# Chapter 9- Coordination Chemistry

## LEVEL-1 QUESTIONS

**1.Define Ligand . Give one example also.**
The ion or molecules which are coordinately bonded to central metalatom in the coordination entity are
called ligands.

**2. Why Coordination compounds are coloured?**
Due to d-d transition.

**3. What is Homoleptic complexes?**
The complexes in which a metal is bound to only one kind of donorgroups. E.g., $[Co(NH3)_6]^{3+}$

**4. What is the Oxidation no. of cobalt in K[Co(CO)4]?**
+1

**5. Amongest the following which is most stable complex is A) $[Fe(H_2O)_6]^{3+}$ B) $Fe(C_2O_4)_3]^{3-}$**
ANS. B

**6.Write IUPAC name of the following $[CO(NH_3)_6Cl_3$**
Hexaaminocobalt(III)chloride

**7. Which isomerisms are shown by following**
**a) $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$**
**b)$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$**
A)Linkage isomerism b)Ionisation isomerism

8. **Explain each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.**
**Answer**
**(i)Coordination entity:**
A coordination entity is an electrically charged radical or species carrying a positive ornegative charge. In a coordination entity, the central atom or ion is surrounded by a suitablenumber of neutral molecules or negative ions ( called ligands)

**(ii)Ligands**
The neutral molecules or negatively charged ions that surround the metal atom in acoordination entity or a coordinal complex are known as ligands. For example,,Cl−, −OH. Ligands are usually polar in nature and possess at least one unshared pair ofvalence electrons.

**(iii)Coordination number:**
The total number of ligands (either neutral molecules or negative ions) that get attached tothe central metal atom in the coordination sphere is called the coordination number of thecentral metal atom. It is also referred to as its ligancy.

**(vi)Coordination polyhedron:**
Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere.

**(v)Homoleptic complexes:**
These are those complexes in which the metal ion is bound to only one kind of a donorgroup.

**(vi)Heteroleptic complexes:**
Heteroleptic complexes are those complexes where the central metal ion is bound to morethan one type of a donor group.

**9. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.**
**Answer**
A ligand may contain one or more unshared pairs of electrons which are called the donorsites of ligands. Now, depending on the number of these donor sites, ligands can be classifiedas follows:
**(a)Unidentate ligands:** Ligands with only one donor sites are called unidentate ligands. Fore.g., , Cl− etc.

**(b)Didentate ligands:** Ligands that have two donor sites are called didentate ligands. Fore.g.,
(a) Ethane-1,2-diamine
(b) Oxalate ion

**(c)Ambidentate ligands:**
Ligands that can attach themselves to the central metal atom through two different atoms arecalled ambidentate ligands.

**10.Write the name of each of the following complex compound**

**(a) $[Co(NH_3)_4(H_2O)_2]Cl_3$**

**(b) $[Pt(NH_3)_4][NiCl_4]$**

**Ans**. (a) Tetraamminediaquacobalt(III)chloride

(b) Tetraammineplatinum(II)tetrachloridonickelate(II)

**11. Write the IUPAC name of $[CrCl_2(en)(NH_3)_2]^+$**

**Ans**. Diamminedichloridoethane-1,2-diamminechromium(III)ion

**12. Why only transition metals are known to form π complexes?**

**Ans.** Transition metals have empty d-orbitals into which the electron-pairs can be donated by ligands containing π electrons, i.e, electrons in their π molecular orbital.

**13. CO is a stronger ligand than $NH_3$. Why?**

**Ans**. Back bonding.

**14. What is crystal field splitting energy?**

Energy difference between eg and t2g level.

**15. Differentiate between:**

a) Didentate and Polydentate ligand

Didentate ligand : Two binding sites

Polydentate ligand: more than two binding sites

**b) Chelate ligand and ambidentate ligand**

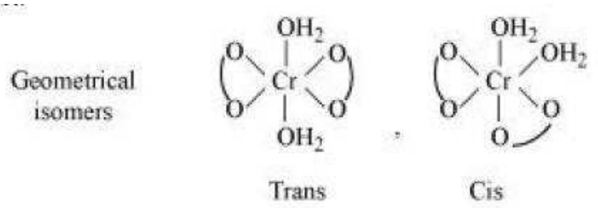
Chelate ligand : Forms cyclic structure.

ambidentate ligand : Bind through either of the atoms.

