

## CBSE NCERT Solutions for Class 12 Chemistry Chapter 9

### Back of Chapter Questions

1. 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
- (iv) Amminebromidochloridonitrito-N-platinate (II)
- (v) Dichloridobis (ethane-1, 2-diamine) platinum (IV) nitrate
- (vi) Iron(III) hexacyanidoferrate(II)

#### Solution:

Rule to write the name of a coordination compound

1. The name of the cation is named first in both positively and negatively charged entities.
2. The ligands name should be arranged in alphabetical order before the name of the central atom.
3. Names of the anionic ligand end in -o, those of the neutral are the same, and the cation ends in -ium.
4. Prefixes mono, di, tri are used to indicate the number of the individual ligands.
5. When the name of the ligands include numerical prefix then the terms bis, tris, tetrakis are used
6. If the complex ion is a cation, the metal is named the same as the element
7. If the complex is anion the name of the metal ends with the suffix -ate.

Therefore, the formula of coordination compounds mentioned are:

- (i) Tetraamminediaquacobalt (III) chloride

Ligands: Ammine( $\text{NH}_3$ ) – neutral

Aqua( $\text{H}_2\text{O}$ ) –neutral

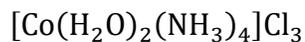
Charge on coordination sphere:

$$3 + 2 \times 0 + 4 \times 0 = x$$

$$x = 3$$

Complex is cationic.

Following the rules for a cationic coordination complex we get the formula as:



(ii) Potassium tetracyanonickelate (II)

Ligands: Cyano(CN) : charge is  $-1$

Charge on coordination sphere:

$$2 + 4 \times -1 = x$$

$$x = -2$$

Complex is anionic.

Following the rules for an anionic coordination complex we get the formula as:



(iii) Tris(ethane- 1, 2-diamine) chromium(III)chloride

Ligands: ethylene diamine(en) : neutral

Charge on coordination sphere:

$$3 + 3 \times 0 = x$$

$$x = 3$$

Complex is cationic.

Following the rules for a cationic coordination complex we get the formula as:



(iv) Amminebromidochloridonitrito-N-platinate (II)

Ligands: ammine( $\text{NH}_3$ ) : neutral

Nitrito( $\text{NO}_2$ ): charge is  $-1$

Bromido:charge is  $-1$

Chlorido: charge is  $-1$

Charge on coordination sphere:

$$2 + 0 - 1 - 1 - 1 = x$$

$$x = -1$$

Complex is anionic.

Following the rules for an anionic coordination complex we get the formula as:



- (v) Dichloridobis (ethane-1, 2-diamine) platinum(IV) nitrate

Ligands: ethylene diamine(en) : neutral

Chlorido – charge is  $-1$

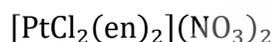
Charge on coordination sphere:

$$4 + 2(-1) + 2 \times 0 = x$$

$$x = 2$$

Complex is cationic.

Following the rules for a cationic coordination complex we get the formula as:



- (vi) Iron(III)hexacyanidoferrate(II)

Ligands: cyano(CN) : charge is  $-1$ .

Charge on coordination sphere:

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

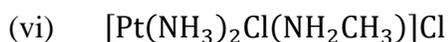
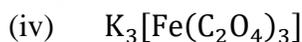
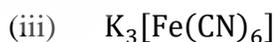
$$x = -4$$

Complex is anionic.

Following the rules for an anionic coordination complex we get the formula as:



2. Write the IUPAC names of the following coordination compounds:



**Solution:**

Rules to write the IUPAC name of coordination compound :

- (i) find the oxidation number of the central atom involved.
- (ii) The cation is named first as is the case with other. This rule applies to both positively and negatively charged coordination entities.
- (iii) Usually, the number of free cation or anions is not given as can easily be calculated by charge
- (iv) For writing the names of complex cation use the following rule.

Names of the ligand in alphabetical order with their quantity as prefix (but do not use mono for one and do not consider first letters of these number denoting prefixes in alphabetisation). This is followed by the name of metal followed by its oxidation number (in Roman numeral) in a bracket like

(0) (I), (II), (III), (-I), (-II) etc.

- (v) For writing the names of complex anion use the following rule.

