Chapter-24

Coordination Chemistry (Optical Isomerism)

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Optical activity is the ability of a chiral molecule to rotate the plane of polarized light, measured by a polarimeter. A chiral molecule (optically active) does not have any plane of symmetry or will produce a non-super imposable mirror image. If a molecule possesses any plane of symmetry or will produce supper imposable mirror image is to be treated as an achiral molecule (optically inactive).

Non-superimposable mirror image is the essential condition for coordination compounds to become optically active (chiral).

Optical isomers are capable to rotate plane-polarized light as right side or clockwise called dextrorotatory (d) and left side or anticlockwise called laevorotatory (l). An equilibrium mixture (1: 1) of d and l isomers that give a net-zero rotation is called a racemic mixture.

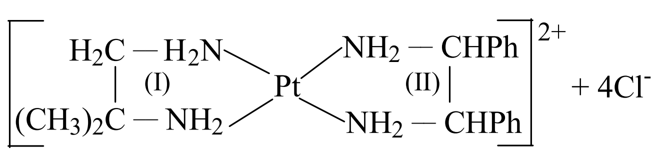
Isomers are mirror images of each other and do not superimposable with each other (called enantiomers) and do not have a plane of symmetry, so they are called chiral compounds or optically active compounds.

In co-ordination compound the optical activity is shown below:

1. Optical isomerism in 4-co-ordination compounds:

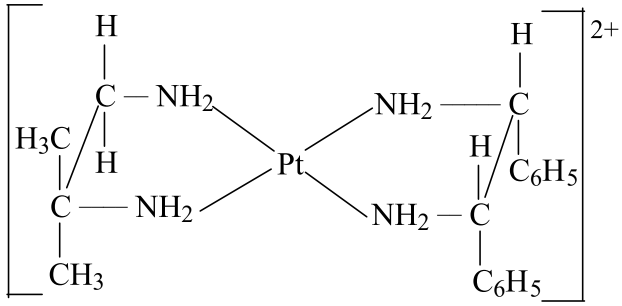
(a) Optical isomerism in *square planar complex*: Optical isomerism is not shown by square planar complex due to four ligands and central metal ion present at the same plane and possess a plane or axis of symmetry.

But Milla and Quibell give an optical isomer of $[Pt(NH_2)CH(C_6H_5)CH(C_6H_5).NH_2(NH_2CH_2C(CH_3)_2NH_2)]^{2+}$ isobutylenediamine-meso-stilbenediamineplatinum(II) cation.



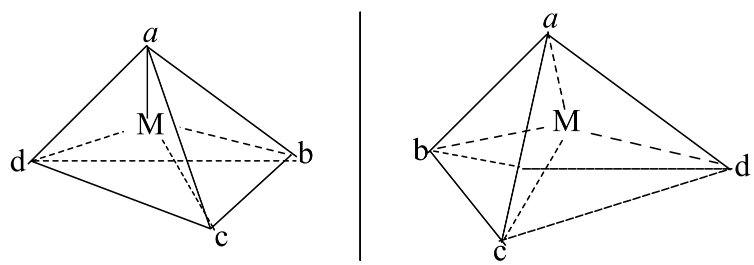
In the above complex cation, there are two rings (1) and (II). When the donor atoms are arranged in a square planar around Pt^{2+} ion, the above structure will have no plane or axis of symmetry,

***i.e.* it is asymmetric and consequently optically active and this complex should give rise to optical isomer** but the tetrahedral shape of this complex is not optically active.



square planar strucutre show optical activity

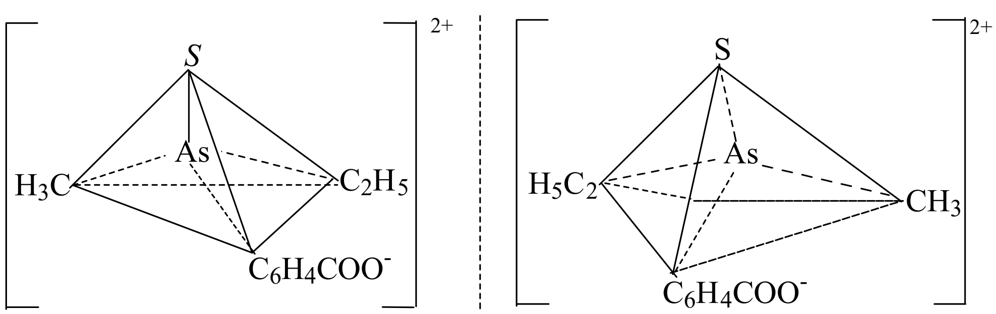
(b) Optical isomerism in *tetrahedral complexes*: The tetrahedral molecule having group [*Mabcd*] type show optical activity as:



both are enantiomers

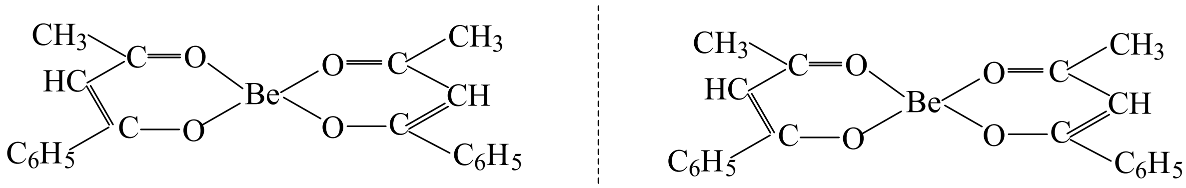
Two optical isomers of tetrahedral complex [*Mabcd*]

e.g. $[As(CH_3)(C_2H_5)S(C_6H_4COO)]^{2+}$ shows optical isomerism as



Mirror plane
both are isomers

It is found that the compounds having two unsymmetric bidentate ligands are easy to resolve into optical isomers such as compounds of Be(II), Zn(II), B(III). Compound bis(benzoylacetonato)beryllium(II) shows two forms.



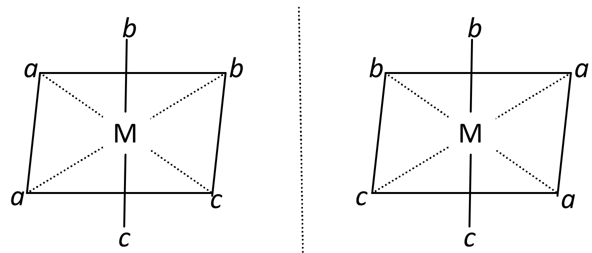
d-form (mirror plane) *l*-form

Both are enantiomorphs.

2. Optical isomerism in 6-co-ordination compounds:

(a) $[Ma_2b_2c_2]^{n\pm}$ type –

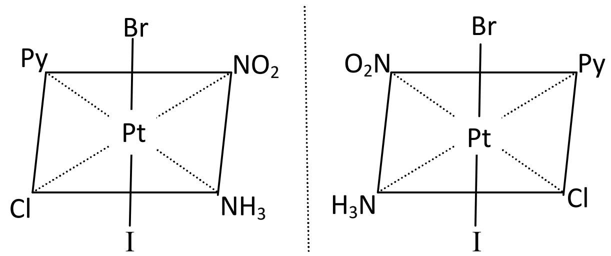
e.g. $[Pt(NH_3)_2(CH_3)_2(C_2H_5)_2]$



cis-form

b) $[Mabcdef]^{n\pm}$ type-

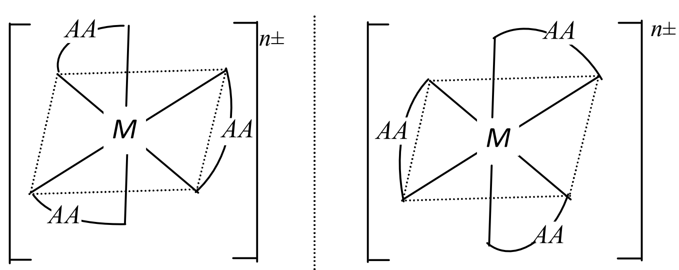
e.g. $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$



