

a) charge of metal ion:-

- Higher the charge on central metal ion higher will be the stability of a complex. For a given metal & same number of ligands,



b) size of metal ion:-

- Smaller the size of metal ion higher is the stability, For a given metal ion & same number of ligands.



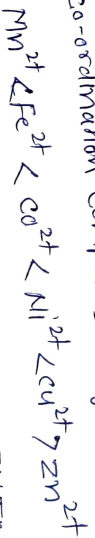
c) Ionic potential:- It is defined as the ratio of charge and size.

$$\text{I.P.} = \frac{\text{charge}}{\text{size}}$$

- Ionic potential will be higher when there is more charge & lesser size. Higher the ionic potential higher will be the stability.

- Two ions having same value of ionic potential will have equal tendency to form complexes.

\* On the basis of above rules the stability order of metal ions to form co-ordination compounds is given as



- This series is known as "IRVING-WILLIAMS" series.

3) Ligand effect:-

- Higher basicity will lead to higher tendency of ligand to donate the electrons & make a stronger bond leading to a stable complex.

-  $\pi$  Acceptance property of ligand also leads to a stronger bond & a stable complex. This behavior is shown by  $\pi$ -acceptor ligands.

e.g.  $\text{CN}^-$ ,  $\text{CO}$ ,  $\text{PR}_3$

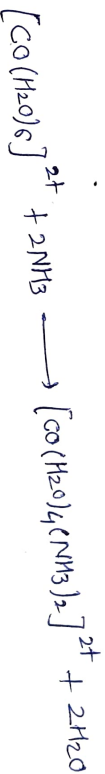
- chelate effect:-

- The polydentate ligands have geometry such that they can form more than 1 co-ordinate bond to the same metal, such ligands are called chelating ligands.

- The complex formed by the coordination of a polydentate ligand to a metal ion is called a chelate complex.

- The complex formed is far more stable than the analogous complex formed by a monodentate ligand. This extra stability in the complex is known as chelate effect.

- consider the formation of non-chelated complex:-

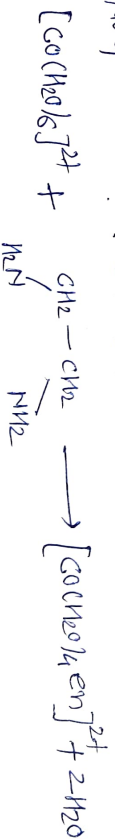


$$\Delta G = \Delta H - T\Delta S$$

- In this case, the change in randomness of the system is almost negligible.

$$\text{i.e. } \Delta S \approx 0$$

$$\text{Now, } \therefore \Delta G = \Delta H$$

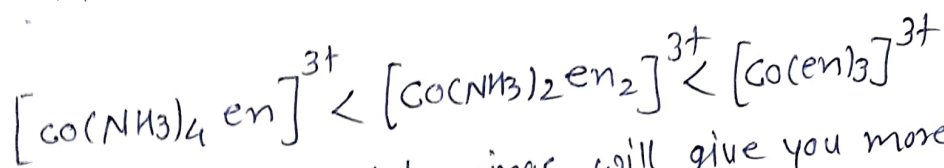


- In this case, due to the formation of a ring there is an increase in entropy of the system

$$\Delta S = +ve; \quad \Delta S > 0 \quad (\because \text{The no. of molecules have increased in the product})$$

$$\Delta G = \Delta H - T\Delta S$$

Now, due to the positive value of  $\Delta S$  the  $\Delta G$  will be more negative leading to higher stability in the chelated complex.



- more no. of chelate rings will give you more stability.

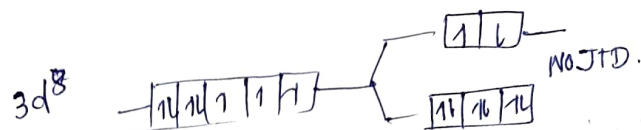
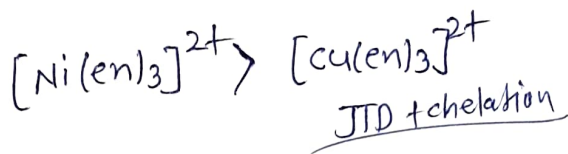
IF a molecule has chelation it has more stability.

IF a molecule has JTD it also leads to higher stability.

But,

IF a molecule has both chelation & JTD will be lesser stable

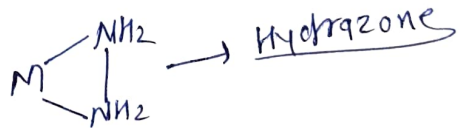
e.g.



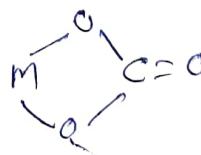
Fe Co Ni Cu



- 3-membered ring is highly unstable.

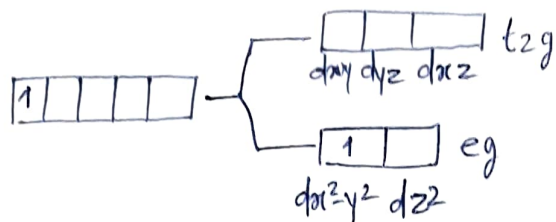


- 4-membered rings are also less stable but are seen with the carbonate ligand



a) Find CFSE for all cases mentioned below.  
 $d^1 - d^{10}$  (tetrahedral)

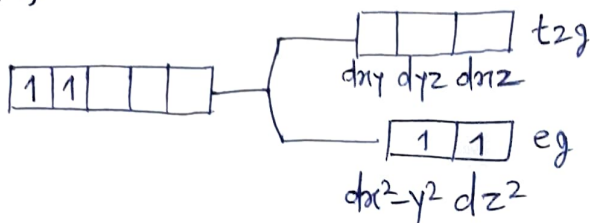
→  
 1)  $d^1$  (td)



$$\text{CFSE} = 1(0.6) + 0(-0.4)$$

$$= 0.6 \Delta_t$$

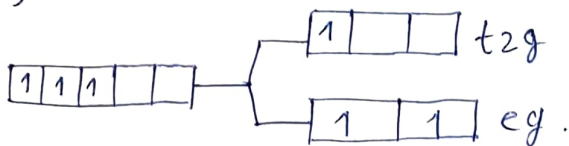
2)  $d^2$  (td)



$$\text{CFSE} = 2(0.6) + 0(-0.4)$$

$$= 1.2 \Delta_t$$

3)  $d^3$  (td)

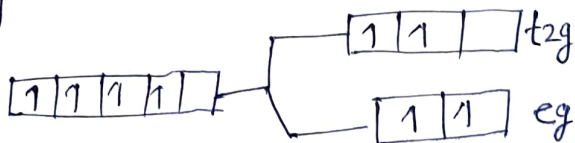


$$\text{CFSE} = 2(0.6) + 1(-0.4)$$

$$= 1.2 - 0.4$$

$$= 0.8 \Delta_t$$

4)  $d^4$  (td)