Names of the ligand in alphabetical order with their quantity as prefix (but do not use mono for one and do not consider first letters of these number denoting prefixes in alphabetisation). This is followed by the name of metal (modified as per rule already specified) followed by its oxidation number (in Roman numeral) in a bracket like (I), (II), (III), (0), (-I), (-II), etc.

- (vi) The neutral complex molecule is named similar to that of the complex cation.

By following the above rules, we get the IUPAC name of the compounds as follows:

- (i) The IUPAC name of the coordination compound  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  :

Central atom = cobalt

Ligand =  $\text{NH}_3$  (ammine)

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

$x = 3$

Complex type = cationic

IUPAC name = Hexamminecobalt(III) chloride

- (ii) The IUPAC name of the coordination compound  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Central atom = cobalt

Ligand =  $\text{NH}_3$  (ammine) is neutral ligand and Cl (chloride) has -1 charge

$$\text{Oxidation state of Co} = x + 5(0) + 1(-1) + 2(-1) = 0$$

$$x = 3$$

Complex type = cationic

IUPAC name = Pentamminechloridocobalt(III) chloride

(iii) The IUPAC names of the coordination compound  $K_3[Fe(CN)_6]$

Central atom = iron

Ligand = CN (cyano)

$$\text{Oxidation state} = 3(+1) + x + 6(-1) = 0$$

$$x = 3$$

Complex type = anionic

IUPAC name = Potassium hexacyanoferrate(III)

(iv) The IUPAC names of the coordination compound  $K_3[Fe(C_2O_4)_3]$

Central atom = iron

Ligand =  $C_2O_4^{2-}$  (oxalate)

$$\text{Oxidation state} = 3(+1) + x + 3(-2) = 0$$

$$x = 3$$

Complex type = anionic

IUPAC name = Potassium trioxalatoferrate(III)

(v) The IUPAC names of the coordination compound  $K_2[PdCl_4]$

Central atom = palladium

Ligand = Cl (chlorido) having -1 charge

$$\text{Oxidation state} = 2(+1) + x + 4(-1) = 0$$

$$x = 2$$

Complex type = anionic

IUPAC name = Potassium tetrachloridopalladate(II)

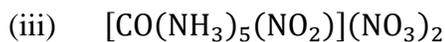
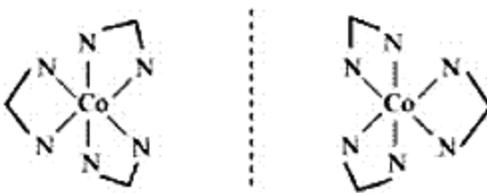
(vi) The IUPAC names of the coordination compound  $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

Central atom = Platinum

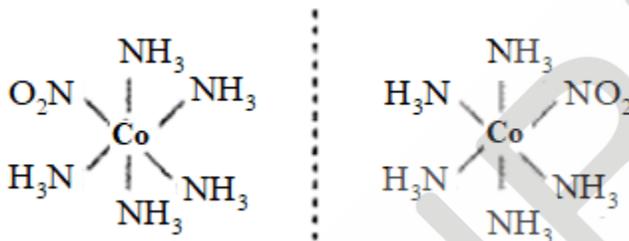
Ligand =  $NH_2CH_3$  (methylamine), Cl (chlorido),  $NH_3$  (ammine)

$$\text{Oxidation state} = x + 2(0) + 1(-1) + 1(0) + 1(-1) = 0$$





A pair of optical isomers:



It can also show linkage isomerism.

4. Give evidence that  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$  are ionisation isomers.

**Solution:**

When ionisation isomers are dissolved in water, they ionise to give different ions. These ions then react differently with various reagents to give different products.



5. Explain on the basis of valence bond theory that  $[\text{Ni}(\text{CN})_4]^{2-}$  ion with square planar structure is diamagnetic and the  $[\text{NiCl}_4]^{2-}$  ion with tetrahedral geometry is paramagnetic.

**Solution:**

Ni is in the +2 oxidation state, i.e., in  $d^8$  configuration.

$d^8$  configuration:

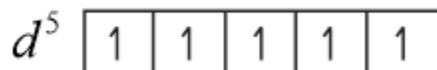




7.  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic. Explain.

**Solution:**

In both  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , Fe exists in the +3 oxidation state i.e., in  $d^5$  configuration.



