

## CHAPTER - 17

# CO-ORDINATION COMPOUNDS

### SYNOPSIS

The transition metals form a large number of complex compounds in which the metal atoms/ions are bound to a number of anions or neutral molecules. Such compounds are called co-ordination compounds. The chemistry of co-ordination compounds is an important area of modern inorganic chemistry and provides insights into the chemical bonding, molecular structure and functioning of vital components of biological systems. Chlorophyll, haemoglobin and vitamin B<sub>12</sub> are co-ordination compounds of magnesium, iron and cobalt respectively. A variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Co-ordination compounds also find applications in electroplating, textile dyeing and medicinal chemistry.

### Werner's theory of co-ordination compounds

The first ideas about the structures of co-ordination compounds were formulated by Alfred Werner, a swiss chemist. He prepared and characterised a large no. of co-ordination compounds and studied their physical and chemical behaviour. Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds like CrCl<sub>3</sub>, CoCl<sub>2</sub> and PdCl<sub>2</sub> have primary valence of 3, 2 and 2 respectively. Werner found that in a series of compounds of CoCl<sub>3</sub> and NH<sub>3</sub>, only some of the chloride ions could be precipitated as AgCl on adding excess of AgNO<sub>3</sub> solution, but some others could not be

1 mole CoCl<sub>3</sub>.6NH<sub>3</sub>(yellow) gave 3 mol AgCl

1 mole CoCl<sub>3</sub>.5NH<sub>3</sub>(purple) gave 2 mol AgCl

1 mol CoCl<sub>3</sub>.4NH<sub>3</sub> (green) gave 1 mol AgCl

1 mol CoCl<sub>3</sub>.4NH<sub>3</sub> (violet) gave 1 mol AgCl

These observations together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either Cl<sup>-</sup> ions or NH<sub>3</sub> molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown below.

### Formulation of CoCl<sub>3</sub>-NH<sub>3</sub> complexes

Colour	Formula	Conductivity in solution corresponds to
Yellow	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> 3Cl <sup>-</sup>	1 : 3 electrolyte
Purple	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup> 2Cl <sup>-</sup>	1 : 2 electrolyte
Green	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup> Cl <sup>-</sup>	1 : 1 electrolyte
Violet	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup> Cl <sup>-</sup>	1 : 1 electrolyte

Although the last two compounds above have identical empirical formula  $\text{CoCl}_3 \cdot 4\text{NH}_3$ , they have different properties they are therefore isomers.

These observations led Werner to propound his theory of coordination compounds. The main postulates are:

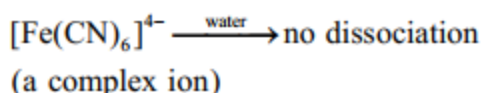
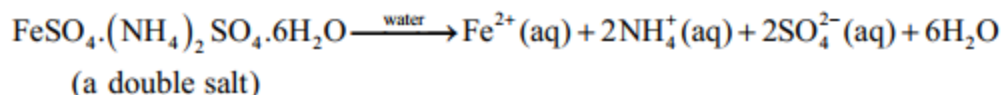
1. In coordination compounds, metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions or both. The secondary valence of a metal is equal to its co-ordination number and is fixed for a metal.
4. The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In the modern theory, such spatial arrangements are called **co-ordination polyhedra**. The species within the square bracket are called **co-ordination entities** and the ions outside the square bracket are called **counter ions**.

Werner further postulated that octahedral, tetrahedral and square planar shapes are more common in coordination compounds of transition metals. Thus  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  are octahedral entities,  $[\text{Ni}(\text{CO})_4]$  is tetrahedral and  $[\text{PtCl}_4]^{2-}$  is square planar.

### Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , Mohr's salt  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , potash alum  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  etc dissociate completely into simple ions when dissolved in water. But complex ions such as  $[\text{Fe}(\text{CN})_6]^{4-}$  of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  do not dissociate into  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions.



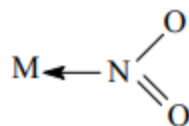
### Ligands

The ions or molecules bound to the central metal atom/ion in the coordination entity are called ligands. These may be simple ions like  $\text{Cl}^-$ , small molecules like  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , larger molecules like  $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$  or even macromolecules such as proteins. Some coordination compounds may contain positively charged ligands also. Eg. of cationic ligands are hydrazinium ion  $\text{NH}_2\text{—NH}_3^+$ , nitrosonium ion  $\text{NO}^+$  etc.