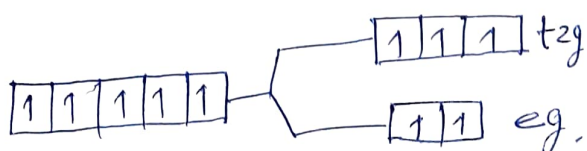


$$\text{CFSE} = 2(0.6) + 2(-0.4)$$

$$= 1.2 - 0.8$$

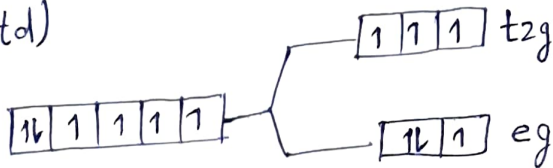
$$= 0.4 \Delta_t$$

5)  $d^5$  (td)



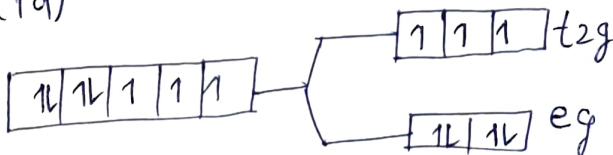
$$\text{CFSE} = 2(0.6) + 3(-0.4) = 1.2 - 1.2 = 0 \Delta_t$$

6)  $d^6(td)$



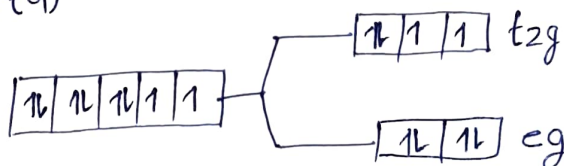
$$\begin{aligned} CFSE &= 3(0.6) + 2(0.4) \\ &= 1.8 - 0.8 \\ &= 1.0 \Delta t \end{aligned}$$

7)  $d^7(td)$



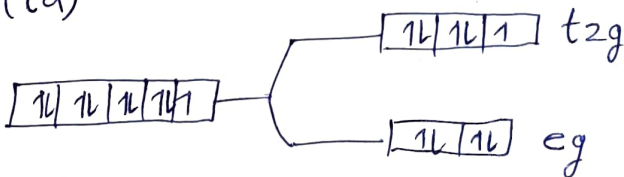
$$\begin{aligned} CFSE &= 4(0.6) + 3(-0.4) \\ &= 2.4 - 1.2 \\ &= 1.2 \Delta t \end{aligned}$$

8)  $d^8(td)$



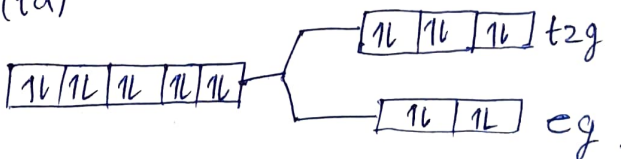
$$\begin{aligned} CFSE &= 5(0.6) + 3(0.4) \\ &= 3.0 + 1.2 \\ &= 4.2 \Delta t \end{aligned}$$

9)  $d^9(td)$



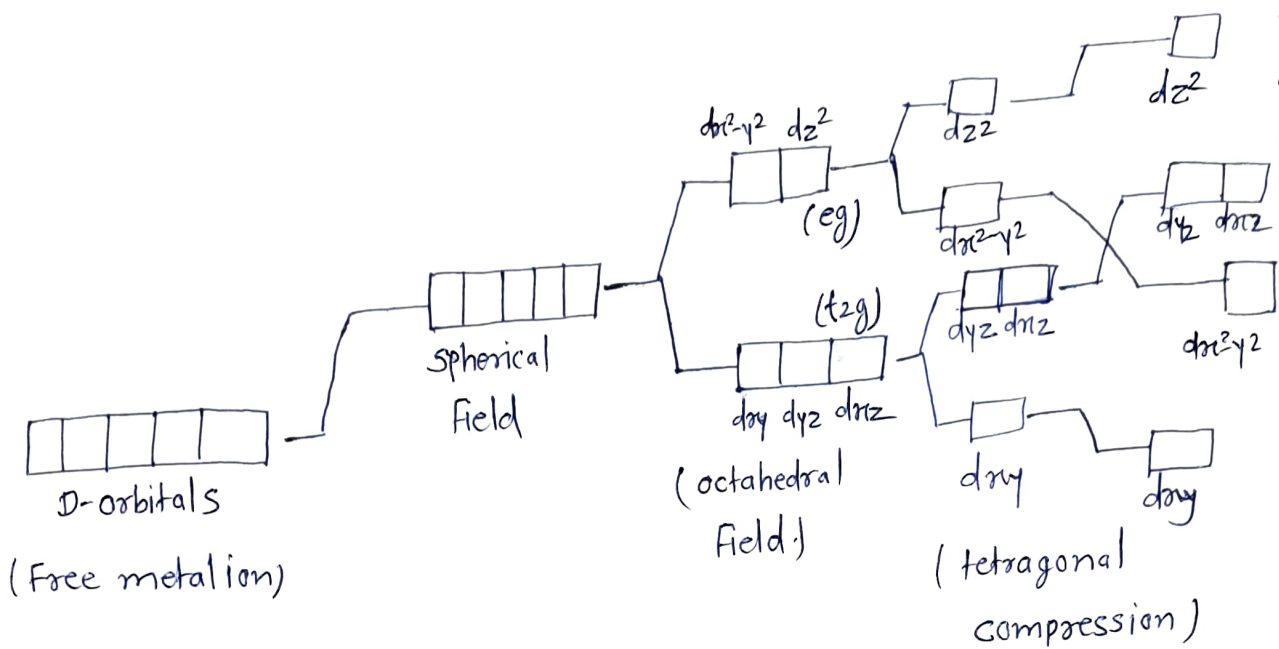
$$\begin{aligned} CFSE &= 6(0.6) + 3(-0.4) \\ &= 3.6 - 1.2 \\ &= 2.4 \Delta t \end{aligned}$$

10)  $d^{10}(td)$



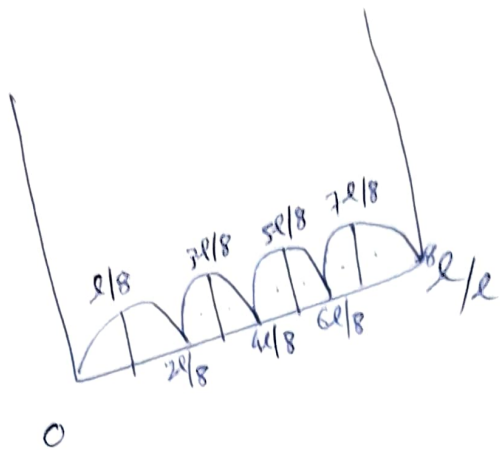
$$\begin{aligned} CFSE &= 10(0.6) + 2(0.4) \\ &= 6.0 + 0.8 \\ &= 6.8 \Delta t \end{aligned}$$

Q) Explain the crystal field splitting square planar complexes with the help of tetragonal compression.