Since  $\text{CN}^-$  is a strong field ligand, it causes the pairing of unpaired electrons. Therefore, there is only one unpaired electron left in the d-orbital.



Therefore,

$$\begin{aligned} \mu &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{3} \\ &= 1.732 \text{ BM} \end{aligned}$$

On the other hand,  $\text{H}_2\text{O}$  is a weak field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

Therefore,

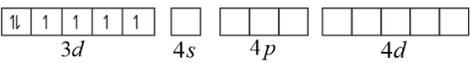
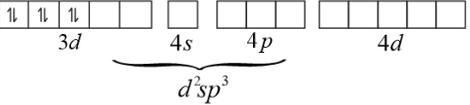
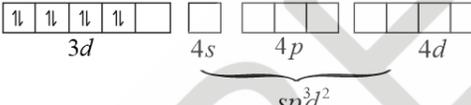
$$\begin{aligned} \mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} \\ &= \sqrt{35} \\ &\cong 6 \text{ BM} \end{aligned}$$

Thus, it is evident that  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic, while  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic.

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

**Solution:**

$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2

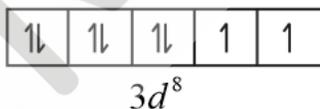
Electronic configuration of cobalt = $d^5$	Electronic configuration of nickel = $d^5$
	
<p><math>NH_3</math> being a strong field ligand causes the pairing. Therefore, Ni can undergo <math>d^2sp^3</math> hybridization.</p> 	<p>If <math>NH_3</math> causes the pairing, then only one 3d orbital is empty. Thus, it cannot undergo <math>d^2sp^3</math> hybridization. Therefore, it undergoes <math>sp^3d^2</math> hybridization.</p> 
<p>If the complex is formed by the use of inner d-orbitals for hybridization it is called inner orbital complex.</p> <p>Hence, it is an inner orbital complex.</p>	<p>If the complex is formed by the use of the outer d-orbitals for hybridization it is called an outer orbital complex.</p> <p>Hence, it forms an outer orbital complex.</p>

9. Predict the number of unpaired electrons in the square planar  $[Pt(CN)_4]^{2-}$  ion.

**Solution:**



In this complex, Pt is in the +2 state. It forms a square planar structure and it undergoes  $dsp^2$  hybridization. Now, the electronic configuration of Pt(+2) is  $5d^8$ .



$CN^-$  being a strong field ligand causes the pairing of unpaired electrons. Since, all the electrons get paired, there are no unpaired electrons in  $[Pt(CN)_4]^{2-}$ .

10. The hexaquo manganese (II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

**Solution:**

$[Mn(H_2O)_6]^{2+}$	$[Mn(CN)_6]^{4-}$
Mn is in the +2 oxidation state	Mn is in the +2 oxidation state
The electronic configuration is $d^5$ .	The electronic configuration is $d^5$
The crystal field is octahedral. Water is a weak field ligand. Therefore, the	The crystal field is octahedral. Cyanide is a strong field ligand. Therefore, the

arrangement of the electrons in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is $t_{2g}^3 e_g^2$ .	arrangement of the electrons in $[\text{Mn}(\text{CN})_6]^{4-}$ is $t_{2g}^5 e_g^0$ .
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Hence, hexaquo manganese (II) ion has five unpaired electrons, while hexacyano ion has only one unpaired electron.

In octahedral field splitting of d orbital is such that 3d orbitals are in ground state where 2d orbitals are in higher energy thus representing as  $t_{2g}, e_g$ .

First the ground state is filled then the higher state.

11. Calculate the overall complex dissociation equilibrium constant for the  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion, given that  $\beta_4$  for this complex is  $2.1 \times 10^{13}$ .

**Solution:**

$$\beta_4 = 2.1 \times 10^{13}$$

The overall complex dissociation equilibrium constant is the reciprocal of the overall stability constant,  $\beta_4$ .

$$\frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}}$$

$$\therefore = 4.7 \times 10^{-14}$$

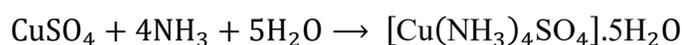
1. Explain the bonding in coordination compounds in terms of Werner's postulates.

