Isomerism in Coordination Compounds :-

The coordination compounds which have the same molecular formula but have their ligands attached to central metal atom in different ways are called isomers. These isomers have different properties. The phenomenon that gives rise to different isomers is called isomerism.

Coordination compounds give rise to a wide variety of isomers due to different structural arrangement of constituent ~~ion~~ atoms.

Isomerism in coordination comp may be divided into two main types.

(A) Structural Isomerism :-

These are the isomers which have different arrangment of ligands around CMI. This isomerism is of following types :

1) Ionization isomerism :-

In this type of isomerism, the compounds are of same composition but yield different ions in soln. This difference arises from the position of groups inside or outside of coordination sphere.

Eg : Violet coloured pentammine bromocobalt (III) sulphate $[Co(NH_3)_5Br]SO_4$ is an ionization isomer of red coloured pentammine sulfato cobalt (III) bromide $[Co(NH_3)_5SO_4]Br$.

The violet comp. in aq soln gives a precipitate with $BaCl_2$ indicating that sulphate ion is outside the coordination sphere whereas it does not gives ppt with $AgNO_3$. Whereas red comp gives a precipitate with $AgNO_3$ shows that bromide ion is outside the coordination sphere and it does not form precipitate with $BaCl_2$.

1. $[Pt(NH_3)_4Cl_2]Br_2$ & $[Pt(NH_3)_4Br_2]Cl_2$
2. $[Co(NH_3)_5NO_3]SO_4$ & $[Co(NH_3)_5SO_4]NO_3$
3. $[Cr(NH_3)_5SO_4]Br$ & $[Cr(NH_3)_5Br]SO_4$.

② Linkage isomerism :

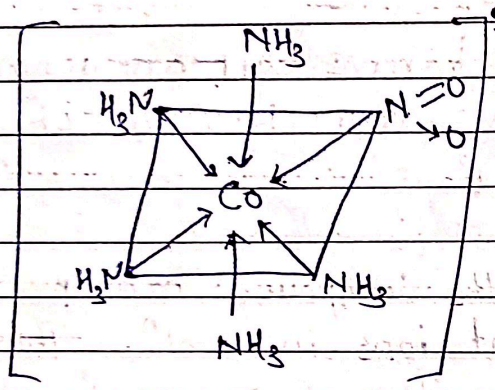
Linkage isomerism is shown by those coordination comp which contain ambidentate ligands, (eg. NO_2^-, SCN^-). Ambidentate ligands are those ligands which coordinate to metal atom through any of their donar atoms. The linking of the ambidentate ligand to the metal atom through two different donar atoms gives two different compounds called as linkage isomers and the phenomenon is called linkage isomerism.

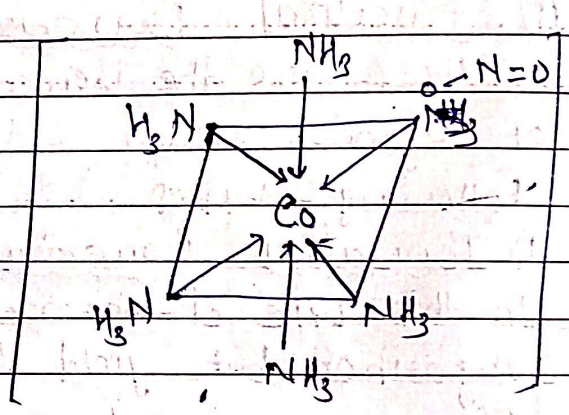
Example :

$:\ddot{O}\leftarrow N=\ddot{O}:$ (Nitrito-N group)

$:\ddot{O}-N=\ddot{O}:$ (Nitrito-O group)

① $[Co(NO_2)(NH_3)_5]Cl_2$ — $[Co(ONO)(NH_3)_5]Cl_2$





Pentaammine nitrito-N-Cobalt (III) ion — Pentaammine nitrito-O-Cobalt (III) ion

fig : Linkage isomers

(i) $[Pt(diph)(SCN)_2]$ - Diphenyldithiocyanato-Splatinum (II) & $[Pt(diph)(NCS)_2]$ - Diphenyldiisocyanato-N-platinum (II)

(ii) $[Co(NH_3)_5\text{-}S\cdot SO_3]Cl$ - Pentaammine thiosulfato-S-cobalt (II) chloride

$[Co(NH_3)_5\text{-}O\cdot SO_2\cdot S]Cl$ - Pentaammine thiosulfato-O-Cobalt (II) Chloride.

③ Coordination Isomerism :

This type of isomerism is shown by those complex comp which are composed of complex cation & complex anion. This type of isomers are obtained when some or all the ligands of both the coordination spheres are

interchanged with each other. Thus both the complex comp of each of following pairs are coordination isomers to each other. In this pairs the central metallic atom in the two coordination sphere may be same or different.

Example:

(i) $[Co(NH_3)_6]\ [Cr(CN)_6]$ & $[Cr(NH_3)_6]\ [Co(CN)_6]$

(ii) $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$ & $[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$

(iii) $[Cu(NH_3)_4]\ [PtCl_4]$ & $[Pt(NH_3)_4]\ [CuCl_4]$.