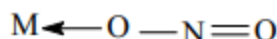
When a ligand is bound to a metal atom/ion through a single donor atom as with  $\text{Cl}^-$ ,  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , the ligand is said to be **monodentate** or **unidentate**. When a ligand can bind through two donor atoms as in  $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$  (ethylene diamine or ethane-1,2-diamine) or  $\text{C}_2\text{O}_4^{2-}$  (oxalate), the ligand is said to be **bidentate** or **didentate** and when several donor atoms are present in a single ligand as in  $\text{edta}^{4-}$ , the ligand is said to be **polydentate** ( $\text{edta}^{4-}$ , for example, is hexadentate)

When a di-or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The no. of ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes are more stable than similar complexes containing unidentate ligands.

A ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples of such ligands are  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  can coordinate either through its N or its O.



Nitrite-N-complex



Nitrito-O-complex

Similarly  $\text{SCN}^-$  ion can coordinate through its S or N atom.

### Co-ordination number

The C.No of a metal atom/ion in a complex is the no.of ligand donor atoms to which the metal is directly bonded. For example in the complex ions  $[\text{PtCl}_6]^{2-}$  and  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  the C. No of Pt and Ni are 6 & 4 respectively. In the complex ions  $[\text{Co}(\text{en})_3]^{3+}$  and  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , the C. No of both Co and Fe is 6 because en and  $\text{C}_2\text{O}_4^{2-}$  are bidentate ligands.

### Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one kind of ligands eg.  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{CO})_4]$  are known as homoleptic. Complexes in which a metal is bound to more than one kind of ligands eg  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  are known as heteroleptic.

### IUPAC nomenclature of coordination compounds

### Isomerism in coordination compounds

Two principal types of isomerism are known among coordination compounds. Each of these can be further subdivided.

#### A) Structural isomerism

**1. Linkage isomerism** : This kind of isomerism arises in a coordination compound containing an ambidentate ligand. eg. The ligand  $\text{NO}_2^-$  (nitrite ion) can bind itself to the central metal either through its N ( $-\text{NO}_2$ ) (nitrito-N-complex) or its O ( $-\text{ONO}$ ) (nitrito-O-complex) giving rise to two isomers which are called linkage isomers.

Eg.  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$   
(yellow) (red)

**2. 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.

Eg:  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$  are ionisation isomers.

**3. Co-ordination isomerism** : Arises when both the cation and the anion of a coordination compound are complexes and the ligands in them may interchange positions.

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

Another eg. is  $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CN})_6]$  and  $[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$   
cation anion cation anion

**4. Solvate isomerism** : This form of isomerism is known as hydrate isomerism when the solvent involved is water. 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.

Eg :  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  and  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  are hydrate isomers.  
                     (violet)                      (grey – green)

## B) Stereoisomerism

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

**1. Geometrical isomerism** : A few typical examples of coordination entities in which geometric isomerism is possible are given below.

C.NO	Shape	Type	Example	No. of geometric isomers
4	Square planar	$[\text{MA}_2\text{B}_2]$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	2(cis and trans)
4	Square planar	$[\text{MAB}_2\text{C}]$	$[\text{Pt}(\text{NH}_3)\text{Cl}_2(\text{Py})]$	2(cis and trans)
4	Square planar	$[\text{MABCD}]$	$[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{Py})]$	3 (2 cis and 1 trans)
4	Square planar	$[\text{M}(\text{A}-\text{B})_2]$	$[\text{Pt}(\text{gly})_2]$	2 (cis and trans)
6	Octahedral	$[\text{MA}_4\text{B}_2]$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	2 (cis and trans)
6	Octahedral	$[\text{MA}_2\text{B}_4]$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	2 (cis and trans)
6	Octahedral	$[\text{MA}_3\text{B}_3]$	$[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$	2 (facial and meridional)
6	Octahedral	$[\text{MA}_2\text{B}_2\text{C}_2]$	$[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$	5
7	Octahedral	$[\text{MA}_2(\text{B}-\text{B})_2]$	$[\text{CoCl}_2(\text{en})_2]^+$	2 (cis and trans)

M is the central metal. A, B, C and D are monodentate ligands. B–B represents a symmetrical bidentate ligand like en. A–B represents an unsymmetrical bidentate ligand like gly (glycinate ion  $\text{NH}_2\text{--CH}_2\text{--COO}^-$ ).

