

# Coordination Compounds

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## Case Study Based Questions

### Case Study 1

Co-ordination compounds show structural isomerism and it is different from the nature of the isomerism which we generally come across in organic compounds. The structural isomers may be classified as ionisation, hydrate, co-ordination and linkage isomers depending upon their nature. The electrical conductivity of these isomers depends upon the number of ions which they furnish upon dissociation in aqueous solution. The isomers belonging to a particular type can also be distinguished from each other with the help of certain tests. In addition to the structural isomerism, the co-ordination compounds are also involved in geometrical and optical isomerism. Whereas optical isomerism is normally shown by octahedral complexes, both octahedral and square planar complexes can exhibit geometrical isomerism.

Read the given passage carefully and give the answer of the following questions:

**Q1. An aqueous solution of  $\text{CoCl}_2$  on addition of excess of concentrated HCL turns blue due to the formation of:**

- a.  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$
- b.  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_4]^{2-}$
- c.  $(\text{CoCl}_4)^{2-}$
- d.  $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2]$

**Q2. Which one is the most likely structure of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  if  $\frac{1}{3}$  of the total chlorine in the compounds is precipitated by adding  $\text{AgNO}_3$  solution?**

- a.  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
- b.  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot (\text{H}_2\text{O})_3$
- c.  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot \text{H}_2\text{O}$
- d.  $(\text{Cr}(\text{H}_2\text{O})_5\text{Cl})\text{Cl}_2 \cdot \text{H}_2\text{O}$

**Q3. One mole of the complex compound  $\text{Co}(\text{NH})_5\text{Cl}_3$  gives 3 mole of ions on dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  to yield two moles of  $\text{AgCl(s)}$ . The structure of the complex is:**

- a.  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$     b.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$   
 c.  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$     d.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Q4. Which of the following will not show geometrical isomerism?

- a.  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$     b.  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$   
 c.  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$     d.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

## Answers

1. (c)  $(\text{CoCl}_4)^{2-}$
2. (c)  $(\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2)\text{Cl} \cdot 2\text{H}_2\text{O}$
3. (d)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
4. (c)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$

## Case Study 2

Metal complexes show different colours due to d-d transitions. The complex absorbs light of specific wavelength to promote the electron from  $t_2$  to  $e$  level. The colour of the complex is due to the transmitted light, which is complementary of the colour absorbed. The wave number of light absorbed by different complexes of Cr ion are given below:

| Complex               | Wave number of light absorbed ( $\text{cm}^{-1}$ ) | Energy of light absorbed (kJ/mol) |
|-----------------------|--|-----------------------------------|
| $[\text{CrA}_6]^{3-}$ | 13640  | 163                               |
| $[\text{CrB}_6]^{3+}$ | 17830  | 213                               |
| $[\text{CrC}_6]^{3+}$ | 21680  | 259                               |
| $[\text{CrD}_6]^{3-}$ | 26280  | 314                               |

Read the given passage carefully and give the answer of the following questions: (CBSE SQP 2023-24)

Q1. Out of the ligands 'A', 'B', 'C' and 'D', which ligand causes maximum crystal field splitting? Why?

OR

Which of the two, 'A', or 'D' will be a weak field ligand? Why?

Q2. Which of the complexes will be violet in colour?  $[\text{CrA}]$  or  $[\text{CrB}]^{3+}$  and why? (Given: If 560-570 nm of light is absorbed, the colour of the complex observed is violet.)

Q3. If the ligands attached to  $\text{Cr}^{3+}$  ion in the complexes given in the table above are water, cyanide ion, chloride ion and ammonia (not in this order) Identify the ligand, write the formula and IUPAC name of the following:

(i)  $[\text{CrA}]^{3+}$

(ii)  $[\text{CrC}_2]^{3+}$

### Answers

1. 'D' causes maximum crystal field splitting. Energy is directly proportional to the wave number. Maximum energy of light is required for an electron to jump from  $t_{2g}$  to  $e_g$  in case of  $(\text{CrD}_6)^{3-}$

OR

'A' will be a weak field ligand. The splitting caused is least in this case as the energy required for electron to jump from  $t_{2g}$  to  $e_g$  is minimum.

2.  $[\text{CrB}]^{3+}$  will be violet in colour because wavelength of light absorbed is 1/17830-560nm for the complex while 1/13640733nm for  $(\text{CrA}_6)^{3-}$  complex.

3. (i)  $(\text{CrCl}_6)^{3+}$  Hexachloridochromate (III) ion

(ii)  $(\text{Cr}(\text{NH}_3)_6)^{3+}$ , Hexaamminechromium (III) ion

A=Cl, B=H<sub>2</sub>O, C = NH<sub>3</sub>, D = CN

### Case Study 3

In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes.

Read the given passage carefully and give the answer of the following questions: (CBSE 2023)

Q1. If  $\text{PtCl}_2 \cdot 2\text{NH}_3$  does not react with  $\text{AgNO}_3$ , what will be its formula?

