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Summary

Description	Two or more compounds having same molecular formula (same molecular weight) but different structural formula and property are known as isomers and the phenomenon is called isomerism. In metal complex the ligand may occupy different types of positions around the central metal atom which are either adjacent to each other (cis isomer) or opposite to one another (trans isomer). So geometrical isomerism is also known as 'cis-trans' isomerism. Geometrical isomerism is very much common in coordination compounds for coordination number 4 and 6.Tetrahedral complexes do not show geometrical isomerism due to all four ligands are equidistant to one another. Square planar complexes with general formula Ma4, Ma3b, Mba3 do not show cis-trans isomerism due to equivalent spatial arrangement. Octahedral complexes with general formula Ma6, Ma5b, Mba5 do not show cis-trans isomerism.
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Chapter-23

Coordination Chemistry (Geometrical Isomerism)

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Isomerism in co-ordination compounds (iso-equal, meros – parts):

Two or more compounds having same molecular formula (same molecular weight) but different structural formula and property are known as *isomers* and the phenomenon is called *isomerism*.

Stereoisomerism

1. **Geometrical isomerism**: In metal complex the ligand may occupy different types of positions around the central metal atom which are either adjacent to each other (*cis isomer*) or opposite to one another (*trans isomer*). So geometrical isomerism is also known as '*cis-trans*' isomerism.

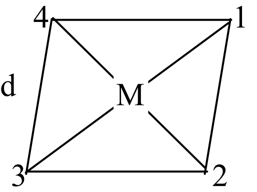
Geometrical isomerism is very much common in coordination compounds for coordination number 4 and 6.

1. Geometrical isomerism in 4-coordination compounds:

A) Tetrahedral complexes: **They do not show geometrical isomerism** due to all four ligands are equidistant to one another.

B) Square planar complexes: Complexes with general formula **Ma_4, Ma_3b, Mba_3 do not show *cis-trans* isomerism** due to equivalent spatial arrangement. *Cis* and *trans* positions in square planar geometry is given below:

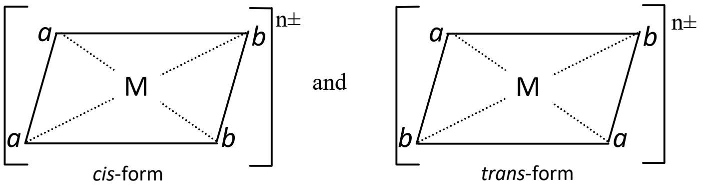
Note : In square planar complexes,
there are four cis positions and
two trans positions **1-2 = 2-3 = 3-4**
1-3 = 2-4 = *trans* **= 1-4 = *cis***



In the general formula below (a,b) represents monodentate ligands, (aa) represent symmetrical bidentate ligand and (ab) represent unsymmetrical bidentate ligand.

Following type of square planar complexes show cis-trans isomerism.

a) $[Ma_2b_2]^{n\pm}$ type:



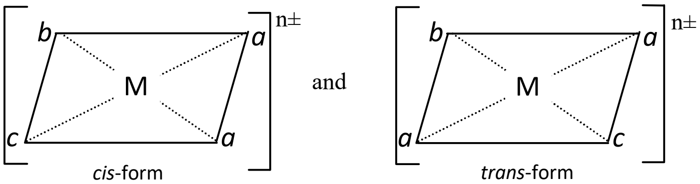
cis-form

trans-form

(*cis-trans* isomer w.r.t. 'a' and 'b')
(Here *M* = metal ion, *a, b* = monodentate ligand)

e.g. $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2(NO_2)_2]$, $[Ni(NH_3)_2Cl_2]$

b) $[Ma_2bc]^{n\pm}$ type:



cis-form

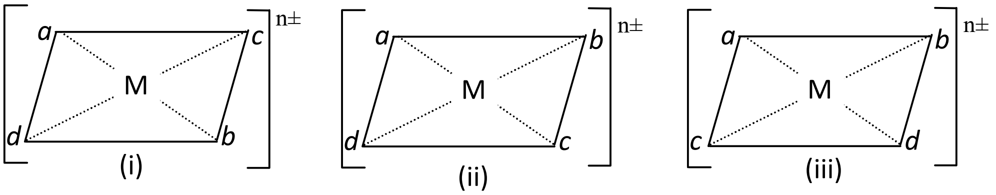
trans-form

Here *M* = metal ion*; a* = neutral ligand (NH_3, Py, H_2O); *b, c* = anionic ligand (Cl^-, Br^-, NO_2^-, SCN^-)

(*cis-trans* isomer w.r.t. 'a')

e.g. $[Pt(Py)_2(NO_2)Cl]$, $[PtCl(NH_3)_2Br]$ etc.

c) $[Mabcd]^{n\pm}$ type: Exist in three isomeric *trans* form.



