Isomerism in Coordination Compounds

Two or more different compounds having the same formula are called isomers. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

1. Stereoisomerism

a) Geometrical isomerism
b) Optical isomerism

2. Structural Isomerism.

a) Coordination isomerism
b) Ionisation isomerism
c) Hydrate isomerism
d) Linkage isomerism

1. Stereoisomers

Stereoisomers have the same atoms, same sets of bonds, but differ in the relative orientation of these bonds.

Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral.

Optical isomers are possible for both tetrahedral and octahedral complexes, but not square planar.

The earliest examples of stereoisomerism involve complexes of Co(III). In 1889, Jorgensen observed purple and green salts of $[CoCl_2(en)_2]+$, which Werner later correctly identified as the *cis-* and *trans-* geometric isomers. In 1911, the first resolution of optical isomers was reported by Werner and King for the complexes cis-$[CoX(NH_3)(en)_2]^{2+}$, where X=Cl⁻ or Br⁻.

Geometric Isomers

The number of geometric isomers expected for common stereochemistries are as follows:

Square Planar:

| Compound type	No. of isomers
Ma_2b_2	2 (cis- and trans-)
Mabcd	3 (use cis- and trans- relations)

here a, b, c, and d refer to monodentate ligands.

A number of examples of these types have been isolated and characterised and they show very different chemical and biological properties. Thus for example, *cis*-$PtCl_2(NH_3)_2$ is an anti-cancer agent (cisplatin) whereas the *trans*- isomer is inactive against cancer (it is toxic), and so not useful in Chemotherapy.
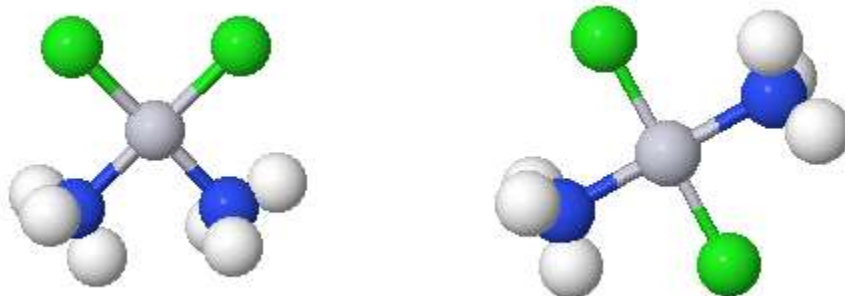
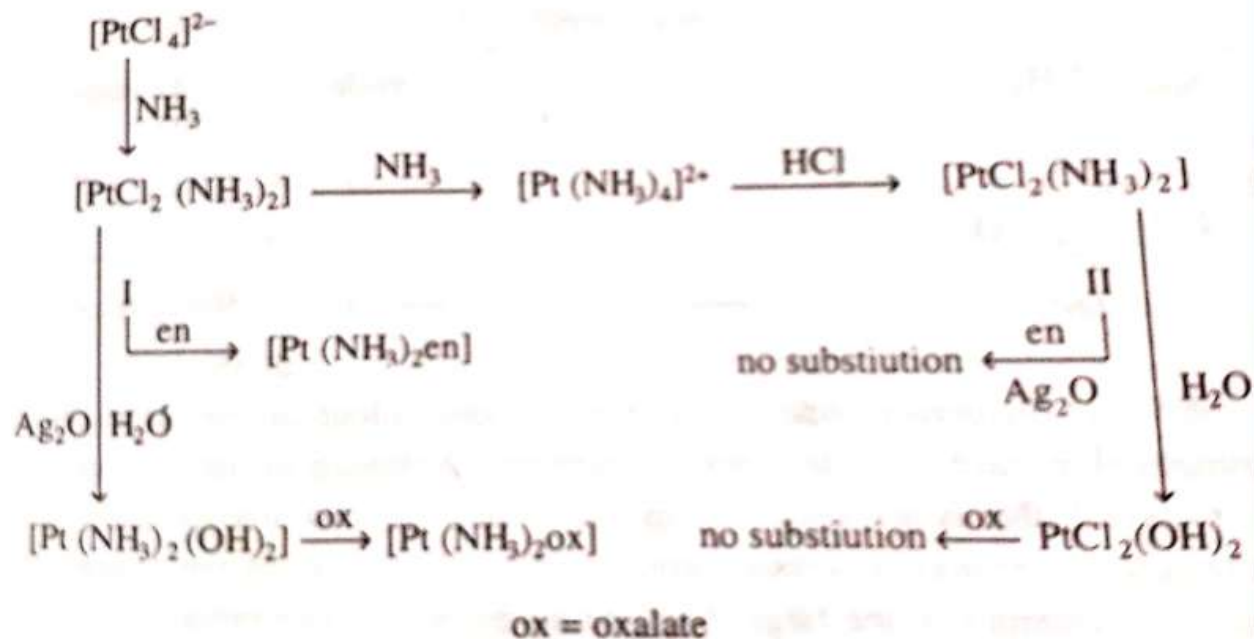

