

Isomerism in Coordination Compounds

Just like organic compounds, coordination complexes exhibit different types of isomerism. It means that there are coordination complexes which have same composition and molecular formula but have different structural arrangements of atoms in the molecule or complex and have different physico-chemical properties. *The compounds of identical composition but showing different properties are regarded as isomers and the phenomenon is called isomerism.* The difference in properties is due to the different structural arrangements of atoms in their molecules. The isomerism may be of two types (a) structural isomerism (b) stereo or space isomerism, which are discussed in this section.

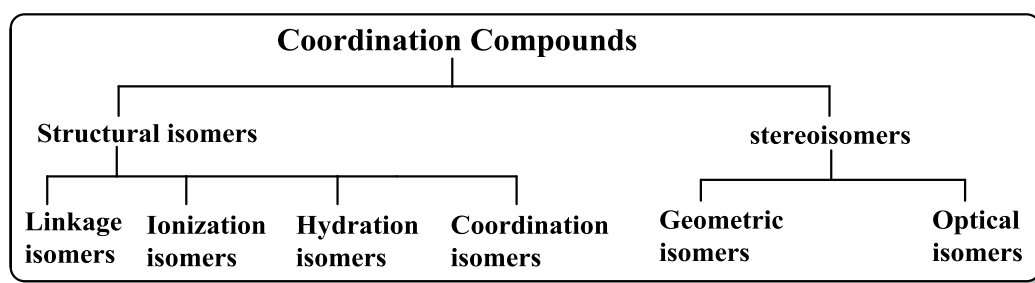


Figure 5.31: Types of isomerism in coordination complexes

5.6.1 Structural Isomerism

This type of isomerism arises due to the differences in linkages of atoms of coordination compounds and may be of the following types.

1. Ionization Isomerism: The compounds having similar empirical composition but producing different ions in solution are called ionization isomers and is observed when the ligands in the coordination sphere are exchanged with the anion present in the ionization sphere. Some examples are given in Table 5.18

Table 5.18: Ionization Isomers

Compound	Isomers	Mode of ionization
$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$	$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$	$[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+ + \text{Br}^-$ $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{SO}_4^{2-}$
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+} + 2\text{Br}^-$ $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]^{2+} + 2\text{Cl}^-$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$ $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{NO}_2^-$ $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]^+ + \text{Cl}^-$

The formation of different ions by the complexes can be confirmed by the qualitative test of the particular ion for example, $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ gives white precipitate of BaSO_4 with BaCl_2 while $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ gives a yellow precipitate of AgBr with AgNO_3 .

2. Hydrate Isomerism: The water molecules in complex compounds may be present as ligands or water of crystallization and the isomerism due to the replacement of coordinated water by anions present outside the coordination sphere is called hydrate isomerism. The best known example is the compound $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ which exists in three isomeric forms, that is, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ is violet in color and ionizes to produce 3Cl^- ions in solution; $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is green and ionizes to produce 2Cl^- ions in solution and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ is also green and ionize to produce only one Cl^- ion in the solution. The action of these isomers over concentrated H_2SO_4 shows the presence of zero, one and two molecules of water of crystallization. The Cl^- ions can be estimated by titrating the solution with AgNO_3 .

3. Coordination Isomerism: If both the cation and anion of a complex compound are complex ions this type of isomerism may be shown by exchange of ligands between the two metal ions. The metal in the complex cation or anion may be same or different. Coordination isomerism is illustrated by the following examples.

Table 5.19: Coordination isomers

Complex	Coordination Isomers
$[\text{Cr}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{SCN})_6]^{3-}$	$[\text{Cr}(\text{NH}_3)_4(\text{SCN})_2]^+[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]^+$
$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{SCN})_6]^{3-}$	$[\text{Cr}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{SCN})_6]^{3-}$
$[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{PtCl}_4]^{2-}$	$[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{CuCl}_4]^{2-}$

4. Coordination Position Isomerism: This type of isomerism is shown by those complexes which contain bridging ligands and arises from the different placement of non-bridging ligands around the central metal ion. Examples of coordination isomerism are shown in Figure 5.32.

