



## Revision Notes

### Class 12 Chemistry

#### Chapter 9 - Coordination Compounds Notes in 30 Minutes

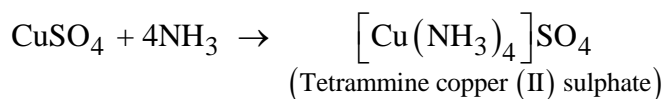
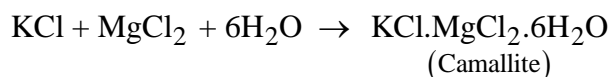
##### 1. Introduction

Coordination compounds are extremely important. It is important to recognize that life would not have been possible without the presence of chlorophyll (Mg - complex) in plants and haemoglobin (Fe- complex) in human blood. The study of these compounds will broaden our understanding of chemical bonding and the physical properties of coordination compounds such as magnetic properties.

##### 2. MOLECULAR OR ADDITION COMPOUNDS

When a solution containing two or more simple stable compounds in molecular proportions is allowed to evaporate, it produces crystals of new substances known as molecular or addition compounds.

Example:



##### 2.1 Types of Molecular compounds

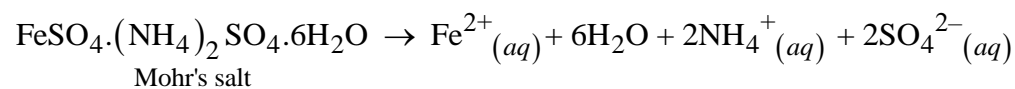
###### 2.1.1 Double Salt

A double salt is a substance formed by combining two different salts that crystallize as a single substance but ionize as two distinct salts when dissolved in



water. These salts lose their identity in solution, which means that when dissolved in water, they test positive for all of the ions present in the salt. eg. Mohr's salt, potash alum.

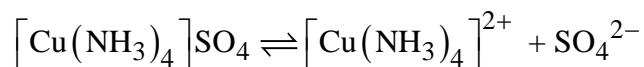
Example:



## 2.2 Coordination Compounds

A coordination compound is a molecular compound formed by the combination of two or more simple molecular compounds that retains its identity both solid and dissolved.

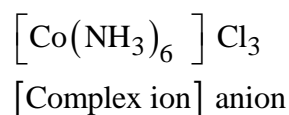
Example:



## 3. COORDINATION COMPOUNDS

A ligand, a central atom, a complex ion, a cation, or an anion make up a coordination compound. In general, the complex ion is written in a square box, and the ion (cation or anion) is written outside the complex ion.

eg:



General formula:  $A_x[\text{ML}_n]/[\text{ML}_n]B_y$  where M is the central metal atom/ion, L is the ligand, A is the cation and B is the anion.



## Some Important Terms pertaining to Coordination Compounds

### 3.1 Coordination entity

It is the fixed central metal atom or ion that is bonded to a specific number of ions or molecules. Six ammonia molecules, for example, are surrounded by three chloride ions in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , a coordination entity.

### 3.2 Central atom/ion

In a specific geometrical arrangement, it is the central cation that is surrounded and coordinately bonded to one or more neutral molecules or negatively charged ions. In the complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , for example,  $\text{Co}^{3+}$  is the central metal ion that is positively charged and is coordinately bonded to six neutral  $\text{NH}_3$  molecules within the coordination sphere. The central metal/ion is also known as Lewis acid.

### 3.3 Ligands

Ligands are ions or molecules that are bound to the coordination entity's central atom/ion. These can be simple ions like  $\text{Cl}^-$ , small molecules like  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , or larger molecules like  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ .

### 3.4 Co-ordination Number (C.N)

The number of atoms in the ligands that are directly bound to the central metal atom or ion by co-ordinate bonds is known as the metal atom's or ion's co-ordination number. It is also the same as secondary valency.

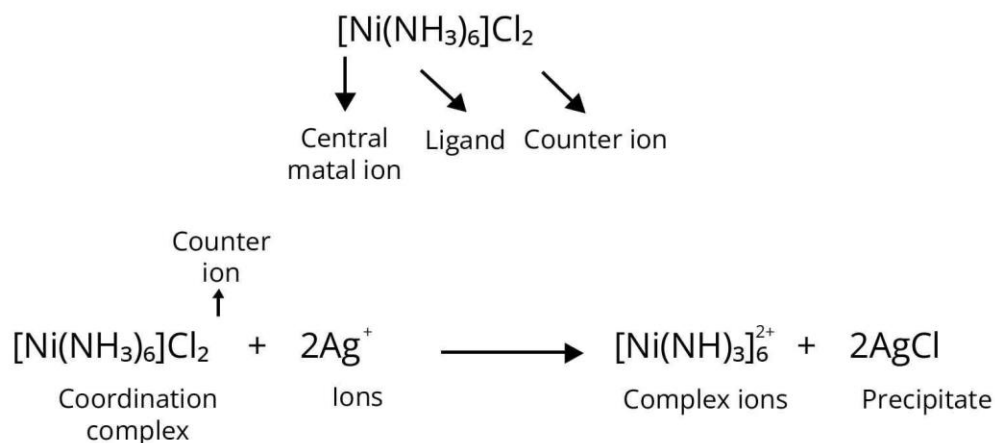
Complex	Coordination number
$\text{K}_4[\text{Fe}(\text{CN})_6]$	6



$[\text{Ag}(\text{CN})_2]^-$	2
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	4
$[\text{Ca}(\text{EDTA})]^{2-}$	6

### 3.5 Coordination sphere

A square bracket surrounds the central metal atom or ion and the ligands that are directly attached to it. This was known as the coordination sphere or the first sphere of attraction. Because the metal ion tightly holds the ligands in the coordination sphere, it behaves as a single unit.



### 3.6 Coordination Polyhedron

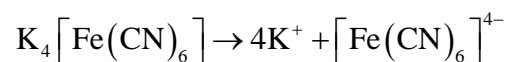


The spatial arrangement of the ligand atoms that are directly attached to the central atom/ion is referred to as a coordination polyhedron.  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , for example, is octahedral,  $[\text{Ni}(\text{CO})_4]$  is tetrahedral, and  $[\text{PtCl}_4]_2$  is square planar.

### 3.7 Oxidation Number of Central Metal Atom

It is defined as the charge that the central metal ion would have if all ligands and electron pairs were removed. It is computed as follows:

Example:



Charge on the complex ion is -4.

Let charge on Fe be x.

Now, the charge on cyanide ions is -1.

$$\Rightarrow x + 6 \times (-1) = -4$$

$$\Rightarrow x = +2$$

Hence, the oxidation number of Fe is +2 (II).

### 3.8 Homoleptic and Heteroleptic Complexes

Homoleptic complexes are those in which the central atom is coordinated with only one type of ligand, such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Heteroleptic complexes are those in which the central atom is coordinated with more than one type of ligand, such as  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ .



## 4. NOMENCLATURE OF COORDINATION COMPOUNDS

### 4.1 Nomenclature

The following rules are followed when naming a complex ion:

- Cations are named first, followed by anions.
- The central metal ion's oxidation state (O.S.) is denoted by a Roman numeral.
- The ligand names are listed first, followed by the name of the central metal ion.
- Anion ligand names that end in 'ide' are changed to 'o', 'ite' are changed to 'ito' and 'ate' are changed to 'ato'
- The unmodified name is used for many ligands that are molecules.
- Positive groups are terminated by *-ium*. For example:  $\text{NH}_2 - \text{NH}_3^+$  hydrazinium.
- When there are multiple ligands of the same type, the prefixes di, tri, tetra, penta, and hexa are used to indicate the number of ligands of that type. An exception occurs when the name of the ligand contains a number, as in ethylenediamine (en). To avoid confusion, bis, tris, and tetrakis are used instead of di, tri, and tetra, and the ligand name is enclosed in brackets. as in bis (ethylenediamine)
- If anion is a complex, metal is followed by 'ate'.