(B) Stereoisomerism :

These isomers contain same atom to atom bonding but differ only in special arrangment of atoms or groups about the CMI. It is possible only in the complexes with coordination no. four & greater than four. These are of two types

(1) Geometrical isomerism

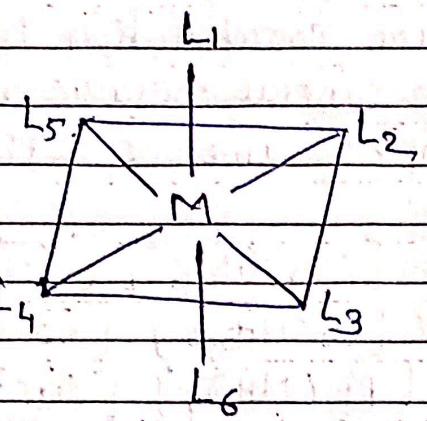
(2) Optical isomerism.

(1) Geometrical isomerism :-

The complex comp which have the same ligands in coordination sphere but relative position of ligands around the CMI is different are called geometrical isomers. In this if the two ligands may occupy positions either adjacent to each other or opposite to each other.

If same kinds of ligands occupy position adjacent to each other it is called as Cis - isomer and if these are opposite to each other, it called trans isomer. Hence geometrical isomerism is also called cis - trans isomerism. It is very common in complexes with coordination number 4 & 6. It is not possible for complexes having C.N. 2 & 3 because in these complexes, all positions are adjacent to one another.

Geometrical isomerism in coordination complexes (C.N. 6):



Cis positions: 1-2, 1-3, 2-3, 3-6, 6-4, 6-5, 3-4, 4-5 & 5-2.

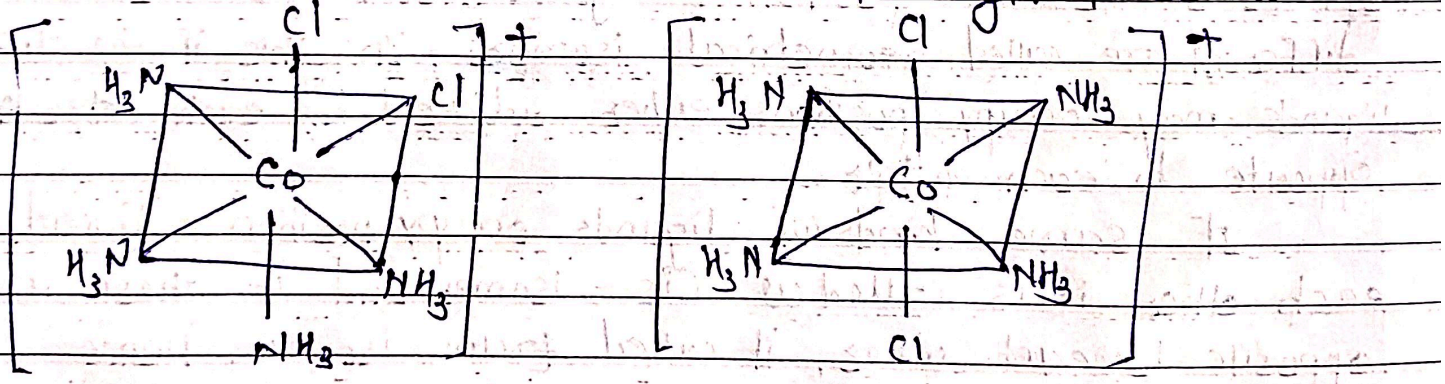
Trans positions: 1-6, 2-4 & 3-5.

In octahedral complex, if two similar ligands are placed on any of the twelve edge of octahedron, they are said to be in cis position. Whereas if two similar ligands are lying on straight line which passes through center they are in trans position.

octahedral complexes of type Ma_4b_2, Ma_4bc, Ma_3b_3, $M(AA)_2b_2$ exists as cis & trans isomers.

① octahedral complexes of Ma_4b_2 and Ma_4bc :-

Example of type Ma_4b_2 is $[Co(NH_3)_4Cl_2]^+$ & Ma_4bc is $[Co(NH_3)_4Cl\cdot NO_2]^+$. The structure of cis & trans isomers of tetraamine dichloro cobalt (III) ion is given below



Cis isomer (Blue or violet) Trans isomer (Green)

Fig: Cis and trans isomers of $[Co(NH_3)_4Cl_2]^+$ ion.

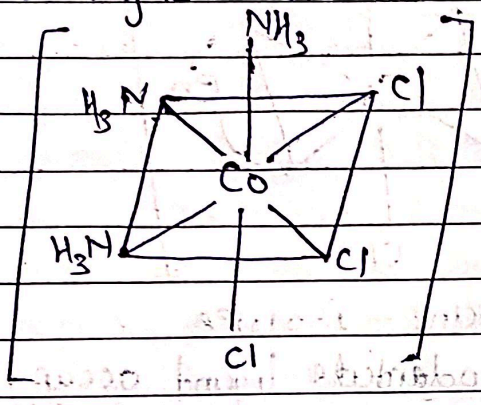
In cis isomer two Cl^- ions occupy adjacent positions while in trans isomers they occupy opposite position.

A large no. of other octahedral complexes of Cr(III), Rh(III), Pt(IV) of this types have been prepared.

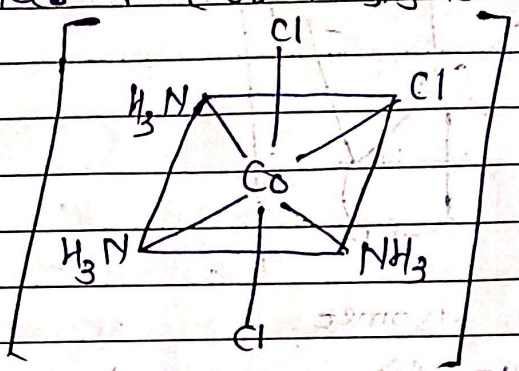
(II) Ma_3b_3 type complex :-

Complexes of this type exist in two isomeric form. In this in cis form, similar groups occupy the corners of one octahedral faces is called facial or fac-isomer. While in trans form they do not is called meridional or mer-isomer.