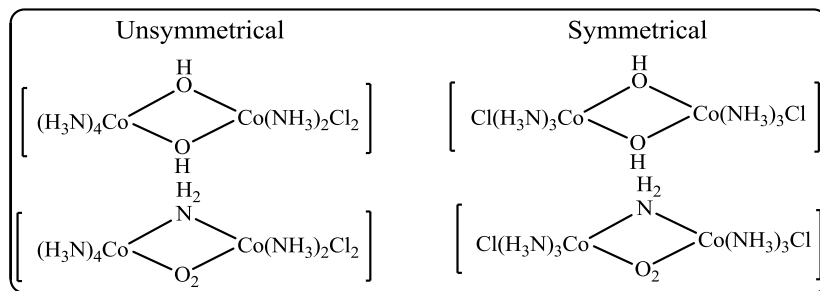


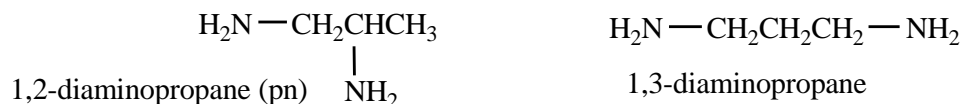
Figure 5.32: Examples of coordination position isomerism. In these compounds NH_3 and Cl^- are placed in an unsymmetrical and symmetrical manner around the $\text{Co}(\text{II})$ ion.

5. Polymerization Isomerism: Isomers having same empirical formula but different formula weight have the same empirical composition and the formulae appear to be polymers of some simple complex compound.

Examples:

1. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$
2. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$

6. Ligand Isomerism: There are certain ligands which exist as isomers and the complexes of these ligands also show isomerism. For example diaminopropane can exist either as 1,2-diaminopropane or 1,3-diaminopropane as shown below:



The isomeric complexes of such types of ligands are known, for example, $[\text{Co}(\text{pn})_2\text{Cl}_2]^+$ and $[\text{Co}(\text{tr})_2\text{Cl}_2]^+$

7. Linkage isomerism: Certain ligands contain two donor atoms and can coordinate to central metal ion through either of these two donors giving isomers. The examples of such ligands are NO_2^- and SCN^- . In former the lone pair is present on nitrogen and oxygen atom and former can coordinate to metal either through nitrogen (M–N bond) or through oxygen (M–O bond) and later through sulphur (M–S bond) or through nitrogen (M–N bond). Therefore two different isomers of nitropentaamminecobalt(III) chlorides; $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ (yellow) and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ (red color), have been reported by S. M. Jørgensen in 1894. Investigations have shown that N-bonded nitro isomer is more stable than O-bonded nitro and conversion of nitrito to nitro could occur simultaneously both in solution and solid state *via* an intramolecular mechanism and the reaction rate is accelerated at elevated temperature. Similar complexes have been prepared with thiocyanate ion. The thiocyanate ligand, usually acts as an S-donor towards soft metal centers, but as a N-donor towards hard metals. Steric effects may also be important, particularly for the bulkier dimethylsulfoxide as ligands.

5.6.2 Stereoisomerism

Stereoisomers have the same ligands, but have different geometric arrangement of the ligands. Stereoisomers include cis and trans isomers, chiral isomers, compounds with different conformations of chelate rings, and other isomers that differ only in the geometry of attachment to the metal ion. In case of compounds which contain the same ligands coordinated to same metal ion, the arrangement of atoms/ligands around the central metal

ion in space is different and this gives rise to stereoisomerism and individual pair of compounds are stereoisomers. This isomerism is of two types: geometrical isomerism and optical isomerism.

A: Geometrical Isomerism

This is also called *cis-trans isomerism* in which the two ligands may occupy the position adjacent to each other (*cis-isomers*) or opposite to each other around the metal atom (*trans-isomers*). The complex compounds in which two ligands are placed adjacent to one other are called *cis-isomers* and in which two ligands occupy opposite position are called *trans-isomers*. Geometrical isomers have identical formulae but differ in physical and chemical properties such as dipole moment due to different placement of ligands. *Trans* isomers have nearly zero dipole moment as the moment due to individual groups cancel out whereas *cis* isomers have dipole moment in the range of 8-12 Deby. The complexes having coordination numbers 2 and 3 do not exhibit geometrical isomerism and it is common for complexes having coordination number 4 and 6.

Geometrical Isomerism in Complexes with Coordination number 4

Geometrical isomerism is not shown by tetrahedral complexes because all the ligands are in adjacent position and all four bond angles are the same. However it is very common in square planar complexes and can be discussed under the following type in which M represents a metal atom and a, b, c and d monodentate ligands; A-A and A-B stand for a symmetrical and unsymmetrical bidentate ligand. In terms of numbering scheme, the two similar ligands at 1,2; 2,3; 3,4 and 1,4 positions give *cis* isomers and at positions 1,3 and 2,4 form *trans* isomers. *Cis* and *trans* isomerism in square planar complexes is discussed here.