**2. Optical isomerism** in coordination compounds arises out of chirality in the coordination entity. Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers or enantiomorphs. The two forms are called dextro (d) and laevo (l) depending upon the direction in which they rotate the plane of polarised light in a polarimeter. Optical isomerism is common in octahedral complexes (C.No = 6) having bidentate ligands.

C.NO	Shape	Type	Example	No. of optical isomers
6	Octahedral	$[\text{M}(\text{A}-\text{A})_3]$	$[\text{Co}(\text{en})_3]^{3+}$ , $[\text{Cr}(\text{ox})_3]^{3-}$	2 (d and l)
6	Octahedral	$[\text{MA}_2(\text{B}-\text{B})_2]$	Cis $[\text{CoCl}_2(\text{en})_2]^+$ trans $[\text{CoCl}_2(\text{en})_2]^+$	2 (d and l) Nil

## Bonding in coordination compounds

Many approaches have been put forward to explain the nature of bonding in coordination compounds. eg. The Valence Bond Theory (VBT) and The Crystal Field Theory (CFT)



Valence bond theory: According to this theory, the metal atom or ion under the influence of the ligands uses its  $(n-1)d$ ,  $ns$ ,  $np$  or  $ns$ ,  $np$ ,  $nd$  orbitals for hybridisation to yield a set of equivalent hybrid orbitals of definite geometry such as octahedral, tetrahedral, square planar etc. These hybridised orbitals overlap with the ligand orbitals that can donate electron pairs for bonding.

C.NO	Type of hybridisation	Orientation of hybrid orbitals in space	Example
4	$sp^3$	Tetrahedral	$[\text{Ni}(\text{CO})_4]$
4	$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$
6	$sp^3d^2$	Octahedral	$[\text{FeF}_6]^{3-}$
6	$d^2sp^3$	Octahedral	$[\text{Fe}(\text{CN})_6]^{3-}$
5	$dsp^3$	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$

Crystal field theory:

This theory is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in the case of anions or dipoles in the case of neutral molecules. The five  $d$ -orbitals in an isolated metal atom/ion have the same energy i.e. they are degenerate. But when negative field due to ligands (either anions or the negative ends of polar molecules like  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) in a complex surround the metal atom/ion, the degeneracy of the  $d$  orbitals is lifted. It results in the splitting of  $d$  orbitals. (crystal field splitting). The pattern of splitting depends upon the nature of the crystal field.

eg:  $t_{2g}$   $\Delta_o$   $\Delta_t$  field strength and ligands.

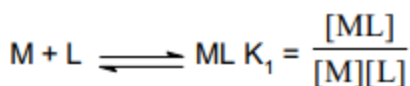
Magnetic properties and colour of coordination compounds.

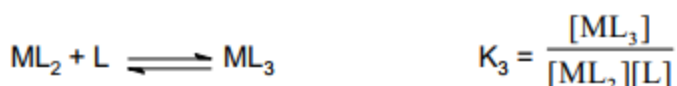
Stability of coordination compounds

The stability of a complex in solution refers to the degree of association between the two species (metal ion and ligands) involved in the equilibrium. The magnitude of the equilibrium constant (stability constant or formation constant) for the association quantitatively expresses the stability of the complex. Thus, for a reaction of the type:



then the larger the stability constant, the higher is the proportion of  $\text{ML}_4$  that exists in the solution. Free metal ions rarely exist in solution so that  $\text{M}$  will usually be surrounded by solvent molecules which will compete with the ligand molecules  $\text{L}$ , and be replaced by them. We generally ignore these solvent molecules for the sake of simplicity and write the four stability constants as follows.





where  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  are called stepwise stability constants or stepwise formation constants.

The overall stability constant or overall formation constant for the process  $M + 4L \rightleftharpoons ML_4$  is

$\beta_4 = \frac{[ML_4]}{[M][L]^4}$ . The stepwise and overall stability constants are therefore related as

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$$

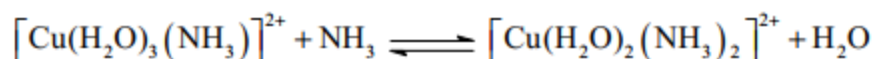
In general,  $\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots K_n$

The reciprocal of the overall formation constant of a complex is called the overall dissociation constant or overall instability constant. Eg: The steps involved in the formation of the tetraammine copper (II) ion from  $[Cu(H_2O)_4]^{2+}$  and  $NH_3$  are:



$$K_1 = \frac{[Cu(H_2O)_3(NH_3)]^{2+}}{[Cu(H_2O)_4]^{2+} [NH_3]} = 1 \times 10^4$$

