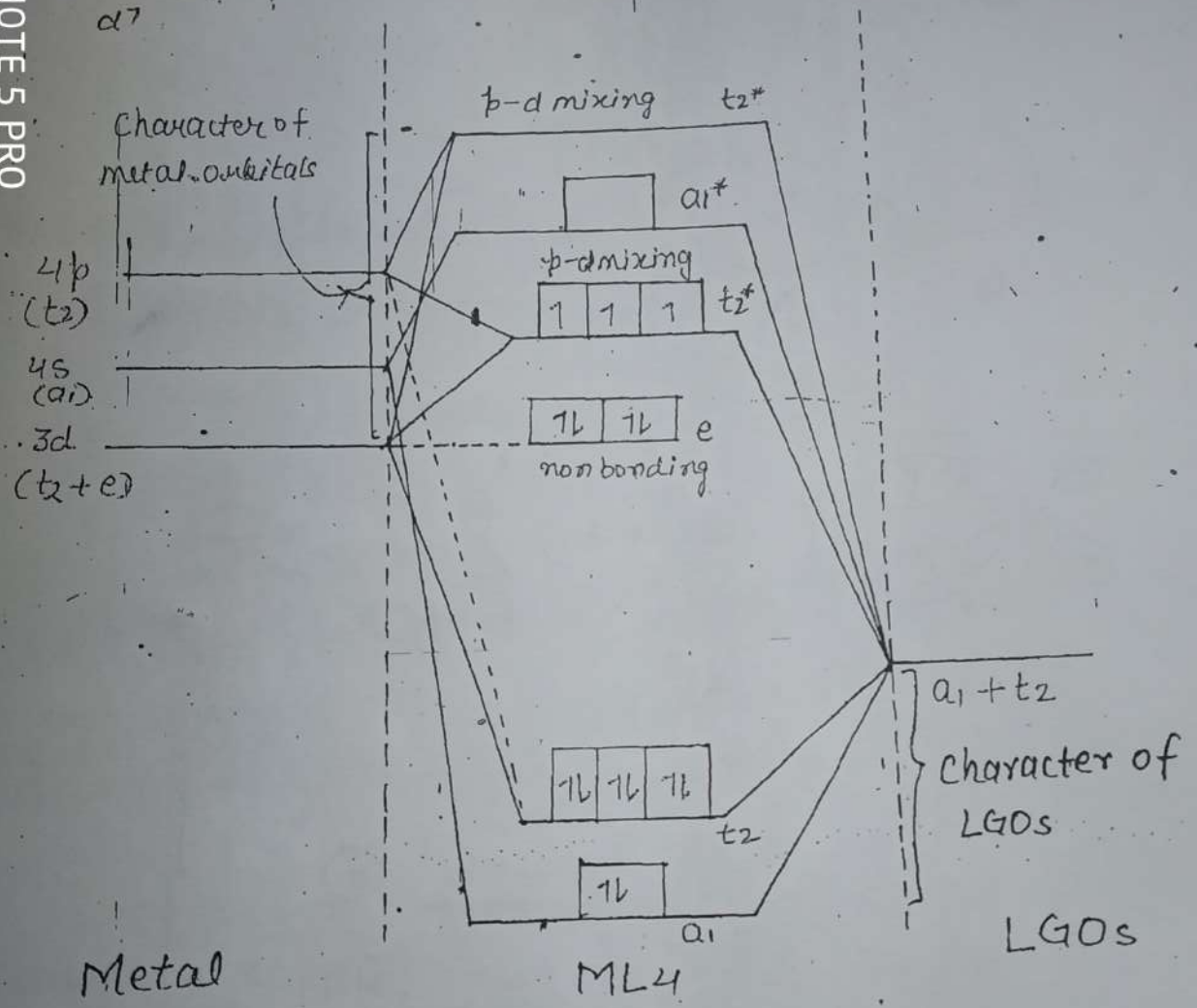
Molecular orbital diagram for σ-bonding in tetrahedral complexes ⇒

Example :-

$[CoCl_4]^{2-}$, $[NiCl_4]^{2-}$

$[CoCl_4]^{2-}$

d^7

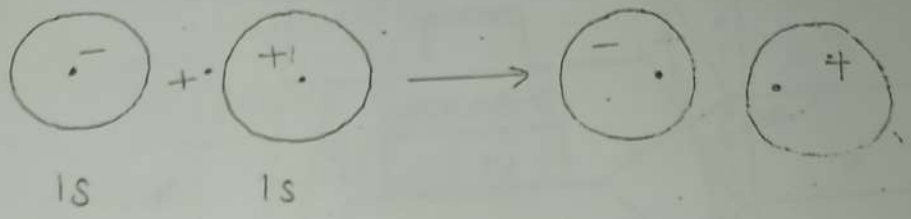


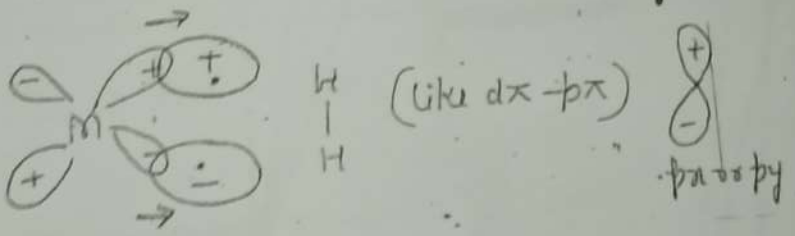
The symmetry of t_2 (4p) and t_2 (3d) are same, therefore both can bonded with ligand's t_2 (p) but as the energy gap b/w t_2 (dxy, dyz, dzx) ~~B/~~ and t_2 (ligand) is less as compared to t_2 (px, py, pz) & metal, there will be more contribution from t_2 (dxy, dyz, dzx) and less contribution from t_2 (px, py, pz).

(4) $d\pi - \sigma^*$ (dominates over $d\pi - d\pi$)

Examples ⇒ R_3P, R_3As, R_2S, H_2 etc. (Having -C-H (σ bonding of alkylgp)

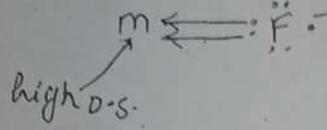
$H_2 \rightarrow 2e^- \rightarrow \sigma 1s^2\ \sigma^* 1s^0$



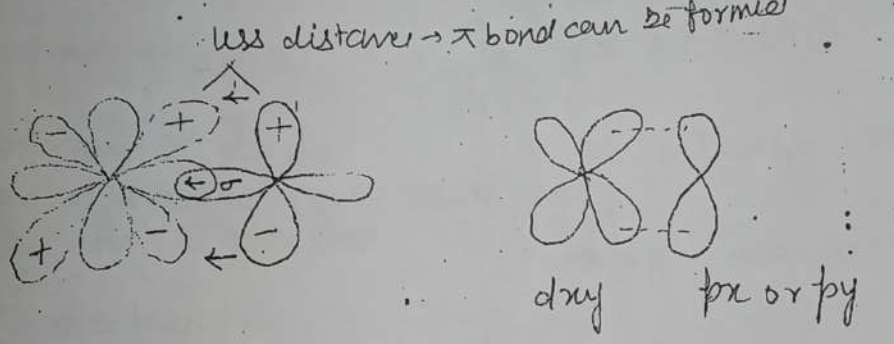


② $d\pi - p\pi$

Examples ⇒ F^-, Cl^-, Br^-, I^-, H_2O, S^{2-}, OH^- etc



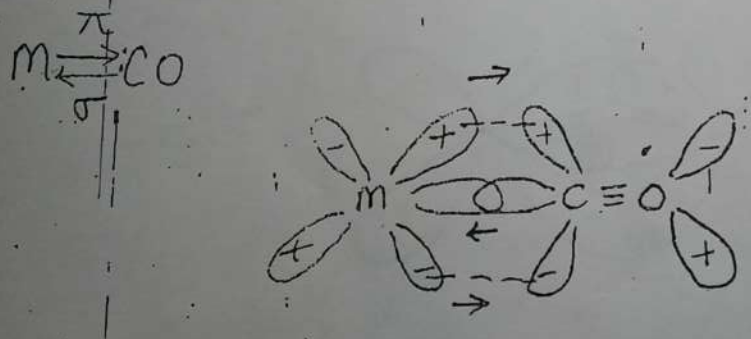
Electron pair is donated from p-orbitals of the ligand to the d-orbitals of the metal.



③ $d\pi - \pi^*$

Examples ⇒ CO, $C\tilde{N}$, NO, bpy, phen, olefins

π-acceptors



π-bond → metal to ligand

electron pair is donated from d-orbitals (t_{2g}) to vacant π^* of the ligands.

Types of π-bonds ⇒

1. $d\pi - d\pi$
2. $d\pi - p\pi$
3. $d\pi - \pi^*$
4. $d\pi - \sigma^*$

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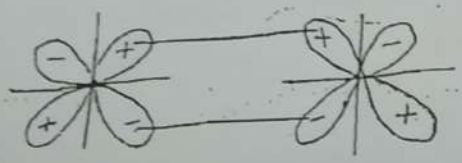
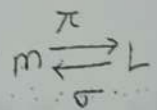
① $d\pi - d\pi$

Examples ⇒ R_3P, R_3As, R_3S etc.

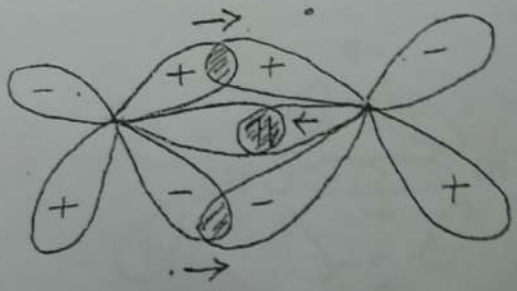
π electrons are donated from metal (t_{2g}) orbitals to vacant d- orbitals of the ligands.





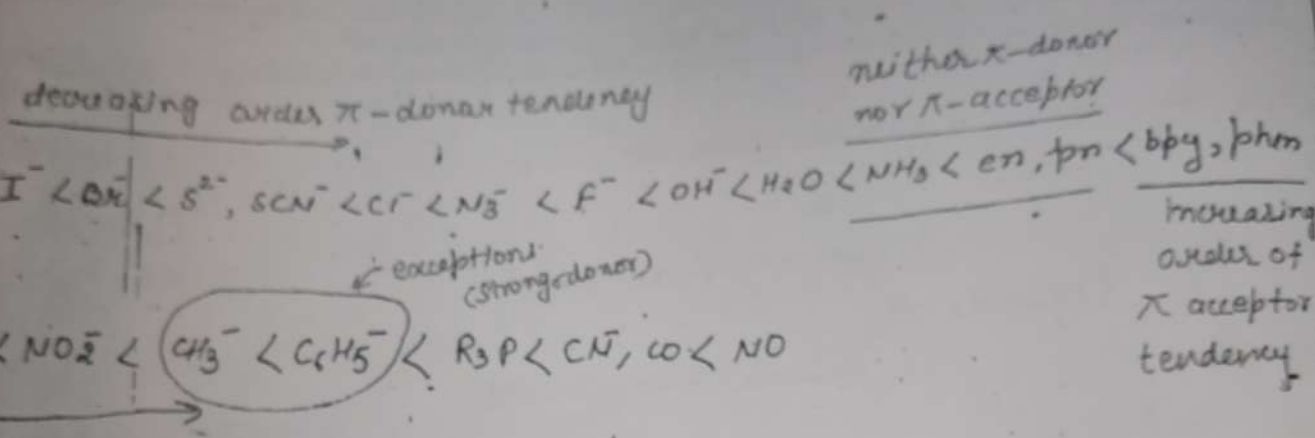
metal — Ligand

Low oxidation states (0, -1, +1 or some times +2)



electrophile → donates e⁻

Na[M(CO)$_x$] ← metal in -1 oxidation state.



Q⇒ $\bar{C}H_3$ and $C_6H_5^-$ are -

(a) only strong σ donor

(b) σ donor and π donor

(c) σ donor and π acceptor

(d) only π-acceptors

π- bonding in octahedral complexes ⇒

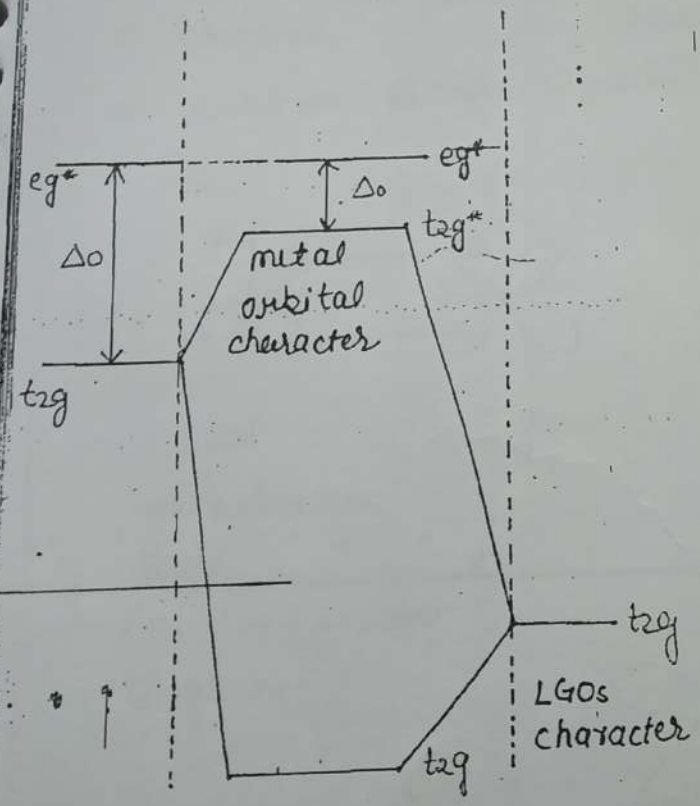
Acc to LFT, ligands may be-

Ligands → π-donors
Ligands → π-acceptors.

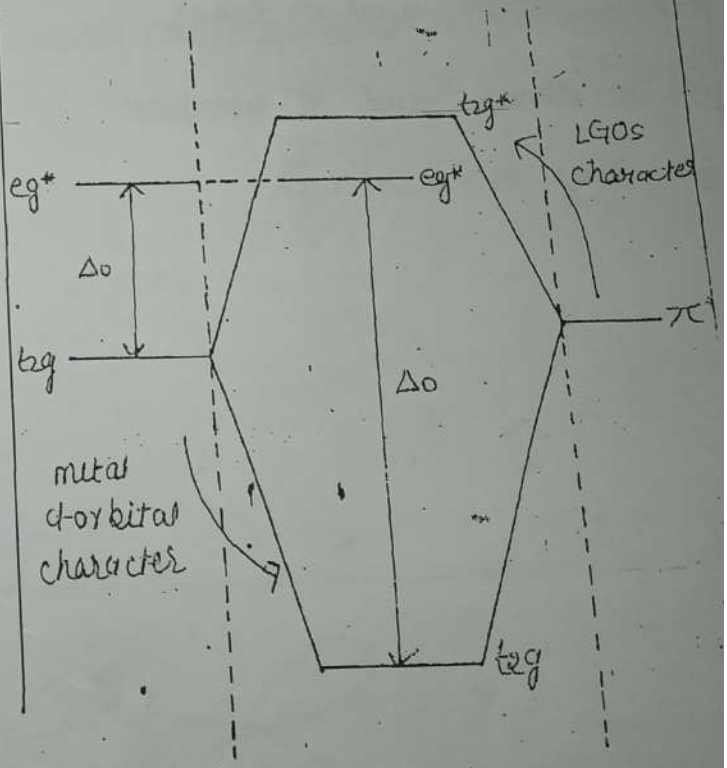
π- donors ⇒ F^-, Cl^-, Br^-, I^-, H_2O, OH^-, S^{2-} etc.