[Ma₂b₂] Type Complexes

These complexes can exist in *cis-trans* isomeric forms as shown in Figure 5.33. Platinum and palladium complexes have such isomers, for example, [Pt(NH₃)₂Cl₂], [Pt(py)₂Cl₂] and [Pd(NH₃)₂(NO₂)₂]. These complexes can be identified by dipole moment measurement. The *cis* isomer has a definite dipole moment since similar groups are on the same side while the *trans* isomer has no dipole moment since similar groups are opposite to one another. The *cis* isomer of [Pt(NH₃)₂Cl₂], is called cisplatin and used as an antitumor agent. Several *cis*-platinum complexes of [Pt(a₂b₂)] type have been found to exhibit anticancer properties. Another example is [Pt(NO₂)₂(NH₃)₂] which exist in *cis* and *trans* forms. Diamminebromochloroplatinum(II) also shows *cis-trans* isomerism.

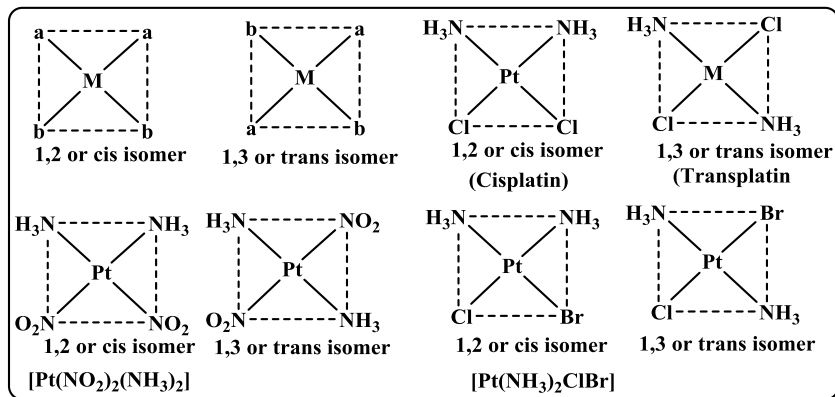


Figure 5.33: Examples of *cis* - *trans* isomerism in complexes of type $[Ma_2b_2]$

$[Ma_2bc]$ Type Complexes

The complexes of this composition can exist in *cis* and *trans* isomeric forms depending on whether 'a' ligands are adjacent or opposite to one other. The complex $[Pt(py)_2NH_3Cl]^+$ and $[PdCl_2BrI]^{2-}$ exist *cis-trans* forms and are shown in in Figure 5.34.

$[Mabcd]$ Type Complexes

The complexes of this type give three isomers and their structures can be written by fixing the position of one ligand (**a**) and then placing the other three ligands **b**, **c** and **d** trans to it (Figure 5.35). Typical examples of this type of complexes are $[Pt(NH_3)(Py)ClBr]$ and $[Pt(NO_2)PyClBr]$. This type of complexes exists in three isomeric forms.

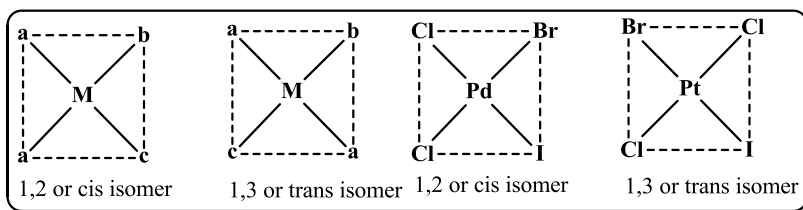


Figure 5.34: Examples of *cis-trans* isomerism in complexes of type $[Ma_2bc]$

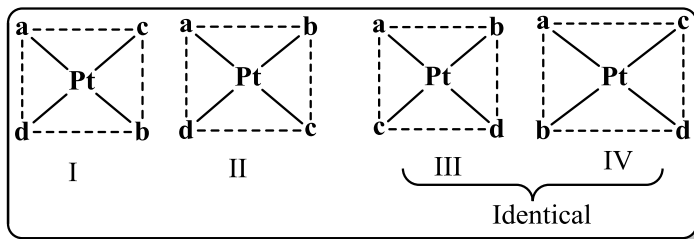


Figure 5.35: Examples of cis-trans isomerism in complexes of type [Mabcd]

[M(AB)₂] Type Complexes

Square planar complexes containing unsymmetrical bidentate ligands of type AB where A and B are the two donor atoms which are different also show geometrical isomerism. This is shown in Figure 5.36. Examples of such complexes are [Pt(gly)₂] and [Cu(gly)₂] where gly stands for glycinato ion NH₂CH₂COO⁻ which has N and O as the donor atoms. Cis-/trans-[Pt(gly)₂] complexes have been synthesized. These complexes have shown antiproliferative activity.

