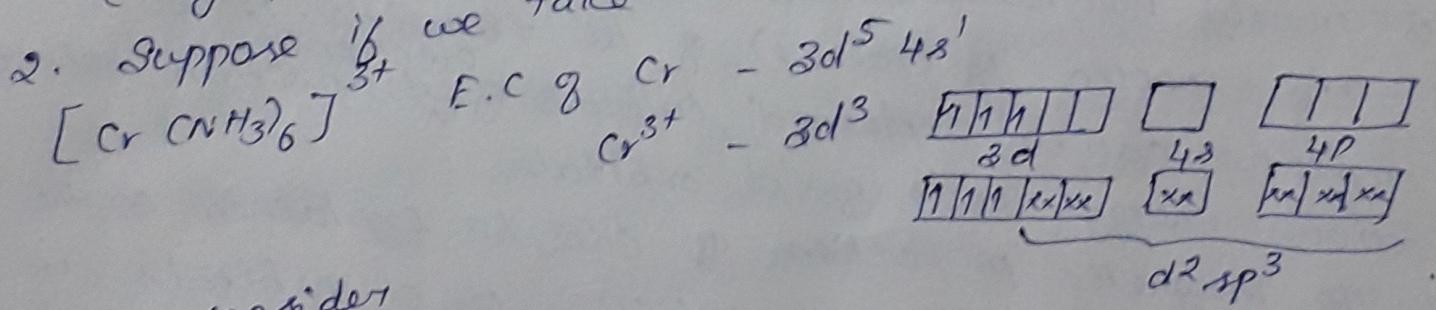


Acc. to this theory

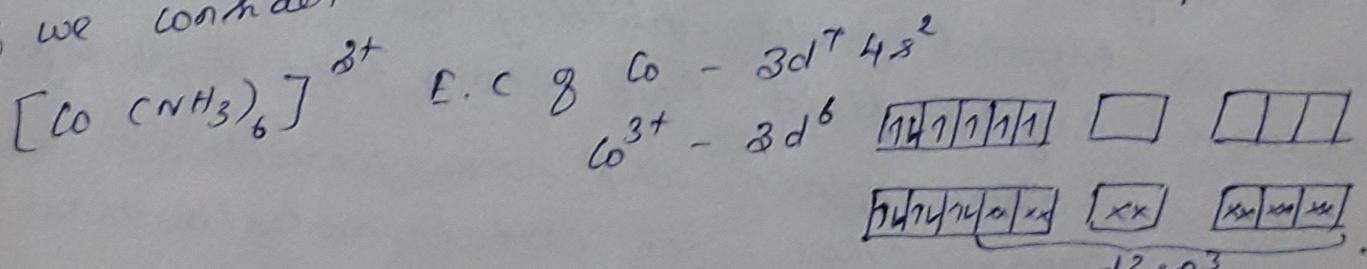
- 1) The central metal ion makes available a no. of empty orbitals for the formation of coordinate bonds.
- 2) Hence the no. of empty orbitals in the metal is the C.N.
- 3) These empty orbitals undergo hybridisation to give rise to new orbitals of equivalent energy before bonding with ligands.
- 4) When we consider ligands, each ligand must contain a lone pair of e⁻s.
- 5) The empty hybrid orbitals of metal overlap with filled orbitals of ligand and thus forms a co-ordinate bond.

Limitations:-

1. It could not explain paramagnetism & diamagnetism.
(mag. properties)
2. Suppose if we take



If we consider



This Co also forms d²s p³ or complex. Note, this theory could not explain why all e⁻s of Co are paired up and why is not so in the case of Cr.

3. It could not explain the interpretation of spectra of complexes. (colour?).
4. It does not take into consideration splitting of energy.

Crystal Field Theory :-

This theory is based on different assumption than VBT. In VBT the bonding between M & L are considered as pure covalent. But in CFT, it is based on the assumption that, the ligands act as point charges and there is no bond in between them. The interaction is purely electrostatic i.e 100% ionic.

