Geometrical Isomerism and Optical Isomerism:

→ In disubstituted complexes, the substituted group may be adjacent or opposite to each other. This gives rise to geometrical isomerism.

→ This type of isomerism is observed in complexes with coordination number 4, 5 and 6.

→ If a molecule is asymmetric, it cannot be superimposed on its mirror image. The molecule and its mirror image have the type of symmetry as shown by the left and right hands and are called an enantiomorphic pair.

→ The two forms are optical isomers. They are called either dextro or laevo (d or l) depending on the direction in which they rotate the plane of polarized light in a polarimeter.

→ Optical isomerism is common in octahedral complexes involving bidentate groups.

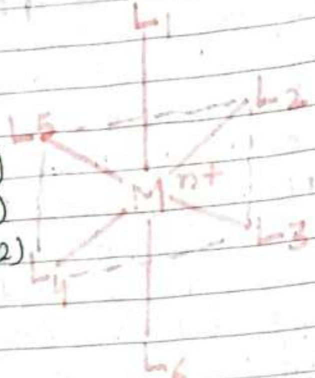
For Coordination Number 6:

(a) All ligands are monodentate, having no chiral centre:

Formula	Possible number of stereoisomers	Possible number of Enantiomer Pairs	Possible number of Geometrical Isomers.
Ma_6	1	0	1
Ma_5b	1	0	1
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
Ma_3bc_2	3	0	3
Ma_2bcd	5	1	4
$Ma_2b_2c_2$	6	1	5
Ma_2b_2cd	8	2	6
Ma_2bcde	15	6	9
$Mabcdef$	30	15	15

M = metal (ion)
a, b, c, d, e & f = monodentate ligands

cis
(1,2) (1,3) (1,4)
(1,5) (2,3) (3,4)
(4,5) (5,2) (6,2)
(6,3), (6,4) or
(6,5)



trans
(1,6), (2,4) and (3,5)

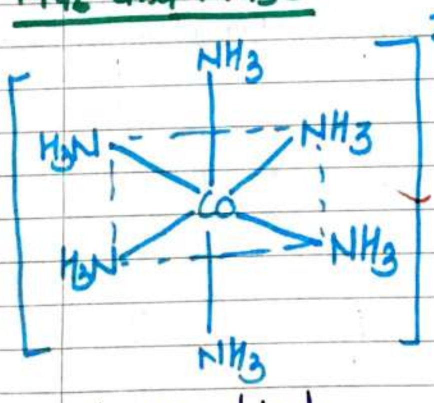
→ In cis - isomers the two similar ligands or some times two different ligands of interest occupy the corners of octahedral adjacent to one another.

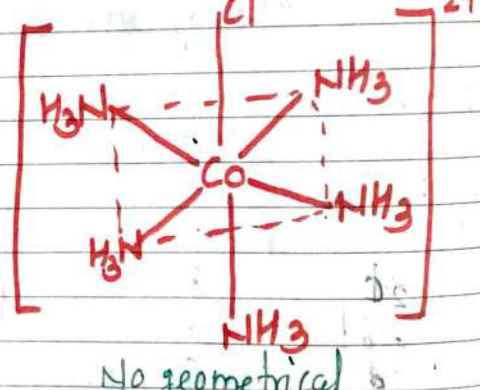
→ In trans- isomers these ligands are lying opposite to one another.

→ In trans- isomers the two ligands under consideration will occupy either of the positions.

Note: Since all the corners of a regular octahedron are equivalent, there are no geometrical isomers of complexes of the type $[Ma_6]^{n\pm}$ & $[Ma_5b]^{n\pm}$

Ma_6 and Ma_5b :

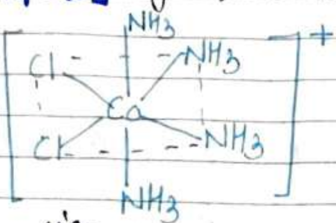




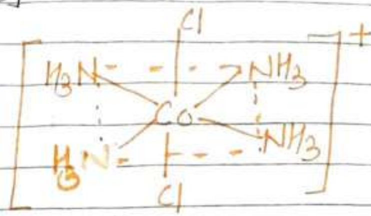
No geometrical
optically inactive
Plane of symmetry present

No geometrical
→ Plane of symmetry +nt
→ optically inactive.

[Ma_4b_2] e.g. $[Co(NH_3)_4Cl_2]^+$



cis-



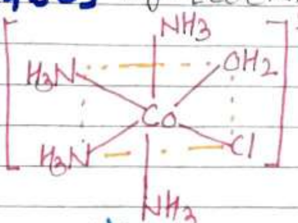
trans.

cis:
→ geometrical present
→ Plane of symmetry present
→ optically inactive.

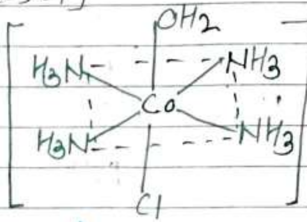
trans:
→ Plane of symmetry pnt.
→ optically inactive.

[Ma_4bc] e.g. $[Co(NH_3)_4(H_2O)Cl]^{2+}$

→



cis.



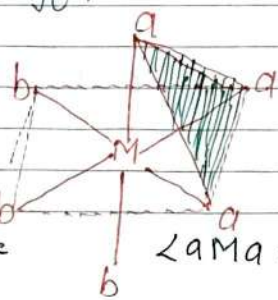
trans.

cis:
→ Geometrical present
→ Plane present
→ optically inactive

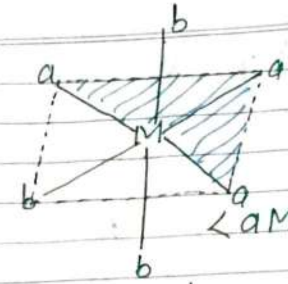
trans:
→ Plane present
→ optically inactive.

[Ma_3b_3] : $[Co(NH_3)_3Cl_3]$

→ When the 3 ligands with the same donor are on the same triangular face of the octahedron, the isomer is given the name facial or fac-isomer.
→ In facial isomer identical 3 ligands forms a triangular face of the octahedron.
→ The angles a-M-a and b-M-b in the facial isomer are all 90°.

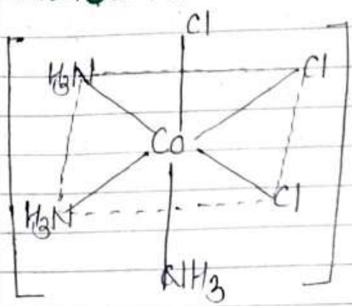


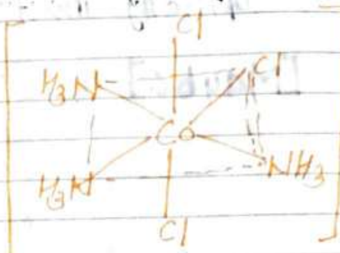
$\angle aMa = \angle bMb = 90°$ (fac-isomer)



$\angle aMa = \angle bMb = 180°$
(mer-isomer)

→ When the 3 ligands are on the same equational plane of the octahedron, the isomer is named meridinal or mer isomer.