Example : Cis and trans isomers of $[Co(NH_3)_3Cl_3]$



Facial or fac-isomer

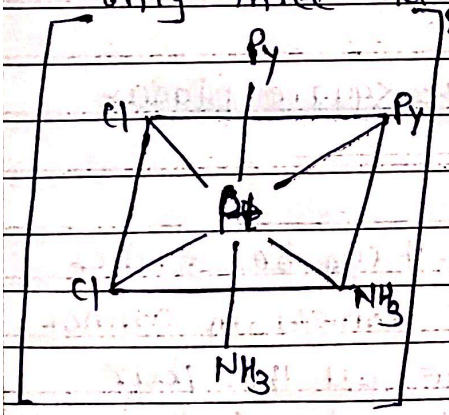


Meridional or mer-isomer

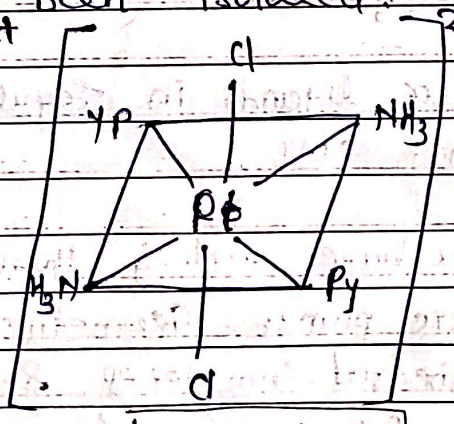
other examples of this type are $[Rh(py)_3Cl_3]$ & $[Cr(H_2O)_3F_3]$ etc.

(III) $Ma_2b_2c_2$ type complex :-

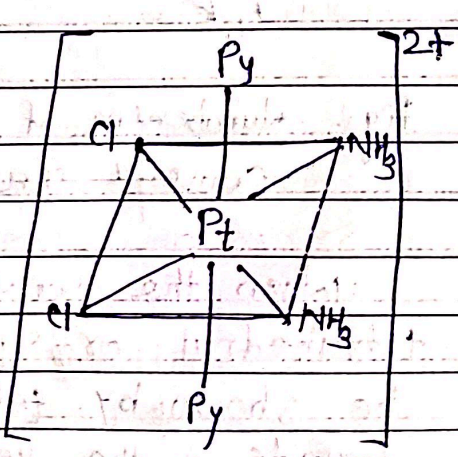
$[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$ ion is an important example of octahedral complexes of $[Ma_2b_2c_2]$ type. Theoretically these type of complexes exist in five geometrical isomers out of which only three have been isolated.

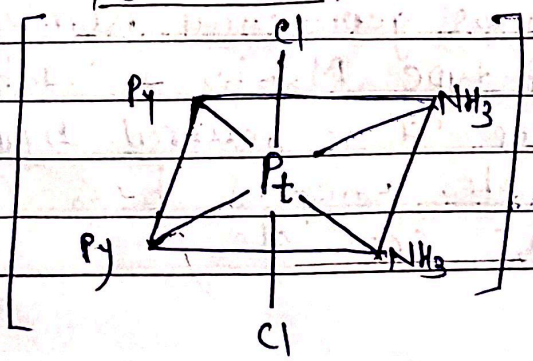


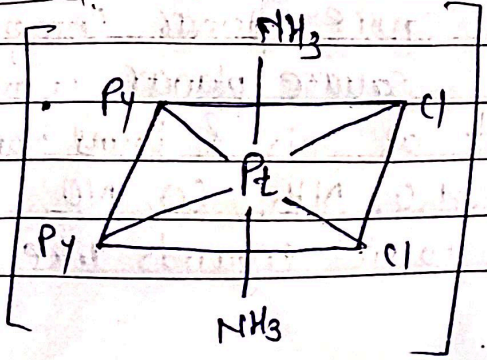
cis-isomer



trans-isomer



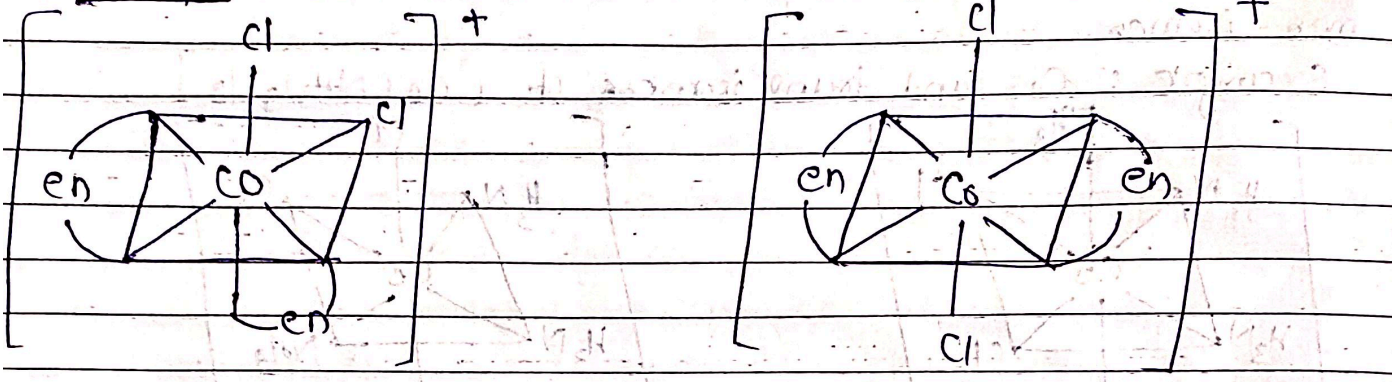




(iv) $[M(AA)_2b_2]$ type complex :-

Here (AA) refers to symmetrical bidentate ligands like ethylene diammine (en), $(NH_2CH_2CH_2NH_2)$, oxalate ion (ox) $(OOC^{\bullet}-COO)^{2-}$ etc. where 'b' refers to anionic ligand.

