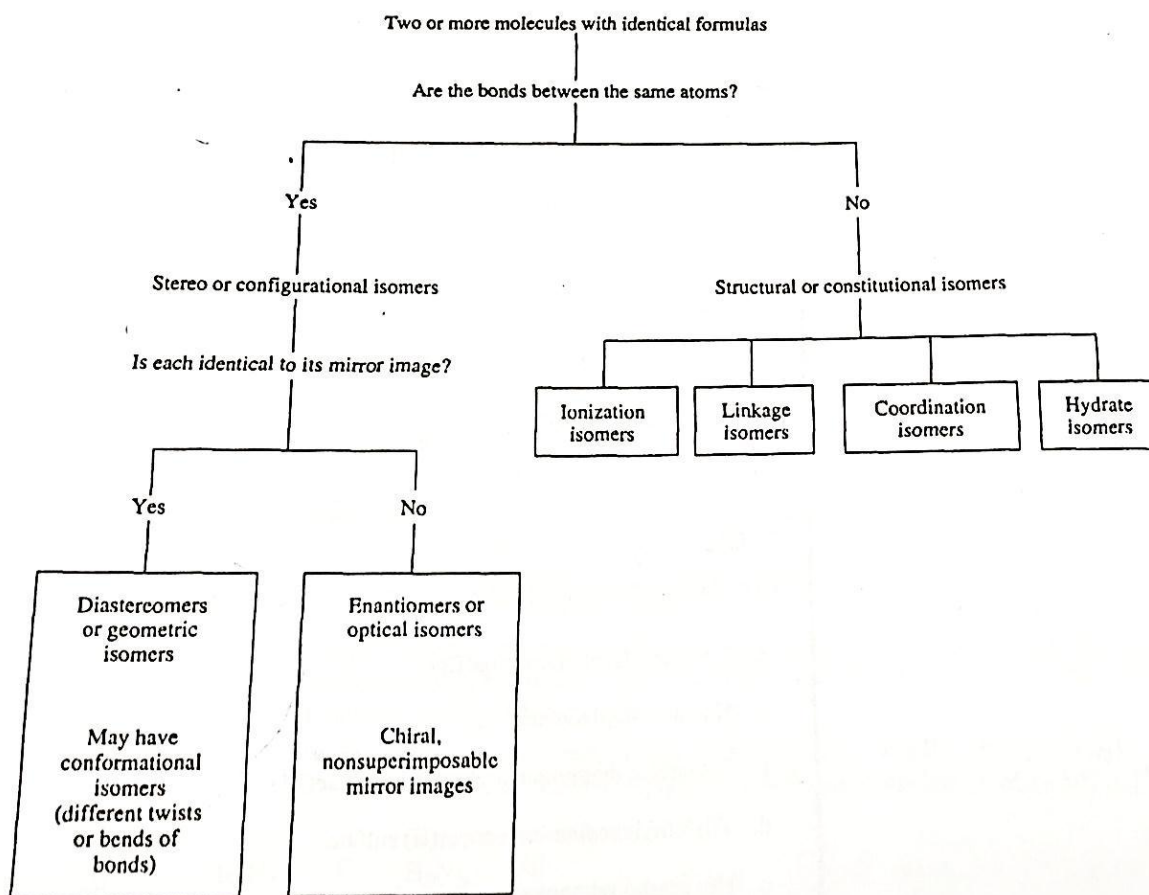


## Isomerism in Coordination Compounds

The coordination compounds which 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.

The number of possible isomers increases with coordination numbers, we limit our discussion to the more common coordination numbers 4 and 6.



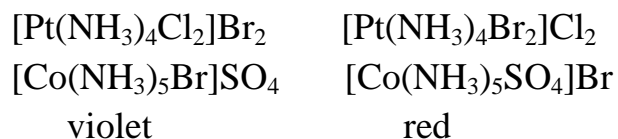
Isomerism include two types; structural isomerism and stereo isomerism

### Structural Isomerism

This isomerism arises due to difference in the structures of complex (coordination compounds). This isomerism include the following:

## 1- Ionization isomerism

Compounds with the same formula, but which give different ions in solution, exhibit ionization isomerization. The difference is in which ion is included as a ligand and which is present to balance the overall charge (the ligands given in coordination sphere and the anions present outside the coordination sphere are exchanged with each other).



## 2-Linkage (ambidentate) isomerism

Some ligands can bond to the metal through different atoms. When an ambidentate ligand having two different donor atoms coordinates to the metal atom through either of its two donor atoms, two different complex compounds are obtained. These compounds are different because they have different structure.

The most common early examples were thiocyanate,  $\text{SCN}^-$ , and nitrite,  $\text{NO}_2^-$ . Class (a) metal ions (hard acids) tend to bond to the nitrogen of thiocyanate and class (b) metal ions (soft acids) bond through the sulfur, but the differences are small and the solvent used influences the bonding.

