

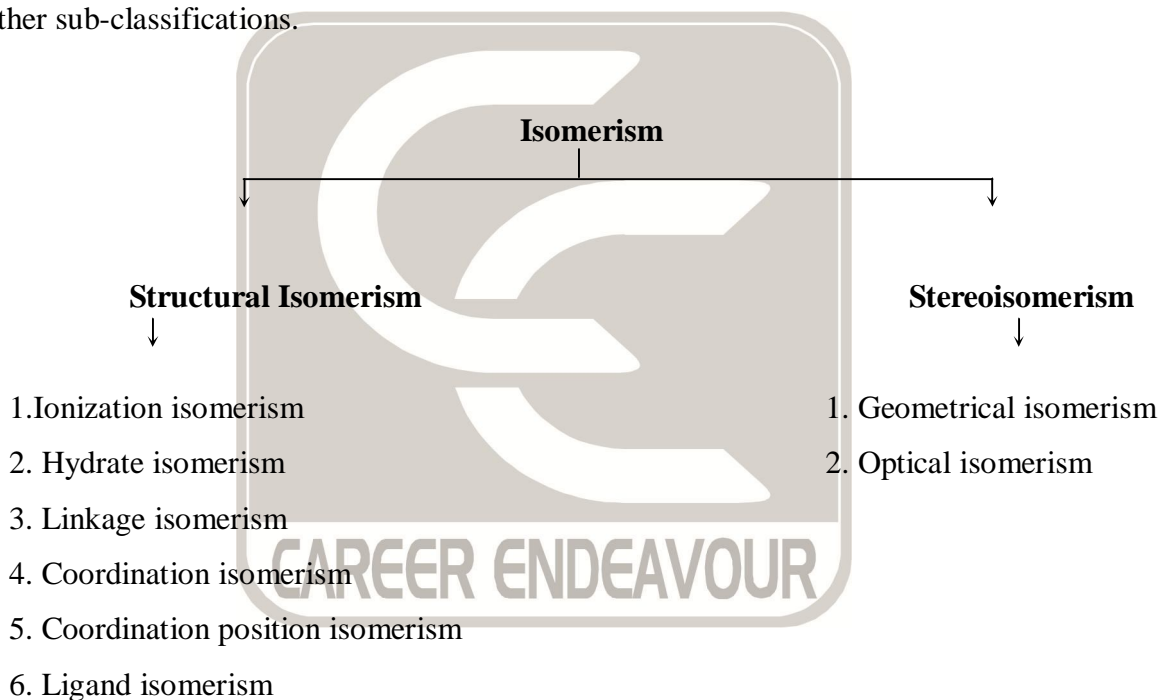
ISOMERISM IN COORDINATION COMPLEXES

UNIT

3

Isomerism in Coordination Complexes

Isomers are compounds having the same number and kinds of atoms arranged differently. The phenomena of existence of isomers is called *isomerism*. Since their structural arrangements are different, the properties of isomers are also different. Isomers can be broadly classified into two types, each type having further sub-classifications.



Structural Isomerism

Structural isomers are those which contain different atom-to-atom bonding sequences. These involve either more than one coordination sphere or different donor atoms of the same ligand in the same coordination sphere.

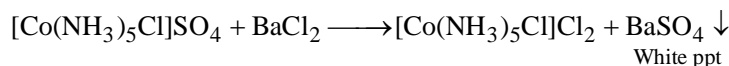
(1) Ionization Isomerism

The isomers which involve exchange of ligands between coordination sphere and ionization sphere are called ionization isomers. Ionisation isomers show different properties. For example,

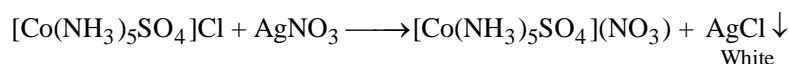
- (a) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and
pentamminechlorocobalt(III) sulfate
 $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

pentamminesulfatocobalt(III) chloride

In pentamminechlorocobalt(III) sulfate complex, the chloro ligand is in the coordination sphere, while the sulfate group is in the ionization sphere. An aqueous solution of this complex, on treatment with barium chloride, yields white precipitates of barium sulfate.



In pentamminesulfatocobalt(III) chloride complex, the sulfato ligand is in the coordination sphere, while the chloride group is in the ionization sphere. With silver nitrate, an aqueous solution of this complex yields white precipitates of silver chloride.



Other examples of ionisation isomers are:

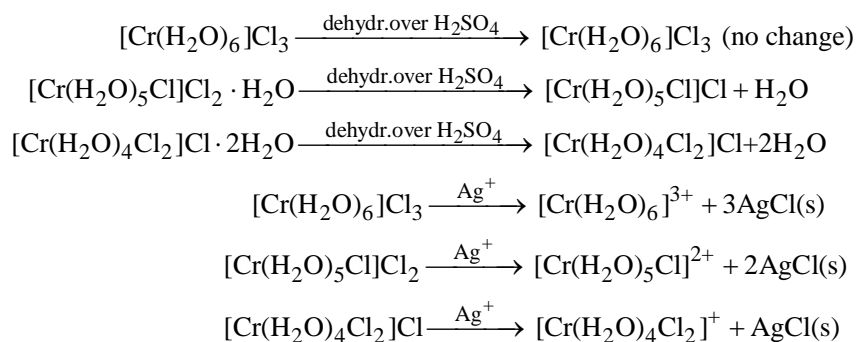
- (a) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (Red violet) and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (Red)
- (b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$
- (c) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and
tetramminedichloroplatinum(IV) bromide
 $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
tetramminedibromoplatinum(IV) chloride
- (d) $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]\text{SCN}$
chlorobis(ethylene diamine)nitrocobalt(III) thiocyanate
 $[\text{Co}(\text{en})_2\text{NO}_2\text{SCN}]\text{Cl}$ and
bis(ethylene diamine)nitrothiocyanato-Scobalt(III) chloride
 $[\text{Co}(\text{en})_2\text{SCNCl}]\text{NO}_2$
chlorobis(ethylene diamine)thiocyanato-S cobalt(III) nitrite

(2) Solvate Isomerism or Hydrate Isomerism

When water (solvent) molecules are interchanged between coordination sphere and ionisation sphere, the resulting isomers are called hydrate (or solvate) isomers.

