

# Coordination Compounds

## Topic 1

1. The main postulates are :

(i) In coordination compounds, metals show two types of linkages (valencies)-primary and secondary.

(ii) The primary valencies are normally ionisable and are satisfied by negative ions.

(iii) The secondary valencies are non-ionisable. These are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.

(iv) The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

2.  $\text{FeSO}_4$  solution when mixed with  $(\text{NH}_4)_2\text{SO}_4$  solution in 1:1 molar ratio forms a double salt  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  which when dissolved in water dissociates into simple ions to give tests for its constituent ions. When  $\text{CuSO}_4$  is mixed with aqueous ammonia a complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is formed which does not give free  $\text{Cu}^{2+}$  ions in the solution.

3. (i) **Coordination entity** : A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example,  $[\text{CoCl}_3(\text{NH}_3)_3]$  is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{PtCl}_2(\text{NH}_3)_2]$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

(ii) **Ligand** : The ion or molecule bound to the central atom/ion in the coordination entity is called ligand. These may be simple ions such as  $\text{Cl}^-$ , small molecules such as  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , larger molecules such as  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  or  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$  or even macromolecules, such as proteins.

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

(iv) **Coordination polyhedron** : The spatial arrangement of the ligand atoms which are directly attached to the central atom/

ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is octahedral,  $[\text{Ni}(\text{CO})_4]$  is tetrahedral and  $[\text{PtCl}_4]^{2-}$  is square planar.

(v) **Homoleptic and heteroleptic complex** : Complexes in which a metal is bound to only one kind of donor groups, e.g.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g.,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ , are known as heteroleptic.

4. Unidentate ligands are those which bind to the metal ion through a single donor atom. e.g.,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ .

Bidentate ligands are those which bind to the metal ion through two donor atoms. e.g., ethane-1,2-diamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ), oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) ion.

Ambidentate ligands are those which can bind to metal ion through two different donor atoms. e.g.,  $\text{NO}_2^-$  and  $\text{SCN}^-$  ion.

5. (i)  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$ ;  $x - 1 = +2$ ;  $x = +3$

(ii)  $[\text{CoBr}_2(\text{en})_2]^+$ ;  $x - 2 = +1$ ;  $x = +3$

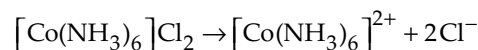
(iii)  $[\text{PtCl}_4]^{2-}$ ;  $x - 4 = -2$ ;  $x = +2$

(iv)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ;  $x - 6 = -3$ ;  $x = +3$

(v)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ ;  $x - 3 = 0$ ;  $x = +3$

6. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion and forms a ring, it is said to be a chelate ligand. The number of such ligating groups is called the denticity of the ligand. Such complexes are called chelate complexes and they tend to be more stable than similar complexes containing unidentate ligands. Example : *EDTA*, *DMG*, etc.

7. (c) : 3 ions are produced by  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ .



8. (c) : Since  $\text{C}_2\text{O}_4^{2-}$  is a bidentate ligand, it forms the most stable complex.

## Topic 2

1. (i) Tetrahydroxozincate(II) ion –  $[\text{Zn}(\text{OH})_4]^{2-}$

(ii) Potassium tetrachloridopalladate(II) –  $\text{K}_2[\text{PdCl}_4]$

(iii) Diamminedichloridoplatinum(II) –  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(iv) Potassium tetracyanonickelate(II) –  $\text{K}_2[\text{Ni}(\text{CN})_4]$

- (v) Pentaamminenitrito-O-cobalt(III) ion –  $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$   
 (vi) Hexaammincobalt(III) sulphate –  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$   
 (vii) Potassium tri(oxalato)chromate(III) –  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$   
 (viii) Hexaammineplatinum(IV) ion –  $[\text{Pt}(\text{NH}_3)_6]^{4+}$   
 (ix) Tetrabromidocuprate(II) ion –  $[\text{Cu}(\text{Br})_4]^{2+}$   
 (x) Pentaamminenitrito-N-cobalt(III) ion –  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$

