Coordination Chemistry-II

Crystal Field Theory and its Application:

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a) Splitting of d-orbitals in different geometries

(octahedral, tetrahedral and square planar),

b)Crystal field stabilization energy (CFSE),

c) Spectrochemical series

d) Jahn Teller Distortion

B. C. College/VI Semester (H)/ Inorg. Chem./ Lecture-4/TKS/ March-2020

Splitting of d-orbitals in octahedral geometry:

Shape of d orbitals and its orientation

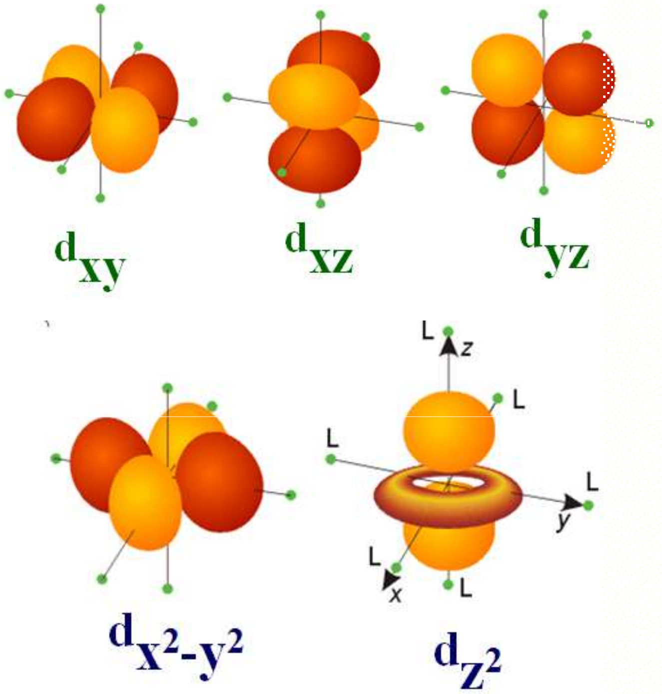


Fig.1

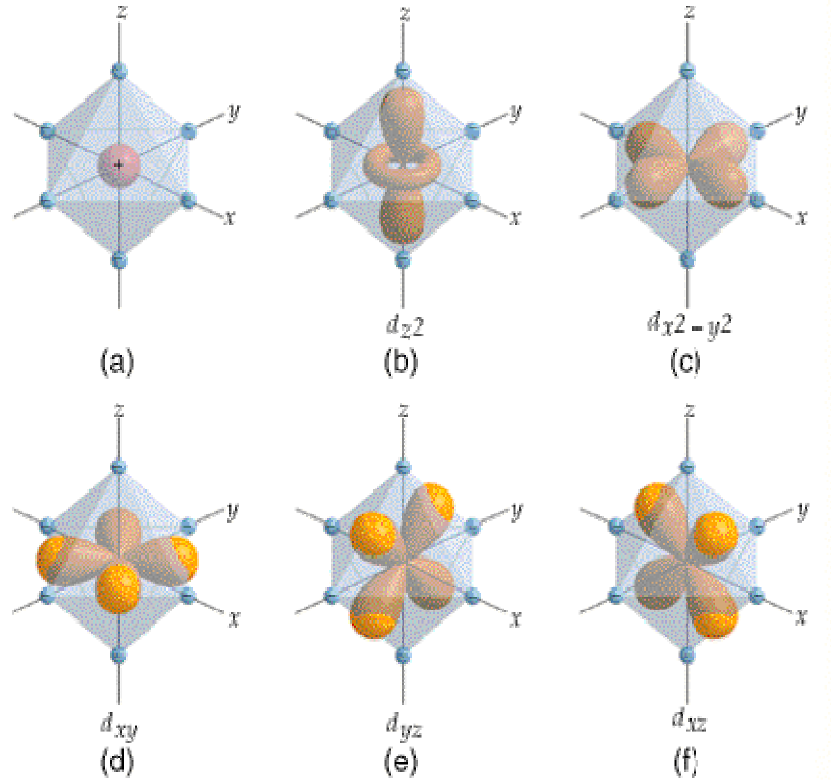


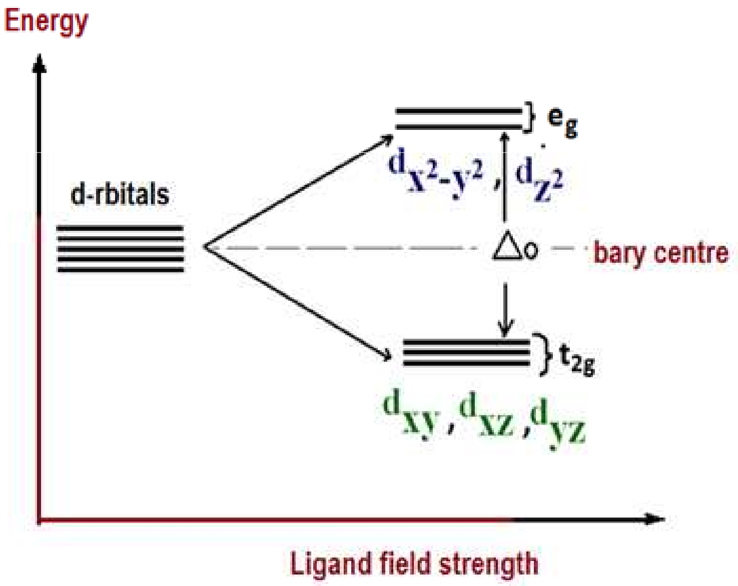
Fig.2

In octahedral geometry only two orbitals (dx^2-y^2 and dz^2) are lying along three axis (x, y and z axis) and other three orbitals (dxy, dxz and dyz) are directed in between axis shown in Fig.2

Splitting of d-orbitals in different geometries (octahedral, tetrahedral and square planar)

- In octahedral geometry two orbitals, dx^2-y^2 and dz^2 are strongly repelled by the ligand field during formation of octahedral complex due to their direct interaction with the ligand and become excited while rest three d orbitals (dxy, dxz and dyz) are stabilized.

