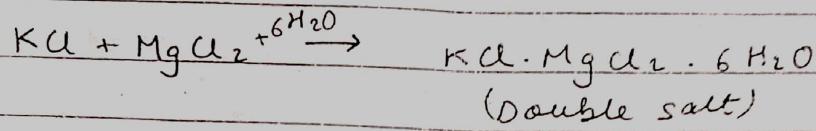


## Coordination chemistry

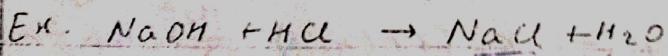
KCl (single salt)

MgCl<sub>2</sub> (" ")



### Simple salt:

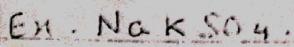
When an acid reacts with an alkali, neutralisation takes place & simple salt is produced.



When dissolved in water, these salts ionise & produce ions in sol<sup>+</sup>.

### Mixed salt:

They contain more than one acidic or basic radicals.



### Molecular or addition compounds:

When sol<sup>+</sup> containing two or more salts in a stoichiometric proportion, is allowed to evaporate we get crystals of compound known as molecular or addition compounds.

They are of two types depending on their

behaviors in aq. sol<sup>n</sup>:

1. Double salt (cattice compound)

These are additional compounds which are stable in solid state but give their constituent ions when dissolved in water or in any other ion solvent. In these compounds, the individual properties of constituent ions are not lost.

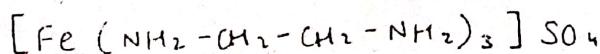
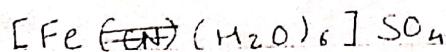
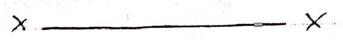
For ex.  $KAlMgCl_2 \cdot 6H_2O$  gives  $K^+$ ,  $Mg^{+2}$  &  $Cl^-$  ions.

Mohr's salt ( $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ )

and potash alum ( $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ )

2. Coordination or complex compounds:

It has been observed that when sol<sup>n</sup> of  $Fe(CN)_6^{4-}$  +  $KCN$  are mixed together & evaporated; potassium ferrocyanide is obtained which in aq. sol<sup>n</sup> does not give test of  $Fe^{+2}$  ions &  $CN^-$  ions, but gives test of  $K^+$  ions and  $[Fe(CN)_6]^{4-}$  ions.



[ ] : ionisation sphere  
 or  
 coordination sphere  
 +ve      -ve      or neutral

∴ Coordination sphere may be anion or cation or both

Acc. to VBT, bond b/w central atom & ligand is  
coord<sup>n</sup> bond (b/w filled & empty orbital)  
 $\text{C}_n \text{ I}_o$  bond

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Date \_\_\_\_\_

③

central atom :

D-block element present in a coordination sphere which may bond with ligands is central atom.

ligands :

It is an ion or molecule which makes bonds with central atom ion in a coordination sphere.

It is an ion or molecule capable of donating a lone pair of  $e^-$  to the central atom.

Valency

→ Primary : oxidation no. charge on coordination sphere

→ Secondary : coordination no.

Coordination no. :

C.N. =  $\sum$  No. of ligands  $\times$  no. of dented nature

Metal ion

Min. O.N.  $\rightarrow$  CN

Fe

$\text{Fe}^{+2} \rightarrow 6$

Au

$\text{Au}^{+} \rightarrow 2$

Ag

$\text{Ag}^0$

Hg

$\text{Hg}^{+2}$

Cu

$\text{Cu}^{+} \rightarrow 2, 4$

Zn

$\text{Zn}^{+2}$

Cd

$\text{Cd}^{+2} \rightarrow 4$

Co

$\text{Co}^{+2} \rightarrow 4, 6, 5$

Ni

$\text{Ni}^{+2} \rightarrow 4, 6$

Pt

$\text{Pt}^{+2} \rightarrow 4$

$\text{Mo}^{+4} \rightarrow 7$ ,  $\text{W}^{+4} \rightarrow 8$

$\text{Cu}^{+2}, \text{Pt}^{+2}, \text{Ni}^{+2}, \text{Mn}^{+2}, \text{Pd}^{+2}, \text{Zn}^{+2}, \text{Ni}^{+}$  have C.N. = 4

$\text{Fe}^0 \rightarrow 5$ ;  $\text{Fe}^{+2}, \text{Fe}^{+3}, \text{Co}^{+3}, \text{Pt}^{+4}, \text{Cr}^{+3}, \text{Cr}^0, \text{Ni}^{+2}, \text{In}^{+3}$  have C.N. = 6

Max. O.N.  $\rightarrow$  CN

$\text{Fe}^{+3} \rightarrow 6$

$\text{Au}^{3+} \rightarrow 4$

$\text{Ag}^{+1} \rightarrow 2$

$\text{Hg}^{+1} \rightarrow 4$

$\text{Cu}^{+2} \rightarrow 4$

$\text{Zn}^{+2} \rightarrow 4$

$\text{Cd}^{+2} \rightarrow 4$

$\text{Co}^{+3} \rightarrow 6$

$\text{Pt}^{+4} \rightarrow 6$

(c)

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Types of ligands :

- On the basis of dented nature or classification based on the no. of donor atoms present
- On the basis of charge
- On the basis of interaction b/w ligands & central atom

\* b) On the basis of charge

Anionic ligands/  
-ve ligands

Ex.  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{Br}^-$ ,  
 $\text{F}^-$ ,  $\text{CO}_3^{2-}$ , etc.

Positive ligands

Ex.  $\text{NO}^+$ ,  $\text{NH}_2-\text{NH}_3^+$ ,  
etc.  $\text{Ph}_3^+$

Neutral ligands

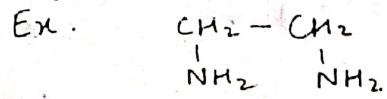
Ex.  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NC}$ ,  
 $\text{CO}$ ,  $\text{C}_6\text{H}_6$ , etc.

a) On the basis of no. of potential donor atoms (denticity)

• Mono-dented -

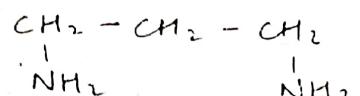
Ligands with only one donor atom. Ex.  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ .

• Bi-dented - (poly-dented starts from bi-dented)  
Ligands with two donor atoms.

