

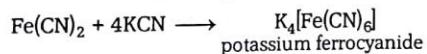
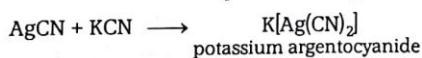
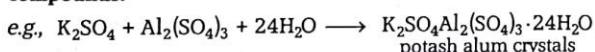
# Coordination Compounds

## JEE Main MILESTONE

- Molecular or Addition Compounds
- Terminology Related to Coordination Compounds
- Werner's Theory
- IUPAC Nomenclature of Mononuclear Coordination Compounds
- Isomerism
- Bonding in Coordination Compounds
- Stability of Complexes
- Importance of Coordination Compounds

### 9.1 Molecular or Addition Compounds

When solutions containing two or more stable salts in simple molecular (stoichiometric) proportions, are evaporated, crystals of new compounds may separate out. These new compounds are called **molecular or addition compounds**.



The addition compounds can be divided into two classes

#### (a) Those which Loose their Identity in Solution i.e., Double Salts

In aqueous solution these addition compounds break down into simpler ions, thus, exhibit the properties of their constituent ions. e.g., an aqueous solution of carnallite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  shows the properties of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  simpler ions. Such addition compounds, which loose their identity in solution, are called '**double salts**'. They only exist in the crystalline state. Some other examples of double salts are potash alum  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  and Mohr salt  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

#### (b) Those which Retain their Identity in Solution i.e., Complex Compounds

In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure e.g., potassium ferrocyanide does not give properties of simple

*Coordination compounds are those compounds in which a central metal atom or ion is attached with a fixed number of groups or molecules (ligands) through coordinate bonds. In other words, these compounds contain complex ions. These are generally formed by transition elements because of their small radii.*

$K^+$ ,  $Fe^{2+}$  and  $CN^-$  ions but gives the properties of  $K^+$  ions and complex ferrocyanide ions,  $[Fe(CN)_6]^{4-}$ . In other words, in these compounds, the **complex ions** retains their identity in the solution. Other example of coordination compounds are  $[Co(NH_3)_6]Cl_3$ ,  $K_2[PtCl_6]$ , etc.

Actually complexes or coordination compounds are the result of acceptance of lone pair of electrons of ligands by the empty orbitals of the metal atom or ion.

## 9.2 Terminology Used in Coordination Compounds

The important terms used to define a complex completely are as follows

### 1. Complex Ions

A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one or more neutral molecules or one or more simple anions or in some cases positive groups also. It exists as a single entity and is usually indicated within square bracket, i.e., [ ]

e.g.,  $[Cu(NH_3)_4]^{2+}$  is a complex ion, which is formed by the combination of four neutral molecules of ammonia with a simple  $Cu^{2+}$  cation. Similarly,  $[Fe(CN)_6]^{4-}$  is a complex ion formed by the combination of six  $CN^-$  anions with a simple  $Fe^{2+}$  cation. In nitroprusside ion,  $[Fe(CN)_5NO]^{2+}$ , five  $CN^-$  ions and one  $NO^+$  (a positively charged ligand) ion are coordinated to  $Fe^{2+}$  ion.

The complex ion carrying a positive charge e.g.,  $[Cu(NH_3)_4]^{2+}$ , is called **cationic complex**, the one with a negative charge e.g.,  $[Fe(CN)_6]^{4-}$  is called **anionic complex** and the one with no charge e.g.,  $[PtCl_2(NH_3)_2]$  is called a **neutral complex**.

Complex ions do not give tests of their constituent ions. e.g.,  $[Cu(NH_3)_4]^{2+}$  does not give test of  $Cu^{2+}$  or  $NH_3$ .

**Homoleptic complex** have only one type of ligands linked to the central metal atom/ion. e.g.,  $[Co(NH_3)_6]^{3+}$  whereas **heteroleptic complex** have more than one type of ligands linked to the central metal atom/ion. e.g.,  $[Co(NH_3)_4Cl_2]$

**Sample Problem 1** Which of the following complexes are homoleptic? [NCERT Exemplar]

- |                         |                            |
|-------------------------|----------------------------|
| (a) $[Co(NH_3)_6]^{3+}$ | (b) $[Co(NH_3)_4Cl_2]^{+}$ |
| (c) $[Ni(CN)_4]^{2-}$   | (d) $[Ni(NH_3)_4Cl_2]$     |

**Interpret** (a,c) Homoleptic complexes have ligands of only one kind. e.g.,  $[Co(NH_3)_6]^{3+}$ ,  $[Ni(CN)_4]^{2-}$

### 2. Central Metal Atom or Ion

Every complex ion contains a metal atom or ion to which one or more neutral molecules or ions are attached. This is known as the **central metal atom** or **ion**. It is sometimes known as the **nuclear atom**. In a complex, the central metal atom or ion behaves as the **electron pair acceptor** or **Lewis acid**.

### 3. Ligands

The central metal ion is surrounded by a number of the anions or the neutral molecules or sometimes positively charged ions possessing at least one lone pair. These surrounded ions are called **Ligands**. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage. In the formation of coordination complexes, the ligands act as the **electron-pair donors** or **Lewis bases**.

e.g., in the complex ions  $[Cu(NH_3)_4]^{2+}$  and  $[Fe(CN)_6]^{4-}$ ,  $NH_3$  and  $CN^-$  are the ligands. Ligands invariably contain one or more atoms (called **donor atoms**) having lone pairs of electrons.

The number of donor groups, from a given ligand, attached to the same central atom, is called the **denticity of the ligand**. Ligands like  $NH_3$ ,  $CH_3NH_2$ ,  $PH_3$  can form only one coordinate bond with the central metal ion. So, their denticity is one.  $H_2N-CH_2-CH_2-NH_2$ ,  $NH_2CH_2COO^-$  have two donor atoms in each molecule or ion and each can form two coordinate bonds with the central metal ion and hence, their denticity is two.

Depending upon the number of donor atoms (or sites), the ligands may be classified into various categories as follows

#### (a) Unidentate or Monodentate Ligands

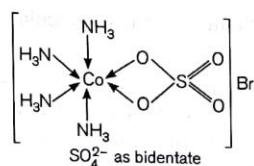
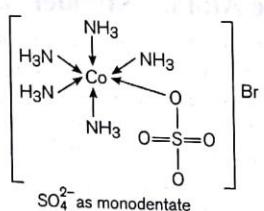
These ligands contain only one donor atom (or site) which is capable of donating an electron pair and thus, attach to the central metal ion only at one point e.g.,  $CN^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $OH^-$ ,  $H_2O$ ,  $NH_3$ ,  $NO_2^-$ ,  $C_2H_5N$  (pyridine) etc.

#### (b) Polydentate or Multidentate Ligands

Ligands which contain two or more such atoms which can simultaneously serve as donor atoms are called **Polydentate or multidentate ligands**. Such ligands attach to the central metal ion at more than one point. Polydentate ligands with two donor sites are called bidentate, and with three, four, five and six donor sites are called tri (or ter), tetra (or quadri), penta and hexa-(or sexi) dentate ligands respectively.

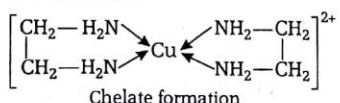
Certain polydente ligands have flexi dentate character, i.e., they do not use all the donor atoms to form a complex e.g., EDTA is a hexadentate ligand but it can also act as a pentadentate or a tetridentate ligand.

**Caution Point** Some ligands like  $\text{SO}_4^{2-}$  ion etc., can act both as a monodentate as well as a bidentate ligand. This is clear from the following examples.



### (c) Chelating Ligands

Polydente ligands, the structures of which permeates the attachment of two or more donor sites at the terminals of a chain to the same metal ion simultaneously, thus, closing one or more rings are called **chelating ligands** and the compounds formed are known as **chelate compounds**. Thus, a chelate may be defined as a ring structure formed by the combination of a polydente ligand having two or more donor atoms at the terminals with a metal ion forming part of the ring. The process of formation of chelates is called **chelation**.



Chelate complexes are more stable than ordinary complexes in which the ligand is monodentate. This increased stability of the compound due to chelation is called the **chelate effect**.

Generally the chelate complexes with five or six membered rings are more stable. Out of these, five membered rings are very stable when they involve saturated ligands, e.g., ethylenediamine contains only single bonds and forms five membered stable ring structures.

On the other hand, six membered ring structures acquire maximum stability when they involve unsaturated

ligands containing conjugate double bonds. This is due to the resonance effects involving metal *d*-orbitals and ligand  $\pi$ -orbital electrons. The stability of the chelate complex is explained on the basis of **entropy effect**. When one end of en (ethylene diamine) is coordinated, the probability of the coordination of the other end is high because this end is bound to stay close to the cation. This shows that it is easier to form a chelate ring than coordinate to two independent molecules. Thermodynamically, the increased stability due to chelation can be attributed to an increase in the degree of freedom of the system. A large entropy change but only small heat of reaction generally accompany the chelation process.

The complex compound having maximum number of rings formed with the ligands, is most stable. A complex  $[M(\text{en})_3]^{3+}$  is less stable than a complex  $[M(\text{EDTA})]^-$  because in the former there are three rings while, the latter involves five rings.

**Sample Problem 2** The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?

[NCERT Exemplar]

- (a)  $[\text{Fe}(\text{CO})_5]$       (b)  $[\text{Fe}(\text{CN})_6]^{3-}$   
 (c)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$       (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

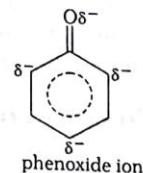
**Interpret** (c)  $(\text{C}_2\text{O}_4)^{2-}$  is a chelating agent  $\left[ \begin{array}{c} \text{COO}^- \\ | \\ \text{C} \\ | \\ \text{COO}^- \end{array} \right]$ , so its complex is more stable than the other given due to chelation.

### (d) Ambidentate Ligands

There are certain ligands, which have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands. Some examples of such ligands are

- $M \leftarrow \text{NO}_2$  (Nitro)  
 $M \leftarrow \text{CN}$  (Cyano)  
 $M \leftarrow \text{SCN}$  (Thiocyanato)  
 $M \leftarrow \text{ONO}$  (Nitrito)  
 $M \leftarrow \text{NC}$  (Isocyano)  
 $M \leftarrow \text{NCS}$  (Isothiocyanato)

Phenoxyde ion also serves as an ambidentate ligand due to resonance. *o*- and *p*- positions of the benzene ring in the phenoxyde ion also become electron donors.



## 4. Coordination Sphere

The central atom and ligands which are directly attached to it, are enclosed in square brackets, called the coordination sphere. The ligands and the metal atom shown inside the square bracket actually behave as a single constituent unit. The bonding between the central metal ion/atom, and the ligands in its coordination sphere is non-ionisable.

## 5. Coordination Number

The total number of ligands attached to the central metal ion through coordinate bond is called the **coordination number** (CN) of the metal ion, e.g., in the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , the coordination number of  $\text{Cu}^{2+}$  is 4 and that of  $\text{Fe}^{2+}$  ion in  $[\text{Fe}(\text{CN})_6]^{4-}$  is 6. The coordination numbers of most common metals are 4 and 6.  $\text{Ag}^+$ ,  $\text{Pt}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  and  $\text{Pt}^{4+}$  ions show only one coordination number, e.g.,  $\text{Ag}^+$  shows CN = 2,  $\text{Pt}^{2+}$  CN = 4 and  $\text{Cr}^{3+}$   $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  and  $\text{Pt}^{4+}$  show CN = 6 only.

In case of polydentate ligands,

Coordination number = No. of ligand  $\times$  its denticity  
e.g., in  $[\text{CoBr}_2(\text{en})_2]^+$ . CN wrt Br = 2

$$\text{Total CN} = 2 + 4 = 6$$

## 6. Oxidation Number or Oxidation State

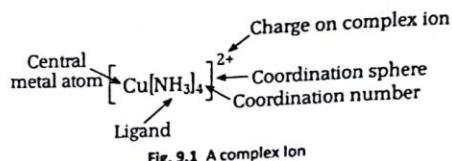
It is a number that represents an electric charge in which a metal atom or ion has or appears to have when combined with ligands, e.g., oxidation number of copper in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is +2 but its coordination number is 4. Similarly, the oxidation number of Fe in  $[\text{Fe}(\text{CN})_6]^{4-}$  is +3 but its coordination number is 6.

## 7. Charge on the Complex Ions

The charge carried by a complex ion is the algebraic sum of the charges carried by central metal ion and the ligands coordinated to the central metal ion, e.g., in the complex ion,  $[\text{Ag}(\text{CN})_2]^-$ ,  $\text{Ag}^+$  ion carries a charge of +1. Therefore, the net charge on the complex ion  $[\text{Ag}(\text{CN})_2]$  is  $+1 - 2 = -1$ . Similarly, in the complex ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $\text{Cu}^{2+}$  ion carries a charge equal to +2 and as  $\text{NH}_3$  molecules are neutral, therefore, the net charge on the complex is +2.

## 8. Representation of a Complex Ion

The terms ligand, central metal, charge on complex ion and coordination number can be illustrated as



**Fig. 9.1 A complex ion**

### 9. Effective Atomic Number [EAN]

In order to explain the stability of the complex Sidgwick proposed effective atomic number abbreviated as EAN, which is defined as the *resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligand*. The effective atomic number (EAN) generally coincides with the atomic number of next inert gas except in some cases.

**Calculation of EAN** EAN can be calculated by the following relation

EAN = Z (atomic number of the metal) - number of electrons lost in the ion formation + number of electrons gained from the donor atoms of the ligands

The EAN's of various metals in their respective complexes is tabulated below

**Table 9.1 EAN of Some Species**

Complex	Oxidation state of metal ion	Atomic number of metal ( $Z$ )	Coordination number	Effective atomic number
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	+3	27	6	$(27 - 3) + (6 \times 2)$ = 36 (Kr)
$\text{K}_4[\text{Fe}(\text{CN})_6]$	2	26	6	$(26 - 2) + (6 \times 2)$ = 36 (Kr)
$\text{Ni}[\text{CO}]_4$	0	28	4	$(28 - 0) + (4 \times 2)$ = 36 (Kr)
$\text{K}_2[\text{PtCl}_6]$	+4	78	6	$(78 - 4) + (6 \times 2)$ = 86 (Rn)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	+3	26	6	$(26 - 3) + (6 \times 2)$ = 35

**Sample Problem 4** Using the EAN rule predict the value of  $x$  in  $\text{Cr}(\text{CO})_x$ .



**Interpret** (c) EAN = 24 - 0 + 2x = 36

$$2x = 12 \quad [\text{i.e., atomic number of nearest noble gas}]$$

$$x = 6$$

Therefore, the formula of the compound is  $\text{Cr}(\text{CO})_6$ .

### 9.3 Werner's Theory

Werner proposed a theory called **Werner's coordination theory** for which he was awarded Nobel prize in 1913. It was the first successful theory, which explained the properties of complexes.

The main postulates of this theory are

1. Metals possess two types of linkages (valencies)
  - (i) primary or principal linkage and
  - (ii) secondary linkage
2. **Primary linkages** (valencies) are **ionisable** and are exhibited by a metal in the formation of its simple salts such as  $\text{CoCl}_3$ ,  $\text{CuSO}_4$  and  $\text{AgCl}$ . In these salts, the primary valencies of Co, Cu and Ag are 3, 2 and 1 respectively. Now a days, **primary valency** is referred to as **oxidation state** of the metal ion.
3. **Secondary linkages** (valencies) are **non-ionisable** and are exhibited by a metal in the formation of its complex ions such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ag}(\text{NH}_3)_2]^+$ . In these complexes, the secondary valencies of  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  are 6, 4 and 2 respectively. The secondary valency is also referred to as **coordination number (CN)** of the metal cation.

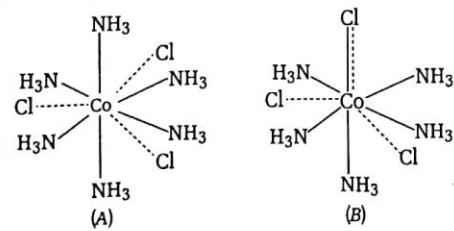
Table 9.2 Werner's Coordination Compounds

Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
(A) $\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$	six ( $\text{NH}_3$ )	three ( $\text{Cl}^-$ )
(B) $\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$	five ( $\text{NH}_3$ ) and one ( $\text{Cl}^-$ )	three ( $\text{Cl}^-$ ) including one ( $\text{Cl}^-$ ) with <b>dual nature</b>
(C) $\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$	four ( $\text{NH}_3$ ) and two ( $\text{Cl}^-$ )	three ( $\text{Cl}^-$ ) including two ( $\text{Cl}^-$ ) with <b>dual nature</b>
(D) $\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (single species)	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (single species)	three ( $\text{NH}_3$ ) and three ( $\text{Cl}^-$ )	three ( $\text{Cl}^-$ ) all with <b>dual nature</b>

From the Table 9.3, it is clear that conduction of the complexes which depends on the number of ions will be in order:  $D < C < B < A$

They are represented as :

[only  $\text{Cl}^-$  ions joined by (.....) will ionise].



4. **Primary linkages** (valencies) are satisfied by negative ions while, **secondary linkages (valencies)** can be satisfied by neutral molecules or negative ions or in some cases positive ions (ligands) **also**. This happens in case of mixed complexes.

5. Every metal atom or ion has a fixed number of secondary linkages. In other words, the coordination number of the metal atom is fixed. Thus, the coordination number gives the total number of neutral molecules of negative or positive groups, which may be directly linked to the metal cation in the formation of its complexes.
6. Every metal has a tendency to satisfy both its primary and secondary linkages (valencies). The ligands satisfying secondary linkages (valencies) are always directed towards fixed positions in space about the central metal atom or ion. Thus, the coordination compounds have a definite geometry (structure or shape).

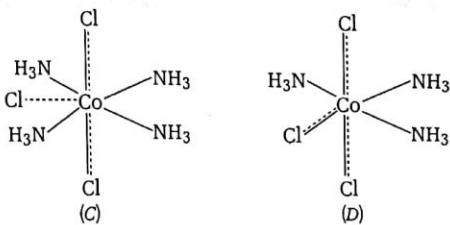
### Werner's Representation

Consider the case of  $\text{CoCl}_3 \cdot x\text{NH}_3$

where maximum value of  $x = \text{CN}$  of  $\text{Co(III)} = 6$

and minimum value of  $x = \text{CN} - \text{ON} = 3$

Various structures are summarized in Table 9.3.



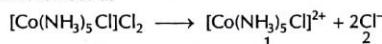
**Sample Problem 5** When 0.1 mole  $\text{CoCl}_3(\text{NH}_3)_5$  is treated with excess of  $\text{AgNO}_3$ , 0.2 mole of  $\text{AgCl}$  are obtained. The conductivity of solution will correspond to

[NCERT Exemplar]

- (a) 1:3 electrolyte
- (b) 1:2 electrolyte
- (c) 1:1 electrolyte
- (d) 3:1 electrolyte

**Interpret** (b) Formation of 0.2 mole of AgCl, from 0.1 mole complex suggest the presence of two  $\text{Cl}^-$  outside the coordination sphere. Thus, the formula of the complex should be  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$ .

This complex ionises as



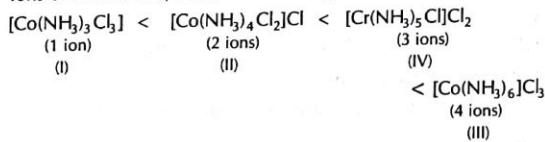
Hence, it is 1:2 electrolyte.

**Sample Problem 6** Arrange the following complexes in the increasing order of conductivity of their solution :

- I.  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  II.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , III.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , IV.  $[\text{Cr}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$  [INCERT Exemplar]

- (a) I < II < III < IV  
 (b) II < I < IV < III  
 (c) I < II < IV < III  
 (d) II < I < III < IV

**Interpret** (c) Ions or molecules present outside the coordination sphere are ionisable. A complex which gives more ions on dissolution, is more conducting.



### Check Point 1

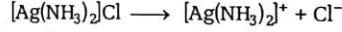
- Why does  $\text{NH}_4^+$  ion not form complexes?
- A freshly prepared aqueous solution of  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$  does not conduct electricity. Is this compound regarded as a weak electrolyte?
- $\text{CuSO}_4$  on mixing with  $\text{NH}_3$  (ratio 1: 4) does not give test for  $\text{Cu}^{2+}$  ions but gives test for  $\text{SO}_4^{2-}$  ions; why?
- Why is  $\text{K}_4[\text{Fe}(\text{CN})_6]$  more conducting as compared to  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ ?

## 9.4 IUPAC Nomenclature of Mononuclear Coordination Compounds

The various rules are applied in naming the coordination compounds according to the IUPAC (International Union of Pure and Applied Chemistry) system are

### Order of Naming Ions

If the complex compound is ionic, the positive ion (cation) whether simple or complex, is named first followed by the negative ion (anion). e.g.,  $\text{K}[\text{BF}_4]$  ionises to  $\text{K}^+$  and  $\text{BF}_4^-$  ions. Here cation ( $\text{K}^+$ ) is simple and it is named first followed by anionic part. Thus,  $\text{K}[\text{BF}_4]$  is named as potassium tetrafluoroborate (III). The complex  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  ionises as



Here, the cation  $[\text{Ag}(\text{NH}_3)_2]^+$  is not a simple one but a complex. Therefore, it is named first and then the anionic part. Thus,  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  is named as diamminesilver (I) chloride. But one word name is given to non-ionic and molecular complexes.

### Naming Ligands

- The number of each kind of ligand is specified using the Greek **prefixes** like di, tri, tetra, penta, and hexa. The term mono is generally not mentioned. If the name of ligand itself is complex, i.e., it includes a numerical prefix, e.g., in case of organic molecules such as dipyridyl or ethylenediamine, then the terms **bis** (for two), **tris** (for three), **tetrakis** (for four), **pentakis** (for five), etc., are used followed by the name of the ligand placed without brackets. e.g.,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is named as tetramminecopper (II) ion and  $[\text{Co}(\text{en})_3]^{3+}$  is named as tris (ethylenediamine) cobalt (III) ion.
- Negative ligands** are normally end in -o, e.g.,

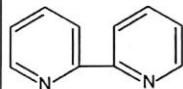
Table 9.3 Different Negative Ligands, Their Charge and Donor Atoms

	Name	Formula	Charge	Name of ligand in the complex	Donor atom/atoms
Monodentate ligands with one unit negative charge	Halide ion	(X = Cl, Br, I)	-1	Halo or halido	X
	Hydroxide ion	:OH <sup>-</sup>	-1	Hydroxo	O
	Cyanide ion	-C≡N	-1	Cyano	C
	Isocyanide	N <sup>+</sup> ≡C <sup>-</sup>	-1	Isocyanido	N
	Nitro ion	NO <sub>2</sub> <sup>-</sup>	-1	Nitro	N
	Nitrito ion	ONO <sup>-</sup>	-1	Nitrito	O
	Thiocyanate ion	SCN <sup>-</sup>	-1	Thiocyanato	S
	Isothiocyanate ion	NCS <sup>-</sup>	-1	Isothiocyanato	N
	Hydride ion	H <sup>-</sup>	-1	Hydrido	H
	Amide ion	NH <sub>2</sub> <sup>-</sup>	-1	Amido	N
	Acetate ion	CH <sub>3</sub> COO <sup>-</sup>	-1	Acetato	O
	Nitrate ion	NO <sub>3</sub> <sup>-</sup>	-1	Nitrato	O
	Cyanate	ONC <sup>-</sup>	-1	Cyanato	O
	Isocyanate	NCO <sup>-</sup>	-1	Isocyanato	N
Monodentate ligands with two negative charges	Sulphate ion	SO <sub>4</sub> <sup>2-</sup>	-2	Sulphato	O
	Oxide ion	O <sup>2-</sup>	-2	Oxo	O
	Peroxide ion	O <sub>2</sub> <sup>2-</sup>	-2	Peroxo	O
	Carbonate ion	CO <sub>3</sub> <sup>2-</sup>	-2	Carbonato	O
	Sulphite ion	SO <sub>3</sub> <sup>2-</sup>	-2	Sulphito	O
	Sulphide ion	S <sup>2-</sup>	-2	Sulphido	S
	Thiosulphate ion	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	-2	Thiosulphato	S
	Imide ion	NH <sup>2-</sup>	-2	Imido	N
Bidentate ligands with one/two negative charges	Oxalate ion (o*x)	COO <sup>-</sup>   COO <sup>-</sup>	-2	Oxalato	Two O-atoms
	Acetyl acetone (a*cac)	CH <sub>3</sub> —C(=O)—CH=C(=O)CH <sub>3</sub>	-1	Acetyl acetonato	Two O-atoms
	Glycinate ion (g*ly)	CH <sub>2</sub> —NH—CH <sub>2</sub> —COO <sup>-</sup>	-1	Glycinato	One N-atom and one O-atom
	* Symbol used				
Polydentate ligands with high negative charges	Ethylenediamine triacetate ion (a pentadentate ligand)	CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup> CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup> CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup> CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup>	-3	EDTA <sup>3-</sup>	Two N-atoms and three O-atoms
	Ethylenediamine tetra-acetate ion (a hexadentate ligand)	CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup> CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup> CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup> CH <sub>2</sub> —N(H) <sub>2</sub> —CH <sub>2</sub> —COO <sup>-</sup>	-4	EDTA <sup>4-</sup>	Two N-atoms and four O-atoms

## 996 JEE Main Chemistry

3. **Neutral ligands** have no special ending e.g.,

Table 9.4 Neutral Ligands

	Name and symbol of ligand	Formula	Charge	Name of ligand on the complex	Donor atom
Neutral monodentate ligands	Ammonia	NH <sub>3</sub>	Zero	Ammine	N
	Water	H <sub>2</sub> O	Zero	Aqua	O
	Phosphine	PH <sub>3</sub>	Zero	Phosphine	P
	Nitrogen oxide	NO	Zero	Nitrosyl	N
	Carbon monoxide	CO	Zero	Carbonyl	C
Neutral polydentate ligands	Pyridine (py)	C <sub>6</sub> H <sub>5</sub> N or 	Zero	Pyridine	N
	Thiourea (tu)	H <sub>2</sub> N—C=S—NH <sub>2</sub>	Zero	Thiourea	S
	Triphenyl phosphine	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Zero	Triphenyl phosphine	P
	Thiocarbonyl	CS	Zero	Thiocarbonyl	S
	Ethylenediamine (en) (a bidentate ligand)	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	Zero	Ethylenediamine	Two N-atoms
	2,2-dipyridyl (dipy) (a bidentate ligand)		Zero	Dipyridyl	Two N-atoms
	Diethylene triamine (dien) (a tridentate ligand)	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	Zero	Diethylene triamine	Three N-atoms
	Triethylene tetramine (trien) (a tetradeятate ligand)	NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> —NH—(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	Zero	Triethylene tetramine	Four N-atoms

**Caution Point** In old system, word aquo was used.

4. **Positive ligands** (which are very few) end in -ium e.g.,

Table 9.5 Positive Ligands

Name and symbol of ligand	Formula	Charge	Name given in the complex	Donor atom
Nitronium ion	NO <sub>2</sub> <sup>+</sup>	+ 1	Nitronium	N
Nitrosonium ion	NO <sup>+</sup>	+ 1	Nitrosonium	N
Hydrazinium ion	NH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	+ 1	Hydrazinium	N

5. The order of the preference of the ligands in the complexes according to the old system was as

- (i) Negative ligands; (ii) Neutral ligands;
- (iii) Positive ligands

There should be no hyphen in between. In case, there are more than one negative or positive ligands, they are listed alphabetically. Thus, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup> are written in the order as chloro, nitro etc.

IUPAC rules 1991 recommended that all ligands whether anions, neutral or positive be arranged alphabetically without any preference order. But the old system has also been retained. Some examples are as

Formula of the complex	Old IUPAC Name	Latest IUPAC Name
[PtCl(NO <sub>2</sub> )(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub>	Chloronitrotetrammine platinum (IV) sulphate	Tetramminechloronitro platinum (IV) sulphate
[CoCl(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)]Cl <sub>2</sub>	Chloroquotetrammine cobalt (III) chloride	Tetramminechloroacobalt (III) chloride

**Note** Always follows latest IUPAC conventions.

6. Certain ligands like NO can act as a neutral as well as unipositive (NO<sup>+</sup>) ligand. In such case, it is very difficult to find the oxidation state and the charge on the ligand from the given formula of the complex.

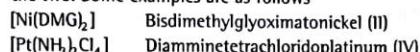
## Hot Spot 1

### NAMING of the Complex Ion

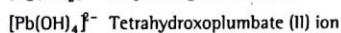
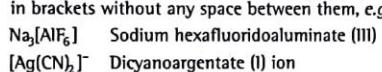
*It is an important topic for JEE Main examination. The level of questions is generally easy so a small practice can help you to solve the problems based on naming and formula writing.*

While naming the complex ion, number and name of the ligands are given first, then the central metal atom followed by its oxidation state indicated by Roman numeral in parenthesis.

- (i) **If the complex ion is a cation,** the name of the central metal ion is given as such followed by its oxidation state indicated by numerals (such as II, III, IV) in the parenthesis at the end of the name of the complex without a space between the two. Some examples are as follows



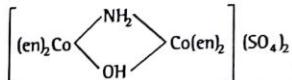
- (ii) **If the complex ion is an anion,** the name of the central atom, is made to end in -ate followed by the oxidation number in brackets without any space between them, e.g.,



- For an acid we have a characteristic ending (ic) e.g.,**  
 $\text{H}_4[\text{Pt}(\text{CN})_6]$  Hexacyanoplatinic (II) acid.

If the complex contains two or more metal ions, it is termed as polynuclear complex. The ligands, which link the two metal atoms, are

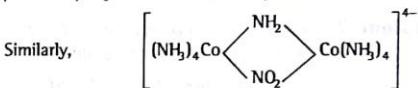
called bridge groups and are separated from the rest complex by hyphens and denoted by the prefix  $\mu$  placed before their names, e.g.,



is named as

bis (ethylenediamine) cobalt (III) - $\mu$  - amido - $\mu$  - hydroxo bis (ethylenediamine) cobalt (III) sulphate

[It can also be named as tetrakis (ethylenediamine)  $\mu$ -amido- $\mu$ -hydroxocobalt (III) sulphate.]



is named as octaammine- $\mu$ -amido- $\mu$ -nitrocobalt (III) ion

It can also be named as

[tetramminecobalt (III)- $\mu$ -amido- $\mu$ -nitrotetrammine cobalt (III) ion].

The following examples illustrate the nomenclature of complexes

- |  |  |
|--|--|
| 1. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$       | Tetraquaquadichloridochromium (III) chloride                     |
| 2. $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$              | Pentaamminecarbonatocobalt (III) chloride                        |
| 3. $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$                         | Diamminesilver (I) chloride                                      |
| 4. $[\text{Co}(\text{en})_2\text{Cl}_2]\text{SO}_4$              | Dichloridobis (ethylenediamine) cobalt (III) sulphate            |
| 5. $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{NO}_3$ | Tetraamminechloridonitrocobalt (III) nitrate                     |
| 6. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2]$                   | Triaminetrinitrocobalt (III)                                     |
| 7. $[\text{Pt}(\text{NH}_3)_2]\text{Cl}_4$                       | Hexaammineplatinum (IV) chloride                                 |
| 8. $[\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)]\text{Cl}_3$   | Triaminetriaquachromium (III) chloride                           |
| 9. $[\text{Co}(\text{en})_2\text{ClO}_4]$                        | Bis (ethylenediamine) difluoridocobalt (III) perchlorate         |
| 10. $\text{Na}_2[\text{SiF}_6]$                                  | Sodium hexafluorosilicate (IV)                                   |
| 11. $\text{Fe}_4[\text{Fe}(\text{CN})_6]$                        | Iron (III) hexacyanoferrate (II) or ferric hexacyanoferrate (II) |
| 12. $\text{Na}_2[\text{CrF}_4\text{O}]$                          | Sodium tetrafluoridooxochromate (IV)                             |
| 13. $\text{K}[\text{BF}_4]$                                      | Potassium tetrafluoridoborate (III)                              |
| 14. $\text{K}_2[\text{OsCl}_5\text{N}]$                          | Potassium pentachloridonitridoosmate (VI)                        |
| 15. $\text{Ni}(\text{CO})_4$                                     | Tetracarbonyl nickel (0)   |
| 16. $\text{K}_4[\text{Ni}(\text{CN})_4]$                         | Potassium tetracyanonickelate (0)                                |
| 17. $[\text{Ni}(\text{dmg})_2]$                                  | Bis (dimethylglyoximo) nickel (II)                               |
| 18. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$                      | Diamminedichloridoplatinum (II)                                  |

## 998 JEE Main Chemistry

19.  $[\text{Cr}(\text{PPh}_3)(\text{CO})_5]$  Pentacarbonyltriphenylphosphinechromium (0)  
 20.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2][\text{Cr}(\text{CN})_6]$  Tetraamminedithiocobalt (III) hexacyanochromate (III)  
 21.  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$  Tetraammine dichloridoplatinum (IV) tetrachloridoplatinate (II)  
 22.  $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$  Pentaamminechromium (III)- $\mu$ -hydroxopentaamminechromium (III) chloride  
 23.  $(\text{C}_6\text{H}_5)_3\text{P} \begin{array}{c} > \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} < \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} < \\ \text{Cl} \end{array} \text{P}(\text{C}_6\text{H}_5)_3$  Chloridotriphenylphosphinepalladium (II)- $\mu$ -dichloro  
chloridotriphenylphosphinepalladium (II)  
 24.  $[(\text{NH}_3)_5\text{Co}-\text{NH}_2-\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$  Decammine- $\mu$ -amidodicobalt (III) nitrate  
 25.  $\left[ (\text{H}_2\text{O})_4\text{Fe} \begin{array}{c} \text{OH} \\ | \\ \text{NO}_2 \end{array} \text{Fe}(\text{H}_2\text{O})_4 \right] \text{SO}_4$  Octaaqua- $\mu$ -hydroxo- $\mu$ -nitrodiiron (III) sulphate  
 26.  $[\text{Mn}(\text{CO})_{12}]$  Dodecacarbonyltrimanganese (0)  
 27.  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$  Bis(cyclopentadienyl)iron (II) or ferrocene  
 28.  $[\text{PtBrCl}(\text{NO}_2)(\text{NH}_3)(\text{Py})]$  Amminebromidochloridoiodidonitropyridineplatinum (IV)  
 29.  $[\text{VO}(\text{acac})_3]$  Bis(acetylacetone)oxovanadium (IV)  
 30.  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$  Sodium bis(thiosulphato) argentate (I)  
 31.  $\text{Na}_3[\text{Ni}(\text{EDTA})]$  Sodium ethylenediaminetetraacetatonickelate (II)  
 32.  $\text{Hg}[\text{Co}(\text{SCN})_4]$  Mercuric tetrathiocyanatocobaltate (II)

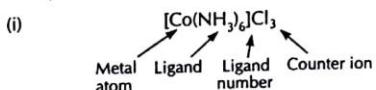
**Sample Problem 7** Select the incorrect match(s) of IUPAC names with the following coordination compounds :

- (i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  Hexaaminocobalt (III) chloride  
 (ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  Pentaamminechloridocobalt (III) chloride  
 (iii)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  Potassium hexacyanoferrate (III)  
 (iv)  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  Potassium trioxalatoferrate (III)  
 (v)  $\text{K}_2[\text{PdCl}_4]$  Potassium tetrachlorido palladate (II)  
 (vi)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$  Diamminechlorido (methylamine) platinum (II) chloride [INCERT]
- (a) (i) only  
 (b) (i), (v) and (vi)  
 (c) (i), (ii) and (iii) only  
 (d) (v) only

### Interpret (a)

- (i) To write the name of cationic complex, the general formula is  
ligand number + ligand names (alphabetically) + metal name + metal oxidation state in parenthesis + counter ion name (counter ion is present outside the coordination sphere.)  
 (ii) To write the name of anionic complex, the general formula is  
counter ion + number of ligands + ligand names (alphabetically) + metal name + 'ate' + (oxidation state of metal).

So write, the name according to above formula



Let the oxidation state of Co be x

$$x + (0)6 + (-1)3 = 0$$

$$x + 0 - 3 = 0$$

$$x = +3$$

So, the name of this complex is hexaamminecobalt (III) chloride.

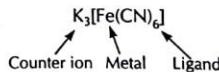


$$x + (0)5 + (-1)1 + (-1)2 = 0$$

$$x + 0 - 3 = 0$$

$$x = +3$$

So, the name of the complex is pentaamminechloridocobalt (III) chloride.



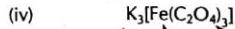
Let the oxidation state of Fe is x

$$(+1)3 + x + (-1)6 = 0$$

$$+3 + x - 6 = 0$$

$$x = +3$$

So, the name of the complex is potassium hexacyanoferrate (III).



Let the oxidation state of Fe is x

$$(+1)3 + x + (-2)3 = 0$$

[As Oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ ) bears -2 charge.]

$$3 + x - 6 = 0$$

$$x = +3$$

So, the name of the complex is potassium trioxalatoferrate (III).



## 9.5 Isomerism

It is a phenomenon, in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. These compounds are called **isomers**. The complexes in which ligands undergo rapid displacement by other ligands, cannot exhibit isomerism as the arrangement is not stable. Such complexes are known as **labile complexes**.

There are two main types of isomerism as seen in coordination compound namely:

- (i) Structural isomerism, (ii) Space or stereoisomerism

## Structural Isomerism

*Structural isomerism is mainly of the following types*

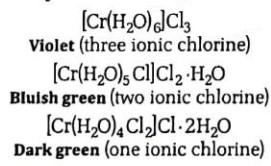
### (a) Ionisation Isomerism

Ionisation isomers yield different ions in solution although they have same composition. This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it, e.g.,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  is red-violet and in solution gives a precipitate of  $\text{BaSO}_4$  with  $\text{BaCl}_2$  confirming the presence of  $\text{SO}_4^{2-}$  ion. On the other hand,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  is red, and does not give test for sulphate ion in the solution, but instead gives a precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$ . Other examples are

- (i)  $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]\text{SO}_4$  and  $[\text{Pt}(\text{NH}_3)_4\text{SO}_4](\text{OH})_2$
  - (ii)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
  - (iii)  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$

### (b) Hydrate Isomerism

Since, water is one of the most effective coordinating agents, therefore the number of water molecules, which may enter into the coordination sphere, may vary resulting in the formation of hydrate isomers, e.g., there are three different hexa-hydrates of chromic chloride with an empirical formula of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . One of these hydrates is violet and the other two are green in colour. All the three differ in the number of molecules of water in the coordination sphere. The formulae, which have been assigned to these hydrate isomers, are



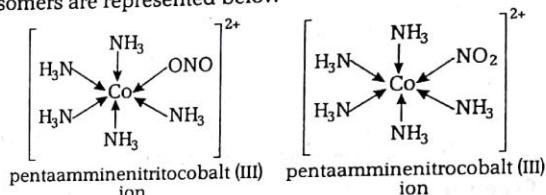
Similarly, other compounds in which hydrate isomerism is observed are

- (i)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$   
 (ii)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl} \cdot \text{Br}]\text{Br} \cdot \text{H}_2\text{O}$

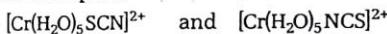
### (c) Linkage Isomerism

(C) **Linkage Isomerism**  
 Isomerism of this type occurs when two or more atoms in a monodentate ligand may function as a donor i.e., when an ambidentate ligand is present. For example, in the case of  $\text{NO}_2^-$  ion either a nitrogen or an oxygen atom may act as donor giving two different isomers. Thus, two different isomers with molecular formula  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$  have been prepared. One isomer has N-atom of  $\text{NO}_2$  group linked to cobalt atom and the other has O-atom linked to cobalt.

This behaviour is analogous to the behaviour of organic nitrites  $R-\text{ONO}$  and nitro compounds  $R-\text{NO}_2$ . The two isomers are represented below



Other example is



#### (d) Coordination Isomerism

This type of isomerism is possible when both positive and negative ions of a salt are complex ions. The two isomers differ in the **distribution of ligands** in the cation and the anion.

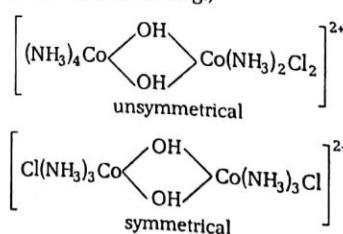
*Some important examples are*

- (i)  $[\text{Co}(\text{NH}_3)_6]_2[\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6]_2[\text{Co}(\text{CN})_6]$   
(ii)  $[\text{Cr}(\text{NH}_2)_6]_2[\text{Co}(\text{C}_2\text{O}_4)_6]$  and  $[\text{Co}(\text{NH}_2)_6]_2[\text{Cr}(\text{C}_2\text{O}_4)_6]$

This type of isomerism may be caused by **interchange of ligand between the two complex ions**.

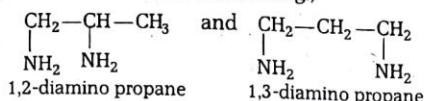
**(e) Coordination Position Isomerism**

(c) **COORDINATION POSITION ISOMERISM**  
This type of isomerism is due to the difference in the distribution of ligands in two coordination centres. Generally, the bridged complexes involving different ligands show this isomerism e.g.



### (f) Ligand Isomerism

This isomerism arises in those complexes in which the two ligands are isomers themselves e.g.,



When these form the complexes, we get ligand isomers. e.g.,  $[\text{Co}(1,2\text{-diaminopropane})_2 \text{Cl}_2]^+$   
 $[\text{Co}(1,3\text{-diaminopropane})_2 \text{Cl}_2]^+$ . This type of isomerism is quite rare.

### Stereoisomerism

This is due to the different relative positions of the ligands. It is of two types

- (a) Geometrical isomerism,
- (b) Optical isomerism

Out of these two, the most thoroughly investigated is the geometrical isomerism.

#### (a) Geometrical Isomerism

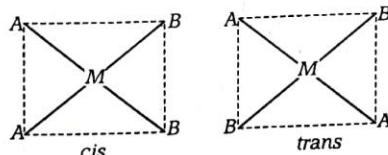
Geometrical isomers differ in the spatial distribution of atoms or groups about the central atom or atom in polynuclear compounds. Those complexes in which the two same ligands occupy adjacent positions to each other or opposite to each other (cis or trans respectively) are able to show this isomerism.

This isomerism cannot be exhibited by coordination compounds having 2 or 3 coordination number as it is not possible to have more than a single arrangement of ligands in space around the central ion in these cases. Geometrical isomerism with respect to the metal has also not been found among **tetrahedral** complexes of type  $MA_4$  or  $MA_3B$  or  $MA_2B_2$  because all the four ligands are equidistant from each other.

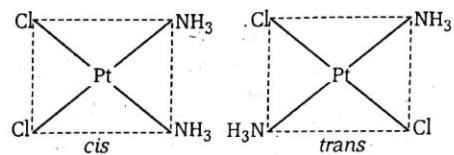
Only square planar and octahedral complexes show this type of isomerism.

#### 1. cis-trans isomerism in square planar complexes is of various types

- (i) Any complex of the type  $MA_2B_2$  can exist in cis-trans form.

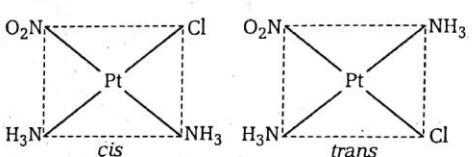


e.g., *cis*-platin or dichlorodiammineplatinum (II),  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  can exist as under

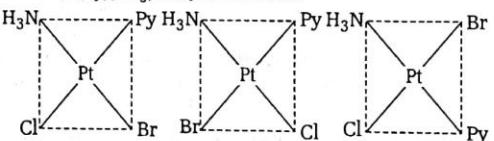


**Caution Point** Square planar complexes of the type  $[M(AA)_2]$ ,  $MA_4$ ,  $MA_3B$  and  $MAB_3$  do not show this isomerism since, all possible spatial arrangements for any of these complexes are identical.

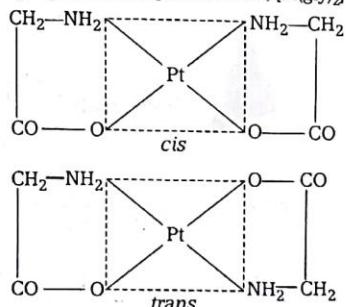
- (ii) In a complex of the type  $MA_2BC$ , also there are cis- and trans-isomers, e.g.,  $[\text{Pt}(\text{NH}_3)_2\text{ClNO}_2]$  can exist as



- (iii) For a complex of the type  $MABCD$ , three geometrical isomers are possible, e.g.,  $[\text{Pt}(\text{Py})(\text{NH}_3)\text{BrCl}]$  can exist as

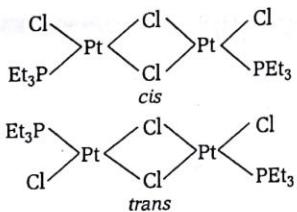


- (iv) The geometrical isomerism can also occur in square planar complexes if the chelate group is not symmetrical, e.g., complex of glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) and platinum i.e.,  $[\text{Pt}(\text{gly})_2]$



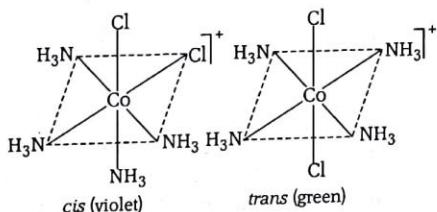
- (v) Geometrical isomerism is also shown by **bridged binuclear** planar complexes of the type,  $M_2A_4X_2$ , e.g.,  $[\text{PtCl}_2\text{PEt}_3]_2$

## 1002 JEE Main Chemistry



2. Various octahedral complexes that show geometrical isomerism are as follows

(i) Octahedral complexes of  $MA_4B_2$  type show *cis-trans* isomerism, e.g., dichlorotetramminecobalt (III) complex ion,  $[Co(NH_3)_4Cl_2]^+$  shows *cis-trans* isomerism as



(ii) An another type of geometrical isomerism called by *fac*-and *mer*-isomerism also occurs in octahedral coordination entities of the type  $[M_{a_2}b_3]$  like  $[Co(NH_3)_3(NO_2)_3]$ . 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 **meridional (mer) isomer**.

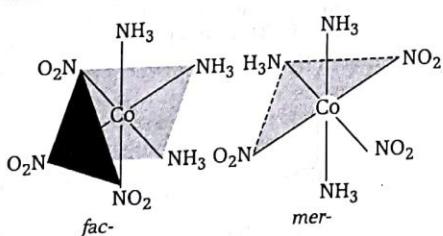
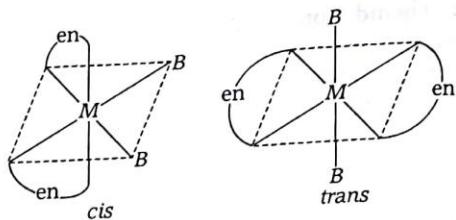


Fig. 9.2 The facial (fac) and meridional (mer) isomers of  $[Co(NH_3)_3(NO_2)_3]$

(iii) Even  $M(AA)_2B_2$  type octahedral complexes also show *cis* and *trans* isomerism where, A-A can be any symmetrical bidentate ligand like ethylenediamine (en) and B can be any anionic ligand, such as  $Cl^-$ ,  $CN^-$ ,  $NO_2^-$  etc.



An example of this type is  $[Pt(en)_2Cl_2]$ .

Octahedral complexes of  $[M_A_5B]$  or  $M(AA)_3$  (where, AA = symmetrical bidentate ligand) do not exhibit geometrical isomerism.

(iv) Complexes having six different ligands  $[M(ABCDEF)]$  shall exhibit geometrical isomerism. Theoretically, fifteen different isomers should be possible. In practice, three isomers of the complex  $[Pt(C_5H_5N)(NH_3)(NO_2)(Cl)(Br)(I)]$  have actually been isolated.

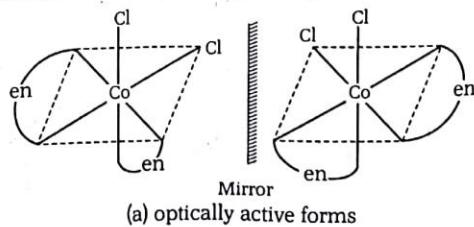
(v) As was observed in square planar complexes, unsymmetrical bidentate ligands also give rise to geometrical isomerism in octahedral complexes of the type  $[M(AB)_3]$ .

### (b) Optical Isomerism

Optical isomerism arises when a compound can be represented by two asymmetrical structures (known as optical isomers). The two isomers are structurally the mirror images of each other (just as in the organic chemistry). Further, it has been found that these mirror image compounds are non-superimposable on each other and they do not possess the plane of symmetry.

**Optical isomerism is common in octahedral complexes involving 2 or 3 symmetrical bidentate groups** (i.e., a group attached to the central atom by two coordinate bonds of the type  $[M(AA)_2X_2]$  and  $[M(AA)_3]$  where, AA = bidentate ligand). This is illustrated as under:

(i) **Example of  $M(AA)_2X_2$  type** *cis*-dichloridobis (ethylenediamine) cobalt (III) ion,  $[Co(en)_2Cl_2]^+$ , the *cis*-form of this complex is optically active and exists in *d* and *l*-forms. Its *trans* form is optically inactive due to the presence of a plane of symmetry as shown below.



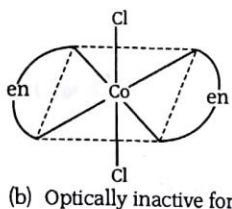
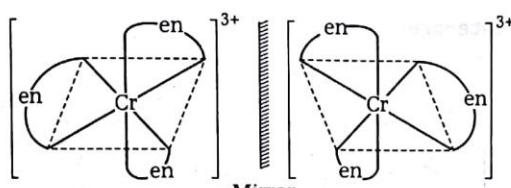


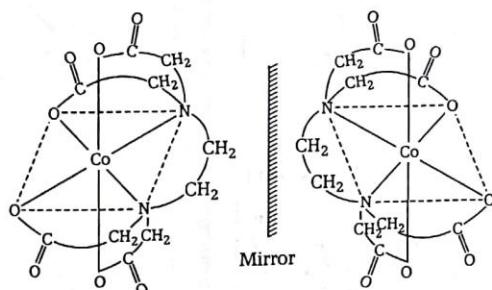
Fig. 9.3 (a) *cis*-dichloro bis(ethylenediamine) cobalt (III) ion  
 (b) *trans*-dichloro bis(ethylenediamine) cobalt (III) ion

- (ii) **Example of  $M(AA)_3$  type octahedral complexes**  $[Cr(en)_3]^{3+}$ , tris (ethylenediamine) chromium (III) ion and  $[Cr(C_2O_4)_3]^{3-}$ , trioxalatochromate (III) ion etc.

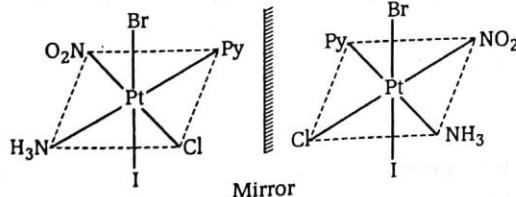


- (iii) **Examples of  $[M(AA)B_2X_2]$  type**  $[CoCl_2(NH_3)_2(en)]^+$ ,

- (iv) **Complexes containing hexadentate ligand** (e.g., ethylenediaminetetraacetic acid) show optical activity, e.g., the anion  $[Co(EDTA)]^-$  exists in two forms.

