

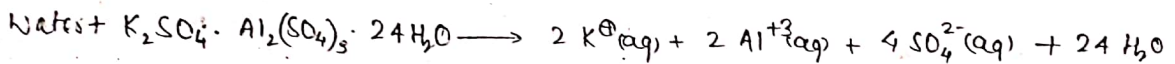
## Co-ordination Chemistry

no. of elements	hybrids	no. of	L. stability
5	sp <sup>3</sup>	108	most stable
6	sp <sup>3</sup>	120	most stable

### Important terms

Double Salt :- Such type of salts which gives the test of all their constituent

- ① S.P.d.f Block element
- ② Fe, Cu, Pb, Zn, Al ions in aqueous solution are called double salts. These exist as sub
- ③ Coordination chemist. in crystalline state e.g. aq. solution of potash alum gives chemical
- ④ sandwich comp. tests of K<sup>+</sup>, Al<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> ions
- ⑤ metal carbonyl.



- ⑥ metal cluster
- ⑦ Rare gas compd.
- ⑧ non stoichiometric oxides
- ⑨ Radioactivity

Co-ordination compounds :- such type of compounds which don't give the chemical test of all the constituent ions in aq. solutions are considered as co-ordination compound. These are also called complex compounds. A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and a complex anion.

Examples →  $\text{K}_4[\text{Fe}(\text{CN})_6]$  → It's aq. sol<sup>n</sup> do not give chemical tests of free CN ion, but give the test of presence of K<sup>+</sup> ion.

↓  
Test show.  $\text{Fe}^{3+}$

non-covalent ligand (anion)  
 complex ion - etc.  
 a<sup>-</sup> chloride  
 complex ion -  
 $SO_3^{2-}$  sulphite  
 $SO_4^{2-}$  sulphate  
 etc. High oxidation state  
 High electronegativity  
 etc. di, tri, tetra, etc.  
 etc.  
 etc.  
 etc.

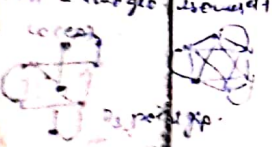
Ligand :- Such electron rich species which can make co-ordination bond(s) with metal atom or ion in a complex compound are called ligands. A ligand may be neutral, anionic or positively charged species. But presence of a pair of electrons must, on ligand.

Neutral Ligands  $\rightarrow H_2O, NH_3, \text{Pyridine}, \text{Benzene}, \text{ethylenediamine}$  etc.  
Anionic ligands  $\rightarrow CN^-, F^-, SO_4^{2-}, BH_4^-,$  etc.  
Cationic ligands  $\rightarrow NH_3^+, N_2^+$  etc.

Co-ordination no. :- The total no. of co-ordination bonds through which a metal atom/ion is bonded with ligands in a complex species are called co-ordin. no.

Co-ordination sphere :- The central metal ion and the ligands which are directly joined to it, are enclosed in a square bracket. this enclosed system is called co-ord. sphere.

Ambidentate ligands :- The ligands which have two or more donor atoms, but forming complexes only one donor atom is attached to the metal ion at a given time, are called ambidentate ligands.



Some examples → ①  $\ominus \text{C} - \text{NO} \neq \text{NO}_2$  ②  $\ominus \text{CN} \neq \ominus \text{NC}$  ③  $\text{NCs}^\ominus \neq \text{SCN}^\ominus$   
 ④ Thiosulphato-S & thiosulphato-O

Classification of ligands denticity or teeth :- No of electro negative atoms (N, O, F), OR No of free lone pairs OR No of anion -ve charge

① Monodentate ligands :- These ligands makes only one co-ord. bond with metal atom/ion. e.g.  $\text{H}_2\text{O}$ ,  $\text{CN}^\ominus$ ,  $\text{NH}_3$ ,  $\text{F}^\ominus$ ,  $\text{CO}$ ,  $\text{NH}_2 - \overset{\oplus}{\text{N}}\text{H}_2$ ,  $\text{NO}^\oplus$

② Bidentate ligands :- Each of such ligand always makes two co-ordination bonds with complex metal atom/ion in a complex comp.  
 Examples → Ethylene diamine (en), Oxalate ion, Glycinate ion etc.

③ Polydentate ligands :-

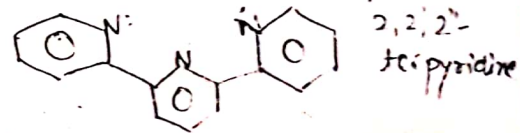
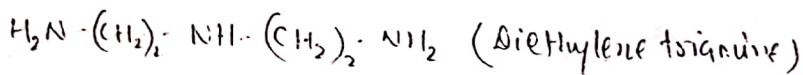
④ Tridentate ligands → 2,2',2''-terpyridine, Diethylene triamine etc

⑤ Tetradentate ligands → Triethylene tetraamine,  $\text{H}_2\text{EDTA}$  etc.

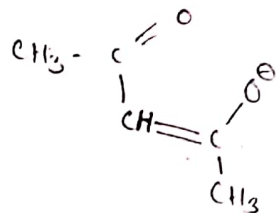
⑥ Pentadentate ligands → Ethylene diamine triacetate

⑦ Hexadentate ligand → Ethylene diamine tetraacetate.

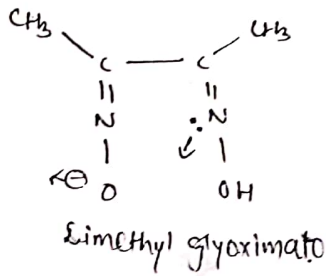
Structures of some ligands



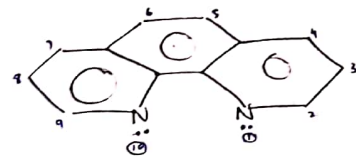




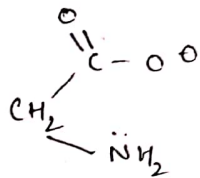
Acetylacetonate



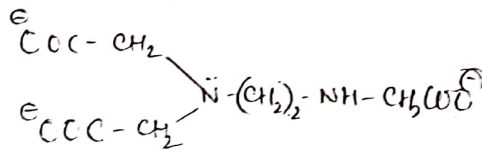
Dimethyl glyoximate



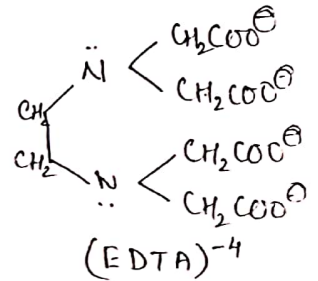
1,10-phenanthroline



Glycinato



Ethylene diamine triacetate

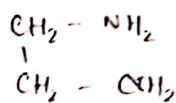


(EDTA)<sup>-4</sup>

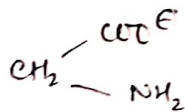
Chelation ! → One or more ring containing complexes which

are formed by polydentate ligands are called complex chelates.

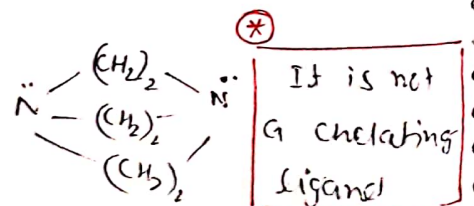
The formation of such rings is called chelation. Structure of the ligand should permit the two or more attachment points necessary for one metal atom/ion. e.g



Chelating ligand



Chelating ligand



\*  
It is not a chelating ligand

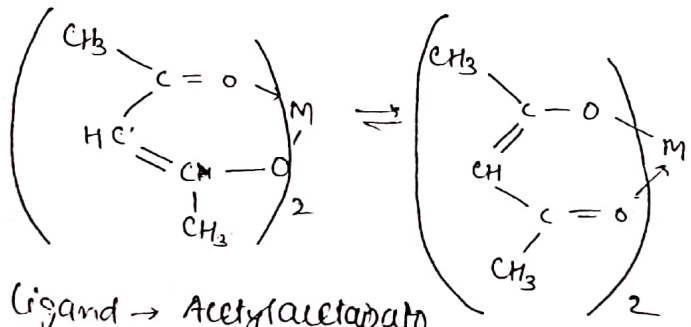
चित्रीत नसल्यामुळे हे चित्रीत

D. delocalisation of  $\pi e^-$   
 E - energy used in forming chelate bond  
 S - strain is very less.

Generally chelates are more stable than open chain complexes due to  $\rightarrow$ 

1. Reduced strain
2. delocalisation of  $\pi$ -es in chelate ring
3. more energy is required to break the two co-ordination bonds simultaneously

Example  $\rightarrow$



The enhanced stability of complexes containing chelated ligands is called chelate effect.

chelating ligand  $\rightarrow$  Acetylacetonate

**Kesner's theory of Co-ordination compounds**

He holds his PhD on this topic and has a Nobel on the same sub-topic.