cis- and *trans*- isomers of [$PtCl_2(NH_3)_2$]

cis- and *trans*- refer to the position of 2 groups relative to each other. In the *cis*- isomer they are "next to each other" i.e. at 90 degrees in relation to the central metal ion, whereas in the *trans*- isomer they are "opposite each other", i.e. at 180 degrees relative to the central metal ion.

```
a
|
|
M ----b       a----M----b
  cis-          trans-
```
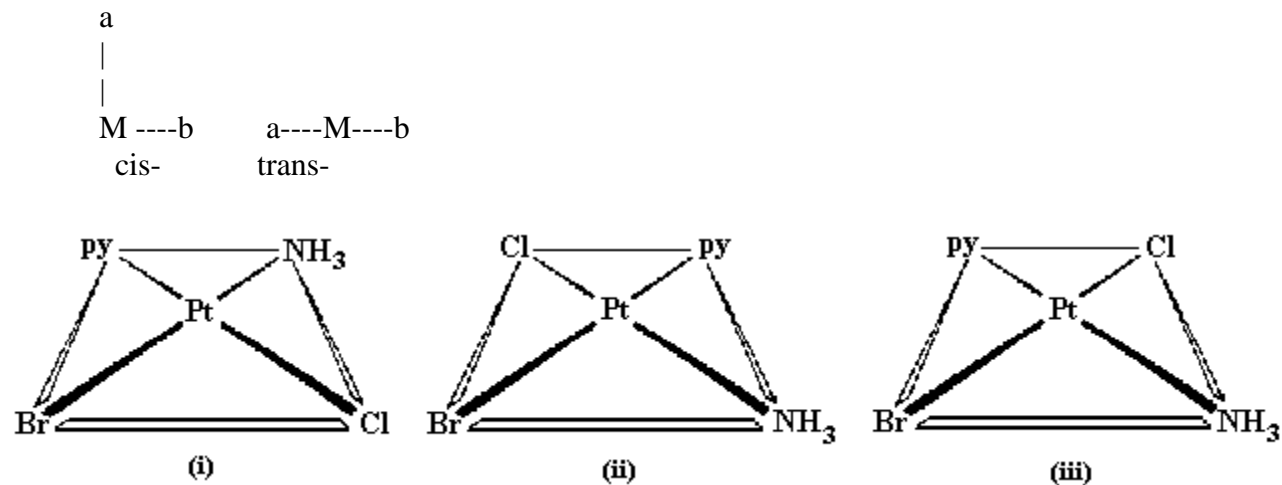

3 geometric isomers of a square planar complex [$PtBrClNH_3(pyr)$].

The first report of the three geometric isomers being isolated and characterised for complexes of the type [Mabcd] was by Il'ya Chernyaev in 1928. The example above was reported by Anna Gel'man in 1948.

The cis- and trans- isomers may be chemically distinguished by the fact that two unidentate ligands only in cis position can be replaced by a bidentate ligand: bidentate ligands cannot span across the square plane to bridge two trans posituins.
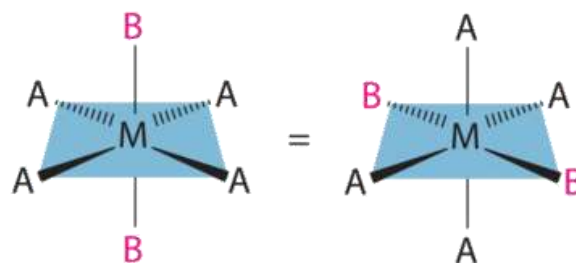
$[PtCl_4]^{2-}$

$$[PtCl_4]^{2-}$$

$$\downarrow NH_3$$

$$[PtCl_2 (NH_3)_2] \xrightarrow{NH_3} [Pt(NH_3)_4]^{2+} \xrightarrow{HCl} [PtCl_2(NH_3)_2]$$

