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# Coordination Chemistry

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## **Introduction :**

*Coordination compound, any of a class of substances with chemical structures in which a central metal atom is surrounded by nonmetal atoms or groups of atoms, called ligands, joined to it by chemical bonds. Coordination compounds include such substances as vitamin B<sub>12</sub> , hemoglobin, and chlorophyll, dyes and pigments, and catalysts used in preparing organic substances.*

- The earliest known coordination compound is the bright red alizarin dye , it is a calcium aluminum chelate complex of hydroxyanthraquinone.*
- Another example of a coordination compound is the substance Prussian blue, with formula  $KFe[Fe(CN)_6]$*
- The branch of chemistry which deals with the study of coordination compounds or metal complexes or complex salts is called coordination chemistry.*
- Nearly 75 % research activities in inorganic chemistry are related with synthesis and applications of coordination compounds.*
- These are having very vast applications in medicines, separations, Purification of metals and catalysis.*

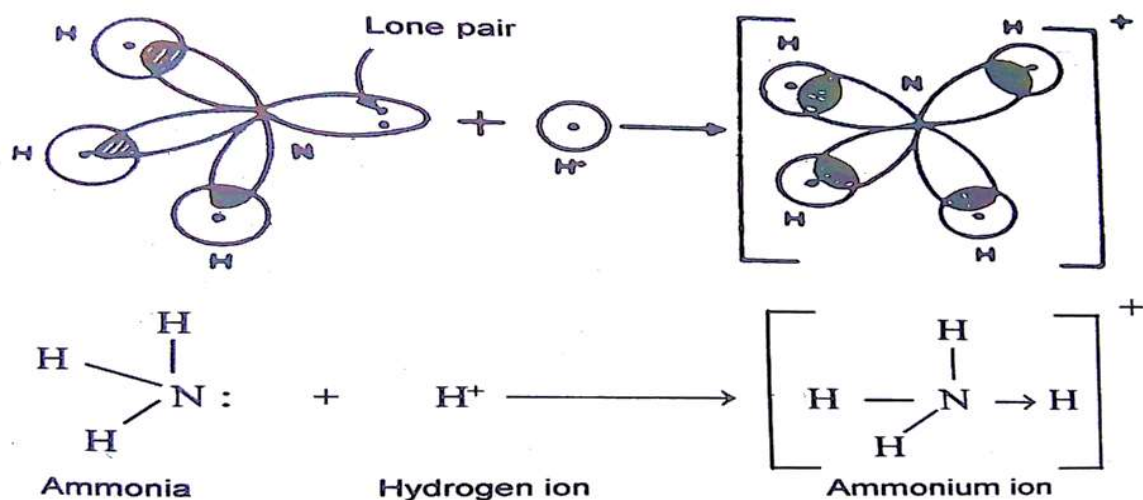
## Coordinate bond :

*A coordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom.*

- It is pointing from by an arrow (  ) pointing from donor to acceptor.  $\text{NH}_4^+$  ,  $\text{NH}_3\text{-BF}_3$  .*
- The atom which donates a pair of electrons is known as donor, while the atom which accept the pair of electrons is called acceptor.*
- Coordinate bond is also known as coionic or semipolar bond .*
- To form coordinate bond donor atom must possess at least one lone pair of electrons.*
- Acceptor atom must have an empty orbital in the valence shell.*
- There should be appreciable overlap between filled and empty orbitals of donor and acceptor atom.*

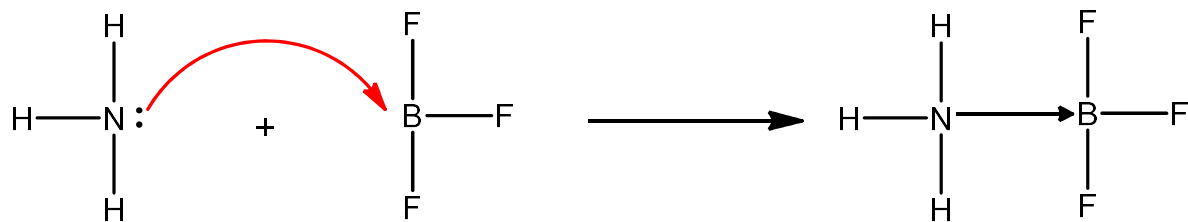
## Formation of $\text{NH}_4^+$

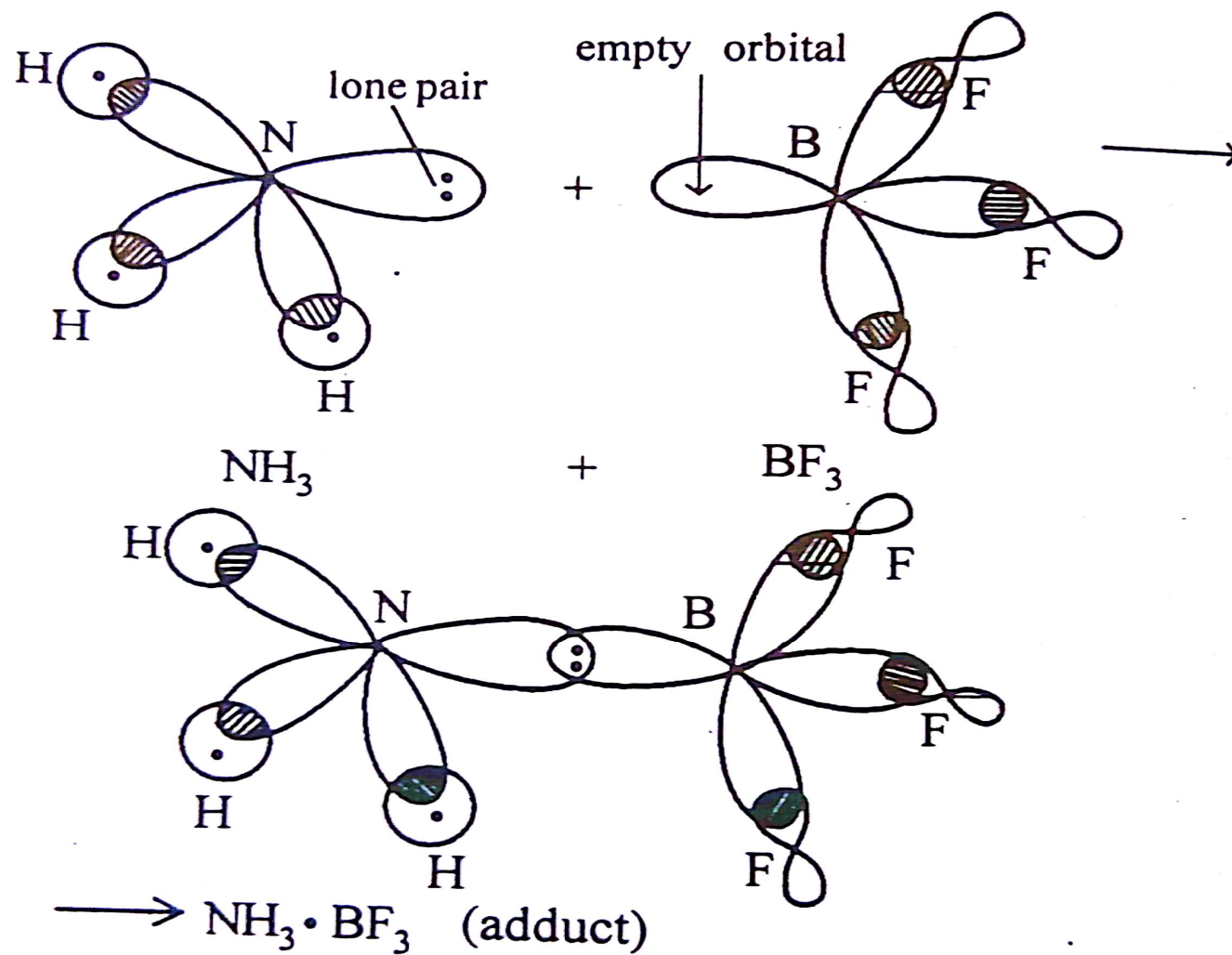
- In ammonia molecule nitrogen is a center atom with  $sp^3$  hybridization*
- Three  $sp^3$  hybrid orbitals of nitrogen with unpaired electrons overlap with half filled  $s$  orbital of hydrogen. The forth  $sp^3$  orbital with lone pair of electrons overlap with empty orbital of the  $\text{H}^+$  to form  $\text{NH}_4^+$*



### Formation of $\text{NH}_3\text{-BF}_3$

- When ammonia is treated with boron trifluoride an adduct is formed. In  $\text{BF}_3$  boron is the central atom .
- Boron is  $\text{sp}^2$  hybridized with one empty 'p' orbital
- In ammonia nitrogen is  $\text{sp}^3$  hybridized with lone pair of electrons in one of the  $\text{sp}^3$  hybrid orbital.
- The filled orbital of ammonia overlap with empty orbital of boron trifluoride to form  $\text{NH}_3\text{-BF}_3$  adduct.