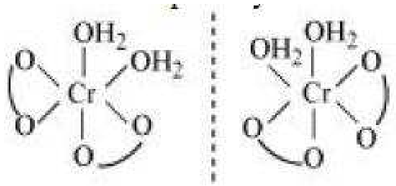
## LEVEL-2 QUESTIONS

**1. Write the possible isomers of $K[Cr(H_2O)_2 (C_2O_4)_2]$.**

Answer: Both geometrical (cis-, trans-) isomers for $K[Cr(H_2O)_2(C_2O_4)_2]$can exist. Also, optical isomers
for cis-isomer exist.



Trans-isomer is optically inactive. On the other hand, cis-isomer is optically active.



2. **Write the IUPAC name of:**

**i) $[Co(NH_3)_5Cl]Cl_2$**

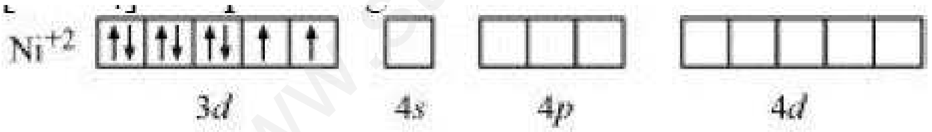
**ii) $[Pt Cl_2 (en)_2](NO_3)_2$**

Answer: (i)Pentamminechloridocobalt III chloride

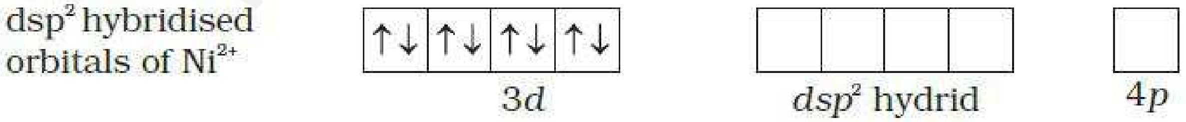
(ii) Dichloridobis(ethane-1,2diammineplatinum IV nitrate.

3. **On the basis of VB theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and $[Ni(Cl)_4]^{2-}$ is tetrahedral is paramagnetic.**

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^8$

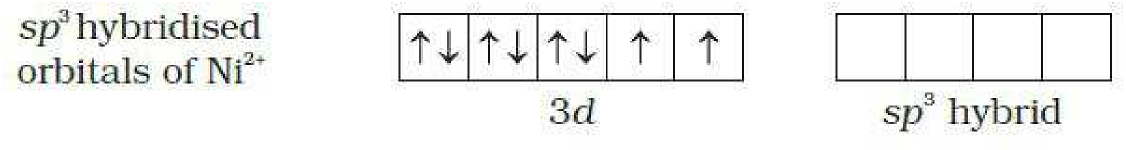


CN is a strong ligand and pairing takes place



Square planar and diamagnetic

In [NiCl4]2- Ni is +2



Cl is a weak ligand pairing will not take place tetrahedral shape paramagnetic nature

**4. Draw the crystal fieid splitting of d orbital in octahedral crystal field. Write the electroni configuration of $d^5$ .**