I

$$\xrightarrow{en} [Pt(NH_3)_2en]$$

$Ag_2O | H_2O$

II

no substiution $\xleftarrow{\text{en}}{Ag_2O}$ H_2O

$$[Pt(NH_3)_2(OH)_2] \xrightarrow{ox} [Pt(NH_3)_2ox] \qquad \text{no substiution} \xleftarrow{ox} PtCl_2(OH)_2$$

ox = oxalate

Octahedral:

Compound type	No. of isomers
MA_4B_2	2 (cis- and trans-)
MA_3B_3	2 (fac- and mer-)
MAA_2b_2	3 (2*cis- and 1 trans-)

here a, and b, represent monodentate ligands and AA is a bidentate ligand.
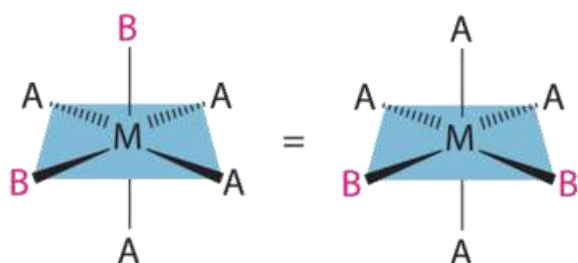
MA₄B₂ octahedral complex, *cis* isomer   **MA₄B₂ octahedral complex, *trans* isomer**
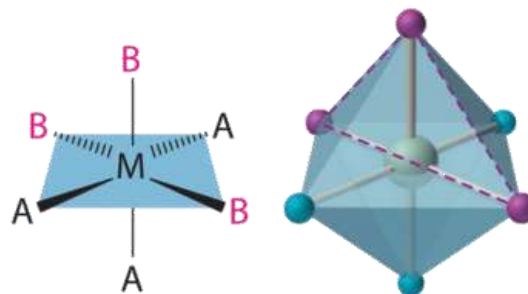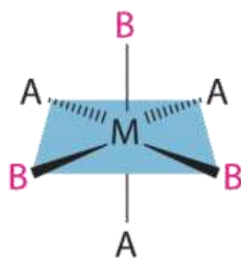
In the second example, new labels are introduced to reflect the relative positions of the ligands around the octahedral structure. Thus; placing the 3 groups on one face of the octahedral gives rise to the *fac*ial isomer and placing the 3 groups around the centre gives rise to the *mer*idional isomer.
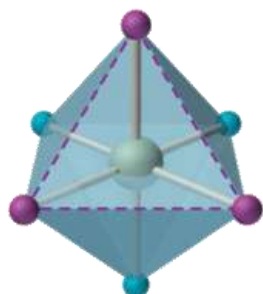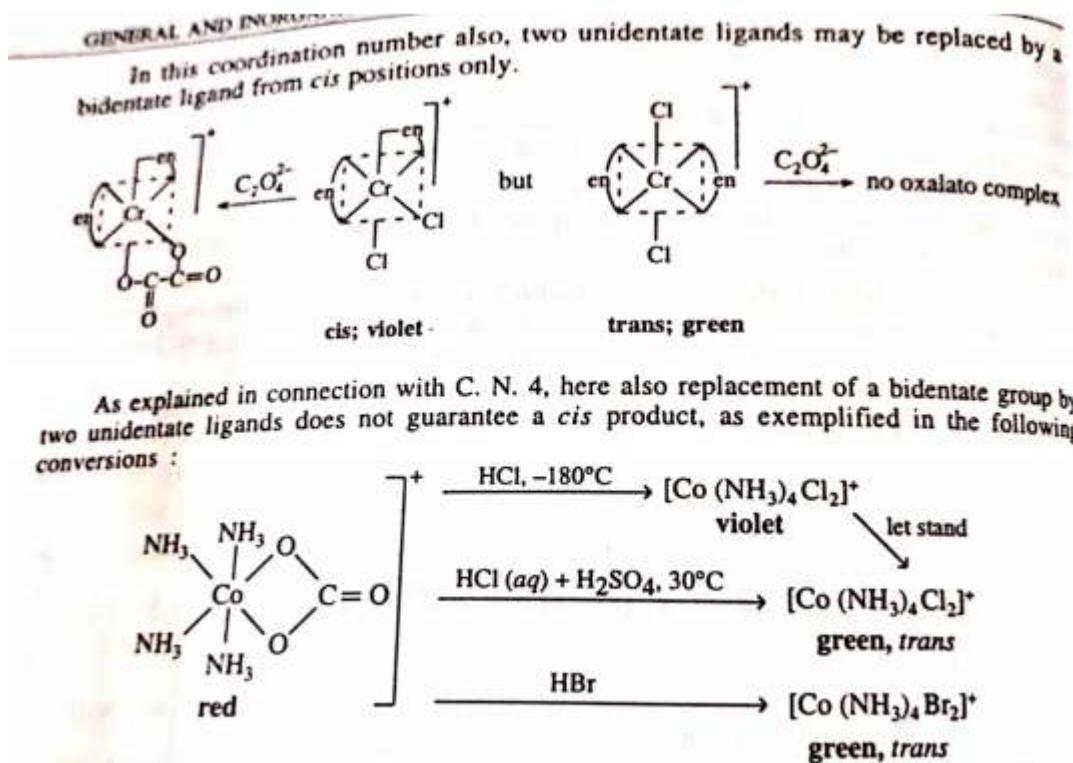
MA₃B₃ octahedral complex, _fac_ isomer