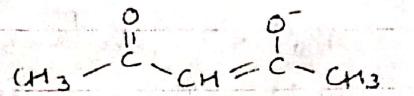
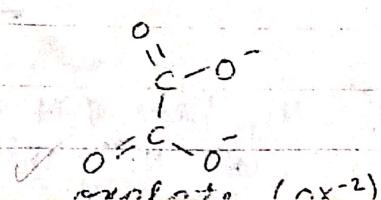


Ethylenediamine ✓  
or

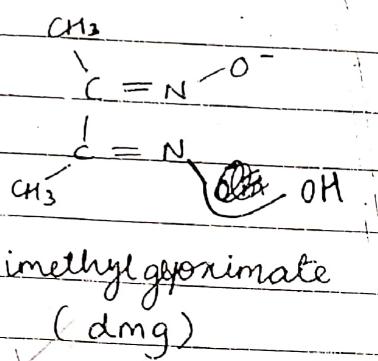
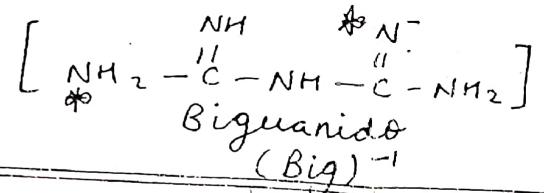
Ethane-1,2-diamine  
✓ (en)



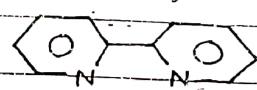
Trimethylenediamine  
(tn) ✓



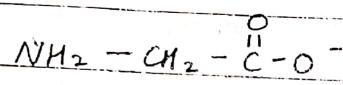
acetylacetone ion  
( $\text{acac}^-$ )



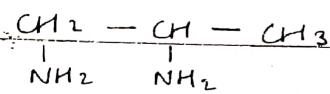
Dimethylglyoximate  
 (dmg)



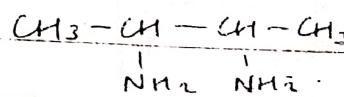
dipyrydyl  
 (dipy)



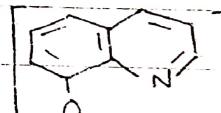
glycinato  
 (gly)



1,2 diaminopropane  
 Propylene diamine  
 (Pn)



Butyl Butylenediamine  
 (bn)

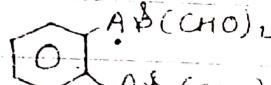


(oxin)<sup>-</sup> (oxinate)

2-Hydroxyquinolinato



1,10 phenanthroline  
 (phen)

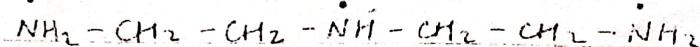


O-phenylene bis(dimethyl arsine)  
 diarylarsine  
 or  
 (D)

Tri-dentate

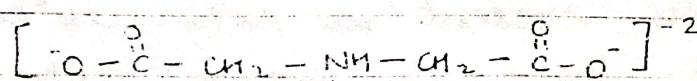
Ligands which have 3 donor atoms.

Ex:



Diethylene triamine

or dien

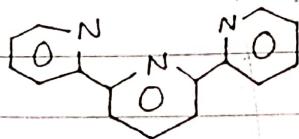


Imino-di-acetato

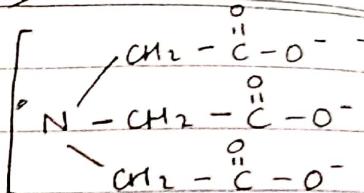
(TNA)<sup>-2</sup>

6

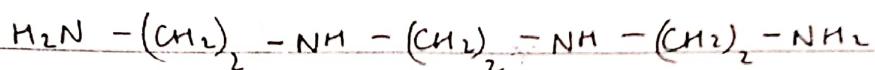
Tetradentate

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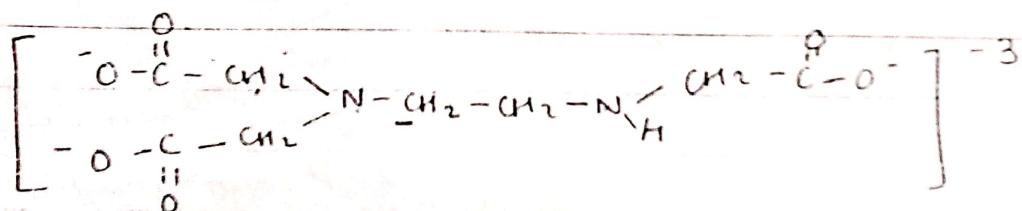
2, 2', 2'' terpyridine  
or  
(terpy)



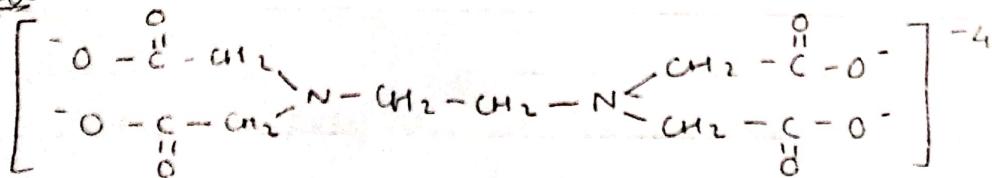
Nitrilotriacetato,  
or  
 $(\text{NTA})^{-3}$



Tri - ethylene tetra amine  
or  
(trien)

Penta

Ethylenediaminetetraacetato  
[EDTA]<sup>-3</sup>

Henna

Ethylenediaminetetraacetato  
[EDTA]<sup>-4</sup>

Poly-dentated ligands have flexibility in dentate character. It is not necessary that all the donor atoms present in poly-dentated ligands should form coordinate bonds with central metal atom. For ex. Ethylenediaminetetraacetic acid [EDTA]<sup>-4</sup>

Flexidentate  $\rightarrow$  denticity depends on comp. formed.

(7)

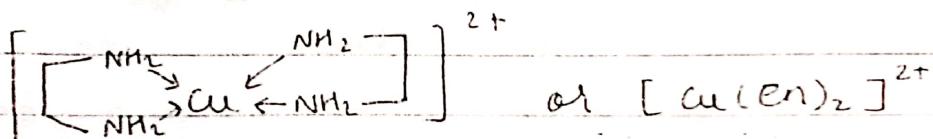
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which is hexa-dented can function as penta-dented, tetra-dented ligands with certain metals.  
Similarly, sulphate ion can also act as mono-dented ligands.

Chelating ligand:

A bi-dented or poly-dented ligand is known as chelating ligand if it produces one or more ring with central atom during bond formation. Chelating ligands form more stable complex.