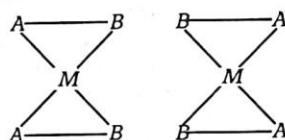


- (v) **Example of  $ML_aL_bL_cL_dL_eL_f$  type** is  $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$ . The optical activity in such complexes is due to the presence of six different ligands around the central atoms.

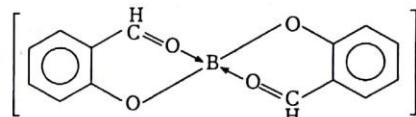


In such a compound fifteen geometrical isomers are possible which can be resolved into optical isomers. Resolution of all the isomers is not achieved.

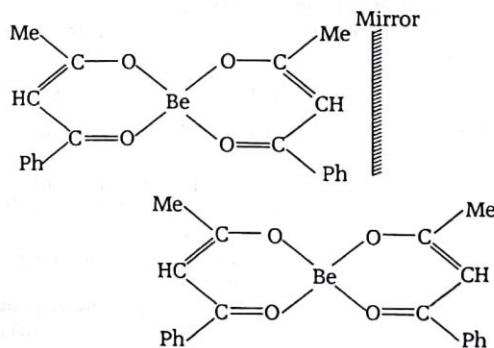
The optical activity has been observed for chelated tetrahedral and square planar complexes but only rarely. In tetrahedral complexes only the type, which occurs in bis-chelates with unsymmetrical ligand has been detected. These have been found in Be(II), B(III), Zn(II) and Cu(II) complexes. They are of the general type as represented below:



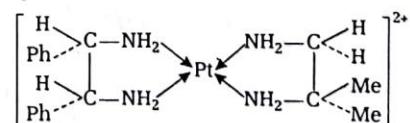
Thus, bis(salicylaldehyde) boron (III) cation has been found to be racemic and resolution has been accomplished.



The two enantiomers of bis (benzoylacetonato) beryllium (II) are shown below :



**Square planar complexes are seldom optically active.** One such compound which has been resolved into two forms is shown below. As can be seen, it has no plane or axis of symmetry.



## Hot Spot 2

### FINDING NUMBER of Stereoisomerism

Questions based on stereoisomers are frequently asked in JEE Main examination. The level of question is generally average and by a small practice, the question can be solved easily.

In order to find number of stereoisomers or whether a compound exhibit stereoisomerism or not, first find the general formula of the complex, and then compare with the following facts.

- Geometrical isomerism is possible in square planar complexes of the type  $MA_2BC$ ,  $MA_2B_2$ ,  $MABCD$ . It is also possible in bridged binuclear planar complexes of the type  $M_2A_4X_2$ . Octahedral complexes of the type  $MA_3B$ ,  $MA_4B_2$ ,  $M(AA)_2B_2$ ,  $[M(ABCDEF)]$  exhibit geometrical isomerism.
- Geometrical isomerism is not possible in square planar complexes of type  $MA_4$  and  $MA_2B$ , tetrahedral complexes of type  $MA_4$ ,  $MA_2B_2$  and  $MABCD$  and octahedral complexes of type  $MA_6$  and  $MA_5B$ . In case of octahedral complexes of the types  $MA_3B$ , the *cis-trans* isomers are also called *fac-mer* isomers.
- Octahedral complexes of the type  $[M(AA)_2X_2]$ ,  $[M(AA)_3]$ ,  $[M(AA)B_2X_2]$  [where, AA = bidentate ligand] generally exhibits optical isomerism.  $[M(\text{EDTA})]$  and  $MABCDEF$  also exhibit optical isomerism. (A, B, C, D, E, F are different monodentate ligands)

**Sample Problem 9** The number of geometrical isomers possible the following coordination entities are respectively.

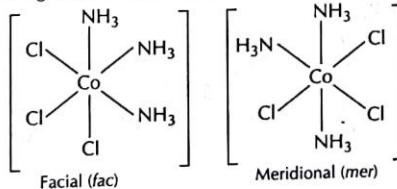
- (i)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{2-}$       (ii)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$       [NCERT]  
 (a) 2, 2      (b) 0, 2      (c) 2, 0      (d) 1, 2

**Interpret** (b) In order to solve such problem recall the following facts

- Geometrical isomerism is exhibited by octahedral complexes of the type  $[MA_3B_3]$ ,  $[MA_2B_4]$  etc., where A and B are monodentate ligands.
- $[M(AA)_3]$  type complex does not exhibit geometrical isomerism, they exhibit optical isomerism.
- When the similar groups occupy adjacent positions, the isomer is called *fac* or *cis*-form, if not, it is called *mer* or *trans*-form.

Thus,

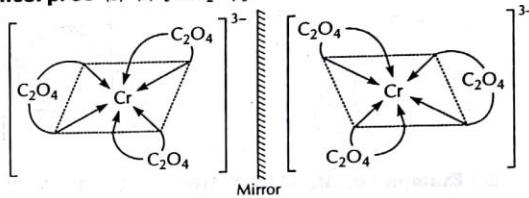
- (i) No geometrical isomer is possible.  
 (ii) Two geometrical isomers are possible for  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$



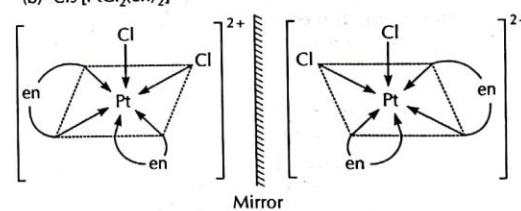
**Sample Problem 10** Trans form of which of the following is optically inactive?

- (a)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (b)  $[\text{PtCl}_2(\text{en})_2]^{2+}$   
 (c)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$   
 (d) All of these

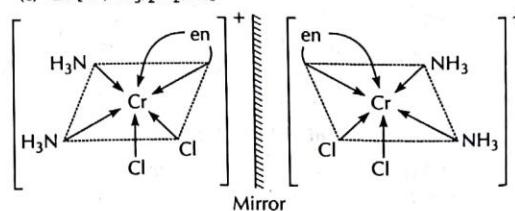
**Interpret** (b) (a)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$



(b)  $\text{Cis-}[\text{PtCl}_2(\text{en})_2]^{2+}$



(c)  $\text{Cis-}[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$



Thus,  $\text{trans-}[\text{PtCl}_2(\text{en})_2]^{2+}$  is optically inactive.

**Sample Problem 11** Which of the following has largest number of isomers? (R = alkyl group, en = ethylenediamine)

- (a)  $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$   
 (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$   
 (c)  $[\text{Ir}(\text{PR}_3)_2\text{H}(\text{CO})]^{2+}$   
 (d)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$

**Interpret** (d) Among the given  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is a  $[\text{M}(AA)_2A_2]$  type complex, thus, it is possible for it to exhibit optical as well geometrical isomerism, which is not possible in case of other given complexes. Thus, it exhibits largest number of isomers.

**Check Point 2**

1. Why do ambidentate ligands show linkage isomerism?
2. Name a ligand, presence of which causes difficulty in finding the oxidation state and charge on the ligands.
3. Why do the complexes in which ligands undergo rapid displacement by other ligands, not show isomerism?
4. Why do the complexes with 2 or 3 coordination number not exhibit geometrical isomerism?
5. *Trans*-dichlorobis (en) cobalt (III) ion is optically inactive while its *cis*-form is optically active. Explain, why?

## 9.6 Bonding in Coordination Compounds

The formation of coordination compounds can be explained electronically by a number of theories like (i) valence bond approach (ii) crystal field theory

### Valence Bond Approach

This was evolved largely through the efforts of **Linus Pauling** based on attempted Lewis-Sidgwick ideas of the coordinate covalent bond. In this approach, the basic assumption made is that the metal-ligand bonds arise by the donation of pairs of electrons from ligands to the metal i.e., through forming the coordinate covalent bond. In order to accommodate these electrons, the metal ion must possess requisite number of vacant orbitals of similar energy. These metal orbitals undergo hybridisation to give a set of hybrid orbitals of equal energy with the approach of the ligands.

*The main assumptions of valence bond approach are*

1. The ions of the transition elements have some incompletely filled *d*-orbitals.
2. Some or all the electrons in the incompletely filled *d*-orbitals are unpaired.
3. It was suggested that sometimes, the unpaired ( $n - 1$ ) *d*-electrons couple as fully as possible prior to bond formation. In this process some ( $n - 1$ ) *d*-orbitals become vacant.
4. Since, the energy of the ( $n - 1$ ) *d*-orbitals is only slightly less than that of *s*-and *p*-orbitals of the *n*th orbitals,

The central metal atom thus, makes available a number of empty orbitals equal to its coordination number for the formation of coordinate bonds with suitable ligand orbitals.

these vacant orbitals mix together to form new equivalent orbitals, called **hybrid orbitals**.

5. Each ligand has at least one sigma orbital containing a lone pair of electrons.
6. The hybrid orbitals formed, take part in the formation of hybrid bonds with the ligands by overlapping. The bond formation takes place by accepting the lone pair of electrons by the hybrid orbitals of the metal from the ligands. Especially the orbitals that would be used for a metal ion of the first series, are the two  $3d$ , one  $4s$  and the three  $4p$ -orbitals. The rest  $3d$  or **inner orbitals on the metal ion do not** participate in the bonding. When ( $n - 1$ ) *d*-orbitals are used in bond formation, the complex formed is called **inner orbital complex**.
7. Sometimes, in place of ( $n - 1$ ) *d*-orbitals, outer *nd*-orbitals are used for hybridisation. The complex, thus, formed is called **outer orbital complex**.
8. The bond hybridisation involved and the resulting geometrical shapes of the complexes are given in the following table

Table 9.6 Relation Between Hybridisation and Geometry of Complexes

Bond hybridisation	Geometrical shape	<i>d</i> -orbital used	Typical example
$d^2sp^3$	octahedral (inner orbital complex)	$d_{z^2}$ and $d_{x^2-y^2}$	$[Fe(CN)_6]^{3-}$
$sp^3d^2$	octahedral (outer orbital complex)	$d_{x^2-y^2}$ and $d_{z^2}$	$[FeF_6]^{3-}$
$sp^3$	tetrahedral		$[Zn(NH_3)_4]^{2+}$
$dsp^2$ or $sp^2d$	square planar	$d_{x^2-y^2}$	$Ni(CN)_4]^{2-}$

9. A given complex is paramagnetic, if one or more unpaired electrons are present in the *d*-subshell. However, if there is no unpaired electrons, then complex is termed as diamagnetic. Pauling made extensive use of magnetic measurements to discover the number of unpaired electrons in a complex and he also differentiated between complexes in which the bonding could be considered as ionic or those in which it was probably covalent.

In deciding whether the hybridisation at the central metal ion of octahedral complexes is  $sp^3d^2$  (outer orbital) or  $d^2sp^3$  (inner orbital) we must know the results of magnetic measurements. These indicate the number of unpaired electrons ( $N$ ). Magnetic moment is given by

$$\mu = \sqrt{N(N + 2)} \text{ BM}$$

(BM is Bohr Magneton)

## Hot Spot 3

### FINDING GEOMETRY

#### and Magnetic Character of Complexes

Questions based on geometry, hybridisation, magnetic character and number of unpaired electrons were frequently asked in the AIEEE and JEE Main examination, thus it is a very important topic for the examination. The level of question is generally average.

In order to find the geometry, hybridisation and magnetic character, follow the following steps

**Step I** Find the oxidation number of central metal atom and write the electronic configuration of **central metal ion**.

**Step II** Find the nature of ligand,

- If it is  $\text{CN}^-$ ,  $\text{NH}_3$ ,  $\text{CO}$ , pair up the unpaired electrons of the metal ion (if they are more than 4 and less than 8 in case of octahedral complex).
- If it is  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{H}_2\text{O}$ , etc., leave the unpaired electrons of the metal ion as such.

**Step III** Now fill the ligand's electrons in empty available orbitals. The orbitals occupied by ligands give an idea about the hybridisation.

**Step IV** From the hybridisation, find geometry (see table 9.7).

**Step V** Also see whether unpaired electrons are present, or not. If they are present, species is paramagnetic, otherwise diamagnetic.

**Step VI** If inner  $[(n - 1)d]$  orbital takes part in hybridisation, the complex is inner orbital, otherwise outer orbital.

The above procedure can be best understood by following examples.

#### 1. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ion

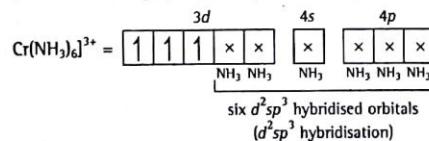
In this ion, oxidation state of Cr is +3.

$$[x + 6 \times 0 = +3 \text{ or } x = +3] \\ \text{Cr}^{3+} = [\text{Ar}] 3d^3 4s^0$$

3d	4s
1   1   1	

$\text{NH}_3$  is a strong field ligand but unpaired electrons are < 4. So, pairing does not occur.

Since, there are six  $\text{NH}_3$  ligands, fill their electrons as



(Here  $x$  = a pair of electrons from ligand)

Since, hybridisation is  $d^3 s^0$ , geometry is octahedral. Because of the presence of three unpaired electrons, it is a paramagnetic complex.

Since  $(n - 1)d$  ( $3d$  orbital) takes part in hybridisation, it is an inner orbital complex.

Other complexes of Cr with similar inner structure are  $[\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ . In a similar way, structure of  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  with  $d^3$ -configuration of  $\text{V}^{3+}$  ion can be explained.

#### 2. $[\text{Co}(\text{NH}_3)_6]^{2+}$

Co is present in +2 oxidation state, so

$$\text{Co}^{2+} = [\text{Ar}] \quad 3d^7 \quad 4s^0$$

1	1	1	1	1	
---	---	---	---	---	--

$\text{NH}_3$  being strong field ligand pair up the unpaired electrons of Co and also transfers one remained unpaired electron into higher energy state, as

$\text{Co}^{2+}$ (hybridised)	3d	4s	4p	5s
1   1   1				1

The inner two  $d$ -orbitals are made available for the required  $d^2 s^3$  hybridisation after maximum pairing of electrons within the  $3d$  level followed by promotion of one  $d$ -electrons to the higher energy level (5s). This is shown below

$[\text{Co}(\text{NH}_3)_6]^{2+}$	3d	4s	4p	5s
1   1   1   x   x   x   x   x   x   x   x   1				

$d^2 s^3$  hybridisation

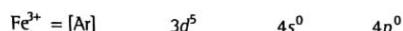
Thus, its geometry is octahedral. It is a paramagnetic complex. Moreover, it is an inner orbital complex.

As the promoted electron (shown above) has low ionisation energy, the complexed central metal ion  $\text{Co}^{2+}$  has a tendency to undergo oxidation easily to  $\text{Co}^{3+}$ . Thus, the paramagnetic complex changes to diamagnetic after oxidation. It should be noted however, that the formation of such inner orbital

**complex and promotion of electron can be brought about only by very strong ligands.**

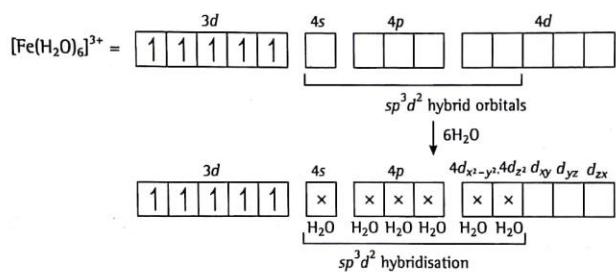
3.  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Here, Fe is present as  $\text{Fe}^{3+}$ .



1	1	1	1	1			
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$\text{H}_2\text{O}$  being weak field ligand is unable to pair up its unpaired electrons, thus, occupy the 4s, 4p and 4d empty orbitals as



Thus, its geometry is octahedral.

Because of the presence of five unpaired electrons, it is paramagnetic.

Since  $nd$  orbitals (4d orbitals) take part in hybridisation (bonding), it is an **outer orbital or high spin complex**.

#### Caution Points

- (i) Electrons of ligands are only the bonding electrons. None of the 3d-electron of Fe take part in bonding.
  - (ii) In  $d^5$  electronic configuration, an octahedral complex can exist in both high spin and low spin forms.
-

# 1008 JEE Main Chemistry

Table 9.7 Geometry and Hybridisation of Some Other Complexes on the Basis of VBT

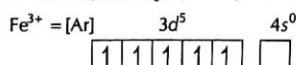
S.N.	Atom/Ion Complex	Configuration	Oxidation state of metal	Type of hybridisation	Geometry (Shape)	No. of unpaired electrons	Magnetic nature																		
1.	$\text{Ni}^{2+}(d^8)$ $[\text{NiCl}_4]^{2-}$	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1 1</td><td>1</td><td></td></tr> <tr><td>1 1 1 1 1</td><td>:</td><td>:</td></tr> </table> <table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1 1</td><td>1</td><td></td></tr> <tr><td>1 1 1 1 1</td><td>:</td><td>:</td></tr> </table> <span style="margin-left: 100px;"><math>sp^3</math></span>	3d	4s	4p	1 1 1 1 1	1		1 1 1 1 1	:	:	3d	4s	4p	1 1 1 1 1	1		1 1 1 1 1	:	:	+2 +2	$sp^3$	Tetrahedral	2 2	Paramagnetic Paramagnetic
3d	4s	4p																							
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1 1 1 1 1	:	:																							
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S.N.	Atom/Ion Complex	Configuration	Oxidation state of metal	Type of hybridisation	Geometry (Shape)	No. of unpaired electrons	Magnetic nature																																																																																																
7.	$\text{Co}^{2+}(\text{d}^7)$ $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	<div style="display: flex; justify-content: space-around; align-items: center;"> <span>3d</span> <span>4s</span> <span>4p</span> </div> <table border="1" style="border-collapse: collapse; text-align: center;"> <tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td></td><td></td><td></td></tr> <tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td></td><td></td><td></td></tr> <tr><td></td><td></td><td></td><td></td><td></td><td>1</td><td>1</td><td>1</td></tr> <tr><td></td><td></td><td></td><td></td><td></td><td>1</td><td>1</td><td>1</td></tr> <tr><td></td><td></td><td></td><td></td><td></td><td>1</td><td>1</td><td>1</td></tr> <tr><td></td><td></td><td></td><td></td><td></td><td>1</td><td>1</td><td>1</td></tr> </table> <p style="margin-left: 20px;"><math>\text{sp}^3\text{d}^2</math></p>	1	1	1	1	1				1	1	1	1	1									1	1	1						1	1	1						1	1	1						1	1	1	+2 +2	$\text{sp}^3\text{d}^2$ (Outer)	Octahedral	3 3	Paramagnetic Paramagnetic																																																
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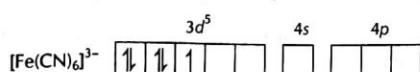
**Sample Problem 12** Which of the following options are correct for  $[\text{Fe}(\text{CN})_6]^{3-}$  complex? [NCERT Exemplar]

- (i)  $\text{d}^2\text{sp}^3$  hybridisation
- (ii)  $\text{sp}^3\text{d}^2$  hybridisation
- (iii) Paramagnetic
- (iv) Diamagnetic
- (a) (i) and (iii)
- (b) (i) and (iv)
- (c) (ii) and (iii)
- (d) (ii) and (iv)

**Interpret** (a) In  $[\text{Fe}(\text{CN})_6]^{3-}$ , Fe is present as  $\text{Fe}^{3+}$ .



$\text{CN}^-$  being strong field ligand pair up these unpaired electrons, so that now the complex have only one unpaired electron as



Now, the two  $3d$ , one  $4s$  and three  $4p$  orbitals hybridise to give six  $\text{d}^2\text{sp}^3$  hybridised orbitals which are occupied by electrons of  $\text{CN}^-$

Since, the complex contain one unpaired electron, it is paramagnetic in nature.

**Sample Problem 13** Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic? [NCERT Exemplar]

- (i)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (ii)  $[\text{Mn}(\text{CN})_6]^{3-}$
- (iii)  $[\text{Fe}(\text{CN})_6]^{4-}$
- (iv)  $[\text{Fe}(\text{CN})_6]^{3-}$
- (a) (i) and (ii) only
- (b) (ii) and (iii) only
- (c) (i) and (iii) only
- (d) All of these

**Interpret** (c)  $\text{Co}^{3+}$  and  $\text{Fe}^{2+}$  contains  $\text{d}^6$  configuration and the unpaired electrons are paired by strong field ligands, i.e.,  $\text{NH}_3$  and  $\text{CN}^-$ , so  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  are diamagnetic complexes.

In  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  unpaired electrons remain even after pairing, so these are paramagnetic.

**Sample Problem 14** Amongst the following ions which one has the highest magnetic moment value? [NCERT]

- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- (c)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- (d) All have same magnetic moment

## 1010 JEE Main Chemistry

**Interpret** (b) More the number of unpaired electrons, higher is the magnetic moment. So, first find the number of unpaired electrons to find magnetic moment.

The oxidation states of metals in the complexes along with the electronic configuration are given

- (a)  $\text{Cr}^{3+}$  :  $3d^3$  configuration; no. of unpaired electrons ( $n$ ) = 3
- (b)  $\text{Fe}^{2+}$  :  $3d^6$  configuration;  $n$  = 4
- (c)  $\text{Zn}^{2+}$  :  $3d^{10}$  configuration;  $n$  = 0

Thus, the complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  with maximum number of unpaired electrons has the highest magnetic moment.

**Sample Problem 15** The spin only magnetic moment of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. Predict the geometry of the complex ion?

- (a) Tetrahedral
- (b) Square planar
- (c) Octahedral
- (d) Trigonal pyramidal

**Interpret** (a) Since, the coordination number of  $\text{Mn}^{2+}$  ion in the complex ion is 4, it will be either tetrahedral ( $sp^3$  hybridisation) or square planar ( $dsp^2$  hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM suggests that it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the  $d$ -orbitals.

### Limitations of Valence Bond Theory

Although this theory described the formation, structure and magnetic behaviour of complexes successfully but it suffers from the following short comings :

1. It involves a number of assumptions.
2. It describes bonding in coordination compounds only qualitatively.
3. It does not offer any explanation for the optical absorption spectra of complexes.
4. It does not describe the detailed magnetic properties of coordination compounds.
5. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
6. It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
7. It does not distinguish between weak and strong ligands.

### Crystal Field Theory

Most of the shortcomings of VBT of coordination compounds were removed in **Crystal Field Theory (CFT)**. It attributes partial covalent character and partial ionic character to bonds. This **theory** was developed by **H. Bethe** and **V. Vleck** (1935) and proved to be more successful in explaining the bonding and properties of coordination complexes. The theory is based upon the fact that the degenerate (meaning energetically alike)  **$d$ -orbitals** of

metal ions are splitted energy wise due to the concentration of point charges in certain specific positions. This is seen because the energy of the orbitals lying in the direction of point charges increases more in comparison to orbitals lying in between the point charges as the electrons in former case experience greater repulsion than in latter case. Thus, energy wise, two groups of orbitals are seen now, one with higher energy and other with lower energy. This splitting of 5 degenerate orbitals of metal ion into two sets of orbitals having different energies is called **crystal field splitting**. In case of octahedral complexes,  $e_g$  set ( $d_{x^2-y^2}, d_{z^2}$ ) is of higher energy while in case of tetrahedral complexes  $t_{2g}$  set ( $d_{xy}, d_{yz}, d_{zx}$ ) has higher energy.

The splitting of  $d$ -orbitals in octahedral and tetrahedral complexes is shown below

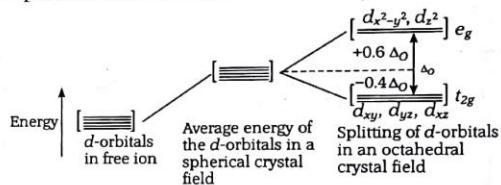


Fig. 9.4  $d$ -orbital splitting in an octahedral crystal field.

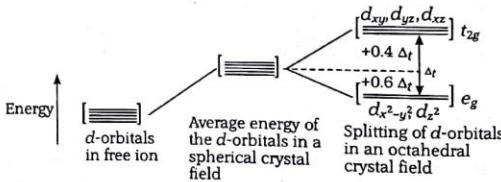


Fig. 9.5  $d$ -orbital splitting in a tetrahedral crystal field

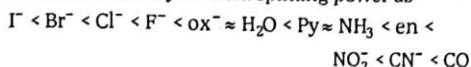
The difference in energy levels is arbitrarily taken to be  $\Delta$ . The set of lower energy stabilises the complex ion by 0.4 units and that with higher energy destabilises the ion by 0.6 units. The gain in energy achieved by preferential filling of electrons in orbitals is called **crystal field stabilisation energy (CFSE)**. Higher the amount of CFSE, greater is the stability of the complex.

The tetrahedral crystal field splitting is only  $4/9$  of the octahedral splitting and there is no known low spin tetrahedral complex.

Here, one point must always be kept in mind that **crystal field theory** considers purely electrostatic attractions between central metal ion and ligands. Factors which affect the magnitude of crystal field splitting are

1. Nature of ligands (the ligands with smaller size, large negative charge, with good  $\sigma$  donor and  $\pi$  acceptor properties will give large crystal field splitting).

ligands are arranged in **spectro chemical series** on the basis of their crystal field splitting power as



It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the  $d$ -orbitals of metal ion in octahedral coordination entities. Obviously, the single  $d$  electron occupies one of the lower energy  $t_{2g}$  orbitals. In  $d^2$  and  $d^3$  coordination entities, the  $d$ -electrons occupy the  $t_{2g}$  orbitals singly in accordance with the Hund's rule. For  $d^4$  ions, two possible patterns of electron distribution arise (i) the fourth electron could either enter the  $t_{2g}$  level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the  $e_g$  level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta_o$  and the pairing energy,  $P$  ( $P$  represents the energy required for electron pairing in a single orbital). *The two options are :*

(i) If  $\Delta_o < P$ , the fourth electron enters in 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.

(ii) 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.

2. Oxidation state of metal ion (More crystal field splitting is seen in metal ions with higher oxidation states).
3. Size of  $d$ -orbital (larger the size, more crystal field splitting is seen).
4. Geometry of the complex (as splitting is different for tetrahedral and octahedral complexes).

The number of unpaired electrons in octahedral and tetrahedral complex having different configuration can be summarised in table 9.9

Table 9.8 Number of Unpaired Electrons in Octahedral and Tetrahedral Complexes

Electronic configuration	Octahedral complex		Number of unpaired electrons	Tetrahedral complex		Number of unpaired electrons
	( $t_{2g}$ set)	( $e_g$ set)		( $e_g$ set)	( $t_{2g}$ set)	
$d^1$	$t_{2g}^1$	$e_g^0$	1	$e^1$	$t_2^0$	1
$d^2$	$t_{2g}^2$	$e_g^0$	2	$e^2$	$t_2^0$	2
$d^3$	$t_{2g}^3$	$e_g^0$	3	$e^2$	$t_2^1$	3
$d^4$ (a)*	$t_{2g}^3$	$e_g^1$	4	$e^2$	$t_2^2$	4
(b)*	$t_{2g}^4$	$e_g^0$	2	$e^4$	$t_2^0$	0
$d^5$ (a)*	$t_{2g}^3$	$e_g^2$	5	$e^2$	$t_2^3$	5
(b)*	$t_{2g}^5$	$e_g^0$	1	$e^4$	$t_2^1$	1
$d^6$ (a)*	$t_{2g}^4$	$e_g^2$	4	$e^3$	$t_2^3$	4
(b)*	$t_{2g}^6$	$e_g^0$	0	$e^4$	$t_2^2$	2
$d^7$ (a)*	$t_{2g}^5$	$e_g^2$	3	$e^4$	$t_2^3$	3
(b)*	$t_{2g}^6$	$e_g^1$	1	$e^4$	$t_2^3$	3
$d^8$	$t_{2g}^6$	$e_g^2$	2	$e^4$	$t_2^4$	2
$d^9$	$t_{2g}^6$	$e_g^3$	1	$e^4$	$t_2^5$	1
$d^{10}$	$t_{2g}^6$	$e_g^4$	0	$e^4$	$t_2^6$	0

\*(a) is the configuration for high spin and (b) is the configuration for low spin complexes]

## 1012 JEE Main Chemistry

**Sample Problem 16** The CFSE for octahedral  $[\text{CoCl}_6]^{4-}$  is  $18,000 \text{ cm}^{-1}$ . The CFSE for tetrahedral  $[\text{CoCl}_4]^{2-}$  will be

[NCERT Exemplar]

- (a)  $18000 \text{ cm}^{-1}$       (b)  $16000 \text{ cm}^{-1}$   
 (c)  $8000 \text{ cm}^{-1}$       (d)  $20000 \text{ cm}^{-1}$

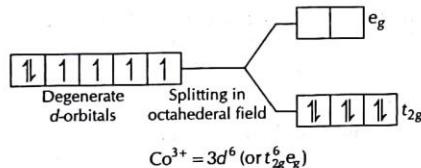
**Interpret** (c)  $\Delta_t = -\frac{4}{9} \Delta_o$

$$= -\frac{4}{9} \times 18000 = 8000 \text{ cm}^{-1}$$

**Sample Problem 17** The electronic configuration of central metal atom/ion in  $[\text{Co}(\text{CN})_6]^{3-}$  is

- (a)  $t_{2g}^5 e_g^0$       (b)  $t_{2g}^4 e_g^2$       (c)  $t_{2g}^6 e_g^0$       (d)  $t_{2g}^4 e_g^3$

**Interpret** (c)  $[\text{Co}(\text{CN})_6]^{3-}$  i.e.,  $\text{Co}^{3+}$



There is no unpaired electron, so it is diamagnetic.

**Sample Problem 18** Arrange the following complex ion in increasing order of crystal field splitting energy. ( $\Delta_o$ ).

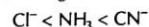
- I.  $[\text{Cr}(\text{Cl})_6]^{3-}$ , II.  $[\text{Cr}(\text{CN})_6]^{3-}$ , III.  $[\text{Cr}(\text{NH}_3)_6]^{3-}$

[NCERT Exemplar]

- (a) I < II < III      (b) II < I < III  
 (c) III < II < I      (d) I < III < II

**Interpret** (d) CFSE is higher when the complex contains strong field ligand. Thus, crystal field splitting energy increases in the order  $[\text{Cr}(\text{Cl})_6]^{3-} < [\text{Cr}(\text{NH}_3)_6]^{3-} < [\text{Cr}(\text{CN})_6]^{3-}$ .

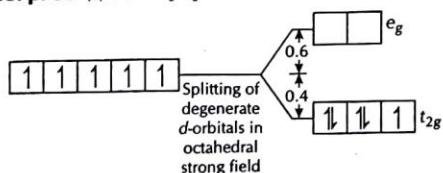
Because the order of field strength is



**Sample Problem 19** The CFSE for  $[\text{Fe}(\text{CN})_6]^{3-}$  is

- (a)  $-1.2$       (b)  $-2.0$       (c)  $-1.8$       (d)  $+1.2$

**Interpret** (c)  $\text{Fe}^{3+} = [\text{Ar}] 3d^5$



$$\begin{aligned} \text{CFSE} &= -(0.4 \times t_{2g} e^-) + 0.6 \times e_g e^- \\ &= -(0.4 \times 5) + 0.6 \times 0 = -2.0 \end{aligned}$$

### Magnetic Properties

The diamagnetic (repulsion from applied magnetic field due to paired electrons) and paramagnetic (attraction from applied magnetic field due to unpaired electron) behaviour of coordination compounds can be explained on the basis of crystal field theory, e.g., Co (III) shows diamagnetic properties in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex and paramagnetic properties in  $[\text{CoF}_6]^{3-}$  complex. Such a difference in behaviour show that there must be some unpaired electrons in latter while former have all paired electrons (magnetic measurement shows the presence of four unpaired electrons in latter). This can be explained on the basis of crystal field theory if you observe the diagrams given below carefully.

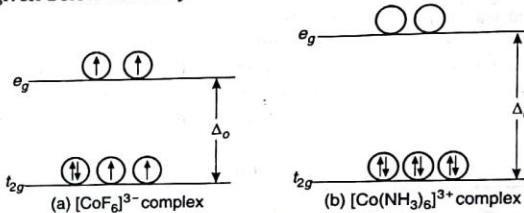


Fig. 9.6 In fig. (a) as  $\Delta_o$  is small, the energy required to pair up the 4th and 5th electron with the electrons in lower d-orbitals ( $t_{2g}$ ) is higher as compared to that required to place the electron in higher d-orbital ( $e_g$ ).

In fig. (b) as  $\Delta_o$  is higher, the energy required to pair up the 4th and 5th electron with the electrons in lower d-orbitals ( $t_{2g}$ ) is lower as compared to that required to place the electron in higher d-orbital ( $e_g$ ).

Magnetic moment ( $\mu$ ) is related to number of unpaired electrons ' $n$ ' as,  $\mu = \sqrt{n(n+2)} \text{ BM}$

**Caution Point** The values of  $n$  calculated by applying the above formula for different magnetic moments are given in the following table :

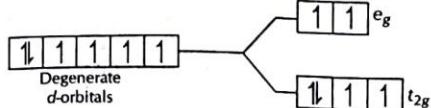
Magnetic moment (BM)	Number of unpaired electrons
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

**Sample Problem 20** The magnetic moment of  $[\text{CoF}_6]^{3-}$  by using CFT is

- [NCERT Exemplar]

- (a) 0      (b) 4.9      (c) 5.9      (d) 1.73

**Interpret** (b)  $[\text{CoF}_6]^{3-}$  i.e.,  $\text{Co}^{3+}$



Configuration of  $\text{Co}^{3+} = 3d^6$  (or  $t_{\text{g}}^4 e_g^2$ )

Number of unpaired electrons ( $n$ ) = 4

$$\begin{aligned}\text{Magnetic moment } (\mu) &= \sqrt{n(n+2)} = \sqrt{4(4+2)} \\ &= \sqrt{24} = 4.9 \text{ BM}\end{aligned}$$

### Colour of the Complexes

A substance appears coloured because it absorbs light at specific wavelengths in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmits or reflects the rest of the wavelength. Each wavelength of visible light represents a different colour. White light, such as sunlight, is a combination of all colours; an object that absorbs all visible light appears black.

When the energy of the photon ( $h\nu$ ) is equal to the difference between the lower and higher  $d$ -orbital energy levels, an electron is promoted from a lower to higher level. If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same as the incident light white and the ion appears colourless.

The coloured nature of solutions of coordination compounds can also be explained on the basis of crystal field theory, because in coordination compounds the energy difference between two sets of  $d$ -orbitals is usually small (as explained by crystal field splitting) thus, excitation of an electron from lower energy to higher energy is very easy and can be achieved even by the absorption of low energy radiations of visible region. As a result of the absorption of such selected wavelengths of visible light, the complexes appeared coloured. Relationship between the  $\lambda$  of light absorbed and the colour observed can be exemplified as

Table 9.9 Wavelength Associated with Different Colours

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue green	Purple

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence, the substance is colourless. For example, removal of water from  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  on heating renders it colourless. Similarly, anhydrous  $\text{CuSO}_4$  is white, but  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour.

**Sample Problem 21** The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes,  $[\text{Co}(\text{NH}_3)_6]^{1+}$ ,  $[\text{Co}(\text{CN})_6]^{1-}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{1+}$ ?

[INCERT Exemplar]

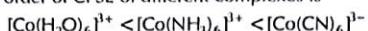
- (a)  $[\text{Co}(\text{CN})_6]^{1-} > [\text{Co}(\text{NH}_3)_6]^{1+} > [\text{Co}(\text{H}_2\text{O})_6]^{1+}$
- (b)  $[\text{Co}(\text{NH}_3)_6]^{1+} > [\text{Co}(\text{H}_2\text{O})_6]^{1+} > [\text{Co}(\text{CN})_6]^{1-}$
- (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{1+} > [\text{Co}(\text{NH}_3)_6]^{1+} > [\text{Co}(\text{CN})_6]^{1-}$
- (d)  $[\text{Co}(\text{CN})_6]^{1-} > [\text{Co}(\text{NH}_3)_6]^{1+} > [\text{Co}(\text{H}_2\text{O})_6]^{1+}$

**Interpret** (c) CFSE (Crystal field stabilisation energy) depends upon the strength of ligands.

Since, the order of splitting tendency of different ligands is as



Hence, the order of CFSE of different complexes is



Since, Energy  $\propto \frac{1}{\text{wavelength } (\lambda)}$

$\therefore$  The order of absorption of wavelength is



### Limitations of CFT

The crystal field theory can explain the spectra of the metal ions and complexes on the assumption that these arise from the transition of electrons from lower energy  $d$ -orbitals to higher energy  $d$ -orbitals. However, the position and intensities of spectral bands calculated on the basis of crystal field theory do not always coincide with those determined experimentally.

Apart from this, a pure electrostatic interaction between central metal ion and ligand fails to explain the relative positions of ligands in spectrochemical series. Along with this there is clear evidence that covalent bonding too makes a significant contribution towards the metal ligand bonding.

In the light of above written facts the crystal field theory was modified so as to include the contribution of covalent bonding in the metal ligand bond and is called **ligand field theory**, which assumes that the extent of covalent character in metal ligand bond is generally low as compared to the extent of the ionic character of the bond that means the conclusions arrived by the crystal field theory are still valid to a larger extent.

### 9.7 Stability of Complexes

The stability of a complex in solution is in fact the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association,

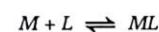
## 1014 JEE Main Chemistry

quantitatively expresses the stability. Thus, if we have a reaction of the type :



then the *larger the stability constant K, the higher the proportion of  $ML_4$  that exists in solution*. Alternatively  $1/K$  values, called the **instability constant**, explain the dissociation of the complex into metal ion and ligands in the solution.

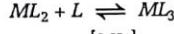
A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex,  $ML_n$  ( $M$  = central metal cation,  $L$  = monodentate ligand and  $n$  = coordination number of metal ion) may be supposed to take place by the following  $n$  consecutive steps.



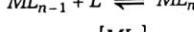
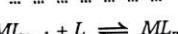
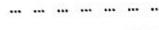
$$K_1 = \frac{[ML]}{[M][L]}$$



$$K_2 = \frac{[ML_2]}{[M][L]}$$



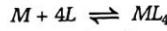
$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$



$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

$K_1, K_2, K_3, \dots, K_n$  are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from  $K_1$  to  $K_n$ .

Alternatively, we can write the **overall stability constant** thus



$$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

The stepwise and overall stability constant are therefore related as follows

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \text{ or more generally,}$$

$$\beta_1 = K_1 \times K_2 \dots \times K_1$$

### Factors Affecting Stability of Complexes

The strength of a complex ion depends upon the following factors

(i) **Higher charge** of the central metal ion i.e., greater ionic potential  $\left( \frac{\text{ionic charge}}{\text{ionic radius}} \right)$  and greater is the stability.

(ii) **Greater base strength** of the ligand, greater will be the stability.

(iii) **Ring formation** (chelation) in structure of the complexes is the chief factor, which **increases** the stability of the complexes in solution.

(iv) If a multidentate ligand happens to be cyclic without any steric effects, a further increase in stability occurs. This is called **macrocyclic effect**.

**Sample Problem 22** Which of the following complexes formed by  $Cu^{2+}$  ions is most stable? [NCERT Exemplar]

$$(a) Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}, \quad \log K = 11.6$$

$$(b) Cu^{2+} + 4CN \rightleftharpoons [Cu(CN)_4]^{2-}, \quad \log K = 27.3$$

$$(c) Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+}, \quad \log K = 15.4$$

$$(d) Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}, \quad \log K = 8.9$$

**Interpret** (b) Stability of complexes depends upon stability constant. Higher the value of  $K$ , more stable is the complex. Since,  $K$  is highest when  $\log K$  is 27.3.

Thus,  $[Cu(CN)_4]^{2-}$  is the most stable complex among the given.

## 9.8 Importance of Coordination Compounds

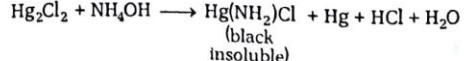
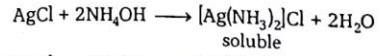
Some important applications of coordination compounds are as follows

### 1. In Qualitative and Quantitative Analysis

(i) Nickel is detected and estimated as its red dimethyl glyoxime complex which is a chelate complex.

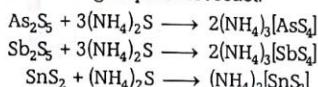
(ii) Mg and Al are estimated as complexes of 8-hydroxyquinoline (oxime).

(iii) The separation of  $Ag^+$  from  $Hg_2^{2+}$  in the first group of analysis is based on the fact that while, silver chloride is soluble in aqueous ammonia,  $Hg_2Cl_2$  forms a black insoluble material.



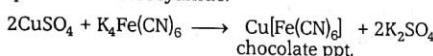
(iv) The separation of IIB group sulphides from IIA group sulphides is based on the fact that sulphides of IIB group form, complex sulphides with yellow

ammonium sulphide which are soluble while, sulphides of IIA group do not react.

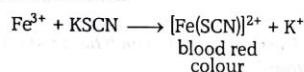


- (v) The detection of  $\text{Cu}^{2+}$  is based on the formation of a blue tetra-ammine copper sulphate complex, which gives a deep blue coloured solution upon addition of  $\text{NH}_3$  to  $\text{Cu}^{2+}$  ions.

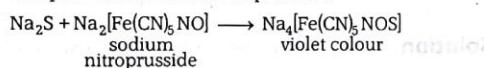
$\text{CuSO}_4 + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   
It also forms a chocolate coloured precipitate with potassium ferrocyanide.



- (vi)  $\text{Fe}^{3+}$  is detected by formation of a blood red coloured complex with KSCN.



- (vii)  $\text{S}^{2-}$  is detected by the formation of a violet-coloured complex with sodium nitroprusside.



- (viii) EDTA is used in the complexometric determination of several metal ions such as  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.

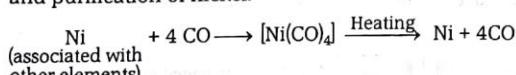
## 2. In the Extraction of Metals

The formation of complex compounds is used in the extraction of some metals e.g., Ag and Au are extracted as follows



It is due to more electropositive nature of Zn as compared to Ag and Au.

**Nickel tetracarbonyl** complex is used for the extraction and purification of nickel.



## 3. In Biological World

Cyclic ligands impart extra stability to coordinate compounds. Thus, Mg in chlorophyll and iron in haemoglobin are stable towards dissociation due to the formation of coordination compounds. Haemoglobin of the blood gets oxygenated through the binding of dioxygen,  $\text{O}_2$  to the ferrous ions in haemoglobin.

## 4. Role of Coordination Compounds in Medicinal Chemistry

(i) The platinum complex  $cis$ -[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (*cis*-platin) is used in the treatment of cancer.

(ii) EDTA complex of calcium is used in the treatment of lead poisoning. Ca-EDTA is a weak complex, when it is administered, calcium in the complex is replaced by the lead present in the body and is eliminated in the urine.

(iii) The excess of copper and iron present in animal system are removed by the chelating ligands *D*-penicillamine and desferroxime *B* via the formation of complexes.

## 5. In Estimation of Hardness of Water

EDTA is a hexadentate ligand and forms complex with various metal ions. This is used in the estimation of hardness of water by a volumetric method. Hardness of water is due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Since, stability constant values of EDTA complex with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are  $10^7$  and  $10^8$  respectively, it helps in selective estimation of different ions.

## 6. In Electroplating of Metals

Coordination compounds are used in **electroplating industry** e.g., gold and silver are electroplated from their coordination compounds, such as  $\text{K}[\text{Ag}(\text{CN})_2]$  or  $\text{K}[\text{Au}(\text{CN})_4]$ .

## 7. As Catalysts

A coordination complex of Ti and Al is used as a catalyst to convert ethylene and propylene into polyethene. Ziegler-Natta catalyst is  $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$  or  $(\text{CH}_3)_3\text{Al}$ .

## 8. In Pigments

Many pigments such as phthalocyanines used in paints are the coordination compounds.

## Check Point 3

- The hexaaqua complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green whereas, the corresponding ammonia complex  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is violet. Explain.
- Explain  $[\text{CoF}_6]^{3-}$  is paramagnetic but  $[\text{Co}(\text{CN})_6]^{3-}$  is diamagnetic.
- Why is ligand field theory also called crystal field theory?
- All the octahedral complexes of  $\text{Ni}^{2+}$  must be outer orbital complexes. Explain, why?

# WORKED OUT

## Examples

**Example 1** Which of the following complexes do not follow EAN rule?

- (a)  $[\text{Fe}(\text{CN})_6]^{4-}$
- (b)  $[\text{Fe}(\text{CN})_6]^{3-}$
- (c)  $\text{Ni}(\text{CO})_4$
- (d)  $[\text{PdCl}_4]^{2-}$

**Solution** (b) According to Sidgwick,

EAN = atomic number of nearest noble gas

In case of  $[\text{Fe}(\text{CN})_6]^{3-}$ ,

$$\begin{aligned}\text{EAN} &= 26 - 3 + 2 \times 6 \\ &= 35\end{aligned}$$

While, the atomic number of nearest noble gas is 36. Thus, it does not follow EAN rule.

**Example 2** An aqueous solution of titanium chloride, when subjected to magnetic measurement, measured zero magnetic moment. The formula of the complex assuming it to be octahedral in aqueous solution is

- (a)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_4$
- (b)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$
- (c)  $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$
- (d)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}$

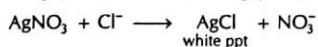
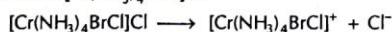
**Solution** (a)  $\text{Ti}_{22} = [\text{Ar}] 3d^2 4s^2$

Since, its magnetic moment is zero, it is present in the form of  $\text{Ti}^{4+}$ . Thus, the formula of the complex is  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_4$  as only in it the oxidation state of Ti is +4.

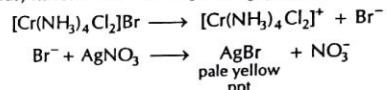
**Example 3** A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms A and B. A reacts with  $\text{AgNO}_3$  producing a white precipitate which was soluble in dilute ammonia solution. B reacts with  $\text{AgNO}_3$  producing a pale yellow precipitate soluble in concentrated ammonia solution. The formulas of A and B are respectively

- (a)  $[\text{Cr}(\text{NH}_3)_4\text{Br}]\text{Cl}_2$ ;  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$
- (b)  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$ ;  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br} \cdot \text{NH}_3$
- (c)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ ;  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$
- (d)  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$ ;  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$

**Solution** (d) Since, the compound A gives white precipitate with  $\text{AgNO}_3$ , which is soluble in dilute ammonia solution, it contains at least one Cl atom outside the coordination sphere. Thus, its formula is  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$ .



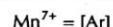
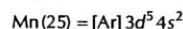
Similarly, compound B gives a yellow precipitate which is soluble in concentrated ammonia solution, it contains a Br atom outside the sphere. Thus, its formula must be  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ .



**Example 4** The complex ion which has no d-electrons in the central metal atom is

- (a)  $[\text{MnO}_4]^-$
- (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (c)  $[\text{Fe}(\text{CN})_6]^{3-}$
- (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

**Solution** (a) In  $[\text{MnO}_4]^-$ , the oxidation state of Mn is +7.

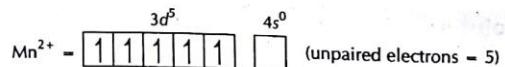


Thus, in  $[\text{MnO}_4]^-$  no d-electron is present.

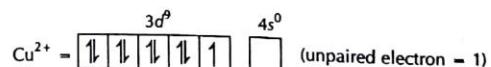
**Example 5** Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by

- (a)  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$
- (b)  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- (c)  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
- (d)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

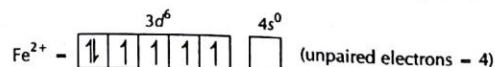
**Solution** (d) In  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , Mn is present as  $\text{Mn}^{2+}$ .



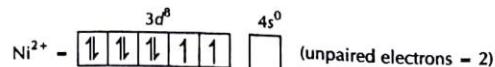
In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Cu is present as  $\text{Cu}^{2+}$ .



In  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , Fe is present as  $\text{Fe}^{2+}$



In  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , Ni is present as  $\text{Ni}^{2+}$



Since, paramagnetic character  $\propto$  unpaired electrons.

Thus,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has the lowest degree of paramagnetism among the given at 298 K.

**Example 6** Which of the following compounds has same oxidation state of the central metal atom in the cationic and anionic part?

- (a)  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$
- (b)  $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$
- (c)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$
- (d)  $\text{K}_4[\text{Ni}(\text{CN})_6]$

**Solution** (b)  $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$

Let the oxidation state of Pt is x.

$$x + 0 \times 4 + x + (-1) \times 4 = 0$$

$$2x = 4$$

$$x = +2$$

Thus, it is the complex in which the central metals atom in cationic and anionic parts have same oxidation state.

**Example 7** The most stable ion is

- (a)  $[\text{Fe}(\text{OH})_5]^{3-}$
- (b)  $[\text{FeCl}_6]^{3-}$
- (c)  $[\text{Fe}(\text{CN})_6]^{3-}$
- (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

**Solution** (c) Stability of complex increases with increase in charge on the central metal ion and with increase in basic strength of ligand.

In  $[\text{Fe}(\text{CN})_6]^{3-}$ , oxidation state of Fe is +3 and basicity of  $\text{CN}^-$  is higher than that of  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{H}_2\text{O}$ . Thus,  $[\text{Fe}(\text{CN})_6]^{3-}$  is the most stable ion among the given.

**Example 8** The pair in which both species have same magnetic moment (spin only value) is

- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, [\text{CoCl}_4]^{2-}$
- (b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- (c)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}, [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
- (d)  $[\text{CoCl}_4]^{2-}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

**Solution** (b) Species having the same number of unpaired electrons, have same magnetic moment because magnetic moment is related with number of unpaired electrons (n) as,  $\mu = \sqrt{n(n+2)}$

$$\text{Cr}^{2+} = [\text{Ar}]3d^4 \quad (4 \text{ unpaired electrons})$$

$$\text{Co}^{2+} = [\text{Ar}]3d^7 \quad (3 \text{ unpaired electrons})$$

$$\text{Mn}^{2+} = [\text{Ar}]3d^5 \quad (5 \text{ unpaired electrons})$$

$$\text{Fe}^{2+} = [\text{Ar}]3d^6 \quad (4 \text{ unpaired electrons})$$

Thus,  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  have same magnetic moment.

**Example 9** Identify the complexes which is expected to be coloured.

- (a)  $[\text{Ti}(\text{NO}_3)_4]$
- (b)  $[\text{Cu}(\text{NCCH}_3)]^+\text{BF}_4^-$
- (c)  $[\text{Fe}(\text{CN})_6]^{4-}$
- (d)  $\text{K}_3[\text{VF}_6]$

**Solution** (d) (a) In  $[\text{Ti}(\text{NO}_3)_4]$ , ON of Ti is +4.

Hence, in  $\text{Ti}(\text{IV})$  ( $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ ) incomplete d-orbital is not present, so it is colourless.