Salient Features :-

1. The central metal ion is surrounded by ligands which contain lone pair of e⁻s.
2. All types of ligands whether they are ionic or molecular in nature are regarded as point charges. For neutral molecule the negative end of the dipole is oriented towards the central metal atom.
3. The attraction between the metal and the ligand is purely electrostatic i.e 100% ionic.
4. The spectra (colour) of the transition metal complexes can be explained in terms of electronic transition between various energy levels of d orbitals.
5. The magnetic properties can be explained on the basis of crystal field splitting of d orbitals in different crystal field (i.e strong field & weak field).
6. It can also explain why some geometries are favoured than other for certain metals. This is because of different CFSE.

d-orbitals into two sets.

Based on the orientation of the axes, five d-orbitals have been grouped into two sets of orbitals (dz^2 & $d_{x^2-y^2}$) having axes. They are also called axial set and to doubly degenerate set.

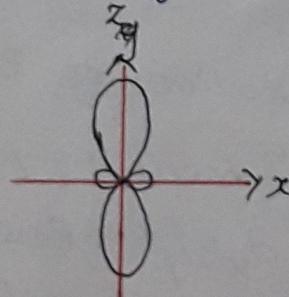
set of orbitals: (dxz , dyz) & between the axes. They are also called triply degenerate sets. The t_{2g} refers to

have the same energy i.e. they are degenerate (energy alike). However on the approach of ligands, the d 's will be repelled by the lone pair of ligands. The repulsion will raise the energy level of the d -orbitals. If all the ligands approaching the central ion are at equal distance ~~from~~ each of the energy of each orbital will increase by same amount. i.e. they will still remain degenerate but they have now higher energy than before. But, this is only a hypothetical situation.

The d orbitals differ in their orientation. The energy of the orbitals lying in the directions of the ligands is raised to a larger extent than that of the orbitals lying in between the ligands.

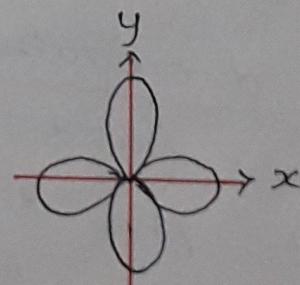
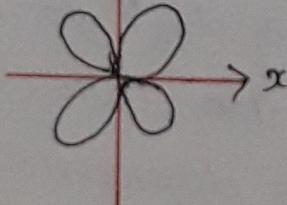
The conversion of five degenerate d -orbitals of the metal ion into two sets of orbitals having different energies is called crystal field splitting or energy level splitting. This concept forms the basis of crystal field splitting theory. Grouping of d -orbitals.

t_{2g} set

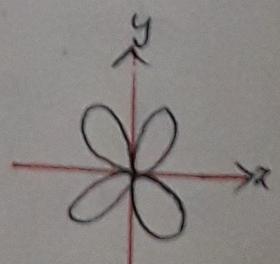
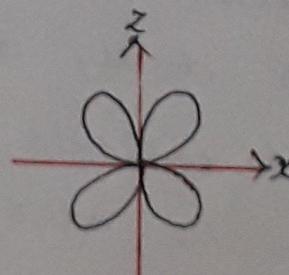


