ISOMERISM IN COORDINATION COMPOUNDS

Compounds with identical molecular formulas but distinct atom arrangements, leading to differences in one or more physical properties, are referred to as isomers, and this phenomenon is termed isomerism. Isomerism can be categorized into two main types:

A. Structural isomerism
B. Stereoisomerism

(A) Structural Isomerism

(i) Ionisation Isomerism

This form of isomerism arises from the exchange of groups between the complex ion and ions outside of it. $[Co\ (NH_3)_5Br]SO_4$ appears red-violet. When its aqueous solution is mixed with $BaCl_2$ solution, a white precipitate of $BaSO_4$ forms, indicating the presence of free SO_4^{2-} ions. In contrast, $[Co\ (NH_3)_5SO_4]Br$ is red. When a solution of this complex is subjected to a sulfate test with $BaCl_2$, it does not yield a positive result. However, it does produce a cream-colored precipitate of AgBr when reacted with $AgNO_3$, thus confirming the presence of free Br^- ions.

Other examples of ionisation isomerism are.

$[Pt\ (NH_3)_4Cl_2]\ Br_2$ and $[Pt\ (NH_3)_4Br_2]\ Cl_2$ and

$[Co(en)_2NO_2.Cl]\ SCN$, $[Co(en)_2NO_2.SCN]\ Cl$ and $[Co(en)_2Cl.SCN]NO_2$.

(ii) Hydrate isomerism

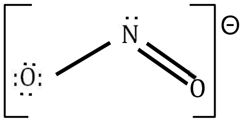
These isomers are formed through the exchange of groups within the complex ion with water. There are three known isomers of $CrCl_3.6\ H_2O$. Conductivity measurements and quantitative precipitation of the ionized Cl^- have led to the following characterizations:

$$[Cr(H_2O)_6]Cl_3$$
$$[Cr(H_2O)_5Cl]Cl_2.H_2O$$
$$[Cr\ (H_2O)_4Cl_2]\ Cl.2H_2O$$

(iii) Linkage Isomerism

This form of isomerism occurs when the ligand binds to the central metal ion of a complex in various manners. These ligands are referred to as ambident ligands.

For instance, the nitrite ion possesses electron pairs that can coordinate with both nitrogen and oxygen atoms.



Ex.

(a) $[Co\ (NH_3)_5\ ONO]\ Cl_2$ and $[Co\ (NH_3)_5\ NO_2]\ Cl_2$

pentaamminenitrito-o-cobalt(III) chloride (red) — pentaamminenitrito-N-cobalt-(III)-chloride (yellow)

(b) $[Mn\ (CO_5).\ SCN]^+$ and $[Mn\ (CO_5)\ (NCS]^+$

pentacarbonylthiocyanto –S-manganese (II) ion — pentacarbonylthiocyanato –N-manganese (II) ion

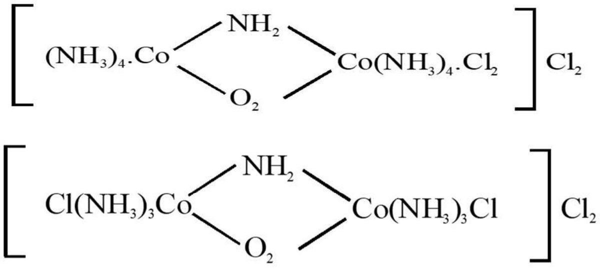
(iv) Co-ordination Isomerism

When both the positively charged cation and negatively charged anion consist of complex ions, isomerism can result from the exchange of ligands between the anion and cation.

For instance, consider [Pt $(NH_3)_4$] [$PtCl_4$] and [PtCl $(NH_3)_3$] [$PtCl_3(NH_3)$]. These isomers are termed coordination isomers.

(v) Co-ordination Position Isomerism

In polynuclear complexes, the exchange of ligands between the metal nuclei leads to the occurrence of coordination position isomerism, as seen in the following example.



Co-ordination position isomers

Polymerisation Isomerism

This This does not constitute a genuine form of isomerism, as it occurs among compounds that share the same empirical formula but possess different molecular formulas. Thus,

[Pt $(NH_3)_2Cl_2$], [Pt $(NH_3)_4$] [$PtCl_4$], [Pt $(NH_3)_4$] [Pt (NH_3) $Cl_3]_2$ and

[Pt $(NH_3)_3Cl]_2[PtCl_4]$ all have the same empirical formula.