- (b) In  $[\text{Cu}(\text{NCCH}_3)]^+\text{BF}_4^-$ , ON of Cu is +1.  
Hence, in  $\text{Cu}(\text{I})$  ( $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$ ) incomplete d-orbital is not present, so it is also colourless.
- (c) In  $[\text{Fe}(\text{CN})_6]^{4-}$ , ON of Fe is +2.  
Hence,  $\text{Fe}(\text{II})$  ( $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$ ) But  $\text{CN}^-$ , being a strong field ligand, causes pairing, thus no unpaired electron is present in d-orbital. Hence, it is also colourless.
- (d) In  $\text{K}_3[\text{VF}_6]$ , ON of V is +3.  
Hence,  $\text{V}(\text{III})$  ( $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$ ) incomplete d-orbitals are present, so it is coloured.

**Example 10** A solution made by dissolving 0.875 g of compound  $\text{Co}(\text{NH}_3)_4\text{Cl}_2$  in 25 g of water freezes at  $-0.56^\circ\text{C}$ . The structural formula of the complex, if cryoscopic constant of water is  $1.86 \text{ K kg mol}^{-1}$ , is

- (a)  $[\text{Co}(\text{NH}_3)_4]\text{Cl}_3$
- (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2$
- (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
- (d)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_2]\text{NH}_3$

$$\text{Solution} \quad (c) -\Delta T_f = 0.56 = i \times 1.86 \times \frac{0.875}{233.5} \times \frac{1000}{25}$$

$$[\because \Delta T_f = i k_f \cdot m]$$

$$\therefore i = 2$$

Hence, the formula of the complex ion is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .

[For details see chapter 2 'solutions']

# Start Practice for JEE Main

## Round I (Topically Divided Problems)

### General Terms Related to Coordination Compounds

1. Potassium ferrocyanide is a
  - (a) complex salt
  - (b) double salt
  - (c) normal salt
  - (d) mixed salt
2. In the compound lithium tetrahydroaluminate, the ligand is
  - (a) H
  - (b)  $H^+$
  - (c)  $H^-$
  - (d) None of these
3. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? [NCERT Exemplar]
  - (a) Thiosulphato
  - (b) Oxalato
  - (c) Glycinato
  - (d) Ethane-1,2-diamine
4. Which of the following species is not excepted to be a ligand? [NCERT Exemplar]
  - (a) NO
  - (b)  $NH_4^+$
  - (c)  $NH_2CH_2CH_2NH_2$
  - (d) CO
5. The oxidation number of cobalt in  $K[Co(CO)_4]$  is [NCERT]
  - (a) +1
  - (b) +3
  - (c) -1
  - (d) -3
6. The coordination number of Pt in  $[Pt(NH_3)_4Cl_2]^{2+}$  ion is
  - (a) 2
  - (b) 4
  - (c) 6
  - (d) 8
7. EDTA has coordination number
  - (a) 3
  - (b) 4
  - (c) 5
  - (d) 6
8. The effective atomic number of cobalt in the complex  $[Co(NH_3)_6]^{3+}$  is
  - (a) 36
  - (b) 24
  - (c) 33
  - (d) 30
9. The pair of the compounds in which both the metals are in the higher possible oxidation state is
  - (a)  $CrO_2Cl_2$ ,  $MnO_4^-$
  - (b)  $[Co(CN)_6]^{3-}$ ,  $MnO_3$
  - (c)  $TiO_3$ ,  $MnO_2$
  - (d)  $[Fe(CN)_6]^{3-}$ ,  $[Co(CN)_6]^{3-}$
10. Given the molecular formula of the hexa coordinated complexes (A)  $CoCl_3 \cdot 6NH_3$  (B)  $CoCl_3 \cdot 5NH_3$  (C)  $CoCl_3 \cdot 4NH_3$ . If the number of coordinated  $NH_3$  molecules in A, B, and C respectively are 6, 5 and 4, primary valency in (A), (B) and (C) are
  - (a) 0, 1, 2
  - (b) 3, 2, 1
  - (c) 6, 5, 4
  - (d) 3, 3, 3
11. In the complex  $K_2Fe[Fe(CN)_6]$ 
  - (a) the complex is high spin complex
  - (b) both Fe atoms are in the same oxidation state
  - (c) the coordination number of iron is 4
  - (d) both Fe atoms are in different oxidation state
12. Complex salt can be made by the combination of  $[Co^{III}(NH_3)_5Cl]F$  with
  - (a)  $Cl^-$
  - (b)  $2Cl^-$
  - (c)  $PO_4^{3-}$
  - (d)  $2K^+$
13. How many ions are produced, from the complex,  $Co(NH_3)_6Cl_2$  in solution? [NCERT]
  - (a) 6
  - (b) 4
  - (c) 3
  - (d) 2
14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? [NCERT]
  - (a)  $CuCN$
  - (b)  $K_3[Co(CN)_6]$
  - (c)  $K[Co(CN)_4]$
  - (d)  $K_2[Co(CN)_4]$
15. When 1 mole of  $CrCl_3 \cdot 6H_2O$  is treated with excess of  $AgNO_3$ , 3 moles of  $AgCl$  are obtained. The formula of the complex is [NCERT Exemplar]
  - (a)  $[CrCl_3(H_2O)_3] \cdot 3H_2O$
  - (b)  $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
  - (c)  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
  - (d)  $[Cr(H_2O)_6]Cl_3$

16. Which of the following ions forms most stable complex compound?  
 (a)  $\text{Fe}^{3+}$                                       (b)  $\text{Mn}^{2+}$   
 (c)  $\text{Ni}^{2+}$                                       (d)  $\text{Cu}^{2+}$
17. Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solution but not in acidic solution. What is the reason for it?  
 (a) In acidic solutions, hydration protects copper ions.  
 (b) In alkaline solution, insoluble  $\text{Cu}(\text{OH})_2$  is precipitated.  
 (c) Copper hydroxide is an amphoteric substance  
 (d) In acidic solutions, protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available
18. Amongst the following, the most stable complex is [NCERT]  
 (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$                                       (b)  $[\text{Fe}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$                                       (d)  $[\text{FeCl}_6]^{3-}$

### Nomenclature of Coordination Compounds

19. The correct IUPAC name of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is [NCERT Exemplar]  
 (a) diamminedichloroplatinum (II)  
 (b) diamminedichloroplatinum (IV)  
 (c) diamminedichloroplatinum (0)  
 (d) dichlorodiammineplatinum (IV)
20. IUPAC name of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$  is [NCERT Exemplar]  
 (a) platinum diaminechloronitrite  
 (b) chloronitrito-N-ammineplatinum (II)  
 (c) diamminechloridonitrito-N-platinum (II)  
 (d) diamminechloronitrito-N-platinum (II)
21. The IUPAC name of the coordination compound  $\text{K}_2[\text{Zn}(\text{OH})_4]$  is  
 (a) potassium tetrahydroxo zinc (II)  
 (b) dipotassium tetrahydroxo zinc (II)  
 (c) potassium tetrahydroxo zincate (II)  
 (d) potassium tetrahydroxo zincate (III)
22. Pick the correct name of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .  
 (a) chloropentamminecobalt (III) chloride  
 (b) chloropentamminecobalt (III)  
 (c) chloropentamminecobalt (II) chloride  
 (d) pentamminechloridocobalt (III) chloride
23. The IUPAC name of  $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O})_2(\text{NH}_3)]$  is  
 (a) potassium amminedicyanodioxoperoxochromate (VI)  
 (b) potassium amminecyanoperoxodioxochromatic (IV)  
 (c) potassium amminecyanoperoxodioxochromium (IV)  
 (d) potassium amminecyanoperoxodioxochromium (IV)
24. The correct name of  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$  is  
 (a) tetrachloroplatinum (II) dichlorotetrammine platinate  
 (b) dichlorodotetrammineplatinum (IV) tetrachlorido platinate (II)  
 (c) tetraminedichloroplatinum (IV) tetrachlorido platinate (II)  
 (d) tetrachloroplatinum (II) tetrammineplatinate (IV)
25. The IUPAC name of  $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$  is  
 (a) tetrachloronickel (II) tetraamminenickel (II)  
 (b) tetraamminenickel (II) tetrachloronickel (II)  
 (c) tetraamminenickel (II) tetrachloronickelate (II)  
 (d) tetrachloronickel (II) tetraamminenickel (0)

### Isomerism in Coordination Compounds

26. The compounds  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$  represent [NCERT Exemplar]  
 (a) linkage isomerism  
 (b) ionisation isomerism  
 (c) coordination isomerism  
 (d) no isomerism
27. The complexes  $[\text{Co}(\text{NH}_3)_6]\text{[Cr}(\text{C}_2\text{O}_4)_3]$  and  $[\text{Cr}(\text{NH}_3)_6]\text{[Co}(\text{C}_2\text{O}_4)_3]$  exhibit  
 (a) geometrical isomerism  
 (b) ionisation energy  
 (c) coordination isomerism  
 (d) linkage isomerism
28. Which of the following cannot show linkage isomerism?  
 (a)  $\text{NO}_2^-$     (b)  $\text{NH}_3$   
 (c)  $\text{CN}^-$     (d)  $\text{SCN}^-$
29. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$  and  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$  are [NCERT Exemplar]  
 (a) linkage isomers                                      (b) coordination isomers  
 (c) ionisation isomers                                      (d) geometrical isomers
30. What kind of isomerism exists between  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (greyish-green)? [NCERT Exemplar]  
 (a) Linkage isomerism                                      (b) Solvate isomerism  
 (c) Ionisation isomerism                                      (d) Coordination isomerism
31. Optical isomerism is shown by octahedral complexes  
 (a) having all monodentate ligands  
 (b) having all the three bidentate ligands  
 (c) having two *trans* bidentate ligands  
 (d) having two *trans* monodentate ligands

## 1020 JEE Main Chemistry

- 32.** Which of the following will exhibit optical isomerism?  
 (a)  $[\text{Cr}(\text{en})(\text{H}_2\text{O})_4]^{3+}$       (b)  $[\text{Cr}(\text{en})_3]^{3+}$   
 (c)  $\text{trans-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$       (d)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- 33.** Which one of the following is expected to exhibit optical isomerism [en = ethylenediamine]?  
 (a)  $\text{Trans-}[\text{Co}(\text{en})_2\text{Cl}_2]$   
 (b)  $\text{Cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$   
 (c)  $\text{Cis-}[\text{Co}(\text{en})_2\text{Cl}_2]$   
 (d)  $\text{Trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- 34.** Indicate the complex ion which shows geometrical isomerism. [NCERT Exemplar]  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$       (b)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]$   
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (d)  $[\text{Co}(\text{CN})_5(\text{NCl})]^{3-}$
- 35.** The total number of possible isomers for the complex compound  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$   
 (a) 6      (b) 5      (c) 4      (d) 3
- 36.** For square planar complex of platinum (II),  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]^{2+}$ , how many isomeric forms are possible?  
 (a) Two      (b) Three  
 (c) Four      (d) Six
- 37.** Among the geometrical isomers of  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$  how many will exhibit optical isomers? [NCERT]  
 (a) 0      (b) 1      (c) 2      (d) All
- 38.** A complex of the type  $[\text{M}(\text{AA})_2\text{X}_2]^{n+}$  is known to be optically active. What does this indicate about the structure of the complex? [NCERT Exemplar]  
 (a) It has an octahedral geometry  
 (b) It is a tetrahedral complex  
 (c) It is a *trans* complex  
 (d) None of the above
- Bonding in Coordination Compounds**
- 39.** Among the following ions, which one has the highest unpaired electrons?  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$       (b)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$       (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- 40.**  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  is  
 (a) pyramidal      (b) pentagonal  
 (c) tetrahedral      (d) square planar
- 41.** Which one is an example of octahedral complex?  
 (a)  $\text{Cu}(\text{NH}_3)_4^{2+}$       (b)  $\text{FeF}_6^{3-}$   
 (c)  $\text{Zn}(\text{NH}_3)_4^{2+}$       (d)  $\text{Ni}(\text{CN})_4^{2-}$
- 42.** The species having tetrahedral shape is  
 (a)  $[\text{NiCl}_4]^{2-}$       (b)  $[\text{Ni}(\text{CN})_4]^{2-}$   
 (c)  $[\text{PdCl}_4]^{2-}$       (d)  $[\text{Pd}(\text{CN})_4]^{2-}$
- 43.** The geometry of  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  are  
 (a) square planar and tetrahedral respectively  
 (b) Both tetrahedral  
 (c) tetrahedral and square planar respectively  
 (d) Both square planar
- 44.** What is the magnetic moment of  $\text{K}_3[\text{FeF}_6]$ ?  
 (a) 3.87 BM      (b) 4.89 BM  
 (c) 5.91 BM      (d) 6.92 BM
- 45.** The value of 'spin only' magnetic moment for one of the following configuration is 2.84 BM. The correct one is  
 (a)  $d^4$  (in weak ligand field)  
 (b)  $d^4$  (in strong ligand field)  
 (c)  $d^3$  (in weak as well as in strong field)  
 (d)  $d^5$  (in strong ligand field)
- 46.** Why do compounds having similar geometry have different magnetic moment? [NCERT Exemplar]  
 (a) Due to different reactivity  
 (b) Due to their labile nature  
 (c) Due to the presence of weak and strong field ligands  
 (d) None of the above
- 47.**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour while  $\text{CuSO}_4$  is colourless why? [NCERT Exemplar]  
 (a) Because  $\text{H}_2\text{O}$  is a strong field ligand than  $\text{SO}_4^{2-}$   
 (b) Because  $\text{SO}_4^{2-}$  is a strong field ligand  
 (c) Because  $\text{CuSO}_4$  is not a complex  
 (d) Because no *d-d* transition is possible in  $\text{CuSO}_4$
- 48.** Among  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{Cl})_6]^{3-}$  species, the hybridisation state of the Fe atom are, respectively.  
 (a)  $d^2sp^3$ ,  $d^2sp^3$ ,  $sp^3d^2$   
 (b)  $sp^3d^2$ ,  $d^2sp^3$ ,  $d^2sp^3$   
 (c)  $sp^3d^2$ ,  $d^2sp^3$ ,  $sp^3d^2$   
 (d) None of the above
- 49.** Amongst  $\text{Ni}(\text{CO})_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$   
 (a)  $\text{Ni}(\text{CO})_4$  is diamagnetic,  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic  
 (b)  $\text{Ni}(\text{CO})_4$  and  $[\text{NiCl}_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic  
 (c)  $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{NiCl}_4]^{2-}$  is paramagnetic  
 (d)  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $\text{Ni}(\text{CO})_4$  is paramagnetic

50.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. This is because of  
 (a) difference in the nature of ligands  
 (b) the presence of unpaired electrons  
 (c) the  $d-d$  transition  
 (d) All of the above [NCERT]
51. On the basis of VBT, find which is an inner orbital complex with 0 magnetic moment? [NCERT Exemplar]  
 (a)  $[\text{Mn}(\text{CN})_6]^{3-}$  (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{FeCl}_6]^{4-}$
52. The low spin tetrahedral complexes are not formed because  
 (a)  $\Delta_t > P$  (b)  $\Delta_t < P$   
 (c)  $\Delta_t \geq P$  (d)  $\Delta_t > \Delta_0$
53. The correct order for the wavelengths of absorption in the visible region for the following is  
 I.  $[\text{Ni}(\text{NO}_2)_6]^{4-}$  II.  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  III.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  [NCERT]  
 (a) I > II > III (b) II > I > III  
 (c) III > II > I (d) III > I > II
54. Calculate the overall complex dissociation equilibrium constant for the  $\text{Cu}(\text{NH}_3)_4^{2+}$  ions, given that  $\beta_4$  for this complex is  $2.1 \times 10^{13}$ .  
 (a)  $8.27 \times 10^{-13}$  (b)  $4.7 \times 10^{-14}$   
 (c)  $2.39 \times 10^{-7}$  (d)  $1.83 \times 10^{14}$
55. Which of the following pair is not correctly matched?  
 (a) Absorption peak for  $[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+} = 21680 \text{ cm}^{-1}$   
 (b) Effective atomic no. of Pt in  $[\text{PtCl}_6]^{2-} = 84$
- (c) Crystal field stabilisation energy of  $d^2$  in weak ligand field  $= (-)0.8 \Delta_o$   
 (d) Example of weak ligand field for  $d^5$  configuration  $= [\text{Mn}^{\text{II}}\text{F}_6]^{4-}$

### Applications of Coordination Compounds

56. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?  
 (a) Haemoglobin is the red pigment of blood and contains iron  
 (b) Cyanocobalamin is  $\text{B}_{12}$  and contains cobalt  
 (c) Chlorophylls are green pigments in plants and contains calcium  
 (d) Carboxypeptidase-A, an enzyme, contains zinc
57. The complex used as an anticancer agent is  
 (a) *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$  (b)  $\text{Na}_2\text{CO}_3$   
 (c) *trans*- $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (d) *cis*- $\text{K}_2[\text{PtCl}_2\text{Br}_2]$
58. Dimethyl glyoxime gives a red precipitate with  $\text{Ni}^{2+}$  which is used for its detection. To get this precipitate readily, the best pH range is  
 (a)  $< 1$  (b) 3–4 (c) 9–11 (d) 2–3
59. When EDTA solution is added to  $\text{Mg}^{2+}$  ion solution, then which of the following statements is not true?  
 (a) Four coordinate sites of  $\text{Mg}^{2+}$  are occupied by EDTA and remaining two sites are occupied by water molecules  
 (b) All six coordinate sites of  $\text{Mg}^{2+}$  are occupied  
 (c) pH of the solution is decreased  
 (d) Colourless  $[\text{Mg-EDTA}]^{4-}$  chelate is formed

### Round II (Mixed Bag)

#### Only One Correct Option

1. The coordination number and oxidation state of Cr in  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  are respectively  
 (a) +6 and +3 (b) 3 and 0  
 (c) 4 and +2 (d) 3 and +3
2. The oxidation state of Fe in the brown ring complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{\text{SO}_4}$  is  
 (a) +3 (b) 0  
 (c) +2 (d) +1
3. Which of the following statements is correct?  
 (a) In  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , the ligand has satisfied both primary and secondary valencies of ferric ion.
- (b) In  $[\text{Cu}(\text{NH}_3)_4]^{\text{SO}_4}$ , the ligand has satisfied only the secondary valency of copper.  
 (c) In  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , the ligand has satisfied only the secondary valency of ferric ion.  
 (d) Both (b) and (c)
4. According to IUPAC nomenclature sodium nitroprusside is named as  
 (a) sodium pentacyanonitrosylferrate (II)  
 (b) sodium pentacyanonitrosylferrate (III)  
 (c) sodium nitroferricyanide  
 (d) sodium nitroferrocyanide

## 1022 JEE Main Chemistry

5. I.  $K_4[Fe(CN)_6]$       II.  $K_3[Cr(CN)_6]$   
 III.  $K_3[Co(CN)_6]$       IV.  $K_2[Ni(CN)_6]$

Select the complexes which are diamagnetic.

- (a) I, II and III      (b) II, III and IV  
 (c) I, III and IV      (d) I, II and IV

6. In spectrochemical series chlorine is above than water, i.e., Cl > H<sub>2</sub>O, this is due to  
 (a) good  $\pi$ -acceptor properties of Cl  
 (b) strong  $\sigma$ -donor and good  $\pi$ -acceptor properties of Cl  
 (c) good  $\pi$ -donor properties of Cl  
 (d) larger size of Cl than H<sub>2</sub>O

7. Mixture X = 0.02 mole of  $[Co(NH_3)_5SO_4]Br$  and 0.02 mole of  $[Co(NH_3)_5Br]SO_4$  was prepared in 2 L of solution

1 L of mixture X + excess AgNO<sub>3</sub> → Y

1 L of mixture X + excess BaCl<sub>2</sub> → Z

Number of moles of Y and Z are

- (a) 0.01, 0.01      (b) 0.01, 0.02  
 (c) 0.02, 0.01      (d) 0.02, 0.02

8. The hybridisation of central metal ion and shape of Wilkinson's catalyst is  
 (a)  $sp^3d$ , trigonal bipyramidal  
 (b)  $sp^3$ , tetrahedral  
 (c)  $dsp^2$ , square planar  
 (d)  $d^2sp^2$ , octahedral

9. An aqueous solution of CoCl<sub>2</sub> on addition of excess of concentrated HCl turns blue due to formation of  
 (a)  $[CoCl_4]^{2-}$       (b)  $[Co(H_2O)_2Cl_4]^{2-}$   
 (c)  $[Co(H_2O)_2Cl_4]^{2-}$       (d)  $[Co(H_2O)_4Cl_2]$

10. Which one of the following complexes is an outer orbital complex?  
 (a)  $[Fe(CN)_6]^{4-}$       (b)  $[Co(NH_3)_6]^{3+}$   
 (c)  $[Ni(NH_3)_6]^{2+}$       (d) None of these

11. Which one of the following has highest number of isomers?  
 (a)  $[Co(NH_3)_5Cl]^{2+}$   
 (b)  $[Co(en)_2Cl_2]^{+}$   
 (c)  $[Ru(NH_3)_4Cl^-]$   
 (d)  $[In(Ph_3)_2H(CO)]^{2+}$

12. In which of the following pairs both the complex show optical isomerism?  
 (a) *Cis*- $[Cr(C_2O_4)_2Cl_2]^{3-}$ ; *cis*- $[Co(NH_3)_4Cl_2]$   
 (b)  $[PtCl(dien)]Cl$ ,  $[NiCl_2Br_2]^{2-}$   
 (c)  $[Co(NO_3)_3(NH_3)_3]$ , *cis*- $[Pt(en)_2Cl_2]$   
 (d)  $[Co(en)_3]Cl_3$ , *cis*- $[Co(en)_2Cl_2]Cl$

13. Match the complex ions given in Column I with the colours given in Column II and assign the correct code :  
 [INCERT Exemplar]

	Column I (Complex ion)		Column II (Colour)
A.	$[Co(NH_3)_6]^{3+}$	1.	Violet
B.	$[Ti(H_2O)_6]^{3+}$	2.	Green
C.	$[Ni(H_2O)_6]^{2+}$	3.	Pale blue
D.	$[Ni(H_2O)_4(en)]^{2+}(aq)$	4.	Yellowish orange
		5.	Blue

Codes

- | A     | B | C | D | A   | B | C | D |
|-------|---|---|---|-----|---|---|---|
| (a) 1 | 2 | 4 | 5 | (b) | 4 | 3 | 2 |
| (c) 3 | 2 | 4 | 1 | (d) | 4 | 1 | 2 |

14. Match the complex species given in Column I with the possible isomerism given in Column II and assign the correct code :  
 [INCERT Exemplar]

	Column I (Complex species)		Column II (Isomerism)
A.	$[Co(NH_3)_4Cl_2]^{+}$	1.	Optical
B.	<i>cis</i> - $[Co(en)_2Cl_2]^{+}$	2.	Ionisation
C.	$[Co(NH_3)_5(NO_2)]Cl_2$	3.	Coordination
D.	$[Co(NH_3)_6][Cr(CN)_6]$	4.	Geometrical
		5.	Linkage

Codes

- | A     | B | C | D | A   | B | C | D |
|-------|---|---|---|-----|---|---|---|
| (a) 1 | 2 | 4 | 5 | (b) | 4 | 3 | 2 |
| (c) 4 | 1 | 5 | 3 | (d) | 4 | 1 | 3 |

15. Match the complex ions given in Column I with the hybridisation number of unpaired electrons given in Column II and assign the correct code :  
 [INCERT Exemplar]

	Column I (Complex ion)		Column II (Hybridisation and number of unpaired electrons)
A.	$[Cr(H_2O)_6]^{3+}$	1.	$dsp^2$ , 1
B.	$[Co(CN)_4]^{2-}$	2.	$sp^3d^2$ , 5
C.	$[Ni(NH_3)_6]^{2+}$	3.	$d^2sp^3$ , 3
D.	$[MnF_6]^{4-}$	4.	$sp^3$ , 4
		5.	$sp^3d^2$ , 2

Codes

- | A     | B | C | D | A   | B | C | D |
|-------|---|---|---|-----|---|---|---|
| (a) 3 | 1 | 5 | 2 | (b) | 4 | 3 | 2 |
| (c) 3 | 2 | 4 | 1 | (d) | 4 | 1 | 3 |

- 16.** Match the coordination compounds given in Column I with the central metal atoms given in Column II and assign the correct code : [NCERT Exemplar]

	Column I (Coordination compound)	Column II (Central metal atom)
A.	Chlorophyll	1. Rhodium
B.	Blood pigment	2. Cobalt
C.	Wilkinson catalyst	3. Calcium
D.	Vitamin B <sub>12</sub>	4. Iron
		5. Magnesium

**Codes**

	A	B	C	D
(a)	5	4	1	2
(b)	3	4	5	1
(c)	4	3	2	1
(d)	3	4	1	2

**More than One Correct Option**

- 17.** Which of the following complexes are heteroleptic? [NCERT Exemplar]

- (a)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$       (b)  $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]^+$   
 (c)  $[\text{Mn}(\text{CN})_6]^{4-}$       (d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$

- 18.** In which of the following, the chemical formula and the name correctly matched?

- (a)  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  — Potassium trioxalatochromate (III)  
 (b)  $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$  — Potassium amminepentachlorido platinate (IV)  
 (c)  $\text{Na}_2[\text{Ni}(\text{EDTA})]$  — Sodium ethylenediaminetetra acetatonickel (I)  
 (d)  $[\text{Ag}(\text{CN})_2]^-$  — Dicyanoargentate (I) ion

- 19.** Which of the following statements is/are false?

- (a)  $[\text{Ni}(\text{CO})_4]$  is high spin complex  
 (b) Weak ligands like  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{OH}^-$  usually form low spin complexes  
 (c)  $[\text{FeF}_6]^{3-}$  is a high spin complex  
 (d) Strong ligand like  $\text{CN}^-$  and  $\text{NO}_2^-$ , generally form high spin complexes

- 20.** An aqueous pink solution of cobalt (II) chloride changes to deep blue on addition of excess of HCl. This is because ..... [NCERT Exemplar]

- (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is transformed into  $[\text{CoCl}_6]^{4-}$   
 (b)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is transformed into  $[\text{CoCl}_4]^{2-}$   
 (c) tetrahedral complexes have smaller crystal field splitting than octahedral complexes  
 (d) tetrahedral complexes have larger crystal field splitting than octahedral complex

- 21.** Identify the optically active compounds from the following [NCERT Exemplar]

- (a)  $[\text{Co}(\text{en})_3]^{3+}$   
 (b)  $\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (c)  $\text{cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (d)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]$

**Assertion and Reason**

**Directions** (Q. Nos. 22 to 26) Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below :

- (a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.  
 (b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.  
 (c) Statement I is true; Statement II is false.  
 (d) Statement I is false; Statement II is true.

- 22.** **Statement I** Ions with more than five  $3d$  electrons have usually slightly larger magnetic moment than calculated on the basis of  $\mu = \sqrt{n(n+2)}$ .

**Statement II** The maximum number of unpaired  $d$ -electrons is five as in  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  and so,  $\mu = 5.92$  for 5 unpaired electrons.

- 23.** **Statement I** Toxic metal ions are removed by the chelating ligands. [NCERT Exemplar]

**Statement II** Chelate complexes tend to be more stable.

- 24.** **Statement I**  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$  and  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$  are reducing in nature. [NCERT Exemplar]

**Statement II** Unpaired electrons are present in their  $d$ -orbitals.

- 25.** **Statement I** Complexes of  $\text{MX}_6$  and  $\text{MX}_5\text{L}$  type ( $X$  and  $L$  are unidentate) do not show geometrical isomerism. [NCERT Exemplar]

**Statement II** Geometrical isomerism is not shown by complexes of coordination number 6.

- 26.** **Statement I**  $d-d$  transition is not possible in  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ .

**Statement II**  $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless.

### Comprehension Based Questions

**Directions** (Q. Nos. 27 to 29)  $\text{CoSO}_4\text{Cl}\cdot 5\text{NH}_3$  exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with  $\text{AgNO}_3$  to give white precipitate, but does not react with  $\text{BaCl}_2$ . Isomer 'B' gives white precipitate with  $\text{BaCl}_2$  but does not react with  $\text{AgNO}_3$ . Answer the following questions. [NCERT Exemplar]

27. Write the structural formulae of A and B respectively
  - (a)  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$
  - (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ ,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$
  - (c)  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$
  - (d)  $[\text{CoClSO}_4(\text{NH}_3)_3](\text{NH}_3)_2$ ,  $[\text{CoSO}_4(\text{NH}_4)_4]\text{NH}_3 \cdot \text{Cl}$
28. Name the type of isomerism involved.
  - (a) Solvated
  - (b) Coordination
  - (c) Ionisation
  - (d) Geometrical
29. Give the IUPAC name of 'B'.
  - (a) Pentaamminesulphatocobalt (III) chloride
  - (b) Pentaamminechloridocobalt (III) sulphate
  - (c) Pentaamminesulphatocobalt (II) chloride
  - (d) tetraamminesulphatecobalt (III) ammonium chloride

**Directions** (Q. Nos. 30 to 32) Splitting energy ( $\Delta_o$ ) can usually be measured from the absorption spectra of the complex ions. In simple cases when light is absorbed by a complex ion, an electron in one of the lower energy orbitals is excited to one of the higher energy orbital. The energy corresponding to the frequency of absorbed light is equal to  $\Delta_o$ .

$\Delta_o$ . If value of  $\Delta_o$  for the complex is in visible region, the complex is coloured and the value of  $\Delta_o$  lies in ultraviolet or infrared region, the complex is colourless. For octahedral complexes, the crystal field stabilisation energy is given by  $\text{CFSE} = [-0.4t_{2g}N + 0.6e_g N']\Delta_o$ , where  $N$  and  $N'$  are number of electrons in  $t_{2g}$  and  $e_g$  orbitals respectively.

30. Among the following pairs of complexes, in which case the  $\Delta_o$  value is higher for the first one?
  - (a)  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - (b)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
  - (c)  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
  - (d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{CN})_6]^{3-}$
31. Which of the following statements is correct?
  - (a) Zinc (II) ion has a zero CFSE for any geometry
  - (b) A solution of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  appear colourless in dil solutions
  - (c) A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green as the value of  $\Delta$  for the  $\text{H}_2\text{O}$  complex is in the visible region
  - (d) All of the above
32. In which of the following complex ion, the metal ion will have  $t_{2g}^6 e_g^0$  configuration according to CFT?
  - (a)  $[\text{Fe}(\text{CN})_6]^{3-}$
  - (b)  $[\text{FeF}_6]^{3-}$
  - (c)  $[\text{Fe}(\text{CN})_6]^{4-}$
  - (d) None of these

### Previous Years' Questions

33. Which among the following will be named as dibromidobis (ethylenediamine) chromium (III) bromide? [AIEEE 2012]
  - (a)  $[\text{Cr}(\text{en})_3]\text{Br}_3$
  - (b)  $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$
  - (c)  $[\text{Cr}(\text{en})\text{Br}_4]^-$
  - (d)  $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$
34. Which of the following facts about the complex  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is wrong? [AIEEE 2011]
  - (a) The complex involves  $d^2sp^3$  hybridisation and is octahedral in shape
  - (b) The complex is paramagnetic
  - (c) The complex is an outer orbital complex
  - (d) The complex gives white precipitate with silver nitrate solution
35. The magnetic moment (spin only) of  $[\text{NiCl}_4]^{2-}$  is [AIEEE 2011]
 

(a) 1.82 BM	(b) 5.46 BM
(c) 2.82 BM	(d) 1.41 BM
36. Among the ligands  $\text{NH}_3$ , en,  $\text{CN}^-$  and  $\text{CO}$ , the correct order of their increasing field strength, is [AIEEE 2011]
  - (a)  $\text{CO} < \text{NH}_3 < \text{en} < \text{CN}^-$
  - (b)  $\text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$
  - (c)  $\text{CN}^- < \text{NH}_3 < \text{CO} < \text{en}$
  - (d)  $\text{en} < \text{CN}^- < \text{NH}_3 < \text{CO}$
37. Which one of the following complex ions has geometrical isomers? [AIEEE 2011]
  - (a)  $[\text{Co}(\text{en})_3]^{3+}$
  - (b)  $[\text{Ni}(\text{NH}_3)_5\text{Br}]^+$
  - (c)  $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
  - (d)  $[\text{Cr}(\text{NH}_3)_4(\text{en})]^{3+}$
38. Which of the following has an optical isomer? [AIEEE 2009]
  - (a)  $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$
  - (b)  $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$
  - (c)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$
  - (d)  $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$
39. Which of the following pairs represents linkage isomers? [AIEEE 2009]
  - (a)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
  - (b)  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
  - (c)  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
  - (d)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$

- 40.** The coordination number and the oxidation state of the element 'E' in the complex  $[E(\text{en})_2(\text{C}_2\text{O}_4)_2]\text{NO}_2$  (where (en) is ethylene diamine) are, respectively. [AIEEE 2008]
- (a) 6 and 2      (b) 4 and 2  
 (c) 4 and 3      (d) 6 and 3
- 41.** In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of  $\Delta_o$  be the highest? [AIEEE 2008]
- (a)  $[\text{Co}(\text{CN})_6]^{3-}$       (b)  $[\text{Co}(\text{C}_2\text{O}_4)_6]^{3-}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$       (d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- 42.** Which one of the following has a square planar geometry? [AIEEE 2007]  
 (At. no. Co = 27, Ni = 28, Fe = 26, Pt = 78)
- (a)  $[\text{CoCl}_4]^{2-}$       (b)  $[\text{FeCl}_4]^{2-}$   
 (c)  $[\text{NiCl}_4]^{2-}$       (d)  $[\text{PtCl}_4]^{2-}$
- 43.** The IUPAC name for the complex  $[\text{Co}(\text{NO}_2)_5(\text{NH}_3)\text{Cl}_2]$  is [AIEEE 2006]
- (a) nitrito-N-pentamminecobalt (III) chloride  
 (b) nitrito-N-pentamminecobalt (II) chloride  
 (c) pentaaminenitrito-N-cobalt (II) chloride  
 (d) pentaaminenitrito-N-cobalt (III) chloride
- 44.** Nickel ( $Z = 28$ ) combines with a uninegative monodentate ligand  $X^-$  to form a paramagnetic complex  $[\text{NiX}_4]^{f^-}$ . The number of unpaired electron (s) in the nickel and geometry of this complex ion are, respectively [AIEEE 2006]
- (a) one, tetrahedral      (b) two, tetrahedral  
 (c) one, square planar      (d) two, square planar
- 45.** Which of the following compounds shows optical isomerism? [AIEEE 2005]

- (a)  $[\text{Co}(\text{CN})_6]^{3-}$       (b)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (c)  $[\text{ZnCl}_4]^{2-}$       (d)  $[\text{Cu}(\text{NH}_3)_4]^{f^+}$
- 46.** The coordination number of a central metal atom in a complex is determined by [AIEEE 2004]
- (a) the number of ligands around a metal ion bonded by sigma bonds  
 (b) the number of ligands around a metal ion bonded by pi bonds  
 (c) the number of ligands around a metal ion bonded by sigma and pi bonds both  
 (d) the number of only anionic ligands bonded to the metal ion
- 47.** The correct order of magnetic moments (spin only values in BM) among the following is [AIEEE 2004]  
 (At. no. Mn = 25, Fe = 26, Co = 27)
- (a)  $[\text{MnCl}_4]^{f^-} > [\text{CoCl}_4]^{f^-} > [\text{Fe}(\text{CN})_6]^{f^-}$   
 (b)  $[\text{MnCl}_4]^{f^-} > [\text{Fe}(\text{CN})_6]^{f^-} > [\text{CoCl}_4]^{f^-}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{f^-} > [\text{MnCl}_4]^{f^-} > [\text{CoCl}_4]^{f^-}$   
 (d)  $[\text{Fe}(\text{CN})_6]^{f^-} > [\text{CoCl}_4]^{f^-} > [\text{MnCl}_4]^{f^-}$
- 48.** One mole of the complex compound  $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ , gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  solution to yield two moles of  $\text{AgCl}(s)$ . The structure of the complex is [AIEEE 2003]
- (a)  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$       (b)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$   
 (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$       (d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}] \text{Cl}_2 \cdot \text{NH}_3$
- 49.** A square planar complex is formed by hybridisation of the following atomic orbitals [AIEEE 2002]
- (a)  $s, p_x, p_y, p_z$       (b)  $s, p_x, p_y, p_z, d$   
 (c)  $d, s, p_x, p_y$       (d)  $s, p_x, p_y, p_z, d, d$

## Answers

**Round I**

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (c)  | 3. (a)  | 4. (b)  | 5. (c)  | 6. (c)  | 7. (d)  | 8. (a)  | 9. (a)  | 10. (b) |
| 11. (b) | 12. (a) | 13. (c) | 14. (d) | 15. (d) | 16. (b) | 17. (d) | 18. (c) | 19. (a) | 20. (c) |
| 21. (c) | 22. (d) | 23. (a) | 24. (c) | 25. (c) | 26. (d) | 27. (c) | 28. (b) | 29. (a) | 30. (b) |
| 31. (b) | 32. (b) | 33. (c) | 34. (a) | 35. (a) | 36. (b) | 37. (a) | 38. (d) | 39. (d) | 40. (d) |
| 41. (b) | 42. (a) | 43. (c) | 44. (c) | 45. (b) | 46. (c) | 47. (d) | 48. (c) | 49. (c) | 50. (d) |
| 51. (b) | 52. (b) | 53. (c) | 54. (b) | 55. (b) | 56. (c) | 57. (a) | 58. (c) | 59. (a) |         |

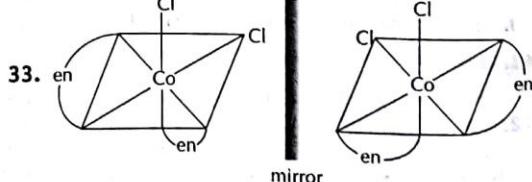
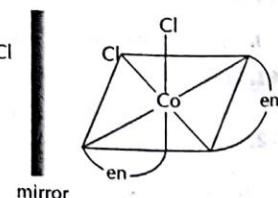
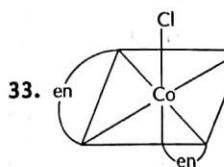
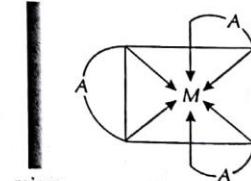
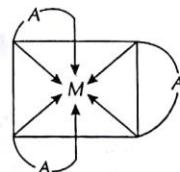
**Round II**

- |           |         |         |         |         |         |           |             |             |           |
|-----------|---------|---------|---------|---------|---------|-----------|-------------|-------------|-----------|
| 1. (a)    | 2. (d)  | 3. (c)  | 4. (b)  | 5. (c)  | 6. (b)  | 7. (a)    | 8. (c)      | 9. (a)      | 10. (c)   |
| 11. (b)   | 12. (d) | 13. (b) | 14. (c) | 15. (a) | 16. (a) | 17. (b,d) | 18. (a,b,d) | 19. (a,b,d) | 20. (b,c) |
| 21. (a,c) | 22. (b) | 23. (a) | 24. (b) | 25. (c) | 26. (c) | 27. (c)   | 28. (c)     | 29. (b)     | 30. (c)   |
| 31. (d)   | 32. (c) | 33. (b) | 34. (c) | 35. (c) | 36. (b) | 37. (c)   | 38. (d)     | 39. (b)     | 40. (d)   |
| 41. (a)   | 42. (d) | 43. (d) | 44. (b) | 45. (b) | 46. (a) | 47. (a)   | 48. (a)     | 49. (c)     |           |

# the Guidance

## Round I

1. In  $K_4Fe(CN)_6$ , the species retains its identity in solid as well as solution state so, it is a complex salt.
2. Lithium tetrahydroaluminate is  $Li[Al(H)_4]$ .
3. Chelating agent coordinates through more than one coordinating sites. Thiosulphate ( $S_2O_3^{2-}$ ) although coordinate through only one coordinating site, so it is not referred as chelating agent.
4. Ligands have tendency to donate its lone pair.  $NH_4^+$  ion have no lone pair so it is unable to behave like a ligand.
5. Oxidation number of Co :  $K[Co(CO)_4]$   
 $x + (4 \times 0) = -1; x = -1$
8. CO ligand has zero oxidation state, that is why  $[Ni(CO)_4]$  is a zero valent metal complex.
10. The complexes can be written as follows  
 $[Co(NH_3)_6]Cl_3, [Co(NH_3)_5 Cl]Cl_2, [Co(NH_3)_4 Cl_4]Cl$   
Hence, number of primary valencies are 3, 2 and 1 respectively.
11. In the complex  $K_2Fe[Fe(CN)_6]$  both the iron atoms are present in the same oxidation state i.e., +2.
12.  $[Co(NH_3)_5 Cl]^{2+} + 2Cl^- \longrightarrow [Co(NH_3)_5 Cl]Cl_2$
13. The complex will dissociate in aqueous solution to produce 3 ions.  
 $Co(NH_3)_6 Cl_2 \xrightarrow{aq} [Co(NH_3)_6]^{2+} + 2Cl^-$
14. When excess of  $KCN(aq)$  is mixed with  $CuSO_4(aq)$ , a complex named potassium tetracyanocuprate (II) is formed. Since,  $CN^-$  ions are strong ligands, the complex is quite stable. It is evident from the stability constant value ( $K = 2.0 \times 10^{27}$ ).  
 $4KCN(aq) + CuSO_4(aq) \longrightarrow K_2[Cu(CN)_4](aq) + K_2SO_4(aq)$   
(soluble)  
 $\downarrow + H_2S$   
No cleavage and no production of  $Cu^{2+}$  ions
15. Formation of 3 mol  $AgCl$  from 1 mole complex suggests the presence of all the three  $Cl^-$  outside the coordination sphere. Thus, the formula of the complex should be  $[Cr(H_2O)_6]Cl_3$ .
16.  $Mn^{2+}$  will have half filled more stable  $d^5$  configuration and without distributing it an outer orbital complex can be formed.
17. In acidic solution, proton coordinates with ammonia to form  $NH_4^+$ .  $NH_4^+$  does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.
18. In all these complexes, Fe is in +3 oxidation state. However, the complex (c) is a chelate because three  $C_2O_4^{2-}$  ions act as the chelating ligands. Thus, the most stable complex is  $[Fe(C_2O_4)_3]^{3-}$ .
19. IUPAC name of  $[Pt(NH_3)_2Cl_2]$  is diamminedi-chloroplatinum (II).
20. IUPAC name of  $[Pt(NH_3)_2Cl(NO_2)]$  is diamminechlorido nitrito-N-platinum (III).
26. The given complexes are not isomers as their composition is not same. (Isomers have same composition but different arrangement and properties.)
27. Coordination isomerism is possible when both positive and negative ions of a salt are complex ions and the two isomers differ in distribution of ligands in the cation and the anion.
29. Complexes having ambidentate ligands like SCN exhibit linkage isomerism.
30. Since the two complexes differ in number of water (solvent) molecules inside and outside the coordination sphere, so they exhibit solvate isomerism.
31. Octahedral complexes containing three bidentate ligands shows optical isomerism. If A is a bidentate ligand then complex of type  $MA_3$  show optical isomerism.



**34.** Octahedral complexes of the type  $[MA_4B_2]^+$  [where A and B are two different monodentate ligands] exhibit geometrical isomerism.

Hence, among the given only  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  exhibit geometrical isomerism.

**35.** 1.  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$

2.  $[\text{Cu}(\text{NH}_3)_3\text{Cl}] \cdot [\text{PtCl}_2(\text{NH}_3)]$

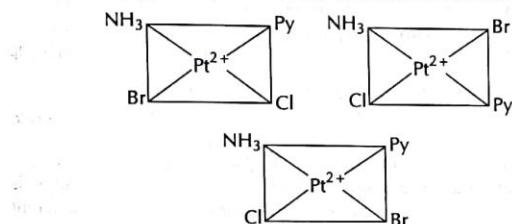
3.  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2] \cdot [\text{PtCl}_2(\text{NH}_3)_2]$  cis

4.  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2] \cdot [\text{PtCl}_2(\text{NH}_3)_2]$  trans

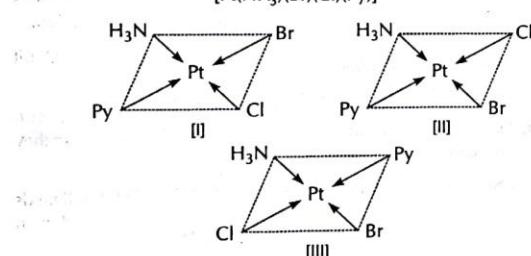
5.  $[\text{Cu}(\text{NH}_3)\text{Cl}_3] \cdot [\text{Pt}(\text{Cl})(\text{NH}_3)_3]$

6.  $[\text{Pt}(\text{NH}_3)_4] \cdot [\text{CuCl}_4]$

**36.**  $[\text{Mabcd}]$  type complexes exist in three isomeric forms.



**37.** Three geometrical isomers are possible for  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$



Optical isomerism is not exhibited by this compound with CN = 4 and square planar geometry, because of the presence of horizontal plane of symmetry.

**38.** An optically active complex of the type  $[\text{M}(AA)_2X_2]^{n+}$  indicates cis-octahedral structure, e.g., cis- $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$  or cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$

**39.**  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has five unpaired electrons.

**40.** Since, hybridisation is  $dsp^2$  so, it is square planar.

**41.** The coordination number in  $[\text{FeF}_6]^{3-}$  is 6, hence it is a octahedral complex.

**42.**  $[\text{NiCl}_4]^{2-}$  has tetrahedral shape. In this complex, Ni is in the +2 oxidation state and  $\text{Ni}^{2+}$  ion always forms tetrahedral complexes.

**43.** Both  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  have  $sp^3$ -hybridisation but later is square planar.

**44.**  $\text{K}_3[\text{FeF}_6]$

$\text{Fe}^{3+} = [\text{Ar}] 3d^5 4s^0$

3d	4s	4p
1 1 1 1 1	□	□ □ □

Number of unpaired electrons = 5

$$\text{Magnetic moment} = \sqrt{5(5+2)} = \sqrt{s(s+2)} \\ = \sqrt{35} = 5.91 \text{ BM}$$

**46.** It is due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and vice-versa, e.g.  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , the former is paramagnetic, and the latter is diamagnetic because  $\text{F}^-$  is a weak field ligand and  $\text{NH}_3$  is a strong field ligand.

**47.** In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  water acts as ligand as a result it causes crystal field splitting. Hence,  $d-d$  transition is possible thus  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is coloured. In the anhydrous  $\text{CuSO}_4$  due to the absence of water (ligand), crystal field splitting is not possible and hence, it is colourless.

3d	4s	4p	4d
$[\text{Fe}] = 1\ 1\ 1\ 1\ 1$	1	□ □	□ □ □ □
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} = 1\ 1\ 1\ 1\ 1$	xx	xx xx xx	xx xx □ □

$sp^3 d^2$  hybridisation

$[\text{Fe}(\text{CN})_6]^{3-} = 1\ 1\ 1\ 1\ 1$	xx	xx xx xx
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$d^2 sp^3$  hybridisation

$[\text{Fe}(\text{Cl})_6]^{3-} = 1\ 1\ 1\ 1\ 1$	xx	xx xx xx	xx xx □ □
---	----	----------	-----------

$sp^3 d^2$  hybridisation

**49.** The electronic configuration of Ni in  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{NiCl}_4]^{2-}$  and  $\text{Ni}^{2+}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$

3d	4s	4p
1 1 1 1 1 xx	xx	xx xx

$dsp^2$

$\text{Ni}^{2+}$  in  $[\text{NiCl}_4]^{2-}$

3d	4s	4p
1 1 1 1 1	xx	xx xx xx

$sp^3$

Ni in  $[\text{Ni}(\text{CO})_4]$

3d	4s	4p
1 1 1 1 1	xx	xx xx xx

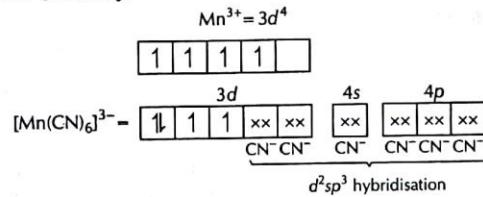
$sp^3$

CO and  $\text{CN}^-$  are strong ligands so, they induces pairing of electrons so, their complexes are diamagnetic while,  $\text{Cl}^-$  is a weak field ligand so, it does not induce the pairing of electrons so, its complex is paramagnetic.

# 1028 JEE Main Chemistry

**50.** In both the complex compounds, Fe is in +2 oxidation state with configuration  $3d^6$ , i.e., it has four unpaired electrons. In the presence of weak  $H_2O$  ligands, the unpaired electrons do not pair up. But in the presence of strong ligand  $CN^-$ , they get paired up. Then, no unpaired electron is left. Due to this difference in the number of unpaired electrons, both complex ions have different colours.

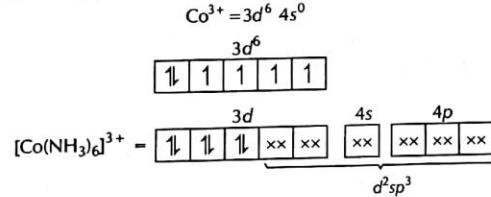
**51.** (a)  $[Mn(CN)_6]^{3-}$



- (i)  $d^2sp^3$  hybridisation
- (ii) Inner orbital complex because  $(n - 1)d$ -orbitals are used.
- (iii) Paramagnetic, as two unpaired electrons are present.
- (iv) Spin only magnetic moment  

$$\mu = \sqrt{n(n+2)} = \sqrt{8} = 2.82 \text{ BM}$$

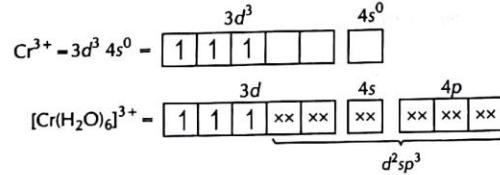
(b)  $[Co(NH_3)_6]^{3+}$



( $NH_3$  pair up the unpaired  $3d$  electrons.)

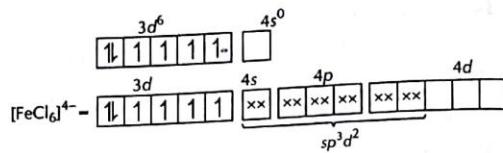
- (i)  $d^2sp^3$  hybridisation
- (ii) Inner orbital complex because of the involvement of  $(n - 1)d$ -orbital in bonding.
- (iii) Diamagnetic, as no unpaired electron is present.
- (iv)  $\mu = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$  (Zero)

(c)  $[Cr(H_2O)_6]^{3+}$



- (i)  $d^2sp^3$  hybridisation
- (ii) Inner orbital complex (as  $(n - 1)d$ -orbitals take part.)
- (iii) Paramagnetic (as three unpaired electrons are present.)
- (iv)  $\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$

(d)  $[Fe(Cl)_6]^{4-}$



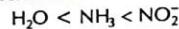
(i)  $sp^3d^2$  hybridisation

- (ii) Outer orbital complex because  $nd$ -orbitals are involved in hybridisation.
- (iii) Paramagnetic (because of the presence of four unpaired electrons).
- (iv)  $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9 \text{ BM}$

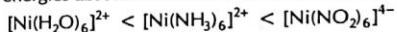
**52.** For tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy, so they are not formed in low spin state.