$3d_{z^2}$

t_{2g} set

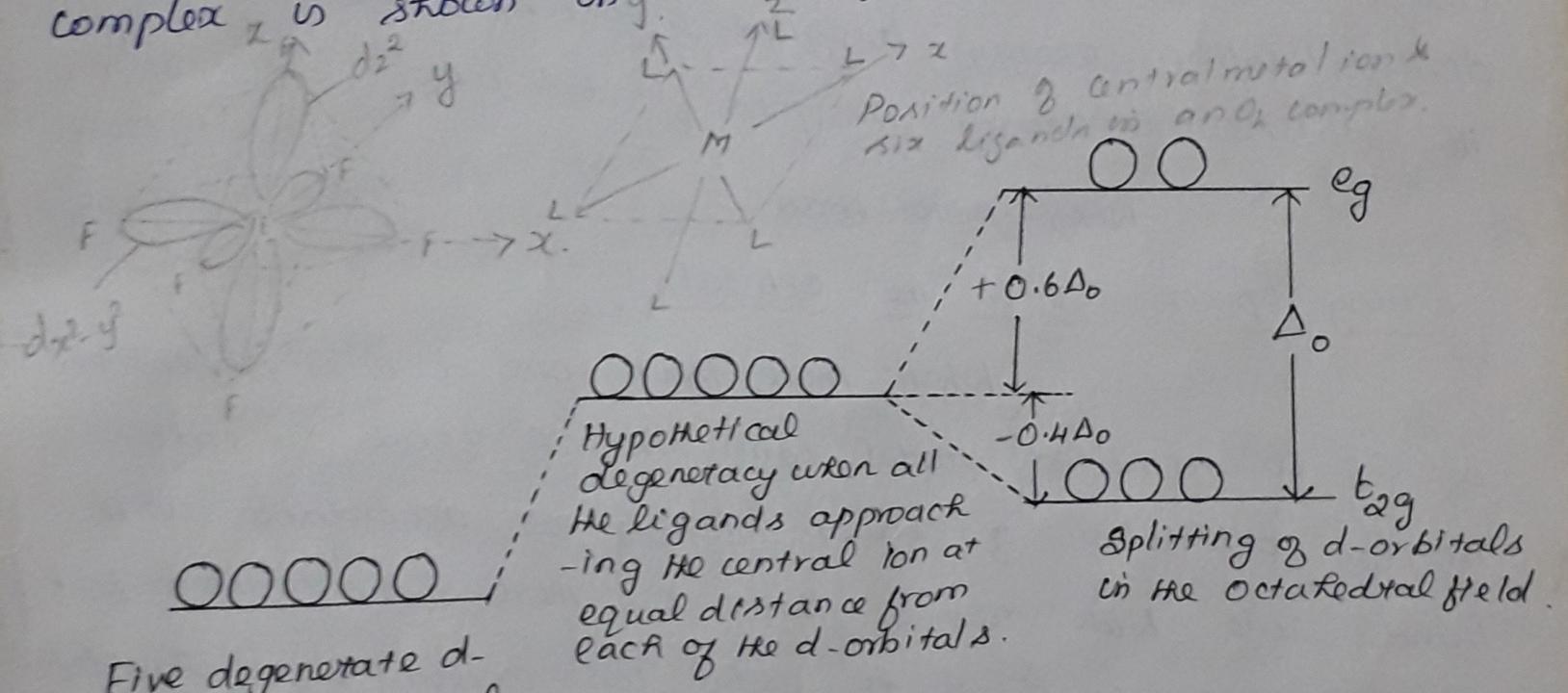


$d_{x^2-y^2}$



In an Octahedral complex, the central metal ion is at the centre and the ligands occupy the six corners of the octahedron.

In the case of octahedral complexes, as the two ligands approach along the axes, the two axial orbitals i.e. $d_{x^2-y^2}$ and d_{z^2} are repelled more than t_{2g} orbitals. In other words, the energy of e_g orbitals increases much more than the energy of t_{2g} orbitals. The phenomenon of crystal field splitting in octahedral complex is shown in the fig.



Five degenerate d-orbitals of free metal ion in the absence of ligand.

The energy difference between t_{2g} and e_g

orbital is denoted by Δ_0 (Δ_0 for O_8 complexes). In an octahedral complex, the energy of the t_{2g} orbital is ~~stabilised by $0.4\Delta_0$ less than~~ that of hypothetical degenerate d-orbitals and the energy of e_g orbital is ~~stabilised by $0.6\Delta_0$ above that of hypothetical degenerate~~ $0.6\Delta_0$ above that of hypothetical degenerate

If an O_6 complex contains one d^5 , that e^- will occupy one of the t_{2g} orbitals. This orbital has an energy -0.4 A.U. less than that of hypothetical degenerate orbitals predicted by pure electrostatic theory. Thus the complex is 0.4 A.U. more ~~less~~ stable than stated by pure electrostatic theory. Hence -0.4 A.U. is called CFSE of the complex, as CFSE. Greater the amount of CFSE of the complex, greater is its stability.

∴ for each e^- entering onto a t_{2g} orbital, the CFSE is -0.4 A.U. and each e^- entering into a e_g orbital, the destabilisation energy assigned is $+0.6 \text{ A.U.}$. In other words, the stabilisation energy assigned is $+0.6 \text{ A.U.}$.

When more than one d^5

Filling up of e^- s in the orbitals!

When more than one d^5 is present on a O_6 co-ordinated metal ion, the e^- s tend to enter the t_{2g} orbitals of lower energy in accordance with Hund's rule. With two or three e^- s there is no problem but when the no. of e^- s in the metal ion exceeds 3, it has two options.