$[\text{Ni}(\text{CN})_4]^{2-}$  : tetracyanonickelate (II) ion

lead – plumbate

gold – aurate

zinc – zincate

tin – stannate

silver – argentate



cobalt – cobaltate

iron – ferrate

aluminium – aluminate

manganese – manganate

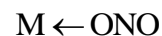
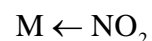
copper – cuprate

chromium – chromate

platinum – platinate

(i) A complex is said to be polynuclear if it contains two or more metal atoms. The prefix –  $\mu$  denotes the bridging ligands that connect the two metal atoms.

(j) Ambidentate ligands can be connected via different atoms.–



(k) When writing (not naming) the complex formula:

\* Complex ion should be enclosed by square brackets and

\* Ligands are placed alphabetically after metal, but first negative ligands, then neutral, then positive.

## 5. WERNER'S THEORY

Werner explained the nature of bonding in complexes and came to the conclusion that the metal in complexes has two different types of valency.

### 5.1 Primary Valency



The oxidation state of the central metal atom or ion determines the primary valency. These are asymmetrical.

**EXAMPLE:** What are the primary valency of  $K_4[Fe(CN)_6]$  and  $[Cu(NH_3)_4]SO_4$  ?

**Ans:** The primary valency of  $K_4[Fe(CN)_6]$  and  $[Cu(NH_3)_4]SO_4$  is 2.

## 5.2 Secondary Valency

Secondary valency refers to the number of ligand atoms that are co-ordinated to the central metal atom. Because these are directional, a complex ion has a specific shape.

**EXAMPLE:** What are the secondary valency of  $[Co(NH_3)_6]Cl_3$  and  $K_4[Fe(CN)_6]$  ?

**Ans:** The secondary valency in  $[Co(NH_3)_6]Cl_3$  is 6.

$K_4[Fe(CN)_6]$ : six ligands are coordinated to Fe. As a result, the secondary valency is 6. Ions attached to complex ions satisfy the primary valency. It is represented by dotted lines. Ionisable valency is another name for primary valency. The ligands satisfy the secondary valency; they are non-ionisable and are represented by a solid line  $[Co(NH_3)_6]Cl_3$

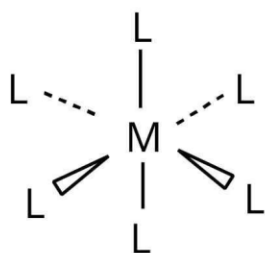
Every element is capable of satisfying both its primary and secondary valencies. When a negative ion is present in the coordination sphere, it exhibits dual behavior. It has the potential to satisfy both primary and secondary valencies.

The ligands that satisfy the secondary valencies are aimed at specific locations in space. The coordination number determines the geometry of the complex ion. If the metal has coordination number 6, the complex is octahedral, which means that six donor atoms of the ligands occupy six positions around the metal octahedrally. If, on the other hand, the coordination number is 4, the complex's geometry can be

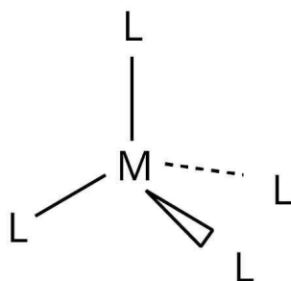




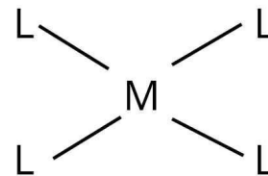
tetrahedral or square planar. This postulate predicted that different types of isomerism would exist in coordination compounds.



Octahedral



Tetrahedral

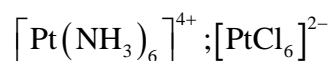
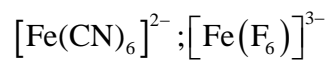
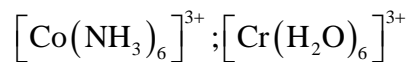
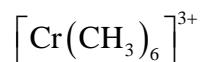


Square planar

Examples:

Octahedral

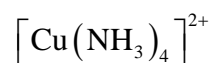
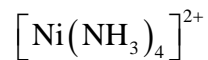
(C·N = 6)



Square planar



( C.  $N = 4$  )



$X = \text{Cl}^-, \text{Br}, \text{I}^-$

Familiar C.N.'s of some common metal ions.

Univalent	C.N	Divalent	C.N.
$\text{Ag}^+$	2	$\text{V}^{2+}$	6
$\text{Au}^+$	2, 4	$\text{Fe}^{2+}$	6
$\text{Ti}^+$	2	$\text{Co}^{2+}$	4, 6
$\text{Cu}^+$	2, 4	$\text{Ni}^{2+}$	4, 6
		$\text{Cu}^{2+}$	4, 6
		$\text{Zn}^{2+}$	4
		$\text{Pd}^{2+}$	4
		$\text{Pt}^{2+}$	4
		$\text{Ag}^{2+}$	4

Trivalent	C.N.	Tetravalent	C.N.
$\text{Sc}^{3+}$	6	$\text{Pt}^{4+}$	6



Cr <sup>3+</sup>	6	Pd <sup>4+</sup>	6
Fe <sup>3+</sup>	6		
Co <sup>3+</sup>	6		
Os <sup>3+</sup>	6		
Ir <sup>3+</sup>	6		
Au <sup>3+</sup>	4		.

## 6. EFFECTIVE ATOMIC NUMBER (EAN)

Sidgwick proposed effective atomic number (EAN), which is defined as the number of electrons gained by the metal atom or ion after gaining electrons from the donor atoms of the ligands. In some cases, the effective atomic number (EAN) coincides with the atomic number of the next inert gas. The following relationship is used to calculate EAN:

$$\text{EAN} = \text{Atomic number of the metal} - \text{number of electrons lost in ion formation} + \text{number of electrons gained from the donor atoms of the ligands. } (2 \times \text{CN})$$

The EAN values of various metals in their complexes are listed below:

Complex	Metal (Oxidation state)	Atomic number of metal	Coordination number	Effective atomic number
$\text{K}_4[\text{Fe}(\text{CN})_6]$	+2	26	6	$(26 - 2) + (6 \times 2) = 36$
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	+2	29	4	$(29 - 2) + (4 \times 2) = 35$
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_4$	+3	27	6	$(27 - 3) + (6 \times 2) = 36$



$\text{Ni}(\text{CO})_4$	0	28	4	$(28-0) + (4 \times 2) = 36$
$\text{K}_2[\text{Ni}(\text{CN})_4]$	+2	28	4	$(28-2) + (4 \times 2) = 34$

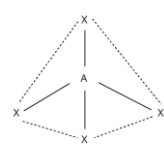
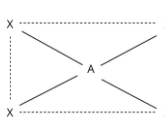
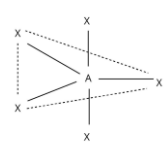
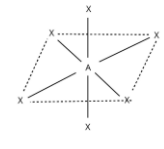
## 7. VALENCE BOND THEORY

Valence Bond Theory (VBT) can explain the bonding in coordination compounds because the d orbitals of the majority of transition metal complexes are incomplete. Valence bond considers orbital hybridization because penultimate d-orbitals are close in energy to s and p-orbitals of the outermost shell, allowing for various types of hybridization.

The following assumption is made by VBT:

- (i) The central metal ion has a number of empty orbitals that can accept electrons donated by the ligands. The coordination number of the metal ion for the specific complex is equal to the number of empty d-orbitals.
- (ii) Strong bonds are formed when the metal orbitals and ligand orbitals overlap. The greater the extent of overlapping, the more stable the complex. Different orbitals (s, p, or d) hybridize to form a set of equivalent hybridized orbitals that participate in ligand bonding.
- (iii) Each ligand contributes two electrons to the central metal ion/atom.
- (iv) The inner orbitals contain non-bonding metal electrons that do not participate in chemical bonding.
- (v) A complex is paramagnetic if it contains unpaired electrons. The complex is diamagnetic if it does not contain an unpaired electron.
- (vi) Under the influence of a strong ligand (CN, CO), electrons can be forced to pair up, thereby violating Hund's rule of multiplicity.