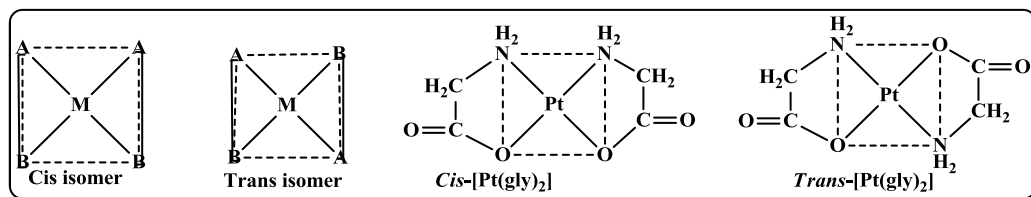


Figure 5.36: Examples of cis-trans isomerism in complexes of the type [M(AB)₂]

Geometrical Isomerism in Complexes with Coordination number Six

The complexes with coordination number six are octahedral in shape which have six equivalent vertices and eight faces. Metal ion/atom lies at the center and positions 1 to 6 are occupied by ligands. These complexes exhibit geometrical isomerism when these contain monodentate ligands **a**, **b**, **c** and **d**, symmetrical bidentate ligands A-A and unsymmetrical bidentate ligands A-B. The two ligands at position 1,2; 1,3; 2,3; 3,6 and 6,4 are *cis* to one other and at position 1,6; 2,4; and 3,5 are *trans* to one other. There are several types of octahedral complexes which exhibit geometrical isomerism, however, only [Ma₄b₂], [Ma₃b₃] and [Mabcd] type complexes will be described here.

a. [Ma₄b₂], [Ma₂b₄] and [Ma₄bc] Type Complexes

The complexes of these types show geometrical isomerism and typical examples are [Co(NH₃)₄Cl₂]⁺ and [Co(NH₃)₄H₂OCl]²⁺. These isomers are illustrated in Figure 5.37.

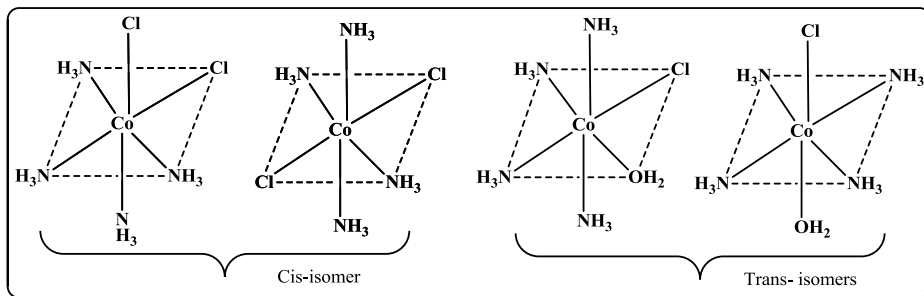


Figure 5.37: Cis-trans isomerism in complexes of Type $[Ma_4b_2]$, $[Ma_2b_4]$, $[Ma_4b_4]$ and $[Ma_4bc]$

b. $[Ma_3b_3]$ Type Complexes

This composition has two geometric isomers, *fac* and *mer*. The *fac*- isomer ("facial") gets its name because all three 'a's are coordinated on one face of the octahedron. The *mer* isomer ("meridional") has the three 'a's coordinated in a plane that includes the metal ion. The **a** and **b** are monodentate ligands. Several complexes of this type are known which exhibit *fac-mer* isomerism. For example $[Rh(py)_3Cl_3]$, $[Pt(NH_3)_3Cl_3]^+$, $[Cr(H_2O)_3F_3]$, $[Ru(H_2O)_3Cl_3]$, $[Pt(NH_3)_3X_3]$ and $[Co(NH_3)_3(NO_2)_3]$. The two isomers of complex $[Co(NH_3)_3(NO_2)_3]$ are shown in Figure 5.38. The Figures show that in *cis* isomer (*fac*) the three NO_2^- ions lie on the corners of one triangular face of octahedron and the NH_3 molecules are present on corners of opposite triangular face.

