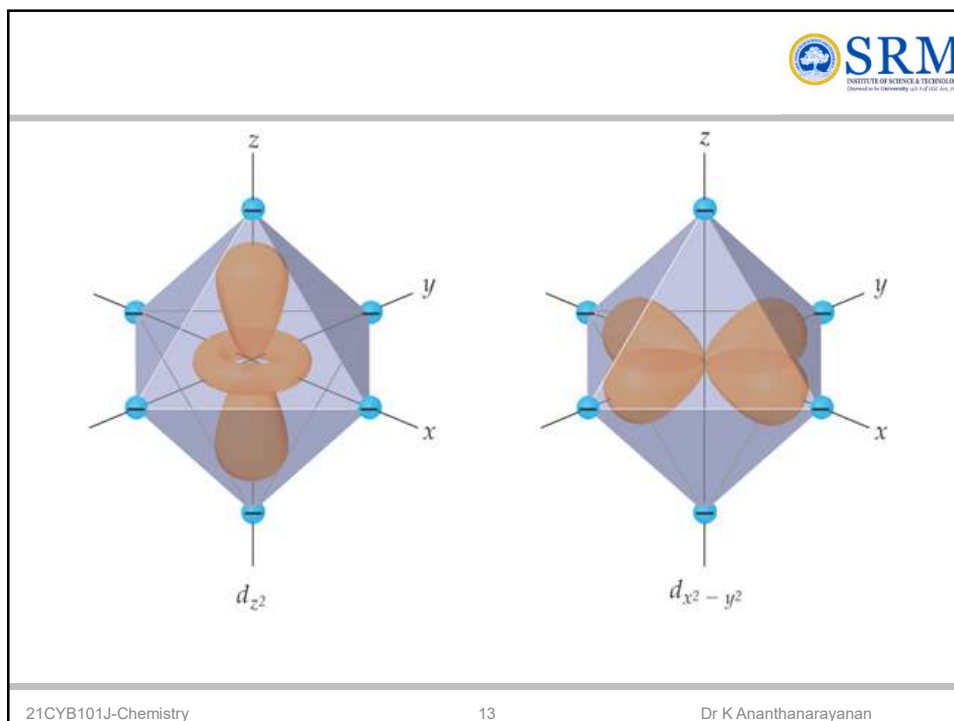


- ❑ In this process, the **electrons in d-orbitals of metal cation are repelled by negative point charge**. This repulsion will raise the energy of all the five d-orbitals
- ❑ If all the ligands approaching the central metal are at an equal distance from each of five d-orbitals, the energy of each of the d-orbitals will raise by the same amount, i.e., all the d-orbitals will still remain degenerate, although they will have now higher than before
- ❑ Since the lobes of the  $d_z^2$  and  $d_{x^2-y^2}$  orbitals ( $e_g$  orbitals) lie directly in the path of approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in three  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals ( $t_{2g}$  orbitals) whose lobes are directed in the space between the path of the approaching ligands. So the energy of  $e_g$  orbitals is increased while that of  $t_{2g}$  is decreased

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## CFT as applied to octahedral complexes



### Crystal field splitting of d-orbitals in octahedral complexes

- ☐ In an isolated atom, these orbitals have the same energy
- ☐ However, in an octahedral complex, the orbitals split into two sets, with the  **$d_{z^2}$  and  $d_{x^2-y^2}$  orbitals** having higher energy than the other three
- ☐ Note that the lobes of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals **point toward the ligands** (represented here by negative charges), whereas the lobes of the **other orbitals point between ligands.**
- ☐ The repulsion is greater in the case of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals.

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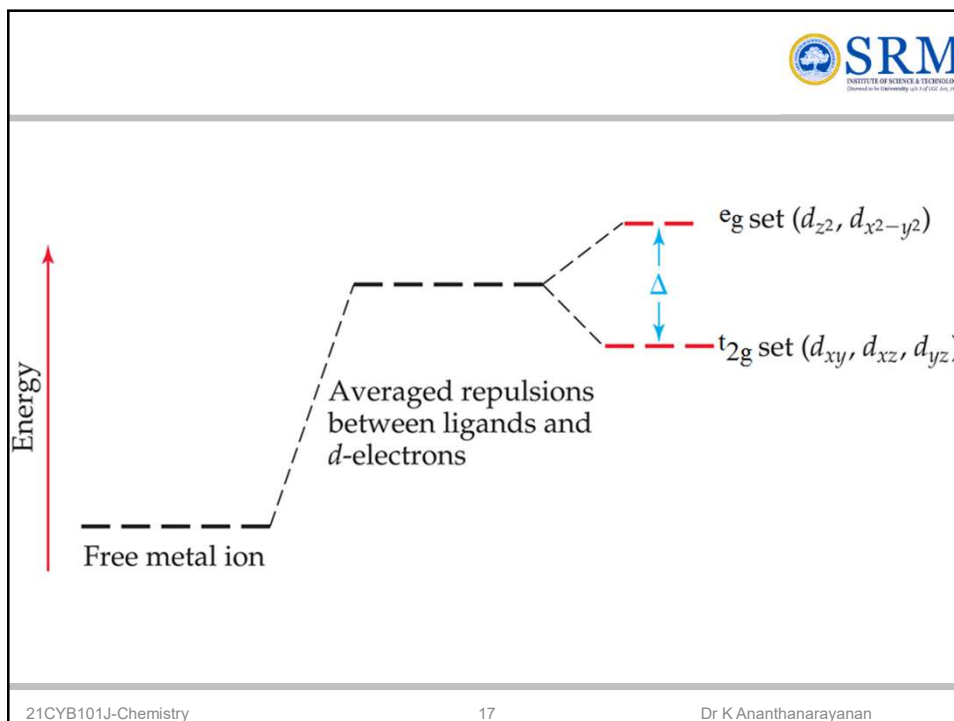
- ☐ Under the influence of approaching ligands, **the five d-orbitals which were originally degenerate** in the free metal cation are **now split into two levels** viz.,  **$t_{2g}$  level** which is triply degenerate and is of lower energy and,  **$e_g$  level** which is doubly degenerate and is of higher energy.
- ☐ **The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting.**