Q2. What is the secondary valency of  $[\text{Co}(\text{en})_3]^{+}$ ?

Q3. (i) Write the formula of Iron (III)

Hexacyanidoferrate (II).

(ii) Write the IUPAC name of  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$ .

OR

Write the hybridisation and magnetic

behaviour of  $[\text{Ni}(\text{CN})_4]^{2-}$

[Atomic number: Ni = 28]

### Answers

1. If  $\text{PtCl}_2 \cdot 2\text{NH}_3$  does not react with  $\text{AgNO}_3$ , then the formula of the compound would be  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .

2. The secondary valency of  $[\text{Co}(\text{en})_3]^{3+}$  is 6 as there are 4  $\text{NH}_3$  molecules and 2  $\text{C}^-$  ions linked to the cobalt atom.

3. (1) The formula is  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

(ii) The IUPAC name of  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$  is pentaammine chlorido cobalt (III) chloride.

OR

In the presence of strong field CN ions, all the electrons are paired up. The empty 3d, 3s and two 4p orbitals undergo  $\text{dsp}^2$  hybridisation to make bonds with CN-ligands in square planar geometry. Hence,  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Coordination compounds are widely present in the minerals, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems and medicine. Alfred Werner's theory postulated the use of two types of linkages (primary and secondary), by a metal atom/ion in a coordination compound. He predicted the geometrical shapes of a large number of coordination entities using the property of isomerism. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to describe the optical properties of these compounds. The Crystal Field Theory (CFT) explains the effect of different crystal fields (provided by the ligands taken as point charges) on the degeneracy of d-orbital energies of the central metal atom/ion.

Read the given passage carefully and give the answer of the following questions: (CBSE 2023)

Q1. When a coordination compound  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  is mixed with  $\text{AgNO}_3$  solution, 2 moles of  $\text{AgCl}$  are precipitated per mole of the compound. Write the structural formula of the complex and secondary valency for Nickel ion.

Q 2. Write the IUPAC name of the ionisation isomer of  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)] \text{Cl}$ .

Q3. Using valence bond theory, predict the geometry and magnetic nature of:

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

(ii)  $[\text{Fe}(\text{CN})_6]^{3-}$

[Atomic number: Ni = 28, Fe = 26]

OR

Give reasons:

(i) Low spin tetrahedral complexes are not formed.

(ii)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inner orbital complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is an outer orbital complex.

[Atomic number: Co = 27, Ni = 28]

## Answers

1. The structural formula of the complex is  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  and the secondary valency for nickel ion is 6 in it.

2. The IUPAC name of the ionisation isomer of  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$  is pentaammine sulphato cobalt

(III) chloride.

3. (i) In  $[\text{Ni}(\text{CO})_4]$ , oxidation state of Ni is zero.

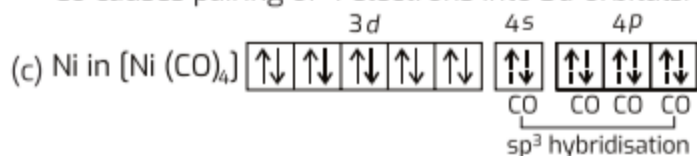
$_{28}\text{Ni} = [\text{Ar}] 3d^8 4s^2$



(b) Ni atom after the rearrangement in presence of strong CO ligands.



Co causes pairing of 4 electrons into 3d-orbitals.



It is diamagnetic as all the electrons present in it are paired.

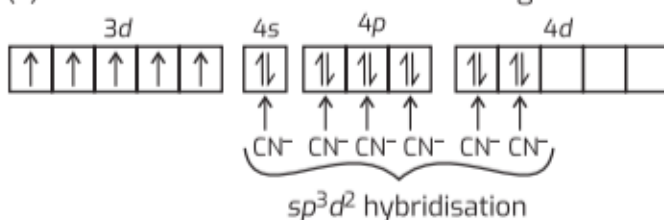
(ii) We have  ${}_{26}\text{Fe} = [\text{Ar}]3d^64s^2$

$\text{Fe}^{3+}$  ion =  $[\text{Ar}]3d^5$

(a)  $\text{Fe}^{3+}$  ion

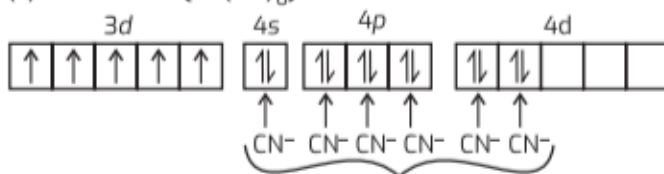


(b)  $\text{Fe}^{3+}$  ion under influence of weak  $\text{F}^-$  ligand



It is strongly paramagnetic in nature.

(c)  $\text{Fe}^{3+}$  ion in  $[\text{Fe}(\text{CN})_6]^{3-}$



Thus,  $[\text{Fe}(\text{CN})_6]^{3-}$  is strongly paramagnetic in nature with  $sp^3d^2$  hybridisation.

