Inorganic

# ISOMERISM IN COORDINATION COMPOUNDS

The compounds with
same molecular formula
different Physical properties
different Chemical properties
different structure

Two kinds

- Structural isomerism
- Stereo isomerism

type of isomerism which arises due to difference in structures of coordination compds.

due to different ligands present in their coordination sphere.

Types
- Ionization Isomerism
- Hydrate Isomerism
- Coordination Isomerism
- Linkage Isomerism

OPPO F19S

# Ionization Isomerism

Cord$^n$. C. Same molecular formula but gives different ions in a solution.

M.F → $Co(NH_3)_5ISO_4$

$[Co(NH_3)_5I]SO_4$ $\quad$ $[Co(NH_3)_5SO_4]I$

$[Co(NH_3)_5I]SO_4 \xrightarrow{H_2O} [Co(NH_3)_5I]^{+2} + SO_4^{-2}$

$[Co(NH_3)_5SO_4]I \xrightarrow{H_2O} [Co(NH_3)_5SO_4]^{+1} + I^{-1}$

OR

Difference in type of ions produced

$[Pt(NH_3)_4Cl_2]Br_2$ $\quad$ $[Pt(NH_3)_4Br_2]Cl_2$

1, 3, ~~4~~ 8, 12, 13, 27, 28, 32

Lead acetate

$Pb(CH_3COO)_2 \rightarrow Pb^{+2} + CH_3COO^-$

aq. sol$^n$ $[Co(NH_3)_5I]SO_4$

$\xrightarrow{H_2O} [Co(NH_3)_5I]^{+2} + SO_4^{-2}$

aq. sol$^n$ of compd + lead acetate

↓

White ppt

↓

due to the rxn $Pb^{+2} + SO_4^{-2}$

↓

$PbSO_4$

Lead acetate

aq. sol$^n$ $[Co(NH_3)_5SO_4]I$

$\xrightarrow{H_2O} [Co(NH_3)_5SO_4]^{+} + I^-$

aq. sol$^n$ of comp + lead acetate

↓

Yellow ppt

↓

$Pb^{+2} + 2I^-$

↓

$PbI_2$

Different color ppt confirms that the both compds ionized differently.

# Hydrate Isomerism (Solvate Isomerism)

→ Same molecular formula

→ different no. of $H_2O$ molecules inside and outside the coord$^n$ sphere.

$CrCl_3 \cdot 6H_2O \rightarrow$
- $[Cr(H_2O)_6]Cl_3$
- $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
- $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

$[Cr(H_2O)_3Cl_3]^0 \cdot 3H_2O$ ✗

$+3 + 0 - 3 = x$

$x = 0$

∴ charge on complex is 0.

& ~~tout~~ to bind $H_2O$, ion dipole ~~a~~ attraction is required so, this is not valid / will not exist.

# Coordination Isomerism :

Both the cation & Anion are complex ions
↓
arises due to interchange of ligand between the complex or two sphere

$[Co(NH_3)_6][Cr(CN)_6] \longleftrightarrow [Cr(NH_3)_6]$ cation $[Co(CN)_6]$ anion

cation anion

$+3+(-1\times 6)=x$
$x=-3$

* Cations always written first then anion

$[Cu(NH_3)_4][PtCl_4]$ $\begin{cases}\text{Total -ve charge} = -4\\ \text{Total positive} = +4\end{cases}$

By permutation & comb$^n$ - possible isomers

→ $[Cu(NH_3)_3Cl]^{+1}$ $[Pt(NH_3)Cl_3]^{-1}$
→ $[Cu(NH_3)_2Cl_2]^{0}$ $[Pt(NH_3)_2Cl_2]^{0}$
→ $[Cu(NH_3)Cl_3]^{-1}$ $[Pt(NH_3)_3Cl]^{+1}$
→ $[CuCl_4]^{-2}$ $[Pt(NH_3)_4]^{+2}$

Second one is not possible, as both the sphere has 0 charge.