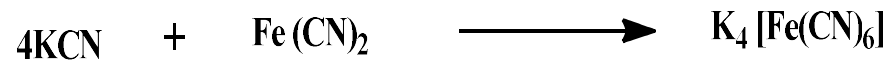
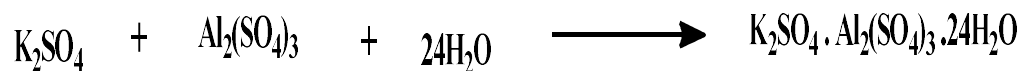
## *Distinction between double salts and complex salts*

### **Double salts**

- These are made up of two or more simple salts
- They exist in crystalline state, in aqueous state dissociate completely into ions.
- Nature of bonding is ionic, weak Vander Walls forces
- Complex ion absent
- The Properties of double salts are same as those of its constituents compounds.
- In double salts metals show their normal valency.
- Double salt loses its identity in solution
- E.g. Mohars salt, Potash alum

### **Complex salts**

- These are made by the combination of simple salt with electron rich ligands
- They exist in solid state as well as in aqueous state.
- Usually nature of bonding is ionic, covalent and coordinate
- Complex ion present
- The properties of coordination compounds are different from its constituent.
- In complex salts metals satisfy two types of valencies, primary and secondary valencies.
- Complex salt retains its identity in solution
- E.g. Potassium ferrocyanide, Tetra ammine copper(II) sulphate



## ***Werner's theory of Coordination Compounds***

***Alfred Werner in 1893, propounded his theory of coordination compounds. For his great work he was awarded with Nobel prize in 1913. The main postulates are:***

- In coordination compounds metals show two types of linkages (valencies)-primary and secondary.***
- The primary valences are normally ionizable and are satisfied by negative ions.***
- The secondary valences are non ionizable. These are satisfied by neutral molecules or negative ions.***
- The secondary valence is equal to the coordination number and is fixed for a metal.***
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.***
- The combining power of metal is divided into two spheres of attraction. The inner sphere is known as coordination sphere and the outer sphere is known as ionization sphere.***

## ***Applications Werner's theory of Coordination Compounds***

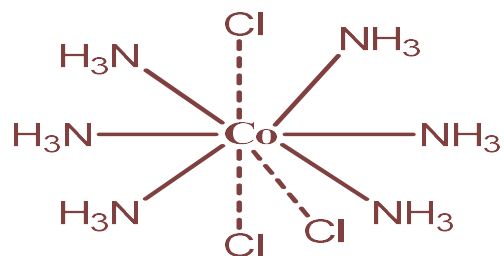
***Structures of various cobalt ammines is based on Werner's theory is given below:***

***Cobalt has a primary valency (oxidation state) of three and exhibit secondary valency (coordination number) of 6. The secondary valencies are represented by thick lines and the primary valency is represented by broken lines.***

- $\text{CoCl}_3 \cdot 6\text{NH}_3$  Complex: In this compound, the coordination number of cobalt is 6 and all the 6 secondary valencies are satisfied by  $\text{NH}_3$  molecules (the black solid lines). The 3 primary valencies are satisfied by chloride ions (the dotted line in fig). These are non-directional in character. These chloride ions are instantaneously precipitated on the addition of silver nitrate. The total number of ions in this case is 4, three chloride ions and one complex ion. The central ion and the neutral molecules or ions satisfying secondary valencies are written in a square bracket while writing the formula of the compound. Hence the complex may be written as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and as shown as in fig.***



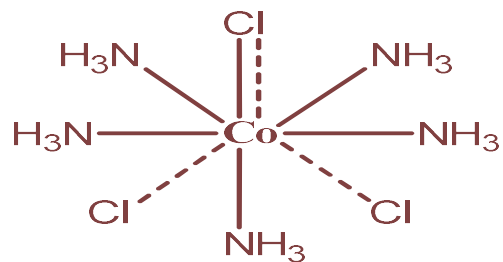
- ***CoCl<sub>3</sub>·5NH<sub>3</sub> complex: In this compound the coordination number of cobalt is also 6 but the number of NH<sub>3</sub> molecule is decreased to 5 from 6 and one remaining position is now occupied by chloride ion. This chloride ion exhibits the dual behavior as it has primary as well as secondary valency. Secondary valency is shown by full line and the primary valency is shown by dotted line in the figure. This structure satisfies the 3 primary and 6 secondary valencies of cobalt. Hence the complex formed may be formulated by writing five ammonia molecules and one chloride ion inside the square brackets and the two chloride ions outside the brackets [CoCl(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub>.***
- ***CoCl<sub>3</sub>·4NH<sub>3</sub> complex: In this compound, two chloride ions exhibit dual behavior of satisfying both Primary and Secondary Valencies. This compound will give precipitate with silver nitrate corresponding to only one Cl<sup>-</sup> ion and the total number of ions in this case is 2. Hence it can be formulated as [CoCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl.***
- ***CoCl<sub>3</sub>·3NH<sub>3</sub> complex: In this compound, three chloride ions satisfy primary as well as secondary valency. No Cl<sup>-</sup> will be precipitated on the addition of silver nitrate at room temperature. Therefore, the complex compound behave as neutral non conducting molecule. It may be formulated as [CoCl<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>].***



**$\text{CoCl}_3 \cdot 6\text{NH}_3$  complex**

**Total no. of ions = 4,**

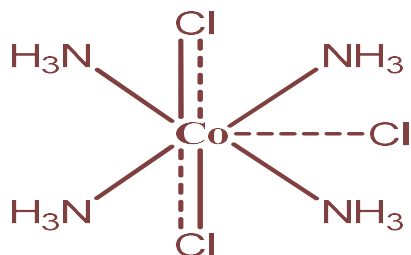
**No. of  $\text{Cl}^-$  precipitated = 3**



**$\text{CoCl}_3 \cdot 5\text{NH}_3$  complex**

**Total no. of ions = 3,**

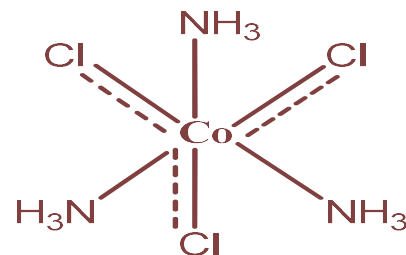
**No. of  $\text{Cl}^-$  precipitated = 2**