OR

(i) For tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy. so they are rarely formed in low spin state.

(ii) As inner d-electrons are involved in the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , it is an inner orbital complex.

But outer (4d) electrons are involved in the hybridisation of the complex  $[\text{Ni}(\text{NH}_3)_6]^{3+}$  so, it is an outer orbital complex.

## Solutions for Questions 4 to 13 are Given Below

### Case Study 4

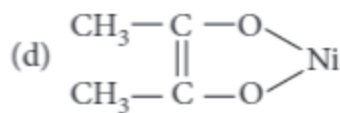
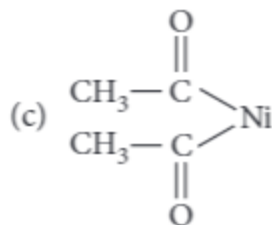
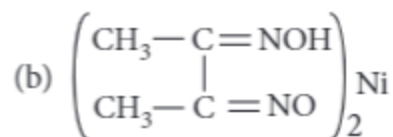
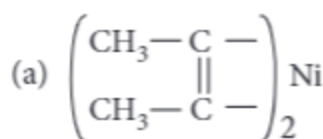
Read the passage given below and answer the following questions :

The molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state are called coordination compounds. Their properties are completely different from the constituents. In coordination compounds, the central metal atom or ion is linked to a number of ions or neutral molecules, called ligands, by coordinate bonds. For example, Dimethyl glyoxime (dmg) is a bidendate ligand chelating large amounts of metals.

When dimethyl glyoxime is added to alcoholic solution of  $\text{NiCl}_2$  and ammonium hydroxide is slowly added to it, a rosy red precipitate of a complex is formed.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The structure of the complex is



(ii) Oxidation number of Ni in the given complex is

(a) +3

(b) +1

(c) +2

(d) zero.

(iii) Hybridisation and structure of the complex is

(a)  $sp^3$ , tetrahedral

(b)  $dsp^2$ , square planar

(c)  $sp^3$ , square planar

(d)  $sp^3d$ , trigonal bipyramidal.

OR

Which of the following is true about this complex?

- (a) It is paramagnetic, containing 2 unpaired electrons.
  - (b) It is paramagnetic, containing 1 unpaired electron.
  - (c) It is paramagnetic, containing 4 unpaired electrons.
  - (d) It is diamagnetic with no unpaired electron.
- (iv) Which one will give test for  $\text{Fe}^{3+}$  ions in the 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)  $\text{Fe}_2(\text{SO}_4)_3$

## Case Study 5

Read the passage given below and answer the following questions :

Coordination compounds are formulated and named according to the IUPAC system.

Few rules for naming coordination compounds are :

- (I) In ionic complex, the cation is named first and then the anion.
- (II) In the coordination entity, the ligands are named first and then the central metal ion.
- (III) When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.

The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) The IUPAC name of the complex  $[\text{Pt}(\text{NH}_3)_3\text{Br}(\text{NO}_2)\text{Cl}]\text{Cl}$  is
- (a) triamminechlorobromonitroplatinum(IV) chloride
  - (b) triamminebromonitrochloroplatinum(IV) chloride
  - (c) triamminebromidochloridonitroplatinum(IV) chloride
  - (d) triamminenitrochlorobromoplatinum(IV) chloride.
- (ii) The IUPAC name of  $[\text{Ni}(\text{CO})_4]$  is
- (a) tetracarbonylnickel(II)
  - (b) tetracarbonylnickel(0)
  - (c) tetracarbonylnickelate(II)
  - (d) tetracarbonylnickelate(0).
- (iii) As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  is
- (a) tetraaquadiamminecobalt(II) chloride
  - (b) tetraaquadiamminecobalt(III) chloride
  - (c) diamminetetraaquacobalt(II) chloride
  - (d) diamminetetraaquacobalt(III) chloride.
- (iv) Which of the following represents correct formula of dichloridobis(ethane-1, 2-diamine)cobalt(III) ion?
- (a)  $[\text{CoCl}_2(\text{en})]^{2+}$
  - (b)  $[\text{CoCl}_2(\text{en})_2]^{2+}$
  - (c)  $[\text{CoCl}_2(\text{en})]^+$
  - (d)  $[\text{CoCl}_2(\text{en})_2]^+$

OR

Correct formula of pentaamminenitro-O-cobalt(III) sulphate is

- (a)  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{SO}_4$
- (b)  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{SO}_4$
- (c)  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_4](\text{SO}_4)_2$
- (d)  $[\text{Co}(\text{ONO})(\text{NH}_3)_4](\text{SO}_4)_2$



## Case Study 6

Read the passage given below and answer the following questions :

Iron forms many complexes in its +2 and +3 oxidation states such as  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (A);  $[\text{Fe}(\text{CN})_6]^{4-}$  (B);  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (C);  $[\text{Fe}(\text{CN})_6]^{3-}$  (D), etc., They exhibit different magnetic properties and undergo different hybridisation of iron.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following statements is correct?