- In a free metal ion all the 5-d orbitals are degenerate.
- In a square planar complex, the metal ion is present at the centre & 4 ligands are present at each corner of metal ion along x & y axis. in a ~~same~~ same plane.
- When the ligands ~~are~~ are at infinite distance from metal ion, the 5-orbitals will not be affected by metal field.
- When the ligands come closer to the metal ion at a certain distance they create a spherical field, all d-orbitals face equal repulsion and are excited equally & remains degenerate only.
- when the attractive forces increase & the ligands approach closest distance to the metal ion the d-orbitals face different magnitude of repulsion. This leads to splitting of d-orbitals into two different states (eg,  $t_{2g}$ )

- But, in square planar complexes the ligands are approaching along the axis but only at  $x$  &  $y$  axis.
- So, the  $z$ -axis goes into compression, as  $z$ -axis is compressed the  $d_{z^2}$  orbitals faces higher magnitude of repulsion, and goes <sup>(eg)</sup> into higher excited state as compared to  $t_{2g}$ -orbitals. ( $d_{xy}, d_{yz}, d_{xz}$ )
- When the  ~~$z$ -axis~~  $z$ -axis completely undergoes tetragonal compression the final crystal field splitting occurs in which  $d_{z^2}$  is at highest energy state &  $d_{xy}$  is at lowest energy state. While  $d_{yz}, d_{xz}$  &  $d_{x^2-y^2}$  are intermediate.



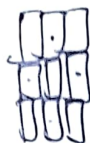
$$\frac{14l}{8}$$

$$\frac{\frac{3}{2} + 1}{2} = \frac{2 + 3}{2} = \frac{5}{2}$$

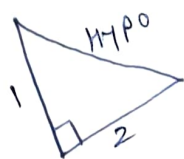
$$\frac{124l}{248}$$

$$\angle \pi = \frac{2}{l} \cdot \frac{l^2}{4}$$

$$\angle \pi = \frac{l}{2}$$



Pythagorean theorem;



$$(\text{Hypotenuse})^2 = (\text{side 1})^2 + (\text{side 2})^2$$

15<sup>2</sup>

$$15^2 - 25^2 - 29^6 - 33^2 - 35^2 - 37^2 - 39^2 - 41^2 - 43^2 - 45^2 - 47^2 - 49^2 - 51^2 - 53^2 - 55^2 - 57^2 - 59^2 - 61^2 - 63^2 - 65^2 - 67^2 - 69^2 - 71^2 - 73^2 - 75^2 - 77^2 - 79^2 - 81^2 - 83^2 - 85^2 - 87^2 - 89^2 - 91^2 - 93^2 - 95^2 - 97^2 - 99^2$$

Southern

sure  
Southern

$$\frac{2}{1} : \frac{2}{3}$$

$$15^2 - 25^2 - 29^2$$

$$\frac{6 \times 2}{3} \quad \frac{12}{3} = 4$$

$$21, 8, 18, 10$$

$$21, 8, 18, 10$$

$$15^2 - 25^2 - 29^6 - 33^2 - 35^2 - 37^2 - 39^2 - 41^2 - 43^2 - 45^2 - 47^2 - 49^2 - 51^2 - 53^2 - 55^2 - 57^2 - 59^2 - 61^2 - 63^2 - 65^2 - 67^2 - 69^2 - 71^2 - 73^2 - 75^2 - 77^2 - 79^2 - 81^2 - 83^2 - 85^2 - 87^2 - 89^2 - 91^2 - 93^2 - 95^2 - 97^2 - 99^2$$



a) Explain the crystal field splitting in square planar complexes with the help of tetragonal compression/compression

q) Find CFSE of all cases mentioned below.

d<sup>1</sup> - d<sup>10</sup> (tetrahedral)

\* Td is always high spin. (No pairing).

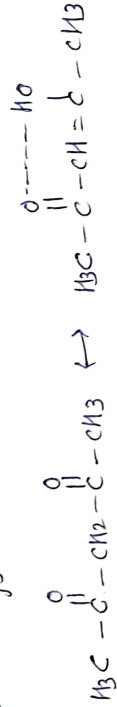


- In case of  $5d^0$  membered ring, 5-membered is more stable when the ligand has only  $\sigma$ -bonds & no  $\pi$ -bonds.

$\pi$ -conjugation.



But, if there is conjugation in the ligand system then six membered rings are more stable.

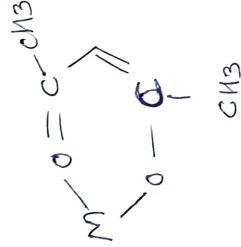


(ac-ac)

keto-enol tautomerism

Acetyl acetone

(Resonance effect)



4) macrocyclic effect-

- macrocyclic ligands are large sized compounds. These ligands have several donor atoms & form multiple chelate rings.  
e.g. porphyrine.

## • kinetic complexes stability of complexes:-

- kinetic stability of a complex is defined as the tendency of a complex to undergo ligand substitution reaction.
- on the basis of kinetic stability the complexes can be classified as inert complexes & labile complexes.
- The complexes in which the substitution is done within 1 min they are termed as labile complexes.
- The complexes in which the substitution its require more than a 1 min. are termed as inert complexes.
- The possibility of substitution reaction is maximum  $\neq$  sq. in the case of octahedral complexes due to it's saturated nature. Also the CFSE calculations are easiest in octahedral complexes so the concept of inertness & lability is applied only to the octahedral complexes.

\* There is no correlation betn thermodynamic stability & kinetic stability of a reaction.

- Thermodynamic stability <sup>formed in more amount.</sup> tells you which product will be formed
- kinetic stability tells you which product will be formed quickly.

## 1) Ligand Substitution reaction in octahedral complex:-

- metal complexes show nucleophilic substitution reactions due to the nucleophilic behaviour of ligands.

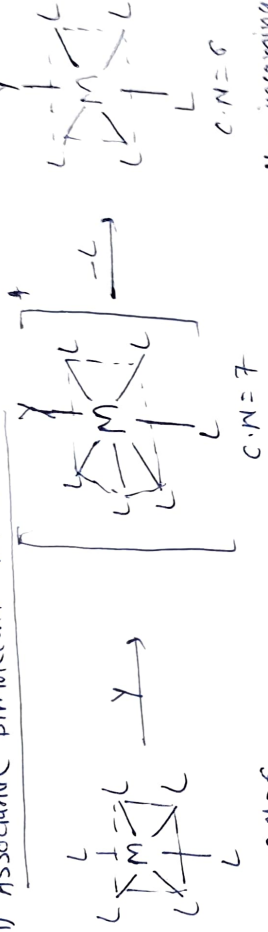


- This reaction can proceed through two different mechanisms

\* molecularity:- It is the no. of reacting species in the slowest step of the reaction.