**$\text{CoCl}_3 \cdot 4\text{NH}_3$  complex**

**Total no. of ions = 2,**

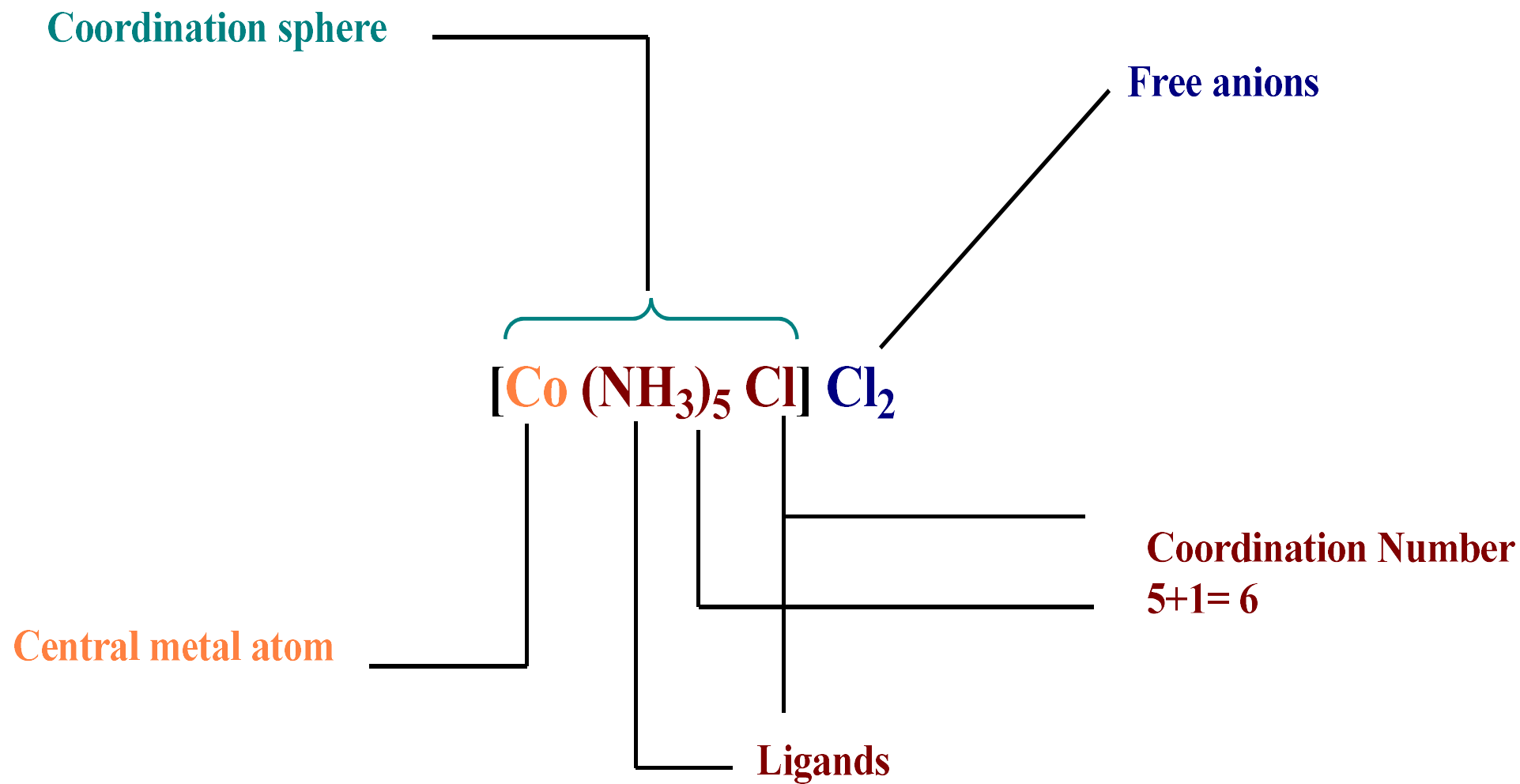
**No. of  $\text{Cl}^-$  precipitated = 1**



**$\text{CoCl}_3 \cdot 3\text{NH}_3$  complex**

**It is neutral molecule,**

**No. of  $\text{Cl}^-$  precipitated = 0**

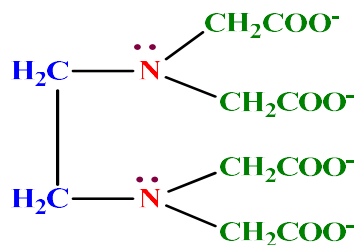


## Terminology in coordination chemistry

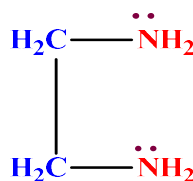
- **Coordination entity** : A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example,  $[\text{CoCl}_3 (\text{NH}_3)_3]$  is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Pt Cl}_2 (\text{NH}_3)_2]$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .
- **Central atom/ion** : In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities:  $[\text{NiCl}_2 (\text{H}_2\text{O})_4]$ ,  $[\text{Co Cl}(\text{NH}_3)_5]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$ , respectively. These central atoms/ions are also referred to as Lewis acids.
- **Ligands** : The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as  $\text{Cl}^-$ , small molecules such as  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , larger molecules such as  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  or even macromolecules, such as proteins. These are classified as  
  
**Unidentate** : When a ligand is bound to a metal ion through a single donor atom, as with  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the ligand is said to be unidentate.

## Terminology in coordination chemistry

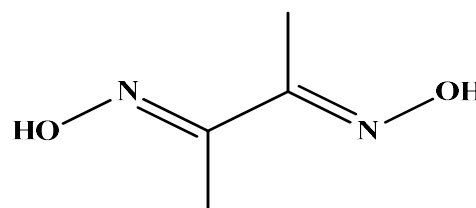
- When a ligand can bind through two donor atoms as in  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethane-1,2-diamine) or  $\text{C}_2\text{O}_4^{2-}$  (oxalate), the ligand is said to be bidentate. Polydentate ligands are those that can bind to the metal ion through several donor atoms. Examples are  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$  and Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ ). EDTA is an important hexadentate ligand that can bind to a central metal ion through two nitrogen and four oxygen atoms.
- When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands
- Ligand which can ligate through two different atoms is called ambidentate ligand. Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly,  $\text{SCN}^-$  ion can coordinate through the Sulphur or nitrogen atom.



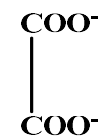
Ethylenediamine tetraacetate



Ethylenediamine



dimethyl glyoxime



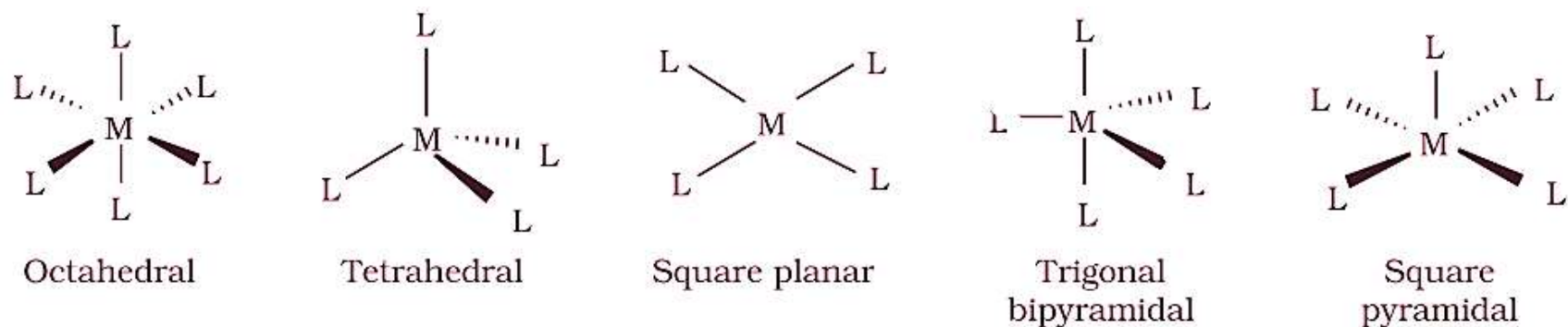
oxalato

**Coordination number** : The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions,  $[\text{PtCl}_6]^{2-}$  and  $[\text{Ni}(\text{NH}_3)_4]^{2+}$ , the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Co}(\text{en})_3]^{3+}$ , the coordination number of both, Fe and Co, is 6 because  $\text{C}_2\text{O}_4^{2-}$  and en (ethane-1,2-diamine) are bidentate ligands.

It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

**Coordination sphere** : The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere. The ionizable groups are written outside the bracket and are called counter ions. For example, in the complex  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , the coordination sphere is  $[\text{Fe}(\text{CN})_6]^{4-}$  and the counter ion is  $\text{K}^+$ .

**Coordination polyhedron**: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is octahedral,  $[\text{Ni}(\text{CO})_4]$  is tetrahedral and  $[\text{PtCl}_4]^{2-}$  is square planar. Fig. below shows the shapes of different coordination polyhedra.



- **Oxidation number of central atom** :The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in  $[\text{Cu}(\text{CN})_4]^{3-}$  is +1 and it is written as Cu(I).
- **Homoleptic and heteroleptic complexes** : Complexes in which a metal is bound to only one kind of donor groups, e.g.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g.,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ , are known as heteroleptic.