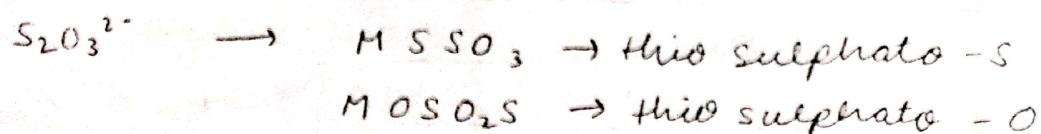
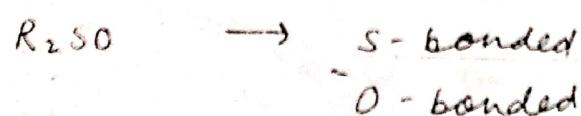
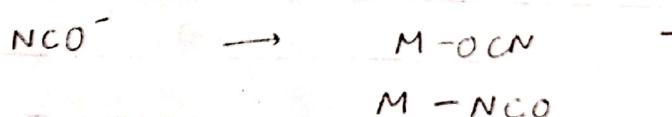
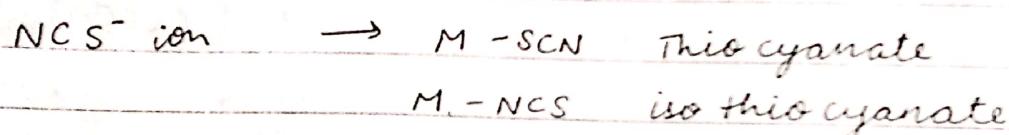
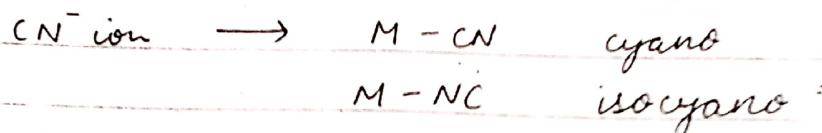
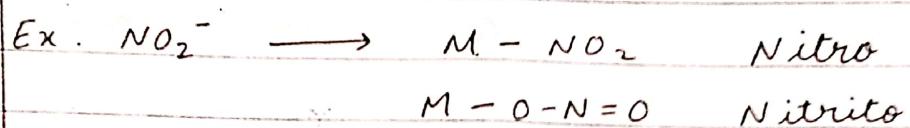
Ex.



Chelating complex.

### Ambi-dentate ligands:

These are ligands which have two or more donor atoms, but in forming complex only one donor atom is attached to metal ion at a given time. Such ligands are ambidentate ligands.



c) On the basis of interaction b/w ligands & central atoms:

i. Classical or simple donor ligands -

Ligands only donate lone pair of  $\text{e}^-$  to central atom

Ex.  $\text{NH}_3$ ,  $\text{NH}_2^-$ ,  $\text{H}_2\text{O}$ , etc.

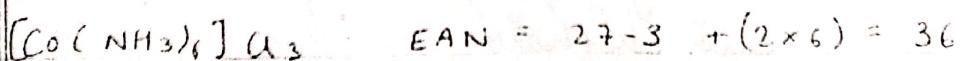
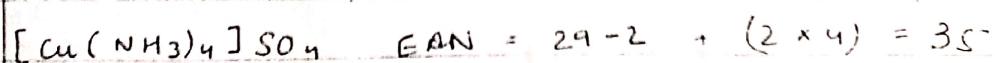
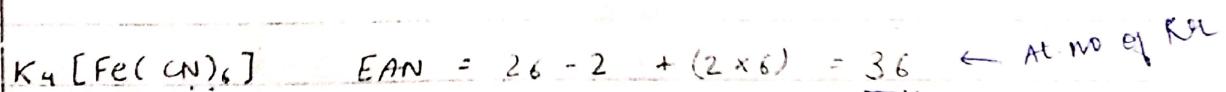
Non-classical ligands or  $\pi$ -acid or  $\pi$ -acceptor ligands - These ligands not only donate their lone pair to central atom but also gain  $\bar{e}$ -cloud from the central atom in their low-lying vacant ( $5\sigma_m$ ) orbitals. This kind of back donation is called synergic effect.

Ex.  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , etc.,  $\text{CN}^-$ ,  $\text{PR}_3$   $R = \text{H/Ph/Et}$   
 Antipriong (NE empty)  $\text{CO}_2$ ,  $\text{NO}^+$ ,  $\text{PF}_3$ .

Effective atomic number (EAN):

$EAN = \text{At. no. of metal} - \text{no. of } \bar{e} \text{ lost in ion formation} + \text{no. of } \bar{e} \text{ gained from the donor atom of ligands}$

It is defined as resultant no. of  $\bar{e}$  with metal atom or ion after gaining  $\bar{e}$  from the donor atoms of the ligand -



EAN concept has been particularly successful for complexes of low-valent metals (i.e. O.N.  $< 4$ )

Sidgwick suggested that complex in which EAN of central atom is equal to at. no. of next noble gas are extra stable but this is found to be incorrect in many complexes. EAN rule is valid in case of

## metal carbonates and metal carbonyls.

Rules for nomenclature :

- Naming of ligands : (according to alphabetical order)

### Naming of -ve ligands

A, E, I, O, U replaced by O

H<sup>-</sup> : Hydrido

O<sup>-2</sup> : oxo

O<sub>2</sub><sup>-2</sup> : Peroxo

O<sub>2</sub>H<sup>-</sup> : perhydroxo = (H<sub>2</sub>O<sub>2</sub>)

F<sup>-</sup> : Fluorido

Cl<sup>-</sup> : Chlorido

Br<sup>-</sup> : Bromido

I<sup>-</sup> : Iodido

CO<sub>3</sub><sup>-2</sup> : Carbonato

C<sub>2</sub>O<sub>4</sub><sup>-2</sup> : Oxalato

CH<sub>3</sub>COO<sup>-</sup> : acetato

EDTA<sup>-4</sup> : Ethylene diamine tetraacetato

SO<sub>4</sub><sup>-2</sup> : Sulphato

SO<sub>3</sub><sup>-2</sup> : Sulphito

S<sup>-2</sup> : Sulphido

HSO<sub>3</sub><sup>-</sup> : Hydrogen sulphito

S<sub>2</sub>O<sub>3</sub><sup>-2</sup> : Thio sulphato

HS<sup>-</sup> : Mercapto

NH<sub>2</sub><sup>-</sup> : Amido or Azaanido

NH<sup>-</sup> : Imido or Azane diido

NO<sub>3</sub><sup>-</sup> : Nitrato

ONO<sup>-</sup> : Nitrito-O / O-nitro

NO<sub>2</sub><sup>-</sup> : Nitro / Nitrito-N / N-nitro

N<sup>-3</sup> : Nitrido

CN<sup>-</sup> : cyano / cyanido

$\text{N}_3^-$  : Azido $\text{SCN}^-$  : thiocyanato - S $\text{NCS}^-$  : iso thiocyanato - N $\text{HCO}_3^-$  : Hydrogen carbonato $\text{S}_4\text{O}_6^-$  : tetra thionoso

If the ligand is an organic anion then the name of ligand does not end with 'o'.