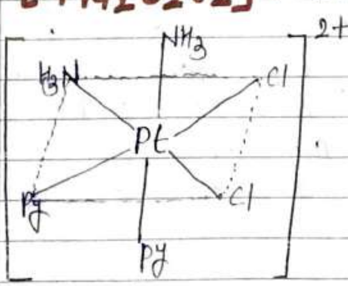
fac-isomer
cis

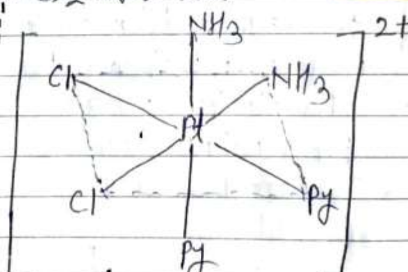
mer-isomer
trans

→ Geometrical isomerism
→ Plane of symmetry present.
→ Optically inactive.

→ Plane of symmetry ~~prt~~.
→ optically inactive.

[$Ma_2b_2c_2$] : [$Pt(NH_3)_2(py)_2Cl_2$]$^{2+}$ 5GI

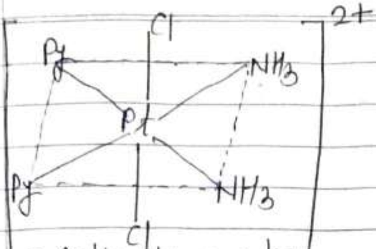




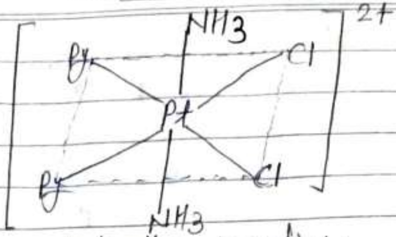
cis-d-isomer — optically active

cis-l isomer — optically active

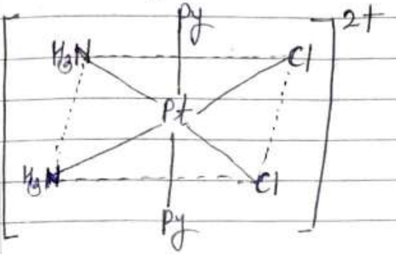
Enantiomers.



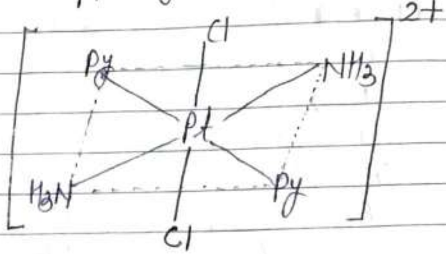
optically inactive



optically inactive



optically inactive



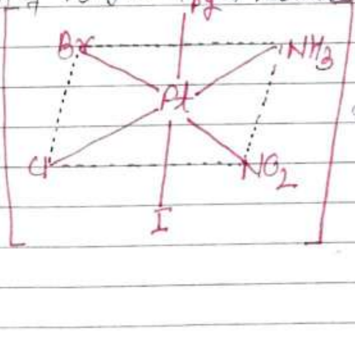
optically inactive

[Mabcdef] : $[\overset{IV}{Pt}(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$

→ There is only one coordination compound of this type.

→ This compound can exist in fifteen possible isomeric forms but only three isomers have been isolated.

→ Each of 15 geometrical isomers is optically active (Chiral)



→ There are 15 pairs of enantiomers (i.e. total number of optical isomers is 30).

When Ligands are bidentate symmetrical and Monodentate Type, having no chiral centre:

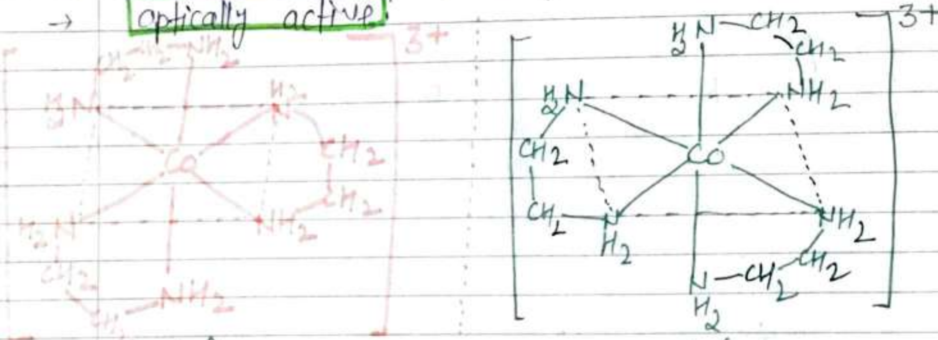
formula	Possible number of stereoisomers	Possible number of Enantiomer Pairs	Possible number of Geometrical Isomers
[M(AA)$_3$]	2	1	1
[M(AA)$_2$a$_2$]	3	1	2
[M(AA)$_2$ab]	3	1	2
[M(AA)a$_4$]	1	0	1
[M(AA)a$_3$b]	2	0	2
[M(AA)a$_2$b$_2$]	4	1	3
[M(AA)a$_2$bc]	6	2	4
[M(AA)abcd]	12	6	6

[M(AA)$_3$]: e.g. $[Co(en)_3]^{3+}$ $[Cr(C_2O_4)_3]^{3-}$

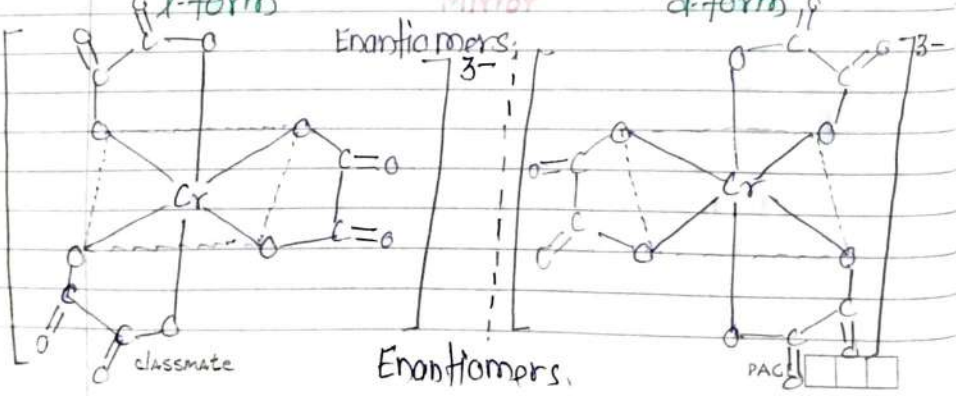
→ Do not show geometrical isomerism

→ Plane or centre of symmetry absent

→ optically active

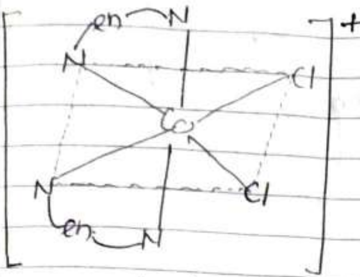


l-form   Mirror   d-form



Enantiomers.

