

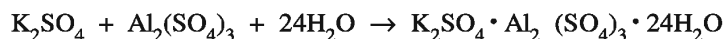
Unit

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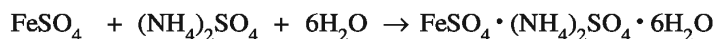
Complex Salts or Co-ordination Compounds

4.1 Introduction

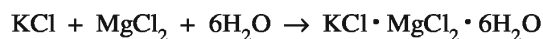
The salt that is obtained according to the laws of chemical combination by combination of two or more salts (compounds) having independent existence and maintains the properties of the original salts is called **double salt**, e.g., if saturated aqueous solution of K_2SO_4 and $Al_2(SO_4)_3$ are mixed and crystallized, then crystals of alum- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ are obtained, which is called double salt. On qualitative analysis of solution of this alum, yellow precipitate with picric acid are obtained. This indicates presence of K^+ , with NaOH gum-like gelatinous precipitates are obtained which indicates presence of Al^{3+} and with $BaCl_2$ gives white precipitates which indicates presence of SO_4^{2-} and thus K_2SO_4 and $Al_2(SO_4)_3$ maintain their properties. Hence it is a double salt. In addition, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ ferrous ammonium sulphate and carnalite are also double salts whose equations are shown below :



Potassium alum



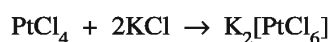
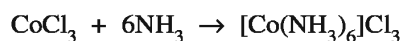
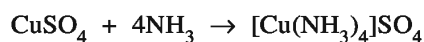
Ferrous ammonium sulphate



Carnalite

Similarly, by combination of two or more compounds of independent existence, according to the laws of chemical combination, compounds obtained with new properties are called **complex salts or co-ordination compounds**, viz. when KCN is added to ferrous cyanide $Fe(CN)_2$, and ferric cyanide $Fe(CN)_3$ are formed and then both of them become soluble. The crystals having formula

$\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$ and $\text{Fe}(\text{CN})_3 \cdot 3\text{KCN}$ are obtained. They are known as potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ and potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ respectively. In these two, the qualitative analysis of Fe^{2+} , Fe^{3+} or CN^- ions cannot be carried out but new ions $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Fe}(\text{CN})_6]^{3-}$ are obtained. In electrolysis; they move towards anode. Equations for preparing some complex salts are given below :



From the equation of CuSO_4 and NH_3 as shown above, it appears that the valency of Cu^{2+} and SO_4^{2-} ions is satisfied even then CuSO_4 combines with four molecules of ammonia and gives complex salt.

The elements in the d-block of modern periodic table, are called transition elements. Among these transition elements, Scandium to Zinc ($Z = 21$ to 30), Yttrium to Cadmium ($Z = 39$ to 48) and Lanthanum to Mercury ($Z = 57$ to 80). That is the elements of fourth, fifth and sixth periods are very important in modern inorganic chemistry. Some of the properties of these elements are same. There is change in their valency and the aqueous solution of their salts are coloured. In the electronic configuration of these transition elements, electrons are arranged successively in d-orbitals. **When (n-1)d, ns and np or ns, np and nd orbitals of the atoms or ions of transition elements are vacant, these transition elements accept electron pairs from negative ions or neutral molecules, which are called complex (co-ordination) compounds.** The bond that is formed between metal ions of metallic elements in this type of compound and the negative ions or neutral molecules is called co-ordinate covalent bond. In these compounds, around the metal ion in the centre of the molecules are arranged negative ions or neutral molecules by co-ordinate covalent bond. Mostly the transition elements have more tendency to form complex compounds.

4.2 Werner's Theory

The question that why the other compounds combine with stable compounds after satisfaction of valency; had become the subject of discussion in the beginning of the nineteenth century. In 1905, Swiss scientist Alfred Werner prepared many new compounds by mixtures of cobalt chloride and ammonia, studied them thoroughly and gave a new theory, which is known as Werner's co-ordination theory. By the Werner's theory many clarifications were made in this field. **Werner obtained different compounds of CoCl_3 and NH_3 viz. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (yellow), $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (purple, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (violet / green) and $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, (bluish green).** Werner received nobel prize for this work in 1913.

The theory given by Werner for the formulas and structures of complex salt is "Certain metals have secondary valency in addition to primary valency. With this it combines strongly with the metal ions, neutral molecules or negative ions in its first attraction sphere []."

According to Werner, metal ion possesses two types of valency. Primary valency or ionizing valency and Secondary valency or non-ionisable valency.

- (i) The primary valency is similar to positive electric charge of positive ion of metal or oxidation number of metal. It forms ionic bond. The other ion combined by this valency becomes free by ionization of compound.

- (ii) Secondary valency is non-ionized. The negative ions or neutral molecules contained with secondary valency are not ionized.
- (iii) Primary valency is satisfied by only negative ions, while secondary valency is satisfied by negative ions or neutral molecules (ligand).
- (iv) The secondary valency of metal ion or metal elements form co-ordinate covalent bond, so the secondary valency is called co-ordination number of metal.
- (v) The co-ordination number of metal ion is definite which is independent of primary valency.
- (vi) Secondary valency being directional, different types of geometrical structures are obtained.

Note : (1) In some complex compounds, the positively charged ligand like ^+NO , $^+\text{NO}_2$ are also seen.

(2) Now it is proved that the some metal ions of transition elements possess more than one co-ordination number.

(3) To understand these geometrical structures, it is important to know the magnetic properties of complex compounds.

The bond between metal ion combined through secondary valency, and ligand is called co-ordinate covalent bond. This is indicated by \rightarrow which indicates the co-ordination site. The electron pair present between metal ion and ligand are given by negative ion or neutral molecule.

The complex ion in complex compounds is shown by [] bracket (first attraction sphere) whereas outside the bracket, on the left side, the positive ion combined by ionic bond is shown viz. In $\text{K}_3[\text{Fe}(\text{CN})_6]$ complex compound $[\text{Fe}(\text{CN})_6]^{3-}$ complex negative ion is combined by ionic bond with positive ion K^+ . Similarly in $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ complex compound $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complex positive ion is combined with negative ion Cl^- by ionic bond.

4.3 Clasification of Ligands

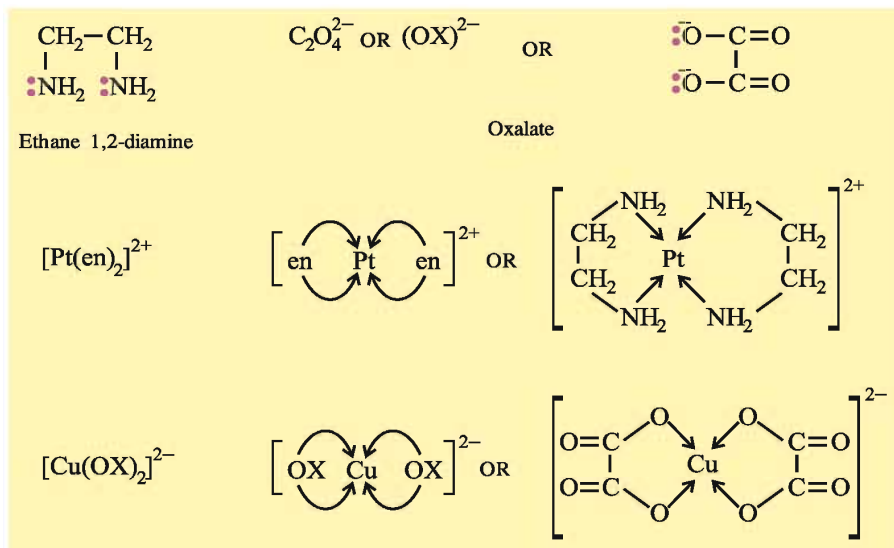
Generally the ligand has a negative electric charge or is a neutral molecule. The classification of ligands is made on the basis of the number of electron pair donating atoms.

(I) Unidentate ligand : If only one atom of ligand of negative ion or neutral molecule donates one atom to metal ion by giving one electron pair and form one co-ordinate covalent bond, then it is called unidentate ligand. Neutral molecules like H_2O , NH_3 , CO and negative ions like Cl^- , CN^- , F^- which combine with metal ion by giving one electron pair; viz. In $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ complex compound, nitrogen atom of each ammonia combine by giving one electron pair to chromium metal ion, it is called unidentate ligand. In $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ complex compounds each molecule of water co-ordinates with chromium metal ion by giving one electron pair, so it is unidentate ligand. In these unidentate ligands, nitrogen atom in ammonia molecule and oxygen atom in water molecule donate one electron pair to metal ion. Hence, the atom present in negative ion or neutral molecule gives electron pair to metal-ion which is called the co-ordinate site of ligand and it is shown as $\text{M} \leftarrow \text{L}$, where M is metal ion and L is ligand.

(II) Didentate ligand : The ligand which can donate two electron pairs and forms two co-ordinate covalent bonds, is called didentate ligand. In this type of ligand two atoms combine with metal ion by giving two electron pairs and form two co-ordinate covalent bonds. Thus, only one ligand satisfies two secondary valencies of metal ion viz. In ethane 1-2 diamine (ethylene diamine-en), its one molecule forms two co-ordinate covalent bonds by giving two electron pairs on two nitrogen atoms, to metal ion.

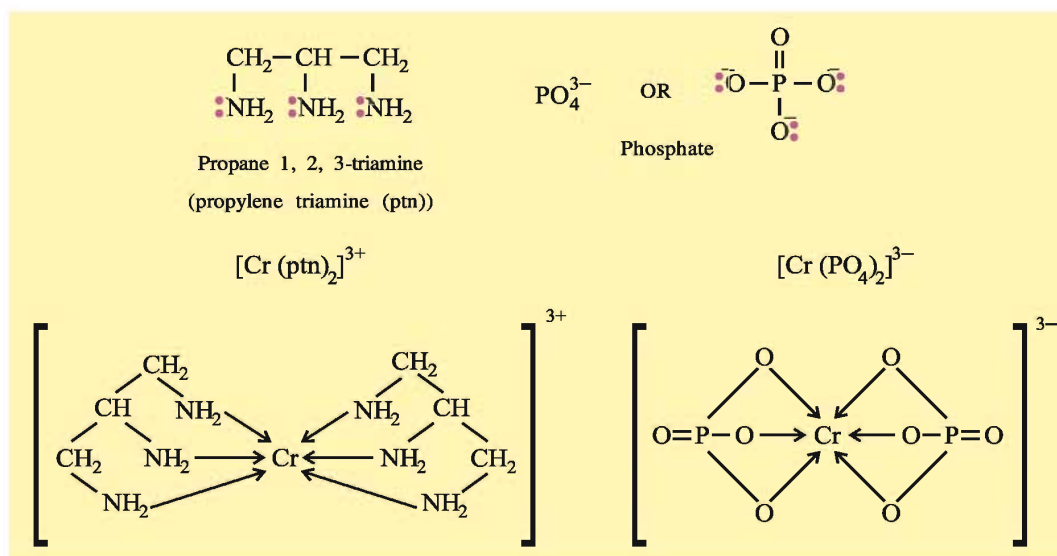
In oxalate (OX^{2-}) negative ion, two electron pairs on two oxygen atoms are given to metal-ion and two co-ordinate covalent bonds are formed.

e.g.,



(III) Tridentate ligand : The ligand in which there are three co-ordination sites is called tridentate ligand. In this type of ligand, three atoms form three co-ordinate covalent bonds by giving three electron pairs. Thus only one ligand satisfies three secondary valencies of metal ion viz. Propane 1-2-3 triamine (Propylene triamine-ptn) one neutral molecule form three co-ordinate covalent bonds by giving three electron pairs on its three nitrogen atoms. Similarly, PO_4^{3-} is a negative ion tridentate ligand.

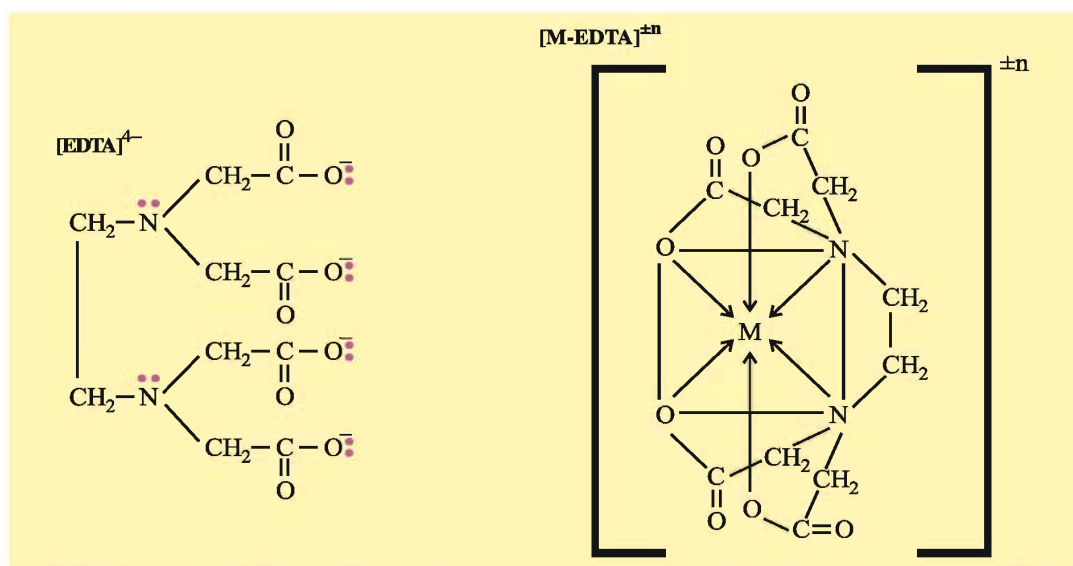
e.g.