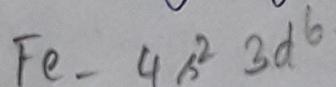
i) Either the e^- may pair up with the e^- s in t_{2g} orbitals.

ii) Or it may enter the higher e_g orbitals.
The filling up of e^- s path is dependent on the strength of ligand. In a strong ligand field, the Δ is large enough to force the e^- s to pair up and fill the t_{2g} d-orbitals. ~~BUT~~ Thus in presence of strong complexes are expected to be

The t_{2g} & e_g orbitals are not large enough to cause the electrons to pair up and hence the electrons enter into t_{2g} orbitals. Thus in presence of weak field they will be high spin complexes.

Ex:- $[\text{Fe}(\text{CH}_2\text{O})_6]^{4+}$ - weak ligand field - High spin complex.

$[\text{Fe}(\text{CN})_6]^{4-}$ - strong ligand field - Low spin complex.



Pairing energy:

The energy required to cause pairing of e^- s in the same orbital is called pairing energy and this energy depends on the type of ligand. It is denoted by the symbol P . If the e^- s prefer to pair up, then the complex will be spin paired or low spin. But when the crystal field splitting A_0 is not large, then the e^- s will remain unpaired. Such a complex will be high spin.

i. If $P > A_0$ i.e. pairing energy is $>$ the e^- s will remain unpaired and that will result in high spin complex.

If $P < A_0$ i.e. pairing energy will be less, the e^- s will be easily paired up and that will result in low spin complex.

[Note: A_0 is higher means the gap between t_{2g} & e_g will be more. In t_{2g} level itself all the e^- s will be paired first and then only they will go to e_g level]. [6 Dq for e_g & 4 Dq for t_{2g} level].

$$[A_0 = 10 Dq, \text{ i.e } 6 Dq \text{ for } e_g \text{ & } 4 Dq \text{ for } t_{2g} \text{ level}]$$

CFSE: The net gain in energy achieved by preferential filling up of stable t_{2g} orbitals and e_g is called CFSE.

Magnetic moment Δ_0 depends on the following factors.

1) Oxidn. state of the metal ion:

Higher the oxidn. state of central metal ion, higher will be the attraction for the ligand metal ion, which results in more crystal field splitting.

2) Higher the no. of d⁻s:

Higher the no. of d⁻s lesser will be the Δ_0 value. i.e. the energy difference between t_{2g} & e_g levels will be less. They occupy t_{2g} & e_g level.

$$\therefore \text{No. of d}^{\text{-}}\text{s} \propto \frac{1}{\Delta_0}$$

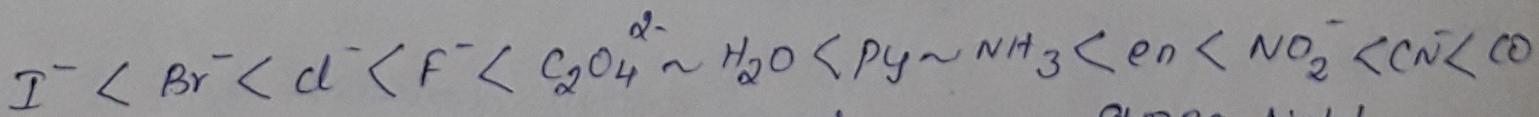
3) Stronger and weaker ligands:

For stronger ligands splitting will be more. Therefore Δ_0 value will be higher. (low spin)

For weaker ligand, pairing will be less & also the value of Δ_0 will be less. (lower splitting power). (high spin).

4) Spectrochemical series:

The common ligands are arranged in the order of their increasing splitting power to cause d-orbital splitting. This series is called spectrochemical series.



Weak field
(high spin)

$\xrightarrow{\text{Increasing CFSE}}$

Strong field
(low spin).

Strong ligands are those which exert a strong field on the central metal ion and hence they have higher splitting power. The weak ligands are those which exert a weak field on the central metal ion. For strong ligand Δ_0 is large.