M-SCN thiocyanato isomer

M-NCS isothiocyanato isomer

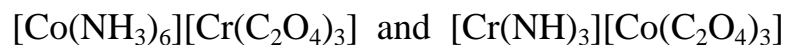
M- $\text{NO}_2$  nitro isomer

M-ONO nitrito isomer



### 3- Coordination isomerism

Examples of a complete series of coordination isomers require at least two metal ions. The total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change, (coordination isomers are obtained when some or all ligands of both the coordination spheres are interchanged with each other)



### 4- Hydrate isomerism

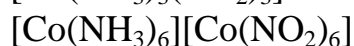
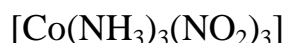
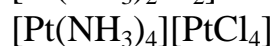
This type of isomerism is similar to ionization isomerism. Hydrate isomers are obtained when  $\text{H}_2\text{O}$  molecules acting as ligands are replaced by the anions present outside the coordination sphere.

The standard example is  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  which can have three distinctly different crystalline compounds, now known as  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet),  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (blue-green) and  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green).

The action of  $\text{AgNO}_3$  solution on these isomers indicates that they have three, two and one  $\text{Cl}^-$  ions respectively outside the coordination sphere.

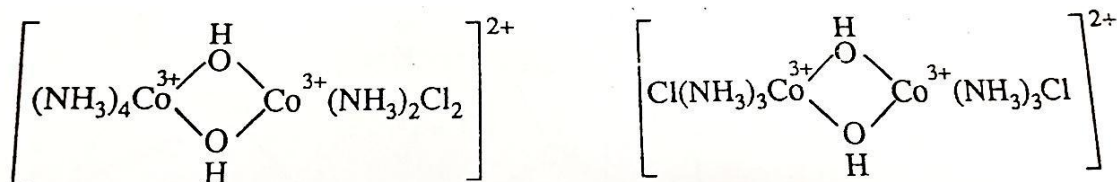
### 5- Polymerization isomerism

This type of isomerism is found in those complex compound whose formulae appear to be polymers of some simple complex compound. All these complex compounds have the same ratio of different metal atoms and ligands in them.



### 6- 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.



## 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:

### 1- Geometrical isomerism

These complex compounds have the same ligands in the coordination sphere but the relative position of the ligands round the central metal atom is different

#### Geometrical isomerism in 4-coordinated complex compounds

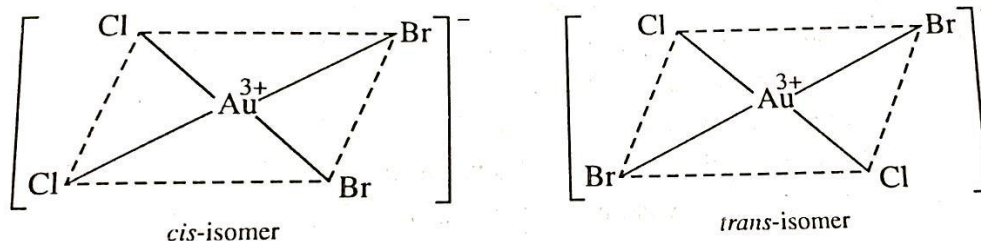
Complexes having central atom with 4-coordination number may have either tetrahedral or square planar geometry. Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in this geometry have adjacent position (cis position) to one another and all the four bond angles are the same ( $109.5^\circ$ ).

#### Geometrical isomerism in square planar complexes

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

Cis and trans isomers of square-planar complexes are common, with platinum(II) being one of the most common metal ions studied.

Examples:  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and  $[\text{AuCl}_2\text{Br}_2]$ .



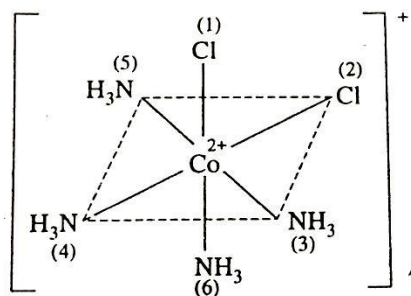
## Geometrical isomerism in 6-coordinated complexes

### Octahedral complexes

We know that a complex compound having central atom with coordination number equal to 6 is octahedral in shape.

[MA<sub>4</sub>B<sub>2</sub>] type complexes where A and B are monodentate ligands may have two isomeric forms called cis and trans. Important examples of octahedral complexes of this type are [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> and [Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>.

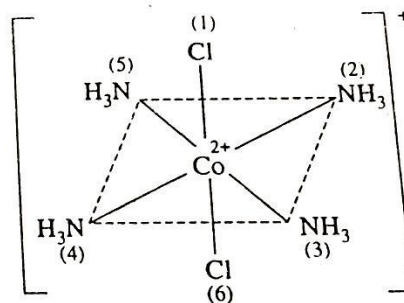
In cis-isomer two Cl<sup>-</sup> ions occupy the adjacent positions of the octahedron while in trans-isomers these ions have the opposite position.