∴ Total 4 coord$^n$ isomers

Indicates diff. in linkage

# Linkage Isomerism :

this kind of isomerism occurs in the complex compds which contain ambidentate ligand.

have two donor atoms but at a time only one atom is directly linked to central atom

eg. $NO_2^-$ , $SCN^-$ , $CN^-$ , $OCN^-$

$ONO^-$ , $NCS^-$ , $NC^-$ , $NCO^-$

① $[Co(NH_3)_5(NO_2)]Cl_2$

$[Co(NH_3)_5(ONO)]Cl_2$

② $[Pt(H_2O)_4(NCS)(NO_2)]^{+2}$

$[Pt(H_2O)_4(NCS)(ONO)]^{+2}$

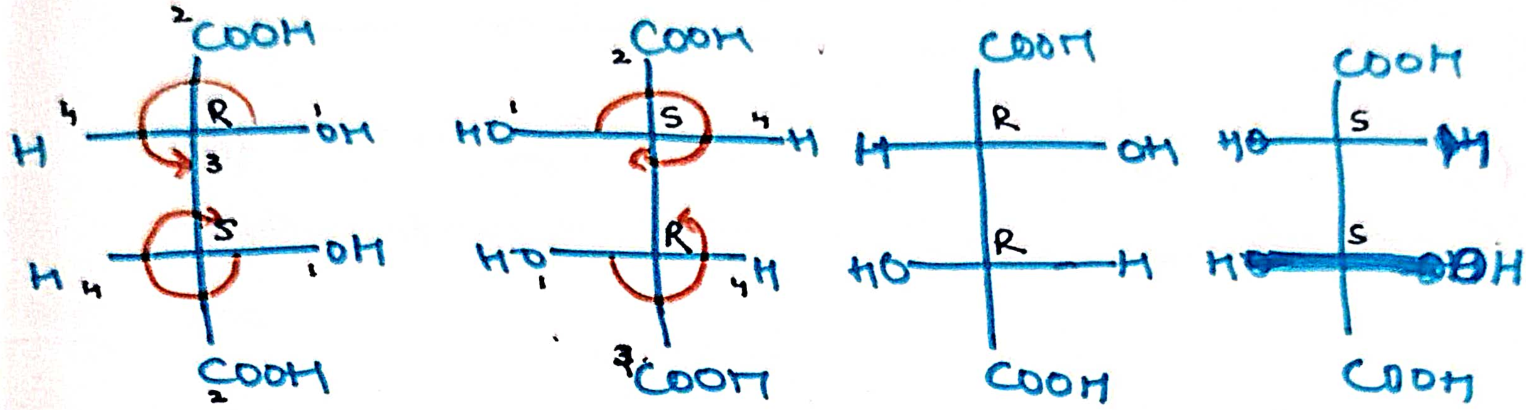
$[Pt(H_2O)_4(SCN)(NO_2)]^{+2}$

$[Pt(H_2O)_4(SCN)(ONO)]^{+2}$

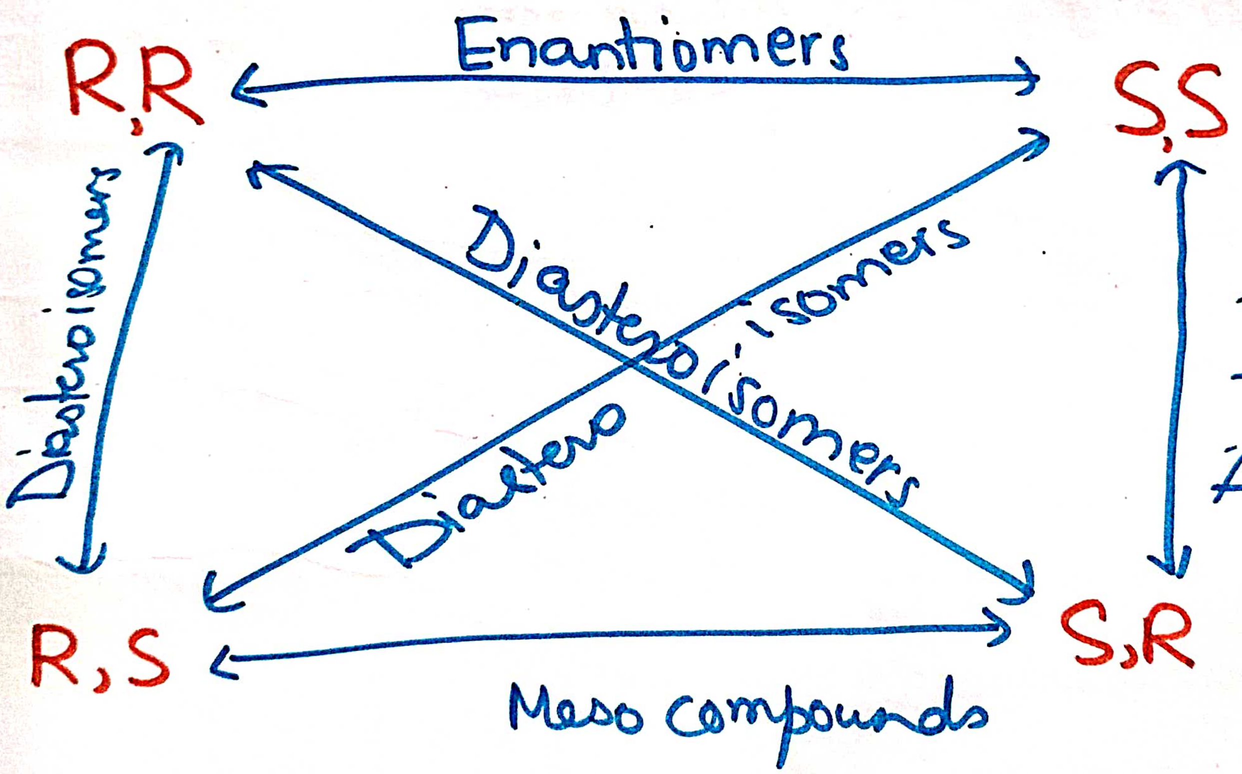
4 linkage isomers.

# Tartaric Acid

→ 2 Chiral C atom
↓
$2^n$ isomers = 4 isomers




(R,S) Tartaric acid S,R R,R S,S



# Stereoisomerism in Transition Metal Complexes or Coordination compds.

Stereoisomerism
due to orientation in space

- Geometrical isomerism
- Optical Isomerism

## CASE I – TETRAHEDRAL COMPLEXES ($sp^3$)

↓

do not show geometrical isomerism as 4 positions are identical.

# Geometrical Isomers

## Isomerism (Coord$^n$ Compds)
ML

- Structural
  - Ionization
  - hydrate
  - Linkage
  - Coordination
- Stereo isomerism
  different in orientat$^n$ of atoms in space.
  - Geometrical Isomers
    in which Ligands occupy different position around the Central metal
    - cis
      adjacent or at 90°
    - Trans
      opposite or at 180°

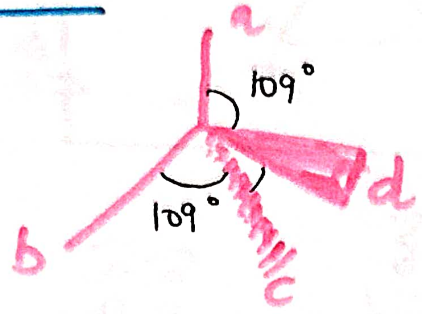
    K/a cis-trans isomers
  - Optical Isomers
    which shows optical activity
    ↓
    Rotates Plane polarized light
    ↓
    d / l.

