

SRIMAAN COACHING CENTRE-TRICHY-UG-TRB CHEMISTRY-  
UNIT-III STUDY MATERIAL- TO CONTACT:8072230063.

2022-23  
SRIMAAN

# SRIMAAN

## UG-TRB

## CHEMISTRY

### UNIT-III- COORDINATION CHEMISTRY

### UG-TRB MATERIALS

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**SRIMAAN COACHING CENTRE-TRICHY.**

**TO CONTACT:8072230063.**

**UG-TRB:CHEMISTRY**

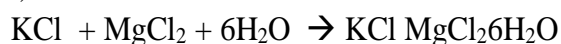


### UNIT-III-COORDINATION CHEMISTRY

When two or more stable compounds are mixed in stoichiometric amounts, two types addition compounds are formed. 1) Double salt and 2) Complex salts.

**Double salts:** Compounds formed by the combination of two or more stable chemical compounds which loses their identity in solution. They breakdown into constituent component. Each constituent ions can be identified.

Eg: Carnalite ( $\text{KCl MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), Mohr's salt ( $\text{FeSO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ), Potash alum ( $\text{K}_2\text{SO}_4 \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ )



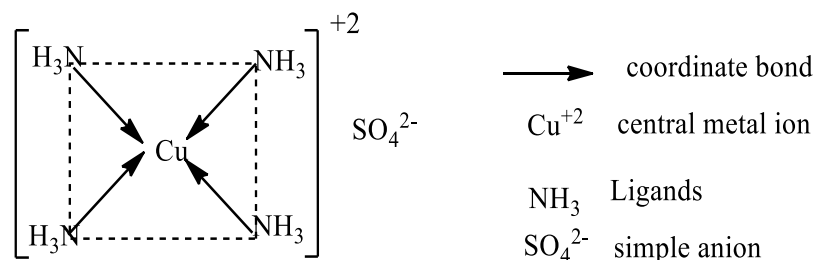
**Complex salts:** "Compounds formed by the combination of two or more stable compounds which retain their identity in solid as well as in solution". They does not breakdown into constituent component. Each constituent ions cannot be identified.

$\text{FeSO}_4 + 6\text{KCN} \rightarrow \text{K}_4[\text{Fe}(\text{CN})_6] + \text{K}_2\text{SO}_4$        $\text{CuSO}_4 + 4\text{NH}_4\text{OH} \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$  Eg:  
Potassiumferrocyanide  $\text{K}_4[\text{Fe}(\text{CN})_6]$       Cupramoniumsulphate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ . Potassium ferrocyanide gives reactions of  $\text{K}^+$  ion but not  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions.

#### Coordination compounds (Complex Compounds):

"A compounds formed by the combination of two are more stable species which retain their identity in the solid as well as dissolved state".

Properties complex compounds are completely different from those of the constituents". A Complex compound contains central metal atom or ion attached to other ions or molecules through the coordinate bond. Eg:  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ .

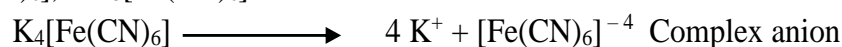


These compounds produce a complex ion in their aqueous solution.

**Types of complex compounds:** Complex compounds are of three types, Anionic, cationic and neutral complex compounds.

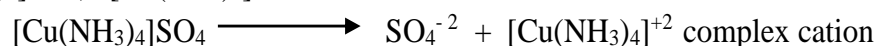
**Anionic complex:** Complex compounds which give negatively charged complex ions in aqueous solution are called anionic complexes.

Eg:  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$



**Cationic complex:** Complex compounds which give positively charged complex ions in aqueous solution are called cationic complexes.

Eg:  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$



**Neutral complex:** Complex compounds which does not ionize in aqueous solution are called neutral complexes.

Eg:  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

**Complex ion:** "A charged species containing central metal atom or ion bonded to other ions or molecules through the coordinate bonds is called complex ion."

**Complex cation:** "A positively charged species containing central metal atom or ion bonded to other ions or molecules through the coordinate bonds is called complex ion."

Eg:  $[\text{Cu}(\text{NH}_3)_4]^{+2}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

**Complex anion:** "A negatively charged species containing central metal atom or ion bonded to other ions or molecules through the coordinate bonds is called complex ion."

Eg:  $[\text{Fe}(\text{CN})_6]^{-4}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$

**Ligands:** "Ions or molecules which donate at least a pair of electron to the central metal atom or ion to form coordinate bond are called ligands".

Ligands bonded to the central metal atom or ion through the coordinate bond ( $\text{M} \leftarrow \text{L}$ ).

Ligands must have at least one lone pair of electrons (Lewis bases).

An atom in a ligand which provide a pair of electron for bonding with metal atom/ion is called **donor atom**.

Eg: Ions like,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_2^+$ ,  $\text{NO}^+$  and neutral molecules like  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  are ligands.

### Classification of Ligands:

Based on the charge carried on them, ligands are classified into negative, positive and neutral ligands.

- Negative ligands: Ligands which carry negative charge, Eg:  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{Br}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,
- Positive ligands: Ligands which carry positive charge, Eg:  $\text{NO}_2^+$  (nitronium)  $\text{NO}^+$  (nitrasonium)
- Neutral ligands: Ligands which carry no charge, Eg:  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_5\text{H}_5\text{N}$  (pyridine) (py),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethylenediamine (en)).  $\text{PH}_3$  (phosphine)  $(\text{C}_6\text{H}_5)_3\text{P}$  Triphenyl phosphine (PPh<sub>3</sub>)

Based on the number of the donor atoms present in them, ligands are classified into monodentate, bidentate, and polydentate ligands.

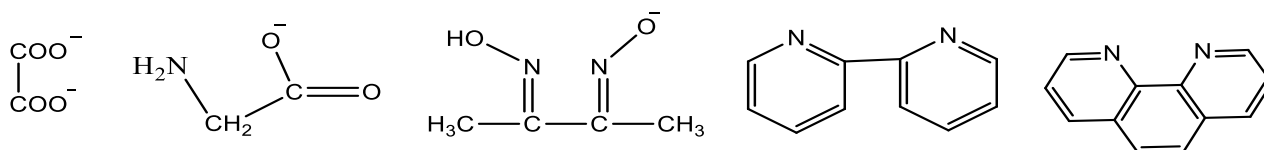
1. **Monodentate Ligands:** Ligands that bonded to central metal atom through one donor atom are called monodentate ligands.

Ex:  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{C}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$  etc.,

2. **Bidentate Ligands:** Ligands that bonded to central metal atom through two donor atom are called bidentate ligand.

Example: (i) ethane-1,2-diamine (en);  $\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$  The ligand has two nitrogen atoms with a lone pair of electrons.

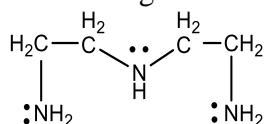
(ii) oxalate ion(ox) (iii) Glycinate ion(gly) (iv) DMG (v) 2,2-dipyridyl (vi) 1,10-Phenanthroline



3) **Polydentate Ligands:** Ligands that bonded to central metal atom through more than two donor atoms present in the molecule are called polydentate ligands.