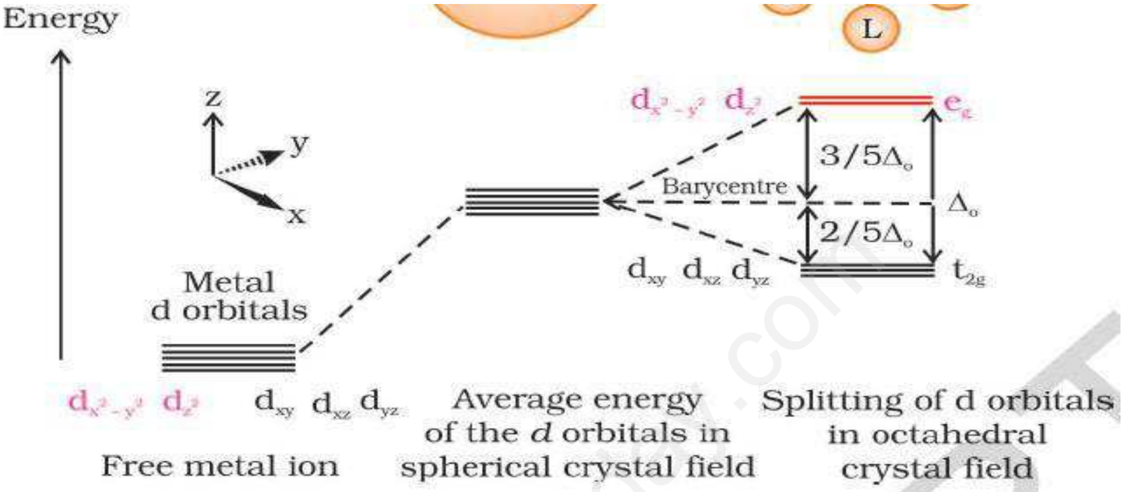


**Fig.9.8:** *d orbital splitting in an octahedral crystal field*

Answer:

Electronic configuration is $t2g^3,eg^2\ p>\Delta_0$

$t2g^5,eg^0\ p<\Delta_0$

5. **Write the optical isomer of $[PtCl_2(en)_2]^{2+}$.**

Answer:

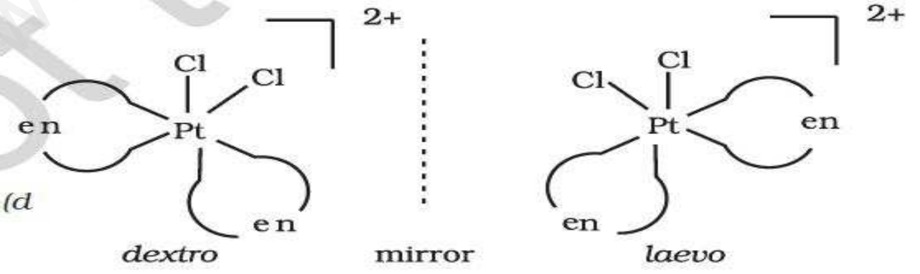


*Fig.9.7 Optical isomers (d and l) of cis-$[PtCl_2(en)_2]^{2+}$*

**6. For the complex $[Fe(en)_2Cl_2]Cl$,(en= ethylene diamine), identify**

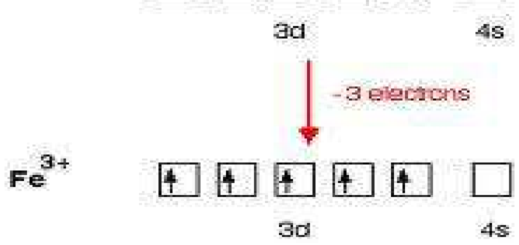
**(i)The oxidation number of iron,**

**Ans:** x + 2(-1) + 0 + (-1) = 0 x = +2 + 1 = +3

**+3 oxidation state**

(ii) The hybrid orbitals and the shape of the complex,
Hybridization = $Sp^3d^2$
Octahedral

(iii) The magnetic behavior of the complex,
Paramagnetic



(iv) The number of geometrical isomers,
2 geometric isomers

(v) Whether there is an optical isomer also and
Yes

(vi) Name of the complex. (At. No. of Fe =26)

Dichloridobis (ethane-1, 2-diamine) Iron (III) chloride

**7.Explain structure of[ $[CO(NH_3)_6]^{3+}$ on the basis of valencebond theory.**
Structure on the basis of valence bond theory
In the diamagnetic octahedral complex $[CO(NH_3)_6]^{3+}$ , the cobalt ion isin +3 oxidation state and has the electronic configuration 3d6. Thehybridisation scheme is as shown in diagram.Six pairs of electrons, one from each NH3 molecule, occupy the six hybrid orbitals.
Thus, the complex has octahedral geometry and is diamagnetic because of theabsence of unpaired electron. In the formation of this complex, since the inner dorbital (3d) is used in hybridisation, the complex, [Co(NH3)6]3+ is called an innerorbital or low spin or spin paired complexes.