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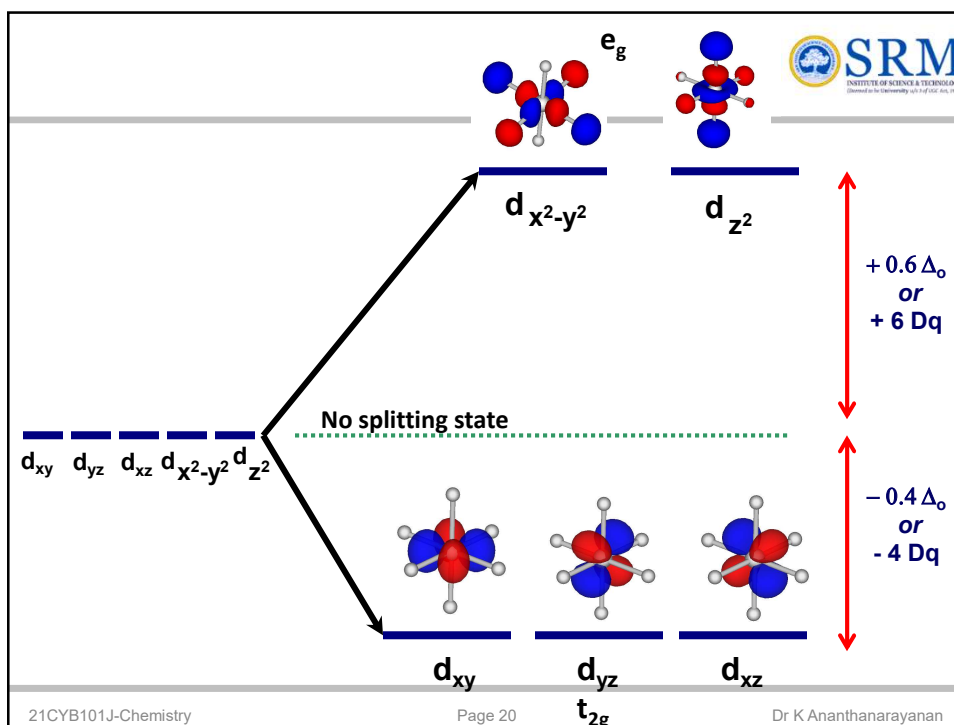
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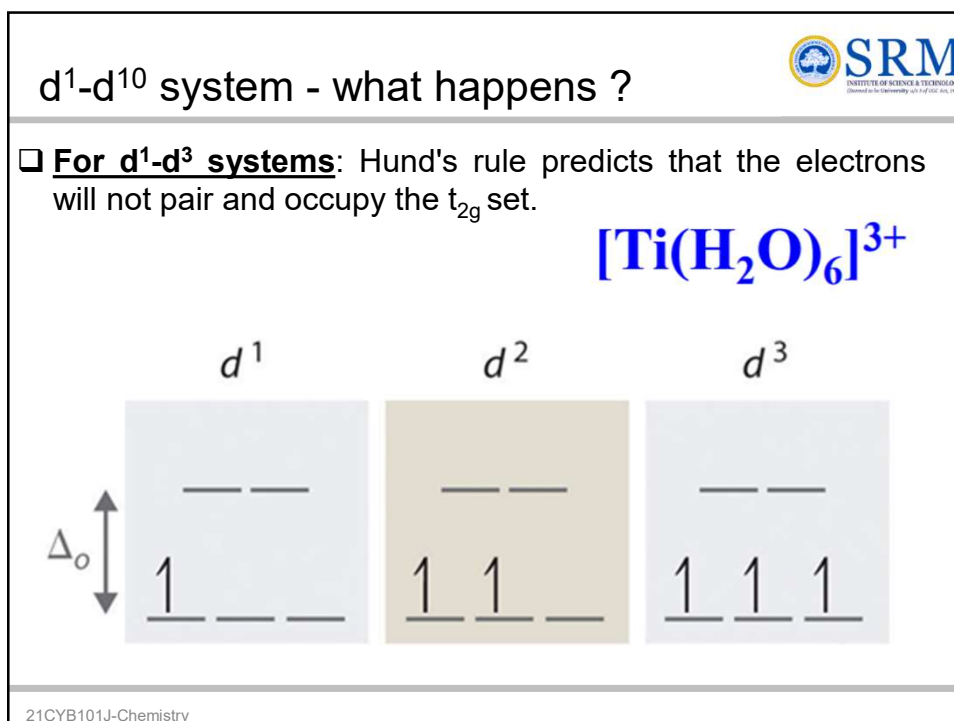
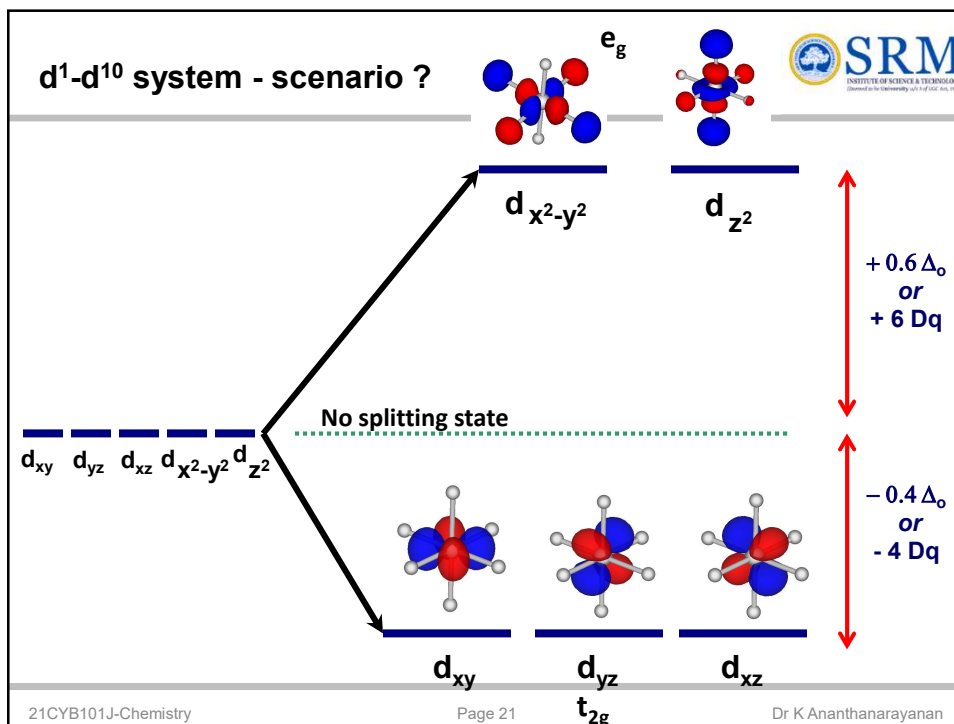