$[M(AA)_2a_2]$: e.g. $[Co(en)_2Cl_2]^+$



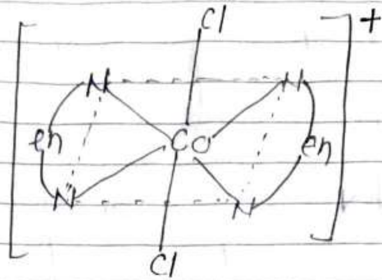
cis-form

↓

Plane of symmetry absent

↓

optically active



trans-form

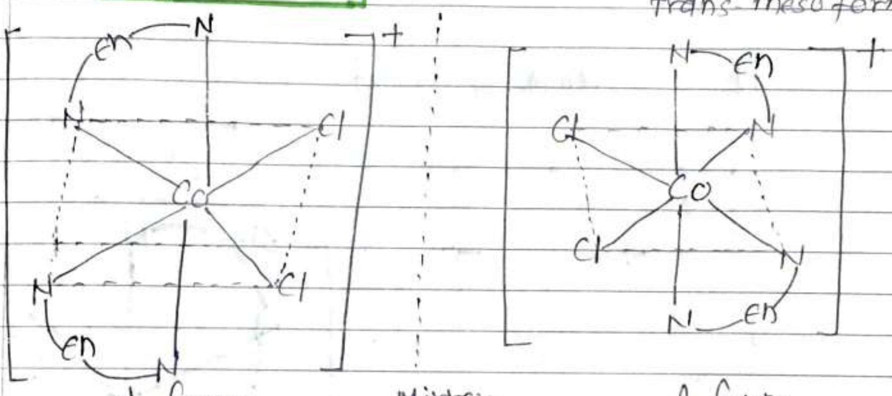
↓

Plane of symmetry prst.

↓

optically inactive

trans-meso form



d-form Mirror l-form

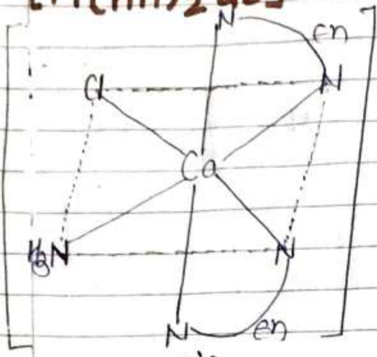
Other examples:

$[Co(en)_2(NO_2)_2]^+$, $[Ir(C_2O_4)_2Cl_2]^{2-}$

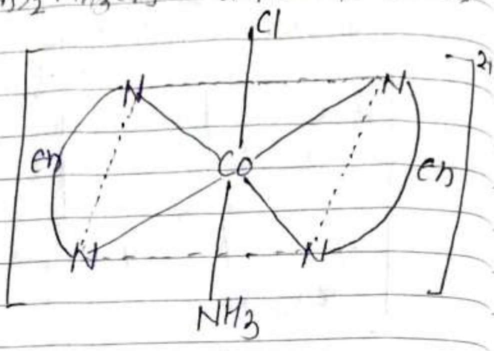
$[Rh(C_2O_4)_2Cl_2]^{2-}$ $[Cr(C_2O_4)_2(H_2O)_2]^-$

$[Ir(C_2O_4)_2Cl_2]^{3-}$ etc.

$[M(AA)_2 gb]$: $[Co(en)_2 NH_3 Cl]^{2+}$ $[Ru(C_2O_4) Py NO_2]^{2-}$



cis

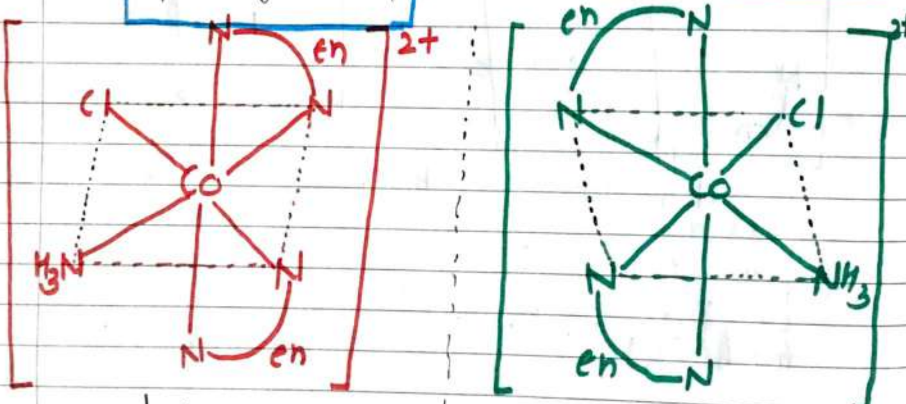


trans

→ In cis-isomer the two monodentate ligands viz. NH_3 and Cl^- occupy the adjacent positions, while in trans-isomer these ligands occupy opposite positions.

cis-isomer → Plane of symmetry absent → **Optically active**

trans-isomer → Plane of symmetry present → **Optically inactive**



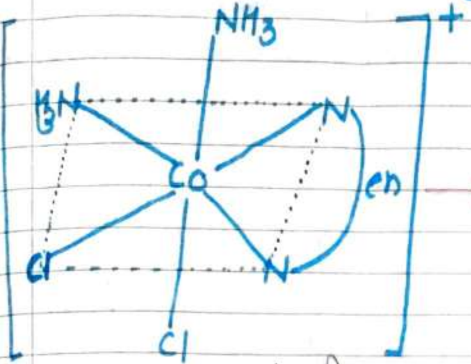
d-isomer Mirror l-isomer

Enantiomers.