π- acceptors ⇒ have vacant π* Examples ⇒ CO, CN^-, NO, olefins, bpy, phen

π-donor

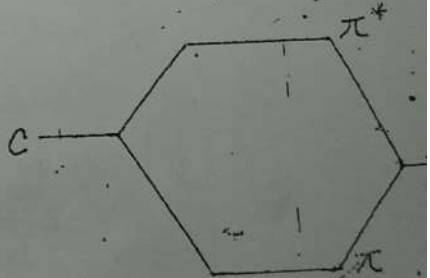


π-acceptor

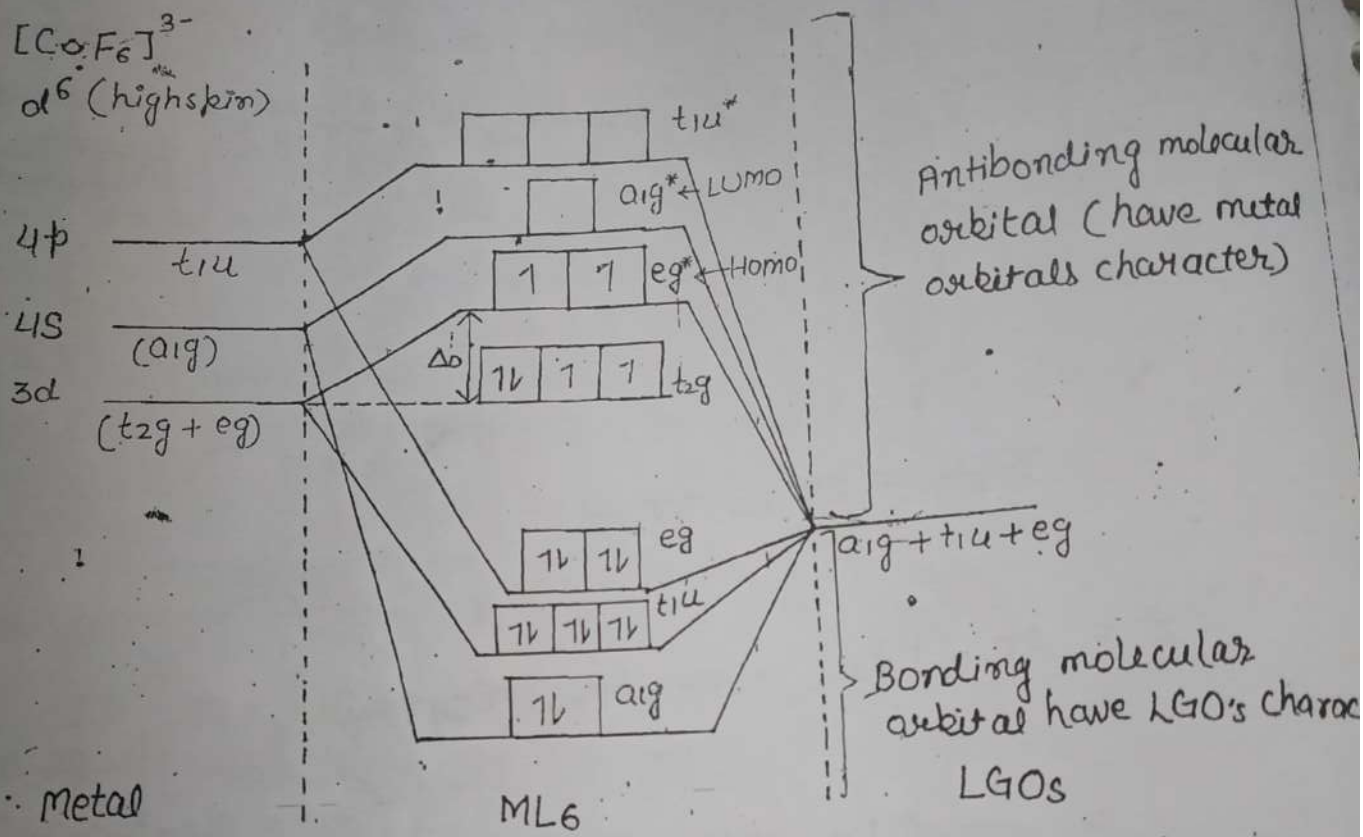


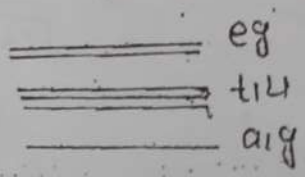
⇒ The symmetry of t2g matches with π* not with π.

⇒ The energy of t2g is comparable with π*.

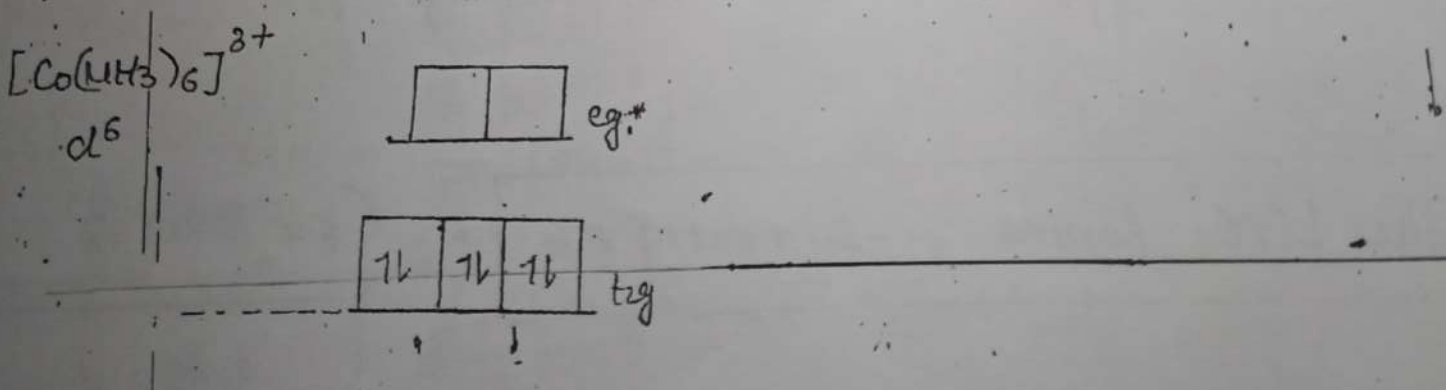


Molecular orbital diagram for octahedral complexes (σ-bonding)



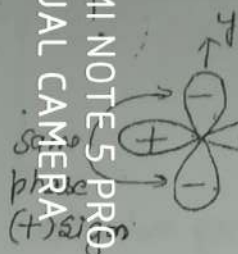


⇒ All 12 e⁻s in Bonding molecular orbital are of ligand because ligand donates its e⁻ to e⁻ deficient metal.



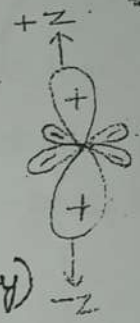
⇒ Ligands have energy lower than metals because ligands are non meta while metals are electropositive.

eg $z x^2-y^2$ $\frac{1}{2}\{\sigma_{+x} + \sigma_{-x} - (\sigma_y + \sigma_{-y})\}$



$= \frac{1}{2}(\sigma_{+x} + \sigma_{-x} - \sigma_y - \sigma_{-y})\left\{\frac{1}{\sqrt{1^2+1^2+1^2+1^2}} = \frac{1}{\sqrt{4}} = \frac{1}{2}\right.$

$\Sigma z^2 = 2\sigma^1_{+z} + 2\sigma_{-z}$



$\Sigma z^2 = 2\sigma_{+z} + 2\sigma_{-z} - (\sigma_{+x} + \sigma_{-x}) - (\sigma_{+y} + \sigma_{-y})$

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

$= \frac{1}{\sqrt{12}}(2\sigma_{+z} + 2\sigma_{-z} - \sigma_{+x} - \sigma_{-x} - \sigma_{+y} - \sigma_{-y})$

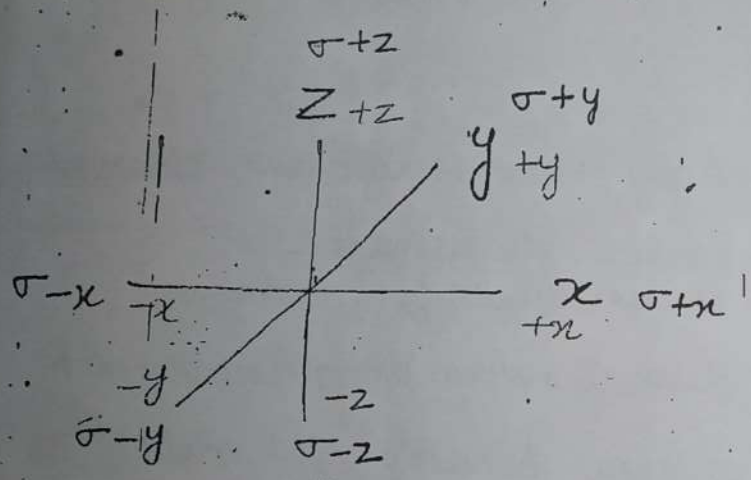
$= \frac{1}{2\sqrt{3}}(2\sigma_{+z} + 2\sigma_{-z} - \sigma_{+x} - \sigma_{-x} - \sigma_{+y} - \sigma_{-y})$

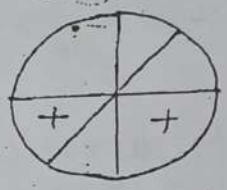
The LGOs having σ-symmetry = 6

$\left\{\begin{array}{l} 6 = 1\,a_1g \\ \quad\quad 3\,t_1u \\ \quad\quad 2\,eg \end{array}\right\}$

and group orbitals (LGOs) ⇒

According to molecular orbitals calculations, the ligand orbitals of all the ligands combine together and form new types of orbitals which have different symmetries and these orbitals are called ligand group orbitals (LGOs).





s- : gerade
(a1g)

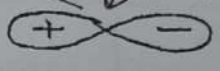
$$a_{1g} = \frac{1}{\sqrt{6}} (\sigma_{+x} + \sigma_{-x} + \sigma_{+y} + \sigma_{-y} + \sigma_{+z} + \sigma_{-z})$$

$$t_{1u} = \frac{1}{\sqrt{2}} (\sigma_{+x} - \sigma_{-x}) \; \Sigma_x$$

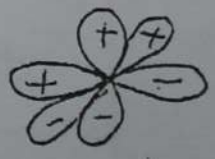
(p-orbital)

↳ sign due to opposite phases

opposite phase



$$\frac{1}{\sqrt{2}} (\sigma_{+y} - \sigma_{-y}) \; \Sigma_y$$



$$\frac{1}{\sqrt{2}} (\sigma_{+z} - \sigma_{-z}) \; \Sigma_z$$

23/08/13

Ligand Field Theory (LFT) or MOT

(Adjusted crystal field theory)

Limitations of CFT ⇒

① A/c to CFT the bonding b/w metal & ligand is purely ionic or electrostatic but in the given example the Ni and CO both are

$Ni(CO)_4$ Ni CO

neutral, hence there is no possibility of ionic bonding, only covalent bonding is possible.

② According to ESR, NQR spectroscopy, there is covalent character b/w metal and ligand. {ESR → Electron spin resonance; NQR → Nuclear Quadrupole resonance}

③ A/c to Nephelauxetic effect (delocalisation of d electrons of metals on ligands) there is covalent bonding b/w metal and ligand.

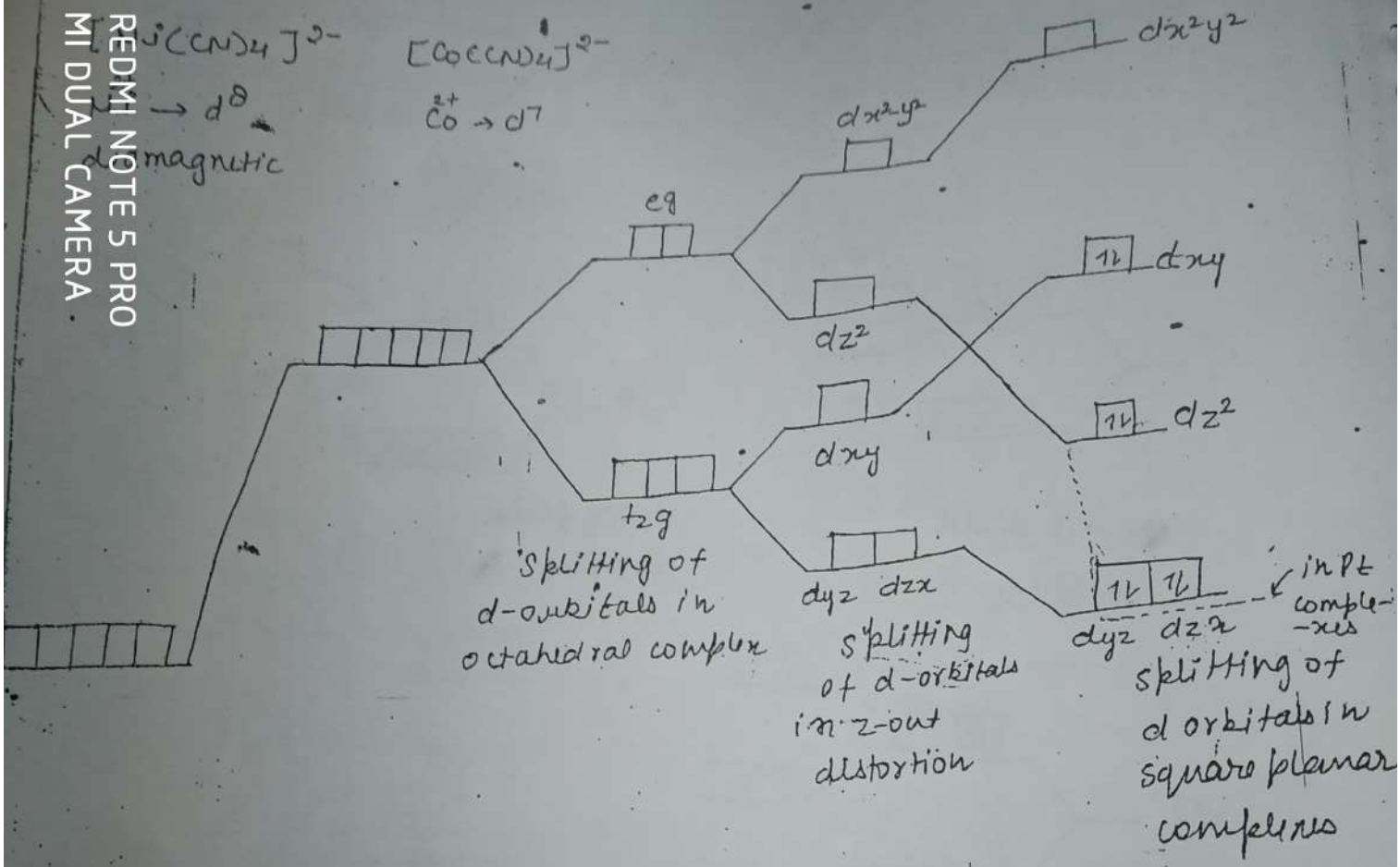
For σ-bonding in octahedral complexes ⇒

metal	s	a_{1g}
	p_x, p_y, p_z	t_{1u}
	d_{xy}, d_{yz}, d_{zx}	t_{2g}
	$d_{x^2-y^2}, d_{z^2}$	e_g

$[Ni(CN)_4]^{2-}$ → d^8 diamagnetic

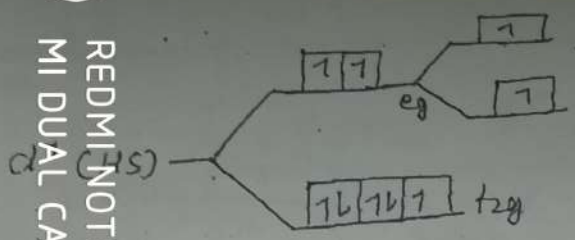
$[Co(CN)_4]^{2-}$

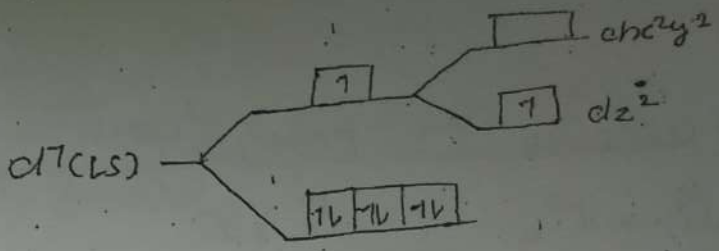
Co^{2+} → d^7

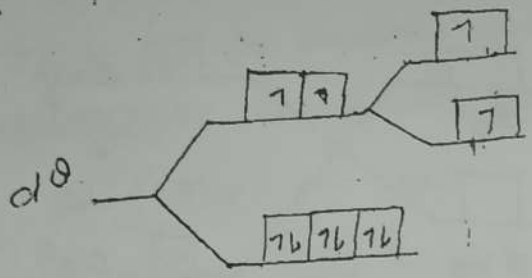


Increasing order of energy of d-orbitals in square planar complexes

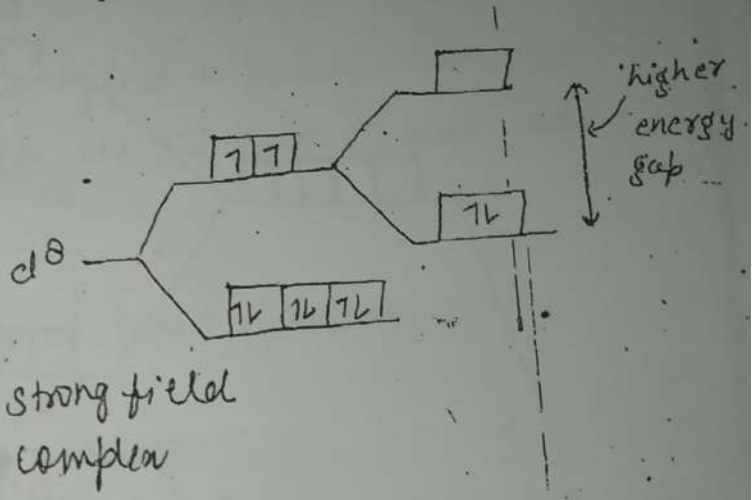
$$d_{yz} = d_{zx} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$