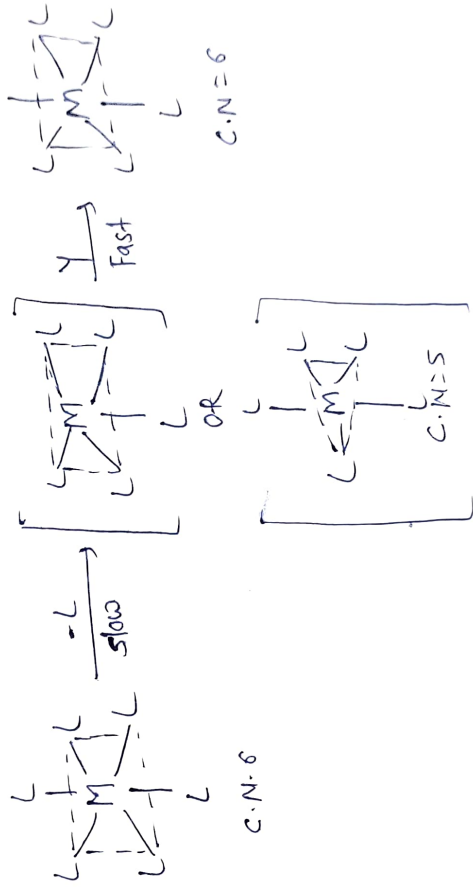
elementary - single step reaction / complex reaction:- Multiple step reaction

### 1) Associative Bimolecular mechanism:-



- The associative mechanism involves a step in which the incoming ligand attacks & an intermediate is formed with one higher C.N. & then one of the ligand leaves to give the product again in same co-ordination number.

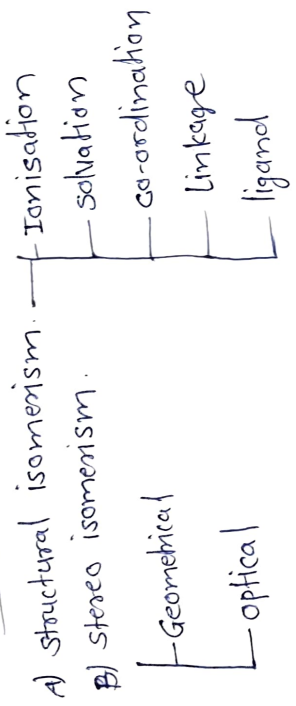
### 2) Dissociative unimolecular mechanism:-



Isomerism:-

- Two species or molecules having same molecular formula but different structural formula.

\* Types of isomerism in co-ordination compounds:-



A) structural isomerism:-

1) Ionisation:-



- when two complexes have same molecular formula but they give different ion on ionisation they are called ionisation isomers.

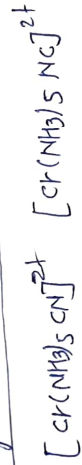
- This type of isomerism is shown by those molecules in which the ions are different inside & outside the co-ordination sphere.

2) solvation / solvate isomerism:-

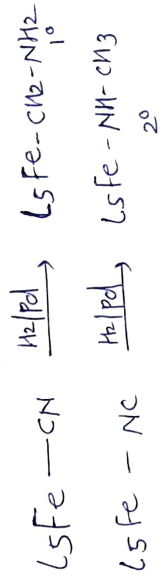


- solvate isomerism arises due to change in position of solvent molecule inside & outside the co-ordination sphere.
- This isomerism is shown only by those complexes which have some solvent molecules bound to the metal centre (e.g.  $H_2O$ ,  $NH_3$ )
- If the solvent is specifically water then the isomerism is called hydrate isomerism.

### 3) Linkage isomerism:-



- linkage isomerism arises due to the presence of ambidentate ligands



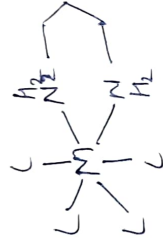
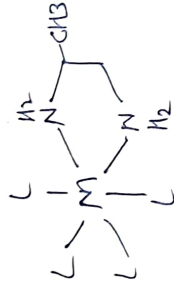
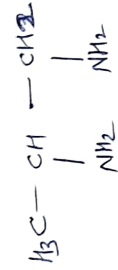
- The linkage isomerism can be detected by the help of oxidation & reduction reactions. Also, the binding mode can be detected with the help of stretching frequency in the IR-spectrum.

### 4) Co-ordination isomerism:-

- co-ordination isomerism is displayed only by those compounds in which the both cation & anion are co-ordination spheres.



## 5] Ligand isomerism:-



- The ligand isomerism is a special case in structural isomerism when the isomerism is shown by ligand itself.

## B] Stereoisomerism:-

- In stereoisomerism same atoms are always coordinated to the metal centre, only the ~~space~~ spatial arrangement changes (connectivity remains same arrangement changes).

### 1] Geometrical isomerism:-

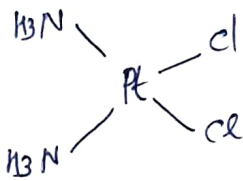
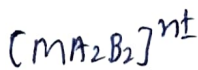
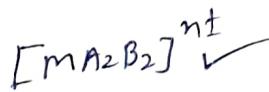
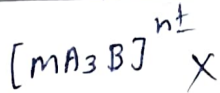
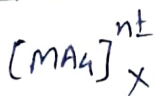
- ~~stere~~ stereoisomerism in which relative position of ligands or specifically donor atoms around the metal centre is different or specifically donor atoms around the metal centre if there are atleast
- Geometrical isomerism can only be displayed if there are atleast two different types of ligands & ~~least~~ atleast 1 of

2 in number.

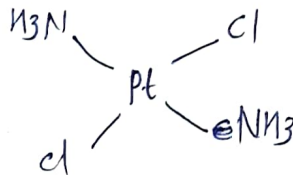
### a) In tetrahedral complexes:-

- No Geometrical isomerism because of there is no relative position concept.

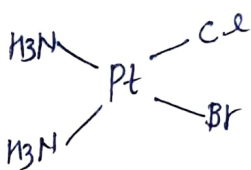
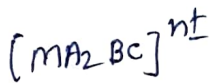
b) In square planar complexes:-



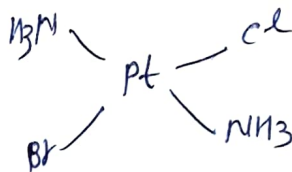
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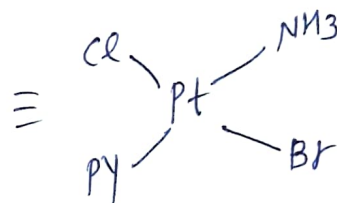
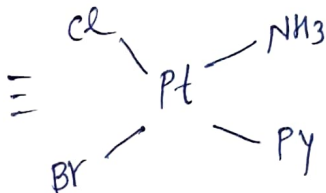
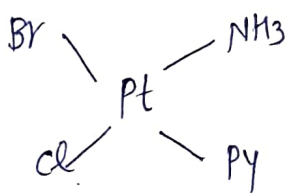
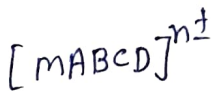
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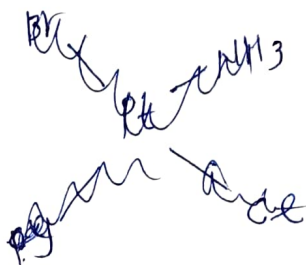
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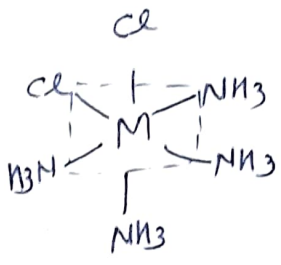
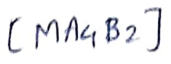
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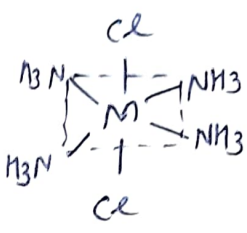
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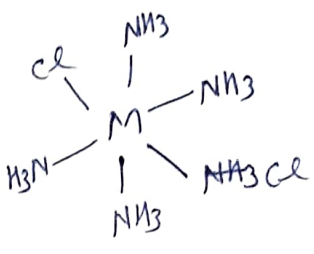
c) In octahedral complexes:-