- (a) (B) is paramagnetic while (C) is diamagnetic.
- (b) Both (B) and (D) are outer orbital complexes.
- (c) Both (A) and (C) are paramagnetic.
- (d) (A) is outer orbital complex and (C) is inner orbital complex.

(ii) The complex having maximum magnetic moment is

- (a) (A) (b) (B) (c) (C) (d) (D)

OR

Which of the following does not represent correct configuration of the  $d$ -orbitals in the given complexes?

- (a) (A) :  $t_{2g}^4 e_g^2$  (b) (B) :  $t_{2g}^6 e_g^0$  (c) (C) :  $t_{2g}^4 e_g^1$  (d) (D) :  $t_{2g}^5 e_g^0$

(iii) The spin only magnetic moment of complexes (A), (B), (C) and (D) are respectively (in BM)

- (a)  $2\sqrt{6}, 0, \sqrt{35}, \sqrt{3}$  (b)  $0, 2\sqrt{6}, \sqrt{35}, \sqrt{3}$  (c)  $\sqrt{15}, 2\sqrt{6}, \sqrt{3}, 0$  (d)  $\sqrt{3}, \sqrt{8}, 0, \sqrt{15}$

(iv) Which of the given complexes are outer orbital complexes?

- (a) (A) and (B) only (b) (B) and (C) only (c) (A) and (C) only (d) (B) and (D) only

## Case Study 7

Read the passage given below and answer the following questions :

To explain bonding in coordination compounds various theories were proposed. One of the important theory was valence bond theory. According to that, the central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands. The appropriate atomic orbitals of the metal hybridise to give a set of equivalent orbitals of definite geometry.

The  $d$ -orbitals involved in the hybridisation may be either inner  $d$ -orbitals i.e.,  $(n-1)d$  or outer  $d$ -orbitals i.e.,  $nd$ . For example,  $\text{Co}^{3+}$  forms both inner orbital and outer orbital complexes, with ammonia it forms  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and with fluorine it forms  $[\text{CoF}_6]^{3-}$  complex ion.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following is not true for  $[\text{CoF}_6]^{3-}$ ?

- (a) It is paramagnetic. (b) It has coordination number of 6.
- (c) It is outer orbital complex. (d) It involves  $d^2sp^3$  hybridisation.

(ii)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of  $3d$ -electrons in the central metal of the complex is

- (a)  $3d_{xy}^1, 3d_{x^2-y^2}^1, 3d_{yz}^1$  (b)  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$
- (c)  $3d_{xy}^1, 3d_{zy}^1, 3d_{z^2}^1$  (d)  $3d_{x^2-y^2}^1, 3d_{z^2}^1, 3d_{xz}^1$

OR

Which of the following is true for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ?

- (a) It is an octahedral, diamagnetic and outer orbital complex.
- (b) It is an octahedral, paramagnetic and outer orbital complex.
- (c) It is an octahedral, paramagnetic and inner orbital complex.
- (d) It is an octahedral, diamagnetic and inner orbital complex.

(iii) The paramagnetism of  $[\text{CoF}_6]^{3-}$  is due to

- (a) 3 electrons
- (b) 4 electrons
- (c) 2 electrons
- (d) 1 electron.

(iv) Which of the following is an inner orbital or low spin complex?

- (a)  $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$
- (b)  $[\text{FeF}_6]^{3-}$
- (c)  $[\text{Co}(\text{CN})_6]^{3-}$
- (d)  $[\text{NiCl}_4]^{2-}$

## Case Study 8

Read the passage given below and answer the following questions :

Valence bond theory considers the bonding between the metal ion and the ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands. In coordination compounds, the interaction between the ligand and the metal ion causes the five  $d$ -orbitals to split-up. This is called crystal field splitting and the energy difference between the two sets of energy level is called crystal field splitting energy. The crystal field splitting energy ( $\Delta_o$ ) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of  $\Delta_o$  and  $P$  (pairing energy).

If  $\Delta_o < P$ , then complex will be high spin.

If  $\Delta_o > P$ , then complex will be low spin.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following ligand has lowest  $\Delta_o$  value?

- (a)  $\text{CN}^-$
- (b)  $\text{CO}$
- (c)  $\text{F}^-$
- (d)  $\text{NH}_3$

(ii) The crystal field splitting energy for octahedral ( $\Delta_o$ ) and tetrahedral ( $\Delta_t$ ) complex is related as

- (a)  $\Delta_t = \frac{1}{2} \Delta_o$
- (b)  $\Delta_t = \frac{4}{9} \Delta_o$
- (c)  $\Delta_t = \frac{3}{5} \Delta_o$
- (d)  $\Delta_t = \frac{2}{5} \Delta_o$

(iii) On the basis of crystal field theory, the electronic configuration of  $d^4$  in two situations : (i)  $\Delta_o > P$  and

(ii)  $\Delta_o < P$  are

- | (i)                  | (ii)             |
|----------------------|------------------|
| (a) $t_{2g}^4 e_g^0$ | $t_{2g}^3 e_g^1$ |
| (b) $t_{2g}^3 e_g^1$ | $t_{2g}^4 e_g^0$ |
| (c) $t_{2g}^3 e_g^1$ | $t_{2g}^3 e_g^1$ |
| (d) $t_{2g}^4 e_g^0$ | $t_{2g}^4 e_g^0$ |

(iv) Using crystal field theory, calculate magnetic moment of central metal ion of  $[\text{FeF}_6]^{4-}$ .