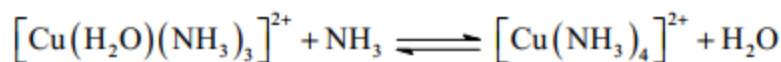
As concentration of  $H_2O$  in the above aq. solution of  $Cu^{2+}$  remains essentially constant, it is ignored.



$$K_2 = \frac{[Cu(H_2O)_2(NH_3)_2]^{2+}}{[Cu(H_2O)_3(NH_3)]^{2+} [NH_3]} = 1 \times 10^{3.2}$$

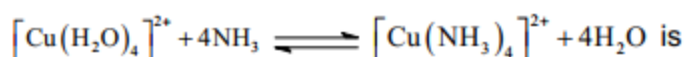


$$K_3 = \frac{[Cu(H_2O)(NH_3)_3]^{2+}}{[Cu(H_2O)_2(NH_3)_2]^{2+} [NH_3]} = 1 \times 10^{2.7}$$



$$K_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu(H_2O)(NH_3)_3]^{2+} [NH_3]} = 1 \times 10^2$$

The overall formation constant ( $\beta_4$ ) for the process



$$\beta_4 = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}(\text{H}_2\text{O})_4]^{2+} [\text{NH}_3]^4} = K_1 \times K_2 \times K_3 \times K_4 = 1 \times 10^{11.9}$$

### Organometallic compounds

An organometallic compound is one in which the metal atom or ion is directly bonded to a carbon atom of an organic group. Organometallics are of two types 1)  $\sigma$  bonded organo metalics. eg. Grignard reagents  $\text{R-MgX}$ , Frankland's compound  $\text{R}_2\text{Zn}$  2)  $\pi$  bonded organometallics eg. dibenzene chromium, Zeise's salt, ferrocene etc.

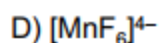
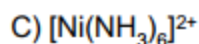
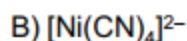
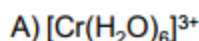
### PART-I (JEE MAIN)

#### SECTION-I- Straight objective type questions

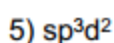
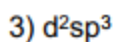
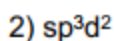
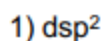
- The primary and secondary valencies of iron in the complex ion  $[\text{Fe}(\text{CN})_6]^{3-}$  are respectively  
 1) 6 and 2                      2) 3 and 6                      3) 2 and 6                      4) 6 and 3
- The correct set of ambidentate ligands is:  
 a)  $\text{C}_2\text{O}_4^{2-}$                       b)  $\text{SCN}^-$                       c)  $\text{NO}_2^-$                       d) en  
 1) a and d only                      2) b and c only                      3) a, b, c and d                      4) a and c only
- IUPAC name of  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  is  
 1) Potassium tris(oxalato)chromate(III)  
 2) Potassium trioxalatochromate(III)  
 3) Tripotassium tris(oxalato)chromate(III)  
 4) Tripotassium trioxalatochromate(III)
- Which types of isomerism are shown by the octahedral complex  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$  ?  
 1) Linkage and optical isomersim  
 2) Linkage and ionisation isomerism  
 3) Geometrical and optical isomerism  
 4) Geometrical and ionisation isomerism
- Identify optically active complex from the following  
 1)  $\text{trans-}[\text{CoCl}_2(\text{en})_2]^+$                       2)  $\text{cis-}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$   
 3)  $[\text{PtCl}_4]^{2-}$                       4)  $[\text{Co}(\text{en})_3]^{3+}$

6. Match List I with List II

**List - I (Complex ion)**



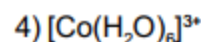
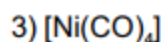
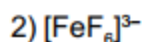
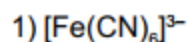
**List - II (Hybridisation)**



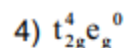
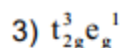
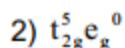
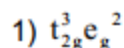
7. The d-orbital involved in hybridization of the metal in  $[\text{CoF}_6]^{3-}$  is



8. Which of the following is both paramagnetic and inner orbital complex?



9. Electronic configuration of central metal ion in  $[\text{Mn}(\text{CN})_6]^{3-}$  is



10. The low spin complex of a  $\text{d}^6$  metal ion in an octahedral field will have the following CFSE:

1)  $-\frac{2}{5}\Delta_0 + P$

2)  $-\frac{12}{5}\Delta_0 + 3P$

3)  $-\frac{2}{5}\Delta_0 + 2P$

4)  $-\frac{12}{5}\Delta_0 + 2P$

11. **Assertion:**  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is violet in colour

**Reason :**  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  absorbs a light corresponding to the energy of violet region and changes from  $t_{2g}^1 e_g^0$  state to  $t_{2g}^0 e_g^1$  state.