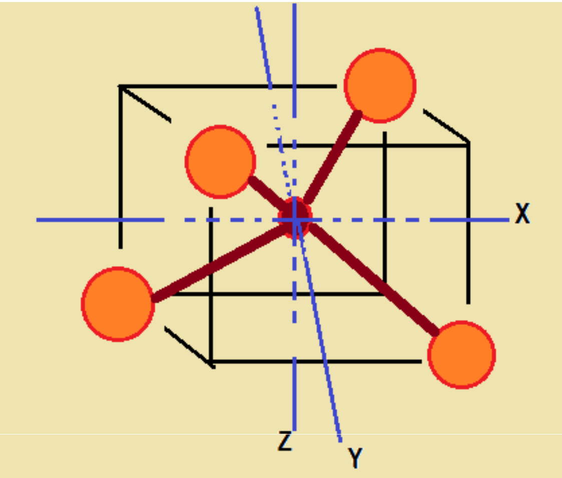
Δo is the d-orbital splitting energy in octahedral field. Its value increases with increasing ligand field strength.
It may be represented as 10Dq.
From bary centre each orbital of (dx^2-y^2, dz^2) e_g set is destabilized by + 6Dq while each orbital of (dxy, dxz and dyz) t_{2g} set is stabilized by - 4Dq.

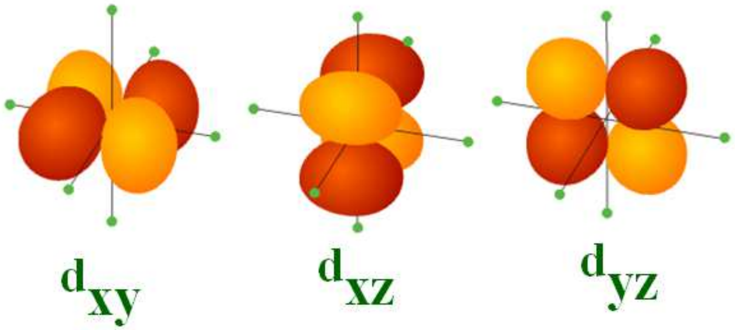


Splitting of d- orbitals in Octahedral Geometry

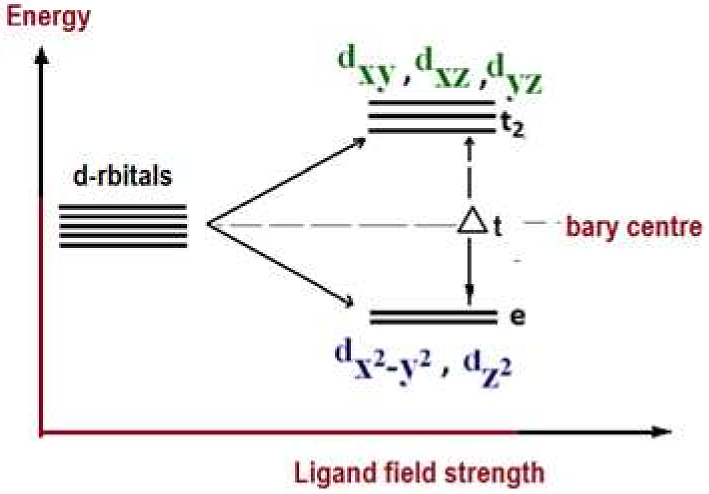
Here 'D' and 'q' represents two expressions.
D $=35ze/4a^5$, **q**$=2er^4/105$
z = charge of the ligand, a =metal-ligand distance ,
r = distance of the electron from the nucleus

Splitting of d-orbitals in tetrahedral geometry:





In tetrahedral geometry three d-orbitals (dxy, dxz and dyz) are strongly repelled by the ligand field due to direct interaction with incoming 4 ligands and become excited. Other two orbitals (dx^2-y^2 , dz^2) are stabilized to the same extent.



Splitting of d- orbitals in Tetrahedral Geometry

The Δt value is lower than Δo due to less number of ligands interaction as compared to Octahedral Complex.

Splitting of d-orbitals in square planar geometry:

If two ligands bonded with dz^2 orbital are removed from a octahedral complex, then it results the square planar complex as shown in Fig.3

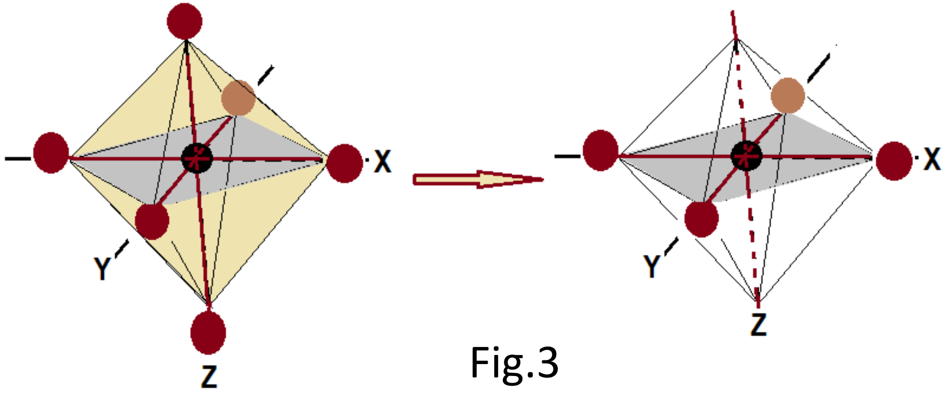


Fig.3

Now in Octahedral Complex, two d-orbitals (dx^2-y^2 , dz^2) are involved in bond formation with six ligands. Four ligands are linked with dx^2-y^2 orbital and two ligands with dz^2 orbital.