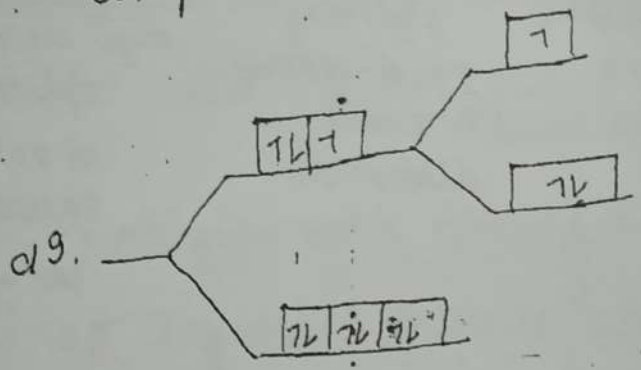


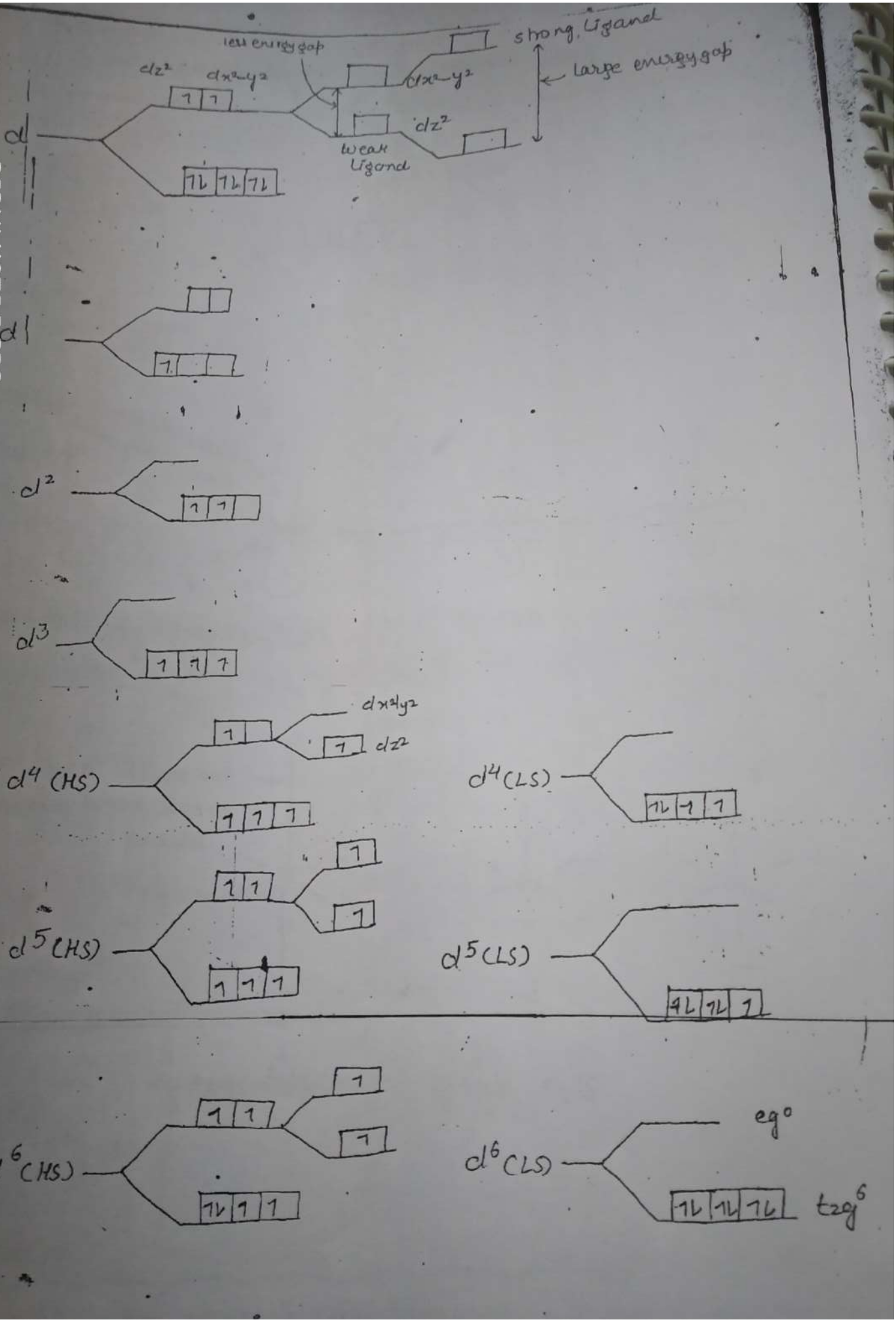


weak field complex



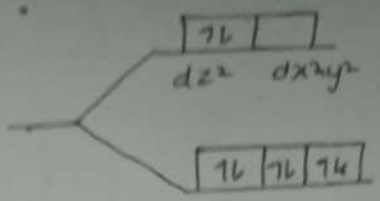
strong field complex

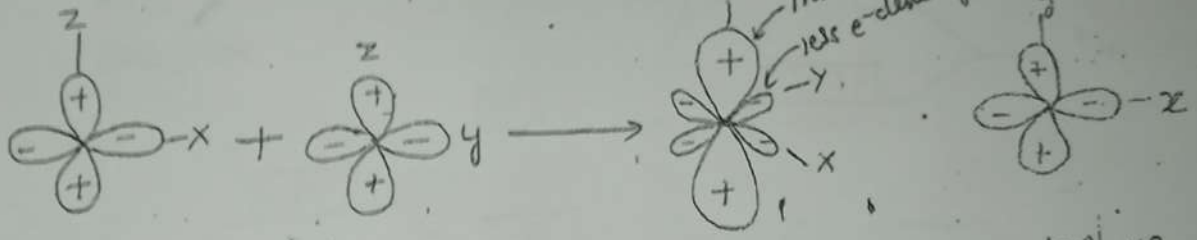



less energy gap
strong ligand
large energy gap
dz^2
dx^2-y^2
dx^2-y^2
dz^2
weak ligand
d
d
d^2
d^3
dx^2y^2
dz^2
d^4 (HS)
d^4(LS)
d^5(HS)
d^5(LS)
d^6(HS)
d^6(LS)
eg^0
t_{2g}^6

Square planar complexes of d^8 configuration :-

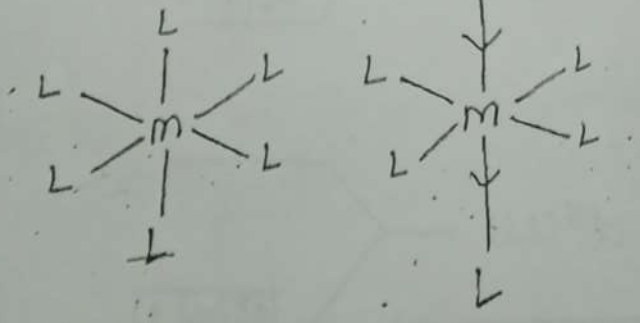
$[Ni(CN)_4]^{2-}$



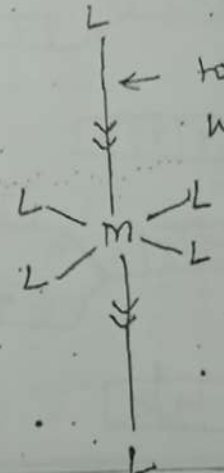


dz^2-x^2 + dz^2-y^2 → $dz^2-x^2-y^2$, dx^2-y^2

$\equiv dz^2$



d^1z^2 $d^0x^2y^2$



d^2z^2 $d^0x^2-y^2$

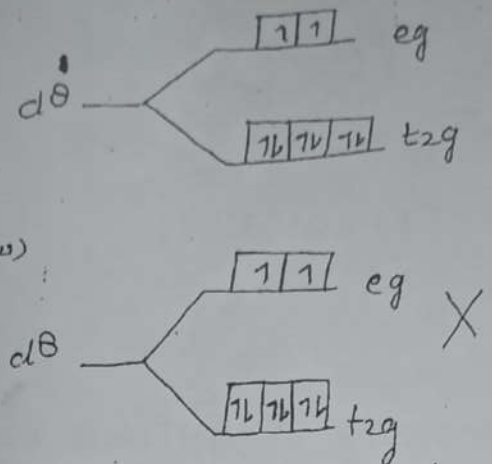
Crystal Field splitting in square planar complexes

$[Ni(H_2O)_6]^{2+}$

$[Ni(NH_3)_6]^{2+}$

(NH_3) → moderate ligand (not strongest nor weakest)

$[Ni(CN)_6]^{4-}$ does not exist.



$[Ni(CN)_4]^{2-}$

Ni forms only square planar complexes with strong ligands while octahedral (or Tetrahedral) complexes with weak ligands.

d^8

$[NiCl_4]^{2-}$ Td

$[Ni(H_2O)_6]^{2+}$

$[Ni(NH_3)_6]^{2+}$ } octahedral

$[Ni(CN)_4]^{2-}$

$[PdCl_4]^{2-}$

$[PtCl_4]^{2-}$

$[Pt(NH_3)_4]^{2+}$

$[Pt(CN)_4]^{2-}$ } square planar

Pd^{2+}, Pt^{2+} form square planar complexes whether the ligand is strong or weak.

Q ⇒ The set of ions expected to show Jahn-Teller distortion is-

(a) Ti (III), Cu (II), Hs Fe (III)
($d^5 \rightarrow t_{2g}^3 e_g^2$)

(b) Cu (I), Ni (II), Hs Fe (III)
($d^{10} \rightarrow t_{2g}^6 e_g^4$, $d^8 \rightarrow t_{2g}^6$)

(c) Cu (II), LS Fe (III), Ti (III)
($d^9 \rightarrow t_{2g}^6 e_g^3$, $d^5 \rightarrow t_{2g}^5 e_g^0$, $d^1 \rightarrow t_{2g}^1 e_g^0$)

(d) LS Fe (III), Mn (II), Cu (I)

Q ⇒ The complex showing John-Teller distortion is-

(a) $Co(NH_3)_6^{3+}$ → $Co^{3+} \rightarrow 3d^6 \rightarrow (t_{2g}^6 e_g^0)$
$_{27}Co \rightarrow 3d^7 4s^2$

(b) $Cr(H_2O)_6^{3+}$ → $Cr^{3+} \rightarrow 3d^3 \rightarrow (t_{2g}^3 e_g^0)$
$_{24}Cr \rightarrow 3d^5 4s^1$

(c) $Cu(H_2O)_6^{2+}$ → $Cu^{+2} \rightarrow 3d^9 \rightarrow t_{2g}^6 e_g^3$
$_{29}Cu \rightarrow 3d^{10} 4s^1$

(d) $[Fe(CN)_6]^{4-}$ → $Fe^{+2} \rightarrow 3d^6 \rightarrow (t_{2g}^6 e_g^0)$
$_{26}Fe \rightarrow 3d^6 4s^2$

Q ⇒ Which one of the following complexes is Jahn-Teller distorted -

(a) $[Co(H_2O)_6]^{3+} \rightarrow d^6 \rightarrow t_{2g}^6 e_g^0$

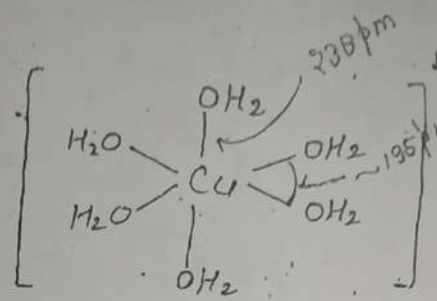
(b) ~~$[Co(NH_3)_6]^{2+} \rightarrow d^7 \rightarrow t_{2g}^5 e_g^2$~~

(c) $[Ni(NH_3)_6]^{2+} \rightarrow d^8 \rightarrow t_{2g}^6 e_g^2$

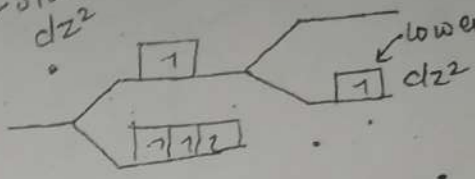
(d) $[Cr(CN)_6]^{3-} \rightarrow d^3 \rightarrow t_{2g}^3 e_g^0$

Consequences of John Teller Distortion ⇒

$[Cu(H_2O)_6]^{2+}$

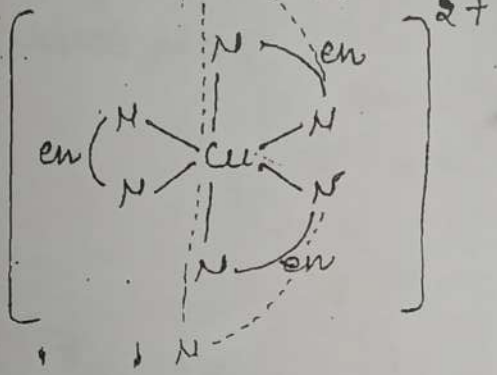


Stable due to stability of d_{z^2}



due to elongation of bond strain increases hence complex becomes unstable

$[Cu(en)_3]^{2+}$

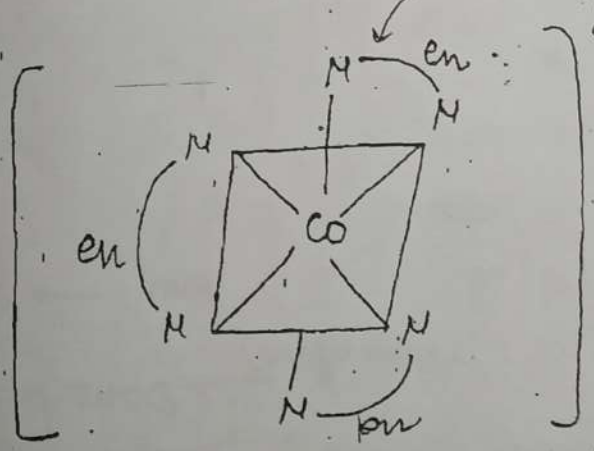


$_{29}Cu = 3d^{10}_{1}4s^{1}$

$Cu^{+2} = 3d^9 \quad t_{2g}^6 e_g^3$

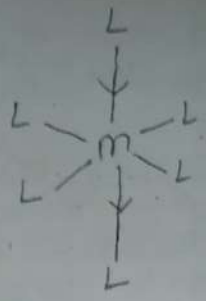
Normal bond → no strain

$[Co(en)_3]^{3+}$



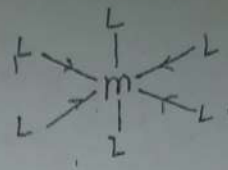
$Co^{+3} = 3d^6 \qquad d^6 \rightarrow (t_{2g}^6 e_g^0)$

$_{27}Co = 8d^7 4s^2$



z-out

(repulsion by 2 ligands)
(more stable)

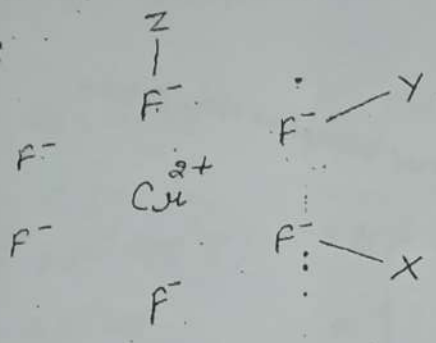


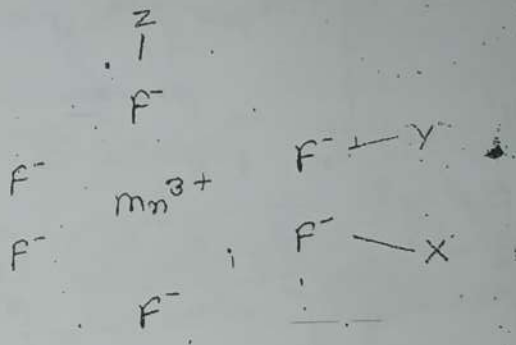
z-in

(repulsion by 4 ligands)
(less stable)

e.g.