## Common types of hybridization

Coordination Number	Hybridization	Shape	Geometry
2	$sp$	Linear	X-A-X
4	$sp^3$	Tetrahedron	
4	$dsp^2$	Square planar	
5	$sp^3d$ or $dsp^3$	Trigonal bipyramidal	
6	$d^2sp^3$ or $sp^3d^2$	Octahedral	

**NOTE:** Inner d-orbitals (3d orbital) have been used for bonding in  $d^2sp^3$  hybridisation; such complexes are known as inner orbital complexes or low spin complexes. The outer d-orbitals (4d orbital) have been used for bonding in  $sp^3d^2$  hybridisation; such complexes are known as outer orbital complexes or high spin complexes.  $\sqrt{n(n+2)}$  where n is the number of unpaired electrons, gives the magnetic moment.



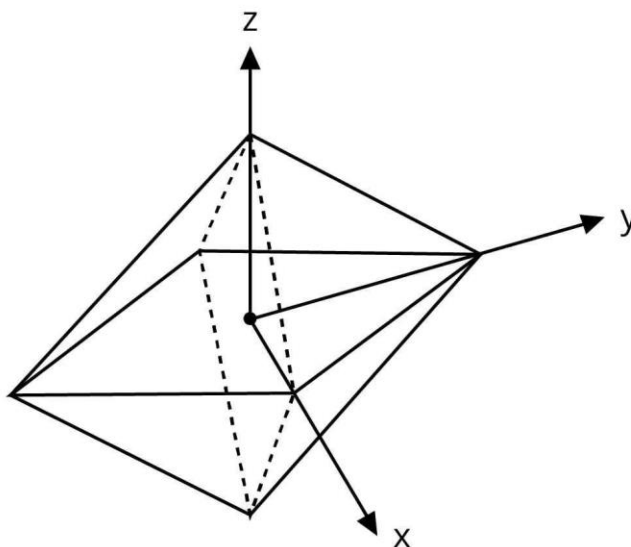
### 7.1 Limitations of VBT

1. The change in ligand and metal ion properties could not be explained.
2. The valence bond theory is silent on why some complexes are more labile than others.
3. The VBT does not explain the existence of inner and outer orbital complexes satisfactorily.
4. The VBT was unable to explain the color of complexes.

## 8. CRYSTAL FIELD THEORY

The valence bond theory is less widely accepted than the Crystal Field Theory. It is assumed that the attraction between a complex's central metal and its ligands is purely electrostatic. The following assumptions are made in the crystal field.

1. Ligands are considered point charges.
2. Metal orbitals and ligand orbitals have no interaction.
3. In the free atom, all of the d orbitals on the metal have the same energy (that is, they are degenerate). However, when a complex is formed, the ligands destroy the degeneracy of these orbitals, resulting in different energies for the orbitals.



## 8.1 Octahedral complexes

The metal is at the center of an octahedral complex, and the ligands are at the six corners. As shown, the directions  $x$ ,  $y$ , and  $z$  point to three adjacent corners of the octahedron. The lobes of the  $e_g$  and  $d_{x^2-y^2}$ ,  $d_{z^2}$  orbitals point along the  $x$ ,  $y$ , and  $z$  axes and the lobes of the  $t_{2g}$   $t_{2g}$  and  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  are located between the axes. The approach of six ligands along the  $x$ ,  $y$ ,  $z$ ,  $-x$ ,  $-y$ , and  $-z$  directions increases the energy of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (which point along the axes) much more than the energy of the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals (which point between the axes). Thus, the  $d$  orbitals split into two groups under the influence of an octahedral ligand field.

Weak field ligands are those that cause only a minor amount of crystal field splitting. Strong field ligands are ligands that cause a large splitting. The common ligands can be arranged in ascending crystal field splitting  $\Delta$ .



## Spectrochemical Series

$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < EtOH < \text{oxalate} < H_2O$

(weak field ligands)  $< EDTA < (NH_3 = \text{pyridine}) < \text{ethylenediamine} < \text{dipyridy}$   
 $< O\text{-phenanthroline} < NO_2 < CN^- < CO$  (strong field ligands)

A pattern of increasing donation is followed:

Halide donors  $< O$  donors  $< N$  donors  $< C$  donors

The total crystal field stabilization energy is given by

$$CFSE_{(\text{octahedral})} = -0.4n_{(t_{2g})} + 0.6n_{(e_g)}$$

where  $n_{t_{2g}}$  and  $n_{e_g}$  are the number of electrons occupying the  $t_{2g}$  and  $e_g$  orbitals respectively. The CFSE is zero for ions with  $d^0$  and  $d^{10}$  configurations in both strong and weak ligand fields. The CFSE is also zero for  $d^5$  configurations in a weak field.

## EFFECTS OF CRYSTAL FIELD SPLITTING

### CFSE and electronic arrangements in octahedral complexes

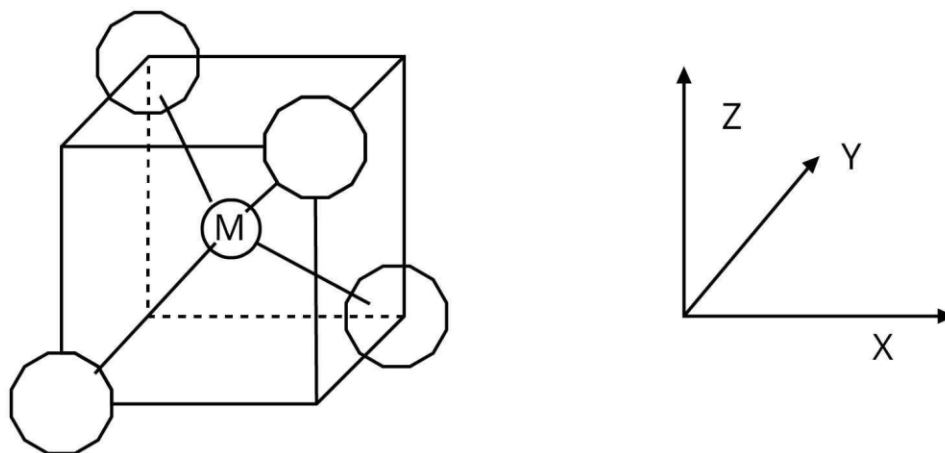




Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	$t_{2g}$	$e_g$	CFSE $\Delta_o$	Spin only magnetic moment $\mu_B$ (D)	$t_{2g}$	$e_g$	CFSE $\Delta_o$	Spin only magnetic moment $\mu_B$ (D)
$d^1$	$\uparrow$		0.4	1.73	$\uparrow$		0.4	1.73
$d^2$	$\uparrow\uparrow$		-0.8	2.83	$\uparrow\uparrow$		-0.8	2.83
$d^3$	$\uparrow\uparrow\uparrow$		-1.2	3.87	$\uparrow\uparrow\uparrow$		-1.2	3.87
$d^4$	$\uparrow\uparrow\uparrow$	$\uparrow$	-0.6	4.90	$\uparrow\downarrow\uparrow$		-1.6	2.83
$d^5$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow$	-0.0	5.92	$\uparrow\downarrow\uparrow\downarrow$		-2.0	1.73
$d^6$	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\uparrow$	-0.4	4.90	$\uparrow\downarrow\uparrow\downarrow$		-2.4	0.00
$d^7$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\uparrow$	-0.8	3.87	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow$	-1.8	1.73
$d^8$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\uparrow$	-1.2	2.83	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\uparrow$	-1.2	2.83
$d^9$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow$	-0.6	1.73	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow$	-0.6	1.73
$d^{10}$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	0.0	0.00	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	0.0	0.00

## 8.2 Tetrahedral Complexes

A cube is related to a regular tetrahedron. As shown, one atom is in the center of the cube, and four of the cube's eight corners are occupied by ligands.



The directions  $x$ ,  $y$ , and  $z$  point to the cube's face centers. The  $e$  orbitals are oriented along the  $x$ ,  $y$ , and  $z$  axes (that is to the centres of the faces). The  $t_2$  orbitals are located between the  $x$ ,  $y$ , and  $z$  axes (that is towards the centres of the edges of the cube). The ligands' approach directions do not exactly coincide with the  $e$  or  $t_2$  orbitals.