→ Coordination No. 4
- Tetrahedral ($sp^3$)
- Square planar ($dsp^2$)

→ Coordination No. 6 → octahedral ($d^2sp^3/sp^3d^2$)

# Geometrical isomerism

## CASE I – Tetrahedral Complex

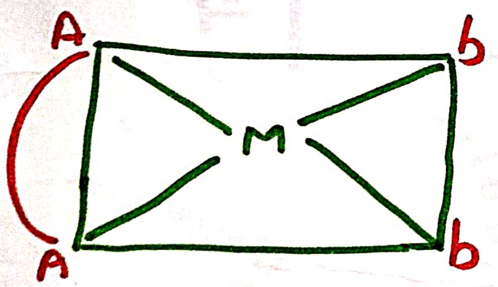



G·I not possible
↓
bcos all four positions are identical
↓
all the positions are at 109° angle wrt to each other

eg $[NiCl_4]^{-2}$
↓
$sp^3$ → No G·I

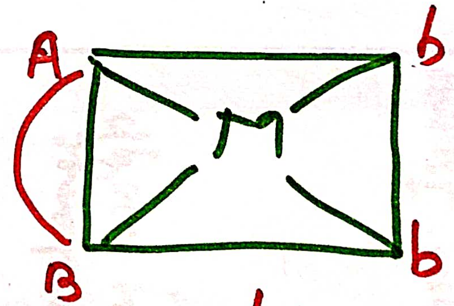
## CASE II – Square Planar Complexes $dsp^2$

$M(AA)b_2$




↓
No change after flip
↓
No G·I

$M(AB)b_2$

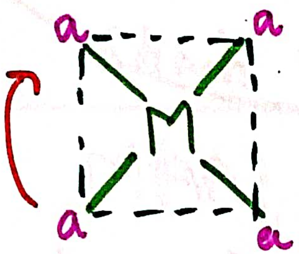



↓
No change after flip
↓
No. Geometrical Isomer

# Geometrical Isomers

## Square planar Complexes (Monodentate Ligand)

**Type** $Ma_4$




(a,a)
(a,a)

↓ Interchange any two gp

Same

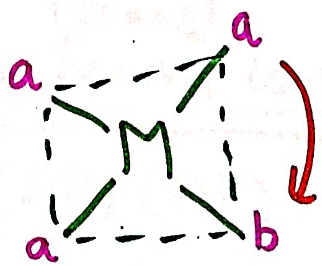
↓

No Geom. Isomer

$[PtCl_4]^{-2}$

**Type** $Ma_3b$

(a,a) (ab)




↓

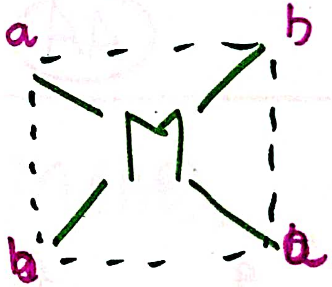
same

↓

No G.I

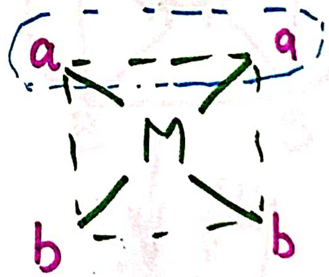
**Type** $Ma_2b_2$

(aa)(bb)
(ab) (ab)




Trans

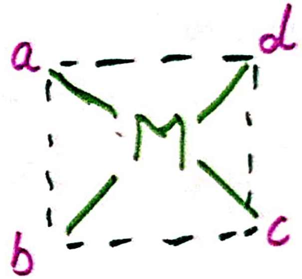
↓




Cis

2 G.Isomers

**Type** $Mabcd$




(ab)(cd)
(ac) (bd)
(ad)(bc)

3 Geom. Isomers

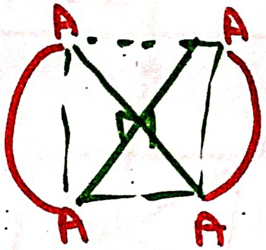
# Geometrical Isomerism
## Square Planar Complexes
### Bidentate ligand