- (a) 1.79 B.M.
- (b) 2.83 B.M.
- (c) 3.85 B.M.
- (d) 4.9 B.M.

OR

Electronic configuration of  $d$ -orbitals in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion in an octahedral crystal field is

- (a)  $t_{2g}^1 e_g^0$
- (b)  $t_{2g}^2 e_g^0$
- (c)  $t_{2g}^0 e_g^1$
- (d)  $t_{2g}^1 e_g^1$

## Case Study 9

Read the passage given below and answer the following questions :

Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both  $\sigma$  and  $\pi$  character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty  $\pi$  or  $\pi^*$  orbitals. These types of ligands are called  $\pi$ -acceptor or  $\pi$ -acid ligands. These interactions increases the  $\Delta_o$  value.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) What is the oxidation state of metal in  $[\text{Mn}_2(\text{CO})_{10}]$ ?

- (a) +1 (b) -1 (c) +2 (d) 0

(ii) Among the following metal carbonyls, the C – O bond order is lowest in

- (a)  $[\text{Mn}(\text{CO})_6]^+$  (b)  $[\text{Fe}(\text{CO})_5]$  (c)  $[\text{Cr}(\text{CO})_6]$  (d)  $[\text{V}(\text{CO})_6]^-$

OR

Which of the following can be reduced easily?

- (a)  $\text{V}(\text{CO})_6$  (b)  $\text{Mo}(\text{CO})_6$  (c)  $[\text{Co}(\text{CO})_4]^-$  (d)  $\text{Fe}(\text{CO})_5$

(iii) The oxidation state of cobalt in  $\text{K}[\text{Co}(\text{CO})_4]$  is

- (a) +1 (b) +3 (c) -1 (d) 0

(iv) Structure of decacarbonyl manganese is

- (a) trigonal bipyramidal (b) octahedral (c) tetrahedral (d) square pyramidal.

## Case Study 10

Read the passage given below and answer the following questions :

Werner, a Swiss chemist in 1892 prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour. He proposed that, in coordination compounds, metals possess two types of valencies, viz. primary valencies, which are normally ionisable and secondary valencies which are non-ionisable. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess of  $\text{AgNO}_3$  solution in cold, but some remained in solution. The number of ions furnished by a complex in a solution can be determined by precipitation reactions. The measurement of molar conductance of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.  
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.  
(c) Assertion is correct statement but reason is wrong statement.  
(d) Assertion is wrong statement but reason is correct statement.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) **Assertion :** The complex  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  does not give precipitate with silver nitrate solution.

**Reason :** The given complex is non-ionisable.



(ii) **Assertion :** The complex  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  gives precipitate corresponding to 2 mol of  $\text{AgCl}$  with  $\text{AgNO}_3$  solution.

**Reason :** It ionises as  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$ .

OR

**Assertion :**  $\text{CoCl}_3 \cdot 4\text{NH}_3$  gives 1 mol of  $\text{AgCl}$  on reacting with  $\text{AgNO}_3$ , its secondary valency is 6.

**Reason :** Secondary valency corresponds to coordination number.

(iii) **Assertion :** 1 mol of  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$  will give 1 mol of  $\text{AgCl}$  on treating with  $\text{AgNO}_3$ .

**Reason :**  $\text{Cl}^-$  ions satisfying secondary valence will not be precipitated.

(iv) **Assertion :**  $\text{CoCl}_3 \cdot 3\text{NH}_3$  is not conducting while  $\text{CoCl}_3 \cdot 5\text{NH}_3$  is conducting.

**Reason :** The complex of  $\text{CoCl}_3 \cdot 3\text{NH}_3$  is  $[\text{CoCl}_3(\text{NH}_3)_3]$  while that of  $\text{CoCl}_3 \cdot 5\text{NH}_3$  is  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ .

## Case Study 11

Read the passage given below and answer the following questions :

Arrangement of ligands in order of their ability to cause splitting ( $\Delta$ ) is called spectrochemical series. Ligands which cause large splitting (large  $\Delta$ ) are called strong field ligands while those which cause small splitting (small  $\Delta$ ) are called weak field ligands. When strong field ligands approach metal atom/ion, the value of  $\Delta_o$  is large, so that electrons are forced to get paired up in lower energy  $t_{2g}$  orbitals. Hence, a low-spin complex is resulted from strong field ligand. When weak field ligands approach metal atom/ion, the value of  $\Delta_o$  is small, so that electrons enter high energy  $e_g$  orbitals rather than pairing in low energy  $t_{2g}$  orbitals. Hence, a high-spin complex is resulted from weak field ligands. Strong field ligands have tendency to form inner orbital complexes by forcing the electrons to pair up. Whereas weak field ligands have tendency to form outer orbital complex because inner electrons generally do not pair up.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** In tetrahedral coordination entity formation, the  $d$  orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

**Reason :** Spectrochemical series is based on the absorption of light by complexes with different ligands.

(ii) **Assertion :** In high spin situation, configuration of  $d^5$  ions will be  $t_{2g}^3 e_g^2$ .

**Reason :** In high spin situation, pairing energy is less than crystal field energy.

OR

**Assertion :**  $\text{F}^-$  ion is a weak field ligand and forms outer orbital complex.

**Reason :**  $\text{F}^-$  ion cannot force the electrons of  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals of the inner shell to occupy  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals of the same shell.

(iii) **Assertion :** The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds.

**Reason :** In spectrochemical series, ligands are arranged in a series of increasing field strength.

(iv) **Assertion :**  $\text{NF}_3$  is a weaker ligand than  $\text{N}(\text{CH}_3)_3$ .

**Reason :**  $\text{NF}_3$  ionizes to give  $\text{F}^-$  ions in aqueous solution.

## Case Study 12

Read the passage given below and answer the following questions :

Ligands are atoms or ions which can donate electrons to the central atoms. Ligands can be monodentate, bidentate or polydentate as well. Few ligands can coordinate with the central atom through more than one site, these are called ambidentate ligands. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelating ligand.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Glycinate ion is an example of monodentate ligand.

**Reason :** Glycinate contains N and O as donor atoms.

OR

**Assertion :** EDTA forms complex with divalent metals of 3d-series in the ratio of 1 : 1.

**Reason :** EDTA has 4 —COOH groups.

(ii) **Assertion :** Oxalate ion is a bidentate ligand.

**Reason :** Oxalate ion has two donor atoms.

(iii) **Assertion :** A chelating ligand must possess two or more lone pairs at such a distance that it may form suitable strain free 5 and 6 membered rings with the metal ion.

**Reason :**  $\text{H}_2\text{N}-\text{NH}_2$  is a chelating ligand.

(iv) **Assertion :** In Zeise's salt coordination number of Pt is five.

**Reason :** Ethene is a monodentate ligand.

## Case Study 13

Read the passage given below and answer the following questions :

For understanding the structure and bonding in transition metal complexes, the magnetic properties are very helpful. Low spin complexes are generally diamagnetic because of pairing of electrons, whereas high spin complexes are usually paramagnetic because of presence of unpaired electrons. Larger the number of unpaired electrons, stronger will be the paramagnetism. However magnetic behaviour of a complex can be confirmed from magnetic moment measurement. Magnetic moment  $\mu = \sqrt{n(n+2)}$  B.M. where  $n$  = number of unpaired electrons. Greater the number of unpaired electrons, more will be the magnetic moment.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Both  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  have same magnetic moment.

**Reason :** Number of unpaired electrons in  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$  are same.

(ii) **Assertion :**  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  is paramagnetic.

**Reason :** The Fe in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  has three unpaired electrons.

(iii) **Assertion :**  $[\text{Co}(\text{en})_3]^{3+}$  is paramagnetic.

**Reason :** It is an inner orbital complex.

(iv) **Assertion :**  $[\text{Ni}(\text{CO})_4]$  is diamagnetic and tetrahedral in shape.

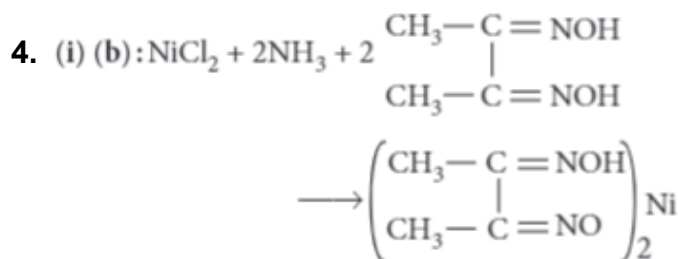
**Reason :**  $[\text{Ni}(\text{CO})_4]$  contains no unpaired electrons and involves  $dsp^2$  hybridisation.

OR

**Assertion :**  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic complex.

**Reason :** It involves  $dsp^2$  hybridisation and there is no unpaired electron.

## HINTS & EXPLANATIONS



(ii) (c)

(iii) (b)

OR

(d): It has no unpaired electrons hence, it is diamagnetic.

(iv) (d): (a) and (b) are coordination compounds hence cannot give free  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions in solution.

(c) and (d) represent simple compounds hence are free to give ions in solution, but only  $\text{Fe}_2(\text{SO}_4)_3$  contains  $\text{Fe}^{3+}$  ions.  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  contains  $\text{Fe}^{2+}$  ions not  $\text{Fe}^{3+}$  ions.

