

Isomerism: →

Co-ordination compounds give different possibilities of binding of ligand atoms. These variations of co-ordination ^{and} orientation of ligand atoms or ions give rise to different possible isomers of co-ordination chemistry.

Isomerism in co-ordination compounds are mainly classified as ~~co-ordination~~

- ① stereoisomer and stereoisomerism
- ② structural isomer and structural isomerism.

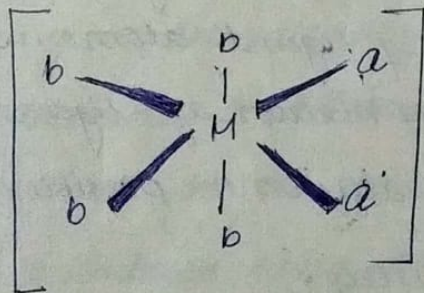
① Stereoisomerism: →

Stereoisomers deals with co-ordinate complexes having different possible ^{stereo-} structural arrangement of the same co-ordination compound. Important iso stereoisomers are geometrical and optical isomers.

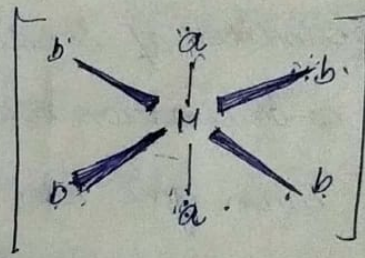
Geometrical isomers: →

Geometrical isomers are classified according to the orientation of ligands arounds the metal atom. →

(A) @ for octahedral MA_2B_4 ~~$[MA_2B_4]$~~ $[MA_2B_4]$ type of complexes (co-ordination no. - 6). the possible geometrical isomers are → "cis and trans" forms. If two 'a' ligands of $[MA_2B_4]$ complex placed on adjacent octahedral position then cis-isomer results. Similarly, if the two 'a' ligands are placed diametrically opposite positions then trans isomer is produced.



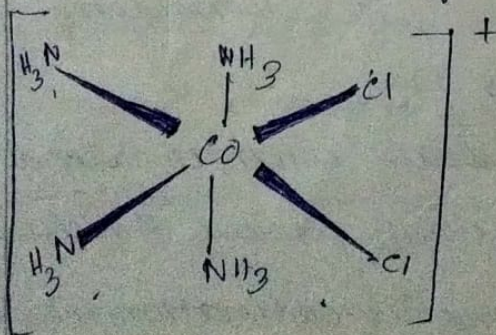
cis-isomer
 C_{2v}



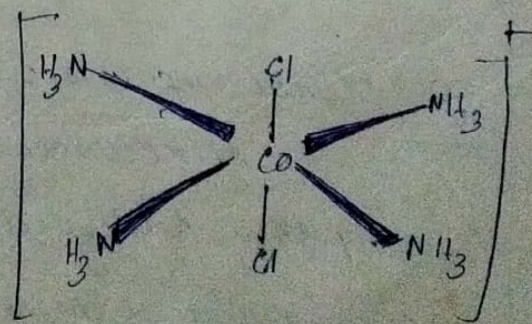
Trans-form
 D_{4h} point group

For eg → $[CoCl_2(NH_3)_4]^+$ can be exhibit

"cis" and "trans" geometrical isomerism.



cis-tetraaminedichloro cobalt(II) ion



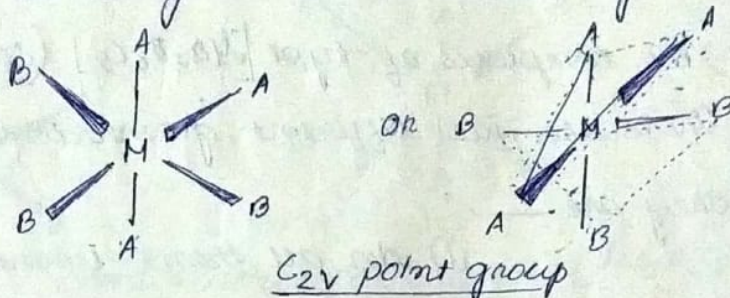
Trans-tetraaminedichloro

Cobalt(II)

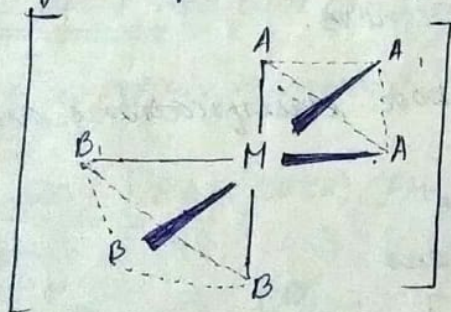
① For $[Ma_3b_3]$ type of complexes there are two ways to define geometrical isomers.