As a result, the  $t_2$  orbitals are closer to the ligand direction than the  $e$  orbitals. The ligands' approach raises the energy of both sets of orbitals. Because they are closest to the ligands, the energy of the  $t_2$  orbitals is increased the most. The crystal field splitting in octahedral complexes is the inverse of that in tetrahedral complexes.

The  $t_2$  orbitals are  $0.4\Delta_o$  higher than the weighted average energy of the two groups (the bary center), while the  $e$  orbitals are  $0.6\Delta_o$  lower.

In tetrahedral complexes, the magnitude of the crystal field splitting  $t$  is much smaller than in octahedral fields. This is due to two factors:

1. Because there are only four ligands rather than six, the ligand field is only two-thirds the size; consequently, the ligand field splitting is also two-thirds the size.



2. The orbital direction does not coincide with the ligand direction. This reduces the crystal field splitting by about two-thirds.

Thus the tetrahedral crystal field splitting  $\Delta_t$  is roughly  $2/3 \times 2/3 = 4/9$  of the octahedral crystal field splitting  $\Delta_o$ .

## 9. ORGANOMETALLIC COMPOUNDS

Organometallic compounds are those that contain at least one carbon-metal bond. The Grignard reagent,  $\text{RMgX}$ , is a well-known example of an organometallic compound in which R is an alkyl group. Organometallic compounds include diethyl zinc  $[\text{Zn}(\text{C}_2\text{H}_5)_2]$ , lead tetraethyl  $[\text{Pb}(\text{C}_2\text{H}_5)_4]$ , ferrocene  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ , dibenzene chromium  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ , and metal carbonyls. Organometallic compounds are divided into three types:

1. Complexes with the sigma ( $\sigma$ )
2. bonded complexes of Pi ( $\pi$ )
3. Complexes with both sigma and pi bonding properties.

### 9.1 Sigma bonded complexes

The metal atom and carbon atom of the ligand are joined together with a sigma bond in these complexes, i.e., the ligand contributes one electron and is thus referred to as a one electron donor.

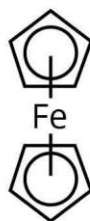
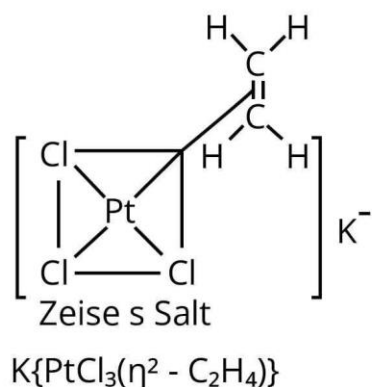
(i) Grignard reagent,  $R-Mg-X$ , where R is an alkyl or aryl group and X is halogen.

(ii) Zinc compounds with the formula  $\text{R}_2\text{Zn}$ , for example,  $(\text{C}_2\text{H}_5)_2\text{Zn}$ . Frankland was the first to isolate this in 1849. Other comparable compounds include  $(\text{CH}_3)_4\text{Sn}$ ,  $(\text{C}_2\text{H}_5)_4\text{Pb}$ ,  $\text{Al}_2(\text{CH}_3)_6$ ,  $\text{Al}_2(\text{C}_2\text{H}_5)_6$ , and  $\text{Pb}(\text{CH}_3)_4$

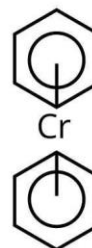


## 9.2 Pi bonded organometallic compounds

These are the compounds of metals that are combined with alkenes, alkynes, benzene, and other ring compounds. In these complexes, the metal and ligand form a bond that involves the pi electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown here:



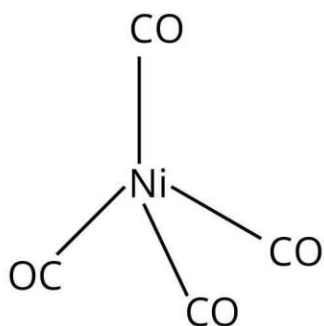
Ferrocene  
 $Fe(\eta^5 - C_2H_5)_2$



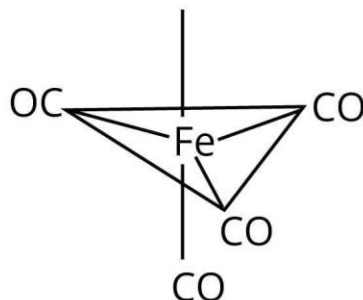
Dibenzene chromium  
 $Cr(\eta^6 - C_6H_6)_2$

## 9.3 Sigma- and Pi-bonded organometallic compounds

This class includes metal carbonyls, which are compounds formed by combining metal and carbon monoxide. These compounds have sigma and pi bonding. Metal atoms in these compounds have no oxidation state. Carbonyls can be monomeric, bridged, or polynuclear in nature.

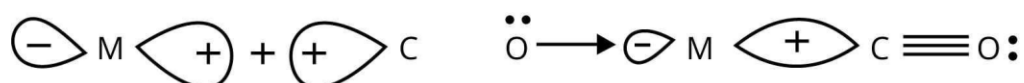


Tetracarbonyl nickel (0)  
 $\text{Ni}(\text{CO})_4$



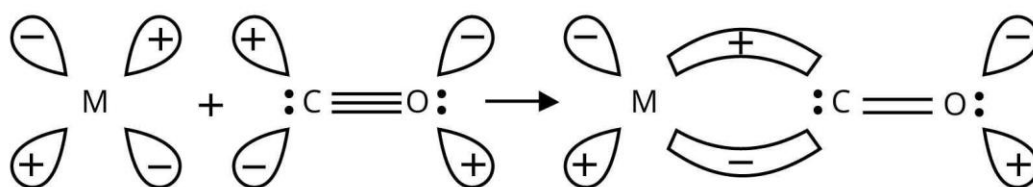
Pentacarbonyl iron (0)  
 $\text{Fe}(\text{CO})_5$

The metal–carbon bond in a metal carbonyl has both the sigma– and pi–character. When a vacant hybrid orbital of the metal atom overlaps with an orbital on the C atom of carbon monoxide containing a lone pair of electrons, a sigma bond is formed.





When a filled orbital of a metal atom overlaps with a vacant antibonding  $\pi^*$  orbital of a carbon monoxide atom, a  $\pi$ -bond is formed. This overlap is also known as metal atom back donation of electrons to carbon. As an example, consider the following:



The  $\pi$ -overlap is perpendicular to the  $\sigma$ -bond nodal plane.

In olefinic complexes, bonding  $\pi$ -orbital electrons are donated to the metal atoms' empty orbital while back bonding occurs from the metal atoms' filled orbital to the antibonding  $\pi$ -orbital of the olefin.

## 10. ISOMERISM

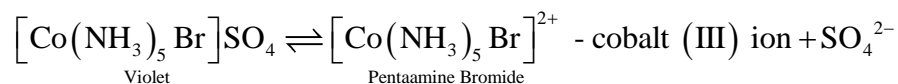
Isomers are compounds that have the same molecular formula but a different structural formula.

### 10.1 Structural Isomerism

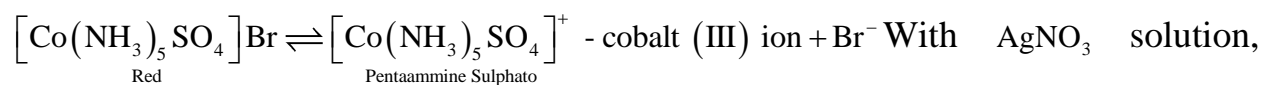


### 10.1.1 Ionisation Isomerism :

This isomerism occurs when the coordination compounds produce different ions in solution. For example, the formula has two isomers.



This isomer produces a white precipitate of  $\text{BaSO}_4$  in a solution of  $\text{BaCl}_2$ .



the above isomer produces a light yellow precipitate.