**Effective atomic number (EAN) :** *Effective atomic number (EAN), number that represents the total number of electrons surrounding the nucleus of a metal atom in a metal complex. It is composed of the metal atom's electrons and the bonding electrons from the surrounding electron-donating atoms and molecules. Thus, the effective atomic number of the cobalt atom in the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is 36, the sum of the number of electrons in the trivalent cobalt ion (24) and the number of bonding electrons from six surrounding ammonia molecules, each of which contributes an electron pair ( $2 \times 6 = 12$ ).*

*The English chemist Nevil V. Sidgwick made the observation, since known as the EAN rule, that in a number of metal complexes the metal atom tends to surround itself with sufficient ligands that the resulting effective atomic number is numerically equal to the atomic number of the noble-gas element found in the same period in which the metal is situated. This rule seems to hold for most of the metal complexes with carbon monoxide, the metal carbonyls, as well as many organometallic compounds.*

*By using this rule, it is possible to predict the number of ligands in these types of compounds and also the products of their reactions. The EAN rule is often referred to as the "18-electron rule" since, if one counts only valence electrons (6 for  $\text{Co}^{3+}$  and  $2 \times 6 = 12$  for 6  $\text{NH}_3$ ), the total number is 18.*



## IUPAC Nomenclature of Coordination Compounds

*The names of coordination compounds are derived by following the principles of additive nomenclature.*

- ❑ The cation is named first in both positively and negatively charged coordination entities.

$K_4[Fe(CN)_6]$  - Potassium hexacyano ferrate (II),  $[Ni(NH_3)_6]Cl_2$  - Hexammine nickel (II) chloride

- ❑ While naming complex ion always named ligands first followed by name of the metal.

$[Fe(CN)_6]^{3-}$  - Hexacyano ferrate (III),  $[Co(en)_3]^{3+}$  - Trisethylenediammine cobalt (III)

- ❑ Ligands are always named according to their alphabetical order, Names of the anionic ligands end in - o, those of neutral and cationic ligands are the same except aqua for  $H_2O$ , ammine for  $NH_3$ , carbonyl for CO and nitrosyl for NO.  $[NiCl_2(H_2O)_4]$  - Tetraqua dichloro nickel (II)

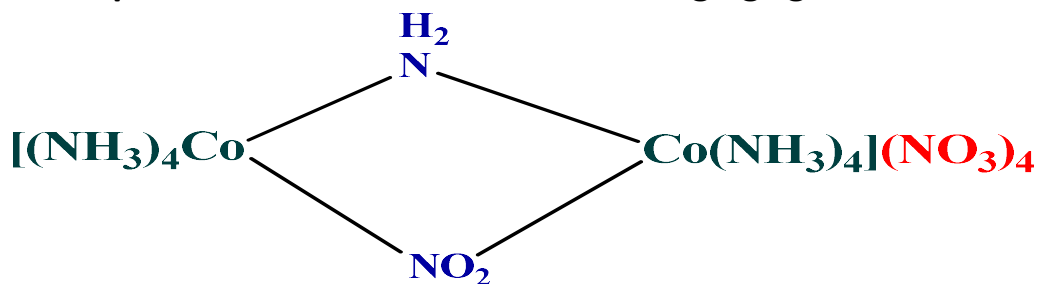
- ❑ Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses.

For example,  $[NiCl_2(PPh_3)_2]$  is named as dichloro bis(triphenylphosphine) nickel (II).

## IUPAC Nomenclature of Coordination Compounds

*The names of coordination compounds are derived by following the principles of additive nomenclature.*

- ❑ Naming the bridging ligands: Ligands that bridge between the two coordination centers designated by Greek word  $\mu$ , which is repeated before the each kind of bridging ligand.



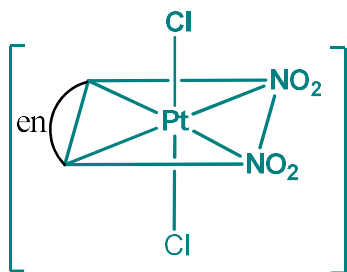
*Octammine  $\mu$ -amido  $\mu$ -nitrito N dicobalt (III) nitrate*

- ❑ Ambidentate ligands are named by placing the symbol of an element attached with metal followed by its name. e.g.  $\text{NO}_2^-$  - when linked through 'N' it is named as nitrito (N) while through 'O' it is named nitrito (O).



### *IUPAC Nomenclature of Coordination Compounds*

- ❑ If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion,  $[\text{Co}(\text{SCN})_4]^{2-}$  is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.
- ❑ The neutral complex molecule is named similar to that of the complex cation.
- ❑ Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
- ❑ Geometrical isomers are named using the prefixes cis or trans or by a numbering system if the structure is complicated.



*1,6 dichloro 4,5 (ethylene diamine) 2,3 dinitrito N platinum (IV)*

- ❑ The solvent of crystallization is named after the name of the complex, number of solvent molecules are designated by Arabic numeral.

$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  – *Tetrammine copper (II) sulphate-1-hydrate.*

## ***Valence Bond Theory (VBT)***

*Many approaches have been put forth to explain the nature of bonding in coordination compounds viz. Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT). Valence Bond Theory was proposed by Linus Pauling to explain the bonding and properties of coordination complexes. The salient features of this theory are as follows:*

- *Coordination compounds consist of complex ions, in which ligand coordinates with the metal.*
- *The central metal atom or ion makes available a number of orbitals equal to its coordination number for bonding with suitable ligand.*
- *These atomic orbitals of metal atom or ion hybridize to give an equal number of hybrid orbitals of equal energy. The type of hybridization decides geometry of the complex.*
- *Each ligand must possess at least one orbital containing a lone pair of electrons.*
- *The inner d-orbitals, i.e.  $(n-1)d$  or the outer d-orbitals, i.e.  $nd$  orbitals of the metal atom or ion may get involved in the hybridization. The complexes formed with the involvement of  $(n-1)d$  orbitals are called inner orbital complexes or low spin complexes. On the other hand, the complexes formed with  $nd$  orbitals are called outer orbital complexes or high spin complexes.*

## Valence Bond Theory (VBT)

- *The formation of sigma covalent bond takes place by axial overlap of vacant hybrid orbitals of the metal with filled orbitals of the ligand.*
- *The strength of bond formed depends upon the extent of overlap.*
- *The compound which contain all the paired electrons is diamagnetic , while which contains one or more unpaired electrons is paramagnetic in nature.*
- *If metal possess filled  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals and ligands with empty  $\pi^*$  orbital, M-L  $\pi$  bonding takes place.*

### Application of Valence Bond Theory (VBT)

#### ❑ Complexes with CN = 4

Two types of complex formation is possible. When the hybridization of metal atom /ion is  **$dsp^2$** , square planar complexes are formed and are low spin or spin restricted or spin paired complexes. Eg.  $[\text{Ni}(\text{CN})_4]^{2-}$

When the hybridization of metal atom /ion is  **$sp^3$** , tetrahedral complexes are formed and are usually high spin or spin free complexes. eg.  $[\text{CuCl}_4]^{2-}$