(IV) Hexadentate ligand : The ligand in which there are six co-ordination sites is called hexadentate ligand. Six atoms of this type of ligand give six electron pairs to metal ion and form six

co-ordinate covalent bonds. Thus, only one ligand satisfies six secondary valencies of metal ion viz. In ethylene diamine tetraacetate (EDTA)⁴⁻, four oxygen atoms and two nitrogen atoms give four electron pairs and two electron pairs respectively to metal ion and form six co-ordinate covalent bonds.

e.g. [M EDTA]^{±n}



Generally, the ligand in which two or more co-ordination sites are there or the ligand in which two or more atoms donate electron pairs to metal ion and form co-ordinate covalent bond, is called multidentate ligand.

Some ligands and their types are shown in table 4.1

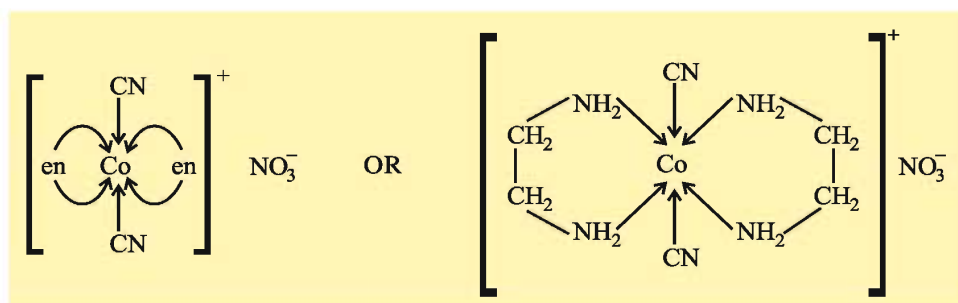
Table 4.1 Some ligands and their types

Type	Ligand	Electric charge
Unidentate Neutral ligand	$\text{H}_2\ddot{\text{O}}:$, $:\text{NH}_3$, $:\text{CO}$, $:\text{NO}$, $\text{CH}_3\ddot{\text{N}}\text{H}_2$, $\text{C}_5\text{H}_5\ddot{\text{N}}$ (py)	0
Unidentate Negative ion ligand	^-OH , F^- , Cl^- , Br^- , I^- , ^-CN , $^-\text{NH}_2$, NO_3^- , NO_2^- , $\text{CH}_3\text{COO}^- (\text{AcO}^-)$, O^{2-} , S^{2-} , N^{3-}	- 1
Unidentate Positive ion ligand	^+NO , $^+\text{NO}_2$,	+ 1
Didentate Neutral ligand	$\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$ (en), $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \quad \quad \\ :\text{NH}_2 \quad :\text{NH}_2 \end{array}$ (pn)	0
Didentate Negative ion ligand	CO_3^{2-} , SO_4^{2-} , $\begin{array}{c} \text{COO}^- \\ \\ \text{COO}^- \end{array} (\text{OX})^{2-}$	- 2
Tridentate Neutral ligand	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ \quad \quad \\ :\text{NH}_2 \quad :\text{NH}_2 \quad :\text{NH}_2 \end{array}$ (ptn)	0

Tridentate Negative ion ligand	$\text{PO}_4^{3-}, \text{AsO}_4^{3-}$	- 3
Hexadentate Negative ion ligand	$ \begin{array}{c} ^-\text{OOC}-\text{CH}_2 \quad \text{N} \quad \text{CH}_2-\text{COO}^- \\ \quad \quad \quad \cdot\cdot \quad \quad \quad \cdot\cdot \\ \quad \quad \quad \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \\ \quad \quad \quad \cdot\cdot \quad \quad \quad \cdot\cdot \\ ^-\text{OOC}-\text{CH}_2 \quad \text{CH}_2-\text{COO}^- \end{array} $ EDTA ion	- 4

When multidentate ligands like en, OX^{2-} , pn, ptn, $(\text{EDTA})^{4-}$ form co-ordinate covalent bond with metal ion, it results into cyclic structure involving central metal ion. Thus, the complex compound formed by ligand and metal ion having cyclic structure is called chelate. The stability of such chelate compounds is more than the stability of simple complex compounds (formed by monodentate ligand).

e.g. $[\text{Co}(\text{CN})_2(\text{en})_2]^+ \text{NO}_3^-$



4.4 Requirements for Formation of Complex Compounds

Some basic requirements are necessary for formation of complex compound. The capacity of transition element metal ions of formation of complex compounds is more than that of other elements.

Basic requirements :

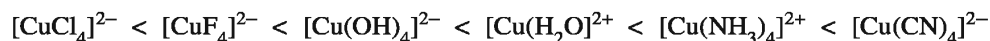
- The ligand must have electron pair which can be easily donated.
- There must be vacant orbitals in the metal ion to receive electron pairs.
- The metal ions should have the symmetry of vacant orbitals same as the symmetry of orbitals of ligand having electron pairs. Hence, co-ordinate covalent bond can be formed by overlapping of orbitals having electron pair in ligand.

These basic requirements are satisfied by metal ions and so complex salts are easily formed. Even then, it is not necessary that each transition element forms complex compounds with equal ease. There is change in capacity of formation of complex compounds according to different oxidation states of metal ions. In addition, there is difference in the stability of the compounds that are formed.

4.5 Stability of Complex Compounds and Strength of Ligand

As the strength of different ligands to form co-ordinate covalent bond varies, stronger ligand possesses more attraction with metal ion. As a result, complexes having stronger ligands possess more stability and the complexes having weak ligand possess less stability. Hence, it can be said that the strength of the complexes is determined on the basis of strength of ligand. The basis of strength of ligand

can be determined by same metal ion combined with different ligands. The order of strength of some complex compounds is as follows : $\text{Cl}^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$

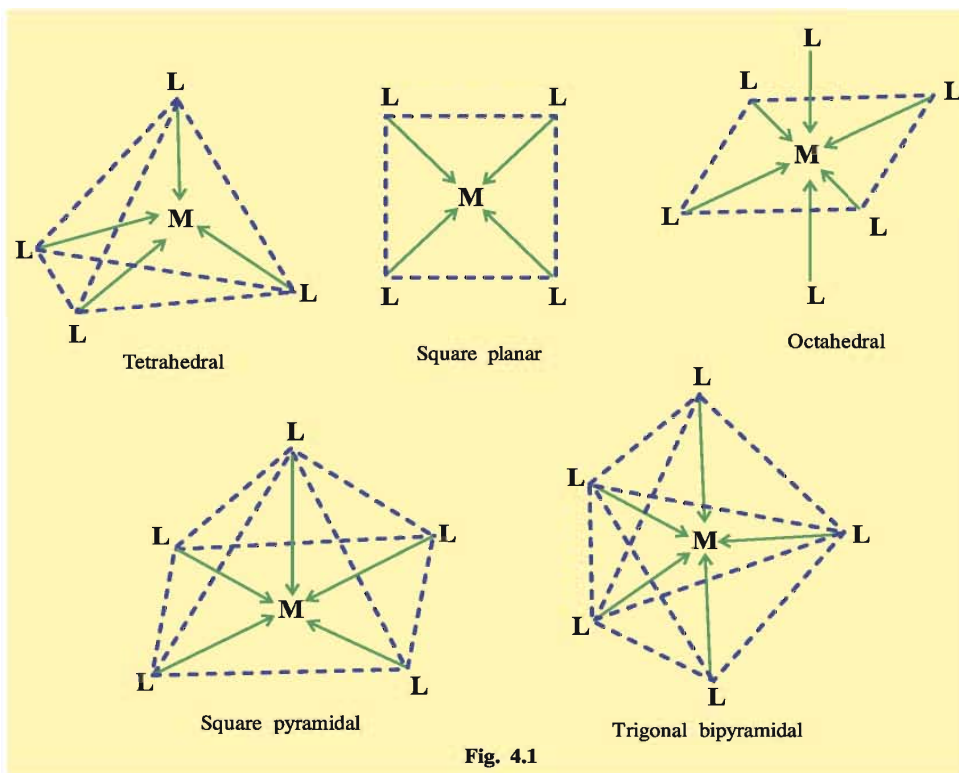


Hence, change in the capacity is seen in the formation of complex ions of metal ions of transition elements according to different conditions.

It is not necessary that any metal ion form only one type of complex salt with ligand. Sometimes different types of ligands form complex compounds with metal ion. This type of complex compounds are called mixed ligand complex compounds. viz. In the complex $[\text{Cr}(\text{NH}_3)_4(\text{CN})_2]\text{NO}_3$, four ammonia molecules and two cyanide ions, total six unidentate ligands are combined. If ligand is of only one type, the complex salts are called simple complex compounds.

As in mixed ligand complex compounds two or more types of ligands combine and form complex compound, similar if only one metal ion is present in any complex compound, then it is called uncentred complex compound, e.g. $\text{K}[\text{MnO}_4]$. If more than one metal ions are present in the complex compound then it is called polycentred complex compound. e.g. $\text{K}_2[\text{Cr}_2\text{O}_7]$.

In uncentred or polycentred complex compounds, the three dimensional arrangement of ligand combined to metal ion are directional, so different geometrical structures formed accordingly are called co-ordination polyhedral. Mostly, the shape of this geometrical structure is tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal.



4.6 Geometry of Complex Ions

The co-ordination number of metal ion and the geometrical structures of ions can be known from the studies of magnetic properties and crystal field theory. It is not necessary that metal ion should possess same co-ordination number and one definite type of geometrical structure containing complex ions. Sometimes, it may happen that the metal ion possesses more than one co-ordination number and even if the co-ordination number remains the same, it can form complex ions having different types of geometrical structures. In most of the metal complex ions, the co-ordination number 4 and 6 are very common and the complex ions showing these co-ordination numbers are found comparatively in larger number.

Co-ordination number 4 : The metal ions possessing co-ordination number 4 form complexes having two types of geometrical structures :

(i) Tetrahedral structure containing complex ions and (ii) square planar structure containing complex ions.

(i) Tetrahedral complex ions : Metal ions form tetrahedral complex ions and they are stable in special conditions. Most of the tetrahedral complex ions are obtained in negative ion form viz. MnO_4^- . While, tetrahedral complex like $[\text{Ni}(\text{CO})_4]$ is obtained in form of neutral molecule.

(ii) Square planar complex ions : Metal ions of only some of the transition elements form square planar complexes. Square planar complexes are formed by combination of Ni^{2+} metal ion with negative ion and / or neutral molecule ligand viz. $\text{K}_2[\text{Ni}(\text{CN})_4]$ and $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$.

In table 4.2 some examples of tetrahedral and square planar complexes possessing co-ordination number 4 of some transition elements in the fourth period are shown.

Table 4.2 Some complexes of transition elements possessing co-ordination number-4

Transition Element	Oxidation state	Electrons of 3d-orbital	Complex compound	Geometrical structure
Mn	+7	$3d^0$	$\text{K}[\text{MnO}_4]$	Tetrahedral
Co	+2	$3d^7$	$\text{K}_2[\text{CoCl}_4]$	Tetrahedral
Ni	0	$3d^{10}$	$\text{K}_4[\text{Ni}(\text{CN})_4]$	Tetrahedral
	+2	$3d^8$	$\text{K}_2[\text{NiCl}_4]$	Tetrahedral
	+2	$3d^8$	$\text{K}_2[\text{Ni}(\text{CN})_4]$	Square planar
	+2	$3d^8$	$[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$	Square planar

Co-ordination number 6 : The complex compounds of metal ions possessing co-ordination number 6 are easily available. The geometrical structures of these complexes are octahedral due to which different ligands deformations are also found viz. $[\text{CrCl}_2(\text{en})_2]\text{NO}_3$ and $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$.

In table 4.3, some examples of octahedral complexes possessing co-ordination number 6 of elements of some transition elements of fourth period are given.

