Name of the Teacher- Sutapa Chakrabarty

Subject: Chemistry

Class: Semester-4

Paper: C9T: Inorganic Chemistry

Topic: Coordination Chemistry

Part 4

Comments- Study the whole lesson thoroughly.Practice effectively " **different types of geometrical and optical isomers".** Also complete the given assignment.

[N.B. - Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

iii) Polymerisation Isomerism :

This type of isomerism is found in those complex compound whose formula appear to be polymers of some simple complex compound. All these complex compound have the same ratio of diff metal atoms and ligands in them.

eg The following complex compounds are polymeris isomer to each other, since ii) and iii) comp appear to be dimer of i) compound and compound iv) appears to be the pentamer of comp i). The ratio $Co^{+3} : NH_3 : NO_2^-$ in all the compounds is 1:3:3.

Complex	No of Co^{+3}	NH_3	NO_2^-
i) $[Co(NH_3)_3(NO_2)_3]$	1	3	3
ii) $[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6
iii) $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6
iv) $[Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$	5	15	15

Valency Isomerism

The term was used by Werner to complex species in which the same gr. is held in one compound by primary valency and in another compd by secondary valency.

eg $[(en)_2Co\langle^{NH_2}_{O_2^{(-)}}\rangle Co(en)_2]X_4$ and $[(en)_2Co\langle^{NH_2 \cdot HX}_{O_2^{(2-)}}\rangle Co(en)_2]X_3$

Stereo Isomerism :-

When two compound contain the same ligands co-ordinated to the same central metal ion but the arrangement of ligand in space is diff, then the compounds are said to be stereoisomer and the phenomenon is known as stereoisomerism.

Stereoisomerism is two types :
i) Geometrical Isomerism or Cis-trans isom
ii) Optical or mirror image Isomerism

i) **Geometrical Isomerism :**

The complex compound which have the same ligand in the co-ordination sphere but the relative position of the ligand around the central metal ion is diff are called geometrical isomers and the phenomenon is called geometrical isomerism.

In a given complex compd the two ligands may occupy positions either adjacent to each other or opposite to each other. The complex compd having two ligands occupying the adjacent positions to each other is called 'cis'-isomer while that in which the two ligands occupy opposite position is called trans isomer. Thus geometrical isomerism is also called 'cis-trans' isomerism.

Geometrical isomerism is not found in complex with co-ordination no. 2 and 3, since in these cases all the positions occupied by the ligands around the central metal atom are adjacent to one another. The Geometrical isomerism is most common with the complex having CN 4 and 6

» Geometrical isomerism 4 'CN' compounds

Complexes having central atom with CN-4 may have either tetrahedral or square planar geometry.

Geometrical isomerism cannot be shown by tetrahedral complexes, since all the 4-ligands in this geometry have adjacent position to one another and all the 4-bond angles are the same.

» Geometrical isomerism in square planar complexes :

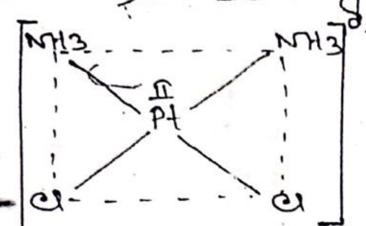
i) $[Ma_4]$, $[Ma_3b]$ $[Mab_3]$ complexes

Square planar complexes of this type donot show geometrical isomerism, since all the possible arrangement of 4-ligands around the central metal atom is the same.

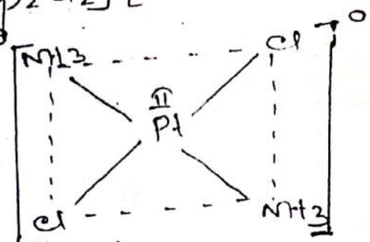
ii) **Ma_2b_2 type complexes :**

Here M = metal ion and 'a' and 'b' are monodentate ligand. Complexes of these type can exist in cis & trans isomers.

eg [$Pt(NH_3)_2Cl_2$] [$Pt(Py)_2Cl_2$] [$Pd(NH_3)_2NO_2$] etc



(cis isomer)
'a'



(trans isomer)
'b'

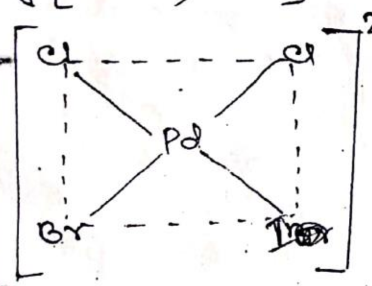
Cis and trans isomers of [$Pt(NH_3)_2Cl_2$]^0

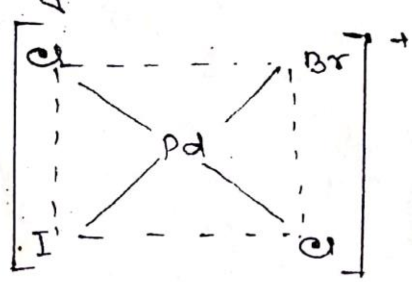
In figure 'a', since both NH_3 molecule and both Cl^- ion are cis to eachother it is called cis isomer. On the otherhand in figure 'b' since both NH_3 mole and both Cl^- ion are trans w.r.to each other it is called trans isomer.

iii) **Ma_2bc type complexes :**

Squareplanar complexes of this type also show cis-trans isomerism.