(i)

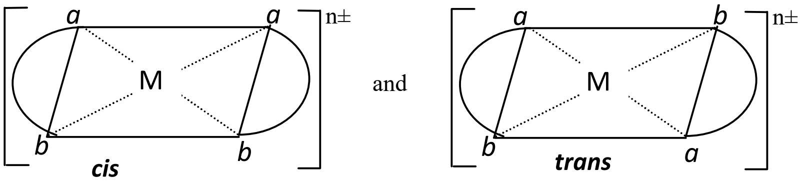
(ii)

(iii)

The structure of these isomers can be written **by fixing the position of one ligand (a) at one corner and placing the other ligands *b, c, d* trans to it.**

e.g. $[Pt(NO_2)(Py)(NH_2OH)NH_3]^+$, $[Pt(NH_3)(Py)(Cl)(Br)]$ etc.

d) $[M(ab)_2]^{n\pm}$: The square planar complexes having unsymmetrical bidentate ligand also show *cis-trans* isomerism as -

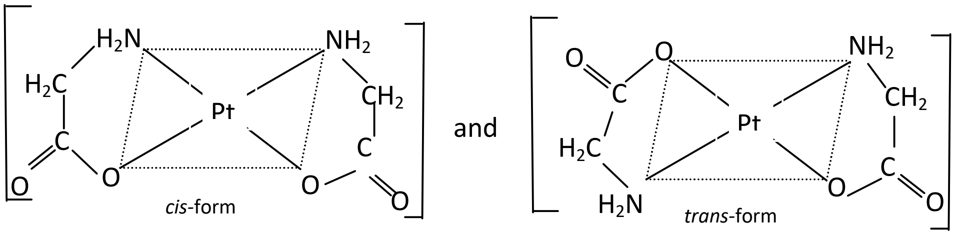


cis

trans

Here M = central metal ion; (ab) = unsymmetrical bidentate ligand such as glycinato (gly^{-1}) etc.

e.g. *cis-trans* isomer of [Pt(gly)$_2$] is given below:



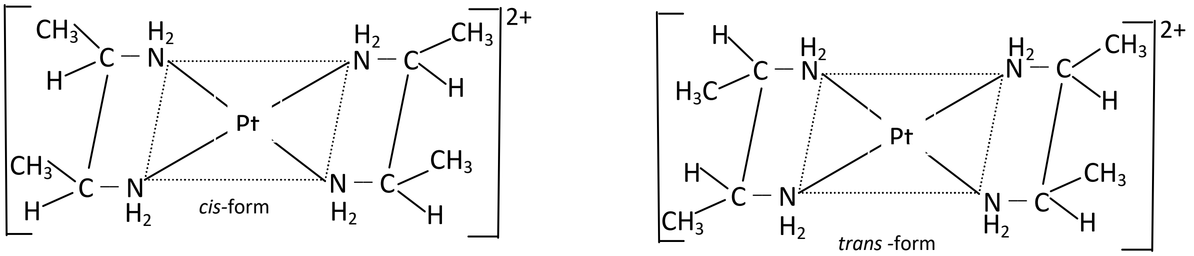
cis-form

trans-form

(*cis-trans* isomer w.r.t. donor atom 'N' and 'O')

e) [*M*(*aa*)$_2$]$^{n\pm}$ type: Square planar complex having symmetrical bidentate chelating ligand also shows *cis-trans* isomerism.

e.g. *cis-trans* isomer of [Pt(NH$_2$CHCH$_3$.CHCH$_3$NH$_2$)$_2$]$^{2+}$ is shown below.

