### Subject: US03CCHE21 **ISOMERISM AMONGS INORGANIC COMPLEXES**

The coordination compounds have the same molecular formula but have their ligands attached to the central metal atom in different ways are called isomers. These isomers have different properties. The phenomenon that gives rise to different isomers is called isomerism.

### **TYPES OF ISOMERISM:**

Isomerism may be classified as under:

### [A]Structural isomerism

- 1. Conformation isomerism
- 2. Ionization isomerism
- 3. Hydrate isomerism
- 4. Coordination isomerism
- 5. Linkage (salt) isomerism
- 6. Coordination position isomerism
- 7. Ligand isomerism
- 8. Polymerization isomerism

## STRUCTURAL ISOMERISM:

### 1. Conformation isomerism:

In this isomerism two isomers have different geometries but are otherwise identical. e.g.  $[Ni^{2+}(P.Et.Ph_2)_2Br_2]$  complex (four coordinated) give two conformation isomers. One of these is tetrahedral, green and paramagnetic while the other form is square planar, brown and diamagnetic. Thus both forms have different geometries but same coordination number i.e. four.

### 2. Ionization isomerism:

Ionisation isomers are the compounds that have the same molecular formula but give different ions in the solution. This occurs due to interchange of the ligand anion of the central metal atom and the external anion associated with the complex.

e.g.  $[Co(NH_3)_5Br]^{+2}SO_4^{-2} \& [Co(NH_3)_5SO_4]^{+1}Br^{-1}$ :  $[Co(NH_3)_5Br]^{+2}SO_4^{-2}$  gives white ppts of BaSO<sub>4</sub> with aq BaCl<sub>2</sub> while [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]<sup>+1</sup>Br<sup>-1</sup> does not. Similarly [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]<sup>+1</sup>Br<sup>-1</sup> gives yellow ppts of AgBr with aq. silver nitrate, while  $[Co(NH_3)_5Br]^{+2}SO_4^{-2}$  does not.

Another examples are [Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Br<sub>2</sub> and [Pt(NH<sub>3</sub>)<sub>4</sub> Br<sub>2</sub>]Cl<sub>2</sub>, [Co(en)<sub>2</sub>NO<sub>2</sub>Cl]SCN & [Co(en)<sub>2</sub>NO<sub>2</sub>SCN]Cl

### [B] Stereoisomerism

- 1. Geometrical isomerism (cis-trans isomerism)
- 2. Optical isomerism

(mirror image isomerism)

### 3. <u>Hydrate isomerism</u>:

e.g

This isomerism arises due to different positions of water molecules in the complex (interchange between complex and rest of the compound). The classic example is that of  $CrCl_3 6H_2O$  that is found in 3-isomeric forms.

$[Cr(H_2O)_6]Cl_3$	[Cr(H <sub>2</sub> O) <sub>5</sub> Cl]Cl <sub>2</sub> H <sub>2</sub> O	[Cr(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]Cl <sub>2</sub> H <sub>2</sub> O
Violet	Blue green	Dark Green
4 ions	3 ions	2 ions
Equi.cond ~425	~250	~130
All chlorine ppted as AgCl	2/3 chlorine ppted	1/3 chlorine ppted
No loss of water in a desicator over conc sulfuric acid.	One $H_2O$ lost over conc sulfuric acid.	Two $H_2O$ lost over conc sulfuric acid.

Other examples are  $[Co Cl(H_2O) en_2]Cl_2$  and  $[Co Cl_2 en_2]Cl H_2O$ ,  $[CrCl_2(H_2O)_2Py_2]Cl$  and  $[CrCl_3(H_2O)_2Py_2]H_2O$ 

### 4. Coordination isomerism:

This can occur only with salts in which both cation and anion parts are complexes and the ligands have a different distribution between the two central metal atoms (i.e. exchange of ligands between two coordination spheres).