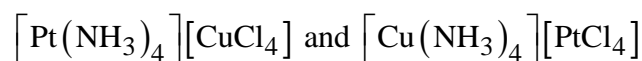
### 10.1.2 Hydrate Isomerism:

When different numbers of water molecules are present inside and outside the coordination sphere, this type of isomerism occurs. This isomerism is best exemplified by the three isomers with the formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ .

$\left[ \text{Cr}(\text{H}_2\text{O})_6 \right] \text{Cl}_3$ ,  $\left[ \text{Cr}(\text{H}_2\text{O})_5 \text{Cl} \right] \text{Cl}_2 \cdot \text{H}_2\text{O}$ , and  $\left[ \text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2 \right] \text{Cl} \cdot 2\text{H}_2\text{O}$  are its Hydrate Isomers.

### 10.1.3 Cordination Isomerism:

This type of isomerism can be found in coordination compounds that contain both cationic and anionic complex ions. To form isomers, the ligands in both the cationic and anionic ions are exchanged. Here are some examples:





### 10.1.4 Linkage Isomerism:

This isomerism occurs in complex compounds containing ambidentate ligands such as  $\text{NO}_2$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{CO}$ . For example,

$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  are linkage isomers because  $\text{NO}_2$  can be linked via N or O.

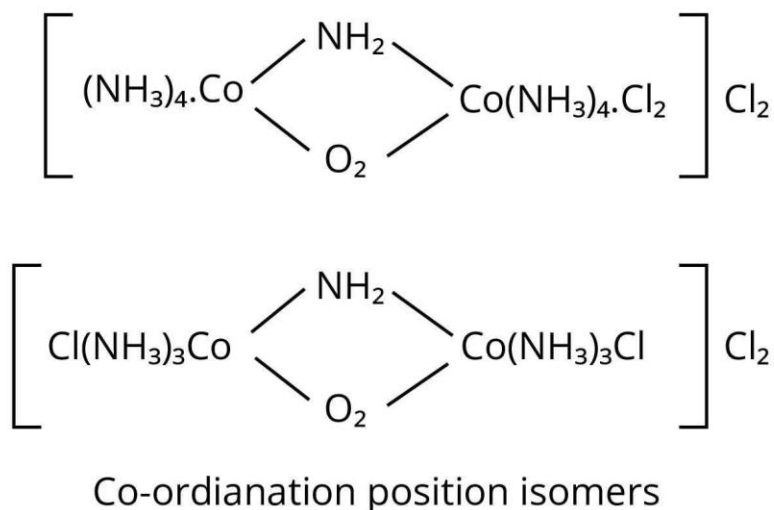
### 10.1.5 Ligand Isomerism:

Some ligands can exist as isomers; for example, diamino propane can exist as both 1, 2-diamino propane (pn) and 1, 3-diamino propane, also known as trimethylene diamine (tn).

### 10.1.6 Coordination position isomerism:

This type of isomerism is exhibited by polynuclear complexes by changing the position of ligands with respect to different metal atoms present in the complex. For example:





## 10.2 Stereo Isomerism

Compounds with stereo isomerism have the same number of atoms or groups in the same position, but the atoms or groups are arranged differently around the central atom.

### 10.2.1 Geometrical Isomerism

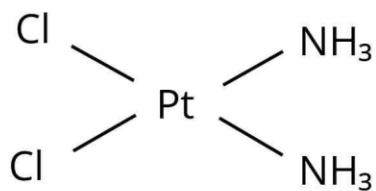
Complex compounds with the same ligands in the coordination sphere but different relative positions of the ligands around the central metal atom are referred to as geometrical isomers, and the phenomenon is referred to as geometrical isomerism.

#### 10.2.1.1 Geometrical Isomerism in square planar complexes

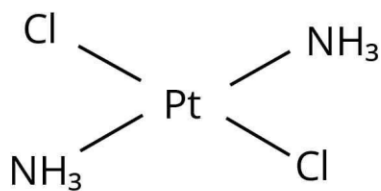


A square planar complex with two similar ligands at opposite positions (180° apart) is called a trans-isomer, while a square planar complex with two similar ligands at adjacent positions (90° apart) is called a cis - isomer.

1. Geometrical isomers (cis and trans) of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

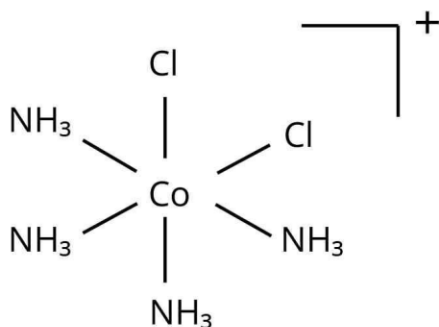


cis

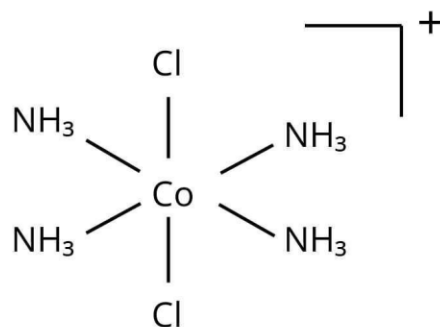


trans

2. Geometrical isomers (cis and trans) of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

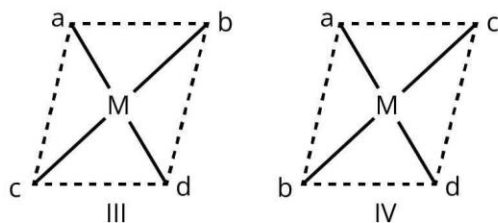
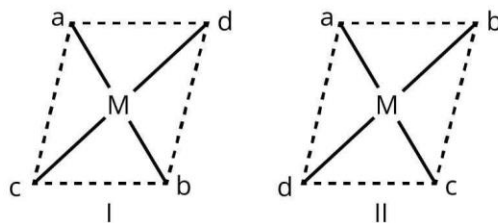


cis

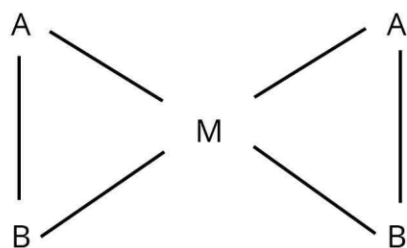


trans

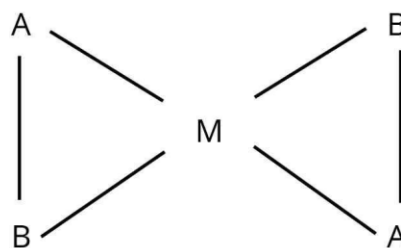
3. Mabcd



Both are identical  
The three isomeric structure of the complex Mabcd.

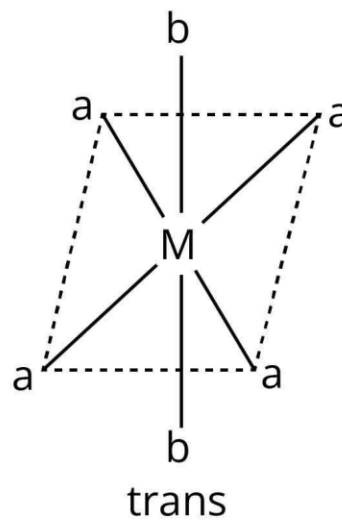
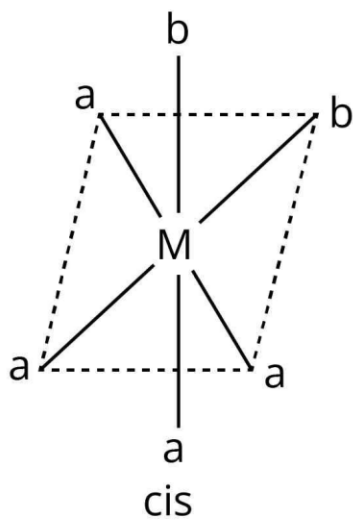
4.  $M(AB)_2$ 