When two similar ligands are mutually adjacent they form cis isomers. When two similar ligand are opposite to each other, trans isomers are formed. When three identical ligands occupy one face of an octahedron, the isomer is said to be facial, or *fac*. In a *fac* isomer, any two identical ligands are adjacent or cis to each other. If these three ligands and the metal ion are in one plane, the isomer is said to be meridional, or *mer*. A *mer* isomer can be considered as a combination of a trans and a cis, since it contains both trans and cis pairs of identical ligands.

In terms of numbering scheme of position in *cis* isomer the three NO_2^- ions are present at position 1,2,3 and this isomer may also be called 1,2,3-isomer or facial (*fac*) isomer. While in the *trans* isomer the three NO_2^- ions lie around one edge of octahedron and the NH_3 molecules are present at the opposite edge and the isomer is called meridional (*mer*) isomer. Similar isomers are possible with some chelating ligands. Examples with monodentate and tridentate ligands are shown in Figure 5.38.

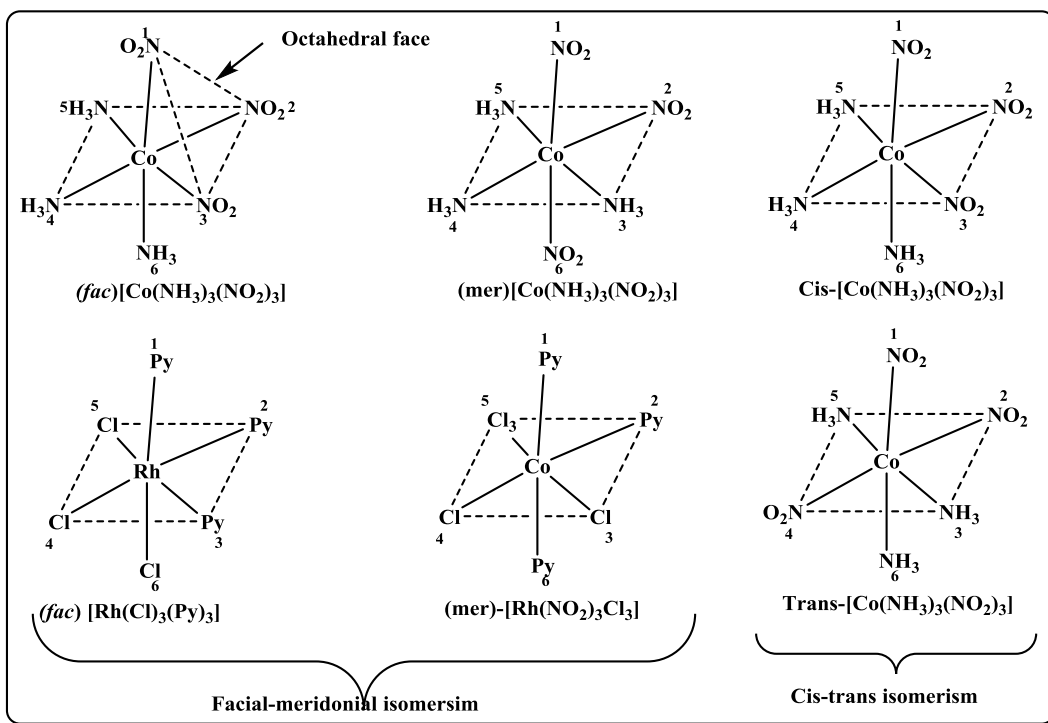


Figure 5.38: *Cis-trans* isomers of the complexes of the type $[Ma_3b_3]$

c. $[M abcdef]$ Type Complexes

Octahedral complexes containing six different monodentate ligands are theoretically known to exist in 15 isomers while only three isomers have been isolated experimentally. The only example is $[Pt(py)(NH_3)(NO_2)(Cl)Br(I)]$ which has been prepared for Pt^{4+} .

d. $[M(A-B)_3]$, $[M(A-A)_2b_2]$ and $[M(A-A)b_2c_2]$ Type Complexes

The octahedral complexes with unsymmetrical bidentate ligand exhibits cis-trans isomerism. In the complexes of the type $[M(A-B)_3]$, $A-B$ is an unsymmetrical ligand in which the two donor atoms A and B are different. An example of this type of complexes is $[Cr(gly)_3]$. In the *cis* isomer the two N and two O atoms of two glycine are placed adjacent while in *trans* isomer these occupy opposite positions. In $[M(A-A)_2b_2]$ and $[M(A-A)b_2c_2]$ type complexes, $A-A$ is symmetrical ligand like ethylenediamine whereas b and c are monodentate ligands. The example of such complexes are $[Co(en)_2(NH_3)_2]^{3+}$ and $[Co(en)(NH_3)_2Cl_2]^+$. The structures of $[M(A-B)_3]$, $[M(A-A)b_2c_2]$ and $[M(A-A)_2b_2]$ are shown in Figure 5.39.