* Bidentate ligand always bind at 90° (cis), not 180° (trans) as it increases strain & molecule becomes unstable

**Symmetrical** (en, $C_2O_4^{-2}$) same donor atoms (AA)

**Asymmetrical** (dmg, glycinate gly) different donor atoms (AB)

$M(AA)_2$

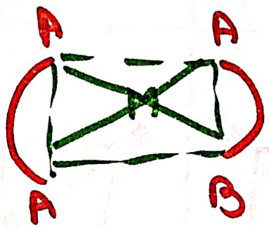



↓ Interchange or flip

Same

No Geo. Isomer

$M(AA)(AB)$

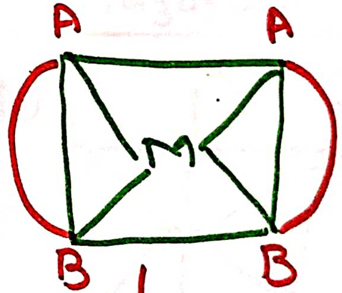



↓ Interchange/flip

Same

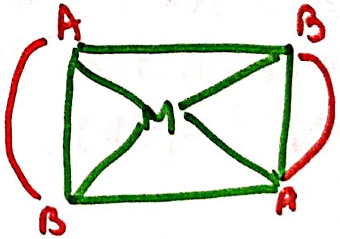
No Geom. Isomers

$M(AB)_2$




Cis

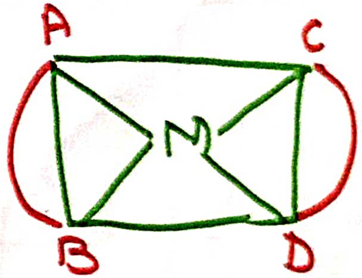
↓ flip




Trans.

2 Geom. Isomers

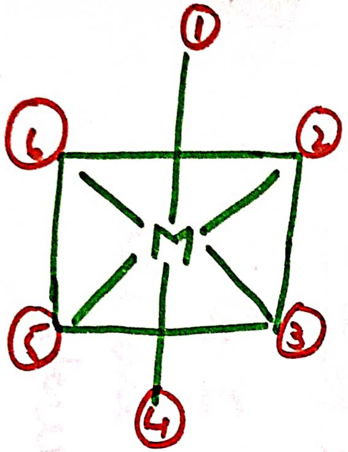
M(AB)(CD)




↓

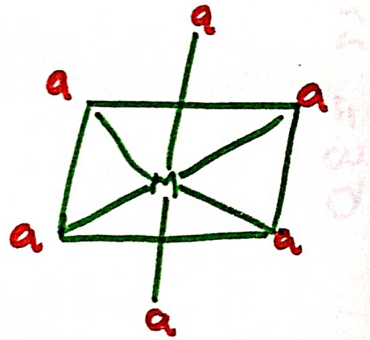
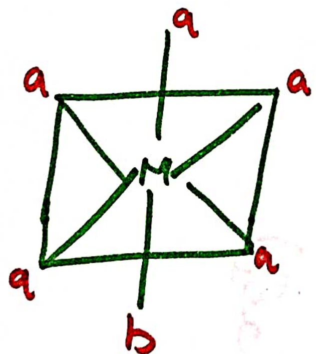
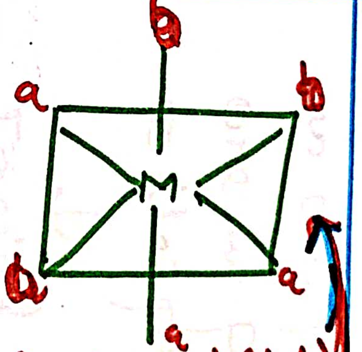
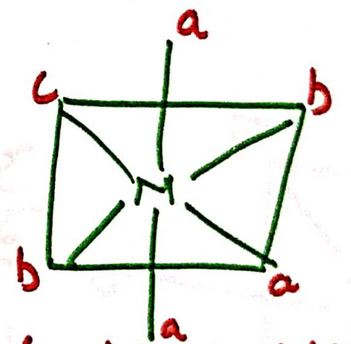
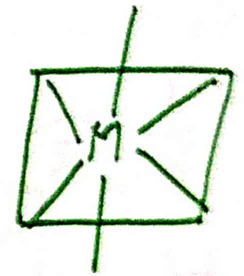
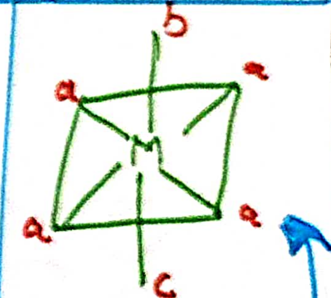
Two Geo. Isomers