 $\text{Ph}^-$  Phenyl $\text{CH}_2=\text{CH}_-$  Vinyl $\text{CH}_3^-$  Methyl

For the  $\pi$  donor ligands prefix  $\eta^x$  is used, where  $\eta$  indicates  $\pi$ -electron donation and  $x$  is known as the capacity of the ligand (no. of atoms involved in the  $\pi$ -donation)

Ex.  $\pi\text{-C}_5\text{H}_5^-$   $\eta^5$  (cyclopentadienyl) $\pi\text{-C}_6\text{H}_6$   $\eta^6$  (Benzene)2 pi bonds  
& 1 lone pair

3 pi bonds

→ Homoleptic complexes : In which metal atom/ion is linked to only 1 type of ligand.  
eg:  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

→ Heteroleptic complexes : In which metal atom/ion is linked to more than 1 type of ligands. eg:  $[\text{Cr}(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Br}_2]^+$

→ Labile complex : complex in which ligands can be easily replaced by other ligands

→ Homonuclear complex : in which only 1 metal atom is present. eg:  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

→ Polymeric complexes : more than 1 metal atom/ion present  
eg) any bridge complex

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### Neutral ligands:

$\text{H}_2\text{O}$  : Aquo / Aqua

$\text{CO}$  : Carbonyl

$\text{NH}_3$  : Ammine

$\text{NO}$  : Nitrosyl

$\text{CS}$  : Thio carbonyl

$\text{NS}$  : Thio nitrosyl

$\text{C}_5\text{H}_5\text{N}$  : Pyridine

$\text{NH}_2-\text{NH}_2$  : Hydrazine

$\text{PH}_3$  : Phosphine

$\text{O}_2$  : di oxygen

$\text{Ph}_3\text{P}$  : tri phenyl phosphine



Dipyridyl

$\text{N}_2$  : di nitrogen

$\begin{matrix} \text{CH}_2 & - \text{CH}_2 \\ | & | \\ \text{NH}_2 & \text{NH}_2 \end{matrix}$  (en) : Ethylene diamine

or  
ethane - 1, 2 - diamine

$\text{NH}_2 - \overset{\text{S}}{\underset{\text{H}}{\text{C}}} - \text{NH}_2$  : Thio urea



acetone

### +ve ligands :

Neutral ligand + iun

$\text{NO}^+$  : Nitrosylium / Nitrosonium

$\text{NH}_2-\text{NH}_3^+$  : Hydrazinium

$\text{H}_3\text{O}^+$  : Hydronium

Indication of no. of ligands:

No. of simple ligands such as  $\text{Cl}^-$ , Acetate ion is indicated by using before them Greek prefix: di, tri, tetra, etc.

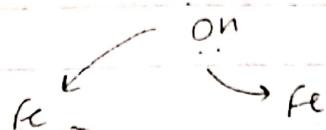
In case of chelating ligands like (en) & trialkyl phosphine which contain prefix di, tri, etc. in their ligand's name, we have bis for 2, tris for 3, tetrakis for 4, penta kis for 5.

Ligands to which these prefixes refer are often placed in parentheses.

Bridge ligands:

Mono dentate ligands may have more than 1 free pair and thus, may simultaneously coordinate w/ two or more atoms. Ligands form 2 sigma bonds with two metal atoms & thus, act as a bridge b/w metal atoms. Such ligands are called bridging ligands & resulting complex is bridge complex.

Ex.  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_3^-$ , etc.



Naming of bridge ligands of bridged poly nuclear complexes:

Complexes having two or more metal atoms are called poly-nuclear complexes. In these complexes bridging grp is indicated in the formula of complex by separating it from the rest of complex by hyphen & by adding the prefix  $\mu$  before its name. Two or more bridging grps of same kind are indicated by di- $\mu$ , tri- $\mu$ .

Naming of central atom: -

If coordination sphere has +ve or 0 charge, then central metals follow English name.

If coordination sphere has -ve charge then central metals follow Latin name.

Latin names:

Iron - Ferrate

Silver - Argentate

Copper - Cuprate

Gold - Aurate

Lead - Plumbate

Tin - Stannate

Chromium - chromate

Platinum - Platinate

Mercury - Mercurate /

Cobalt - Cobaltate

Nickel - Nickelate

Aluminum - Aluminate

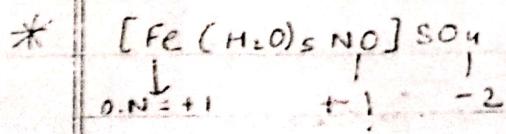
Q. Name the following compounds:

1.  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$  - Hexa ammine platinum (IV) chloride
2.  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}\text{Cl}]\text{Cl}$  - Tetra ammine aqua chloride cobalt (II) chloride
3.  $[\text{Cu}(\text{en})_2]\text{SO}_4$  - Bis (ethylene diamine) copper (II) sulphate
4.  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  - Tetra aqua di chloride chromium (III) ion
5.  $[\text{Fe}(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)]\text{SO}_4$  - Tetra aqua oxalato iron (III) sulphate
6.  $[\text{Cr}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{NO}_3$  - Tetra ammine chloride  $\text{o-nitro}$  chromium(III) nitrate
7.  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  - Di ammine silver (I) chloride
8.  $[\text{Co}(\text{NH}_3)_5\text{Cl}(\text{NCS})]\text{Cl}_2$  - Penta ammine isothiocyanato-N cobalt(II) chloride
9.  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl}$  - Triis triphenyl phosphine rhodium (I) chloride
10.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  - Potassium hexa cyanido ferrate (V)
11.  $\text{K}_3[\text{Fe}(\text{CN})_6]$  - Potassium hexa cyanido ferrate (VI)
12.  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  - Potassium tri oxalato <sup>chromate</sup> chromium (VI)
13.  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$  - Potassium dichlorido de oxalato cobaltate (III)
14.  $\text{K}_2[\text{HgI}_4]$  - Potassium tetra iodido mercurate (II)
15.  $\text{K}_2[\text{PtCl}_6]$  - Potassium hexa chloride platinate (IV)
16.  $\text{Na}[\text{Ag}(\text{CN})_2]$  - Sodium di cyanide argenteate (I)