Primary valency: - anion satisfied, No of oxidation state  
 Secondary: - non ionic, or non-ionic valency - satisfied - anion or neutral ligand.

Two types of valencies are shown by metal atom/ion in complexes.

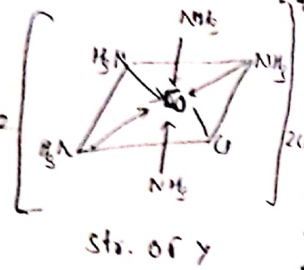
- Primary valency  $\rightarrow$  It is always satisfied by anions. It corresponds to oxidation state of the metal ion. It is also called ionic valency.
- Secondary valency: It is non ionic or non-ionic. It is either satisfied

14.1

anion or neutral ligand. These are shown by thick lines

Kerner has work done on complexes of Co(III) with ammonia

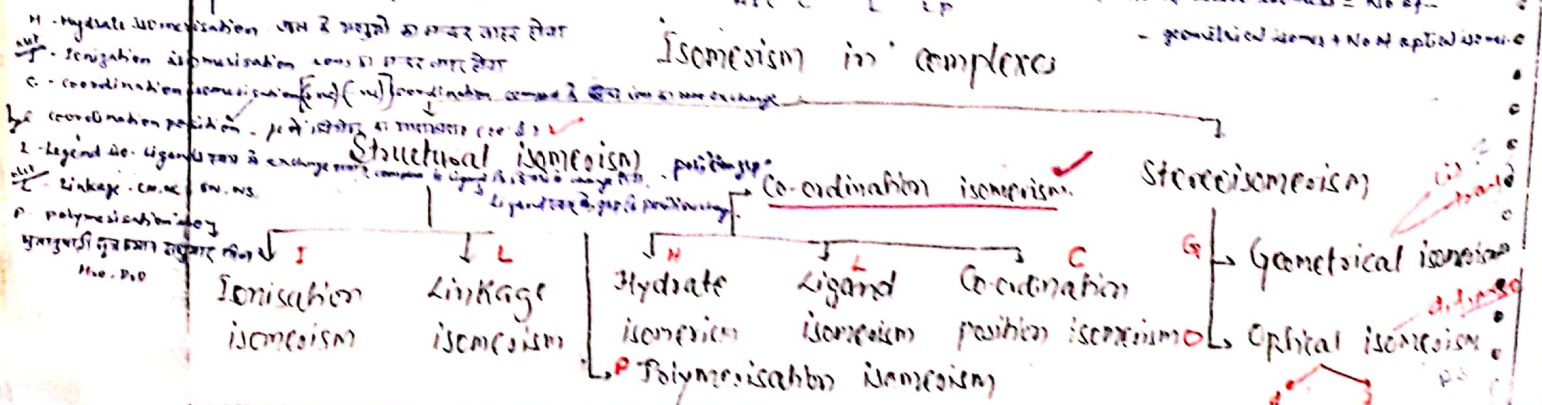
- (A)  $CoCl_3 \cdot 6NH_3 + 3AgNO_3 \rightarrow 3AgCl + [Co(NH_3)_6](NO_3)_3$
- (B)  $CoCl_3 \cdot 5NH_3 + 2AgNO_3 \rightarrow 2AgCl + [Co(NH_3)_5Cl](NO_3)_2$
- (C)  $CoCl_3 \cdot 4NH_3 + AgNO_3 \rightarrow AgCl + [Co(NH_3)_4Cl_2]NO_3$
- (D)  $CoCl_3 \cdot 3NH_3 + AgNO_3 \rightarrow \text{No reaction}$



Starting comp. of Co(III) in reactions (A), (B), (C) & (D) shows 4, 3, 2, 1 no. of particles in the aq. solution which is measured by elevation

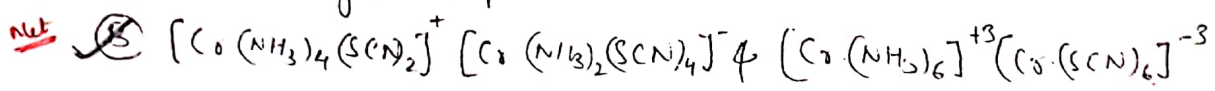
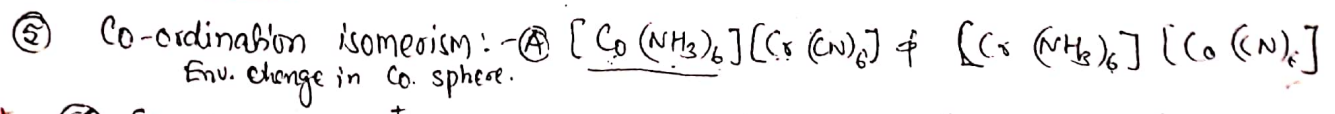
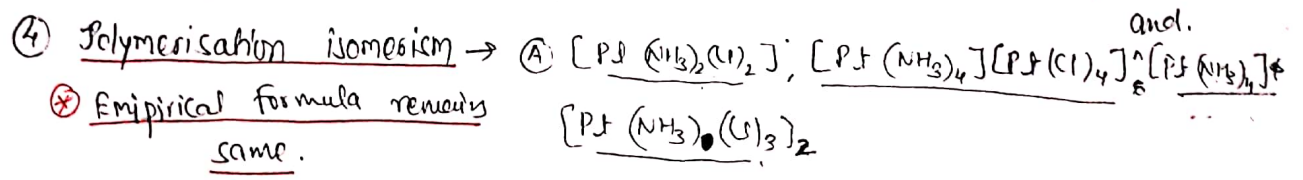
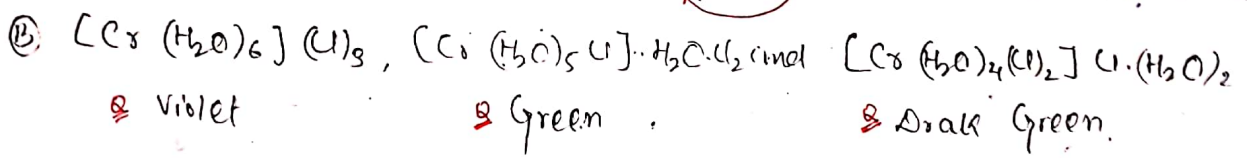
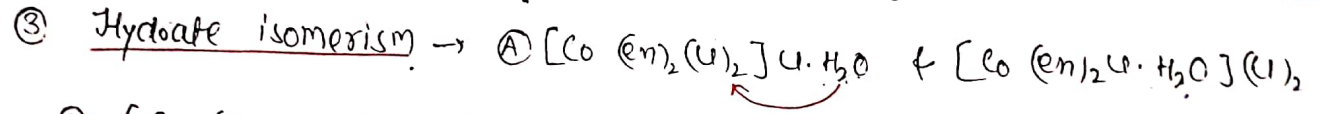
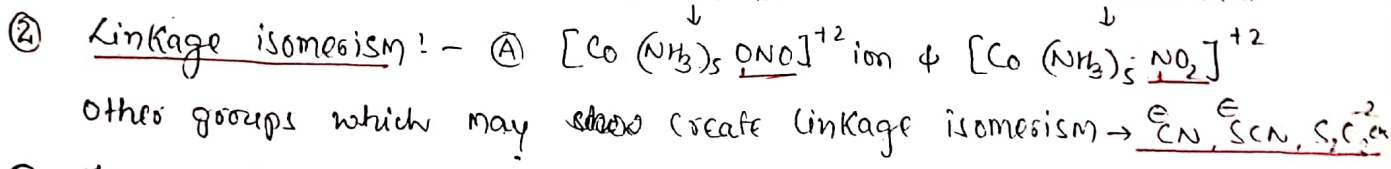
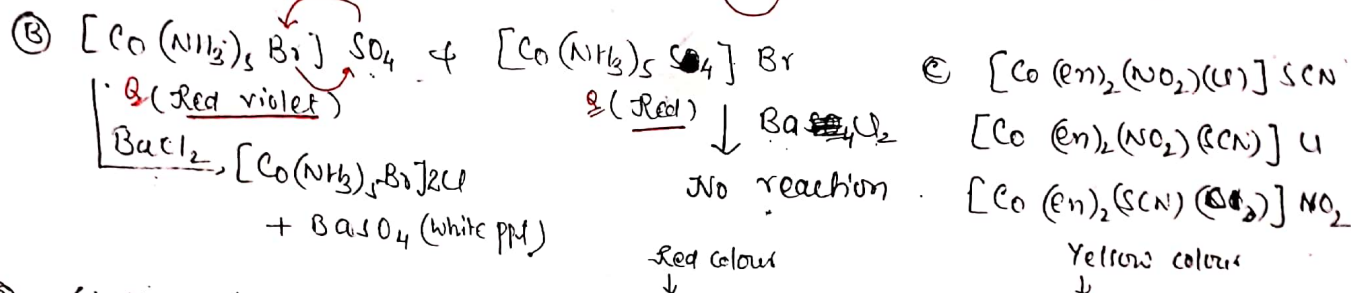
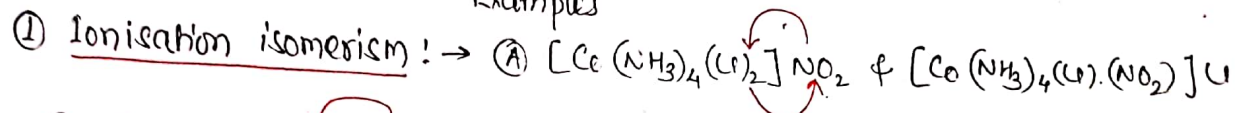
no. of particles in the aq. solution which is measured by elevation in b.p. method