Example : Cis and trans isomer of $[Co(en)_2Cl_2]^+$.

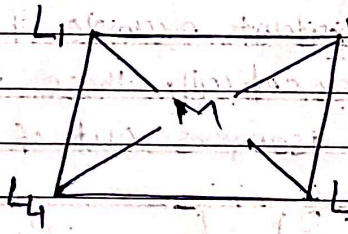


Cis -isomer trans - isomer

In cis isomer two same monodentate ligand occupy the adjacent position while in trans isomer, ligands occupy opposite position.

Some examples are $[Co(en)_2(NO_2)_2]^{2+}$, $[Ni(ox)_2Cl_2]^+$ etc.

Geometrical isomerism in square planar complexes (C.N. 4):



Cis position : 1-4, 2-3, 1-2 & 3-4

Trans position : 1-3 & 2-4.

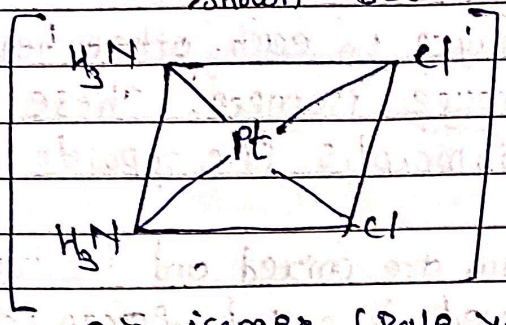
Fig: Numbering of four ligands in regular square planar complex around CM.

When the complex have C.N. 4 then it can be either tetrahedral or square planar. Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in the geometry have adjacent position (ci's). only square planar complexes shows geometrical isomerism.

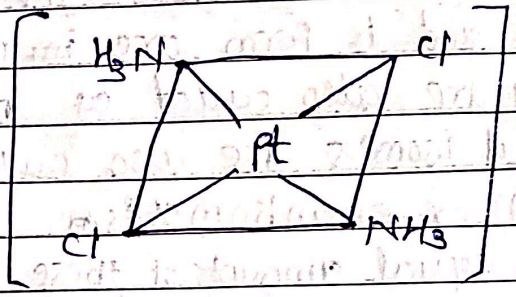
Square planar complexes of type Ma_2b_2 & Ma_2bc exist as cis & trans isomers. Here 'a' is neutral ligand like H_2O, NH_3, CO, NO, C_5H_5N etc. whereas 'b' & 'c' are ionic ligands like Cl^-, NO_2^-, SCN^- etc.

(i) Ma_2b_2 type complex :

In this complex four bonds are coplanar with CMI. Example : Cis and trans isomer of $[Pt(NH_3)_2Cl_2]$ as shown below



Cis - isomer (Pale yellow)

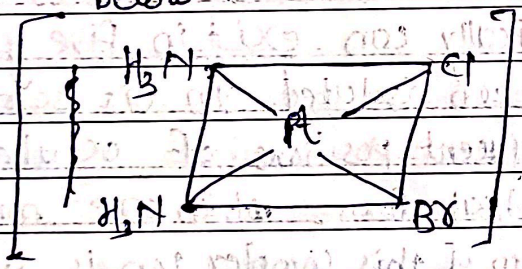


Trans - isomer (Dark yellow)

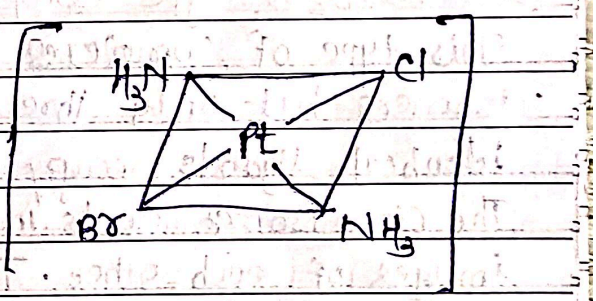
In cis isomer, both NH_3 molecules & Cl^- ions are adjacent to each other whereas in trans isomer both NH_3 & Cl^- ions are diagonally opposite to each other.

(ii) Ma_2bC type complex :

The complexes of this type also show cis & trans isomerism. example : Cis & trans isomers of $[Pt(NH_3)_2ClBr]$ as shown below :



Cis - isomer



Trans - isomer

Optical isomerism :-

There are certain substances which can rotate the plane of polarised light. These so are called optically active substances.

(i) The isomer which rotate plane of polarised light in clockwise direction is said to be dextro-rotatory or d - form. d-form represented by (+) sign.

(ii) The isomer which rotates plane of polarised light in anti-clockwise direction is called levo-rotatory or l - form. It is represented by (-) sign.

(iii) since d & l form capable of rotating plane of polarised light these are said to be optically active form or

optical isomers and this phenomenon is called optical activity or optical isomerism. These two form have exactly identical physical and chemical properties but they differ in their action on polarised light.

(b) d and l form are ~~im~~ mirror images to each other hence they are also called as mirror-image isomers. These ophical isomers are also called enantiomorphs (i.e. opposite form) or enantiomerism.