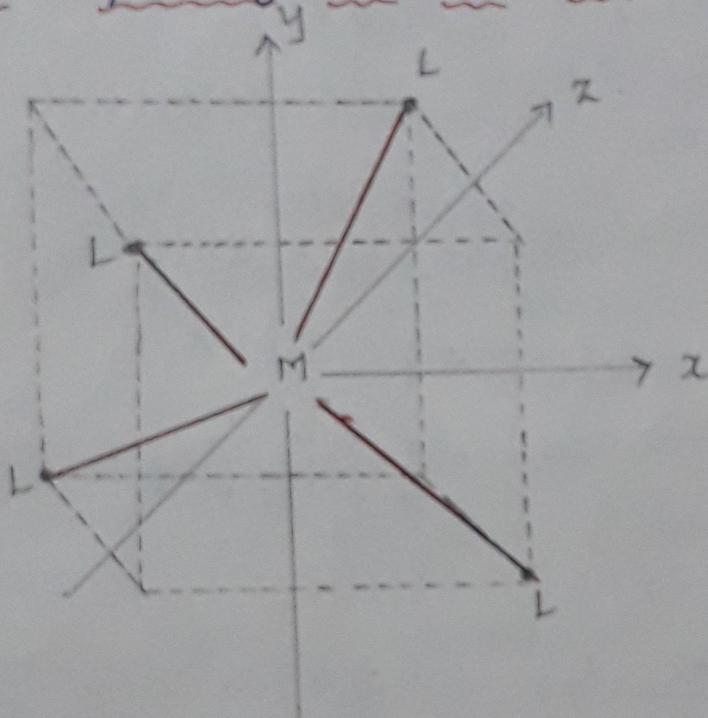
Value of one t_{2g} level = $-0.4 \Delta_0 - \frac{2}{5} \Delta_0$

Value of one e_g level = $+0.6 \Delta_0 + \frac{3}{5} \Delta_0$ Among 3 orbitals
 Δ_0 2 e_g orbitals
 energy is reduced.

d^1	\uparrow	$-\quad e_g$	-	
	<u>1</u>	$-t_{2g}$	$1 \times 0.4 \Delta_0$	$-0.4 \Delta_0$
d^2	<u>—</u>	$-\quad e_g$	-	$-0.8 \Delta_0$
	<u>1</u> <u>1</u>	$-t_{2g}$	$2 \times 0.4 \Delta_0$	
d^3	<u>—</u>	$-\quad e_g$	-	$-1.2 \Delta_0$
	<u>1</u> <u>1</u> <u>1</u>	$-t_{2g}$	$3 \times 0.4 \Delta_0$	
d^4	<u>1</u>	$-\quad e_g$		
(cor)	<u>1</u> <u>1</u> <u>1</u> <u>1</u>	t_{2g}	$3 \times 0.4 + (1 \times -0.6) \Delta_0$	$+0.6 \Delta_0$
For Pairing	<u>1V</u> <u>1</u> <u>1</u>	t_{2g}	$-1.2 + 0.6 \Delta_0$	$-1.6 \Delta_0 + 1P$
	<u>1</u> <u>1</u>	e_g	$2 \times (-0.6) \Delta_0$	
d^5	<u>1</u> <u>1</u> <u>1</u> <u>1</u>	t_{2g}	$3 \times -0.4 \Delta_0$	0
			$-(1.2 + 1.2) \Delta_0$	
(cor)	<u>—</u>	$-\quad e_g$	-	
d^5	<u>1V</u> <u>1V</u> <u>1</u>	t_{2g}	$5 \times -0.4 \Delta_0$	$-2 \Delta_0 + 2P$
	<u>1</u> <u>1</u>	e_g	$2 \times (-0.6) \Delta_0$	
d^6	<u>1V</u> <u>1</u> <u>1</u>	t_{2g}	$4 \times 0.4 \Delta_0$	$-0.4 \Delta_0$
			$-1.6 + 1.2$	
(cor)	<u>1V</u> <u>1V</u> <u>1V</u>	t_{2g}	$5 \times 0.4 \Delta_0$	$-2.4 \Delta_0 + 3P$
	<u>1</u>	$-\quad e_g$	$1 \times (+0.6) = +0.6 \Delta_0$	
d^7	<u>1V</u> <u>1V</u> <u>1V</u>	t_{2g}	$6 \times 0.4 = 2.4 \Delta_0$	$1.8 \Delta_0 + 3P$
	<u>1</u> <u>1</u>	e_g	$2 \times 0.6 = -1.2 \Delta_0$	
(cor)	<u>1V</u> <u>1V</u> <u>1</u>	t_{2g}	$5 \times 0.4 = 2 \Delta_0$	$0.8 \Delta_0$