Isomerism in complexes



most have not superimposable mirror image & absent of all axes of symmetry

Examples



\* axis of symmetry having compd. may be optically active or may not be chiral.  
 or chiral

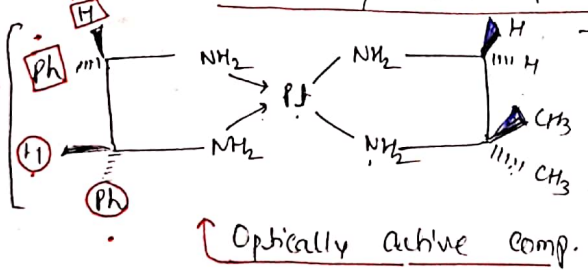






Stereoisomerism in square planar complexes → These complexes only show geometrical isomerism. Optical isomerism is not shown by these complexes due to presence of mirror plane except following exception

4 3 (1) 2 PH SO.  
Not mirror of mirror plane.  
(1) (2)  
(PH)



Mills & Quibell forms this comp.  
due to its mirror image not super imposable  
\* absence of plane of symmetry  
\* to make geometrical isomers these should think only about positions possibilities of minimum no. ligand present.

Possible geometrical square planar complexes → 2-2 different ligand

(A)  $[MA_4]^{n\pm}$ ,  $[MA_3B]^{n\pm}$  and  $[MAB_3]^{n\pm}$  → do not show geom. isomerism.

(B)  $[MA_2B_2]^{n\pm}$  → Two geom. isomers  
 cis-isomer:  $\begin{bmatrix} A & B \\ A & B \end{bmatrix}^{n\pm}$  (IR active)  
 trans-isomer:  $\begin{bmatrix} A & B \\ B & A \end{bmatrix}^{n\pm}$  (IR inactive)

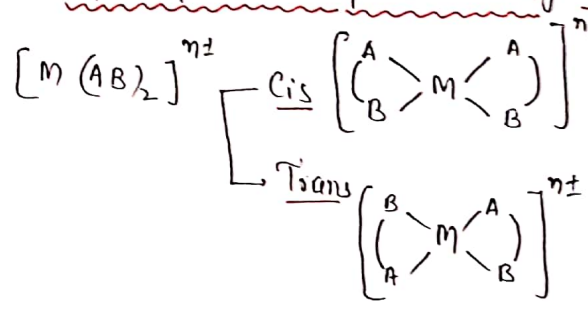
(C)  $[MA_2BC]^{n\pm}$  → Two geom. isomers  
 cis-isomer:  $\begin{bmatrix} A & B \\ A & C \end{bmatrix}^{n\pm}$   
 trans-isomer:  $\begin{bmatrix} B & A \\ A & C \end{bmatrix}^{n\pm}$

(D)  $[M(ABCD)]^{n\pm}$  → e.g.  $[Pt(NH_3)(Py)(Br)(Cl)]$   
 Three isomers are possible  
 cis-isomer:  $\begin{bmatrix} A & B \\ D & C \end{bmatrix}^{n\pm}$   
 trans-isomer:  $\begin{bmatrix} A & C \\ D & B \end{bmatrix}^{n\pm}$   
 All of these will be IR active

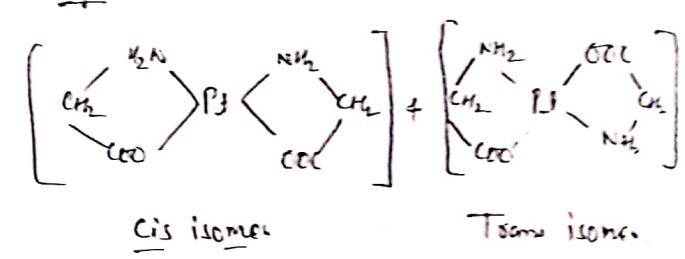
(1) BC only by 90° (2) DC by 90°

180° are same group - trans.  
 90° are same group - cis

⑤ Square planar complexes having unsym. bidentate ligand → Two geom. isomers



Example

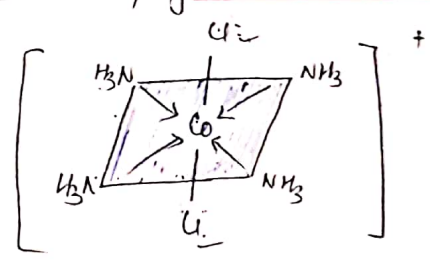


Stereoisomerism in octahedral complexes

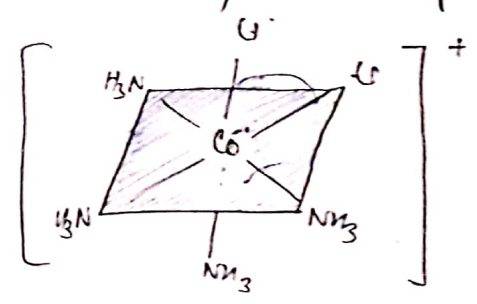
①  $[MA_6]^{n\pm}$  &  $[MA_5B]^{n\pm}$  → Neither show geom. isomerism nor optical isomerism

②  $[MA_4B_2]^{n\pm}$  → Only geometrical isomerism is shown by these complexes.