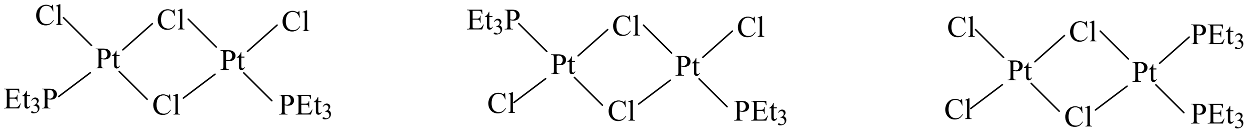


cis-form

trans -form

(*cis-trans* isomer w.r.t. peripheral –CH$_3$ group)

f) [*M*$_2$*a*$_2$*X*$_4$] type: Bridged binuclear square planar complexes also show *cis-trans* isomerism as follows –



cis-form **(i)**

trans-form **(ii)**

unsymmetrical form **(iii)**

(*cis-trans* isomer w.r.t. peripheral – Cl and PEt$_3$ group)

This molecule also show unsymmetrical isomers which are shown above **(iii)**.

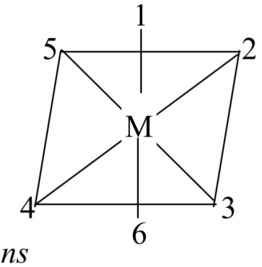
2. Geometrical isomerism in 6-coordination compounds (octahedral compounds):

Complexes with general formula **Ma_6, Ma_5b, Mba_5 do not show *cis-trans* isomerism.**

Note : We know that a regular octahedron has eight faces and six equivalent vertices. In this complex, metal ion is placed at the centre and ligands are placed at the vertices. The position of *cis* and *trans* are

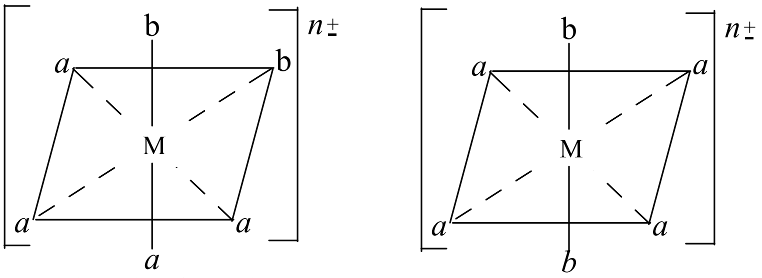
1-2 = 1-5 = 2-5 = 2-3 = 3-4 = 3-6 = 4-6 = 4-5 = *cis*

1-6 = 2-4 = 3-5 = *trans*



Following type octahedral compounds show cis-trans isomerism.

a) $[Ma_4b_2]^{n\pm}$ type: In *cis* isomer two 'b' are adjacent in position while in *trans* two 'b' are opposite to each other.



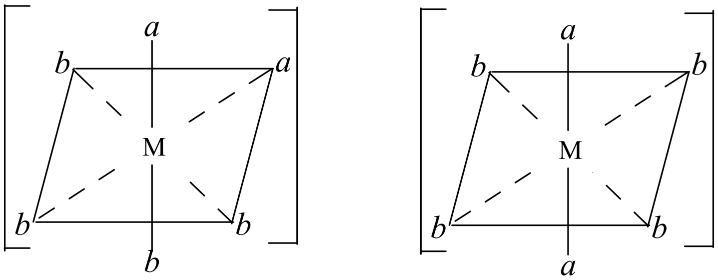
cis-form (1,2-isomer)

trans-form (1,6-isomer)

(*cis-trans* isomer w.r.t. 'b')

e.g. $[Co(NH_3)_4Cl_2]^+$ and $[Fe(CN)_4(NH_3)_2]^{-1}$

b) $[Ma_2b_4]$ type:



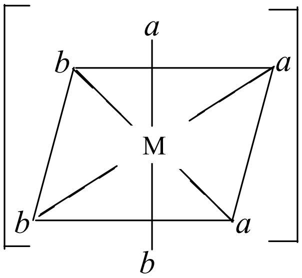
cis-form (1,2-isomer)

trans-form (1,6-isomer)

(*cis-trans* isomer w.r.t. 'a')

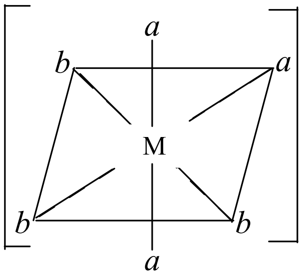
e.g. $[Co(NO_2)_2(NH_3)_4]$.

c) $[Ma_3b_3]^{n\pm}$ type:



cis-form (facial isomer)

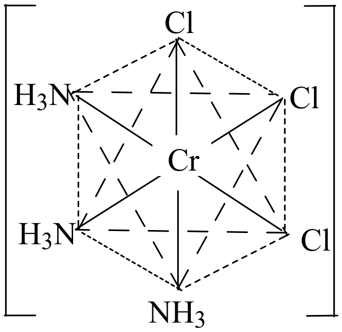
(*same ligands placed in two opposite* triangular *faces*)



trans-form (peripheral isomer)

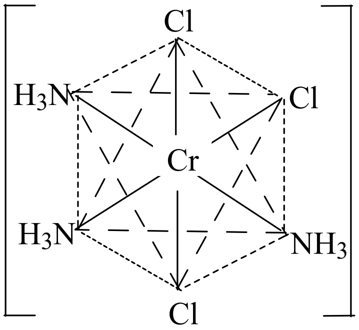
(triangular *faces disturbed by exchange of one ligand*)

e.g. $[Cr(NH_3)_3Cl_3]$ is found in two forms to one isomer, the three Cl^- ions are on triangular face and the three NH_3 molecules are on the opposite triangular face of the regular tetrahedron. So it is known as facial isomer (*cis* isomer). While in other isomer the Cl^- ions are arranged around on the edge of octahedron and NH_3 on opposite edges. So it is known as *peripheral isomer* (*trans* isomer). **It can also be named as Fac - Mer Isomerism, where 'Fac' denotes *cis* form and 'Mer' denotes *trans* form as** shown below:



facial isomer

(Fac or *cis* form)

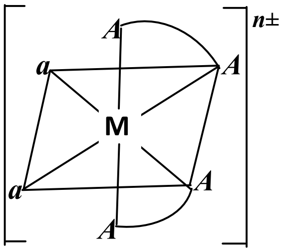


peripheral isomer

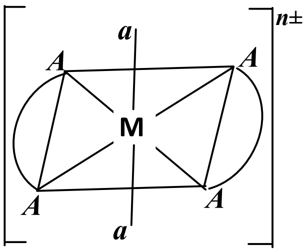
(Mer or *trans* form)

In the 'Fac Isomer' (Fac = Face), the 3 similar ligands are arranged at the 3 corners of a face of the octahedral and in the 'Mer Isomer', the 3 similar ligands are arranged in an arc around the middle of the octahedron (Mer = Meridian).

d) $[M(AA)_2a_2]^{n\pm}$ type: Octahedral complexes having monodentate (*a*) and symmetrical bidentate ligands (*AA*) also show *cis-trans* isomerism.



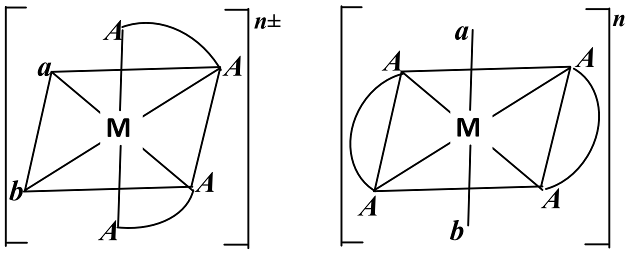
(*a's cis*)



(*a's*

e.g. $[Co(en)_2Cl_2]^+$, $[Co(en)_2(NO_3)_2]^+$, $[Co(C_2O_4)_2Cl_2]^-$ etc.

e) $[M(AA)_2ab]^{n\pm}$ type: The complexes having bidentate ligand (*AA*) and two different monodentate ligands (*a, b*) show *cis-trans* isomerism as follows

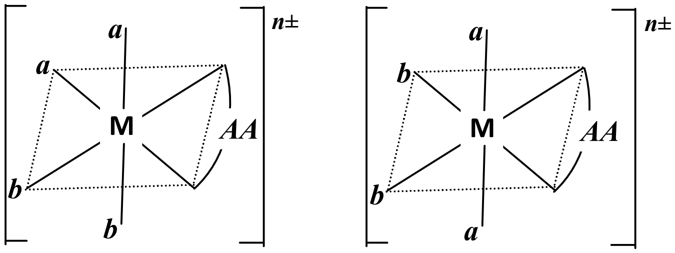


(*cis*-form) **(*trans* -form)**

(*cis-trans* isomer w.r.t. symmetrical bidentate ligand ‘AA’)

e.g. $[Co(en)_2(NH_3)(Cl)]^{2+}$, $[Ru(Py)(C_2O_4)_2(NO)]$ etc.

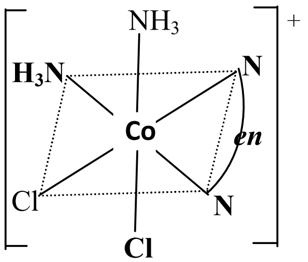
f) $[M(AA)a_2b_2]^{n\pm}$ type:



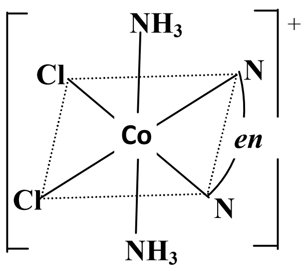
(*cis*-form) **(*trans*-form)**

(*cis-trans* isomer w.r.t. monodentate ligand ‘a’)

e.g. $[Co(en)(NH_3)_2(Cl_2)]^+$ having following *cis-trans* form.

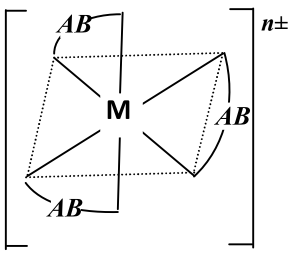


(*cis*-isomer)

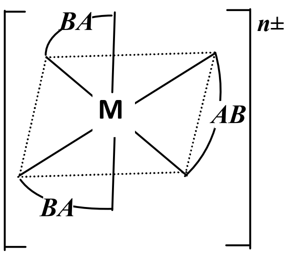


(*trans*-isomer)

g) $[M(AB)_3]^{n\pm}$ type: Octahedral complexes having unsymmetrical bidentate chelating agent ‘*AB*’, (*A* and *B* show two different co-ordinating atoms of the ligand) show *cis-trans* isomerism.

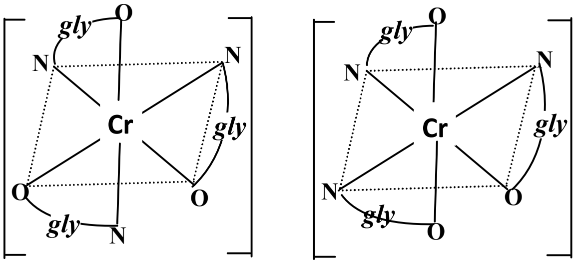


(*cis*isomer)



(*trans*-isomer)

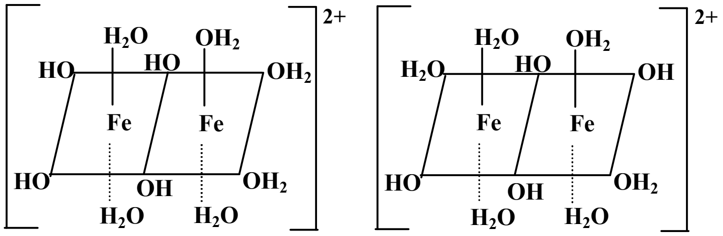
e.g. $[Cr(gly)_3]$ → triglycinatochromium (III) have following *cis* and *trans* isomer.



(*cis*- **(*trans*-isomer)**

(*cis-trans* isomer w.r.t. donor atom)

h) $[M_2a_4b_6]^{n\pm}$ type: In case of polynuclear complex, e.g., $[Fe_2(OH)_4(H_2O)_6]^{2+}$, the geometrical isomers are given below.



***cis* isomer** ***trans* isomer**

(cis w.r.t. left hand side OH and right hand side H_2O; trans w.r.t. diagonally opposite OH and H_2O)

In the above example the two OH groups act as bridges and correct respective octahedral components of the overall structure. **This isomerism is also known as *bridge isomerism*.**

Related Questions

Q.1. The one that is not expected to show geometrical isomerism is
a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$
b) $[Ni(en)_3]^{2+}$
c) $[Ni(NH_3)_2Cl_2]$
d) $[Pt(NH_3)_2Cl_2]$
***Ans.* (c) $[Ni(NH_3)_2Cl_2]$, doesn't exhibit geometrical isomerism because it has tetrahedral geometry.**

Q.2. The complex that can show *fac*- and *mer*-isomers is:
a) $[Pt(NH_3)_2Cl_2]$ **b) $[Co(NH_3)_3(NO_2)_3]$**
c) $[Co(NH_3)_4Cl_2]^+$ **d) $[CoCl_2(en)_2]$**
***Ans.* (*b*)**
Octahedral coordination entities of the type $[Ma_3b_3]$ shows geometrical isomers: *fac* and *mer* isomers. Among the given complexes, the complex with general formula $[Ma_3b_3]$ is $[Co(NH_3)_3(NO_2)_3]$.