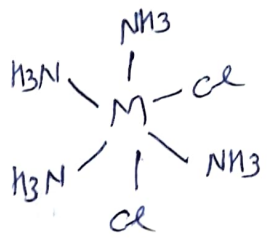
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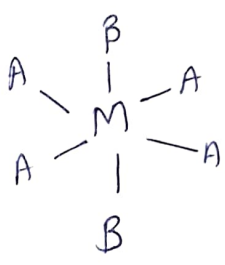
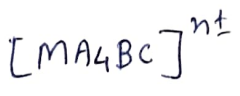
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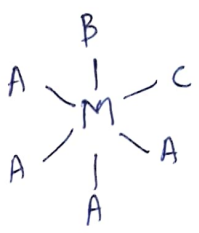
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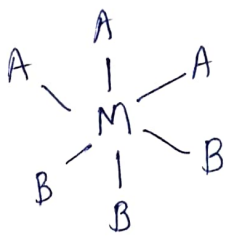
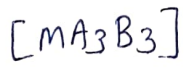
cis.



trans

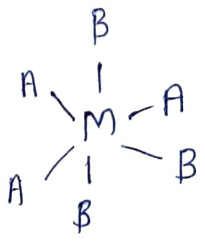


cis.



Facial isomer (Fac)

cis isomer

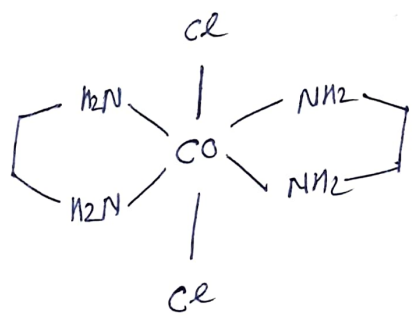


meridional isomer. (Mer)

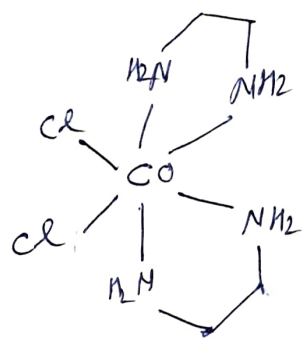
trans



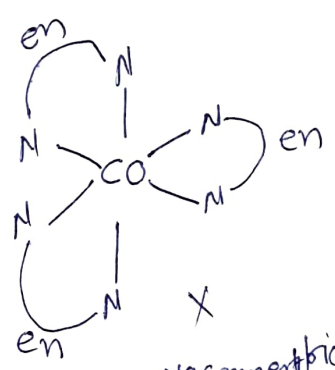
$[M(AA)_2(B)_2]$



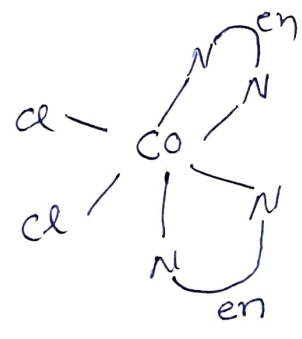
trans.



|||



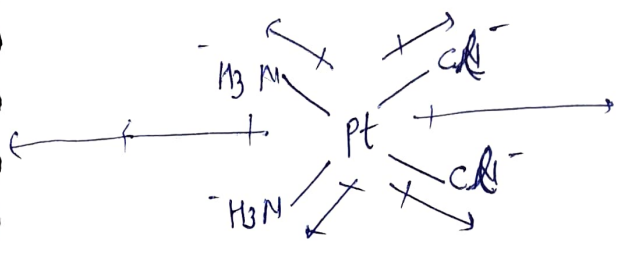
No Geometrical isomerism



cis

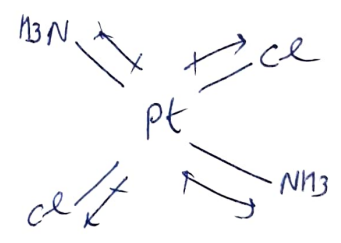
Q) How will you confirm the presence of geometrical isomerism by chemical or physical methods, for detecting geometrical isomerism in co-ordination compounds.

1. Dipole moment :-



$\mu \neq 0$

$\mu \neq 0$

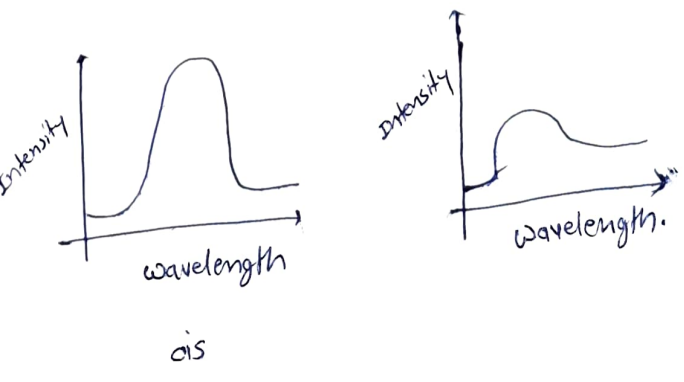


$\mu = 0$

- The dipole moment of cis-isomers is always far greater than the trans isomer.

2) UV-Spectra:-

- A trans-isomer is more symmetrical & d laporte's selection is less  $\therefore$  the UV transitions will be less intense as compared to the cis-isomer. relaxation selection is