Example



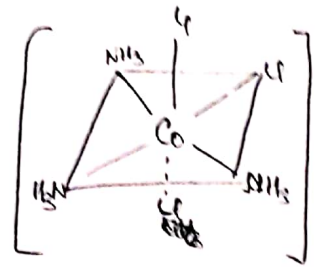
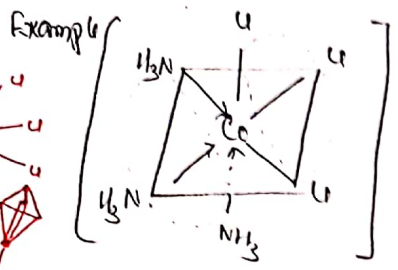
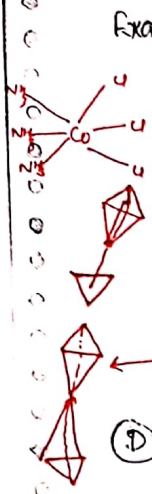
Trans (or) 1,6-isomer



Cis (or) 1,2-isomer

Both isomers are optically inactive due to plane of symmetry

6.1  
 ©  $[MA_3B_3]^{±n}$  type complexes → These complexes show only geometrical isomerism

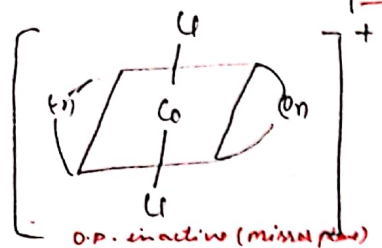


Both isomers are optically inactive due to plane of symmetry  
 e.g. →  $C_{2v}$

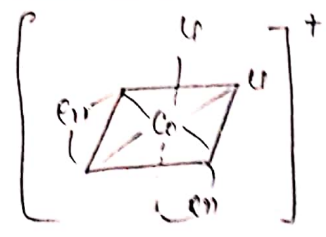
Cis or 1,2,3-isomer ( $P_6 \rightarrow C_{3v}$ ) Trans-isomer (1,2,6-isomer)

Facial isomer (Fac-isomer) Meridional isomer

©  $[M(AA)_2X_2]^{±n}$  type complexes → These complexes show geometrical isomerism as well as optical isomerism.



Trans isomer



Cis isomer (o.p. active)

Cis isomer can exhibit enantiomerism.

So that possible stereoisomers for  $[M(AA)_2X_2]^{±n} = \text{Three}$

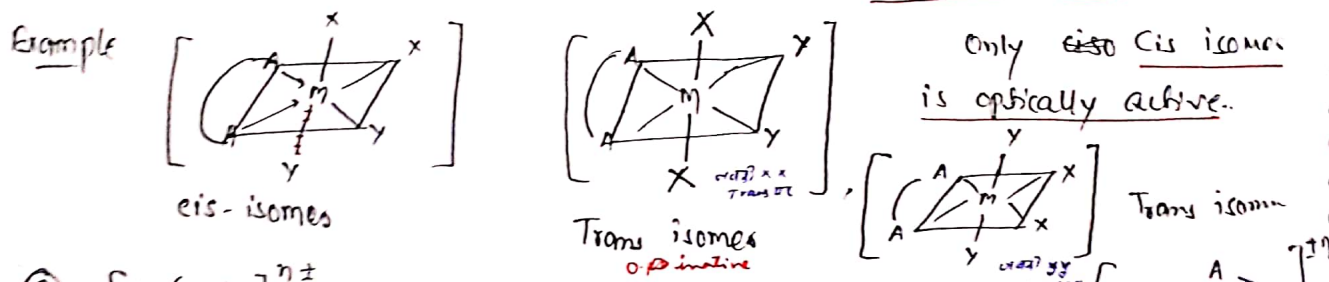
o.ganic except cis o.p. inactive  
 biogan central atom o.p. inactive

©  $[M(AA)_2XY]^{±n}$  → Shows geometrical as well as optical isomerism  
 Possible stereoisomers = Three (Cis-isomer is optically active - same as above)

\* bidentate or chelating ligand must add at two neighbouring sites & bidentate ligand must not trans position in octahedron



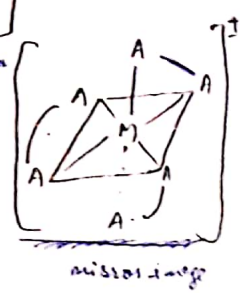
(F)  $[M(AA)_2X_2Y_2]^{\pm n}$  type complexes  $\rightarrow$  It shows geometrical as well as optical isomerism. Possible stereoisomers for this  $\rightarrow$  Three + 1 = four



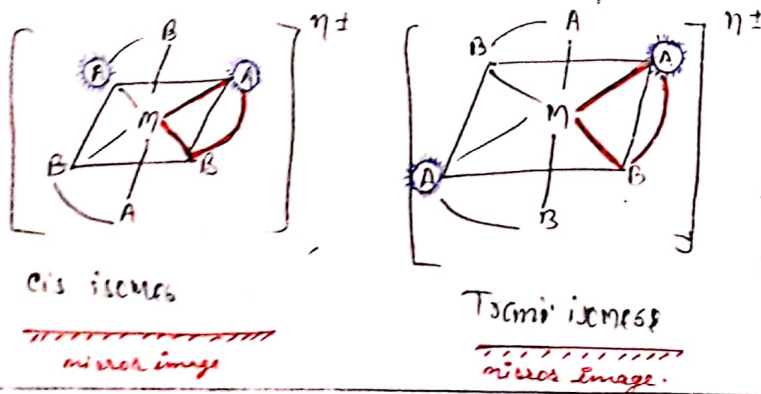
(G)  $[M(AA)_3]^{\pm n}$  type complexes  $\rightarrow$  Shows only optical isomerism

Possible optical isomers = Two  $\rightarrow$  enantiomers.

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



(H)  $[M(AA)_2B_2]^{\pm n}$  type complexes  $\rightarrow$  These exhibit both type of isomerism



Since both isomers are optically active, so that four stereoisomers are possible for such complexes.

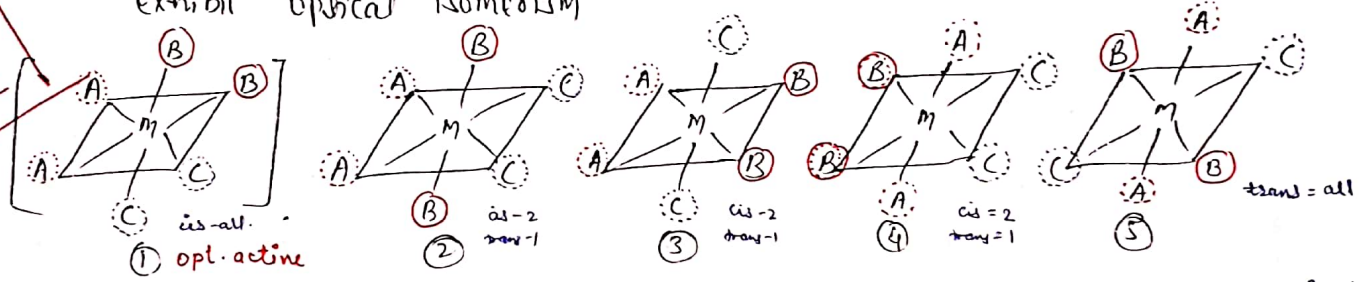
MABF  
for

(I)  $[M(ABCDEF)]^{\pm n}$  type complexes  $\rightarrow$  Possible geometrical isomers = 15

Since each isomer is optically active, so that 30 optical isomers are possible for such a complex. Total = 15 geo + 30 op = 45

(J)  $[MA_2B_2C_2]^{\pm n}$  type complexes: - Five types of geometrical isomers are possible such type of complexes in which only one isomer exhibit optical isomerism

*Handwritten notes:*  
 cis-2  
 trans-1  
 only 1 opt. active

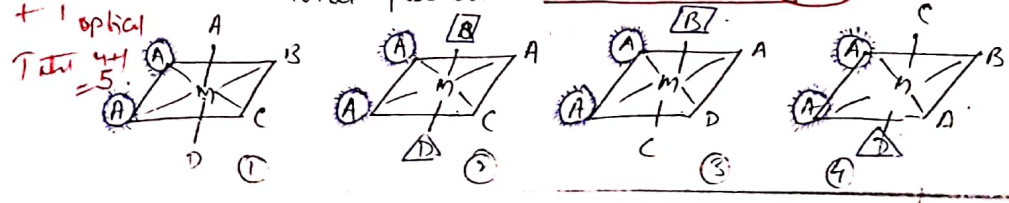


Only (1) isomer is optically active. 5 geometrical + 1 optical

So that possible stereoisomers for such a complex = Six - (6)

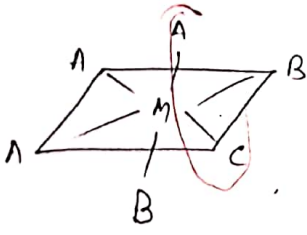
(K)  $[MA_3B_2CD]^{\pm n}$  type complexes  $\rightarrow$  Possible geom. isomers = four, Opt. isomers = One

geo. four = 1 2 3 4 Total possible stereoisomers = five

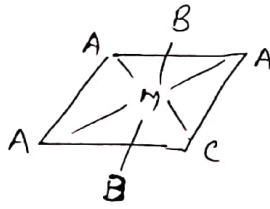


Only (1) isomer is optically active

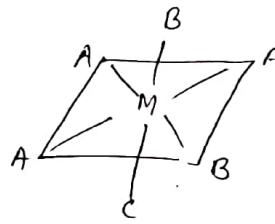
②  $[MA_3B_2C]^{n\pm}$  type complexes  $\rightarrow$  Three geometrical isomers are possible in which only one isomer can show optical isomerism.