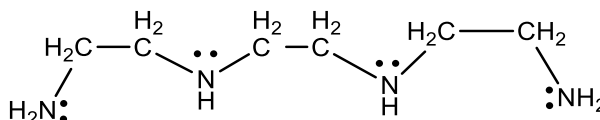
a. **Tridentate Ligands:** Ligands that bonded to central metal atom through three donor atoms are called Tridentate Ligands.

Example: diethylene triamine (dien) Dien has three nitrogen atoms with lone pair of electrons.



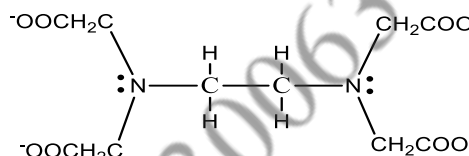
b. **Tetradentate Ligands:** Ligands that bonded to central metal atom through four donor atoms are called Tetradentate Ligands.

Example: Triethylenetetramine(trien):



c. **Hexadentate Ligands:** Ligand that bonded to central metal atom through six donor atoms are called Hexadentate Ligand.

Eg: Ethylene diamine tetra acetate (EDTA)



**Denticity:** The number of atoms (ligating atoms) in a ligand, which donate electron pair is called Denticity.

**Chelating Ligand:**

“*Bidentate or Polydentate ligand bonded to the same central metal atom or ion through two or more donor atoms forming a ring structure is called Chelating ligand.*”

Bidentate or polydentate ligands hold the metal ion like a claw.

Complexes containing polydentate ligands are chelate complexes. Eg:  $[\text{Cu}(\text{en})_2]$



**Ambidentate ligands:** Monodentate ligand bonded to central metal atom through different donor atom is called ambidentate ligand.

Eg:  $-\text{NO}_2$  (nitrito-N),  $-\text{ONO}$  (nitrito-O),  $-\text{SCN}$  (thiocyanato-S),  $-\text{NCS}$  (thiocyanato-N)

**Coordination Number:**

“*The number of coordinate bonds between the ligands and central metal atom or ion in the complex is called coordination number.*”

Ex: (1) Coordination number of copper in cuprammonium sulphate,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  is 4, that is four ammonia molecules bonded to the central copper metal ion through the coordinate bond.

(2) Coordination number of iron in potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is 6, that is six cyanide ions bonded to the central iron metal ion through the coordinate bond.

**Coordination sphere or coordination entity** “*The central metal atom or ion together with molecules or ions coordinated to it is called coordination sphere.*”

In writing the formula of the coordination compound, the coordination sphere is written inside the square brackets [ ]. It does not ionize to give the constituent ions. The ionisable species are written outside the square bracket.

For example, in cuprammonium sulphate, the part  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is coordination sphere.

**Oxidation number of central metal in complex:**

It is charge possessed by the central metal atom in the complex compound.

Oxidation state of the central metal ion is calculated by the usual method. In a molecules, the sum of oxidation number of all the atoms or groups is equal to zero.

In ions, the sum of the oxidation number of the all the atoms or groups is equal to charge on the ion.

Eg: The oxidation number Fe in  $K_4[Fe(CN)_6]$ ;

Let  $x$  is the oxidation state of Fe

$$+1 \times 4 + x + 6(-1) = 0, \quad x = +2$$

The oxidation number of Cu in  $[Cu(NH_3)_4]SO_4$ ;

Let  $x$  is the oxidation state of Cu

$$x + 4(0) + 1(-2) = 0, \quad x = +2$$

The oxidation number of Ni in  $[Ni(CO)_4]$ ;

Let  $x$  is the oxidation state of Ni

$$x + 4(0) = 0, \quad x = 0$$

The Oxidation number of Co in  $[Co(H_2O)_6]^{+3}$

Let  $x$  is the oxidation state of Co

$$x + 6(O) = +3, \quad x = +3$$

### IUPAC Nomenclature of coordination compounds:

Name of the simple cation	Names of the ligands in alphabetical order	Name of the central metal atom or ion	(Oxidation No. of the central metal in roman numerical)	Name of simple anion
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1. Names of the complex compounds begin with small letter.

2. **Order of naming ions:** The cation is named first, followed by the name of anion.

Ex: In  $K_4[Fe(CN)_6]$ , the name of  $K^+$  and in  $[Co(NH_3)_6]Cl_3$ , name of  $[Co(NH_3)_6]^{3+}$  is written first.

2. **Name of coordination sphere:** Names of the ligands are written first followed by the name central metal atom. The name of coordination sphere is written as one word.

3. **Naming of the ligands:** a) The name of different ligands are written in the alphabetic order of their names.

Eg: In  $[Pt BrCl(NO_2)NH_3]$ . The order of writing the name of the ligands is ammino, bromo, chloro, nitrito-N

b) Names of negative ligands end with 'O'. Eg:  $Cl^-$  (chloro),  $OH^-$  (hydroxo),  $CN^-$  (cyano) etc,

c) Names of the positive ligands end with 'ium'.  $NO^+$  (nitrosonium),  $NH_2^-$   $NH_3^+$  (hydrazinium),  $NO_2^+$  (nitronium)

d) Names of neutral ligands in a majority of cases is the same as the name of the molecules.

Eg:  $H_2NCH_2CH_2NH_2$  (ethylenediamine),  $C_5H_5N$  (peridine),  $(C_6H_5)_3P$  (triphenylphosphene)

However, for a few neutral ligands, special names are used.  $H_2O$  (aqua),  $NH_3$  (ammine),  $NO$  (nitrosyl),  $CO$  (carbonyl).

4. **Numerical prefix to indicate the number of ligands:** If more than one same kind ligands are present in the complex, the number of ligands are indicated by Greek prefixes di, tri, tetra, penta, hexa, etc.

Eg: Dichloro indicates, two  $Cl^-$  ligands; Pentaqua denotes five  $H_2O$  ligands,

If the ligand itself contain Greek prefix di, tri, tetra, etc., then number of ligands are indicated by the prefixes bis, tris, tetrakis, pentakis, followed by the name of the ligand in bracket.

Eg:  $(H_2NCH_2CH_2NH_2)_2$  as bis(ethylenediamine)  $((C_6H_5)_3P)_6$  hexakis(triphenylphosphine).

5. **Naming of the central metal atom or ion:**

(a) In a neutral or cationic complex no change in the name of the central metal atom.

Eg:  $[Ni(CO)_4]$ , tetracarbonyl nickel.

(b) In an anionic complexes the name of the metal atom or ion end with suffix – 'ate', such as cobaltate, cuprate, chromate. Ferrate, Argentate, Nickelate, Zincate, (Latin names)

Eg:  $K_4[Fe(CN)_6]$ ; potassium hexacyanoferrate.

6. **Oxidation state of the central metal ion:** The oxidation state of the central metal atom /ion is denoted by Roman numeral in small bracket.

Eg:  $[Ni(CO)_4]$ ; tetracarbonylnickel(0)

$K_4[Fe(CN)_6]$ ; potassium hexacyanoferrate (II)

7. **Bridging ligand:** A ligand which is attached directly to two metal atoms/ions is called a bridging ligand,

The name of the bridging ligand is indicated by adding the prefix  $\mu$ -before the name of the ligand.