Choose the correct option

1) Both assertion and reason are true and reason is the correct explanation of assertion.

2) Both assertion and reason are true but reason is not the correct explanation of assertion.

3) Assertion is true but reason is false.

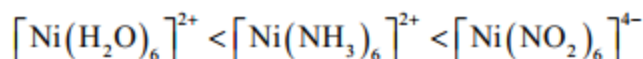
4) Assertion is false but reason is true.



12. The correct set of d-orbitals on central metal that is lower in energy with respect to barycentre in a tetrahedral crystal field is



13. **Assertion:** The wavelength of absorption for the complexes increases in the order



**Reason:** Crystal field strength of ligands increases in the order  $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$

Choose the correct option

- 1) Both assertion and reason are true and reason is the correct explanation of assertion.
  - 2) Both assertion and reason are true but reason is not the correct explanation of assertion.
  - 3) Assertion is true but reason is false.
  - 4) Assertion is false but reason is true.
14. Choose the incorrectly matched pair
- 1)  $[\text{Mn}_2(\text{CO})_{10}] \rightarrow$  no bridging CO ligands are present in the structure
  - 2) Desferrioxime B  $\rightarrow$  a chelating ligand used for removal of excess of iron
  - 3)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} \rightarrow$  more stable than the complex,  $[\text{Fe}(\text{NH}_3)_6]^{3+}$
  - 4)  $[\text{Rh}(\text{PPh}_3)_2\text{Cl}_2] \rightarrow$  Wilkinson's catalyst used for hydrogenation of alkenes

### SECTION-II - Numerical Type Questions

15. The total number of geometrical isomers possible for  $[\text{Pt}(\text{Cl})(\text{Br})(\text{NH}_3)(\text{py})]$  is —
16. The total number of  $90^\circ \text{Cl}-\text{Co}-\text{Cl}$  bond angles present in the facial isomer of  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  is —

### PART-II (JEE ADVANCED)

#### Section-III - Only one option correct type

17. Which of the following pairs of complexes are isomeric with each other but their aqueous solutions exhibit different molar conductivities?
- 1)  $[\text{PtCl}_2(\text{NH}_3)_2] \text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
  - 2)  $[\text{CoCl}_2(\text{NH}_3)_4]\text{NO}_2$  and  $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$
  - 3)  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$  and  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$
  - 4)  $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$

18. A solution containing 0.319 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was passed through cation exchange resin and the acid liberated was titrated with a standard solution of NaOH. This required  $28.5 \text{ cm}^3$  of 0.125 M NaOH. The correct formula of the complex is: (Given molar mass of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} = 266.5 \text{ g mol}^{-1}$ )
- 1)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
  - 2)  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
  - 3)  $[\text{CrCl}_2(\text{H}_2\text{O})_5]\text{Cl} \cdot \text{H}_2\text{O}$
  - 4)  $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$
19. The compounds that can display geometrical isomerism among the following are
- i)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$
  - ii)  $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$
  - iii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
  - iv)  $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^{2+}$
  - v)  $[\text{Pt}(\text{Gly})_3]^{3-}$
  - vi)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$
- A) iii, iv and vi only      B) i, ii, iii, iv and vi only      C) iii, iv, v and vi only      D) iii and iv only

#### Section IV - One or more option correct type

20. Select the correct statement(s) regarding metal carbonyls
- A) Metal-carbon bond possesses both  $\sigma$  and  $\pi$  character
  - B) The bond order of metal-carbon bond increases with decrease in the positive oxidation state of the metal
  - C) Metal-carbon  $\pi$  bond is formed by the donation of electron pair from a filled d-orbital of metal into vacant  $\pi^*$  orbital of carbon monoxide
  - D) The bond order of carbon-oxygen bond decreases with decrease in the positive oxidation state of the metal
21. Choose the correct statement(s)
- A)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  is red in colour whereas  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$  is yellow in colour
  - B) Two isomers of the octahedral  $\text{Co}(\text{NH}_3)_5\text{Br}(\text{SO}_4)$  can be distinguished by treatment with barium chloride solution
  - C) Both facial and meridional isomers of  $\text{CoCl}_3(\text{NH}_3)_3$  are optically inactive
  - D) Cis-isomer of  $[\text{PtCl}_2(\text{en})_2]$  exists as a pair of enantiomers