cis

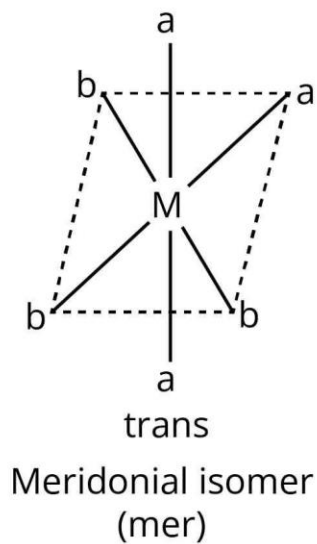
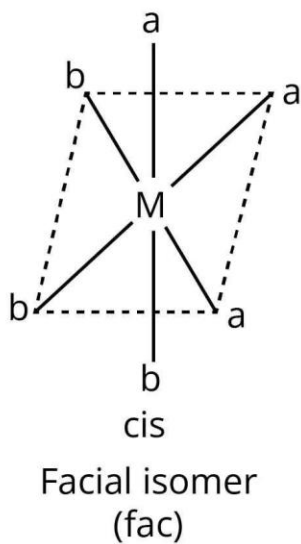


trans

**10.2.1.2 Geometrical Isomerism in octahedral complexes**1.  $Ma_4b_2$



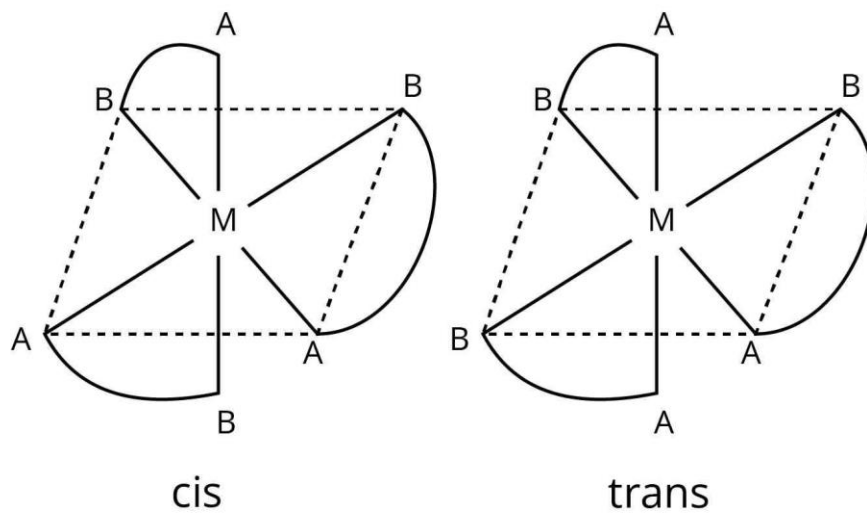
2.  $Ma_3b_3$



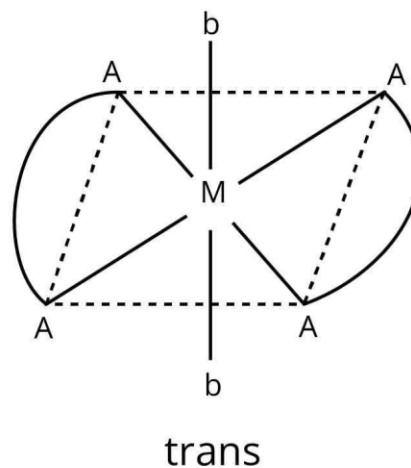
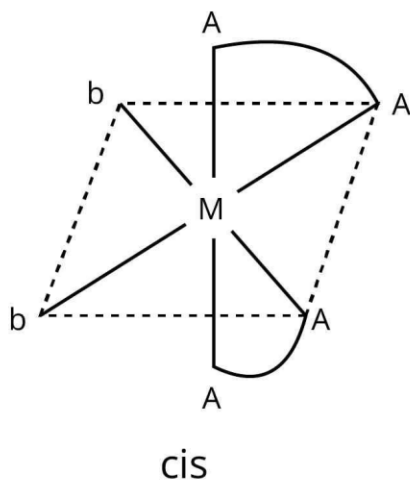


3.  $Mabcdef$ : They form 15 isomers

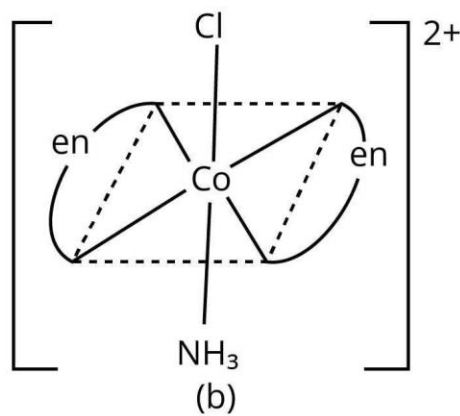
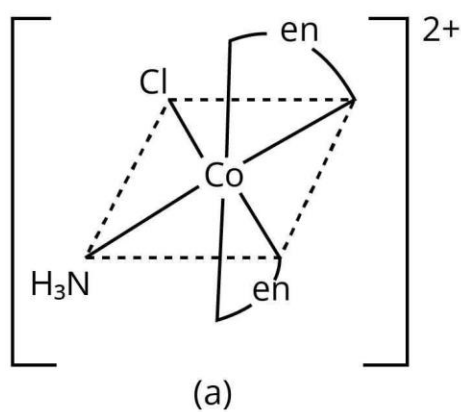
4.  $M(AB)_3$



5.  $M(AA)_2b_2$



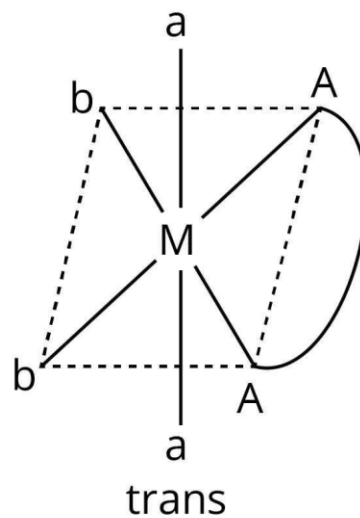
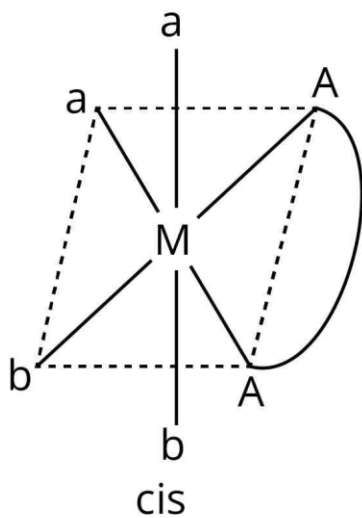
6.  $M(AA)_2bc$



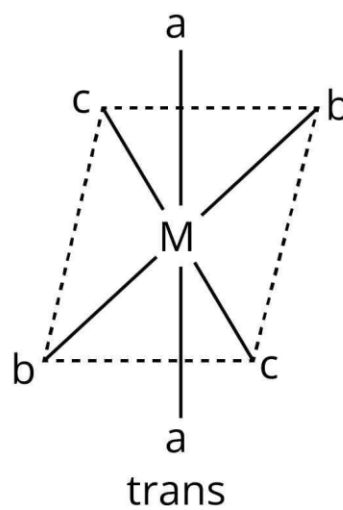
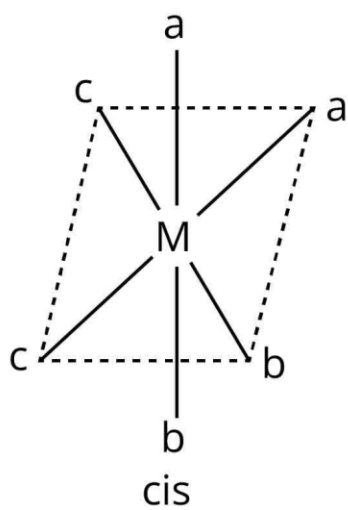
Cis and trans-isomers  $[Co^{III}(en)_2(NH_3)(Cl)]^{2+}$  ion