**Solution:**

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 satisfied by both negative and neutral ions.
  - (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 definite geometry of the coordination compound.
  - (iii) Primary valencies are usually ionizable, while secondary valencies are non-ionizable.
2.  $\text{FeSO}_4$  solution mixed with  $(\text{NH}_4)_2\text{SO}_4$  solution in 1: 1 molar ratio gives the test of  $\text{Fe}^{2+}$  ion but  $\text{CuSO}_4$  solution mixed with aqueous ammonia in 1: 4 molar ratio does not give the test of  $\text{Cu}^{2+}$  ion. Explain why?

**Solution:**



Both the compounds i.e.,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  and  $[\text{Cu}(\text{NH}_3)_4\text{SO}_4] \cdot 5\text{H}_2\text{O}$  fall under the category of addition compounds with only one major difference i.e., the former is an example of a double salt, while the latter is a coordination compound.

A double salt is an addition compound that is stable in the solid state but that which breaks up into its constituent ions in the dissolved state. These compounds exhibit individual properties of their constituents.

For example:  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  breaks into  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions. Hence, it gives a positive test for  $\text{Fe}^{2+}$  ions.

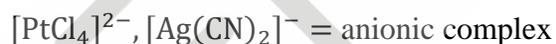
A coordination compound is an addition compound which retains its identity in the solid as well as in the dissolved state. However, the individual properties of the constituents are lost. This happens because  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$  does not show the test for  $\text{Cu}^{2+}$ . The ions present in the solution of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$  are  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $\text{SO}_4^{2-}$ .

3. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

**Solution:**

- (i) Coordination entity:

A coordination entity is an electrically charged radical or species carrying a positive or negative charge. In a coordination entity, the central atom or ion is surrounded by a suitable number of neutral molecules or negative ions (called ligands). For example:



- (ii) Ligands

The neutral molecules or negatively charged ions that surround the metal atom in a coordination entity or a coordinational complex are known as ligands. For example,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ,  $-\text{OH}$ . Ligands are usually polar in nature and possess at least one unshared pair of valence electrons.

- (iii) Coordination number:

The total number of lone pairs donated by ligands (either neutral molecules or negative ions) attached to the central metal atom in the coordination sphere is called the coordination number of the central metal atom. It is also called as ligancy.

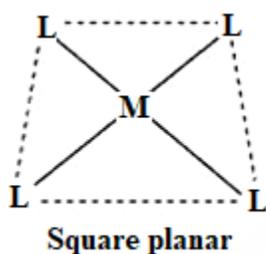
For example:

- (a) In the complex,  $K_2[PtCl_6]$ , there are six chloride ions attached to Pt in the coordinate sphere. Therefore, the coordination number of Pt is 6.
- (b) Similarly, in the complex  $[Ni(NH_3)_4]Cl_2$ , the coordination number of the central atom (Ni) is 4.
- (iv) Coordination polyhedron:

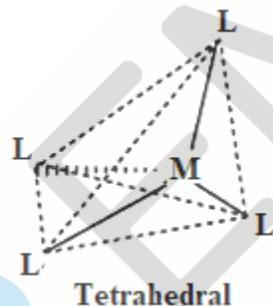
Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere.

For example:

(a)



(b) Tetrahedral



(v) Homoleptic complexes:

These are those complexes in which the metal ion is bound to only one kind of a donor group. For e.g.:  $[Co(NH_3)_6]^{3+}$ ,  $[PtCl_4]^{2-}$  etc.

(vi) Heteroleptic complexes:

Heteroleptic complexes are those complexes where the central metal ion is bound to more than one type of a donor group.

For e.g.:  $[Co(NH_3)_4Cl_2]^+$ ,  $[Co(NH_3)_5Cl]^{2+}$

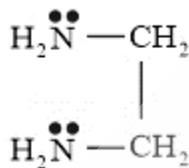
4. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

**Solution:**

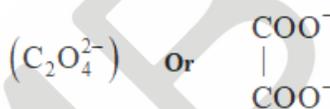
A ligand may contain one or more unshared pairs of electrons which are called the donor sites of ligands. Depending upon the number of these donor sites, ligands can be classified as follows:

- (a) Unidentate ligands: Ligands with only one donor sites are called unidentate ligands. For e.g.,  $\ddot{\text{N}}\text{H}_3$ ,  $\text{Cl}^-$  etc.
- (b) Didentate ligands: ligands that have two donor sites are called didentate ligands. E.g.,

- (1) Ethane-1, 2-diamine

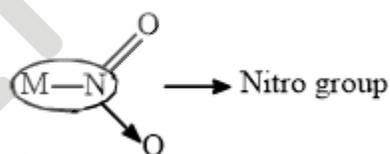


- (2) Oxalate ion

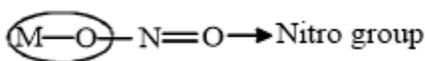


- (c) Ambidentate ligands:

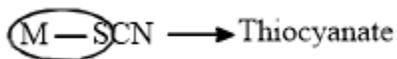
Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands. For example:



(The donor atom is N)

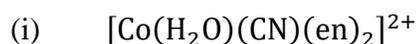


(The donor atom is oxygen)



(The donor atom is S)

5. Specify the oxidation numbers of the metals in the following coordination entities:



- (ii)  $[\text{CoBr}_2(\text{en})_2]^+$   
(iii)  $[\text{PtCl}_4]^{2-}$   
(iv)  $\text{K}_3[\text{Fe}(\text{CN})_6]$   
(v)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$

**Solution:**

- (i)  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$

Let the oxidation number of Co be x.

The charge on the complex is +2

$\text{H}_2\text{O}$  is neutral ligand so its oxidation number = 0

CN is negatively charged ligand and its oxidation number = -1

(en) is neutral ligand so its oxidation number = 0



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

$$x - 1 = +2$$

$$x = +3$$

- (ii)  $[\text{Pt}(\text{Cl})_4]^{2-}$

Let the oxidation number of Pt be x.

Cl is negatively charged ligand and its oxidation number = -1

The charge on the complex is -2.



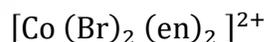
$$x + 4(-1) = -2$$

$$x = +2$$

- (iii)  $[\text{Co}(\text{Br})_2(\text{en})_2]^{2+}$

Br is negatively charged ligand and its oxidation number = -1

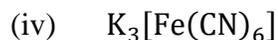
(en) is neutral ligand so its oxidation number = 0



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

$$x - 2 = +2$$

$$x = +4$$



Let the oxidation number of Fe be x.

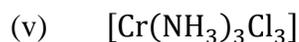
CN is negatively charged ligand and its oxidation number = -1

The oxidation number of k = +1.



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

$$x = +3$$



Let the oxidation number of Cr be x.

Cl is negatively charged ligand and its oxidation number = -1

$NH_3$  is neutral ligand and its oxidation number = 0

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

$$x = +3$$

6. Using IUPAC norms write the formulas for the following:

- (i) Tetrahydroxozincate(II)
- (ii) Potassium tetrachloridopalladate(II)
- (iii) Diamminedichloridoplatinum(II)
- (iv) Potassium tetracyanonickelate(II)
- (v) Pentaamminenitrito-o-cobalt(III)
- (vi) Hexaamminecobalt(III) sulphate
- (vii) Potassium tri(oxalato)chromate(III)
- (viii) Hexaammineplatinum(IV)
- (ix) Tetrabromidocuprate(II)
- (x) Pentaamminenitrito-N-cobalt(III)

**Solution:**

- (i) Tetrahydroxozincate(II) :

Central metal atom is zinc and the oxidation number of Zn = +2.

Hydroxide (OH) is negatively charged ligand and its oxidation number = -1

$$\text{Charge on complex} = 4(-1) + (+2) = x$$

$x = -2$  (complex is negatively charged )

Hence the complex is  $[\text{Zn}(\text{OH})_4]^{-2}$

(ii) Potassium tetrachloridopalladate(II) :

Central metal atom is palladate (Pd) and the oxidation number of Pd = +2.

chlorido (Cl) is negatively charged ligand and its oxidation number = -1

Charge on complex =  $4(-1) + (+2) = x$

$x = -2$  (complex is negatively charged )

Potassium has +1 oxidation number so to balance the charge on complex two potassium ions present in complex.