CuF_2 , MnF_3





$Cu^{2+} \rightarrow 3d^9 \rightarrow t_{2g}^6 e_g^3$

(coz F is weak ligand)

z out

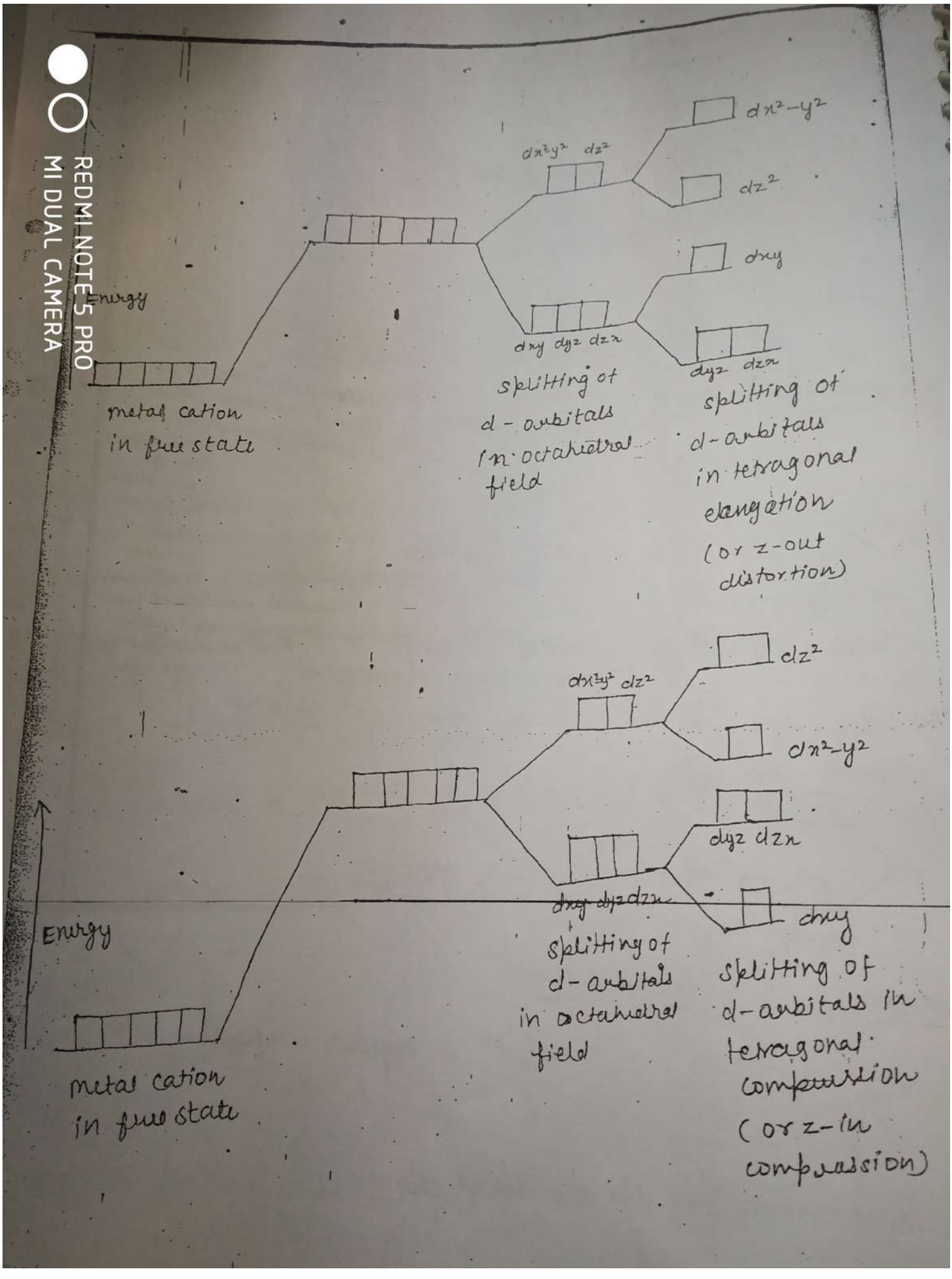
(e⁻ will enter in dz^2)

$Mn^{3+} \rightarrow 3d^4$

z out

(e⁻ will enter in dz^2)

(Fluorine always makes ionic bond with metals.)



Conditions for strong distortion ⇒

t_{2g} → symmetrically filled

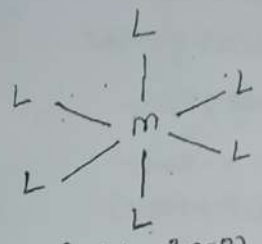
e_g → unsymmetrically filled

t_{2g} ⇒ d^4 (HS) → $t_{2g}^3 e_g^1$

d^7 (LS) → $t_{2g}^6 e_g^1$

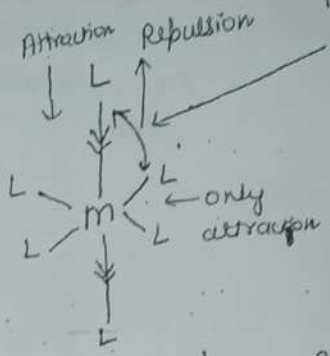
d^9 → $t_{2g}^6 e_g^3$

Tetragonal elongation ⇒



d^3 ($t_{2g}^3 e_g^0$)

d^4(HS) → $t_{2g}^3 e_g^1$

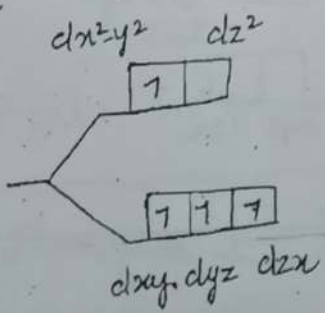


The distance b/w these two ligands increases, steric repulsion decreases → M–L bond decreases at x, y plane ligand fine d orbital is d^4 means nuclear area also ↑ so metal attracts ligand more as compared to in $t_{2g}^3 e_g^0$

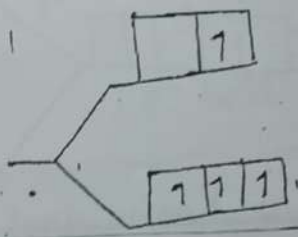
$t_{2g}^3 e_g^1$ $d_{z^2}^1$ $d_{x^2-y^2}^0$

(Tetragonal elongation → z-out distortion)

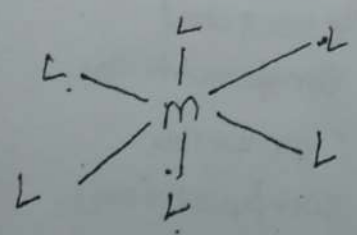
d^4 ⇒ d_{xy}^1 d_{yz}^1 d_{zx}^1 $d_{z^2}^1$ $d_{x^2-y^2}^0$ OR $d_{x^2-y^2}^1$ $d_{z^2}^0$

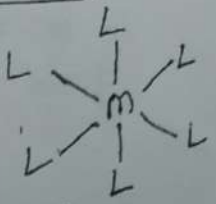


OR



Tetragonal compression ⇒





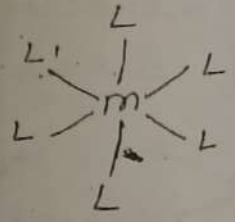
← Regular octahedron

(z-in distortion) d_{xy}^1 d_{yz}^1 d_{zx}^1 $d_{x^2-y^2}^1$ $d_{z^2}^0$

e.g. → d^3 ($t_{2g}^3 e_g^0$), d^5 (HS) → ($t_{2g}^3 e_g^2$)

d^6 (LS) → ($t_{2g}^6 e_g^0$), d^8 ($t_{2g}^6 e_g^2$)

d^{10} ($t_{2g}^6 e_g^4$)



d^3 → d_{xy} d_{yz} d_{zx}

← no distortion ; regular octahedron

② conditions for slight distortion ⇒

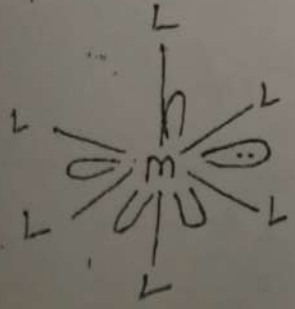
t_{2g} → unsymmetrically filled

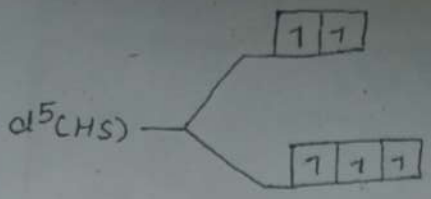
e_g → symmetrically filled

e.g. → d^1 ($t_{2g}^1 e_g^0$), d^2 ($t_{2g}^2 e_g^0$)

d^4 (LS) → ($t_{2g}^4 e_g^0$), d^5 (LS) → ($t_{2g}^5 e_g^0$)

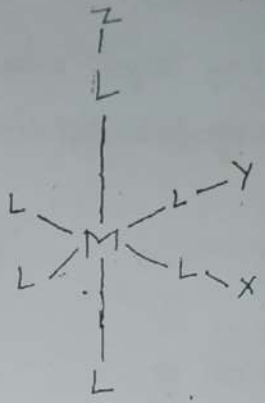
d^6 (HS) → ($t_{2g}^4 e_g^2$), d^7 (HS) → ($t_{2g}^5 e_g^2$)



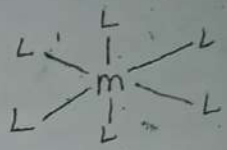


electronically non degenerate

Regular octahedron (All the M-L bond lengths same)



Tetragonal elongation OR Zout OR Tetragonal distortion (M-L bond lengths on Z axis large)



Tetragonal compression (OR Z-in) M-L bond length on Z-axis are shorter

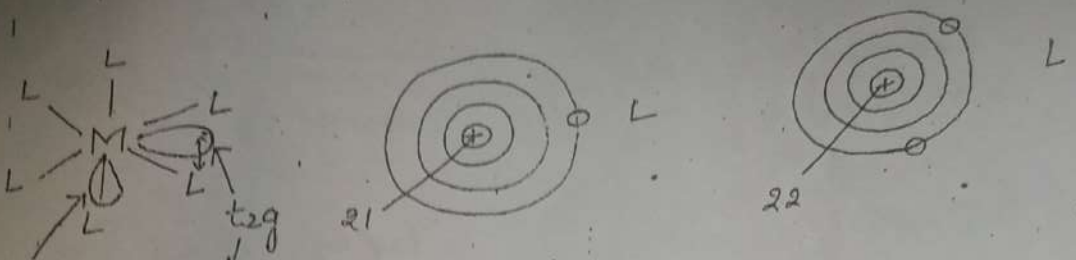
10/09/13

Conditions for Jahn Teller distortion ⇒

① No distortion conditions ⇒

t_{2g} symmetrically filled

e_g symmetrically filled



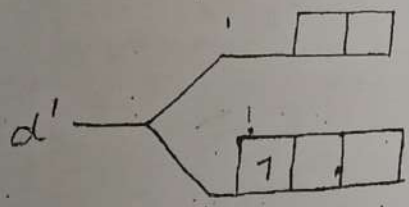
eg
↓
along the axis
↓
more repulsion
↓
small CFSE

t2g
↓
b/w the axis
↓
less repulsion
↓
large CFSE

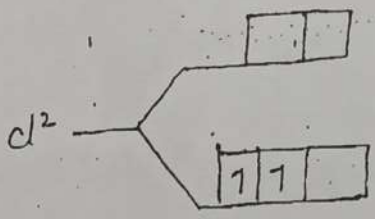
Tetragonal distortion, or John Teller distortion ⇒

John Teller Theorem ⇒ Any non linear molecule in its electronically degenerate state is unstable and undergoes some sort of distortion to remove its degeneracy, lowers energy and change in symmetry (lower in symmetry).

Ex:-

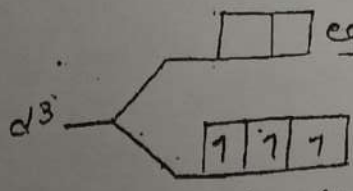


Triply degenerate electronically

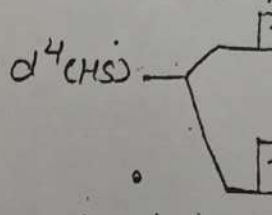


d_{xy} d_{yz}, d_{xy} d_{zx},

d_{yz} d_{zx} electronically triply degenerate



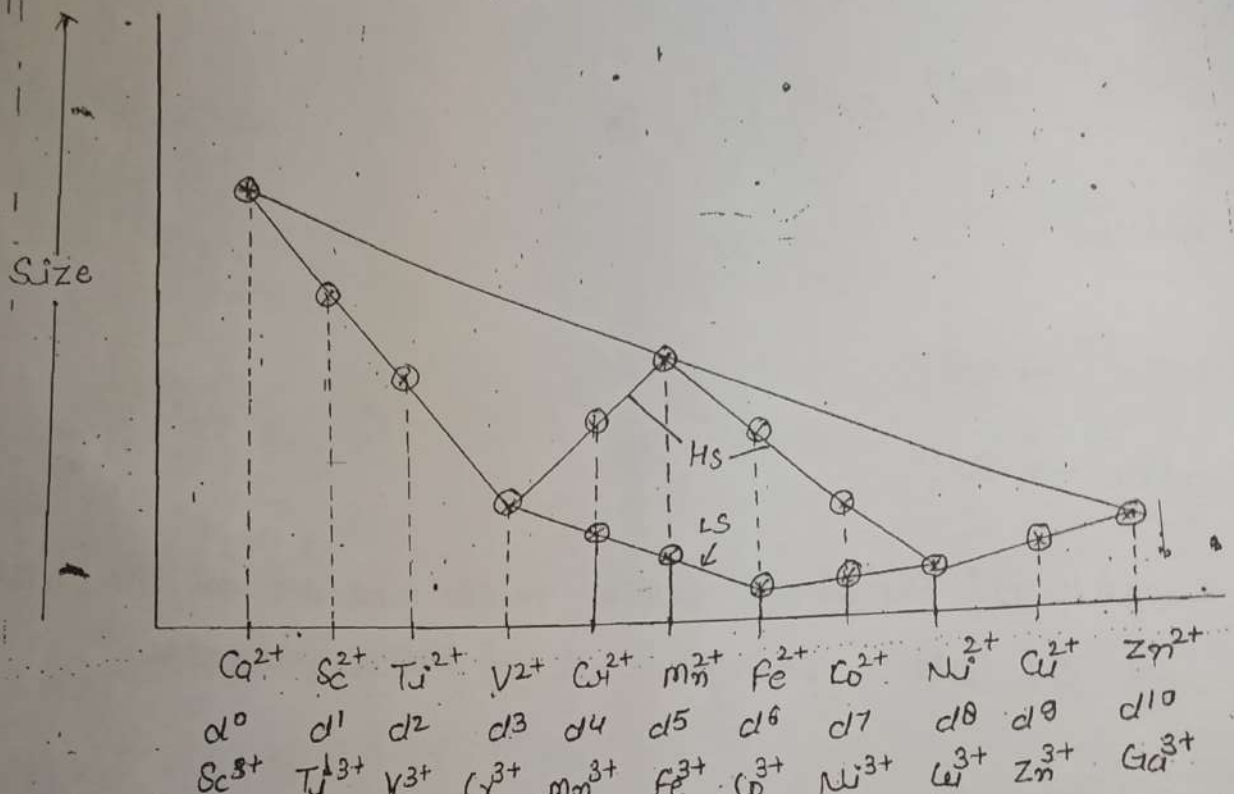
electronically non degenerate



electronically doubly degenerate

	HS Electronic configuration	CfSE	LS Electronic configuration	CfSE
d^0	$t_{2g}^0 e_g^0$	0	$t_{2g}^0 e_g^0$	0
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_0$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_0$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_0$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_0$	$t_{2g}^4 e_g^0$	$-1.6\Delta_0$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$+2.0\Delta_0$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_0$	$t_{2g}^6 e_g^0$	$-2.4\Delta_0$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_0$	$t_{2g}^6 e_g^1$	$-1.8\Delta_0$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_0$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_0$		
d^{10}	$t_{2g}^6 e_g^4$	0		

Size of complex ions



CFSE

$[Ca(H_2O)_6]^{2+}$ 0 — Ca^{2+}

$[Sc(H_2O)_6]^{2+}$ $-0.4\Delta_o$ — Sc^{2+}

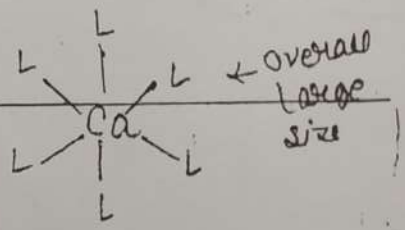
$[Ti(H_2O)_6]^{2+}$ $-0.8\Delta_o$

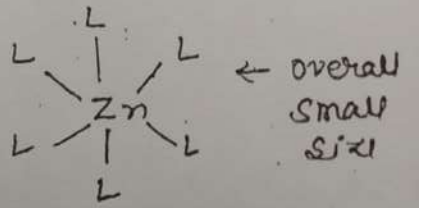
-1.2

$-0.6\Delta_o$

$[Zn(H_2O)_6]^{2+}$ — Zn^{2+}

Size decreases





Q. Which of the following set of transition metal ions lie on the straight line of lattice energy curve of their fluorides?