Eg:  $-(OH)_2-$  di- $\mu$ -hydroxo.

8. Name of the complex ion end with ion.

Negative ligands			Negative ligands			Negative ligands		
Formula	Name	Donor atom	Formula	Name	Donor Atom	Formula	Name	Donor atom
$F^-$	fluoro	F	$CH_3COO^-$	acetate	O	$O^{2-}$	oxido	O
$Cl^-$	chloro	Cl	$S^{2-}$	sulphido	S	$O_2^-$	superoxido	O
$Br^-$	Bromo	Br	$CO_3^{2-}$	carbonato	O	$NO_2^-$	nitrito-N	N
$I^-$	Iodo	I	$NH_2^-$	amido	N	$ONO^-$	nitrito -O	O
$OH^-$	hydroxo	O	$NH_2^-$	imido	N	$NO_3^-$	nitrato	O
$CN^-$	cyano	C	$SCN^-$	thiocyanato-S	S	$C_2O_4^{2-}$	oxalato(ox)	O
$H^-$	hydrido	H	$NCS^-$	thiocyanato-N	N	$SO_4^{2-}$	sulphato	O
Neutral Ligands			Positive Ligands					
Formula	Name	Donor Atom	Formula	Name	Donor Atom			
$H_2O$	aqua	O	$NO^+$	nitosonium	N			
$NH_3$	ammine	N	$NO_2^+$	nitronium	N			
CO	carbonyl	C	$H_2N-NH_3^+$	hydrazinium	N			
NO	nitrosyl	N	$H_3O^+$	hydronium	O			
$C_5H_5N$	pyridine(py)	N						
$H_2NCH_2CH_2NH_2$	ethylene diamine(en)	N						
$PH_3$	phosphine	P						
$Ph_3P$	triphenyl phosphine	P						

#### IUPAC name of some coordination compounds

Formula	IUPAC Names
1. $[Fe(CO)_5]$	pentacarbonyliron(0)
2. $K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III)
3. $K_2[Cu(CN)_4]$	potassium tetracyanocuprate(II)
4. $K_3[Cr(C_2O_4)_3]$	potassium trioxalatochromate(III)
5. $Na_3[Co(NO_2)_6]$	sodium hexanitrito-N-cobaltate (III)
6. $[Zn(OH)_4]^{2-}$	tetrahydroxozincate (II) ion
7. $[CrCl(H_2O)_5]Cl_2$	petaaquachlorochromium (III) Chloride
8. $[CuBr_4]^{2-}$	tetrabromocuprate(II) ion
9. $[CoCl_2(NH_3)_4]^+$	tetraamminedichlorocobalt(III)ion
10. $[CrCl_3(NH_3)_3]$	triamminetrichlorochromium(III)
11. $[Co(NH_3)_6]Cl_3$	hexaammincobalt(III) chloride
12. $[Co(ONO)(NH_3)_5]Cl_2$	pentaamminenitrito-O-cobalt(III) chloride
13. $[Cr(NO_2)_3(NH_3)_3]$	triamminetrinitrito-N-chromium(III)
14. $[Co(NH_3)_5(H_2O)]Cl_3$	pentaammineaquacobalt(III) chloride
15. $[Ag(NH_3)_2]Cl$	diamminesilver(I) Chloride
16. $[PtCl_4(NH_3)_2]$	diamminetetrachloroplatinum(IV)

17. $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	tetraamminecopper(II) sulphate
18. $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	tetraammineplatinum(II)tetrachloroplatinate (II)
19. $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	trioxalatocobaltate(III) ion
20. $[\text{Co}(\text{en})_3]_2 (\text{SO}_4)_3$	tris(ethanediamine)cobalt(III) sulphate
21. $[\text{CoClCNNO}_2(\text{NH}_3)_3]$	triamminechlorocyanonitrito-Ncobalt(III)
22. $[\text{Cr}(\text{en})_3]\text{Cl}_3$	tris(ethylenediamine)chromium(III) Chloride
23. $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	tertapridineplatinum(II)tetrachloroplatinate(II)
24. $[\text{Fe}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$	hexaamminoiron(III)hexacyanochromate(III)
25. $(\text{NH}_4)_2[\text{CuCl}_4]$	ammonium tetrachlorocuprate(II)
24. $[\text{Fe}(\text{C}_5\text{H}_5)_2]$	bis(cyclopentadienyl)iron(0)
25. $[(\text{C}_2\text{O}_4)_2\text{Cr}(\text{OH})_2\text{Cr}(\text{C}_2\text{O}_4)_2]^{4-}$	$\mu$ -dihydroxotetraoxalatodichromate(III)ion
26. $[(\text{NH}_3)_5\text{Co}-(\text{NH}_2)-\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$	$\mu$ -amidodecaamminedicobalt(III) nitrate
26. $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$	$\mu$ -hydroxodecaamminedichromium(III) chloride
$\left[ (\text{NH}_3)_4\text{Co} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NO}_2 \end{array} \text{Co}(\text{NH}_3)_4 \right] (\text{NO}_3)_4$	$\mu$ -amido- $\mu$ -nitrito-Noctaamminedicobalt(III) nitrate
$\left[ (\text{en})_2\text{Co} \begin{array}{l} \nearrow \text{NH} \\ \searrow \text{O} \\ \text{H} \end{array} \text{Co}(\text{en})_2 \right]^{+3}$	$\mu$ -hydroxo- $\mu$ -imido-tetrakis(ethylenediamine)dicobalt(III) ion
$[(\text{H}_2\text{O})_4\text{Fe}(\text{OH})_2\text{Fe}(\text{H}_2\text{O})_4]\text{SO}_4$	di- $\mu$ -hydroxooctaaquadiiron(II) sulphate
$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	
$[\text{PdI}_2(\text{NO}_2)_2(\text{H}_2\text{O})_2]$	
$[\text{Cr}(\text{PPh}_3)(\text{CO})_5]$	
$\text{Na}_2[\text{CrOF}_4]$	
$\text{Na}[\text{AlH}_4]$	
$\text{Na}_2[\text{Ni}(\text{EDTA})]$	
$\text{K}_4[\text{Mo}(\text{CN})_8]$	
$[\text{PtCl}_2(\text{NH}_3)_4][\text{PtCl}_4]$	

### Writing the Formula of the Complex compound from its IUPAC names:

symbol of simple cation  $\left[ \begin{array}{l} \text{symbol of central} \\ \text{metal ion} \end{array} \left( \begin{array}{l} \text{-Ve ligands in alphabetical} \\ \text{order of the symbol} \end{array} \right) \left( \begin{array}{l} \text{Neutral ligands in alphabetical} \\ \text{order of the symbol} \end{array} \right) \right] \text{Symbol of simple anion}$

Write the formula of the following coordination compounds.