# Geometrical Isomerism → Octahedral complexes




Cis → (1,2) (1,3) (1,5) (1,6)
90°  (4,2) (4,3) (4,5) (4,6)
(2,3) (3,5) (5,6) (6,2)

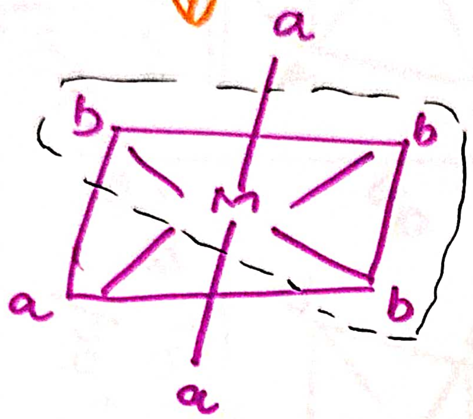
Trans → (1,4) (2,5) (6,3)
180°
opposite

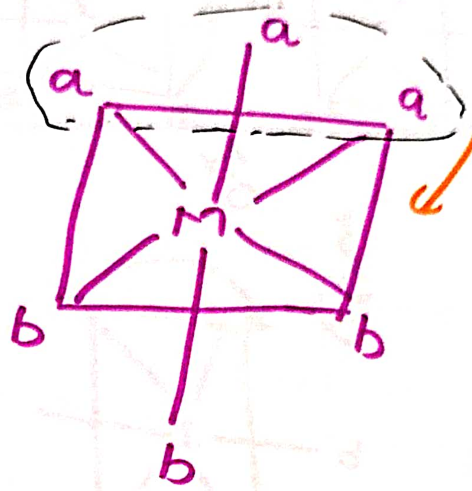
| $[Ma_6]$ | $[Ma_5b]$ | $[Ma_4b_2]$ | $[Ma_3b_2c]$ | $[Ma_3bcd]$ | $[Ma_4bc]$ |
|---|---|---|---|---|---|
|  |  |  |  |  |  |
| (aa) (aa) (aa) | (aa)(aa)(ab) | (aa) (aa) (bb)<br>(ab) (ab) (aa) | (aa)(ac) (bb)<br>(ab) (bc) (aa)<br>(ab) (ab) (ac) | (aa)(ab) (cd)<br>(aa) (ad)(bc)<br>(aa)(ac)(bd)<br>(ab)(ac)(ad) | (aa) (aa)(bc)<br>(ab) (ac)(aa) |
| ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| No G.I | No G.I | 2 Isomers | GI = 3 | 4 G.I | 2 isomers<br>Geom. |

## $Ma_3b_3$

(aa) (bb) (ab)
(ab) (ab) (ab)

2-Geo. Isomers





When three gps are in same plane

↓

Meridonial
(mer)

When two gps are in one plane & third one is perpendicular to that plane

↓

Facial ( )
(fac)