Hence the complex is  $\text{K}_2[\text{PdCl}_4]$

(iii) Diamminedichloridoplatinum(II) :

Central metal atom is platinum (Pt) and the oxidation number of Pt = +2.

chlorido (Cl) is negatively charged ligand and its oxidation number = -1

ammine ( $\text{NH}_3$ ) is neutral ligand and its oxidation number = 0

Charge on complex =  $2(0) + 2(-1) + (+2) = x$

$x = 0$  (complex is neutral )

Hence the complex is  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(iv) Potassium tetracyanonickelate(II)

The central metal atom is nickel (Ni) and the oxidation number of Ni = +2.

cyano (CN) is negatively charged ligand and its oxidation number = -1

Charge on complex =  $4(-1) + (+2) = x$

$x = -2$

Potassium has +1 oxidation number so to balance the charge on complex two potassium ions present in complex.

Hence the complex is  $\text{K}_2[\text{Ni}(\text{CN})_4]$

(v) Pentaamminenitrito-o-cobalt(III) :

Central metal atom is cobalt (Co) and the oxidation number of Co = +3.

nitrito-o- ( $\text{ONO}$ ) is negatively charged ligand and its oxidation number = -1

ammine ( $\text{NH}_3$ ) is neutral ligand and its oxidation number = 0

Charge on complex = 5 (0) + 1 (-1) + (+3) =  $x$

$x = 2$  (complex is positively)

Hence the complex is  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$

(vi) Hexaamminecobalt(III) sulphate :

The central metal atom is cobalt (Co) and the oxidation number of Co = +3.

ammine ( $\text{NH}_3$ ) is neutral ligand and its oxidation number = 0

$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$

(vii) Potassium tri(oxalato)chromate(III)

Central metal atom is chromium (Cr) and the oxidation number of Cr = +3.

Oxalate ( $\text{C}_2\text{O}_4$ ) is negatively charged ligand and its oxidation number = -2

Charge on complex = 3 (-2) + (+3) =  $x$

$x = -3$

Potassium has +1 oxidation number so to balance the charge on complex three potassium ions present in complex

Hence the complex is  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$

(viii) Hexaammineplatinum(IV) :

The central metal atom is platinum (Pt) and the oxidation number of Pt = +4.

ammine ( $\text{NH}_3$ ) is neutral ligand and its oxidation number = 0

Charge on complex = 6 (0) + (+4) =  $x$

$x = +4$

Hence the complex is  $[\text{Pt}(\text{NH}_3)_6]^{4+}$

(ix) Tetrabromidocuprate(II) :

Central metal atom is copper (Cu) and the oxidation number of Cu = +2.

bromido (Br) is negatively charged ligand and its oxidation number = -1

Charge on complex = 4(-1) + (+2) =  $x$

$x = -2$

Hence the complex is  $[\text{Cu}(\text{Br})_4]^{2-}$

(x) Pentaamminenitrito-N-cobalt(III) :

The central metal atom is cobalt (Co) and the oxidation number of Co = +3.

nitro ( $\text{NO}_2$ ) is negatively ligand and its oxidation number = -1

ammine ( $\text{NH}_3$ ) is neutral ligand and its oxidation number = 0

Charge on complex =  $+3 + (-1) + 5(0) = x$

$x = +2$

Hence the complex is  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{+2}$

7. Using IUPAC norms write the systematic names of the following:

- (i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- (ii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
- (iii)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
- (iv)  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$
- (v)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- (vi)  $[\text{NiCl}_4]^{2-}$
- (vii)  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$
- (viii)  $[\text{Co}(\text{en})_3]^{3+}$
- (ix)  $[\text{Ni}(\text{CO})_4]$

**Solution:**

- (i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Let the oxidation number of Co be x.

$\text{NH}_3$  is neutral ligand its name is ammine and its oxidation number = 0

the oxidation number of Cl = -1.

The oxidation number of central metal atom =

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

$$x = +3$$

The complex is positively charged

So the name of the compound is Hexaamminecobalt(III) chloride

- (ii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$

Let the oxidation number of Pt be x.

$\text{NH}_3$  is neutral ligand its name is amine and its oxidation number = 0

$\text{NH}_2\text{CH}_3$  is a neutral ligand its name is methylamine and its oxidation number = 0

The oxidation number of Cl = -1.