2. (i) Hexaammincobalt(III) chloride  
 (ii) Diamminechloridomethylamineplatinum(II) chloride  
 (iii) Hexaaquatitanium(III) ion  
 (iv) Tetraamminechloridonitrito-N-cobalt (III)chloride  
 (v) Hexaaquamanganese (II) ion  
 (vi) Tetrachloridonickelate(II) ion  
 (vii) Hexaamminenickel(II) chloride  
 (viii) *Tris* (ethane-1, 2-diamine)cobalt(III) ion  
 (ix) Tetracarbonylnickel (0)

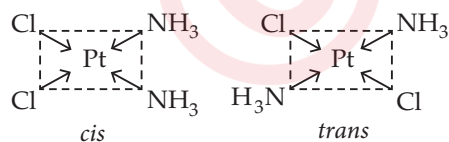
3. Among coordination compounds, there are two main types of isomerism.

- (I) Stereoisomerism  
 (II) Structural isomerism

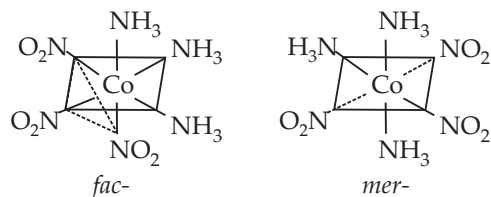
#### Stereoisomerism :

(i) **Geometrical isomerism** : This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula  $[\text{MX}_2\text{L}_2]$  (X and L are unidentate), the two identical ligands may be arranged adjacent to each other in a *cis*-isomer, or opposite to each other in a *trans* isomer.

Another type of geometrical isomerism occurs in octahedral coordination entities of the type  $[\text{Ma}_3\text{b}_3]$  like  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ . If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (*fac*) isomer. When the positions are around the meridian of the octahedron, we get the meridional (*mer*) isomer.

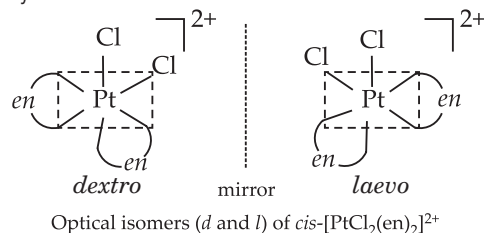


Geometrical isomers  
*cis* and *trans* isomers of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



The facial (*fac*) and meridional (*mer*) isomers of  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

(ii) **Optical isomerism** : Optical isomerism is common in octahedral complexes involving bidentate ligands. In a coordination entity of the  $[\text{PtCl}_2(\text{en})_2]^{2+}$ , only the *cis*-isomer shows optical activity.



Optical isomers (*d* and *l*) of  $\text{cis}-[\text{PtCl}_2(\text{en})_2]^{2+}$

#### Structural isomerism

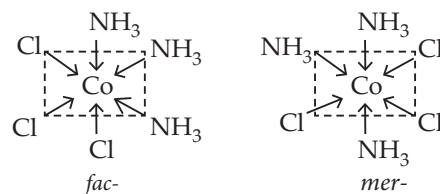
(i) **Linkage isomerism** : Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand,  $\text{NCS}^-$ , which may bind through the nitrogen to give *M-NCS* or through sulphur to give *M-SCN*. This behaviour was seen in the complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ , which is obtained as the red form, in which the nitrite ligand is bound through oxygen ( $-\text{ONO}$ ), and as the yellow form, in which the nitrite ligand is bound through nitrogen ( $-\text{NO}_2$ ).