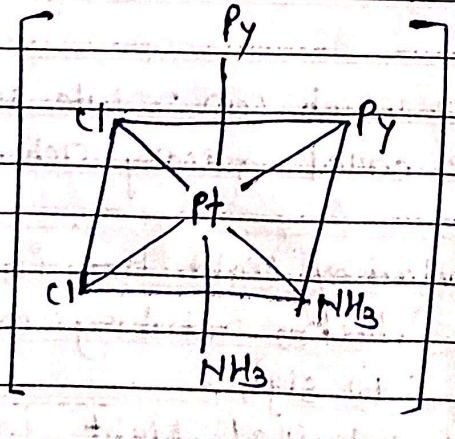
(3) If equal amount of these d & l form are mixed and dissolve in water, no optical activity is observed, is called racemic form (dl form).

Complexes with coordination no. 4 & 6 show this type of isomers. This type of isomerism is exhibited by chiral molecule i.e, molecule which do not have plane of symmetry

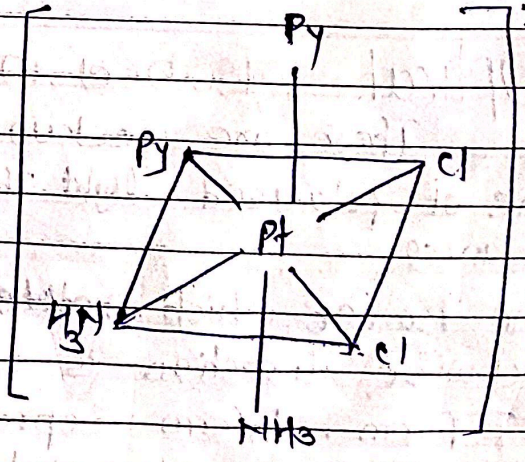
Optical isomerism in complexes with C.N. 6 :-

(1) $Ma_2b_2c_2$ type complex :

This type of complexes theoretically can exist in five geometrical isomers but only three have been isolated. In cis isomer two identical ligands occupy the adjacent positions of octahedron. The cis-isomer exists in two ophical forms which are mirror images of each other. Trans form of this complex ion is symmetrical and hence is ophically inactive form which is known as trans-meso form.

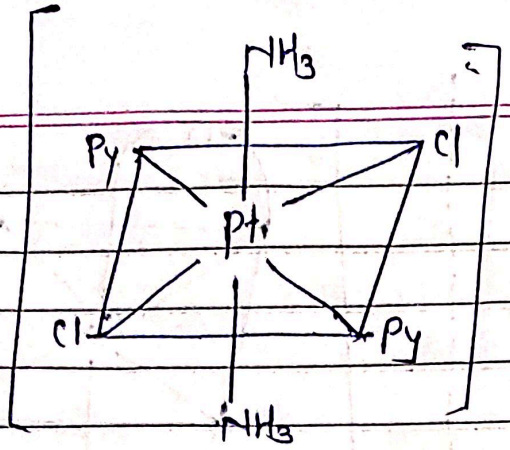


cis-d-isomer



mirror

cis-l-~~Form~~ isomer

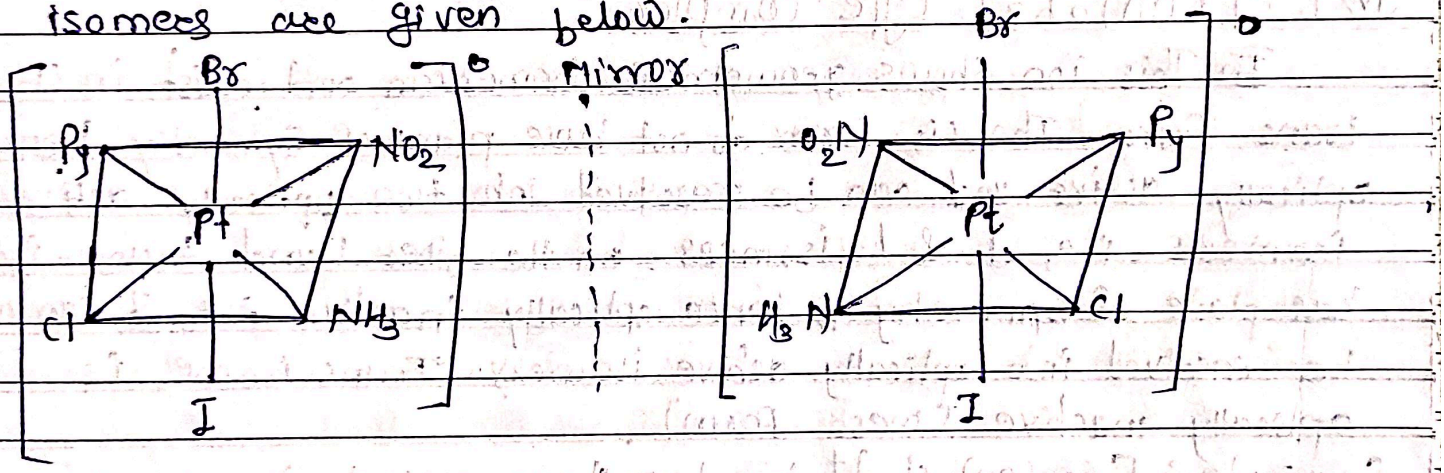


Trans - isomer (optically inactive)

Fig: optical isomers of $[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$ ion.

(ii) Mabcdef type complex :-

$[Pt(Py)(NH_3)(NO_2)ClBr]$ is the only example of this type. Theoretically this complex can exist in 15 geometrical isomers. Each of ~~these~~ these 15 geometrical isomers exist in optically active d- and l- form, giving total of 30 optically active isomers. d- and l- isomers for one of this 15 geometrical isomers are given below.