e.g.  $[Cr(NH_3)_6]^{+3}[Cr(SCN)_6]^{-3} \& [Cr(NH_3)_4(SCN)_2]^+[Cr(NH_3)_2(SCN)_4]^-$  (same central atom)

$$[Co(NH_3)_6]^{+3}[Cr(CN)_6]^{-3} \& [Cr(NH_3)_6]^{+3}[Co(CN)_6]^{-3}$$
 (different central atom)

### 5. Linkage isomerism:

This arises when the ligand can coordinate either of two different donor atoms (ambidentate ligands), e.g.  $NO_2^-$  ion may attach with the central ion either through O atm or through N atom. i.e.  $[Co(NH_3)_5-ONO]^{+2}$  and  $[Co(NH_3)_5-NO_2]^{+2}$ . Other ligands are SCN<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>-2</sup> etc.

### 6. Coordination position isomerism:

In some of the polynuclear complexes, interchange of the non-bridging ligands between the two metal nuclei takes place, which is given to rice to coordinate position isomerism. e.g.



### 7. Ligand isomerism:

Some of the ligands themselves are capable of existing as isomers, e.g. diaminopropane can exist isomers as 1, 2-diaminopropane (pn) and 1, 3-diaminopropane (tn).



When these ligands are associated with metal to form complexes, the complexes are isomers of each other.

### e.g. $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$ ions



### 8. Polymerisation isomerism:

This type of isomerism is found in polymers of some simple complex compound. They have the same ratio of different metal atoms and ligands in them. Following complex compounds are polymerisation isomers to each other, since (ii) and (iii) complexes appear to be dimer of (i) complex and (iv) complex appears to be the pentamer of (i) complex. The ratio of  $Co^{3+}$ : NH<sub>3</sub> : NO<sub>2</sub><sup>-</sup> in all the complexes is 1: 3 : 3.

Complex compound	No. of Co <sup>3+</sup>	No. of NH <sub>3</sub>	No. of NO <sub>2</sub>
(i) $[Co(NH_3)_3(NO_2)_3]$	1	3	3
(ii) $[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6
(iii) $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6
(iv) $[Co(NH_3)_5(NO_2)_3][Co(NO_2)_6]$	5	15	15

### **STEREOISOMERISM** or **SPACE ISOMERISM**:

When two compounds have same ligands but its arrangement in space is different is known as space isomerism. There are two forms of stereoisomerism.

- 1. Geometrical Isomerism
- 2. Optical Isomerism

### **GEOMETRICAL ISOMERISM or CIS-TRANS ISOMERISM:**

### **<u>4-Coordinate complexes</u>:**

The arrangement of four ligands around the central metal atom may be tetrahedral or square planar.

#### **Tetrahedral complexes:**

A regular tetrahedral species  $[Ma_4]$ ,  $[Ma_2b_2]$  or [Mabcd] can exist in only one geometrical form (no geometrical isomers) since arrangement of every ligand atom or group around the central atom in space is equivalent.

#### **Square planar complexes:**

The long established facts that there are two distinct forms of  $[Pt(NH_3)_2Cl_2]$  led Werner to propose a planar structure for 4-coordinate Pt(II) complexes. A planar species  $[Ma_2b_2]$  can exist in 1,2 or cis and 1,3 or trans form. Tsherniaev isolated the three forms predicted for the planar species [Mabcd] of the complex  $[Pt(NH_3)(NH_2OH)Py(NO_2)]Cl$ providing elegant support to the Werner's postulation. The planar structure of 4-coordinate complexes has since then been confirmed by physical methods of structure determination like dipole moment measurement, vibrational spectroscopy and X-ray diffraction. Planar complexes are formed by the central metal ions like Co(II), Ni(II), Cu(II), Au(III), Pd(II) having d<sup>7</sup>, d<sup>8</sup> or d<sup>9</sup> configuration.

No stereoisomers are possible for planar species of the type [Ma<sub>4</sub>], [Ma<sub>3</sub>b] or [Mab<sub>3</sub>] because all possible arrangements of a and b for each of these types are exactly equivalent.

Following types of complexes show geometrical isomers.

#### (i) <u>Complexes containing only monodentate ligand</u>:

Following types of complexes exist.