$[M(AA)_2a_2b_2]$: e.g. $[Co(en)_2(NH_3)_2Cl_2]^+$

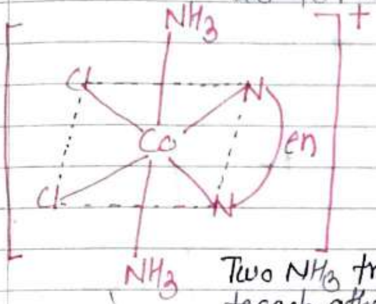
$[Co(C_2O_4)(NH_3)_2(NO_2)_2]^-$

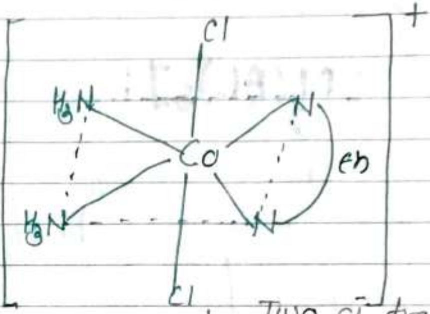
One cis & two trans. **Total G.I = 03**



→ Plane/centre of symmetry absent
↓
optically active

cis-form





Two NH_3 trans to each other

Two Cl^- trans to each other

Two trans isomers.

↓

Plane of symmetry present

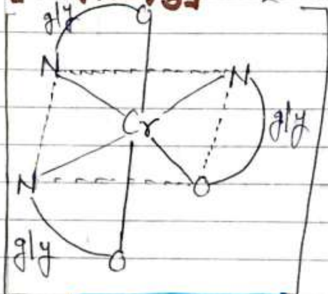
↓

optically inactive

When Ligands are Bidentate unsymmetrical and Monodentate Type having no chiral centre:

Formula	Possible number of stereoisomers	Possible number of Enantiomer Pairs	Possible number of Geometrical Isomers
$[M(AB)_3]$	4	2	2
$[M(AB)_2a_2]$	8	3	5
$[M(AB)_2ab]$	11	5	6
$[M(AB)a_4]$	1	0	1
$[M(AB)a_3b]$	4	1	3
$[M(AB)a_2b_2]$	6	2	4
$[M(AB)a_2bc]$	12	5	7
$[M(AB)abcd]$	24	12	12

$[M(AB)_3]$: $[Cr(gly)_3]$



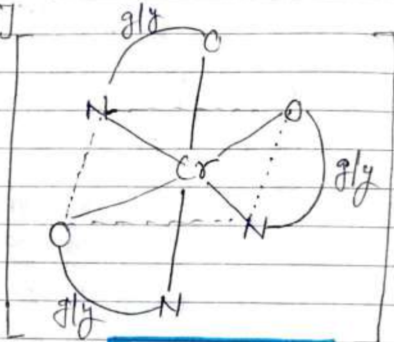
cis- isomer

↓

Plane of symmetry absent

↓

Optically active



trans isomer

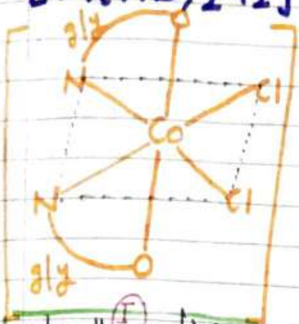
↓

Plane of symmetry absent

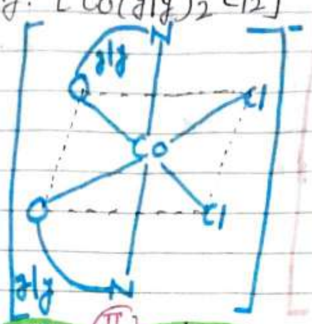
↓

Optically active

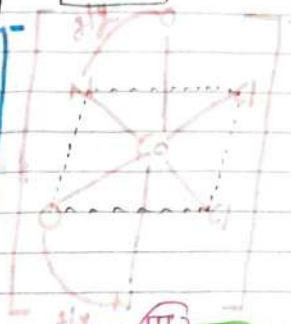
$[M(AB)_2a_2]$: e.g. $[Co(gly)_2Cl_2]^-$ 5 GI



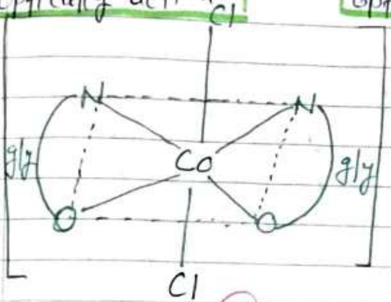
(I) optically active



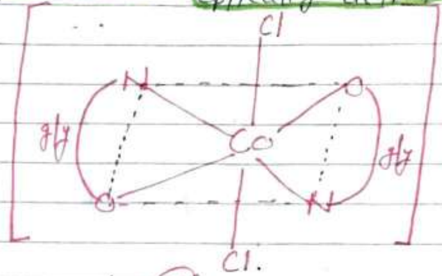
(II) optically active



(III) optically active

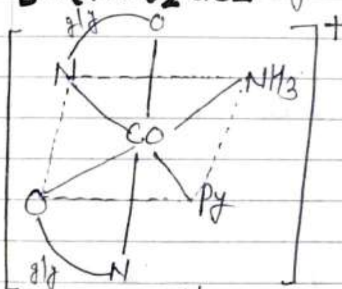


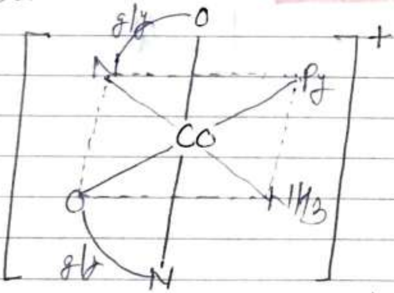
(IV) optically inactive

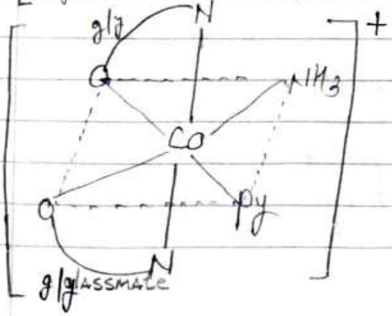


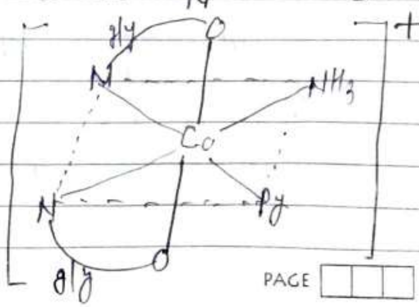
(V) optically inactive

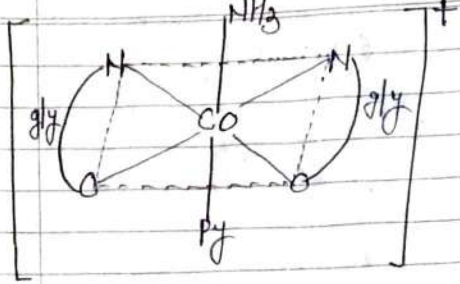
$[M(AB)_2ab]$ e.g. $[Co(gly)_2(NH_3)(Py)]^+$ 6 GIs