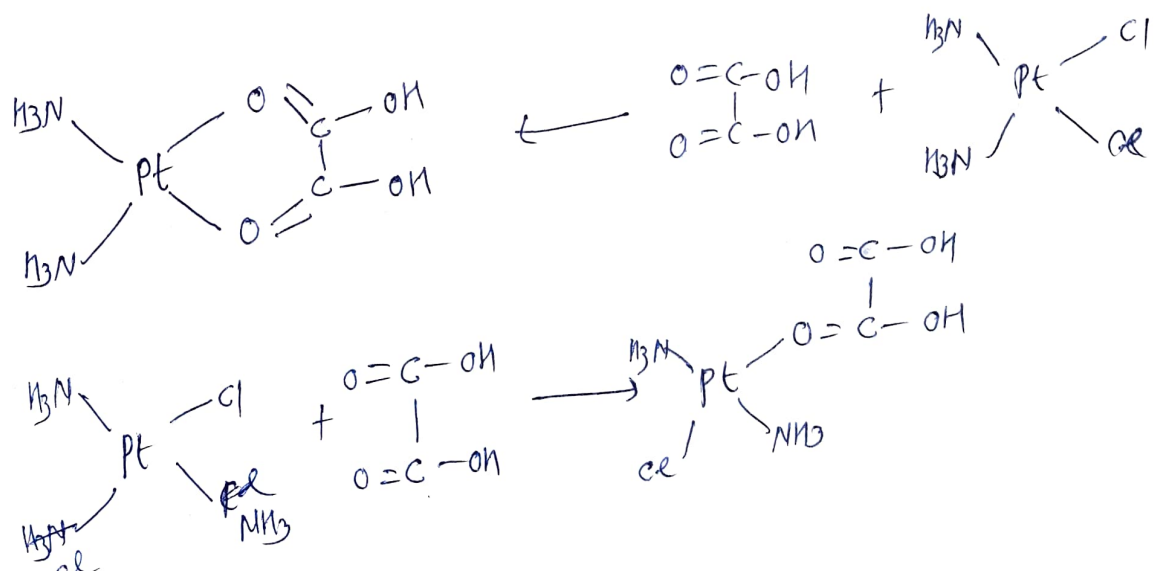
3) IR-Spectra:-

- Essential condition of IR-spectra is that it shows only those bands in which there is a change in dipole moment during vibrations.

- As the trans isomer is more-symmetric the no. of IR-bands are lesser in it's case than associated with the cis-isomer.

4) chemical method:-

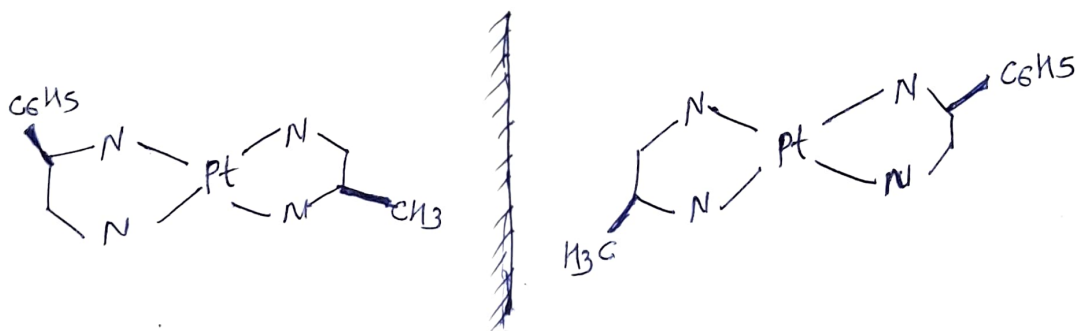
- The detection of geometrical isomerism can be done by reacting them with bidentate ligands.



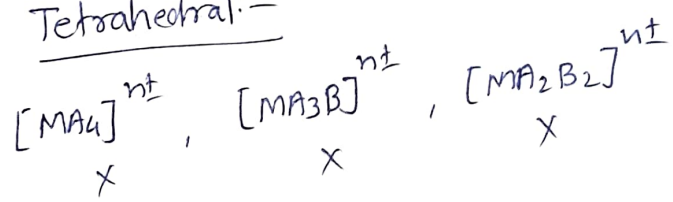
2) optical isomer:-

a) square planar: - most of the  $sp$ -complexes possess molecular plane of symmetry even when all four ligands are different.

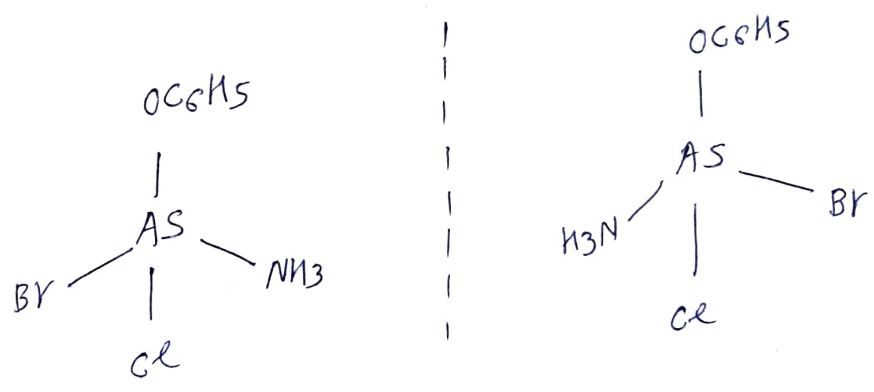
∴ square-planar complexes rarely show optical isomerism.  
- ~~Some~~ some of the exceptional cases are.



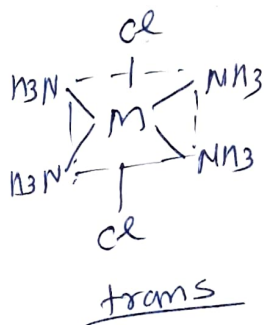
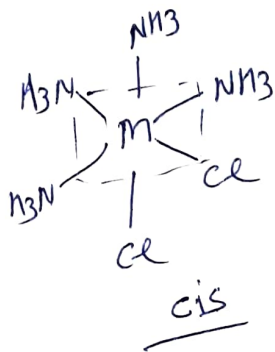
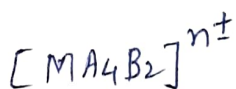
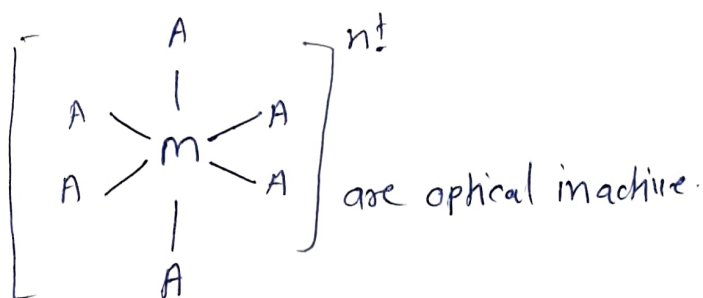
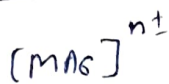
b) Tetrahedral:-



$[MABCP]^{n\pm}$  will show optical isomerism.

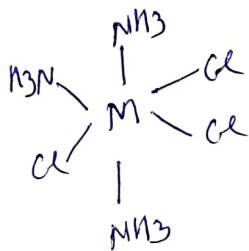
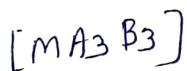


c) octahedral:-

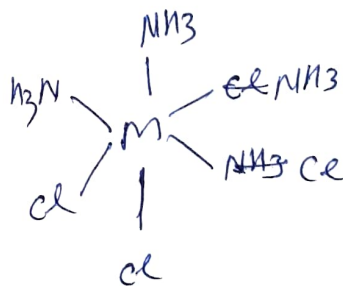


inactive

Both of the cis & trans isomer possess plane of symmetry  
 $\therefore$  Both are optically inactive.