Table 4.3 Some complexes possessing co-ordination number 6 of transition elements

Transition Element	Oxidation state	Electrons of 3d-orbital	Complex compound (Octahedral structure)
Cr	0	3d ⁶	[Cr(CO) ₆]
	+1	3d ⁵	K ₄ [Cr(CN) ₅ (NO)]
	+3	3d ³	K[Cr(NH ₃) ₂ (CO ₃) ₂]
	+4	3d ²	K ₂ [CrF ₆]
Mn	+2	3d ⁵	[Mn(H ₂ O) ₆]Cl ₂
	+3	3d ⁴	[Mn(en) ₃]Cl ₃
Fe	+2	3d ⁶	K ₄ [Fe(CN) ₆]
	+3	3d ⁵	Na ₃ [Fe(OX) ₃]
Co	+2	3d ⁷	Na ₄ [Co(NO ₂) ₆]
	+3	3d ⁶	[Co(NH ₃) ₆]Cl ₃
	+4	3d ⁵	K ₂ [CoF ₆]
Ni	+2	3d ⁸	[Ni(H ₂ O) ₆]Cl ₂
	+3	3d ⁷	K ₃ [Ni(CN) ₆]
	+4	3d ⁶	K ₂ [NiF ₆]

4.7 Hybridization of Orbitals of Metal Ions of Complex Compounds and Magnetic Properties

Most of the metal ions have geometrical structures- tetrahedral, square planar or octahedral. To understand this geometrical structures, hybridization of metal-ion orbitals and magnetic property are very useful.

sp³ hybridization : When one 4s-orbital and three 4p_x, 4p_y, 4p_z orbitals overlap with one another and get hybridised, then new four hybrid orbitals are produced. These four orbitals are called sp³ hybrid orbitals. The energy value of these four hybrid orbitals are same and are extended towards the four corners from the centre of the tetrahedral. Also, the angle between any two sp³ hybrid orbitals is 109°28'. Hence, if the metal ion orbitals in complex ion hybridization of sp³ type, then the geometrical structure of complex compounds is tetrahedral.

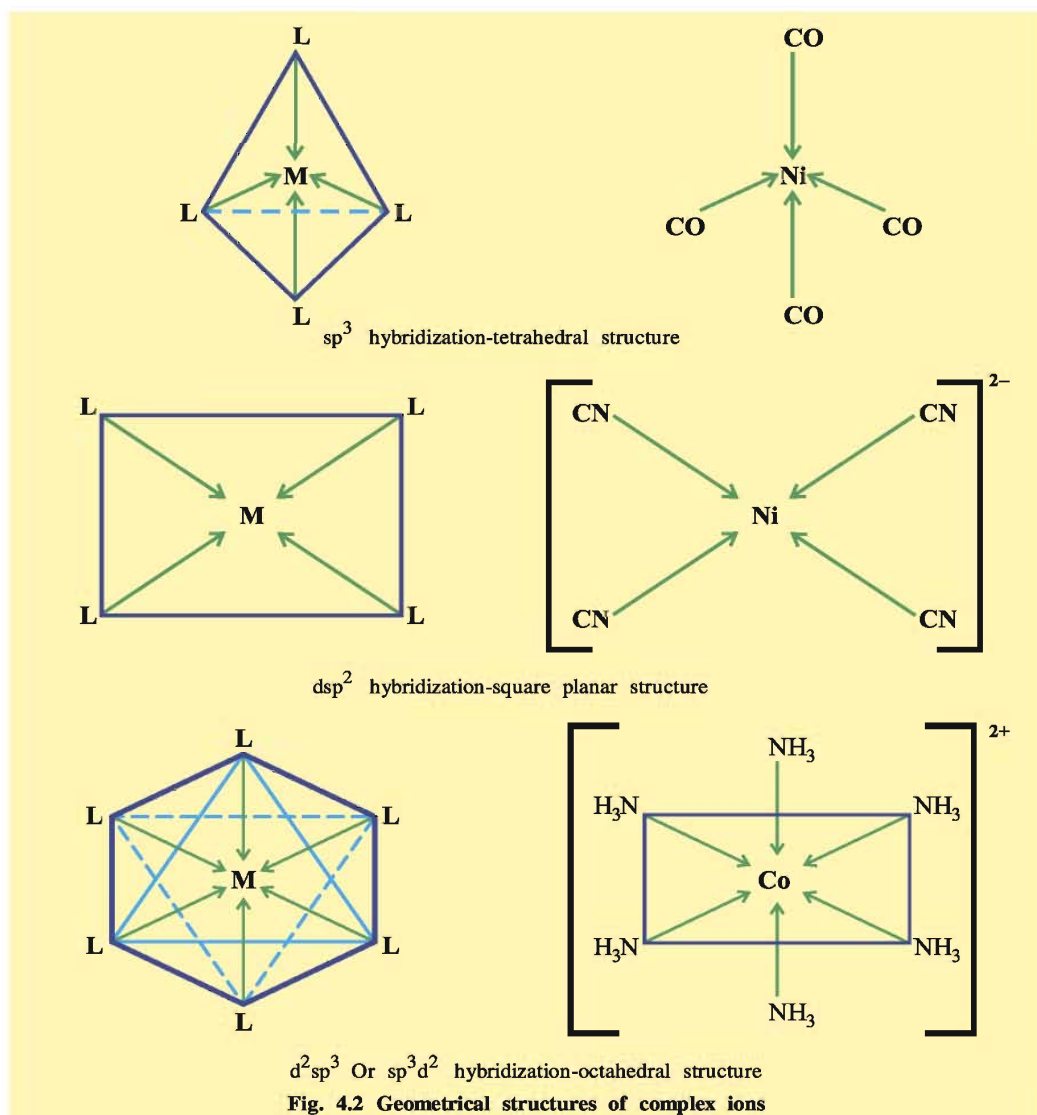
dsp² hybridization : When one 3d-orbital, one 4s-orbital and two 4p_x, 4p_y orbitals of metal ion overlap with one another and get hybridized, new four hybrid orbitals are produced. These four hybrid orbitals are called dsp² hybrid orbitals. The value of energy of these four hybrid orbitals is same and are extended towards four corners from the centre of the plane square. Also, the angle between any two nearby dsp² orbital is 90°. Hence, if the hybridization of metal ion orbitals in compound, is of dsp² type then, the geometrical structure of metal in the compound becomes of dsp² type; then the geometrical structure of complex compounds is square planar.

d²sp³ hybridization : When two 3d-orbitals, one 4s-orbital and three 4p_x, 4p_y, 4p_z orbitals overlap with one another and get hybridized, then new six hybrid orbitals are produced. These hybrid orbitals are called d²sp³ hybrid orbitals. The value of energy of these six hybrid orbitals is same and it

is extended to six corners of octahedral from the centre of that octagon. Also, all these hybrid orbitals are on X-axis, Y-axis and Z-axis to one another. So the angle between any two nearby d^2sp^3 orbitals is 90° . Hence, the complex compounds in which the hybridization of metal ion in complex compound is of d^2sp^3 type, the geometrical structure of this complex compound is octahedral.

sp^3d^2 hybridization : Sometimes, sp^3d^2 hybridisation can occur to produce octahedral structure when 3d-orbitals of metal ion are not available, then one 4s-orbital, three $4p_x$, $4p_y$, and $4p_z$ orbitals and two 4d-orbitals overlap with one another and sp^3d^2 hybridization occurs. Here also, in sp^3d^2 hybridization the geometrical structure is octahedral.

Hence, it can be said that in octahedral structure d^2sp^3 or sp^3d^2 hybridization occurs. To determine which type of hybridization is possessed by study of magnetic properties becomes very essential. In fig. 4.2 the geometrical structures of complex molecules or ions on the basis of sp^3 , dsp^2 , d^2sp^3 or sp^3d^2 hybridization are shown.



Magnetic properties : If the electrons of 3d-orbital of the metal ion are paired in transition element in any complex then the complex is called diamagnetic. If there are unpaired electrons then the complex is called paramagnetic. The theoretical value of magnetic moment can be found out by the equation $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons. The unit of this value is BM (Bohr magneton).

The magnetic moment of complex compounds of metal ions of transition elements is dependent on geometrical structure, type of ligand etc. In the detailed study of complex compounds, the calculation of magnetic moment is very helpful. In table 4.1, the theoretical and experimental values of magnetic moment of Sc^{2+} to Zn^{2+} (d^1 to d^{10}) ions are given.

Table 4.4 Unpaired electrons and magnetic moment of M^{2+} ions of transition elements

Ion	$3d^n$	Unpaired Electrons	Magnetic moment (μ) BM	
			Theoretical value	Experimental value
Sc^{2+}	d^1	1	1.73	1.73 – 1.74
Ti^{2+}	d^2	2	2.83	2.76
V^{2+}	d^3	3	3.87	3.86
Cr^{2+}	d^4	4	4.90	4.80
Mn^{2+}	d^5	5	5.92	5.96
Fe^{2+}	d^6	4	4.90	5.00 – 5.50
Co^{2+}	d^7	3	3.87	4.40 – 5.20
Ni^{2+}	d^8	2	2.83	2.90 – 3.40
Cu^{2+}	d^9	1	1.73	1.80 – 2.20
Zn^{2+}	d^{10}	0	0	0

4.8 IUPAC Nomenclature of Complex Compounds

There are different types of ligand for variety of complex compounds with various metal elements. Also many complex compounds possessing mixed ligands are prepared. In the earlier times, the names of the complex compounds were given on the basis of metal ion and their colours. Werner had named the complexes obtained from cobalt chloride and ammonia on the basis of their colours viz. greenio cobaltic ammonium chloride, violetio cobaltic ammonium chloride, purpleo cobaltic ammonium chloride etc. As many complexes were being formed, the accurate names of complex compounds could not be given. Hence to have accuracy in the names of the complex compounds, IUPAC method was used. The IUPAC nomenclature of monocentric complex compounds is done according to the definite rules as shown below :

- (i) In showing name of ionic complex compound, the positive ion is written first and then the name of negative ion, is mentioned.
- (ii) In complex compound co-ordination sphere [] in naming is done according to the rules.
 - (a) In nomenclature in co-ordination sphere the name of ligand according to English alphabates is first shown and then the name of the metal is written.

- (b) For the ligands having negative electric charge, the suffix 'O' is joined with the name of the ligand viz OH^- hydroxo, CN^- cyano, NH_2^- amido, NO_2^- nitro, ONO^- nitrito, NO_3^- nitratato, SCN^- thiocyanato, CNO^- cyanato, CO_3^{2-} carbonato, O^{2-} oxo, OX^{2-} oxalato, PO_4^{3-} phosphato, AsO_4^{3-} arsenato etc. As per IUPAC rules, 2004, Cl^- is written as chlorido instead of chloro and Br^- as bromido instead of bromo.
- (c) The neutral ligand is shown according to its original name viz. $\text{CH}_3 \cdot \text{NH}_2$ methyl amine, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ethane 1-2 diamine, $\text{NH}_2-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{CH}_2-\text{NH}_2$ propane-1,2,3-triamine $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ propane 1,2-diamine but as exception H_2O aqua, NH_3 ammine, CO carbonyl, NO nitrosyl etc. are written.
- (d) If the number of ligand of only one type is more than 1, then according to the number of ligands 2, 3, 4, 5, 6, the words di, tri, tetra, penta, hexa etc are used as prefix respectively. If organic ligand is there, and the prefix is a number, then ligand is placed in bracket and for numbers 2, 3, 4 etc. corresponding bis, tris, tetrakis prefix are added.
- (e) If there is monocentred complex ion, in which only one metal ion, then there is definite order of showing its name.
- (i) If the complex is negative ion, then write names of ligand successively. The suffix 'ate' is joined with metal ion and then its oxidation state is shown in () bracket in Roman numbers viz. ferrate (II), ferrate (III), chromate (III), manganate (VII), cobaltate (III), nickelate (II), molybdate (VI).
- (ii) If the complex is positive ion or neutral molecule, then first writing the name of ligand successively, the name of metal is added at the end and its oxidation state is shown in () bracket, in Roman numbers. The whole part of complex positive ion, negative ion and neutral molecule is placed in the square bracket [].

The formulae and IUPAC names of some complex compounds on the basis of these rules are given below :

Formula	IUPAC
$\text{K}[\text{MnO}_4]$	Potassium tetraoxomanganate(VII)
$\text{Na}_2[\text{CoCl}_4]$	Sodium tetrachloridocobaltate(II)
$[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel(0)
$\text{K}_2[\text{NiCl}_4]$	Potassium tetrachloridenickelate(II)
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II)ion
$[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$	Tetraamminecopper(II)chloride
$[\text{Cr}(\text{CO})_6]$	Hexacarbonylchromium(0)