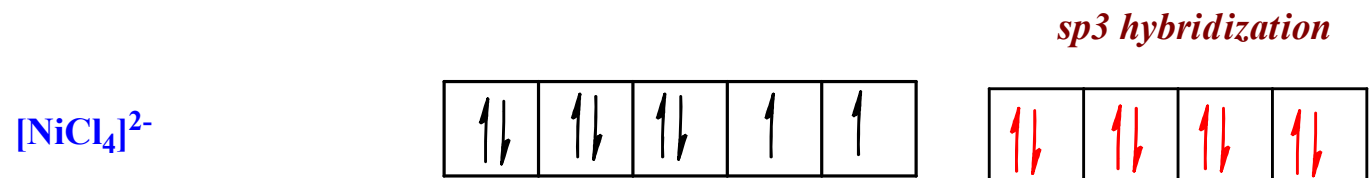
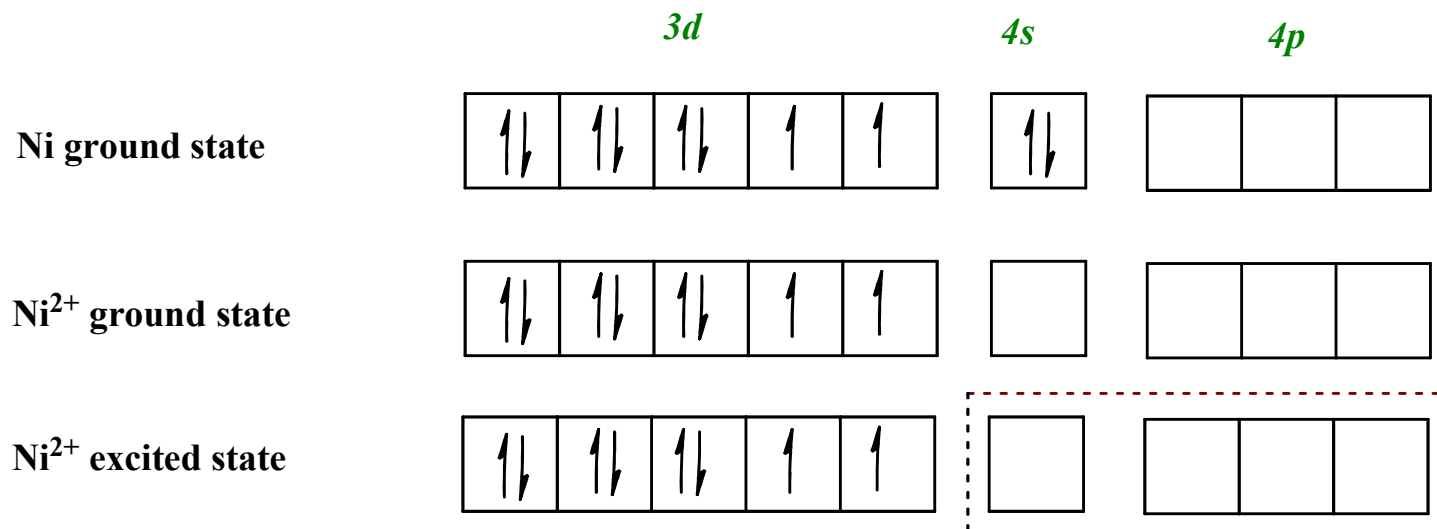
#### ❑ Complexes with CN = 6

When the CN=6 of the central metal atom/ion is 6 then possible hybridization are  **$d^2sp^3$  or  $sp^3d^2$**  in both the cases the geometry of the complex is an octahedral.

### ***Tetrahedral complexes***

***In tetrahedral complexes one s and three p orbitals are hybridized to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for  $[\text{NiCl}_4]^{2-}$***

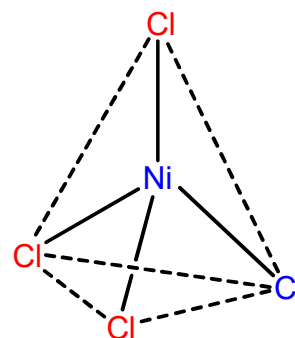
- Here nickel is in +2 oxidation state and the ion has the electronic configuration  $[\text{Ar}] 3d^8$ .***
- The  $\text{Ni}^{2+}$  get excited when come in intimate contact with  $\text{Cl}^-$  ligands.***
- The vacant one 4s and three 4p orbitals of  $\text{Ni}^{2+}$  undergo  $sp^3$  hybridization to form four  $sp^3$  hybrid orbitals.***
- The resulting four  $sp^3$  hybrid orbitals are directed towards the four corners of regular tetrahedron.***
- Each hybrid orbital overlap with the filled ligand orbital to form a sigma bond.***
- The complex possess two unpaired electrons so it is paramagnetic in nature.***
- The hybridization scheme is as shown in diagram.***



Electrons of Ni<sup>2+</sup>

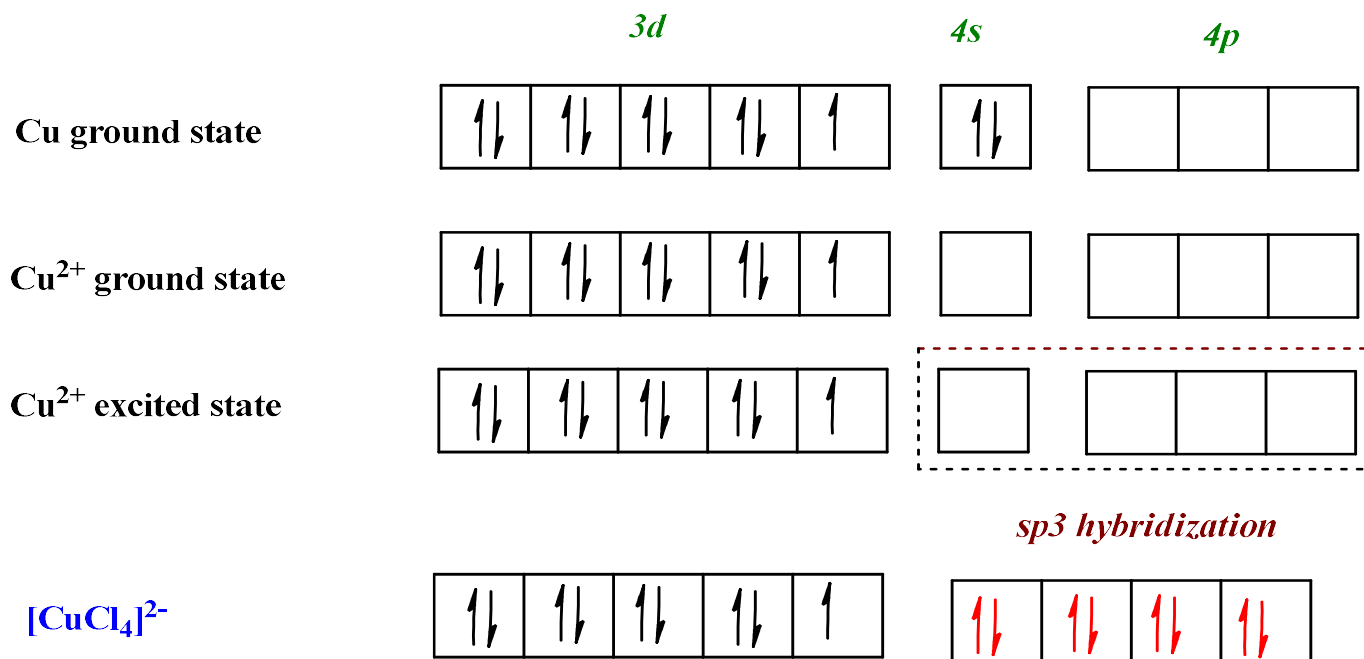


Electrons of Chloro ligands



*Tetrahedral*

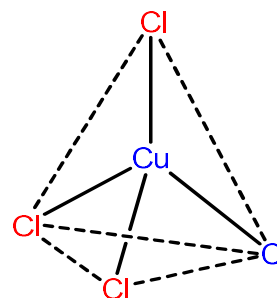
**$[\text{CuCl}_4]^{2-}$  Tetra chloro cuprate (II)**