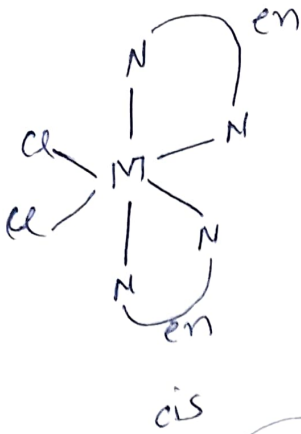
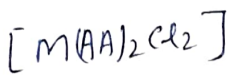


trans | meridional

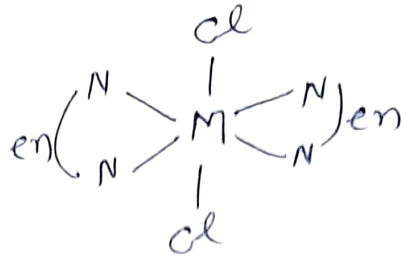


cis | facial

inactive

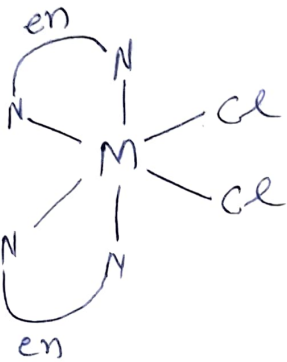


Active

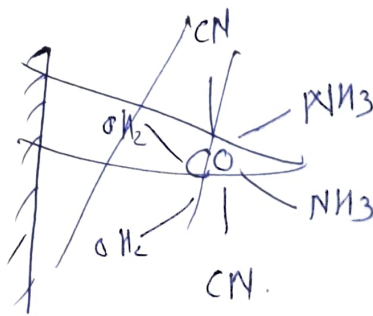
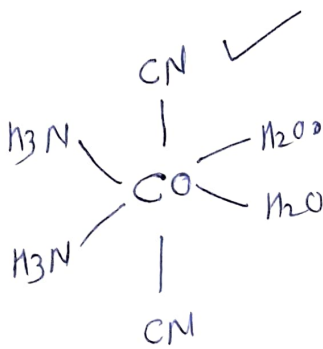


trans.

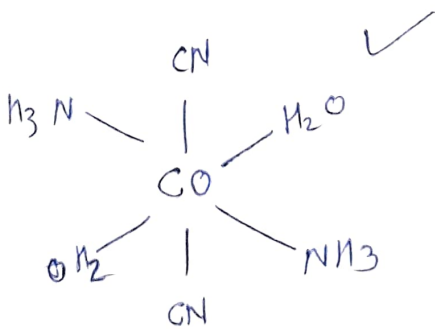
Inactive



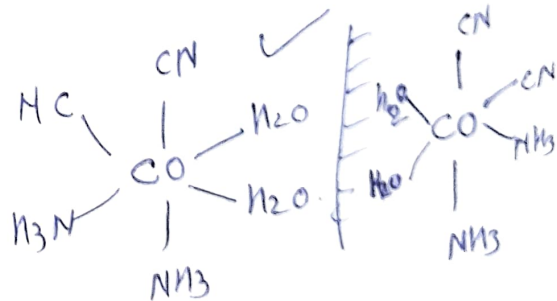
Q)  $[Co(CN)_2(H_2O)_2(NH_3)_2]^+$  draw all stereoisomers [10m] [2023]

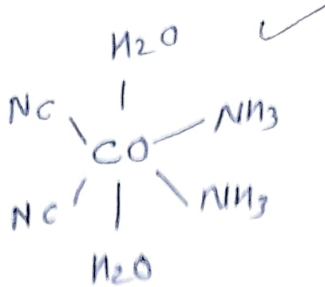
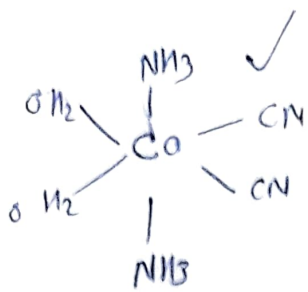


optical



trans.





## • Nomenclature of co-ordination compounds:-

- 1) If a co-ordination compound is ionic then the cation is named first followed by the name of anion. The cation and anion names are separated by a space.
- 2) If a co-ordination compound is neutral the name of the compound is written in a single word.
- 3) If a co-ordination compound is a complex ion then the ligands are named first. In the name of complex ion the ligands are named first in alphabetical order before the name of metal ion or atom. The prefix di, tri, tetra are not used to determine the alphabetical order.
- 4) The oxidation number of metal cation or atom is written in roman numerals in parentheses ( ) immediately after the name of the metal without any space.
- 5) If the complex contains more than 1-ligand of particular kind then prefix like di, tri, tetra, penta are used for 2, 3, 4, 5 & hence forth.
- 6) If the name of a ligand itself contains the prefix di, tri, tetra then the prefix is bis, tris, tetrakis, pentakis must be used to specify the no. of ligands.
- 7) The prefix bis, tris are also used for complex ligands.
 

e.g.  $(\text{C}_6\text{H}_5\text{NH}_2)_2$   
           ↓  
       bis methylamine.
- 8) The names of anionic ligands end with letter 'o'. They are usually obtained by changing anion ending with Ido to -o, ite to ito (nitrite -nitrito), ate to ato



g) The vowel ending the numeral prefix of the ligand will not be ignored while writing the name.

e.g. tetraqua  $\rightarrow$  tetraaqua

tetraamine  $\rightarrow$  tetraamine

- Mono is an exception

10) For a complex ion if the metal is a cation or neutral the usual name of metal is used, but if the complex ion is anionic it is added at the end of the name of metal replacing -ium or other suffix

water

aqua

$\text{NH}_3$

ammine

$\text{Cl}^-$

chloro/chlorido

$\text{en}^-$

ethylene-1,2-diamine.

$\text{OH}^{2-}$

oxalato

$\text{NO}_2^-$

Nitrito - N

$\text{ONO}^-$

Nitrito - O

$\text{NO}_3^-$

Nitrate

$\text{CN}^-$

cyanido or cyano

$\text{NC}^-$

isocyanido or isocyano

$\text{SCN}^-$

Thiocyanato

$\downarrow$   
(thiocyano)

isothiocyanato

$\text{NCS}^-$

Carbonyl

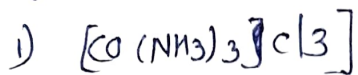
CO



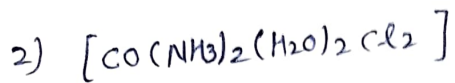
NO

Nitrosyl

e.g.



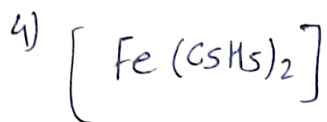
triammine trichlorocobalt(III)



diammine diaqua dichloro cobalt(II)



tetracarbonyl Nickel(0)



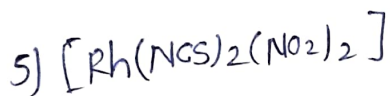
Bis(cyclopentadienyl)ferrous(II)

Bis(cyclopentadienyl) iron

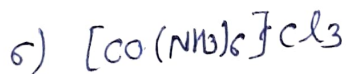
C<sub>5</sub>H<sub>5</sub><sup>-</sup>



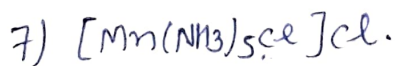
cyclopentadi-ene  
+  
cyclopentadienyl  
anion.



diisothiocyanatodi(nitro ~~thio~~-N) rhodium(IV)



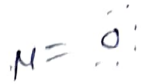
Hexaammine cobalt(III) chloride



Pentaamminechloro manganese(II) chloride.



