

ISOMERISM IN transition Compds

→ same mol formula but different properties

→ Phenomenon is isomerism

Structural

- 1) Ionisation isomerism
- 2) Hydrate isomerism
- 3) Coordination isomerism
- 4) Linkage isomerism

Stereoisomerism

- 1) Geometrical isomerism
- 2) Optical isomerism

Structural Isomerism: same formula, different structural arrangement of atom / gpe around the central atom.

1. Ionisation Isomerism: → same mol. formula

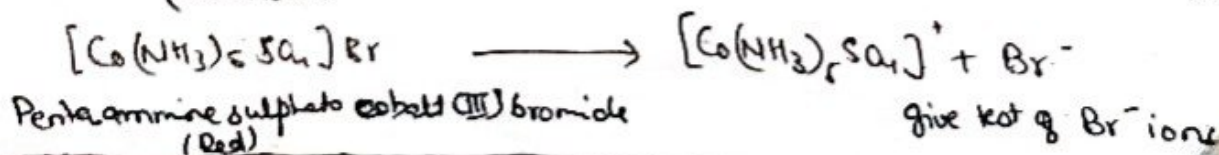
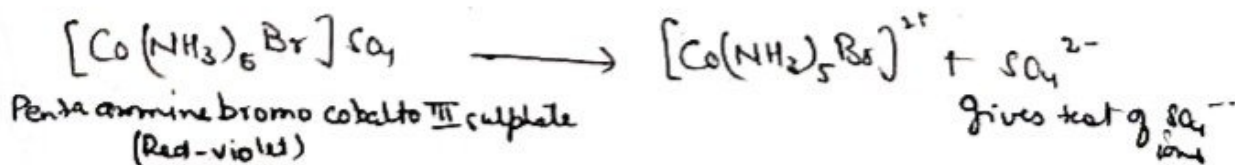
^{gives}
→ different ions in solⁿ

In this type of isomerism, the difference arises from the interchange of groups within / outside the coordⁿ sphere. So these isomers give different ion in solⁿ.

for eg^s, there are 2 isomers of the compd $\text{Co}(\text{NH}_3)_5\text{BrSO}_4$

→ one is red-violet and forms ppt w/ BaCl_2 which indicates SO_4^{2-} ion is outside the coordⁿ sphere.

→ Second one is red & does not form ppt w/ BaCl_2 but forms ppt of AgBr w/ AgNO_3 indicating bromide ion outside the sphere.



②

Stereoisomers: Isomers \bar{c} same mol formula ^{and position} but have different spatial arrangements around central atom.

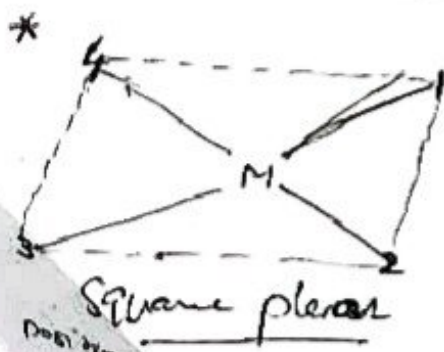
Two types $\left\{ \begin{array}{l} \text{Geometrical Isomerism} \\ \text{Optical Isomerism} \end{array} \right.$

1) Geometrical Isomerism: It is due to ligands occupying different positions around the central ion. Positions can be either adjacent to one another or opposite to one another, which are referred as cis form & trans form respectively.

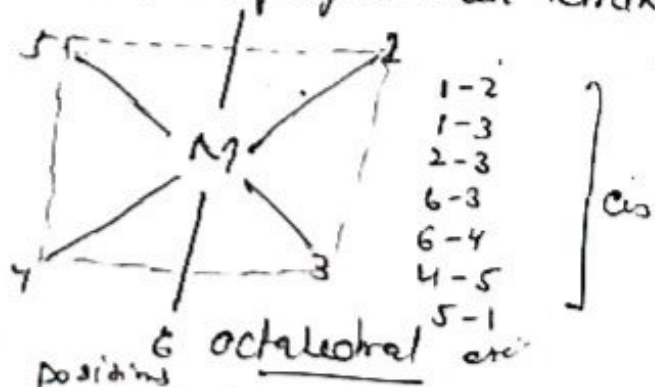
- Also k/d as cis-trans isomers.
- very common in coordⁿ compds, due to different coordⁿ no.'s varying from 2-9.
- Geometrical isomerism of compds with CN 4 & 6 is very imp & discussed.

i) Geometrical isomerism in complexes \bar{c} CN-4

Complexes \bar{c} CN 4 adopt tetrahedral / square planar geometry. In tetrahedral, geometrical isomerism is not possible bcos all the positions are adjacent in tetrahedral.