- tetraammineaquachlorocobalt(III) chloride.  $[\text{CoCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$
- potassium tetrahydrozincate(II)  $\text{K}_2[\text{Zn}(\text{OH})_4]$
- $\mu$ -hydroxodecaaquadiiron(III) Chloride  $[(\text{H}_2\text{O})_5\text{Fe}(\text{OH})-\text{Fe}(\text{H}_2\text{O})_5]\text{Cl}_5$
- potassium dibromocarbonylchlorodicyanoferrate(III)  $\text{K}_2[\text{FeBr}_2\text{Cl}(\text{CN})_2\text{CO}]$

### Valence Bond Theory of Coordination Compounds(Linus Pauling)

The valence bond theory for the formation of coordination compounds is based on the following assumptions,

- The central metal provides adequate number of vacant atomic orbitals for bonding with ligands.  
The number of vacant orbitals provided by the central metal atom or ion is equal to its coordination number.
- The appropriate vacant orbitals of central metal atom undergo hybridization to give equal number of identical orbitals  
called hybrid orbitals. The hybrid orbitals are directed to definite directions around the central metal atom.
- The Vacant hybrid orbital of central metal overlap with orbital of ligand containing lone pairs of electrons to form  
coordinate bond.
- The geometry of the complex depends on the number of hybrid orbitals and type of hybridization.
- The complex containing unpaired electrons is paramagnetic and the complex which does not contain unpaired electrons is diamagnetic.

6. If the inner d-orbitals are used in hybridization are called inner d-orbital complexes Or Low spin complexes(No or less number of unpaired electrons)

If the outer d-orbitals are used in hybridisation are called outer d-orbital complexes or High spin complexes(One or more unpaired electrons)

Type of Hybridisation and Geometry of Coordination sphere

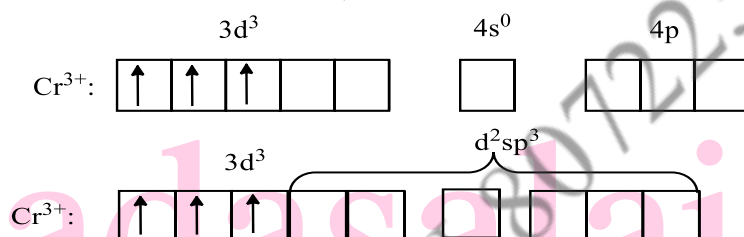
Coordination Number	Type of Hybridization	Geometry of coordinate sphere	Example
2	Sp	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$
3	$sp^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$sp^3$	Tetrahedral	$[\text{NiCl}_4]^{2-}$ $[\text{Ni}(\text{CO})_4]$
4	$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Cu}(\text{NH}_3)_4]^{2+}$
5	$dsp^3$	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$
6	$d^2sp^3$	Octahedral	$[\text{Co}(\text{NH}_3)_6]^{3+}$
6	$sp^3d^2$	Octahedral	$[\text{CoF}_6]^{3-}$

Formation of the Coordination compounds, geometry and magnetic property can be illustrated based on VBT in the following examples:

**Formation, geometry and Magnetic property of hexaaquachromium(III) ion  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  :**

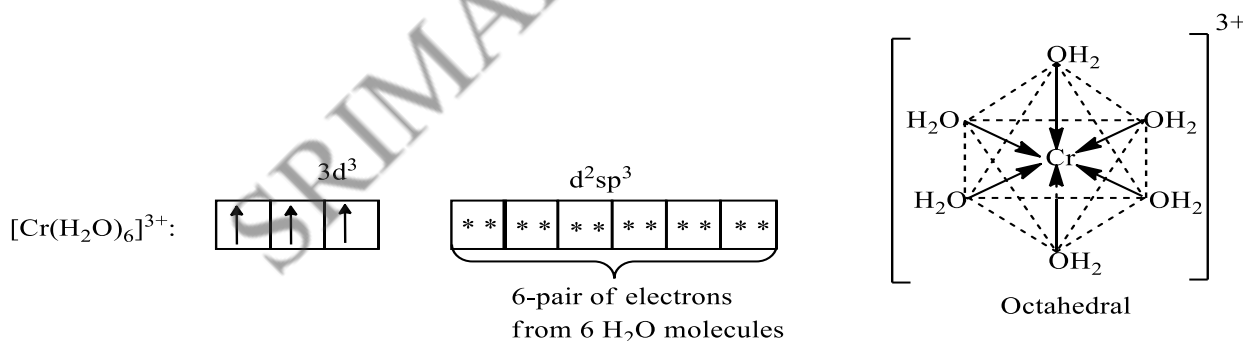
In this complex the central metal atom is Cr, Cr (At. No.24) has outer electronic configuration  $3d^5 4s^1 4p^0$ .

In this complex Cr has oxidation state of +3,  $\text{Cr}^{3+}$  ion has the outer electronic configuration  $3d^3 4s^0 4p^0$



The two 3d- orbitals, one 4s orbital and three 4p- orbitals mix up to form six  $d^2sp^3$  hybrid orbitals. The hybrid orbitals are directed to the each corners of the octahedron.

The empty hybrid orbital of central metal atom overlap with the filled orbitals of the ligand to form coordinate bonds.



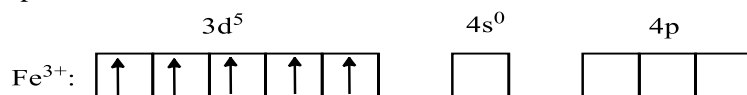
This Complex ion is **paramagnetic**, because it has 3 unpaired electrons. The complex ion is **octahedral** shape, due to  $d^2sp^3$  hybridisation.

Note: In the formation of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complex ion, the inner d-orbital (3d) is used in hybridization. Hence, this complex is called '**inner orbital**' complex. The inner d-orbital complex is expected to have less number of unpaired electrons or no unpaired electrons such complex is called '**low spin**' or '**spin paired**' complex.

**Formation, geometry and Magnetic property of hexacyanoferrate (III) ion  $[\text{Fe}(\text{CN})_6]^{3-}$  :**

In this complex ion the central metal atom is Fe, Fe (At. No.26) has outer electronic configuration  $3d^6 4s^2 4p^0$ .

In this complex Fe has +3 oxidation state.  $\text{Fe}^{3+}$  ion has the outer electronic configuration  $3d^5 4s^0 4p^0$

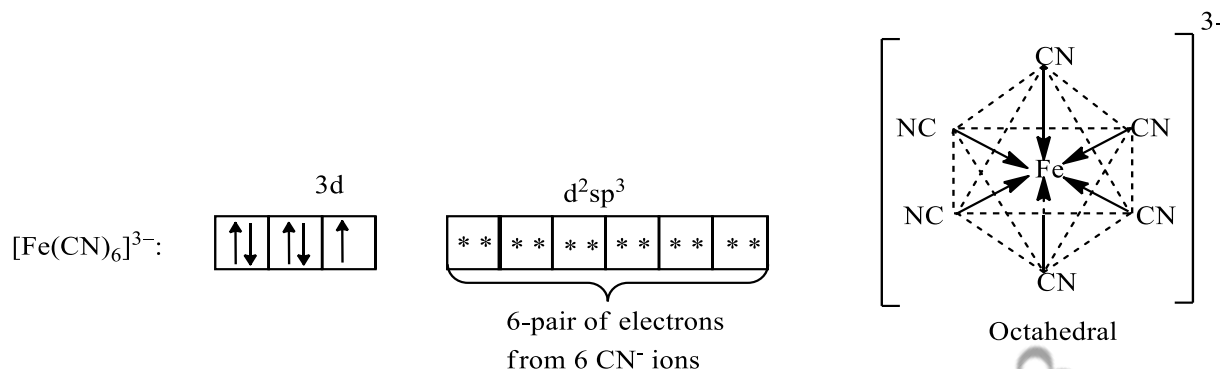


When the ligands approach the metal ion, the electrons in the d-orbitals are forced to paired up and provide two vacant d-orbitals



Then two 3d- orbitals, one 4s- orbital and three 4p- orbitals mix up to form six  $d^2sp^3$  hybrid orbitals. The hybrid orbitals are directed to the each corners of the octahedron.