(B) Stereoisomerism

Isomers in which atoms maintain the same bonding order but exhibit distinct spatial arrangements are referred to as stereoisomers, and the phenomenon is termed stereoisomerism.

(i) Geometrical Isomerism

This isomerism category emerges within heteroleptic complexes because of the multiple potential geometric configurations of the ligands. Geometrical isomerism is frequently observed in coordination compounds with coordination numbers 4 and 6.

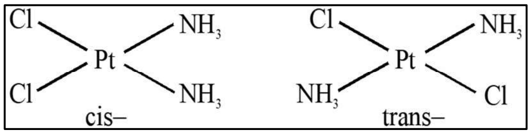
Coordination Number Four

Tetrahedral Complex

Geometrical isomerism cannot be exhibited by tetrahedral compounds because, as commonly understood, all four positions within a tetrahedral geometry are equivalent.

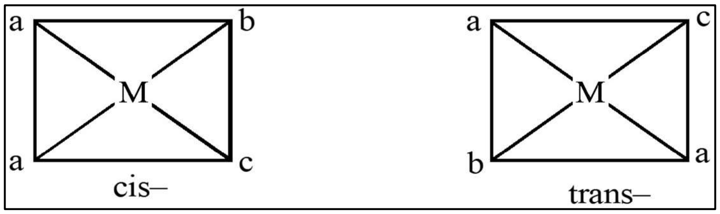
Square Planar Complex

In a square planar complex with the formula [Ma_2b_2] (where 'a' and 'b' are unidentate ligands), the two ligands 'a' can be positioned either next to each other in a cis isomer or opposite to each other in a trans isomer, as illustrated.

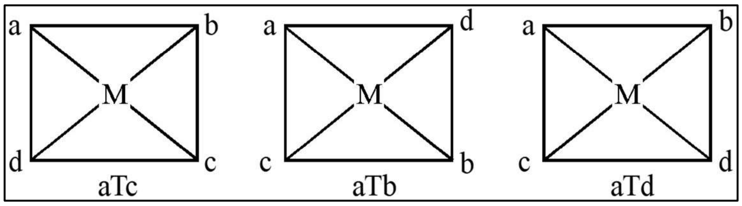


Geometrical isomers (cis and trans) of Pt $(NH_3)_2Cl_2$.

Square planar complex of the type Ma_2bc (where a, b, c are unidentate) shows two geometrical isomers.



Square planar complex of the type Mabcd (where a, b, c, d are unidentates) shows three geometrical isomers.

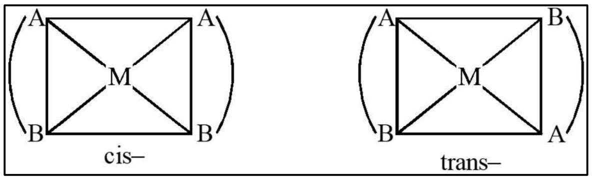


Example is [Pt (NH_3) BrCl(py)]. Three isomers of the complex

[Pt (NH_3) (NH_2OH) (py)$(NO_2)]^+$ have been isolated and identified.

Square planar complex of the type $M(AB)_2$ (where AB are unsymmetrical bidentate) shows two geometrical isomers.

Example is $[Pt(gly)_2]$ in which gly is unsymmetrical ligand.



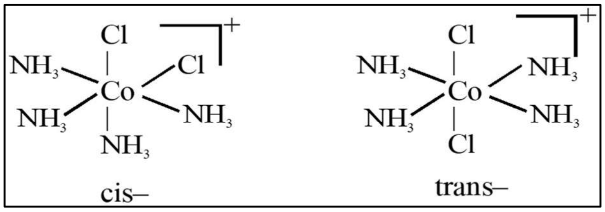
Similarly, M(AB)(CD) also shows two geometrical isomers.

Note: $M(AA)_2$, (where AA are symmetrical bidentate) does not show geometrical isomerism.

e.g., $[Cu(en)_2]^{2+}$ $[Pt(ox)_2]^{2-}$, etc.

Coordination Number Six

Geometrical isomerism is also possible in octahedral complexes.