Generally metal ions with d^8 Electronic configuration form Square Planar complex, as no strong bond is formed along dz^2 orbital that contains 2 electrons in square planar field. (Fig.4)

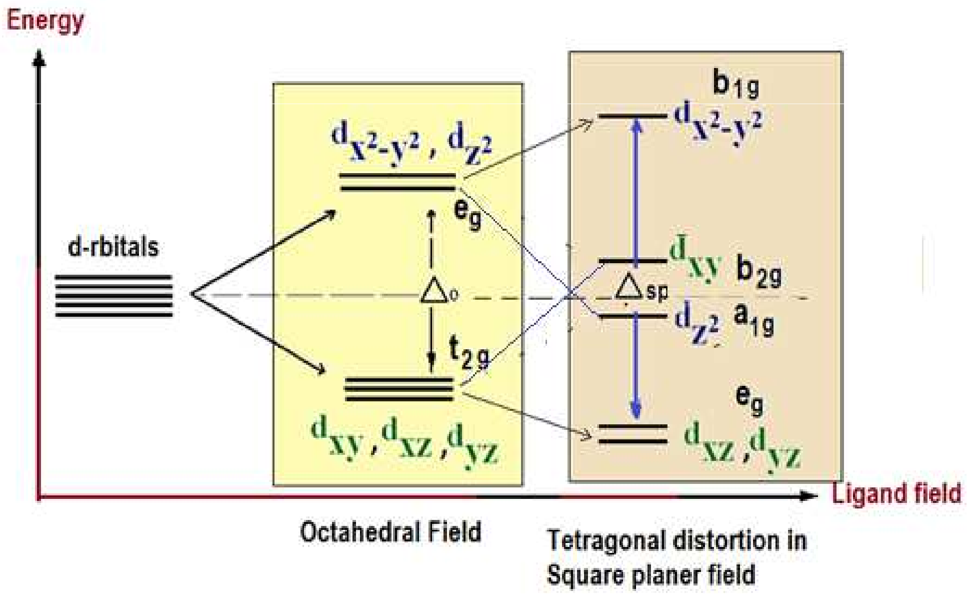
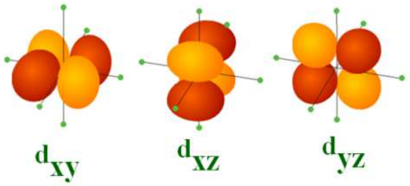


Fig.4

Splitting Energy of d-orbitals in octahedral, tetrahedral and square planar



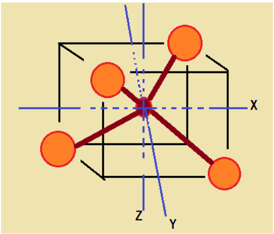


Fig.5

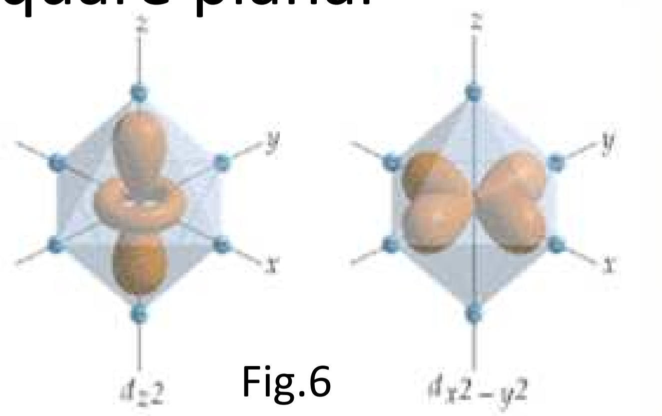


Fig.6

$\Delta o > \Delta t$, and it is related as $\Delta t=(4/9)\ \Delta o$. Because more number of ligands approach to two d-orbitals of metal center of Octahedral complex as compared to tetrahedral complex.

On the other hand $\Delta sp > \Delta o$ and it is approximately equal to 1.3 Δo.

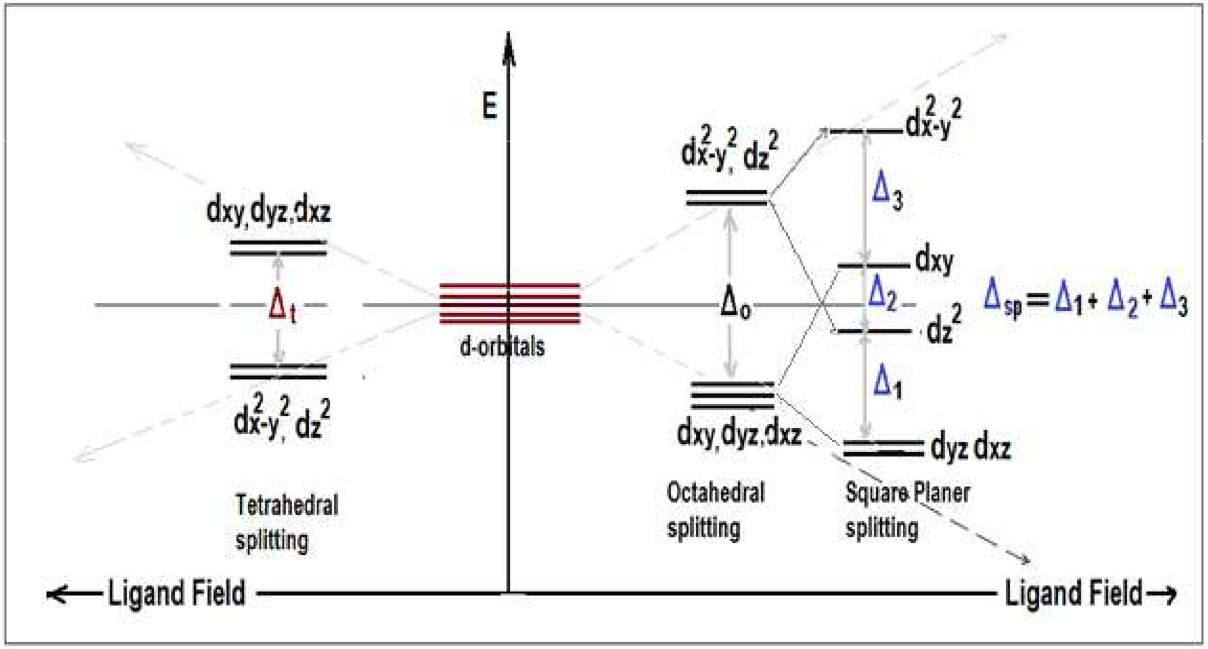
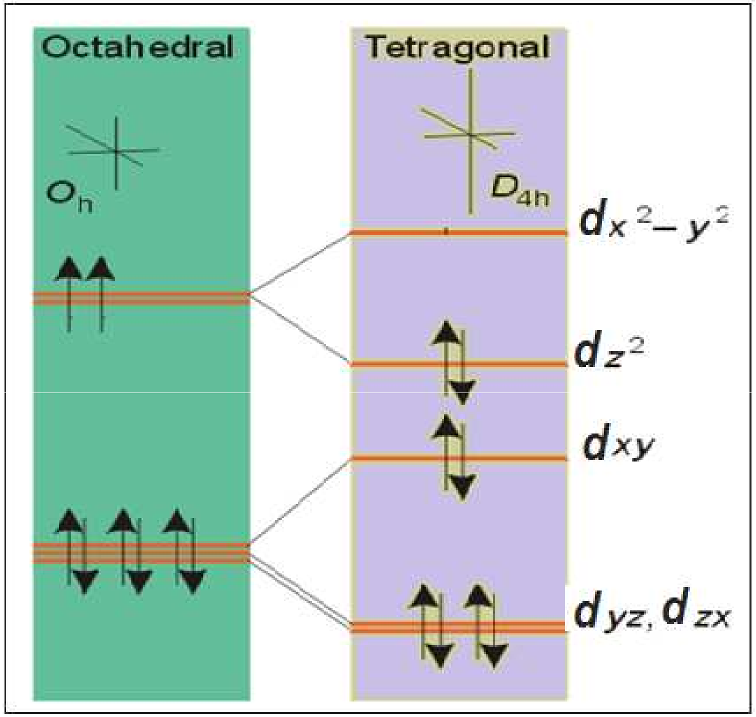