(a) cis-isomer

(a) cis-isomer (1,2-dichlorotetrammine cobalt (III) ion). (yellow-brown)

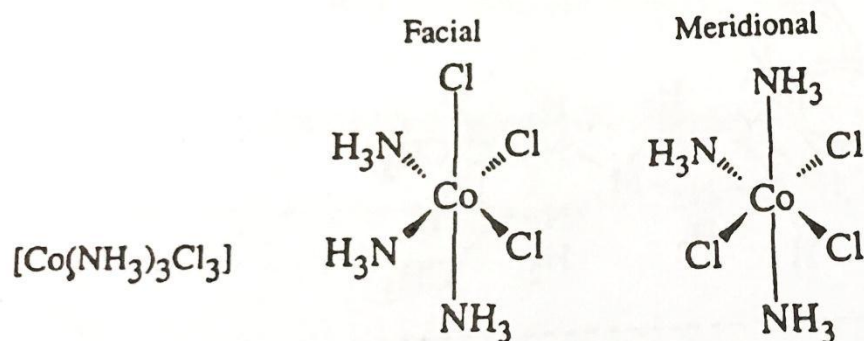
OR



(b) trans-isomer

(b) trans-isomer (1, 6-dichlorotetrammine cobalt (III) ion). (yellow)

[MA<sub>3</sub>B<sub>3</sub>] type complexes may have two isomeric forms called fac- and mer-(facial and meridional). Fac isomers have three identical ligands on one triangular face; mer isomers have three identical ligands in a plane bisecting the molecule. Similar isomers are possible with some chelating ligands.



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

When the solution of certain complex compounds are placed in the path of a plane-polarized light, 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 polarized 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 following forms:

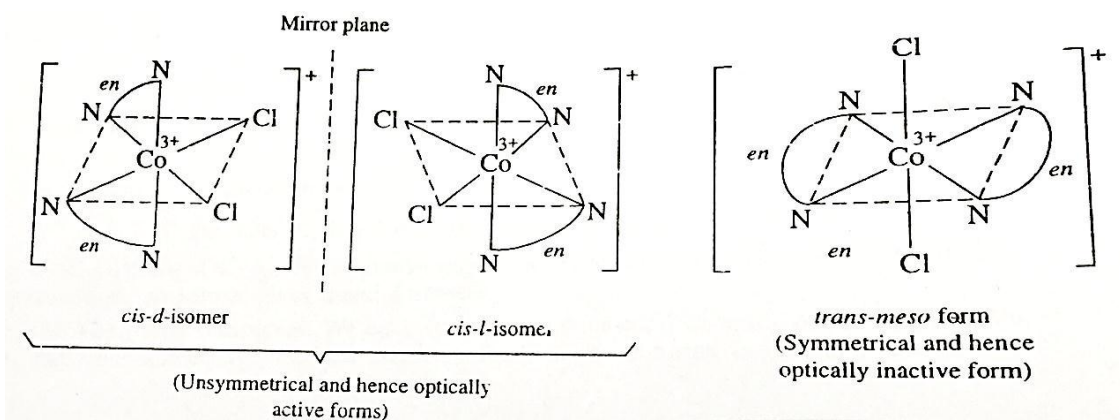
- 1- One which rotates the plane of polarized light towards right (in clockwise direction) is said to be dextro-rotatory or d-form. d-form is also represented by placing (+) sign before its name or formula.
- 2- One which rotates the plane of polarized light towards left (anti-clockwise direction) is called levo-rotatory or l-form. l-form is also represented by putting (-) sign before its name or formula.

\*The d- and l- forms have exactly identical physical and chemical properties, although they differ in their action on polarized light.

\*\* The d- and l- forms are mirror images to each other just as left hand is the mirror image of the right hand.

- 3- The isomer which is not capable of rotating the plane of polarized light is called optically inactive. Such an isomer is called meso, racemic, dl- or ( $\pm$ ) form.

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



## Effective Atomic Number (EAN)

In main group chemistry, we have encountered the octet rule in which the electronic structures of many main group compounds can be rationalized on the basis of a valance shell requirement of 8 electrons. Similarly, in organometallic chemistry, the electronic structure of many compounds are based on a total valance electron count of 18 on the central metal atom. As in the case of octet rule, there are many exceptions to the 18-electron rule.

On the bases of his concept of coordinate bond, Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through L- M bonding, the total number of electrons on the central atom, including those gained from ligands in the bonding, is called the effective atomic number (EAN) of the central metal ion.