MA₃B₃ octahedral complex, _mer_ isomer

[Mabcdef] is expected to give 15 geometric isomers. In the case of [PtBrClI(NO₂)(NH₃)(pyr)], several of these were isolated and characterised by Anna Gel'man and reported in 1956. Optical isomers are possible for each of these 15 forms, making a total of 30 isomers.

The _cis-_ isomer of MAA₂b₂ may also exhibit optical isomerism although we will concentrate largely on optical isomers of the type M(AA)₃ (see below).

GENERAL AND INORG....

In this coordination number also, two unidentate ligands may be replaced by a bidentate ligand from _cis_ positions only.

but

 $C_2O_4^{2-}$ ⟶ no oxalato complex

cis; violet   trans; green

As explained in connection with C. N. 4, here also replacement of a bidentate group by two unidentate ligands does not guarantee a _cis_ product, as exemplified in the following conversions :

red

$\xrightarrow{\text{HCl, }-180°C}$ [Co (NH₃)₄Cl₂]⁺
violet   ↘ let stand

$\xrightarrow{\text{HCl (aq) + H}_2\text{SO}_4,\ 30°C}$ [Co (NH₃)₄Cl₂]⁺
green, _trans_

$\xrightarrow{\text{HBr}}$ [Co (NH₃)₄Br₂]⁺
green, _trans_

2. Optical Isomers

Optical isomers are related as non-superimposable mirror images and differ in the direction with which they rotate plane-polarised light. These isomers are referred to as enantiomers or enantiomorphs of each other and their non-superimposable structures are described as being asymmetric.
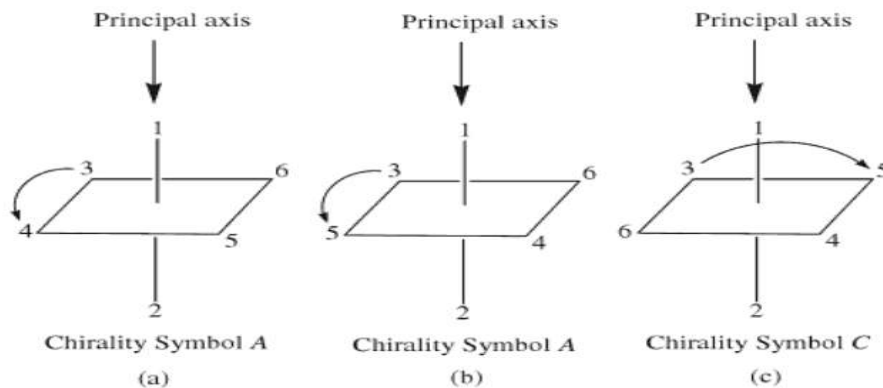
Various methods have been used to denote the absolute configuration of optical isomers such as R or S, Λ or Δ or C and A. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use and that for bis and tris bidentate complexes the absolute configuration be designated Lambda Λ (left-handed) and Delta Δ (right-handed).