7.  $M(AA)a_2b_2$



8.  $Ma_2b_2c_2$



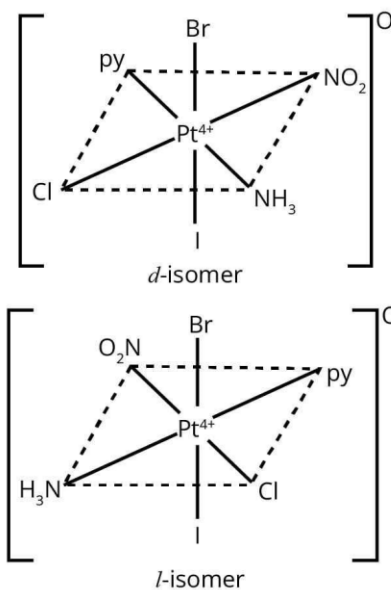




## Optical Isomerism in octahedral complexes

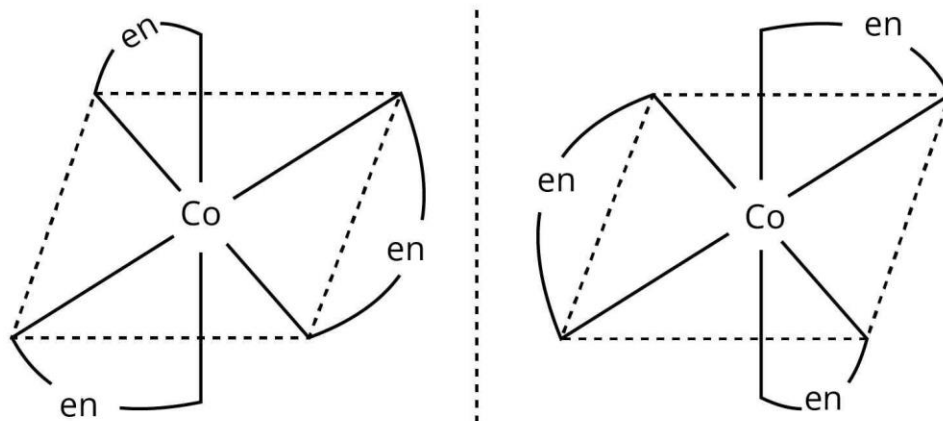
### 1. Mabcdef

**Example:** Draw the optical isomers of  $[\text{Pt}(\text{Cl})(\text{Br})(\text{I})(\text{py})(\text{NO}_2)(\text{NH}_3)]$



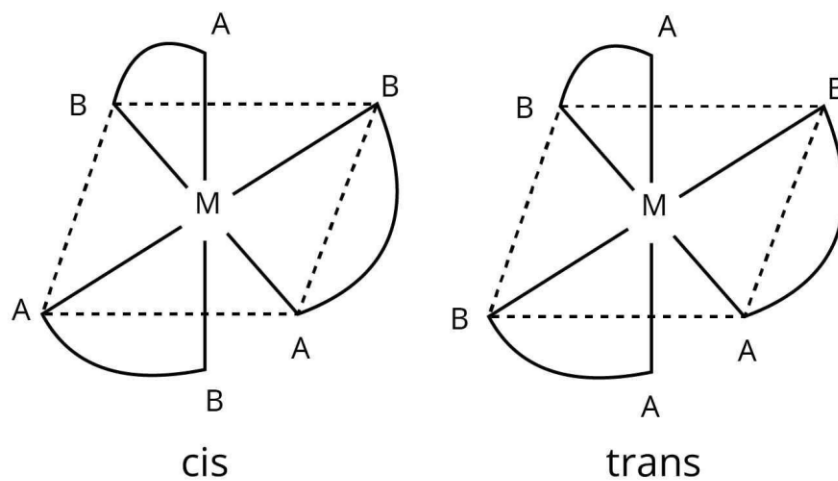
### 2. $M(\text{AA})_3$

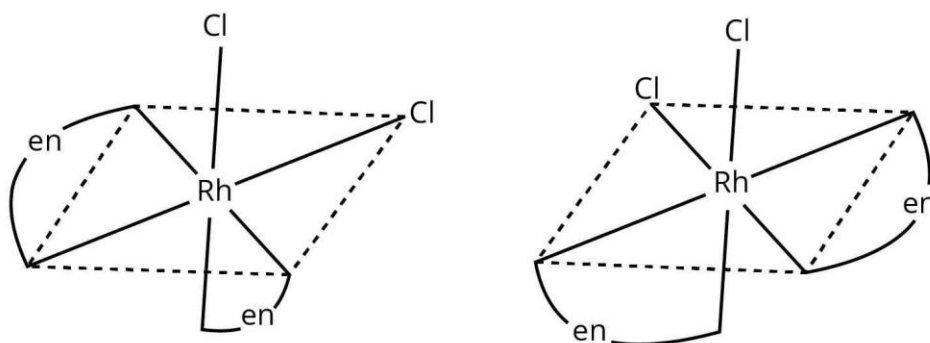
**Example:** Draw the optical isomers of  $[\text{Co}(\text{en})_3]^{3+}$

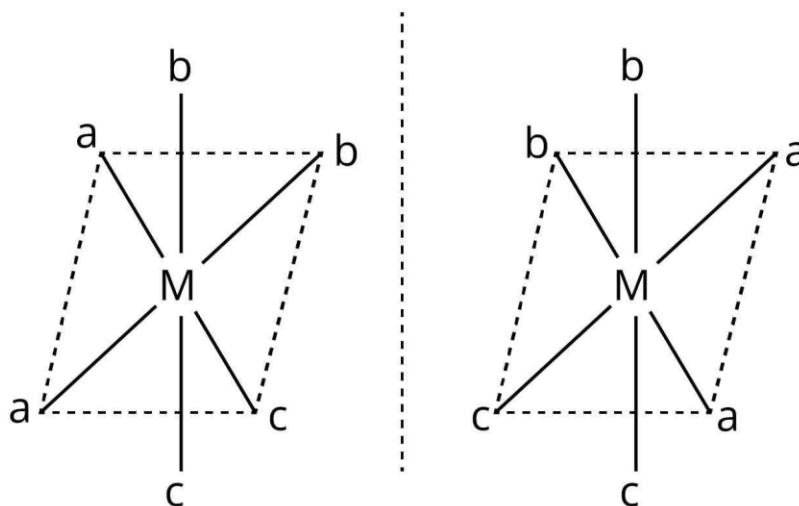


The two optical isomeric forms of the complex  $[\text{Co}(\text{en})_3]^{3+}$

3.  $M(\text{AB})_3$

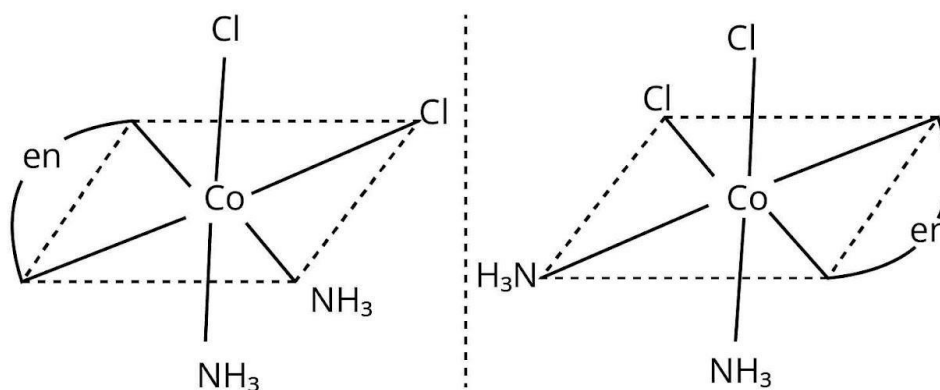


**4. cis  $M(AA)_2b_2$** **Example:** Draw the optical isomers of  $[\text{RhCl}_2(\text{en})_2]^+$ Optical active isomers of cis  $[\text{RhCl}_2(\text{en})_2]^+$ **5. Cis  $Ma_2b_2c_2$**