(a) Mn^{2+}, Zn^{2+}, Ca^{2+}

(b) Mn^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}

(c) Mn^{2+}, Zn^{2+}, Fe^{3+}

(d) Ca^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+}, Ga^{3+}

Ans. (c)

$_{30}Zn^{2+} \rightarrow 3d^{10}$

$_{31}Ga^{3+} \rightarrow 3d^{10}$

Q ⇒ which of the above set of metal ions lie on the straight line of lattice energy curve of their fluorides?

Ans ⇒ (d)

$Ca^{+2}F_2^{-1}$

$Sc^{+2}F_2^{-1}$

$Ti^{+2}F_2^{-1}$

$V^{+2}F_2^{-1}$

$Cr^{+2}F_2^{-1}$

$Mn^{+2}F_2^{-1}$

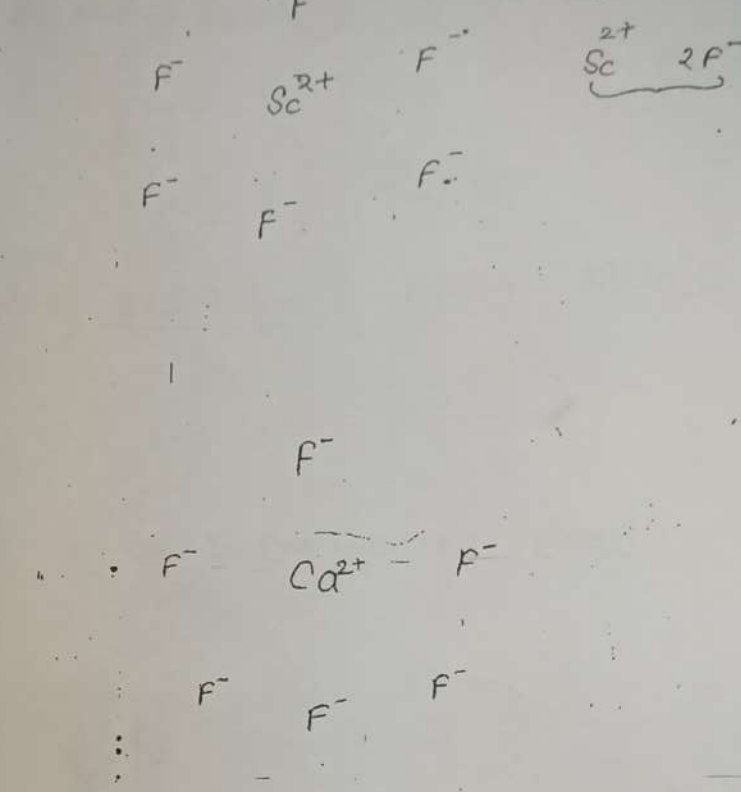
$Fe^{+2}F_2^{-1}$

$Co^{+2}F_2^{-1}$

$Ni^{+2}F_2^{-1}$

$Cu^{+2}F_2^{-1}$

$Zn^{+2}F_2^{-1}$



d^4 (LS) $\rightarrow$ $t_{2g}^4 eg^0$ CFSE $= -1.6\Delta_o$

d^5 (LS) $\rightarrow$ $t_{2g}^5 eg^0$ CFSE $= -2.0\Delta_o$

d^6 (LS) $\rightarrow$ $t_{2g}^6 eg^0$ CFSE $= -2.4$

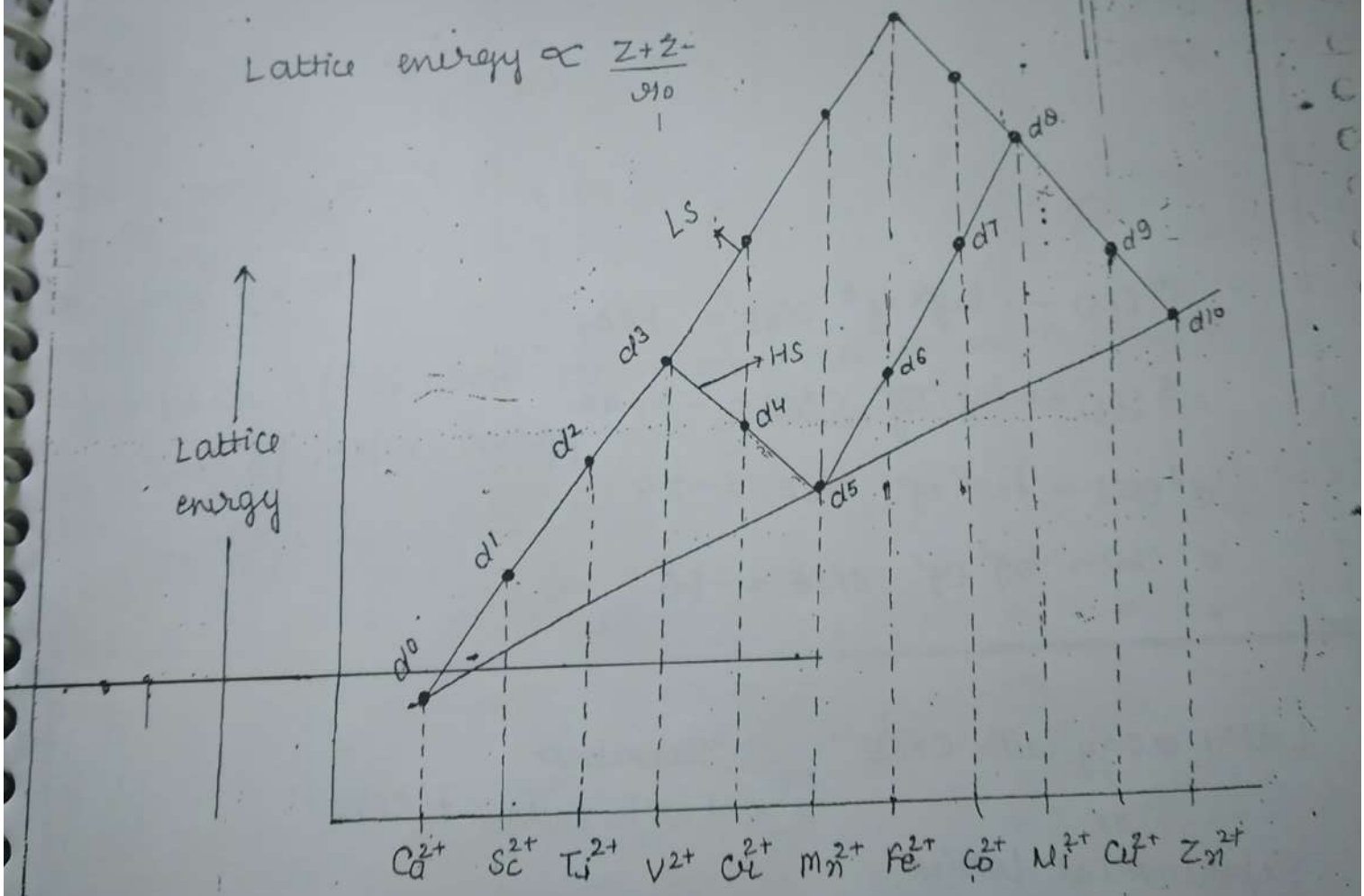
d^7 (LS) $\rightarrow$ $t_{2g}^6 eg^1$ CFSE $= -1.8$

Lattice energy with CFSE or Experimental Lattice energy = Theoretical Lattice energy + CFSE

Lattice Energy ⇒ When one mole of an ionic crystal is formed from its constituent gaseous ions, some energy released → which is called lattice energy.

$$\text{Lattice energy} = \frac{-NAZ^+Z^-}{r_0}\left(1-\frac{1}{n}\right)$$

$$\text{Lattice energy} \propto \frac{Z^+Z^-}{r_0}$$



Lattice energy of diposition transition metals of first transition series.

Q7 The experimental hydration energy for Co^{2+} ion is $-540\ KJ\,mol^{-1}$ and $\Delta o = 12000\ cm^{-1}$. Calculate hydration energy without CFSE.

Given: $1KJ = 83.7\ cm^{-1}$

$1KKal = 4.18\ KJ$

$= 4.18 \times 83.7\ cm^{-1}$

$= 351\ cm^{-1}$

Soln. ⇒

Hydration energy without CFSE = Exp. hydration energy − CFSE

$Co^{2+} \rightarrow 3d^7 \rightarrow t_{2g}^5 e_g^2$

$CFSE = -0.8\Delta o$

$= -0.8 \times 12000$

$= -9600\ cm^{-1}$

$= \frac{-9600}{83.7}\ KJ$

$= -114.6\ KJ$

Hydration E = $-540 - (-114.6)$

$= -425.4\ KJ\,mol^{-1}$

$[Ca(H_2O)_6]^{2+} \rightarrow 3d^0 \longrightarrow t_{2g}^0 e_g^0$

$CFSE = 0$

$[Sc(H_2O)_6]^{2+} \rightarrow 3d^1 \rightarrow t_{2g}^1 e_g^0$

$CFSE = -0.4\Delta_o$

Experimental hydration energy = Theoretical or calculated hydration E + CFSE

$[Ti(H_2O)_6]^{2+} \longrightarrow 3d^2 \rightarrow t_{2g}^2 e_g^0 \rightarrow CFSE = -0.8\ \Delta_o$

$[V(H_2O)_6]^{2+} \longrightarrow 3d^3 \rightarrow t_{2g}^3 e_g^0 \rightarrow CFSE = -0.4X3 = -1.2\ \Delta_o$

* $[Cr(H_2O)_6]^{2+} \rightarrow 3d^4 \longrightarrow t_{2g}^3 e_g^1 \rightarrow CFSE = -0.4X3 + 0.6X1 = -0.6\ \Delta_o$

* $[Mn(H_2O)_6]^{2+} \rightarrow 3d^5 \rightarrow t_{2g}^3 e_g^2 \rightarrow CFSE = -0.4X3 + 0.6X2 = -1.2 + 1.2 = 0$

$[Fe(H_2O)_6]^{2+} \longrightarrow 3d^6 \rightarrow t_{2g}^4 e_g^2 \rightarrow CFSE = -0.4\Delta_o$

$[Co(H_2O)_6]^{2+} \rightarrow 3d^7 \rightarrow t_{2g}^5 e_g^2 \rightarrow CFSE = -0.4X5 + 0.6X2 = -0.8\ \Delta_o$

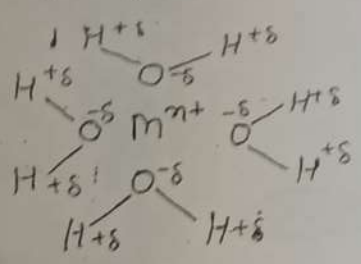
$[Ni(H_2O)_6]^{2+} \rightarrow 3d^8 \rightarrow t_{2g}^6 e_g^2 \rightarrow CFSE = -0.4X6 + 0.6X2 = -1.2\Delta_o$

* $[Cu(H_2O)_6]^{2+} \rightarrow 3d^9 \rightarrow t_{2g}^6 e_g^3 \rightarrow CFSE = -0.4X6 + 0.6X3 = -0.6\ \Delta_o$

* $[Zn(H_2O)_6]^{2+} \rightarrow 3d^{10} \rightarrow t_{2g}^6 e_g^4 \rightarrow CFSE = -0.4X6 + 0.6X4 = 0$

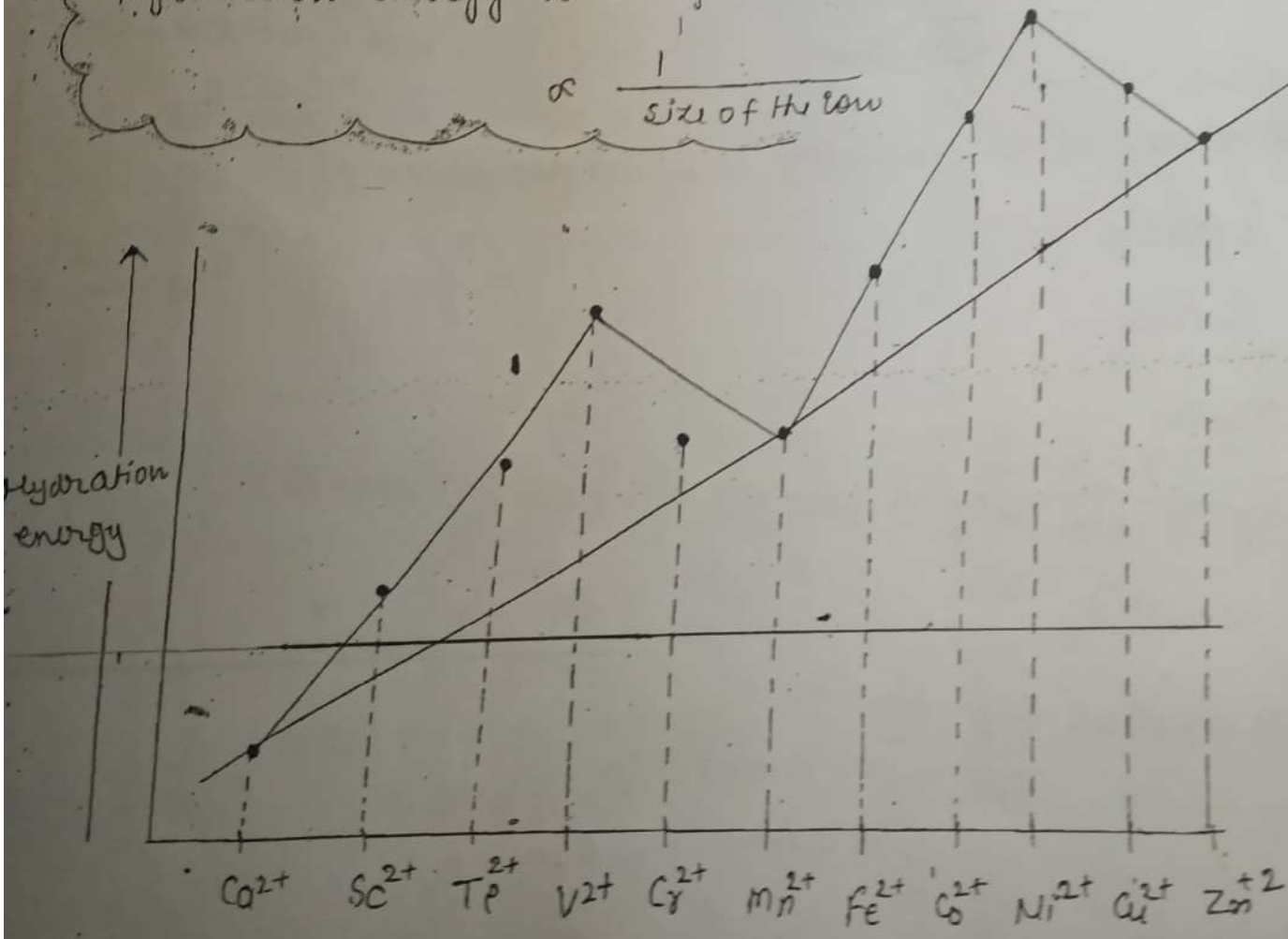
Hydration Energy ⇒

Hydration ⇒ Gathering of water molecules around cation or anion is k/a hydration. In this process some amount of energy is released - which is known as hydration energy. This energy is used to break the ionic bond.