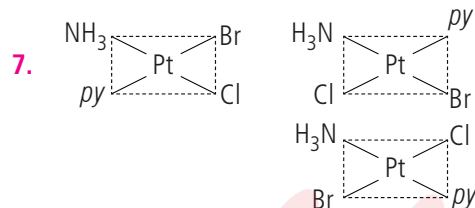
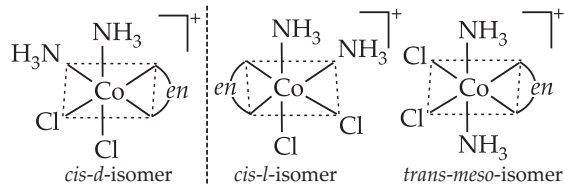
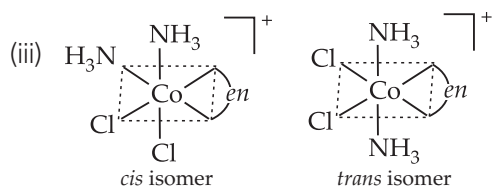
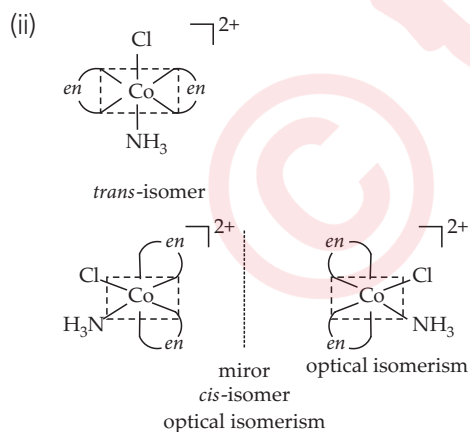
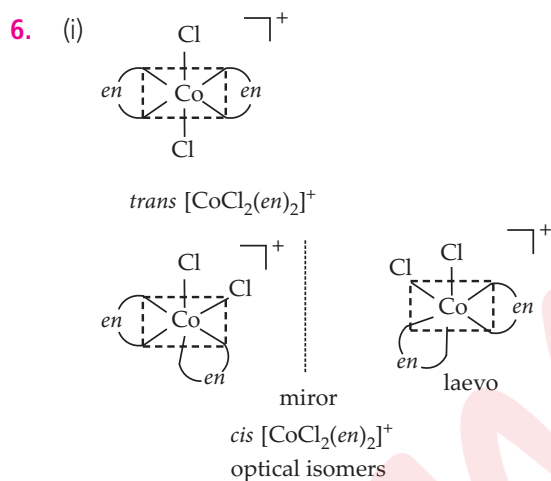
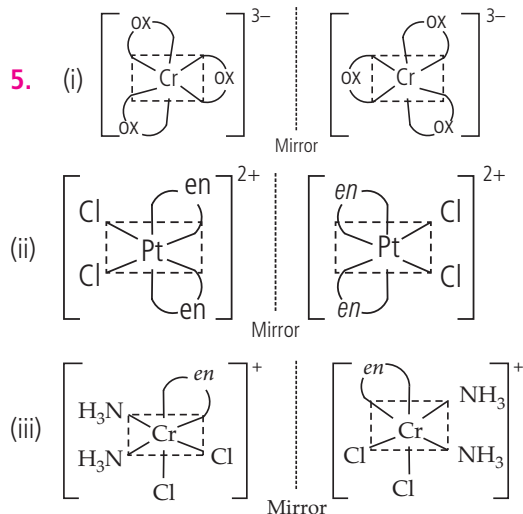
(ii) **Coordination isomerism** : This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ , in which the  $\text{NH}_3$  ligands are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

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

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

4. (i) Zero  
 (ii) Two - Facial and meridional.





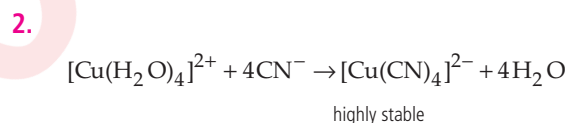
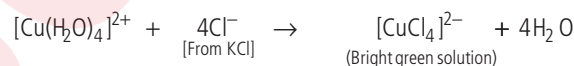
All will show optical isomerism

### Topic 3

1. (i) Aqueous  $CuSO_4$  solution contains  $[Cu(H_2O)_4]^{2+}$  ions which impart blue colour. When KF is added,  $H_2O$  being weak field ligand can be replaced by  $F^-$  forming  $[CuF_4]^{2-}$  ions which impart green colour.



(ii) When KCl is added,  $Cl^-$  ligand replaces  $H_2O$  forming  $[CuCl_4]^{2-}$  ions which has bright green colour.