This is a somewhat special case of the above interchange of ligands involving neutral solvate molecules. The best known example involves isomers of “chromic chloride hydrates” of which three are known:

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. These differ in their reactions:



(3) Linkage Isomerism

Linkage isomerism is the existence of coordination compounds that have the same composition differing with the connectivity of the metal to a ligand. Typical ligands that give rise to linkage isomers. $\bar{\text{S}}\text{CN}$ (thiocyanato) and $\bar{\text{N}}\text{CS}$ (isothiocyanato)

e.g. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ are linkage isomers.
 (yellow colour) (Red colour)

(4) Coordination Isomerism

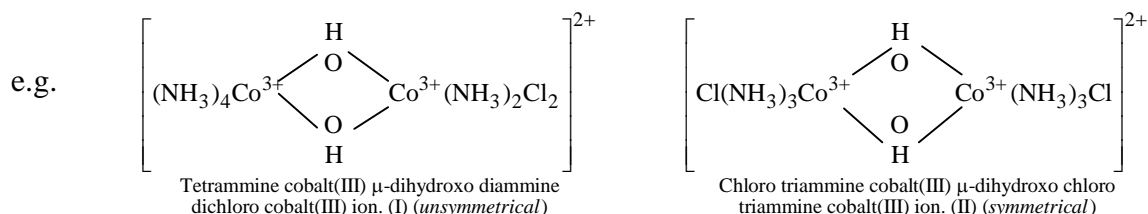
Salts that contain complex cations and anions may exhibit isomerism through the interchange of ligands between cation and anion. For example, both hexaamminecobalt(III) hexacyanochromate(III), $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and its coordination isomer, $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, are known. Another example is $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$ in which the isomers differ in color (as a result of the d^9 Cu^{2+} chromophore), being violet and green, respectively.

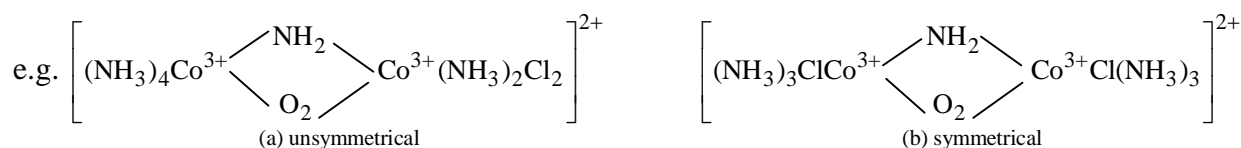
Coordination isomers are obtained when some or all ligands of both the coordination spheres are interchanged with each other. In these pairs the central metallic atom in the two coordination spheres may be the same or different.

- (i) $[\text{Cr}^{3+}(\text{NH}_3)_6]^{3+} [\text{Cr}^{3+}(\text{CN})_6]^{3-}$ and $[\text{Cr}^{3+}(\text{NH}_3)_4(\text{CN})_2]^+ [\text{Cr}^{3+}(\text{CN})_4(\text{NH}_3)_2]^-$
- (ii) $[\text{Pt}^{2+}(\text{NH}_3)_4]^{2+} [\text{Pt}^{2+}\text{Cl}_4]^{2-}$ and $[\text{Pt}^{2+}(\text{NH}_3)_3\text{Cl}]^+ [\text{Pt}^{2+}\text{Cl}_3(\text{NH}_3)]^-$
- (iii) $[\text{Co}^{3+}(\text{NH}_3)_6]^{3+} [\text{Cr}^{3+}(\text{CN})_6]^{3-}$ and $[\text{Co}^{3+}(\text{CN})_6]^{3-} [\text{Cr}(\text{NH}_3)_6]^{3+}$

(5) Coordination Position Isomerism

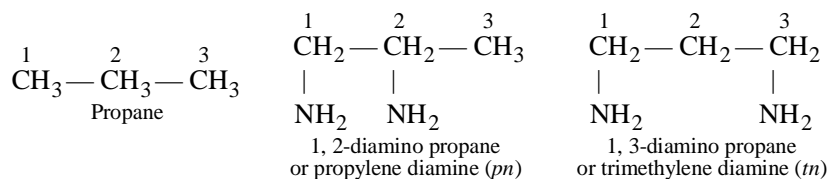
This type of isomerism is shown by those complex compounds which contain bridging ligands and arises when the non-bridging ligands are differently placed round the central metal atom. Thus (I) and (II) are coordination position isomers to each other, since NH_3 molecules and Cl^- ions (non-bridging ligands) are differently placed round the two Co^{3+} ions.





(6) Ligand Isomerism

Diamine derivatives of propane exist in two isomeric forms which are called 1, 2-diamino propane or propylene diamine (*pn*) and 1, 3-diamino propane or trimethylene diamine (*tn*). The structures of propane, *pn* and *tn* are given below:



pn and *tn* both are bidentate (neutral) ligands. When these ligands get coordinated to the metal atom, two isomers are obtained. These are called ligand isomers and the isomerism is called ligand isomerism. $[\text{Co}^{3+}(\text{pn})_2\text{Cl}_2]^+$ and $[\text{Co}^{3+}(\text{tn})_2\text{Cl}_2]^+$ are ligand isomers.

Stereo Isomerism

Stereo isomerism is exhibited by those compounds which have the same position of atoms or groups but these atoms or groups have different arrangement round the central atom. Stereo isomerism may be of two types viz. geometrical (or cis-trans) isomerism and optical (or d-l or mirror-image) isomerism.