Electrons of  $\text{Cu}^{2+}$



Electrons of Chloro ligands



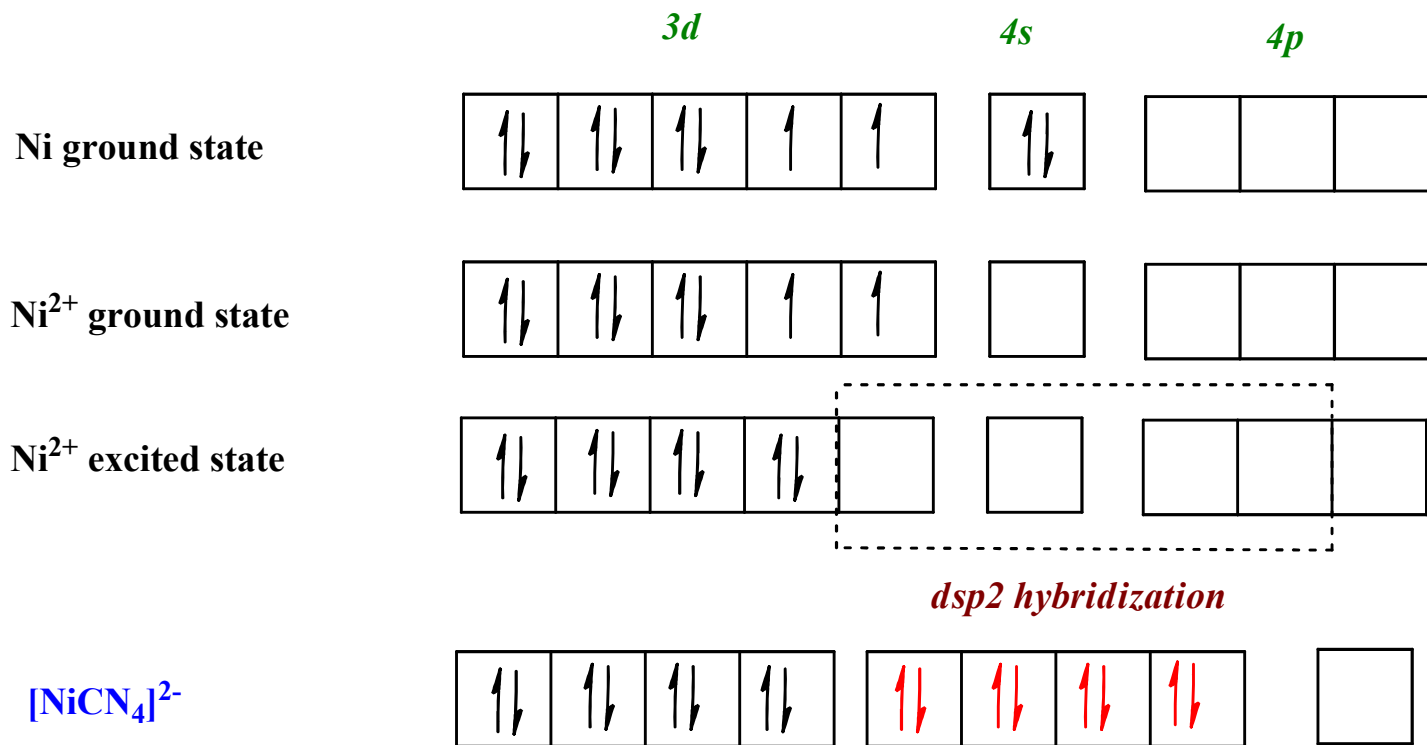
*Tetrahedral*



## ***Square planar complexes***

***In square planar complexes one d, one s and two p orbitals are hybridized to form four equivalent orbitals oriented in square planar manner . This is illustrated below for  $[\text{NiCN}_4]^{2-}$***

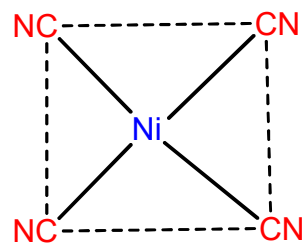
- Here nickel is in +2 oxidation state and the ion has the electronic configuration  $[\text{Ar}] 3d^8$  .***
- The  $\text{Ni}^{2+}$  get excited when come in intimate contact with  $\text{CN}^-$  ligands.***
- Here cyanide ( $\text{CN}^-$ )being a strong field ligand forces nickel electrons inside to pair up.***
- The vacant one 3d, one 4s and two 4p orbitals of  $\text{Ni}^{2+}$  undergo dsp<sup>2</sup> hybridization to form four dsp<sup>2</sup> hybrid orbitals.***
- The resulting four dsp<sup>2</sup> hybrid orbitals are directed towards the four corners to form square planar geometry .***
- Each hybrid orbital overlap with the filled ligand orbital to form a sigma bond.***
- The complex possess all the electrons paired so it is diamagnetic in nature.***
- The hybridization scheme is as shown in diagram.***



Electrons of Ni<sup>2+</sup>



Electrons of Cyano ligands



*Square planar*

## Octahedral complexes

When CN of metal in a complex is 6, geometry of complex will be octahedral. Here observed hybridization is  $sp^3d^2$  or  $d^2sp^3$ . Two 'd', one 's', and three 'p' orbitals involved in the hybridization accounting octahedral geometry. When inner 'd' orbitals i. e.  $(n-1)$  d orbitals are used for the hybridization ( $d^2sp^3$ ), complex formed is called inner orbital complex, while when outer d orbitals i. e. nd orbitals are used for the hybridization ( $sp^3d^2$ ), complex formed is called outer orbital complex. Linus Pauling referred inner orbital complex as hypoligated complexes, while outer orbital complex as hyperligated complexes. Usually inner orbital complexes are low spin complexes while those of outer orbital complexes are high spin complexes.

e.g.  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{CoF}_6]^{3-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$

### ***Formation of $[\text{FeF}_6]^{3-}$ Hexafluoro ferrate (III)***

- ***In this complex iron is the central metal ion with +3 oxidation state***
- ***The electronic configuration of  $\text{Fe}^{3+}$  is  $[\text{Ar}] 3d^5$ .***
- ***The  $\text{Fe}^{3+}$  get excited when come in intimate contact with  $\text{F}^-$  ligands.***
- ***$\text{F}^-$  being a weak field ligand and hence no internal rearrangement of 'd' electrons of  $\text{Fe}^{3+}$  is possible.***
- ***One 4s, three 4p and two 4d orbitals of  $\text{Fe}^{3+}$  are undergo hybridization i.e.  $sp^3d^2$ .***
- ***Each hybrid orbital overlap with the filled ligand orbital to form a sigma bond.***
- ***The complex possess five unpaired electrons so it is highly paramagnetic in nature.***
- ***The hybridization scheme is as shown in diagram.***

**$[\text{FeF}_6]^{3-}$  Hexafluoro ferrate (III)**

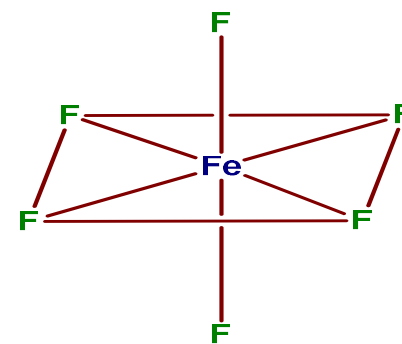
	<i>3d</i>	<i>4s</i>	<i>4p</i>	<i>4d</i>
<b>Fe in GS</b>	$\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow\downarrow$		
<b><math>\text{Fe}^{3+}</math> in GS</b>	$\uparrow \uparrow \uparrow \uparrow \uparrow$			
<b><math>\text{Fe}^{3+}</math> in ES</b>	$\uparrow \uparrow \uparrow \uparrow \uparrow$			
		<i>sp3d2 hybridization</i>		
<b><math>[\text{FeF}_6]^{3-}</math></b>	$\uparrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$		



**Electrons of  $\text{Fe}^{3+}$**



**Electrons of Fluoro ligands**



**Octahedral**

### ***Formation of $[\text{FeCN}_6]^{3-}$ Hexacyano ferrate (III)***

- ***In this complex iron is the central metal ion with +3 oxidation state***
- ***The electronic configuration of  $\text{Fe}^{3+}$  is  $[\text{Ar}] 3d^5$ .***
- ***The  $\text{Fe}^{3+}$  get excited when come in intimate contact with  $\text{CN}^-$  ligands.***
- ***$\text{CN}^-$  being a strong field ligand and hence internal rearrangement of 'd' electrons of  $\text{Fe}^{3+}$  takes place.***
- ***Two 3d, One 4s, and three 4p orbitals of  $\text{Fe}^{3+}$  are undergo hybridization i.e.  $d^2sp^3$ .***
- ***Each hybrid orbital overlap with the filled ligand orbital to form a sigma bond.***
- ***All the electrons in the complex are paired so it is diamagnetic in nature.***
- ***The hybridization scheme is as shown in diagram.***