**53.** We know that, CFSE is higher for the complex having strong field ligand and varies inversely with wavelength.

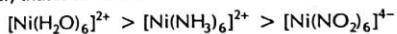
In all the given complexes, the metal ion is  $Ni^{2+}$ . The increasing field strengths of the ligands present as per electrochemical series are in the order :



The energies absorbed for excitation will be in the order :



As  $E = \frac{hc}{\lambda}$ , i.e.,  $E \propto \frac{1}{\lambda}$ ; the wavelengths will be in the opposite order, that is as follows



**54.** Dissociation constant is the reciprocal of  $\beta_4$ , the stability constant.

Overall complex dissociation equilibrium constant =  $\frac{1}{\beta_4}$

$$= \frac{1}{2.1 \times 10^{-13}} = 4.7 \times 10^{-14}$$

**55.** EAN of Pt in  $[PtCl_6]^{2-} = 86$

**56.** Chlorophyll are green pigment in plant and contain magnesium instead of calcium.

**57.** Cis-isomer of  $[Pt(NH_3)_2Cl_2]$  is used as an anticancer drug for treating several type of malignant tumours. When it is injected into the blood stream, the more reactive Cl groups are lost so, the Pt atom bonds to a N-atom in guanosine (a part of DNA). This molecule can bond to two different guanosine units and by bridging between them it upsets the normal reproduction of DNA.

**58.** The reaction carried out in alkaline pH, i.e., 9 – 11.

**59.**  $[H_2EDTA]^{2-} + Mg^{2+} \longrightarrow [MgEDTA]^{2-} + 2H^+$

- (a) In this complex, four donor sites are occupied by oxygen and two donor sites are occupied by nitrogen.
- (b) This complex is six coordinated.
- (c) Complex  $[MgEDTA]^{2-}$  is colourless.
- (d) Increase in  $[H^+]$  decreases pH of the solution.

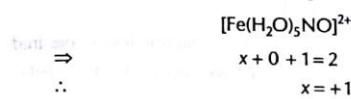
## Round II

- 1.** Its coordination number will be 6 because it is bonded with three bidentate ligands.

Let  $x$  be the oxidation state of Cr.

$$\therefore x + 3(-2) + 3(+1) = 0 \Rightarrow x = +3$$

- 2.** Let the oxidation state of Fe in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  is  $x$ .



Hence NO exists as nitrosyl ion ( $\text{NO}^+$ ).

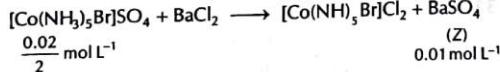
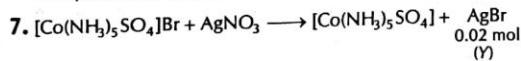
- 3.** In  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , the ligands are negative which is present in coordination spheres shows a dual behaviour. It may satisfy both primary and secondary valencies while neutral ligand satisfied only secondary valencies.

- 4.** IUPAC name of sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  is sodium pentacyanotrosoyl ferrate (III) because in it NO is neutral ligand and the oxidation number of Fe is III, which is calculated as

$$\begin{aligned} & 2 \times \text{O.N. of Na} + \text{O.N. of Fe} + 5 \times \text{O.N. of CN} \\ & \quad + 1 \times \text{O.N. of NO} = 0 \\ & 2 \times (+1) + \text{O.N. of Fe} + 5 \times (-1) + 1 \times 0 = 0 \\ \therefore & \text{O.N. of Fe} = 5 - 2 = +3 \end{aligned}$$

- 5.** Structure  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{K}_3[\text{Co}(\text{CN})_6]$ ,  $\text{K}_2[\text{Ni}(\text{CN})_4]$  are diamagnetic.

- 6.** When ligands are arranged in ascending order of crystal field splitting energy,  $\Delta$ , they produced a spectrochemical series. In comparison to  $\text{H}_2\text{O}$ , Cl is a strong  $\sigma$  donor and good  $\pi$ -acceptor, therefore, it is a strong ligand than  $\text{H}_2\text{O}$ . Hence, in the spectrochemical series is Cl is above than water.



- 8.** Wilkinson's catalyst,  $(\text{Ph}_3\text{P})_3\text{RhCl}$

$$\text{Rh}^+ = [\text{Kr}] 4d^8 s^0$$

i.e.,  $dsp^2$  hybridisation.

Rh atom in Wilkinson's catalyst is  $dsp^2$  hybridised giving a square planar shape to the molecule.

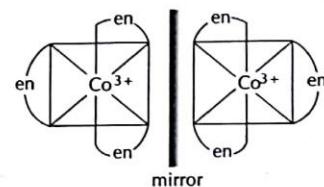
- 9.**  $\text{CoCl}_2$  is a weak Lewis acid, It reacts with chloride ions to produce salt containing the tetrahedral  $[\text{CoCl}_4]^{2-}$  ion.  $\text{CoCl}_2$  is blue when anhydrous, and a deep magenta colour when hydrated, for this reason it is widely used as an indicator for water.

- 10. Complex ion Hybridisation of central atom**

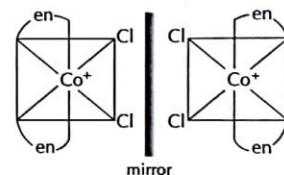
$[\text{Fe}(\text{CN})_6]^{4-}$	$d^2sp^3$ (inner)
$[\text{Co}(\text{NH}_3)_6]^{3+}$	$d^2sp^3$ (inner)
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	$sp^3d^2$ (outer)

- 11.**  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  shows geometrical as well as optical isomerism.

- 12.**  $[\text{Co}(\text{en})_3]\text{Cl}_3$  i.e.,  $[\text{Co}(\text{en})_3]^{3+}$



cis-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl i.e., cis-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>



- 13.** In  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , Co is present as  $\text{Co}^{3+}(d^6)$  and  $\text{NH}_3$  is a strong field ligand, so unpaired electrons = 0.

So, it is yellowish orange.

In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , Ti is present as  $\text{Ti}^{3+}(d^1)$  so it contains one unpaired electron. It is pale blue in colour.

In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , Ni is present as  $\text{Ni}^{2+}(d^8)$  so it have two unpaired electrons. It is of green colour.

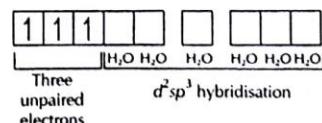
$[\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+}$  is violet as en is a strong field ligand.

- 14.**  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  exhibits geometrical isomerism. Cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  because of the absence of symmetry elements exhibits optical isomerism.

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  because of the presence of ambidentate ( $\text{NO}_2$ ) ligand exhibit linkage isomerism.  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  exhibits coordination isomerism because here cation and anion both are complex.

- 15.** In  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , Cr is present as  $\text{Cr}^{3+}$ .

$$\text{Cr}^{3+} = 3d^3, 4s^0, 4p^0$$

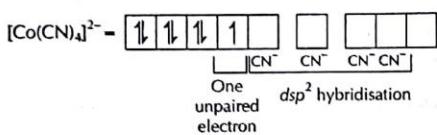


## 1030 JEE Main Chemistry

In  $[\text{Co}(\text{CN})_4]^{2-}$ , Co is present as  $\text{Co}^{2+}$

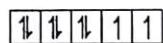
$$\text{Co}^{2+} = 3d^7, 4s^0, 4p^0$$

[ $\text{CN}^-$  being strong field ligand pair up the unpaired d electrons.]

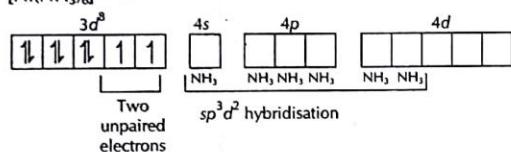


(c) In  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , Ni is present as  $\text{Ni}^{2+}$ .

$$\text{Ni}^{2+} = [\text{Ar}] 3d^8, 4s^0$$



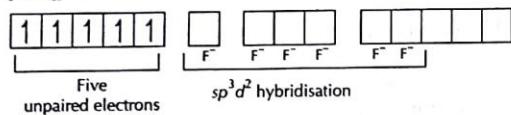
$[\text{Ni}(\text{NH}_3)_6]^{2+} =$



(d) In  $[\text{MnF}_6]^{4-}$ , Mn is present as  $\text{Mn}^{2+}$ .

$$\text{Mn}^{2+} = 3d^5, 4s^0$$

$[\text{MnF}_6]^{4-} =$



16. Chlorophyll contains Mg, blood pigment, i.e., haemoglobin contains iron (Fe), Wilkinson catalyst contains Rh (rhodium) and vitamin B<sub>12</sub> have cobalt metal.

17. Heteroleptic complexes are those in which more than one kind of ligands are present. e.g.,  $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]^{4+}$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  etc.

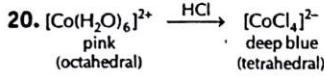
18. Three names and formulas are correctly matched.

$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  — Potassium trioxalatochromate (III)

$\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$  — Potassium amminepentachloroplatinate (IV)

$[\text{Ag}(\text{CN})_2^-]$  — Dicyanoargentate (I) ion

19.  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{OH}^-$  are weak field ligands usually form high spin complexes.  $\text{CN}^-$  and  $\text{NO}_2^-$  are strong field ligands usually form low spin complexes.  $[\text{Ni}(\text{CO})_4]$  is a low spin complex.



The colour changes because crystal field splitting is more in case of octahedral complexes as compared to tetrahedral complexes.

21.  $[\text{Co}(\text{en})_3]^{3+}$  and  $cis-[\text{Co}(\text{en})_2\text{Cl}_2]^{+}$  are optically active compounds because of the absence of symmetry elements.

22. The slightly larger value of  $\mu$  than expected from the formula  $\mu = \sqrt{n(n + 2)}$  is due to a small contribution from the magnetic orbital angular momentum of the electrons to the magnetic moment.

23. Chelating agents form more stable complexes thus, these are used to remove toxic metal ions.

24.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$  contains Cr as  $\text{Cr}^{2+}$ , which is less stable than  $\text{Cr}^{3+}$ , so it has higher tendency to get oxidised or it is a better reducing agent.

Similar is true for  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ . Both the complex have unpaired electrons in their d-orbitals.

25.  $MX_6$  and  $MX_5L$  type complexes do not exhibit geometrical isomerism although many 6 coordinated complexes like complex of the type  $MA_3B_3$  exhibits geometrical isomerism.

26. Both  $[\text{Ti}(\text{H}_2\text{O})_6]^{1+}$  and  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  are colourless due to the absence of free electrons in  $3d$  subshell.

27. 'A' gives precipitate with  $\text{AgNO}_3$ , so in it Cl is present outside the coordination sphere.

'B' gives precipitate with  $\text{BaCl}_2$ , so in it  $\text{SO}_4^{2-}$  is present outside the coordination sphere.

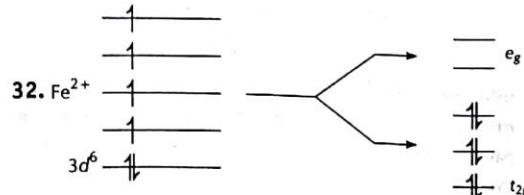
So, A- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$   
B- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

28. Ionisation isomerism (as give different ions when subjected to ionisation.)

29. [B] Pentaamminechloridocobalt (III) sulphate.

30. In complexes  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ , central metal cations have same oxidation state as well as same ligands and they fall in same group, but  $\Delta_o$  of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+} > \Delta_o$  of  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  because Rh<sup>3+</sup> has high  $Z_{\text{eff}}$  value than Co<sup>3+</sup>.

31.  $\Delta_o$  is so large for  $[\text{Fe}(\text{CN})_6]^{4-}$  that its absorption peak is in ultraviolet region.  $\Delta_o$  for  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is so small that its absorption peak is in infrared region.



$\text{CN}^-$  is a strong field ligand, therefore  $\Delta_o > \Delta_P$  and hence, pairing of electrons takes place.

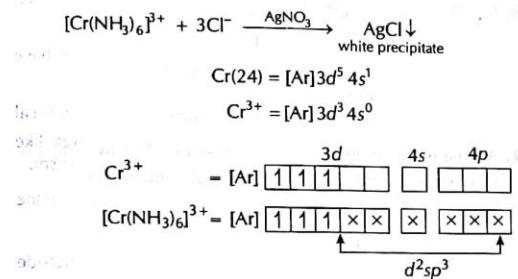
- 33.** Two Br, two (en) and one Cr are parts of complex. Charge on the complex is

$$\left. \begin{array}{l} 2(\text{Br}) = -2 \\ 2(\text{en}) = 0 \\ 1(\text{Cr}) = +3 \end{array} \right\} = +1$$

Thus, complex ion is  $[\text{Cr}(\text{en})_2\text{Br}_2]^{+}$ .

Since, anion is bromide thus, complex is  $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ .

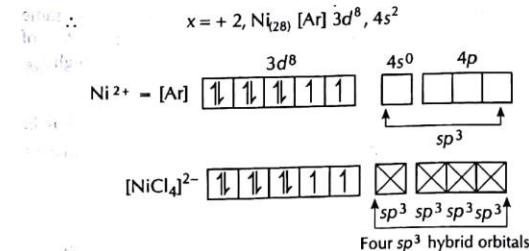
- 34.**  $[\text{Cr}(\text{NH}_3)_6]^{3+} \quad \text{Cl}_3 \rightleftharpoons$   
coordinate sphere ionisable



Indicates lone-pair of  $\text{NH}_3$  donated to Cr

- (a)  $d^2sp^3$ -hybridisation, octahedral. Thus, correct.
- (b) There are three unpaired electrons, hence paramagnetic. Thus, correct.
- (c)  $d^2sp^3$ -inner orbital complex, thus incorrect.
- (d) Due to ionisable  $\text{Cl}^-$  ions, white precipitate with  $\text{AgNO}_3$ , thus, correct.

- 35.**  $[\text{NiCl}_4]^{2-}$ ; oxidation number of Ni,  $x - 4 = -2$



$sp^3$ -hybrid orbitals, tetrahedral

$\text{Cl}^-$  is a weak field ligand and thus, unpaired electrons are not paired. Lone pairs from 4  $\text{Cl}^-$  are accommodated in four  $sp^3$  hybrid orbitals.

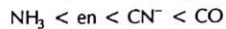
N = unpaired electrons = 2, paramagnetic

Magnetic moment (spin only)

$$= \sqrt{N(N+2)} \text{ BM}$$

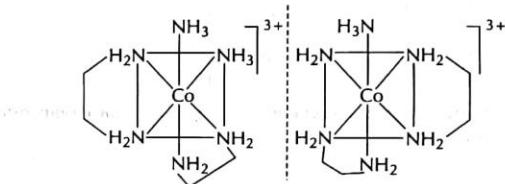
$$= \sqrt{8} = 2.828 \text{ BM}$$

- 36.** Based on spectrochemical series, ligands arranged in increasing order of crystal field strength are as



	Complex	Isomerism shown
(a)	$[\text{Co}(\text{en})_3]^{3+}$	Optical only
(b)	$[\text{Ni}(\text{NH}_3)_6\text{Br}]^+$	No geometrical isomer
(c)	$[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$	Cis and trans
(d)	$[\text{Cr}(\text{NH}_3)_4(\text{en})]^{3+}$	No geometrical isomer

- 38.** Cis-form of  $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$  is optically active.



- 39.** Linkage isomerism are caused due to presence of ambidentate ligands.  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$  are linkage isomers due to SCN, ambidentate ligands.

- 40.** en,  $\text{CH}_2-\text{NH}_2$  is a bidentate ligand.

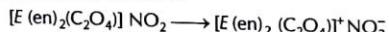


Hence, coordinating head are six

$$(\text{en} : 2 \times 2 = 4 + (\text{ox}) 2)$$

Coordination number 6

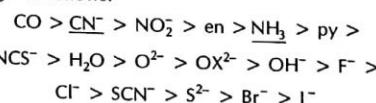
Complex can be ionised as



Oxidation number  $x + 0 + (-2) = +1$

$\Rightarrow$  Oxidation number,  $x = 3$

- 41.** CFSE (crystal field splitting energy) for octahedral complex,  $\Delta_o$  depends on the strength of negative ligand. Spectrochemically it has been found that the strength of splitting is as follows:



- 42.**  $\text{Cl}^-$  is a weak ligand but  $\text{Cl}^-$  cause the pairing of electrons with large  $\text{Pt}^{2+}$  and consequently give  $dsp^2$  hybridisation and square planar geometry.

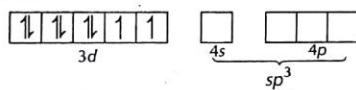
- 43.**  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$

Pentaamminenitrito-N-cobalt (III) chloride

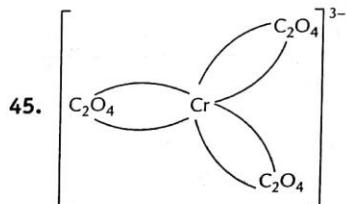
## 1032 JEE Main Chemistry

44.  ${}_{28}\text{Ni} = [\text{Ar}] 4s^2, 3d^8$

${}^{+}\text{Ni}^{2+} = [\text{Ar}] 3d^8$



Nickel has two unpaired electrons and geometry is tetrahedral due to  $sp^3$  hybridisation.



Mirror image is not superimposable, hence optical isomerism is possible.

46. Coordination number is the maximum covalency shown by a metal or metal ion. It is the maximum number of ligands attached to metal by sigma bonds or coordinate bonds.

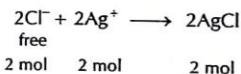
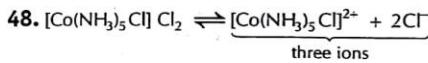
47. Number of unpaired electrons in  $[\text{Fe}(\text{CN})_6]^{4-}$  is zero.

$$\text{Thus, magnetic moment} = \sqrt{n(n+2)} = 0 \text{ BM}$$

(n = unpaired electrons)

$$n \text{ in } [\text{MnCl}_4]^{2-} = 5, \sqrt{35} \text{ BM}$$

$$n \text{ in } [\text{CoCl}_4]^{2-} = 3, \sqrt{15} \text{ BM}$$



49. A square planar geometry is the result of  $dsp^2$  hybridisation where inner d sub-shell ( $d_{x^2-y^2}$  orbital) participates.

# Coordination Compounds and Organometallics

Some coordination compounds are  
very different to simple salts in strength to heat  
and in having noble metals to which they are  
not soluble in water. These salts are called  
base lattice. It has notable one like copper salt of  
 $\text{CO}_2\text{OH}_2\text{Mg}^{+2}\text{CN}^{-}\text{H}_2\text{O}\text{Li}^+\text{H}_2\text{O}_2\text{O}_2\text{Li}^+$ . It is to make  
changes in colour or to affect the properties  
of other substances.

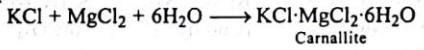
It is not known how the salt of noble metals are but some  
are colourless and others are brownish.

One of the most important properties of transition metals is that they form coordination or complex compounds. These compounds play a vital role in our lives. The importance of these compounds can be realised from the fact that life would not have been possible without the existence of **chlorophyll** (Mg-complex) in plants and **haemoglobin** (Fe-complex) in the blood of animals. One of the earliest known coordination compound is prussian blue which was accidentally prepared in 1704 by a Berlin colour maker, Diesbach, by strongly heating animal wastes and sodium carbonate in an iron container. In 1753, Macquer prepared potassium ferrocyanide by treating prussian blue with alkali. In 1799, Tassaert obtained an orange compound,  $\text{CoCl}_3 \cdot 6\text{NH}_3$ , by allowing a mixture of cobalt chloride and aqueous ammonia to stand in air. During the next fifty years, numerous compounds of this type containing cobalt, platinum, chromium and iron were discovered. The field of such compounds has expanded very fast in recent years and coordination compounds are playing important roles in analytical chemistry, polymerization reactions, metallurgy and refining of metals, organic synthesis, electroplating, photography, biochemistry, water purification, textile dyeing and bacteriology. In addition, the study of these compounds has enlarged our understanding of chemical bonding, certain physical properties such as spectral and magnetic properties and metabolic processes. In this chapter some basic aspects regarding coordination compounds are discussed.

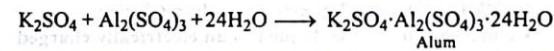
## 15.1 MOLECULAR OR ADDITION COMPOUNDS

When solutions containing two or more simple stable compounds in molecular proportions are allowed to evaporate,

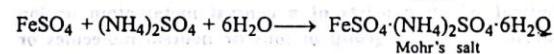
crystals of new substances are obtained. These substances are termed **molecular** or **addition compounds**. Some common examples are:



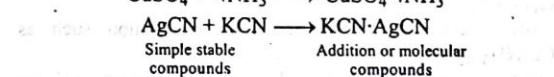
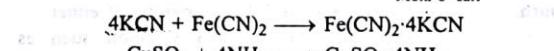
Carnallite



Alum



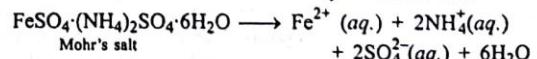
Mohr's salt



Simple stable                      Addition or molecular  
compounds                      compounds

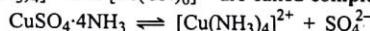
The molecular or addition compounds are of two types:

(i) **Double salts or Lattice compounds :** The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called **double salts or lattice compounds**. Their solution have the same properties as the mixture of individual compounds. For example, when Mohr's salt,  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ , is dissolved in water, it exhibits the properties of  $\text{FeSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , i.e., they produce  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions in solution. Thus, each ion has its identity in double salt.



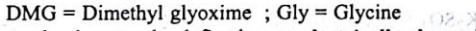
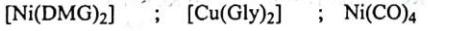
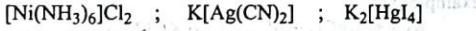
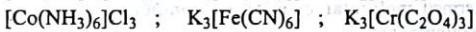
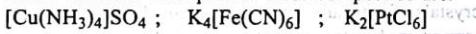
Carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; potash alum,  
 $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , etc., are the examples of double salts.

**(ii) Coordination or complex compounds :** The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions, are called **coordination compounds**. The properties of their solutions are different than those of their constituents. When crystals of  $\text{CuSO}_4 \cdot 4\text{NH}_3$  are dissolved in water there is hardly any evidence for the presence of  $\text{Cu}^{2+}$  ions or ammonia molecules. A new ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of  $\text{Fe}(\text{CN})_6 \cdot 4\text{KCN}$  does not give tests of  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions but gives the test for a new ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ . The ions  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  are called **complex ions**.



Thus, a coordination or complex compound may be defined as a molecular compound that results from the combination of two or more simple stable molecular compounds and retains its identity in the solid as well as in dissolved state. The properties of such compounds are totally different than individual constituents. A coordination compound contains very often but not always a complex ion.

Some of the common examples of these compounds are:



A complex ion may be defined as an electrically charged radical which consists of a central metal atom or ion surrounded by a group of ions or neutral molecules or both. A coordination compound, thus, consists of either,

(i) a simple cation and a complex anion such as  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , or

(ii) a complex cation and a simple anion such as  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , or

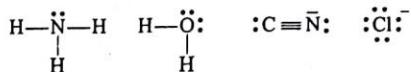
(iii) a complex cation and a complex anion such as  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ , or

(iv) a neutral molecule such as  $\text{Cu}(\text{Gly})_2$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Ni}(\text{DMG})_2$ , etc.

## 15.2 TERMINOLOGY OF COORDINATION COMPOUNDS

Before further discussion, it is necessary to explain some important terms used in the study of coordination compounds. These are discussed here.

**1. Ligands :** The neutral molecules; anions or cations which are directly linked with the central metal atom or ion in a complex ion are called **ligands**. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage. With few exceptions, free ligands have at least one electron pair that is not engaged in bonding. Some examples are:



The ligand acts as a donor as it donates one or more electron pairs to the central metal atom or ion which acts as an acceptor. The ligands are thus Lewis bases and central metal ions or atoms are Lewis acids. The formation of a complex ion involves following two things:

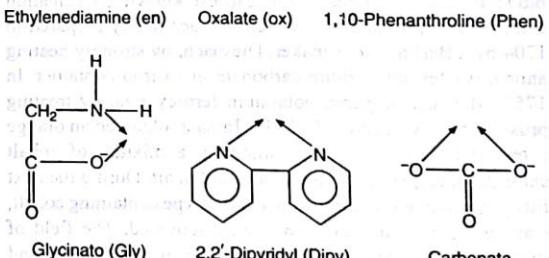
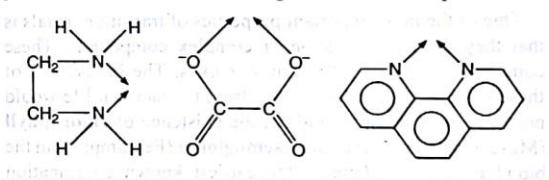
(i) Ligands should have lone pair or pairs of electrons which can be donated to the central metal ion or atom.

(ii) The central atom or ion should have vacant orbitals of nearly equivalent energy as to accommodate the electrons donated by ligands. This condition is easily fulfilled by atoms or ions of transition metals.

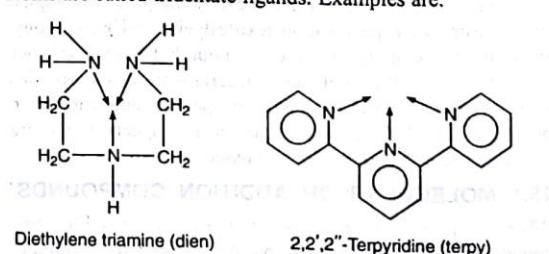
**Types of ligands :** Ligands can be of following types depending on the number of donor atoms present in them.

**(i) Mono- or unidentate ligands :** They have one donor atom, i.e., they supply only one electron pair to central metal atom or ion.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ ,  $\text{CO}$ , etc., are examples of monodentate ligands.

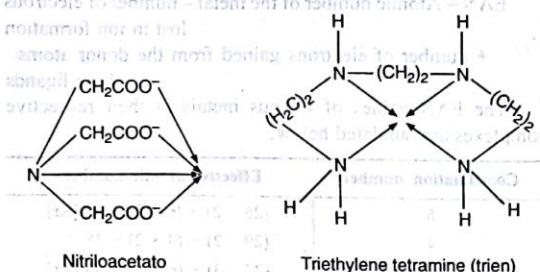
**(ii) Bidentate ligands :** Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. Some examples are:



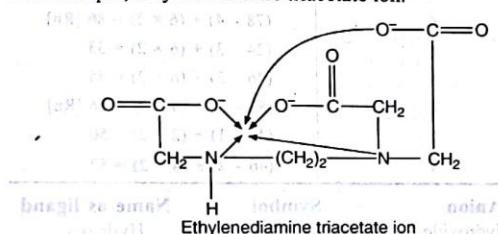
**(iii) Tridentate ligands :** The ligands having three donor atoms are called tridentate ligands. Examples are:



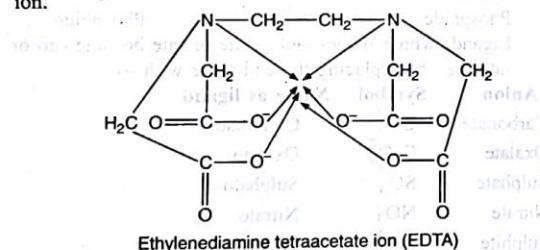
(iv) **Tetradeятate ligands :** These ligands possess four donor atoms. Examples are:



(v) **Pentadeятate ligands :** They have five donor atoms. For example, ethylenediamine triacetate ion.



(vi) **Hexadeятate ligands :** They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.

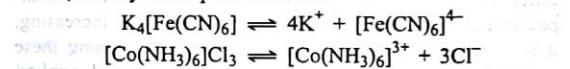


- Note :**
- The ligands having two or more donor atoms are also called polydentate or multidentate ligands.
  - A multidentate ligand is known as a chelating ligand if on coordination it results in formation of a closed or cyclic ring. The complexes thus formed are called *Chelates*. The chelates are comparatively more stable than ordinary complexes.
  - Polydentate ligands have **flexideterminate** character. It is not necessary that all the donor atoms present in the polydentate ligands should form coordinate bonds with central metal atom or ion. For example, ethylenediamine tetraacetic acid (EDTA) which is hexadentate ligand can function as pentadentate or tetradeятate ligand with certain metal ions. Similarly sulphate ion can also act as monodentate ligand.
  - There are certain ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion. Such ligands are called **ambidentate** ligands. Some examples of such ligands are:

1. **Ligand field**:  $M \leftarrow NO_2^-$  (nitro),  $M \leftarrow ONO^-$  (nitrito)  
 $M \leftarrow CN^-$  (cyanide),  $M \leftarrow NC^-$  (isocyano)  
 $M \leftarrow SCN^-$  (thiocyanate),  $M \leftarrow NCS^-$  (isothiocyanate)

2. **Coordination number :** The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion. It is actually the number of chemical bonds which the ligands form with the central metal atom or ion. For example, in  $[Cu(NH_3)_4]^{2+}$  the coordination number of copper is 4, in  $[Co(en)]^{3+}$  the coordination number of cobalt is 6 as (en) is the bidentate ligand. The most common coordination numbers exhibited by metal ions are 2, 4 and 6. The light transition metals exhibit 4 and 6 coordination numbers while heavy transition metals may exhibit coordination number more than 6. It has been observed that in a particular oxidation state, a metal prefers to exhibit the same coordination number.

3. **Coordination sphere :** The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket. This has been called coordination sphere or first sphere of attraction. It behaves as a single unit because the ligands present in the coordination sphere are held tightly by the metal ion. Any ion present outside this sphere is separated from the complex when the compound is dissolved in the water, on any other polar medium.



The charge on the complex ion is the algebraic sum of the charges carried by central metal ion and the ligands attached to it. For illustration, see following examples:

**Example 1.** Assign the charge on the following ions:

- (a)  $[Hg(CN)_4]^x$ , (b)  $[Co(NH_3)_2Cl_4]^x$ , (c)  $[Fe(CN)_6]^{x-}$ .
- Solution.** (a) The oxidation state of Hg in the complex is +2  
 $So \ x = +2 + 4 \times (-1) = -2$ , i.e.,  $[Hg(CN)_4]^{2-}$

- (b) The oxidation state of Co in the complex is +3

$$So \ x = +3 + 2 \times 0 + 4 \times (-1) = -1, \text{ i.e., } [Co(NH_3)_2Cl_4]^-$$

- (c) The oxidation state of Fe in the complex is +2

$$So \ x = +2 + 6 \times (-1) = -4, \text{ i.e., } [Fe(CN)_6]^{4-}$$

If the oxidation state of Fe in the complex is +3

$$x = +3 + 6 \times (-1) = -3, \text{ i.e., } [Fe(CN)_6]^{3-}$$

**Example 2.** Determine the oxidation state of metal in the complex ion,  $[PtCl_6]^{2-}$ .

**Solution.** Charge on the complex ion = Oxidation state of metal + charge on ligands

$$-2 = x + 6 \times (-1)$$

$$\text{or } x + 6 = +4$$

The oxidation state of Pt in the complex ion is +4.

**4. Effective atomic number (EAN) :** Ligands, are attached with the central metal ion through donor atoms. Each

donor atom donates one electron pair to the central metal ion, i.e., the central metal atom or ion gains electrons from the donor atoms. In order to explain the stability of the complex, Sidgwick proposed **effective atomic number** abbreviated as EAN, which is defined as the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands. The effective atomic number (EAN) generally coincides with the atomic number of next

inert gas in some cases. EAN is calculated by the following relation:

$$\text{EAN} = \text{Atomic number of the metal} - \text{number of electrons lost in ion formation} + \text{number of electrons gained from the donor atoms of the ligands}$$

The EAN values of various metals in their respective complexes are tabulated below:

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	+2	26	6	(26 - 2) + (6 × 2) = 36 [Kr]
[Cu(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub>	+2	29	4	(29 - 2) + (4 × 2) = 35
[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	+3	27	6	(27 - 3) + (6 × 2) = 36 [Kr]
Ni(CO) <sub>4</sub>	0	28	4	(28 - 0) + (4 × 2) = 36 [Kr]
K <sub>2</sub> [Ni(CN) <sub>4</sub> ]	+2	28	4	(28 - 2) + (4 × 2) = 34
K <sub>2</sub> [PtCl <sub>6</sub> ]	+4	78	6	(78 - 4) + (6 × 2) = 86 [Rn]
K <sub>3</sub> [Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]	+3	24	6	(24 - 3) + (6 × 2) = 33
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	+3	26	6	(26 - 3) + (6 × 2) = 35
K <sub>2</sub> [HgI <sub>4</sub> ]	+2	80	4	(80 - 2) + (4 × 2) = 86 [Rn]
[Ag(NH <sub>3</sub> ) <sub>2</sub> ]Cl	+1	47	2	(47 - 1) + (2 × 2) = 50
K <sub>2</sub> [PdCl <sub>4</sub> ]	+2	46	4	(46 - 2) + (4 × 2) = 52

### 15.3 NOMENCLATURE OF COORDINATION COMPOUNDS

Since several thousands of complexes (coordination compounds) are known and the number is constantly increasing, it is necessary to adopt a uniform system of naming these compounds. The International Union of Pure and Applied Chemistry (IUPAC) published rules for the systematic naming of coordination compounds in 1957. Some modifications in these rules were made in 1962 and 1971.

However, trivial names for certain coordination compounds are still in use, e.g., K<sub>4</sub>[Fe(CN)<sub>6</sub>] and K<sub>3</sub>[Fe(CN)<sub>6</sub>] are called as potassium ferrocyanide and potassium ferricyanide even today.

The following rules are adopted these days for naming all types of coordination compounds:

(1) If a coordination compound is ionic, the name of cation is given first whether or not it is the complex ion followed by the name of the anion just like naming a simple salt. The names of cation and anion are separated by a space.

(2) Within a complex ion, the ligands are named first followed by the metal ion.

#### Names of the Ligands

(i) Anionic ligands ending with ide are named by replacing -ide with suffix -o or replacing -e by -o.

Anion	Symbol	Name as ligand
Chloride	Cl <sup>-</sup>	Chlorido
Bromide	Br <sup>-</sup>	Bromido
Cyanide	CN <sup>-</sup>	Cyano
Oxide	O <sup>2-</sup>	Oxo
Peroxide	O <sub>2</sub> <sup>2-</sup>	Peroxo

Anion	Symbol	Name as ligand
Hydroxide	OH <sup>-</sup>	Hydroxo
Sulphide	S <sup>2-</sup>	Sulphido
Amide	NH <sub>2</sub> <sup>-</sup>	Amido
Nitride	N <sup>3-</sup>	Nitrido
Phosphide	P <sup>3-</sup>	Phosphido
Ligands whose names end in -ite or -ate become -ito or -ato, i.e., by replacing the ending -e with -o.		

Anion	Symbol	Name as ligand
Carbonate	CO <sub>3</sub> <sup>2-</sup>	Carbonato
Oxalate	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Oxalato
Sulphate	SO <sub>4</sub> <sup>2-</sup>	Sulphato
Nitrate	NO <sub>3</sub> <sup>-</sup>	Nitrato
Sulphite	SO <sub>3</sub> <sup>2-</sup>	Sulphito
Acetate	CH <sub>3</sub> COO <sup>-</sup>	Acetato
Nitrite	{ONO <sup>-</sup> (bonded through oxygen) nitrito NO <sub>2</sub> <sup>-</sup> (bonded through nitrogen) nitro}	

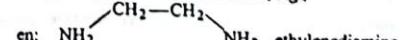
(ii) Neutral ligands are given the same names as the neutral molecule. For example, ethylenediamine as a ligand is named ethylenediamine in the complex. However, two very important exceptions to this rule are:

H<sub>2</sub>O Aquo (Aqua) NH<sub>3</sub> Ammine;

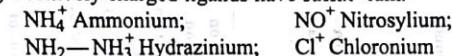
Other exceptions are:

CO Carbonyl; NO Nitrosyl;  
CS Thiocarbonyl; NS Thionitrosyl

Note : In the case of poly-dentate amino ligands we use single 'm' in the spelling, i.e., amine is written, e.g.,



(iii) Positively charged ligands have suffix -ium.



(iv) If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc.

However, when the name of the ligand includes a number, e.g., dipyridyl, ethylenediamine, then *bis*, *tris*, *tetrakis* are used in place of *di*, *tri*, *tetra*, etc.

(v) Order of naming ligands : When more than one type of ligands are present, they are named in alphabetical order without separation by hyphen. This rule has come in force after 1971 convention.

Note : In the old system, the ligands are named in the order of (i) negative (ii) neutral and (iii) positive without separation by hyphens. (iv) When there are several ligands of same kind, these are listed alphabetically.

For example, in the complex  $[\text{Cr}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]^+$ , the ligands are named in the order of ammine, chlorido and nitro in accordance to new convention. However, according to old convention, the ligands are named in the order of chlorido, nitro and ammine (first negative ligands in alphabetical order and then neutral ligand).

(3) The oxidation state of the central metal is shown by Roman numeral in bracket immediately following its name.

(4) Complex positive ions and neutral coordination compounds have no special ending but complex negative ions always end in the suffix -ate. In most of the cases, the suffix -ate is fixed to English names of the metals but in some cases -ate is fixed with Latin names of metals.

Name of components present in coordination sphere are written in continuum.

e.g.,  $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$  Potassium pentacyanonitrosylferrate(II)

Continuum

Element	Metal as named in anionic complex
Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

Note : In the case of mercury we may use both **mercurate** and **hydrazinate**.

(5) The name of the neutral coordination compound is given in one word only as the name of  $\text{Ni}(\text{CO})_4$  is tetracarbonylnickel (0).

The following examples will make the rules more clear.

#### Coordination compounds containing cationic complex ion :

$[\text{Pt}(\text{NH}_3)_6\text{Cl}_4]$	Hexaammineplatinum(IV) chloride
$[\text{CO}(\text{NH}_3)_4\text{H}_2\text{OCl}]\text{Cl}$	Tetraammineaquochloridocobalt(III) chloride
$[\text{Cu}(\text{en})_2\text{SO}_4]$	Bis (ethylenediamine) copper(II) sulphate
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$	Tetraquodichloridochromium(III) ion

$[\text{Fe}(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)]_2\text{SO}_4$	Tetraaquooxalatoiron(III) sulphate
$[\text{Cr}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{NO}_3$	Tetraamminechloridonitrochromium(III) nitrate
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Diammine silver(I) chloride
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$	Pentaammineisothiocyanatocobalt(III) chloride
$[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Rh}\text{Cl}$	<i>Tris</i> (triphenylphosphine) rhodium(I) chloride

#### Coordination compounds containing complex anionic ion :

$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate (II)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate (III)
$\text{K}_2[\text{Cr}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatochromate (III)
$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$	Potassium dichloridodioxalatocobaltate (III)
$\text{K}_2\text{HgI}_4$	Potassium tetraiodidomercurate (II)
$\text{K}_2[\text{PtCl}_6]$	Potassium hexachloridoplatinate (IV)
$\text{Na}[\text{Ag}(\text{CN})_2]$	Sodium dicyanoargentate (I)
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II) ion
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrocobaltate (III)
$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Potassium pentacyanonitrosyl ferrate (II)

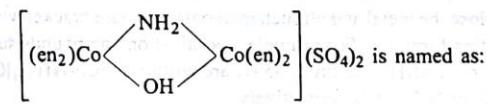
#### Coordination compounds containing complex cationic and anionic ions :

$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	Hexaamminechromium (III) hexacyanocobaltate (III)
$[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$	Tetraammineplatinum (II) tetrachloridocuprate (II)
$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$	Hexaamminechromium (III) trioxalatocobaltate (III)
$[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	Tetrapyridine platinum (II) tetrachloridoplatinate (II)

#### Non-ionic coordination compounds :

$\text{Fe}(\text{CO})_5$	Pentacarbonyliron(0)
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triaminetrinitro cobalt (III)
$\text{Cu}(\text{Gly})_2$	Diglycinato copper (II)
$\text{Ni}(\text{DMG})_2$	<i>Bis</i> (dimethylglyoximato) nickel (II)

(6) Bridging groups in bidentate ligands : In a polyatomic complex which contains two or more central metal ions, the ligands which act as bridge between two metal atoms, the Greek letter  $\mu$  (mu) separated by a hyphen is written before their names. For example, the complex



*Bis* (ethylenediamine) cobalt(III)- $\mu$ -amido- $\mu$ -hydroxo *bis* (ethylenediamine) cobalt(III) sulphate

Or

*Tetrakis* (ethylenediamine)- $\mu$ -amido- $\mu$ -hydroxodicobalt (III) sulphate.

The complex  $\left[ (\text{H}_2\text{O})_4\text{Fe} \begin{array}{c} \text{OH} \\ | \\ \text{OH} \end{array} \text{Fe}(\text{H}_2\text{O})_4 \right] (\text{SO}_4)_2$  is named as:

Tetraaquoiron(III) - $\mu$ -dihydroxotetraaquoiron(III) sulphate.

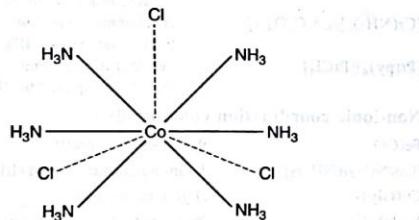
### 15.4 WERNER'S COORDINATION THEORY

Werner, in 1893, proposed coordination theory to explain the properties and structures of various metal ammines of cobalt, chromium, platinum, etc. It was first successful attempt which satisfactorily described the formation of coordination compounds from stable molecules. The important postulates of coordination theory are:

- Every element exhibits two types of valencies:  
(a) Primary valency and (b) Secondary valency.

In modern terminology, primary valency corresponds to the oxidation state of the central metal and secondary valency represents the coordination number of the metal. Primary valency is satisfied by negative ions. This is also called **principal, ionisable or ionic valency**. Its attachment to the metal is shown by dotted lines.

The secondary valency is satisfied by neutral molecules or negative ions. This valency is non-ionic or non-ionisable. The donor atoms of the ligands which satisfy the coordination number are directly attached to the metal atom and shown by thick lines. Thus, the coordination compound,  $\text{CoCl}_3 \cdot 6\text{NH}_3$ , may be represented as:

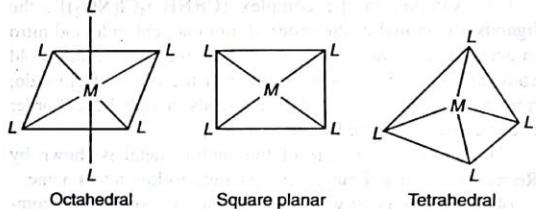


Every metal has a fixed coordination number. For example,  $\text{Co}(\text{III})$  and  $\text{Pt}(\text{IV})$  were recognised as having coordination number 6 while  $\text{Cu}(\text{II})$  has 4. In order to designate materials held by secondary valencies, it has become customary to enclose the metal and all such materials in square bracket when writing formulae. For example, coordination compounds such as  $\text{CoCl}_3 \cdot 6\text{NH}_3$  and  $\text{PtCl}_4 \cdot 6\text{NH}_3$  are written as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$  respectively.

2. Every element tends to satisfy both its primary and secondary valencies. A negative ion when present in the coordination sphere shows a dual behaviour. It may satisfy both primary and secondary valencies. The presence of negative ion in the coordination sphere reduces the charge on the complex ion by the amount of charge possessed by it and the negative ions present in the coordination sphere are not ionised. Thus, the following coordination compounds will have varying number of ionisable chlorine atoms but coordination number remains the same.

Coordination compounds	Modern formula	Charge on the cation	Coordination number	Primary valency (secondary val.)	Total no. of ions
$\text{PtCl}_4 \cdot 6\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	+4	6	4	5
$\text{PtCl}_4 \cdot 5\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	+3	6	4	4
$\text{PtCl}_4 \cdot 4\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	+2	6	4	3
$\text{PtCl}_4 \cdot 3\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	+1	6	4	2
$\text{PtCl}_4 \cdot 2\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	0	6	4	Non-electrolyte

3. The ligands which satisfy the secondary valencies are directed towards fixed positions in space. The geometry of the complex ion depends on the coordination number. If the metal



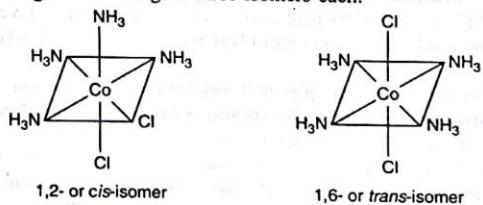
has coordination number 6, the complex is octahedral, i.e., six positions around the metal are occupied by six donor atoms of the ligands octahedrally. On the other hand, if the coordination number is 4, the geometry of the complex may be tetrahedral or square planar. This postulate predicted the existence of different types of isomerism in coordination compounds.

#### Examples :

Octahedral	Square planar	Tetrahedral
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$[\text{Ni}(\text{CN})_4]^{2-}$	$[\text{Ni}(\text{CO})_4]$
$[\text{Co}(\text{NH}_3)_6]^{3+}$ ; $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Ni}(\text{NH}_3)_4]^{2+}$	$[\text{CuX}_4]^{2-}$ ; $[\text{ZnCl}_4]^{2-}$
$[\text{Fe}(\text{CN})_6]^{4-}$ ; $[\text{Fe}(\text{F}_6)]^{3-}$	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$[\text{NiX}_4]^{2-}$
$[\text{Pt}(\text{NH}_3)_6]^{4+}$ ; $[\text{PtCl}_6]^{2-}$		

$$X = \text{Cl}^-, \text{Br}^-, \text{I}^-$$

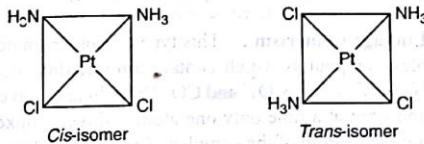
In  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , Werner was able to isolate two isomers. He predicted an octahedral structure for coordination number 6 because only octahedral structure can form two isomers (1, 2- and 1, 6-). The planar hexagonal and trigonal prism arrangements will give three isomers each.



Similarly, the existence of two geometrical isomers of the complex,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , was proved by accepting square planar configuration.

The postulates of Werner's coordination theory were actually based on experimental evidences rather than theoretical. A large number of metal ammines were studied by Werner using molar conductance values as to ascertain the number of ions per molecule and chemical methods such as precipitation of  $\text{Cl}^-$  by  $\text{AgNO}_3$  as to determine the number of ionisable  $\text{Cl}^-$  ions per molecule. The following experimental data regarding cobalt ammines well supported the postulates that the secondary

valency of 6 is maintained in all the cobalt ammines and when the  $\text{Cl}^-$  ion enters the coordination sphere, it decreases the positive charge on the complex ion by one unit.



Molecular formula	Molar conductance	No. of ions in molecules	Ionisable $\text{Cl}^-$ ions (precipitation with $\text{AgNO}_3$ )	Secondary valency	Ionic formulation
$\text{CoCl}_3\text{NH}_3$	430	4	3	6	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3\text{NH}_3\cdot\text{H}_2\text{O}$	430	4	3	6	$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$
$\text{CoCl}_3\text{NH}_3$	250	3	2	6	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3\text{NH}_3$	100	2	1	6	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3\text{NH}_3$	0	Non-electrolyte		6	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

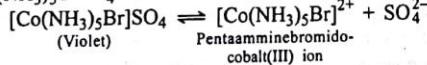
## 15.5 ISOMERISM IN COORDINATION COMPOUNDS

The compounds having same molecular formula but different physical and chemical properties on account of different structures are called **isomers** and the phenomenon as isomerism. Isomerism in coordination compounds may be divided into two main types:

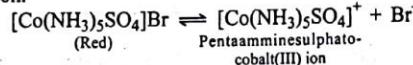
(1) Structural isomerism, (2) Stereo-isomerism

**1. Structural isomerism :** It is displayed by compounds that have different ligands within their coordination spheres. The different types of structural isomerism shown by coordination compounds are discussed below:

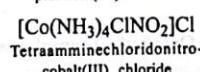
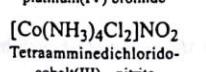
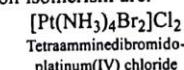
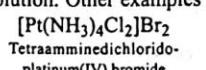
**(i) Ionisation isomerism :** This type of isomerism arises when the coordination compounds give different ions in solution. For example, there are two isomers of the formula  $\text{Co}(\text{NH}_3)_5\text{BrSO}_4$ .



This isomer gives a white precipitate of  $\text{BaSO}_4$  with  $\text{BaCl}_2$  solution.



Above isomer gives light yellow precipitate with  $\text{AgNO}_3$  solution. Other examples of ionisation isomerism are:

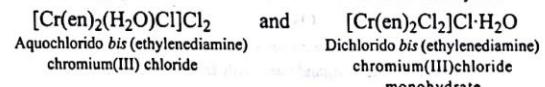
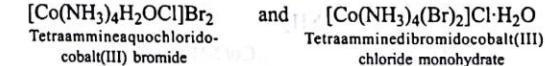


**(ii) Hydrate isomerism :** This type of isomerism arises when different number of water molecules are present inside and outside the coordination sphere. This isomerism is best illustrated by the three isomers that have the formula  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ .

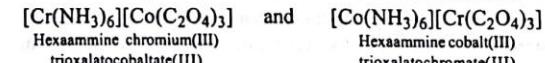
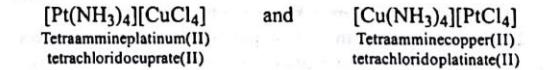
(a)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ —Violet. All the six water molecules are coordinated to Cr. It has three ionisable chloride ions.

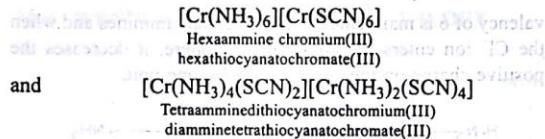
(b)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\cdot\text{H}_2\text{O}$ —Green. Five water molecules are coordinated to Cr. It has two ionisable chloride ions. One water molecule outside the coordination sphere can be easily lost.

(c)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ —Green. Four water molecules are coordinated to Cr. It has one ionisable  $\text{Cl}^-$  ion. Other examples of hydrate isomerism are:

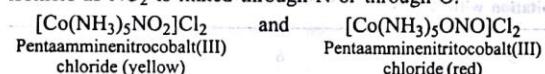


**(iii) Coordination isomerism :** This type of isomerism is observed in the coordination compounds having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers. Some examples are :

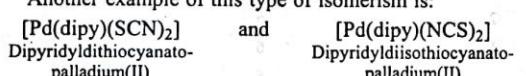




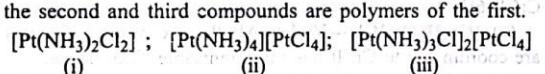
**(iv) Linkage isomerism :** This type of isomerism occurs in complex compounds which contain **ambidentate** ligands like  $\text{NO}_2^-$ ,  $\text{SCN}^-$ ,  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{CO}$ . These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex. These types of isomers are distinguished by infra-red (I.R.) spectroscopy. For example,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  are linkage isomers as  $\text{NO}_2^-$  is linked through N or through O.