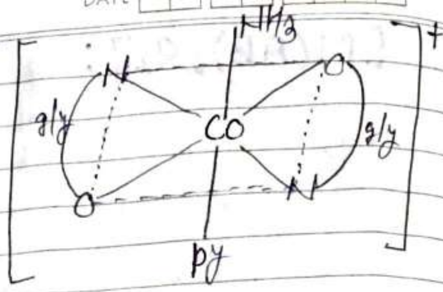






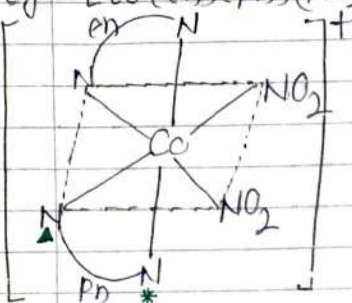




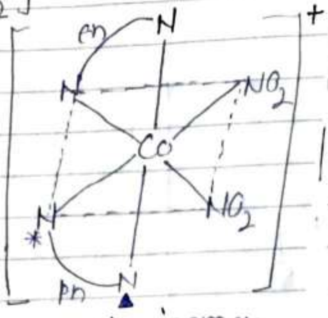


Geometrical Isomerism in Octahedral Complexes Containing Optically Active Bidentate Ligands:

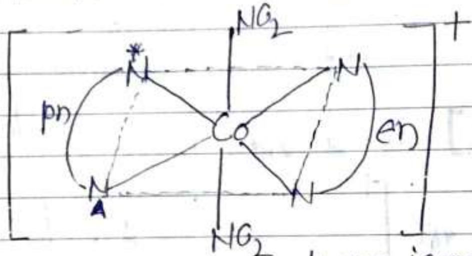
e.g. $[Co(en)(pn)(NO_2)_2]^+$



cis- isomer

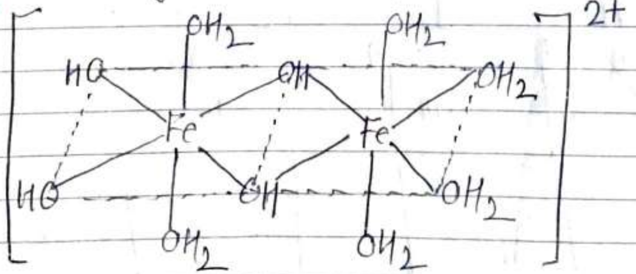


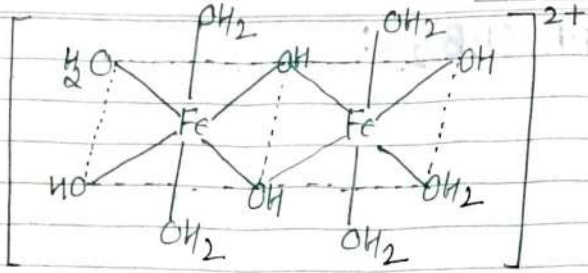
cis- isomer

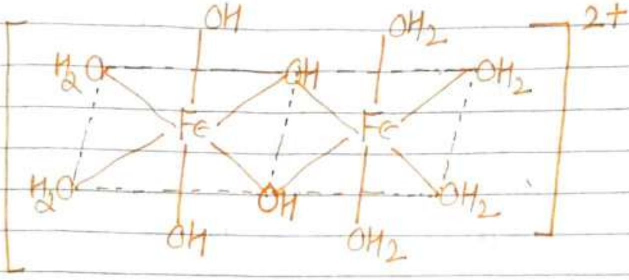


trans- isomer

Geometrical Isomerism in Octahedral Polynuclear Complexes: e.g $[Fe_2(OH)_4(H_2O)_6]^{2+}$

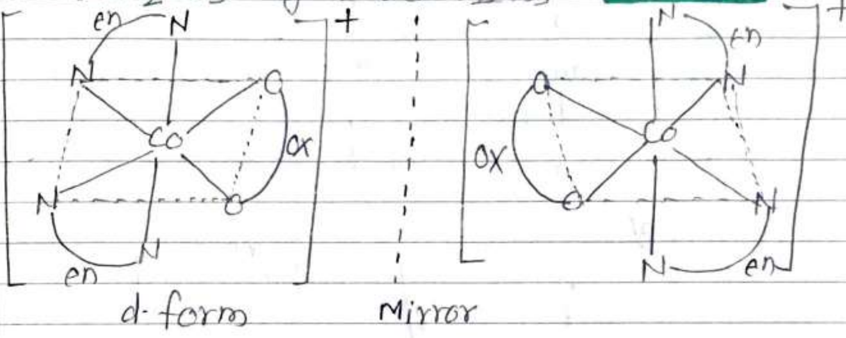




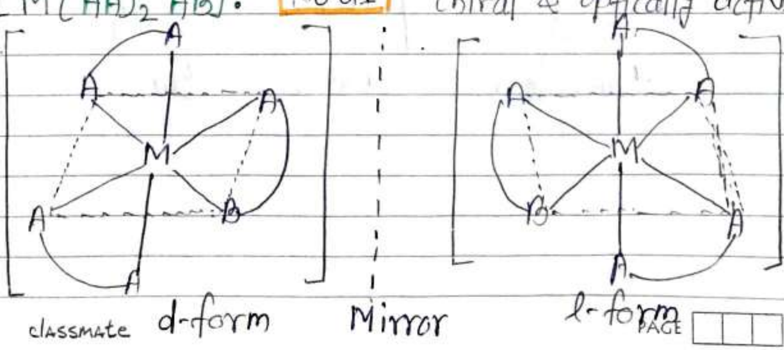


Other Cases of Optical Isomerism in Octahedral Complexes:

1. $[M(AA)_2BB]$: e.g. $[Co(en)_2(ox)]^+$ **No GI**

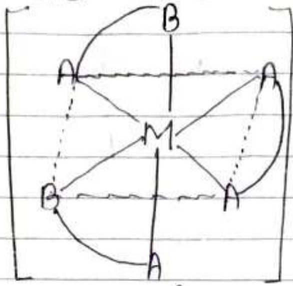


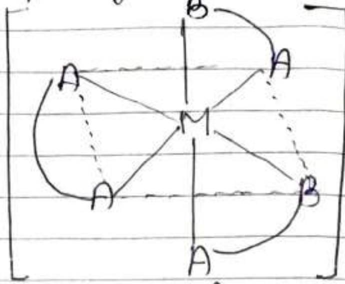
2. $[M(AA)_2AB]$: **No GI** Chiral & optically active.