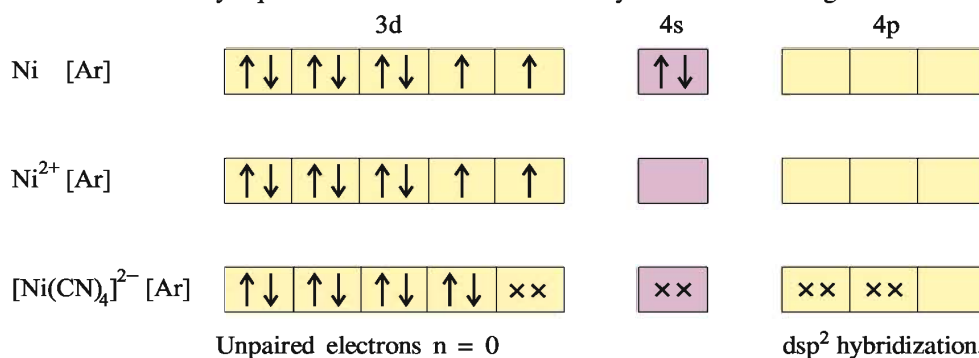
$[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{SO}_4$	Tetraamminediaquanickel(II)sulphate
$[\text{Cr}(\text{OX})_3]^{3-}$	Trioxalatochromate(III)ion.
$[\text{Co}(\text{en})_2(\text{CN})_2]\text{Cl}$	Dicyanobis(ethane-1,2-diamine)cobalt(III)chloride
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)
$(\text{NH}_4)_2[\text{MoO}_4]$	Ammonium tetraoxomolybdate(VI)
$\text{K}_2[\text{CrF}_6]$	Potassium hexafluoridoochromate(IV)
$\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$ (Sodium nitroprusside)	Sodiumpentacyanonitrosoniumferrate(II)
$\text{Na}_4[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrocobaltate(II)
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{OX})_2]$	Ammonium diamminedioxalatocobaltate(III)
$[\text{Pt}(\text{Pn})_2\text{CO}_3]\text{SO}_4$	Carbonatobis(propane-1,3-diammine)platinum(II)sulphate
$[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$	Diammineargentun(I) dicyanoargentate(I)
$[\text{Cr}(\text{en})_3][\text{Cr}(\text{OX})_3]$	Tris(ethane-1,2-diamine)chromium(III)trioxalatochromate(III)
$[\text{Pt}(\text{NH}_3)_2\text{ClNO}_2]$	Diamminechloridonitroplatinum(II)
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$	Tetramminecarbonatocobalt(III)chloride.
$[\text{Cr}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{NO}_3$	Tetraamminechloridonitritochromium(III)nitrate
$\text{Na}_2[\text{Ni}(\text{EDTA})]$	Sodium ethylenediamminetetraacetatonickelate(II)
$[\text{Pt}(\text{Py})_4][\text{PtBr}_4]$	Tetrapyridineplatinum(II)tetrabromidoplatinate(II)
$[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$	Dichloridodi(methanamine)copper(II)
$[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{SCN})_6]$	Hexaamminechromium(III)hexathiocyanatochromate(III)

Formula from the IUPAC name of the complex

- Tetrammineaquachloridocobalt(III)chloride
 $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
- Potassium tetrahydroxozincate(II)
 $\text{K}_2[\text{Zn}(\text{OH})_4]$
- Sodium trioxalatoaluminate(III)
 $\text{Na}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
- Dichloridobis(ethane-1,2-diamine)cobalt(III)ion.
 $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
- Pentacyrbonyliron(0)
 $[\text{Fe}(\text{CO})_5]$

4.9 Geometrical Structures and The Magnetic Properties of Complex Compounds

$[\text{Ni}(\text{CN})_4]^{2-}$ complex ion : In tetracyano nickelate (II) four CN^- strong ligands are combined with Ni^{2+} metal ion. In this compound, four ligands are joined and so possesses square planar or tetrahedral structure. Here the electronic configuration of Ni metal and Ni^{2+} ion are $[\text{Ar}]3d^84s^2$ and $[\text{Ar}]3d^8$ respectively. The arrangement of eight electrons in 3d-orbitals is shown in the following figure. The orbitals are shown by square blocks and the electrons by vertical arrow sign \uparrow or \downarrow .



Unpaired electrons $n = 0$

dsp^2 hybridization.

Hence $\mu = 0 \text{ BM}$

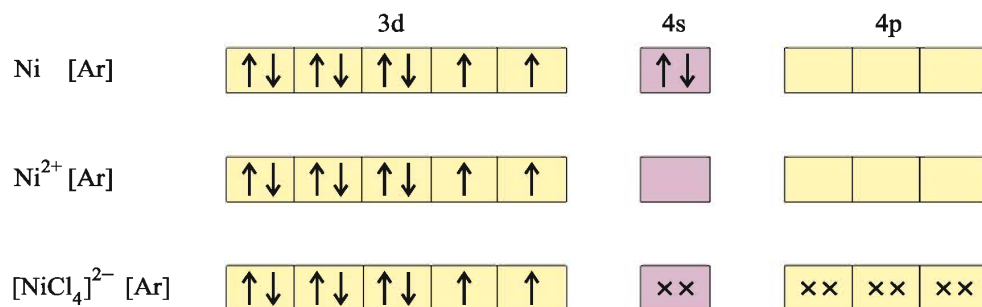
In one square block, the vertical arrows in opposite directions show electron pairs in which the rotation of both the electrons is in opposite directions. Here Ni^{2+} metal ion combines with four CN^- strong ligand and forms complex ion. Each CN^- strong ligand gives one electron pair to Ni^{2+} metal ion. Hence Ni^{2+} metal ion receives four electron pairs from four ligands.

If the structure of $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar, then dsp^2 type hybridization occurs in Ni^{2+} metal ion. For this, one 3d-orbital, one 4s-orbital and two 4p-orbitals take part in hybridization of dsp^2 , orbitals having equal energy are produced. For this, the arrangement of eight electrons in 3d-orbitals of Ni^{2+} metal ion, the charge is necessary because of the strong ligand like CN^- . In this two unpaired electrons in 3d-orbital, one unpaired electron of 3d-orbital enters into the other 3d-orbital having unpaired electron and forms a pair. As a result one 3d-orbital becomes vacant.

[Note : Because of strong ligands like CN^- , NH_3 and CO , the unpaired electrons get paired in rearrangement of electrons.]

This vacant one 3d-orbital, one 4s-orbital and two 4p-orbitals overlap and form dsp^2 four hybrid orbitals and arrange at 90° angle in square planar form. In the four dsp^2 orbitals produced, this four electrons pairs coming from four strong ligand CN^- , get arranged, which are shown by $\times\times$ sign. **Here $[\text{Ni}(\text{CN})_4]^{2-}$ complex possesses dsp^2 hybridization and its all 3d-orbitals have paired electrons and so it becomes diamagnetic and its geometric structure is square planar.**

$[\text{NiCl}_4]^{2-}$ complex ion : In tetrachlorido nickelate (II) complex ion, Ni^{2+} metal ion is combined with four weak Cl^- ligands. As CN^- strong ligand comes nearer to the metal ion because it possesses more attraction, while weak Cl^- ligand does not come near to metal ion because it possesses less attraction. Hence, the 3d-orbital of Ni^{2+} ion is not capable of forming co-ordinate covalent bond with four Cl^- weak ligand. Hence, the rearrangement of electrons in 3d-orbitals if Ni^{2+} metal ion is not required. Here, one 4s, and three 3d-orbitals take part in hybridization and form sp^3 hybrid orbitals having same energy, which is arranged at the angle of $109^\circ 28'$ tetrahedrally in which the four electron pairs coming from four weak Cl^- ligand are arranged.



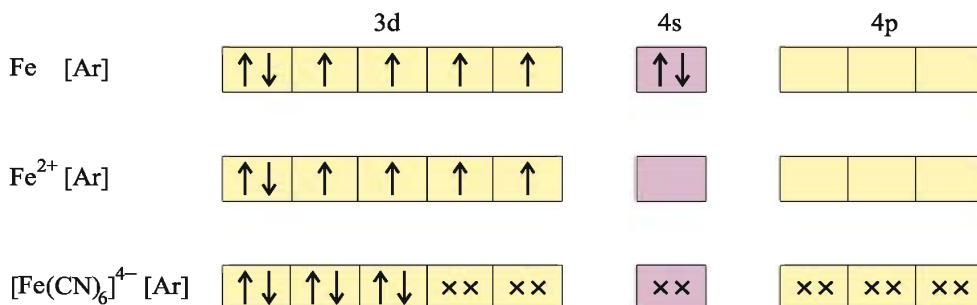
Unpaired electrons $n = 2$

sp^3 hybridization

Hence, $\mu = 2.83$ BM

Because of this [NiCl₄]²⁻ complex ion has sp^3 type of hybridization and its geometrical structure becomes tetrahedral. As there are two unpaired electrons in two 3d-orbitals, the theoretical value of its magnetic moment becomes 2.83 BM and the value of experimental magnetic moment is 2.90 BM. So it becomes paramagnetic.

[Fe(CN)₆]⁴⁻ complex ion (Ferrocyanide ion) : In hexacyano ferrate (II) complex ion Fe²⁺ metal ion has combined with six CN⁻ strong ligand and so it possesses octahedral structure. Here, the electronic configuration of Fe metal and Fe²⁺ ion are [Ar] 3d⁶4s² and [Ar]3d⁶ respectively. The arrangement of six electrons in 3d-orbitals is shown below :



Number of unpaired electrons $n = 0$

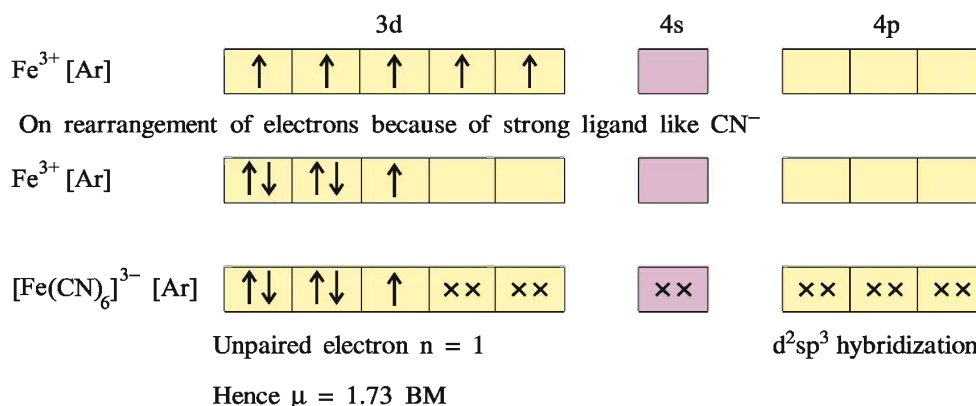
d^2sp^3 hybridization

Hence, $\mu = 0$ BM

In Fe²⁺ ion d^2sp^3 type hybridization occurs. Octahedral structure is obtained in this hybridization. In d^2sp^3 hybridization, the inner 3d-orbital takes part.

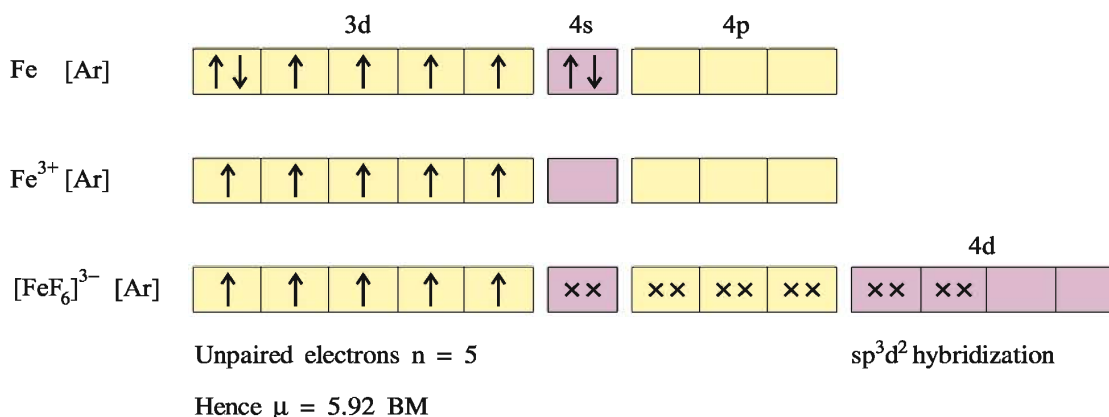
For d^2sp^3 hybridisation there must be two 3d-orbitals vacant in Fe²⁺ metal ion. For this, the rearrangement of six electrons in 3d-orbitals is necessary i.e. as the CN⁻ ion is a strong ligand, total six electrons form three electron pairs and get arranged in 3d-orbitals. As a result the vacated two 3d-orbitals, one 4s-orbital and three 4p-orbitals overlap and form d^2sp^3 hybridization; six d^2sp^3 hybrid orbitals having same energy, produced in the above are arranged octahedrally. In d^2sp^3 hybrid orbitals six electron pairs coming from six CN⁻ strong ligand are arranged. **Here, [Fe(CN)₆]⁴⁻ complex ion possesses d^2sp^3 type hybrid orbitals and its geometrical structure is octahedral. In the 3d-orbitals of this complex only paired electrons are there and so it becomes diamagnetic.**

$[\text{Fe}(\text{CN})_6]^{3-}$ Hexacyanoferrate (III) ion (Ferricyanide ion) : In hexacyanoferrate (III) complex ion, the oxidation state of Fe is +3 and its coordination number is 6. The electronic configuration of Fe^{3+} metal ion in this complex compound is $[\text{Ar}] 3d^5$. As CN^- is a strong ligand, rearrangement of electrons in 3d-orbitals is necessary. On rearrangement of five electrons in 3d-orbitals, two orbitals become paired and one electron remains unpaired in 3d-orbital. Hence, two 3d-orbitals, one 4s-orbital and three 4p orbitals overlap and form d^2sp^3 type hybridization. Six electron pairs coming from strong ligand CN^- are arranged in six d^2sp^3 hybrid orbitals having same energy. Here, $[\text{Fe}(\text{CN})_6]^{3-}$ complex ion possesses d^2sp^3 hybridization.



$[\text{Fe}(\text{CN})_6]^{3-}$ complex ion possesses d^2sp^3 hybridization whose geometrical structure is octahedral. As there is one unpaired electron in its 3d-orbit it becomes paramagnetic and the theoretical value of magnetic moment becomes 1.73 B.M. and the experimental value is about 1.8 BM.