Another example of this type of isomerism is:

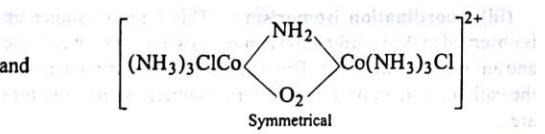
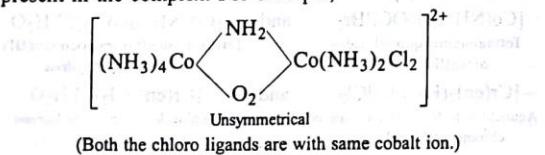


**(v) Polymerisation isomerism :** This type of isomerism exists in compounds having same stoichiometric composition but different molecular compositions. The molecular compositions are simple multiples of the simplest stoichiometric arrangement. For example in the following three compounds, the second and third compounds are polymers of the first.



[Note : (ii) and (iii) compounds are actually not the examples of polymerisation, i.e., (i) compound is not acting as a monomer due to its low reactivity in the formation of (ii) and (iii) compounds.]

**(vi) Coordination position isomerism :** This type of isomerism is exhibited by polynuclear complexes by changing the position of ligands with respect to different metal atoms present in the complex. For example,



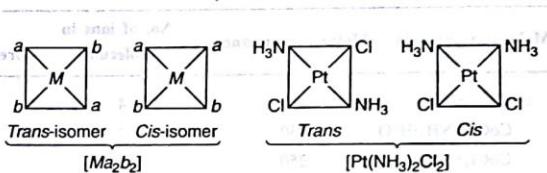
**2. Stereo-isomerism :** Compounds are stereo-isomers when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space. Stereo-isomerism is of two types, viz., geometrical isomerism and optical isomerism.

**(1) Geometrical isomerism :** This isomerism is due to ligands occupying different positions around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as *cis-trans* isomerism.

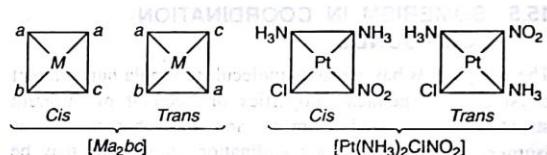
Geometrical isomerism is very much common in coordination number 4 and 6 complexes.

**Square planar complexes** (coordination number four) exhibit geometrical isomerism.

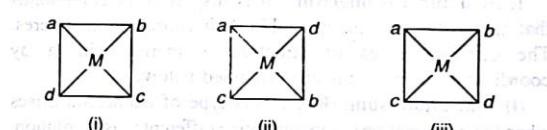
(i) Complexes with general formula,  $Ma_2b_2$  (where both  $a$  and  $b$  are monodentate) can have *cis*- and *trans*-isomers.



(ii) Complexes with general formula,  $Ma_2bc$  can have *cis*- and *trans*-isomers.

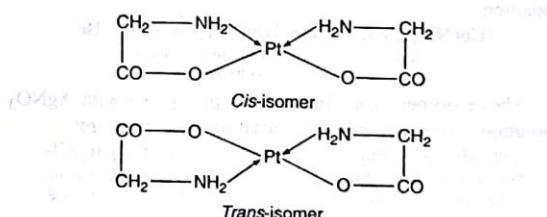


(iii) Complexes with general formula,  $Mabcd$  can have three isomers.



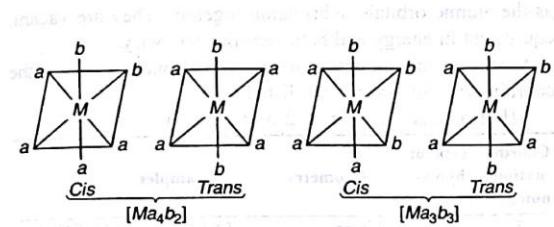
**Example :**  $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{NO}_2)(\text{py})]\text{NO}_2$ .

(iv) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism. For example, platinum glycinate complex,  $[\text{Pt}(\text{Gly})_2]$ , exhibits geometrical isomerism.



Octahedral complexes of the type  $Ma_4b_2$  and  $Ma_3b_3$  exhibit geometrical isomerism.

## Coordination Compounds and Organometallics



**Example :**  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

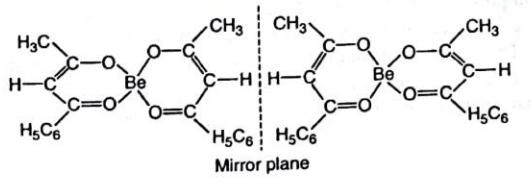
Octahedral complexes of general formula,  $Mabdef$ , can have fifteen geometrical isomers.

- Note:**
- Geometrical isomerism is not observed in complexes of coordination number 2 and 3.
  - Geometrical isomerism is not observed in complexes of coordination number 4 of tetrahedral geometry.
  - The complexes of general formulae,  $Ma_3b$  or  $Mab_3$ , or  $Ma_4$ , of square planar geometry do not show geometrical isomerism.
  - The complexes of general formula,  $Ma_6$  and  $Ma_5b$ , of octahedral geometry do not show geometrical isomerism.

**(2) Optical isomerism :** A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers. The optical isomers are pair of molecules which are non-superimposable mirror images of each other. The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure. The isomer which rotates the plane of polarised light to right direction is termed **dextro** (*d*-form) while the isomer which rotates the plane of polarised light to left direction is termed **laevo** (*l*-form). The two optically active isomers are collectively called **enantiomers**. Enantiomers are mirror image to each other and their physical properties are different.

Optical isomerism is expected in tetrahedral complexes of the type  $Mabcd$  but no optical isomer has been isolated until now.

However, compounds containing two unsymmetrical bidentate ligands have been resolved into optical isomers and are known for Be(II), Zn(II) and B(III). For example, Bis-benzoylacetonato-beryllium(II) exhibits optical isomerism.



Optical isomers rarely occur in square planar complexes on account of the presence of axis of symmetry.

Optical isomerism is very common in octahedral complexes.

Octahedral complexes of general formulae,

$[Ma_2b_2c_2]^{n\pm}$ ,  $[Mabcdef]$ ,  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$ ,

(where AA = symmetrical bidentate ligands)

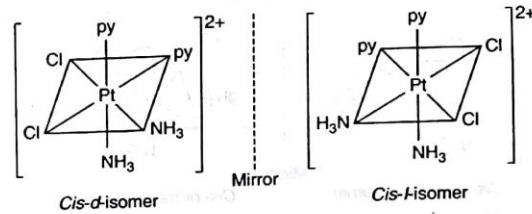
$[M(AA)_2ab]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$

(where AB unsymmetrical ligands)

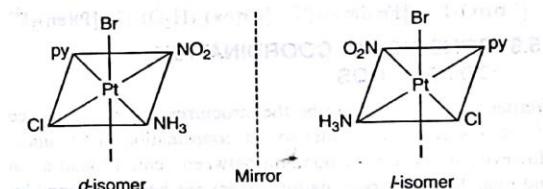
show optical isomerism.

**Examples :**

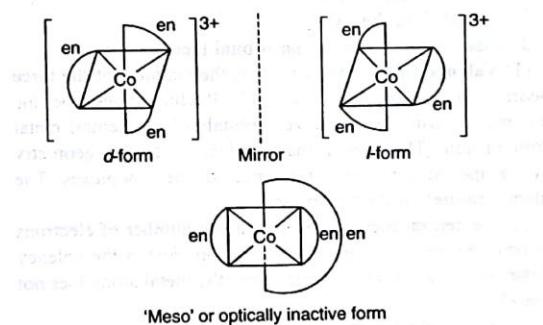
(a)  $[Ma_2b_2c_2]^{n\pm}$ ;  $[\text{Pt}(\text{py})_2(\text{NH}_3)_2\text{Cl}_2]^{2+}$



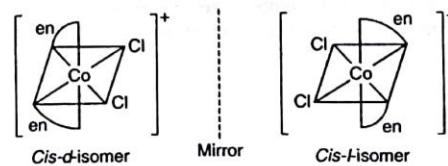
(b)  $[Mabcdef]$ :



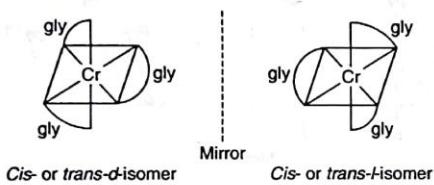
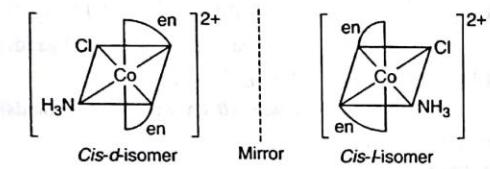
(c)  $[M(AA)_3]^{n\pm}$ ;  $[\text{Co}(\text{en})_3]^{3+}$



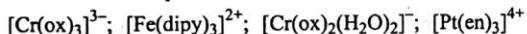
(d)  $[M(AA)_2a_2]^{n\pm}$ ;  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$



*Trans* form of  $[M(AA)_2a_2]^{n\pm}$  does not show optical isomerism.



Some more examples are :



## 15.6 BONDING IN COORDINATION COMPOUNDS

Werner was first to describe the structures and the existence of various types of isomerism in coordination compounds. However, the nature of bonding between central metal atom and ligands in the coordination sphere has been explained by the three well-known theories. These theories are :

1. Valence bond theory
2. Crystal field theory
3. Ligand field or molecular orbital theory

(1) **Valence bond theory** : It is the simplest of the three theories and was developed mainly by Pauling. It describes the bonding in terms of hybridized orbitals of the central metal atom or ion. The theory mainly deals with the geometry (*i.e.*, shape) and magnetic properties of the complexes. The salient features of the theory are:

(i) The central metal loses a requisite number of electrons to form the ion. The number of electrons lost is the valency of the resulting cation. In some cases, the metal atom does not lose electrons.

(ii) The central metal ion or atom (as the case may be) makes available a number of empty *s*-, *p*- and *d*-atomic orbitals equal to its coordination number. These vacant orbitals hybridize together to form hybrid orbitals which are same in the number

as the atomic orbitals hybridizing together. They are vacant, equivalent in energy and have definite geometry.

Some of the common hybridized orbitals met in the coordination compounds are listed below:

(For details see chapter 2 on valency.)

Coordination number	Type of hybridization	Geometry	Examples
2	$sp$	Linear	$[Ag(NH_3)_2]^+$ ; $[Ag(CN)_2]^-$
3	$sp^2$	Trigonal planar	$[HgI_3]^-$
4	$sp^3$	Tetrahedral	$Ni(CO)_4$ , $[Ni(X_4)]^{2-}$ $[ZnCl_4]^{2-}$ , $[CuX_4]^{2-}$ where $X = Cl^-$ , $Br^-$ , $I^-$
	$dsp^2$	Square planar	$[Ni(CN)_4]^{2-}$ , $[Cu(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$
5	$dsp^3$	Trigonal bipyramidal	$Fe(CO)_5$ , $[CuCl_5]^{3-}$
	$sp^3d$	Square pyramidal	$[SbF_5]^{2-}$
6	$d^2sp^3$ or $sp^3d^2$	Octahedral (Inner orbital) (Outer orbital)	$[Cr(NH_3)_6]^{3+}$ ; $[Fe(CN)_6]^{3-}$ $[Fe(H_2O)_6]^{2+}$ ; $[Ni(NH_3)_6]^{2+}$ $[FeF_6]^{3-}$

(iii) The non-bonding electrons of the metal occupy the inner orbitals. These are grouped in accordance with Hund's rule, however, under the influence of some strong ligands, there may be some re-arrangement of electrons in the atomic orbitals (against Hund's rule). The *d*-orbitals participating in this process of hybridization may be either  $(n-1)d^2sp^3$  or  $nsp^3d^2$ . The complexes thus formed are referred to as inner or low spin and outer or high spin complexes, respectively.

(iv) The ligands have at least one  $\sigma$ -orbital containing a lone pair of electrons. Vacant hybrid orbitals of the metal atom or ion overlap with the  $\sigma$ -orbitals containing lone pair or electrons of the ligands to form  $M \leftarrow$  ligand  $\sigma$ -bond. This bond is called coordinate bond (a special type of covalent bond) and possesses a considerable amount of polarity.

(v) It is possible to predict the magnetic properties of the complex if the geometry of the complex ion (*or vice-versa*) is known. If the complex contains unpaired electrons, it is paramagnetic in nature whereas if it does not contain unpaired electrons, *i.e.*, all are paired, the complex is diamagnetic in nature. Complexes having unpaired electron are coloured.

The number of unpaired electrons and the geometries of the complex ions having central metal ion with configurations  $d^1$  to  $d^9$  are related to each other as shown below:

The shapes and magnetic nature of some of the common complexes of metals of 3d-series have been described on the basis of valence bond theory in the table on the next page:

$d^x$ Configuration	Number of unpaired electrons for different geometries			
	Tetrahedral ( $sp^3$ )	Square planar ( $dsp^2$ )	Octahedral	
			Inner orbitals ( $d^2sp^3$ )	Outer orbitals ( $sp^3d^2$ )
$d^1$	1	1	1	1
$d^2$	2	2	2	2
$d^3$	3	3	3	3
$d^4$	4	4	2	4
$d^5$	5	3	1	5
$d^6$	4	2	0	4
$d^7$	3	1	1	3
$d^8$	2	0	(Shifted to higher orbits) 0	2
$d^9$	1	1	(2 electrons shifted) 1 (3 electrons shifted)	1

**Limitations of valence bond theory :** The valence bond theory was fairly successful in explaining qualitatively the geometry and magnetic properties of complexes. However, it has a number of limitations.

(i) The theory does not offer any explanation about the spectra of complex (why most of the complexes are coloured).

(ii) Sometimes the same metal ion assumes different geometry when formation of complex ion takes place. The theory is unable to explain why at one time the electrons are rearranged against the Hund's rule while at other times the electronic configuration is not disturbed.

(iii) The theory does not offer an explanation for the existence of inner-orbital and outer-orbital complexes.

(iv) The theory does not explain why certain complexes are labile while others are inert.

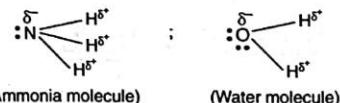
(v) In the formation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , one electron is shifted from  $3d$  to  $4p$ -orbital. The theory is silent about the energy availability for shifting such an electron. Such an electron can be easily lost, then why  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex does not show reducing properties.

(vi) The changes in energies of the metal orbitals on formation of complex are difficult to calculate mathematically.

**(2) Crystal field theory :** Crystal field theory was proposed by H. Bethe (1929) and Van Vleck (1932) and was originally applied to ionic crystals to explain their optical properties and is, therefore, called **crystal field theory**. However, this theory was applied to the study of coordination compounds in 1950s. The valence bond theory represents the ligand metal bond as covalent, with an electron pair, shared

between the metal and the ligand donor atom. This theory is frequently used but it is not adequate to explain properties of complexes such as colour and magnetism. Currently, the bonding in coordination complexes is usually described by crystal field theory or ligand field theory. This theory accounts for more satisfactory explanation for the properties of complexes especially colour and magnetism. The main points of the theory are:

(i) According to crystal field theory, the bonding in complex ions is purely electrostatic. This theory regards the ligand atoms of ionic ligands such as  $\text{F}^-$ ,  $\text{Cl}^-$  or  $\text{CN}^-$  as negative point charges (also called point charges) and if the ligand molecules are neutral, these are regarded as point dipoles or simply dipoles, the negative end pointing towards central metal ion.



(ii) The complex is regarded as a combination of a central metal ion surrounded by ligands which act as point charges or point dipoles. The arrangement of ligands around the central metal ion or atom is such that the repulsion between these negative points or dipoles is minimum.

(iii) Interactions between positively charged nucleus of the central metal ion or atom and the negatively charged ligands are of two types:

**Geometry (shape) and magnetic nature of some of the complexes  
(Application of valence bond theory)**

Atom / ion / complex (1)	Configuration (2)	Oxidation state of metal (3)	Type of hybridization (4)	Geometry shape (5)	No. of unpaired electrons (6)	Magnetic nature (7)
Ni <sup>2+</sup> ( $d^8$ )		+2			2	Paramagnetic
[NiCl <sub>4</sub> ] <sup>2-</sup>		+2	$sp^3$	Tetrahedral	2	Paramagnetic
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>		+2	$dsp^2$	Square planar	0	Diamagnetic
Ni		0	$dsp^2$		2	Paramagnetic
Ni(CO) <sub>4</sub>		0	$sp^3$	Tetrahedral	0	Diamagnetic
[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>		+2	$sp^3d^2$ (Outer)	Octahedral	2	Paramagnetic
Mn <sup>2+</sup> ( $d^5$ )		+2			5	Paramagnetic
Mn(CN) <sub>6</sub> <sup>4-</sup>		+2	$d^2sp^3$ (Inner)	Octahedral	1	Paramagnetic
[MnCl <sub>4</sub> ] <sup>2-</sup>		+2	$sp^3$	Tetrahedral	5	Paramagnetic
Cu <sup>2+</sup> ( $d^9$ )		+2			1	Paramagnetic
[CuCl <sub>4</sub> ] <sup>2-</sup>		+2	$sp^3$	Tetrahedral	1	Paramagnetic
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>		+2	$dsp^2$	Sqaure planar	1	Paramagnetic

Contd. ...

(1)	(2)	(3)	(4)	(5)	(6)	(7)
$\text{Cr}^{3+}(d^3)$	3d      4s      4p 	+3			3	Paramagnetic
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$d^2\text{sp}^3$ 	+3	$d^2\text{sp}^3$ (Inner)	Octahedral	3	Paramagnetic
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	4d $\text{sp}^3\text{d}^2$ 	+3	$\text{sp}^3\text{d}^2$ (Outer)	Octahedral	3	Paramagnetic
$\text{Co}^{3+}(d^6)$		+3			4	Paramagnetic
$[\text{CoF}_6]^{3-}$	$\text{sp}^3\text{d}^2$ 	+3	$\text{sp}^3\text{d}^2$ (Outer)	Octahedral	4	Paramagnetic
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Rearrangement $d^2\text{sp}^3$ 	+3	$d^2\text{sp}^3$ (Inner)	Octahedral	0	Diamagnetic
$\text{Co}^{2+}(d^7)$		+2			3	Paramagnetic
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$\text{sp}^3\text{d}^2$ 	+2	$\text{sp}^3\text{d}^2$ (Outer)	Octahedral	3	Paramagnetic
$\text{Fe}^{2+}(d^6)$		+2			4	Paramagnetic
$[\text{Fe}(\text{CN})_6]^{4-}$	Rearrangement $d^2\text{sp}^3$ 	+2	$d^2\text{sp}^3$ (Inner)	Octahedral	0	Diamagnetic
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$\text{sp}^3\text{d}^2$ 	+2	$\text{sp}^3\text{d}^2$ (Outer)	Octahedral	4	Paramagnetic
$[\text{Fe}(\text{NH}_3)_6]^{2+}$	Same	+2	$\text{sp}^3\text{d}^2$ (Outer)	Octahedral	4	Paramagnetic
$\text{Fe}^{3+}(d^5)$		+3			5	Paramagnetic
$[\text{Fe}(\text{CN})_6]^{3-}$	$d^2\text{sp}^3$ 	+3	$d^2\text{sp}^3$ (Inner)	Octahedral	1	Paramagnetic
Fe		0			4	Paramagnetic
$\text{Fe}(\text{CO})_5$	$\text{dsp}^3$ 	0	$\text{dsp}^3$ (Inner)	Trigonal bipyramidal	0	Diamagnetic

(a) The attractive forces arise due to the positive metal ion and the negatively charged ligands or the negative end of a polar neutral molecules. For example, in the case of complex ion,  $[Fe(CN)_6]^{3-}$ , the interactions are between  $Fe^{3+}$  ion and negatively charged  $CN^-$  ions whereas in the complex;  $[Cr(NH_3)_6]^{3+}$ , the interactions are between  $Cr^{3+}$  ion and negatively charged ends of ammonia molecules. These attractive forces bind the ligands to the metal ion. The bonds between metal and the surrounding ligands are purely ionic. This theory does not consider any orbital overlapping.

(b) The repulsive forces arise between the lone pairs on the ligands and electrons in the  $d$ -orbitals of the metal or atom. The crystal field theory mainly focuses on these repulsive forces. These forces are responsible for causing a considerable effect on the relative energies of the  $d$ -orbitals of the central metal ion or atom.

(iv) In a free transition metal or ion, there are five  $d$ -orbitals which are designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The five  $d$ -orbitals are divided into two sets depending on the nature of their orientation in space.

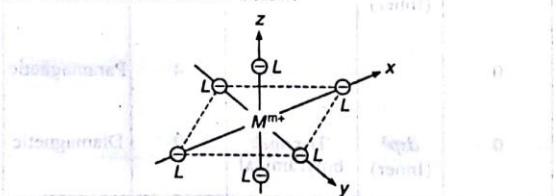
(a) The three  $d$ -orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) which orient in the regions between the coordinate axes are designated as  $t_{2g}$  orbitals (pronounced as "t-two-g").  $t_{2g}$ -orbitals are three-fold degenerate. These are non-axial orbitals.

(b) The other two orbitals ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) which orient along the axes are called  $e_g$  orbitals (pronounced as "e-g").  $e_g$  orbitals are two fold degenerate. These are also called axial-orbitals.

[The names  $t_{2g}$  and  $e_g$  are derived from spectroscopic terms.]

In a free transition metal ion or atom, all the five  $d$ -orbitals have same energy, i.e., they are degenerate. However, when the ligands approach the central metal ion or atom, the electrons of the  $d$ -orbitals of the central metal ion or atom are repelled by lone pairs of the ligands. As a result of these interactions, the degeneracy of  $d$ -orbitals of the metal ion is lost depending on the orientation of ligands in space. The  $d$ -orbitals split into two sets of orbitals having different energies. This is called crystal field splitting. It is the basis of crystal field theory. The extent of splitting depends on the number of ligands and their position around the metal atom or ion. The splitting is different in different structures with different coordination numbers.

**Splitting of  $d$ -orbitals in octahedral complexes :** Let us consider an octahedral complex,  $[M L_6]^{n+}$ , in which the central metal ion is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown below.



The electrons in  $d$ -orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. This repulsion increases the energy of all the five  $d$ -orbitals. If all the ligands approaching the metal cation are at an equal distance from each of  $d$ -orbitals (i.e., the ligand field is spherically symmetrical), the energy of each of the five  $d$ -orbitals increases by the same amount, i.e., all the  $d$ -orbitals remain degenerate, although they possess higher energy. However, this is not possible as it is only hypothetical situation.

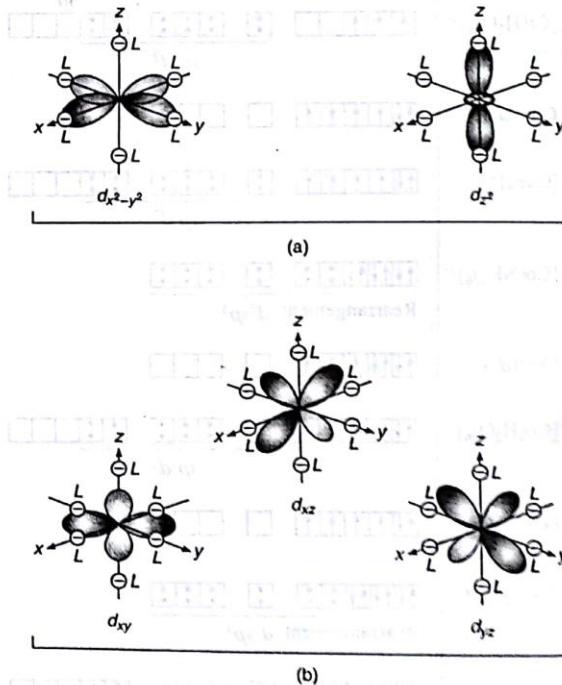
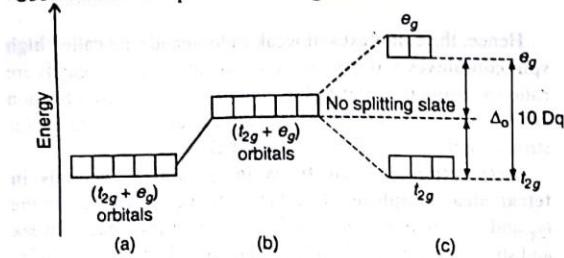


Fig. 15.1 The shapes of the five  $d$ -orbitals and their orientations with respect to an octahedral array of charged ligands

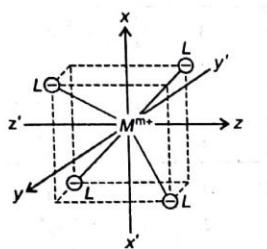
Since the lobes of two  $e_g$  orbitals lie in the path of approaching ligands see, Fig. 15.1 (a), the electrons in these orbitals experience greater force of repulsion than those in  $t_{2g}$  orbitals whose lobes are directed in space between the path of the ligands see Fig 15.1 (b), i.e., energy of  $e_g$  orbitals is increased while that of  $t_{2g}$  orbitals is decreased.

Thus, an energy difference exists between two sets of orbitals. This energy difference is called **crystal field splitting energy** and is represented by  $\Delta_O$  (the subscript O stands for octahedral). It measures the crystal field strength of the ligands. The crystal field splitting occurs in such a way that average energy of the  $d$ -orbitals does not change.



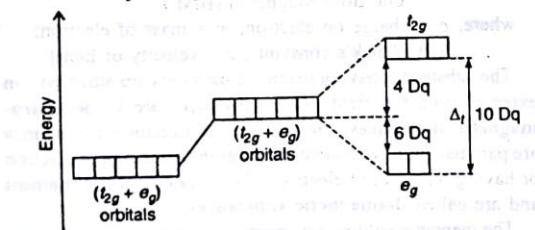
**Fig. 15.2** Crystal field splitting of  $d$ -orbitals in an octahedral complex (a) Five degenerate  $d$ -orbitals of free metal cation (b) Hypothetical degenerate  $d$ -orbitals at higher energy level under spherically symmetrical ligand field (c) Splitting of  $d$ -orbitals under the influence of ligands.

Thus, three orbitals lie at an energy that is  $\frac{2}{5} \Delta_O$  below the average  $d$ -orbital energy and two  $d$ -orbitals lie at an energy



$\frac{3}{5} \Delta_O$  above the average energy. The energy gap between  $t_{2g}$  and  $e_g$  sets is also denoted by  $10 \text{ Dq}$ . Energy of  $t_{2g}$  orbitals is  $4 \text{ Dq}$  less than that of hypothetical degenerate  $d$ -orbitals and that of  $e_g$  orbitals is  $6 \text{ Dq}$  above that of the hypothetical degenerate  $d$ -orbitals. Thus,  $t_{2g}$  set loses an energy equal to  $0.4 \Delta_O$  or  $4 \text{ Dq}$  while  $e_g$  set gains an energy equal to  $0.6 \Delta_O$  or  $6 \text{ Dq}$ .

**Crystal field splitting in tetrahedral complexes :** The tetrahedral arrangement of four ligands surrounding the metal ion  $M^{m+}$  may be depicted as shown in Fig. 15.3.



**Fig. 15.3** Crystal field splitting of  $d$ -orbitals in a tetrahedral complex

The three  $d$ -orbitals, i.e.,  $t_{2g}$  orbitals are close to the approaching ligands. As a result of this, the  $t_{2g}$  electrons suffer more repulsion than  $e_g$  electrons. The energy of  $t_{2g}$  orbitals

increases more than  $e_g$  orbitals. The splitting is shown in Fig. 15.3.

The energy gap between two sets of orbitals is designated as  $\Delta_t$  (The subscript  $t$  indicates tetrahedral complex). It is observed that  $\Delta_t$  is considerably less than  $\Delta_O$ . It has been found that,

$$\Delta_t = \frac{4}{9} \Delta_O$$

**Spectrochemical series :** For any given metal cation, the magnitude of crystal field splitting energy depends on the nature of the ligands. The greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it. The ligands which affect only a small degree of crystal field splitting are termed **weak field ligands** while those which affect a large splitting are called **strong field ligands**.

When the ligands are arranged in order of the magnitude of crystal field splitting, the arrangement, thus, obtained is called **spectrochemical series**.

$$\begin{aligned} I^- &> Br^- < Cl^- < NO_3^- < F^- < OH^- < OX^{2-} < H_2O < py \\ &\quad \text{Weak field ligands} \\ &= NH_3 < en < dip < \sigma\text{-Phen} < NO_2^- < CN^- < CO \\ &\quad \text{Strong field ligands} \end{aligned}$$

From the above arrangement it is clear that ligands before  $H_2O$  such as  $I^-$ ,  $NO_3^-$ ,  $OH^-$ , etc., are weak field ligands while the ligands after  $H_2O$  such as  $NO_2^-$ ,  $CN^-$ ,  $CO$ , etc., are strong field ligands. Stronger field ligands cause greater crystal splitting i.e.,  $\Delta_O$  value for octahedral complex is high.

Besides the nature of ligands, there are some other factors which affect the crystal field splitting energy. These factors are:

(i) **The identity of the metal :** The crystal field splitting,  $\Delta_O$ , is about 50 per cent higher for the second transition series compared to the first whereas the third series is about 25 per cent higher than second. There is small increase in the crystal field splitting along each series.

(ii) **The oxidation state of the metal :** Generally, the higher the oxidation state of the metal, the greater the crystal field splitting. For example, most of the cobalt (II) complexes have low values of  $\Delta$  whereas all cobalt (III) complexes have high values of  $\Delta$ .

(iii) **The number of ligands :** The crystal field splitting for a tetrahedral environment is about  $4/9$  that for an octahedral environment.

**Distribution of  $d$ -electrons in  $t_{2g}$  and  $e_g$  orbitals in octahedral complexes :** The distribution of  $d$ -electrons in  $t_{2g}$  and  $e_g$  orbitals takes place on the basis of the nature of ligands. Two cases may arise.

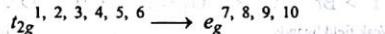
(i) **When the ligands are weak :** Under the influence of weak ligands, the energy difference,  $\Delta_O$ , between  $t_{2g}$  and  $e_g$  sets is relatively small and hence all the five  $d$ -orbitals may be supposed to be degenerate, i.e., all the  $d$ -orbitals have nearly the same energy and the distribution of electrons in  $t_{2g}$  and  $e_g$

sets occurs according to Hund's rule, i.e., electrons will pair up only when each of the five  $d$ -orbitals is at least singly occupied. When the ligands are weak, the first three electrons numbered 1, 2, 3 go to  $t_{2g}$  set, those numbered 4, 5 go to  $e_g$  set, those numbered 6, 7, 8 go to  $t_{2g}$  set and the remaining two electrons numbered 9, 10 will occupy  $e_g$  set. This can be shown as:



In complexes of weak ligands,  $\Delta_O$  is less than  $P$  ( $P$  is called average pairing energy which is the energy required to pair two electrons in the same orbital).  $\Delta_O$ , the octahedral crystal field splitting energy, tends to force as many electrons to  $t_{2g}$  set while  $P$  tends to prevent the electrons to pair in the  $t_{2g}$  level.

**(ii) When the ligands are strong :** Under the influence of strong ligands, the energy difference between  $t_{2g}$  and  $e_g$  sets is relatively high and thus the distribution of  $d$  electrons in  $t_{2g}$  and  $e_g$  sets does not obey Hund's rule. The first electrons numbered 1, 2, 3, 4, 5, 6 will go to  $t_{2g}$  set and remaining four electrons numbered 7, 8, 9 and 10 will go to  $e_g$  set.



For these complexes,  $\Delta_O$  is higher than  $P$ . The above points are summarised in the following table:

$d^x$ ions	Strong field (Low spin) complexes $\Delta_O > P$			Weak field (High spin) complexes $\Delta_O < P$			Common examples
	Config- uration	No. of unpaired electrons	Spin	Config- uration	No. of unpaired electrons	Spin	
$d^1$	$t_{2g}^1 e_g^0$	1	1/2	$t_{2g}^1 e_g^0$	1	1/2	Ti <sup>3+</sup>
$d^2$	$t_{2g}^2 e_g^0$	2	1	$t_{2g}^2 e_g^0$	2	1	V <sup>3+</sup>
$d^3$	$t_{2g}^3 e_g^0$	3	3/2	$t_{2g}^3 e_g^0$	3	3/2	Cr <sup>3+</sup>
$d^4$	$t_{2g}^4 e_g^0$	2	1	$t_{2g}^3 e_g^1$	4	2	Mn <sup>3+</sup>
$d^5$	$t_{2g}^5 e_g^0$	1	1/2	$t_{2g}^3 e_g^2$	5	5/2	Mn <sup>2+</sup> , Fe <sup>3+</sup>
$d^6$	$t_{2g}^6 e_g^0$	0	0	$t_{2g}^4 e_g^2$	4	2	Fe <sup>2+</sup> , Co <sup>3+</sup>
$d^7$	$t_{2g}^6 e_g^1$	1	1/2	$t_{2g}^5 e_g^2$	3	3/2	Co <sup>2+</sup>
$d^8$	$t_{2g}^6 e_g^2$	2	1	$t_{2g}^6 e_g^2$	2	1	Ni <sup>2+</sup>
$d^9$	$t_{2g}^6 e_g^3$	1	1/2	$t_{2g}^6 e_g^3$	1	1/2	Cu <sup>2+</sup>
$d^{10}$	$t_{2g}^6 e_g^4$	0	0	$t_{2g}^6 e_g^4$	0	0	Zn <sup>2+</sup>

The following conclusions are derived from the table:

(i) The distribution of electrons of  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$  and  $d^{10}$  in  $t_{2g}$  and  $e_g$  sets for both strong and weak octahedral ligands fields is the same.

(ii) For each of  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  there is difference in the arrangement of electrons in weak and strong ligands field.

(iii) Weak field complexes of  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  ions have greater number of unpaired electrons than those of strong field complexes and thus, the resultant spins of weak field complexes have higher value than strong field complexes.

Hence, the complexes of weak field ligands are called **high spin complexes** and the complexes of strong field ligands are called **low spin complexes**. Calculations show that coordination entities with four to seven  $d$  electrons are more stable for strong field as compared to weak field cases.

**Distribution of  $d$  electrons in  $t_{2g}$  and  $e_g$  orbitals in tetrahedral complexes.** The distribution of  $d$ -electrons in the  $t_{2g}$  and  $e_g$  sets in a tetrahedral complex in presence of weak and strong ligands field has been shown in the following table:

$d^x$ ions	Weak field (High spin) complexes			Strong field (Low spin) complexes			Spin
	Config- uration	No. of unpaired electrons	Spin	Config- uration	No. of unpaired electrons		
$d^1$	$t_{2g}^0 e_g^1$	1	1/2	$t_{2g}^0 e_g^1$	1	1/2	
$d^2$	$t_{2g}^0 e_g^2$	2	1	$t_{2g}^0 e_g^2$	2	1	
$d^3$	$t_{2g}^1 e_g^2$	3	$1\frac{1}{2}$	$t_{2g}^0 e_g^3$	1	1/2	
$d^4$	$t_{2g}^2 e_g^2$	4	2	$t_{2g}^0 e_g^4$	0	0	
$d^5$	$t_{2g}^2 e_g^2$	5	$2\frac{1}{2}$	$t_{2g}^1 e_g^4$	1	1/2	
$d^6$	$t_{2g}^3 e_g^3$	4	2	$t_{2g}^2 e_g^4$	2	1	
$d^7$	$t_{2g}^3 e_g^4$	3	$1\frac{1}{2}$	$t_{2g}^3 e_g^4$	3	$1\frac{1}{2}$	
$d^8$	$t_{2g}^4 e_g^4$	2	1	$t_{2g}^4 e_g^4$	2	1	
$d^9$	$t_{2g}^5 e_g^4$	1	1/2	$t_{2g}^5 e_g^4$	1	1/2	
$d^{10}$	$t_{2g}^6 e_g^4$	0	0	$t_{2g}^6 e_g^4$	0	0	

**Magnetic nature :** The transition metal complexes containing one or more unpaired electrons possess a definite value of magnetic moment. An unpaired electron because of its spin is equivalent to an electric current flowing in a circular conductor. Hence, it behaves as a magnet.

[The magnetic moment is expressed as :

$$\mu = \frac{e\hbar}{4\pi mc} = 9.274 \times 10^{-21} \text{ erg gauss}^{-1}$$

= one Bohr Magnetons (B.M.)

where,  $e$  = charge on electron;  $m$  = mass of electron;

$\hbar$  = Planck's constant;  $c$  = velocity of light]

The substances having magnetic moments are attracted in external magnetic field. Such substances are termed **paramagnetic substances**. Most of the coordination compounds are paramagnetic. The substances having no unpaired electron or having only paired electrons show zero magnetic moment and are called **diamagnetic substances**.

The magnetic nature or magnetic moment of a coordination compound, thus, depends on the number of unpaired electrons. The magnetic moment is approximately given by the relation,

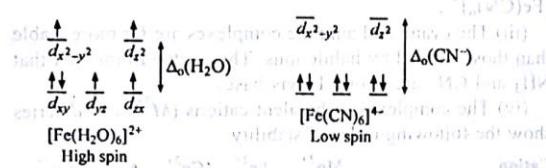
$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)} \text{ B.M.}, \text{ where } n \text{ is the number of unpaired electrons. This relationship is used to}$$

calculate the number of unpaired electrons in a complex ion. The values of  $n$  calculated by applying the above formula for different magnetic moments are given in the following table:

Magnetic moment (B.M.)	Number of unpaired electrons
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

The actual number of unpaired electrons in a complex can be found by magnetic measurements and in general, experimental findings support predictions based on crystal field splitting. However, a distinction between low and high spin complexes can be made only if the metal ion contains more than three and less than eight  $d$ -electrons. The high spin complex,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  has four unpaired electrons and is paramagnetic, whereas the low spin complex,  $[\text{Fe}(\text{CN})_6]^{4-}$  has no unpaired electrons and is diamagnetic.

**Colour :** A substance appears coloured because it absorbs light at specific wavelengths in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmits or



reflects the rest of the wavelength. Each wavelength of visible light represents a different colour. White light, such as sunlight, is a combination of all colours; an object that absorbs all the visible light appears black. The following table shows the relationship of wavelength absorbed to observed colour.

Wavelength absorbed (nm)	400	450	490	570	600	650	700
Colour observed	(violet)	(blue)	(blue-green)	(yellow)	(orange)	(red)	Green

When the energy of the photon ( $h\nu$ ) is equal to the difference between the lower and higher  $d$ -orbital energy levels, an electron is promoted from a lower to higher level. If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same as the incident light white and the ion appears colourless.

Spectroscopic analysis offers the best means of measuring crystal field splitting. The  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion provides a simple example, because  $\text{Ti}^{3+}$  has only one 3  $d$ -electron.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion absorbs light in the visible region. The wavelength corresponding to maximum absorption is 498 nm. This enables us to calculate the crystal field splitting.

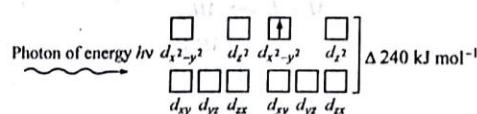
$$\text{Energy required to excite one ion} = \Delta = h\nu = h \times \frac{c}{\lambda}$$

where  $h$  = Planck's constant  $= 6.63 \times 10^{-34}$  Js  
and  $c$  = velocity of light  $= 3.00 \times 10^8$  ms $^{-1}$

$$\Delta = \frac{(6.63 \times 10^{-34}) \times (3.00 \times 10^8)}{498 \times 10^{-9}} \text{ J}$$

$$= 3.99 \times 10^{-19} \text{ J}$$

This is the energy for one ion to excite. Thus, the energy required for one mole of ions,  $\Delta = 3.99 \times 10^{-19} \times 6.02 \times 10^{23} = 240,000 \text{ J mol}^{-1} = 240 \text{ kJ mol}^{-1}$



Experiments with coordination complexes have revealed that for a given metal ion, some ligands cause a small energy separation of the  $d$ -orbitals, whereas others cause a large separation, i.e., different ligands may bring different colours to the complex ions of the same metal ion. For example, the data for several cobalt, (III) complexes are presented in the following table:

The colours of some complexes of  $\text{Co}^{3+}$  ion.

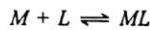
Complex ion	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of complex observed
$[\text{Co}(\text{F})_6]^{3-}$	700	Red	Green
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	600	Yellow	Dark green
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	600	Yellow	Blue-green
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow-orange
$[\text{Co}(\text{en})_3]^{3+}$	470	Blue	Yellow-orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale-yellow

The absorption maxima among the listed complexes ranges from 700 nm for  $[\text{CoF}_6]^{3-}$  to 310 nm for  $[\text{Co}(\text{CN})_6]^{3-}$ . The ligands change from member to member in the series and it is concluded that the energy of light absorbed by the complex is related to different crystal field splitting,  $\Delta_O$ , caused by different ligands. Fluoride ion causes the smallest splitting of the  $d$ -orbitals among the complexes listed, whereas cyanide causes the largest splitting.

Spectra of complexes of other metals provide similar results. This supports the spectrochemical series. The ability of crystal field theory to explain differences in the colour of transition metal complexes is one of the strengths of this theory.

### 15.7 STABILITY OF COORDINATION COMPOUNDS IN SOLUTIONS

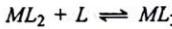
A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex,  $ML_n$  ( $M$  = central metal cation,  $L$  = monodentate ligand and  $n$  = coordination number of metal ion) may be supposed to take place by the following  $n$  consecutive steps:



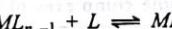
$$K_1 = \frac{[ML]}{[M][L]}$$



$$K_2 = \frac{[ML_2]}{[ML][L]}$$



$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$



$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

$K_1, K_2, K_3, \dots, K_n$  are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from  $K_1$  to  $K_n$ .

The overall stability constant,  $K$ , is given as:



$$K = K_1 \cdot K_2 \cdot K_3 \cdots K_n = \frac{[ML_n]}{[M][L]^n}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively,  $1/K$  values called **instability constant** explain the dissociation of the complex into metal ion and ligands in the solution.

The values of stability constants for some of the complexes are given below:

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	$4.5 \times 10^{11}$
$[Ag(NH_3)_2]^+$	$1.6 \times 10^7$
$[Co(NH_3)_6]^{2+}$	$1.12 \times 10^6$
$[Co(NH_3)_6]^{3+}$	$5.0 \times 10^{33}$
$[AgCl_2]^-$	$1.11 \times 10^5$

$[AgBr_2]^-$	1.28 $\times 10^7$
$[Ag(CN)_2]^-$	$1.0 \times 10^{22}$
$[Cu(CN)_4]^{2-}$	$2.0 \times 10^{27}$
$[Fe(CN)_6]^{3-}$	$7.69 \times 10^{43}$

From the above values, some conclusions are drawn :

(i) The values of stability constants differ widely depending on the nature of the metal ion and the ligand. In general, **higher the charge density on the central ion, the greater is the stability of its complexes, i.e., the higher value of charge**

**radius of the ion, the greater is the stability of its complexes. Electronegativity of the central ion influences the stability. The higher the electronegativity of the central ion, the greater is the stability of its complexes.**

The more basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and therefore, the greater is the stability of the complexes formed by it.

(ii) The higher the oxidation state of the metal, the more stable is the complex. The charge density of  $Co^{3+}$  ion is more than  $Co^{2+}$  ion and thus,  $[Co(NH_3)_6]^{3+}$  is more stable than  $[Co(NH_3)_6]^{2+}$ . Similarly,  $[Fe(CN)_6]^{3-}$  is more stable than  $[Fe(CN)_6]^{4-}$ .

(iii) The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that  $NH_3$  and  $CN^-$  are strong Lewis bases.

(iv) The complexes of bivalent cations ( $M^{2+}$ ) of  $3d$ -series show the following order of stability:

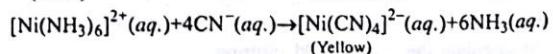
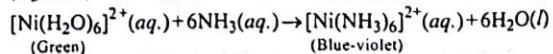
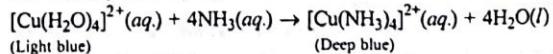
Cation	$Mn^{2+}$	$Fe^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$
Ionic size	0.91	0.83	0.82	0.78	0.69
Stability of the complex	decreases →				

(v) Chelating ligands form more stable complexes as compared to monodentate ligands.

### 15.8 PREPARATION OF COORDINATION COMPOUNDS

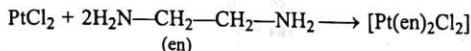
Coordination compounds are generally prepared by the application of the following methods:

**1. Ligand substitution reactions :** A reaction involving the replacement of the ligands attached to the central metal ion in the complex by other ligands is called a ligand substitution reaction. Transition metal ions in aqueous solution form complex ions by bonding with water molecules. These water molecules are then replaced by ligands to form the desired complex.

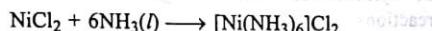


i.e., tetraamminecopper sulphate,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , is formed by addition of ammonia solution to copper sulphate solution and potassium tetracyanonickelate(II) is obtained by the addition of potassium cyanide solution to hexaamminenickel(II) sulphate solution.

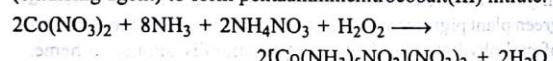
**2. Direct mixing of reagent :** Dichloro bis (ethylenediamine) platinum(II) is prepared by adding platinum chloride ( $\text{PtCl}_2$ ) to ethylenediamine.



Similarly, hexaamminenickel(II) chloride is obtained by direct reaction between solid nickel chloride ( $\text{NiCl}_2$ ) and liquid ammonia.



**3. Redox reactions :** In these reactions, either oxidation or reduction is involved. Cobalt(II) nitrate reacts with aqueous ammonium nitrate and aqueous ammonia in presence of  $\text{H}_2\text{O}_2$  (oxidising agent) to form pentaamminenitrocobalt(III) nitrate.

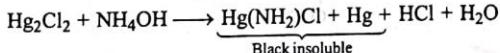
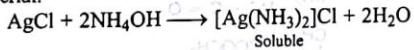


### 15.9 IMPORTANCE OF COORDINATION COMPOUNDS

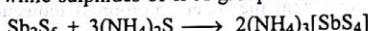
The complexes are of immense importance on account of their applications in various fields. During complex formation there are drastic changes in the properties of metal atom or ion and these changes in properties are made use of in the applications of metal complexes.

**1. Analytical chemistry :** Coordination compounds find their applications in both qualitative and quantitative methods of analysis.

(a) The separation of  $\text{Ag}^+$  from  $\text{Hg}_2^{2+}$  in the first group of analysis is based on the fact that while silver chloride is soluble in aqueous ammonia and  $\text{Hg}_2\text{Cl}_2$  forms a black insoluble material.



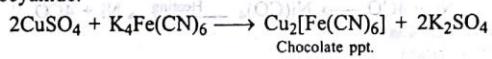
(b) The separation of II B group sulphides from II A group sulphides is based on the fact that sulphides of II B group form complex sulphides with yellow ammonium sulphide which are soluble while sulphides of II A group do not react.



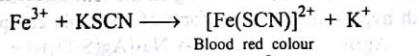
(c) The detection of  $\text{Cu}^{2+}$  is based on the formation of a blue tetraammine copper sulphate complex which gives a deep blue coloured solution.



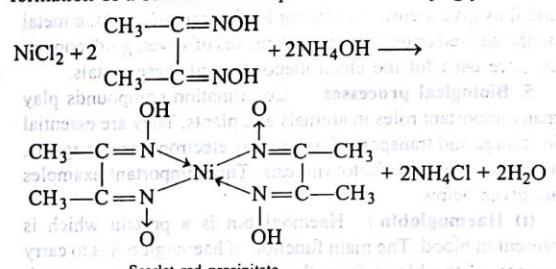
It also forms a chocolate coloured precipitate with potassium ferrocyanide.



(d)  $\text{Fe}^{3+}$  is detected by formation of a blood red coloured complex with KSCN.

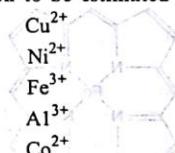


(e) The detection and estimation of  $\text{Ni}^{2+}$  is based on the formation of a scarlet red complex with dimethyl glyoxime.



(f) Many ligands (organic reagents) are used for the gravimetric estimation of a number of metal ions.

**Metal ion to be estimated      Organic reagent used**



Benzoin oxime

Dimethyl glyoxime

1,10-phenanthroline

8-hydroxyquinoline

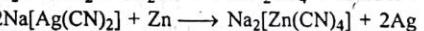
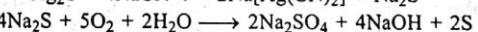
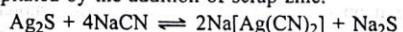
$\alpha$ -nitroso  $\beta$ -naphthol

(g) EDTA is used as a complexing agent in volumetric analysis of metal ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ .

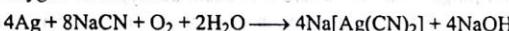
(h) The coordination compounds of the transition metals exhibit a variety of colours. This property is utilised in colorimetric analysis for the estimation of many metals.

(i) Other analytical applications of coordination compounds are oxidation-reduction indicators, estimation of hardness in water, sequestering reagents and solvent extraction.

**2. Metallurgical operations :** Silver and gold are extracted by the use of complex formation. Silver ore is treated with sodium cyanide solution with continuous passing of air through solution. Silver dissolves as a cyanide complex and pure silver is precipitated by the addition of scrap zinc.



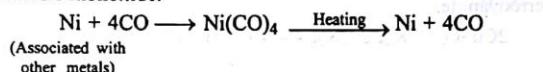
Native Ag and Au also dissolve in NaCN solution in presence of oxygen of the air.



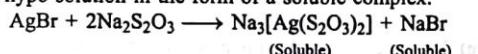
Ag and Au are precipitated by addition of scrap zinc.

Nickel is extracted by converting it into a volatile complex, nickel carbonyl by use of carbon monoxide (Mond's process).

The complex decomposes on heating again into nickel and carbon monoxide.



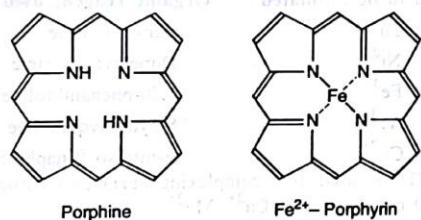
**3. Photography :** In photography, the image on the negative is fixed by dissolving all the remaining silver halides with hypo solution in the form of a soluble complex.



**4. Electroplating :** Metal complexes release metal slowly and thus give a uniform coating in electroplating of the metal on the desired object. Cyano complexes of silver, gold, copper, etc., are used for the electrodeposition of these metals.