**8. Write the formulas for the following coordination compounds:**
**i. Tetraamminediaquacobalt(III) chloride**
**ii. Potassium tetracyanonickelate(II)**
**iii. Tris(ethane−1,2−diamine) chromium(III) chloride**
Answer
i. $[Co(H_2O)_2(NH_3)_4]Cl_3$
ii. $K_2[Ni(CN)_4]$
iii. $[Cr(en)_3]Cl_3$

**11. Write the IUPAC names of the following coordination compounds:**
**i. $[Co(NH_3)_6]Cl_3$**

**ii. $[Co(NH_3)_5Cl]Cl_2$**
**iii. $K_3[Fe(CN)_6]$**
Answer Hexaamminecobalt(III) chloride
Pentaamminechloridocobalt(III) chloride
Potassium hexacyanoferrate(III)

**12. Indicate the types of isomerism exhibited by the following complexes anddraw the structures for these isomers:**
**i. $K[Cr(H_2O)_2(C_2O_4)_2]$**
**ii. $[Co(en)_3]Cl_3$**
**iii. $[Co(NH_3)_5(NO_2)](NO_3)_2$**
**Answer** Both geometrical (*cis*-, *trans*-) isomers for K[Cr(H2O)2(C2O4)2]can exist. Also, optical isomers
for *cis*-isomer exist.*Trans*-isomer is optically inactive. On the other hand, *cis*-isomer is optically active.

**(ii)** Two optical isomers for[Co(en)3]Cl3exist.Two optical isomers are possible for this structure.

**(iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$**
A pair of optical isomers. It can also show linkage isomerism.
**$[Co(NH_3)_5(NO_2)](NO_3)_2$**and **$[Co(NH_3)_5(ONO)](NO_3)_2$**

It can also show ionization isomerism.
[Co(NH3)5(NO2)](NO3)2 and [Co(NH3)5(NO3)](NO3)(NO2)

**13. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral.Why?**
**Answer** Though both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral, their magneticcharacters are different. This is due to a difference in the nature of ligands. Cl− is aweak field ligand and it does not cause the pairing of unpaired 3*d* electrons. Hence,$[NiCl_4]^{2-}$ is paramagnetic.

In $Ni(CO)_4$, Ni is in the zero oxidation state i.e., it has a configuration of $3d^8\ 4s^2$.But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3*d* electrons.Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to *sp*3hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

**14. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.**
**Answer**
$[Pt(CN)_4]^{2-}$, In this complex, Pt is in the +2 state. It forms a square planar structure. Thismeans that it undergoes dsp2 hybridization. Now, the electronic configuration of Pd(+2) is5*d*8.
CN− being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in$[Pt(CN)_4]^{2-}$

## LEVEL-3 QUESTIONS

**1. Explain the bonding in coordination compounds in terms of Werner's postulates.**
**Answer**
Werner's postulates explain the bonding in coordination compounds as follows:

**(i)** A metal exhibits two types of valencies namely, primary and secondary valencies.Primary valencies are satisfied by negative ions while secondary valencies are satisfiedby both negative and neutral ions.

(In modern terminology, the primary valency corresponds to the oxidation number of themetal ion, whereas the secondary valency refers to the coordination number of the metalion.

**(ii)** A metal ion has a definite number of secondary valencies around the central atom.Also, these valencies project in a specific direction in the space assigned to the definitegeometry of the coordination compound.

**(iii)** Primary valencies are usually ionizable, while secondary valencies are non-ionizable.

2. **Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.**

**Answer**

The splitting of the *d* orbitals in an octahedral field takes palce in such a way that ,experience a rise in energy and form the *eg*level, while *dxy, dyz*and*dzx* experience a fall inenergy and form the *t2g* level.