5. (i) (c): Ligands are named in alphabetical order irrespective of their charge.

(ii) (b)

(iii) (d)

(iv) (d)

OR

(b): Ligand  $\text{NO}_2^-$  is ambidentate ligand as it can donate electrons through either nitrogen ( $\text{NO}_2$ ) or oxygen ( $\text{ONO}$ ).

6. (i) (c): (A):  $sp^3d^2$  hybridisation (outer orbital)

No. of unpaired electrons = 4

(B):  $d^2sp^3$  hybridisation (inner orbital)

No. of unpaired electrons = 0

(C):  $sp^3d^2$  hybridisation (outer orbital)

No. of unpaired electrons = 5

(D):  $d^2sp^3$  hybridisation (inner orbital)

No. of unpaired electron = 1

(ii) (c): It has 5 unpaired electrons.

OR

(c): As  $\text{H}_2\text{O}$  is a weak ligand so, it should be  $t_{2g}^3 e_g^2$

(iii) (a): Magnetic moments of (A), (B), (C) and (D) are respectively

$$\sqrt{4(4+2)}, 0, \sqrt{5(5+2)}, \sqrt{1(1+2)}$$

(iv) (c)

7. (i) (d): It involves  $sp^3d^2$  hybridisation and not  $d^2sp^3$ .



(ii) (b) : Magnetic moment of 3.83 B.M. suggests that it has 3 unpaired electrons,

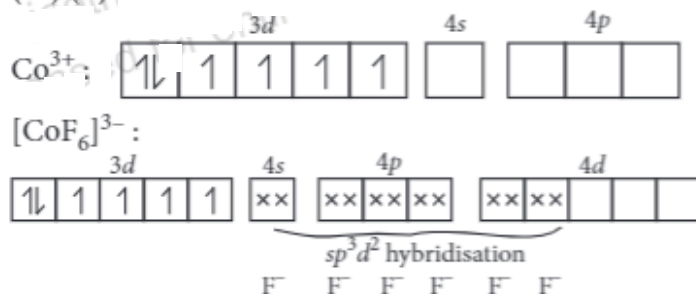
$$\therefore n = 3 \text{ i.e., } \text{Cr}^{3+} : 3d^3$$

It involves  $d^2sp^3$  hybridisation so correct distribution of electrons is  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$ .

OR

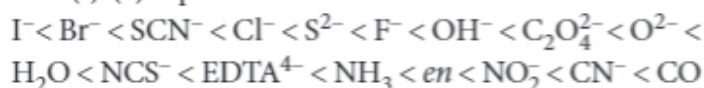
(d) :  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is  $d^2sp^3$  hybridised with all electrons paired hence, it is diamagnetic and inner orbital complex.

(iii) (b) :



(iv) (c) : Inner orbital complexes are formed with strong ligands as they force electrons to pair up and hence the complex will be either diamagnetic or will have less number of unpaired electrons.

8. (i) (c) : Spectrochemical series :



(ii) (b)

(iii) (a) : When  $\Delta_o > P$ , the electrons paired up in the  $t_{2g}$  level rather than going to the  $e_g$  level, so

$$\text{when } \Delta_o > P : t_{2g}^4 e_g^0$$

$$\text{and } \Delta_o < P : t_{2g}^3 e_g^1$$

$$(iv) (d) : \text{Fe}^{2+} : 3d^6 \Rightarrow t_{2g}^4 e_g^2$$

(Since,  $\text{F}^-$  is a weak field ligand)

Hence four unpaired electrons are present.

Magnetic moment ( $\mu$ )

$$= \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9 \text{ B.M.}$$

OR

(a) : In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , Ti is in +3 oxidation state and there is only one electron in  $d$ -orbital.

9. (i) (d) : Oxidation state of Mn in  $[\text{Mn}_2(\text{CO})_{10}]$  is zero.

(ii) (d) : In  $[\text{V}(\text{CO})_6]^-$ , the anionic carbonyl complex can delocalise more electron density to antibonding

$\pi$ -orbital ( $d\pi$ - $p\pi$  back bonding) of CO and thus lowers the bond order.

OR

(a) :  $\text{V}(\text{CO})_6$  can be easily reduced to  $[\text{V}(\text{CO})_6]^-$ .

$\text{V}(\text{CO})_6$  has a total of 17 bonding electrons, hence it is very reactive and unstable.  $[\text{V}(\text{CO})_6]^-$  on the other hand has complete set of 18 bonding electrons as an electron is added into the bonding orbital when  $\text{V}(\text{CO})_6$  gets reduced to  $[\text{V}(\text{CO})_6]^-$ . All others have 18 bonding electrons.