# Formation of $[\text{FeCN}_6]^{3-}$ Hexacyano ferrate (III)

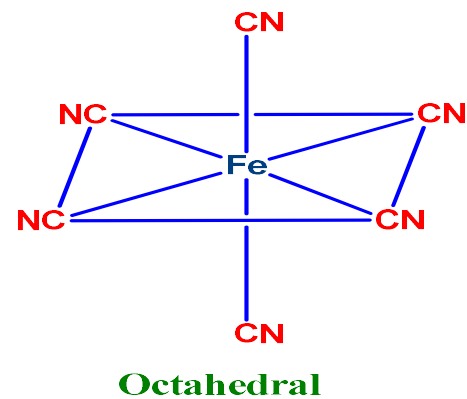
	3d	4s	4p	4d
Fe in GS	$\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$	$\uparrow\downarrow$		
$\text{Fe}^{3+}$ in GS	$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$			
$\text{Fe}^{3+}$ in ES	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$			
	<i>d2sp3 hybridization</i>			
$[\text{FeCN}_6]^{3-}$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$		



Electrons of  $\text{Fe}^{3+}$



Electrons of Cyano ligands



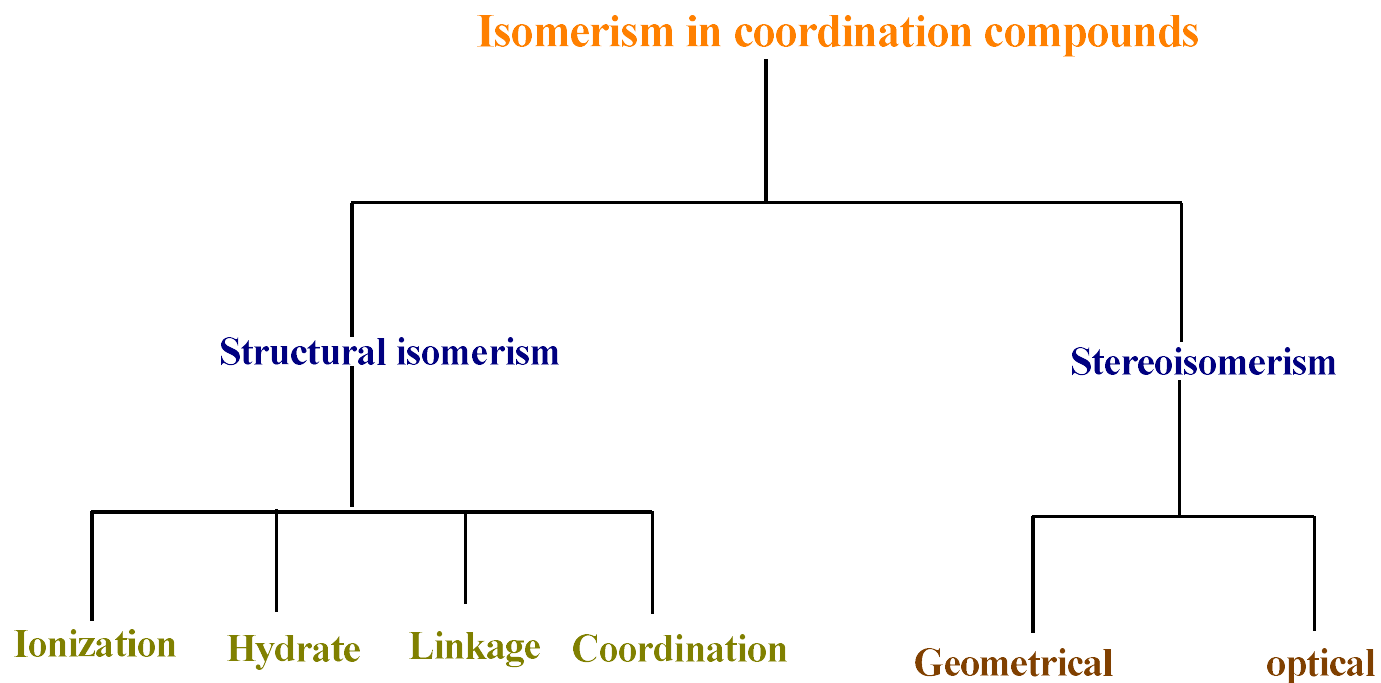
## Limitations of VBT:

- ☐ This theory fails to explain the colour of the complexes.
- ☐ This theory fails to explain the magnetic properties of the complexes quantitatively.
- ☐ It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- ☐ It does not account the splitting of 'd' orbitals of metal.
- ☐ This theory does not provide an explanation for the relative energies of the different geometries of the complexes.
- ☐ It does not give any idea about reactivity of complexes.
- ☐ Relative strength of ligands is not explained properly.



## *Isomerism in Coordination Compounds*

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.



➤ **Ionisation Isomerism:**

*This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .*



➤ **Solvate Isomerism:**

*This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and its solvate isomer  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (grey-green).*

➤ **Linkage Isomerism:**

*Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand,  $\text{NCS}^-$ , which may bind through the nitrogen to give  $\text{M-NCS}$  or through Sulphur to give  $\text{M-SCN}$ .*

*Jorgensen discovered such behavior in the complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ , which is obtained as the red form, in which the nitrite ligand is bound through oxygen ( $-\text{ONO}$ ), and as the yellow form, in which the nitrite ligand is bound through nitrogen ( $-\text{NO}_2$ ).*

➤ **Coordination Isomerism:**

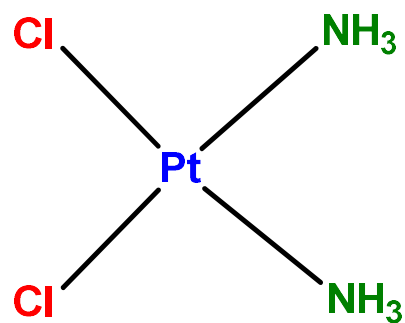
*This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ , in which the  $\text{NH}_3$  ligands are bound to  $\text{Co}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Cr}^{3+}$ . In its coordination isomer  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ , the  $\text{NH}_3$  ligands are bound to  $\text{Cr}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Co}^{3+}$ .*

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement.

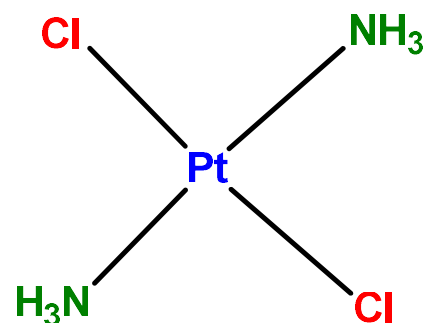
Structural isomers have different bonds. A detailed account of these isomers are given below.

### *Geometric Isomerism:*

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found with coordination numbers 4 and 6. In a square planar complex of formula  $[M X_2 L_2]$  (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted in Fig.



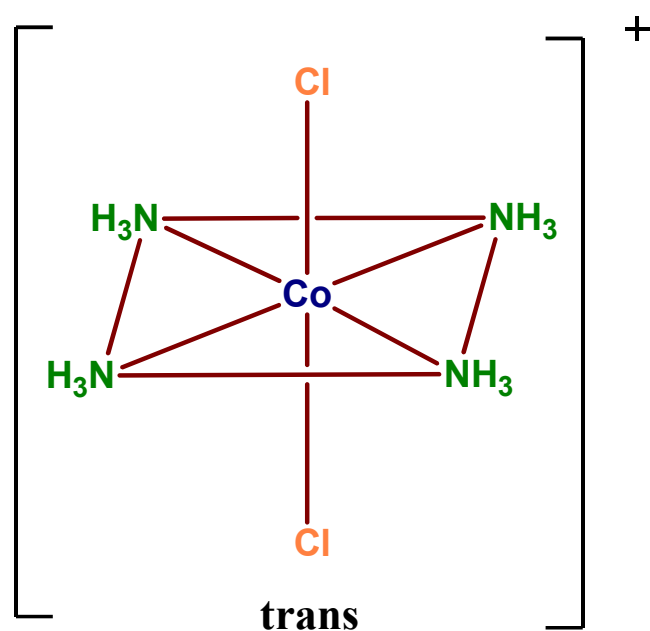
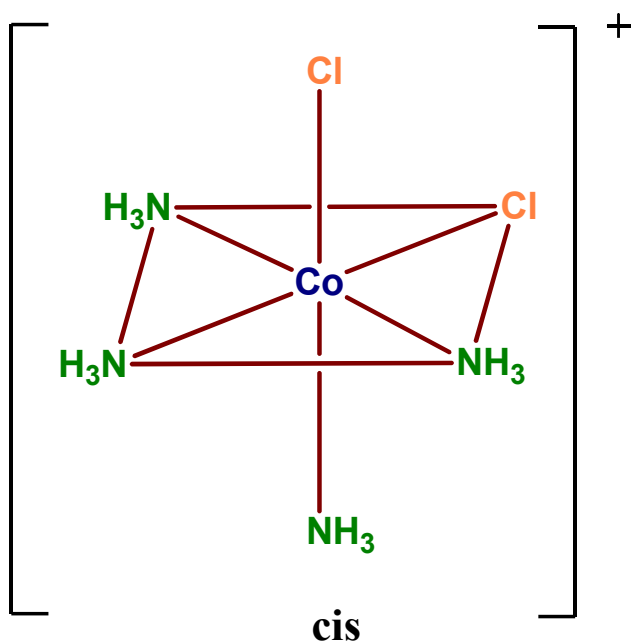
cis