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- ❑ The energy gap between  $t_{2g}$  and  $e_g$  sets is denoted by  $\Delta_o$  or  $10 Dq$  where  $o$  in  $\Delta_o$  indicates an octahedral arrangement of the ligands around the central metal cation.
  - ❑ This energy difference arises because of the difference in electrostatic field exerted by the ligands on  $t_{2g}$  and  $e_g$  sets of the orbitals of the central metal cation.  $\Delta_o$  or  $10 Dq$  is called crystal field splitting energy.
  - ❑ It is important to note that the splitting of the  $d$  orbitals in a crystal field does not change the total energy of the five  $d$  orbitals:
  - ❑ The two  $e_g$  orbitals increase in energy by  $0.6\Delta_o$ , whereas the three  $t_{2g}$  orbitals decrease in energy by  $0.4\Delta_o$ . Thus the total change in energy is  $2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0$ .
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- ❑ The **energy of  $t_{2g}$  orbitals is  $0.4 \Delta_o (=4 Dq)$  below** than that of hypothetical degenerate d-orbitals and the energy of  **$e_g$  orbitals is  $0.6 \Delta_o (=6 Dq)$  above** than that of hypothetical degenerate d-orbitals.
- ❑ So  $t_{2g}$  set loses an energy equal to  $0.4 \Delta_o (=4 Dq)$  while  $e_g$  set gains an energy equal to  $0.6 \Delta_o (=6 Dq)$ .
- ❑ The **loss and gain in energies in  $t_{2g}$  and  $e_g$  orbitals is shown by - and + signs respectively**
- ❑  $\Delta_o$  is measured in  $\text{cm}^{-1}$ .

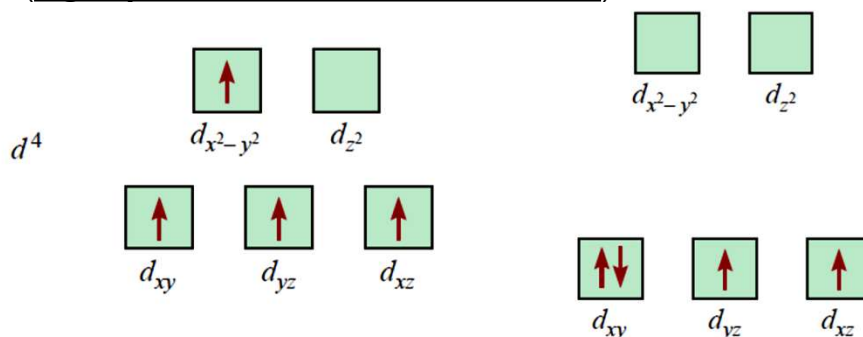




## d<sup>4</sup> system - what happens ?



- For d<sup>4</sup>-d<sup>7</sup> systems (there are two possibilities): Either put the electrons in the t<sub>2g</sub> set and therefore pair the electrons (low spin case or strong field situation) or put the electrons in the e<sub>g</sub> set, which lies higher in energy, but the electrons do not pair (high spin case or weak field situation).