3. [M(AA)(AB)$_2$]: GI present

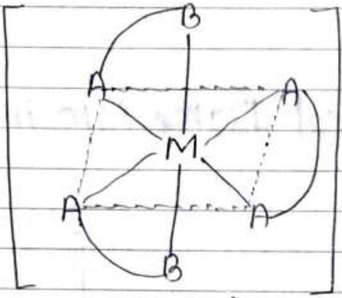
→ All GIs are chiral and optically active.

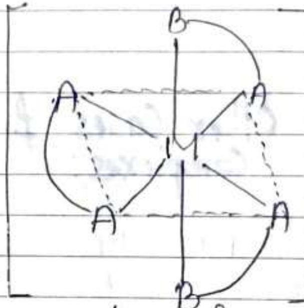




cis form — Mirror — cis-form

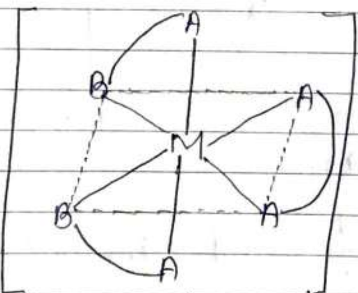
d-form — l-form

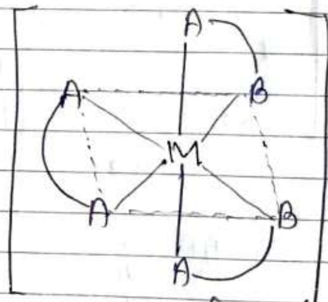




trans-form — Mirror — trans-form

d-form — l-form



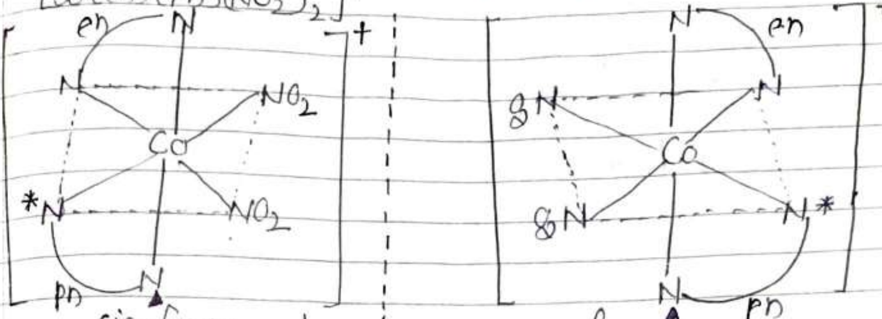


trans-form — Mirror — trans form

d- — l

Octahedral Complexes with Optically Active Ligands:

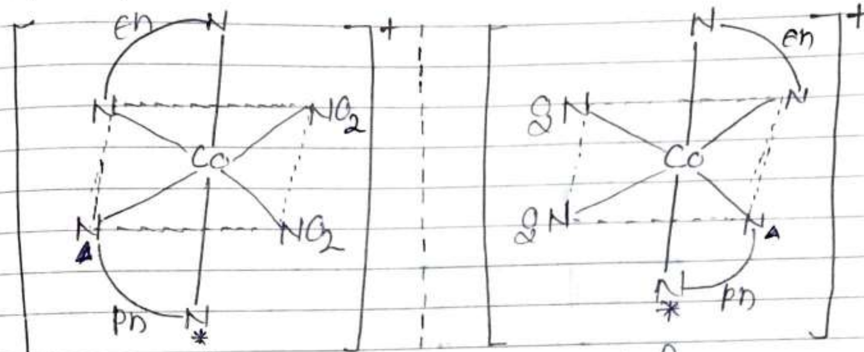
$[Co(en)(pn)(NO_2)_2]^+$



cis-form d | l

→ **optically active**

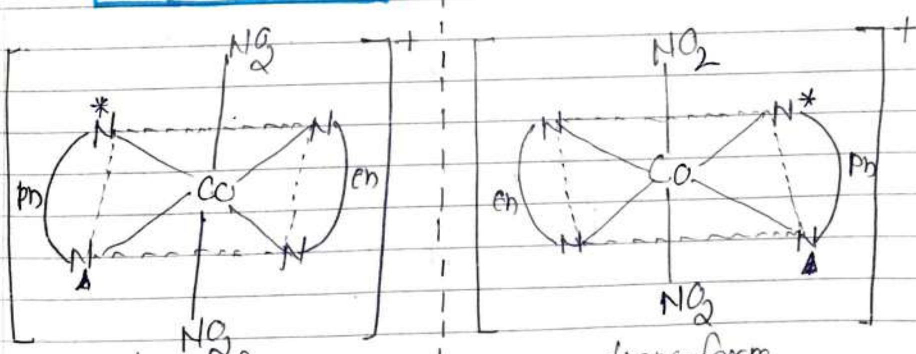
Mirror



cis-form | Mirror | l-form

d

→ **optically active**



trans-form | mirror | trans-form

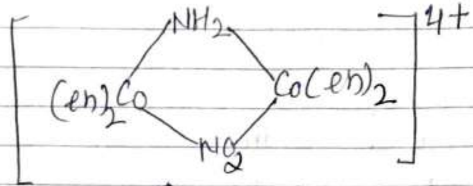
d | | l

optically active

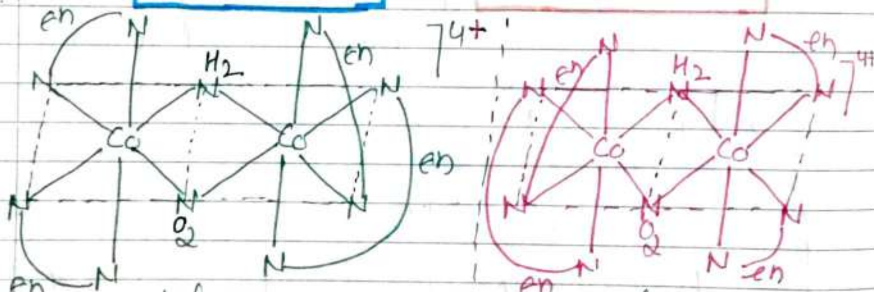
Octahedral Complexes with Polydentate Ligands ($EDTA^{4-}$):

→ No. GI
→ Chiral and optically active.