### (a) $[Ma_2b_2]^{\pm n}$ type:

Here M is the central ion and a and b are monodentate ligands. Complexes of this type exist following cis-trans isomers.

 $[Pt(NH_3)_2Cl_2], Pd(NH_3)_2(NO_3)_2]$ 



In all complexes (i.e. cis-trans isomer) all four bonds are coplanar with the central atom.

Similarly  $[Pd(NH_3)_2(NO_3)_2]$  also show cis-trans isomer.

### (b) $[Ma_2bc]^{\pm n}$ type:

In this type a is any neutral ligand such as  $NH_3$ , py,  $H_2O$  and b and c are anionic ligands like  $Cl^-$ ,  $Br^-$ ,  $NO_2^-$  etc.

e.g.  $[Pt(NH_3)_2CINO_2]$ ,



### (c) [Mabcd] <sup>±n</sup> type:

Pt(II) forms a number of complexes of this type. Complexes of this type exist in three isomeric forms as shown below.



examples are  $[Pt(NH_3)ClBrNO_2]$ ,  $[Pt(NH_3)_2pyClBr]$ ,  $[Pt(NO_2)py(NH_3)(NH_2OH)]^+$ ,  $[Pt(C_2H_4)(NH_3)ClBr]$ 

#### (ii) Square planar complexes containing unsymmetrical bidentate chelating ligands:

Complexes containing unsymmetrical bidentate chelating ligands can also exist cis and trans isomers of type  $[M(AB)_2]^{\pm n}$ , where AB is unsymmetrical bidentate chelating ligands containing A and B are two end of the ligand.

e.g.  $[Pt(gly)_2]$  where gly is NH<sub>2</sub>-CH<sub>2</sub>COO<sup>-</sup> (glycine ion), exist following cis-trans isomers



(iii) Square planar complexes containing symmetrical bidentate chelating ligands:

Complexes containing unsymmetrical bidentate chelating ligands can also exist cis and trans isomers of type  $[M(AA)_2]^{\pm n}$ , where AA is symmetrical bidentate chelating ligands.

### e.g. $[Pt(NH_2CH(CH_3)CH(CH_3)NH_2)_2]^{+2}$



(iv) Bridged binuclear planar complexes of M<sub>2</sub>a<sub>2</sub>b<sub>4</sub> type:

In this type of complexes cis and trans isomers as well as the unsymmetrical form also exist as shown below.

e.g.  $[Pt(PEt_3)Cl_2]_2$ 



### **<u>6-Coordinate complexes</u>:**

6-Coordination is the most common and hence the most extensively studied coordination in coordination chemistry. Three possible arrangements of six ligands around the central metal atom, namely

- (1) Planar hexagonal
- (2) trigonal prismatic
- (3) octahedral

The physical and chemical evidence, especially those based on isomerism have shown that the arrangement of six ligands in a 6-coordinate complex is always octahedral with all six positions equivalent.

#### **Octahedral complexes:**

The arrangement of six ligand in a regular octahedral complex round the central metal ion can be represented as shown below:



#### **Octahedral Complexes containing monodentate ligands:**

In this complexes,  $[Ma_6]^{\pm n}$ ,  $[Ma_5b]^{\pm n}$  and  $[Mab_5]^{\pm n}$  types are not show geometrical isomerism. Following types are show isomerism.

#### (i) $[Ma_4b_2]^{\pm n}$ type:

In this type of complexes two 'b' ligands have adjacent position for cis isomers, while in trans form two 'b' ligands are diagonally opposite to each other as shown below.