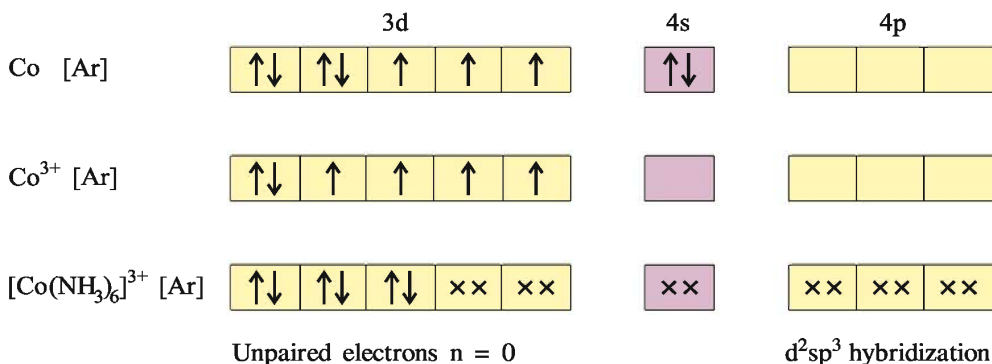
$[\text{FeF}_6]^{3-}$ complex ion : In hexafluorido ferrate (III) ion, six weak F^- ligands combine with Fe^{3+} metal ion. As six F^- weak ligands are combined with Fe^{3+} metal ion, this complex compound possesses sp^3d^2 hybridisation and octahedral structure. In this complex ion in 3d-orbitals, five unpaired electrons are there and so it becomes paramagnetic. Its theoretical value of magnetic moment is 5.92 B.M.



If ligand had been strong, the electrons present in 3d-orbitals would have rearranged but as F^- is a weak ligand, the rearrangement of five electrons in 3d-orbital does not take place. So one 4s-orbital, three 4p-orbitals and two 4d-orbitals, aggregating six orbitals overlap and sp^3d^2 hybridization occurs. In this six sp^3d^2 hybrid orbitals having same energy, six electron pairs coming from six weak F^- ligand are

arranged. Here, $[\text{FeF}_6]^{3-}$ complex ion possesses sp^3d^2 hybridization. So, its geometrical structure is octahedral and complex is paramagnetic. Generally, the basis of d^2sp^3 hybridisation or sp^3d^2 hybridisation is dependent on the strength of ligand.

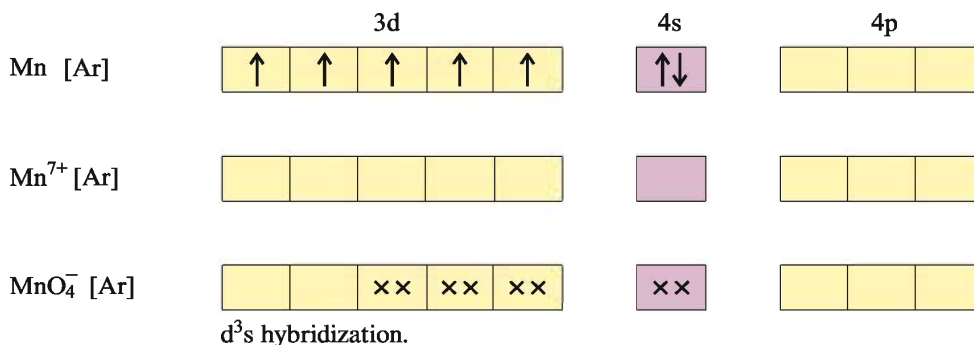
$[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ion : In hexaamminecobalt (III) complex ion the oxidation state of cobalt is +3. The electronic configuration of Co metal and Co^{3+} metal ion are $[\text{Ar}]3\text{d}^74\text{s}^2$ and $[\text{Ar}]3\text{d}^6$ respectively. Here, in Co^{3+} metal ion, the six electrons- one in 3d-orbital are paired and in four other 3d-orbitals unpaired electrons are present. When the strong ligand NH_3 gives six electron pairs to Co^{3+} metal ion, it forms six co-ordinate covalent bonds, the hybridization of Co^{3+} ion, is of d^2sp^3 and six electron pairs of six NH_3 strong ligand are arranged in six hybrid orbitals. Here, to have d^2sp^3 hybridization, two 3d-orbitals must be vacated. NH_3 being a strong ligand, there is rearrangement of six electrons in 3d-orbitals and become paired and two 3d-orbitals remain vacant. Two 3d-orbitals, one 4s-orbital and three 4p-orbitals overlap and d^2sp^3 hybridization occurs so that six hybrid orbitals having same energy get arranged octahedrally.



Hence diamagnetic $\mu = 0$ BM

Here, $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex possesses d^2sp^3 of hybridization and the complex becomes octahedral. As there is no unpaired electron in 3d-orbitals, the complex becomes diamagnetic.

$[\text{MnO}_4]^-$ complex ion : In tetraoxomanganate (VII) complex, four O^{2-} weak ligands are combined with Mn^{7+} metal ion, so it possesses tetrahedral structure. The electronic configuration of Mn metal and Mn^{7+} metal ion are $[\text{Ar}]3\text{d}^54\text{s}^2$ and $[\text{Ar}]3\text{d}^0$ respectively. Here 3d and 4s-orbitals are vacant. In Mn^{7+} metal ion, one 4s and three 3d-orbitals overlap and d^3s type hybridization occurs. In d^3s hybridisation, four hybrid orbitals having same energy are arranged on the four corners of tetrahedral. Four electron pairs of oxygen ions from co-ordination covalent bonds in hybrid orbitals.



In $[\text{MnO}_4]^-$ complex ion there is d^3 hybridization. The co-ordinate bonds formed by O^{2-} weak ligand electrons undergo d-d transition in d-orbital, so that even though there is no unpaired electron in Mn^{7+} of MnO_4^- , it gives coloured ion.

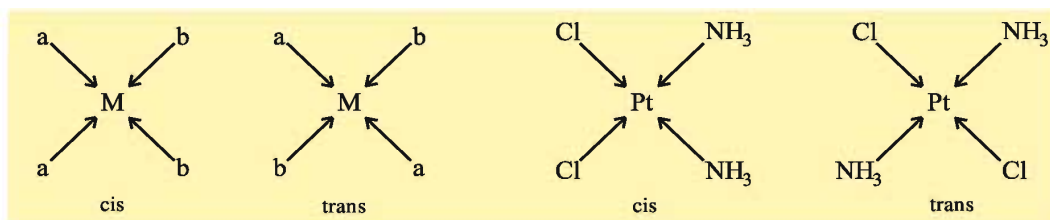
4.10 Isomerism in Complex Compounds

The complex compounds whose molecular formulae are same but the structural formulae are different, are called isomers of each other. Complex compounds possess geometrical isomerism, optical isomerism and structural isomerism.

Geometrical isomerism : Geometrical isomerism is generally observed in square planar and octahedral complex ions. If the two same ligands combined to metal ion are in nearby position to each other, then that isomer is called cis isomer and if they are in opposite positions then the isomer is called trans isomer.

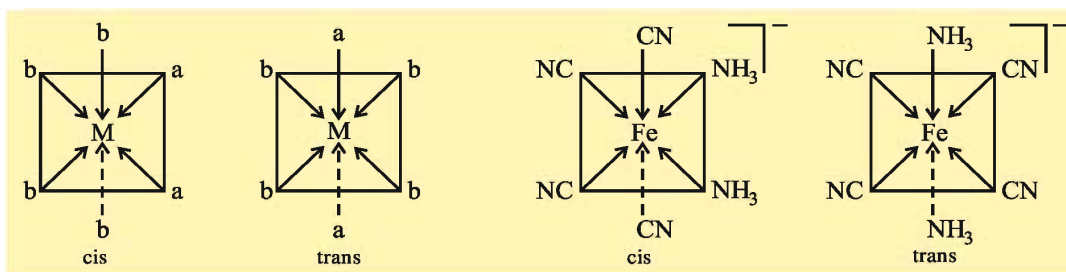
In the square planar structure if there are M metal ion and two different types of two ligands a and b combine then two geometrical isomerism cis and trans are produced

e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



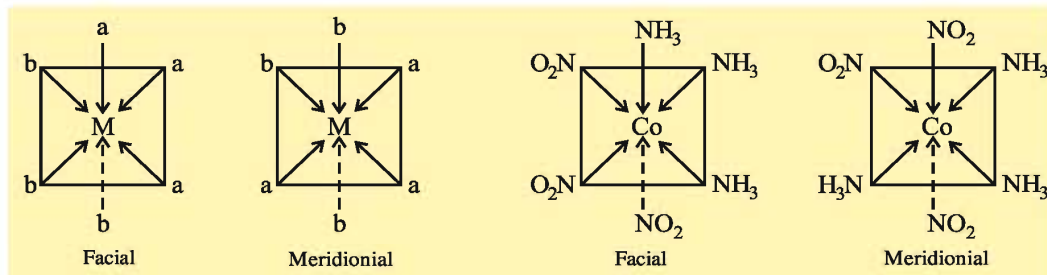
In octahedral structure, if M is metal ion and two ligands of type a and four ligands of type b are there, then two types of geometrical isomerism cis and trans are produced

e.g. $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$



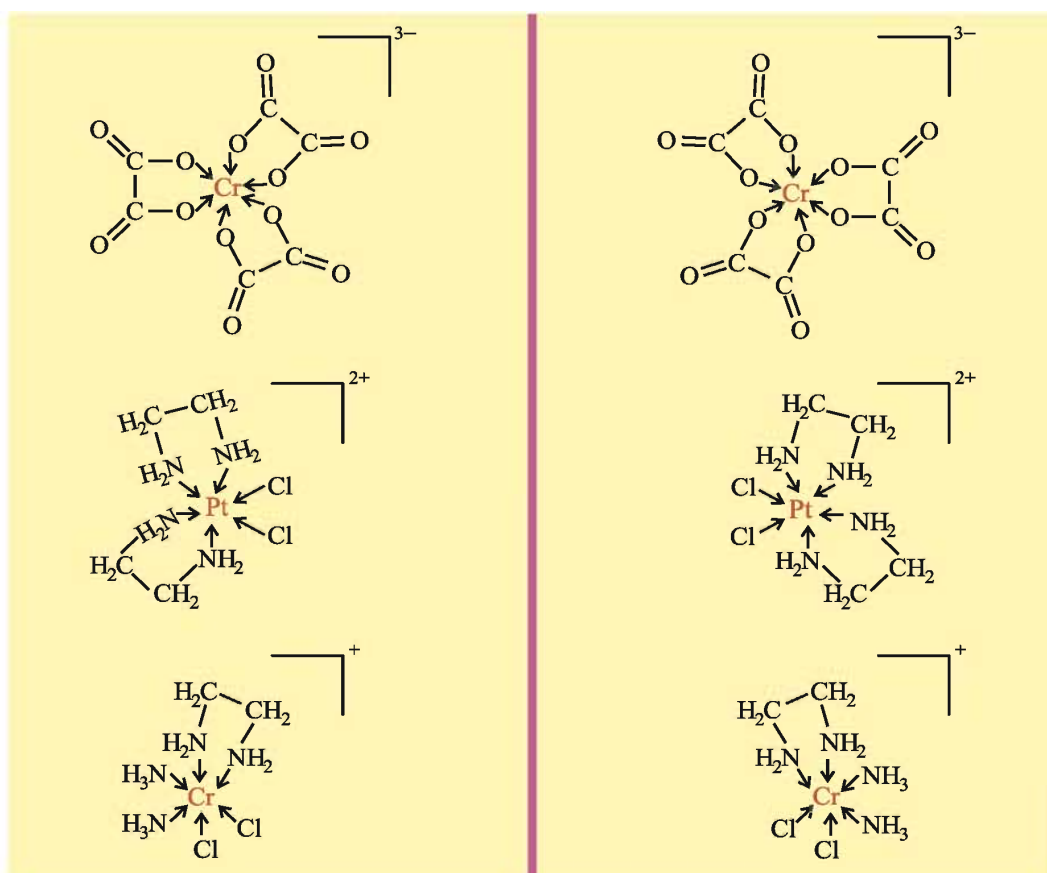
In octahedral structure, if M is metal ion and three ligands of two types a and b are present then two types geometrical isomerism-facial and meridional- are produced

e.g. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$



Optical isomerism : Optical isomerism is generally observed in octahedral complex-chelate ions. There are certain complex compounds in which molecular formula and structural formulas are same, but the two isomers produced, because of directional arrangement of ligands in it. They are mirror images to each other and the superimposition of two isomers on each other is not possible. This type of complex ions possess property of chirality and they are called optical isomers. **The main difference between these two isomers is that both the isomers rotate the plane polarized light to left or right in directions opposite to each other.** If it rotates angle of rotation on left side, then that isomer is called *l* (levo) or (–) and one which rotates angle of rotation on right side, then that isomer is called *d* (dextro) or (+). The equal proportion mixture of dextro and levo isomers is called racemic, *dl* or (±) mixture.

e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, $\text{cis} [\text{PtCl}_2(\text{en})_2]^{2+}$, $[\text{CrCl}_2(\text{NH}_3)_2(\text{en})]^+$

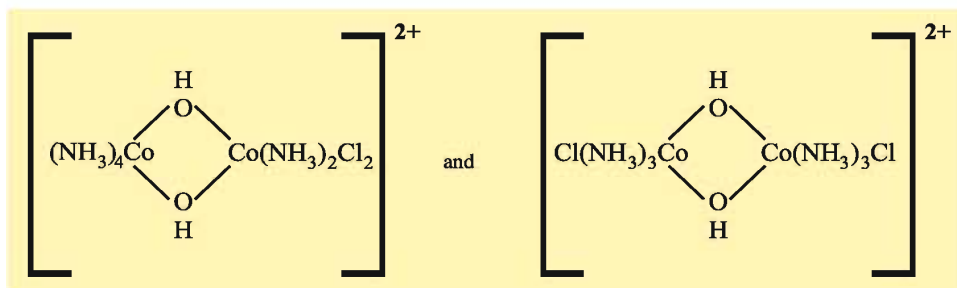


Structural isomerism : Various types of isomerism as compared to organic chemistry are observed because of different geometrical arrangements and different types of bonds in structural isomerism co-ordination. (i) Linkage isomerism (ii) Co-ordination isomerism (iii) Ionic isomerism (iv) Hydration isomerism.