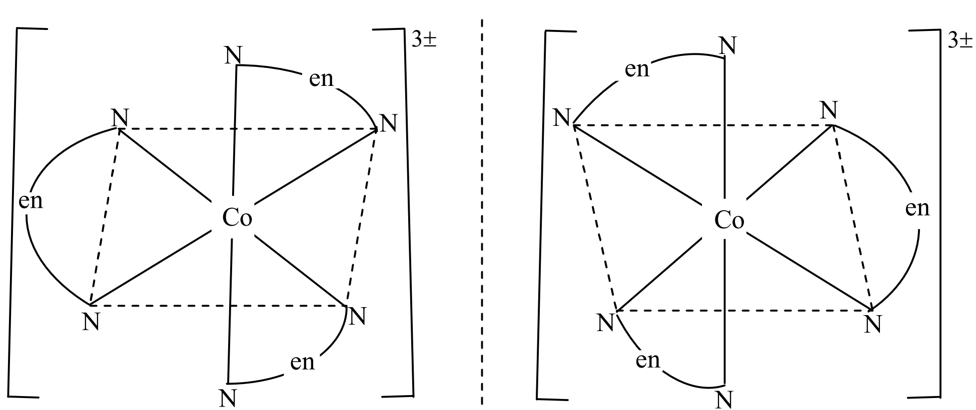
dextro-isomer *laevo-isomer*

c) $[M(AA)_3]^{n\pm}$ type – Here, *AA* = symmetrical bidentate chelating ligand.

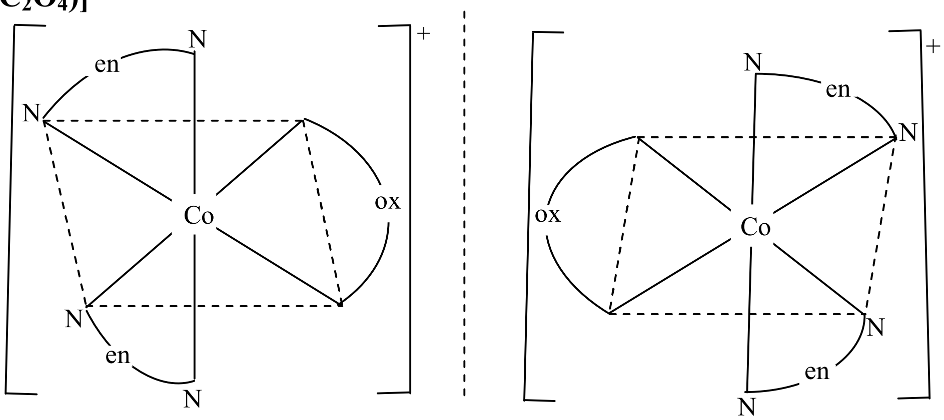
e.g. $[Cr(C_2O_4)_3]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(Ph)_3]^{3+}$, $[Pt(en)_3]^{4+}$ etc.



(*d*-isomer) (*l*-isomer)