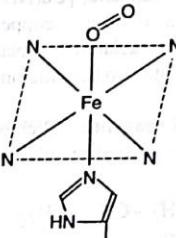
**5. Biological processes :** Coordination compounds play many important roles in animals and plants. They are essential in storage and transport of oxygen, as electron transfer agents, as catalysts and in photosynthesis. Three important examples are given below:

(i) **Haemoglobin :** Haemoglobin is a protein which is present in blood. The main function of haemoglobin is to carry oxygen in the blood from the lungs to the tissues where it delivers the oxygen molecules to myoglobin. The quadridentate macrocyclic ligand, the porphine molecule is an important



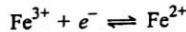
part of haemoglobin structure. The two  $\text{H}^+$  ions bonded to nitrogen atoms are displaced and the metal ion coordinate simultaneously with all the four nitrogen atoms. The complex formed from porphine is called **porphyrin**. The Fe-complex is called **heme**. Haemoglobin molecule consists four heme groups embedded in a protein molecule. The iron in the heme group has the oxidation number +2. It is coordinated to the four nitrogen donor atoms in the porphine group and also, to a nitrogen donor atom in a ligand group which is attached to the protein. The sixth ligand is a water molecule, which binds to the  $\text{Fe}^{2+}$  ion on the other side of the ring to complete the octahedral complex. Under these conditions, the haemoglobin molecule is called deoxyhaemoglobin and has a blue colour. The water ligand can be replaced readily by molecular oxygen to form red coloured oxyhaemoglobin. This haemoglobin flows from lungs to tissues where it is again deoxygenated.

The iron-heme complex is present in another class of proteins, called **cytochromes**. Cytochromes act as electron carriers which also play an essential part in metabolic processes.

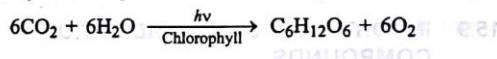


Oxy-haemoglobin

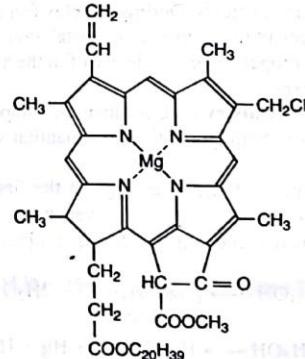
In cytochromes iron undergoes rapid reversible redox reactions.



(ii) **Chlorophyll :** The chlorophyll molecule, which plays an essential role in photosynthesis also contains the porphyrin ring but the metal ion there is  $\text{Mg}^{2+}$  rather than  $\text{Fe}^{2+}$ . It is a green plant pigment and acts as a photosensitizer in the synthesis of carbohydrates in plants. It is structurally similar to heme.



### COMPOUNDS



Structure of Chlorophyll

A molecule of chlorophyll can add one or two molecules of water axially. These coordinated water molecules through hydrogen bonding help the other chlorophyll molecules to associate with each other.

(iii) **Vitamin B<sub>12</sub>** : It is a complex of cobalt with a quadridentate ligand which is similar to porphyrin ligand of haemoglobin. It has been observed that vitamin B<sub>12</sub> is active only when cobalt is present in +1 oxidation state. It is a red crystalline substance which is slightly soluble in water. It is not found in plants but is found in all animal tissues. It is present mainly in milk, eggs, cheese and meat.

It is essential growth factor for many microorganisms.

**6. Plant growth :** Plants require a number of nutrients for healthy growth. Essential nutrients include a number of metals such as Fe, Zn, Cu, Mn, Mo, etc. For example, the deficiency of iron brings a disorder in plants known as **iron chlorosis**. This disorder affects the yield of fruit from citrus trees. Iron in +3 state present in the soil is mostly hydrolysed to form insoluble iron hydroxide  $\text{Fe(OH)}_3$ , which cannot be taken up by plants. To overcome iron deficiency, the complex  $\text{Fe(III)-EDTA}$  is added to the soil. This complex is soluble in water and readily enters the roots of trees and reach to various parts of the plants where it is converted into useful compounds.

**7. In medicinal field :** (i) The complex of calcium with EDTA is used for the treatment of lead poisoning. Lead readily replaces calcium in the complex and lead-EDTA complex is finally eliminated from the body in urine.

(ii) The platinum complex  $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  known as **cis-platin** is used as an antitumor agent in the treatment of cancer.

### 15.10 ORGANOMETALLIC COMPOUNDS

Compounds that contain at least one carbon-metal bond are called organometallic compounds. Zeise, in 1830, prepared the first organometallic compound by the action of ethylene on a solution of potassium chloroplatinate(II). In the last four decades, enormous work has been done in this field and many fascinating compounds have been synthesised and investigated. Grignard reagent,  $\text{RMgX}$  is a familiar example of organometallic compounds where  $R$  is an alkyl group. Diethyl zinc [ $\text{Zn}(\text{C}_2\text{H}_5)_2$ ], lead tetraethyl [ $\text{Pb}(\text{C}_2\text{H}_5)_4$ ], ferrocene [ $\text{Fe}(\text{C}_5\text{H}_5)_2$ ], dibenzene chromium [ $\text{Cr}(\text{C}_6\text{H}_6)_2$ ], metal carbonyls are other examples of organometallic compounds. The compounds of metalloids such as germanium and antimony and non-metallic elements such as boron and silicon are also included under this classification.

Organometallic compounds may be classified in three classes:

1. Sigma ( $\sigma$ ) bonded complexes,
2. Pi ( $\pi$ ) bonded complexes,
3. Complexes containing both  $\sigma$ - and  $\pi$ -bonding characteristics.

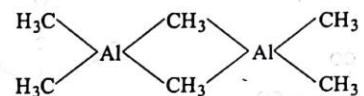
**1. Sigma bonded complexes :** In these complexes, the metal atom and carbon atom of the ligand are joined together by a sigma bond, i.e., the ligand contributes one electron and is, therefore, called one electron donor. Examples are:

(i) Grignard reagent,  $\text{R}-\text{Mg}-\text{X}$  where  $\text{R}$  is an alkyl or aryl group and  $\text{X}$  is a halogen.

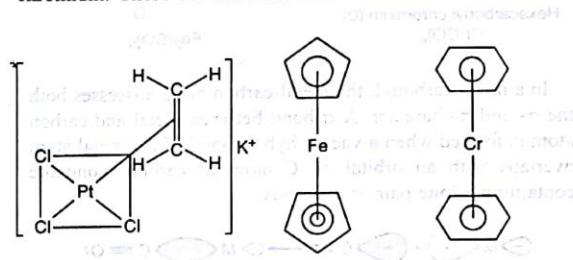
(ii) Zinc compounds of the formula  $\text{R}_2\text{Zn}$  such as  $(\text{C}_2\text{H}_5)_2\text{Zn}$ . This was first isolated by Frankland in 1849. Other similar compounds are  $(\text{CH}_3)_4\text{Sn}$ ,  $(\text{C}_2\text{H}_5)_4\text{Pb}$ ,  $\text{Al}_2(\text{CH}_3)_6$ ,  $\text{Al}_2(\text{C}_2\text{H}_5)_6$ ,  $\text{Pb}(\text{CH}_3)_4$ , etc.

$\text{Al}_2(\text{CH}_3)_6$  is a dimeric compound and has a structure similar to diborane,  $\text{B}_2\text{H}_6$ . It is an electron deficient compound and

two methyl groups act as bridges between two aluminium atoms.



**2.  $\pi$ -bonded organometallic compounds :** These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the  $\pi$  electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown here :

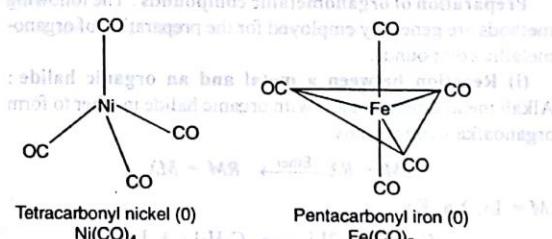


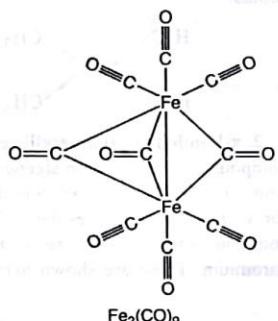
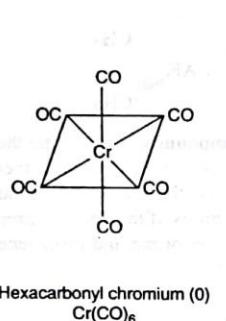
Zeise's salts  
 $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$   
 Ferrocene  
 $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$   
 Dibenzene chromium  
 $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$

The number of carbon atoms bound to the metal in these compounds is indicated by the Greek letter 'η' (eta) with a number. The prefixes  $\eta^2$ ,  $\eta^5$  and  $\eta^6$  indicate that 2, 5 and 6 carbon atoms are bound to the metal in the compound.

**3.  $\sigma$ - and  $\pi$ -bonded organometallic compounds :** Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. These compounds possess both  $\sigma$ - and  $\pi$ -bonding. The oxidation state of metal atoms in these compounds is zero. Carbonyls may be monomeric, bridged or polynuclear. Carbonyls are mainly formed by the transition metals of VIth, VIIth and VIIIth groups.

Some well known examples are :

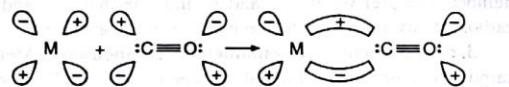




In a metal carbonyl, the metal-carbon bond possesses both the  $\sigma$ - and  $\pi$ -character. A  $\sigma$ -bond between metal and carbon atom is formed when a vacant hybrid bond of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.



Formation of  $\pi$ -bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding  $\pi^*$  orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon. It has been shown below:

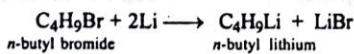
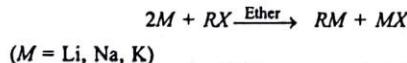


The  $\pi$ -overlap is perpendicular to the nodal plane of  $\sigma$ -bond.

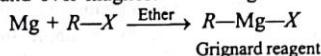
In olefinic complexes, the bonding  $\pi$ -orbital electrons are donated to the empty orbital of the metal atom and at the same time back bonding occurs from filled orbital of the metal atom to the antibonding  $\pi$ -orbital of the olefin.

**Preparation of organometallic compounds :** The following methods are generally employed for the preparation of organometallic compounds:

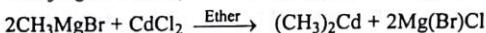
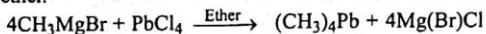
(i) **Reaction between a metal and an organic halide :** Alkali metal directly reacts with organic halide in ether to form organoalkali compounds.



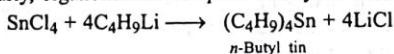
Grignard reagent is prepared when haloalkane in ether is allowed to stand over magnesium turnings for a few hours.



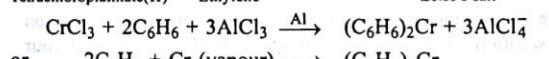
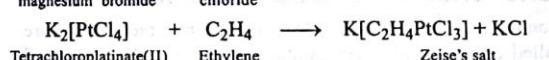
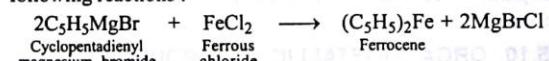
(ii) **By use of Grignard reagent :** Tetraalkyl derivatives of silicon, germanium, tin and lead are prepared by the reaction of Grignard reagent and the metal halide. The reaction is carried in ether.



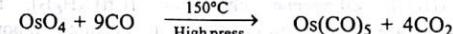
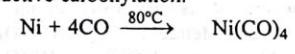
Similarly, organolithium compounds may be used.



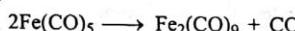
(iii)  $\pi$ -complexes such as ferrocene, Zeise's salt and dibenzene chromium are prepared by the application of following reactions :



(iv) Metal carbonyls are formed by direct carbonylation of the metal or reductive carbonylation.



Bridged carbonyls can be obtained by photolysis of monomeric carbonyls.



**Applications of organometallic compounds :** The applications of organometallic compounds are numerous. Some important ones are mentioned here:

1. Tetraethyl lead (TEL) is used as antiknock compound in gasoline.

2. Silicones are used as polymers of unique properties.

3. Organoalkali and Grignard reagents are used in many organic synthetic reactions.

4. The extraction and purification of nickel is based on the formation of organometallic compound,  $\text{Ni}(\text{CO})_4$ .

5. Organometallic compounds are used as homogeneous and heterogeneous catalysts. Wilkinson's catalyst,  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$  is used as homogeneous catalyst in the hydrogenation of alkenes. Zeigler Natta catalyst [ $\text{TiCl}_4$  and triethyl aluminium] acts as a heterogeneous catalyst in the polymerisation of ethylene into polyethylene.

### SOME SOLVED EXAMPLES

**Example 1.** What is the coordination number of the central metal ions in the following complexes?

- (i)  $[Cu(NH_3)_4]^{2+}$
- (ii)  $[Fe(C_2O_4)_3]^{3-}$
- (iii)  $[Pt(en)_2Cl_2]$
- (iv)  $[Mo(CN)_8]^{4-}$
- (v)  $[Fe(EDTA)]^-$
- (vi)  $[Pd(H_2O)_2(ONO)_2I_2]$

**Solution :** (i)  $NH_3$  is monodentate ligand.

Points of attachment with  $Cu^{2+} = 4 \times 1 = 4$

C.N. of  $Cu^{2+} = 4$

(ii)  $C_2O_4^{2-}$  is a bidentate ligand.

Points of attachment with  $Fe^{3+} = 3 \times 2 = 6$

C.N. of  $Fe^{3+} = 6$

(iii) 'en' is a bidentate ligand and  $Cl^-$  is a monodentate ligand.

Points of attachment with  $Pt^{2+} = 2 \times 2 + 2 \times 1 = 6$

C.N. of  $Pt^{2+} = 6$

(iv)  $CN^-$  is a monodentate ligand.

Points of attachment with  $Mo^{4+} = 8 \times 1 = 8$

C.N. of  $Mo^{4+} = 8$

(v) EDTA is a hexadentate ligand.

Points of attachment with  $Fe^{3+} = 6 \times 1 = 6$

C.N. of  $Fe^{3+} = 6$

(vi) Points of attachment with

$Pd^{4+} = 2 \times 1 + 2 \times 1 + 2 \times 1 = 6$

C.N. of  $Pd^{4+} = 6$

**Example 2.** Calculate the oxidation state of the central metal atom in the following:

- (i)  $[Co(NH_3)_5Cl]^{2+}$
- (ii)  $K_4[Fe(CN)_6]$
- (iii)  $[Co(NO_2)_2(py)_2(NH_3)_2]NO_3$
- (iv)  $Ni(CO)_4$
- (v)  $[Fe(EDTA)]^-$

**Solution :** (i)  $x + 5 \times (0) - 1 = +2$   
 $x = +2 + 1 = 3$  Oxi. state of Co = +3

(ii)  $4 \times (+1) + x + 6 \times (-1) = 0$   
or  $x = +6 - 4 = +2$  Oxi. state of Fe = +2

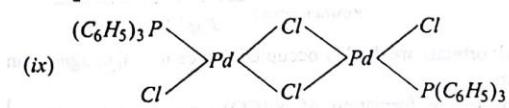
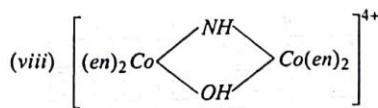
(iii)  $x + 2 \times (-1) + 2 \times (0) + 2 \times (0) - 1 = 0$   
or  $x = +2 + 1 = +3$  Oxi. state of Co = +3

(iv)  $x + 4 \times (0) = 0$   
or  $x = 0$  Oxi. state of Ni = 0

(v)  $x + 1 \times (-4) = -1$   
or  $x = +4 - 1 = +3$  Oxi. state of Fe = +3

**Example 3.** Give the IUPAC names of the following compounds:

- (i)  $K_3[Al(C_2O_4)_3]$
- (ii)  $[Pt(NH_3)_4(NO_2)Cl]SO_4$
- (iii)  $K_3[Cr(CN)_6]$
- (iv)  $[Co(NH_3)_5ONO]Cl_2$
- (v)  $[Cr(NH_3)_5CO_3]Cl$  [I.I.T. 1996]
- (vi)  $[Cr(NH_3)_5(NCS)][ZnCl_4]$  [I.I.T. 1997]
- (vii)  $KAu(CN)_2$



**Solution :**

- (i) Potassium trioxalatoaluminate(III)
- (ii) Tetraammine chloronitroplatinum(IV) sulphate
- (iii) Potassium hexacyano chromate(III)
- (iv) Pentaamminenitritocobalt(III) chloride
- (v) Pentaammine carbonatochromium (III) chloride
- (vi) Pentaammine isothiocyanatochromium (III) tetrachlorozincate (II)
- (vii) Potassium dicyanoaurate (I)
- (viii) Bis (ethylenediamine) cobalt (III)- $\mu$ -imido- $\mu$ -hydrobis (ethylene diammine) cobalt (III) ion
- (ix) Chlorotriphenylphosphine palladium (II)- $\mu$ -dichlorochlorotriphenylphosphine palladium (II).

**Example 4.** Name the type of isomerism exhibited by the following isomers:

- (i)  $[Cr(NH_3)_6][Cr(CN)_6]$  and  $[Cr(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$
- (ii)  $[Co(py)_2(H_2O)_2Cl_2]Cl$  and  $[Co(py)_2(H_2O)Cl_3]H_2O$
- (iii)  $[Pt(NH_3)_4Br_2]Cl_2$  and  $[Pt(NH_3)_4Cl_2]Br_2$
- (iv)  $[Co(NH_3)_5NO_2]Cl_2$  and  $[Co(NH_3)_5ONO]Cl_2$

**Solution :** (i) Coordination isomerism

- (ii) Hydrate isomerism
- (iii) Ionisation isomerism
- (iv) Linkage isomerism

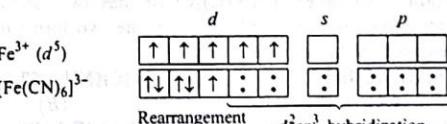
**Example 5.** How would you account for the following?

- (a)  $[Fe(CN)_6]^{3-}$  is weakly paramagnetic while  $[Fe(CN)_6]^{4-}$  is diamagnetic.

(b)  $Ni(CO)_4$  possesses tetrahedral geometry while  $[Ni(CN)_4]^{2-}$  is square planar.

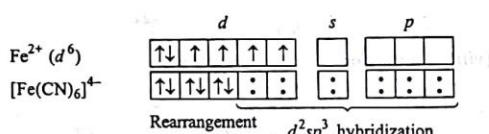
(c)  $[Ni(CN)_4]^{2-}$  is diamagnetic while  $[NiCl_4]^{2-}$  is paramagnetic.

**Solution :** (a)  $[Fe(CN)_6]^{3-}$  involves  $d^2sp^3$  hybridization.



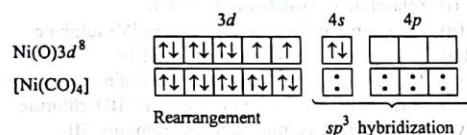
One  $d$ -orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[Fe(CN)_6]^{4-}$  involves also  $d^2sp^3$  hybridization but it has  $Fe^{2+}$  ion as central ion.

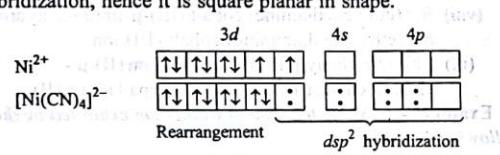


All orbitals are doubly occupied, hence it is diamagnetic in nature.

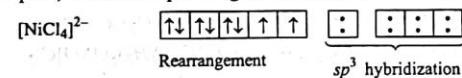
(b) In the formation of  $[\text{Ni}(\text{CO})_4]$ , nickel undergoes  $sp^3$  hybridization, hence it is tetrahedral in shape.



In the formation of  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{Ni}^{2+}$  ion undergoes  $dsp^2$  hybridization, hence it is square planar in shape.



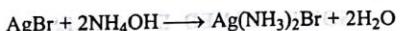
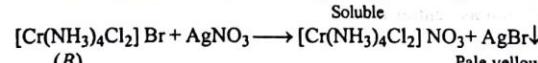
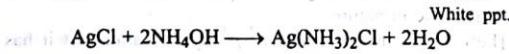
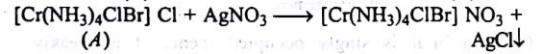
(c) In  $[\text{Ni}(\text{CN})_4]^{2-}$  all orbitals are doubly occupied, hence it is diamagnetic while in  $[\text{NiCl}_4]^{2-}$ , two orbitals are singly occupied, hence it is paramagnetic in nature.



Strong field ligands like  $\text{CN}^-$ ,  $\text{CO}$ , en,  $\text{NO}_2^-$  have very strong electron donating tendency, hence electrons of central metal ion pair up against Hund's rule (low spin complex).

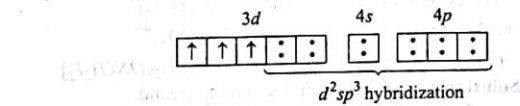
**Example 6.** A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms (A) and (B). The form (A) reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate the magnetic moments (spin-only value). [I.I.T. 2001]

**Solution :** Complex,  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$ , has two isomers. Since, coordination number of Cr is six, the two forms may be represented in the following way:



Soluble

The state of hybridization of chromium in both the complexes is  $d^2sp^3$ . Chromium is in trivalent state ( $\text{Cr}^{3+}$ ).



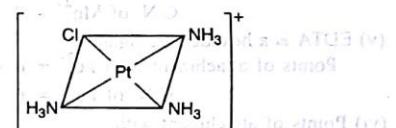
As three unpaired electrons are present,

$$\text{The magnetic moment} = \sqrt{n(n+2)} \text{ B.M.} \\ = \sqrt{3 \times 5} \text{ B.M.} = 3.87 \text{ B.M.}$$

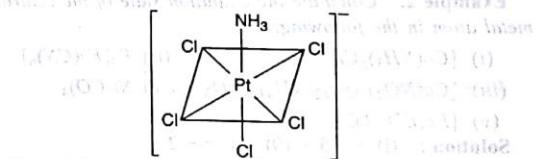
**Example 7.** Platinum II forms square planar complexes and platinum IV gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures:

- (a)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$       (b)  $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$   
 (c)  $[\text{Pt}(\text{NH}_3)_2\text{ClNO}_2]$       (d)  $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^{2+}$

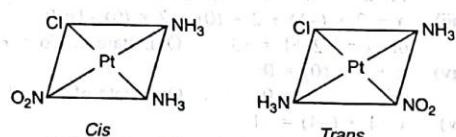
**Solution :** (a) No isomers are possible for a square planar complex of the type  $MA_3B$ .



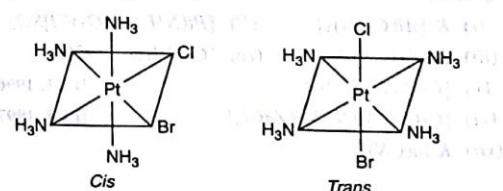
(b) No isomers are possible for an octahedral complex of the type  $MAB_5$ .



(c) Cis and trans isomers are possible for a square planar complex of the type  $MA_2BC$ .



(d) Cis and trans isomers are possible for an octahedral complex of the type  $MA_4BC$ .



**Example 8.** Answer the following:

(a) Why ligand field theory is also called crystal field theory?

(b) What is crystal field splitting?

(c) What are  $t_{2g}$  and  $e_g$  orbitals?

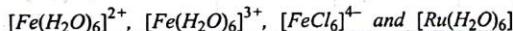
**Solution :** (a) According to this theory, the bond between metal ion and ligands is ionic, i.e., the electrostatic interactions are similar to those present in the crystals amongst the ions. That is why, the ligand field theory is also called crystal field theory.

(b) In the free transition metal atom or ion, all the five  $d$ -orbitals are degenerate but under the influence of ligands when complex formation occurs, the  $d$ -orbitals are split into two sets of orbitals  $t_{2g}$  and  $e_g$  orbitals. This is called crystal field splitting.

(c) Under the influence of ligands, when complex formation occurs, the five degenerate  $d$ -orbitals are split into two types of  $d$ -orbitals  $t_{2g}$  (three degenerate orbitals,  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ ) and  $e_g$  (two degenerate orbitals,  $d_{z^2}$  and  $d_{x^2-y^2}$ ). Both sets have different energies.

In octahedral complexes,  $t_{2g}$  orbitals possess low energy in comparison to  $e_g$  orbitals while in tetrahedral complexes,  $t_{2g}$  orbitals possess high energy in comparison to  $e_g$  orbitals.

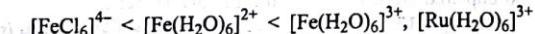
**Example 9.** Arrange the following complexes in order of increasing crystal field splitting:



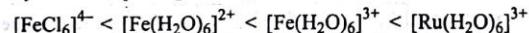
**Solution :** The strength of the splitting depends on the ligand, the charge on the metal and the position of the metal in the periodic table.

Ligand  $\text{Cl}^-$  is lower in the spectrochemical series than  $\text{H}_2\text{O}$ . Thus,  $[\text{FeCl}_6]^{4-}$  has low splitting relative to others.

In  $[\text{FeCl}_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  complexes, iron is in its +2 oxidation state but the metal is in +3 oxidation state in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$  complexes. The complexes with +3 oxidation states have larger splitting.

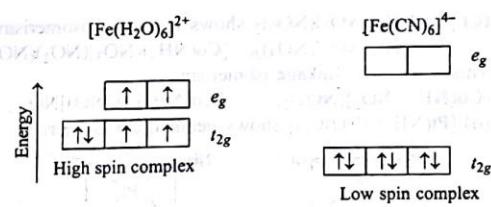


Three complexes contain iron, a metal with 3d valence electrons but the fourth contains ruthenium with 4d valence electrons. The metal with 4d electrons has larger splitting in comparison to the metal with 3d electrons. Thus, the order of crystal field splitting in the given complexes is:



**Example 10.** For each octahedral complex ion,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ , draw an orbital splitting diagram and predict the number of unpaired electrons and the magnetic nature.

**Solution :**  $\text{Fe}^{2+}$  has  $3d^6$  configuration.  $\text{H}_2\text{O}$  is a weak-field ligand so it forms high spin complex while  $\text{CN}^-$  is a strong-field ligand and forms low spin complex. The orbital splitting diagrams are shown ahead:



The  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  has four unpaired electrons and hence, it is paramagnetic in nature. The  $[\text{Fe}(\text{CN})_6]^{4-}$  has no unpaired electrons and hence, it is diamagnetic in nature.

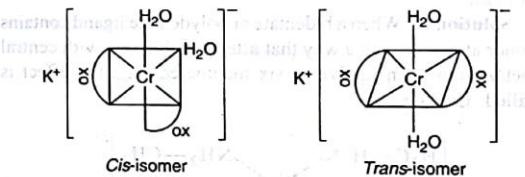
**Example 11.** Explain when hexacyano complexes of metals in their +2 oxidation state are usually yellow, but the corresponding hexaaqua compounds are often blue or green.

**Solution :** The ligand,  $\text{CN}^-$  is near the top of the spectrochemical series, it generates a relatively large energy gap between the two sets of  $d$ -orbitals. The hexacyano complexes are yellow because they absorb high-energy indigo light. The corresponding aqua complexes have a much smaller crystal field splitting energy. They absorb orange or red light, thus appearing blue or green.

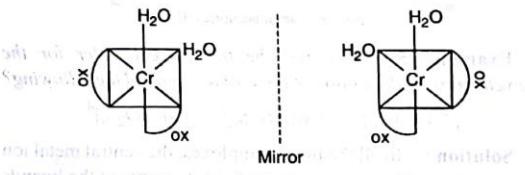
**Example 12.** Indicate the types of isomerism exhibited by the following complexes and draw the structures of these isomers.

- (a)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$       (b)  $[\text{Co}(\text{en})_3]\text{Cl}_3$   
 (c)  $[\text{Co}(\text{NH}_3)_5\text{NO}] (\text{NO}_3)_2$       (d)  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$

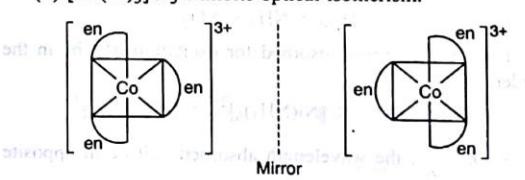
**Solution :** (a)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$  shows geometrical isomerism.



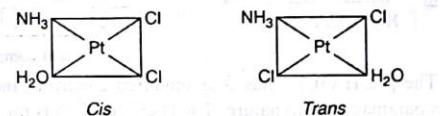
Cis-isomer exhibits optical isomerism.



(b)  $[\text{Co}(\text{en})_3]\text{Cl}_3$  exhibits optical isomerism.



- (c)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$  shows ionisation isomerism.  
 $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$ ,  $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_2)(\text{NO}_3)$   
 This also shows linkage isomerism.  
 $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$ ,  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{NO}_3$   
 (d)  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$  shows geometrical isomerism.

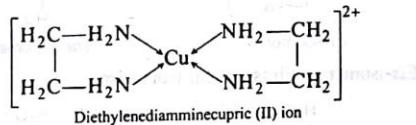


Solution :

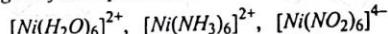
Complex	IUPAC name	Oxidation state	Electronic configuration	Coordination number	Stereochemistry	Magnetic moment
(i) $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$	Potassium diaquodioxalatochromate (III) hydrate	+3	$3d^3$	6	Octahedral $d^2sp^3$ -hybridization	$\sqrt{3 \times 5} = 3.87 \text{ B.M.}$
(ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Pentaamminechloridocobalt (III) chloride	+3	$3d^6$	6	Octahedral	0
(iii) $\text{CrCl}_3(\text{py})_3$	Trichloridotripyridinechromium (III)	+3	$3d^3$	6	Octahedral	$\sqrt{3 \times 5} = 3.87 \text{ B.M.}$
(iv) $\text{Cs}[\text{FeCl}_4]$	Caesium tetrachloridoferrate (III)	+3	$3d^5$	4	Tetrahedral	$\sqrt{5 \times 7} = 5.92 \text{ B.M.}$
(v) $\text{K}_4[\text{Mn}(\text{CN})_6]$	Potassium hexacyanomanganate (II)	+2	$3d^5$	6	Octahedral	$\sqrt{1 \times 3} = 1.73 \text{ B.M.}$

Example 14. What is meant by chelate effect? Give an example.

Solution : When a bidentate or polydentate ligand contains donor atoms in such a way that after coordinating with central metal atom forms a five or six membered ring, the effect is called 'Chelate effect'.



Example 15. What will be the correct order for the wavelengths of absorption in the visible region of the following?



Solution : In all the three complexes, the central metal ion is the same, hence, the increasing field strengths of the ligands from the spectrochemical series are in the order:



Thus, the energies absorbed for excitation will be in the order:



As  $E = \frac{hc}{\lambda}$ , the wavelength absorbed will be in opposite order.

Example 13. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number of the central atom in the complex. Also give stereochemistry and magnetic moment of the complex.

- (i)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$
- (ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- (iii)  $\text{CrCl}_3(\text{py})_3$
- (iv)  $\text{Cs}[\text{FeCl}_4]$
- (v)  $\text{K}_4[\text{Mn}(\text{CN})_6]$

Example 16. Using valence bond theory explain the geometry and magnetic behaviour of pentacarbonyliron (III).

Solution :

Fe ( $Z=26$ )	$\begin{array}{ c c c c c c } \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & & \\ \hline \end{array}$
$[\text{Fe}(\text{CO})_5]$	$\begin{array}{ c c c c c } \hline \uparrow & \uparrow & \uparrow & \uparrow & \times \\ \hline \end{array}$	$\begin{array}{ c } \hline \times \\ \hline \end{array}$	$\begin{array}{ c c c c } \hline \times & \times & \times & \times \\ \hline \end{array}$

$dsp^3$ -hybridization

Hence,  $[\text{Fe}(\text{CO})_5]$  has trigonal bipyramidal geometry and as no unpaired electron is present, it is diamagnetic.

Example 17.  $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $\text{Ni}(\text{CO})_4$  is diamagnetic though both are tetrahedral. Why?

Solution : In  $\text{Ni}(\text{CO})_4$ , the oxidation state of nickel is zero and CO is a strong ligand. Due to strong ligand field, the unpaired electrons of 3d-orbitals get paired by 4s-electrons.

Ni ( $Z=28$ )	$\begin{array}{ c c c c c c } \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow \\ \hline \end{array}$	$\begin{array}{ c c c c } \hline & & & \\ \hline \end{array}$
Ni (0)	$\begin{array}{ c c c c c } \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}$	$\begin{array}{ c c c c } \hline & & & \\ \hline \end{array}$	$\begin{array}{ c c c c } \hline & & & \\ \hline \end{array}$

$sp^3$ -hybridization

In  $[\text{NiCl}_4]^{2-}$ , the oxidation state of nickel is +2 and  $\text{Cl}^-$  is a weak ligand. Due to weak ligand field, there is no regrouping of electrons.

$3d$	$4s$	$4p$
$\begin{array}{ c c c c c c } \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}$	$\begin{array}{ c } \hline \uparrow \\ \hline \end{array}$	$\begin{array}{ c c c c } \hline & & & \\ \hline \end{array}$

$sp^3$ -hybridization

$[\text{Ni}(\text{Cl}_4)]^{2-}$ —Paramagnetic

**Example 18.** Draw crystal field energy level diagrams and predict the number of unpaired electrons for the following complexes:

- (a)  $[\text{FeCl}_4]^-$  (tetrahedral)    (b)  $[\text{NiCl}_4]^{2-}$  (tetrahedral)  
 (c)  $[\text{Cr}(\text{en})_3]^{3+}$  (octahedral)

**Solution :**

(a)	(b)	(c)
$\text{Cl}^-$ is weak field ligand. Thus, the complex is high spin. All the five orbitals are singly occupied.	$\text{Cl}^-$ is a weak field ligand. Thus, the complex is high spin.	$(\text{en})$ is a strong field ligand. The electrons occupy the orbitals of lower energy.
$\uparrow \uparrow \uparrow$ $\uparrow \uparrow$	$\uparrow \downarrow \uparrow \uparrow$ $\uparrow \downarrow$	$\uparrow \uparrow$
No. of unpaired electrons = 5	No. of unpaired electrons = 2	No. of unpaired electrons = 3

**Example 19.** Explain why nearly all tetrahedral complexes are high spin?

**Solution :** Because none of the orbitals point directly at the ligands in tetrahedral geometry and there are only four

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

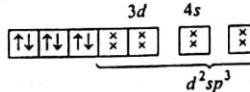
- Highest molar conductivity is exhibited by :  
 (a)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$     (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (c)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$     (d)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$   
**Ans. (a)**  
 [Hint :  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  gives maximum number of ions in solution. Thus, it shows highest molar conductivity.  
 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$   
 Total ions = 4]
- The complex,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is known to exist in two different coloured forms. This is due to :  
 (a) ionisation isomerism    (b) optical isomerism  
 (c) geometrical isomerism    (d) linkage isomerism  
**Ans. (c)**
- The IUPAC name of  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$  is :  
 (a) tetraamminedichloroplatinum (IV) tetrachloroplatinate (III)  
 (b) tetraamminedichloroplatinum (II) tetrachloroplatinate (III)  
 (c) tetraamminedichloroplatinum (III) tetrachloroplatinate (II)  
 (d) tetraamminedichloroplatinum (IV) tetrachloroplatinate (II)  
**Ans. (d)**
- Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ?

[A.I.E.E.E. 2005]

- (a)  $[\text{Cr}(\text{CN})_6]^{3-}$     (b)  $[\text{Co}(\text{CN})_6]^{3-}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$     (d)  $[\text{Mn}(\text{CN})_6]^{3-}$

**Ans. (b)**

[Hint :  $\text{Co}^{3+}$ , E.C. =  $[\text{Ar}] 3d^6$



No unpaired electron paramagnetism = 0]

ligands instead of six (as in octahedral geometry), the crystal field splitting in tetrahedral complexes is only about half of that in octahedral complexes. Consequently,  $\Delta$  is almost always smaller than spin-pairing energy  $P$ , and nearly all tetrahedral complexes are high spin.

**Example 20.** Why are metals complexed in biological systems?

**Solution :** There are two main reasons. These are:

- (i) Uncomplexed metal ions, e.g.,  $\text{Fe}(\text{III})$  may not dissolve in water at physiological pH.
- (ii) Uncomplexed metal ions may not have the required oxidation state. For example, in vitamin  $\text{B}_{12}$ , cobalt has +1 oxidation state which is not stable when uncomplexed.

**Example 21.** Name two coordination compounds which are biologically important.

**Solution :** (i) Haemoglobin—an iron complex—the red pigment in the blood that transports oxygen.

(ii) Chlorophyll—a magnesium complex—a green pigment in plants acts as a catalyst (photosensitizer) in the synthesis of carbohydrates.

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

- In which of the following pairs both the complexes show optical isomerism ? [A.I.I.M.S. 2005]  
 (a) *cis*- $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$ , *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$   
 (b)  $[\text{Co}(\text{en})_3]\text{Cl}_3$ , *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$   
 (c)  $[\text{PtCl}(\text{dien})]\text{Cl}$ ,  $[\text{NiCl}_2\text{Br}_2]^{2-}$   
 (d)  $[\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3]$ , *cis*- $[\text{Pt}(\text{en})_2\text{Cl}_2]$   
**Ans. (b)**
- Two complexes given below are :



- (a) geometrical isomers    (b) position isomers  
 (c) optical isomers    (d) identical

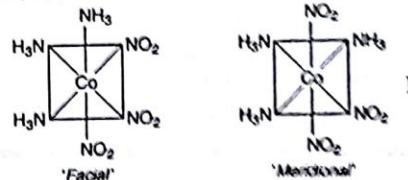
**Ans. (d)**

[Hint : Both represent the same molecule.]

- The number of geometrical isomers of  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$  are :  
 (a) 2    (b) 3  
 (c) 4    (d) nil

**Ans. (a)**

[Hint : The complex exhibits two geometrical isomers (i) facial and (ii) meridional.



8. Which of the following is a  $\pi$ -acid ligand?  
 (a)  $\text{NH}_3$  (b)  $\text{CO}$   
 (c)  $\text{F}^-$  (d)  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

Ans. (b)

[Hint : Ligands which are capable of accepting an appreciable amount of  $\pi$  electron density from the metal atom into  $\pi$  or  $\pi^*$  orbitals of their own are called  $\pi$ -acceptor or  $\pi$ -acid ligands such as  $\text{CO}$ .]

9. Wilkinson's catalyst is :  
 (a)  $\text{TiCl}_4$  and  $\text{Al}(\text{C}_2\text{H}_5)_3$  (b)  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$   
 (c)  $\text{TiCl}_4$  and  $(\text{C}_6\text{H}_5)_3\text{P}$  (d) none of these

Ans. (a)

10. Which of the following systems has maximum number of unpaired electrons or maximum paramagnetism?  
 (a)  $d^4$  (octahedral) (b)  $d^9$  (octahedral)  
 (c)  $d^7$  (octahedral) (d)  $d^5$  (octahedral)

Ans. (d)

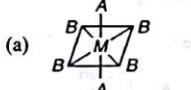
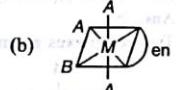
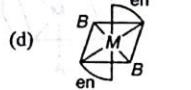
[Hint :  $d^5$  system has five unpaired electrons.]

11. The tetrahedral crystal field splitting is only . . . . of the octahedral splitting.  
 (a)  $1/9$  (b)  $2/9$  (c)  $4/9$  (d)  $5/9$

Ans. (c)

12. Which order is correct in spectrochemical series of ligands?  
 (a)  $\text{Cl}^- < \text{F}^- < [\text{C}_2\text{O}_4]^{2-} < \text{NO}_2^- < \text{CN}^-$   
 (b)  $\text{CN}^- < [\text{C}_2\text{O}_4]^{2-} < \text{Cl}^- < \text{NO}_2^- < \text{F}^-$   
 (c)  $[\text{C}_2\text{O}_4]^{2-} < \text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{CN}^-$   
 (d)  $\text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{CN}^- < [\text{C}_2\text{O}_4]^{2-}$

Ans. (a)

13. The phenomenon of optical activity will be shown by :  
 (a)   
 (b)   
 (c)   
 (d) 

Ans. (b)

14. The number of isomers possible for square planar complex,  $\text{K}_2[\text{PdClBr}_2\text{SCN}]$  are :  
 (a) 2 (b) 3 (c) 4 (d) 6

Ans. (c)

[Hint : Two geometrical isomers and two linkage isomers (-SCN and -CNS).]

15. The pair in which both species have same magnetic moment (spin only value) is:  
 [A.I.I.M.S. 2006]

- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, [\text{CoCl}_4]^{2-}$   
 (b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}, [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$   
 (d)  $[\text{CoCl}_4]^{2-}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Ans. (b)

[Hint : Same magnetic moment = Same number of unpaired electrons  
 $= \sqrt{n(n+2)}$   
 where  $n$  = number of unpaired electrons]

Co<sup>2+</sup> =  $3d^7$ , 3 unpaired electrons  
 Cr<sup>2+</sup> =  $3d^4$ , 4 unpaired electrons  
 Mn<sup>2+</sup> =  $3d^5$ , 5 unpaired electrons  
 Fe<sup>2+</sup> =  $3d^6$ , 4 unpaired electrons]

16. The pair in which both species have iron is: [A.I.I.M.S. 2006]

- (a) nitrogenase, cytochromes  
 (b) carboxypeptidase, haemoglobin  
 (c) haemoglobin, nitrogenase  
 (d) haemoglobin, cytochromes

Ans. (d)

17. The ligands in anticancer drug 'cis-platin' are:  
 [A.I.I.M.S. 2006]

- (a)  $\text{NH}_3, \text{Cl}$  (b)  $\text{NH}_3, \text{H}_2\text{O}$   
 (c)  $\text{Cl}, \text{H}_2\text{O}$  (d)  $\text{NO}, \text{Cl}$

Ans. (a)

18. Match List-I with List-II and select the correct answer using codes given below the lists:

List-I	List-II
Metal ions	Magnetic moments (B.M.)

A.  $\text{Cr}^{3+}$  (a)  $\sqrt{35}$

B.  $\text{Fe}^{2+}$  (b)  $\sqrt{30}$

C.  $\text{Ni}^{2+}$  (c)  $\sqrt{24}$

D.  $\text{Mn}^{2+}$  (d)  $\sqrt{15}$

1.  $\sqrt{35}$

2.  $\sqrt{30}$

3.  $\sqrt{24}$

4.  $\sqrt{15}$

5.  $\sqrt{8}$

(a) A-1, B-3, C-5, D-4  
 (b) A-2, B-3, C-5, D-1  
 (c) A-4, B-3, C-5, D-1  
 (d) A-4, B-5, C-3, D-1

Ans. (c)

[Hint : Magnetic moment =  $\sqrt{n(n+2)}$

Cr<sup>3</sup>— $3d^3 = \sqrt{3 \times 5} = \sqrt{15}$

Fe<sup>2+</sup>— $3d^6 = \sqrt{4 \times 6} = \sqrt{24}$

Ni<sup>2+</sup>— $3d^8 = \sqrt{2 \times 4} = \sqrt{8}$

Mn<sup>2+</sup>— $3d^5 = \sqrt{5 \times 7} = \sqrt{35}$

19. In  $\text{Fe}(\text{CO})_5$ , the Fe-C bond possesses: [A.I.E.E. 2006]

- (a)  $\pi$  character only (b)  $\sigma$  character only

- (c) ionic character only (d) both  $\pi$  and  $\sigma$  characters

Ans. (d)

20.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in the chromium present in the complex is: [C.B.S.E. 2006]

- (a)  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$

- (b)  $3d_{xy}^1, 3d_{yz}^1, 3d_z^1$

- (c)  $3d_{(x^2-y^2)}^1, 3d_z^1, 3d_{xz}^1$

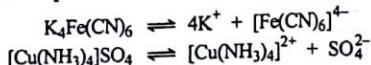
- (d)  $3d_{xy}^1, 3d_{(x^2-y^2)}^1, 3d_{yz}^1$

Ans. (a)

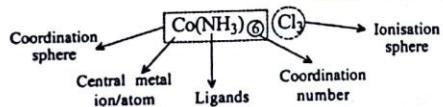
[Hint : Magnetic moment indicates that there are three unpaired electrons present in chromium. These must be present in lower energy orbitals which are  $3d_{xy}$ ,  $3d_{yz}$  and  $3d_{zx}$ .]

**—: SUMMARY AND IMPORTANT POINTS TO REMEMBER :—**

1. When solutions of two or more simple stable compounds in molecular proportions are allowed to evaporate, crystals of new compounds may be formed. These compounds are termed **molecular or addition compounds**. Addition compounds are of two types : (i) Double salts or lattice compounds, and (ii) Coordination or complex compounds.
2. The addition compounds which are stable in solid state but are broken down into individual constituents when dissolved in water are called **double salts**. Mohr's salt, potash alum, carnallite, etc., are some examples of double salts.
3. The addition compounds which retain their identity in solid state as well as in solution are termed **coordination or complex compounds**. In these compounds at least one complex ion is present. In complex ion, a metal atom or ion is surrounded by a number of groups through coordination.
4. Complex compounds are mainly formed by transition metals but to a small extent by other metals such as magnesium in chlorophyll. Transition metals form complexes due to the following reasons:  
(i) Small size, (ii) high nuclear charge, (iii) a number of vacant orbitals of equivalent energy where the electrons donated by ligands are accommodated.
5. The neutral molecules, anions or cations which are directly linked with the central metal atom or ion in a complex ion are called **ligands**. The ligand at least consists one donor atom having a lone pair of electrons which it can donate to metal atom or ion. Ligands can be classified on the basis of number of donor atoms. They are termed monodentate, bidentate, tridentate, etc. The ligands having two or more donor groups are called polydentate. Polydentate ligand is known as **chelating ligand** if on coordination it results in the formation of a closed or cyclic ring structure. The complexes, thus, formed are called **chelates**.
6. The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as **coordination number** of the metal atom or ion. It is actually the number of chemical bonds which the ligands form with central metal atom or ion. The most common coordination number are 4 or 6. The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket. This is called **coordination sphere**. It behaves as a single unit. The ions present outside the coordination sphere form **ionisation sphere**.



Charge on the complex ion = oxidation number of metal ion  
+ charge on the ligands



7. Effective atomic number (EAN) is defined as the resultant number of electrons with the metal atom or ion after gaining electrons from donor atoms after ligands.

EAN = atomic number of the metal – number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands.

8. The following points are followed in naming complex compounds :

- (i) Cation is named first followed by anion.
- (ii) In the coordination sphere, the ligands are named alphabetically. Anionic ligands ending with -ide are named by replacing -ide by suffix -o or by replacing -e by -o. Ligands whose names end in -ite or -ate become -ito or -ato, i.e., by replacing the ending -e with -o. Neutral ligands are given the same names as the neutral molecules. However, H<sub>2</sub>O is named aqua and NH<sub>3</sub> ammine. Positively charged ligands have suffix -ium. If the number of a particular ligand is more than one, the number is indicated by using di, tri, tetra, penta, etc. However, when the name of the ligand includes a number, then bis, tris, etc., are used.
- (iii) The oxidation state of the central metal is shown by Roman numeral in bracket immediately following its name.
- (iv) Complex positive ions and neutral coordination compounds have no special ending but complex negative ions always end in the suffix -ate.

9. Coordination compounds exhibit structural isomerism as well as stereoisomerism. Structural isomerism is displayed when different ligands are present within coordination spheres. The coordination compounds exhibit various types of structural isomerism.

- (i) **Ionisation isomerism** : Isomers give different ions in solution.

Examples : [Co(NH<sub>3</sub>)<sub>5</sub>Br]Cl; [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Br.

- (ii) **Hydrate isomerism** : Isomers having H<sub>2</sub>O as a ligand or as water of hydration.

Examples : [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>; [CrCl(H<sub>2</sub>O)<sub>5</sub>]Cl<sub>2</sub>·H<sub>2</sub>O; [CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl·2H<sub>2</sub>O.

- (iii) **Coordination isomerism** : The ligands are interchanged in both the cationic and anionic ions.

Examples : [Co(NH<sub>3</sub>)<sub>6</sub>][Cr(CN)<sub>6</sub>]; [Cr(NH<sub>3</sub>)<sub>6</sub>][Co(CN)<sub>6</sub>].

- (iv) **Linkage isomerism** : This type of isomerism exists when ambidentate ligand is present.

Examples : [Co(NH<sub>3</sub>)<sub>5</sub>ONO]Cl<sub>2</sub>; [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub>.

10. **Stereoisomerism** : It arises on account of the different positions and arrangement of ligands in space around the metal ion. It is of two types : (a) geometrical and (b) optical. Geometrical isomerism is common in coordination number 4 (square planar) and coordination number 6 compounds. This type of isomerism is termed *cis-trans* isomerism. When the ligands occupy adjacent positions, the isomer is called *cis*-form and when opposite positions, the isomer is termed *trans*-isomer. The square planar complexes having general formulae

$Ma_2b_2$ ,  $Ma_2bc$  or  $Mabcd$  show *cis-trans* isomerism. Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism.

Geometrical isomerism is not observed in complexes of coordination numbers 2 and 3. Square planar complexes of the type  $Ma_4$ ,  $Ma_3b$  and  $Mab_3$  do not show geometrical isomerism. Geometrical isomerism is also not observed in tetrahedral complexes.

Octahedral complexes of the type  $Ma_4b_2$ ,  $Ma_2b_4$ ,  $Ma_4bc$  and  $Ma_3b_3$  exhibit geometrical isomerism.

11. A coordination compound which can rotate the plane of polarised light is said to be optically active. The optical isomers are pair of molecules which are non-superimposable mirror image of each other. The isomer which rotates the plane of polarised light to right direction is termed dextro while the isomer which rotates the plane of polarised light to left direction is termed laevo form. Optical isomerism is very common in octahedral complexes. Octahedral compounds of general formulae  $[Ma_2b_2c_2]^{n\pm}$ ,  $[Mabcdef]$ ,  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$ ,  $[M(AA)_2ab]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$  where  $AA$  = symmetrical bidentate ligands and  $AB$  = unsymmetrical bidentate ligands.
12. Werner, in 1893, proposed the coordination theory to explain the properties and structures of various metal ammines. The important postulates of the theory are:
  - (a) Every element exhibits two types of valencies : (i) Primary valency and (ii) Secondary valency. Primary valency corresponds to oxidation state of metal and secondary valency represents the coordination number of the metal. Primary valency is satisfied by negative ions and is ionisable. The secondary valency is satisfied by neutral molecules or negative ions or both. This valency is non-ionic. Metal and neutral molecules or negative ions which satisfy secondary valency are enclosed in square bracket and termed as coordination sphere.
  - (b) Every element tends to satisfy both its valencies. A negative ion when present in coordination sphere shows a dual behaviour. It satisfies both primary and secondary valencies. The presence of negative ion in the coordination sphere reduces the charge on the complex ion by the amount of charge possessed by it and the negative ions present in the coordination sphere are not ionised.
  - (c) The ligands in coordination sphere are directed towards fixed positions in space. The geometry of the complex ion depends on coordination number. If the coordination number is 6, the complex is octahedral. On the other hand, if the coordination number is 4, the geometry of the complex may be tetrahedral or square planar.
13. Valence bond theory describes the bonding in complexes in terms of two-electron, coordinate-covalent bonds resulting from overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands:  $sp$  (linear);  $sp^3$  (tetrahedral);  $dsp^2$  (square planar) and  $d^2sp^3$  and  $sp^3d^2$  (octahedral).