eg [$Pd(Cl_2)BrI$]$^{2-}$, [$Pt(Py)_2(NH_3)Cl$]$^+$ etc



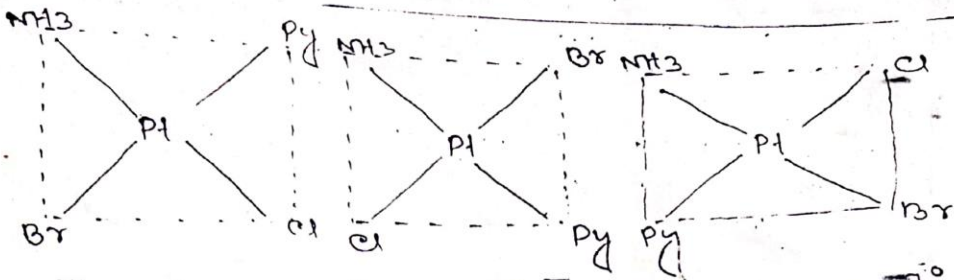


iv) **Mabcd type complexes :**

Complexes of this type exist in three isomeric form

eg: [$Pt(NH_3)(Py)(Cl)Br$]^0 [$Pt(NO_2)(Py)(NH_3)(NH_2OH)$]$^+$

[$Pt(C_2H_4)(NH_3)(Cl)Br$]^0

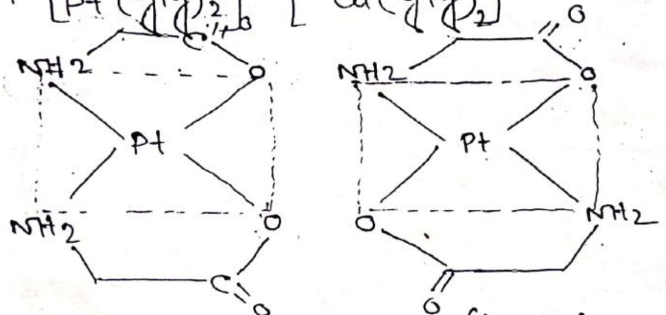


Three isomeric forms of $[Pt(NH_3)(Py)(Cl)(Br)]^0$.

v) $[M(ab)_2]$ complexes

Here M = central metal ion and 'ab' represent an unsymmetrical bidentate ligand in which 'a' and 'b' are two diff. co-ordinating atoms. complexes of this type also exist in cis and trans isomer.

eg: $[Pt(gly)_2]^0$ $[Cu(gly)_2]^0$

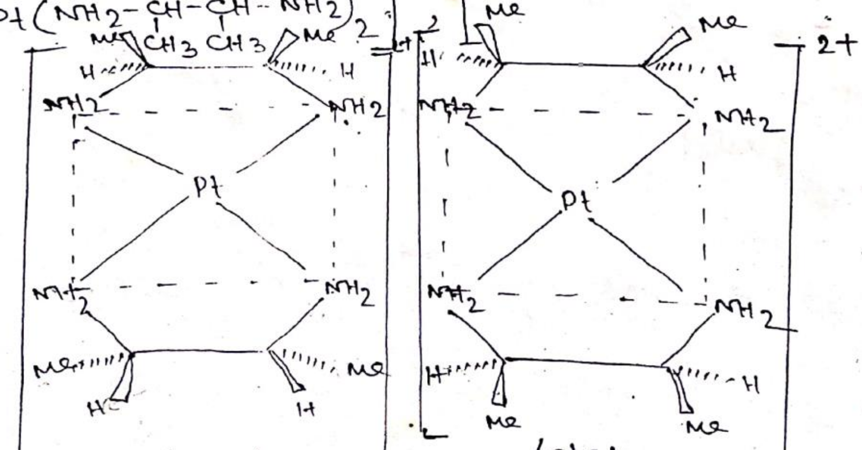


(cis) (trans).

vi) $[M(aa)_2]$ complexes

Such type of complexes also have cis and trans isomers

eg. $[Pt(NH_2-CH(CH_3)-CH(CH_3)-NH_2)_2]^{2+}$

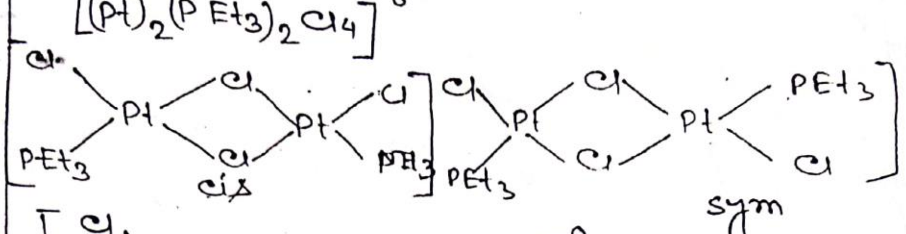


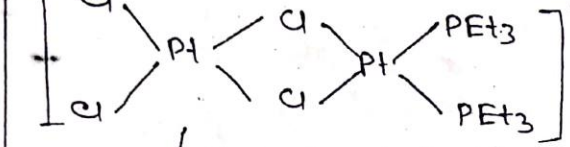
(trans) (cis)

vii) $[M_2a_2b_4]$ type complexes.

In bridged bineuclear squareplanar complexes cis-trans isomers as well as the unsymmetrical isomers are possible.

$[(Pt)_2(PEt_3)_2Cl_4]^0$





(unsymmetrical)

Geometrical isomerism in octahedral complexes

The following type of octahedral complexes show geometrical isomerism.

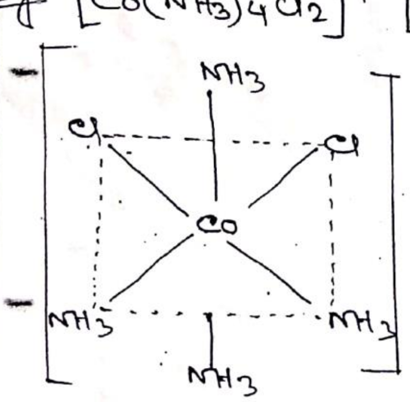
i) $[Ma_6]$ $[Ma_5b$ & $M(aa)_3]$ type complexes:

This type of complexes donot exhibit geometrical isomerism.

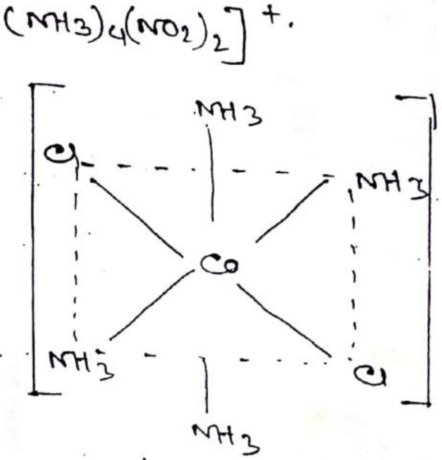
ii) $[Ma_4b_2]$ type complexes:

These complexes exist in cis and trans isomers

Eg: $[Co(NH_3)_4Cl_2]^+$ $[Co(NH_3)_4(NO_2)_2]^+$.



cis



trans

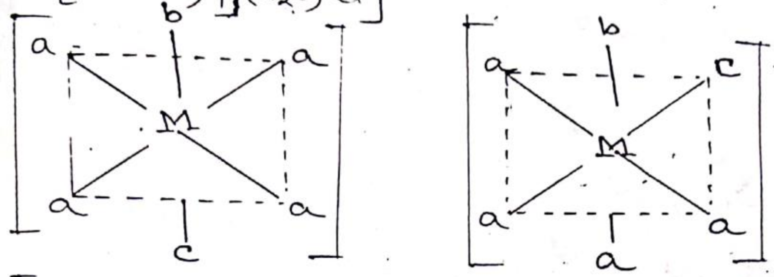
Cis and trans isomers of $[Co(NH_3)_4Cl_2]^+$