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- ❑ For d4 ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the  $t_{2g}$  level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the  $e_g$  level.
- ❑ ***Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta o$  and the pairing energy,  $P$  ( $P$  represents the energy required for electron pairing in a single orbital).***
- ❑ The two options are:

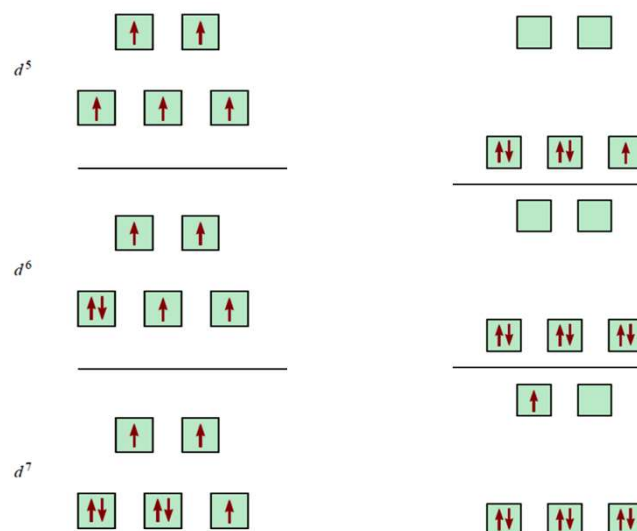


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- ☐ If  $\Delta o < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$
- ☐ Ligands for which  $\Delta o < P$  are known as **weak field ligands** and form **high spin complexes**.
- ☐ If  $\Delta o > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ .
- ☐ Ligands which produce this effect are known as **strong field ligands** and form **low spin complexes**.

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## $d^5 - d^7$ system – two scenarios !



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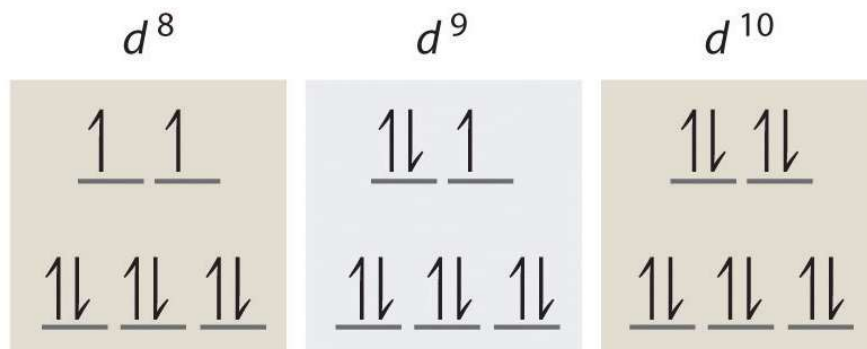
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## $d^8 - d^{10}$ system - what happens ?



- The number of unpaired electrons in  **$d^8-d^{10}$  is same** in case of both low or high spin (similar to **as in  $d^1-d^3$** ).



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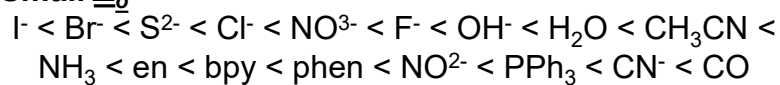
## Spectrochemical series



The common ligands can be arranged in the order of their increasing splitting power to cause d-orbitals splitting. This series is called as spectrochemical series and is given below:

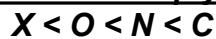
Ligand effect on  $\Delta_o$  :