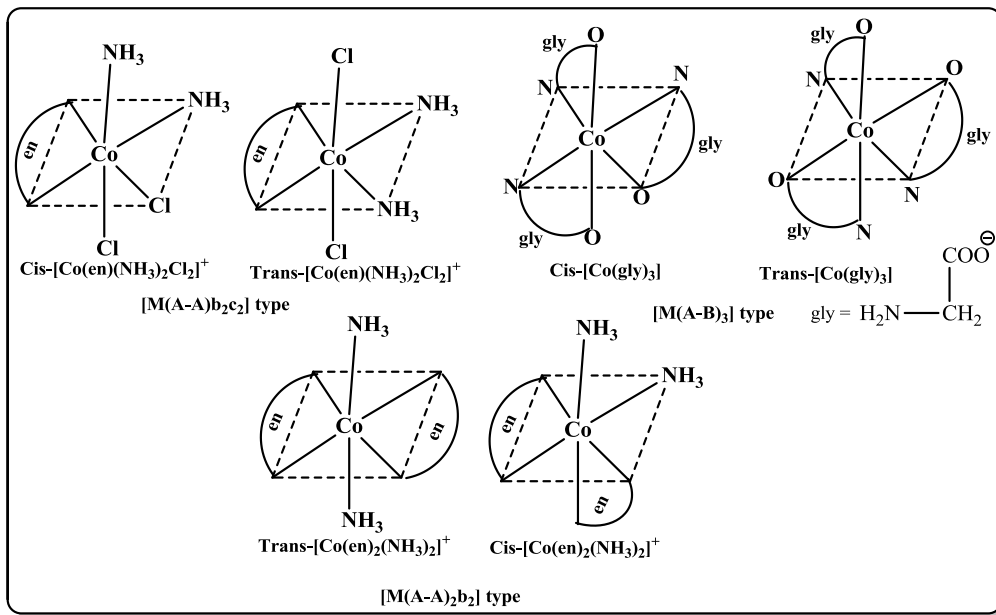


Figure 5.39: Cis-trans isomerism in complexes of the type $[M(A-A)b_2c_2]$ and type $[M(A-B)_3]$ type complexes

B: Optical Isomerism

There are certain compounds which have the ability to rotate the plane polarized light through certain degree either to left or right when light passes through their solution. This property is called optical activity and such compounds are said to be optically active compounds. There are three conditions for a complex to be optically active.

1. It should be asymmetric i.e. should have no plane of symmetry.
2. The complex and its mirror image should not be super imposable.
3. It should contain as far as possible all different ligands.

The optically active coordination complexes are of two types.

A. Those complexes which rotate the plane of polarized light to right are called dextro rotatory and are represented by placing either $-d-$ or $(+)$ sign before the name or formula of the compound.

B. Those compounds which rotate the plane of polarized light to left are called levo rotatory and are represented by placing either $l-$ or $(-)$ sign before the name or formula of the compound. *These two forms which have similar chemical and physical properties are*

called optical isomers and the phenomenon is called optical isomerism. These are mirror image of one another. Optical isomerism is discussed in different types of coordination compounds in this section.

1. Optical Isomerism in four coordinated complexes

The complexes of this type may be tetrahedral or square planar and can exhibit isomerism.

(a) Tetrahedral complexes: Majority of the tetrahedral complexes are optically inactive. The complexes of the type $[Ma_4]$ and $[Ma_3b]$ type are optically inactive while complexes of the type $[Mabcd]$ show optical isomerism and one such example is $[As(CH_3)(C_2H_5)(S)(C_6H_5COO^-)]^{2+}$ ion which exists in two isomeric forms as shown in Figure 5.40.