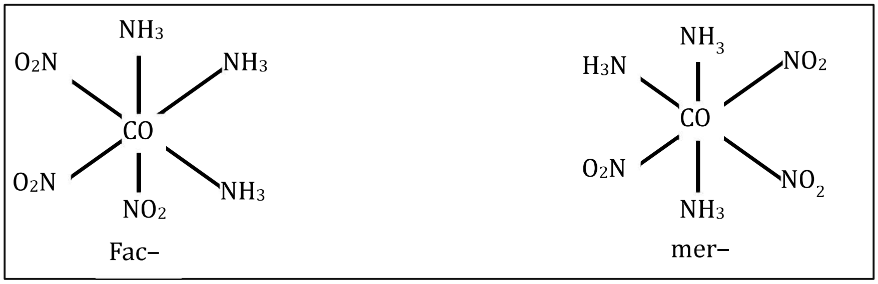
Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

The provided information includes the count of potential isomers and the spatial configurations of ligands around the central metal ion in the respective complexes.

(I) Complexes containing only unidentate ligands

(i)	Ma_2b_4	–	2	(aa)(bb)(bb) (ab)(ab)(bb)
(ii)	Ma_4bc	–	2	(aa)(aa)(bc) (aa)(ab)(ac)
(iii)	Ma_3b_3			

Complexes with the formula Ma_3b_3, featuring monodentate ligands 'a' and 'b,' can exhibit two distinct isomeric variations known as fac– and Mer–. Facial isomers have three identical ligands located on one triangular face, while meridional isomers feature three identical ligands within a plane that bisects the molecule. These same isomeric forms can also be observed in complexes with certain chelating ligands.



Fac– mer–

The facial(fac) and meridional(mer) isomers of $[Co(NH_3)_3(NO_2)_3]$.

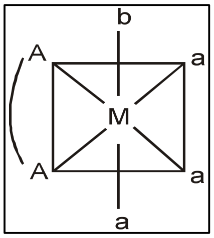
Unsymmetrical bidentate ligands also show fac-mer isomerism.

(iv)	Ma_3b_2c	–	3	(aa)(ab)(bc) (aa)(bb)(ac) (ab)(ab)(ac)
(v)	Ma_3bcd	–	4	(aa)(ab)(cd) (aa)(ac)(bd) (aa)(ad)(bc) (ab)(ac)(ad)
(vi)	$Ma_2b_2c_2$	–	5	(aa)(bb)(cc) (aa)(bc)(bc) (bb)(ac)(ac) (cc)(ab)(ab) (ab)(ac)(bc)
(vii)	Ma_2b_2cd	–	6	
(viii)	Ma_2bcde	–	9	
(ix)	Mabcdef, $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$	–	15	

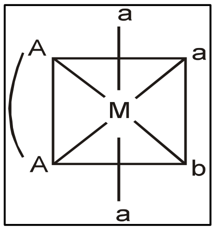
Note: Ma_6 and Ma_5b have only one form.

(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)a_3b$ – Two geometrical isomers are possible.

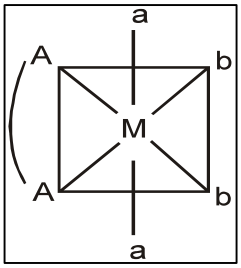


bTa

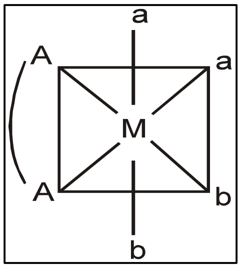


aTa

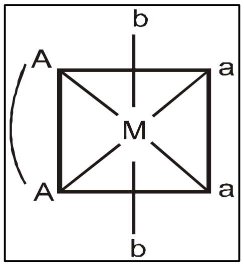
(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.



aTa



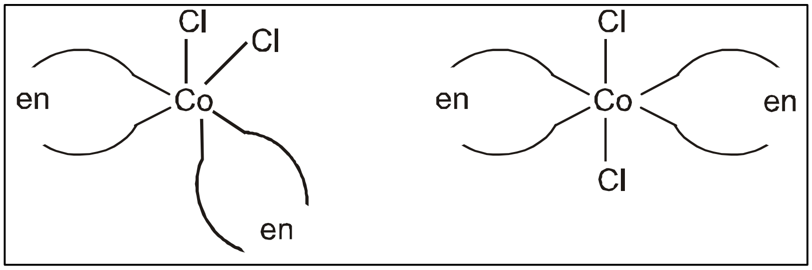
aTb



bTb

Note: With $[M(AA)b_4]$, only one form is possible. M(AA)abcd have six geometrical isomers.

(iii) $M(AA)_2a_2$ – Two geometrical isomers are possible.