**Small  $\Delta_o$**



**Large  $\Delta_o$**

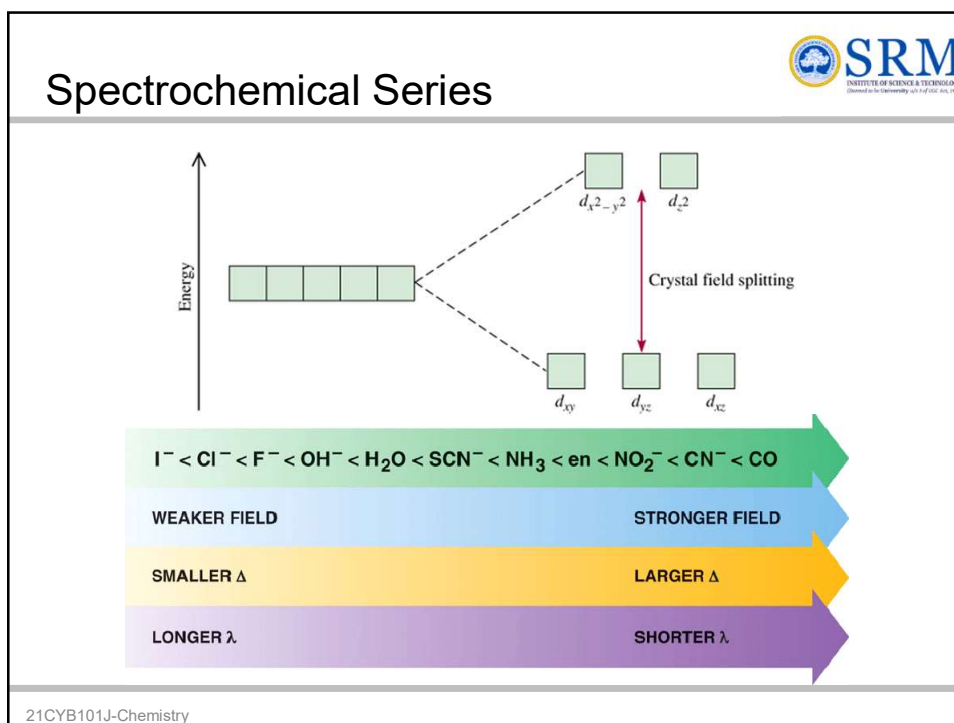
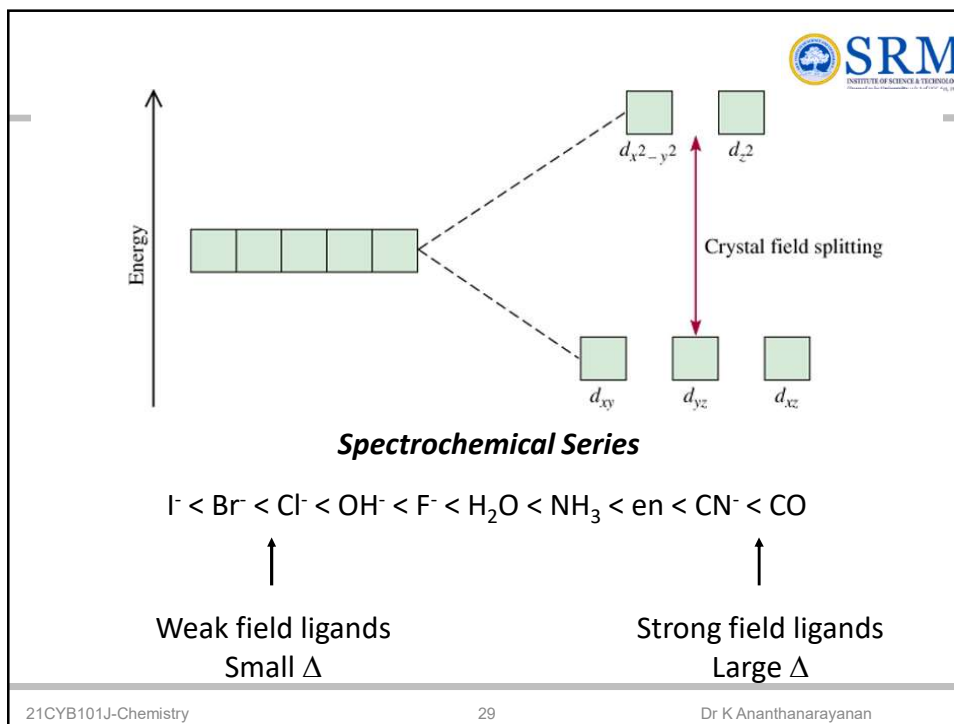
**Or more simply :**



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## Electronic configuration

Filling up  $t_{2g}$  and  $e_g$  orbitals with electrons in octahedral complexes: High spin and low spin octahedral complexes:

### 1. When the ligands are weaker:

- ☐ The energy difference,  $\Delta_o$  between  $t_{2g}$  and  $e_g$  is relatively small and the energy of all five d-orbitals is supposed to be the same.
- ☐ The filling of  $t_{2g}$  and  $e_g$  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.

- $d^1 = t_{2g}^1 e_g^0$
- $d^2 = t_{2g}^2 e_g^0$
- $d^3 = t_{2g}^3 e_g^0$
- $d^4 = t_{2g}^3 e_g^1$
- $d^5 = t_{2g}^3 e_g^2$
- $d^6 = t_{2g}^4 e_g^2$
- $d^7 = t_{2g}^5 e_g^2$
- $d^8 = t_{2g}^6 e_g^2$
- $d^9 = t_{2g}^6 e_g^3$
- $d^{10} = t_{2g}^6 e_g^4$