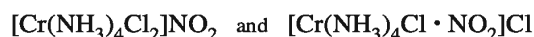
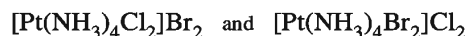
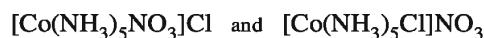
(i) Linkage isomerism : NO_2^- ion combines with metal ion with nitrogen atom through co-ordination and acts as nitro ($-\text{NO}_2$) ligand or through any one of the oxygen by co-ordination and act as nitrito (ONO^-) ligand. Thus one ligand forms isomers by bonding of different atoms. Some of the examples are given below :

$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$ pentaamminenitrocobalt (III) ion and $[\text{Co}(\text{O} \cdot \text{NO})(\text{NH}_3)_5]^{2+}$ pentaammine nitrito cobalt (III) ion and $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is yellow brown coloured and $[\text{Co}(\text{O} \cdot \text{NO})(\text{NH}_3)_5]\text{Cl}_2$ is of red colour. Similarly CNS^- ion can be co-ordinated through nitrogen or sulphur and gives different isomers like. $[\text{Mn}(\text{CO})_5\text{SCN}]^+$ and $[\text{Mn}(\text{CO})_5\text{NCS}]^+$.

(ii) Co-ordination isomerism : When in co-ordination compounds, both positive ion and negative ion are complex ions then there is exchange between the two in the co-ordination sphere and isomers are formed e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$ $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}$ $[\text{Co}(\text{CN})_6]^{3-}$; $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}$ $[\text{CuCl}_4]^{2-}$. This type of isomerism is observed when metal ion is in different oxidation states. e.g. $[\text{Pt}^{\text{III}}(\text{NH}_3)_4]$ $[\text{Pt}^{\text{IV}}\text{Cl}_6]$ and $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_2]$ $[\text{Pt}^{\text{III}}\text{Cl}_4]$ **specific type of co-ordination isomerism is called position isomerism which is observed in cyclic complex compounds.**



(iii) Ionisation isomerism : The compounds whose proportion by weight and the component are same but they give different ions in solution, then that type of isomerism is called ionization isomerism. e.g.



(iv) Hydration isomerism : This type of isomerism is a special type of ionization isomerism. Three isomeric forms of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are known.

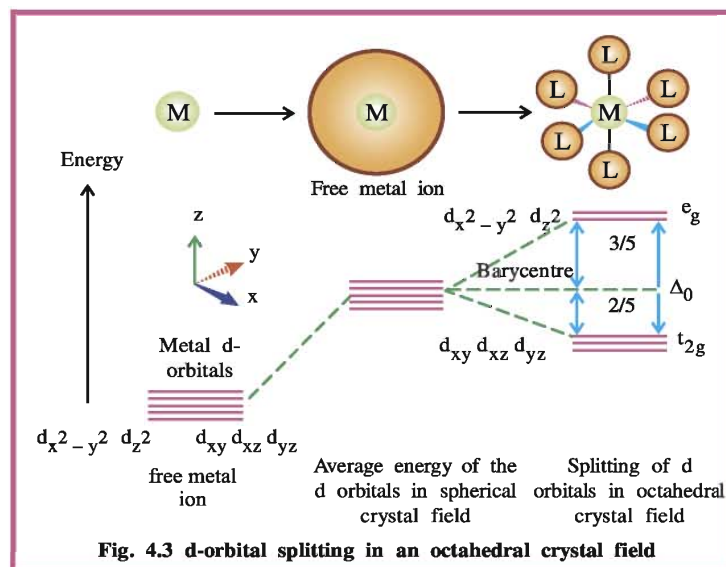
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet). If it is kept over H_2SO_4 , it does not lose water and 3Cl^- and 3Ag^+ ions take part in precipitation.
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (gray green). If it is placed over H_2SO_4 , then it loses one molecule of water and 2Cl^- ions take part in precipitation with 2Ag^+ ions.
- If $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (green) is placed over H_2SO_4 it loses 2 molecules of water and Cl^- ion takes part in precipitation with Ag^+ ion. Here, both ionization and hydration isomerisms are found. In such isomers, difference in their physical and chemical as well as colour is found.

Limitations of valence bond theory : When co-ordination compounds are formed, the valence bond theory is mostly applied for magnetic nature and structural formation. It has following limitations :

- (i) It consists of some assumptions.
- (ii) It cannot interpret quantitatively the magnetic information.
- (iii) It is not able to explain the colours of co-ordination compounds.
- (iv) It cannot interpret quantitatively thermodynamics and kinetic stabilities of co-ordination compounds.
- (v) It does not make exact prediction regarding the tetrahedral and square planar structures of four co-ordination number complexes.
- (vi) It cannot distinguish the weak and strong ligands.

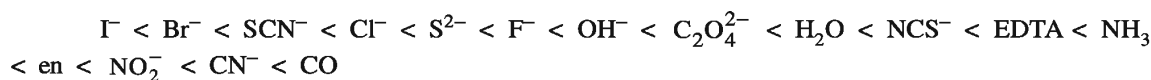
4.11 Crystal Field Theory

Crystal Field Theory (CFT) is known as electrostatic model in which it is believed that there is ionic bond between metal and ligand. According to this theory, negatively charged ligand or polar neutral molecule forms ionic bond with metal ion. All the five types of d-orbitals are degenerate (same energy) in free gaseous form of metal atom or ion (Fig. 4.2). In addition to this, if there is spherical negatively charged field having spherical symmetry around the metal atom or ion, even then d-orbitals remain degenerate but when ligands are arranged around the metal atom or ion then the d-orbitals do not remain degenerate but gets split (fig. 4.3). The splitting of orbitals depends on the nature of crystal field.



(A) Crystal field splitting in octahedral complexes : In octahedral complex, there are six ligands around the metal atom or ion. Here there is repulsion between electrons of d-orbital and electrons of ligand (or between negative ions); $d_{x^2-y^2}$ and d_{z^2} orbitals arranged on this axis experience more repulsion with ligand and will be raised in energy, while there is less repulsion between d_{xy} , d_{yz} , d_{xz} orbitals arranged between the axes, with ligand. Hence, their average energy of spherical crystal field decreases. As the degeneracy of these orbits is removed, it results into three orbitals having lower energy t_{2g} and higher energy possessing e_g orbitals. This type of phenomenon is called crystal field splitting. The splitting of energy of orbitals observed in octahedral complex is shown by Δ_0 . Thus, in e_g orbitals there will be increase by $\frac{3}{5}\Delta_0$ and there will be $\frac{2}{5}\Delta_0$ decrease in energy of three t_{2g} orbitals.

The splitting of crystal field (Δ_0) depends on electric charge of metal ion and ligand. Some ligands produce strong field, so that the splitting of orbitals is more in proportion. While certain ligands produce weak field so that the splitting of orbitals is less in proportion. Generally, the series of ligands on the basis of increase in strength of fields by ligands, can be shown as below :



The above series is called spectrochemical series. If in the metal ion, there are 1, 2 or 3 electrons in d-orbitals, then their arrangement will be in t_{2g} orbitals having low energy, according to Hund's rule. But if there are 4 electrons (d^4) in the d-orbitals then there are two possibilities as follows :

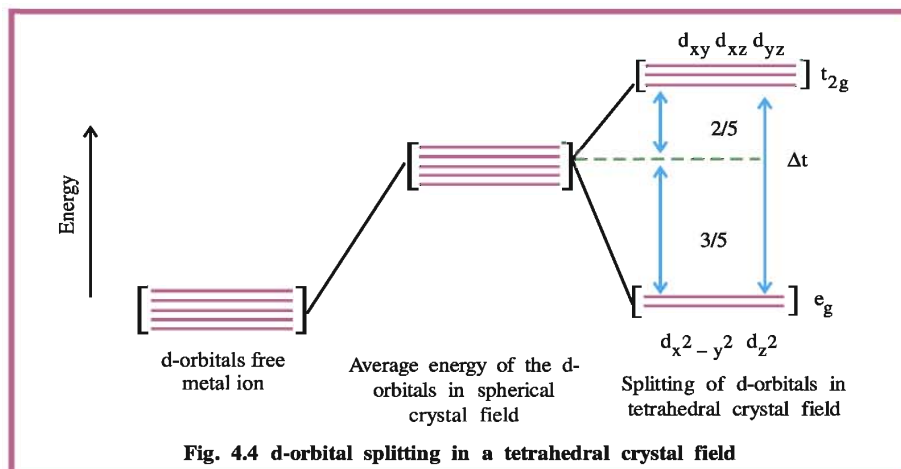
- The fourth electron will be arranged by pairing with any one electron present in t_{2g} orbitals.
- The fourth electron will be arranged in e_g orbital neglecting giving energy for pairing.

Which of the above two possibilities can be possible depends on the splitting of crystal field (Δ_0) and on reactive magnitude energy of pairing; p .

- If $\Delta_0 < p$ then the fourth electron will be arranged in e_g orbital so that electronic structure will be $t_{2g}^3 e_g^1$. For the ligands producing weak field, $\Delta_0 < p$ and form complexes having higher spins.
- If $\Delta_0 > p$ then the fourth electron will be arranged in t_{2g} orbital so that the electronic structure will be $t_{2g}^4 e_g^0$ for ligands producing strong field $\Delta_0 > p$ and for complexes having low spins.

Experimental findings suggest that for complexes having d^4 to d^7 electronic configuration the ligands having stronger field give more stability than complexes having weak field.













(B) Crystal Field Splitting in Tetrahedral Complexes : In the formation of tetrahedral structure, the splitting of d-orbitals is in opposite nature to octahedral complexes. Like octahedral, if tetrahedral complex possesses equal distance between, metal, ligand, metal-ligand, then $\Delta_t = \frac{4}{9} \Delta_0$. Hence if the value of Δ_t is not sufficiently high, pairing of electrons does not occur. Hence low spin is observed in less proportions. The splitting of d-orbitals in tetrahedral structure is shown in the fig. 4.4.



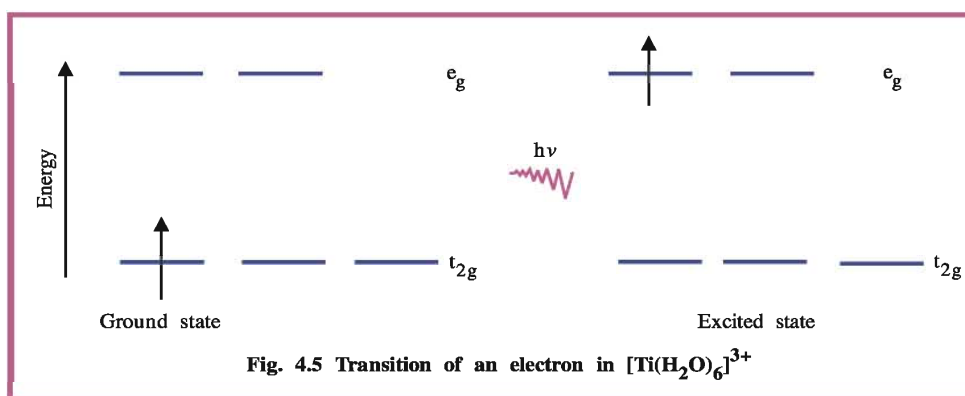
Colour in co-ordination compounds : We have studied earlier that the transition metal complexes exhibit wide variety of colours, which is one of their important properties. **This means that when white light passes through the sample, then it forms definite visible spectrum.** Others are removed from the white light. Hence, for a long time white light is not obtained. The absorption of colour is one complementary matter. The complementary colour is dependent on the wavelength. If complex absorbs green colour, then it will be seen red.

In the table 4.5 absorption of different wavelengths and observed colours are shown.