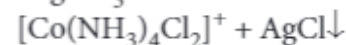
(iii) (c) :  $\text{K}[\text{Co}(\text{CO})_4]$

$$+1 + (x) + 4(0) = 0 \text{ or } x = -1$$

(iv) (d) :  $\text{Mn}_2(\text{CO})_{10}$  is made up of two square pyramidal  $\text{Mn}(\text{CO})_5$  units joined by Mn - Mn bond.

10. (i) (a)

(ii) (d) :  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} + \text{AgNO}_3 \longrightarrow$



Thus it gives precipitate of 1 mol of AgCl.

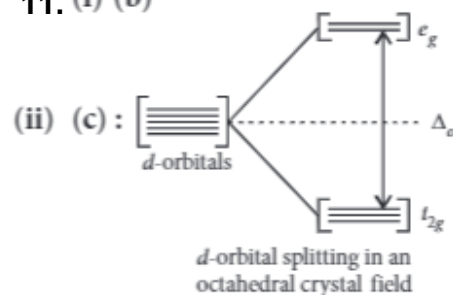
OR

(b) :  $\text{CoCl}_3 \cdot 4\text{NH}_3$  gives 1 mol AgCl on reaction with  $\text{AgNO}_3$ , hence the complex can be represented as  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ .

(iii) (a) : The  $\text{Cl}^-$  ions outside the coordination sphere can only be precipitated.

(iv) (a)

11. (i) (b)



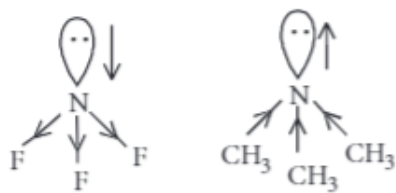
$\therefore$  In high spin situation,  $\Delta_o < P$ , in  $d^5$  configuration, 4<sup>th</sup> and 5<sup>th</sup> electron are added to  $e_g$  rather than  $t_{2g}$ . So, configuration of  $d^5$  ion will be  $t_{2g}^3 e_g^2$ .

OR

(a)

(iii) (b)

(iv) (c) : Due to high electronegativity of F-atoms, the lone pair of N-atom in  $\text{NF}_3$  molecule cannot be ligated easily. Whereas in  $\text{N}(\text{CH}_3)_3$ ,  $\text{CH}_3$  group is an electron releasing group, thus lone pair of N-atom in  $\text{N}(\text{CH}_3)_3$  molecule can be ligated easily.



Except, nitrogen fluoride, all other halides hydrolyse in water.

12. (i) (d): Glycinate ion is an example of bidentate ligand. It contains N and O as donor atoms.

OR

(b) : EDTA is a hexadentate ligand. It forms complex with central metal in the ratio 1 : 1 in which it binds through two nitrogen atoms and four oxygen atoms.

(ii) (a)

(iii) (c) :  $\text{H}_2\text{N} - \text{NH}_2$  does not act as chelating ligand. The coordination by hydrazine leads to a three member highly unstable strained ring and thus it does not act as chelating agent.

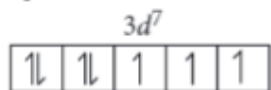
(iv) (d): In Zeise's salt, coordination no. of Pt is 4. Ethylene is a monodentate ligand.

13. (i) (a): Spin only magnetic moment,  $\mu = \sqrt{n(n+2)}$  where  $n$  = number of unpaired electrons.

As the number of unpaired electrons in  $\text{Cr}^{2+}$  ( $[\text{Ar}]3d^4$ ) and  $\text{Fe}^{2+}$  ( $[\text{Ar}]3d^6$ ) are same, hence  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  will have same magnetic moment.

(ii) (a):  $\text{Fe}^+ : [\text{Ar}] 3d^6 4s^1$

When the weak field ligand  $\text{H}_2\text{O}$  and strong field ligand  $\text{NO}^+$  attack, the configuration changes as follows :  $\text{Fe}^+ : [\text{Ar}] 3d^7 4s^0$



$\therefore \text{Fe}^+$  has 3 unpaired electrons.

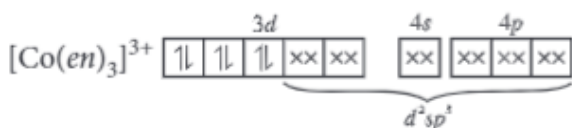
(iii) (d) :  $\text{Co}^{3+}$   $3d^6$   $4s^0$

|                      |            |            |            |            |
|----------------------|------------|------------|------------|------------|
| $\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |
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In presence of strong ethylenediamine ligand the electrons get paired.

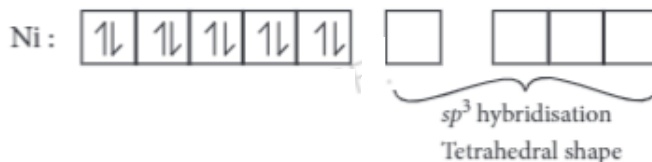


Thus inner orbital complex with no unpaired electrons.

(iv) (c) :  $[\text{Ni}(\text{CO})_4]$  contains Ni(0).



CO is strong ligand thus,



OR

(a)