It means in cis form 'b' ligands lie on any of the twelve edges of the octahedron and in trans form 'b' ligands are at end of the straight line passes through the central atom.

e.g.  $[Co(NH_3)_4Cl_2]^+$  is well known example for this type. In cis isomers, two Cl<sup>-</sup> ions are at the adjacent position (i.e. 1,2-position) while ln trans isomers two Cl<sup>-</sup> ions are opposite to each other (i.e. 1,6-position) as shown below.



cis-form or (1,2)-isomer

trans-form or (1,6)-isomer

#### (ii) $[Ma_3b_3]^{\pm n}$ type:

Two isomers are exist (i.e. cis, trans) as shown below



cis-form or (1,2,3)-isomer

trans-form or (1,2,6)-isomer

In cis isomers, three 'a' occupy 1, 2 and 3 positions and in trans isomers 1, 2 and 6 positions.



cis-form or (1,2,3)-isomer trans-form or (1,2,6)-isomer

In cis isomer, three  $Cl^{-}$  ions are on the triangular face of the octahedron and three  $NH_3$  molecules are on the opposite triangular face of the octahedron hence is called facial isomer.

In trans isomer, three  $Cl^{-}$  ions are around the edge of the octahedron and three  $NH_3$  molecules are at the opposite edge of the octahedron, hence is called peripheral isomer.

#### (iii) [Mabcdef]<sup>±n</sup>type:

In this type of complexes there are 15 different geometrical isomers in which all have optical isomers. Only one compound known is  $[Pt(py)(NH_3)(NO_2)ClBrI]$ . In this compound only three forms are obtained but no attempt has been made to isolate all the 15 isomers.



#### **Octahedral Complexes containing monodentate and symmetrical bidentate ligands:**

#### (i) $[M(AA)_2a_2]^{\pm n}$ type:

Here (AA) is a symmetrical bidentate chelating ligand having ends A. Cis and trans forms are show below.



In cis isomer, 'a' are cis to each other and in trans isomers 'a' are trans to each other. e.g.  $[Co(en)_2(NO_2)_2]^+$ ,  $[Ir(C_2O_4)_2Cl_2]^2^-$ ,  $[Rh(C_2O_4)_2Cl_2]^2^-$ ,  $[Cr(C_2O_4)_2(H_2O_2)_2]^-$  etc.



In cis isomer two Cl<sup>-</sup> ions are cis to each other and trans isomers two Cl<sup>-</sup> ions are trans to each other.

#### (ii) $[M(AA)_2ab]^{\pm n}$ type:

Following geometrical isomers are exist



e.g.  $[Co(en)_2(NH_3)Cl]^{2+}$ ,  $[Ru(py)(C_2O_4)_2(NO)]^-$  etc.



### (iii) $[M(AA)a_2b_2]^{\pm n}$ type:

Following Cis-trans (geometrical) isomers are exist.



<u>Octahedral Complexes containing unsymmetrical bidentate chelating ligands:</u> i.e.  $[M(AB)_3]^{\pm n}$  type:

In this type AB is an unsymmetrical bidentate chelating ligand which is having A and B two ends shown below.





### VARIOUS METHODS TO DISTINGUISH BETWEEN CIS AND TRANS ISOMERS:

#### (1) **Dipole moment:**

Jensen has shown that the Pt(II) complexes of  $[PtA_2X_2]$  type(where A = substituted phosphine, arsine and X = halogen) have their dipole moment equal to zero or between 8 & 12 debye units. If the dipole moment is equal to zero then individual moments have cancelled one another, so these are trans isomers. If  $\mu \neq 0$  (i.e. 8-12) are cis isomer.

#### (2) X -ray crystal analysis:

X-ray crystal analysis and dipole moment measurements of several Pt(II) complexes have confirmed the square planarity of the bond around the central metal. This arrangement has also been established for 4- coordinated complexes of Pt(II), Ag(II), Cu(II) and Au(II).

#### (3) IR technique:

The trans complexes such as  $[Co(NH_3)_4Cl_2]^+$  or  $[Co(NH_3)_2Cl_2]^+$ , the Cl-M-Cl symmetrical stretching vibration produce no change in the dipole moment of the molecule. Hence no band corresponding to this vibration is observed in IR spectra.



However, in the cis form, the symmetrical as well as unsymmetrical stretching vibration produce change in the dipole moment, hence in cis isomer will show large number of bands due to Cl-M-Cl stretching.