The vacant hybrid orbital of central metal atom overlap with the filled orbitals of the ligand to form coordinate bonds.

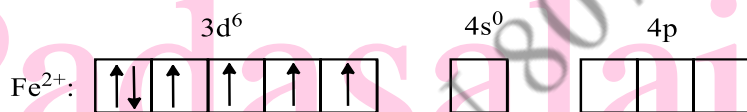


This complex ion is **paramagnetic**, because it has one unpaired electron. And it has **octahedral shape** due to  $d^2sp^3$  hybridisation.

In this complex ion, the inner d-orbitals are involved in hybridization, hence it is '**inner d- orbital complex**'. The inner d-orbital complex is expected to have a less number of unpaired electrons such complex is called '**low spin**' complex.

#### Formation, geometry and Magnetic property of hexacyanoferrate(II) ion $[\text{Fe}(\text{CN})_6]^{4-}$ :

In this complex ion the central metal atom is Fe, Fe(At. No.26) has outer electronic configuration  $3d^64s^24p^0$ . In this complex iron is in the +2 oxidation state.  $\text{Fe}^{2+}$  ion has the outer electronic configuration  $3d^64s^04p^0$ .

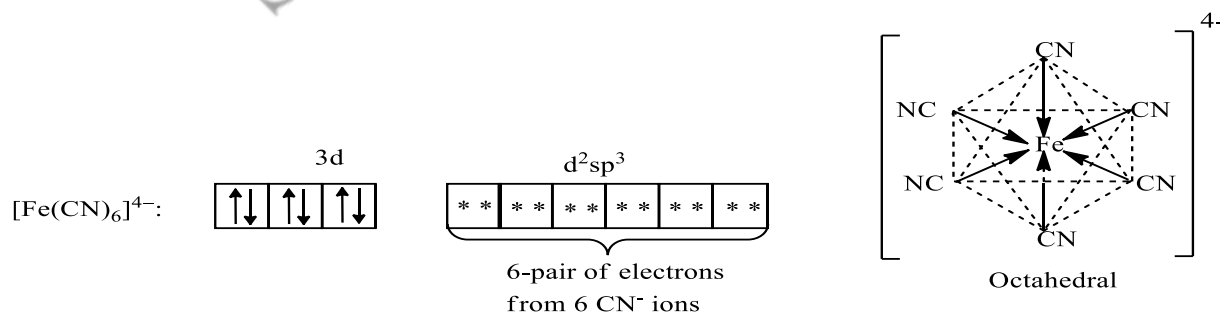


When the  $\text{CN}^-$  ligands approach the metal ion, the electrons in the d-orbitals are forced to paired up, this provide two vacant d-orbitals.



Then two 3d- orbitals, one 4s- orbital and three 4p- orbitals mix up to form six  $d^2sp^3$  hybrid orbitals. The hybrid orbitals are directed to the each corners of the octahedron.

The vacant hybrid orbital of central metal atom overlap with the filled orbitals of the ligand to form coordinate bonds.



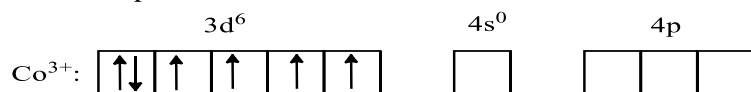
This complex ion is **diamagnetic**, because it has no unpaired electrons. It has **octahedral structure** due to  $d^2sp^3$  hybridisation

In the formation of  $[\text{Fe}(\text{CN})_6]^{4-}$  complex, inner d-orbitals (3d) are used in hybridization. Hence, this complex is called '**inner orbital**' complex. The inner d-orbital complex is expected to have less number of unpaired electrons or no unpaired electrons such complex is called '**low spin**' or '**spin paired**' complex.

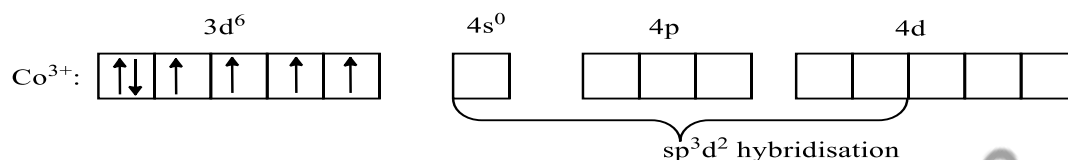
**Formation, geometry and magnetic property of hexafluorocobaltate (III) ion  $[\text{CoF}_6]^{3-}$  :**

In this complex ion the central metal atom Co (At. No.27) has outer electronic configuration  $3d^7 4s^2 4p^0$ .

In this complex oxidation state of Co is +3. then  $\text{Co}^{3+}$  ion has the outer electronic configuration  $3d^6 4s^0 4p^0$ .

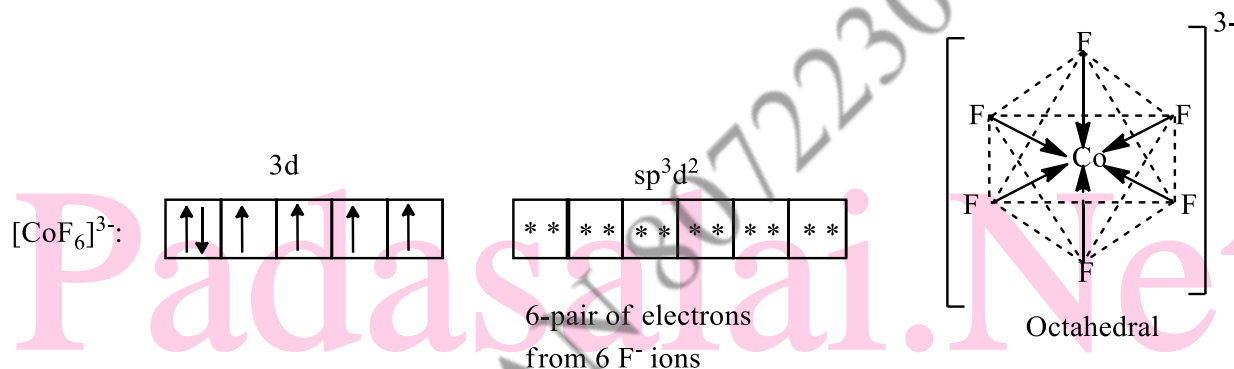


While forming fluoro complex, electrons continue to remain unpaired in 3d orbital. Electrons in d-orbitals are not forced to pair up.



The vacant one 4s-orbital, three 4p-orbitals and two 4d-orbitals of outer shell involve in  $sp^3 d^2$  hybridisation. The hybrid orbitals are directed to the each corner of the regular octahedron.