22. The pair(s) of complexes wherein both exhibit tetrahedral geometry is/are

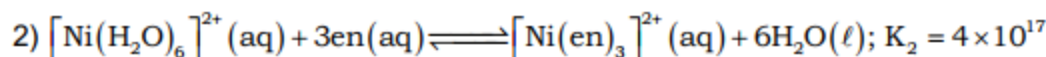
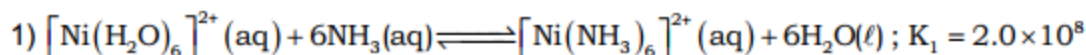
- A)  $[\text{FeCl}_4]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$                       B)  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{CoCl}_4]^{2-}$
- C)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$                       D)  $[\text{Cu}(\text{Py})_4]^+$  and  $[\text{Cu}(\text{CN})_4]^{3-}$

23. In which of the following options, electronic configuration of the metal is correctly represented?

- A)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \rightarrow t_{2g}^4 e_g^2$                       B)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} \rightarrow t_{2g}^3 e_g^2$
- C)  $[\text{FeCl}_4]^- \rightarrow t_{2g}^3 e_g^2$                       D)  $[\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow t_{2g}^6 e_g^0$

### **Section V - Numerical type questions**

24. The formation constants at 273 K for the ammonia and ethylenediamine complexes of Nickel (II) are as follows:



If the enthalpy change for the reactions  $\Delta H_1^0$  and  $\Delta H_2^0$  are equal (since both complexes contain six Ni-N bonds) the value of  $\Delta S_2^0 - \Delta S_1^0$  is  $30x \text{ JK}^{-1} \text{ mol}^{-1}$ . The value of  $x$  is ..... (Use  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $\log 2 = 0.3$ )

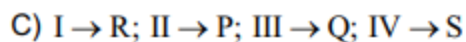
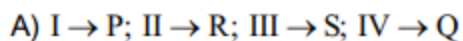
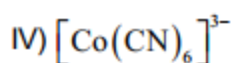
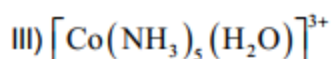
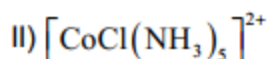
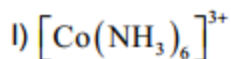
25. Total number of isomers for the complex  $[\text{Co}(\text{en})_2(\text{NO}_2)(\text{SCN})]$  and  $[\text{Pt}(\text{Gly})_3]^{3-}$  is .....

26.  $\text{EDTA}^{4-}$  is ethylenediaminetetraacetate ion. The total number of N-Co-O bond angles in  $[\text{Co}(\text{EDTA})]^-$  is .....

27. If the CFSE of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is  $-96.0 \text{ kJ mol}^{-1}$ , this complex will absorb maximum at wavelength \_\_\_\_\_ nm (Use  $N_A = 6 \times 10^{23} \text{ mol}^{-1}$ ,  $h = 6.4 \times 10^{-34} \text{ Js}$ )

**Section-VI - Matrix match type**

28. Match the following

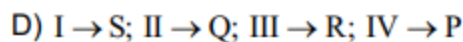
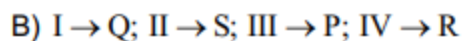
**Column-I (Compound)****Column-II (Colour)**

P) Violet

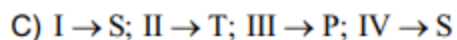
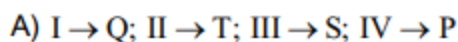
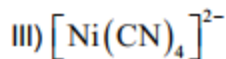
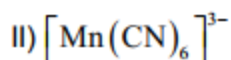
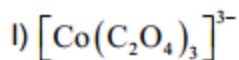
Q) Red

R) Yellow-orange

S) Pale yellow



29. Match the following

**Column-I (Complex)****Column-II (Spin only magnetic moment)**

P) 4.90 BM

Q) 3.87 BM

R) 2.84 BM

S) 0.00 BM

T) 5.92 BM