(1) Geometrical (or cis-trans) Isomerism

- The complex compounds which have the same ligands in the coordination sphere but the relative position of the ligands round the central metal atom is different are called geometrical isomers and the phenomenon is called geometrical isomerism.
- The complex compound having two ligands occupying the adjacent positions to each other is called *cis-isomer* while that in which the two ligands occupy opposite positions is called *trans-isomer*. Thus geometrical isomerism is also called *cis-trans* isomerism.
- Geometrical isomerism is not found in complex compound with coordination number 2 and 3.
- Geometrical isomerism is most common with the complex compounds having coordination number 4 and 6.

(i) Geometrical Isomerism in 4-coordinated Complex Compounds

Complexes having central m with 4-coordination number may have either tetrahedral or square planar geometry.

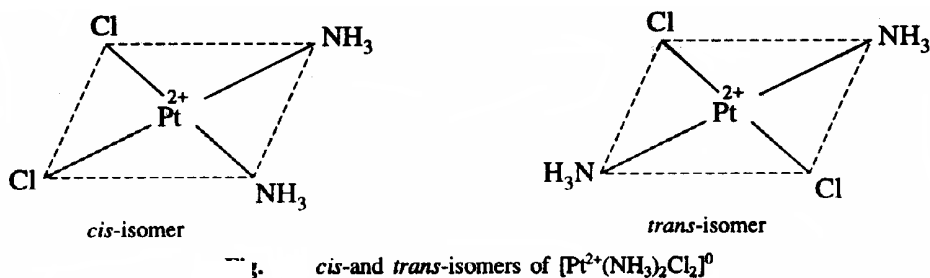
(ii) Geometrical Isomerism in Tetrahedral complexes

Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in this geometry have adjacent position (i.e., *cis* position) to one another and all the four bond angles are the same ($= 109.5^\circ$).

(iii) Geometrical Isomerism in Square Planar Complexes

A square planar complex having similar ligands at adjacent positions (90° apart) is called *cis*-isomer while a square planar complex having two similar ligands at opposite positions (180° apart) is called *trans*-isomer.

- (1) **[Ma₂b₂] type complexes** : Important examples of square planar complexes of this type are $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^0$, $[\text{Pt}(\text{py})_2\text{Cl}_2]^0$, $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]^0$ etc. These complexes exist in *cis*- and *trans*-isomers.



- (2) **[Ma₂bc] type complexes** : Square planar complexes of this type also show *cis-trans* isomerism. For example $[\text{Pd}^{2+}\text{Cl}_2\text{BrI}]^{2-}$ ion exists in *cis* and *trans* isomers as shown below.

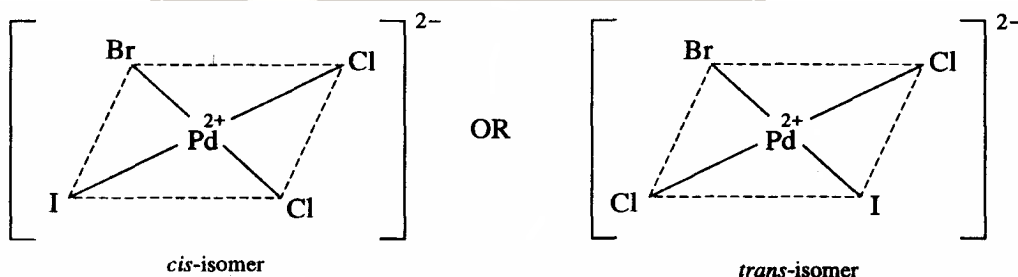


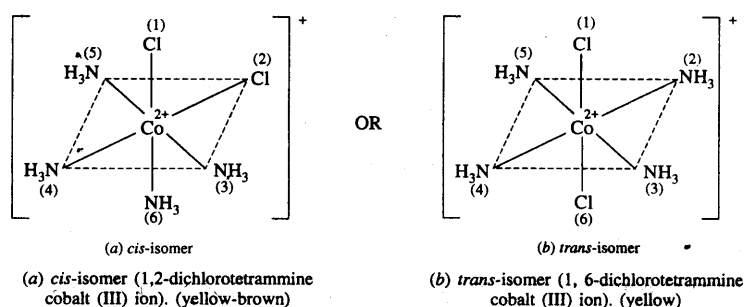
Fig. *Cis*- and *trans*-isomers of $[\text{Pd}^{2+}\text{Cl}_2\text{BrI}]^{2-}$ ion.

$[\text{Pt}^{2+}(\text{py})_2(\text{NH}_3)\text{Cl}]^+$ is another example of square planar complex of $[\text{Ma}_2\text{bc}]$ type which exists in *cis*- and *trans*-isomers.

Geometrical Isomerism in 6-coordinated Complexes : Octahedral Complexes

A complex compound having central atom with coordination number equal to 6 is octahedral in shape. In an octahedral complex, if two similar ligands are placed on any of the twelve edges of the octahedron, they are said to be in *cis* position. On the other hand, if two similar ligands are lying on a straight line which passes through the centre (where the metal ion is placed), they are said to be in *trans* position.