The vacant hybrid orbital of central metal atom overlap with the filled orbitals of the ligand to form coordinate bonds.



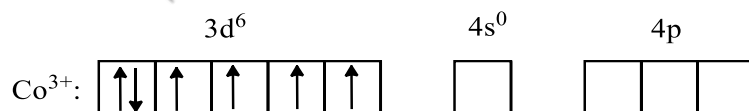
This complex ion is **paramagnetic**, because it has four unpaired electrons. It has **octahedral structure** due to  $sp^3 d^2$  hybridisation.

Note: The octahedral complex  $[\text{CoF}_6]^{3-}$  uses outer d-orbitals (4d) in hybridization ( $sp^3 d^2$ ), hence it is called '**outer orbital**' complex. The outer d-orbital complex is expected to have a more number of unpaired electrons such complex is called '**high spin**' or '**spin free**' complex.

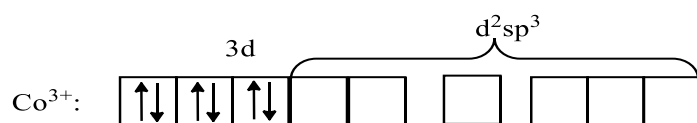
**Formation, geometry and Magnetic property of hexamminecobalt (III) ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  :**

In this complex ion the central metal atom is Co, Co (At. No.27) has outer electronic configuration  $3d^7 4s^2 4p^0$ .

In this complex ion Co has oxidation state of +3,  $\text{Co}^{3+}$  ion has the outer electronic configuration  $3d^6 4s^0 4p^0$ .

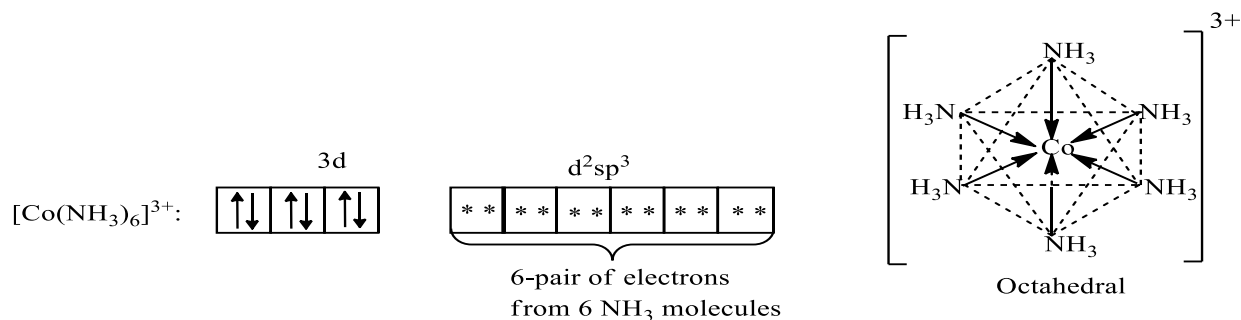


When the  $\text{NH}_3$  ligands approach the metal ion, the electrons in the d-orbitals are forced to paired up, this provide two vacant d-orbitals.



Then two 3d-orbitals, one 4s-orbital and three 4p-orbitals mix up to form six  $d^2 sp^3$  hybrid orbitals. The hybrid orbitals are directed to the six corners of the octahedron.

The vacant hybrid orbital of central metal atom overlap with the filled orbitals of the ligand to form coordinate bonds.

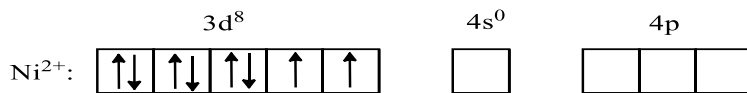


This complex ion is **diamagnetic**, because no unpaired electrons. Complex ion is **octahedral in shape** because of  $d^2sp^3$  hybridisation.

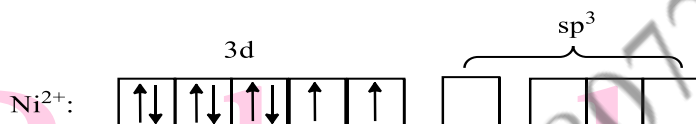
Note: In the formation of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex, the inner d-orbital (3d) is used in hybridization. Hence, this complex is called '**inner orbital**' complex. The inner d-orbital complex is expected to have less number of unpaired electrons or no unpaired electrons such complex is called '**low spin**' or '**spin paired**' complex.

### Formation, geometry and Magnetic property of tetrachloronickelate(II) ion $[\text{Ni}(\text{Cl})_4]^{2-}$ :

In this complex ion the central metal atom is Ni, Ni (At. No.28) has outer electronic configuration  $3d^8 4s^2 4p^0$ . In this complex ion Ni has oxidation state of +2,  $\text{Ni}^{2+}$  ion has the outer electronic configuration  $3d^8 4s^0 4p^0$

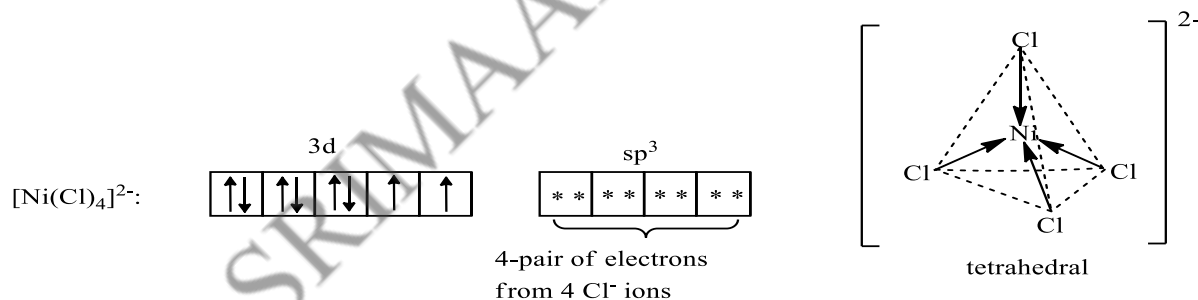


When the  $\text{Cl}^-$  ligands approach the metal ion, the electrons in the d-orbitals are remains unpaired (electrons are not paired)



Then one 4s- orbital and three 4p- orbitals mix up to form four  $sp^3$  hybrid orbitals. The hybrid orbitals are directed to the four corners of the tetrahedron.

The vacant hybrid orbital of central Ni-metal ion overlap with the filled orbitals of the chloride ligand to form coordinate bonds.

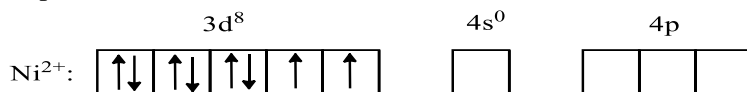


This complex ion is **Paramagnetic**, because of two unpaired electrons. Complex ion is **tetrahedral in shape** due to  $sp^3$  hybridisation.