6. cis  $M(AA)b_2c_2$

**Example:** Draw the optical isomers of  $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$



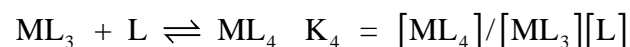
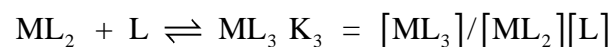
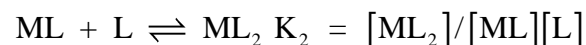


## 7. cis $M(AA)_2bc$

## 11. STABILITY OF COORDINATION COMPOUNDS

The degree of association between the two species involved in the state of equilibrium is referred to as the stability of a complex in solution. If we get a reaction like this:  $M+4L \rightleftharpoons ML_4$

The greater the stability constant, the greater the proportion of  $ML_4$  in solution. Because free metal ions are rare in solution,  $M$  is usually surrounded by solvent molecules, which compete with and eventually replace the ligand molecules,  $L$ . To keep things simple, we ignore the solvent molecules and write the four stability constants as follows:



where  $K_1, K_2$ , etc are known as stepwise stability constants. Alternatively, we can express the overall stability constant as follows:



## 12. IMPORTANCE AND APPLICATIONS OF COORDINATION COMPOUNDS

### 1. Analytical chemistry:

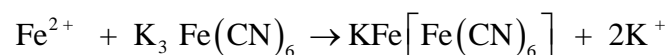


The analytical applications of coordination chemistry are in

**(a) Qualitative and quantitative analysis:**

Metal ions react with a variety of ligands to form colored coordination compounds. These reactions are used to detect metal ions. The formed colored complexes can be used to estimate metals using traditional or instrumental methods such as gravimetry or colorimetry. The following are some examples:

The addition of potassium ferrocyanide solution detects the presence of iron ions ( $Fe^{3+}$ ), resulting in the formation of the Prussian blue complex.



**(b) Volumetric analysis:**

(b) Volumetric analysis:

Titration with EDTA can be used to determine the hardness of water.  $Ca^{2+}$  and  $Mg^{2+}$ , the metal ions that cause hardness, form stable complexes with EDTA.

**2. Metal extraction and purification:**

Metals such as silver and gold are extracted by forming water-soluble cyanide complexes with the ore. By adding zinc to the solution, pure gold can be extracted. Metals can also be purified by forming and then decomposing their coordination compounds. For example, after extraction, impure nickel can be converted to pure nickel by first converting it to nickel carbonyl and then decomposing it.

**3. Catalysis:**

Catalysts for coordination compounds are used in critical commercial processes. For example:



- (a) In the formation of polyethene, the Ziegler-Natta catalyst ( $TiCl_4$  and trialkyl aluminium) is used as a catalyst.
- (b) In the hydrogenation of alkenes, the Wilkinson catalyst -  $RhCl(PPh_3)_3$  is used.
- (c) Various rhodium complexes, such as  $[Rh(CO)_2I_2]$ ,  $[Rh(Cl)(CO)(PPh_3)_2]$ , or  $[Rh(Cl)(CO)_2]_2$  are used as catalysts in the Monsanto acetic acid process in the presence of  $CH_3I, I_2$ , or HI as activator.

#### 4. Electroplating:

Gold, silver, and copper coordination compounds are used as components in baths used for electroplating articles made of other metals with these metals.  $K[Ag(CN)_2]$  is used as an electrolyte in silver plating;  $K[Au(CN)_2]$  is used as an electrolyte in gold plating; and  $K_3[Cu(CN)_4]$  is used as an electrolyte in copper plating.

Coordination complexes are important biological compounds. Chlorophyll, for example, is a  $Mg^{2+}$  complex. This green pigment is essential for photosynthesis in plants. Similarly, haemoglobin, the red pigment found in blood, is a  $Fe^{2+}$  coordination complex, and vitamin B12, an essential nutrient, is a  $Co^{3+}$  complex.

**6. Medicinal uses:** In the treatment of metal poisoning, complexing or chelating agents are used, in which a coordination complex is formed between the toxic metal in excess metal and the complexing agent. EDTA, for example, is used to treat lead poisoning. When EDTA is injected intravenously into the bloodstream, it traps lead, forming a compound that is excreted in the urine. Mercury, arsenic, aluminum, chromium, cobalt, manganese, nickel, selenium, zinc, tin, and thallium are other heavy metal poisonings that can be treated similarly with chelation therapy. Similarly, D-penicillamine and desferrioxamine B, chelating ligands, are used to remove excess copper and iron, respectively.



### 13. COORDINATION COMPOUNDS AND COMPLEX IONS

(a) Coordination compounds are those in which the central metal atom is linked to a number of ligands (ions or neutral molecules) via coordinate bonds, i.e. by these ligands donating lone pairs of electrons to the central metal atom ion.

If such a compound has a positive or negative charge, it is referred to as a complex ion, for example,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . Hence Co-ordination compounds are also those that contain complex ions, such as  $K_4[\text{Fe}(\text{CN})_6]$ ,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , and so on. In general, a complex ion is denoted by  $[\text{ML}_n]^{\pm x}$  where M is the metal ion, L represents ligands, n is the coordination number of metal ion and x is the net charge on the complex.

(b) Four types of complexes are shown below:

(i) Cation as complex ion, (carrying a net positive charge) e.g.,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  in  $[\text{Cr}(\text{NH}_3)_6] \text{Cl}_3$ .

(ii) Anion as complex ion, (carrying a net negative charge) e.g.,  $[\text{Fe}(\text{CN})_6]^{3-}$  in  $\text{K}_3[\text{Fe}(\text{CN})_6]$ .

(iii) Cation and anion both as complex ions. Carrying both positive and negative charge.

For e.g.,  $[\text{Pt}(\text{Py})_4][\text{PtCl}_4]$

(iv) Neutral complex (A complex carrying no net charge) e.g.,  $[\text{Ni}(\text{CO})_4]$  etc.

### 14. TERMINOLOGY OF COORDINATION COMPOUNDS

#### 14.1 Centre of Coordination (Central atom/ion or Acceptor atom/ion):

The centre of coordination is the cation or neutral atom to which one or more ligands (neutral molecules or anions) are attached or coordinated. As an acceptor,





the central atom/ion must have empty orbitals in order to accommodate electron pairs donated by the ligand's donor atom. This explains why transition metals with empty d-orbitals readily form coordination compounds.

For example in the complexes  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  and  $[(\text{CN})_6]^{3-}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  respectively are the central ions.

## 14.2 Ligands

A ligand or coordinating group is an atom, ion, or molecule that can donate at least two electrons to the central atom to form a coordinate bond (or dative linkage). The atom in a ligand that actually donates the electron pair is referred to as the donor atom. The ligands function as Lewis bases by donating one or more electron pairs to the central metal atoms or ions, which function as Lewis acids by accepting electrons.

### 14.2.1 Types of Ligands:

Ligands are classified based on how many lone pair electrons they donate to the central metal atom or ion.

- (a) Monodentate or unidentate ligands: These ligands have a single donor atom that donates only one electron pair to the central metal atom.
- (b) Bidentate ligands: Ligands with two donor atoms and the ability to link with the central metal in two positions are referred to as bidentate ligands.
- (c) Tridentate Ligand: The ligands that possess three donor atoms are called tridentate ligands
- (d) Tetradentate ligand: These ligands have four donor atoms.
- (e) Pentadentate ligands: They have five donor atoms
- (f) Hexadentate Ligands: They have six donor atoms.



### 14.2.2 Chelating ligands:

A bidentate or polydentate ligand is referred to as a chelating ligand if it forms a cyclic ring structure upon coordination. Chelates are the complexes that result from this process. Chelates with 5 or 6 membered rings are more stable. Due to steric hindrance, larger group ligands form more unstable rings than smaller group ligands.

### 14.2.3 Ambidentate ligands:

The ligands that have two donor atoms but only one donor atom is attached to the metal atom at a time when forming complexes. These ligands are known as ambidentate ligands. As an example:



## 15. COORDINATION NUMBER (C.N)

The number of atoms in the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as the metal atom or ion's coordination number. It is also the same as secondary valency.