Ⓐ

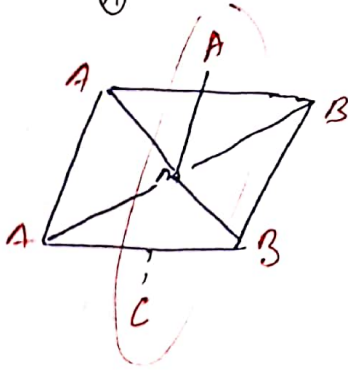


Ⓑ



Ⓒ

Only isomer Ⓐ can show optical isomerism  
So that total no. of stereoisomers = four



$Ag^+$   $\rightarrow$  Linear (sp)  
 $Co/Fe$   $\rightarrow$  octahedral  
 $Ni$   $\rightarrow$  s.p. (But  $NiCO_4 \rightarrow Td$ )  
 $Pt$   $\rightarrow$  s.p. ( $[NiX_4]^{2-}$ )  
 $Hg^{2+}, Ag^+$   $\rightarrow$  Trigonal planar



Nature of Metal-Ligand bonding in complexes  
given by London & Hittler.

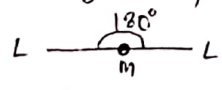
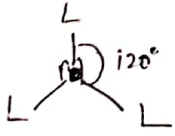
1. Valence bond theory:- (Contribution to this theory → Pauling & Slater 1935)

*Hybridisation is not complete  
 than 2 for each coord. bond  
 formation*

- This theory based upon following assumptions
- Central metal atom/ion in complexes provides hybridised orbitals to ligands for the formation of co-ordination bonds. Hybridised orbitals of metal atom/ion are vacant, equivalent in energy and have definite geometry. *ligand need vacant orbital to make coordination bond.*
  - No. of hybridised orbitals = co-ordination no. of metal atom/ion = n
  - During the complex formation, metal atom/ion accept lone pairs of e<sup>-</sup> from ligands in vacant hybridised orbitals and co-ordination bonds are formed.

Co-ordination no., hybridised orbitals and molecular geometry

*complex compd.  
 in 3 p. or d-orb.  
 not free & hybridised  
 for each ligand  
 for coordination  
 bond could be 2 or 3  
 or 4 - bond.  
 complex compd. of  
 central atom must be  
 d<sup>0</sup> block 3d element  
 or 4d 5d element*

Co. No.	Type of hybrid.	molecular geometry
2	sp	Linear 
3	sp <sup>2</sup>	Trigonal planar 

*for hybridisation use:  
 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup>, 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup>  
 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>10</sup> 4f<sup>14</sup>  
 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>10</sup>*

Example  
 [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, [As(CN)<sub>2</sub>]<sup>-2</sup>  
 [HSI<sub>3</sub>]<sup>0</sup>, [As(R<sub>3</sub>P)<sub>3</sub>]<sup>+</sup>

Ni(CO)<sub>4</sub> - sp<sup>3</sup>  
 Ni(CN)<sub>4</sub><sup>2-</sup> - dsp<sup>2</sup>

\* p block element  
 ↓  
 central atom p  
 ↓  
 hybridization  
 used  
 ↓  
 d orbitals  
 sp<sup>3</sup>d<sup>2</sup>  
 sp<sup>3</sup>d  
 sp<sup>2</sup>d

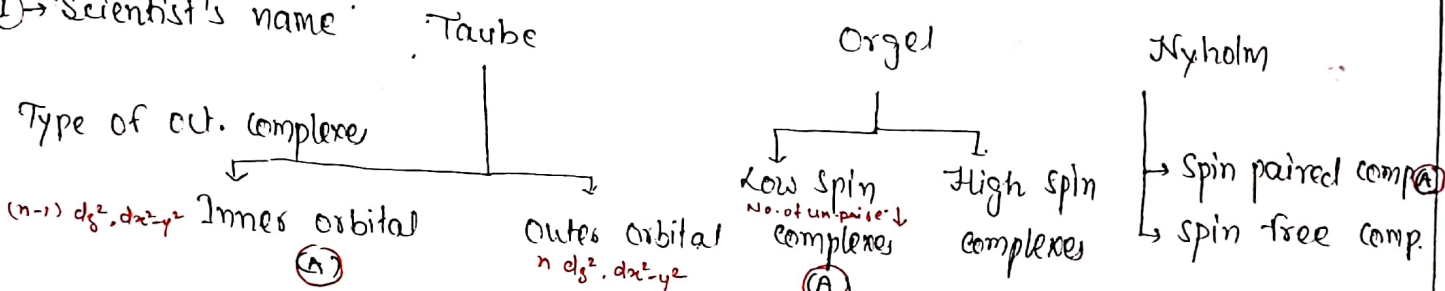
complex compd.  
 ↓  
 distortion in geometry  
 John-Teller  
 Jahn-Teller  
 irregularities  
 eg. eg. Cu<sup>2+</sup>  
 S<sup>2-</sup>

Co. No.	Type of Hyb	Molecular geometry	Example
4	sp <sup>3</sup>	Regular Tetrahedral Note: - No d-orbitals used.	[Ni(CO) <sub>4</sub> ], [Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> , [ZnCl <sub>4</sub> ] <sup>2-</sup> [CuX <sub>4</sub> ] <sup>2-</sup> , [MnX <sub>4</sub> ] <sup>2-</sup> , [NiX <sub>4</sub> ] <sup>2-</sup> x=Br, I, Cl
4	dsp <sup>2</sup> (dx <sup>2</sup> -y <sup>2</sup> or (n-1) <sup>th</sup> shell)	Square planar ↓ use d-dx <sup>2</sup> -y <sup>2</sup> no of l is four.	[Ni(CN) <sub>4</sub> ] <sup>2-</sup> , [Ni(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> , [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> [PtCl <sub>4</sub> ] <sup>2-</sup>
5	dsp <sup>3</sup> (n-1)dz <sup>2</sup> , ns, np <sup>3</sup>	Trigonal bipyramidal	[CuCl <sub>5</sub> ] <sup>3-</sup> , [Fe(CO) <sub>5</sub> ], [Mn(CO) <sub>5</sub> ] <sup>0</sup> [Pt(SnCl <sub>3</sub> ) <sub>2</sub> ] <sup>-3</sup> , [Co(CNCH <sub>3</sub> ) <sub>5</sub> ] <sup>+</sup>
5	sp <sup>3</sup> d ns, np <sup>3</sup> , ndx <sup>2</sup> -y <sup>2</sup>	Square pyramidal (dx <sup>2</sup> -y <sup>2</sup> )	[SbF <sub>5</sub> ] <sup>-2</sup> , [Ni(CN) <sub>5</sub> ] <sup>3-</sup> [MnCl <sub>5</sub> ] <sup>-2</sup> , [InCl <sub>5</sub> ] <sup>-2</sup> , Sb(Ph) <sub>5</sub>
6	d <sup>2</sup> sp <sup>3</sup> d(n-1)dz <sup>2</sup> , dz <sup>2</sup> -y <sup>2</sup> , ns, np <sup>2</sup>	Octahedral, (Inner orbital) (dx <sup>2</sup> -y <sup>2</sup> )	[Fe(CN) <sub>6</sub> ] <sup>-3</sup> , [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>+3</sup> etc
	sp <sup>3</sup> d <sup>2</sup> ns, np <sup>3</sup> , ndz <sup>2</sup> , ndx <sup>2</sup> -y <sup>2</sup>	Octahedral (outer orbital)	[FeF <sub>6</sub> ] <sup>-3</sup> , [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>+2</sup> [Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>+3</sup> , [Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>

Pauling has made a use of magnetic measurements to find out the no. of unpaired in a complex.