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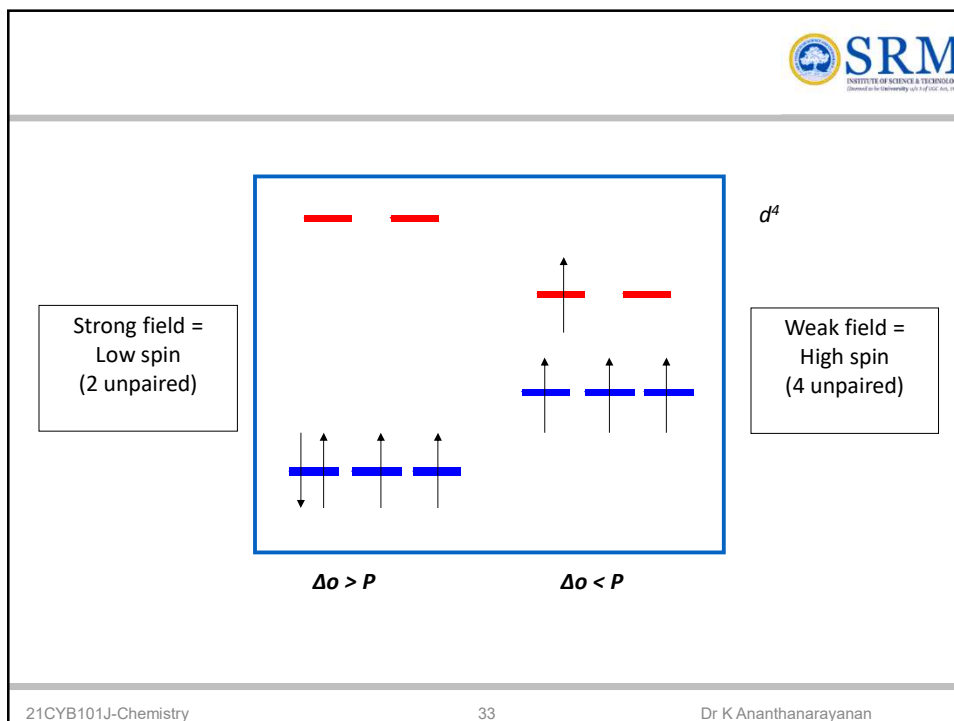
### 2. When the ligands are stronger:

The energy difference,  $\Delta_o$  between  $t_{2g}$  and  $e_g$  is relatively large and the filling of  $t_{2g}$  and  $e_g$  orbitals **does not obey Hund's rule**, so **all three  $t_{2g}$  set are filled up first and then two  $e_g$  sets are filled.**

- $d^1 = t_{2g}^1 e_g^0$
- $d^2 = t_{2g}^2 e_g^0$
- $d^3 = t_{2g}^3 e_g^0$
- $d^4 = t_{2g}^4 e_g^0$
- $d^5 = t_{2g}^5 e_g^0$
- $d^6 = t_{2g}^6 e_g^0$
- $d^7 = t_{2g}^6 e_g^1$
- $d^8 = t_{2g}^6 e_g^2$
- $d^9 = t_{2g}^6 e_g^3$
- $d^{10} = t_{2g}^6 e_g^4$

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## Charge on the metal ion



- ❑ **Increasing the charge on a metal ion** has two effects: the **radius of the metal ion decreases**, and **negatively charged ligands are more strongly attracted to it**.
- ❑ **Both factors decrease the metal–ligand distance**, which in turn causes the **negatively charged ligands to interact more strongly with the d orbitals**.
- ❑ Consequently, **the magnitude of  $\Delta_o$  increases** as the **charge on the metal ion increases**.
- ❑ Typically,  **$\Delta_o$  for a tripositive ion is about 50% greater than for the dipositive ion of the same metal**; for example, for  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $\Delta_o = 11,800 \text{ cm}^{-1}$ ; for  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ ,  $\Delta_o = 17,850 \text{ cm}^{-1}$ .

High spin      Low spin

$d^4$

$d^5$

$d^6$

$d^7$

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- Orbital diagrams for the high spin and low-spin octahedral complexes corresponding to the electron configurations  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$ .
- No such distinctions can be made for  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$ , and  $d^{10}$ .

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## CFSE for $d^7$ high spin case

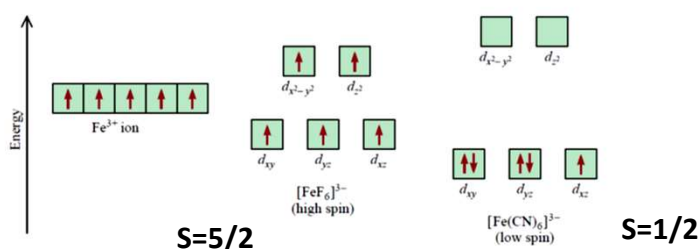
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CFSE(7 electrons) = (5 electrons stabilised by  $(-0.4\Delta_{\text{oct}})$ ) + (2 electrons destabilized by  $(+0.6\Delta_{\text{oct}})$ )

=  $-2.0\Delta_{\text{oct}} + 1.2\Delta_{\text{oct}} = -0.8\Delta_{\text{oct}}$

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## Spin, calculation



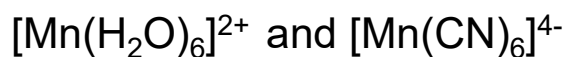
- Because  $\text{F}^-$  is a weak-field ligand, the five  $d$  electrons enter five separate  $d$  orbitals with parallel spins to create a high-spin complex.
- The cyanide ion is a strong-field ligand, on the other hand, so the energy needed to promote two of the five  $d$  electrons to higher  $d$  orbitals is too much, and therefore a low-spin complex is formed

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## Complexes, example, Spin ??