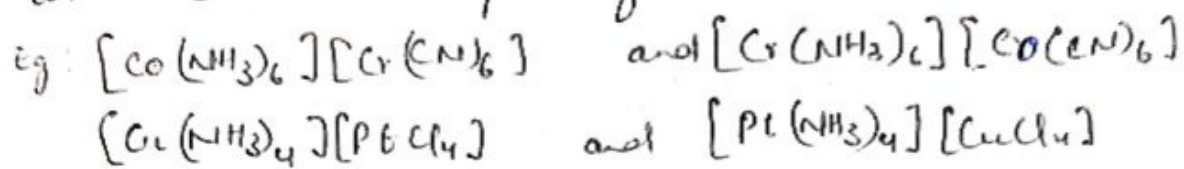


positions
 $\left. \begin{array}{l} 1-2 \\ 2-3 \\ 3-4 \\ 4-1 \end{array} \right\} \text{cis}$
 $\left. \begin{array}{l} 1-3 \\ 2-4 \end{array} \right\} \text{trans}$

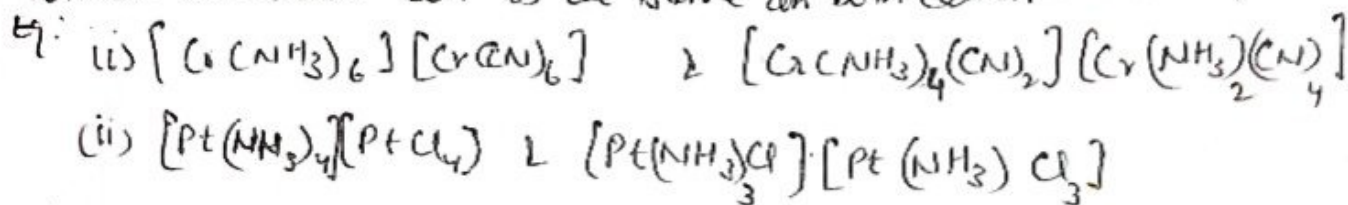


positions
 $\left. \begin{array}{l} 1-2 \\ 2-3 \\ 3-4 \end{array} \right\} \text{cis}$
 $\left. \begin{array}{l} 1-6 \\ 2-4 \\ 3-5 \end{array} \right\} \text{trans}$

3) Coordination Isomerism: This type of isomerism occurs in compds containing both cationic & anionic complexes and the isomers differ in the distribution of ligands in the coordination sphere of cationic & anionic parts.



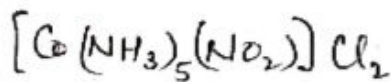
This type of isomerism is also shown by compds in which the metal ion is the same in both cation & anion complex:



4) Linkage Isomerism: Compds have same mol formula but differ in the mode of linkage/attachment of a ligand to the metal atom or ion are called linkage isomers.

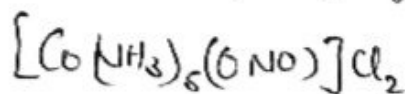
For eg: NO_2^- (Nitro) ion, N- as well as O-atom can donate their lone pairs. This gives rise to isomerism.

eg: Pentaammine cobalt(III) chloride containing NO_2^- gp in complex



Yellow brown

Pentaammine nitro cobalt(III) chloride



Red

Pentaammine nitrito cobalt(III) chloride

The unidentate ligands which can bind to the central atom thru a donor atom are also called ambidentate ligands.

Some of ambidentate ligands are

-CN \rightarrow Cyano (thru C)

-SCN \rightarrow thiocyanato (thru S)

-NC \rightarrow isocyano (thru N)

-NCS \rightarrow isothiocyanato (thru N)

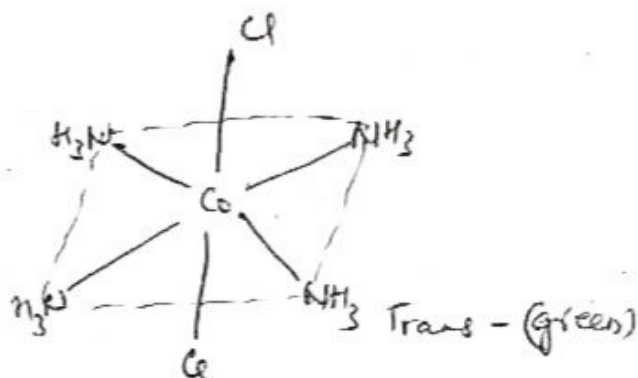
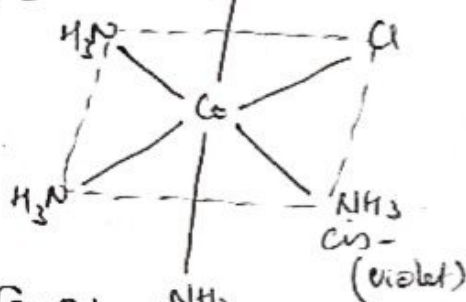
(ii) Geometrical isomerism in CN. 6

→ CN. 6 complex adopt octahedral complexes.