In one isomer, three-A ligands lie in one plane and the three-B ligands lie in a \perp plane.

This complex is designated the "mer-isomer," (for meridional) because each set of ligands can be regarded as lying on the meridian of a sphere.



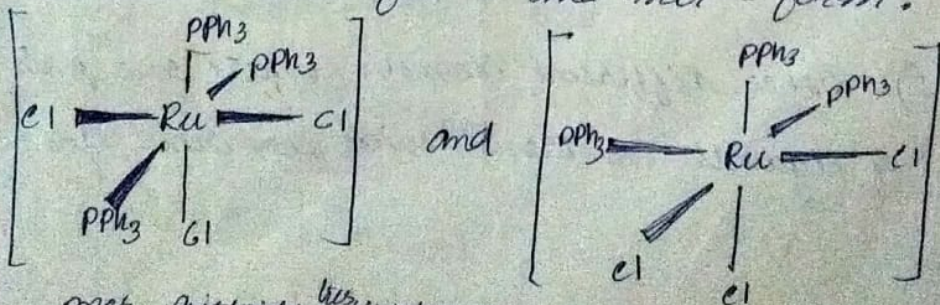
In 2nd isomer, all three-A (and B) ligands are adjacent and occupy the corner of one triangular-face of the octahedron. This complex is designated as fac isomer, (for facial).



fac-isomer.

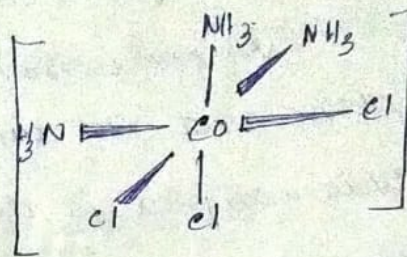
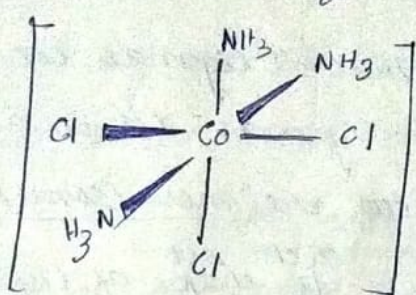
C_{2v} point group

For eg: \rightarrow ~~[PtCl₃(PPh₃)₃]~~ $[RuCl_3(PPh_3)_3]$ exhibit geometrical isomerism with "fac" and "mer" form.



mer-trichlorotris(triphenylphosphine) and fac-trichlorotris(triphenylphosphine)

Similarly, $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ exhibit geometrical isomerism with "fac" and "mer" isomerism.



fac \rightarrow fac-triamminotrichloro cobalt(III)

mer \rightarrow mer-triamminotrichloro cobalt(III)

(*) For complexes of type $[\text{MA}_2\text{B}_2\text{C}_2]$ (Co- no-6).

There are five different geometrical isomers.

They are —

(1) An all trans-isomers.

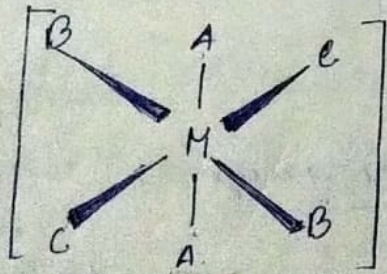
(2) Three different isomers where one pair of ligands are trans with the other two cis.

(3) An enantiomeric pair of all cis-isomers.

Ex.