For the molecule to be optically active it should be asymmetric which means it should not have a plane of symmetry. Some tetrahedral complexes of beryllium(II), boron(III) and zinc(II) with unsymmetrical bidentate ligands have been resolved into optical isomers. For example, the complexes of boron and beryllium like bis(benzoylacetato)beryllium(II) have been found to be optically active. The complex $[Be(C_6H_5COCHCOCH_3)_2]$ and its mirror-image are shown in Figure 5.40. The complex $[Be(C_6H_5COCHCOCH_3)_2]$ has no plane of symmetry and its mirror image is not superimposable.

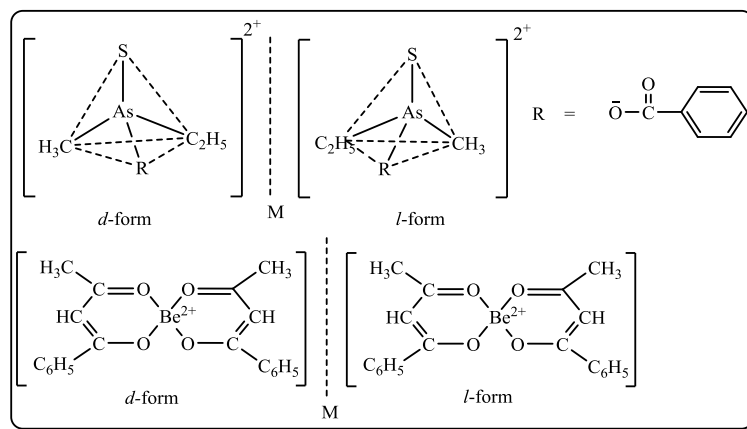


Figure 5.40: Optical isomerism in $[As(CH_3)(C_2H_5)(S)(C_6H_5COO)]^{2+}$ and $[Be(C_6H_5COCHCOCH_3)_2]$

(b) Square planar complexes

In square planar complexes the metal and the ligands are coplanar so that the molecule has a plane of symmetry. Therefore, such complexes rarely show optical isomerism. But some

complexes of Pd^{2+} and Pt^{2+} with isobutylene diamine meso stilbene diamine and ethylenediamine tetra acetic acid have been prepared and resolved into the optically active isomers as shown in Figure 5.41.

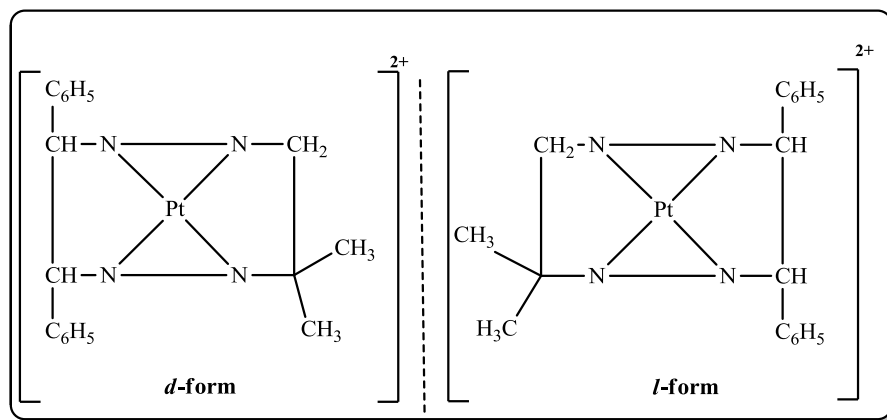


Figure 5.41: Optical isomerism in complexes in isobutylene diamine meso stilbenediamine platinum (II)

2. Optical Isomerism in six coordinated complexes

[Ma_4b_2] and [Ma_3b_3] Type Complexes

These type of complexes do not show optical isomerism. However the complexes of the [$\text{Ma}_2\text{b}_2\text{c}_2$] type are optically active. For example $\text{cis-}[\text{Pt}(\text{NH}_3)_2(\text{py})_2\text{Cl}_2]^{2+}$ exists in two optical isomers. The *trans*-form is optically inactive as the molecule has a plane of symmetry. These two optically active forms are shown in Figure 5.42.

[Mabcdef] Type Complexes

This type of complexes should be optically active and one example of an octahedral complex of this type is $[\text{Pt}(\text{py})(\text{NH}_3)(\text{NO}_2)\text{ClBrI}]$. It can theoretically exist in 15 geometrical isomers each of which exists in optical isomeric active form. One form, for example is shown in Figure 5.42.