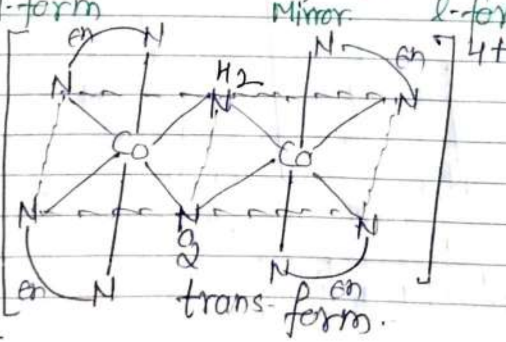
Bridged Binuclear Octahedral Complexes:



- cis-form → Chiral → **Optically active**
- trans-form → Achiral → **Optically inactive**



cis d-form   Mirror   l-form

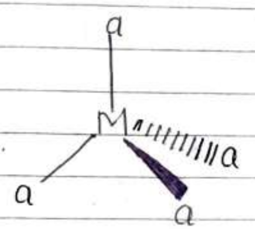


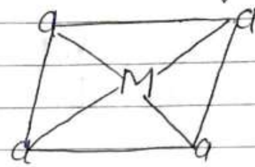
trans-form.

Stereoisomerism in Coordination No. 4

C.No 4
Two geometry

- Tetrahedral geometry
- Square Planar geometry

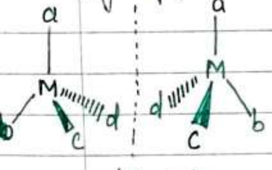




For Td Geometry

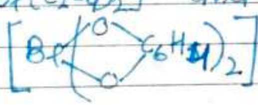
(No GI
Optical absent in Ma_4, Ma_2b_2 & Ma_3b)

① → If ligands are different, then no GI.
→ Only optical

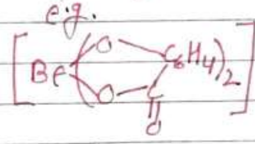


dl pair.

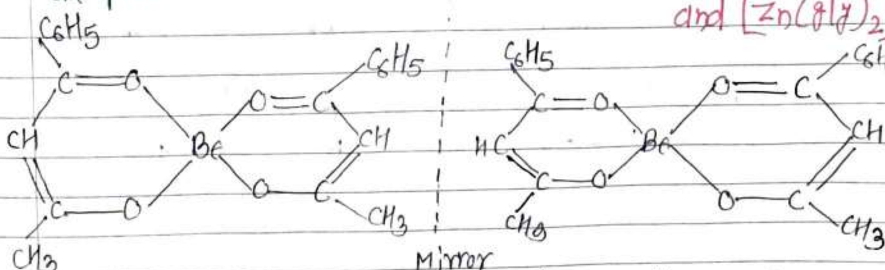
② If symmetrical bidentate ligands having no chiral center are present, then the complexes are optically inactive. e.g. $[Zn(acac)_2]$, $[Be(C_2O_4)_2]^{2-}$ and



③ If unsymmetrical bidentate ligands are present then the compound will be optically active. e.g.



and $[Zn(gly)_2]$



bis (benzoylacetonato) beryllium (II)

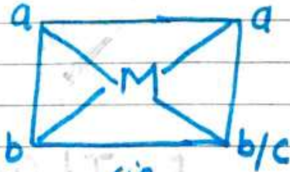
For Square Planar Geometry :

1. GIs absent in $[Ma_4]$ $[Ma_3b]$ $[M(AA)_2]$ $[M(AA)a_2]$ and $[M(AB)a_2]$
where a and b = simple bidentate ligands
AA = Symmetrical bidentate ligand
AB = Unsymmetrical bidentate ligand

→ Chiral centre absent.

2. for $[Ma_2b_2]$ and $[Ma_2bc]$
Two GIs

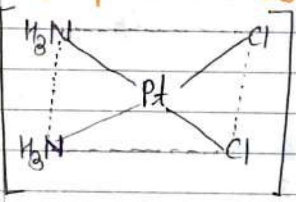
trans



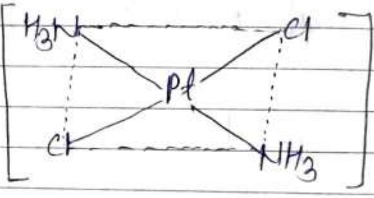
cis

Geometrical isomers of complexes of the type $[Ma_2b_2]$ & $[Ma_2bc]$

e.g. of $[Ma_2b_2]$

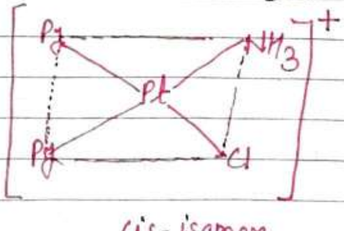


cis

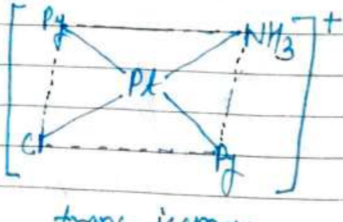


trans.

e.g. of $[Ma_2bC]$: $[Pt(NH_3)_2PyCl]^+$, $[Pt(Py)_2(NH_3)Cl]^+$
$[Pt(NH_3)_2(NO_2)Cl]$ etc.



cis-isomer

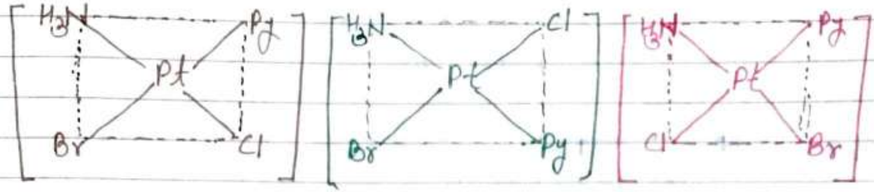


trans-isomer

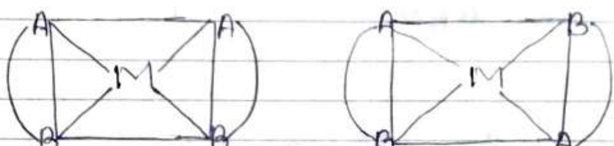
3. $[Mabcd]$ **3 GIs**

For this isomers cis and trans terminology is not applicable or it is to be mentioned with respect to a, b or b, c etc.