Fig.7

Square planar complexes:

Square planar complexes are quite common for the **d^8 metals in the 4th and 5th periods:** **Rh(I), Ir(I), Pt(II), Pd(II) and Au(III).**

*The **lower transition** metals have **large ligand field** stabilization energies, favoring **four-coordinate complexes.***



*Square planar complexes are rare for **the 3rd period metals. Ni(II)** generally forms tetrahedral complexes. **Only with very strong ligands such as CN$^-$, square planar geometry is seen with Ni(II).***

Crystal field stabilization energy (CFSE)

- The coordination compound is formed through the splitting of d-orbitals in different ligand fields. The overall stabilization energy achieved by the complex due to splitting of d-orbitals is termed as **crystal field stabilization energy (CFSE)** in terms of **Dq** value and **pairing energy (P)**.
- For Tetrahedral geometry , if electronic arrangement is like this $\mathbf{e^m}$ ($dx^2\text{-}y^2$, dz^2), $\mathbf{t_2^m}$ (dxy, dyz, dxz) where **m, n** are the number of electron/s present in the respective set of orbitals then for high spin complex, the CFSE will be $[(\mathbf{m} \times -{}^3/_5\, \Delta_t)+(\mathbf{n} \times {}^2/_5\, \Delta_t)]$.

For $CoCl_4^{2-}$, a $\mathbf{d^7}$ system **tetrahedral complex**, the electronic arrangement is $\mathbf{e^4}$ ($dx^2\text{-}y^2$, dz^2), $\mathbf{t_2^3}$ (dxy, dyz, dxz) and **CFSE** is $=[(4 \times -{}^3/_5\, \Delta_t)+(3 \times {}^2/_5\, \Delta_t]$

$= (-{}^{12}/_5\, \Delta_t + {}^6/_5\, \Delta_t) = \mathbf{-\,{}^6/_5\, \Delta_t}$

- Now we know $\Delta_t = {}^4/_9\, \Delta_o$, So, CFSE of $\mathbf{CoCl_4^{2-}}$ is $= -\,{}^6/_5 \times {}^4/_9\, \Delta_o = -\,{}^8/_{15}\, \Delta_o$

$= -\,{}^8/_{15} \times 10Dq = \mathbf{-\,{}^{16}/_3\, Dq}$

Crystal field stabilization energy (CFSE):

Octahedral Complex

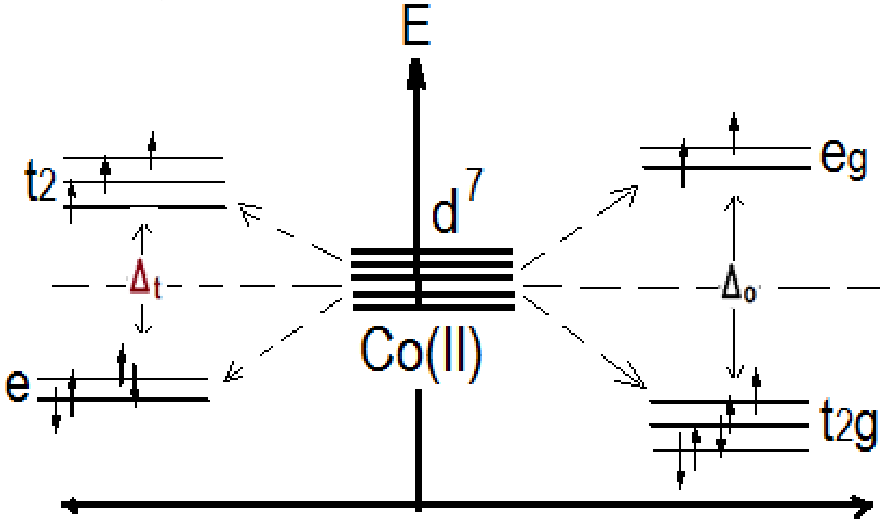
- For octahedral geometry , if electronic arrangement is like this $\mathbf{t_{2g}^{m}}$ (dxy, dyz, dxz), $\mathbf{e_g^{m}}$ (dx^2-y^2, dz^2), where **m, n** are the number of electron/s present in the respective set of orbitals, then for high spin complex, the CFSE will be $[(\mathbf{m} \text{ x } -{}^{2}/_{5}\, \Delta_o)+(\mathbf{n} \text{ x } {}^{3}/_{5}\, \Delta_o)]$.