# Concept of octahedral complexes

① → Scientist's name

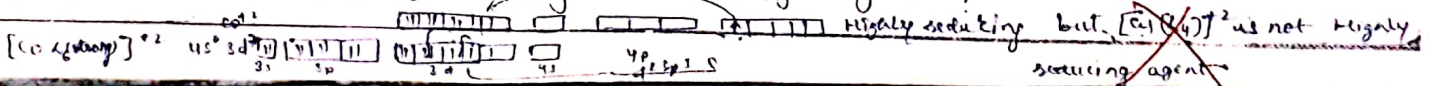


Those octahedral complexes which involves  $d_{z^2}$  &  $d_{x^2-y^2}$  orbitals of  $n^{th}$  shell in  $sp^3d^2$  hybridisation are called outer orbital complexes. Since in these complexes ions the no. of unpaired e<sup>-</sup> is equal to the no. of unpaired e<sup>-</sup> in the metal ions, so these are also called high spin complexes or spin free complexes.

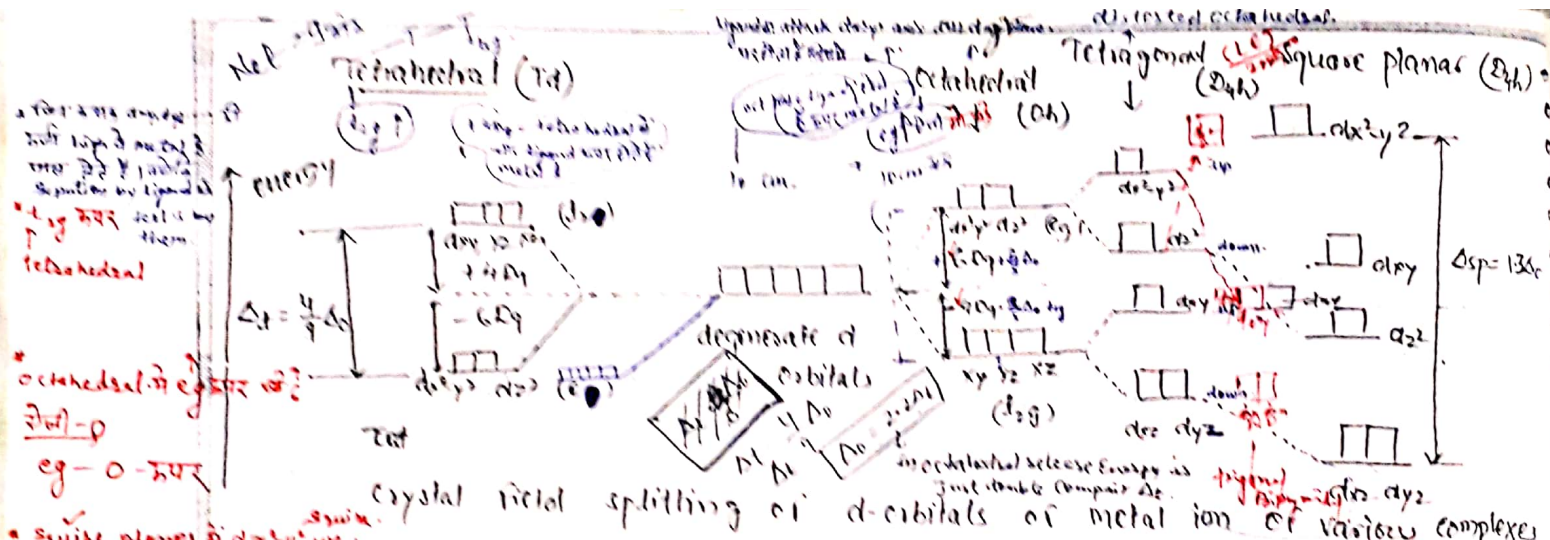
Such octahedral complexes in which  $d_{z^2}$  &  $d_{x^2-y^2}$  orbitals of  $(n-1)^{th}$  shell are involved in  $d^2sp^3$  hybridisation are called inner orbital complexes. Since no. of unpaired e<sup>-</sup> decreased after the formation of these complexes, so that these are also called low spin complexes or spin paired complexes.

→ All the octahedral complexes of  $Ni^{2+}$  are outer orbital complexes

~~Q~~ Explain →  $[Co(NH_3)_6]Cl_2$  is a good reducing agent?







• Tetrahedral  
 $\Delta_t = \frac{4}{9} \Delta_o$   
 • Octahedral में eg ऊपर त<sub>2g</sub> नीचे - 0 ऊपर  
 • Square planar में dxy ऊपर  
 • Tetrahedral में dxy ऊपर

Maximum energy of orbitals  
 • Oct. eg dx<sup>2</sup>-y<sup>2</sup>, dz<sup>2</sup>  
 • Tet. - t<sub>2g</sub> dxy, dxz, dyz  
 • Trigonal bipyramidal - dxy, dxz, dyz  
 • Square planar - dxy  
 • Trigonal bipyramidal - dxy  
 • Square planar - dxy  
 • Oct. - eg  
 • Tetrahedral - t<sub>2g</sub>, e<sub>g</sub>

S.No.	e. no.	Structure	dxy	dxz	dyz	dx <sup>2</sup> -y <sup>2</sup>	dz <sup>2</sup>
1	6	Octahedral	free	-4.00	-4.00	6.00	6.00
2	4 equal to No.	Tetrahedral	1.76	1.76	1.76	-2.67	-2.67
3	4 of coordination	Square planar	2.28	-5.14	-5.14	11.28	-4.28
4	5 bond	Trigonal bipyramidal	-1.82	-2.72	-2.72	-1.82	7.04
5	5	Square pyramidal (tetragonal)	-1.86	-4.57	-4.57	9.14	1.86
6	8	Cubic (tet.)	3.56	3.56	3.56	-5.84	-5.84
7	12	Icosahedral	0.00	0.00	0.00	0.00	0.00

Pairing Energy  $\times$   $Z_{eff}$ . The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting. This concept of crystal field splitting makes the basis of CFT.

The energy gap between  $t_{2g}$  and  $e_g$  sets is denoted by  $10 Dq$  or  $\Delta_o$  (for octahedral complexes) and  $\Delta_t$  for tetrahedral complexes.  $10 Dq$  is called crystal field splitting energy.

C.F.S.E =  $\sum n \times \Delta_o + P_{energy}$ . The value of  $10 Dq$  can be calculated by UV spectrum

C.S.S.E =  $\sum n \times \Delta_o + P_{for}$  a given compound in terms of  $KJ mol^{-1}$   $\therefore$  CFSE for this =  $\frac{20300}{18} \times 4 = 8120 cm^{-1}$

$10 Dq = \frac{\sum KJ mol^{-1}}{8.37}$  e.g.  $[Ti(H_2O)_6]^{+3}$  complex shows a peak at  $20300 cm^{-1}$  in UV spectrum.