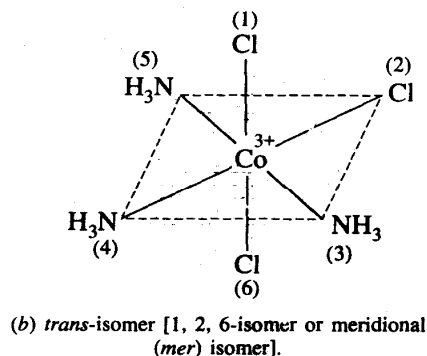
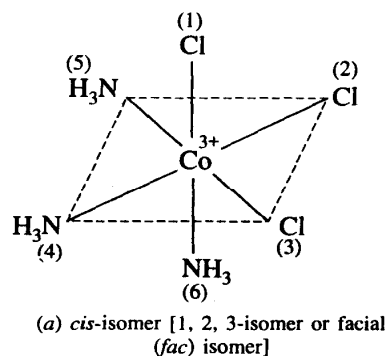
- (1) **[Ma₄b₂] type complexes** :



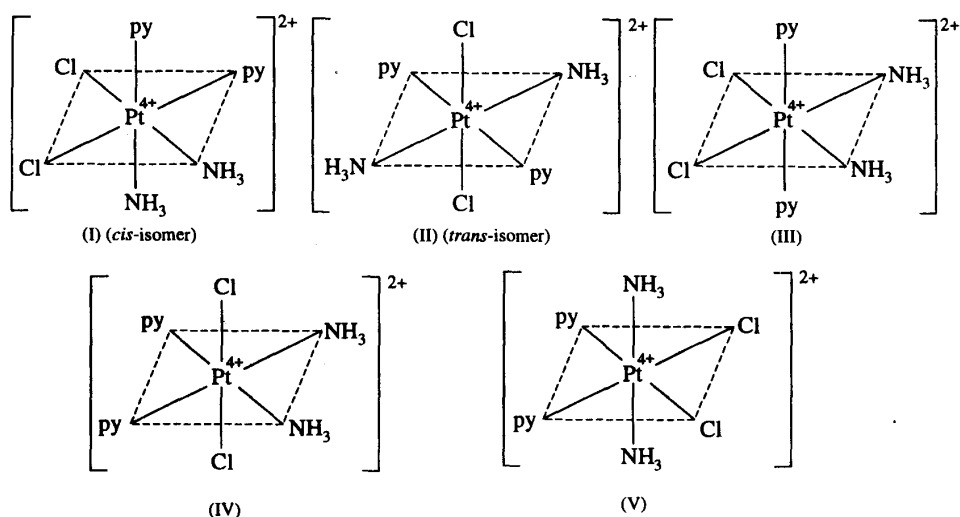
(2) **[Ma₃b₃] type complexes** : [Co(NH₃)₃Cl₃], [Co(NH₃)₃(NO₂)₃], [Cr(H₂O)₃F₃], [Cr(NH₃)₃Cl₃], [Rh(py)₃Cl₃], [Ru(H₂O)₃Cl₃], [Ir(H₂O)₃Cl₃], [Pt(NH₃)₃Br₃]⁺, [Pt(NH₃)₃I₃]⁺ etc. are important examples of octahedral complexes of [Ma₃b₃] type. Two geometrical isomers are for complex Ma₃b₃.

- The ligands of one type may form an equilateral triangle on one of the faces (called facial isomer).
- In other isomer, the ligands of one type occupy the positions such that two are opposite (or trans) to each other, called meridional isomer.

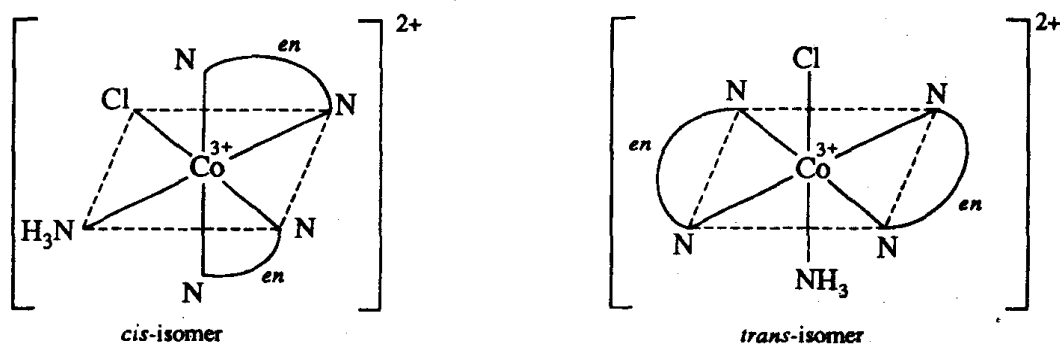
As an example these isomers for [Co³⁺(NH₃)₃Cl₃]⁰ have been shown below.



(4) **[Ma₂b₂c₂] type complexes** : [Pt⁴⁺(NH₃)₂(py)₂Cl₂]²⁺ ion is an important example of octahedral complex of [Ma₂b₂c₂] type. This ion can exist theoretically in five geometrical isomers that have been shown below., but it is only three isomers that have been actually isolated. It may be noted from the figure that (I) form is a *cis*-form since in this form two identical ligands are occupying adjacent positions. Form (II) is a *trans*-form because in it the two identical ligands are placed at opposite positions.



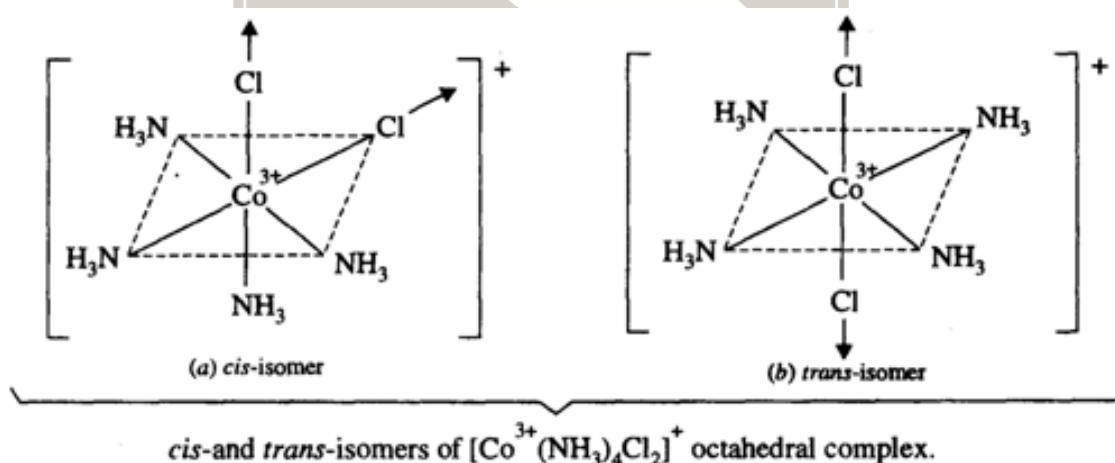
(9) **[M(AA)₂ab] type complexes** : [Co³⁺(*en*)₂(NH₃)Cl]²⁺ is an important example of octahedral complex of [M(AA)₂ab] type. This complex ion exists in *cis*- and *trans*-isomers. In *cis*-isomer the two monodentate ligands *viz.* NH₃ and Cl⁻ occupy the adjacent (i.e., *cis*) positions while in *trans*-isomer these ligands occupy opposite (i.e., *trans*) positions [Ru³⁺(C₂O₄)₂(py)(NO₂)]²⁻ also exists in *cis*- and *trans*-isomers.