$$\begin{array}{lll}
 d^8 & & \\
 \text{1L} & \text{1L} & \text{1L} \quad t_{2g} \quad 6 \times 0.4 = 2.4 \text{d}_{\circ} + 39 & \text{1.02} \\
 & & 3 \times (-0.6) = 1.8 \text{d}_{\circ} & \text{value} \\
 \text{1L} & \text{1L} & \text{1L} \quad e_g \quad 0.6 \text{d}_{\circ} \\
 \text{1L} & \text{1L} & \text{1L} \quad t_{2g} \quad 6 \times 0.4 = 2.4 \text{d}_{\circ} + 49 & 0.6 \text{d}_{\circ} \\
 \text{1L} & \text{1L} & \text{1L} \quad e_g \quad 4 \times (-0.6) = 2.4 \text{d}_{\circ} - 15 & \text{to comp} \\
 \text{1L} & \text{1L} & \text{1L} \quad t_{2g} \quad 6 \times 0.4 = 2.4 \text{d}_{\circ} & 200 \\
 & & & 0 \text{d}_{\circ} \\
 \end{array}$$

Crystal Field splitting in t_{d} complexes:-



The coordination no. for t_{d} complex is 4 and the 4 ligands are arranged around the central metal atom at alternate corners of the cube. Here the 4 ligands are situated in a manner that they lie in between the three axes x, y, z . It means that the three t_{2g} orbitals of the metal ion will be in the direction of ligands where the lobes of e_g orbitals will be pointing away from the axes. \therefore The t_{2g} orbitals will be raised in energy than e_g orbitals (lower energy), and hence the degeneracy of the five d-orbitals will be removed.

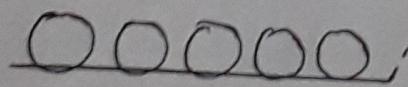
where t stands for t_{1d} and it is estimated that,

value of $\Delta_t \approx -4/9$ t , i.e. Δ_t is always less than t .

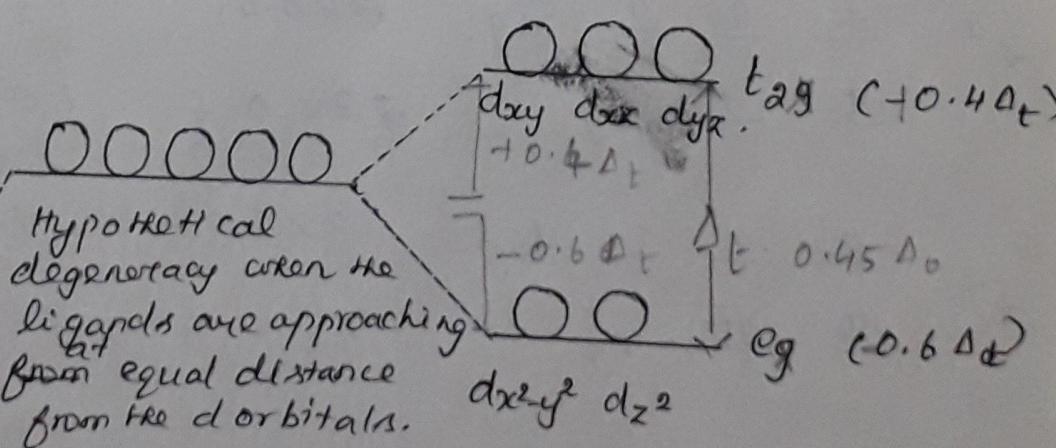
The sign denotes that the order of splitting in T_d complexes is just reverse that of O_h complexes. The reason for the smaller value of Δ_t is partly due to lesser no. of ligands in T_d field.

Here an e^- entering into t_{1g} level will be stabilized by $-0.6 \Delta_t$ and an e^- entering into t_{2g} level will be destabilized by $+0.4 \Delta_t$.