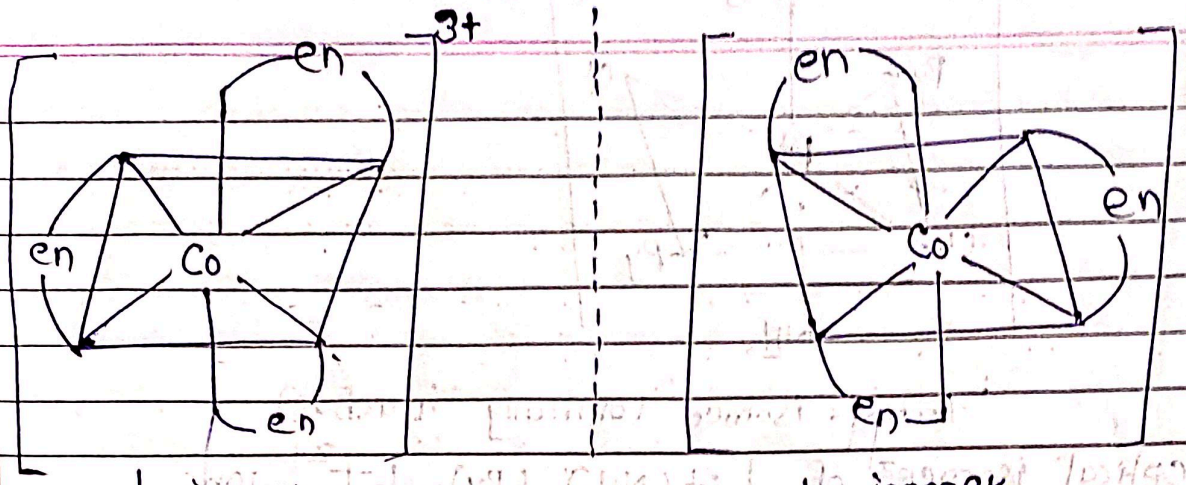


d- isomer l- isomer

Fig: optical (d- & l- isomer) isomers of ~~$[Pt(Py)(NH_3)(NO_2)Br]$~~ $[Pt(Py)(NH_3)(NO_2)ClBr]$.

(iii) $[M(AA)_3]$ type complex :-

(AA) is symmetrical bidentate ligand. Example of this type is $[Co(en)_3]^{3+}$. In this complex their is no plane of symmetry so it is optically active and resolved into dextro and ~~laevo~~ leavo form. for example d- and l- form of $[Co(en)_3]^{3+}$ ion shown as follows.



d-isomer l-isomer

Fig: optical isomers of $[Co(en)_3]^{3+}$ ion.

only octahedral complexes have ability to show optical activity or optical isomer hence these complex have octahedral shape. Neither hexagonal nor trigonal prismatic geometry of 6-coordinated complexes can show optical activity.

Examples: $[Co(ox)_3]^{3-}$, $[Pt(en)_3]^{4+}$, $[Fe(diph)_3]^{2+}$ etc.

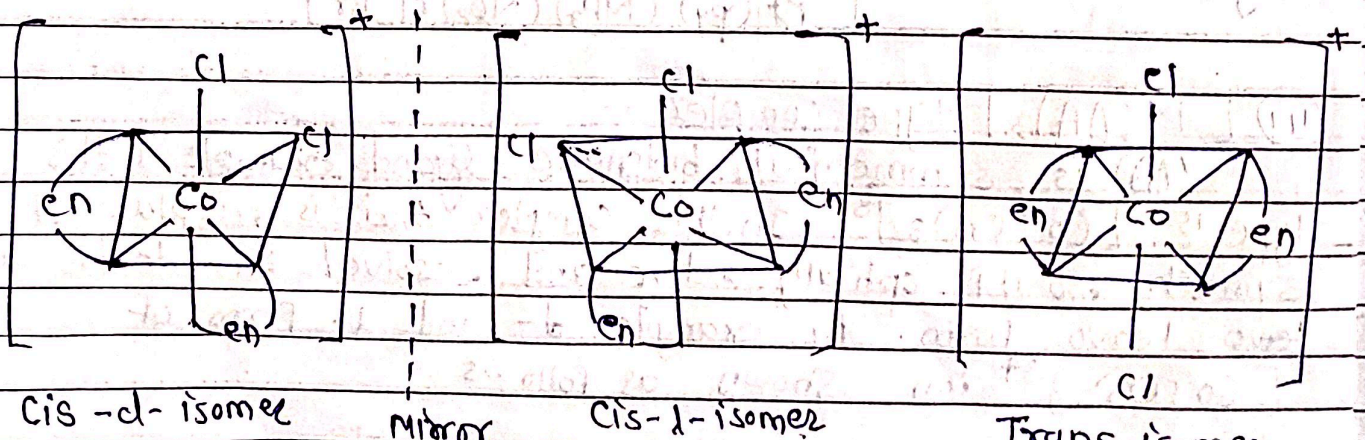
(iv) $[M(AA)_2b_2]$ type complex:

This ion shows geometrical isomerism and exist in cis & trans form. The cis-form do not have plane of symmetry hence optically active and can be resolved into two optically active isomers i.e, d- & l-isomers. on the other hand trans-isomer has plane of symmetry & hence optically inactive i.e, it can not be resolved into optically active isomers. Trans isomer is optically inactive (meso-form).

Example: $[Co(en)_2Cl_2]^+$ ion has three optical isomers viz.