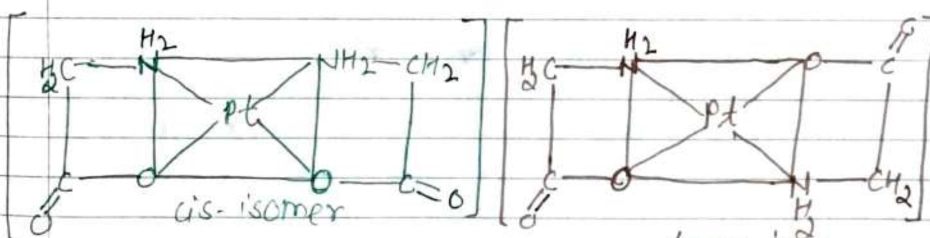
e.g $[Pt(NH_3)(Py)ClBr]$



4. $[M(AB)_2]$: **Two GIs are possible**



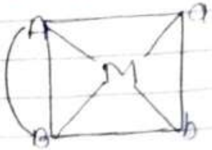
cis-isomer trans. isomer

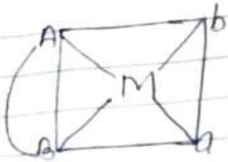


cis- isomer

trans- Isomer

5. [M(AB)ab] : Two GIs

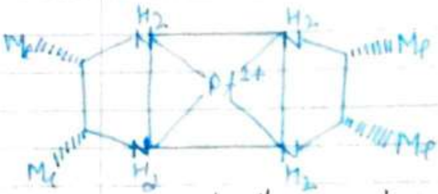




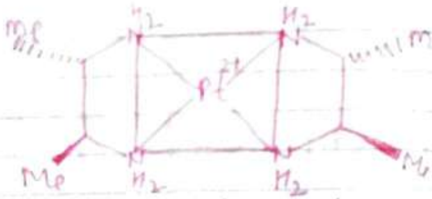
6. [M(AA)$_2$] : can show geometrical isomerism if the ligand AA has a chiral centre.

e.g. $[Pt(bn)_2]^{2+}$

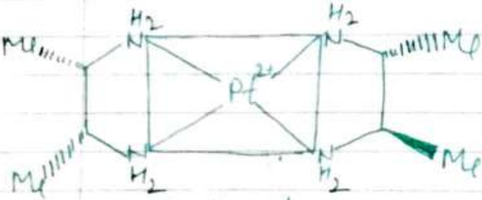
bn = $CH_3-\underset{NH_2}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH}}-CH_3$



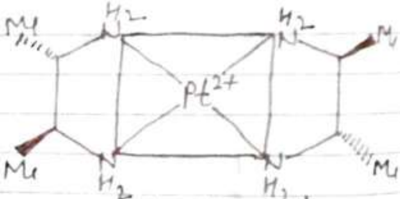
optically inactive



optically inactive



optically active



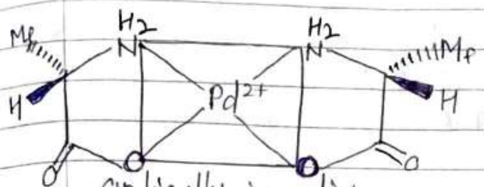
optically active.

optically inactive

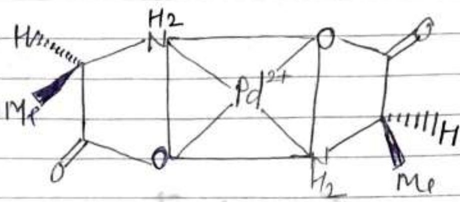
7. $[M(AB)_2]$ can show geometrical as well as optical isomerism if the ligand AB has a chiral centre.

e.g. $[Pd(NH_2-CH(CH_3)-COO^-)]$

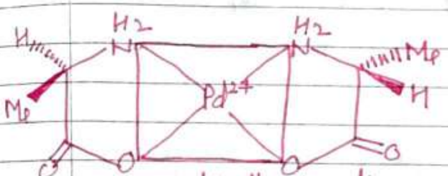
→ 4 GIs



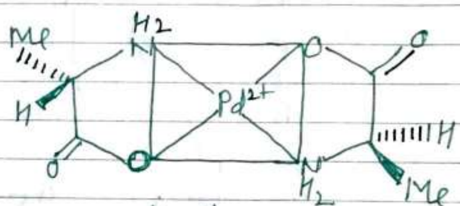
optically inactive cis-isomer
Plane of symmetry present.



optically active trans.

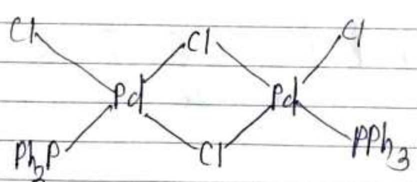


optically inactive cis-isomer

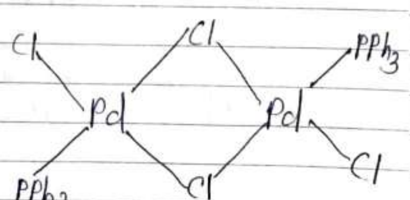


optically inactive
→ centre of symmetry +nt
trans-isomer.

8. **Bridged Binuclear Square Planar Complexes $M_2a_2b_4$ type:** e.g. $[Pd_2Cl_4(PPh_3)_2]$



cis.

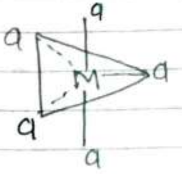


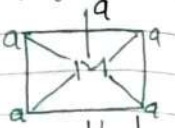
trans.

For Coordination Number 5

→ Two possible geometries

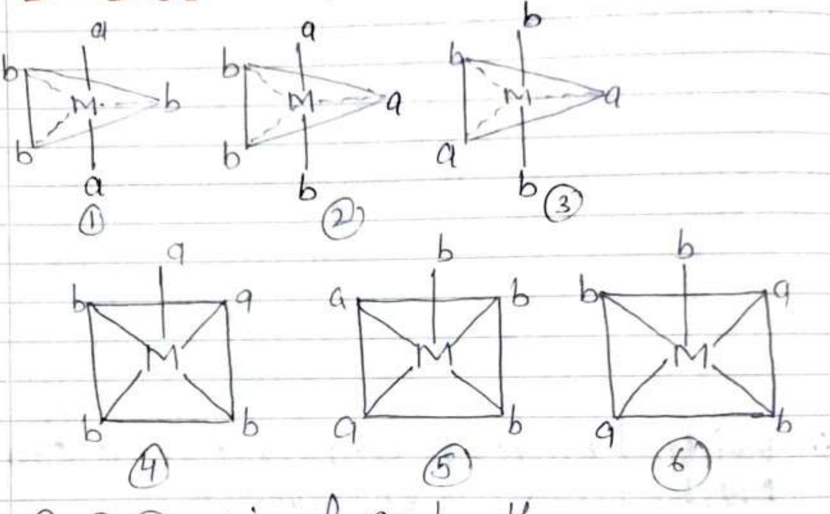
Trigonal Bipyramidal (TBP) | Square Pyramidal





These two are also called as allogon isomers.

$[Ma_2b_3]$ → 6 possible GIs



①, ② ③ gis of each othe

→ one of ①, ② ③ and one of ④, ⑤, ⑥ are allogon isomers of each other.