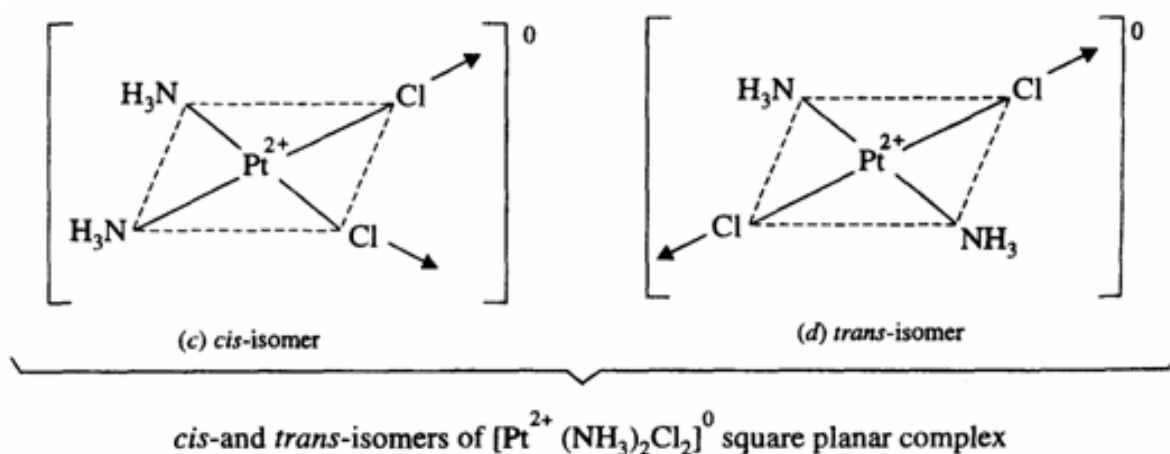


To Distinguish between *cis*- and *trans*-isomers

The following methods may be used to distinguish between *cis* and *trans*-isomers.

- (1) **Dipole moments measurements** : The Pt(II) complexes $[Pt^{2+}A_2X_2]$ type, where A = substituted phosphine, arsine or stilbine such as $(C_2H_5)_3P$, $(C_2H_5)_3As$ or $(C_2H_5)_3Sb$ and X = a halogen, have their dipole moments (μ) either equal to zero or between 8 and 12 Debye units. In the compounds with $\mu = 0$, the individual moments have cancelled one another and so these are *trans*-isomers. The compound with $\mu = 8 - 12$ Debye units are *cis*-isomers.
- (2) **Infra-red spectroscopic technique** : In a *trans* octahedral complex such as $[Co^{3+}(NH_3)_4Cl_2]$ or in *trans* square planar complex like $[Pt^{2+}(NH_3)_2Cl_2]^0$ the Cl-metal-Cl symmetrical stretching vibration produces no change in the dipole moment of the molecule and thus no band corresponding to this vibration is observed in the infra-red spectrum. However, in the *cis*-form of each compound, the symmetrical stretching vibration as well the unsymmetrical stretching vibration produce appreciable changes in the dipole moment; hence the infra-red spectrum of the *cis*-isomer will contain a large number of bands due to Cl-metal-Cl stretching.





Optical (or *d-l* or mirror-image) Isomerism

When the solution of certain complex compounds are placed in the path of a *plane-polarised light* (the waves of the plane-polarised light vibrate only in one direction; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. This property of a complex of rotating the plane of polarised light is called its optical activity and the complex possessing this property is said to be optically active. Optically active complexes are said to exist in the following forms:

- One which rotates the plane of polarised light towards right (i.e., in clockwise direction) is said to be dextro-rotatory or *d*-form. *d*-form is also represented by placing (+) sign before its name or formula.
- One which rotates the plane of polarised light towards left (i.e., in anti-clockwise direction) is called levo-rotatory or *l*-form. *l*-form is also represented by putting (–) sign before its name or formula. (+), dextro, and (–), levo. The *d*- and *l*-forms have the following characteristics: (i) Since *d*- and *l*-forms are capable of rotating the plane of polarised light, these are said to be optically active forms or optical isomers. These two forms have exactly identical physical and chemical properties. (ii) *d*- and *l*-forms are mirror images to each other. Thus *d*- and *l*-forms can not be superimposed on each other and hence *d*- and *l*-forms are also called *mirror-image isomers* or *enantiomer*.
- The isomer which is not capable of rotating the plane of polarised light is called optically inactive. Such an isomer is called meso, racemic, dl-or (\pm) form. A racemic substance is composed of 50% *d*- and 50% *l*-form.