## Mabcdef →

G.I → 15

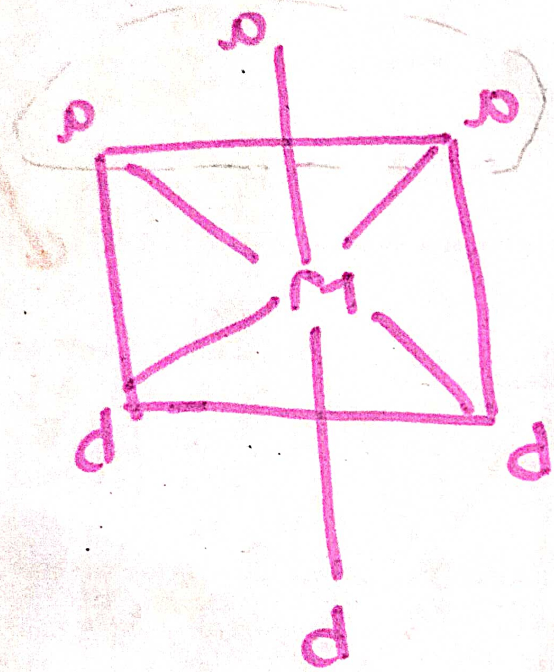
all are O.A

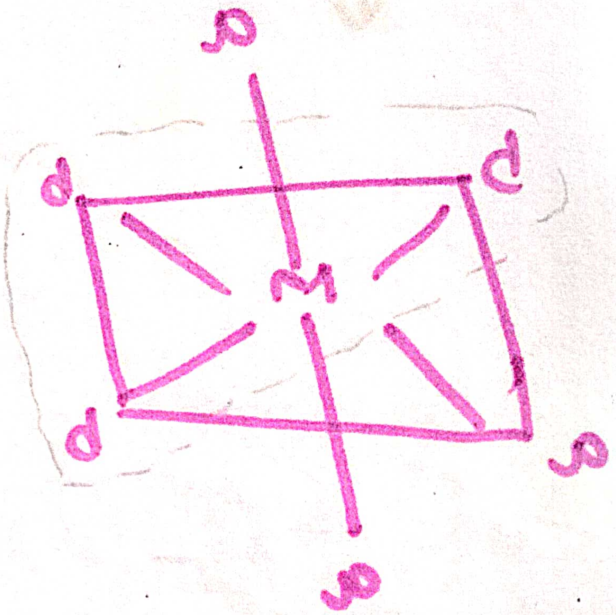
∴ stereoisomers = 30

Ma₃b₃

(aa)(bb)(ab)
(ab)(ab)(ab)

2-Geo Isomers





When two gps are in one plane & the other are is perpendicular to that plane

↓

Facial (fac)

When three gps are in same plane

↓

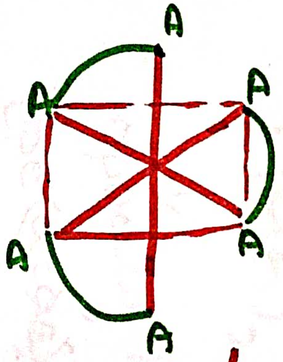
~~meridional~~

Meridional (mer)