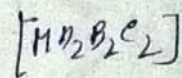
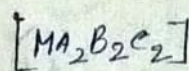
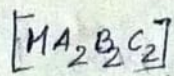
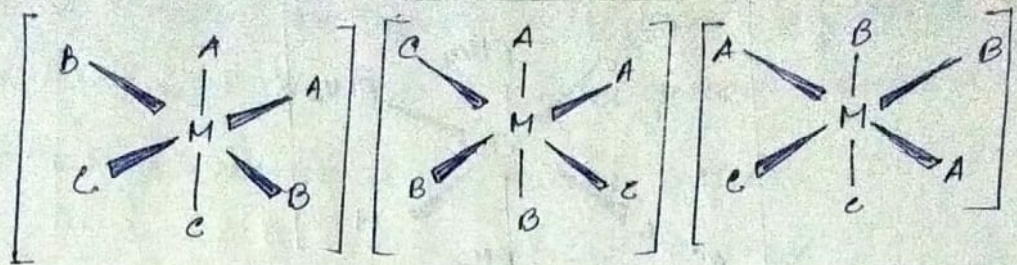
Examples of the above classifications are given below \rightarrow

1) An all trans isomers.

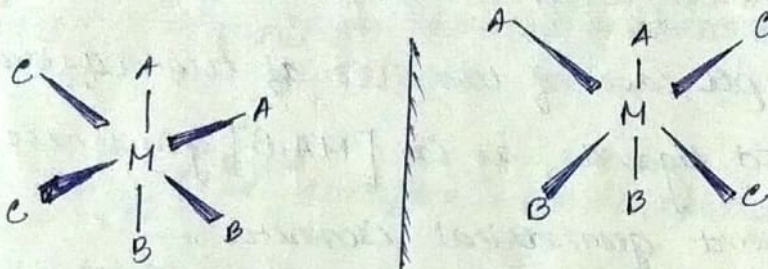


Trans- $[\text{MA}_2\text{B}_2\text{C}_2]$

2) Three different isomers where one pair of ligands are trans with the other two cis.



③ All enantiomeric pairs of all six isomers.



enantiomeric pairs of cis $[MA_2B_2C_2]$

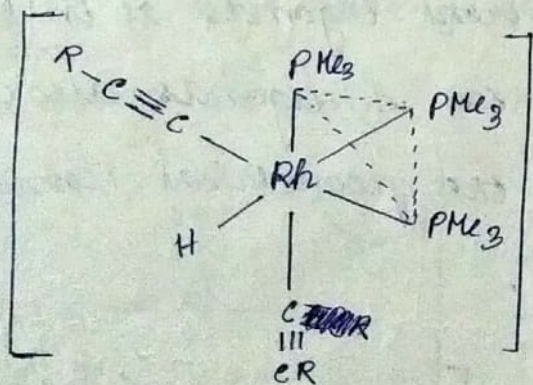
④ More complicated compositions such as $[MA_2B_2CD]$

or, $[MA_3B_2C]$ result in more extensive geometrical isomerism.

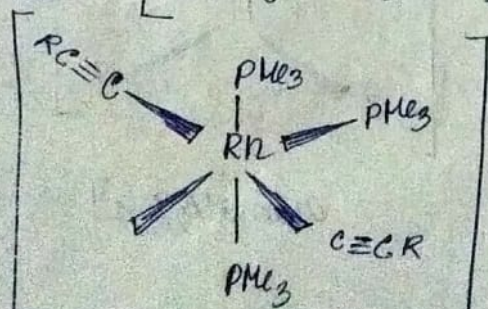
For eg: \rightarrow Rhodium compounds $[Rh(H)(C\equiv CR)_2(PMe_3)_3]$

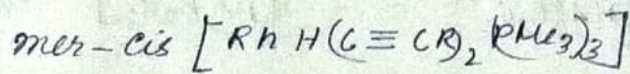
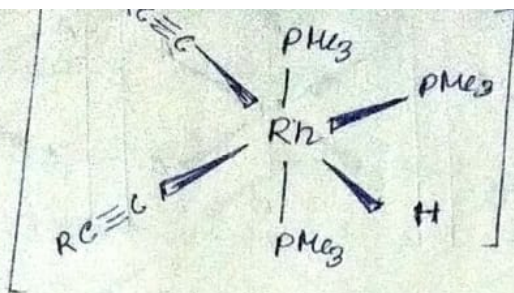
exists as three different isomeric form.

① fac - $[Rh(H)(C\equiv CR)_2(PMe_3)_3]$



② mer - $[Rh(H)(C\equiv CR)_2(PMe_3)_3]$



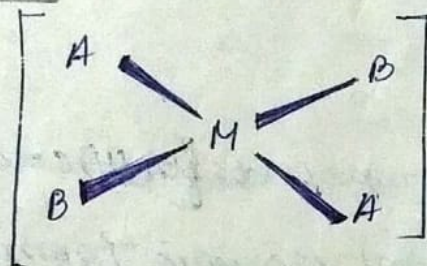


(B) Complexes with co-ordination no four.

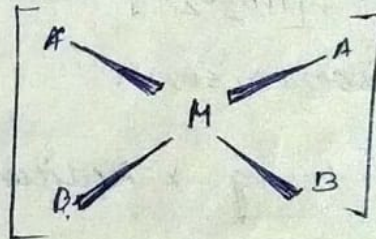
(i) The simple case of two sets of two different monodentate ligands as in $[MA_2B_2]$, gives rise to two different geometrical isomers —

cis and trans form.

For eg: →

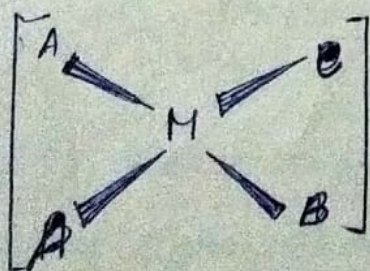


Trans-form

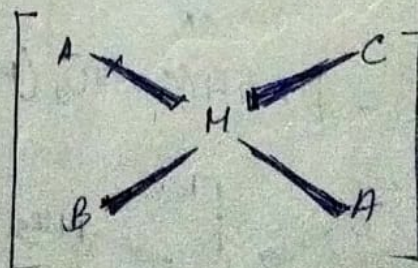


Cis-form.

(ii) With three different ligands as in $[MA_2BC]$ the locations of the two A ligands also allow as to distinguish the geometrical isomers as cis and trans.

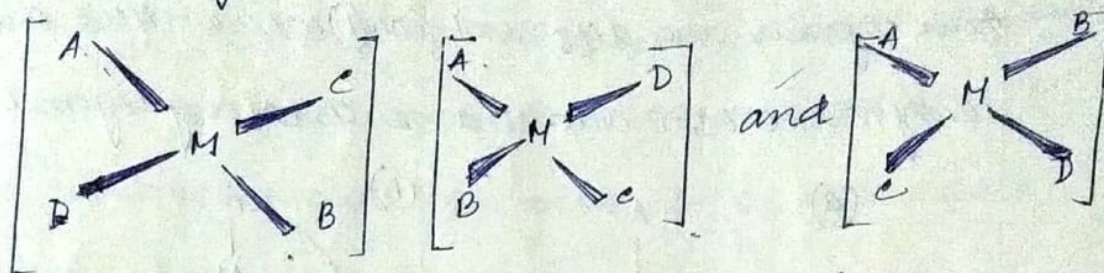


Cis $[MA_2BC]$



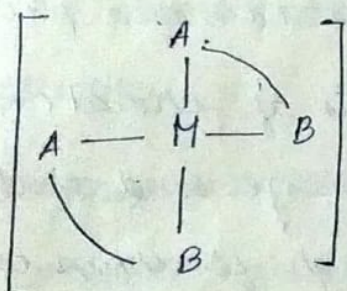
Trans $[MA_2BC]$

(iii) when there are four different ligands as in $[MABCD]$ there are three different isomers. and their geometries are shown below.

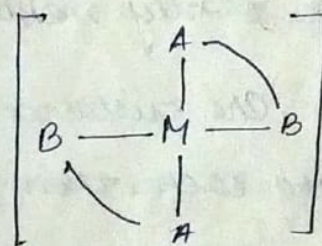


$[MABCD]$, A trans B $[MABCD]$, A trans to C $[MABCD]$, A trans to D.