Diagram.

3.**What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.**

**Answer**

A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values. The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands. Also, strong field ligands cause higher splitting in the *d* orbitals than weak field ligands.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < H^- < CN^- < NH_3 < en < SO_3^{2-} < NO_2^- < phen < CO$

**4. Discuss the nature of bonding in metal carbonyls**.

**Answer** The metal-carbon bonds in metal carbonyls have both σ and π characters. A σ-bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacantorbital of the metal. A π bond is formed by the donation of a pair of electrons from the filledmetal *d* orbital into the vacant anti-bonding π* orbital (also known as back bonding of thecarbonyl group). The σ bond strengthens the π bond and vice-versa. Thus, a synergic effect iscreated due to this metal-ligand bonding. This synergic effect strengthens the bond betweenCO and the metal.

**5. What is meant by the *chelate effect*?**

**Answer** When a ligand attaches to the metal ion in a manner that forms a ring, then themetal-ligand association is found to be more stable. In other words, we can say thatcomplexes containing chelate rings are more stable than complexes without rings. This isknown as the chelate effect.

**6. Discuss briefly giving an example in each case the role of coordination compounds in:**

**(i) biological system**

**(ii) medicinal chemistry**

**(iii) analytical chemistry**

**Answer**

(i) **Role of coordination compounds in biological systems:**

We know that photosynthesis is made possible by the presence of the chlorophyll pigment.This pigment is a coordination compound of magnesium. In the human biological system,several coordination compounds play important roles. For example, the oxygen-carrier ofblood, i.e., haemoglobin, is a coordination compound of iron.

(ii) **Role of coordination compounds in medicinal chemistry:**
Certain coordination compounds of platinum (for example, *cis*-platin) are used for inhibitingthe growth of tumours.
(iii) **Role of coordination compounds in analytical chemistry:**
During salt analysis, a number of basic radicals are detected with the help of the colourchanges they exhibit with different reagents. These colour changes are a result of thecoordination compounds or complexes that the basic radicals form with different ligands.
(iii) **Role of coordination compounds in extraction or metallurgy of metals:**
The process of extraction of some of the metals from their ores involves the formation of complexes. For example, in aqueous solution, gold combines with cyanide ions to form$[Au(CN)_2]^-$. From this solution, gold is later extracted by the addition of zinc metal.

**7. What will be the correct order for the wavelengths ofabsorption in the visible region for the following:$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$**
**Answer :**The central metal ion in all the three complexes is the same. Therefore, absorption in the visibleregion depends on the ligands. The order in which the CFSE values of the ligands increases in the spectrochemical series is as follows:$H_2O < NH_3 < NO$

Hence, the wavelengths of absorption in the visible region will be in the order:
$[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

**8.Discuss briefly giving an example in each case the role of coordination compounds in:**
**(i) biological system**
**(ii) medicinal chemistry**
**(iii) analytical chemistry**
**(iv) extraction/metallurgy of metals**

Answer :

(i) Role of coordination compounds in biological systems:
We know that photosynthesis is made possible by the presence of the chlorophyll pigment. This pigment is a coordination compound of magnesium. In the human biological system, several coordination compounds play important roles. For example, the oxygen-carrier of blood, i.e., haemoglobin, is a coordination compound of iron.
(ii) Role of coordination compounds in medicinal chemistry:
Certain coordination compounds of platinum (for example, *cis*-platin) are used for inhibiting the growth of tumours.
(iii) Role of coordination compounds in analytical chemistry:
During salt analysis, a number of basic radicals are detected with the help of the colour changes they exhibit with different reagents. These colour changes are a result of the coordination compounds or complexes that the basic radicals form with different ligands.
(iii) Role of coordination compounds in extraction or metallurgy of metals:
The process of extraction of some of the metals from their ores involves the formation of complexes. For example, in aqueous solution, GOLD combines with cyanide ions to form $[Au(CN)_2]$. From this solution, gold is later extracted by the addition of zinc metal.