# Geometrical Isomerism - $\boxed{\text{Bidentate Ligand}}$

## Octahedral Complexes

### $M(AA)_3$



↓

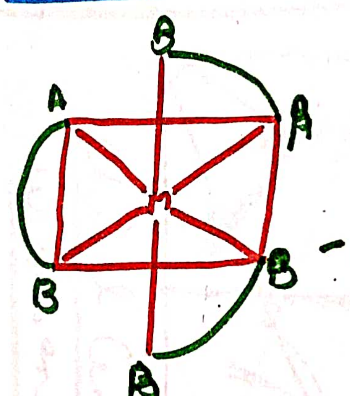
No G.I

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

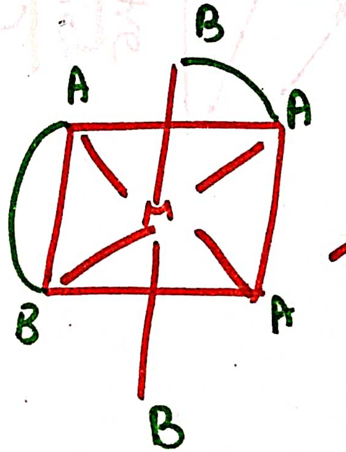
No POS → O.A

Total Stereo Isomers → 2

### $M(AB)_3$



- Fac



- Mer

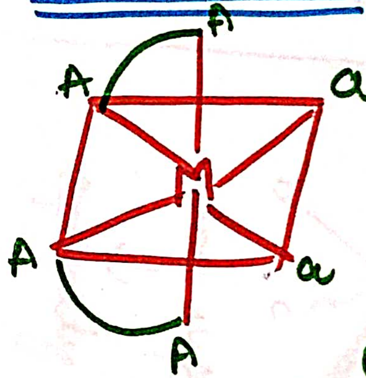
↓

2 G.I

Eg $[Co(gly)_3]$

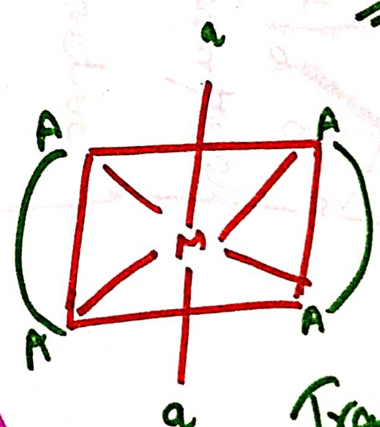
### $M(AA)_2bc$ / $M(AA)_2a_2$

eg. $[Co(en)_2Cl_2]^{+1}$



Cis

O.A



Trans

O.I

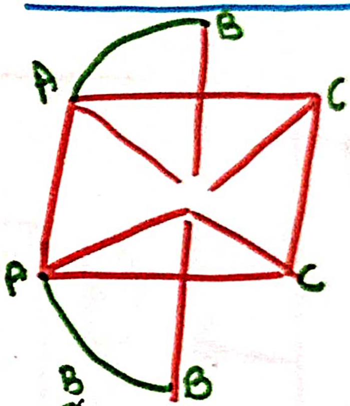
↓

2 = Geo. Isomers

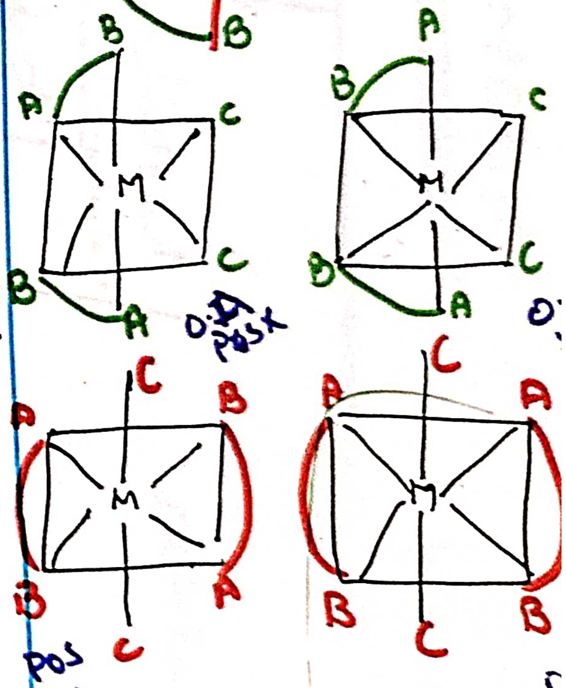
eg $[Co(en)_2NH_3Cl]^{+2}$

### $M(AB)_2C_2$

$[Co(gly)_2Cl_2]$



O.A
POS ×



O.A
POS ×

O.

POS
O.I

5 Geometrical Is