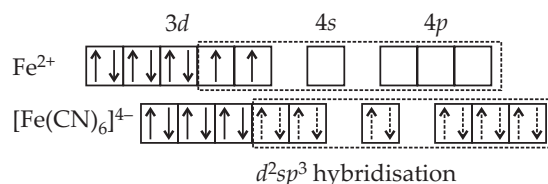


$CN^-$  is a strong field ligand, therefore,  $[Cu(CN)_4]^{2-}$  is highly stable and has large value of stability constant. On passing  $H_2S$ ,  $CuS$  is not formed because this coordination entity does not give  $Cu^{2+}$  ion.

3. (i)  $[Fe(CN)_6]^{4-}$ : Fe(26) has electronic configuration  $[Ar] 4s^2 3d^6$ .



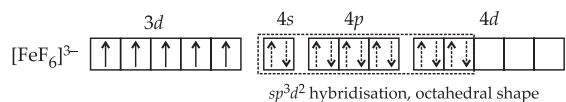
$CN^-$  ion causes pairing of electrons because it is a strong field ligand.



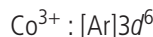
It has octahedral shape and is diamagnetic in nature due to absence of unpaired electrons.

(ii)  $[FeF_6]^{3-}$ : Fe(26) has electronic configuration  $[Ar] 4s^2 3d^6$ .  $Fe^{3+}$ :  $[Ar] 3d^5$

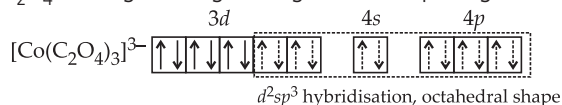
$F^-$  being a weak field ligand, does not cause pairing of electrons.



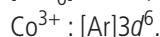
(iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ : Co(27) has electronic configuration  $[\text{Ar}] 4s^2 3d^7$ .



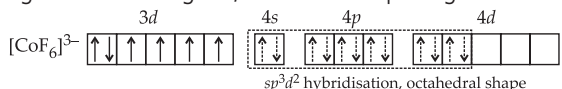
$\text{C}_2\text{O}_4^{2-}$  being a strong field ligand causes pairing of electrons.



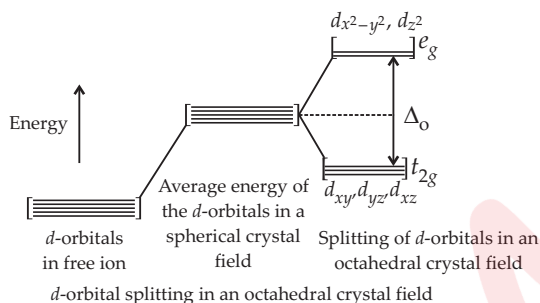
(iv)  $[\text{CoF}_6]^{3-}$ : Co(27) has electronic configuration  $[\text{Ar}] 4s^2 3d^7$ .



$\text{F}^-$  being a weak field ligand, cannot cause pairing of electrons.



4. Let us assume that the six ligands are positioned symmetrically along the cartesian axes, with metal atom at the origin.



As the ligands approach, first there is an increase in energy of  $d$ -orbitals relative to that of the free ion just as would be the case in a spherical field.

The orbitals lying along the axes ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) get repelled more strongly than  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals which have lobes directed between the axes.

The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals get raised in energy and  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals are lowered in energy relative to the average energy in the spherical crystal field. Thus, the degenerate set of  $d$ -orbitals get split into two sets: the lower energy orbitals set,  $t_{2g}$  and the higher energy orbitals set,  $e_g$ . The energy is separated by  $\Delta_o$  (CFSE).

5. The crystal field splitting,  $\Delta_o$ , depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which, the splitting will be large whereas others produce weak fields and consequently result in small splitting of  $d$ -orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:  $\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{EDTA}^{4-} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$

Such a series is termed as spectrochemical series.

If  $\Delta_o < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the

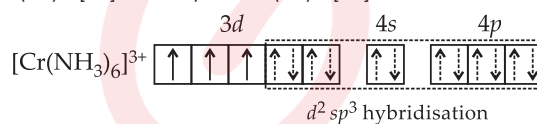
configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_o < P$  are known as weak field ligands and form high spin complexes. If  $\Delta_o > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect are known as strong field ligands and form low spin complexes.