So value of  $10 Dq = \frac{20300}{8.37} \approx 242.53 KJ mol^{-1}$   $\therefore 1 KJ mol^{-1} = 83.7 cm^{-1}$

Factors influencing the magnitude of  $10 Dq$  - (A) Nature of metal ion

(1) Different charges on the cation of the same metal  $\rightarrow$  charge  $\propto 10 Dq$   
 e.g.  $10 Dq$  for  $[Fe(H_2O)_6]^{+2} = 10,400 cm^{-1}$ , & for  $[Fe(H_2O)_6]^{+3} = 13,700 cm^{-1}$

(2) Different charges on the cation of different metals  $\rightarrow$  charge  $\propto 10 Dq$  in some d series.  
 e.g.  $10 Dq$  for  $[V(H_2O)_6]^{+2} = 12,400 cm^{-1}$ ,  $10 Dq$  for  $[Cr(H_2O)_6]^{+3} = 17,400 cm^{-1}$   
3d<sup>3</sup> system 3d<sup>5</sup> system

Principle for metal:  
 1.  $10 Dq \propto \frac{1}{d}$  (No. of metal ions same charge but stability of complex  $\propto$  smallness of size)

SL - strong ligand, WL - weak ligand. H.S. - High Spin, L.S. - Low Spin, octahedral, Jahn Teller distortion + tetragonal

- distortion. विक्षिप्ति SD - strong distortion, High unpaired. Noe-  
 LD - Light distortion

\* No high spin square planar complexes have been observed as yet. configurations of asymmetry of strong distortion, high e- unsymmetry arrangement } not 5d distortion.  
 Examples  $\rightarrow [Ni(CN)_4]^{-2}$ ,  $[PdCl_4]^{-2}$ ,  $[Pt(NH_3)_4]^{+2}$ ,  $[PtCl_4]^{-2}$  and  $[AuCl_4]^{-}$   
 All of these has  $d^8$  electronic system. In first Transition series

Only strong ligands like  $CN^-$  can form square planar complexes. But heavier metals like Pd, Pt, Au etc can form square planar complexes with halides due to high value of  $\Delta_o$   $Dq$  (High charge density. paramagnetic)

Bond angles in Tetrahedral Complexes

$\angle eg-M-L = 54^\circ 44'$ ,  $\angle t_{2g}-M-L = 35^\circ 16'$   
 $eg = 54.4^\circ$ ,  $t_{2g} = 35.1^\circ$

\*  $t_{2g}$  orbitals are more repelled by ligands as compare to  $eg$  orbitals in tetrahedral complexes due to less distance. In tetrahedral complexes pairing energy is larger than  $\Delta_o$ , due to this pairing of  $e$  is not possible till each  $t_{2g}$  &  $eg$  orbitals has 1e each.

- \* Favourable conditions for formation of  $Td$  complexes over octahedral
- 1) Larger size of ligands
  - 2) Low oxidation state of central metal ion
  - 3) Ligands are weak
  - 4) Generally el. conf.  $\rightarrow d^0, d^3, d^8, d^9, d^6$

$d^0$  Ms. Octa. (W.L.)  
 $d^1$  L.S. tetrahedral (S.L.)  
 octahedral  $\rightarrow eg^2 t_{2g}^3$   
 $d^1$  } 3d distortion e- (eg,  $t_{2g}, e_g, t_{2g}$ )  
 $d^2$  } slight distort.  
 $d^2$  No distortion  
 $d^4$  } W.L. (W.L.)  
 $d^4$  } S.D. (W.L.)  
 $d^5$  } No Dis  
 $d^6$  } L.D.  
 $d^7$  } L.D.  
 $d^8$  } No D.  
 $d^9$  } S.D.  
 $d^{10}$  } No Dis  
 $d^0$  } tetrahedral  
 $d^1$  } Ni-W.L.  
 $d^2$  } (msym) eg  
 $d^3$  } No Dis  
 $d^4$  } High Spin  
 $d^5$  } High Spin  
 $d^6$  } High Spin  
 $d^7$  } High Spin  
 $d^8$  } High Spin  
 $d^9$  } High Spin  
 $d^{10}$  } High Spin



- \* Favourable conditions for formation of octahedral complexes  $d^1 - d^9$  SSC
- ① Small size of ligands (less steric hindrance) S - small size of ligand
  - ② High positive charge on metal ion S - strong ligand
  - ③ Ligands are strong C - charge high on metal

- \* Favourable conditions for square planar complexes use  $d^8 - d^9$  (vacant)  $d^8$  eg.  $[PtCl_4]^{2-}$
- ① Electronic configuration  $\rightarrow d^8$
  - ② Strong ligands ~~set~~ set C.D.
  - ③ High charge density on metal ion.

Applications of CFT.

① Explanation of geometry of complexes: - By considering the above favourable conditions we can predict the geometry of the complex

② No. of unpaired e and explanation of magnetism of complexes - Using this theory, no. of unpaired e's can be calculated and we can determine magnetic moment of given complex

$$\mu = \sqrt{n(n+2)}$$

B.M. of D,  $n = \text{no. of unpaired } e's$

\* Since mag. moment generated by orbital motion of  $e's$  is quenched by ligand due to their closer approach.

③ Explanation of colours of complexes  $\rightarrow$  following two processes are responsible for colour generation in complexes.

- ① d-d electronic transition
- ② charge transfer spectra

only in metal d-orbital.

between metal-ligand

C.D  $\rightarrow$  d-d transition of e<sup>-</sup>  
charge transfer spectra

Heat of hydration  
 $\Delta H \propto m \cdot \downarrow$  size  
 practically observed  
 theoretical expected  
 At. No.  
 $\Delta H \propto \frac{1}{r}$   
 Simple hydration energy  
 But  $d^0, d^5, d^{10}$  are theoretical = practical  
 C.F.S.E. = zero  
 hydration + C.F.S.E.  
 because  $H_2O$  w.l.  
 lattice energy  $\propto \frac{1}{r}$   
 Heat of hydration complex  
 C.F.S.E. zero  $d^0, d^5, d^{10}$   
 generally  
 According to this theorem, for a nonlinear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy, and lower the energy.  
 by J-T distortion octahed  $\xrightarrow{J-T-D}$  tetragonal  $\xrightarrow{J-T-D}$  square planar.

\* LMCT :- Ligand to metal charge transfer  
 colour intensity  $(B) > (A)$ , higher the positive charge on metal ion, higher will be changes of charge transfer from ligand to metal.

Examples  $\rightarrow$  (1) LMCT is responsible for the familiar deep purple colour of  $MnO_4^-$  (This process is facilitated by the high oxidation state of metal).  
 Other examples in which LMCT process is responsible for colour generation

- (A)  $CdS \rightarrow$  Ligand  $\pi_p \rightarrow$  metal  $5s$
- (B)  $HgS \rightarrow$  Ligand  $\pi_p \rightarrow$  metal  $6s$
- (C)  $PbO \rightarrow$  Ligand  $\pi_p \rightarrow$  metal  $6s$
- (D)  $CoO_3^+ \rightarrow$  Ligand  $\pi_p \rightarrow$  metal  $3d$
- (E)  $Fe_2O_3 \rightarrow$  Ligand  $\pi_p \rightarrow$  metal  $3d$
- (F)  $HgI_2 \rightarrow$  Ligand  $\rightarrow$  metal
- (G)  $BiI_3$  and  $PbI_2 \rightarrow$  Ligand  $\rightarrow$  metal (Orange Red) (Yellow)
- (H)  $[CuCl_4]^{2-} \rightarrow$  Ligand  $\rightarrow$  metal  $3d$

Colour of  $I_2$  is violet in  $CCl_4$  but change to brown in benzene due charge transfer process from benzene to iodine.

(4) Explanation of distorted complexes  $\rightarrow$  Jahn-Teller Theorem.

According to this theorem, for a nonlinear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy, and lower the energy.  
 by J-T distortion octahed  $\xrightarrow{J-T-D}$  tetragonal  $\xrightarrow{J-T-D}$  square planar.