In cis isomer, two Cl^- ions occupy the adjacent position of the octahedron while in trans isomer these ion has opposite position.

iii) [Ma_4bc] type

This type of complexes show cis and trans isomers.

eg. $[Co^{III}(NH_3)_4(H_2O)Cl]^{2+}$



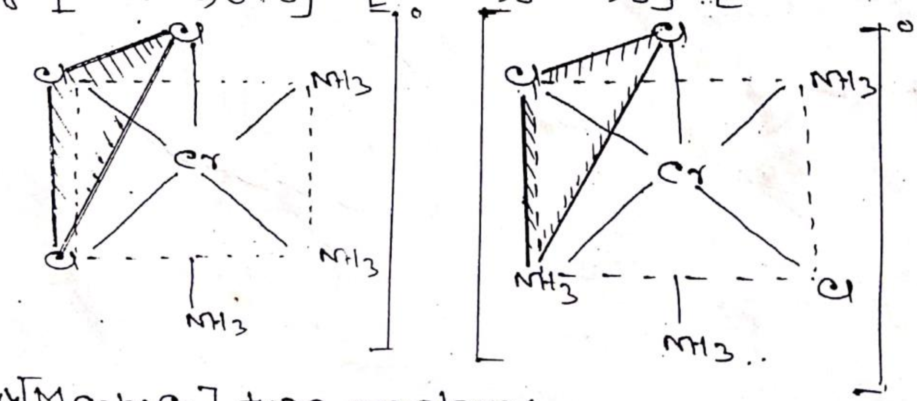
iv) [Ma_3b_3] complexes

This type of complexes exhibit two geometrical isomers;

i) The ligands of one type may form an equilateral triangle on one of the faces called facial or 'fac' isomer.

ii) The ligands of one type may occupy three positions such that two are trans to each other is called meridional or 'Mer' isomer.

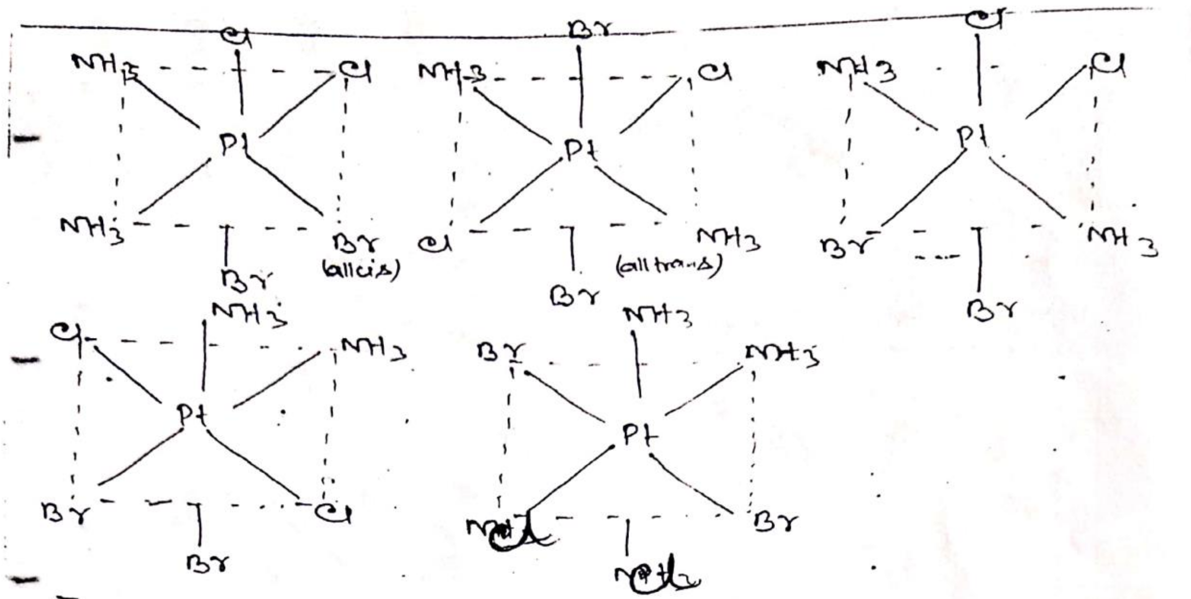
eg. $[Cr(NH_3)_3Cl_3]^0$ $[Co(NH_3)_3(NH_2)_3]^0$ $[Co(NH_3)Cl_3]^0$ etc.



v) [$Ma_2b_2c_2$] type complexes.

This type of complexes exhibit 5 geometrical isomers.

eg. $[Co(NH_3)_2Cl_2Br_2]^-$, $[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$



vi) [M abcdef] type complexes :

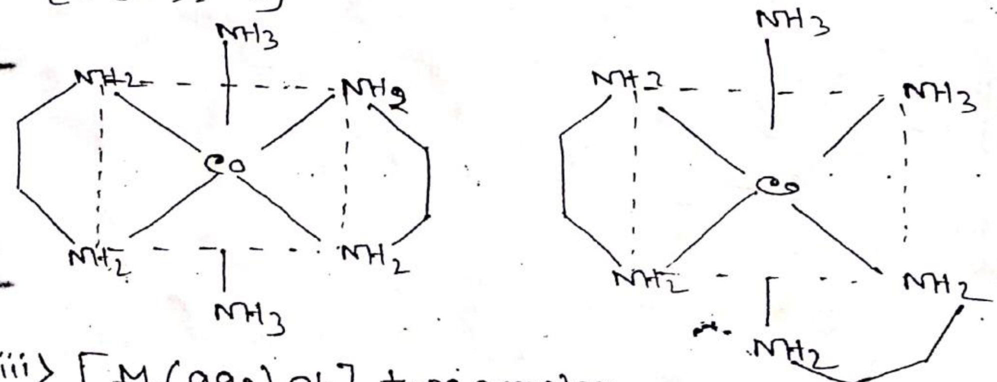
Octahedral complexes which have diff. monodentate ligands exhibit 15 geometrical isomer.