6. The difference in energies of two sets of  $d$ -orbitals  $t_{2g}$  and  $e_g$  is called crystal field splitting energy ( $\Delta_o$ ).

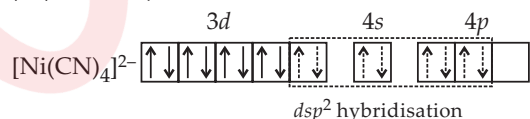
(i) If  $\Delta_o < P$ , the configuration will be  $t_{2g}^3 e_g^1$  and it is there in case of weak field ligands and high spin complex will be formed.

(ii) If  $\Delta_o > P$ , the configuration will be  $t_{2g}^4 e_g^0$  and it is in case of a strong field ligands and low spin complex will be formed.

7.  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ :



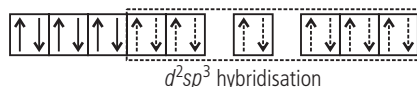
It is paramagnetic due to presence of unpaired electrons



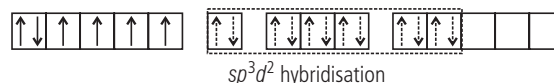
It has square planar shape and is diamagnetic due to absence of unpaired electrons.

8.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  has unpaired electrons due to weak  $\text{H}_2\text{O}$  ligands which absorb light from visible region and radiate complementary colour *i.e.*, green whereas  $[\text{Ni}(\text{CN})_4]^{2-}$  does not have any unpaired electron due to strong  $\text{CN}^-$  ligand, therefore, does not absorb light from visible region hence, it is colourless.

9. In  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $\text{CN}^-$  is a strong field ligand hence, pairing of electrons takes place.



In  $[\text{Fe}(\text{H}_2\text{O})_6]^{4+}$ ,  $\text{H}_2\text{O}$  is a weak ligand hence, pairing does not take place

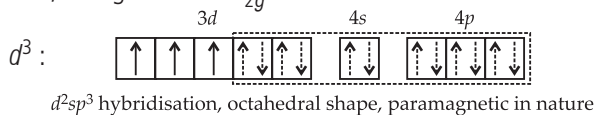


Both ligands show different magnitude of crystal field splitting energy due to different nature hence, absorb different wavelengths and show different colours.

10. (i)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$

Potassiumdiaquadioxalatochromate(III) hydrate

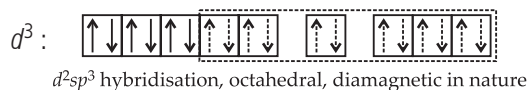
Oxidation state = +3

C.N. = 6, configuration =  $t_{2g}^3$ 

$$\mu = \sqrt{n(n+2)} = \sqrt{3 \times 5} = \sqrt{15} = 3.87 \text{ B.M.}$$

(ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 

Pentaamminechloridocobalt(III) chloride

Co(27) :  $4s^2 3d^7$  $\text{Co}^{3+}$  :  $4s^0 3d^6$ 

The oxidation state of Co = +3

C.N. = 6

Configuration =  $t_{2g}^6$ 

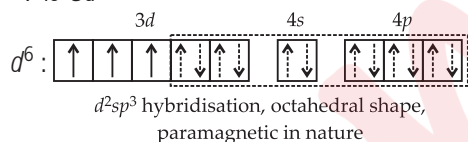
$$\mu = 0 \text{ B.M.}$$

(iii)  $[\text{CrCl}_3(\text{py})_3]$ 

Trichloridotripyridinechromium(III)

Coordination No. of Cr = 6

Oxidation state = +3

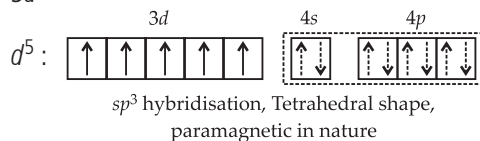
Configuration =  $t_{2g}^3 e_g^0$ Cr(24) :  $4s^1 3d^5$  $\text{Cr}^{3+}$  :  $4s^0 3d^3$ 

$$\mu = \sqrt{n(n+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

(iv)  $\text{Cs}[\text{FeCl}_4]$  Caesium tetrachloridoferrate (III)