C

17.  $[\text{Ni}(\text{CN})_4]^-$  - Tetra cyanido nickelate(IV) ion
18.  $\text{Na}_3 [\text{Co}(\text{NO}_2)_6]$  - Sodium hexa nitro cobaltate (III)
19.  $\text{K}_3 [\text{Fe}(\text{CN})_5 \text{NO}]$  - Potassium penta cyanido nitrosyl ferrate(II)
20.  $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$  - Hexa ammine chromium (III)  
hexa cyanido cobaltate (III)
21.  $[\text{Pt}(\text{NH}_3)_4] [\text{CuCl}_4]$  - Tetra ammine platinum (II)  
tetra chlorido cuprate (II)
22.  $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{C}_2\text{O}_4)_3]$  - Hexa ammine chromium (III)  
Tri oxalato cobaltate (III)
23.  $[\text{Pt}(\text{Py})_4] [\text{PtCl}_4]$  - Tetra pyridine platinum (II)  
tetra chlorido platinato (II)
24.  $\text{Fe}(\text{CO})_5$  - Penta carbonyl iron (0)
25.  $[\text{Co}(\text{NO}_2)_3 (\text{NH}_3)_3]$  - Tri ammine trinitro cobalt (III)
- 26.  $\text{Cu}(\text{gly})_2$  - Di glycinate copper (II)
- 27.  $\text{Ni}(\text{DMG})_2$  - Bis di methyl glyoximato nickel (II)
- \* 28.  $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{a. } 2\text{H}_2\text{O}$  - Tetra aqua di chlorido chromium (III) chloride di hydrate
29.  $[(\text{NH}_3)_5 \text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5] \text{Cl}_5$  -  $\mu$ -hydroxido bis (penta ammine penta ammine chromium(III)- $\mu$ -hydroxido penta ammine chromium(III) chloride
30.  $[(\text{H}_2\text{O})_4 \text{Co} \begin{smallmatrix} \text{ON} \\ \swarrow \\ \text{NH}_3 \end{smallmatrix} \text{Co} \begin{smallmatrix} \text{ON} \\ \searrow \\ \text{NH}_3 \end{smallmatrix} (\text{NH}_3)_4] \text{SO}_4$
31.  $[(\text{en})_2 \text{Co} \begin{smallmatrix} \text{N}^+ \\ \text{ON} \\ \swarrow \\ \text{en} \end{smallmatrix} \text{Co} \begin{smallmatrix} \text{N}^+ \\ \text{ON} \\ \searrow \\ \text{en} \end{smallmatrix} (\text{en})_2] (\text{SO}_4)_2$
32.  $[(\text{H}_2\text{O})_4 \text{Fe} \begin{smallmatrix} \text{ON} \\ \swarrow \\ \text{en} \end{smallmatrix} \text{Fe}(\text{H}_2\text{O})_4] (\text{SO}_4)_2$

33.  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$  - Bis (cyclopenta dienyl) iron (II)
34.  $\text{NO}_2[\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]]$  - Sodium penta cyanido nitro-silium ferrate (II)
35.  $\text{K}_4[\text{FeO}_4]$  - Potassium tetra oxido ferrate (IV)
36.  $\text{K}_2[\text{Co}(\text{N}_3)_4]$  - Potassium tetra azido cobaltate (II)
37.  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_4]\text{NO}_3$  - Tetra ammine sulphate cobalt (III) nitrate
38.  $\text{Li}[\text{AlH}_4]$  - lithium tetra hydrido aluminate (II)
39.  $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$  - Potassium ammine di cyanido di oxo per oxo chromate (II)



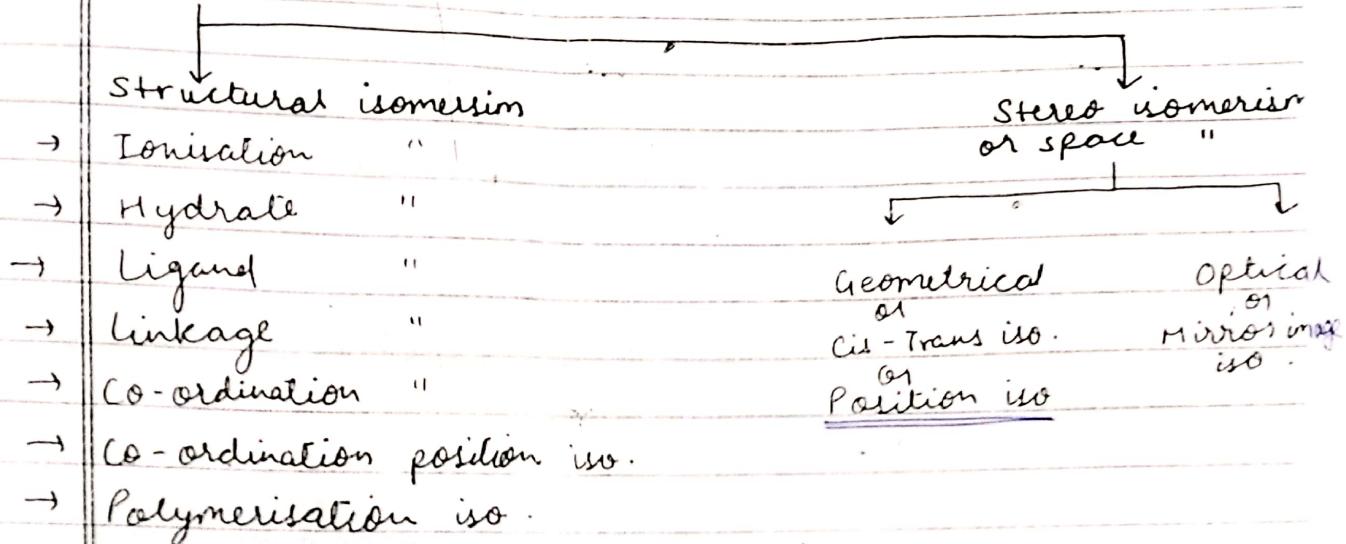
30.  $\rightarrow$  Bis (ethane-1,2-diamine) cobalt (III)  $\mu$ -amido- $\mu$ -hydroxo bis (ethane-1,2-diamine) cobalt (III) sulphate

or,

Tetra bis (ethane-1,2-diamine)- $\mu$ -amido- $\mu$ -hydroxo di cobalt (III) sulphate

32. Tetra aquo iron (III)  $\xrightarrow{\text{di-}} \mu$ -hydroxo - tetra aquo Iron (III) sulphate

### Isomerism :

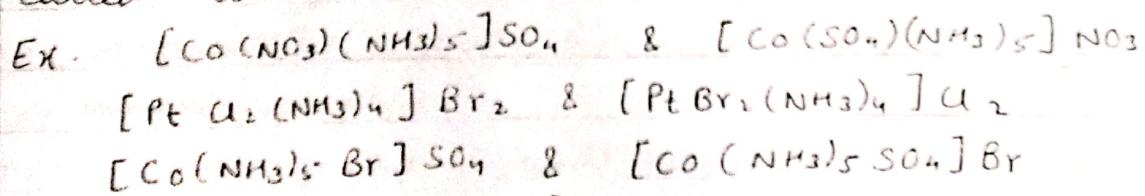


### Structural isomerism :

This isomerism arises due to difference in structure of coordination compounds.

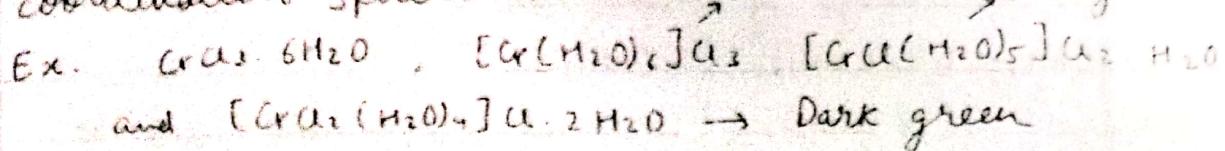
#### 1. Ionisation iso. :-

Complexes which have same empirical formula but give different ions in sol's on ionisation are called ionisation isomers.