We can determine which octahedral complexes will be subject to Jahn-Teller distortions by considering ground state degeneracies,

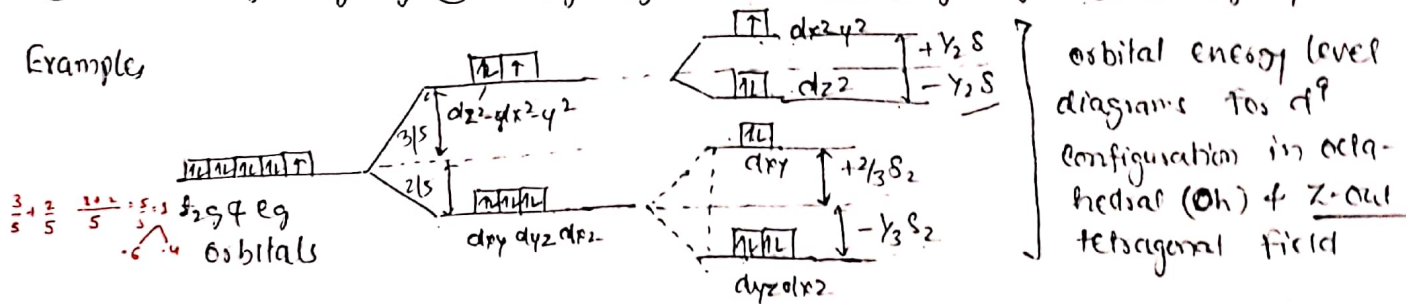
Configurations for which Jahn Teller distortions are expected in ML<sub>6</sub> complexes

} both high & low spin	d <sup>1</sup>	d <sup>2</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>9</sup>
				(low spin)	(high spin)		high & low spin

⊛ Generally strong distortions occur in following cases

- Ⓐ d<sup>4</sup> - e<sub>g</sub><sup>3</sup> t<sub>2g</sub><sup>1</sup> Ⓑ t<sub>2g</sub><sup>6</sup> e<sub>g</sub><sup>3</sup> - d<sup>9</sup> Ⓒ t<sub>2g</sub><sup>6</sup> e<sub>g</sub><sup>2</sup> - d<sup>8</sup> Ⓓ t<sub>2g</sub><sup>6</sup> e<sub>g</sub><sup>3</sup> - d<sup>9</sup>

Example



⊚ Cu<sup>+2</sup> ion (d<sup>9</sup>-system), splitting of d-orbitals due to Jahn Teller distortion.

It means, the net lowering of the electronic energy in case of e<sub>g</sub> level is  $\delta/2$ . This net energy equal to  $-\delta/2$ , might be called the J.T. stabilisation energy and provides the driving for the distortion.

Examples having distorted structure → (All the distances in pm)

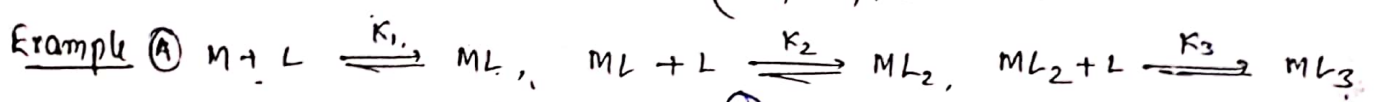
S. No.	d <sup>n</sup> compound	Short distances (pm)	Long distances (pm)	Comment
①	d <sup>9</sup> CuF <sub>2</sub> (CuF <sub>6</sub> ) <sup>2-</sup>	4F at 193 <small>(bond distance)</small>	2F at 227 <small>(bond distance)</small>	Z-out effect
②	d <sup>9</sup> CuF <sub>2</sub> · 2H <sub>2</sub> O	2F at 190 2O at 194	2F at 247	Z-out effect
③	d <sup>9</sup> K <sub>2</sub> CuF <sub>4</sub>	4F at 199	2F at 222	Z-out effect
④	d <sup>9</sup> CuCl <sub>2</sub>	4Cl at 230	2Cl at 295	Z-out effect
⑤	d <sup>9</sup> CuCl <sub>2</sub> · 2H <sub>2</sub> O	2Cl at 229 2O at 196	2Cl at 294	Z-out effect
⑥	d <sup>9</sup> [Cu(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	4N at 207	2N at 262	Z-out effect
⑦	d <sup>8</sup> empirical formula CoF <sub>2</sub>	4F at 200	2F at 243	
⑧	d <sup>4</sup> MnF <sub>2</sub>	2F at 179 2F at 191	2F at 209	
⑨	d <sup>4</sup> K <sub>2</sub> MnF <sub>5</sub> · H <sub>2</sub> O	4F at 183	2F at 207	

Since in every distorted structure having complex, J. T. stabilisation energy is released, which makes stable to given complex.



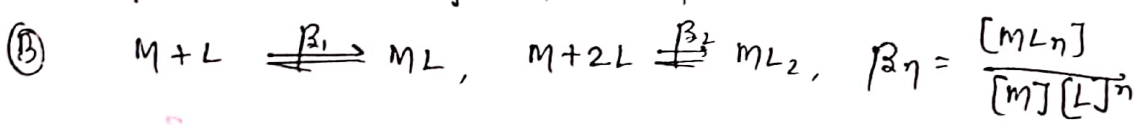
### Stability of complexes in aqueous solutions

Stepwise formation of complexes, stepwise formation constants ( $K_1, K_2, K_3 \dots$  etc) and overall formation constants ( $\beta_1, \beta_2, \beta_3 \dots$  etc)



So that  $K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$  Generally  $K_1 > K_2 > K_3 > K_4$

Reason  $\rightarrow$  When more and more ligands move into the co-ordination zone, less and less aqua molecules are available to fresh ligands for replacement. and greedyness of metal ion towards es decreases.



$\beta_n = K_1 \cdot K_2 \cdot K_3 \dots K_n$  , stability constant increase then stability of complex also increase.

$\Delta H^\ddagger$  Thermodynamic stability  $\rightarrow$  stable and unstable complexes (stability const)

$\Delta G^\ddagger$  Kinetic stability  $\rightarrow$  labile and inert complexes

The stability of a complex depends on the reaction energy while the lability of a compound depends on activation. The complexes in which the ligands are rapidly replaced by others.

are called labile while those in which substitution occurs slowly are termed inert complexes. *unstable complex* → *stable complex*.

labile complex  
↳  
we can easily change their ligand by new ligand & they show the character of lability very fast.

① Outer orbital octahedral complexes → Generally these complexes are labile. *unstable* *activation* labile and inert complexes (V.B.T. explanation)

e.g.  $Mn^{+2}$   $Fe^{+2}$   $Fe^{+3}$   $Co^{+2}$   $Ni^{+2}$   $Cu^{+2}$   $Cr^{+2}$   $M^{+2}$

$d^5$   $d^6$   $d^5$   $d^7$   $d^8$   $d^9$   $d^4$

*37904*  $Fe^{+3}$   
 $M^{+3}$   $M^{+4}$  - inert

Reason → metal ligand bonds are weak in  $sp^3d^2$  hybridised complexes as compare to  $d^2sp^3$  hybridised complexes.

② Inner orbital octahedral complexes →

① Such complexes which has at least one  $d$ -orbital of  $t_{2g}$  set empty → Labile complexes.

② Inert inner orbital octahedral complexes → each  $d$ -orbital of  $t_{2g}$  set contains at least one  $e^-$ .



Explanation according to CFT. → *distorted octahedral*

① Order of lability →  $d^6 < d^3 < d^4 < d^5$  → For low spin complexes - *with strong ligand.*

② High spin complexes of  $d^3$  system reacts slowly - inert

③ High spin octahedral complexes of  $d^5$  system reacts fastly - labile

④ Both high spin & low spin of  $d^8$  are inert (V.B.T. predicts opposite results)  *$L_2$   $ML_2$  complex*

Factors affecting the lability of a complex

- ① Charge of the central<sup>M</sup> ion  $\propto 1/\text{lability}$
- ② Radius of the central<sup>M</sup> ion  $\propto \text{lability}$
- ③ Charge to radius ratio  $\propto \frac{1}{\text{lability}}$
- ④ Geometry of complex  $\rightarrow$  4-co-ordinated system <sup>weak bond</sup>  $>$  6-co-ordinated sys.

Factors affecting the stability of complexes

① Properties of the central metal atom  $\rightarrow$

Stability increasing factors  $\rightarrow$  High charge, small size

✓ Natural order of stability  $\xrightarrow{\text{Net}}$   $\text{Mn}^{+2} < \text{Fe}^{+2} < \text{Co}^{+2} < \text{Ni}^{+2} < \text{Cu}^{+2} > \text{Zn}^{+2}$   
 (Irving-William order) (Stability order of high spin complexes)

Explanation for this series  $\rightarrow$  charge/radius ratio

② Properties of ligands  $\rightarrow$  chelate effect, size & charge of ligand, steric effects, chelate ring size, basic character of ligand.

The relative stability of high spin octahedral  $[\text{M}^n\text{L}_6]^{+2}$  complexes of the 1<sup>st</sup> T. series