eg. $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]^0$

vii) $[M(AA)_2(a)_2]$ type

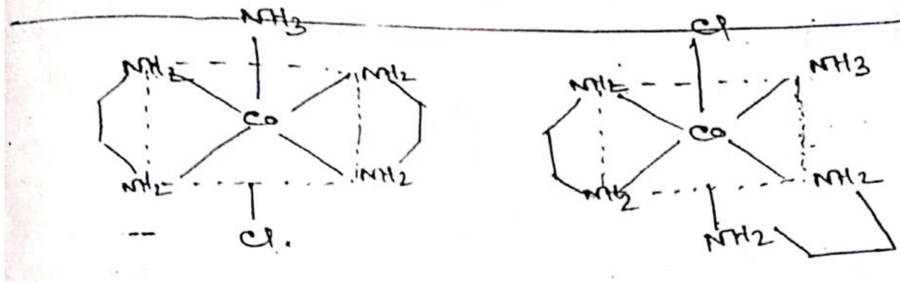
Here 'aa' represents a symmetrical bidentate ligand in which 'a' and 'a' two identical co-ordinating atoms. This type complexes exist in cis and trans isomer.

eg $[Co(en)_2(NH_3)_2]^{3+}$ $[Co(en)_2(NO_2)_2]^+$ $[Cr(en)_2Cl_2]^+$ $[Co(en)_2Cl_2]^+$



viii) $[M(aa)_2ab]$ type complex.

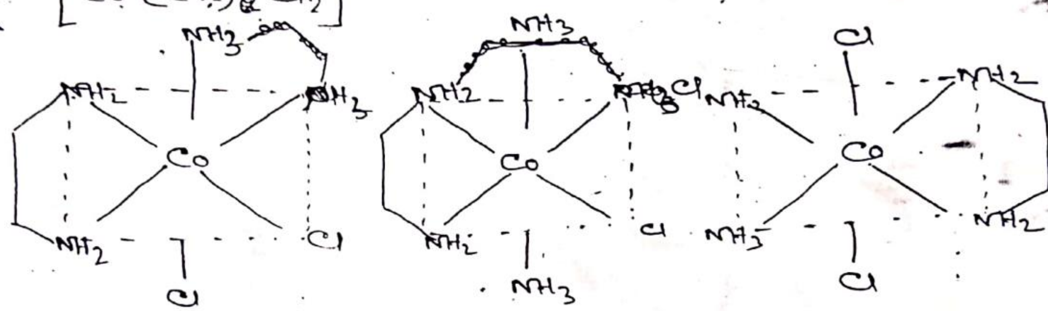
eg $[Co(en)_2NH_3Cl]^{2+}$



ix) $[M(aa)a_2b_2]$ complexes :

Complexes of this type exist in three isomers (1-cis, 2-trans)

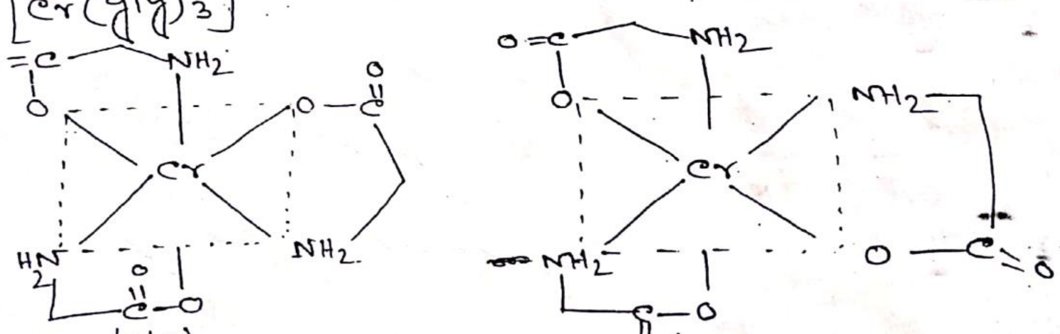
eg: $[Co(en)_2\,^{(NH_3)}Cl_2]^+$



x) $[M(ab)_3]$

Here 'ab' represents an unsymmetrical bidentate ligand in which 'a' and 'b' are two diff. co-ordinating atoms. complexes of this type exist in two geometrical isomers.

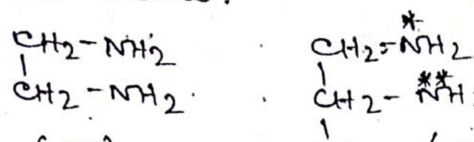
$[Cr(gly)_3]^0$



(cis) (trans)

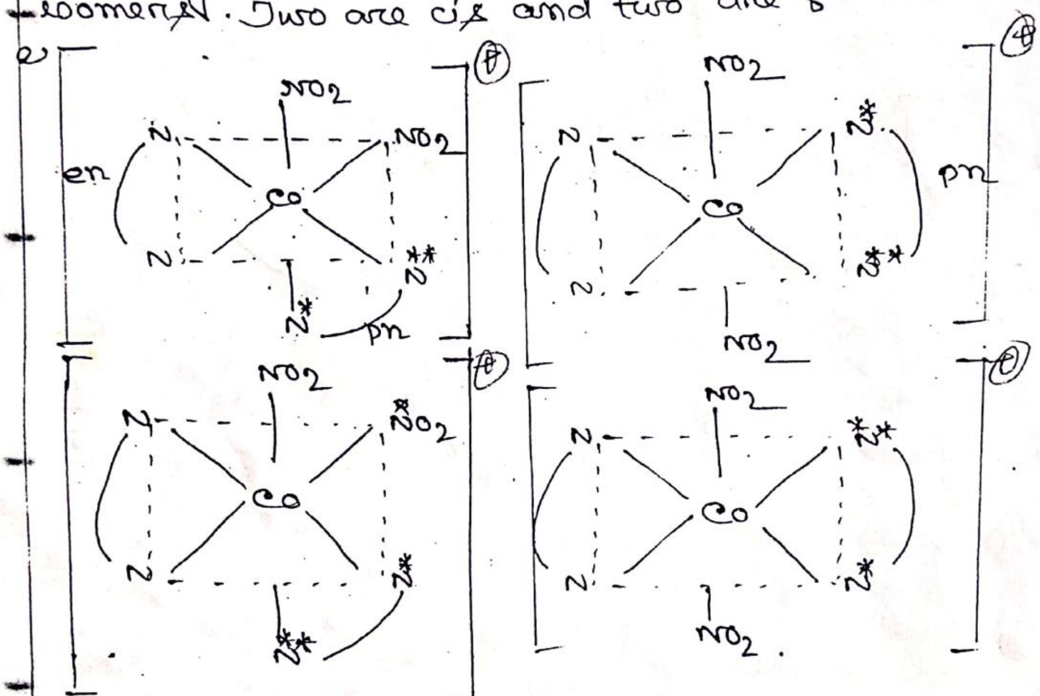
xi) Octahedal complex containing optically active bidentate ligand.