#### 2. Hydrated iso. :

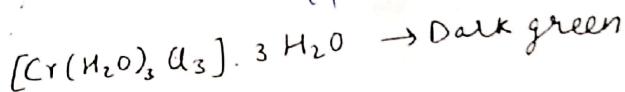
This type of isomerism arises due to different pos<sup>n</sup> of water molecule inside & outside of the coordination sphere.



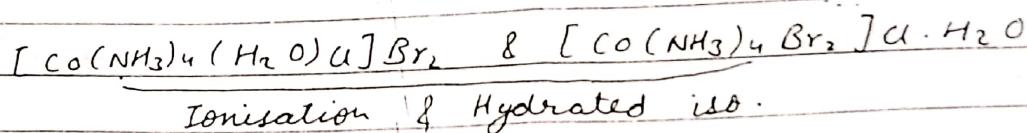
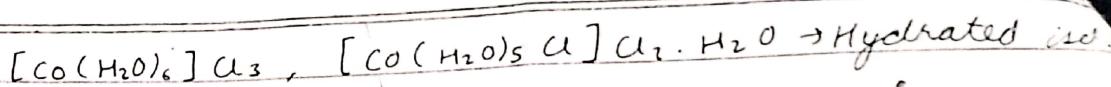
Violet → Does not lose water over  $\text{HgSO}_4$  & also all  $\text{Cr}^{+3}$  ions are immediately ppt.d by  $\text{Ag}^+$

Pale green → Lose water over  $\text{HgSO}_4$ , 2  $\text{Cr}^{+3}$  ions are ppt.d by  $\text{Ag}^+$

Dark green → loses water, 1  $\text{Cr}^{+3}$  ion ppt.d

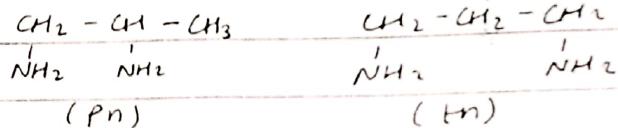


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### 3. Ligand isomers:

Some ligands themselves are capable of existing as isomers. Ex.

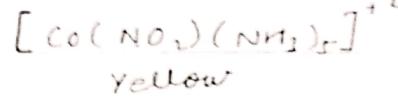
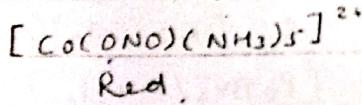
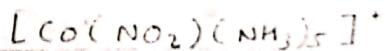


### 4. Linkage isomers:

This type of isomerism is found in those complexes in which ligands can coordinate with central metal ion through either of two atoms.

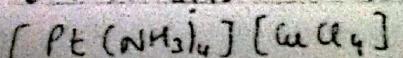
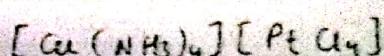
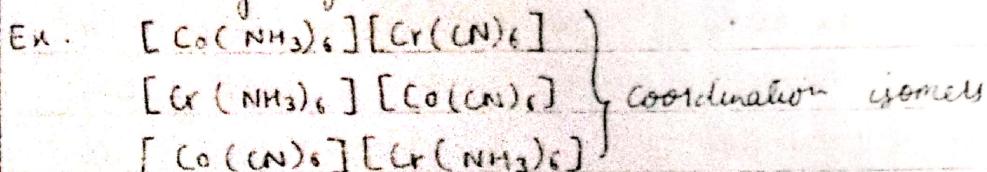
Ambi-dentate ligands are involved in linkage isom.

Ex.

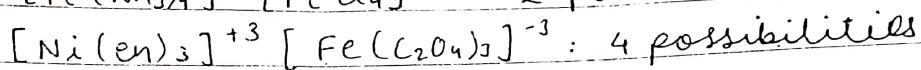
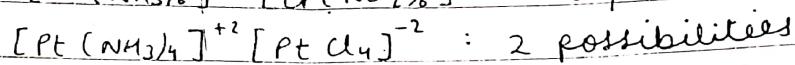
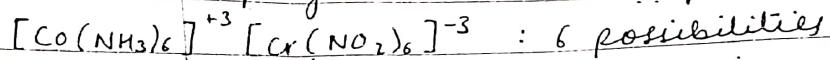


### 5. Coordination isomers:

Coordination compounds made up of cationic & anionic coordination spheres show this isomerism due to interchange of cationic & anionic ligands or due to interchange of central atoms.

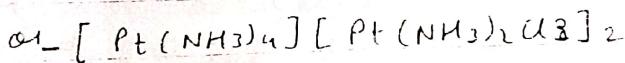
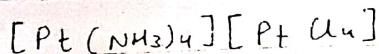
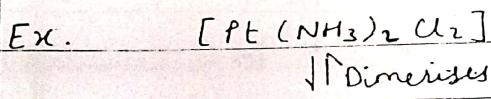


Some such isomers are expected to have significant differences in their physical & chemical properties.



#### → 6. Polymerisation isomers:

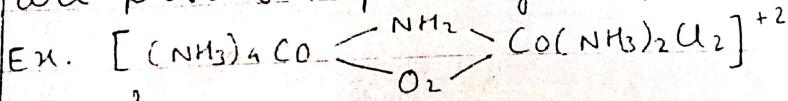
They denote this is not true isomerism because it occurs b/w compounds having same empirical formula but different molecular weight. Molecular compositions are simple multipliers of simplest stoichiometric co<sub>n</sub>t arrangement.



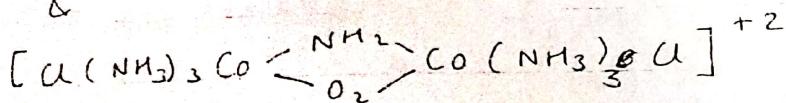
#### → 7. Coordination position isomers

This isomerism arises in poly-nuclear complexes. An interchange of ligands b/w different metal nuclei in poly-nuclear complex

To interchange the ligands b/w metal nuclei which are present as part of complex, is possible.