Hydration energy ∝ charge on the ion

$$\propto \frac{1}{\text{size of the ion}}$$



for dipositive metal ions of 3d series transition metal

$FeCr_2O_4$

Note ⇒ Spinals having Cr^{3+} ions → Normal spinels

	Oh	Td
$Fe^{+2} \rightarrow 3d^6$	$t_{2g}^4 e_g^2$ $CFSE = -0.4\Delta_o$	$e^3 t_2^3$ $CFSE = -0.27\Delta t$
$Cr^{+3} \rightarrow 3d^3$	$t_{2g}^3 e_g^0$ $CFSE = (-0.4 \times 3 + 0.6 \times 0)\Delta_o$ $= -1.2\Delta_o$	$e^2 t_2^1$ $CFSE = -0.27 \times 2 + 0.18 \times 1$ $= -0.54 + 0.18$ $= -0.36\Delta t$
$Fe^{+2} \rightarrow 3d^4$	$t_{2g}^3 e_g^1$ $CFSE = (-0.4 \times 3 + 0.6 \times 1)\Delta_o$ $= -1.2 + 0.6 = -0.6\Delta_o$	$e^2 t_2^2$ $CFSE = -0.27 \times 2 + 0.18 \times 2$ $= -0.54 + 0.36$ $= -0.18\Delta t$

Q ⇒ which of the following is a normal spinel ?

(i) $NiCrO_4$

(ii) $FeCrO_4$

(iii) $MnCo_3O_4$

(a) only (i) (b) only (i) and (ii) (c) only (ii) and (iii)

(d) (i), (ii), (iii)

$Ni^{2+} \rightarrow 3d^8 \rightarrow t_{2g}^6 e_g^2$

$CFSE = (-2.4 + 1.2)\Delta_o$

$= -1.2\Delta_o$

$Cr^{3+} \rightarrow 3d^3 \rightarrow CFSE = -1.2\Delta_o$

(4) $NiFe_2O_4$

	octahedral	Tetrahedral
$Ni^{+2} \rightarrow 3d^8$	$t_{2g}^6 e_g^2$	$d^8 \rightarrow e^4 t_2^4$
	$CFSE = (-0.4\times6 + 0.6\times2)\Delta o$	$CFSE = (-0.27\times4 + 0.18\times4)\Delta t$
	$= (-2.4 + 1.2)\Delta o$	$= -1.08 + 0.72$
	$= -1.2\Delta o$	$= -0.36\Delta t$
$Fe^{+2} \rightarrow 3d^6$	$t_{2g}^4 e_g^2$	$d^6 \rightarrow e^3 t_2^3$
	$CFSE = (-0.4\times4 + 0.6\times2)\Delta o$	$CFSE = (-0.27\times3 + 0.18\times3)\Delta t$
	$= -1.6 + 1.2$	$= -0.81 + 0.54$
	$= -0.4\Delta o$	$= -0.27\Delta t$
$Fe^{+3} \rightarrow 3d^5$	$t_{2g}^3 e_g^2$	$d^5 \rightarrow e^2 t_2^3$
	$CFSE = (-0.4\times3 + 0.6\times2)\Delta o$	$CFSE = (-0.27\times2 + 0.18\times3)$
	$= 0$	$= -54 + 0.54$
		$= 0$

Ni^{+2} → octahedral
Fe^{+3} → tetrahedral
O^{2-} → lattice point
} inverse

③ Co_3O_4

octahedral

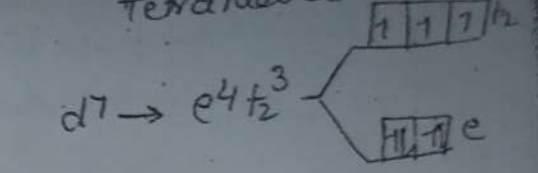
$Co^{2+} \rightarrow 3d^7$ $\quad t_{2g}^5 e_g^2$

$CFSE = (-0.4 \times 5 + 0.6 \times 2)\Delta_o$

$= -0.800$

Tetrahedral

$d^7 \rightarrow e^4 t_2^3$



$CFSE = (-0.27 \times 4 + 0.18 \times 3)\Delta_o$

$= (-1.08 + 0.54)\Delta_o$

$= -0.54\,\Delta_o$

$Co^{3+} \rightarrow 3d^6$ $\quad t_{2g}^4 e_g^2$

$CFSE = (-0.4 \times 4 + 0.6 \times 2)$

$= -0.4$

$t_{2g}^6 e_g^0$

$CFSE = -0.4 \times 6 + 0.6 \times 0$

$CFSE = -2.4$

d^6 $\quad e^4 t_2^2$

$CFSE = (-0.27 \times 4 + 0.18 \times 2)$

$= (-1.08 + 0.36)$

$= -0.72\,\Delta_o$

$d^6 \rightarrow e^3 t_2^3$

$CFSE = (-0.27 \times 3 + 0.18 \times 3)$

$= (-0.81 + 0.54)$

$= -0.27\,\Delta_o$

$Co^{2+} \rightarrow$ tetrahedral (hs)

$Co^{3+} \rightarrow$ octahedral

} normal

(2) Fe_3O_4

octahedral

Tetrahedral

$Fe^{2+} \rightarrow 3d^6$ $\quad t_{2g}^4 e_g^2$ $\quad e^3 t_2^3$

$CFSE = (-0.4 \times 4 + 0.6 \times 2)\Delta_o$

$= -0.4\Delta_o$

$CESE = [-0.27 \times 3 + 0.18(3)]\Delta_o$

$= (-0.81 + 0.54)\Delta_o$

$= -0.27\Delta_o$

$Fe^{3+} \rightarrow d^5$ $\quad t_{2g}^3 e_g^2$ $\quad d^5\ e^2 t_2^3$

$CFSE = 0$ $\quad CFSE = 0$

Fe^{2+} → octahedral

Fe^{3+} → Tetrahedral } Inverse spinel

O^{2-} → Lattice Point

Spinels having Fe^{+3} ions — inverse spinels

03/09/13

Example ⇒

1) Mn_3O_4

	Octahedral	Tetrahedral
$Mn^{2+} \rightarrow 3d^5$	$t_{2g}^3 e_g^2$	$d^5 \rightarrow e^2 t_2^3$
	$CFSE = (-0.4 \times 3 + 0.6 \times 2)\Delta_o$	$CFSE = [-0.27 \times 2 + 0.18 \times 3]\Delta_t$
	$= 0$	$= 0$
$Mn^{3+} \rightarrow 3d^4$	$t_{2g}^3 e_g^1$	$d^4 \rightarrow e^2 t_2^2$
	$CFSE = (-0.4 \times 3 + 0.6 \times 1)\Delta_o$	$CFSE = (-0.4 \times 2 + 0.6 \times 2)\Delta_t$
	$= -0.6\Delta_o$	$= -0.48\Delta_t$

$= [-0.27 \times 2 + 0.6 \times$

$= [-0.27 \times 2 + 0.18 \times 2]$

$= -0.18\Delta_o$

$O^{2-} \rightarrow$ Lattice Point

$Mn^{3+} \rightarrow$ Octahedral

$Mn^{2+} \rightarrow$ Tetrahedral

} Normal spinel

Inverse spinels :-

O^{2-} → constitute lattice points

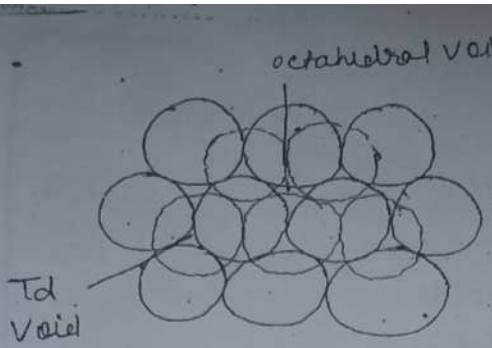
B^{3+} → occupy $\frac{1}{8}$th of the Td voids

B^{3+} → occupy $\frac{1}{4}$th of the Oh voids

A^{2+} → occupy $\frac{1}{4}$th of the Oh voids

Lattice points	Oh voids	Td voids
4	4	8
Normal $O^{2-} = 4$	B^{3+} $4 \times \frac{1}{2} = 2$	$8 \times \frac{1}{8} = 1$
Inverse $O^{2-} = 4$.	B^{3+} $4 \times \frac{1}{4} = 1$	$B^{3+} = 8 \times \frac{1}{8} = 1$
	A^{2+} $4 \times \frac{1}{4} = 1$	

$A_1 B_2 O_4$



No. of tetrahedral voids = 2 × No. of lattice points

No. of Oh voids = No. of lattice points

No. of Td voids = 2 × No. of Oh voids
= 2 × No. of lattice points

① Normal spinels ⇒

O^{2-} → constitute lattice points

A^{2+} → occupy $\frac{1}{8}^{th}$ of the tetrahedral voids

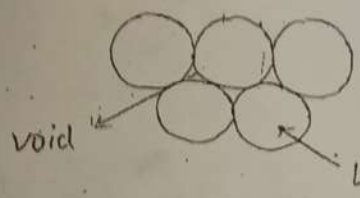
B^{3+} → occupy half of the octahedral voids

Lattice Points	Octahedral Voids	Tetrahedral Voids
4	4	8
$O^{2-} = 4$	B^{3+} $4 \times \frac{1}{2} = 2$	$8 \times \frac{1}{8} = 1$

A^{2+} B^{3+} O^{2-} | AB_2O_4
1 2 4

Larger size ion (in general anion) → Constitute lattice point

Smaller size ion (In general cation) → occupy voids

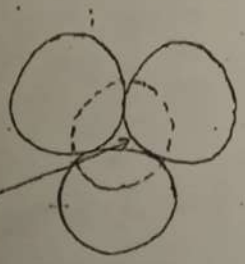


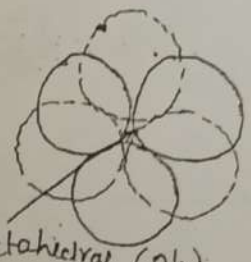
Voids or interstitial sites or interstices or hole → unoccupied space

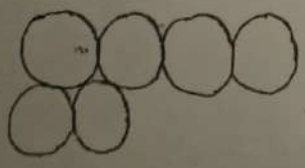
Two types voides :

① Tetrahedral voides

② octahedral voides







Applications of CFSE ⇒

(1) Spinels ⇒

Mixed oxides having formula AB_2O_4 or AB_2S_4 / AB_2Se_4

A ⟶ +2 oxidation state → Mg^{2+}, Ca^{2+}, Sn^{2+}, Ba^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}

B ⟶ +3 oxidation state → Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}

A and B either same or different atoms.

Examples ⇒ $\overset{+2}{Ni}\overset{+3}{Fe_2}O_4$ $\quad$ $\overset{+2}{NiO}\cdot\overset{+3}{Fe_2}O_3$

Mn_3O_4 — $\overset{+2}{Mn}\cdot\overset{+3}{Mn_2}O_4$ $\quad$ $MnO\cdot Mn_2O_3$

Fe_3O_4 $\quad$ $\overset{+2}{FeO}\cdot\overset{+3}{Fe_2}O_3$

Classification :-

① Normal spinels ② Inverse spinels

O^{2-} → Lattice Points

metal ions ⟶ occupy Voids

d^4 (LS) → t_{2g}^4 eg^0 CFSE = $-0.4 \times 4\Delta_o + P$

d^5 (LS) → t_{2g}^5 eg^0 CFSE = $-0.4 \times 5\Delta_o + 2P$

d^6 (LS) → t_{2g}^6 eg^0 CFSE = $-0.4 \times 6\Delta_o + 2P$

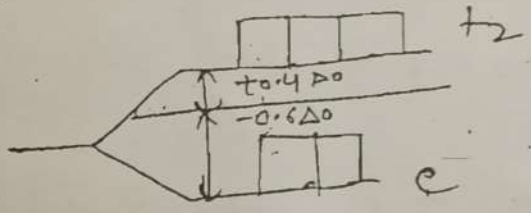
d^7 (LS) → t_{2g}^6 eg^1 CFSE = $[-0.4 \times 6 + 0.6 \times 1]\Delta_o + P$

HS ⟶ No pairing energy

CFSE in tetrahedral complexes ⇒

HS

$d^n \rightarrow e^p\ t_2^q$



$CFSE = [-0.6p + 0.4q]\Delta t$

$\Delta t = \frac{4}{9}\Delta_o$

$CFSE = [-0.27p + 0.18q]\Delta t$

Q7 A complex $[Cr L_6]^{2+}$ absorbs at $15000 cm^{-1}$.

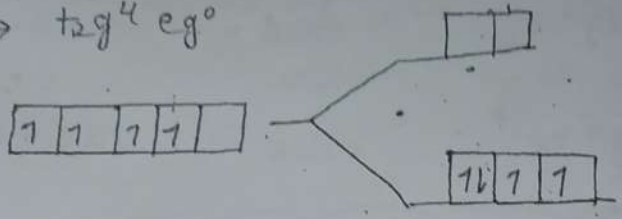
$P = 12000 cm^{-1}$. Calculate CFSE.

L = monodentate, neutral ligand.

$Cr^{2+} \rightarrow {}_{24}Cr \rightarrow 3d^5 4s^1$

$\downarrow$

$3d^4 \rightarrow t_{2g}^4 e_g^0$



$\Delta_o > P \rightarrow LS$

$\Delta_o < P \rightarrow HS$

$\Delta_o = P$ HS and LS are in equilibrium

Here $15000 cm^{-1} (\Delta_o) > 12000 cm^{-1} (P) = LS$

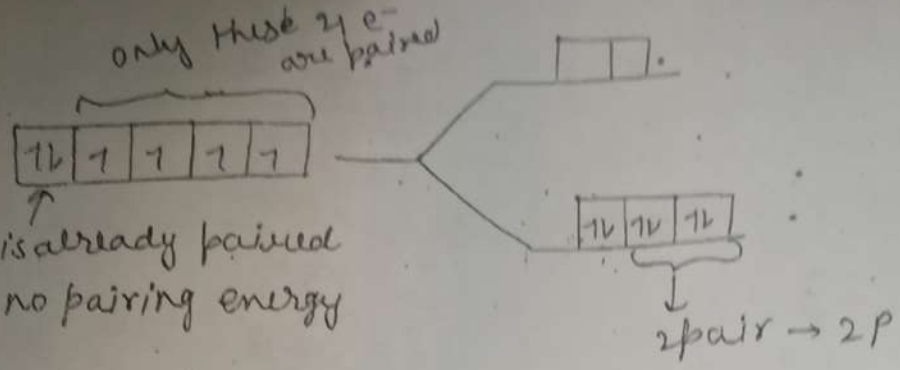
$t_{2g}^4 e_g^0$

~~$-0.4 \times 4 +$~~

~~$-1.6 + P$~~

$= -0.4 \times 4 \times 15000 + 12000$

$= -12000 cm^{-1}$

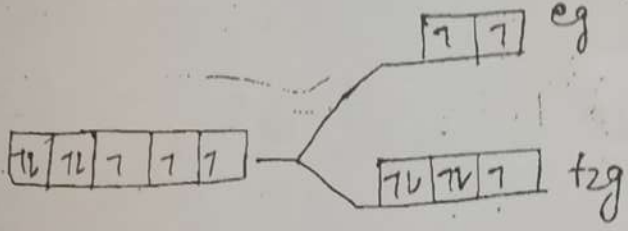


$-0.4 \times 6 + 0.6 \times 0 + 2P$

$-2.4 + 2P$ ✓

Q⇒ d^7 HS → $t_{2g}^5\ e_g^2$

CFSE = ?