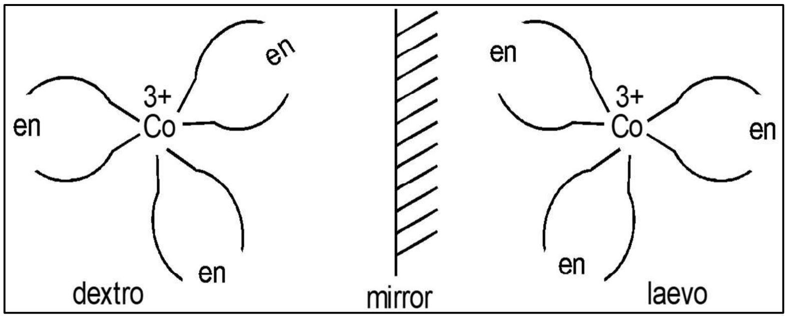
Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

(ii) Optical Isomerism

A coordination compound capable of rotating the plane of polarized light is referred to as optically active. When coordination compounds share the same formula but differ in their ability to change the orientation of polarized light, they are described as displaying optical isomerism, and their molecules are optical isomers. Optical isomers are non-superimposable mirror images and are known as enantiomers. Molecules or ions that cannot be superimposed are termed chiral, which is a result of the absence of symmetry elements in the complex. These two forms are labeled as dextro (d) and laevo (l) based on the direction in which they rotate the plane of polarized light in a polarimeter (d rotates to the right, l to the left).

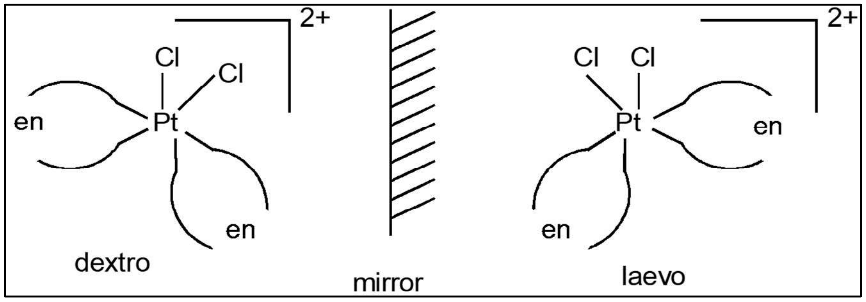
Octahedral Complex

Optical isomerism frequently occurs in octahedral complexes that feature bidentate ligands. For example, $[Co(en)_3]^{3+}$ has d and ℓ forms as given below.



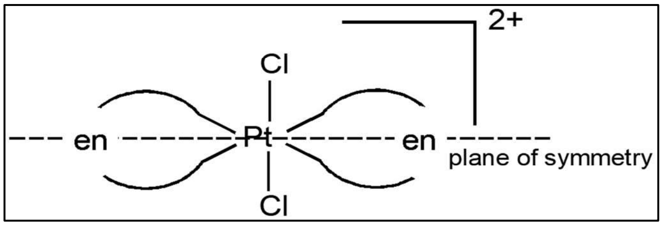
d and ℓ of $[Co(en)_3]^{3+}$

Cis-isomer of [PtCl2(en)2]2+ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.

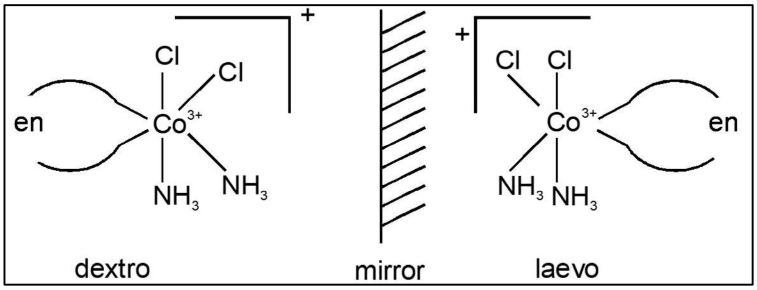


d and ℓ of cis-$[PtCl_2(en)_2]^{2+}$

But trans isomer of $[PtCl_2(en)_2]^{2+}$ does not show optical isomerism.