#### (4) **Grinberg's method:**

It is chemical method in which a chelating ligand having two donor atoms react with cis and trans isomers. In cis isomer, two donor atoms of chelating ligand coordinate to the central atom at two cis positions and form five or six membered ring, while in trans form, chelating ligand coordinate to the central atom by any one of the donor atoms and acts as a monodentate ligand i.e. not form a ring complexes with trans form.

The chelating ligands used are oxalic acid  $(COOH)_2$ , glycine  $(H_2N-CH_2-COOH)$  and ethylenediamine  $(H_2N-CH_2-CH_2-NH_2)$ .

Oxalic acid and glycine ligands example are given below with [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]



#### (5) Kurnakov's method:

Kurnakov utilised the phenomena of trans effect in distinguishing the cis and trans isomers of squar planar complexes of  $[PtA_2X_2]$  type by treating them with thiourea. i.e. (tu) e.g.  $[Pt(NH_3)_2Cl_2]$ 



In cis isomer both Cl<sup>-</sup> ion are trans to NH<sub>3</sub> ligands, so because of trans effect Cl<sup>-</sup> ions are replaced by tu (Thiourea) and from  $[Pt(NH_3)_2(tu)_2]^{+2}$  (i.e. I)

Now in [I] bothNH<sub>3</sub> are trans to tu, hence tu is replaced by tu and from  $[Pt(tu)_4]^{+2}$ .

In the case of trans isomers, the trans effect is smaller, so we get  $[Pt(NH_3)_2tu_2]^{+2}$ .

### **OPTICAL ISOMERISM OR MIRROR IMAGE ISMERISM:**

When the solutions of complexes are placed in the path of plane polarized light, then light rotates its plane through a certain angle either to the left side or right side. This property of the complex of rotating planes of polarized light is called its optical activity and the complexes possessing this property are said to be optically active.

Optically active complexes are said to exist in the following forms:

- a) Which rotates plane of polarized light towards right side (clockwise direction) is said to be dextro-rotetory or *d*-form. It is also represented by (+) sign.
- b) Which rotates plane of polarized light towards the left side (anticlockwise direction) is said to be laevo-rotatory or *l*-form. It is also represented by (-) sign.

(+) and (-) refer to the sign of rotation of an optical isomer.

The d- and l-form have following characteristics

- (i) Since *d* and *l* forms are capable of rotating the plane of polarized light, they are said to be optically active or optical isomers. This phenomenon is called optical isomerism or optical activity. Both isomers have exactly identical physical and chemical properties.
- (ii) If *d* and *l* forms are mirror images to each other and not superimposed on each other, they are called enantiomerism.

c) Which is not capable of rotating the plane polarized light is called optically inactive. This isomer is called racemic- $[dl, or (\pm)]$  from which is made up of 50% d & 50% l-form. In racemic form, one form rotates the plane of polarized light in one direction and is balanced by another form in the opposite direction.

#### **Condition for a molecule to show optical isomerism:**

1. The molecule should be asymmetric which never has a plane of symmetry.

It means the molecule is divided by an imaginary plane in such a way that part of one side of the plane is the mirror image of the other side of the plane. Which is called a plane of symmetry and it is always inactive while molecules which have no plane of symmetry are optically active and hence show optical isomerism.

2. An asymmetric molecule cannot be superimposed on its mirror image.

### **Optical isomerism in 4-coordinate complexes:**

Mirror image isomerism is not possible tetrahedral and square planar complexes of type  $[Ma_4]$ ,  $[Ma_3b]$  and  $[Mab_3]$ .

#### **Square planar complexes**

Square planar complexes seldom show optical isomerism:

Optical isomerism is rarely observed in planar complexes because all four ligands and central atoms are lying in the same plane. Hence, complexes have a **plane of symmetry**. It cannot show optical isomerism even though all ligands are different. In 1935 Mills and Quibell succeeded in resolving isobutylenediaminemesostilbenediamineplatinum(II)chloride (i.e.  $[Pt(NH_2CH(C_6H_5)CH(C_6H_5)(NH_2)(NH_2CH_2C(CH_3)_2NH_2)]Cl_2$  complex into highly stable enantiomorphs. This complex shows optical isomerism. This in fact, provided a very elegant proof of the planar arrangement of four Pt(II) valences. If the structure were tetrahedral, it would have a plane of symmetry and hence it will not be optically active.