Priorities are assigned for mononuclear coordination systems based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog (CIP rules). These rules use the coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number (smallest CIP number). For example the hypothetical complex $[Co\ Cl\ Br\ I\ NH_3\ NO_2\ SCN]^{2-}$ would assign the I- as 1, Br as 2, Cl as 3, SCN as 4, NO_2 as 5 and NH_3 as 6.
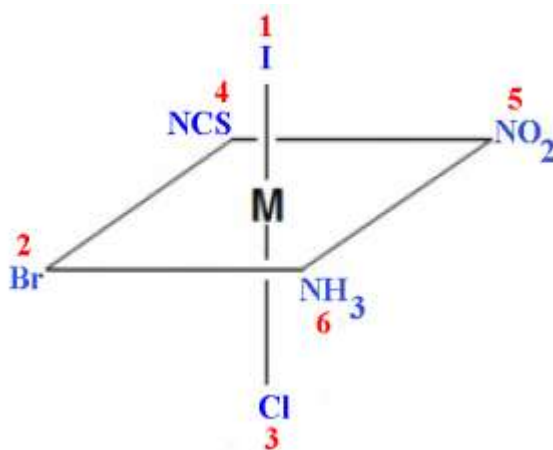

Here is one isomer where the I and Cl, and Br and NO_2 were found to be *trans-* to each other.

The reference axis for an octahedral centre is that axis containing the ligating atom of CIP priority 1 and the trans ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference. In the example shown above this would be C.

Principal axis   Principal axis   Principal axis

Chirality Symbol A   Chirality Symbol A   Chirality Symbol C

(a)   (b)   (c)

The two optical isomers of $[Co(en)_3]^{3+}$ have identical chemical properties and just denoting their absolute configuration does NOT give any information regarding the direction in which they rotate plane-polarised light. This can ONLY be determined from measurement and then the isomers are further distinguished by using the prefixes (-) and (+) depending on whether they rotate left or right.

left-handed Λ isomer   and right-handed Δ isomer

Λ   Δ
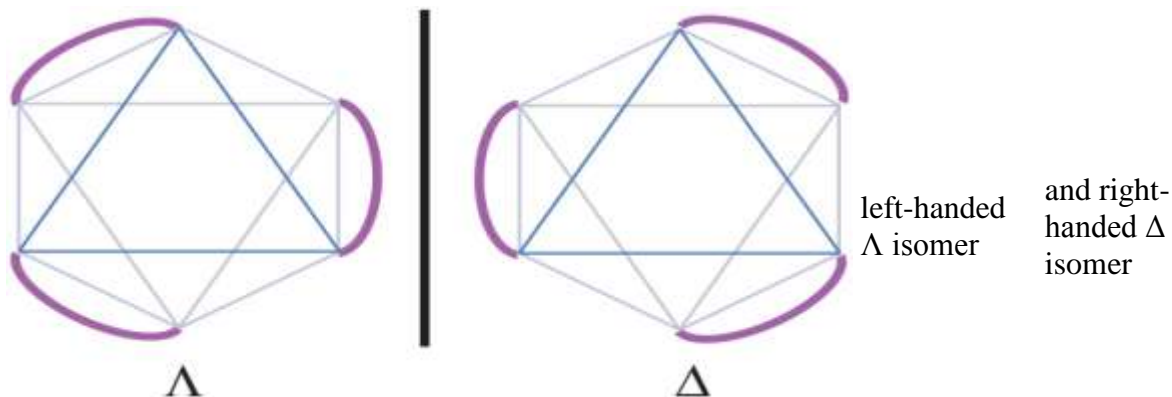
To add to the confusion, when measured at the sodium D line (589nm), the tris(1,2-diaminoethane)M(III) complexes (M= Rh(III) and Co(III)) with **IDENTICAL** absolute configuration, rotate plane polarised light in **OPPOSITE** directions!
The left-handed (Λ)-$[Co(en)_3]^{3+}$ isomer gives a rotation to the right and therefore corresponds to the (+) isomer.

Since the successful resolution of an entirely inorganic ion (containing no C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers e.g. $(NH_4)_2Pt(S_5)_3.2H_2O$.

For tetrahedral complexes, R and S would be used in a similar method to tetrahedral Carbon species and although it is predicted that tetrahedral complexes with 4 different ligands should be able to give rise to optical isomers, in general they are too labile and cannot be isolated.