Since the magnitude of ~~ext~~ crystal field splitting in T_d field (Δ_t) is small and is always less than pairing energy i.e. $\Delta_t < P$, \therefore only high spin T_d complexes are formed although low spin complexes are theoretically possible in some config.



Five degenerate d orbitals of a free metal ion.



Splitting of d orbitals in T_d field.

For T_d complex t_2 instead of $t_{1g} \times 0$ instead of t_{1g}

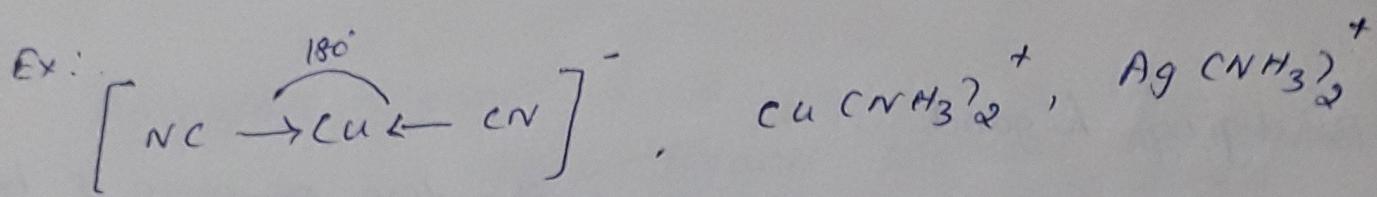
as there is no centre of symmetry, b/c the ligands are

d^1	$\underline{1}$	$\underline{\underline{1}}$	t_{eg}	$1 \times 0.6 \Delta t$	$-0.6 \Delta t$
d^2	$\underline{1}$	$\underline{1}$	t_{eg}	2×0.6	$-1.2 \Delta t$
d^3	$\underline{1}$	$\underline{1}$	t_{eg}	$1 \times (-0.6)$	-0.4
	$\underline{1}$	$\underline{1}$	t_{eg}	2×0.6	-1.2
d^4	$\underline{1}$	$\underline{1}$	t_{eg}	$2 \times (-0.4)$	-0.8
	$\underline{1}$	$\underline{1}$	t_{eg}	2×0.6	1.2
d^5	$\underline{1}$	$\underline{1}$	t_{eg}	$3 \times (-0.4)$	-1.2
	$\underline{1}$	$\underline{1}$	t_{eg}	2×0.6	1.2
d^6	$\underline{1}$	$\underline{1}$	t_{eg}	$3 \times (-0.4)$	-1.2
	$\underline{1}$	$\underline{1}$	t_{eg}	2×0.6	1.2
d^7	$\underline{1}$	$\underline{1}$	t_{eg}	$3 \times (-0.4)$	-1.2
	$\underline{1}$	$\underline{1}$	t_{eg}	4×0.6	2.4
d^8	$\underline{1}$	$\underline{1}$	t_{eg}	$4 \times (-0.4)$	-1.6
	$\underline{1}$	$\underline{1}$	t_{eg}	4×0.6	2.4
d^9	$\underline{1}$	$\underline{1}$	t_{eg}	$5 \times (-0.4)$	-2.0

Co-ordination no.: and stereochemistry of complexes

1. Co-ordination no.: 2 :

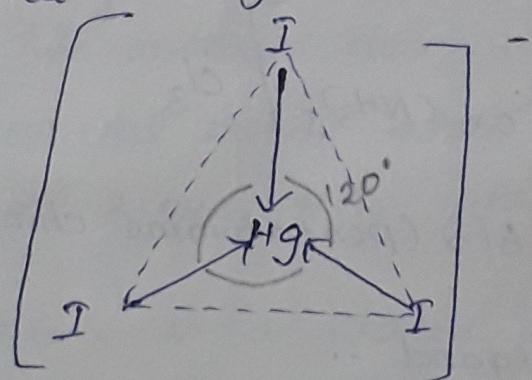
The complexes having C.N. = 2 are linear and show minimum ligand-ligand repulsion.