This structure has no plane of symmetry and hence is unsymmetrical and optically active and gives optical isomer.

### **Tetrahedral complexes:**

(i) Asymmetric tetrahedral molecule(i.e. it should have no plane of symmetry) where all the ligands are different (i.e. [Mabcd] type) show optical isomerism.



e.g. mirror image isomers of As<sup>+3</sup> ion complex,  $[As(CH_3)(C_2H_5)S(C_6H_4COO)]^{+2}$  are shown below



(ii) Optical isomers are known for the complexes of Be(II), Zn(II) and B(III) with unsymmetrical bidentate ligands have been made and show optical isomerism e.g. bis(benzoleacetonato)beryllem(II), [Be(C<sub>6</sub>H<sub>5</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>]



the above complex no centre or plane of symmetry are not superimposed on each other. So it will give d- and l- form.

### **Optical isomerism in 6-Coordinate complexes:**

The octahedral configuration of the 6 coordinate complex requires the existence not only of the geometrical isomerism of the kind discussed earlier but also of mirror image isomerism leading to optical activity.

Optical activity is very common in the following types of octahedral complexes:

### Octahedral complexes containing only monodentate ligands: (i) $[Ma_2b_2c_2]^{\pm n}$ type:

It has two optical isomers as shown below.



### e.g. $[Co(NH_3)_2Cl_2(NO_2)_2]^{-1}$

### (ii) [Mabcdef] $]^{\pm n}$ type:

Only Pt(IV) complexes are existing. There are 15 geometrical isomers, each of which could exist in d- and l- form (i.e. each of which a non superimposable mirror image arises) to give a total of 30 isomers.

For one form of  $[Pt(py)(NH_3)(NO2)(Cl)(Br)(I)]$ , the optical isomers are shown below.



Octahedral complexes containing only symmetrical bidentate chelating ligands:

### (i) $[M(AA)_3]^{\pm n}$ type:



Here AA is a symmetrical bidentate chelating ligand which may be neutral molecule or negative ions.

e.g.  $[Co(en)_3]^{+3}$ ,  $[Co(pn)_3]^{+3}$ ,  $[Pt(en)_3]^{+3}$ ,  $[Cr(C_2O_4)_3]^{+3}$ ,  $[Cd(pn)_3]^{+2}$ ,  $[Fe(C_2O_4)_3]^{-3}$ 

 $[Co(en)_3]^{+3}$  give two isomers as shown below.



# Octahedral complexes containing monodentate and symmetrical bidentate chelating ligands:

#### (i) $[M(AA)_2a_2]^{\pm n}$ type:

Here AA is the symmetrical bidentate chelating and a is the monodentate ligand. e.g.  $[Co(en)_2Cl_2]^+$ : This complex has two geometrical isomers (i.e. cis-trans isomers). In cis isomer there is no plane of symmetry, hence it show optical active isomer as shown below.



In trans isomers there is a plane of symmetry, hence it is optically inactive and shows meso form as shown below.



#### (ii) $[M(AA)_2ab]^{\pm n}$ type:

These complexes also exist in three forms in which two form are optically active and third form is inactive as shown below.



#### (iii) $[M(AA)a_2b_2]^{\pm n}$ type:

These complexes also exist in three forms in which two forms are optically active and the third form is inactive as shown in below figure.



#### Octahedral complexes containing optically active ligand:

 $[Co(en)(pn)(NO_2)_2]^+$  is an example of such type of octahedral complexes. the cis form will give two optical isomers as shown below.



### **Octahedral complexes containing polydentate ligand:**

The complexes having polydentate ligands like EDTA<sup>-4</sup> i.e.  $[Co(EDTA)]^-$  exists in two optical isomers (*d*-form and *l*-form) as shown below.