&

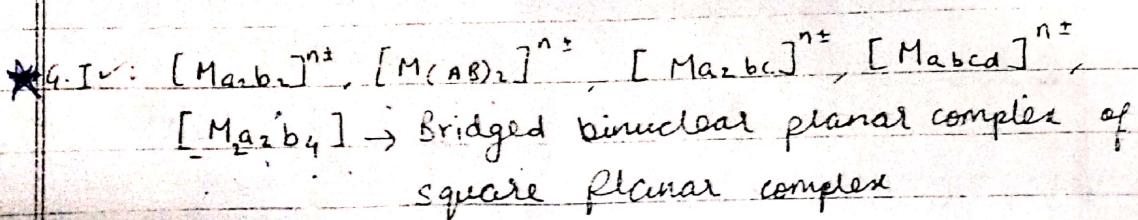
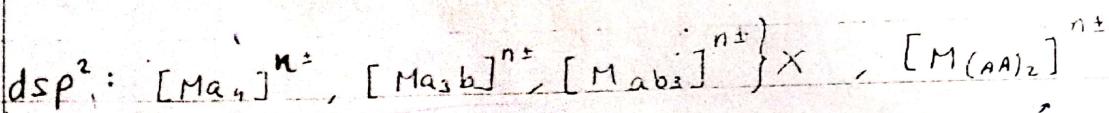
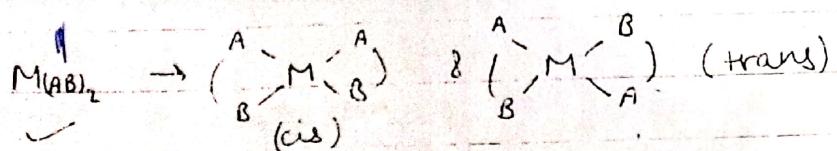
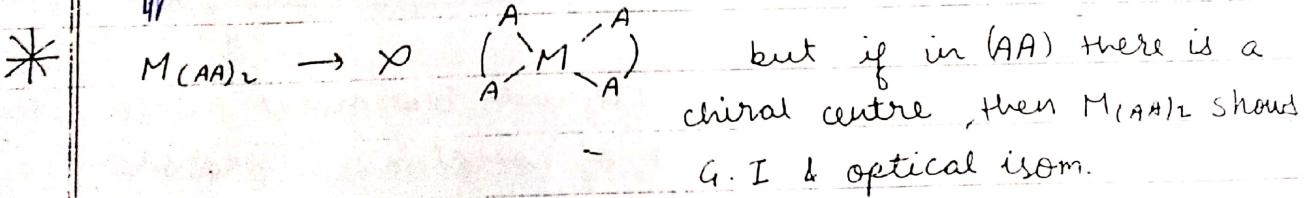
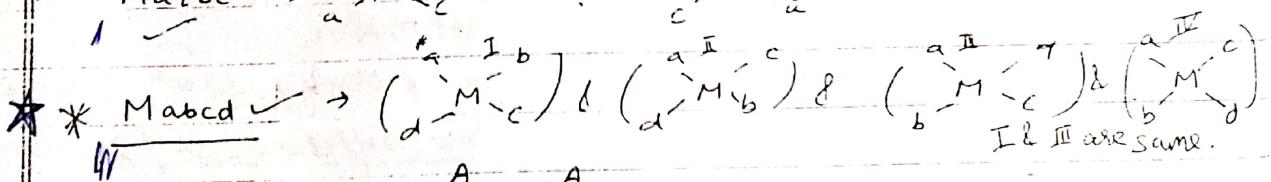
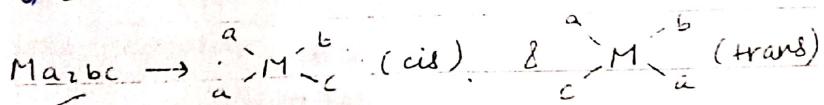
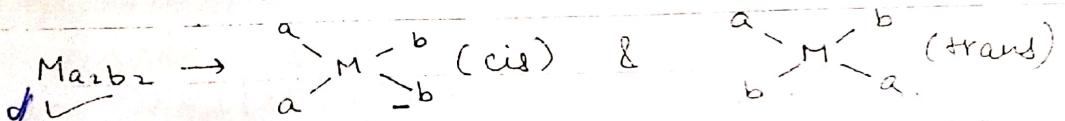
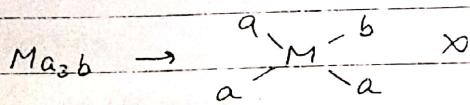
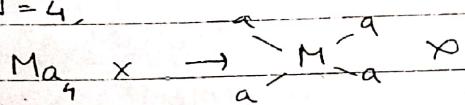


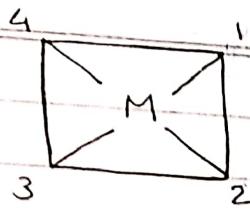
Stereo isomers → G.I :  
→ O.I,

G.I :

$CN = 4 \rightarrow sp^3 \Rightarrow$  tetrahedral ✗ (no geometrical iso.)  
 $\downarrow \rightarrow d\,sp^2 \Rightarrow$  square planar ✓ (geometrical iso.)

$CN = 6 \rightarrow sp^3 d^2 \checkmark$  Octahedral  
 $\downarrow \rightarrow d^2 sp^3 \checkmark$

Ex.  $CN = 4$ ,

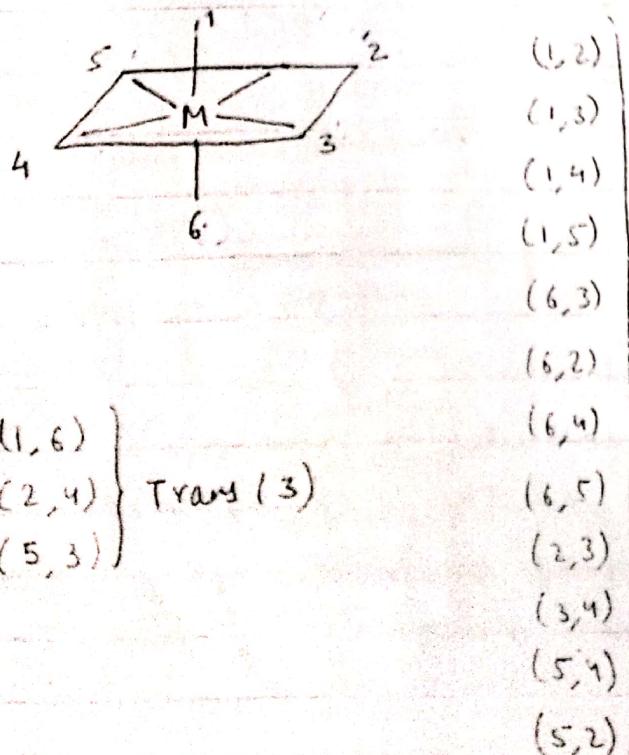
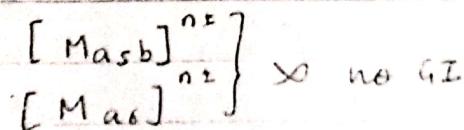
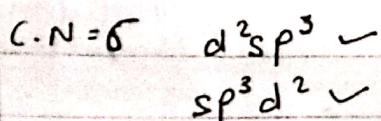
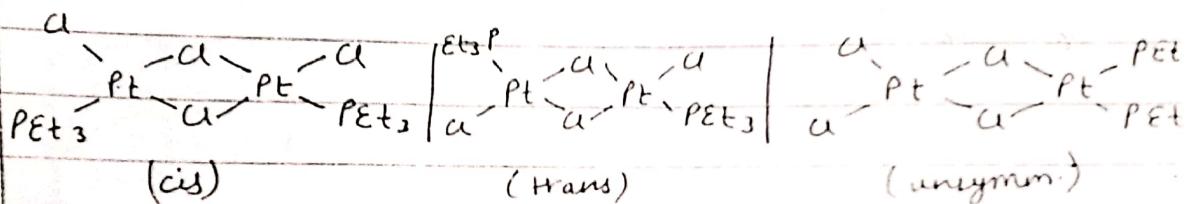