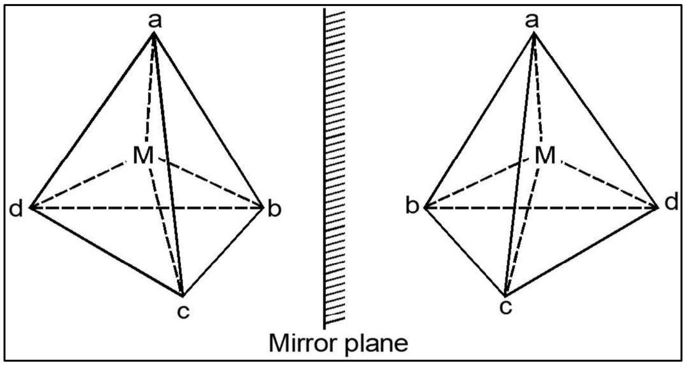


cis- $[Co(NH_3)_2Cl_2(en)]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.

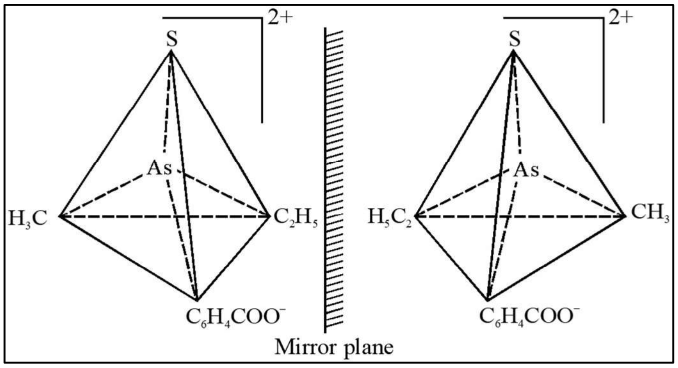


Tetrahedral Complex

Optical isomerism can be anticipated in tetrahedral complexes of the [Mabcd] type, akin to a tetrahedral carbon atom.



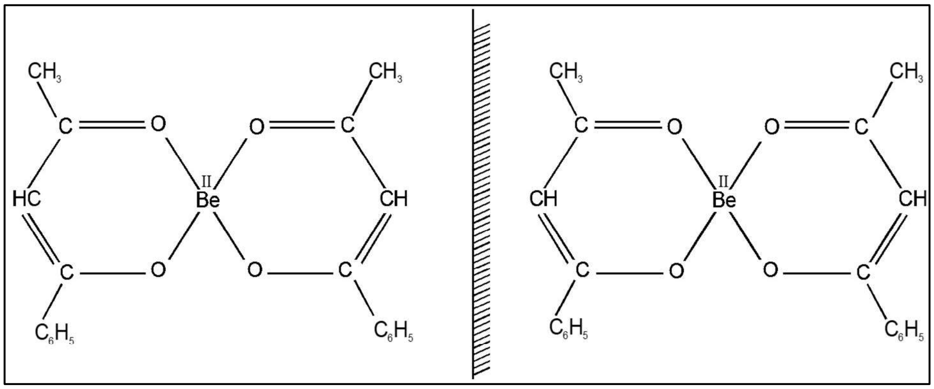
(i) For example [As (III)(CH_3) (C_2H_5) (S)(C_6H_4COO)]$^{2+}$, shows optical isomerism as given below.



It's important to understand that the presence of four distinct groups around the central metal ion isn't the sole prerequisite for a complex to exhibit mirror-image isomerism. The key factor is the molecule's asymmetry. (i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

(ii) Tetrahedral complexes involving beryllium (Be), boron (B), copper (II), and zinc (II) with unsymmetrical bidentate ligands have been separated into optical isomers. To confer chirality to the complex, it's essential for the chelating ligand to be unsymmetrical, even though it may not necessarily be asymmetric or chiral by itself.

An example is bis(benzoylacetate) Be (II) complex, [$(C_6H_5COCHCOCH_3)_2Be$]^0 whose mirror-image isomers are shown in figure.



It's worth observing in the illustration that the complex lacks both a center and a plane of symmetry, and the two forms cannot be overlaid or superimposed upon each other. This explains the resolution of the complex into d-and ℓ-forms.

Square Planar Complex

Optical isomerism is not commonly observed in square planar complexes. The plane defined by the four ligating atoms and the metal ion is regarded as a mirror plane, which precludes the presence of chirality. Nevertheless, even though it is uncommon, a four-coordinated Pt (II) complex can be an exception to this rule.

$[Pt\ (II)(NH_2.CH(C_6H_5).CH(C_6H_5NH_2).\ (NH_2.CH_2.C(CH_3)\ _{2.NH2})]^{2+}$ which has square-planar shape has been resolved into two forms by Mills and Quibell in 1935.