  For $[Co(H_2O)_6]^{2+}$, a **d^7** system **Octahedral complex**, the electronic arrangement is $\mathbf{t_{2g}^{5}}$ (dxy, dyz, dxz), $\mathbf{e_g^{2}}$ (dx^2-y^2, dz^2),

  and **CFSE** is $=[(5 \text{ x } -{}^{2}/_{5}\, \Delta_0)+(2\text{x } {}^{3}/_{5}\, \Delta_o] = -4/5\, \Delta_o$

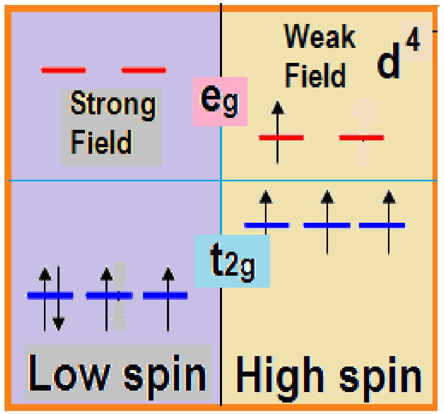
  $=-\,{}^{4}/_{5}$ x 10Dq = **- 8 Dq.**

Therefore crystal field stabilization energy of Co(II), a d^7 system in octahedral field (-8Dq) is higher than that of tetrahedral field (- ${}^{16}/_{3}$ Dq or -5.33Dq)

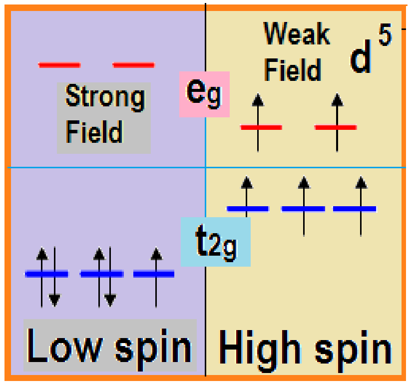


Crystal field stabilization energy (CFSE):

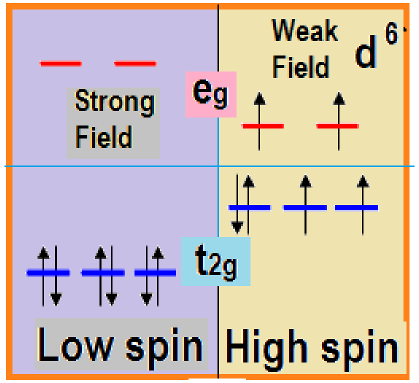
Octahedral Complex



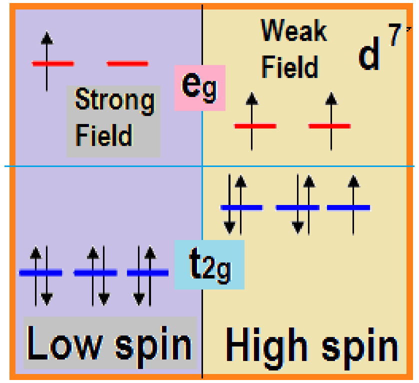
(g)



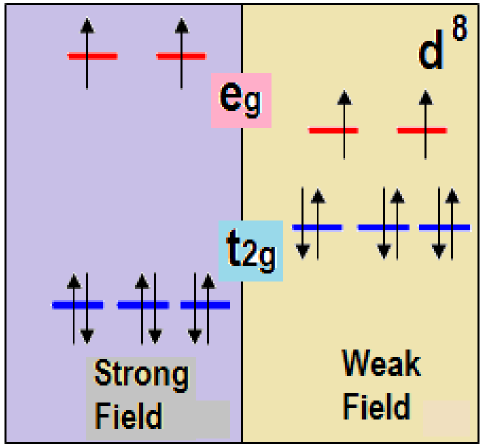
(a)



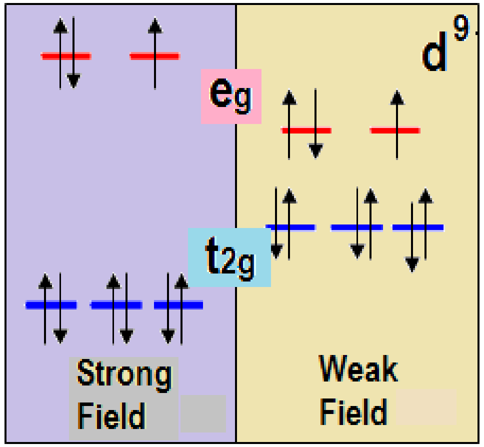
(b)



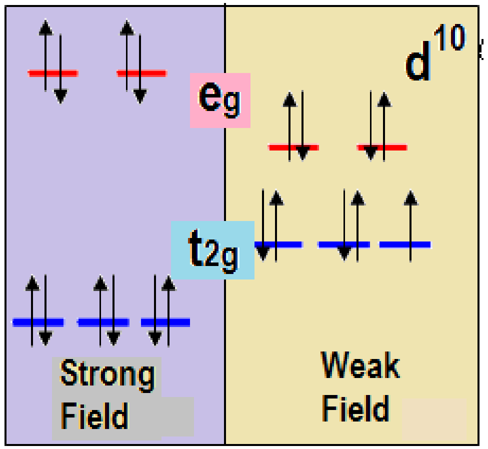
(c)



(d)



(e)



(f)

CFSE Calculation:

Octahedral Complex

(g) d^4 system:

- **High Spin** (t_{2g}^3, e_g^1) , CFSE = (3x-4Dq) +(1x6Dq)=**-6Dq**
- **Low Spin** (t_{2g}^4, e_g^0), CFSE = (4x-4Dq)+ P =**-12Dq+P**
- **(a) d^5 system:**
- **High Spin** (t_{2g}^3, e_g^2) , CFSE = (3x-4Dq) +(2x6Dq)= **-0Dq**
- **Low Spin** $((t_{2g}^5, e_g^0)$, CFSE = (5x-4Dq)+2 P =**-20Dq+2P**
- **(b) d^6 system:**
- High Spin (t_{2g}^4, e_g^2) , CFSE = (4x-4Dq) +(2x6Dq)=**-4Dq**
- **Low Spin** $((t_{2g}^6, e_g^0)$, CFSE = (6x-4Dq)+ 2P =**-24Dq+2P**
- **(c) d^7 system:**
- High Spin (t_{2g}^5, e_g^2) , CFSE = (5x-4Dq) +(2x6Dq)=**-8Dq**
- **Low Spin** $((t_{2g}^6, e_g^1)$, CFSE = (6x-4Dq)+ P =**-24Dq+P**
-

(d) d^8 system:

(t_{2g}^6, e_g^2)
CFSE = (6x-4Dq) +(2x6Dq)
= **-12Dq**

(d) d^9 system:

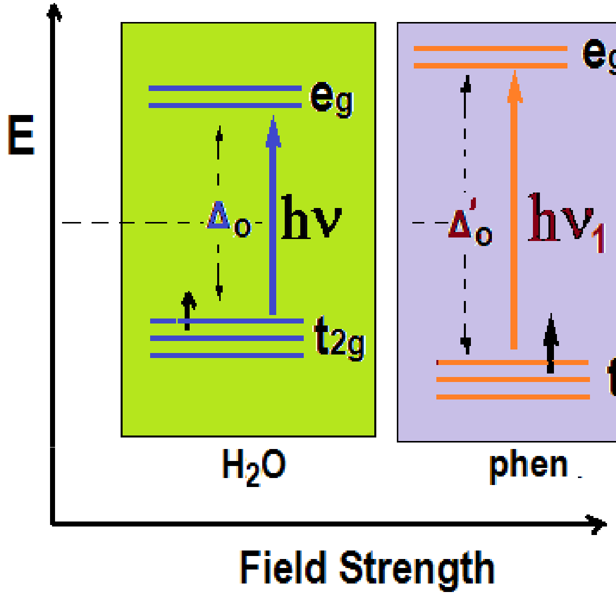
(t_{2g}^6, e_g^3)
CFSE = (6x-4Dq) +(3x6Dq)
= **-6Dq**

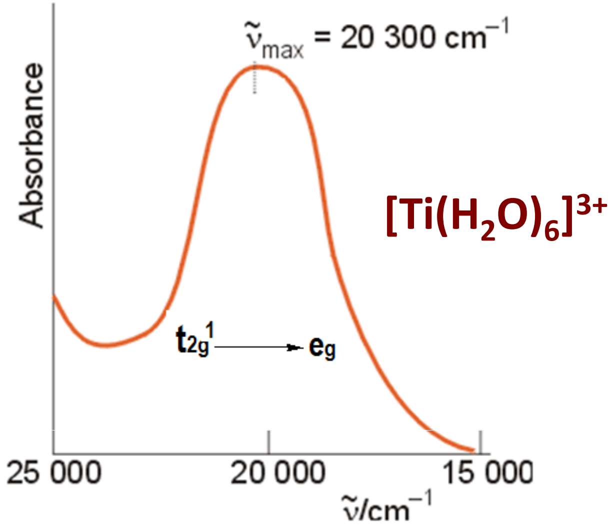
(d) d^{10} system:

(t_{2g}^6, e_g^4)
CFSE = (6x-4Dq) +(4x6Dq)
= **-0Dq**

[P = Pairing Energy]: one 'P' means 1 e^- from e_g set orbital is paired in t_{2g} set for low spin complex. 2 'P' means 2 e^- from e_g set orbital are paired in t_{2g} set for low spin complex.

Spectrochemical series and relation with 10Dq value





Generally the color of the coordination compound arises due to spin allowed d-d transition, $\mathbf{t_{2g}} \rightarrow \mathbf{e_g}$ for octahedral complexes and $\mathbf{e} \rightarrow \mathbf{t_2}$ for tetrahedral complexes. Now the energy separation (Δ_o and Δ_t) between two sets of d- orbitals $\mathbf{t_{2g}} \rightarrow \mathbf{e_g}$ or $\mathbf{e} \rightarrow \mathbf{t_2}$ depends on the nature of ligands **i.e. ligand strength. The color the Complex depends on Δ_o or Δ_t value, that is on the frequency (ν) of the absorption during transition.**

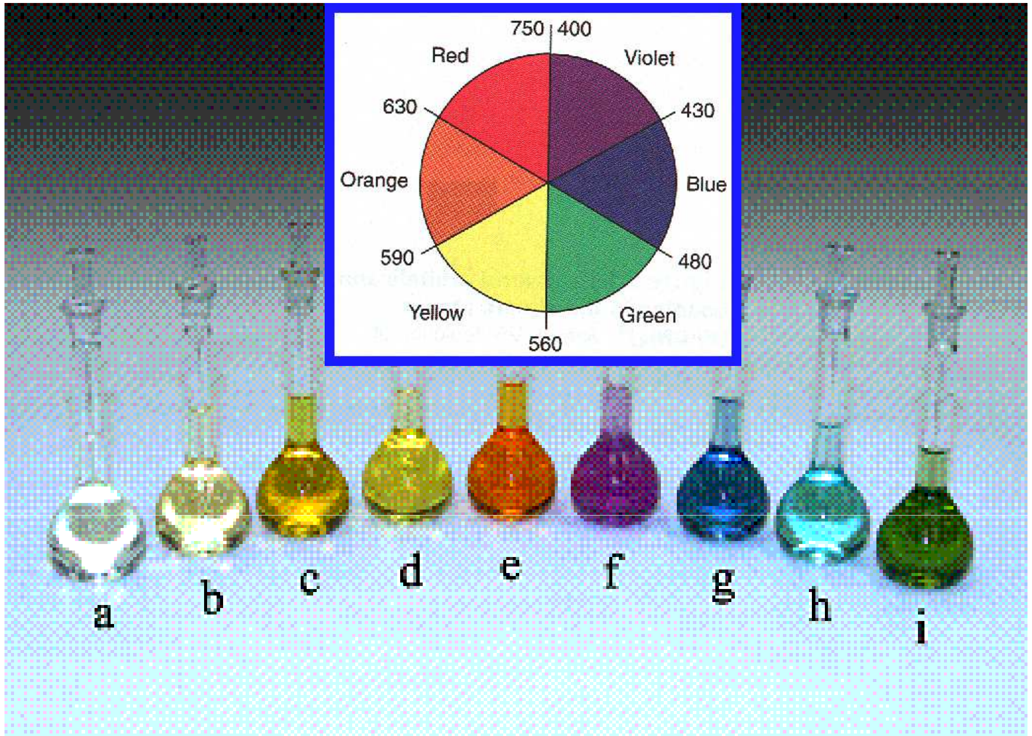
Spectrochemical series

The complexes of cobalt (III) with different ligands.