$[Co(en)(pn)(NO_2)_2]^+$ is an important eg of such type of complexes. Here 'en' and 'pn' are ethylene diamin and 1,2-diaminopropane respectively. Both of this ligands are bidentate and their structures are given below.

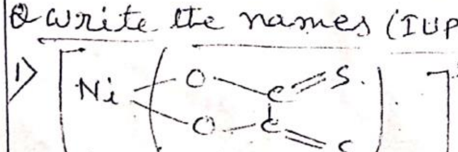


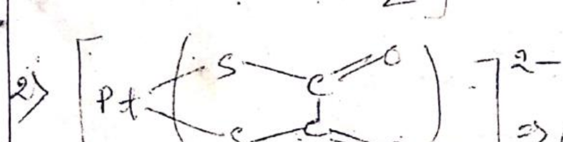
(en) (pn)

This type of complexes exhibit four geometrical isomers. Two are cis and two are trans.



Q write the names (IUPAC) of the following compounds

1)  ⇒ Bis(dithiooxalato-O,O')-Nickelate(II) ion,

2)  ⇒ Bis(dillhiooxalato-S,S')-Platinate(II) ion

Optical Isomerism in four coordinated tetrahedral complexes :

S.S. Das
Bajkul &
Nandakumar

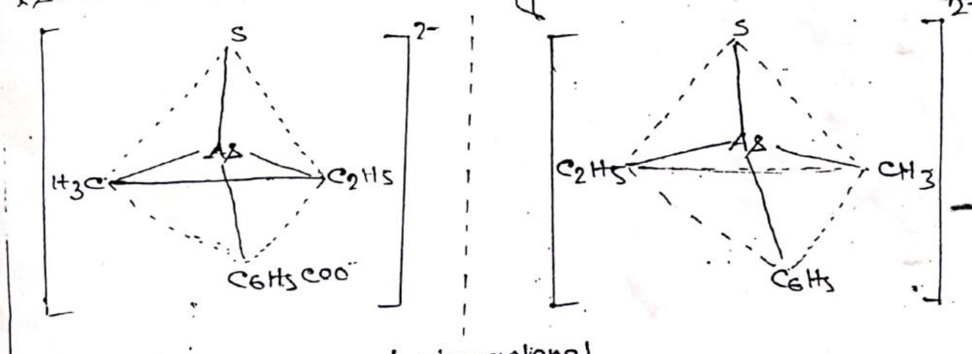
1. $[Ma_4]$, $[Ma_2b_2]$ $[Ma_3b]$ type complexes

Tetrahedral complexes of $[Ma_4]$, $[Ma_2b_2]$ and $Ma_3b]$ type are not able to show optical isomerism because all the possible arrangements of the ligands around the central metal ion are exactly equivalent.

2. [Mabcd] type complexes

Since the central metal atom in tetrahedral complex of [Mabcd] type is surrounded by four diff. ligands the tetrahedral complex of this type is expected to produce a pair of enantiomers.

eg $[\overset{III}{As}(Me)(Et)(S)(C_6H_5COO^-)]^{2-}$ exist in two optical isomers as shown in figure below;



Tetrahedral complexes of symmetrical bidentate ligand

Tetrahedral complexes of Be(II), B(III) and Zn(II) with symmetrical bidentate lig. resolves into optical isomers. Some eg of Td-complexes of this type are. Bis (Salicyldehydato) Boron (III) ion and Bis (Benzoyl acetonato) Berullium (II) whose optical isomers are given below

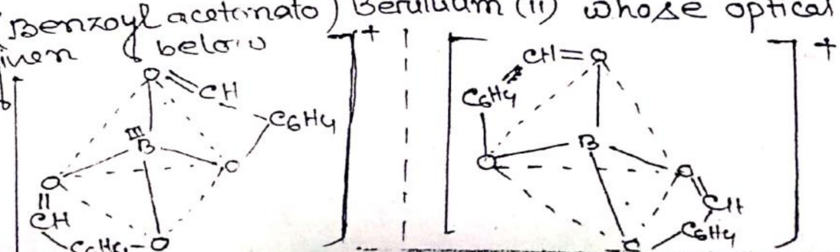
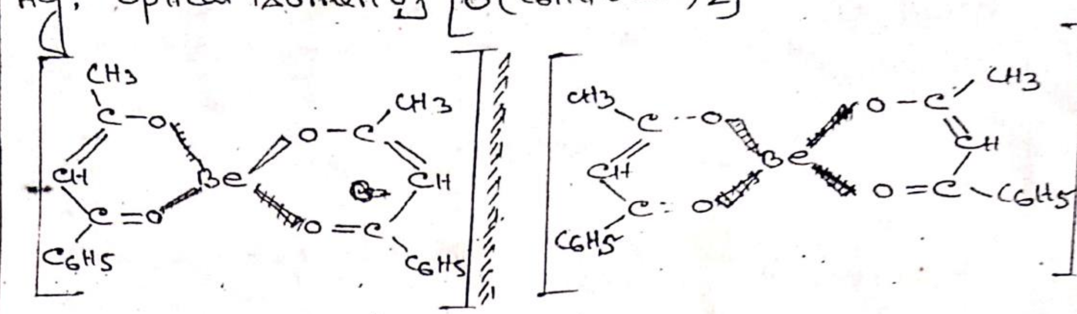
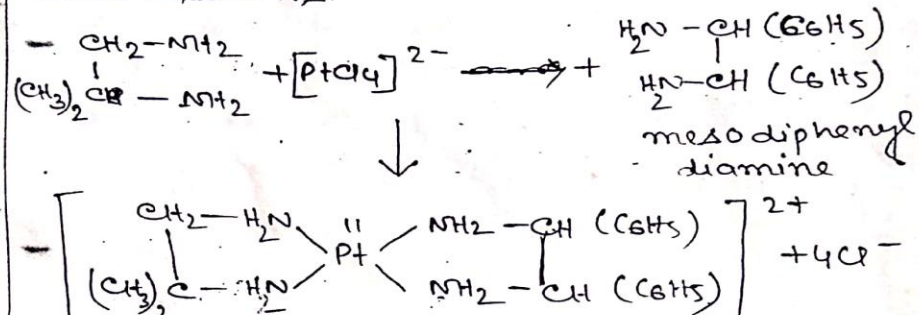


Fig: Optical isomer of $[B^{II}(C_6H_4OCHO)_2]^+$ ion.