Conditions for a Molecule to Show Optical Isomerism

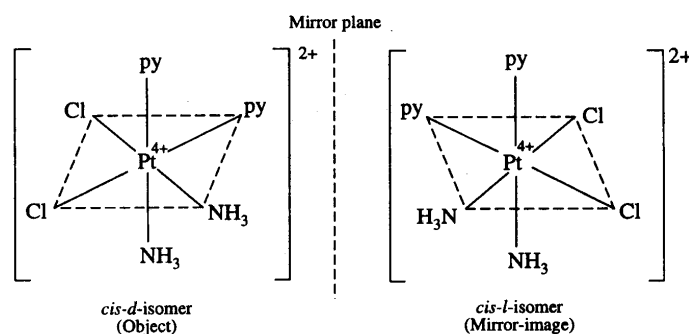
A molecule in which the grouping of the atoms is asymmetric is called an asymmetric or dissymmetric molecule. An asymmetric molecule has the following features:

- An asymmetric molecule never has a plane of symmetry (also called mirror-image plane) which is defined as an imaginary plane dividing the molecule in such a way that the part of it on one side of the plane is the mirror image of that on the other side of the plane. The molecules possessing such a plane of symmetry are always optically inactive while those having no plane of symmetry are optically active and hence show optical isomerism.
- An asymmetric molecule cannot be superimposed on its mirror image.

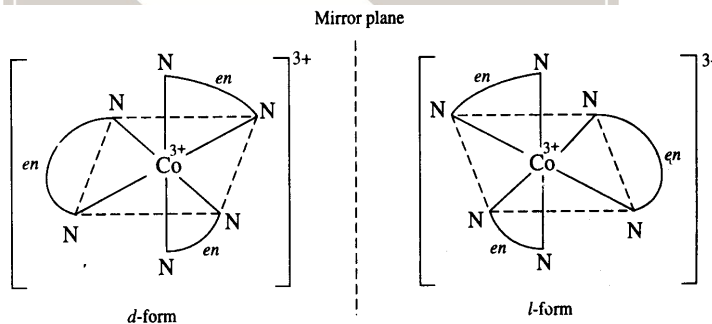
Thus the most necessary and sufficient condition for a molecule to show optical isomerism (i.e., to exist in *d*- and *l*-forms) is that the molecule should be asymmetric, (i.e., it should have no plane of symmetry) and should not be superimposable on its mirror image.

Optical Isomerism in 6-coordinated Complexes : Octahedral Complexes

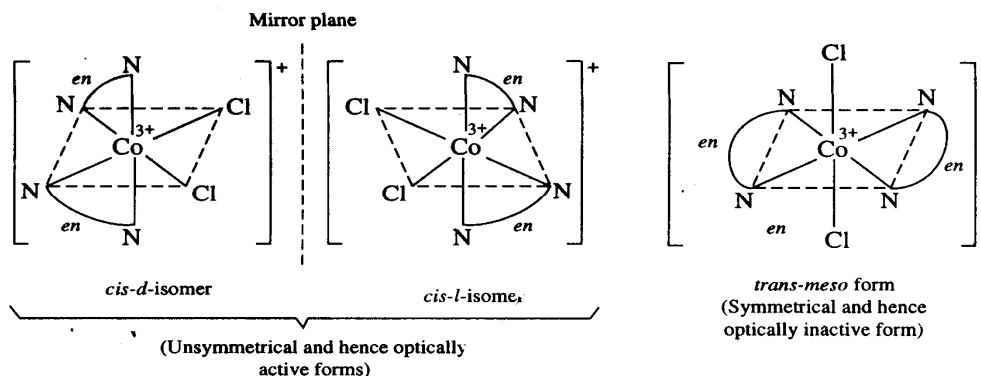
- (1) **[Ma₄b₂] and [Ma₃b₃] type complexes :** (a) Octahedral complexes of [Ma₄b₂] type exist in *cis*- and *trans*-isomers. Both these isomers are optically inactive due to the presence of symmetry and hence do not show optical isomerism.
- (b) Octahedral complexes of [Ma₃b₃] type exist in *cis* (or facial) and *trans* (or meridional) isomers. Both these isomers are optically inactive and hence do not show optical isomerism.
- (2) **[Ma₂b₂c₂] type complexes :** [Pt⁴⁺(NH₃)₂(py)₂Cl₂]²⁺ ion is an important example of octahedral complex of [Ma₂b₂c₂] type. *Cis*-isomer exists in two optical (mirror-image) isomers which are mirror-image to each other. *Trans*-form of this complex ion is symmetrical and hence is optically inactive form. Thus it is a *trans-meso form*.



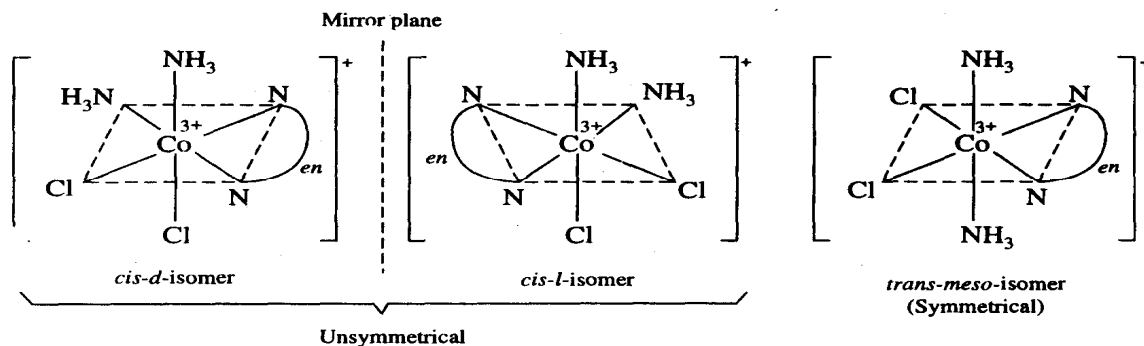
- (3) **[M(AA)₃] type complexes :** Due to the absence of a plane or centre of symmetry, the octahedral complexes of this type are resolvable into *dextro* and *levo* forms. For example *d*- and *l*-forms of [Co³⁺(en)₃]³⁺ ion are shown below. Other example [Cr³⁺(ox)₃]³⁻.