$-0.4 \times 5 + 0.6 \times 2 = -02.0 + 1.2$

$= -0.8\Delta_o$

(a) $-\frac{4}{5}\Delta_o + 3P$

✓(b) $-\frac{4}{5}\Delta_o + 2P$ (wrong a/c to logic but right a/c to examina

(c) $-\frac{9}{5}\Delta_o + 3P$

(d) $-\frac{9}{5}\Delta_o + 2P$

The answer of this ques. should be $-\frac{4}{5}\Delta_o$ as there is no pairing energy in HS complexes.

d^4 (HS) → $t_{2g}^3\ e_g^1$

CFSE = $[-0.4\times3 + 0.6\times1]\Delta_o$

= $-0.6\,\Delta_o$

d^4 (LS) → $t_{2g}^4\ e_g^0$

CFSE = $-0.4\times4\ \Delta_o + 1P$

= $-1.6\,\Delta_o + P$

$d^n = t_{2g}^p\ e_g^q$

resultant → experimental

$$\boxed{CFSE = [-0.4p + 0.6q]\Delta_o + mP}$$

Theoretical → actual CFSE → exact CFSE

P = pairing energy or mean pairing energy ↓ energy required for pairing electrons

m = no. of paired electrons caused by the ligands or (occurs during the complex formation)

d^6 (LS) → $t_{2g}^6\ e_g^0 + 3P$ ✗

$-0.4\times6 + 0.6\times0$

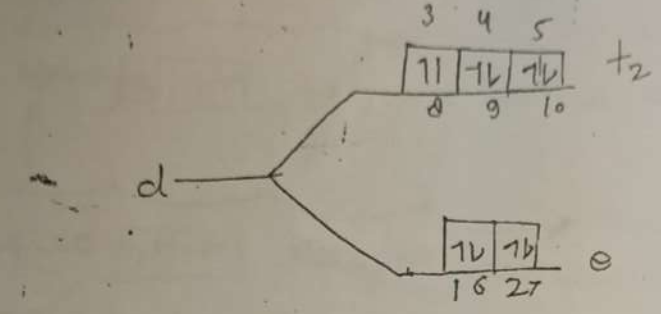
$-2.4 + 3P$

[no pairing energy in high spin complexes.]

Electron distribution in tetrahedral complexes ⇒

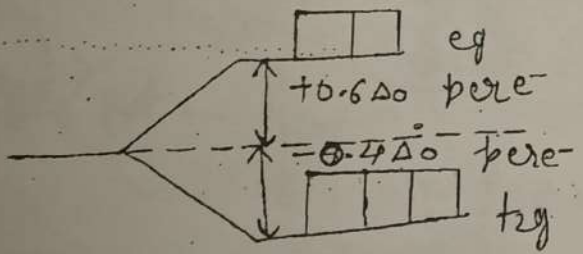
Tetrahedral complexes are high spin complexes.

$$\Delta t = \frac{4}{9}\Delta o$$



1. $e^{1,2} \longrightarrow t_2^{3,4,5} \longrightarrow e^{6,7} \longrightarrow t_2^{8,9,10}$

Crystal field stabilization energy in octahedral complexes =



$d^1 \longrightarrow t_{2g}^1\ eg^0$ CFSE $= -0.4\Delta o$

$d^2 \longrightarrow t_{2g}^2\ eg^0$ $= -0.4 \times 2\ \Delta o$

$= -0.8\ \Delta o$

$d^3 \longrightarrow t_{2g}^3\ eg^0$ $= -0.4 \times 3$

$= -1.2\ \Delta o$

Above electron distribution is valid for-

① only 3d series elements

② for +2, +3 oxidation state

③ +4 oxidation state → how spin complexes whether the ligand is strong or weak

Co^{3+} forms LS complexes with most of the ligands exept halides

④ 4d and 5d series transition mytals in +3 oxidation state form LS complexes whether the ligand are weak or strong.

⑤ +2 oxidation of 5d series - LS :

+2 " " " 4d series - LS (in general)

eg ① $K_2[NiF_6] \rightarrow {}_{28}Ni = {}_{25}Mi^{3+} = 3d^5 4d^2$ $3d^8 4s^2$

$3d^6 \rightarrow t_{2g}^6 e_g^0$

② $[Co(H_2O)_6]^{3+} \rightarrow Co^{3+} \rightarrow 3d^6 \rightarrow t_{2g}^6 e_g^0$

③ $[Co(NH_3)_6]^{2+} \rightarrow Co^{2+} \rightarrow 3d^7 \rightarrow t_{2g}^5 e_g^2$ ← low o.s. no pairing

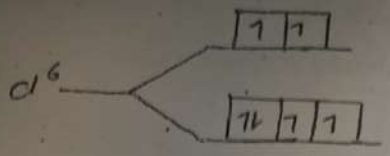
---

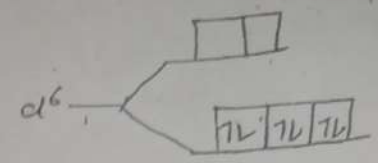
④ $[Rh(H_2O)_6]^{3+} \rightarrow 4d^6 \rightarrow t_{2g}^6 e_g^0$

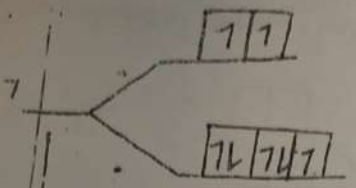
⑤ $[IrF_6]^{3-} \rightarrow 5d^6 \rightarrow t_{2g}^6 e_g^0$

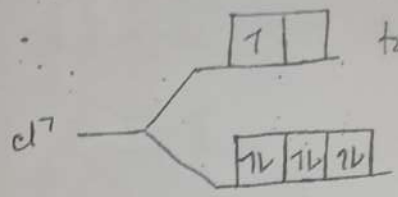
⑥ $[Fe(CN)_6]^{4-} \rightarrow 3d^6 \rightarrow t_{2g}^6 e_g^0$

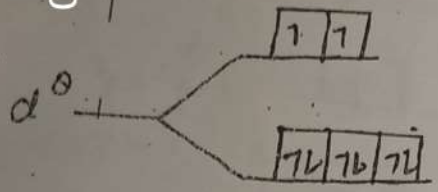
⑦ $[Fe(CN)_6]^{3-}$ $3d^5 \rightarrow t_{2g}^5 e_g^0$

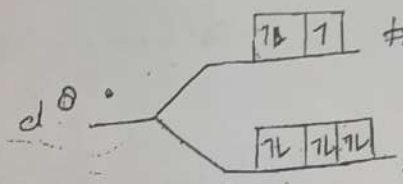


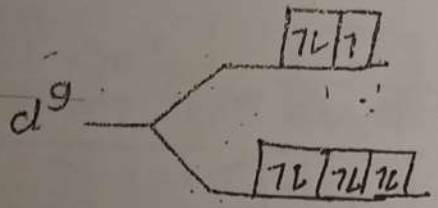


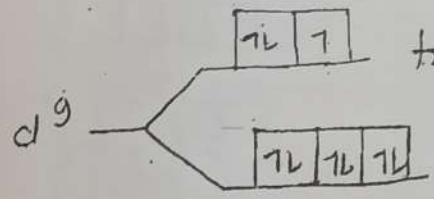


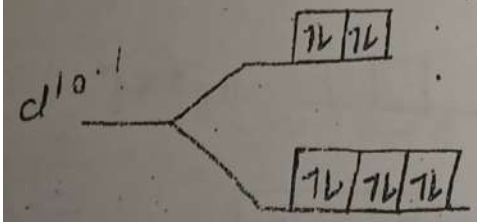


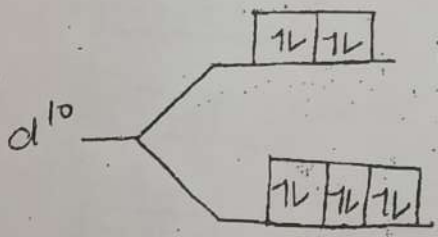












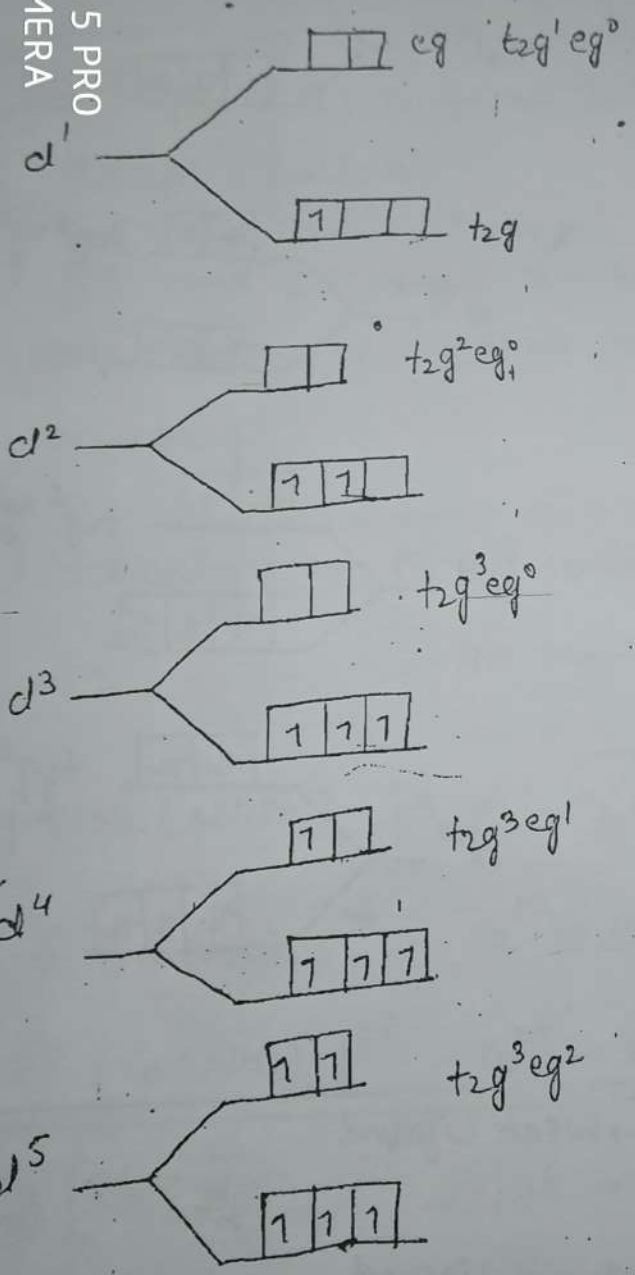
d^4, d^5, d^6, d^7 → HS → weak ligand
→ LS → strong ligand

d^1, d^2, d^3 → complexes

d^8, d^9, d^{10} → complexes

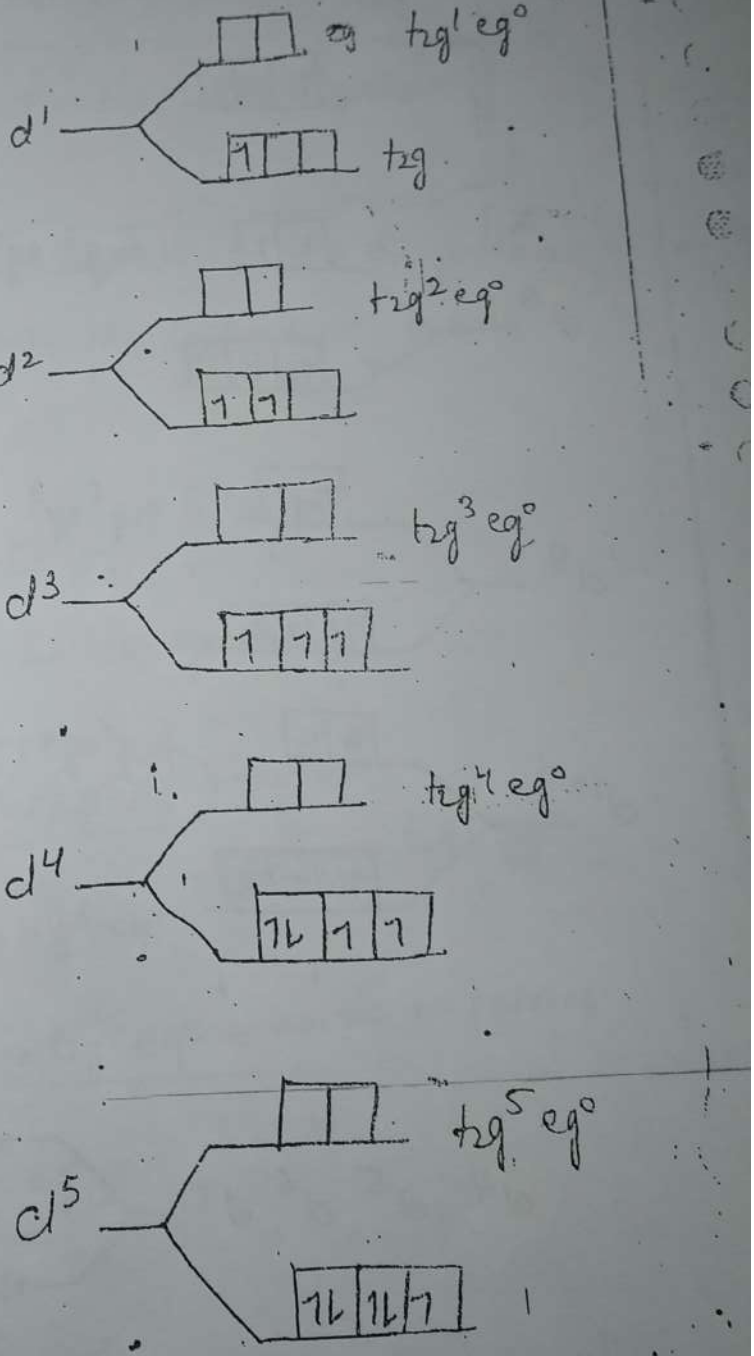
High spin or
Spin free complexes

pairing of e⁻s
(weak field complexes)



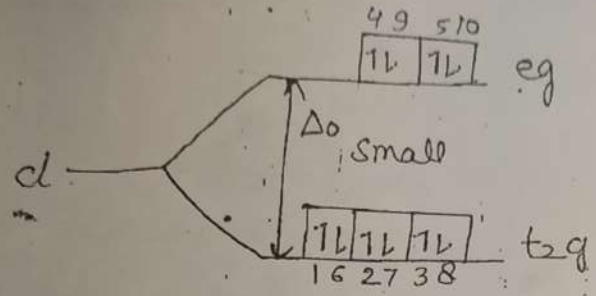
Low spin or spin
paired complexes

pairing of e⁻s
(strong field complexes)



Electron distribution in octahedral complexes ⇒

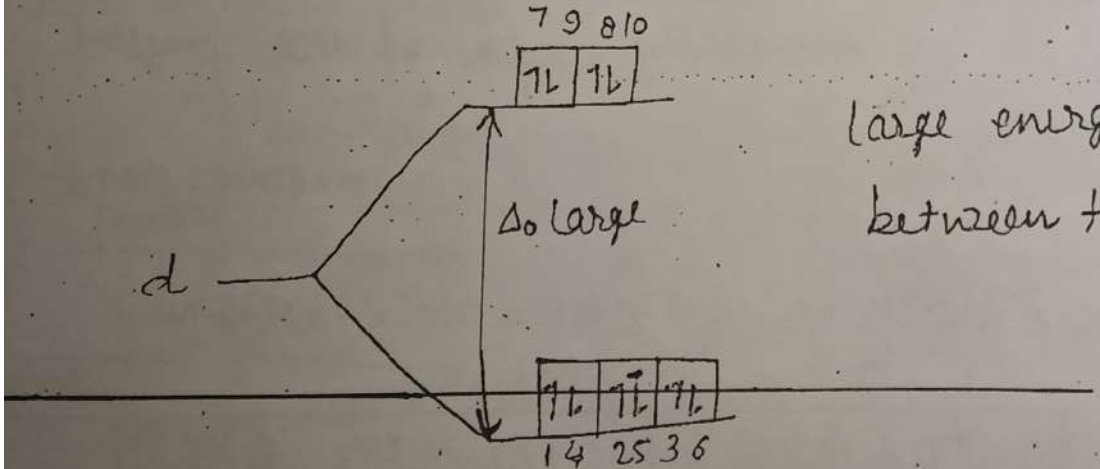
(1) weak ligand, or weak ligand complexes ⇒



energy of t_{2g} and eg comparable

$$d \longrightarrow t_{2g}^{1,2,3} \longrightarrow eg^{4,5} \longrightarrow t_{2g}^{6,7,8} \longrightarrow eg^{9,10}$$

(2) strong field or strong ligand complexes ⇒



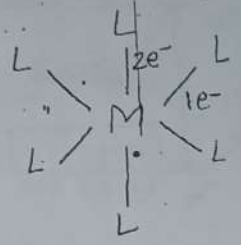
large energy difference between t_{2g} and eg

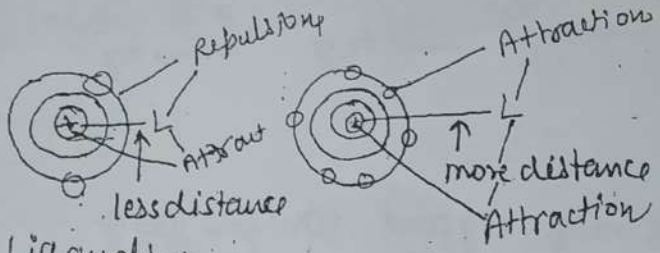
$$d \longrightarrow t_{2g}^{1,2,3,4,5,6} \longrightarrow eg^{7,8,9,10}$$

(c) No. of d-electrons ⇒

$$\Delta_o \propto \frac{1}{\text{d-electrons}}$$

$d^9 \rightarrow t_{2g}^6 \; eg^3$





(2) Nature of the Ligands ⇒

Spectrochemical series ⇒ Arrangement of ligands in the increasing order of their crystal field splitting power.

moderate strong ligand

weak end

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < OX < OH^- < H_2O < NCS^-$

weak ← → Strong

$< NH_3, py < en, pn, tn < bpy, phen < NO_2^- < CH_3^-, C_6H_5$

$< R_3P < CN^- < CO < NO$ strong end

Factors affecting magnitude of Δ ⇒

(a) Nature of metal:-

Oxidation state ⇒ Higher the oxidation state, more will be the magnitude of Δ.

eg. $[Co(NH_3)_6]^{3+}$ > $[Co(NH_3)_6]^{2+}$

Higher the oxidation state of metal → more it will attract ligand → more will be splitting

**

(b) Principle quantum number of d-orbitals ⇒

Δ_o increases by 30-50% on moving 3d to 4d and further increases by 30-50% on moving 4d to 5d series in a group.