(iv) $[M(AB)_2]$ i.e. complex with bidentate ligands having different M. groups. can also give rise to geometrical isomers with cis and trans form.

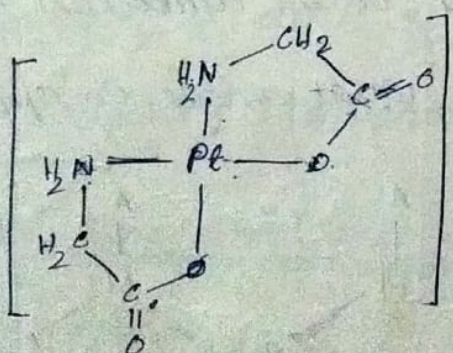


cis- $[M(AB)_2]$

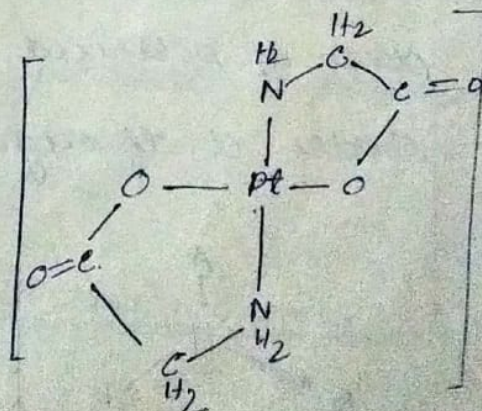


trans- $[M(AB)_2]$

For eg. $\rightarrow [Pt(\text{glycinato})_2]$ complex. can exhibit cis and trans isomers.



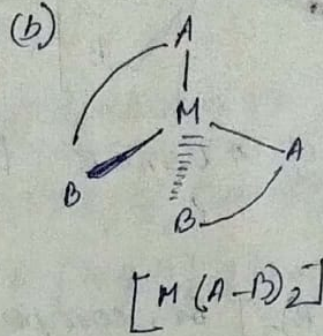
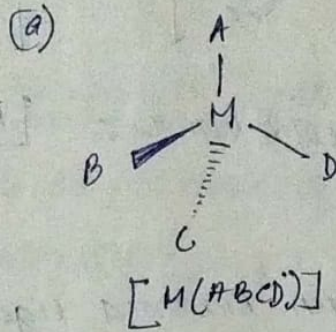
cis- $[Pt(\text{glycinato})_2]$



trans- $[Pt(\text{glycinato})_2]$

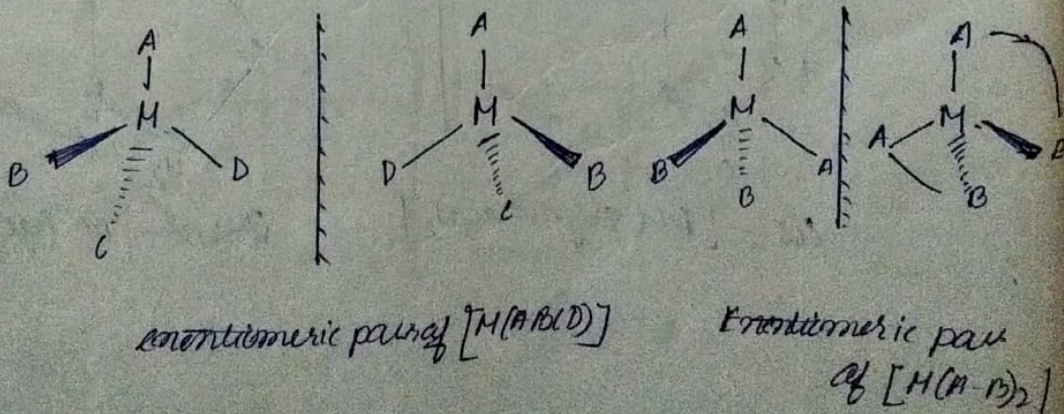
(c) Tetrahedral complexes.

are only isomers of tetrahedral complexes normally encountered are those (a) where either all four ligands are different; or (b) where there are two unsymmetrical bidentate & chelating ligands.



The molecules are chiral, not superimposable on their mirror image, and the two mirror image isomers jointly make up an enantiomeric pair.