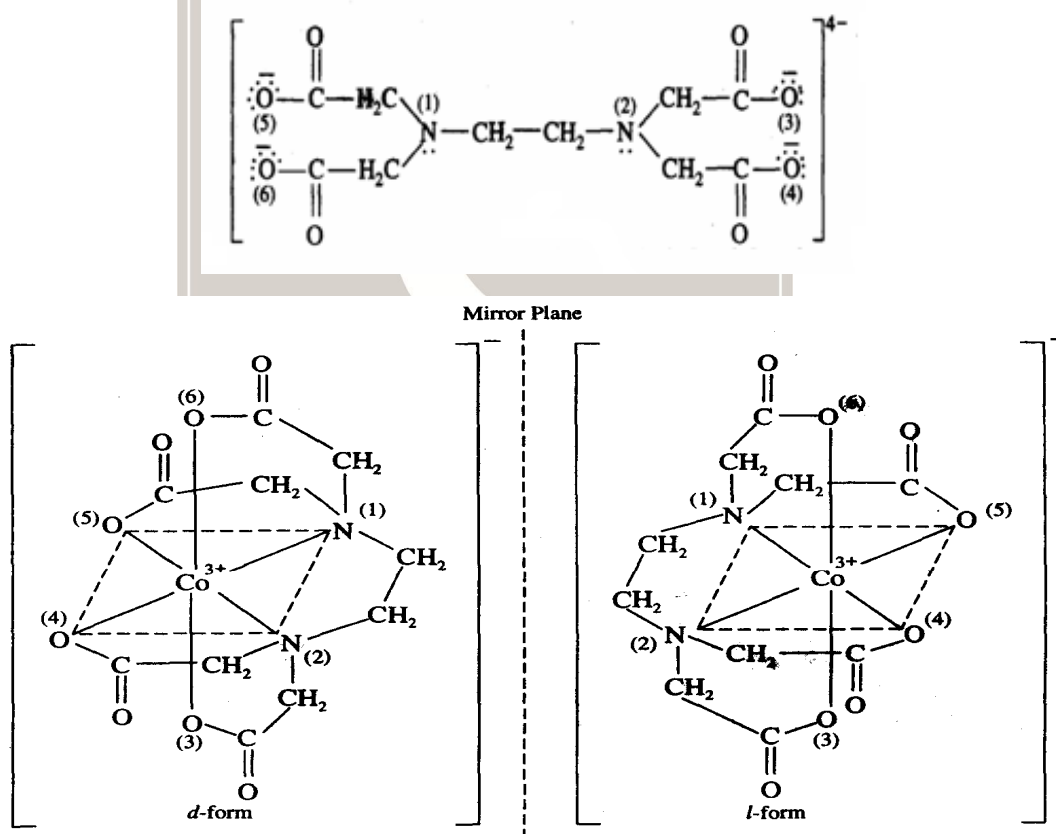
- (4) **[M(AA)₂a₂] type complexes :** Example of this type is [Co³⁺(en)₂Cl₂]⁺ ion. This ion shows geometrical isomerism and hence exists as *cis*- and *trans*- isomers. The *cis*-isomer does not have any plane or centre of symmetry and hence is optically active.



- (5) **[M(AA)₂b₂] type complexes** : One example of this type is $[\text{Co}^{3+}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ ion. This ion exists in *cis*- and *trans*-isomers. *Cis*-isomer is optically active and hence gives optically active *d*- and *l*-forms. On the other hand *trans*-isomer is optically inactive and hence does not give any optical active isomer.



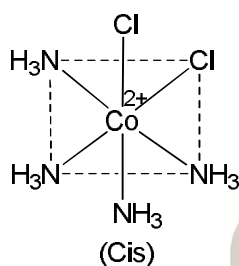
- (6) **Octahedral complexes containing polydentate ligands** : Complex containing hexadentate ligand (polydentate ligand) like ethylene diamine tetraacetate ion also exists in two optical isomers namely *d*- and *l*-isomers. Ethylene diamine tetraacetate ion is abbreviated as EDTA^{4-} and its structure is given as follows:



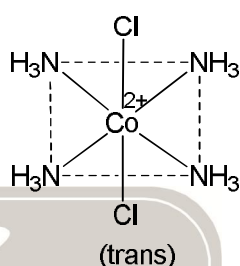
SOLVED PROBLEM

1. The existence of two different coloured complexes of $\text{Co}(\text{NH}_3)_4\text{Cl}_2$ is due to
- (a) optical isomerism (b) linkage isomerism
(c) geometrical isomerism (d) coordination isomerism

Soln. The existence of two different coloured complexes of $[\text{Co}^{2+}(\text{NH}_3)_4\text{Cl}_2]$ is due to geometrical isomerism.



1, 2-dichlorotetramine cobalt (II)
(yellow - brown)



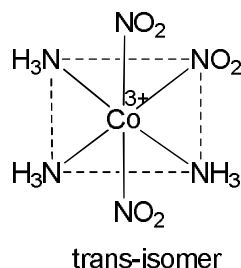
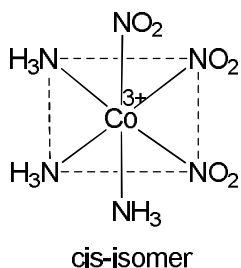
1, 6-dichlorotetramine cobalt (II) ion
(yellow)

Correct answer is (c)

2. The isomerisms that are possible in the Co(III) complexes $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ respectively are
- (a) coordination and position (b) optical and linkage
(c) geometrical and linkage (d) optical and optical

Soln. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3] \rightarrow$ Geometrical isomerism possible

The ligand of one type may form an equilateral triangle on one of the faces (called facial or cis isomer) and the other isomer, the ligands of one type occupy the positions such that two are opposite (or trans) to each other, called meridional or trans isomer.



$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 \rightarrow$ linkage isomerism possible

Here, NO_2 ligands having two potentially ligating atoms that are capable of bonding through one type of donor atom in the situation but a different donor atom in another complex.