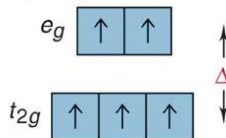
No field

Maximum number of unpaired electrons

A Free  $\text{Mn}^{2+}$  ion $S=5/2$ 

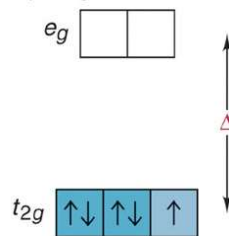
Weak-field ligand

High-spin complex

 $E_{\text{pairing}} > \Delta$ B  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  $S=5/2$ 

Strong-field ligand

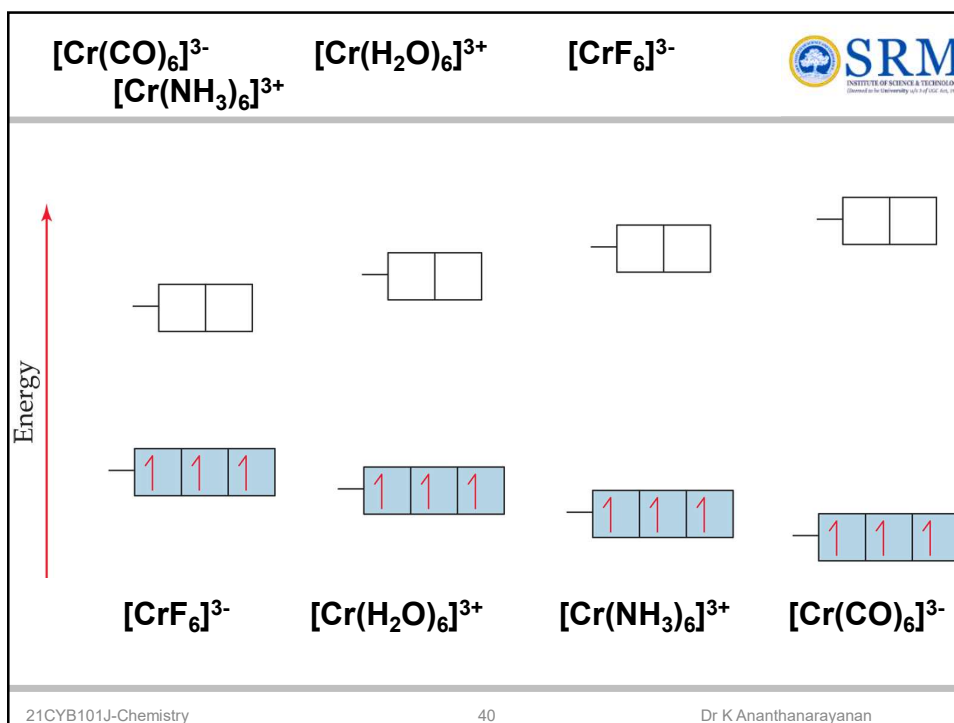
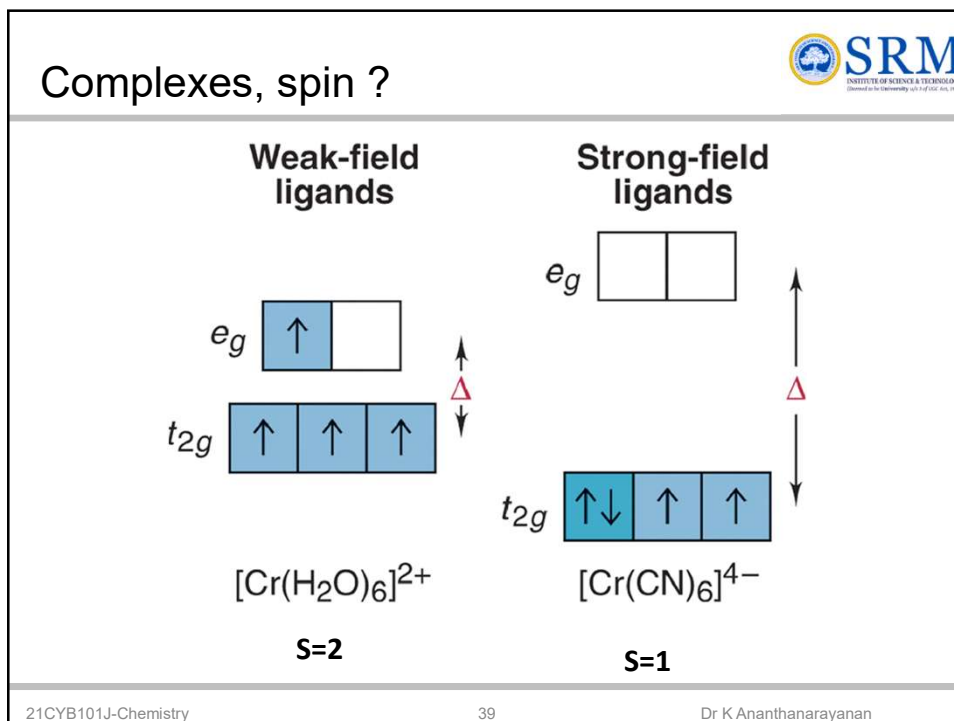
Low-spin complex