This theory explains with reasonable success the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and explanation about optical properties of coordination compounds.

#### Examples :

##### (a) Octahedral complexes :

- (i) Inner orbital (low spin) complexes involving  $d^2sp^3$  hybridization:  
 $[Fe(CN)_6]^{3-}$ ,  $[Co(CN)_6]^{3-}$ ,  $[Cr(NH_3)_6]^{3+}$ ,  $[Co(NH_3)_6]^{3+}$ , etc.
- (ii) Outer orbital (high spin) complexes involving  $sp^3d^2$  hybridization:  
 $[CoF_6]^{3-}$ ,  $[Fe(H_2O)_6]^{3+}$ ,  $[MnF_6]^{3-}$ ,  $[Ni(NH_3)_6]^{2+}$ , etc.

##### (b) Tetrahedral complexes involving $sp^3$ hybridization:

- $[NiCl_4]^{2-}$ ,  $[Cu(Cl_4)]^{2-}$ ,  $Ni(CO)_4$ ,  $[Zn(NH_3)_4]^{2+}$ , etc.
- (c) Square planar complexes involving  $dsp^2$  hybridization:  
 $[Ni(CN)_4]^{2-}$ ,  $[Cu(NH_3)_4]^{2+}$ , etc.

14. Crystal field theory assumes that the metal-ligand bonding is entirely ionic. Because of electrostatic repulsions between the  $d$  electrons and the ligands, the  $d$ -orbitals are raised in energy and are differentiated by an energy separation called the crystal field splitting,  $\Delta$ . In octahedral complexes the  $d_{z^2}$ ,  $d_{x^2-y^2}$  orbitals (e.g., set of orbitals) have higher energy than  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals (e.g., set of orbitals). Tetrahedral complexes exhibit just opposite splitting pattern.

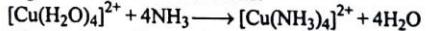
The colours of complexes are due to electronic transitions from one set of  $d$ -orbitals to another and the transition energies depend on the position of ligand in the spectro-chemical series. Weak field ligands give small  $\Delta$  values and strong field ligands give large  $\Delta$  values. Crystal field theory accounts for magnetic properties of complexes in terms of the relative values of  $\Delta$  and the spin pairing energy. Small  $\Delta$  values favour high spin complexes (maximum number of unpaired  $d$  electrons) and large  $\Delta$  values favour low spin complexes.

15. In general, higher the charge density on the central ion, the greater is the stability of its complexes. Electronegativity of the central ion also influences the stability. The higher the oxidation state of the metal, the more stable is the complex. The more basic ligand forms the complex with greater stability. The cyano and ammine complexes are far more stable than those formed by halide ions.

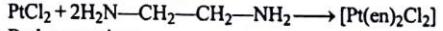
Chelating ligands form more stable complexes as compared to monodentate ligands.

16. Coordination compounds are generally prepared by the application of :

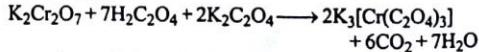
##### (a) Ligand substitution reactions:



##### (b) Direct mixing of reagent:



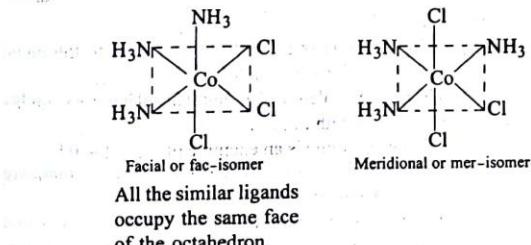
##### (c) Redox reaction:



17. The complexes find applications in various fields:

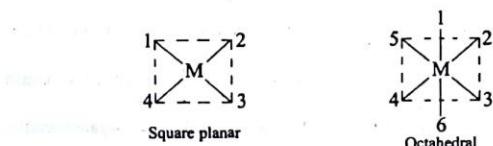
- (a) Analytical chemistry— $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , etc., are tested in the form of complexes.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  ions are estimated volumetrically by EDTA. Many ions are quantitatively estimated by using a number of organic ligands.
- (b) Coordination complexes of transition metals exhibit a variety of colours. This forms the basis of colorimetric estimations.
- (c) Complexes act as oxidation-reduction indicators and sequestering reagents. Hardness of water is estimated by use of EDTA.
- (d) Silver and gold are extracted by the use of complex formation.
- (e) Fixing of negative is done in photography by use of hypo solution. It forms soluble complex with silver bromide.
- (f) During electroplating, complexes are used in electrolytic bath.
- (g) *Cis*-platin,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , is used in the treatment of cancer.  
British anti-lewisite (BAL) is used as antidote for treating poisoning by As, Hg, Au, Bi, Pb and Cd.
- (h) Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg, vitamin B<sub>12</sub> is a complex of cobalt.
18. Compounds that contain at least one carbon-metal bond are called organometallic compounds. Organometallic compounds may be classified in three classes.
- (a) Sigma ( $\sigma$ ) bonded complexes (b) pi ( $\pi$ ) bonded complexes  
(c) complexes containing both  $\sigma$  and  $\pi$ -bonding.  
Grignard reagent ( $R-\text{Mg}-X$ ), zinc compounds ( $R_2\text{Zn}$ ),  $\text{Al}_2(\text{CH}_3)_6$ , etc., are  $\sigma$ -bonded organometallic compounds. Zeise's salts, ferrocene, dibenzene chromium are  $\pi$ -bonded complexes. Metal carbonyls are examples of both  $\sigma$  and  $\pi$ -bonded organometallic compounds.
19. (a) Ligands with more than six donor groups form unstable rings due to steric hindrance.
- (b) Chelating ligands form more stable complexes than the monodentate ligands. Chelates with five membered rings including metal atom are more stable if these do not contain double bonds. Chelates with six membered rings are more stable if the ligands contain conjugate double bonds.
- (c) Complex formed with a cyclic polydentate ligand is more stable than complex formed with a non-cyclic ligand.

20. (a) The complexes of the type  $MA_3B_3$  can form the following two types of geometrical isomers.



All the similar ligands occupy the same face of the octahedron.

- (b) In square planar complexes, positions 1,2; 2,3; 3,4 and 1,4 are *cis* while 1,3 and 2,4 are *trans* with respect to each other. In octahedral complexes, positions 1,2; 1,3; 1,4 and 1,5 are *cis* while 1,6; 2,4 and 3,5 are *trans* with respect to each other.



21. (a) Ferrocene  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$  and dibenzene chromium  $[\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2]$  are called sandwiched compounds.

- (b) Potassium hexanitrocobaltate(III),  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  is called Fischer's salt.  
(c) Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg and vitamin B<sub>12</sub> is a complex of Co.

22. (a) Organo-arsenic compounds are used as remedy for syphilis.  
(b) Zeigler-Natta catalyst,  $R_3\text{Al}$ , mixed with  $\text{TiCl}_3$  or  $\text{TiCl}_4$  is used in low temperature polymerisation of alkenes.  
(c) Wilkinson's catalyst,  $(\text{Ph}_3\text{P})_3\text{RhCl}$  is used in the hydrogenation of alkenes.  
(d) Ethyl mercury chloride is used to prevent the infection of young plants.  
(e) Tetraethyl lead (TEL) is an important anti-knock compound added to petrol used in internal combustion engines.  
(f) Grignard reagent and several other organo metallics and good reagents for the synthesis of compounds.

## QUESTIONS

**1. Fill in the blanks :**

- A ligand donates at least one  $e^-$  to the metal atom/ion to form a complex.
- The primary valency of a central metal ion in a complex is satisfied with  $\sigma$  bonds.
- Ethylenediamine is an example of a bidentate ligand.
- According to Werner's coordination theory, there are 2 kinds of valency and 5 EAN.
- The total number of electrons on the central metal atom/ion including those gained by bonding is called EAN.
- $[Co(NH_3)_5SO_4]Br$  and  $[Co(NH_3)_5Br]SO_4$  show ionization isomerism.
- The IUPAC name of  $Fe(CO)_5$  is pentacarbonyl iron(0).
- The formula of potassium trioxalatoaluminate(III) is  $K_3[Al(C_2O_4)_3]$ .
- On valence bond theory the geometry of  $Ni(CO)_4$  is tetrahedral.
- $K_4Fe(CN)_6$  is considered to be a complex but potash alum is double salt.
- Grignard reagent is a  $\pi$ -bonded organometallic compound.
- $[Co(NH_3)_6]^{3+}$  is diamagnetic while  $[COF_6]^{3-}$  is paramagnetic.
- The type of magnetism exhibited by  $[Mn(H_2O)_6]^{2+}$  ion is paramagnetic [I.I.T. 1994].
- The IUPAC name of  $[Co(NH_3)_6]Cl_3$  is hexamminecobalt(III) [I.I.T. 1994].
- The IUPAC name of  $Na_3[Co(NO_2)_6]$  is sodium hexanitroferrate(II).
- The complex,  $[Cr(NH_3)_6]Cl_3$  has octahedral shape.
- One molecule of  $[Pt(NH_3)_6]Cl_4$  gives 5 ions in solution and requires 1 mol of  $AgNO_3$  for complete precipitation of chloride ions.
- $[Pt(NH_3)(NH_2OH)(py)(NO_2)]NO_3$  has planar shape and has 2 geometrical isomers.
- Geometrical isomerism is not observed in complexes of coordination number 4 of  $Sc^{3+}$  geometry.
- Trans form of  $[M(AA)_2a_2]^{n+}$  complex does not show optical isomerism.
- Dimethyl glyoxime is used from the gravimetric estimation of  $Ni^{2+}$  ion. volumetric
- EDTA is used as a complexing agent in estimation of metal ions like  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Zn^{2+}$  ions.

**2. Whether the following statements are True or False:**

- Coordination compounds are mainly known for transition metals. T
- Coordination number and oxidation state of a metal means the same thing. F
- Tetrahedral complexes cannot show geometrical isomerism. T
- A bidentate ligand has 3 coordination sites. F
- The IUPAC name of  $[CuCl_4]^{2-}$  is tetrachlorido cuprate(II). T

- Ambidentate ligands can show linkage isomerism. T
- Stability of coordination compounds increases with increase in charge density of the metal ions. T
- Valence bond theory explains the colour of the coordination compounds. F
- Valence bond theory explains the geometry and magnetic nature of the coordination compounds. T
- $Fe(CO)_5$  has trigonal bipyramidal geometry. T
- $[NiCl_4]^{2-}$  is diamagnetic in nature. F
- The pair  $[Cr(H_2O)_6]Cl_3$  and  $[Cr(H_2O)_4Cl_2]ClH_2O$  shows ionisation isomerism. F
- EAN rule is followed by  $K_4Fe(CN)_6$  complex. T
- $Al_2(CH_3)_6$  is a dimeric compound and has a structure similar to diborane. T
- Carbonyls are organometallic compounds. T

**3. Match the following:**

- |                        |   |                                      |
|------------------------|---|--------------------------------------|
| 1. Double salt         | e | (a) $[Co(NH_3)_3Cl_3]$               |
| 2. Zeise's salt        | h | (b) Hexadentate                      |
| 3. Neutral molecule    | a | (c) Bidentate                        |
| 4. EDTA                | b | (d) Paramagnetic                     |
| 5. $Ni(CO)_4$          | g | (e) $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ |
| 6. $[Cr(NH_3)_6]^{3+}$ | d | (f) $K_4Fe(CN)_6$                    |
| 7. Low spin complex    | f | (g) Diamagnetic                      |
| 8. Glycine             | c | (h) An organometallic compound       |

**4. Indicate 'principal' and 'secondary' valencies of central metal ion in the following complexes:**

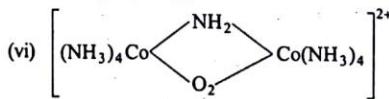
- |                            |     |                        |     |
|----------------------------|-----|------------------------|-----|
| (a) $[Cr(NH_3)_6]Cl_3$     | 3 6 | (b) $K_4[Fe(CN)_6]$    | 2 6 |
| (c) $[Pt(NH_3)_2Cl_2]$     | 2 4 | (d) $K_2[PtCl_4]$      | 2 4 |
| (e) $[Co(NH_3)_5H_2O]Cl_3$ | 3 6 | (f) $[Cu(NH_3)_4]SO_4$ | 2 4 |

**5. Determine the effective atomic number of the metal atom in the following:**

- |                       |     |                         |     |
|-----------------------|-----|-------------------------|-----|
| (a) $[Cr(CO)_6]$      | 3   | (b) $[Fe(CN)_6]^{3-}$   | 3 5 |
| (c) $[Co(CN)_6]^{4-}$ | 3 7 | (d) $[Ni(NH_3)_6]^{2+}$ | 3 8 |
- [Cr = 24; Fe = 26; Co = 27 and Ni = 28 as atomic numbers]

**6. Write down the IUPAC names of the following complexes:**

- |                           |                                 |
|---------------------------|---------------------------------|
| (i) $K_4[Mo(CN)_8]$       | (ii) $Co[(en)_2Cl(ONO)]^+$      |
| (iii) $[Cr(PPh_3)(CO)_5]$ | (iv) $[Pt(NH_3)_4Cl_2][PtCl_4]$ |
| (v) $(NH_4)_2[Cr(NCS)_6]$ |                                 |



**7. Write the formulae of the following complexes:**

- Diamminechlorido (ethylenediamine) nitroplatinum (IV) chloride.
- Calcium hexacyanoferrate (II).
- Tetraamminecobalt (III)- $\mu$ -amino- $\mu$ -nitrotetraammine-cobalt (III) nitrate.

- (d) Dichlorido bis (ethylenediamine) cobalt (III) sulphate.  
 (e) Sodium tetrahydroxoaluminate (III).  
 (f) Potassium ethylenediamine tetraacetate ferrate (II).  
 (g) Hexaammine chromium(III) hexacyanocobaltate(III).
8. Combination of Pt(IV), NH<sub>3</sub>, Cl<sup>-</sup> and K<sup>+</sup> results in the formation of seven complexes and one such complex is [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub>.  
 (i) Write the formulae of the other six members of the series.  
 (ii) Name these complexes according to the IUPAC system of nomenclature.  
 (iii) Which will have highest molar conductivity?  
 (iv) Which of these is non-ionic?  
 (v) What is the coordination number and oxidation state of Pt in these complexes?
9. How many ions per mole of the following complexes are present in their solutions?  
 (i) [Co(NH<sub>3</sub>)<sub>6</sub>(en)<sub>2</sub>Cl]<sup>2+</sup>   (ii) [Ag(NH<sub>3</sub>)<sub>2</sub>]Br  
 (iii) [Pt(NH<sub>3</sub>)<sub>4</sub>]PtCl<sub>4</sub>   (iv) [Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>2</sub>  
 (v) Cu<sub>2</sub>[Fe(CN)<sub>6</sub>]<sup>4-</sup>
10. Which of the following names are correct?  
 (i) K<sub>3</sub>[Fe(CN)<sub>5</sub>NO] : Potassium pentacyanonitrosyl ferrate (II).  
 (ii) Na<sub>2</sub>[Ni(EDTA)] : Sodium ethylenediaminetetraacetato nickel (I).  
 (iii) [Co(NH<sub>3</sub>)<sub>5</sub>CO<sub>3</sub>]Cl : Pentaamminecarbonatocobalt (III) chloride.  
 (iv) K<sub>3</sub>[Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] : Potassium *tris* (oxalato) aluminate (III).  
 (v) K<sub>2</sub>[Zn(OH)<sub>4</sub>] : Potassium tetrahydroxozincate(II).  
 (vi) K<sub>2</sub>[PtF<sub>6</sub>] : Potassium hexafluoridoplatinate(IV).  
 (vii) [Co(en)<sub>3</sub>]Cl<sub>3</sub> : Triethylenediamminecobalt(III) chloride.  
 (viii) Hg[Co(CNS)<sub>4</sub>] : Mercury tetrathiocyanatocobalt(II).
11. What type of isomers are the following?  
 (i) [(CO)<sub>5</sub>MnSCN] and [(CO)<sub>5</sub>MnNCS]  
 (ii) [Co(en)<sub>3</sub>][Cr(CN)<sub>6</sub>] and [Cr(en)<sub>3</sub>][Co(CN)<sub>6</sub>]  
 (iii) [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>3</sub>]SO<sub>4</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]NO<sub>3</sub>  
 (iv) [Co(py)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>]Cl and [Co(py)<sub>2</sub>(H<sub>2</sub>O)Cl<sub>3</sub>]H<sub>2</sub>O
12. Describe a simple chemical test that would allow you to distinguish between the compounds, [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Br.
13. How many geometrical isomers are there for:  
 (a) [Co(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>]<sup>-</sup>, octahedral?  
 (b) [AuCl<sub>2</sub>Br<sub>2</sub>]<sup>-</sup>, square planar?  
 (c) [CoCl<sub>2</sub>Br<sub>2</sub>]<sup>-</sup>, tetrahedral?
14. What are the types of hybridization involved in the following geometrical shapes of the complex?  
 (a) Square planar   (b) Tetrahedral   (c) Octahedral
15. Explain the geometry and magnetic nature of the following complex ions on the basis of valence bond theory.  
 (i) [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>   (ii) [Fe(CN)<sub>6</sub>]<sup>4-</sup>   (iii) [FeF<sub>6</sub>]<sup>3-</sup>  
 (iv) [MnCl<sub>4</sub>]<sup>2-</sup>   (v) [Ni(CN)<sub>4</sub>]<sup>2-</sup>   (vi) [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>

## 16. Explain the following:

- (i) All the octahedral complexes of Ni<sup>2+</sup> must be outer-orbital complexes.

[Ans.]

During rearrangement only one 3d-orbital may be made available by pairing the electrons. Thus, inner  $d^2sp^3$  hybridization is not possible. So, only  $sp^3d^2$  (outer) hybridization can occur.]

- (ii) [CoF<sub>6</sub>]<sup>3-</sup> is paramagnetic but [Co(CN)<sub>6</sub>]<sup>3-</sup> is diamagnetic.

[Ans. In [CoF<sub>6</sub>]<sup>3-</sup>, Co<sup>3+</sup> undergoes  $sp^3d^2$  hybridization. Four d-orbitals are singly occupied. Hence, it is paramagnetic.

Rearrangement       $sp^3d^2$  hybridization

In [Co(CN)<sub>6</sub>]<sup>3-</sup>, Co<sup>3+</sup> undergoes  $d^2sp^3$  hybridization.

No-orbital is singly occupied. Hence, it is diamagnetic.]

Rearrangement       $d^2sp^3$  hybridization

- (iii) The magnetic moment of [MnCl<sub>4</sub>]<sup>2-</sup> is 5.92 B.M.

[Ans. In [MnCl<sub>4</sub>]<sup>2-</sup> ion, Mn<sup>2+</sup> ion undergoes  $sp^3$  hybridization. It contains 5d-orbitals singly occupied. Hence, it has high value of magnetic moment.]

$sp^3$  hybridization

- (iv) NH<sub>4</sub><sup>+</sup> ion does not form complexes.

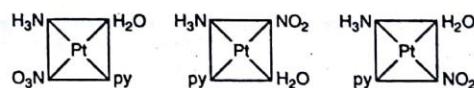
[Ans. NH<sub>4</sub><sup>+</sup> ion does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.]

- (v) (SCN)<sup>-</sup> shows linkage isomerism in coordination compounds.

[Ans. (SCN)<sup>-</sup> group can coordinate with metal atom either through S-atom or N-atom giving two isomers. Thus, it shows linkage isomerism.]

- (vi) Three geometrical isomers of the square planar complex, [Pt(NH<sub>3</sub>)(H<sub>2</sub>O)(py)(NO<sub>2</sub>)]<sup>+</sup>, are possible.

[Ans.]

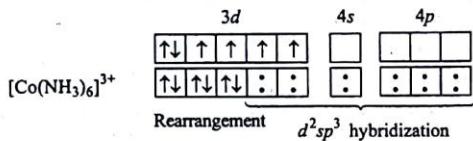


Three different arrangements corresponding to three geometrical isomers are possible.]

17. Find out the hybridization, geometry and magnetic moment of the complexes:

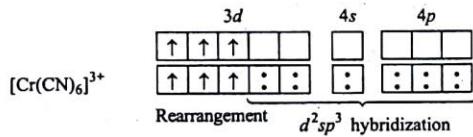
(i) [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>   (ii) [Cr(CN)<sub>6</sub>]<sup>3-</sup>

[Ans. The oxidation state of cobalt in the complex is +3. The electronic configuration of  $\text{Co}^{3+}$  ion is:



Octahedral, zero magnetic moment.

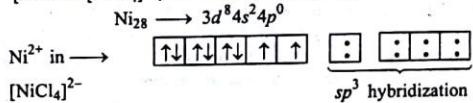
The oxidation state of chromium in the complex is +3. The electronic configuration of  $\text{Cr}^{3+}$  ion is:



Octahedral, mag. moment =  $\sqrt{3 \times (3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$

18. Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{Ni}(\text{CO})_4$ . Write the hybridization of atomic orbitals of the transition metal in each case. [I.I.T. 2000]
19. Deduce the structures of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  considering the hybridization. Calculate the magnetic moment (spin only) of the species. [I.I.T. 2002]

[Ans. In  $[\text{NiCl}_4]^{2-}$ ,  $\text{Cl}^-$  is weak field ligand.

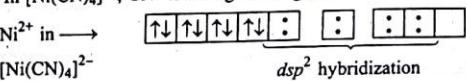


$[\text{NiCl}_4]^{2-}$  is a tetrahedral complex.

Number of unpaired electrons in  $\text{Ni}^{2+} = 2$

Magnetic moment ' $\mu$ ' =  $\sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.82 \text{ B.M.}$

In  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{CN}^-$  is strong field ligand.



$[\text{Ni}(\text{CN})_4]^{2-}$  is a square planar complex.

Number of unpaired electrons in  $\text{Ni}^{2+} = 0$

Magnetic moment ' $\mu$ ' =  $\sqrt{n(n+2)} = 0$

20. What are the main features of the ligand field theory?

21. How does crystal field theory explain:  
 (i) high spin and low spin states of complexes  
 (ii) magnetism of complexes  
 (iii) colour of the complexes.
22. (a) What are organometallic compounds? How are these compounds classified?  
 (b) How is ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$  prepared? Draw its structure.
23. (a) Describe at least three applications of coordination compounds.  
 (b) Describe the application of organometallic compound in homogeneous catalysis.
24. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

## ANSWERS

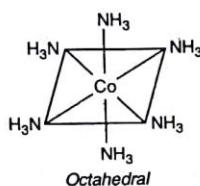
- (i) electron pair (ii) anions (iii) bidentate (iv) two, primary, secondary (v) effective atomic number (vi) ionisation (vii) pentacarbonyliron (0) (viii)  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  (ix) tetrahedral (x) a double salt (xi)  $\sigma$ -bonded (xii) paramagnetic (xiii) paramagnetic (xiv) hexaammine cobalt (III) chloride (xv) sodium hexanitrocobaltate(III) (xvi) octahedral (xvii) five, 4 molecules (xviii) square planar, three (xix) tetrahedral (xx) optical (xxi)  $\text{Ni}^{2+}$  (xxii) volumetric.
- (i) True (ii) False (iii) True (iv) False—has two coordination sites (v) True (vi) True (vii) True (viii) False (ix) True (x) True (xi) False—paramagnetic in nature (xii) False—hydrate isomerism (xiii) True (xiv) True (xv) True.
- (1—e); (2—h); (3—a); (4—b); (5—g); (6—d); (7—f); (8—c).
- (a) 3 and 6 (b) 2 and 6 (c) 2 and 4 (d) 2 and 4 (e) 3 and 6 (f) 2 and 4.
- (a) 36 (b) 35 (c) 37 (d) 38.
- (i) Potassium octacyanomolybdate(IV) (ii) Chlorido bis (ethylene-diamine) nitrito cobalt (III) ion (iii) Pentacarbonyl triphenylphosphinechromium (0) (iv) Tetraamminedichloroplatinum (IV) Tetrachloroplatinate (II) (v) Ammonium hexaisothiocyanato chromate (III) (vi) Tetraamminecobalt (III) - $\mu$ -amido- $\mu$ -peroxotetraammine

cobalt (III) ion (vii) Potassium tetrafluoridoborate (III) (viii) Copper hexacyanoferrate(II).

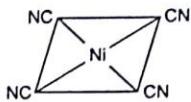
- (a)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{en})\text{NO}_2]\text{Cl}$  (b)  $\text{Ca}_2[\text{Fe}(\text{CN})_6]$   
 (c)   
 (d)  $[\text{Co}(\text{CN})_2\text{Cl}_2]\text{Cl}_3$  (e)  $\text{Na}[\text{Al}(\text{OH})_4]$   
 (f)  $\text{K}_2[\text{Fe}(\text{EDTA})]$  (g)  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- (i)  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ ;  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$ ;  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$ ;  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ ;  $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$ ;  $[\text{PtCl}_6]^{2-}$   
 (ii) Pentaamminechloroplatinum (IV) chloride; Tetraammine dichloroplatinum(IV) chloride, Triammine trichlorido platinum(IV) chloride; Diamminetetrachloroplatinum(IV); Amminepentachlorido platinum (IV) ion; Hexa chloroplatinate (IV) ion.  
 (iii)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$  (iv)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  (v) 6 and 4.
- (i) 3 mole of ions,  $[\text{Co}(\text{NH}_3)(\text{en})_2\text{Cl}]^+$  +  $2\text{Cl}^-$  (ii) 2 mole of ions,  $[\text{Ag}(\text{NH}_3)_2]^+$  +  $\text{Br}^-$  (iii) 2 mole of ions,  $[\text{Pt}(\text{NH}_3)_4]^2+$  +  $[\text{PtCl}_4]^{2-}$  (iv) 3 mole of ions,  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$  +  $2\text{Cl}^-$  (v) 3 mole of ions,  $2\text{Cu}^{2+}$  +  $[\text{Fe}(\text{CN})_6]^{4-}$ .

10. (i), (iii), (v) and (vi) are correct.
11. (i) Linkage (ii) Coordination (iii) Ionisation (iv) Hydrate.
12.  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  gives which precipitate with barium chloride solution while  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  gives light yellow precipitate with  $\text{AgNO}_3$  solution.
13. (a) Two, *cis*- and *trans*- (b) Two, *cis*- and *trans*- (c) No isomerism is exhibited.
14. (a)  $dsp^2$  (b)  $sp^3$  (c)  $d^2sp^3$  or  $sp^3d^2$ .
15. (i) Octahedral, Paramagnetic (ii) Octahedral, Diamagnetic (iii) Octahedral, Paramagnetic (iv) Tetrahedral, Paramagnetic (v) Square planar, Diamagnetic (vi) Square planar, Paramagnetic.

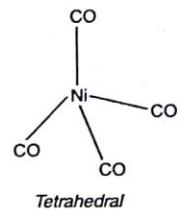
18.  $[\text{Co}(\text{NH}_3)_6]^{3+}$   $d^2sp^3$  hybridization



$[\text{Ni}(\text{CN})_4]^{2-}$   $dsp^2$  hybridization



$[\text{Ni}(\text{CO})_4]$   $sp^3$  hybridization



### BRAIN STORMING PROBLEMS

1. Write down the IUPAC names of the following complexes :
  - (i)  $(\text{NH}_4)_2[\text{FeF}_5\text{H}_2\text{O}]$
  - (ii)  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ReO}_4)_3$
  - (iii)  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{C}_2\text{O}_4)_3]$
  - (iv)  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]_3$
  - (v)  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]_3$
  - (vi)  $\text{K}_4[\text{Mo}(\text{CN})_8]$
  - (vii)  $(\text{NH}_4)_2[\text{Cr}(\text{NH}_3)(\text{NCS})(\text{S})]$
  - (viii)  $[\text{Bi}(\text{SC}(\text{NH}_2)_2)_2](\text{SO}_4)$
  - (ix)  $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$
2.  $[\text{V}(\text{CO})_6]$  has a magnetic moment corresponding to one unpaired electron. Draw a valence bond structure for this molecule. What is geometrical structure of complex?
3. Indicate whether of the following complexes are low spin or high spin complexes:
 

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	0 unpaired electron
$\text{K}_4[\text{Cr}(\text{CN})_6]$	2 unpaired electrons
$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	0 unpaired electron
$(\text{NH}_4)_2[\text{FeF}_5\text{H}_2\text{O}]$	5 unpaired electrons
4. Arrange the following complexes in increasing order of molar conductivity (on the basis of Werner's theory) :
  - (a)  $\text{K}[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_4]$
  - (b)  $[\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3]$
  - (c)  $[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)_3][\text{Co}(\text{NO}_2)_6]$
  - (d)  $\text{Mg}[\text{Cr}(\text{NH}_3)(\text{NO}_2)_5]$

[Ans. (b) < (a) < (d) < (c)]
5. Write down the formula corresponding to the following IUPAC names.
  - (i) Aluminium tetrachloridoaurate(III)
  - (ii) Diamminesilver(I) hexacyanoferrate(II)
  - (iii) Tetrahydroxodioquaoluminate(III) ion
  - (iv) Hexaamminecobalt(III) tetrachloridodiammine chromate(III)
  - (v) Hexaamminenickel(II) hexanitrocobaltate(III)

[Ans. (i)  $\text{Al}[\text{AuCl}_4]_3$  (ii)  $[\text{Ag}(\text{NH}_3)_2]_4[\text{Fe}(\text{CN})_6]$  (iii)  $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$  (iv)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NH}_3)_2\text{Cl}_4]_3$  (v)  $[\text{Ni}(\text{NH}_3)_6]_2[\text{Co}(\text{NO}_2)_6]_2$ ]

6. How many geometrical isomers are possible for each of the following complexes? Draw the structure of each isomer:

- (a)  $\text{Pt}(\text{NH}_3)_2(\text{SCN})_2$
- (b)  $[\text{CoCl}_2\text{Br}_2]^{2-}$  tetrahedral
- (c)  $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$
- (d)  $\text{Pt}(\text{en})\text{Cl}_2$
- (e)  $[\text{Cr}(\text{en})_2\text{Br}_2]^+$
- (f)  $[\text{Rh}(\text{en})_3]^{3+}$

[Ans. (a) Two (b) None (c) Two (d) None (e) Two (f) None]

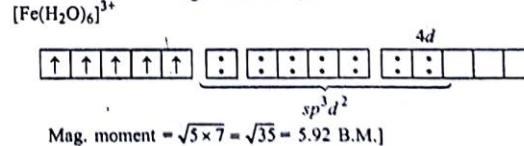
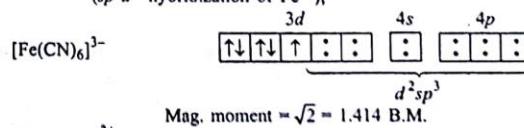
7. Which of the following complexes can exist as optical isomers (enantiomers)? Draw the structure of each enantiomer:

- (a)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
- (b)  $[\text{Co}(\text{NH}_3)_4(\text{en})]^{3+}$
- (c)  $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
- (d)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^{2+}$

[Ans.

- (a)
- (c)
8.  $[\text{Fe}(\text{CN})_6]^{3-}$  ion has magnetic moment of 1.41 B.M. while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment of 5.92 B.M. Explain.

[Ans.  $[\text{Fe}(\text{CN})_6]^{3-}$  has one unpaired electron ( $d^2sp^3$  hybridization of  $\text{Fe}^{3+}$ ) while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has five unpaired electrons ( $sp^3d^2$  hybridization of  $\text{Fe}^{3+}$ ),



9. Match the geometry (given in column A) with the complex (given in column B).

(A)	(B)
(i) Tetrahedral	(a) $[\text{Cu}(\text{NH}_3)_4]^2-$
(ii) Octahedral	(b) $[\text{Ag}(\text{NH}_3)_2]^+$
(iii) Square planar	(c) $\text{Fe}(\text{CO})_5$
(iv) Trigonal bipyramidal	(d) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
(v) Linear	(e) $[\text{NiCl}_4]^{2-}$

[Ans. (i - e); (ii - d); (iii - a); (iv - c); (v - b)]

10. How many ions are given by the following complexes in aqueous solution?

(i) $\text{Ni}(\text{CO})_4$	(ii) $\text{CoCl}_3 \cdot 5\text{H}_2\text{O}$
(iii) $\text{PtCl}_4 \cdot 6\text{NH}_3$	(iv) $\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3$

[Ans. (i) No ionisation

(ii)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}] \text{Cl}_2 \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_5\text{Cl}]^{2+} + 2\text{Cl}^-$ ; three ions

(iii)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4 \rightleftharpoons [\text{Pt}(\text{NH}_3)_6]^{4+} + 4\text{Cl}^-$ ; five ions

(iv)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$  no ionisation]

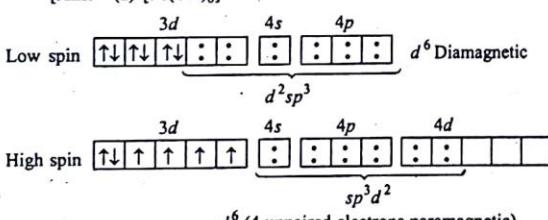
11. What  $d$  electron configurations exhibit both high and low spin in octahedral complexes?

[Ans.  $d^4, d^5, d^6, d^7$ ]

12. Depict high spin and low spin configurations for each of the following complexes. Tell whether each is diamagnetic or paramagnetic. Give the number of unpaired electrons for the paramagnetic complexes:

(a) $[\text{Fe}(\text{CN})_6]^{4-}$	(b) $[\text{Co}(\text{NH}_3)_6]^{3+}$
(c) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	(d) $[\text{CrF}_6]^{4-}$

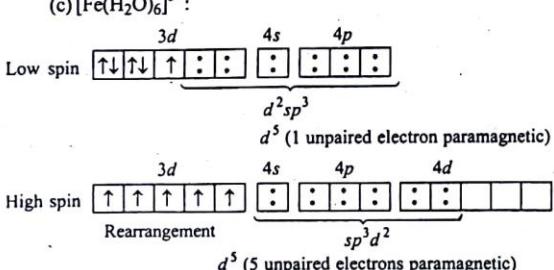
[Ans. (a)  $[\text{Fe}(\text{CN})_6]^{4-}$ :



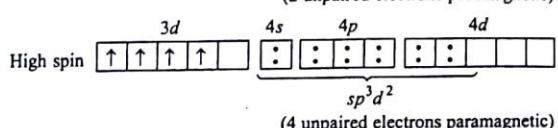
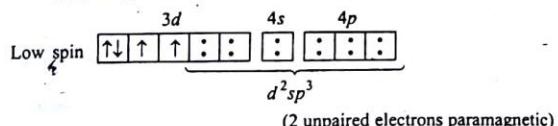
(b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ :  $d^6$  Case depiction as in (a)

Low spin diamagnetic; high spin paramagnetic (4 unpaired electrons)

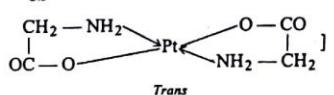
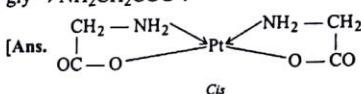
(c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ :



(d)  $[\text{CrF}_6]^{4-}: d^4$  Case



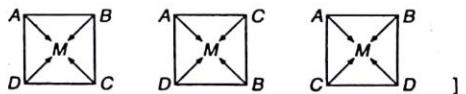
13. Draw the structure of geometrical isomers of  $[\text{Pt}(\text{gly})_2]$  where  $\text{gly} \rightarrow \text{NH}_2\text{CH}_2\text{COO}^-$ .



14. How many geometrical isomers with formula  $[MABCD]$  e.g.,  $[\text{Pt}(\text{NH}_3)(\text{py})(\text{NH}_2\text{OH}) \text{NO}_2]^+$  are possible?

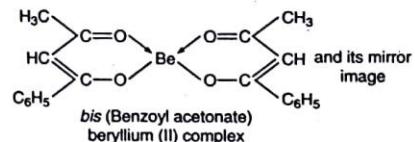
[Ans. 3]

[Hint :



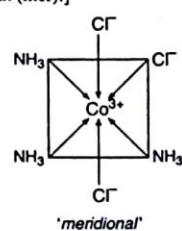
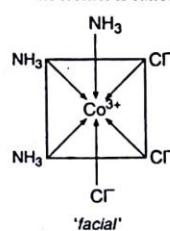
15. Give the example of a tetrahedral complex showing optical activity.

[Ans.]

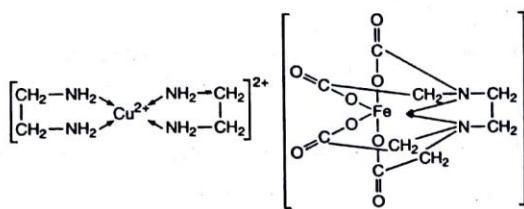


16. What are *facial* and *meridional* isomers? Explain with examples.

[Ans. For the complexes of the type  $[\text{Ma}_3\text{b}_3]$  e.g.,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  and  $[\text{Rh}(\text{py})_3\text{Cl}_3]$ ; the isomer is called *facial* (fac) when all similar ligands occupy same face of an octahedron as shown below. When all similar ligands are not on the same face then the isomer is called *meridional* (mer).]

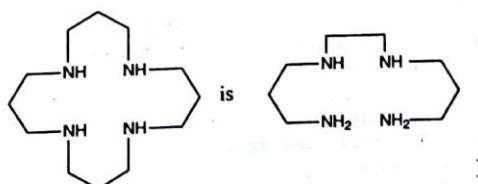


17. Explain why  $[\text{Cu}(\text{en})_2]^{2+}$  is less stable than  $[\text{Fe}(\text{EDTA})]^-$ ?  
 [Ans.  $[\text{Cu}(\text{en})_2]^{2+}$  has four rings in the structure. On the other hand  $[\text{Fe}(\text{EDTA})]^-$  has five rings in the structure.

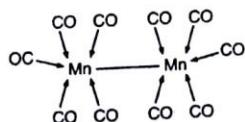


Greater is the number of rings of chelation, more is the stability of complex. Thus,  $[\text{Fe}(\text{EDTA})]^-$  is more stable than  $[\text{Cu}(\text{en})_2]^{2+}$ .

18. What do you understand by macrocyclic effect?  
 [Ans. Thermodynamic stability of a complex formed with a cyclic polydentate ligand is increased when compared to the complex formed with a non-cyclic ligand.



19. The EAN of each Mn ( $Z = 25$ ) in  $\text{Mn}_2(\text{CO})_{10}$  is 36. What is the structure of this complex?  
 [Ans. EAN = 25 (electrons from Mn atom) + 10 (electrons from five CO ligand) + 1 (electron from Mn - Mn bond)  
 Thus, structure will be:



20. How many different structures are possible for each of the following complex ions?

- (a)  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$       (b)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$   
 (c)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$       (d)  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{3+}$

[Ans. Draw the structures yourself.]

21. The hexaaqua complex,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , is green, whereas the corresponding ammonia complex,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , is violet. Explain.

[Ans.  $\text{NH}_3$  is a stronger ligand than  $\text{H}_2\text{O}$ , so  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  will absorb higher energy light than  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ . Being green,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is probably absorbing red light while violet,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is probably absorbing higher energy yellow-green light.]

22. Which of the following metal ions cannot form both high-spin and low-spin octahedral complexes?

- (a)  $\text{Ti}^{3+}$       (b)  $\text{Co}^{2+}$   
 (c)  $\text{Fe}^{2+}$       (d)  $\text{Cu}^{2+}$

[Ans. (a) and (d)]

23. Rank the following complex ions in order of increasing Δ:  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Cr}(\text{NO}_2)_6]^{3-}$ .

[Ans.  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{NO}_2)_6]^{3-}$ .]

24. The value of Δ for  $[\text{RhCl}_6]^{3-}$  is 243 kJ mol<sup>-1</sup>. What wavelength of light will promote an electron from the  $t_{2g}$  set to the  $e_g$  set? What is the colour of the complex?

[Hint :  $\Delta = h\nu = h \cdot \frac{c}{\lambda}$  for one electron

$$\text{or } \lambda = \frac{h \cdot c}{\Delta} = \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1} \times 6.02 \times 10^{23}}{243 \times 10^3 \text{ J}} \\ = 492 \times 10^{-9} \text{ m} = 492 \text{ nm, orange}]$$

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### OBJECTIVE QUESTIONS

Note : Choose the correct answer out of given alternatives for each question.

1. Ethylene diamine is an example of a ..... ligand.  
 (a) monodentate  (b) bidentate   
 (c) tridentate  (d) hexadentate
2. How many EDTA molecules are required to make an octahedral complex with a  $\text{Ca}^{2+}$  ion? [A.I.E.E.E. 2006]  
 (a) Six  (b) Three   
 (c) One  (d) Two   
 [Hint : Only one molecule is required as EDTA is a hexadentate ligand.]
3. The coordination number and oxidation number of  $X$  in the following compound  $[X(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$  will be:  
 [Haryana (P.M.T.) 2006]  
 (a) 10 and 3  (b) 2 and 6   
 (c) 6 and 3  (d) 6 and 4
4. Which one will give  $\text{Fe}^{3+}$  ions in solution?  
 (a)  $[\text{Fe}(\text{CN})_6]^{3-}$    
 (b)  $[\text{Fe}(\text{CN})_6]^{2-}$    
 (c)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$    
 (d)  $\text{Fe}_2(\text{SO}_4)_3$
5. Which of the following is non-ionisable?  
 (a)  $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$   (b)  $\text{Pt}(\text{NH}_3)_3\text{Cl}_4$    
 (c)  $\text{Pt}(\text{NH}_3)_4\text{Cl}_4$   (d)  $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$
6. What is the coordination number of Cr in  $\text{K}_3\text{Cr}(\text{ox})_3$ ?  
 (a) 6  (b) 5   
 (c) 4  (d) 3
7. What is the oxidation state of iron in  $\text{K}_4\text{Fe}(\text{CN})_6$ ?  
 (a) 6  (b) 4   
 (c) 3  (d) 2
8. What is the value of  $x$  on the  $[\text{Ni}(\text{CN})_4]^x$  complex ion?  
 (a) +2  (b) -2   
 (c) 0  (d) +4
9. The oxidation state of Ni in  $\text{Ni}(\text{CO})_4$  is:  
 (a) 0  (b) 1   
 (c) 2  (d) 4
10. The EAN of cobalt in the complex ion  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is:  
 (a) 27  (b) 36   
 (c) 33  (d) 35
11. The formula of the complex *tris* (ethylene diamine) cobalt(III) sulphate is:  
 (a)  $[\text{Co}(\text{en})_2\text{SO}_4]$   (b)  $[\text{Co}(\text{en})_3\text{SO}_4]$    
 (c)  $[\text{Co}(\text{en})_3]_2\text{SO}_4$   (d)  $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$
12. The IUPAC name for the complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  is:  
 [A.I.E.E.E. 2006]  
 (a) nitrito-N-pentaammine cobalt (III) chloride   
 (b) nitrito-N-pentaammine cobalt (II) chloride   
 (c) pentaammine nitrito-N-Cobalt (II) chloride   
 (d) pentaammine nitrito-N-Cobalt (III) chloride
13. The IUPAC name of  $\text{Ni}(\text{CO})_4$  is:  
 (a) tetracarbonyl nickelate(0)   
 (b) tetracarbonyl nickelate(II)
14. The number of chloride ions which would be precipitated, when  $\text{CrCl}_3 \cdot 4\text{NH}_3$  is treated with silver nitrate solution:  
 (a) 3  (b) 2   
 (c) 1  (d) 0
15.  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  are related to each other as:  
 (a) ionisation isomers  (b) linkage isomers   
 (c) coordination isomers  (d) geometrical isomers
16.  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  are related to each other as: [P.M.T. (M.P.) 1993]  
 (a) geometrical isomers  (b) linkage isomers   
 (c) coordination isomers  (d) ionisation isomers
17. An octahedral complex is formed when central metal atom undergoes hybridization amongst the orbitals:  
 (a)  $sp^3$   (b)  $dsp^2$    
 (c)  $sp^3d$   (d)  $sp^3d^2$
18. Which one of the following does not give a white precipitate with silver nitrate solution?  
 (a)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$    
 (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$   (d)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
19. Which of the following has the highest molar conductivity in solution?  
 (a)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$   (b)  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$    
 (c)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$   (d)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_2]\text{Cl}$
20. Geometrical isomerism is found in coordination compounds having coordination number:  
 (a) 2  (b) 3   
 (c) 4 (tetrahedral)  (d) 6
21. Which one of the following will be able to show geometrical isomerism? [B.V.(Pune) 2006]  
 (a)  $MA_4$   (b)  $MA_3B$    
 (c)  $MABCD$   (d)  $M(AA)_2$
22. Optical isomerism is not shown by the complex:  
 (a)  $[\text{Cr}(\text{ox})_3]^{3-}$    
 (b)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  (*cis*-form)   
 (c)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  (*trans*-form)   
 (d)  $[\text{Cr}(\text{en})_3]^{3+}$    
 ox=oxalate; en=ethylenediamine
23. Theoretically, the number of geometrical isomers expected for octahedral complex,  $[Mabcdef]$  is:  
 (a) 0  (b) 15   
 (c) 12  (d) 30
24. The IUPAC name of complex,  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  is:  
 [P.M.T. (M.P.) 1993]  
 (a) potassium alumino oxalate   
 (b) potassium trioxalatoaluminate(III)   
 (c) potassium aluminium(III) oxalate   
 (d) potassium trioxalatoaluminate(VI)
25. The complex that violates the EAN is:  
 (a) potassium ferrocyanide

- (b) potassium ferricyanide  
 (c) tetracarbonyl nickel  
 (d) hexaammine cobalt(III) chloride
26. The hybridization in  $\text{Ni}(\text{CO})_4$  is:  
 (a)  $sp$        (b)  $sp^2$         
 (c)  $sp^3$        (d)  $dsp^2$
27.  $\text{K}_4\text{Fe}(\text{CN})_6$  is called: [C.P.M.T. 1988; C.B.S.E. 1990]  
 (a) potassium hexacyanoferrate(II)  
 (b) potassium ferricyanate  
 (c) potassium ferricyanide  
 (d) prussian blue
28. The hybridization of Fe in  $\text{K}_3\text{Fe}(\text{CN})_6$  is:  
 (a)  $sp^3$        (b)  $dsp^3$         
 (c)  $sp^3d^2$        (d)  $d^2sp^3$
29. The complex,  $[\text{Ni}(\text{CN})_4]^{2-}$  has:  
 (a) linear structure  
 (b) tetrahedral structure  
 (c) square planar structure  
 (d) octahedral structure
30. All ligands are:  
 (a) Lewis acids       (b) Lewis bases  
 (c) neutral       (d) none
31. Which of the following is paramagnetic?  
 (a) Potassium ferrocyanide  
 (b) Potassium ferricyanide  
 (c) Hexaammine cobalt(III) chloride  
 (d) Tetracarbonyl nickel(0)
32. Among the following ions which one has the highest paramagnetism: [I.I.T. 1993]  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$        (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$         
 (c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$        (d)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- [Hint : Larger the number of unpaired electrons, the more it has paramagnetism. The outer configurations are;  $\text{Cr}^{3+}-3d^3$ ;  $\text{Fe}^{2+}-3d^6$ ,  $\text{Cu}^{2+}-3d^9$ ;  $\text{Zn}-3d^{10}$ ]
33. Which one of the following is paramagnetic in nature?  
 (a)  $\text{Ni}(\text{CO})_4$        (b)  $[\text{Ni}(\text{CN})_4]^{2-}$         
 (c)  $[\text{NiCl}_4]^{2-}$        (d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
34. Which one of the following complexes is diamagnetic in nature?  
 (a)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$        (b)  $[\text{FeF}_6]^{3-}$         
 (c)  $[\text{Co}(\text{NH}_3)_6]$        (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
35. Which of the following complexes does not have tetrahedral geometry?  
 (a)  $\text{Ni}(\text{CO})_4$  (diamagnetic)  
 (b)  $[\text{MnCl}_4]^{2-}$  (5 unpaired electrons)  
 (c)  $[\text{Ni}(\text{CN})_4]^{2-}$  (diamagnetic)  
 (d)  $[\text{NiCl}_4]^{2-}$  (2 unpaired electrons)
36. The complex  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  has ..... structure:  
 (a) square planar       (b) tetrahedral        
 (c) pyramidal       (d) pentagonal
37. The coordination number of copper in the complex formed by adding excess of ammonia in copper sulphate solution is:  
 (a) 4       (b) 3        
 (c) 2       (d) 6
38. The scientist who explained structures and isomerism in the coordination complexes is:  
 (a) Sidgwick       (b) Pauling        
 (c) Powell       (d) Werner
39. Which one is not an organometallic compound?  
 (a)  $\text{RMgX}$        (b)  $(\text{C}_2\text{H}_5)_4\text{Pb}$         
 (c)  $(\text{CH}_3)_4\text{Sn}$        (d)  $\text{C}_2\text{H}_5\text{ONa}$
40. The formula of the ferrocene is:  
 (a)  $[(\text{C}_5\text{H}_5)_2\text{Fe}]$        (b)  $[\text{Fe}(\text{CN})_6]^{3-}$         
 (c)  $[\text{Fe}(\text{CN})_6]^{2-}$        (d)  $[\text{Fe}(\text{CO})_5]$
41.  $\pi$ -bonding is not involved in: [A.F.M.C. 1997]  
 (a) ferrocene       (b) dibenzene chromium        
 (c) Zeise's salt       (d) Grignard reagent
42. Wilkinson's catalyst contains:  
 (a) rhodium       (b) iron        
 (c) aluminium       (d) cobalt
43. The number of unpaired electrons in  $d^6$ , low spin, octahedral complex is:  
 (a) 4       (b) 2        
 (c) 1       (d) 0
44. Which of the following systems has maximum number of unpaired electrons?  
 (a)  $d^4$  (octahedral, low spin)        
 (b)  $d^6$  (tetrahedral)        
 (c)  $d^6$  (octahedral, low spin)        
 (d)  $d^9$  (octahedral)
45. The IUPAC name of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is: [A.I.E.E.E. 2005]  
 (a) potassium ferrocyanide        
 (b) potassium ferricyanide        
 (c) potassium hexacyanoferrate(II)        
 (d) potassium hexacyanoferate(III)
46. The oxidation number of Pt in  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$  is: [M.L.N.R. 1993]  
 (a) +1       (b) +2        
 (c) +3       (d) +4
47. Amongst  $\text{Ni}(\text{CO})_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$ : [I.I.T. 1991]  
 (a)  $\text{Ni}(\text{CO})_4$  and  $[\text{NiCl}_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic        
 (b)  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CO})_4]$  is paramagnetic        
 (c)  $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{NiCl}_4]^{2-}$  is paramagnetic        
 (d)  $\text{Ni}(\text{CO})_4$  is diamagnetic and  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic
48. Identify the complexes which are expected to be coloured: [I.I.T. 1994]  
 (a)  $[\text{Ti}(\text{NO}_3)_4]$        (b)  $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$         
 (c)  $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$        (d)  $\text{K}_3[\text{VF}_6]$
- [Hint :  $\text{Ti}^{4+} = 3d^0$ ;  $\text{Cu}^+ = 3d^{10}$ ;  $\text{Cr}^{3+} = 3d^3$ ;  $\text{V}^{3+} = 3d^2$ ]
49. Vitamin B-12 contains:  
 (a) cobalt       (b) magnesium        
 (c) iron       (d) nickel
50. Chlorophyll contains:  
 (a) magnesium       (b) iron        
 (c) cobalt       (d) nickel