(a) two optically active cis isomers (i.e, d- & -l form).

(b) one optically inactive trans isomer (meso form).



Cis-d-isomer Mirror Cis-l-isomer Trans isomer

Fig: optical isomers of $[Co(en)_2Cl_2]^+$ ion.

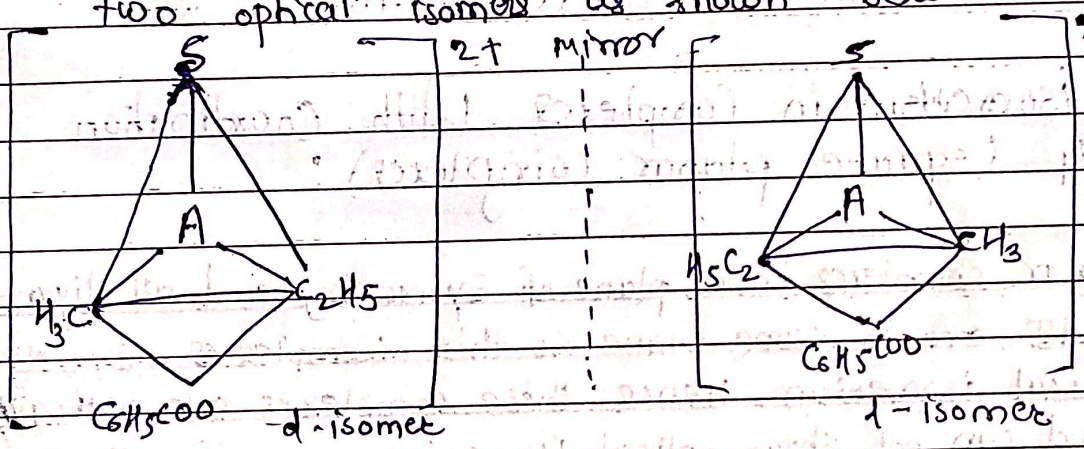
Optical isomerism in complexes with C.N. 4 (tetrahedral complexes) :-

In tetrahedral complexes there is no plane of symmetry hence it should exhibit optical isomerism.

(i) [Mabcd] type complex :

Since the central metal ion in this type surrounded by four different ligands, the tetrahedral complex of this type shows pair of enantiomorphs.

Example: $[As(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$ ion exists in two ophical isomers as shown below -



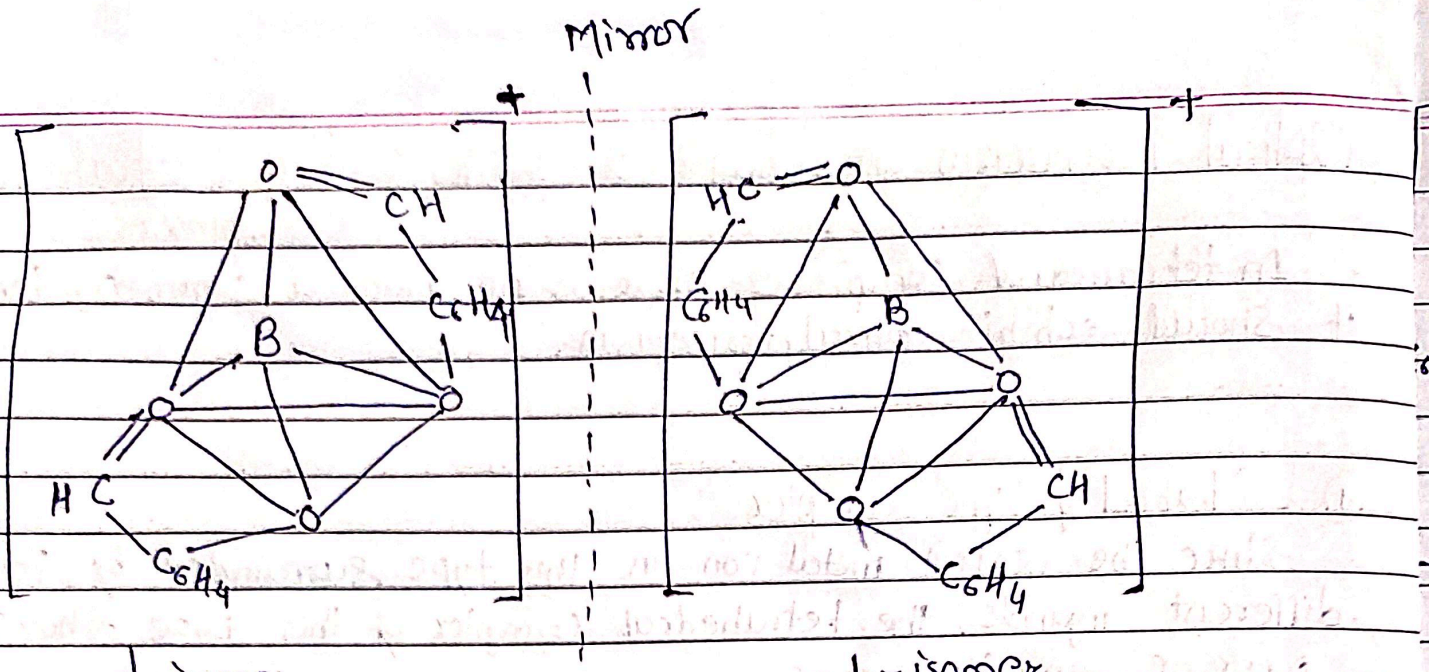
In above example four different groups around CMI is not only requirement for to show complex mirror-image isomerism. The most important requirement is that the molecule should be asymmetric i.e. it should have no plane of symmetry so that it can exist in two mirror-image form.