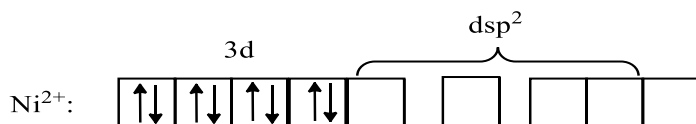
Note: In the formation of  $[\text{Ni}(\text{Cl})_4]^{2-}$  complex ion, d-orbitals are not involved in hybridization,

### Formation, geometry and Magnetic property of tetracyanonickelate(II) ion $[\text{Ni}(\text{CN})_4]^{2-}$ :

In this complex ion the central metal atom is Ni, Ni (At. No.28) has outer electronic configuration  $3d^8 4s^2 4p^0$ . In this complex ion Ni has oxidation state of +2,  $\text{Ni}^{2+}$  ion has the outer electronic configuration  $3d^8 4s^0 4p^0$

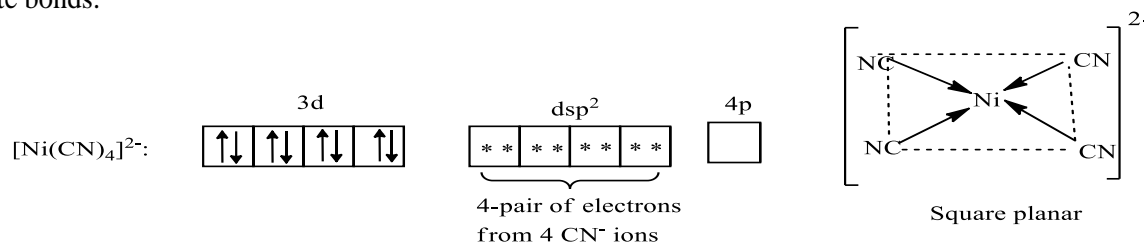


When the  $\text{CN}^-$  ion ligands approach the metal ion, the unpaired electrons in the d-orbitals are forced to pair to form one vacant d-orbital.



Then one 3d-orbital, one 4s-orbital and two 4p-orbitals mix up to form four  $dsp^2$  hybrid orbitals. The hybrid orbitals are directed to the four corners of the Square plane.

The vacant hybrid orbital of central Ni-metal ion overlap with the filled orbitals of the  $CN^-$  ligand to form coordinate bonds.



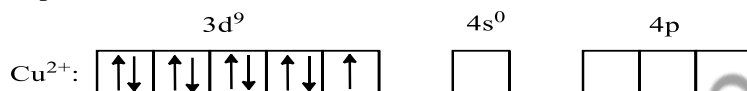
This complex ion is **Diamagnetic**, because of no unpaired electrons. Complex ion has **Square planar shape** due to  $dsp^2$  hybridisation.

Note: In the formation of  $[Ni(CN)_4]^{2-}$  complex ion, inner 3d-orbital is used up in hybridization, hence it is inner d-orbital complex and low spin complex.

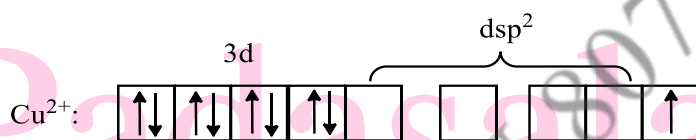
### Geometry and Magnetic property of tetraamminecopper(II) ion $[Cu(NH_3)_4]^{2+}$ :

In this complex ion the central metal atom is Cu, Cu (At. No.29) has outer electronic configuration  $3d^{10}4s^14p^0$ .

In this complex ion Cu has oxidation state of +2,  $Cu^{2+}$  ion has the outer electronic configuration  $3d^94s^04p^0$

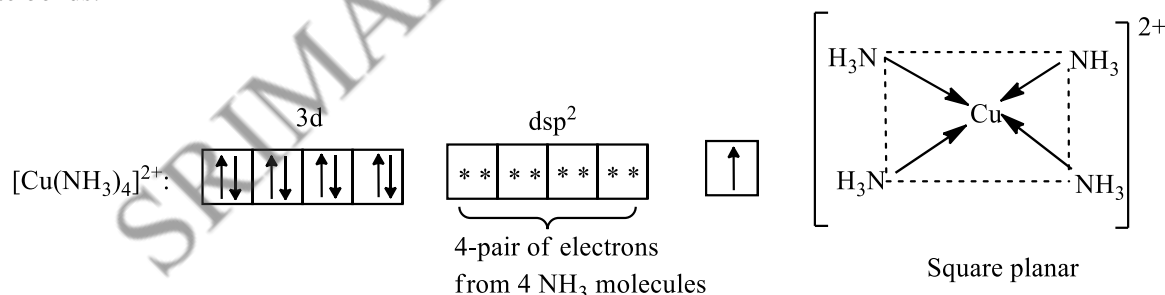


When the  $NH_3$  ligands approach the copper metal ion, the unpaired electron is promoted to one of the vacant 4p-orbital.



Then one 3d-orbital, 4s-orbital and two 4p-orbital mix up to form four  $dsp^2$  hybrid orbitals. The hybrid orbitals are directed to the each corners of the Square plane.

The vacant hybrid orbital of central Cu-metal ion overlap with the filled orbitals of the  $NH_3$  ligand to form coordinate bonds.



This complex ion is **Paramagnetic**, because of one unpaired electron in 4p-orbital. Complex ion has **Square planar shape** because of  $dsp^2$  hybridisation.

Note: In the formation of  $[Cu(NH_3)_4]^{2+}$  complex ion, the inner 3d-orbital is used up in hybridization, hence it is inner d-orbital complex with one unpaired electron.

Though Valence bond theory explains the structure and magnetic nature of coordination compounds, it has the following **Limitations of VBT**:

VBT is based on a number of assumptions.

It is not able to account for spectral property (colour) of coordination compounds.

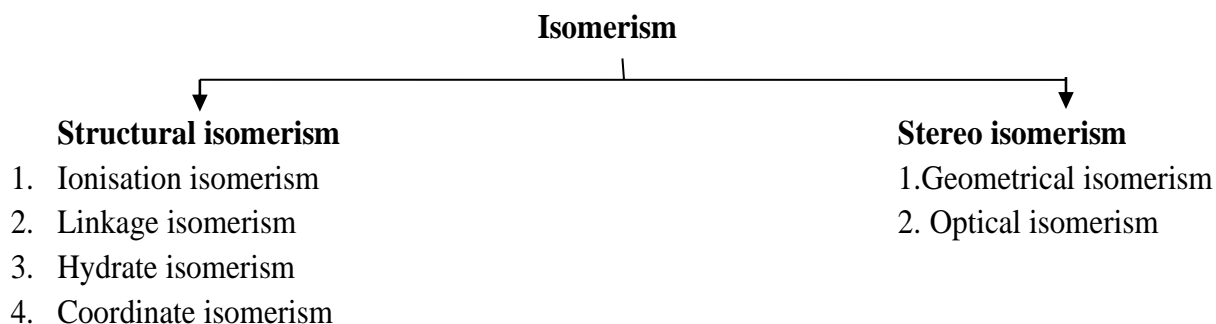
It is not able to explain thermodynamic or kinetic stabilities of coordination compounds.

It is not able to explain pairing or non-pairing of electrons in d-orbitals.

It has no concept of weak and strong ligands.

**Isomerism in coordination compounds**

Compounds with same chemical formula but different properties are called isomers and the phenomenon is called isomerism.