trans

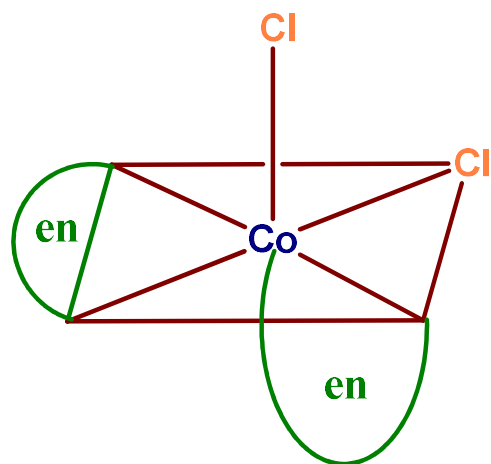
### Geometric Isomerism:

Other square planar complex of the type  $\text{MABXL}$  (where A, B, X, L are unidentate ligands) shows three isomers—two cis and one trans. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behavior is possible in octahedral complexes of formula  $[\text{MX}_2\text{L}_4]$  in which the two ligands X may be oriented cis or trans to each other. e.g.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

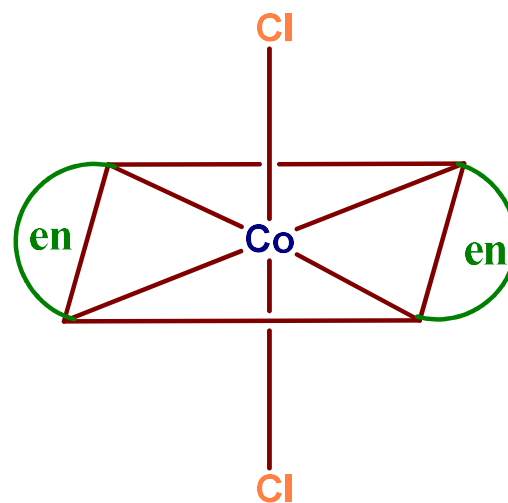


### *Geometric Isomerism:*

This type of isomerism also arises when didentate ligands L-L [e.g.,  $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$  (en)] are present in complexes of formula  $[\text{MX}_2(\text{L-L})_2]$ . e.g.  $[\text{CoCl}_2(\text{en})_2]$ .



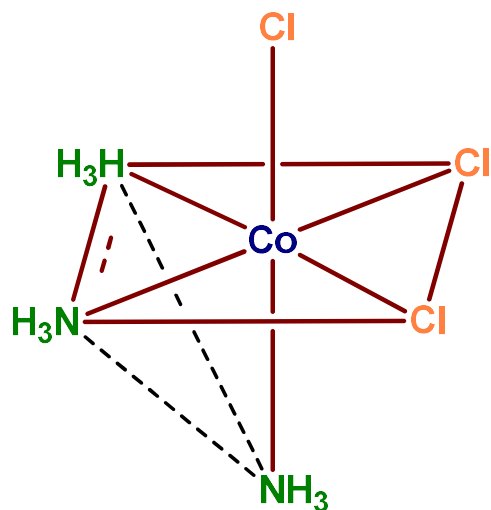
cis



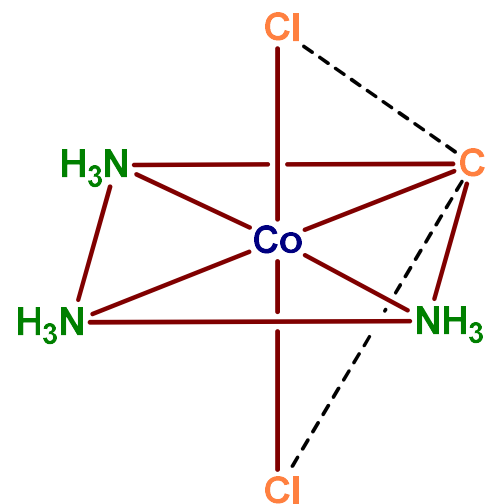
trans

### Geometric Isomerism:

Another type of geometrical isomerism occurs in octahedral coordination entities of the type  $[Ma_3b_3]$  like  $[Co(NH_3)_3(Cl)_3]$ . If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer



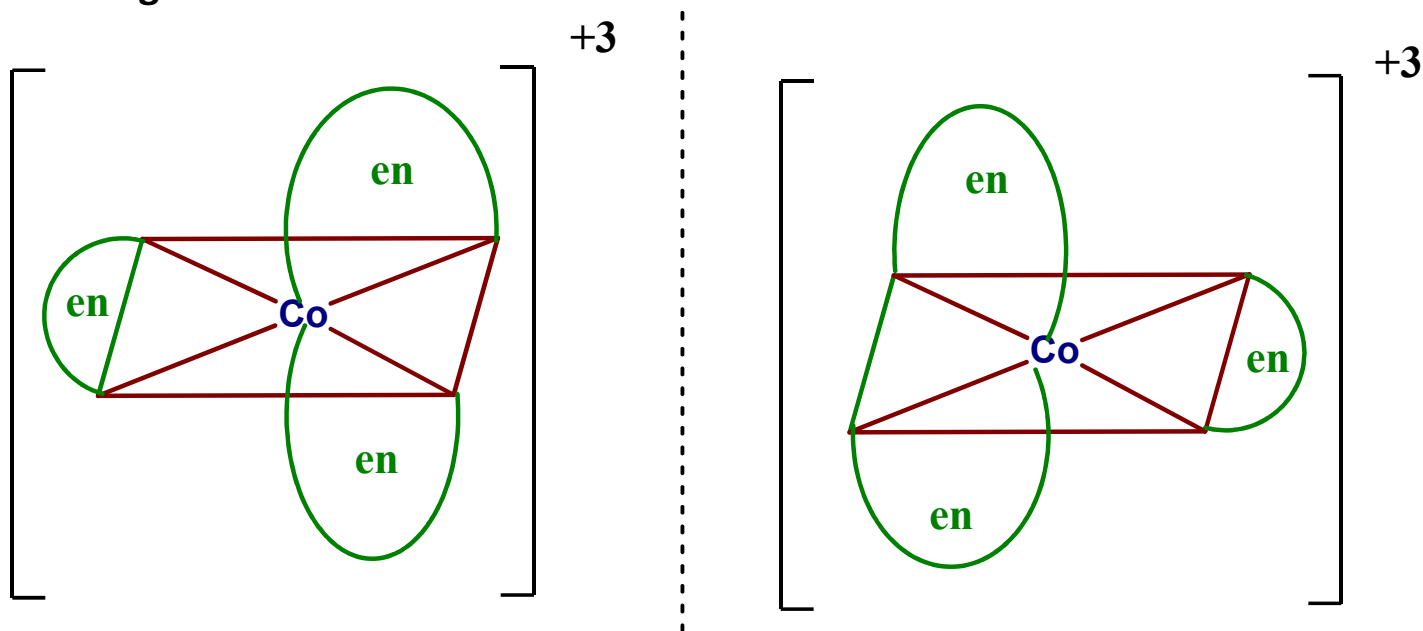
facial (fac)



meridional (mer)

### Optical Isomerism:

Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands.





In a coordination entity of the type  $[\text{CoCl}_2(\text{en})_2]$ , only the cis-isomer shows optical activity, trans form is optically inactive due to the presence of plane of symmetry.