Δ_o increase

3d ——(by 30-50%)——→ 4d ——(30-50%)——→ 5d

Co^{3+}

Rh^{3+} | Δ_o ↓

Ir^{3+}

On moving down in a group, the size of the element (cation here) increases, therefore shielding effect of nucleus decreases and ligand can approach more the cation, resulting in more splitting.

distance b/w dxy, dyz, dzx orbitals and the ligand $= \frac{a}{2}$

diagonal of face $= a\sqrt{2}$

distance b/w face dx^2y^2, dz^2 and ligand $= \frac{a\sqrt{2}}{2}$

$$\Delta t = \frac{4}{9}\Delta_o = 0.45\,\Delta_o$$

Reasons of low Δt in tetrahedral complexes than octahedral complexes ⇒

① No. of ligands are $\frac{2}{3}$rd of the octahedral complex.

$$6 \times \frac{2}{3} = 4$$

② In case of octahedral complexes the ligands dx^2-y^2 axis is present at approx. '0' distance to the ligand while in tetrahedral complexes, dx^2-y^2 do orbital is present at $\frac{a\sqrt{2}}{2}$ distance apart from ligand which is equivalent to $\frac{2}{3}$ as-

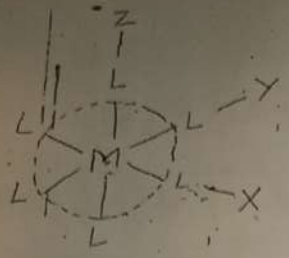
$$\frac{a\sqrt{2}}{2} = \frac{a \times 1.414}{2} = a \times 0.7 \simeq a \times \frac{2}{3}$$

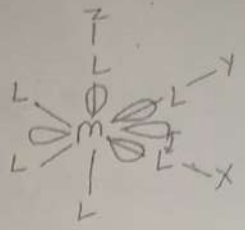
Therefore the overall decrease of energy of tetrahedral complexes as compared to octahedral complexes is-

$$\frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$$

↑ due to no. of ligand

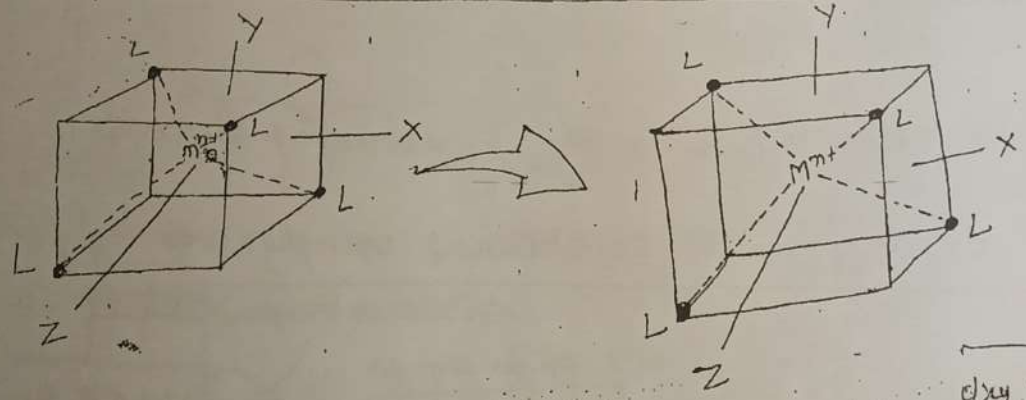
↑ due to distance of dx^2-y^2 orbital

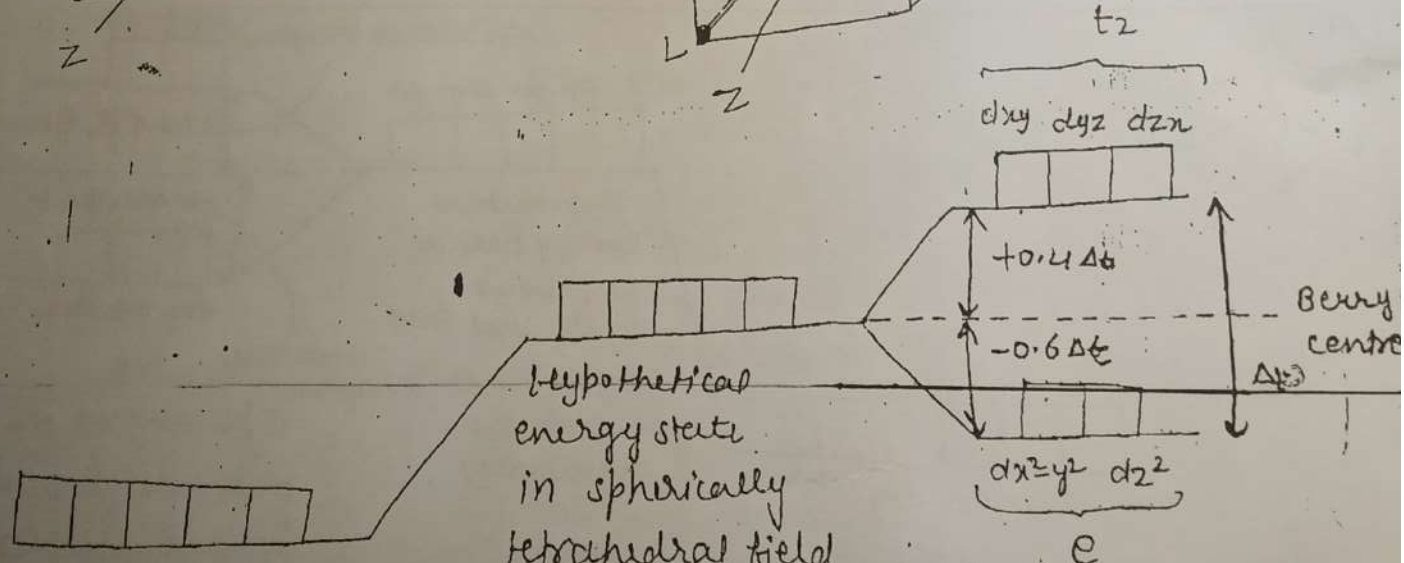




The separation of d-orbitals into 2 different energy levels called crystal field splitting and the separation of gap in ~~orbitals~~ is called crystal field stabilization energy.
energy states (t2g & eg)

Splitting of d-orbitals in tetrahedral complexes ⇒





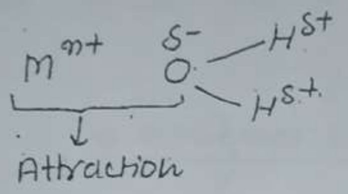
$$\Delta t \approx \frac{4}{9} \Delta_o$$

Postulates ⇒

(1) Ligands
- negative Ligands → Point changes (F^-, Cl^-)
- Neutral Ligands → Point dipoles or dipoles (NH_3, H_2O)

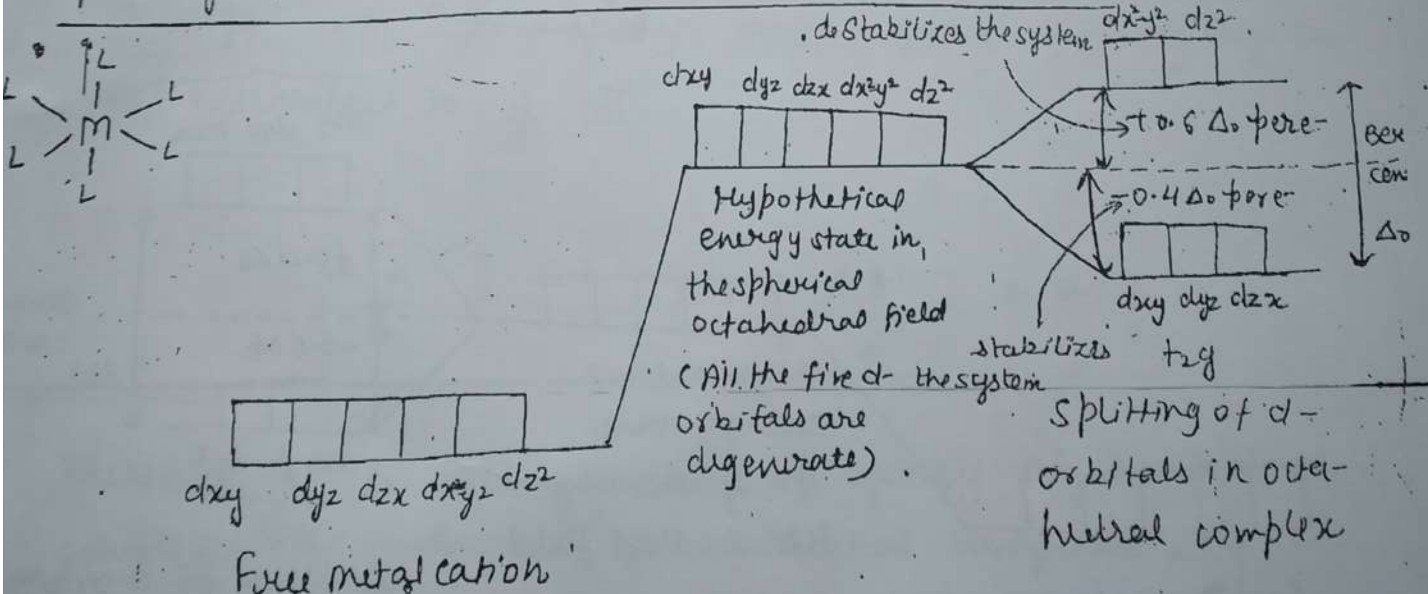
(2) Ionic bond b/w the metal cation & ligand. (No overlapping of orbitals)

(3) Negative end of the Ligands approaches the metal cation.

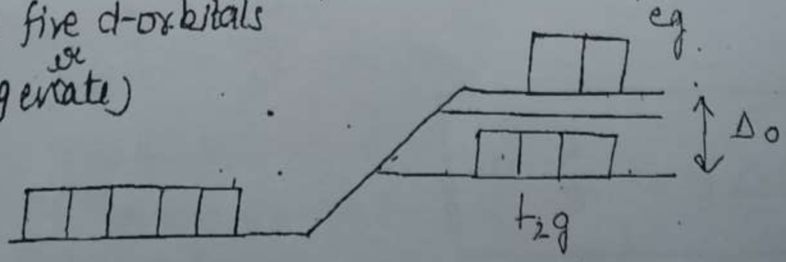


(4) Splitting of d-orbitals in the presence of ligands.

Splitting of d-orbitals in octahedral complexes ⇒



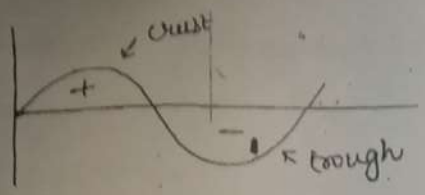
Splitting of d-orbitals in octahedral complex



$+0.6\,\Delta o$ or $6\,Dq$

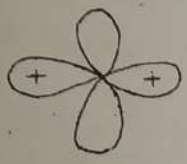
$-0.4\,\Delta o$ or $-4\,Dq$

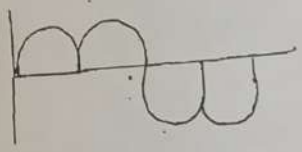
$\Delta o = 10\,Dq$



s —  — gerade

p —  — ungerade

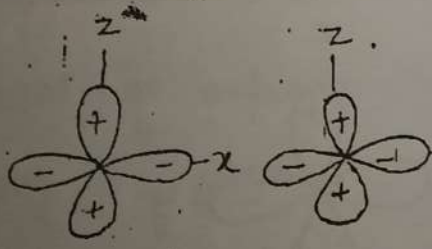
d —  — gerade

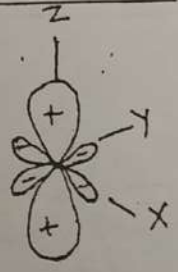


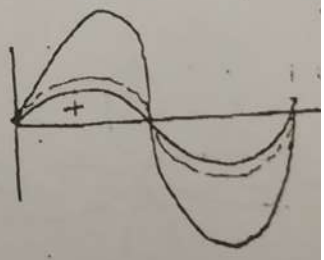
f → u

g → g

h → u







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

dependent

$d_{z^2-x^2-y^2} \equiv d_{z^2}$

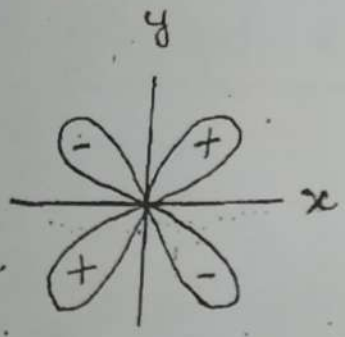
③ Crystal Field Theory (CFT)

⇒ Given by Bethe and van Vlack.

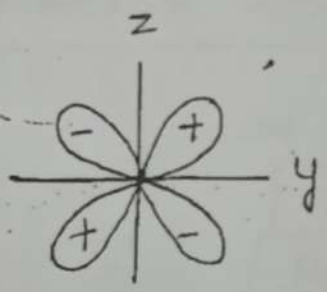
⇒ First applied for ionic crystal, therefore it is called as crystal field theory.

Shape of d-orbitals ⇒

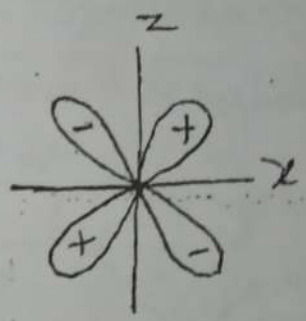
$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$



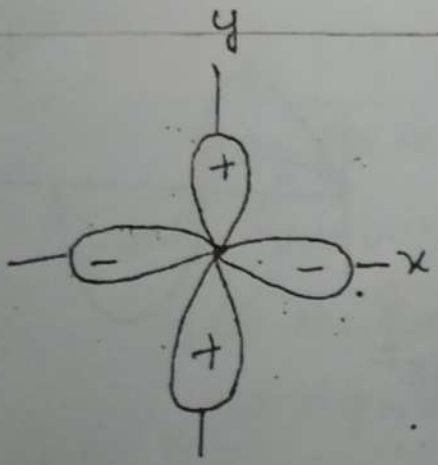
d_{xy}



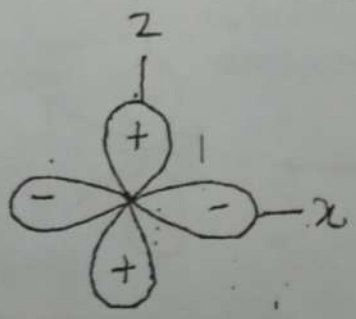
d_{yz}



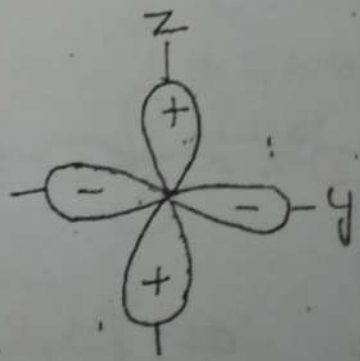
d_{zx}



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



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



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