(ii) $[M(AA)_2]$ type complex :

AA is a symmetrical bidentate ligand. Tetrahedral complexes of Be(II), B(III) & Zn(II) with such type of ligands have been made and resolved into optically active forms.

Example : ① $[B(C_6H_4OCHO)_2]^+$ → bis(salicylaldehydato) boron (III).

other example is $[Be(C_6H_5COCHCH_3(O)_2]$ → bis(benzoylacetonato) beryllium (II).



d-isomer l-isomer

Fig: optical isomers of $[B(C_6H_4OCHO)_2]^+$ ion.

Optical isomerism in Complexes with Coordination No. 4 (square planar complexes):

Square planar complexes have plane of symmetry and all ligands around CMI are in same plane so this complexes rarely have optical isomerism. Hence these complexes are optically inactive and can not show optical isomerism even if all the four ligands are different. However Mills and Quibell have succeeded in resolving optical isomers of isobutylene diammine meso-stilbene diammine platinum (II) ion. This has been resolved into highly stable enantiomorphs. Here isobutylene diammine, $NH_2-CH_2-C(CH_3)_2-NH_2$ is bidentate ligand & meso-diphenyl ethylene diamine (meso-stilbene diamine) $NH_2-CH(C_6H_5)-CH(C_6H_5)-NH_2$ (bidentate ligand) react with $[PtCl_4]^{2-}$ forming a square planar complex of isobutylene diammine meso-stilbene diammine platinum (II) ion.

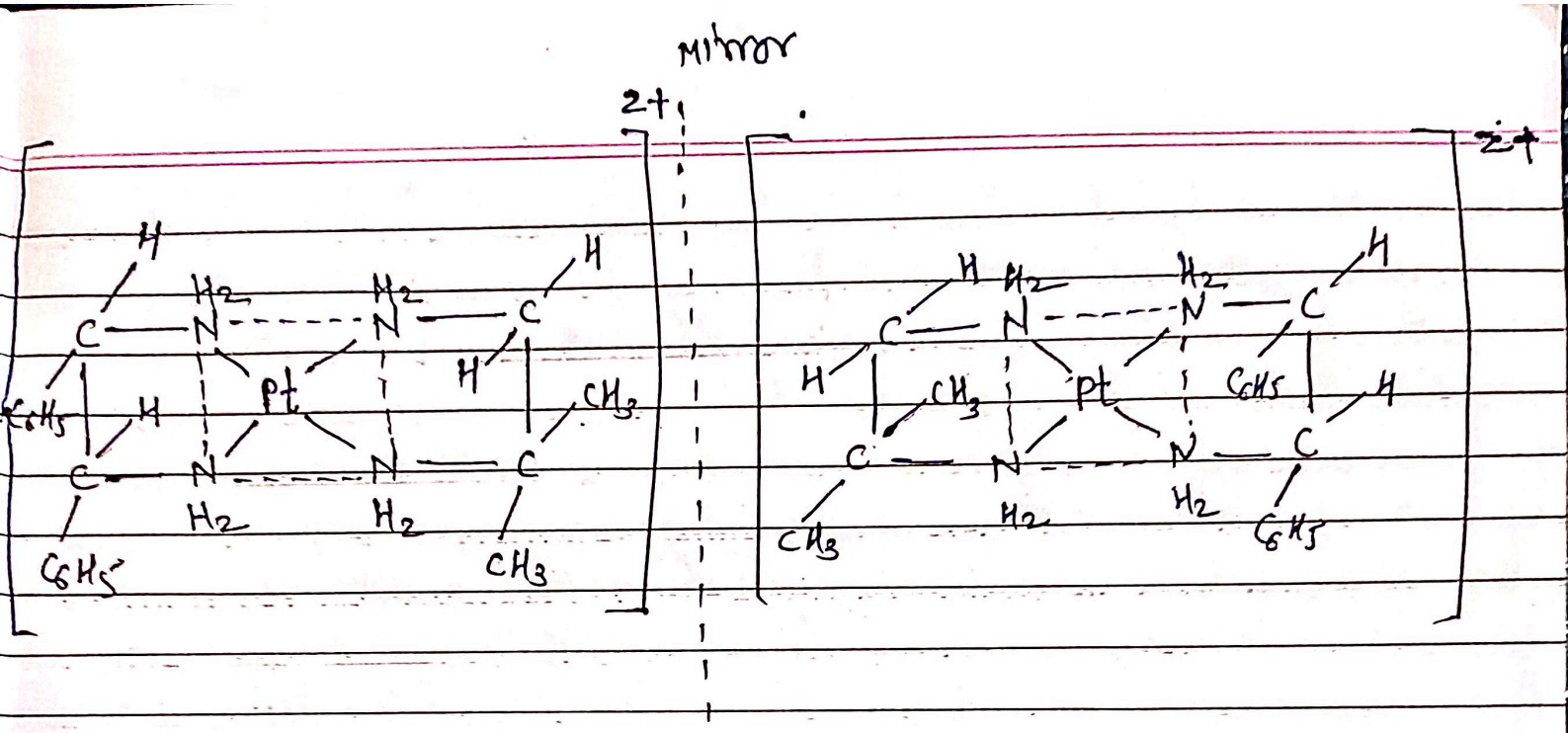


Fig : optical isomers of $[Pt(NH_2-CH(C_6H_5)-CH(C_6H_5)-NH_2)(NH_2-CH_2-C(CH_3)_2-NH_2)]^{2+}$ ion.