Table 4.5 Absorbed wavelength of light and observed colour of complex compounds

Co-ordination compounds	Absorbed light wavelength nm	Absorbed colour of light	Colour observed of co-ordination compounds
$[\text{CoCl}(\text{NH}_3)_3]^{2+}$	535	Yellow 	Violet 
$[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$	500	Bluish green 	Red 
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue 	Yellowish orange 
$[\text{Co}(\text{CN})_6]^{3+}$	310	Ultraviolet 	Light yellow 
$[\text{Cu}(\text{H}_2\text{O})]^{2+}$	600	Red 	Blue 
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Bluish green 	Light violet 

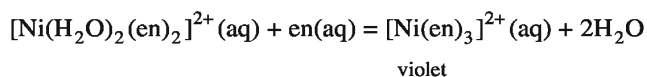
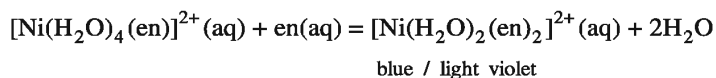
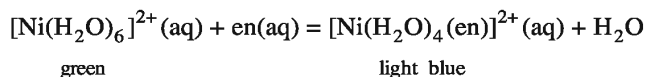
The colours of co-ordination compounds can be explained on the basis of crystal field theory. e.g. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, which has violet colour. This is octahedral complex in which one electron of d-orbital from metal ion complex is in stable state at t_{2g} one electron. (One electron Ti^{3+} is of $3d^1$ system) e_g state is vacant. If photon energy is by absorption of photon with yellow-green light, then the electron goes from t_{2g} layer to e_g layer ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Because of this, violet colour is shown. (As shown in fig. 4.5).



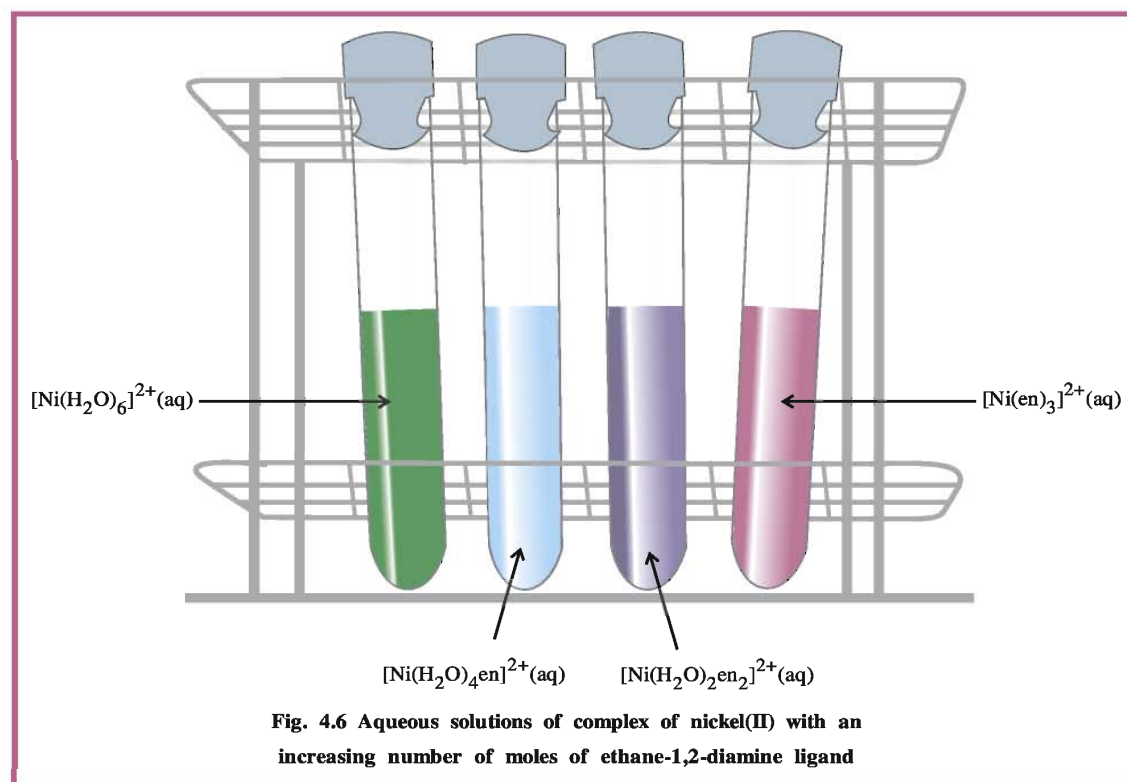
Here, one point is to be noted that in the absence of ligand, there is no splitting in crystal field. So the substance is colourless viz. $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$; when heated water is removed and so it is changed to colourless substance. Similarly anhydrous CuSO_4 is white while $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is of blue colour.

The effect of ligand in complex can be explained by the example of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. This complex is formed by dissolving NiCl_2 in water. Now, if didentate ligand ethane 1,2 diamine (en) is slowly added

so that the molar ratio of en and Ni (en:Ni); is 1:1, 2:1, 3:1, the corresponding change in colour of complex is as follows :



This series of colours is shown in fig. 4.6



The magnetic properties, colour and the formation of structures of complex compounds can be successfully explained by crystal field model. The effect of many diversities is observed in charge of ligand and the ionic ligands. The position of anionic ligand is observed at the lower end in the spectrochemical series. Also there is no covalent bond character in bonding of central atom and that ligand. Thus, the limitation of CFT led to the development of field of study of molecular orbital theory.

The importance and uses (applications) of complex compounds : Co-ordination compounds. have wide range of applications and hence are very useful in mineral nutrition of plants and animals. It plays an important role in analytical chemistry. It possesses great utility in metallurgy, biological system and industries and drugs. They can be described as follows :

- Co-ordination compounds are useful in quantitative and qualitative methods in chemical analysis. We are familiar with the colour produced by their reaction on the basis of number of ligands with metal ions, (especially chelating ligands). Because of the results of the co-ordination compounds, the information about their proportion can be inferred and analysis can be carried out by classical and different instrumental methods. e.g. EDTA, DMG (Dimethyl glyoxime), α -nitroso- β -naphthol, cupferron, etc.
- By titration of hard water with Na_2EDTA the hardness of water can be determined. Ca^{2+} and Mg^{2+} ions give stable complexes with EDTA. The measurement of the order of stability of calcium and magnesium complexes with these ions can be carried out.
- In some important metal reactions such as silver or gold form important complexes. e.g. Gold is combined with cyanide in presence of oxygen and water, combine and solution of $[\text{Au}(\text{CN})_2]^-$ is prepared from this solution. Gold can be obtained in metal form by addition of zinc.
- From co-ordination compounds, like successive decomposition reacts, the metals are formed by purification of metals. e.g. $[\text{Ni}(\text{CO})_4]$ obtained from impure nickel. Then pure nickel is obtained from it by decomposition.
- Co-ordination compounds are very important in biological systems. The dye matter chlorophyll formed by magnesium is responsible for photosynthesis. Iron containing co-ordination compound haemoglobin dye-matter conducts O_2 and so red colour of blood is observed. Cobalt contains co-ordination compound vitamin B_{12} or cyanocobalamine which is antimitotic of pernicious anemia. The other compounds which are substances having biological importance are in enzyme formed by formation of compound with metal viz. carboxypeptidase and carbonic anhydrase (catalysts of biological system-Enzymes).
- Co-ordination compounds are useful as catalysts in many industrial reactions e.g. Rhodium complex $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ which is useful as Wilkinson catalyst in dehydrogenation of alkanes.
- By electroplating with silver and gold soft, attractive replicas are prepared through handicraft. Replicas can be made from complexes $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$ solutions also can be prepared from simple metal ion solutions.
- Film is stabilized by washing with solution of hypo (sodium thiosulphate) in white and black photography which is soluble in non-decomposable AgBr whose formation takes place from complex ion $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.
- In medicinal chemistry, chelate therapy is the important emerging method. For diagnosis of problem like presence of poisonous property of metals in plants and animals is a useful example. To remove the excess proportion of copper and iron, chelating ligands D-Penicillamine and desferrioxime are used for formation of co-ordinate compounds. EDTA is used for diagnostic test for poisoning of lead. From some co-ordinate compounds, the compound like platinum is useful in inhibiting the growth of tumours. e.g. cisplatin and related compound.

SUMMARY

- The salt that is obtained when two or more salts having independent existence combine according to the laws of combination and which maintain the properties of original salts is called double salt e.g. Alum is a double salt.
- Similarly, the compound that is obtained when two or more salts having independent existence combine according to laws of chemical combination and compound having new properties, formed is called complex compound. e.g. $K_3[Fe(CN)_6]$ is a complex salt.
- Most of the complex compounds are formed by elements of d-block (transition elements). In the electronic configuration of these elements, there is successive arrangement of electrons in d-orbitals. when the atom or ion of transition elements has vacant $(n-1)d$, ns and np or ns , np and nd orbitals, these transition elements accept negative ions or neutral molecules and they form the compounds which are called complex compounds. In this type of compounds, the bond that is formed between metal ions of elements and the negative ion or neutral molecules is called co-ordinate covalent bond. Around the centre of the metal ions of the molecules of these compounds, the negative ions or neutral molecules are combined with co-ordinate covalent bond.
- Alfred Werner, first of all gave the theory for complex compounds which is known as Werner's co-ordination theory. Some metals have the secondary valency in addition to their primary valency. By this the ions of that metal combine strongly with the negative ion or neutral molecules in first attraction sphere [].
- According to Werner's theory, the metal ion possesses two types of valencies : Primary valency and secondary valency.
- The primary valency of the metal is equal to its oxidation number or equal to the positive electric charge of the positive ion, which forms ionic bond, so that it gets ionized. The negative ion combines with primary valency.
- The secondary valency depends on the vacant orbitals in metal ion. The secondary valency is satisfied by negative ions or neutral molecules. It does not get ionized. The secondary valency mentions its co-ordination number. The secondary valency is fixed for the metal ion but now, it has been proved that the transition metal ions possess more than one co-ordination number. As the secondary valence being directional determines the geometrical shape of complex compound. From the magnetic properties also the shape of complex can be determined. e.g. In $[Cr(NH_3)_6]Cl_3$, Cr is metal ion and six molecules of neutral molecule ammonia (NH_3) are combined with it by secondary valency which do not get ionized. Hence, the co-ordination number is six. Three Cl^- are combined by primary valency which gets ionized. Hence the primary valency of Cr is three.
- Ligand is an ion having negative electric charge or neutral molecule. The classification of ligand is made on the basis of the number of electron pair donating atoms.

- If the negative ion or neutral molecule in the ligand forms one co-ordinate covalent bond by giving one electron pair to metal ion, then it is called unidentate ligand. Neutral molecules like H_2O , NH_3 , CO , NO and negative ions like Cl^- , Br^- , CN^- act as unidentate ligands.
- The ligand which donates two electron pairs to metal ion, and form two co-ordinate covalent bonds is called didentate ligand. e.g. ethane 1,2-diamine (en), neutral and SO_4^{2-} , CO_3^{2-} negative ions act as didentate ligands.
- The ligand in which three co-ordinate sites are indicated then it is called tridentate. In this type of ligand the atoms donate three pairs of electrons to metal ion and form three co-ordinate covalent bonds. e.g. Propane-1, 2, 3-triamine (ptn) neutral and PO_4^{3-} , AsO_4^{3-} act as negative tridentate ligand.
- Six atoms in EDTA, (ethylene diaminetetracetate) ion, the six atoms donate six electron pairs and form six co-ordinate covalent bonds, which act as hexadentate ligand.
- Generally, the ligand in which two or more than two co-ordination sites are indicated, or the ligand in which two or more than two atoms form co-ordinate covalent bonds by donating electron pairs to metal ion is called polydenate ligand, which combines with metal ion and form complex compounds. They are called chelate compounds which are cyclic and possess higher stability.
- The basic requirements for formation of complex compounds are ligand which can easily donate electron pairs, there must be vacant d-orbitals in the metal ion to accept electron pairs and the metal ion should have the symmetry same as that of the ligand.

The ion satisfying these basic requirements can easily form complex compounds.

- The strength of formation of co-ordinate covalent bonds of different ligands being different, the stronger ligand possesses more attraction towards metal ion and form strong coordinate covalent bond. As a result, the stability of complex having strong ligand is more and the weak ligand containing complex compounds have less stability e.g. The strength of $[\text{Ni}(\text{CN})_4]^{2-}$ is more than that of $[\text{NiCl}_4]^{2-}$.
- A complex compound, in which different types of ligands combine with metal ion and form complex compound, is called mixed ligand complex. If in any of the complex compounds only one metal ion is present, then it is called unicentred complex compound. If in any complex compound, more than one metal ions are present then it is called polycentred complex compound. In such unicentred or polycentred complex compounds, the three dimensional arrangement of ligand, the different geometrical structures are produced in co-ordination compounds, it is called polyhedra. Mostly the geometrical structures are of shapes-tetrahedral square planar, octahedral square pyramidal, trigonal bipyramidal. To understand these geo-

metrical structures, the hybridization of orbitals of metal ion and magnetic properties are very useful. sp^3 hybridisation, dsp^2 hybridisation, d^3s hybridization in metal ions of co-ordination number four is seen. In sp^3d^2 hybridization and d^2sp^3 hybridization, the metal ions of transition elements is seen in metal ions having co-ordination number six. The metal ions of transition elements, magnetic moments of complex compounds of ions, their geometrical structures, types of ligands etc. are described.