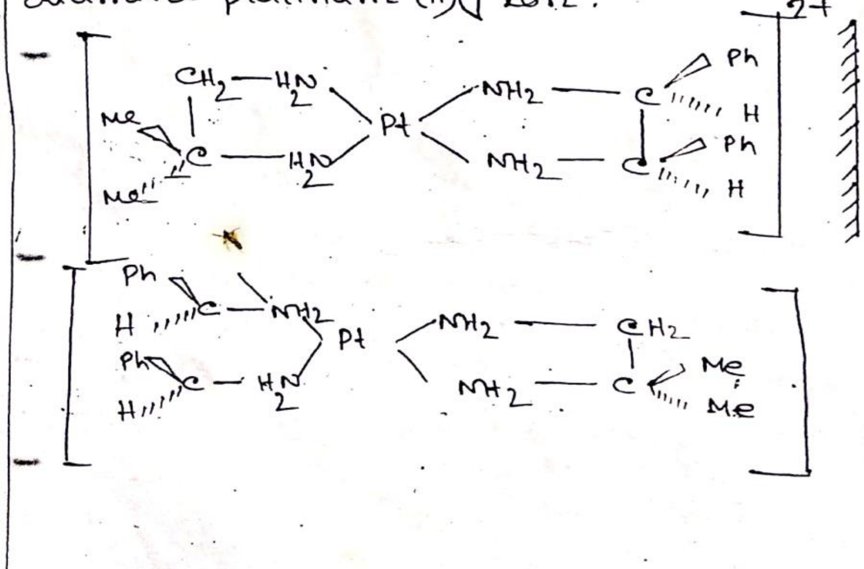


Optical Isomerism in square planar complexes:

i) Isobutylene diamine and meso diphenyl ethylene diamine react with $[PtCl_4]^{2-}$ ion and forms a squareplanar complex which exist in two optically active isomers.



Formation of isobutylene diamine meso stilbene diamine platinum (II) ion.



Optical isomerism in Six-co-ordinated (octahedral complexes) :

1. [Ma_4b_2] [Ma_3b_3] type complexes :

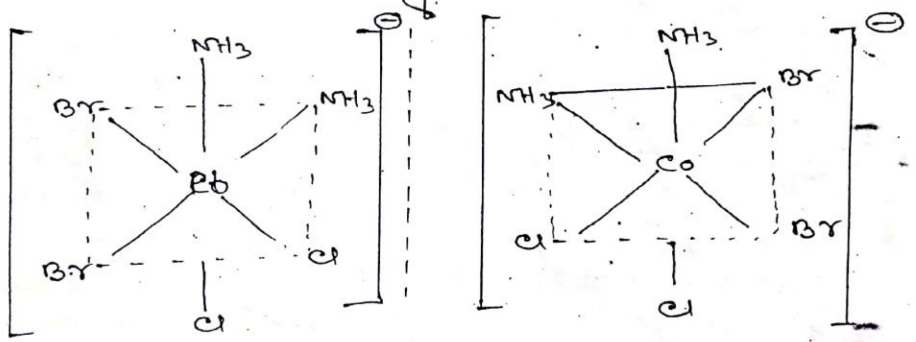
The octahedral complexes of [Ma_4b_2] type exist in cis and trans isomers. Both these isomers are optically inactive due to the presence of symmetry and do not show optical isomerism.

The octahedral complexes of Ma_3b_3 type exist in 'fac' and 'mer' isomers. Both these isomers are optically inactive and hence donot show optical isomerism.

ii) [$Ma_2b_2c_2$] type complexes :

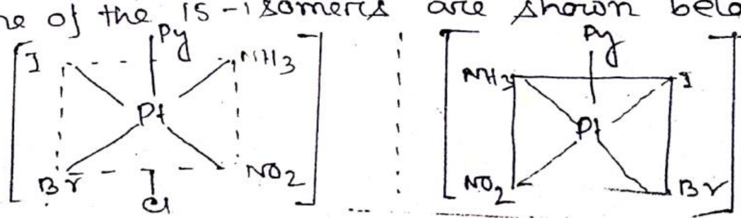
These type of complexes can exist in 5-geometrical isomers. The cis isomer exist in two optical isomers. The other four isomers are symmetrical and hence are optically inactive.

eg



iii) [Mabcdef] type complexes :

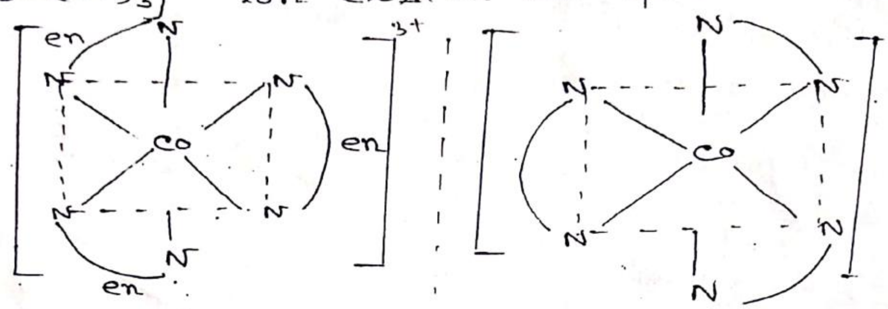
This type of complexes can exist in 15-geometrical isomers. Each of these 15-isomers exist in optically active 'd' and 'l' forms given a total 30-active isomers. The two-optically isomer of one of the 15-isomers are shown below.



(iv) $[M(aa)_3]$ type complexes :

Due to the absence of plane of symmetry or centre of symmetry the octahedral complexes of this type are resolvable into dextro and levo form

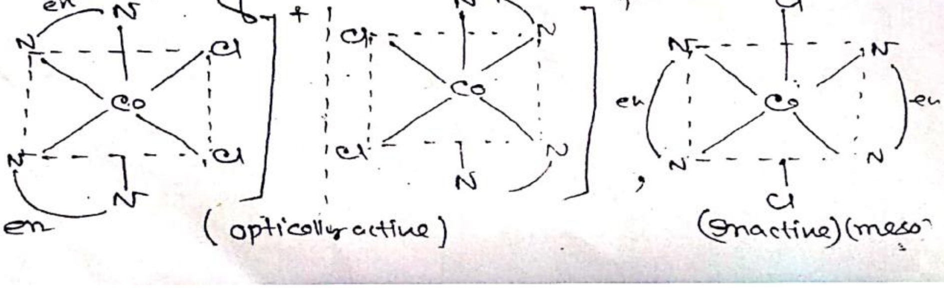
eg: $[Co(en)_3]^{+3}$ ion exist in two optical isomers



The other eg are $[Cr(ox)_3]^{3-}$, $[Pt(en)_3]^{4+}$ etc

(v) $[M(aa)_2a_2]$ type complexes.