Oxidation state = +3

Coordination No. = 4

Configuration =  $t_{2g}^3 e_g^2$ Fe (26) :  $4s^2 3d^6$  $\text{Fe}^{3+}$  :  $4s^0 3d^5$ 

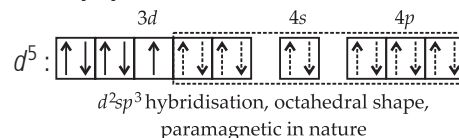
It is paramagnetic due to presence of 5 unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{5 \times 7} = \sqrt{35} = 5.92 \text{ B.M.}$$

(v)  $\text{K}_4[\text{Mn}(\text{CN})_6]$ , Potassium hexacyanomanganate(II)

Oxidation state = +2

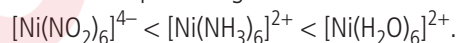
Coordination no. = 6

Configuration =  $t_{2g}^5$ Mn(25) :  $[\text{Ar}] 4s^2 3d^5$  $\text{Mn}^{2+}$  :  $[\text{Ar}] 4s^0 3d^5$ 

$$\mu = \sqrt{n(n+2)} = \sqrt{1 \times 3} = 1.732 \text{ B.M.}$$

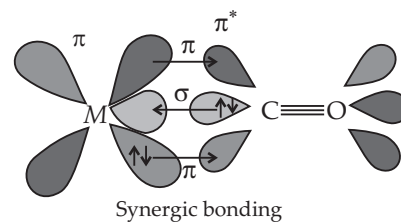
11. (i)  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$ , O.S. = +3, C.N. = 6,  $3d^6$  configuration =  $t_{2g}^6 e_g^0$ (ii)  $\text{cis}[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ , O.S. = +3, C.N. = 6,  $d^3$  configuration =  $t_{2g}^3$ (iii)  $(\text{NH}_4)_2[\text{CoF}_4]$ , O.S. = +2, C.N. = 4,  $d^7$  configuration =  $t_{2g}^5 e_g^2$ (iv)  $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$ , O.S. = +2, C.N. = 6,  $d^5$  configuration =  $t_{2g}^3 e_g^2$ 12. In spectrochemical series the order of the given ligands is  $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$ . Hence, the wavelength of light will be absorbed in the opposite order since  $E = \frac{hc}{\lambda}$ .

Hence, the order of absorption of light will be

13. Electronic configuration of  $\text{Ti}^{3+}$  is  $[\text{Ar}] 3d^1$ . Due to the presence of ligands, its five  $d$ -orbitals are split into two sets of orbitals three with lower energy and other two with higher energy. So, there occurs  $d-d$  transitions between these two sets of orbitals. In ground state, the only  $d$ -electron is present in any one of the three  $d$ -orbitals with lower energy. After absorbing light energy in the visible region of the spectra, this  $d$ -electron is promoted to the other set of  $d$ -orbitals with higher energy. As it absorbs in green and yellow regions of the visible spectra the transmitted light is red and violet *i.e.*, purple.14. (b) :  $\text{Cr}^{3+} - 3d^3$ ,  $\text{Fe}^{2+} - 3d^6$ ,  $\text{Zn}^{2+} - 3d^{10}$ Since  $\text{Fe}^{2+}$  has 4 unpaired electrons, it has highest magnetic moment.

## Topic 4

1.

The metal-carbon bond in metal carbonyls possess both  $\sigma$  and  $\pi$  character. The  $M-C$   $\sigma$  bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.

The  $M-C \pi$  bond is formed by the donation of a pair of electrons from a filled  $d$ -orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

2. (i) Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin  $B_{12}$ , cyanocobalamin, the anti-pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

(ii) There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by

the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*-platin and related compounds.

(iii) Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime),  $\alpha$ -nitroso- $\beta$ -naphthol, cupron, etc.

(iv) Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity  $[Au(CN)_2]^-$  in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.