 $E_{\text{pairing}} < \Delta$ C  $[\text{Mn}(\text{CN})_6]^{4-}$  $S=1/2$ 

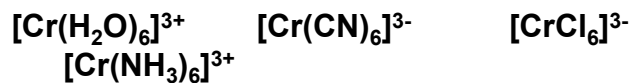
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Predict and rank in decreasing  $\lambda$



$[\text{CrCl}_6]^{3-} \quad \Delta_o = 13640 \text{ cm}^{-1}$

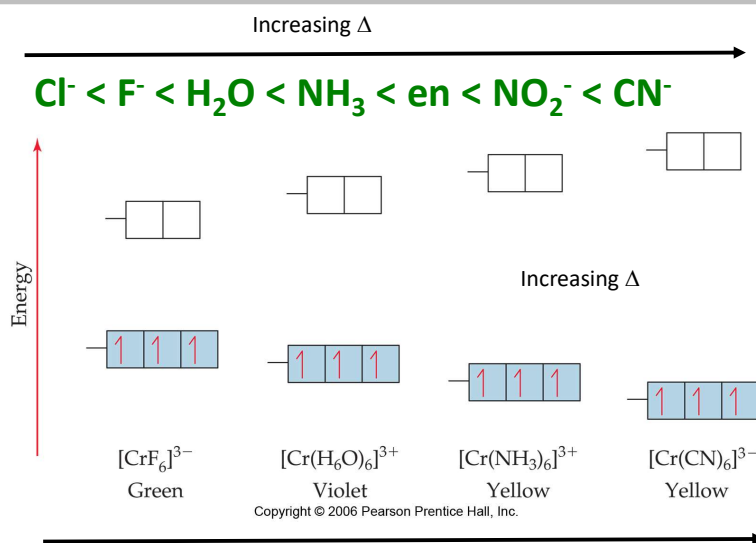
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} \quad \Delta_o = 17830 \text{ cm}^{-1}$

$[\text{Cr}(\text{NH}_3)_6]^{3+} \quad \Delta_o = 21680 \text{ cm}^{-1}$

$[\text{Cr}(\text{CN})_6]^{3-} \quad \Delta_o = 26280 \text{ cm}^{-1}$

**$\Delta_o$  increases with increase of ligand field strength so wavelength decreases**

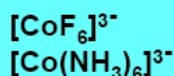
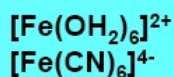
Spectrochemical series (strength of ligand interaction)



## Configuration, Spin state, $\Delta_o$ ??



### Complex



Complex	Config.	$\Delta_o$ , $\text{cm}^{-1}$	spin-state
$[\text{Fe}(\text{OH}_2)_6]^{2+}$	$d^6$	10,400	high-spin
$[\text{Fe}(\text{CN})_6]^{4-}$	$d^6$	32,850	low-spin
$[\text{CoF}_6]^{3-}$	$d^7$	13,000	high-spin
$[\text{Co}(\text{NH}_3)_6]^{3-}$	$d^7$	23,000	low-spin



**Which of the following complexes of  $\text{Ti}^{3+}$  exhibits the shortest wavelength absorption in the visible spectrum:  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ;  $[\text{Ti}(\text{en})_3]^{3+}$ ;  $[\text{TiCl}_6]^{3-}$ ?**

- ☐ The wavelength of the absorption is determined by the magnitude of the splitting between the  $d$ -orbital energies in the field of the surrounding ligands.
- ☐ The larger the splitting, the shorter the wavelength of the absorption corresponding to the transition of the electron from the lower- to the higher-energy orbital.
- ☐ The splitting will be largest for ethylenediamine, en, the ligand that is highest in the spectrochemical series.
- ☐ Thus, the complex with the shortest wavelength absorption is  $[\text{Ti}(\text{en})_3]^{3+}$ .

## Magnetic moment values of complex compounds



- ❑ CFT can be used to find out the number of unpaired electrons ( $n$ ) in a given complexes.
- ❑ Paramagnetic compounds (and atoms) are attracted to magnetic fields while diamagnetic compounds (and atoms) are repelled from magnetic fields.
- ❑ Paramagnetic compounds have unpaired electrons while in diamagnetic compounds the electrons all have paired spins.

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## Spin only magnetic moment



- ❑ **The substitution of  $n$  value in the spin-only formula,  $\mu = \sqrt{n(n+2)}$  B.M gives the value of magnetic moment of the given complex**
- ❑ From the knowledge of  $\mu$  value the valence state of the central metal cation and the nature of bonding in the complex (whether the complex is high spin or low spin) can be known

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

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

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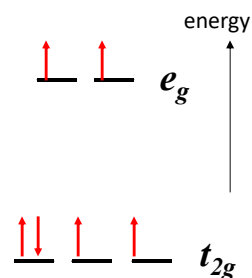
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### What is the magnetic moment of $[\text{CoCl}_6]^{3-}$

- $[\text{CoCl}_6]^{3-}$  is high spin Co(III). High-spin Co(III) is  $d^6$  with four unpaired electrons, so  $n = 4$ .

- We have  $\mu_{\text{eff}} = \sqrt{n(n+2)}$

Approx. 4.9 BM



## 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.