The existence of a pair of chiral complexes that are each others mirror image and that have life times that are long enough for them to be separable, this called optical isomerism. Optical isomers are so called because they are optically active. In the sense that one enantiomer rotates the plane of polarized light in one direction and other rotates it through an equal angle in opp. dir.



Optical isomerism :-

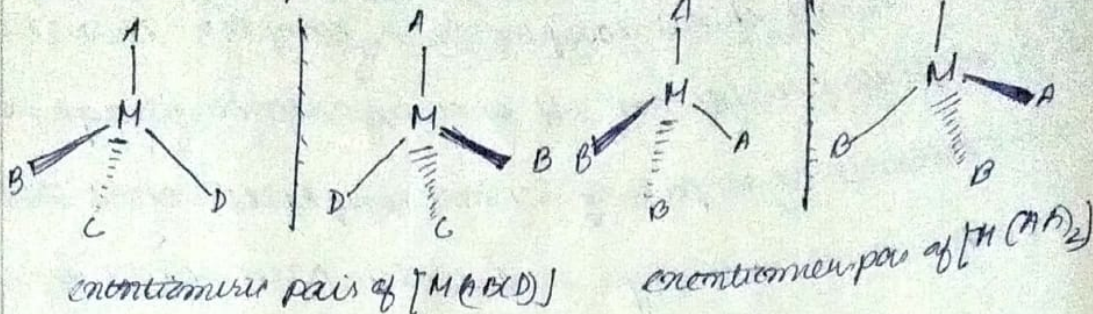
A chiral complex is a complex that is not superimposable on its mirror image. The existence of a pair of chiral complexes that are each other's mirror image and which have lifetimes that are long enough for them to be separable, is called optical isomerism. The two mirror image isomers jointly make up an enantiomeric pair. The optical isomers are so called because they are optically active in the sense that one enantiomer rotates the plane of polarized light in one direction and the other rotates through an equal angle in the opposite direction.

~~The eq: is~~ The formal criterion of chirality is the absence of an axis of improper rotation (S_n axis). The existence of such a symmetry element is applied by the presence of either a mirror plane through the central atom or a centre of inversion, if either of these elements is present the complex is achiral.

Complexes with co-ordination no-4 :-

(a) Tetrahedral complexes with co-ordination no-4 exhibit optical isomerism. Complexes of the type $[MA_2B_2]$ and $[M(AB)_2]$ exist and

enantiomeric pairs,

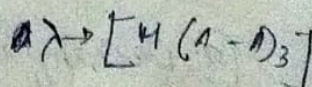
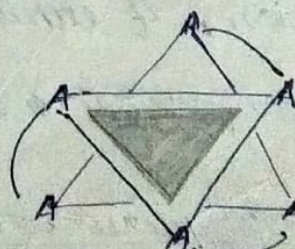
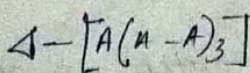
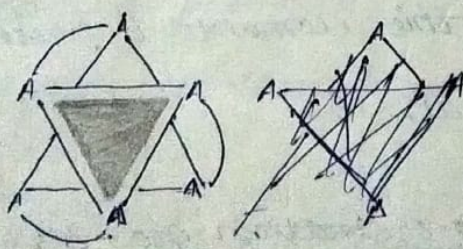
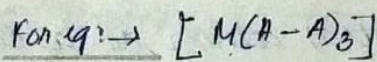


(b) Complexes with co-ordination no-6.