\*The ligands are usually found to donate two electrons, for example  $\text{Cl}^-$ ,  $\text{H}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and etc

Ligand	Electrons donated by ligands
H	2 ( $\text{H}^-$ )
Cl, Br, I	2 ( $\text{X}^-$ )
OH, OR	2 ( $\text{OH}^-$ , $\text{OR}^-$ )
CN	2 ( $\text{CN}^-$ )
$\text{CH}_3$ , $\text{CR}_3$	2 ( $\text{CH}_3^-$ , $\text{CR}_3^-$ )
NO (bent $\text{M}-\text{N}-\text{O}$ )	2 ( $\text{NO}^-$ )
NO (linear $\text{M}-\text{N}-\text{O}$ )	2 ( $\text{NO}^+$ )
CO, $\text{PR}_3$	2
$\text{NH}_3$ , $\text{H}_2\text{O}$	2
$=\text{CRR}'$ (carbene)	2
$\text{H}_2\text{C}=\text{CH}_2$ (ethylene)	2
CNR	2
$=\text{O}$ , $=\text{S}$	4 ( $\text{O}^{2-}$ , $\text{S}^{2-}$ )
$\eta^3\text{-C}_3\text{H}_5$ ( $\pi$ -allyl)	2 ( $\text{C}_3\text{H}_5^+$ )
$\equiv\text{CR}$ (carbyne)	3
$\equiv\text{N}$	6 ( $\text{N}^{3-}$ )
Ethylenediamine (en)	4 (2 per nitrogen)
Bipyridine (bipy)	4 (2 per nitrogen)
Butadiene	4
$\eta^5\text{-C}_5\text{H}_5$ (cyclopentadienyl)	6 ( $\text{C}_5\text{H}_5^-$ )
$\eta^6\text{-C}_6\text{H}_6$ (benzene)	6
$\eta^7\text{-C}_7\text{H}_7$ (cycloheptatrienyl)	6 ( $\text{C}_7\text{H}_7^+$ )

The EAN rule is helpful for organometallic compounds and carbonyl complexes, which obey in most cases this rule.

**[Cr(CO)<sub>6</sub>]** A Cr atom has 6 electrons outside its noble gas core. Each CO is considered to act as a donor of two electrons. The total electron count is therefore:

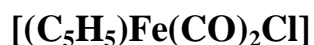
$$\begin{array}{rcl} \text{Cr} & & 6 \text{ electrons} \\ 6(\text{CO}) & 6 \times 2 \text{ electrons} = & 12 \text{ electrons} \\ & & \text{Total} = 18 \text{ electrons} \end{array}$$

[Cr(CO)<sub>6</sub>] is therefore considered an 18-electron complex. It is thermally stable; for example, it can be sublimed without decomposition. [Cr(CO)<sub>5</sub>], a 16-electron species, and [Cr(CO)<sub>7</sub>], a 20-electron species, on the other hand, are much less stable and are known only as transient species. Likewise, the 17-electron [Cr(CO)<sub>6</sub>]<sup>+</sup> and 19-electron [Cr(CO)<sub>6</sub>]<sup>-</sup> are far less stable than the neutral, 18-electron [Cr(CO)<sub>6</sub>].

Similarly the formation of olefin complexes and metallocenes may be explained the EAN rule.

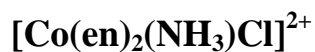
Olefins donate 2 electrons / double bond

ethelene	2 electrons
butadien	4 electrons
benzene	6 electrons
cyclopentadienyl	6 electron



$$\begin{array}{rcl} \text{Fe(II)} & & 6 \text{ electrons} \\ \text{C}_5\text{H}_5 & & 6 \text{ electrons} \\ 2(\text{CO}) & & 4 \text{ electrons} \\ \text{Cl}^- & & 2 \text{ electrons} \\ & & \text{Total} = 18 \text{ electrons} \end{array}$$





$\text{Co}^{3+}$	6 electrons
$2\text{en}$	$2 \times 4 = 8$ electrons
$\text{NH}_3$	2 electrons
$\text{Cl}^-$	2 electrons
Total = 18 electrons	

In addition, metal-metal bonds must be counted. A metal-metal single bond counts as one electron per metal, for example in the dimeric complex  $(\text{CO})_5\text{Mn-Mn}(\text{CO})_5$  the electron count per manganese atom is

Mn	7 electrons
$5(\text{CO})$	10 electrons
Mn-Mn bond	1 electrons
Total = 18 electrons	

### Application of EAN rule

With the help of EAN rule, the magnetic property of the complex ions can be predicted. It has been observed that the complex ions whose central metal atom obeys EAN rule are diamagnetic. For example, since the ion  $\text{Co}^{3+}$  in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  obeys EAN rule and hence this ion is diamagnetic. Experimentally this ion has also been found diamagnetic.

Sidgwick and Bose have suggested that the complex ions whose central metal atom does not obey EAN rule are generally paramagnetic.