Complex compounds show two types of isomerism namely (a) structural isomerism and (b) stereoisomerism.

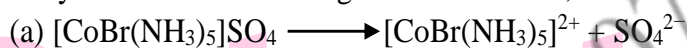
(a) Structural isomerism is due to difference in the arrangement of atoms or groups in the molecule.

There are different types of structural isomerism. They are (1) ionization isomerism (2) linkage isomerism (3) hydrate isomerism or solvate isomerism (4) coordination isomerism.

(1) **Ionisation isomerism:** Two or more coordination compounds have same molecular formula but produce different ions in solution. In this type of isomerism, there is an exchange of ions inside and outside the coordination sphere.

Ex: (i)  $[\text{Co}(\text{NH}_3)_5 \text{Br}]\text{SO}_4$  and  $[\text{CoSO}_4(\text{NH}_3)_5]\text{Br}$

They ionize in solution to give different ions,  $\text{SO}_4^{2-}$  and  $\text{Br}^-$  as shown below:



Compound (a) gives a white precipitate with barium chloride solution but compound (b) does not give a precipitate with barium chloride solution.

(ii)  $[\text{PtCl}_2(\text{NH}_3)_4] \text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$

(iii)  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{CoBr}_2(\text{NH}_3)_4]\text{Cl}_2$

(2) **Linkage isomerism:** Two or more coordination compounds have the same molecular formula but a ligand is bonded to central metal atom through different donor atoms.

Ex:  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$  and  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$

In  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ ,  $\text{NO}_2^-$  ligand is bonded through N-atom and is called Nitrito-N, in

$[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$ ,  $\text{NO}_2^-$  ligand is bonded through O-atom is called as Nitrito-O.

A few other ligands which give rise to linkage isomerism are: (i)  $-\text{CN}^-$  (cyano-C) and  $-\text{NC}^-$  (cyano-N)

(ii)  $-\text{SCN}^-$  (thiocyanato-S) and  $-\text{NCS}^-$  (thiocyanato-N).

Ex:  $[\text{Cr}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2$  and  $[\text{Cr}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$

Ligand that can be bonded through different donor atoms are known as ambidentate ligand.

(3) **Hydrate isomerism or solvate isomerism:** Two or more coordination compounds have the same molecular formula but differ in number of water molecules as ligands and water of hydration.

Ex: (i)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ; (ii)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ; (iii)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

Compound (i) has 6 water molecules as ligand, compound (ii) has 5 water molecules as ligand and compound (iii) has 4 water molecules as ligand.

(4) **Coordination isomerism:** Two or more Coordination compounds having same molecular formula but different complex cation and complex anion. They are formed by the exchange of meta ions between the complex cation and complex anion.

Ex:  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

Ex:  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$

Ex:  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{PtCl}(\text{NH}_3)_3][\text{PtCl}_3(\text{NH}_3)]$

Ex:  $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$

### (b) Stereo Isomerism

Stereo isomers have same chemical formula and chemical bonds but they have different spatial arrangement. Stereo isomerism is of two different type as (1) geometrical isomerism and (2) optical isomerism.

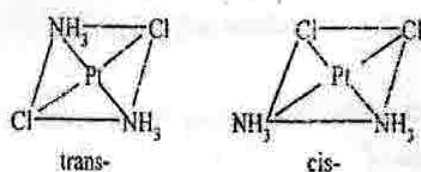
**Geometrical isomerism or cis-trans isomerism:** Two or more coordination compound having same molecular formula but differ in the special arrangement of two similar ligands. They are also called cis-trans isomers.

Square planar and octahedral complexes containing at least two similar ligands can form cis and trans isomers. Similar ligands are present on same side is cis isomers and trans isomer have similar ligand in opposite side.

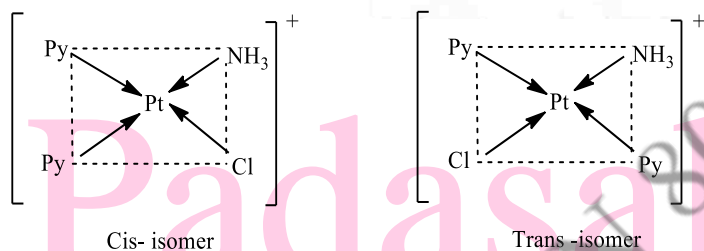
#### Geometrical isomers in Square planar complex:

In a square planar complex, the four ligands and the central metal atom or ion lie in the same plane

Ex:  $[\text{PtCl}_2(\text{NH}_3)_2]$  has two geometrical isomers i) cis- platin and ii) trans-platin



Ex:  $[\text{PtCl}(\text{NH}_3)(\text{ph})_2]^+$  has two geometrical isomers (cis and trans)



Other example,  $[\text{PdBr}_2\text{ClI}]$

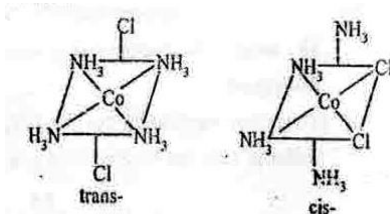
In tetrahedral geometry, all the four positions are identical and hence geometric isomers are not possible.

Geometric isomerism is also found in molecule involving didentate ligands.

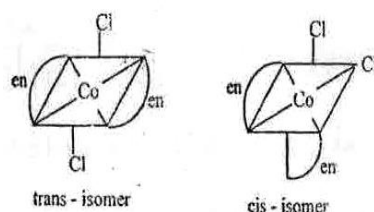
Cis- trans isomers exist in complexes containing unsymmetrical bidentate ligands Ex:  $[\text{Pt}(\text{gly})_2]$  (gly= Glycinato ligand)

#### Geometrical isomers in Octahedral(coordination number six) complexes:

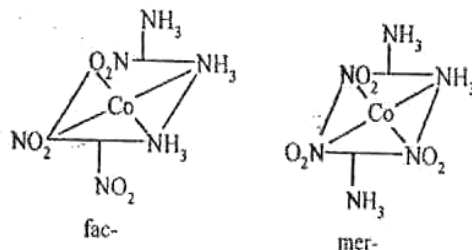
Ex: Geometrical isomerism in Octahedral complex like  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$



Ex:  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  cis and trans isomer coordination sphere are



In octahedral complexes of type  $Ma_3b_3$  like  $[Co(NH_3)_3(NO_2)_3]$  two different types of geometric isomers are possible. When the donor atoms of similar ligands are at the corners of an octahedral face, we have facial isomer (fac- or cis) when the donor atoms of similar ligands are present around the meridian of the octahedrons we get meridional (mer- or trans) isomer.



EX:  $[RhCl_3(Py)_3]$ ,  $[CrF_3(H_2O)_3]$  etc.,

2. **Optical Isomerism:** Two or more complex compounds having same molecular formula but different in the direction of rotation of plane polarized light are called optical isomers.

These are non-superimposable mirror images to each other are called 'enantiomers'. These isomers are optically active. Dextro or d-isomer rotates plane polarized light to right (clockwise) and l-isomer or laevo isomer rotates plane polarized light to left (anticlockwise) direction.

Optical isomers are observed among octahedral complexes containing didentate ligands like (en)

Ex:  $[Co(en)_3]^{3+}$

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