$[Co(en)_2Cl_2]^+$ ion is an eg of this type of complexes. This ion shows two geometrical isomers – one is cis and another is trans form. The cis isomer does not have any plane or centre of symmetry and hence is optically active. ie, The cis isomer can be resolved into two optically active isomers. On the other hand the trans isomer has a plane of symmetry and hence is optically inactive (meso). Consequently this ion has three isomers, two optically active corresponding to cis config. and one optically inactive corresp. to trans configuration.



(optically active) (inactive) (meso)

The other eg. of this type of complexes are $[Co(en)_2(NO_2)_2]^+$, $[Ir(ox)_2Cl_2]^{2-}$ and $[Cr(ox)_2(H_2O)_2]^-$ etc.

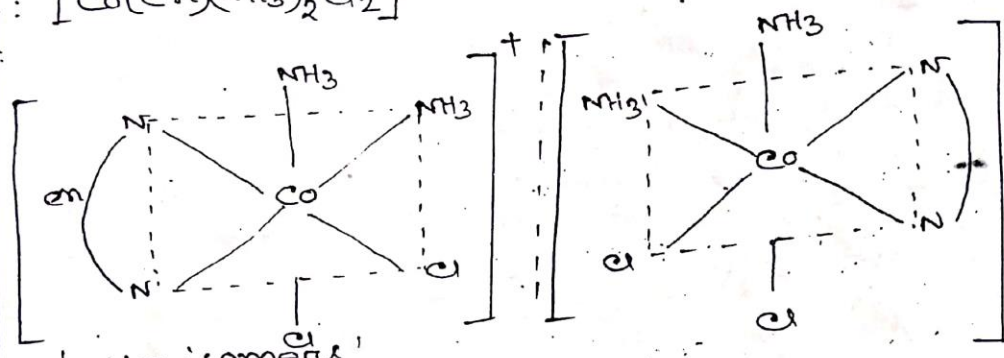
vi) $[M(aa)_2ab]$ type complexes :

(Same as above iv)

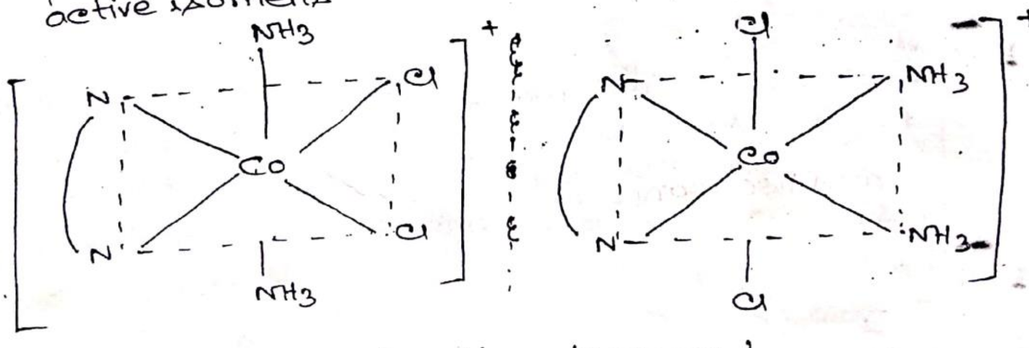
vii) $[M(aa)_2b_2]$ type complexes :

This type of complexes exist in three geometrical isomers. The cis isomer is optically active and hence gives optically active 'd' and 'l' forms, on the other hand the other two geometrical isomers are optically inactive.

eg : $[Co(en)(NH_3)_2Cl_2]^+$



'active isomers'



'two optically inactive isomers'

viii) $[M(ab)_3]$ type complexes :

The octahedral complexes of this type exist in two geometrical isomers. Each of these forms is optically active and hence each give a pair of optical isomers eg: $[Cr(gly)_3]^0$

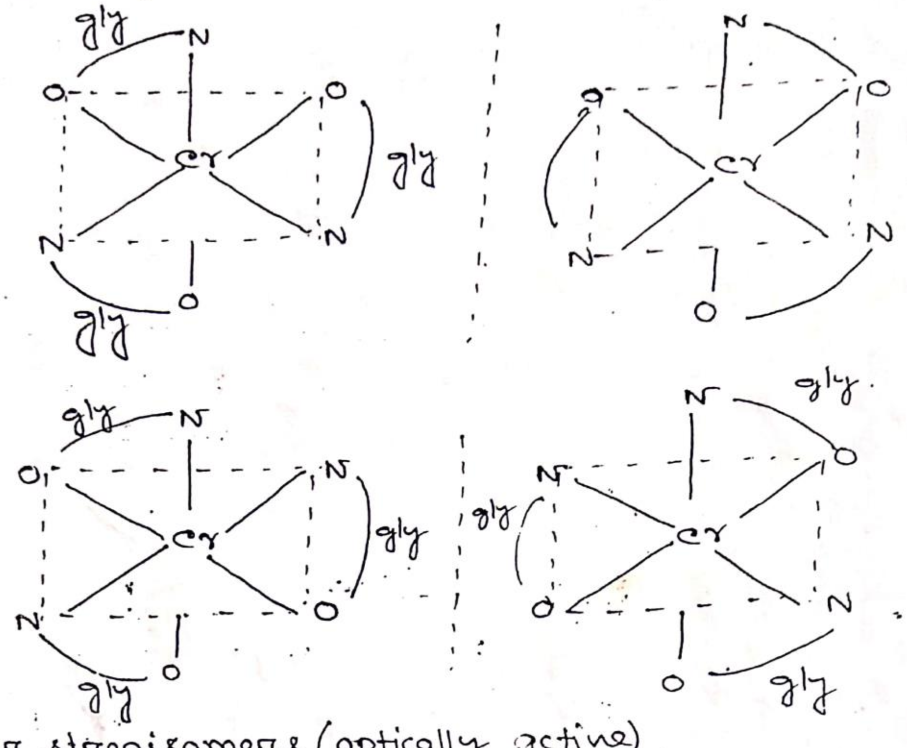
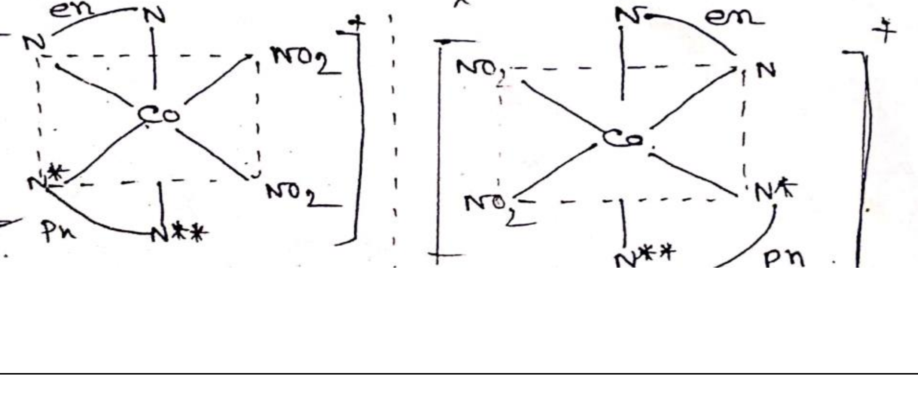