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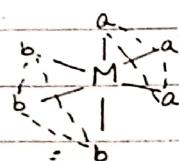
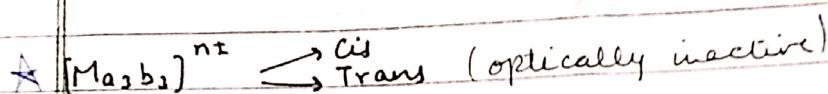
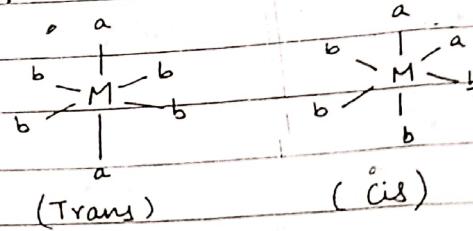
 $(4, 3), (1, 2) \Rightarrow \text{cis}$  $(1, 3), (4, 2) \Rightarrow \text{Trans}$ 
 $[\text{Pt}(\text{P}(\text{Et}_3)_2)]_2 \rightarrow \text{Total no. of isomers}$ 

= 3

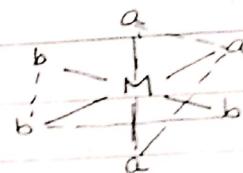
Symm.                          Unsymm.  
 cis + Trans



$M_{ab}^{2}$ :

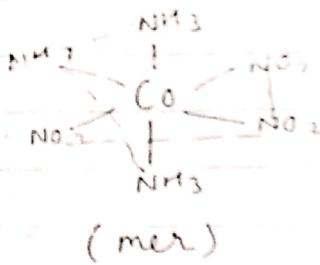
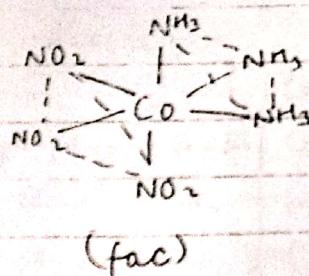


cis (Facial isomers)  
or fac isomers



Meridional  
Trans (Meridional or mer)  
or peripheral "

Ex.  $[Co(NO_2)_3(NH_3)_3]$



Optical isomers:

Conditions for molecules to show O.I.:

1. No plane of symmetry (no symmetry).
2. Molecules should be non-superimposable with its mirror image.

C.N = 4 :  $sp^3 \checkmark \rightarrow M_{abcd} \checkmark$   
 $a \neq b \neq c \neq d$   
 $dsp^2 \times$

$[M_{abbc}] \times$

$[M_{abbc}] \times$

$[M_{ac}] \times$

C.N = 6 :  $d^2sp^3 \checkmark$   
 $sp^3d^2 \checkmark$

# Stereoisomerism in Octahedral Complexes

Types of complex	Geometrical Isomers (Cis + Trans)	Optical Isomers (O.A. + O.Inactive)	Total S.I.
$[M_{4}a_{2}b_{2}]^{n\pm}$	2(1Cis + 1Trans)	No Optical Isomers	2
$[M_{4}a_{2}bc]^{n\pm}$	2(1Cis + 1Trans)	No Optical Isomers	2
$[M_{3}a_{3}b_{3}]^{n\pm}$	2(1Cis + 1Trans)	No Optical Isomers	2
$[M_{3}a_{2}b_{2}c]^{n\pm}$	3(1Cis + 2Trans)	No Optical Isomers	3
$[M_{3}a_{2}bcd]^{n\pm}$	4(1Cis + 3Trans)	5(2 + 3)	5
$[M_{2}a_{2}b_{2}c_{2}]^{n\pm}$	5(1Cis + 4Trans)	6(2 + 4)	6
$[M_{2}a_{2}b_{2}cd]^{n\pm}$	6(2Cis + 4Trans)	8(4 + 4)	8
$[M_{2}a_{2}bcde]^{n\pm}$	9(6Cis + 3Trans)	15(12 + 3)	15
$[Mabcdef]^{n\pm}$	15(Cis & trans not defined)	30(30 + 0)	30

Types of complex	Geometrical Isomers (Cis + Trans)	Optical Isomers (O.A. + O.Inactive)	Total S.I.
$[M(AA)_3]^{n\pm}$	No Geometrical Isomers	2(2 + 0)	2
$[M(AA)_2b_2]^{n\pm}$	2(1Cis + 1Trans)	2(2 + 1)	3
$[M(AA)_2bc]^{n\pm}$	2(1Cis + 1Trans)	3(2 + 1)	3
$[M(AA)b_2c_2]^{n\pm}$	3(1Cis + 2Trans)	4(2 + 2)	4
$[M(AA)b_2c]^{n\pm}$	2(1Cis + 1Trans)	No Optical Isomers	2
$[M(AA)b_2cd]^{n\pm}$	4(2Cis + 2Trans)	6(4 + 2)	6
$[M(AA)bcde]^{n\pm}$	6(Cis & trans not defined)	12(12 + 0)	12

Types of complex	Geometrical Isomers (Cis + Trans)	Optical Isomers (O.A. + O.Inactive)	Total S.I.
$[M(AB)_3]^{n\pm}$	2(1Cis + 1Trans)	4(4 + 0)	4
$[M(AB)_2c_2]^{n\pm}$	5(1Cis + 4Trans)	8(6 + 2)	8
$[M(AB)_2cd]^{n\pm}$	6(2Cis + 4Trans)	11(10 + 1)	11
$[M(AB)c_2d_2]^{n\pm}$	4(2Cis + 2Trans)	6(4 + 2)	6
$[M(AB)c_2d]^{n\pm}$	3(1Cis + 2Trans)	4(2 + 2)	4
$[M(AB)c_2de]^{n\pm}$	7(4Cis + 3Trans)	12(10 + 2)	12
$[M(AB)cdef]^{n\pm}$	12(Cis & trans not defined)	24(24 - 0)	24