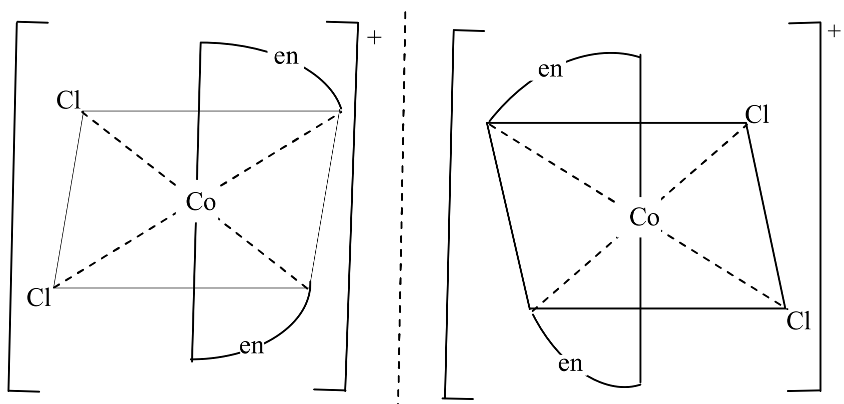


d) $[M(AA)_2(BB)]^{n\pm}$ type –
e.g. $[Co(en)_2(C_2O_4)]^+$



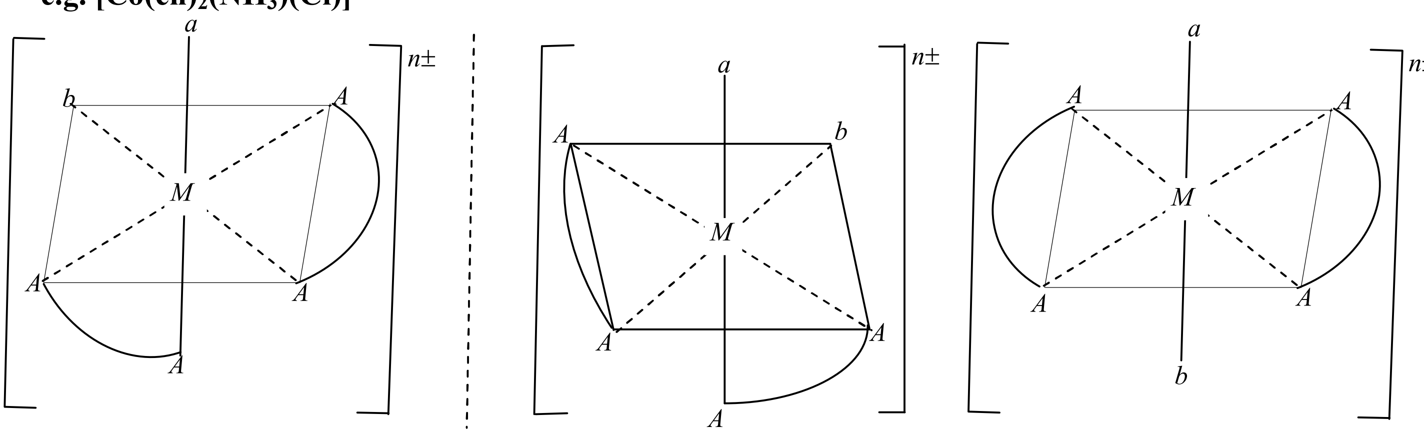
cis-form

e) $[M(AA)_2a_2]^{n\pm}$ type – Here, *AA* = bidentate chelating agent, *a* = unidentate ligand
e.g. $[Co(en)_2Cl_2]^+$



l-form
d-form
cis-form

f) $[M(AA)_2ab]^{n\pm}$ type – Here, *AA* = bidentate ligand, *a, b* = monodentate ligand.
e.g. $[Co(en)_2(NH_3)(Cl)]^{2+}$



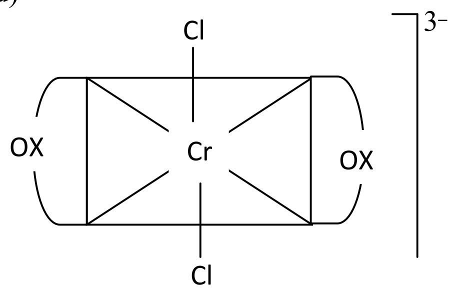
d-form
l-form
Meso-form

Meso-form (*trans* form) contains vertical plane of symmetry and is optically inactive (achiral).

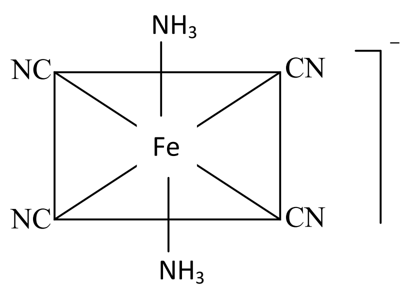
Related Questions

Q.1. The complex that can show optical activity is
a) *trans*-$[Cr(Cl_2)(ox)_2]^{3-}$
b) *trans*-$[Fe(NH_3)_2(CN)_4]^-$
c) *cis*-$[Fe(NH_3)_2(CN)_4]^-$
d) *cis*-$[CrCl_2(ox)_2]^{3-}$ (ox = oxalate)

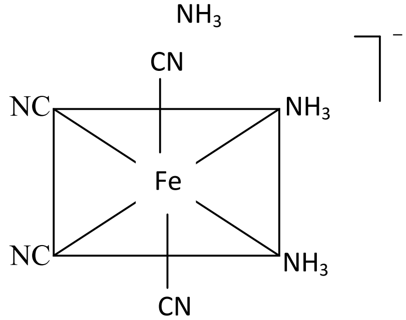
Ans. (d)

(a) 

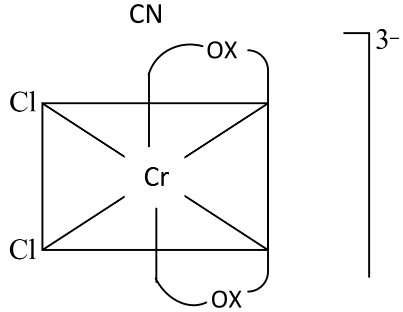
⇒ *trans*-$[Cr(Cl_2)(OX)_2]^{3-}$ will give super-imposable mirror image. (Optically inactive)

(b) 

⇒ *trans*-$[Fe(NH_3)_2(CN)_4]^-$ will also give super-imposable mirror image. (Optically inactive)

(c) 

⇒ *cis*-$[Fe(NH_3)_2(CN)_4]^-$ has also plane of symmetry and it is also optically inactive.