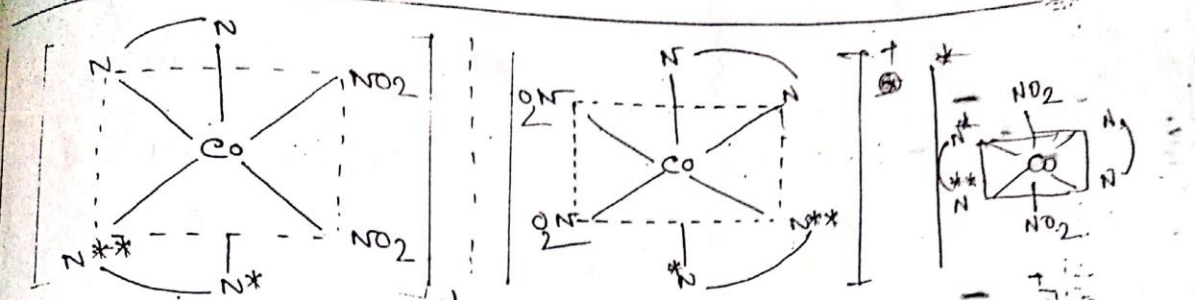
fig: four streoisomers (optically active).

ix) Octahedral complexes containing optically active ligands :

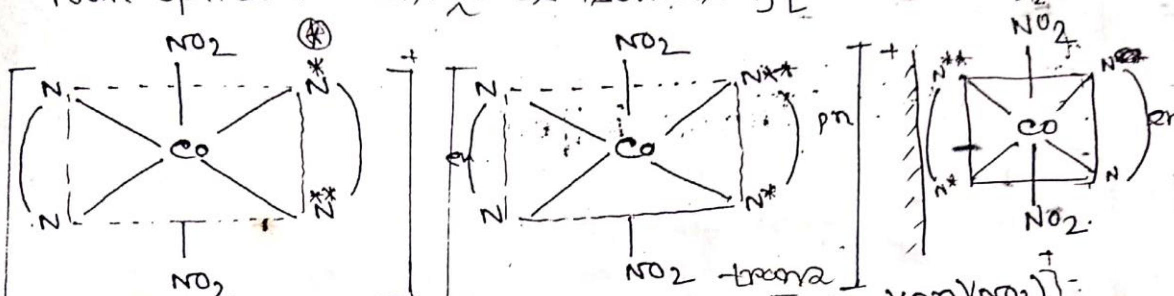
eg: $[\overset{III}{Co}(en)(pn)(NO_2)_2]^+$ ion is an eg. of such type of octahedral complexes. This ion exist in four geometrical isomers. Out of these four isomers, two are cis isomers and two are trans isomers. Since both cis and trans isomers are unsymmetrical and hence are optically active i.e. each of the two cis and two trans isomers can be resolved to give optical isomers.

~~On the other hand since both trans isomers are symmetrical and hence are~~ optically inactive.





four optical isomers of ~~two~~ cis isomers of $[Co(en)(pn)(NO_2)_2]^+$

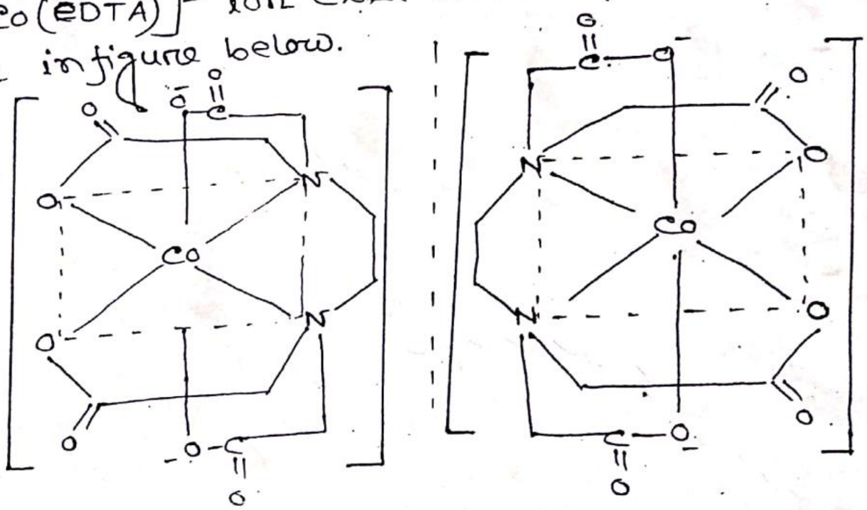


~~Two trans~~ four optically inactive isomers of $[Co(en)(pn)(NO_2)_2]^+$

Octahedral complexes containing polydentate ligands

Complex containing hexadentate ligand like $EDTA]^{4-}$ ion exist in two optical isomers.

eg : $[Co(EDTA)]^{2-}$ ion exist in two optical isomers shown in figure below.



Solve the following problems :

Draw the structures and write the names of all possible isomers of the following complexes.

1.) $[Co(NH_3)_5NO_2]^{2+}$

2.) $[Pt(SCN)(NH_3)_3]^{+}$

3.) $[Co(NH_3)_4Cl_2]^{+}$

4.) $[Pt(en)Cl_2Br_2]$

5.) $[Pt(NH_3)_4Cl_2]^{2+}$

6.) $[Pt(NH_3)(NH_2OH)(Py)(NO_2)]^{+}$