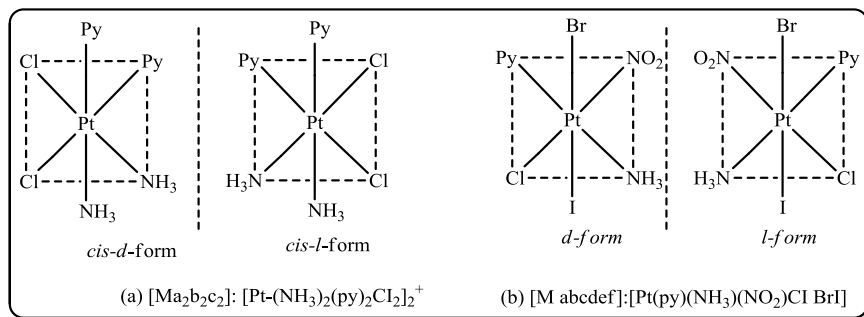


Figure 5.42: Optical isomerism in complexes $[Pt(NH_3)_2(py)_2Cl_2]^{2+}$ and $[Pt(py)(NH_3)(NO_2)Cl BrI]$

$[M(A-A)_3]$ Type Complexes

This type of complexes show optical isomerism and some examples are $[Co(en)_3]^{3+}$; $[Cr(ox)_3]^{3-}$; $[Co(pn)_3]^{3+}$ and $[Pt(en)_3]^{4+}$. The two optical isomers of $[Co(en)_3]^{3+}$ are shown in Figure 5.43.

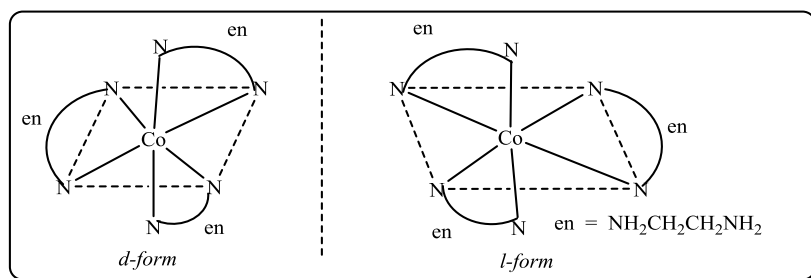


Figure 5.43: Optical isomerism in the $[M(A-A)_3]$ type complex

The hexadentate ligand, EDTA, forms complex with Co^{3+} ion which exists in *d*- and *l*-form as shown in Figure 5.44.

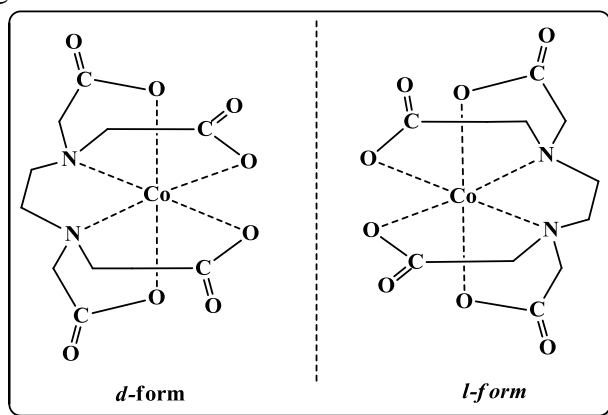


Figure 5.44: Optical isomerism in [Co(EDTA)]

The complex ion $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ has *cis* and *trans* isomers. The *cis* isomer is optically active as it has no plane of symmetry while *trans* isomer is optically inactive because it has a plane of symmetry and exist in optically inactive or meso form. The optically active isomers are shown in Figure 5.45.

Other examples include $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$, $[\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{2-}$, $[\text{Rh}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{2-}$ and $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$

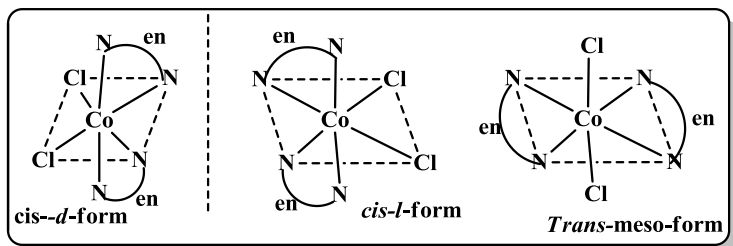


Figure 5.45: Optical isomerism in the $[\text{M}(\text{A}-\text{A})_2 \text{a}_2]$ type complexes