(a) CN^{-}, (b) NO_2^{-},

(c) phen, (d) en,

(e) NH_3, (f) gly, (g) H_2O, (h) ox^{2-}, (i) CO_3^{2-}.



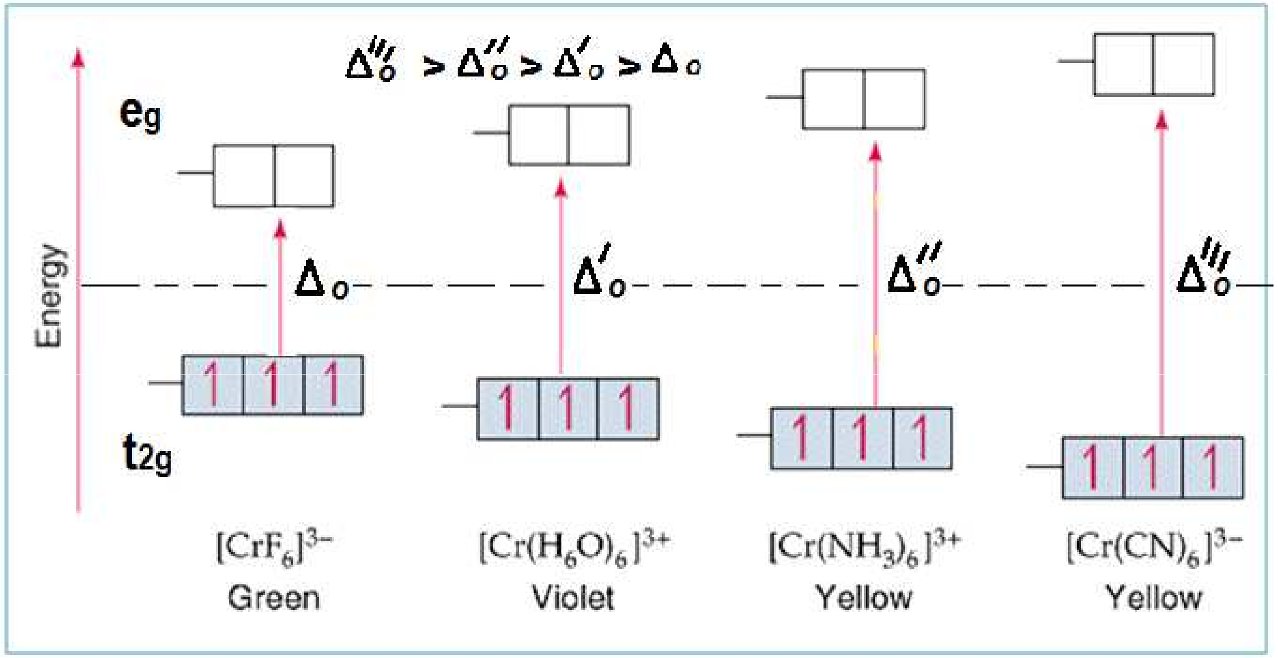
Spectrochemical series : Increasing order of d-orbital splitting efficiency of ligands

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

Spectrochemical series



Cr(III) complex with different weak field ligand to a strong field ligand, Δo increases and the color of the complex changes from green to yellow.

Tetragonal Distortion:

Jahn-Teller distortion

- Generally the octahedral geometry of coordination compounds suffer distortion from their ideal structure i.e. all the bond distances of six ligands of octahedral compounds (ML_6) are not equals length. Sometimes the two axial bonds are elongated or compressed as shown in the fig.7.

Jahn-Teller Theorem:

It states that any non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion to remove the degeneracy and to achieve a lower energy.

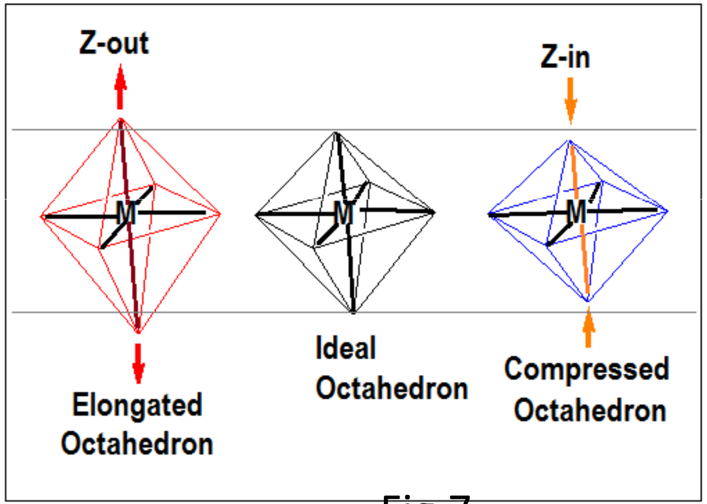


Fig.7

The Jahn-Teller effect predicts which structures will distort depending on its electronic arrangements. But it does not predict the nature or extent of the distortion. The effect is most often seen when the 'orbital degeneracy' is associated with orbitals which are pointed directly towards the ligands.

Tetragonal Distortion:

Jahn-Teller distortion

- In octahedral complexes, the **J-T effect** is most pronounced in **high spin d^4, low spin d^7 and d^9 configurations**, as the degeneracy occurs in the **e_g set** of orbitals.