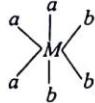
51. Which of the following compounds is not coloured? [A.I.I.M.S. 1997]  
 (a)  $\text{Na}_2[\text{CuCl}_4]$      (b)  $\text{Na}_2[\text{CdCl}_2]$       
 (c)  $\text{K}_4[\text{Fe}(\text{CN})_6]$      (d)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
52. The number of geometrical isomers of  $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$  is: [C.B.S.E. 1997]  
 (a) 0     (b) 2      
 (c) 3     (d) 4
53. The total number of possible isomers of the compound,  $[\text{Cu}(\text{NH}_3)_4]^{\text{II}}[\text{PtCl}_4]^{\text{II}}$ , are: [C.B.S.E. 1998]  
 (a) 3     (b) 5      
 (c) 4     (d) 6
54. The geometry of  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PPH}_3)_2\text{Cl}_2$  are: [I.I.T. 1999]  
 (a) both square planar      
 (b) tetrahedral and square planar respectively      
 (c) both tetrahedral      
 (d) square planar and tetrahedral respectively
55. What is the shape of  $\text{Fe}(\text{CO})_5$  molecule? [C.B.S.E. 2000]  
 (a) Tetrahedral     (b) Octahedral      
 (c) Trigonal bipyramidal     (d) Square pyramidal
56. Mg is an important component of which biomolecule occurring extensively in living world? [C.B.S.E. 2000]  
 (a) Haemoglobin     (b) Chlorophyll      
 (c) Florigen     (d) ATP
57. The complex ion which has no *d* electrons in the central metal atom is (At. No. Cr = 24, Mn = 25, Fe = 26, Co = 27): [I.I.T. (S) 2001]  
 (a)  $[\text{MnO}_4]^-$      (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$      (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
58. The correct order of hybridization of the central atom in following species  $\text{NH}_3$ ,  $[\text{PtCl}_4]^{2-}$ ,  $\text{PCl}_5$ ,  $\text{BCl}_3$  is (At. No. of Pt = 78): [I.I.T. (S) 2001]  
 (a)  $dsp^2$ ,  $dsp^3$ ,  $sp^2$  and  $sp^3$       
 (b)  $sp^3$ ,  $dsp^2$ ,  $dsp^3$ ,  $sp^2$       
 (c)  $dsp^2$ ,  $sp^2$ ,  $dsp^3$ ,  $sp^3$       
 (d)  $dsp^2$ ,  $sp^3$ ,  $sp^2$ ,  $dsp^3$
59. Some salts although containing two different metallic elements give test for one of them in solution. Such salts are: [A.I.I.M.S. 2001]  
 (a) complex salt     (b) double salt      
 (c) normal salt     (d) none
60. Which of the following gives maximum number of isomers? [C.B.S.E. 2001]  
 (a)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$      (b)  $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$       
 (c)  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{en})_2]$      (d)  $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^+$
61. Coordination number of Ni in  $[\text{Ni}(\text{C}_2\text{O}_4)_3]^{4-}$  is: [C.B.S.E. 2001]  
 (a) 3     (b) 6      
 (c) 4     (d) 5
62. Which of the following organometallic compounds is  $\sigma$  and  $\pi$  bonded? [C.B.S.E. 2001]  
 (a)  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$      (b)  $[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$       
 (c)  $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$      (d)  $[\text{Al}(\text{CH}_3)_3]$
63. Which statement is incorrect? [C.B.S.E. 2001]  
 (a)  $\text{Ni}(\text{CO})_4$ —Tetrahedral, paramagnetic      
 (b)  $[\text{Ni}(\text{CN})_4]^{2-}$ —Square planar, diamagnetic      
 (c)  $[\text{Ni}(\text{CO})_4]$ —Tetrahedral, diamagnetic      
 (d)  $[\text{NiCl}_4]^{2-}$ —Tetrahedral, paramagnetic
64. Which of the following cannot show linkage isomerism? [D.C.E. 2001]  
 (a)  $\text{NO}_2^-$      (b)  $\text{SCN}^-$       
 (c)  $\text{CN}^-$      (d)  $\text{NH}_3$
65. Consider the following complex:  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$   
 the coordination number, oxidation number, number of *d*-electrons and number of unpaired *d* electrons on the metal are respectively: [S.C.R.A. 2001]  
 (a) 6, 3, 6, 0     (b) 7, 2, 7, 1      
 (c) 7, 1, 6, 4     (d) 6, 2, 7, 3
66. In electroplating of copper, K  $[\text{Ag}(\text{CN})_2]$  is used instead of  $\text{AgNO}_3$ . The reason is: [C.B.S.E. 2002]  
 (a) a thin layer of Ag is formed on Cu      
 (b) more voltage is required      
 (c)  $\text{Ag}^+$  ions are completely removed from solution      
 (d) less availability of  $\text{Ag}^+$  ions, as Cu cannot displace Ag from  $[\text{Ag}(\text{CN})_2]^-$  ion
67. Both geometrical and optical isomerisms are shown by: [C.E.T. (Chandigarh) 2002]  
 (a)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$      (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$       
 (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$      (d)  $[\text{Crx}_3]^{3-}$
68. In  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , the isomerism shown is: [A.I.E.E.E. 2002]  
 (a) ligand     (b) optical      
 (c) geometrical     (d) ionisation
69. Atomic numbers of Cr and Fe are respectively 25 and 26, which of the following is paramagnetic with spin of electron? [C.B.S.E. 2002]  
 (a)  $\text{Cr}(\text{CO})_6$      (b)  $[\text{Fe}(\text{CO})_5]$       
 (c)  $[\text{Fe}(\text{CN})_6]^{4-}$      (d)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$
70. The hypothetical complex chlorodiaquatriamine cobalt (III) chloride can be represented as : [C.B.S.E. 2002]  
 (a)  $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]\text{Cl}_2$       
 (b)  $[\text{Co}(\text{NH}_3)_3\text{H}_2\text{OCl}_3]$       
 (c)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}]$       
 (d)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3\text{Cl}_3]$
71. The type of isomerism present in nitropentaammine chromium (III) chloride is: [A.I.E.E.E. 2002]  
 (a) optical     (b) linkage      
 (c) ionisation     (d) polymerisation
72. Development of a photographic plate involves the use of: [P.M.T. (Kerala) 2003]  
 (a) an oxidising agent     (b) a complexing agent      
 (c) a neutralising agent     (d) a precipitating agent      
 (e) a reducing agent

73. In the coordination compound  $K_4[Ni(CN)_4]$ , the oxidation state of nickel is: [A.I.E.E. 2003]  
 (a) -1       (b) 0        
 (c) +1       (d) +2
74. One mole of the complex compound  $Co(NH_3)_5Cl_3$ , gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $AgNO_3$  solution to yield two moles of  $AgCl(s)$ . The structure of the complex is: [A.I.E.E. 2003]  
 (a)  $[Co(NH_3)_5Cl]Cl_2$         
 (b)  $[Co(NH_3)_3Cl_3]2NH_3$         
 (c)  $[Co(NH_3)_4Cl_2]Cl\cdot NH_3$         
 (d)  $[Co(NH_3)_4Cl_2]Cl_2\cdot NH_3$
75. Among the following, which is not the  $\pi$ -bonded organometallic compound: [C.B.S.E. (Medical) 2003]  
 (a)  $(CH_3)_4Sn$        (b)  $Cr(\eta^6-C_6H_6)_2$         
 (c)  $Fe(\eta^5-C_5H_5)_2$        (d)  $K[PtCl_3(\eta^2-C_2H_4)]$
76. According to the IUPAC nomenclature, sodium nitroprusside is named as: [C.B.S.E. (Medical) 2003]  
 (a) sodium nitro-ferrocyanide        
 (b) sodium pentacyanonitrosyl ferrate (II)        
 (c) sodium nitroferricyanide        
 (d) sodium pentacyanonitrosyl ferrate (III)
77. The number of unpaired electrons in the complex ion  $[CoF_6]^{3-}$  is: [C.B.S.E. (Medical) 2003]  
 (a) 3       (b) 4        
 (c) 0       (d) 2
78. Which of the following octahedral complexes does not show geometrical isomerism ( $A$  and  $B$  are monodentate ligands)? [C.B.S.E. (Medical) 2003]  
 (a)  $[MA_3B_3]$         
 (b)  $[MA_4B_2]$         
 (c)  $[MA_5B]$         
 (d)  $[MA_2B_4]$
79. The geometry of  $[Ni(CN)_4]^{2-}$  and  $[NiCl_4]^{2-}$  ions are: [A.F.M.C. 2003]  
 (a) tetrahedral        
 (b) square planar        
 (c) square planar, tetrahedral respectively        
 (d) tetrahedral and square planar respectively
80. Complexes with bidentate ligands are called: [P.M.E.T. 2003]  
 (a) ligands       (b) chelates        
 (c) complexes       (d) none of these
81. The complex used as an anticancer agent is: [A.I.I.M.S. 2003; B.H.U. 2007]  
 (a) *mer*- $[Co(NH_3)_3Cl_3]$        (b) *Cis*- $[PtCl_2(NH_3)_2]$         
 (c) *Cis*- $K_2[PtCl_2Br_2]$        (d)  $Na_2[CoCl_4]$
82. The ligand called  $\pi$ -acid is: [A.I.I.M.S. 2003]  
 (a) CO       (b)  $NH_3$         
 (c)  $C_2O_4^{2-}$        (d) ethylene diamine
83. The effective atomic number of cobalt in the complex  $[Co(NH_3)_4]^{3+}$  is: [P.E.T. (M.P.) 2003]  
 (a) 36       (b) 33        
 (c) 24       (d) 30
84. The possible number of optical isomers in  $[Co(en)_2Cl_2]^+$  are: [P.E.T. (M.P.) 2003]  
 (a) 2       (b) 3        
 (c) 4       (d) 6
85. Mixture of  $[X] = 0.02$  mole of  $[Co(NH_3)_5SO_4]Br$  and 0.02 mole of  $[Co(NH_3)_5Br] SO_4$  was prepared in 2 litre of solution; 1 litre of mixture  $[X] +$  excess  $AgNO_3 \rightarrow [Y]$   
 1 litre of mixture  $[X] +$  excess  $BaCl_2 \rightarrow [Z]$   
 No. of moles of  $[Y]$  and  $[Z]$  are: [I.I.T. (S) 2003]  
 (a) 0.01, 0.01       (b) 0.02, 0.01        
 (c) 0.01, 0.02       (d) 0.02, 0.02
86. In the process of extraction of gold,  
 Roasted gold ore +  $CN^- + H_2O \rightarrow [X] + OH^-$   
 $[X] + Zn \rightarrow [Y] + Au$   
 Identify  $[X]$  and  $[Y]$ : [I.I.T. (S) 2003]  
 (a)  $[X] = [Au(CN)_2]^-$ ,  $[Y] = [Zn(CN)_4]^{2-}$         
 (b)  $[X] = [Au(CN)_4]^{3-}$ ,  $[Y] = [Zn(CN)_4]^{2-}$         
 (c)  $[X] = [Au(CN)_2]^-$ ,  $[Y] = [Zn(CN)_6]^{4-}$         
 (d)  $[X] = [Au(CN)_4]^-$ ,  $[Y] = [Zn(CN)_6]^{2-}$
87. Which of the following forms with an excess of  $CN^-$ , a complex having coordination number two? [A.I.I.M.S. 2004]  
 (a)  $Cu^{2+}$        (b)  $Ag^+$         
 (c)  $Ni^{2+}$        (d)  $Fe^{2+}$
88. Which of the following is not considered as an organometallic compound? [A.I.I.M.S. 2004]  
 (a) Ferrocene       (b) *Cis*-platin        
 (c) Zeise's salt       (d) Grignard reagent
89. Which of the following does not have optical isomer? [A.I.I.M.S. 2004]  
 (a)  $[Co(en)_3]Cl_3$        (b)  $[Co(NH_3)_3Cl_3]$         
 (c)  $[Co(en)_2Cl_2]Cl$        (d)  $[Co(en)(NH_3)_2Cl_2]Cl$
90. Which of the following is considered to be an anticancer species? [C.B.S.E. (P.M.T.) 2004]  
 (a)   
 (b)   
 (c)   
 (d)
91. Among  $[Ni(CO)_4]$ ,  $[Ni(CN)_4]^{2-}$  and  $[NiCl_4]^{2-}$  species, the hybridization states of the Ni-atom are respectively: [C.B.S.E. (P.M.T.) 2004]  
 (a)  $sp^3$ ,  $dsp^2$ ,  $dsp^2$        (b)  $sp^3$ ,  $dsp^2$ ,  $sp^3$         
 (c)  $sp^3$ ,  $sp^3$ ,  $dsp^2$        (d)  $dsp^2$ ,  $sp^3$ ,  $sp^3$
92. Considering  $H_2O$  as a weak-field ligand, the number of unpaired electrons in  $[Mn(H_2O)_6]^{2+}$  will be: [C.B.S.E. (P.M.T.) 2004]  
 (a) three       (b) five        
 (c) two       (d) four

93. Which of the following does not have a metal carbon bond?  
 (a)  $\text{Al}(\text{OC}_2\text{H}_5)_3$   (b)  $\text{C}_2\text{H}_5\text{MgBr}$    
 (c)  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$   (d)  $\text{Ni}(\text{CO})_4$
94. The correct order of magnetic moments is:  
 [A.I.E.E.E. 2004]  
 (a)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$    
 (b)  $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$    
 (c)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$    
 (d)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$
95. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?  
 [A.I.E.E.E. 2004]  
 (a) Chlorophyll is a green pigment in plants and contains calcium   
 (b) Haemoglobin is the red pigment of blood and contains iron   
 (c) Cyanocobalamin is  $\text{B}_{12}$  and contains cobalt   
 (d) Carboxypeptidase A is an enzyme and contains zinc
96. Which one of the following complexes is an outer orbital complex?  
 [A.I.E.E.E. 2004]  
 (a)  $[\text{Fe}(\text{CN})_6]^{4-}$   (b)  $[\text{Mn}(\text{CN})_6]^{4-}$    
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   (d)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
97. Which one is an organometallic compound?  
 [M.P. (P.E.T.) 2004]  
 (a) Lithium acetate   
 (b) Lithium methoxide   
 (c) Lithium dimethylamide   
 (d) Methyl lithium
98. The species having tetrahedral shape is:  
 [I.I.T. 2004;  
 A.I.I.M.S. 2007]  
 (a)  $[\text{PdCl}_4]^{2-}$   (b)  $[\text{Ni}(\text{CN})_4]^{2-}$    
 (c)  $[\text{Pd}(\text{CN})_4]^{2-}$   (d)  $[\text{NiCl}_4]^{2-}$
99. Which one of the following complexes will have four isomers?  
 (a)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$    
 (b)  $[\text{Co}(\text{PPh}_3)_2(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$    
 (c)  $[\text{Co}(\text{en})_3]\text{Cl}_3$    
 (d)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$
100. Which of the following shall form an octahedral complex?  
 (a)  $d^4$  (low spin)  (b)  $d^8$  (high spin)   
 (c)  $d^6$  (low spin)  (d) All of these
101. Which of the following has a square planar geometry?  
 [A.I.E.E.E. 2007]  
 (a)  $[\text{PtCl}_4]^{2-}$   (b)  $[\text{CoCl}_4]^{2-}$    
 (c)  $[\text{FeCl}_4]^{2-}$   (d)  $[\text{NiCl}_4]^{2-}$
102. Which of the following will give a pair of enantiomorphs?  
 [C.B.S.E. 2007]  
 (a)  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$   (b)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$    
 (c)  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$   (d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$
103. The  $d$  electron configurations of  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  are  $3d^4$ ,  $3d^5$ ,  $3d^6$ ,  $3d^8$  respectively. Which of the following aqua complexes will exhibit the minimum paramagnetic behaviour?  
 [C.B.S.E. 2007]  
 (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   (b)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$    
 (c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$   (d)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
104. Which of the following statements is not correct?  
 [P.E.T. (Kerala) 2007]  
 (a) The complexes  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  differ in state of hybridization of nickel   
 (b) The complexes  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  differ in geometry   
 (c) The complexes  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  differ in the magnetic properties   
 (d) The complexes  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  differ in primary valencies of nickel   
 (e) Nickel ion has the same secondary valency in the complexes  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$
105. Both  $\text{Co}^{3+}$  and  $\text{Pt}^{4+}$  have a coordination number of 6. Which of the following pairs of complexes will show approximately the same electrical conductance for their  $0.001M$  aqueous solutions?  
 [P.E.T. (Kerala) 2007]  
 (a)  $\text{CoCl}_3 \cdot 4\text{NH}_3$  and  $\text{PtCl}_4 \cdot 4\text{NH}_3$    
 (b)  $\text{CoCl}_3 \cdot 3\text{NH}_3$  and  $\text{PtCl}_4 \cdot 5\text{NH}_3$    
 (c)  $\text{CoCl}_3 \cdot 6\text{NH}_3$  and  $\text{PtCl}_4 \cdot 5\text{NH}_3$    
 (d)  $\text{CoCl}_3 \cdot 6\text{NH}_3$  and  $\text{PtCl}_4 \cdot 3\text{NH}_3$    
 (e)  $\text{CoCl}_3 \cdot 5\text{NH}_3$  and  $\text{PtCl}_4 \cdot 6\text{NH}_3$
106. Facial-meridional isomerism is associated with which one of the following complexes? [M = central metal]  
 [P.M.T. (Kerala) 2007]  
 (a)  $[\text{M}(\text{AA})_2]$   (b)  $[\text{MA}_3\text{B}_3]$    
 (c)  $[\text{M}(\text{AA})_3]$   (d)  $[\text{MABCD}]$    
 (e)  $[\text{MA}_4\text{B}_2]$
107. The increasing order of the crystal field splitting power of some common ligands is:  
 [P.M.T. (Kerala) 2007]  
 (a)  $\text{H}_2\text{O} < \text{OH}^- < \text{Cl}^- < \text{F}^- < \text{CN}^-$    
 (b)  $\text{H}_2\text{O} < \text{Cl}^- < \text{OH}^- < \text{CN}^- < \text{F}^-$    
 (c)  $\text{CN}^- < \text{H}_2\text{O} < \text{OH}^- < \text{F}^- < \text{Cl}^-$    
 (d)  $\text{F}^- < \text{CN}^- < \text{OH}^- < \text{Cl}^- < \text{H}_2\text{O}$    
 (e)  $\text{Cl}^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{CN}^-$
108. Which one of the following is a tridentate ligand?  
 [P.M.T. (Kerala) 2007]  
 (a)  $\text{NO}_2^-$   (b) Oxalate ion   
 (c) Glycinate ion  (d) Diene   
 (e) EDTA
109. The dark blue colour of the solution formed when excess of ammonia is added to a solution of copper(II) sulphate is due to the presence of the ion:  
 [P.M.T. (Kerala) 2007]  
 (a)  $[\text{Cu}(\text{OH})_4(\text{H}_2\text{O})_2]^{2+}$   (b)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$    
 (c)  $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{4+}$   (d)  $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$    
 (e)  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$
110. If  $\text{AgNO}_3$  solution is added in excess to  $1M$  solution of  $\text{CoCl}_3 \cdot x\text{NH}_3$ , one mole of  $\text{AgCl}$  is formed. What is the value of  $x$ ?  
 [E.A.M.C.E.T. (Med.) 2007]  
 (a) 1  (b) 2   
 (c) 3  (d) 4
111. Assign the hybridization, shape and magnetic moment of  $\text{K}_2[\text{Cu}(\text{CN})_4]$ :  
 [J.E.E. (Orissa) 2007]  
 (a)  $sp^3$  tetrahedral, 1.73 B.M.   
 (b)  $dsp^2$ , square planar, 1.73 B.M.

- (c)  $sp^3$ , tetrahedral, 2.44 B.M.  
 (d)  $dsp^2$ , square planar, 2.44 B.M.

112. Octahedral complex,



- (a) *cis*  
 (b) *trans*  
 (c) *mer*  
 (d) *fac*

[D.C.E. (Engg.) 2007]



### ASSERTION-REASON TYPE QUESTIONS

The questions given below consist of Assertion (A) and Reason (R). Use the following key to select the correct answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).  
 (b) If both (A) and (R) are correct but (R) is not correct explanation for (A).  
 (c) If (A) is correct but (R) is incorrect.  
 (d) If both (A) and (R) are incorrect.  
 (e) If (A) is incorrect but (R) is correct.
113. (A)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  does not give a white precipitate with  $\text{AgNO}_3$  solution. (R) Chlorine is not present in the ionising sphere.
114. (A) The ligands, thiocyanato ( $\text{SCN}^-$ ) and isothiocyanato ( $\text{NCS}^-$ ) are ambidentate. (R) The ligands form linkage isomers.
115. (A)  $\text{Ni}(\text{CO})_4$  is diamagnetic in nature. (R) Ni-atom undergoes  $sp^3$  hybridization.
116. (A) *Cis*-isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  shows optical activity. (R) *Cis*-isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  is a symmetric molecule.
117. (A) Complexes containing three bidentate groups such as  $[\text{Cr}(\text{ox})_3]^{3-}$  and  $[\text{Co}(\text{en})_3]^{3+}$  do not show optical activity. (R) Octahedral complex,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  shows geometrical isomerism.
118. (A) Tetrahedral complexes do not show geometrical isomerism. (R)

- (R) The relative positions of the ligands in the tetrahedral complex are the same w.r.t. each other.
119. (A)  $\text{Ti}(\text{OC}_6\text{H}_5)_4$  is an organometallic compound.  
 (R) Acetate ion can form a chelate.
120. (A) EAN of Cr in its complexes is always 36.  
 (R) Oxidation state of Cr in  $\text{Cr}(\text{CO})_6$  is zero.
121. (A)  $\text{K}_3\text{Fe}(\text{CN})_6$  is a low spin complex.  
 (R)  $\text{Fe}^{2+}$  ion in this complex undergoes  $sp^3d^2$  hybridization.
122. (A) Coordination isomerism occurs when both cation and anion are complex.  
 (R) The complexes with coordination number 6 form octahedral complexes involving either  $sp^3d^2$  or  $d^2sp^3$  hybridization.
123. (A) Metals possess two types of valencies-primary and secondary. The primary valency is not ionisable while secondary valency is ionisable.  
 (R) The IUPAC name of  $\text{K}_3\text{Fe}(\text{CN})_6$  is potassium ferricyanide.
124. (A) After splitting of *d*-orbitals during complex formation, the orbitals form two sets of orbitals  $t_{2g}$  and  $e_g$ .  
 (R) Splitting of *d*-orbitals occurs only in the case of strong field ligands such as  $\text{CN}^-$ .
125. (A) Ferrocene is a  $\pi$ -bonded complex.  
 (R) All organometallic compounds are  $\pi$ -bonded complexes.
126. (A) All inner orbital complexes are diamagnetic.  
 (R) Inner orbital complexes contain only paired orbitals.
127. (A) Organometallic compounds are those which have one or more metal-carbon bonds.  
 (R) Metallic carbonyls are organometallic compounds having both  $\sigma$  and  $\pi$ -bonds.
128. (A) In octahedral complexes, the three orbitals ( $d_{xy}, d_{yz}, d_{zx}$ ) are stable and of low energy while the two orbitals ( $d_{x^2-y^2}, d_{z^2}$ ) are unstable and have high energy.  
 (R) In octahedral complexes, the three *d*-orbitals ( $d_{xy}, d_{yz}, d_{zx}$ ) experience less repulsion from the ligands while two *d*-orbitals ( $d_{x^2-y^2}, d_{z^2}$ ) experience more repulsion from the ligands due to their shapes.
129. (A)  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$  does not show optical isomerism.  
 (R) It has a plane of symmetry.

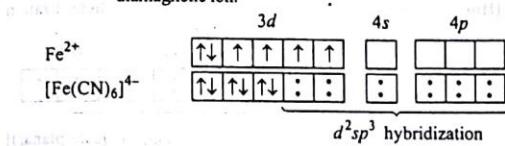
### ANSWERS : OBJECTIVE QUESTIONS

- |          |          |          |          |          |          |          |                 |          |          |
|----------|----------|----------|----------|----------|----------|----------|-----------------|----------|----------|
| 1. (b)   | 2. (c)   | 3. (c)   | 4. (d)   | 5. (a)   | 6. (a)   | 7. (d)   | 8. (b)          | 9. (a)   | 10. (b)  |
| 11. (d)  | 12. (d)  | 13. (c)  | 14. (c)  | 15. (a)  | 16. (b)  | 17. (d)  | 18. (d)         | 19. (a)  | 20. (d)  |
| 21. (c)  | 22. (c)  | 23. (b)  | 24. (b)  | 25. (b)  | 26. (c)  | 27. (a)  | 28. (d)         | 29. (c)  | 30. (b)  |
| 31. (b)  | 32. (b)  | 33. (c)  | 34. (c)  | 35. (c)  | 36. (a)  | 37. (a)  | 38. (d)         | 39. (d)  | 40. (a)  |
| 41. (d)  | 42. (a)  | 43. (d)  | 44. (b)  | 45. (d)  | 46. (b)  | 47. (c)  | 48. (c) and (d) | 49. (a)  | 50. (a)  |
| 51. (b)  | 52. (b)  | 53. (c)  | 54. (b)  | 55. (c)  | 56. (b)  | 57. (a)  | 58. (b)         | 59. (a)  | 60. (d)  |
| 61. (b)  | 62. (b)  | 63. (a)  | 64. (d)  | 65. (a)  | 66. (d)  | 67. (a)  | 68. (b)         | 69. (d)  | 70. (a)  |
| 71. (b)  | 72. (b)  | 73. (b)  | 74. (a)  | 75. (a)  | 76. (b)  | 77. (b)  | 78. (c)         | 79. (c)  | 80. (b)  |
| 81. (b)  | 82. (a)  | 83. (a)  | 84. (b)  | 85. (a)  | 86. (a)  | 87. (b)  | 88. (b)         | 89. (b)  | 90. (c)  |
| 91. (b)  | 92. (b)  | 93. (a)  | 94. (a)  | 95. (a)  | 96. (d)  | 97. (d)  | 98. (d)         | 99. (d)  | 100. (d) |
| 101. (a) | 102. (b) | 103. (b) | 104. (d) | 105. (c) | 106. (b) | 107. (c) | 108. (d)        | 109. (e) | 110. (d) |
| 111. (b) | 112. (d) | 113. (a) | 114. (a) | 115. (b) | 116. (c) | 117. (e) | 118. (a)        | 119. (d) | 120. (e) |
| 121. (c) | 122. (b) | 123. (d) | 124. (c) | 125. (c) | 126. (d) | 127. (b) | 128. (a)        | 129. (a) |          |

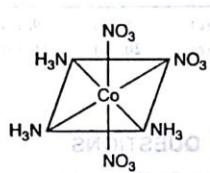
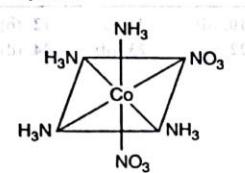
### QUESTIONS FOR IIT ASPIRANTS

1. The coordination number and oxidation number of  $M$  in the complex,  $[M(NH_3)_5SO_4]Cl$  are:  
 (a) 10, 3    (b) 6, 4    (c) 2, 6    (d) 6, 3
2.  $CuSO_4 \cdot 5H_2O$  is a coordination compound. It can be represented as:  
 (a)  $[Cu(H_2O)_4]SO_4 \cdot H_2O$     (b)  $[Cu(H_2O)_3]SO_4 \cdot 2H_2O$   
 (c)  $[Cu(H_2O)_2]SO_4 \cdot 3H_2O$     (d)  $[Cu(H_2O)_5]SO_4$
3. The complex/complex ion, which shows optical activity is:  
 (a)  $[Cr(H_2O)_4Cl_2]^{+}$     (b)  $[Co(H_2O)_2(NH_3)_2Cl_2]^{+}$   
 (c)  $[Co(NH_3)_6]^{3+}$     (d)  $[Co(CN)_5NC]$
- [Hint : ]
- 4.
- 
- The above splitting of  $d$ -orbitals takes place in the formation of:  
 (a) tetrahedral complexes  
 (b) square-planar complexes  
 (c) octahedral complexes  
 (d) both tetrahedral and square-planar complexes
5. Which of the following pairs of complexes are isomeric with each other but their aqueous solutions exhibit different molar conductivities?  
 (a)  $[PtCl_2(NH_3)_4]Br_2$  and  $[Pt(NH_3)_4Br_2]Cl_2$   
 (b)  $[Co(NH_3)_4Cl_2]NO_2$  and  $[Co(NH_3)_4ClNO_2]Cl$   
 (c)  $[Co(NH_3)_5NO_2]Cl_2$  and  $[Co(NH_3)_5ONO]Cl_2$   
 (d)  $[Co(NH_3)_5Br]SO_4$  and  $[Co(NH_3)_5SO_4]Br$
- [Hint : They are ionisation isomers but their molar conductivities are different due to different magnitude of charge on the cation and anion.]
6. Three arrangements are shown for the complex,  $[Co(en)(NH_3)_2Br_2]^{+}$ . Which one is the wrong statement?
- 
- (a) I and II are geometrical isomers  
 (b) II and III are optical isomers  
 (c) I and III are optical isomers  
 (d) II and III are geometrical isomers
7. The donor sites of EDTA ligand are:  
 (a) O atoms only  
 (b) N atoms only  
 (c) Two N atoms and four O atoms  
 (d) Three N atoms and three O atoms
- [Hint : The structure of EDTA ion is :
- 
- 1, 2 are donor N atoms and 3, 4, 5, 6 are donor O atoms.]
8. Which of the following can act as ligand but does not have any lone or unshared pair of electrons?  
 (a)  $C_2H_4$     (b)  $NH_3$     (c)  $H_2O$     (d)  $Cl^-$
- [Hint :  $C_2H_4$  does not possess an unshared lone pair but it can act as π-acid ligand.]
9. A complex is prepared by mixing  $CoCl_3$  and  $NH_3$ . 0.1 M solution of the complex was found to freeze at  $-0.372^\circ C$ . The formula of the complex is:  
 [Molar depression constant of water =  $1.86^\circ C/m$ .]  
 (a)  $[Co(NH_3)_6]Cl_3$     (b)  $[Co(NH_3)_5Cl]Cl_2$   
 (c)  $[Co(NH_3)_4Cl_2]Cl$     (d)  $[Co(NH_3)_3Cl_3]$
- [Hint :  $\Delta T_f = i \times K_f \times m = i \times 1.86 \times 0.1$   
 or     $0.372 = 0.186 \times i$   
 or     $i = 2$   
 This shows that the complex gives two ions in solution.  
 Thus, the formula of the complex is  $[Co(NH_3)_4Cl_2]Cl$ .  
 $[Co(NH_3)_4Cl_2]Cl \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + Cl^-$ ]
10. Which statement is wrong ?  
 (a) All the octahedral complexes of  $Ni^{2+}$  are outer orbital complexes.  
 (b)  $(SCN)^-$  shows linkage isomerism in coordination compounds.  
 (c) All ligands are Lewis bases.  
 (d)  $NH_4^+$  ion can act as a ligand.
- [Hint :  $NH_4^+$  ion does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.]
11. Which of the following is correct ?  
 (a) The IUPAC name of  $Mn_3(CO)_{12}$  is dodecacarbonyl tri-manganese (0).  
 (b) The IUPAC name of  $K[BF_4]$  is tetrafluoroboron potassium (I).  
 (c) The IUPAC name of  $K_3[Al(C_2O_4)_3]$  is potassium trioxalate aluminium (III).  
 (d) The IUPAC name of  $K_4Fe(CN)_6$  is potassium ferrocyanide.

12. Which of the following is not correct ?  
 (a)  $[\text{Fe}(\text{CN})_6]^{4-}$  is weakly paramagnetic  
 (b)  $[\text{Fe}(\text{CN})_6]^{4-}$  is strongly paramagnetic  
 (c)  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic  
 (d)  $[\text{NiCl}_4]^{2-}$  is paramagnetic
- [Hint :  $[\text{Fe}(\text{CN})_6]^{4-}$  involves  $d^2sp^3$  hybridization. As  $\text{CN}^-$  is a strong ligand, the pairing of electrons occurs, thus, it is a diamagnetic ion.



13. The number of geometrical isomers of  $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$  are:  
 (a) 0    (b) 2  
 (c) 3    (d) 4
- [Hint :



14. The complex ion which has no  $d$  electron in the central metal atom is : [At. No. Cr = 24, Mn = 25, Fe = 26, Co = 27]  
 (a)  $\text{MnO}_4^-$     (b)  $[\text{Co}(\text{NH}_3)_6]^{3-}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{4-}$     (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
15. In  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , the isomerism shown is :  
 (a) ligand    (b) geometrical  
 (c) optical    (d) ionisation
16.  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  differ in :  
 (a) geometry, magnetic moment                             (b) magnetic moment, colour  
 (c) geometry, hybridization                                 (d) hybridization, number of unpaired electrons
- [Hint :  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic.  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  has pale green colour while  $[\text{Fe}(\text{CN})_6]^{4-}$  has yellow colour.]

17. Complexes formed in the following methods are :  
 (i) cyanide process for extraction of silver  
 (ii) Mond's process for extraction of nickel  
 (iii) photographic fixing process  
 (iv) removal of  $\text{Ca}^{2+}$  ions from hard water by EDTA.
- I           II           III           IV
- (a)  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$     $\text{Ni}(\text{CO})_4$     $[\text{Ag}(\text{CN})_2]^-$     $[\text{Ca}(\text{EDTA})]^{2-}$   
 (b)  $[\text{Ag}(\text{CN})_2]^-$     $\text{Ni}(\text{CO})_4$     $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$     $[\text{Ca}(\text{EDTA})]^{2-}$   
 (c)  $[\text{Ag}(\text{CN})_2]^-$     $\text{Ni}(\text{CO})_6$     $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$     $[\text{Ca}(\text{EDTA})]^{2-}$   
 (d)  $[\text{Ag}(\text{CN})_4]^{3-}$     $\text{NiO}$     $[\text{Ag}(\text{S}_2\text{O}_3)]^-$     $[\text{Ca}(\text{EDTA})]^{2-}$
18. Which of the following statements is not correct ?  
 (a) Higher the charge density on the central ion, the greater is the stability of its complexes

- (b) Chelating ligands form more stable complexes as compared to monodentate ligands  
 (c) The higher the oxidation state of the metal, the more stable is the complex  
 (d) The cyano and ammine complexes are less stable than those formed by halide ions

19. Match the correct organic ligands used for the estimation of  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions.

(i) Dimethyl glyoxime	(ii) 1, 10-phenanthroline	(III)
(I)	(II)	
(a) $\text{Al}^{3+}$	$\text{Fe}^{3+}$	$\text{Ni}^{2+}$
(b) $\text{Fe}^{3+}$	$\text{Ni}^{2+}$	$\text{Al}^{3+}$
(c) $\text{Ni}^{2+}$	$\text{Fe}^{3+}$	$\text{Al}^{3+}$
(d) $\text{Fe}^{3+}$	$\text{Al}^{3+}$	$\text{Ni}^{2+}$

20. The EAN of a metal carbonyl,  $M(\text{CO})_x$  is 36. The atomic number of metal is 24. The value of  $x$  is :  
 (a) 6    (b) 5  
 (c) 4    (d) 3

- [Hint :  $EAN = 36 = 2 \times x + 24$ ]

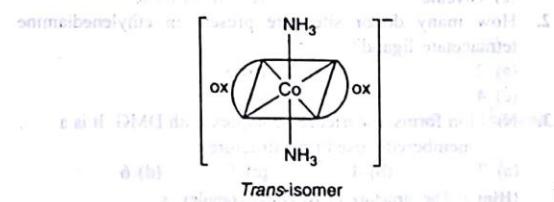
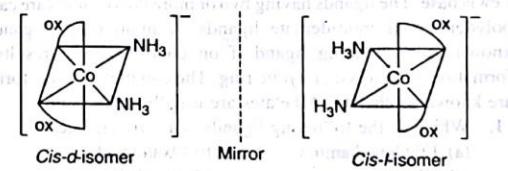
21.  $M-L$ -bonds in carbonyl possess :

- (a) only sigma character  
 (b) only pi( $\pi$ ) character  
 (c) both sigma ( $\sigma$ ) and pi ( $\pi$ ) characters  
 (d) none of the above

22. The number of possible isomers of an octahedral complex,  $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]^{+}$  is:

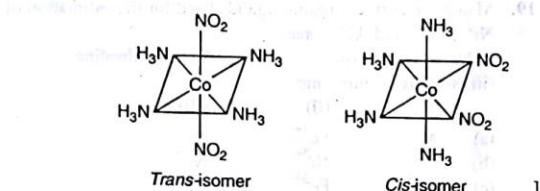
- (a) 1    (b) 2  
 (c) 3    (d) 4

- [Hint : ]



23.  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$  exhibits:  
 (a) ionisation isomerism, geometrical isomerism and optical isomerism  
 (b) linkage isomerism, geometrical isomerism and optical isomerism  
 (c) linkage isomerism, ionisation isomerism and optical isomerism  
 (d) linkage isomerism, geometrical isomerism and ionisation isomerism

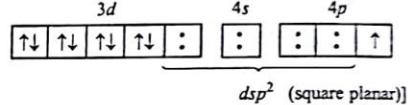
- [Hint : (i)  $\text{NO}_2$  is an ambidentate group. It can show linkage isomerism.  
(ii) The complex can show ionisation isomerism with the complex  $[\text{Co}(\text{NH}_3)_4\text{NO}_2\text{Cl}] \text{NO}_2^-$ .  
(iii) The complex shows geometrical isomerism.]



24. When excess of ammonia is added to copper sulphate solution, the deep blue coloured complex is formed. The complex is:

- (a) tetrahedral, paramagnetic
- (b) tetrahedral, diamagnetic
- (c) square planar, diamagnetic
- (d) square planar, paramagnetic

[Hint :  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex is formed by  $dsp^2$  hybridization and one electron is shifted to  $4p$ -orbital.



$dsp^2$  (square planar)

## ANSWERS

### Questions for IIT Aspirants

1. (d)    2. (a)    3. (b)    4. (c)    5. (d)    6. (b)    7. (c)    8. (a)    9. (c)    10. (d)    11. (a)    12. (b)  
13. (b)    14. (a)    15. (c)    16. (b)    17. (b)    18. (d)    19. (c)    20. (a)    21. (c)    22. (c)    23. (d)    24. (d)

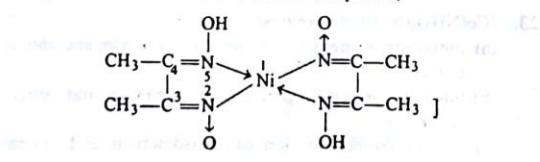
## ● THOUGHT TYPE QUESTIONS

### Thought 1

The neutral molecules, anions or cations which are directly linked with a central metal atom or ion in a complex are called **ligands**. A ligand is a species that is capable of donating an electron pair or pairs to the central metal atom or ion. It acts as a Lewis base. The ligands having two or more donor atoms are called polydentate or multidentate ligands. A multidentate ligand is known as a chelating ligand if on coordination it results in formation of a closed or cyclic ring. The complexes, thus, formed are known as chelates. Chelates are usually more stable.

1. Which of the following ligands can form chelates?  
(a) Ethylenediamine    (b) Oxalic acid  
(c) Glycine    (d) All of these
2. How many donor sites are present in ethylenediamine tetraacetate ligand?  
(a) 2    (b) 3  
(c) 4    (d) 6
3.  $\text{Ni}^{2+}$  ion forms a scarlet red complex with DMG. It is a ..... membered closed ring structure.  
(a) 3    (b) 4    (c) 5    (d) 6

[Hint : The structure of Ni-DMG complex is,



4. Which of the following is not a chelate?  
(a) *Cis*-platin—a drug used in the treatment of cancer

- (b) Haemoglobin—a protein present in blood
- (c) Chlorophyll—a green plant pigment which acts as a photosensitizer in the synthesis of carbohydrates
- (d) Vitamin  $\text{B}_{12}$ —it is a cobalt (I) complex which is essential for growth of animals

5. Which of the following statements are correct about stability of chelates?
  - (a) As the number of rings in complex increases, stability of chelate also increases.
  - (b) A chelate having five membered ring is more stable if it contains double bonds.
  - (c) A chelate having six membered ring is more stable if it does not contain double bonds.
  - (d) Chelating ligands are atleast bidentate ligands.
6. Chelate effect refers to :
  - (a) increase in reactivity of complex because of chelation
  - (b) increase in stability of complex due to chelation
  - (c) increase in conductivity of complex due to chelation
  - (d) decrease in stability of complex due to chelation

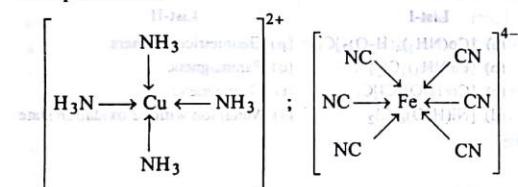
### Thought 2

Coordination compounds play a vital role in our lives. The importance of these compounds can be realised from the fact that life would not have been possible without the existence of chlorophyll in plants and haemoglobin in the blood of the animals. The field of such compounds has expanded very fast in recent years and coordination compounds are playing important roles in analytical chemistry, polymerisation reactions, metallurgy and refining of metals, organic synthesis, electroplating, biochemistry, water purification, textile dyeing and bacteriology.

1. The hardness of water is estimated by :  
 (a) Conductivity method (b) EDTA method  
 (c) Titrimetric method (d) Distillation method
2. A reagent used for identifying nickel ion is :  
 (a) Potassium ferrocyanide (b) Phenolphthalein  
 (c) Dimethyl glyoxime (d) EDTA
3. Lead poisoning in the body can be removed by :  
 (a) Zeise's salt (b) Ferrocene  
 (c) Cis-platin (d)  $[\text{Ca}(\text{EDTA})]^{2-}$
4. Extraction of Ag from sulphide ore and removal of unreacted silver halide from photographic plate involve complexes :  
 (a)  $[\text{Ag}(\text{CN})_2]^-$ ,  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$   
 (b)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ,  $[\text{Ag}(\text{CN})_2]^-$   
 (c)  $[\text{Ag}(\text{CN})_2]^-$  in both (d)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  in both
5. Which is used in cancer chemotherapy?  
 (a) Cis-platin (b) Zeise's salt  
 (c) Ferrocene (d) Fischer's salt

**Thought 3**

When crystals of  $\text{CuSO}_4 \cdot 4\text{NH}_3$  are dissolved in water, there is hardly any evidence for the presence of  $\text{Cu}^{2+}$  ions or ammonia molecules. A new ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of  $\text{Fe}(\text{CN})_6^{4-}$  does not give tests of  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions but gives test of a new ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ . The ions  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  are called complex ions. These ions are represented as :



1. The primary and secondary valency of copper in the complex  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$  are:  
 (a) 2, 4 (b) 4, 2 (c) 0, 4 (d) 1, 4
2. The EAN of Fe in  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is :  
 (a) 24 (b) 30 (c) 36 (d) 38
3. The hybrid state of Cu in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is :  
 (a)  $sp^3$  (b)  $sp^2d$   
 (c)  $sp^3d^2$  (d)  $dsp^2$
4.  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is :  
 (a) square planar (b) octahedral  
 (c) tetrahedral (d) none of these

5. Which one of the following statements is correct?  
 (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is diamagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is paramagnetic  
 (b)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic  
 (c) Both are paramagnetic (d) Both are diamagnetic
6. For a complex ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ :  
 (a) stability constant is  $[\text{Cu}(\text{NH}_3)_4]^{2+}/[\text{Cu}^{2+}][\text{NH}_3]^4$   
 (b) stability constant is  $[\text{Cu}^{2+}][(\text{NH}_3)_4]/[\text{Cu}(\text{NH}_3)_4]^{2+}$   
 (c) stability is more if instability constant is higher  
 (d) stability is less if stability constant is higher

**Thought 4**

The coordination number of  $\text{Ni}^{2+}$  is 4.

- $\text{NiCl}_2 + \text{KCN} \longrightarrow A$  (Cyano complex)  
 $\text{NiCl}_2 + \text{Conc. HCl (excess)} \longrightarrow B$  (Chloro complex)
1. The IUPAC names of A and B are: [I.I.T. 2006]  
 (a) Potassium tetracyanonickelate(II), potassium tetrachloridonickelate(II)  
 (b) Tetracyanopotassiumnickelate(II), tetrachloridopotassiumnickelate(II)  
 (c) Tetracyanonickel(II), tetrachloridonickel(II)  
 (d) Potassium tetracyanonickel(II), potassium tetrachloridonickel(II)
2. Predict the magnetic nature of A and B:  
 (a) both are diamagnetic  
 (b) A is diamagnetic and B is paramagnetic with one unpaired electron  
 (c) A is diamagnetic and B is paramagnetic with two unpaired electrons  
 (d) both are paramagnetic
3. The hybridization of A and B are:  
 (a)  $dsp^2, sp^3$  (b)  $sp^3, sp^3$   
 (c)  $dsp^2, dsp^2$  (d)  $sp^3d^2, d^2sp^3$

[Hint : Cyano complex  $\text{K}_2[\text{Ni}(\text{CN})_4]$   
 Potassium tetracyanonickelate(II)  
 Chloro complex  $\text{K}_2[\text{NiCl}_4]$   
 Potassium tetrachloridonickelate(II)]

Cyano complex	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
	3d	4s	3d	4p	$dsp^2$ diamagnetic			

Chloro complex	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\vdots$	$\vdots$	$\vdots$
	3d	4s	3d	4p	$sp^3$ paramagnetic			

**ANSWERS**

- Thought 1** 1. (d) 2. (d) 3. (c) 4. (a) 5. (a, d) 6. (b)
- Thought 2** 1. (b) 2. (c) 3. (d) 4. (a) 5. (a)
- Thought 3** 1. (a) 2. (c) 3. (d) 4. (b) 5. (b) 6. (a)
- Thought 4** 1. (a) 2. (c) 3. (a)

**● MULTIPLE MATCHING PROBLEMS FOR IIT ASPIRANTS**

**Coordination Compounds and  
Organometallic Compounds**

1. Match the compounds in List-I with their classification in List-II:

List-I	List-II
(a) LiAlH <sub>4</sub>	(p) Reducing agent
(b) KClMgCl <sub>2</sub> ·6H <sub>2</sub> O	(q) Double salt
(c) K <sub>2</sub> SO <sub>4</sub> ·Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O	(r) Alum
(d) NaBH <sub>4</sub>	(s) Complex hydride

2. Match the ligands in List-I with their classification in List-II:

List-I	List-II
(a) EDTA	(p) Monodentate
(b) DMG	(q) Chelating ligand
(c) Ethylenediamine	(r) Bidentate
(d) CN <sup>-</sup>	(s) Hexadentate

3. Match the complexes in List-I with their informations in List-II:

List-I	List-II
(a) [Cu(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub>	(p) $dsp^2$
(b) [Pt(NH <sub>3</sub> ) <sub>2</sub> Cl] <sub>2</sub>	(q) Octahedral
(c) K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	(r) $sp^3d^2$
(d) [Fe(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub>	(s) Square planar

4. Match List-I with List-II:

List-I	List-II
(a) $d^2sp^3$	(p) Outer orbital octahedral complex
(b) $sp^3d^2$	(q) High spin complex
(c) K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	(r) Low spin complex
(d) [Fe(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub>	(s) Inner orbital octahedral complex

5. Match List-I with List-II:

List-I	List-II
(a) Ferrocene	(p) Iron present
(b) Mn <sub>2</sub> (CO) <sub>10</sub>	(q) Cobalt
(c) Vitamin B <sub>12</sub>	(r) Metal-metal bonding
(d) Herme	(s) Sandwich structure

6. Match List-I with List-II:

List-I	List-II
(a) [MnCl <sub>6</sub> ] <sup>2-</sup>	(p) One unpaired electron
(b) [Fe(CN) <sub>6</sub> ] <sup>4-</sup>	(q) $d^2sp^3$
(c) [CoF <sub>6</sub> ] <sup>3-</sup>	(r) $sp^3d^2$
(d) [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	(s) Four unpaired electrons

7. Match the complexes in List-I with their coordination number in the List-II:

List-I	List-II
(a) [Co(en) <sub>3</sub> ] <sup>3+</sup>	(p) 6
(b) [Ca(EDTA)] <sup>2-</sup>	(q) 4
(c) [Ni(CO) <sub>4</sub> ]	(r) 2
(d) [Ag(NH <sub>3</sub> ) <sub>2</sub> ]Cl	(s) 5
(e) [Fe(CO) <sub>5</sub> ]	(t) 10

8. Match the hybridization in List-I with its inference in complex compounds List-II:

List-I	List-II
(a) $sp$	(p) Octahedral
(b) $sp^3$	(q) Tetrahedral
(c) $sp^3d^2$	(r) Linear
(d) $d^2sp^3$	(s) Do not show geometrical isomerism

9. Match the complexes in List-I with their stereoproperties in List-II:

List-I	List-II
(a) [CoCl <sub>3</sub> (NH <sub>3</sub> ) <sub>3</sub> ]	(p) Show facial form
(b) [Cr(OX) <sub>3</sub> ] <sup>3-</sup>	(q) Cis form is optically active
(c) [CrCl <sub>2</sub> (OX) <sub>2</sub> ]	(r) Trans form is optically inactive
(d) [RhCl <sub>3</sub> (Py) <sub>3</sub> ]	(s) Show meridian form

10. Match the complexes in List-I with their properties listed in List-II:

List-I	List-II
(a) [Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	(p) Geometrical isomers
(b) [Pt(NH <sub>3</sub> ) <sub>2</sub> Cl] <sub>2</sub>	(q) Paramagnetic
(c) [Co(H <sub>2</sub> O) <sub>5</sub> Cl]Cl	(r) Diamagnetic
(d) [Ni(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>2</sub>	(s) Metal ion with +2 oxidation state

**ANSWERS**

1. (a-p, s) (b-q) (c-q, r) (d-p, s)  
 2. (a-q, s) (b-q, r) (c-q, r) (d-p)  
 3. (a-p, s) (b-p, s) (c-q) (d-q, r)  
 4. (a-r, s) (b-p, q) (c-r, s) (d-p, q)  
 5. (a-p, s) (b-r) (c-q) (d-p)

6. (a-p, q) (b-p, q) (c-r, s) (d-r, s)  
 7. (a-p) (b-p) (c-q) (d-r) (e-s)  
 8. (a-r, s) (b-q, s) (c-p) (d-p)  
 9. (a-p, s) (b-q, r) (c-q, r) (d-p, s)  
 10. (a-p, q, s) (b-p, r, s) (c-q, s) (d-q, s)