$(\text{NH}_3)_5\text{CO-ONO}\text{Cl}_2$ and $(\text{NH}_3)_5\text{CO-NOO}\text{Cl}_2$

Correct answer is (c)

3. The complexes $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}\cdot\text{H}_2\text{O}$ are examples of
- (a) Ionization isomerism (b) linkage isomerism
(c) geometric isomerism (d) optical isomerism

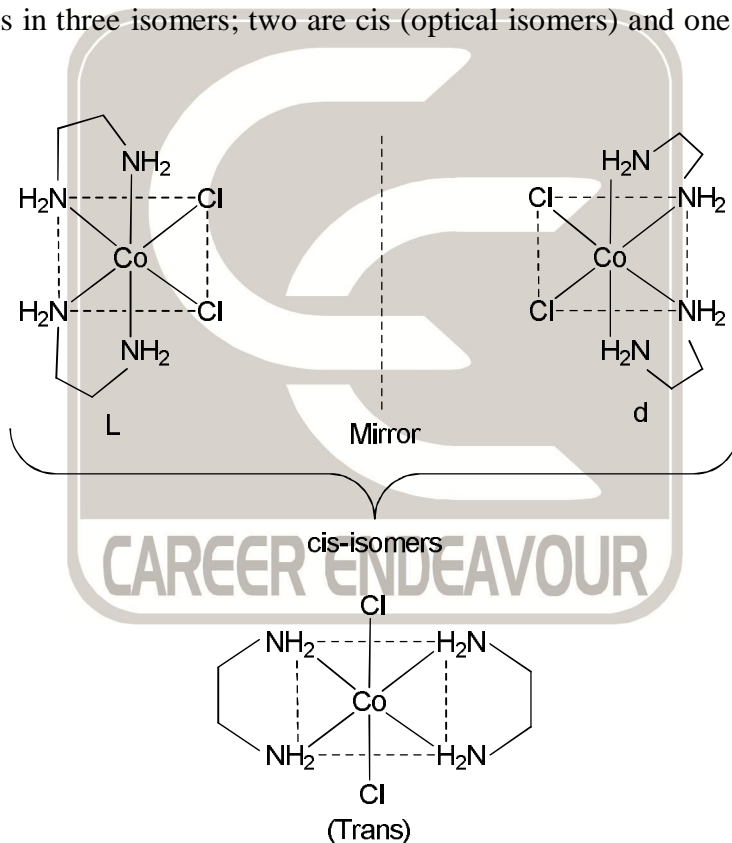
Soln. The isomers which involve exchange of ligands between coordination sphere and ionization sphere are called ionization isomers.

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}\cdot\text{H}_2\text{O}$ is a ionization isomers, because, Br_2 and $\text{H}_2\text{O}\cdot\text{Cl}$ exchange between coordination sphere and ionization sphere.

Correct answer is (a)

4. The total number of isomers of $\text{Co}(\text{en})_2\text{Cl}_2$ is
- (a) 4 (b) 3 (c) 6 (d) 5

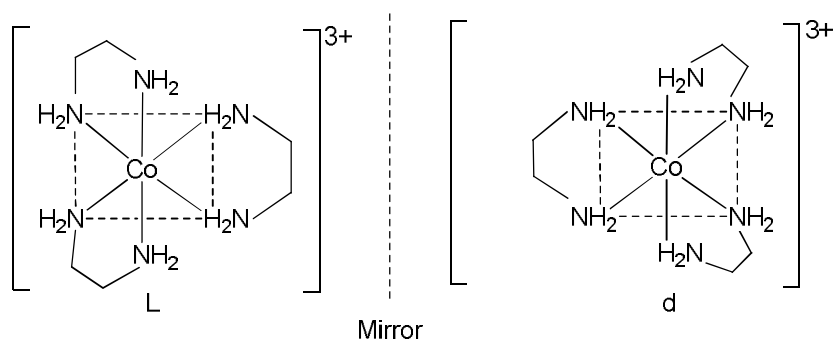
Soln. $\text{Co}(\text{en})_2\text{Cl}_2$ exists in three isomers; two are cis (optical isomers) and one is trans, en is a ethylene diamine



Correct answer is (b)

5. The complex that exists as a pair of enantiomers is
- (a) $\text{trans}-[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$ (b) $\text{cis}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{4+}$
(c) $[\text{Pt}(\text{PPh}_3)(\text{Cl})(\text{Br})(\text{CH}_3)]^-$ (d) $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$

Soln. $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$ exists in a pair of enantiomers.

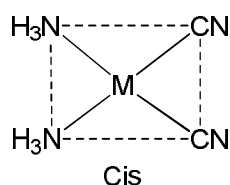


Correct answer is (d)

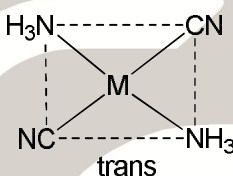
6. The number of possible isomers for the square planar mononuclear complex $[(\text{NH}_3)_2\text{M}(\text{CN})_2]$ of a metal M is

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

Soln. The possible isomers of $[(\text{NH}_3)_2\text{M}(\text{CN})_2]$ are



and



Thus, the number of possible isomers is 2

Correct answer is (a)

7. The complexes $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_2$ and $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ are

(a) linkage isomers (b) positional isomers
(c) ionization isomers (d) optical isomers

Soln. These are ionization isomers because, NO_2 and Cl exchange between ionization sphere and coordination sphere respectively.

Correct answer is (c)

8. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ constitute an example of **[JNU-2004, Biotech]**

(a) linkage isomerism (b) ionisation isomerism
(c) coordination isomerism (d) optical isomerism

Soln. Ionisation isomerism arise due to difference in the position of groups being inside or outside the coordination sphere of the complex.

For example : $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (Violet compound with Co — Br bond) and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (Red compound with Co — SO_4 bond).

Correct option is (b)