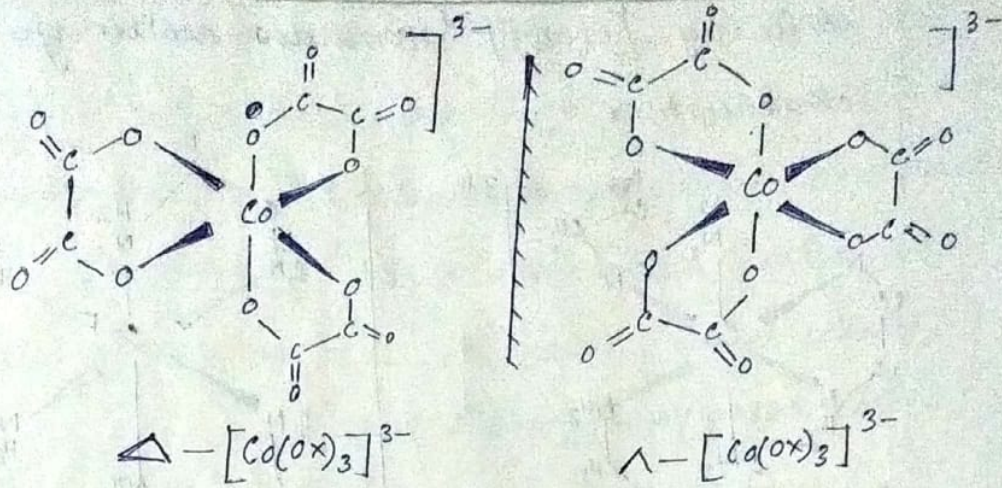
Octahedral complexes (CO-6) exhibit optical isomerism \rightarrow

(1) ~~Comp~~ Octahedral complexes having three bidentate ligand, result in the existence of enantiomers.

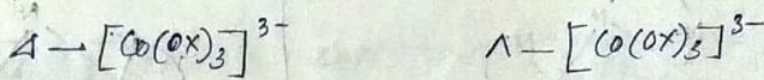
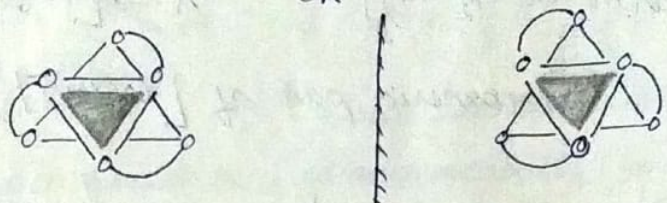
one way of looking at the optical isomers that arises in complexes of this nature is to imagine a view along a three-fold rotation axis ~~and~~ of the regular octahedron and noting the handedness of the helices formed by the ligands.



Few important examples of such type of complexes are $[Mn(acac)_3]$, $[Co(ox)_3]^{3-}$, $[Co(en)_3]^{3+}$ etc.

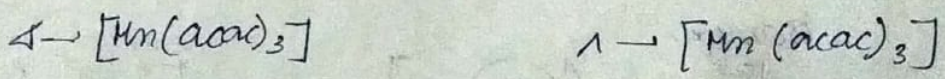
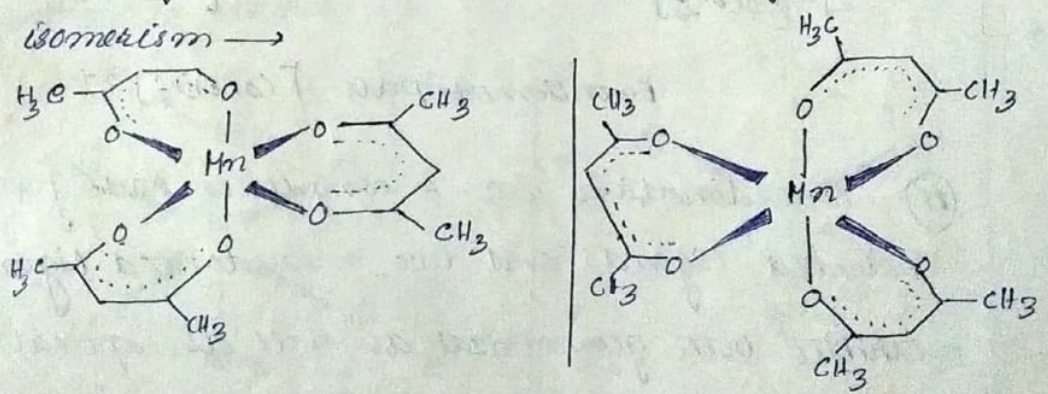


enantiomeric pair of $[Co(ox)_3]^{3-}$
'OR'