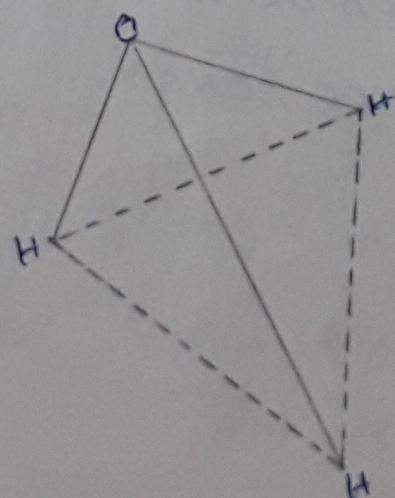
2. Co-ordination no.: 3 :

The complexes having C.N. = 3, show two possible geometries.

i) Equilateral triangle. Ex: $[\text{HgI}_3]^-$



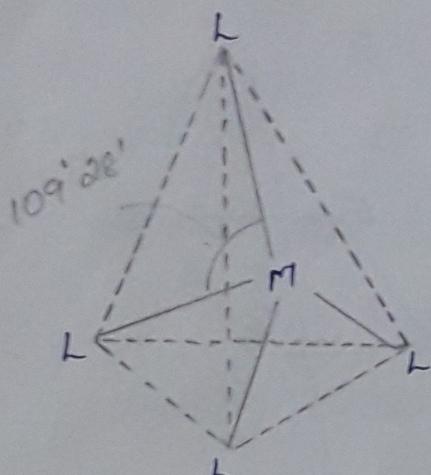
ii) Trigonal pyramidal. H_3O^+ .



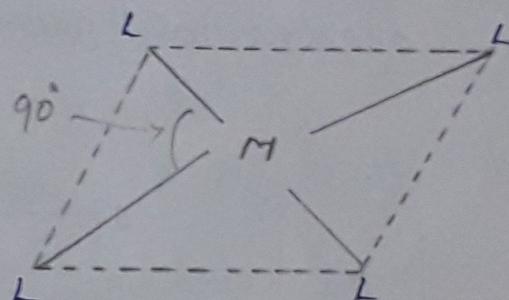
Complexes with $C.N = 4$ may be T_d or square planar in geometry.

Ex:- T_d geometry - $ZnCl_4^{2-}$, $Cu(CN)_4^{2-}$, $Ni(CO)_4^0$.

Sq. planar " - $[Cu(CN)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$.



T_d .



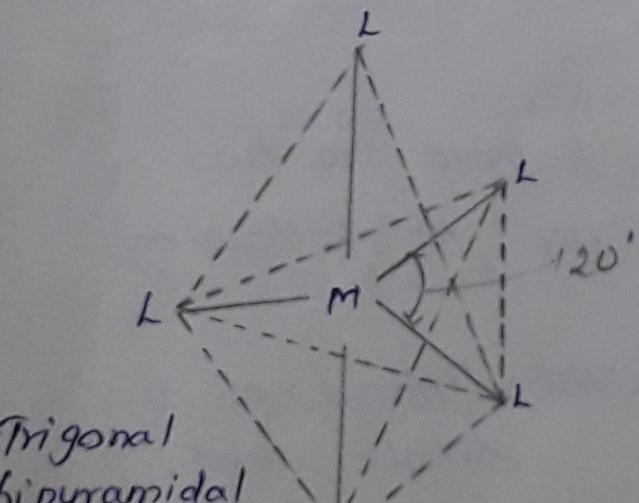
Sq. planar.

4. Co-ordination number 5:

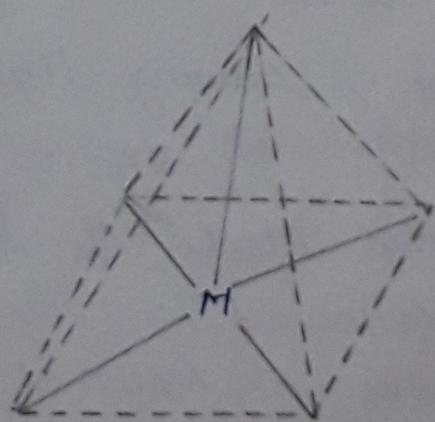
Complexes with $C.N = 5$ may be trigonal bipyramidal or square pyramidal.

Trigonal bi-pyramidal - $Fe(CO)_5$, $CuCl_5^{3-}$, $SnCl_5^-$

Square pyramidal - $[NiBr_3(C_2H_5)_3P_2]$



Trigonal bipyramidal



Square pyramidal