~~Pentaaquanitrosyliron(III) sulphate~~



Pentaaquanitrosyliron(III) sulphate



1  
Potassium ferricyanide

~~Potassium ferrocyanide~~

~~Potassium ferrocyanide~~

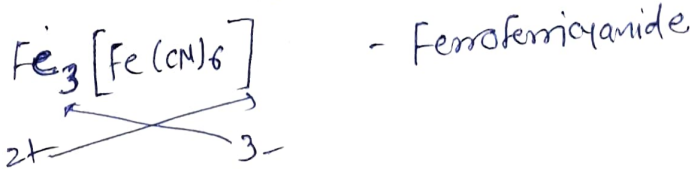
Potassium hexacyanidoferrate (II)



Iron hexacyanidoferrate (II)



Iron hexacyanidoferrate (II)

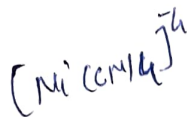


Ferro -  $2^+$

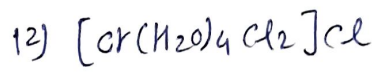
Ferri -  $3^+$



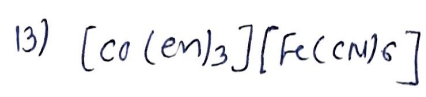
Ferrous hexacyanidoferrate (III)



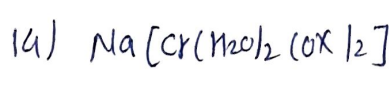
18  
12  
9



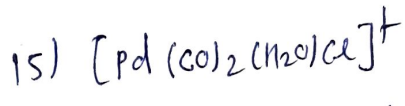
Tetraaqua dichlorochromium(III) chloride



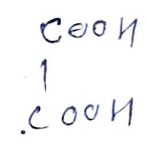
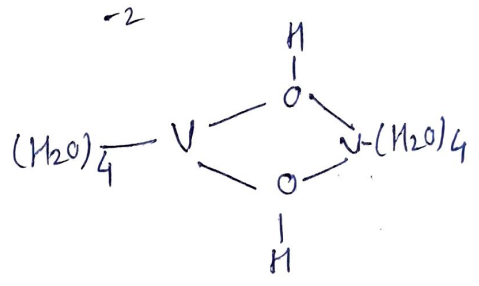
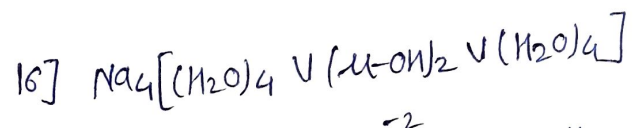
tris(ethylenediamine)cobalt(III) hexacyanido ferrate  
tris(ethylenediamine)cobalt(III) hexacyanido ferrate(III)



sodium diaquadioxalatochromate(III)  
sodium diaqua bisoxalatochromate(III)



aqua dicarbonylchloro palladium(II)



ethane-1,2-dioic acid

$\mu$  - represents the presence of bridged ligand.

~~di-hydroxobis~~

di- $\mu$ -hydroxobis(tetraaqua)vanadate(I)

$4 + (-2) + x = 0$

$x = -2$

## • Kinetic stability:

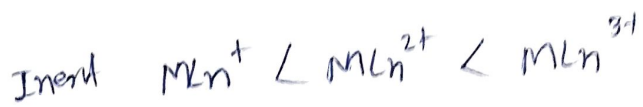
### 1) Inertness & lability in octahedral complex:

#### • Factors affecting:

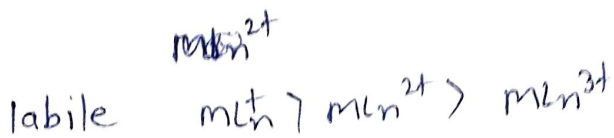
#### 1) oxidation state of metal ion:

- Higher the oxidation state more is the inertness.

O.S & Inertness.



| w.r.t. metal is same



### 2) Non-transition metal v/s Transition metal:

- ~~non~~ Transition metals means those which have vacant d-orbital.

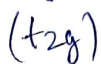
- Non T.S. metals are more labile  
e.g. Zn, Cd, & Hg.

\* In non-transition metal complexes lability increases down the group as size increases.

\* In Transition metal, lability decreases down the group as  $Z_{eff}$  increases.

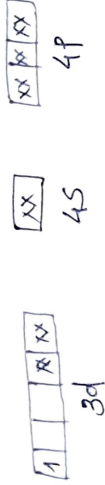
### 3) Electronic configuration:-

- There are two factors depending on the configuration of metal ion leading to its lability either it should have low lying vacant d-orbitals or it should have a low CFSE value.



e.g.  $[Ti(H_2O)_6]^{3+}$

$d^{(oh)}$  - labile.



- This complex contains low lying vacant d-orbitals ( $t_{2g}$ ) are available where the formation of a associative intermediate can easily take place & the reaction can be carried out quickly.  $\therefore$  The  $d^{(oh)}$  complexes are generally labile

$d^2(oh)$  - labile



$d^3(oh)$  (inter) (High CFSE)



$d^4$   
 $HS \rightarrow$  low CFSE  $\rightarrow$  labile  
 $LS \rightarrow$  High CFSE  $\rightarrow$  inert

$d^5$   
 $HS \rightarrow$  low CFSE  $\rightarrow$  labile  
 $LS \rightarrow$  High CFSE  $\rightarrow$  inert.



$0$   
 (H.S.) (L.S.)

$d^6$   
 $HS \rightarrow$  low CFSE  $\rightarrow$  labile  
 $LS \rightarrow$  High CFSE  $\rightarrow$  inert



$-0.4 \Delta_0$   
 (H.S.) (L.S.)

$2.4 \Delta_0$   
 (L.S.)

$d^7(\text{oh}) \xrightarrow{\text{LS}} \text{low CFSE} \rightarrow \text{labile}$   
 $d^7(\text{oh}) \xrightarrow{\text{HS}} \text{High CFSE} \rightarrow \text{inert}$



$d^7(\text{oh}) \xrightarrow{\text{LS}} \text{labile (due to weak Strong J.T.D)}$

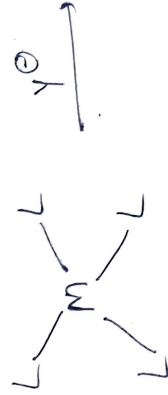
$\tau\text{-1.8 Do (L.S)}$

$d^8(\text{oh}) \rightarrow \text{Inert}$

$d^9(\text{oh}) \rightarrow \text{labile (due to J.T.D)}$

## II] substitution in square planar complexes:-

1) ~~Associative~~ bimolecular mechanism



C.N = 4



C.N = 5



- The substitution in square planar complexes is affected by multiple effects one of them is trans effect.