(d) 

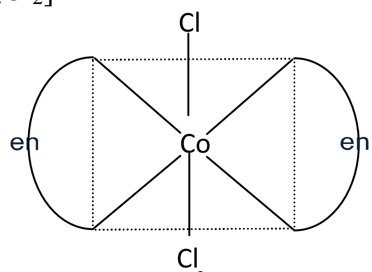
⇒ *cis*-$[CrCl_2(OX)_2]^{3-}$ will give non-supper imposable mirror image. So, it is optically active.

So, option (d) is correct.

Q.2. Consider the complex ions, *trans*- $[Co(en)_2Cl_2]^+$ (*A*) and *cis*-$[Co(en)_2Cl_2]^+$ (*B*). The correct statement regarding them is
a) both (*A*) and (*B*) cannot be optically active
b) (*A*) can be optically active, but (*B*) cannot be optically active
c) both (*A*) and (*B*) can be optically active
d) (*A*) cannot be optically active, but (*B*) can be optically active

Ans. (d)

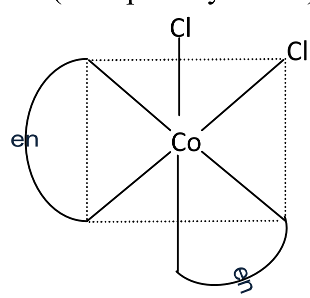
(*A*) trans-$[Co(en)_2Cl_2]^+$



trans-form
(A)

(*A*) is a *trans*-form and shows plane of symmetry. It will produce supper imposable mirror image which makes it optically inactive (not optically active).

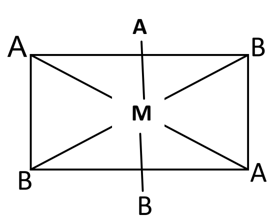
(*B*) *cis*-$[Co(en)_2Cl_2]^+$

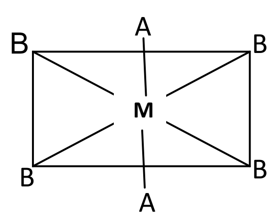


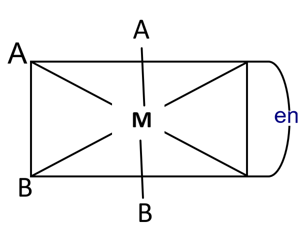
cis-form
(*B*)

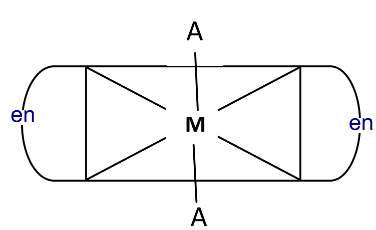
cis-form does not contain any plane of symmetry and it will produce non-supper imposable mirror image which makes it optically active.

Q.3. The one that will show optical activity is (en = ethane – 1, 2-diamine)

(a)


(b)


(c)


(d)


Ans. (*c*)

Optical activity is the ability of a chiral molecule to rotate the plane of polarized light, measured by a polarimeter. A chiral molecule does not have any plane of symmetry or will produce non-supper imposable mirror image. If a molecule possesses any plane of symmetry or will produce supper imposable mirror image is to be treated as an achiral molecule.

Here, options (a), (b) and (d) are trans form and will produce supper imposable mirror image. Hence these are achiral (optically inactive). Only option (c), cis form, will produce non-supper imposable mirror image and is chiral (optically active).

Reference Books:

1. Introduction to Coordination Chemistry, Geoffrey A. Lawrance

2. Coordination chemistry, Joan Ribas Gispert

3. Coordination Chemistry, 20: Invited Lectures Presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, 10-14 December 1979, D. Banerjea

4. Comprehensive Coordination Chemistry III, Gerard Parkin, Edwin C Constable, Lawrence Que

5.https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Coordination_Chemistry/Complex_Ion_Equilibria/Stability_of_Metal_Complexes_and_Chelation

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