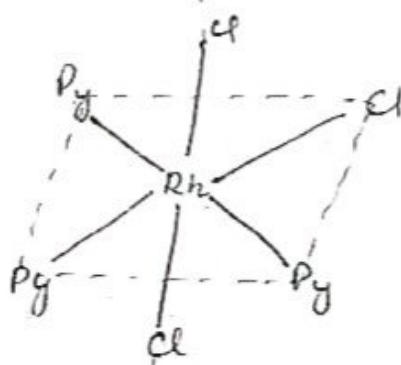
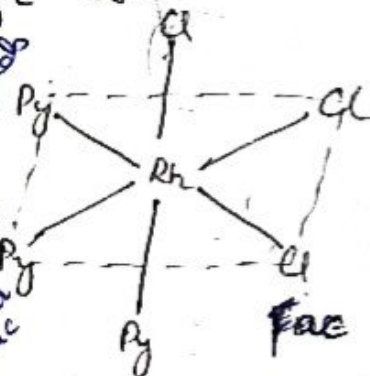
a) Octahedral complexes of type MA_4X_2 , MA_2X_4 , MA_3X_3 etc. exhibit geometrical isomerism -

Eg $[Co(NH_3)_4Cl_2]^+$

(i)



(ii) $[Rh(Py)_3Cl_3]$

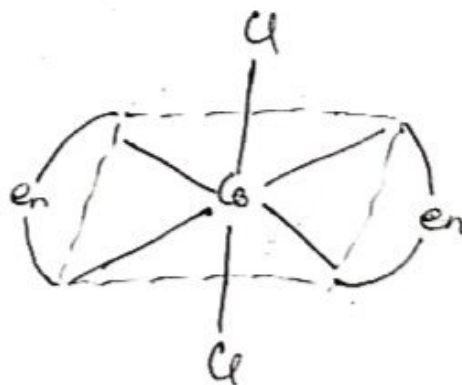
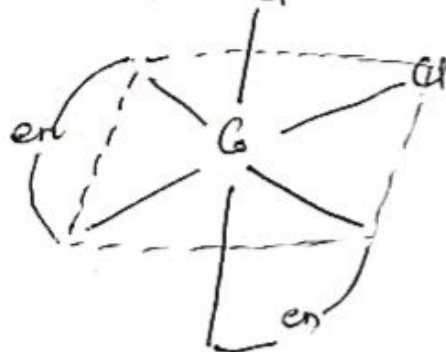


when 3 bidentate ligands occupy one face of an octahedral complex it is fac isomer or fac

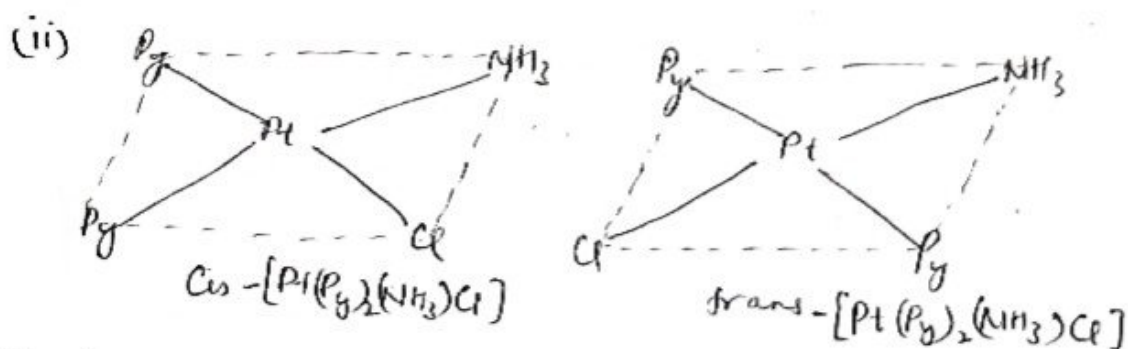
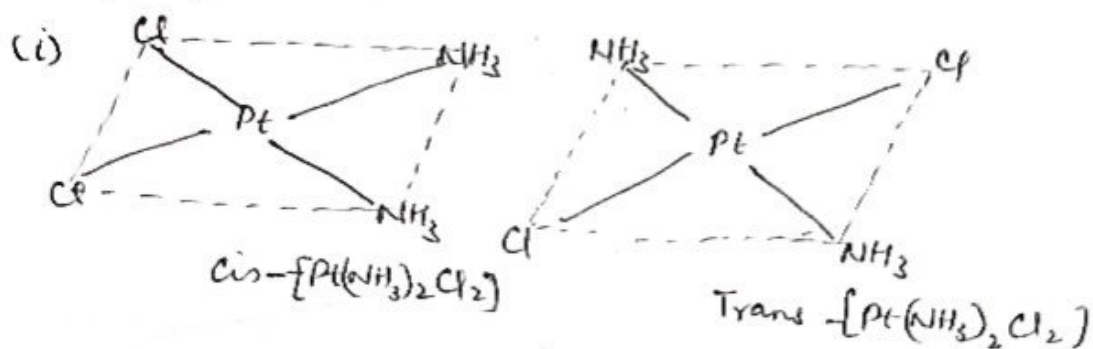
(b) Octahedral complexes of type $M(AA)_2X_2$ & $M(AA)_3X_2$