Q.3. Among (A) – (D), the complexes that can display geometrical isomerism are

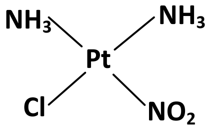
(A) $[Pt(NH_3)_3Cl]^+$ (B) $[Pt(NH_3)Cl_5)^-$
(C) $[Pt(NH_3)_2Cl(NO_2)]$ (D) $[Pt(NH_3)_4ClBr]^{2+}$
a) (D) and (A) b) (C) and (D)
c) (A) and (B) d) (B) and (C)

Ans. **(*b*)**

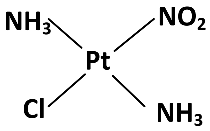
(A) $[Pt(NH_3)_3Cl]^+$: No geometrical isomerism
(B) $[Pt(NH_3)Cl_5]^-$: No geometrical isomerism
(C) $[Pt(NH_3)_2Cl(NO_2)]$: has 2 geometrical isomers
(D) $[Pt(NH_3)_4ClBr]^{2+}$: exhibit geometrical isomerism.

All Pt^{2+} complexes with coordination number equals to 4 are square planar.

(C) The two NH_3 ligands could arrange in *cis* or *trans* positions.
There are two geometrical isomers.



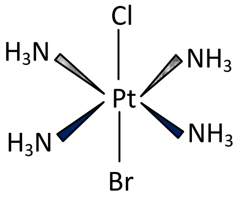
cis



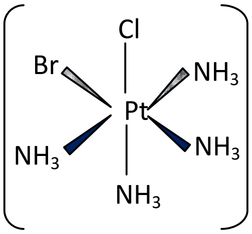
trans

(D) $[Pt(NH_3)_4ClBr]$: Two geometrical isomers Coordination number = 6,Octahedral geometry.

02 geometrical isomers *cis* or *trans w.r.t. –Cl and Br because they are minimum in number.*



trans



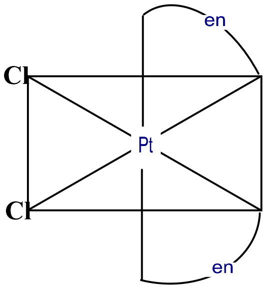
Cis

Q.4. The species that can have a *trans*-isomer is (en = ethane–1, 2-diamine, ox = oxalate)

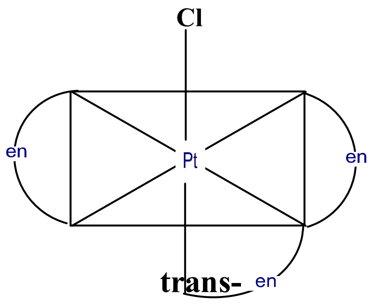
a) $[Pt(en)Cl_2]$ b) $[Cr(en)_2(ox)]^+$
c) $[Pt(en)_2Cl_2]^{2+}$ d) $[Zn(en)Cl_2]$

Ans. **(*c*)**

$[Pt(en)_2(Cl_2)]^{2+}$ with formula $[M(aa)_2b_2]$ can show geometrical isomerism as follows:



cis-
(optically
active)
(I)



trans-
(optically
inactive)
(II)

Q.5. The number of geometric isomers that can exist for square planar $Pt(Cl)(py)(NH_3)(NH_2OH)^+$ is (py = pyridine)

a) 2 b) 3 c) 4 d) 6

Ans. b), it belongs to $[Mabcd]^{n\pm}$ type

Q.6. Which one of the following complex ions has geometrical isomers?

a) $[Co(en)_3]^{3+}$
b) $[Ni(NH_3)_5Br]^+$
c) $[Co(NH_3)_2(en)_2]^{3+}$
d) $[Cr(NH_3)_4(en)]^{3+}$
Ans. c), it belongs to $[M(AA)_2a_2]^{n\pm}$ type.

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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