- The nomenclature of complex compounds keeping in mind the rules of IUPAC is carried out. In complex compounds the rules are applicable.
- In nomenclature in co-ordination sphere, the name of the ligand according to English alphabets are first mentioned. Then the name of metal is written. The suffix "O" is attached after the name of negatively charged ligand. The name of the neutral ligand is mentioned as its original name. If the number of same ligand is more than the one the prefixes di, tri, tetra...etc. are applied. In the prefix of organic ligand, the prefix is a number then the ligand is placed in bracket and the prefix bis, tris, are attached. If the complex is negative ion then the name of ligand is written first and, in the end the suffix 'ate' is applied to the metal ion. Its oxidation state is shown in Roman number in bracket. If the complex is positive ion or neutral molecule, then successively writing the name of ligand, the name of metal is added at the end and oxidation state is shown in the Roman number.
- The geometry of complex compounds and magnetic properties of the complex depends on the hybridization in it. In complexes having co-ordination number 6 if strong ligand is attached with metal ion in complex, the oxidation state is shown in Roman numbers.
- In complex compounds, the geometrical structures are dependent on hybridization in it. In complex having co-ordination number 4, if the strong ligand is combined with metal ion then dsp^2 hybridization takes place in the complex and the structure is square planar. The example of this are $[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$ etc. If the co-ordination number is 4 in the complex, and the weak ligand combines with the metal ion then sp^3 hybridization takes place e.g. $[NiF_4]^{2-}$, $[Ni(H_2O)_4]^{2+}$, etc. If the co-ordination number in complex ion is six, and the strong ligand is combined with metal ion, then d^2sp^3 hybridization and if weak ligand is combined with metal ion, then sp^3d^2 hybridization takes place, e.g. In $[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$ d^2sp^3 hybridization is there, while in $[FeF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ sp^3d^2 hybridization is there. In MnO_4^- and CrO_4^{2-} there is d^3s hybridization, there are no unpaired electrons in d-orbital due to Mn^{7+} and Cr^{6+} oxidation states; but d-d transition takes place by electrons of ligand, and so it becomes coloured.
- Three types of isomerism are observed in complex compounds-geometrical isomerism, optical isomerism and structural isomerism.

- In geometrical isomerism, complex compounds having co-ordination number four- ML_2A_2 type, cis and trans isomerism is observed. In complex compounds having co-ordination number six - ML_4A_2 type, cis and trans while in ML_3A_3 facial and meridional isomerism are observed. In optical isomerism, leavo and dextro isomers are observed.
- In structural isomerism, ionic isomerism, hydration isomerism, co-ordination number isomerism and linkage isomerism are observed.
- In formation of co-ordination compounds the magnetic nature and structural formation with the help of valence bond theory; it has limitations. It cannot interpret the quantitatively the magnetic information and can not explain about the colour in co-ordination compounds. It can not give meaning of thermodynamical stability of co-ordination compounds, also it is not able to detect the difference between weak and strong ligand. To overcome these limitations the crystal field theory (CFT) was presented.
- Crystal field theory is known as electrostatic model in which it is believed that there is ionic bond between metal ion and ligand. According to this theory negatively charged ligand or neutral molecule forms ionic bond. In free metal atom in gaseous state, all the five types of d-orbitals are of equal energy (degenerate) but when ligands are arranged around the metal atom or ion in the complex, the d-orbitals do not remain of equal energy but get splitted. The splitting of orbitals depends on the nature of the crystal field.
- The crystal field splitting (Δ_0) depends on the field produced by electric charge of metal ion and the ligand. Some ligands produce strong field and so splitting is in more proportion. Some ligands produce weak field, so that the splitting is in less proportion. The series of ligands on the basis of the strength of the field produced by ligand can be shown as below :

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$$
 : Spectrochemical series.
- Metal complexes have large magnitude of colours. When the white light passes through the sample, then it forms a specific visible spectrum and the remaining colours of white light are removed. The absorption of colour by complex compounds is dependent on wavelength. If green colour is absorbed then it appears of red colour.
- The colour of co-ordination compounds can be explained on the basis of crystal field theory e.g. $[Ti(H_2O)_6]^{3+}$ violet colour, $[Ni(H_2O)_6]^{2+}$ green colour, and $[Ni(en)_3]^{2+}$ violet colour,
- Co-ordination compounds have great importance. They have immense utility value in nutrition of minerals in plants and animals, analytical chemistry, metallurgy, biological systems and industries. They are also used in various drugs.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) What type of bond is $L \rightarrow M$ in complex compounds ?
(A) Ionic (B) Metallic
(C) Co-ordinate covalent (D) Covalent
- (2) Who gave metal co-ordination theory ?
(A) Albert Werner (B) Schrodinger
(C) August Hofmann (D) Alfred Werner.
- (3) What is the nature of ligand in complex compounds ?
(A) Bronsted-Lowry base (B) Lewis base
(C) Lewis acid (D) Arrhenius acid.
- (4) Which of the following cannot act as ligand ?
(A) H_2O (B) NO_3^- (C) CO_2 (D) CO
- (5) Which of the following compounds is a double salt ?
(A) Potassium permanganate (B) Ferrous ammonium sulphate
(C) Ammonium chromate (D) All the given.
- (6) What is the primary valency of metal ion in the complex $[Co(en)_2Cl_2]NO_3$?
(A) 4 (B) 6 (C) 2 (D) 3
- (7) What is the electrical charge of pentacarbonyl iron (0) complex ?
(A) one (B) two (C) three (D) zero
- (8) What is the secondary valency of metal ion in $[Cr(NH_3)_4OX]NO_3$?
(A) 2 (B) 4 (C) 6 (D) 8
- (9) What is the valency of Fe which does not ionize in $K_3[Fe(OX)_3]$?
(A) Three (B) Four (C) Six (D) One
- (10) How many ions are obtained by ionization of $(NH_4)_2[MoO_4]$ complex compound in aqueous solution ?
(A) 2 (B) 4 (C) 0 (D) 3
- (11) How many ions will be obtained by ionization of ferric hexacyanoferrate(III) complex compound ?
(A) 7 (B) 4 (C) 2 (D) 3

- (12) What is the geometrical shape of $K_4[Ni(CN)_4]$?
 (A) Octahedral (B) Square planar
 (C) Tetrahedral (D) Trigonal pyramidal
- (13) Which of the following is not the chelating ligand ?
 (A) en (B) ptn (C) OX^{2-} (D) CO
- (14) O^{2-} is the example of what type of ligand ?
 (A) Didentate (B) Tridentate (C) Unidentate (D) Hexadentate.
- (15) How many co-ordination sites are in edta ligand ?
 (A) six (B) four (C) three (D) two
- (16) What will be the hybridization in $[Ni(CN)_4]^{2-}$ complex ion ?
 (A) sp^3 (B) dsp^2 (C) sp^3d^2 (D) d^2sp^3
- (17) Which of the following compounds possesses paramagnetic property ?
 (A) $[Ni(NH_3)_4]^{2+}$ (B) $[Fe(CN)_6]^{4-}$ (C) $[Co(NH_3)_6]^{3+}$ (D) $[Fe(CN)_6]^{3-}$
- (18) By which of the following, poisoning of lead in the body can be removed ?
 (A) ptn (B) EDTA (C) pn (D) OX^{2-}
- (19) Which complex is used to stop the growth of tumour in body ?
 (A) Chlorophyll (B) Cisplatin (C) Haemoglobin (D) Ferrocene.
- (20) What is the colour of $[Ni(H_2O)_6]^{2+}$ complex compound ?
 (A) Violet (B) Green (C) Blue (D) Pink
- (21) Mention the electric charge on edta.
 (A) 6- (B) 2- (C) 3- (D) 4-
- (22) Which of the following complex ion does not possess tetrahedral shape ?
 (A) $[MnO_4]^-$ (B) $[Ni(CO)_4]$ (C) $[Ni(CN)_4]^{2-}$ (D) $[Cu(NH_3)_4]^{2+}$
- (23) What is theoretical magnetic moment of complex compound $K_2[NiF_4]$?
 (A) 1.73 BM (B) 2.83 BM (C) 3.87 BM (D) Zero.
- (24) Which of the following ligands acts as strongest ligand ?
 (A) Cl^- (B) NH_3 (C) CO (D) CN^-
- (25) The number of Cl^- combined by secondary valency in $[Fe(NH_3)_4Cl_2]Cl$ is
 (A) 1 (B) 2 (C) 3 (D) 0

- (26) Which of the following complex ions is most stable ?
 (A) $[\text{FeCl}_6]^{3-}$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (C) $[\text{Fe}(\text{NH}_3)_6]^{3+}$ (D) $[\text{Fe}(\text{CN})_6]^{4-}$
- (27) Which of the following complex ions does not possess optical isomerism ?
 (A) $[\text{Co}(\text{en})(\text{NH}_3)_4]^{2+}$ (B) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$
 (C) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{2+}$ (D) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^+$
- (28) Aqueous solution of which complex will be possessing high conductance ?
 (A) Hexamminecobalt(III)chloride
 (B) Tetramminedichloridocobalt(III)chloride
 (C) Pentamminechloridocobalt(III)chloride
 (D) Triamminetrichloridocobalt(III)
- (29) Which of the following is the correct order of spectrochemical series ?
 (A) $\text{Cl}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{NO}_2^- < \text{CN}^-$ (B) $\text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{CN}^- < \text{C}_2\text{O}_4^{2-}$
 (C) $\text{CN}^- < \text{C}_2\text{O}_4^{2-} < \text{Cl}^- < \text{NO}_2^- < \text{F}^-$ (D) $\text{C}_2\text{O}_4^{2-} < \text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{CN}^-$
- (30) Which transition of electrons will be observed in the following when Ti^{3+} ion having complex absorbs visible light ?
 (A) $t_{2g}^0 e_g^1 \rightarrow t_{2g}^1 e_g^0$ (B) $t_{2g}^2 e_g^0 \rightarrow t_{2g}^1 e_g^1$ (C) $t_{2g}^1 e_g^1 \rightarrow t_{2g}^0 e_g^2$ (D) $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$
- (31) The co-ordination number, oxidation number, number of electrons in d-orbital and number of unpaired electrons is respectively in complex $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{ClO}_4$
 (A) 6, 3, 6, 0 (B) 7, 2, 7, 1 (C) 5, 2, 6, 4 (D) 6, 2, 7, 3

2. Answer the following questions in brief :

- (1) What is meant by double salt ?
- (2) What is meant by complex salt ?
- (3) How many types of valencies, the metal ion possesses in complex compound ? and which ?
- (4) Write the valencies of metal ion in $[\text{Fe}(\text{CN})_6]^{4-}$ complex compound.
- (5) What type of ligands are PO_4^{3-} and O^{2-} ?
- (6) What type of bonds are present of the metal ion in complex compound ?
- (7) What is meant by co-ordination site ?
- (8) What is called ligand ?
- (9) Why are the geometrical shapes produced in complexes ?
- (10) What is meant by co-ordination covalent bond ?
- (11) What is meant by secondary valency ? By which type of ions is it satisfied ?

- (12) What is meant by polydentate ligand ? Give any one example.
- (13) What is meant by chelate complex ? Give any one example.
- (14) Draw the structure of $[M-EDTA]^{\pm n}$
- (15) What is meant by mixed ligand complex ? Give an example.
- (16) What is meant by uncentred and polycentred complex compounds ? Give an example.
- (17) Give two examples of complex ions having co-ordination number 4 for different magnetic moments.
- (18) Explain chelate therapy.
- (19) In refining of which metal, the use of complex compounds is made ?
- (20) Describe the use of edta.
- (21) Mention limitations of crystal field theory.
- (22) What type of isomerism is observed in $[Cr(NH_3)_4Cl_2]NO_2$?
- (23) Mention how many types of isomerism are there in $[Pt(en)_2Cl_2]^{2+}$ complex ion and mention them.
- (24) Give two examples of complex ions having sp^3d^2 hybridisation.
- (25) Describe Werner's co-ordination theory.

3. Answer the following questions :

- (1) Explain the difference between double salt and complex salt.
- (2) What is called tridentate ligand ? Explain giving example.
- (3) Explain giving example, hexadentate ligand.
- (4) Mention the basic requirements for the formation of complex compounds.
- (5) Explain stability of complex compounds.
- (6) Explain sp^3d^2 and dsp^2 hybridisation.
- (7) Explain the hybridization and geometrical structure of MnO_4^- complex ion.
- (8) Explain geometrical isomerism.
- (9) Explain optical isomerism.
- (10) Write limitations of valence bond theory.
- (11) Explain crystal field theory.
- (12) Explain the application of complexes in biological systems and photography.

4. Answer the following questions in detail :

- (1) Write the points of Werner's co-ordination theory.
- (2) What is meant by ligand ? Explain its classification.

- (3) Explain the hybridization of orbitals of metal ions in complex compounds and the magnetic properties.
- (4) Explain the geometrical structures and magnetic properties of the following complex compounds with the help of hybridization. $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{FeF}_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{NiCl}_4]^{2-}$
- (5) Explain in detail the structural isomerism with examples.
- (6) Explain crystal field splitting in octahedral complexes and write the limitations of crystal field theory.
- (7) Explain in detail, "Colour in co-ordination compounds."
- (8) Describe the importance and applications of co-ordination compounds.
- (9) Write the IUPAC names of the complex compounds shown below :