AA → symmetrical bidentate ligand such as ethylenediamine (en) or oxalate^{ion} (ox) etc.

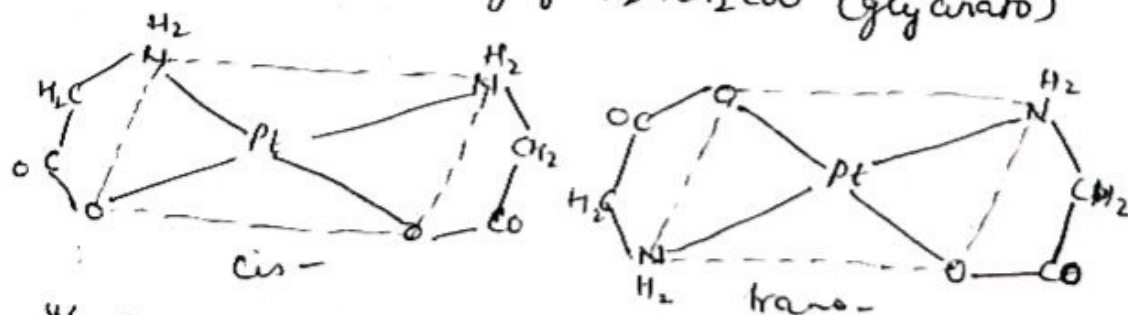
eg. $[Co(en)_2Cl_2]^+$



- (a) Square planar complexes of the type MA_2X_2 , MA_2XY , $MABX_2$, ~~$MABXY$~~ can exist as geometrical isomers (where A & B are neutral ligands such as H_2O , NH_3 , CO , NO , C_5H_5N whereas X & Y are anionic ligands such as Cl^- , NO_2^- , CN^- , SCN^- etc.)
for eg.



- (b) Square planar complexes containing unsymmetrical bidentate ligand such as $[M(AB)_2]$ also show geometrical isomerism for eg. $[Pt(gly)_2]$ where $gly = H_2NCH_2COO^-$ (glycinate)



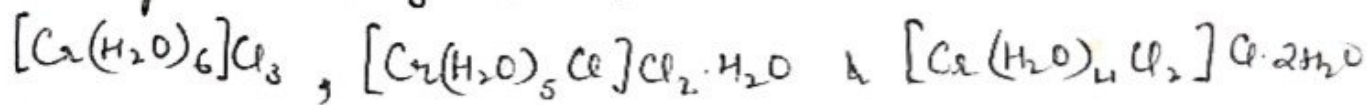
* Square planar complexes of type MA_4 , MA_3X , MAX_3 will not show geometrical isomerism bco in each case, spatial arrangement of complexes are same.

Other compds showing ionisom. are

- (i) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$ 2 $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{ONO}_2)]\text{Cl}$
 (ii) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ 4 $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
 (iii) $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{ONO}_2)]\text{Cl}$ 2 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$

2) Hydrate Isomerism: compd. w/ same mol. formula but differ in no. of H_2O molecules present as ligands / as molecules of hydration are k/d Hydrate isomers.
 → Similar to ionisation isomerism, in which water molecules may occur inside & outside the coordⁿ sphere as a coord. ligand or as a water of hydration.

for example: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ have 3 isomers



(i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \Rightarrow$ It does not lose H_2O when treated w/ conc H_2SO_4 & 3 Cl^- ions are pptd w/ AgNO_3

(ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O} \Rightarrow$ It ~~does not~~ loses one water molecule when treated w/ conc H_2SO_4 & 2 Cl^- ions are pptd w/ AgNO_3

(iii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O} \Rightarrow$ It loses 2 water molecules when treated w/ conc H_2SO_4 & one Cl^- ion is pptd w/ AgNO_3 .

Similarly, the following 2 isomers are hydrate isomers:

