Chapter 5
Coordination Chemistry

Questions 1.
The sum of primary valance and secondary valance of the metal M in the complex $[M(en)_2(Ox)]Cl$ is ……………..
(a) 3
(b) 6
(c) -3
(d) 9
Answer:
(d) 9

Question 2.
An excess of silver nitrate is added to 100ml of a 0.01M solution of penta aquachlorido chromium (III) chloride. The number of moles of AgCl precipitated would be ……………..
(a) 0.02
(b) 0.002
(c) 0.01
(d) 0.2
Answer:
(b) 0.002

Question 3.
A complex has a molecular formula $MSO_4Cl. 6H_2O$. The aqueous solution of it gives white precipitate with Barium chloride solution and no precipitate is obtained when it is treated with silver nitrate solution. If the secondary valence of the metal is six, which one of the following correctly represents the complex?
(a) $[M(H_2O)_4Cl] SO_2. 2H_22O$
(b) $[M(H_2O)_6] SO_4$
(C)$[M(H_2O)_5Cl] SO_4. H_2O$
(d) $[M(H_2O)_3Cl] SO_4. 3H_2O$
Answer:
(c) $[M(H_2O)_5Cl]SO_4. H_2O$

Question 4.
Oxidation state of Iron and the charge on the ligand NO in $[Fe(H_2O)_5NO] SO_4$ are ……………..
(a) +2 and 0 respectively
(b) +3 and 0 respectively
(c) +3 and -1 respectively
(d) +1 and +1 respectively
Answer:
(d) +1 and +1 respectively

Question 5.
As per IUPAC guidelines, the name of the complex $[CO(en)_2(ONO)Cl]Cl$ is ……………..
(a) chlorobisethylenediaminenitritocobalt (III) chloride
(b chloridobis (ethane-1, 2-diamine) nitro k – Ocobaltate (III) chloride
(c) chloridobis (ethane-1, 2-diammine) nitrito k – Ocobalt (II) chloride
(d) chloridobis (ethane-1, 2-diamine) nitro k – Ocobalt (III) chloride

Answer:
(d) chloridobis (ethane-1, 2-diamine) nitro k – Ocobalt (III) chloride

Question 6.
IUPAC name of the complex $K_3[Al(C_2O_4)_3]$ is ……………..
(a) potassiumtrioxalatoaluminium (III)
(b) potassiumtrioxalatoaluminate (II)
(c) potassiumtrisoxalatoaluminate (III)
(d) potassiumtrioxalatoaluminate (III)
Answer:
(d) potassiumtrioxalatoaluminate (III)

Question 7.
A magnetic moment of 1.73BM will be shown by one among the following ……………..
(a) $TiCl_4$
(b) $[COCl_6]^{4-}$
(c) $[Cu(NH_3)_4]^{2+}$
(d) $[Ni(CN)_4]^{2-}$

Answer:
(c) $[Cu(NH_3)_4]^{2+}$

Question 8.
Crystal field stabilization energy for high spin d^5 octahedral complex is ……………..
(a) $-0.6\Delta_0$
(b) 0
(c) $2(P - \Delta_0)$
(d) $2(P + \Delta_0)$
Answer:
(b) 0

Question 9.
In which of the following coordination entities the magnitude of Δ_0 will be maximum?
(a) $[CO(CN)_6]^{3-}$
(b) $[CO(C_2O_4)_3]^{3-}$
(c) $[CO(H_2O)_6]^{3+}$
(d) $[CO(NH_3)_6]^{3+}$
Answer:
(a) $[CO(CN)_6]^{3-}$

Question 10.
Which one of the following will give a pair of enantiomorphs?
(a) $[Cr(NH_3)_6][CO(CN)_6]$
(b) $[CO(en)_2Cl_2]Cl$
(c) $[Pt(NH_3)_4][PtCl_4]$
(d) $[CO(NH_3)_4Cl_2]NO_2$
Answer:
(b) $[CO(en)_2Cl_2]Cl$

Question 11.
Which type of isomerism is exhibited by $[Pt(NH_3)_2Cl_2]$?
(a) Coordination isomerism
(b) Linkage isomerism
(c) Optical isomerism
(d) Geometrical isomerism
Answer:
(d) Geometrical isomerism

Question 12.
How many geometrical isomers are possible for [Pt (Py) (NH_3) (Br) (Cl)]?
(a) 3
(6) 4
(c) 0
(d) 15
Answer:
(a) 3

Question 13.
Which one of the following pairs represents linkage isomers?
(a) $[Cu(NH_3)_4]$ $[PtCl_4]$ and $[Pt(NH_3)_4]$ $[CuCl_4]$
(b) $[CO(NH_3)_5(NO_3)]SO_4$ and $[CO(NH_3)_5(ONO)]$
(c) $[CO(NH_3)_4(NCS)_2]Cl$ and $[CO(NH_3)_4(SCN)_2]Cl$
(d) both (b) and (c)
Answer:
(c) $[CO(NH_3)_4(NCS)_2]Cl$ and $[CO(NH_3)_4(SCN)_2]Cl$

Question 14.
Which kind of isomerism is possible for a complex $[CO(NH_3)_4Br_2]Cl$?
(a) geometrical and ionization
(b) geometrical and optical
(c) optical and ionization
(d) geometrical only

Answer:
(a) geometrical and ionization

Question 15.
Which one of the following complexes is not expected to exhibit isomerism?
(a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$
(b) $[Pt(NH_3)_2 Cl_2]$
(C) $[CO(NH_3)_5SO_4]Cl$
(d) $[Fe(en)_3]^{3+}$
Answer:
(d) $[Fe(en)_3]^{3+}$

Question 16.
A complex in which the oxidation number of the metal is zero is ……………..
(a) $K_4[Fe(CN)_6]$
(b) $[Fe(CN)_3(NH_3)_3]$
(c) $[Fe(CO)_5]$
(d) both (b) and (c)
Answer:
(c) $[Fe(CO)_5]$

Question 17.
Formula of tris (ethane-1, 2-diamine) iron (II) phosphate ……………..
(a) $[Fe(CH_3 – CH(NH_2)_2)_3]\ (PO_4)_3$
(b) $[Fe(H_2N – CH_2 – CH_2 – NH_2)_3]\ (PO_4)$
(c) $[Fe(H_2N – CH_2 – CH_2 – NH_2)_3](PO_4)_2$
(d) $[Fe(H_2N – CH_2 – CH_2 – NH_2)_3](PO_4)_2$
Answer:
(d) $[Fe(H_2N – CH_2 – CH_2 – NH_2)_3](PO_4)_2$

Question 18.
Which of the following is paramagnetic in nature?
(a) $[Zn(NH_3)_4]^{2+}$
(b) $[CO(NH_3)_6]^{3+}$
(c) $[Ni(H_2O)_6]^{2+}$
(d) $[Ni(CN)_4]^{2-}$
Answer:
(c) $[Ni(H_2O)_6]^{2+}$

Question 19.
Facmer isomerism is shown by ……………..
(a) $[CO(en)_3]^{3+}$
(b) $[CO(NH_3)_4(Cl)_2]^{+}$
(c) $[CO(NH_3)_3(Cl)_3]$
(d) $[CO(NH_3)_5Cl]SO_4$
Answer:
(c) $[CO(NH_3)_3(Cl)_3]$

Question 20.

Choose the correct statement.
(a) Square planar complexes are more stable than octahedral complexes
(b) The spin only magnetic moment of $[Cu(Cl)_4]^{2-}$ is 1.732 BM and it has square planar structure.
(c) Crystal field splitting energy (Δ_0) of $[FeF_6]^{4-}$ is higher than the (Δ_0) of $[Fe(CN)_6]^{4-}$
(d) crystal field stabilization energy of $[V(H_2O)_6]^{2+}$ is higher than the crystal field stabilization of $[Ti(H_2O)_6]^{2+}$

Answer:
(d) crystal field stabilization energy of $[V(H_2O)_6]^{2+}$ is is higher than the crystal field stabilization of $[Ti(H_2O)_6]^{2+}$

II. Answer the following questions

Question 1.
Write the IUPAC names for the following complexes.

1. $Na_2\ [Ni(EDTA)]$
2. $[Ag(CN)_2]^-$
3. $[CO(en)_3]_2(SO_4)_3$
4. $[CO(ONO)(NH_3)_5]^{2+}$
5. $[Pt(NH_3)_2Cl(NO_2)]$

Answer:
1. $Na_2[Ni(EDTA)]$
= Sodium Ethyicncdiaminetctraacetatonickcate (II)
(or)
Sodium 2, 2′, 2”, 2” – (ethane – 1, 2 – diyldinitrilo) tetraacetatonickelate (II)

2. $[Ag(CN)_2]^1$
= dicyanidoargentate (I) ion

3. $[CO(en)_3]_2(SO_4)_3$
= tris (ethylenediamine) cobait (III) sulphate

4. $[CO(ONO)(NH_3)_5]^{2+}$
= Pentaammincnitrito – kOCobalt (III) ion.

5. $[Pt(NH_3)_2Cl(NO_2)]$
= diamminedichloridonitrito – kN platinum (II)

Question 2.
Write the formula for the following coordination compounds.

1. potassiumhexacyanidoferrate (II)
2. petacarbonvliron(O)
3. pentaammineriitrito – k – N – cobalt(III)ion
4. hexaamminecobalt (III) sulphate
5. sodiumtetrafluoridodihydroxidoch romate (III)

Answer:

1. potassiurnhexacyanidoferrate (ll) = $K_4[Fe(CN)_6]$
2. petacarbonyliron(O) = $[Fe(CO)_5]$
3. pentaamminenitrito – KN – cobalt (III) ion $[CO(NH_3)_5NO_2]^{2-}$
4. hexaamminecobalt (III) sulphate $[CO(CN)_6]_2(SO_4)^3$
5. sodiumtetrafluoridodihyclroxidochromate (III) = $Na_3[CrF_4(OH)_2]$

Question 3.
Arrange the following in order of increasing molar conductivity

1. $Mg[Cr(NH_3)(Cl)_5]$
2. $[Cr(NH_3)_5Cl]_3\ [COF_6]_2$
3. $[Cr(NH_3)_3Cl_3]$

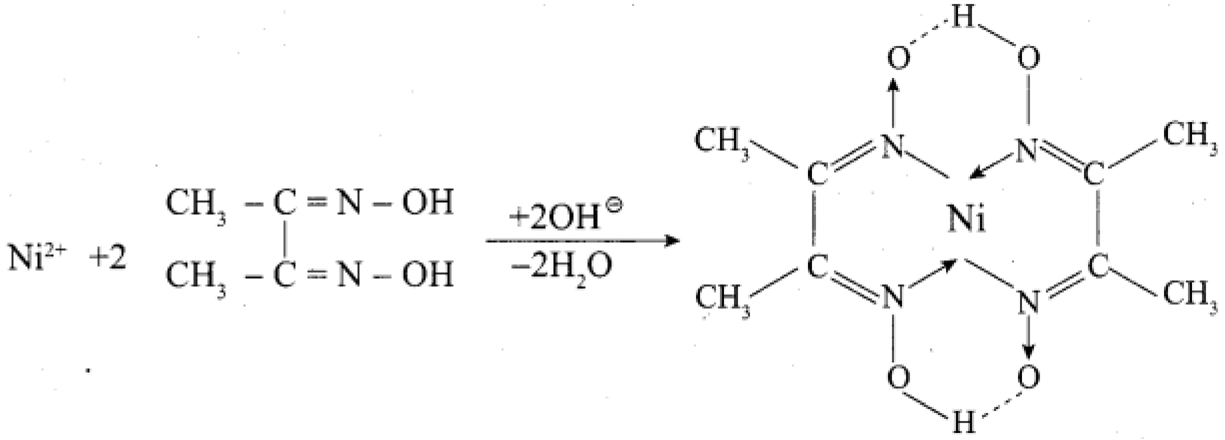
Answer:
These complexes can ionise in solution as:

1. $Mg[Cr(NH_3)(Cl)_5] = Mg^{2+}\ [Cr(NH_3)\ (Cl)_5]^{2-}$
2. $[Cr(NH_3)_5Cl]_3\ [COF_6]_2 = [Cr(NH_3)_5Cl]^{2+} + [COF_6]^{3-}$
3. $[Cr(NH_3)_3Cl_3]$ = does not ionize

As the number of ions in solution increases, their molar conductivity also increases. Therefore, conductivity follows the order:
$[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]_3\ [COF_6]_2 < Mg[Cr(NH_3)(Cl)_5]$

Question 4.
Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction.
Answer:
1. Ni^{2+} ions present in Nickel chloride solution is estimated accurately for forming an insoluble complex called $[Ni(DMG)_2]$.

2. Nickel ion reacts with alcoholic solution of DMG in the presence of ammonical medium, to give rosy red precipitate of [Ni(DMG)$_2$] complex.



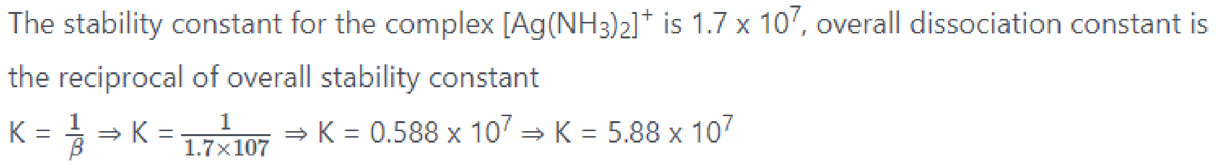
Nickel bis(dimethylglyoximate)
(Rosy red precipitate)

Question 5.
$[CuCl_4]^{2-}$ exists while $[CuI_4]^{2-}$ does not exist why?
Answer:
1. In $[CuI_4]^{2-}$ complex, the size of chloride ion is less hence exist. But in $[CuI_4]^{2-}$ the bigger iodide ion makes the compound unstable.
2. When copper cation comes in contact with iodide anion, iodide get oxidised to iodine molecule hence the formation of the above complex ion does not take place. Hence $[CuI_4]^{2-}$ exists while $[CuI_4]^{2-}$ does not exist.

Question 6.
Calculate the ratio

$$\frac{[Ag^+]}{[Ag(NH_3)_2]^+}$$

in 0.2 M solution of NH_3. If the stability constant for the complex $[Ag(NH_3)_2]$+ is 1.7 x 10^7
Answer:



The stability constant for the complex $[Ag(NH_3)_2]^+$ is 1.7 x 10^7, overall dissociation constant is the reciprocal of overall stability constant

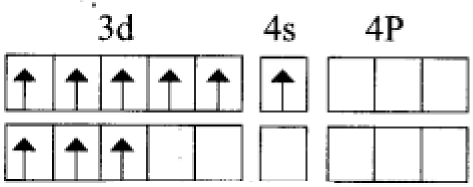
$K = \frac{1}{\beta} \Rightarrow K = \frac{1}{1.7 \times 107} \Rightarrow K = 0.588 \times 10^7 \Rightarrow K = 5.88 \times 10^7$

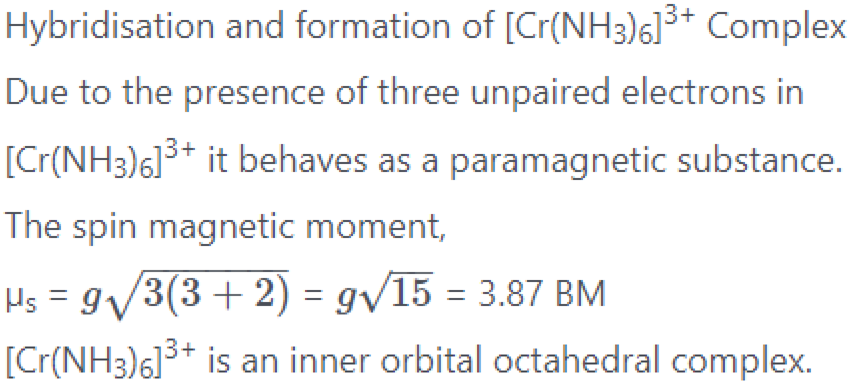
Question 7.
Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.
Answer:

- Cis – platin is used as an antitumour drug in cancer treatment.

- Biologically important compounds.
    - Haemoglobin – Oxygen carrier in blood.
    - Chlorophyll – useful in photo systhesis in plants.

Question 8.
Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Cr(NH)_4]^{2-}$ is diamagnetic.
Answer:
1. $[Cr(NH_3)_6]^{3+}$
In this complex Cr is in the +3 oxidation state. Electronic configuration of Cr atom.
Electronic configuration of Cr^{3+} ion 172 Chemistry 12





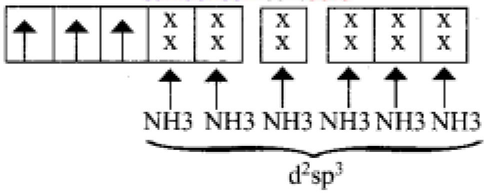
Hybridisation and formation of $[Cr(NH_3)_6]^{3+}$ Complex

Due to the presence of three unpaired electrons in $[Cr(NH_3)_6]^{3+}$ it behaves as a paramagnetic substance.

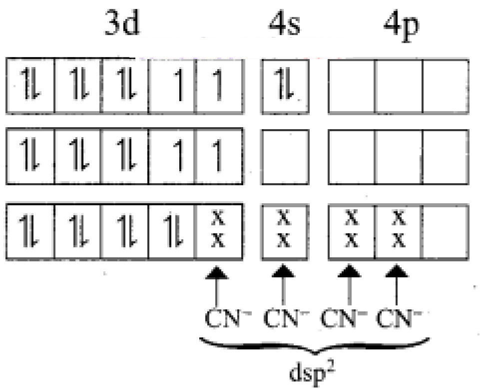
The spin magnetic moment,

$$\mu_s = g\sqrt{3(3+2)} = g\sqrt{15} = 3.87 \text{ BM}$$

$[Cr(NH_3)_6]^{3+}$ is an inner orbital octahedral complex.



2. $[Ni(CN)_4]^{2-}$
in this complex Ni is in the +2 oxidation state. Electronic configuration of Ni atom.
Electronic configuration of Ni^{2+} ion. Hybridisation and formation of $[Ni(CN)_4]^{2-}$ Complex



Since CN⁻ is strong field ligand, hence the electrons in 3d orbitais are forced to pair up and there is no unpaired electron in $[Ni(CN)_4]_2$, hence it should be diamagnetic substance.

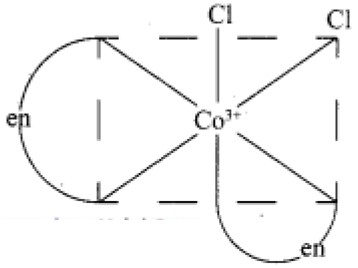
Question 9.

Draw all possible geometrical isomers of the complex $[CO(en)_2CI_2]^+$ and identify the optically active isomer.

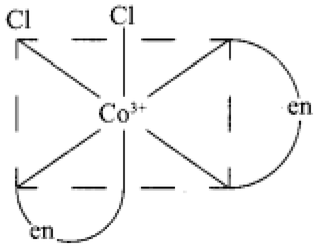
Answer:

1. Cis – $[CO(en)_2CI_2]^+$

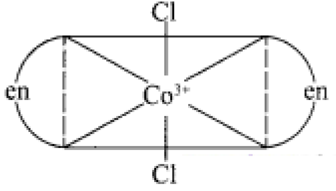
(a)



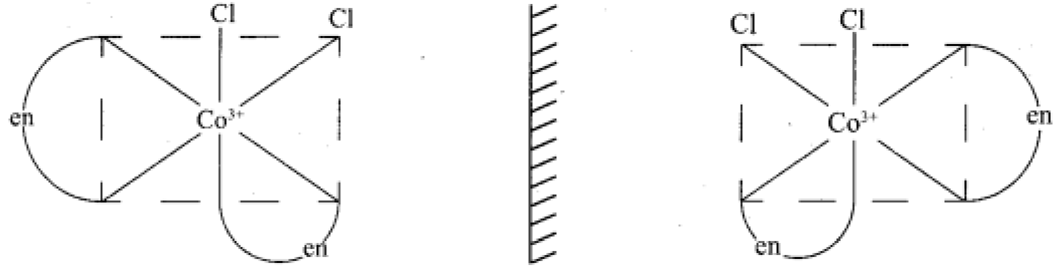
(b)



2. Trans $[CO(en)_2CI_2]^+$



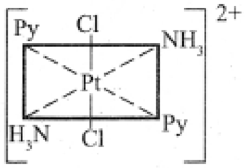
The coordination complex $[CO(en)_2CI_2]^+$ has three isomers two optically active cis forms and the optically inactive trans form.



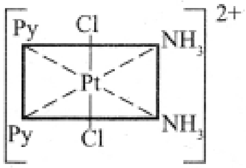
(Structure of optically active two cis form)

Question 10.
$[Ti(H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain.
Answer:
Ti in $[Ti(H_2O)_6]^{3+}$ is in +3 oxidation state. Sc in $[Sc(H_2O)_6]^{3+}$ is in +3 oxidation state. The outer electronic configuration of Sc, Ti and their trivalent ions are,
SC: $3d^1\ 4S^2$
SC^{3+}: $3d^0$
Ti: $3d^2\ 4S^2$
Ti^{3+}: $3d^1$
Ti^{3+}has one unpaired electron in 3d orbital and they undergoes d-d transition. This electron can be promoted to a higher energy level by light absorption. Therefore $[Ti(H_2O)_6]^{3+}$ is coloured. In the case of $[Sc(H_2O)_6]^{3+}$ there is no electron in 3d orbital of Sc^{3+}, hence there is no possibility of light absorbance. Therefore $[Sc(H_2O)_6]^{3+}$ is colourless.

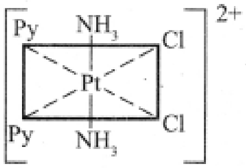
Question 11.
Give an example for complex of the type $[Ma_2b_2c_2]$ where a,b,c are monodentate ligands and give the possible isomers.
Answer:
The octahedral complexes of $[Ma_2b_2c_2]$ type can exist in five geometrical isomers. The five geometrical isomers for the complex ion $[PtCl_2(NH_3)_2(py)_2]^{2+}$are shown below.



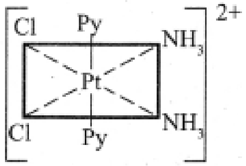
(I)



(II)



(III)



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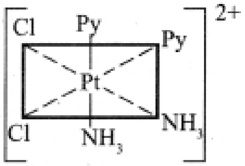
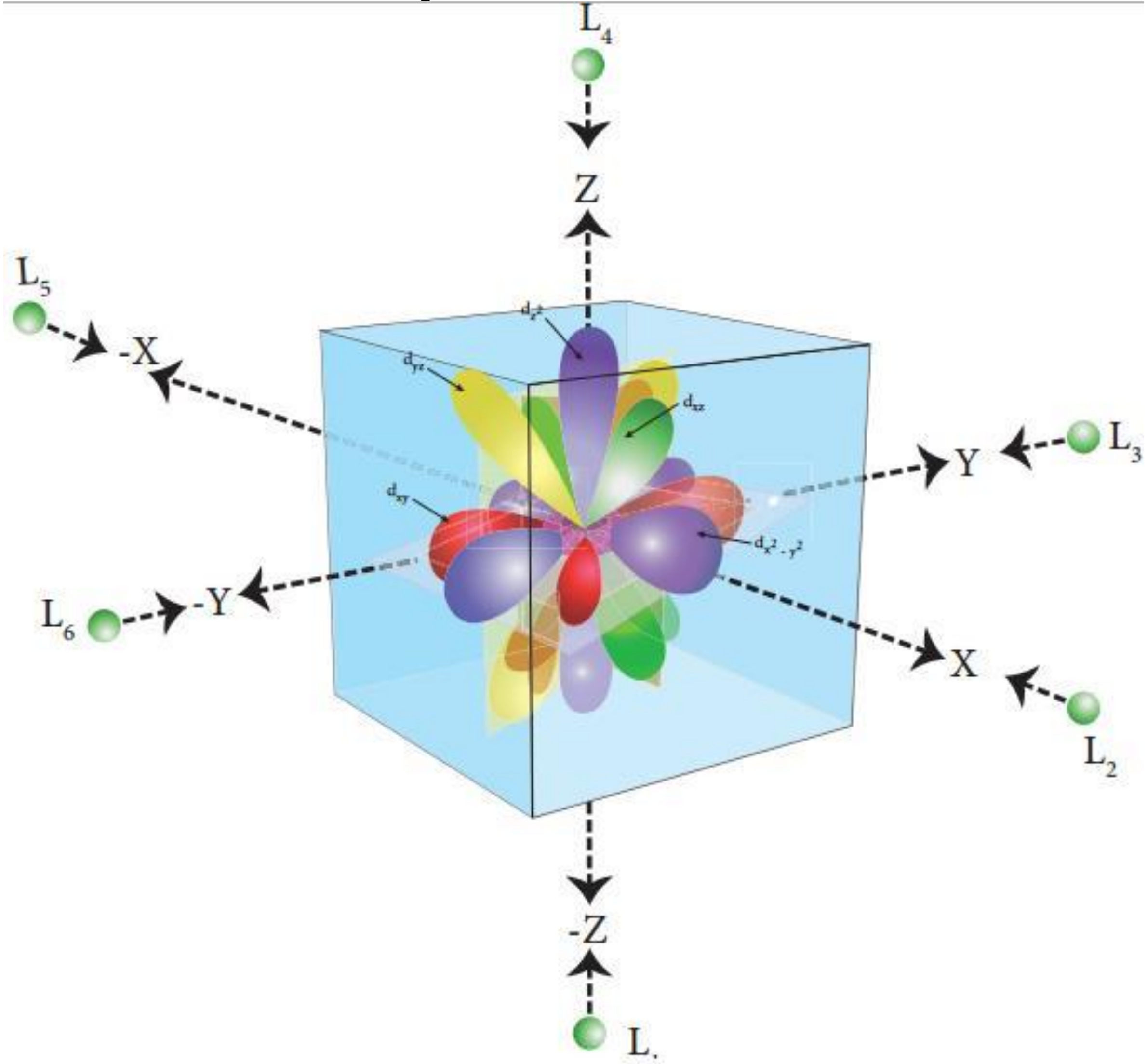


(V)

Question 12.
Give one test to differentiate $[CO(NH_3)_5Cl]\ SO_4$ and $[CO(NH_3)_5SO_4]\ Cl$.
Answer:

Question 13.
In an octahedral crystal field, draw the figure to show the splitting of d orbitals.
Answer:

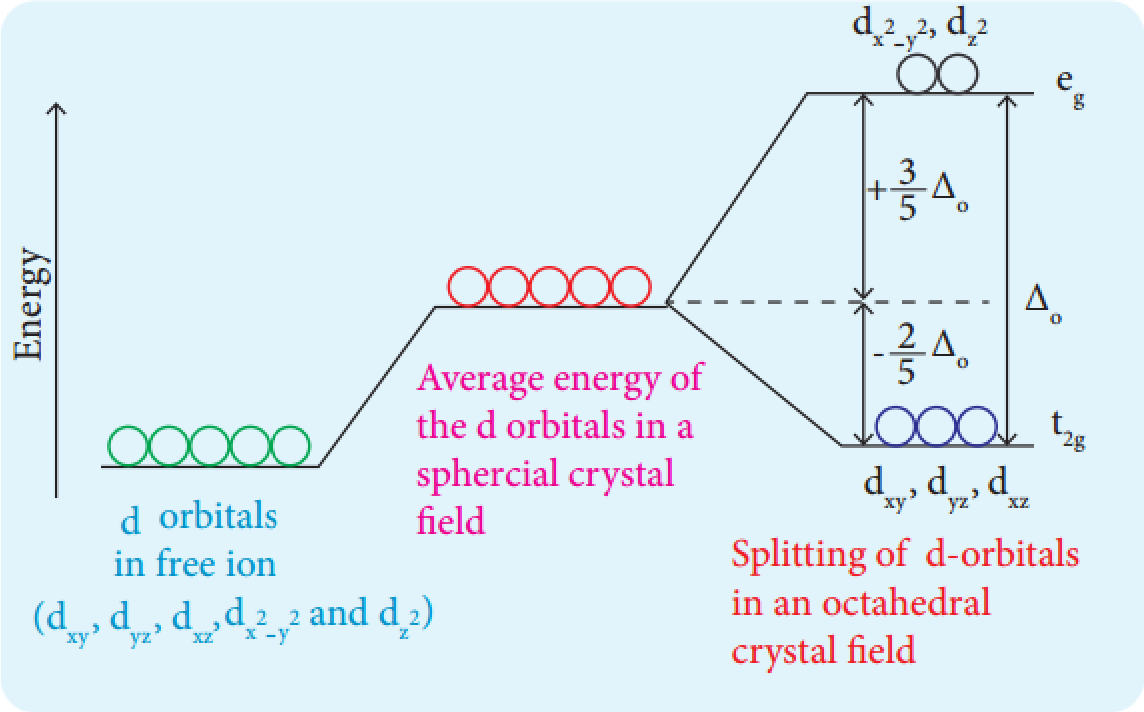
Step 1:
In an isolated gaseous state, all the five d orbitals of the central metal ion are degenerate. Initially, the ligands form a spherical field of negative charge around the metal. In this filed, the energies of all the five d orbitals will increase due to the repulsion between the electrons of the metal and the ligand.



octahedral ligand field

Step 2:
The ligands are approaching the metal atom in actual bond directions. To illustrate this let us consider an octahedral field, in which the central metal ion is located at the origin and the six ligands are coming from the +x, -x, +y, -y, +z and -z directions as shown below. As shown in the figure, the orbitals lying along the axes $dx^2-y^2$and dz^2 orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and d_{zx}). Thus the degenerated orbitals now split into two sets and the process is called crystal field splitting.

Step 3:
Up to this point the complex formation would not be favoured. However, when the ligands approach further, there will be an attraction between the negatively charged electron and the positively charged metal ion, that results in a net decrease in energy. This decrease in energy is the driving force for the complex formation.



Crystal field splitting in octahedral field

During crystal field splitting in the octahedral field, in order to maintain the average energy of the orbitals (barycentre) constant, the energy of the orbitals $d_{x^2-y^2}$ and d_{z^2} (represented as t_{2g} orbitals) will increase by $3/5\Delta_0$ while that of the other three orbitals d_{xy}. d_{yz} and d_{zx} (represented as t_{2g} orbitals) decrease by $2/5\Delta_0$. Here, Δ_0 represents the crystal field splitting energy in the octahedral fiel

Question 14.
What is linkage isomerism? Explain with an example.
Answer:
This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ ion through either of its two different donor atoms. For examples – $[CO(NH_3)_5ONO]Cl_2$ – (Pentaammine nitrito cobalt (III) chloride) – O – attached. (Red in colour).$[CO(NH_3)_5NO_2]Cl_2$ – (Pentaammine nitro cobalt (III) chloride) – N – attached (Yellow-brown in colour).

Question 15.
Write briefly about the applications of coordination compounds in volumetric analysis.
Answer:

Hardness of water is due to the presence of $Ca^{2+}$and Mg^{2+} ions in water. EDTA forms stable complexes with Ca^{2+} and Mg^{2+}. So the total hardness of water can be estimated by simple volumetric titration of water with EDTA.

Question 16.
Classify the following ligand based on the number of donor atoms,

1. NH_3
2. en
3. ox^{2-}
4. triaminotriethylamine
5. pyridine

Answer:

1. NH_3 – Monodentate ligands (N – Donor atom)
2. en – Bidentate ligand (2N – Donor atom)
3. ox^{2-} – Bidentate ligand (2O – Donor atom)
4. triaminotriethylamine – Tridentate ligand (3N – Donor atom)
5. pyridine – Monodentate ligand (N – Donor atom)

Question 17.
Give the difference between double salts and coordination compounds.
Answer:
Double Salt:

1. A double salt is' a compound prepared by the combination of two different salt components.
2. Completely dissociate into its ions in water.
3. Give simple ions when added to water.
4. It can be easily analyzed by determining the ions present in the aqueous solution.
   Example : Potash alum $K_2SO_4 . Al_2(SO_4)_3. 24H_2O$

Coordination compounds (Complex salt):

1. A complex salt is a compound composed of a central metal atom having coordination bonds with ligands around it.
2. Do not completely dissociate into its ions in water.
3. Do not give simple ions.
4. It cannot be easily analyzed by determining the ions in the aqueous solution.
   Example: Potassium ferro cyanide $K_4[Fe(CN)_6]$

Question 18.
Write the postulates of Werner's theory.

Answer:
1. The central metal ion in any complex ion/compound exhibits two types of valencies, these are (a) Primary valency (b) Secondary valency.

2. The primary valency is ionisable and corresponds to the oxidation state of the metal joining the central ion.

3. The secondary valency is non – ionisable. Every central ion has a fixed number of secondary valencies. This number is called the coordination number of the central ion.

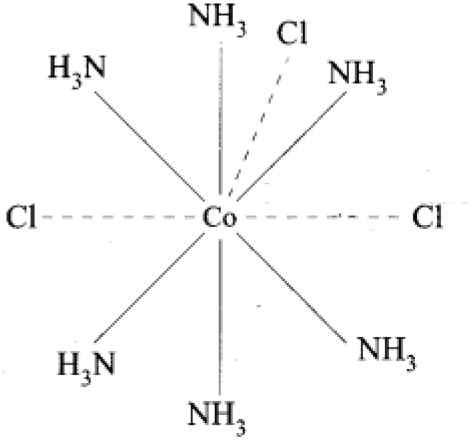
4. The primary valency of the metal ion is always satisfied by a negative ion. The attachment of the central metal ion to the negative ligand is shown by dotted lines.

5. The secondary valencies are satisfied by either negative ions or neutral molecules. The secondary valencies are shown by their lines. The molecules or ions that satisfy secondary valency are called ligands.

6. The ligands which satisfy the secondary valencies must point out in the definite directions in space. Whereas the primary valencies are non – directional in nature. The spatial arrangement of the secondary valencies around the central metal ion is called coordination polyhedron.

7. The secondary valencies are responsible for isomerism in the coordination compounds,

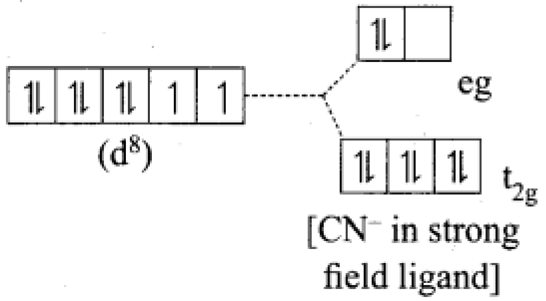
8. Werner's representation of $[CO(NH_3)_6]Cl_3$



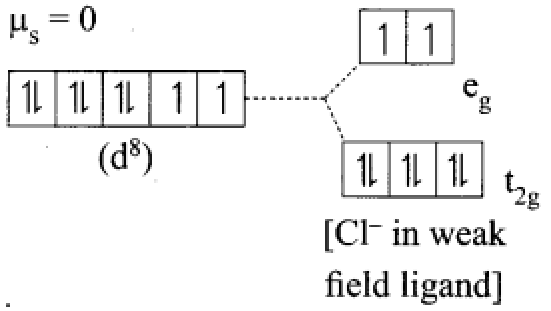
Question 19.
$[Ni(CN)_4]^{2-}$ is diamagnetic, while $[Ni(CN)_4]^{2-}$ is paramagnetic, explain using crystal field theory.

Answer:
1. $[Ni(CN)_4]^{2-}$

Ni = $3d^8$ $4s^2$
Ni^{2+} = $3d^8$



Nature of the complex – Low spin (Spin paired)
Ligand filled elelctronic configuration of central metla ion, t_{2g}^6 e_g^6. Magnetic property – No unpaired electron (CN^- is strong filled ligand), hence it is diamagnetic Magnetic moment – $\mu_s = 0$
2. $[Ni(CN)_4]^{2-}$
Ni = $3d_8$ $4S_2$
Ni^{2+} = $3d^8$



Nature of the complex – high spin
Ligand filled electronic configuration of central metal ion, t_{2g}^6 e_g^6. Magnetic property – Two unpaired electron (CL^- is weak field ligand). Hence it is paramagnetic Magnetic moment – it is paramagnetic

Question 20.
Why tetrahedral complexes do not exhibit geometrical isomerism.
Answer:
In tetrahedral geometry

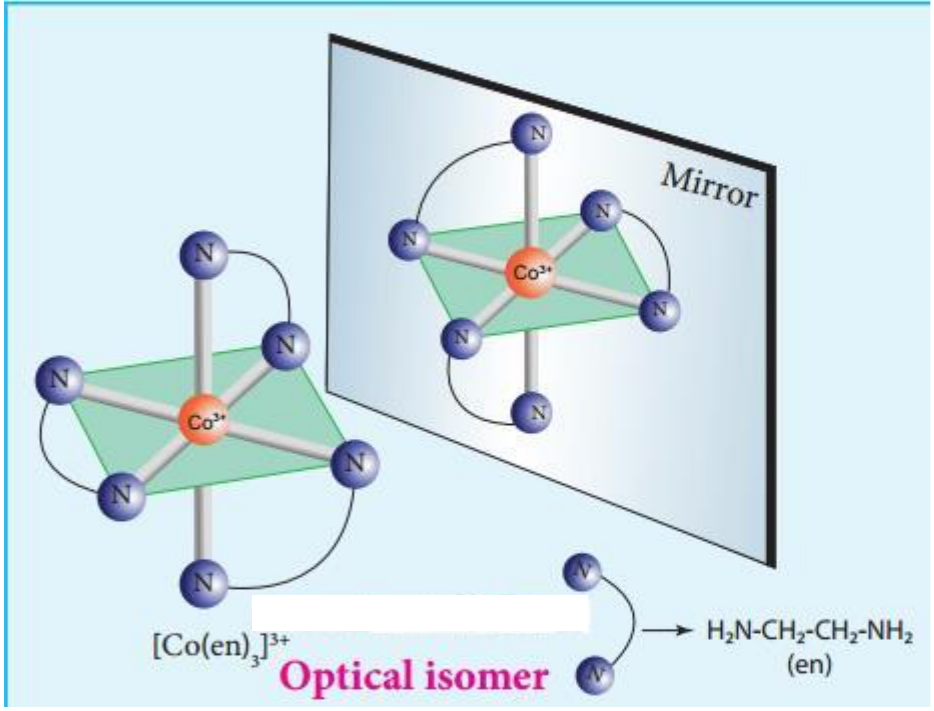
1. All the four ligands are adjacent or equidistant to one another.
2. The relative positions of donor atoms of ligands attached to the central metal atom are same with respect to each other.
3. It has plane of symmetry. Therefore, tetrahedral complexes do not exhibit geometrical isomerism.

Question 21.
Explain optical isomerism in coordination compounds with an example.
Answer:

1. Coordination compounds which possess chairality exhibit optical isomerism similar to organic compounds.
2. The pair of two optically active isomers which are mirror images of each other are called enantiomers.
3. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called d (dextrorotatory) and 1 (levorotatory) forms respectively.
4. The octahedral complexes of type $[M(xx)3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism.

Examples:

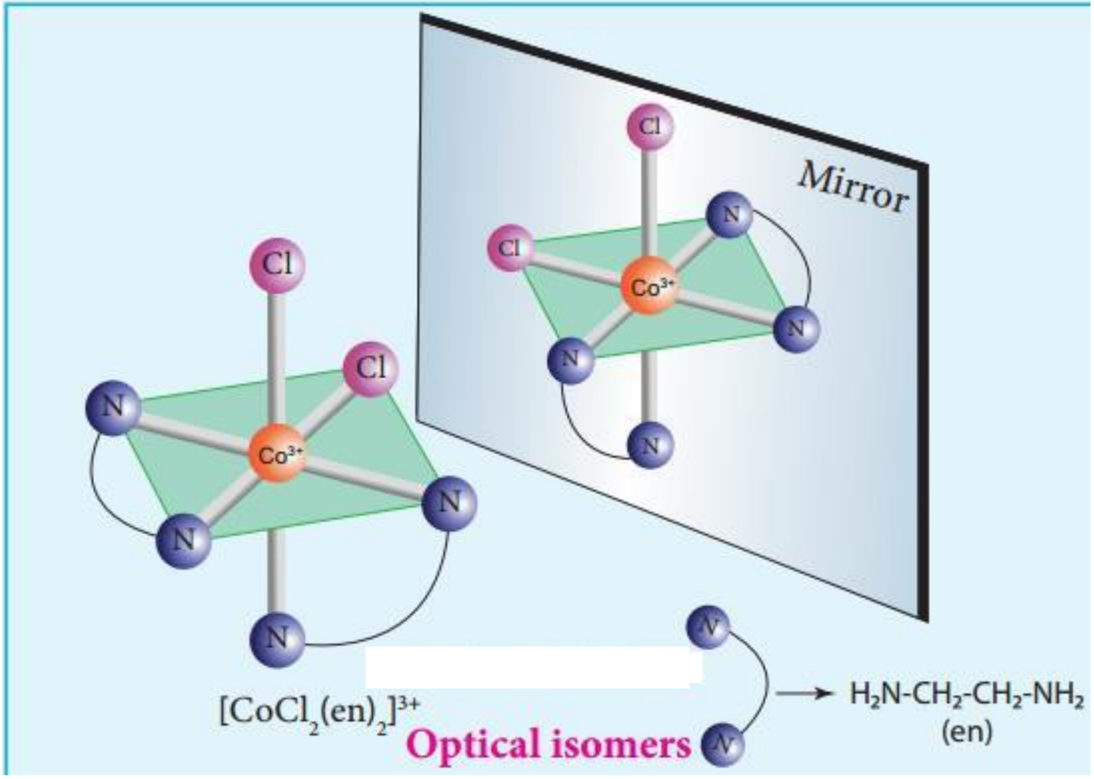
1. The optical isomers of $[Co(en)_3]^{3+}$ are shown below.



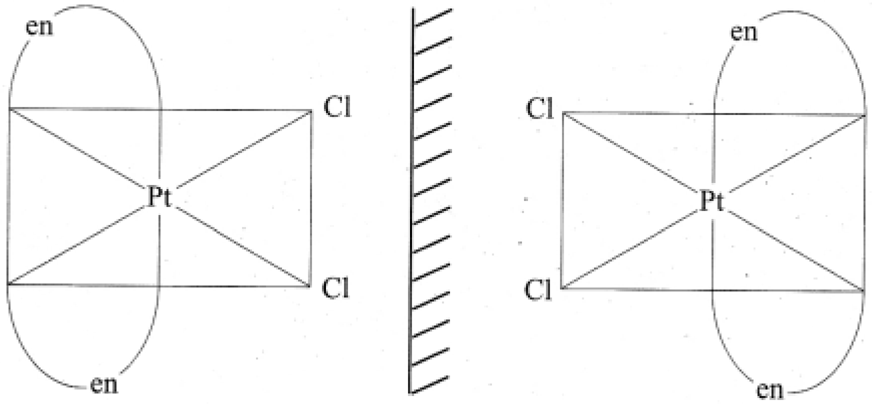
Optical isomer

2. The coordination complex $[COCl_2(en)_2]^+$ has three isomers, two optically active cis forms

and one optically inactive trans form. These structures are shown below.



3. In a coordination compound of type [Pt $Cl_2(en)_2]^{2+}$, two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optically active isomerism because the whole molecule is asymmetric.

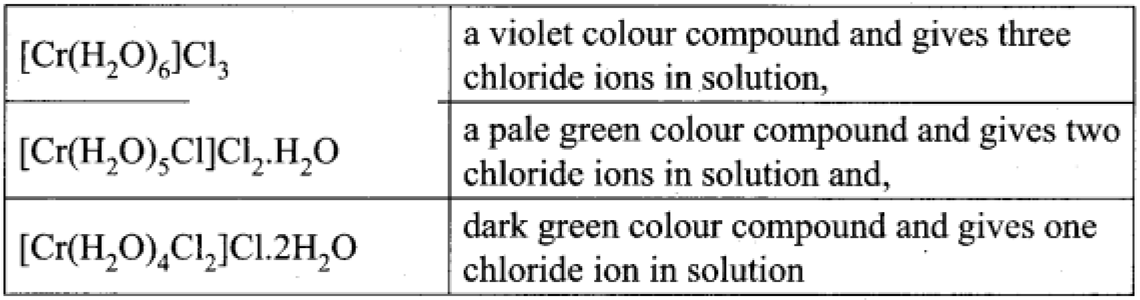


Optical isomers of Cis$[PtCl_2(en)_2]^{2+}$

Question 22.
What are hydrate isomers? Explain with an example.

Answer:
The exchange of free solvent molecules such as water, ammonia, alcohol etc., in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called solvate isomers. If the solvent molecule is water, then these isomers are called hydrate isomers. For example, the complex with chemical formula $CrCl_3$. $6H_2O$ has

three hydrate isomers as shown below.



$[Cr(H_2O)_6]Cl_3$	a violet colour compound and gives three chloride ions in solution,
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	a pale green colour compound and gives two chloride ions in solution and,
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	dark green colour compound and gives one chloride ion in solution

Question 23.
What is crystal field splitting energy?
Answer:
1. In an octahedral complex, the d – orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy.

2. The d orbitals lying along the axes dx^2, dy^2 and dz^2 orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and d_{zx}). Thus the degenerate d – orbitals now split into two sets and the process is called crystal filled splitting.

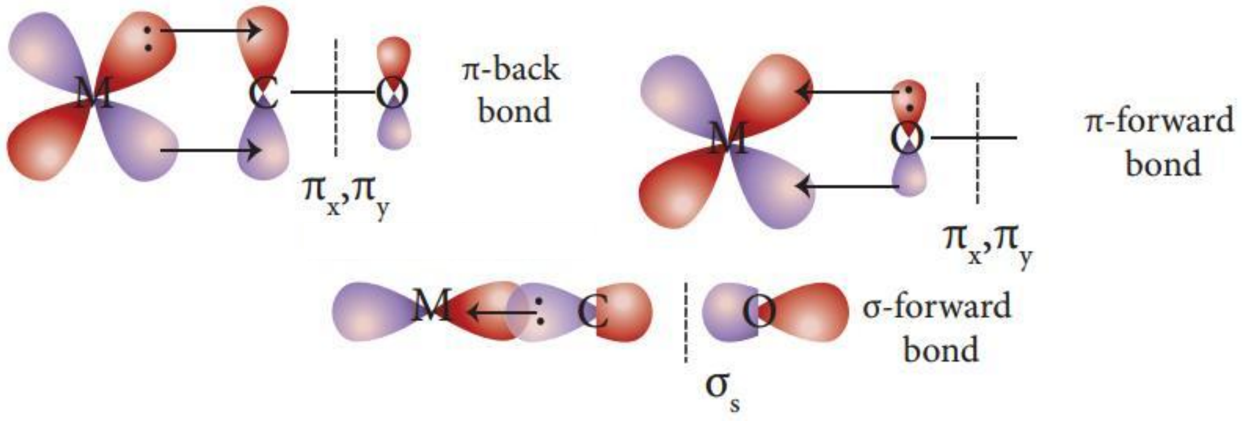
Question 24.
What is crystal field stabilization energy (CFSE) ?
Answer:
The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand field (ELF) and the isotropic field (Eiso).
CFSE (ΔE_0) = $\{E_{LF}\} - \{E_{iso}\}$
= $\{n_{t2g}(-0.4) + n_{6g}(0.6)\,\Delta_0 - n_pP\} - \{n'_pP\}$
Here n_{tg} is the number of electrons in t, orbitals
n_{eg} is the number of electrons in e orbitals
n_p is the number of electrons in the ligand field
n'_p is the number of electrons in the isotropic field
Question 25.
A solution of $[Ni(H_2O)_6]^{2+}$ is green, whereas a solution of $[Ni(CN)_4]^{2-}$ is colorless – Explain.
Answer:
1. In $[Ni(H_2O)_6]^{2+}$, Ni is in +2 oxidation state with the configuration $3d^8$, i.e., it has two unpaired electrons which do not pair up in the presence of weak H_2O ligand. Hence, it is coloured. The d – d transtion absorbs red light and the complementary light emitted is green.
2. In the case of $[Ni(CN)_4]^{2-}$ Ni is again in +2 oxidation state with the configuration $3d^8$, but in the presence of strong CN^- ligand the two impaired electrons in the 3d orbitals pair up. Thus there is no unpaired electron present. Hence it is colourless. Therefore, a solution of $[Ni(H_2O)_6]^{2+}$ is green, whereas a solution of $[Ni(CN)_4]^{2-}$ is colourless.

Question 26.
Discuss briefly the nature of bonding in metal carbonyls.
Answer:
1. In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.

2. The first component is an electron pair donation from the carbon atom of carbonyl ligand into a vacant d – orbital of central metal atom. This electron pair donation forms $M \xleftarrow{\sigma \text{ bond}} CO$ sigma bond.

3. This sigma bond formation increases the electron density in metal d- orbitals and makes the metal electron rich.

4. In order to compensate for this increased electron density, a filled metal d-orbital interacts with the empty π* orbital on the carbonyl ligand and transfers the added electron density back to the ligand. This second component is called π – back bonding. Thus in metal carbonyls, electron density moves from ligand to metal through sigma bonding and from metal to ligand through pi bonding, this synergic effect accounts for strong M ← CO bond in metal carbonyls. This phenomenon is shown diagrammatically as follows.



Question 27.
What is the coordination entity formed when an excess liquid ammonia is added to an aqueous solution copper sulphate?
Answer:
When excess liquid ammonia is added to an aqueous solution of copper sulphate to give tetraamminecopper (II) sulphate

$$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

(Copper Sulphate) (Ammonia) (tetraamminecopper (II) Sulphate)

Therefore, the coordination entity is $[Cu(NH_3)_4]^{2+}$

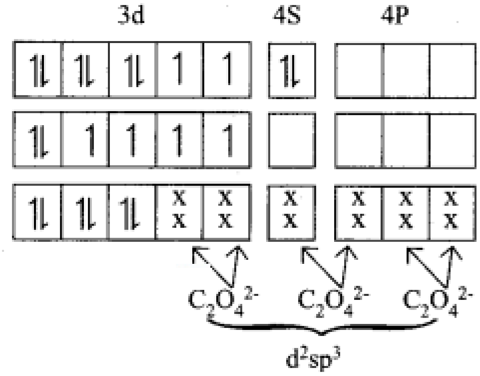
Question 28.

On the basis of VB theory explain the nature of bonding in $[CO(C_2O_4)_3]^{3-}$.

Answer:

In the complex entity $[CO(C_2O_4)_3]^{3-}$, the Co is in +3 oxidation state. The outer electronic configuration of CO^{3+} is $3d^6$. The oxalato ligand is fairly strong field ligand. So it faces the 3d electrons in CO^{3+} to pair up and make two of the 3d orbitals available for bonding. As a result, CO^{3+} shows d^2sp^2 hybridisation. Electronic configuration of Co atom Electronic configuration of CO^{3+} ion Hybridisation and formation of $[CO(C_2O_4)_3]^{3-}$

- There is no unpaired electron in$[CO(C_2O_4)_3]^{3-}$
  Thus$[CO(C_2O_4)_3]^{3-}$
- During the formtion of $[CO(C_2O_4)_3]^{3-}$, two of the 3d-orbitals are used in bonding. Therefore it is an inner orbital (low spin) complex.
- The $[CO(C_2O_4)_3]^{3-}$ has the octahedral geometry



Question 29.

What are the limitations of VB theory?

Answer:

- It does not explain the colour of the complex.
- It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
- It does not provide a quantitative explana¬tion as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example, $[Fe(CN)_6]^{4-}$ is diamagnetic (low spin) whereas $[FeF_6]^{4-}$ is paramagnetic (high spin).

Question 30.

Write the oxidation state, coordination number, nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $K_4[Mn(CN)_6]$.

Answer:

Oxidation state	$K_4[Mn(CN)_6]$ $4(+1) + x + 6(-1) = o$; $x = +2$
Coordination number	6
Nature of ligand	$CN^{\ominus}$ Monodentate ligand
Magnetic property	Mn – $3d^5\ 4s^2$ system Mn^{2+} – $3d^5$ system 3d $K_4\ [Mn(CN)_6]$ - $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}\boxed{}$ It has one unpaired electron. Therefore it is paramagnetic nature
Electronic configuration in octahedral crystal field	$CN^{\ominus}$ is strong field ligand therefore, $t_{2g}^{5}\ e_{g}^{0}$