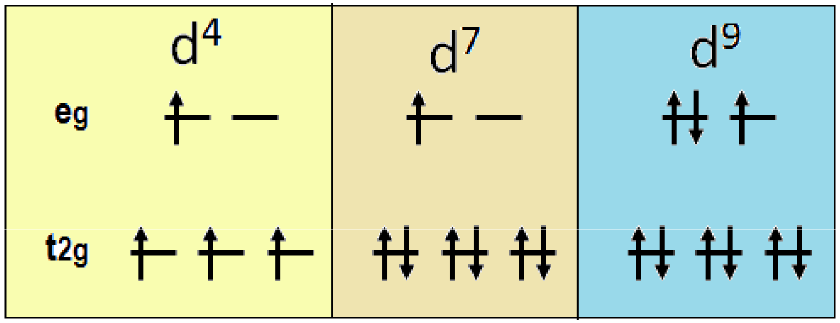


Fig.8

In octahedral complexes, **e_g set** of orbitals are pointed to the ligands and uneven distribution of electrons in this set of orbitals leads to **J-T distortion** to remove its degeneracy.

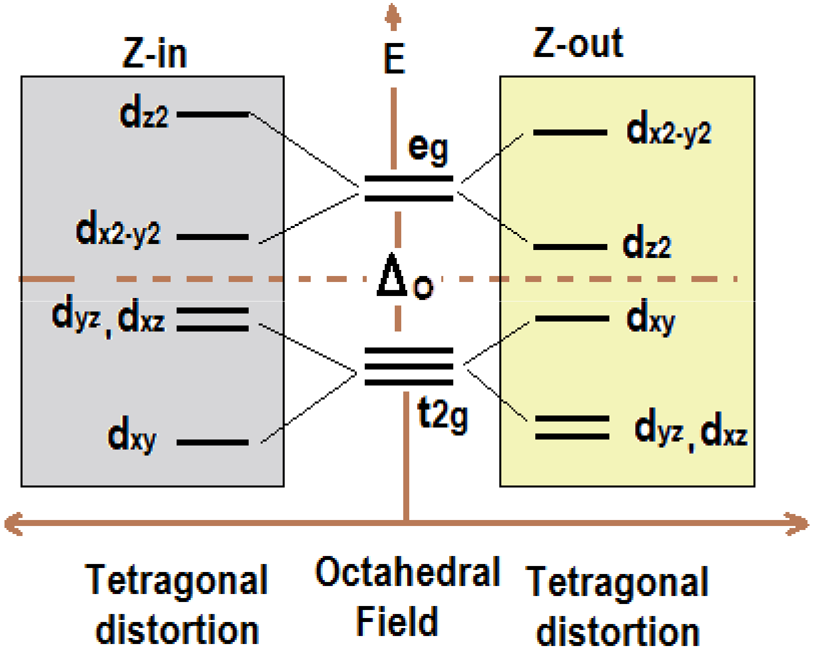


Fig.9

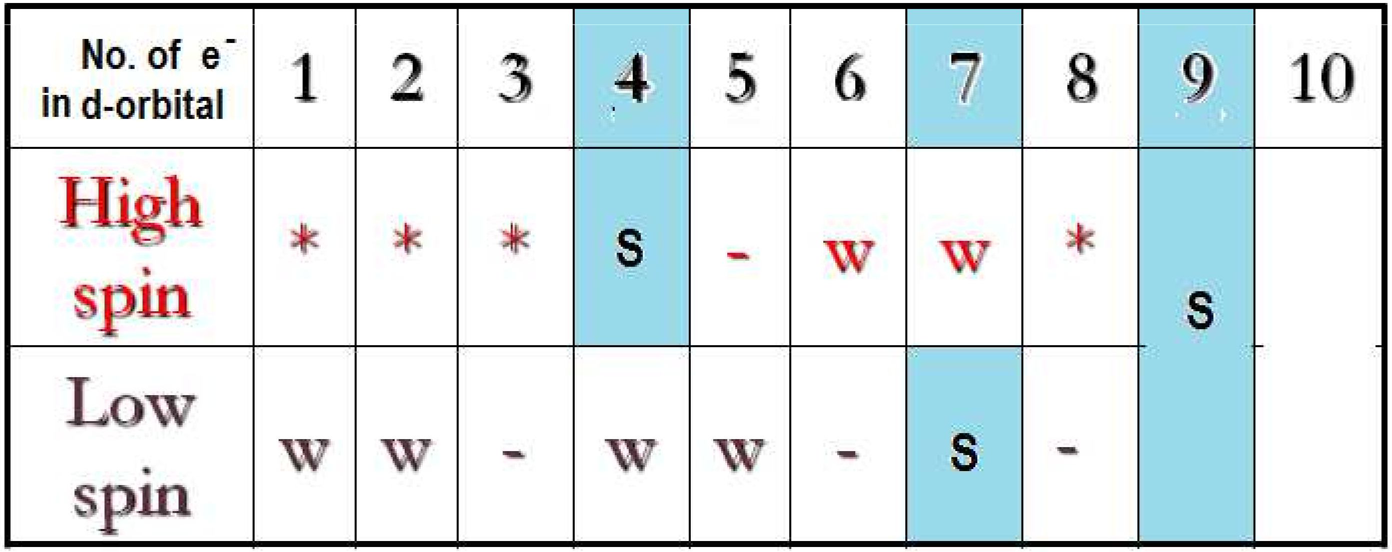
Tetragonal Distortion:

Jahn-Teller distortion

- In octahedral complexes, like $[Cr(H_2O)_6]^{2+}$, **high spin d^4** system, $[Co(en)_3]^{2+}$, **low spin d^7** system, $[Cu(H_2O)_6]^{2+}$, **d^9** system, **configurations ,** the **J-T effect** is pronounced effectively.

The strength of the Jahn-Teller effect is tabulated below:

(w=weak, s=strong)



No. of e^- in d-orbital	1	2	3	4	5	6	7	8	9	10
High spin	*	*	*	s	-	w	w	*	s	
Low spin	w	w	-	w	w	-	s	-		