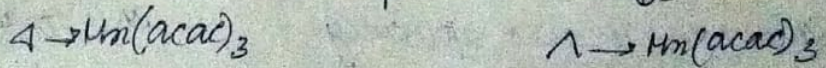


enantiomeric pair of $[Co(ox)_3]^{3-}$

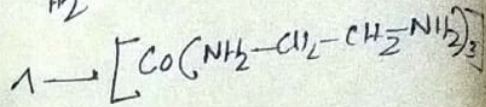
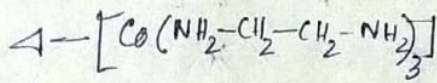
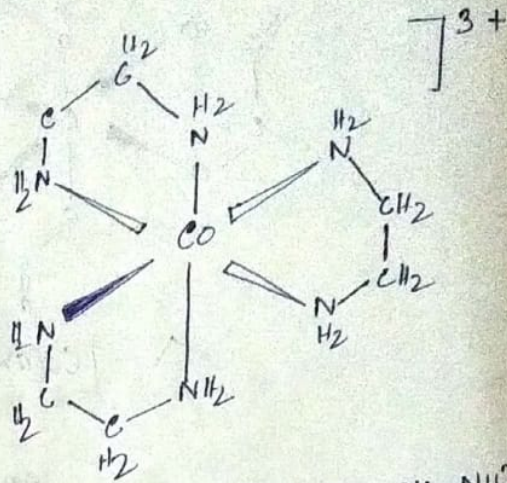
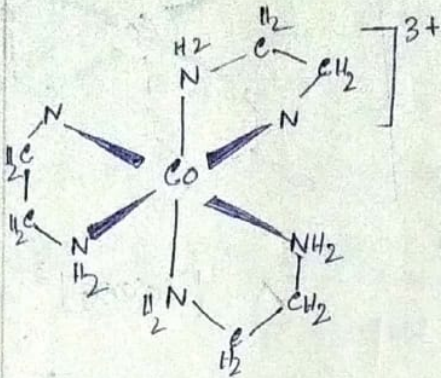
Similarly, $M(acac)_3$ can also exhibit geometrical isomerism \rightarrow



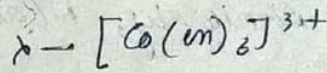
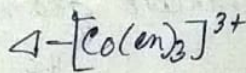
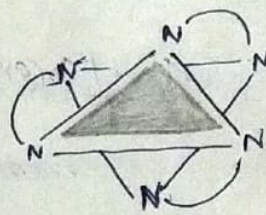
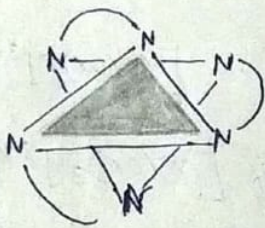
Enantiomeric pair of $[Mn(acac)_3]$



similarly, $[\text{Co(en)}_3]^{3+}$ can also exhibit geometrical isomerism \rightarrow

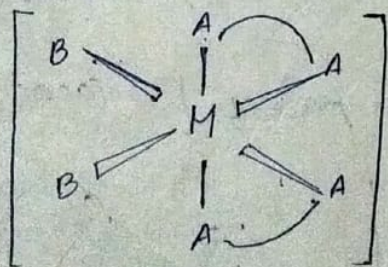


enantiomeric pair of $[\text{Co(en)}_3]^{3+}$

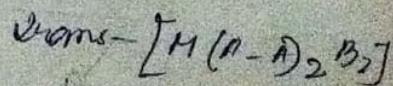
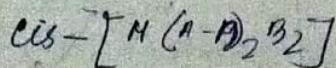
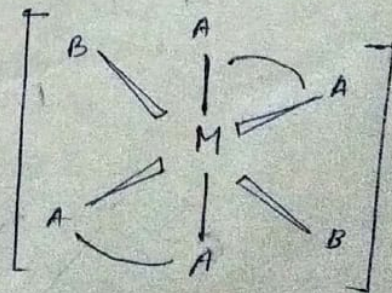


Enantiomeric pair $[\text{Co(en)}_3]^{3+}$

(21) Co-ordination no-6 complexes having two bidentate ligands and two monodentate ligands exhibits both geometrical as well as optical isomers.



and



this form is also optically active. (Diastereomers)

this form is optically inactive.