The oxidation number of central metal atom =

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

$$x = 2$$

The complex is positively charged

So the name of the compound is Diamminechlorido(methylamine) platinum(II) chloride



Let the oxidation number of Ti be x.

$\text{H}_2\text{O}$  is neutral ligand its name is aqua and its oxidation number = 0

The oxidation number of central metal atom =

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

$$x = +3$$

The complex is positively charged

So the name of the compound is Hexaqua titanium(III) ion



Let the oxidation number of Co be x.

$\text{NH}_3$  is a neutral ligand its name is amine and its oxidation number = 0

Cl and  $\text{NO}_2$  is negatively charged ligand. Their name is chlorido and nitrito-N respectively and their oxidation number is = 0

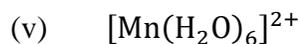
The oxidation number of central metal atom =

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

$$x = +3$$

The complex is positively charged

So the name of the compound is Tetraamminichloridonitrito-N-Cobalt (III) chloride



Let the oxidation number of Mn be x.

$\text{H}_2\text{O}$  is neutral ligand its name is aqua and its oxidation number = 0

The oxidation number of central metal atom =

$$x + 6(0) = +2$$

$$x = +2$$

the complex is positively charged

So the name of the compound is Hexaquamanganese(II) ion



Let the oxidation number of Ni be x.

Cl is negatively charged ligand its name is chlorido and its oxidation number = -1

The oxidation number of central metal atom =

$$x + 4(-1) = -2$$

$$x = +2$$

The complex is negatively charged

So the name of the compound is Tetrachloridonickeltate(II) ion



Let the oxidation number of Ni be x.

$\text{NH}_3$  is neutral ligand its name is ammine and its oxidation number = 0

The oxidation number of central metal atom =

$$x + 6(0) + 2(-1) = 0$$

$$x = +2$$

The complex is positively charged

So the name of the compound is Hexaamminenickel(II) chloride



Let the oxidation number of Co be x.

en is neutral ligand its name is ethane-1,2-diamine and its oxidation number = 0

The oxidation number of central metal atom =

$$x + 3(0) = +3$$

$$x = +3$$

the complex is positively charged

So name of compound is Tris(ethane-1, 2-diamine) cobalt(III) ion



Let the oxidation number of Ni be x.

CO is neutral ligand its name is carbonyl and its oxidation number = 0

The oxidation number of central metal atom =

$$x + 4(0) = 0$$

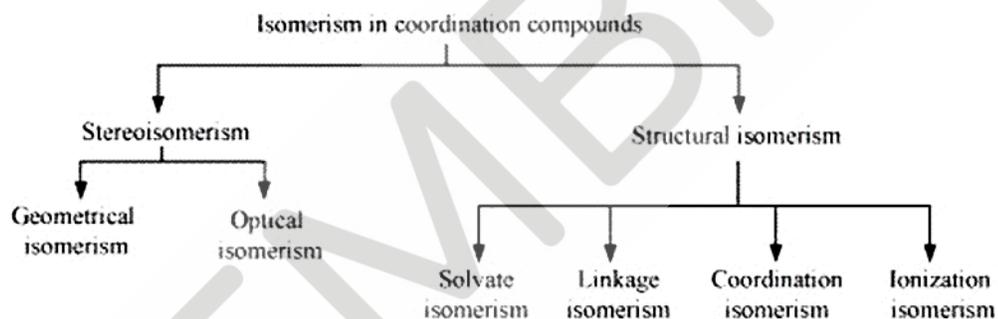
$$x = 0$$

Complex is neutral

So the name of the compound is Tetracarbonylnickel(0)

8. List various types of isomerism possible for coordination compounds, giving an example of each.

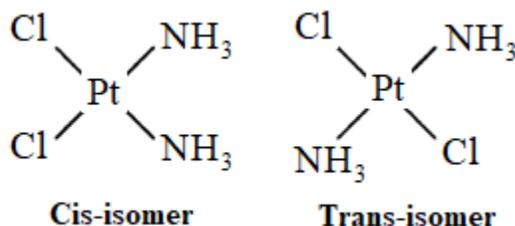
**Solution:**



- (a) Geometric isomerism:

This type of isomerism is common in heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands. For example:

When the coordination number is 4. The tetrahedral compounds do not show geometrical isomerism as we all know that all four positions are equivalent in a tetrahedral geometry. So moving on to square planar complexes there are different possibilities depending upon the formula of the compound



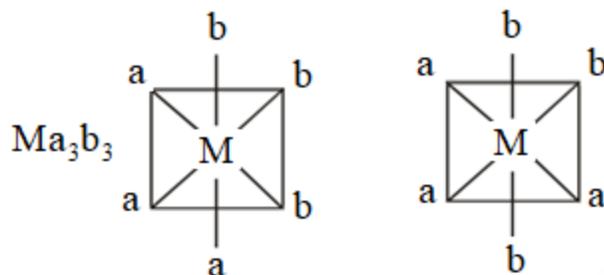
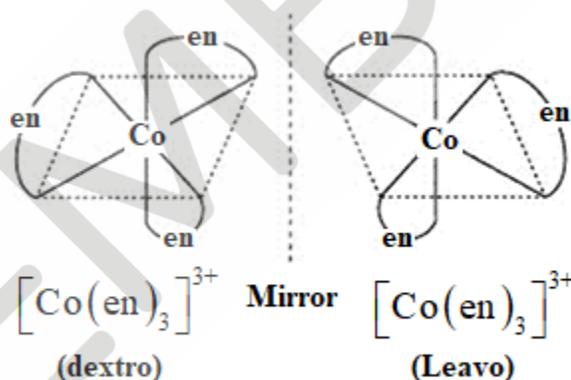


Diagram 1 is facial or (fac), and Diagram 2 is meridional.

- (b) **Optical isomerism:** A Coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have the same formula but differ in their ability 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. This is due to the absence of elements of symmetry in the complex.

This type of isomerism arises in chiral molecules; Isomers are mirror images of each other and are non-superimposable.



- (c) **Linkage isomerism:** This type of isomerism is found in complexes that contain ambidentate ligands.

For example,  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$  has two isomeric forms having red and yellow colours. The red coloured isomer is  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$  named as pentaamminenitrito-O-cobalt (III) cation while the yellow isomer is formulated as  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$ . It is named as pentaamminenitrito-N-cobalt (III) cation. In the first cation, we have  $\text{Co} - (\text{ONO})$  link, while in the second case,  $\text{NO}_2$  coordinates to the metal ion through the nitrogen atom,  $\text{Co} - (\text{NO}_2)$ .

- (d) **Coordination isomerism:**

This type of isomerism arises when the ligands are interchanged between cationic and anionic entities of different metal ions present in the complex.



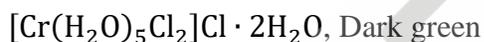
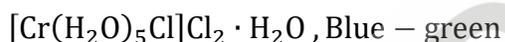
These isomers are expected to have significant differences in their physical and chemical properties.

(e) Ionisation isomerism:

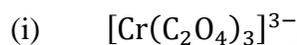
This type of isomerism arises when a counter ion replaces a ligand within the coordinator sphere. Thus, complexes that have the same composition, but furnish different ions when dissolved in water are called ionisation isomers. For e.g., (i)  $\text{Co}(\text{NH}_3)_5\text{SO}_4\text{Br}$  and  $\text{Co}(\text{NH}_3)_5\text{Br}[\text{SO}_4]$ .

(f) Solvate isomerism:

Solvate isomers differ by whether or not the solvent molecule is directly bonded to the metal ion or merely present as a free solvent molecule in the crystal lattice.

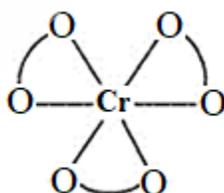


9. How many geometrical isomers are possible in the following coordination entities?



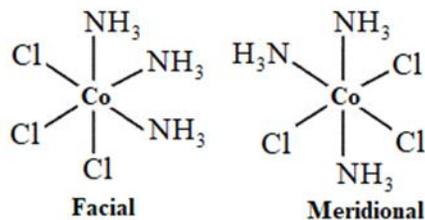
**Solution:**

(i) For  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , no geometric isomer is possible as it is a bidentate ligand.



Two geometrical isomers are possible.

Facial or (fac), two triangular faces such that each corner is occupied by similar ligands. or meridional (If the three ligands and the metal ion are in one plane, the isomer is said to be meridional)

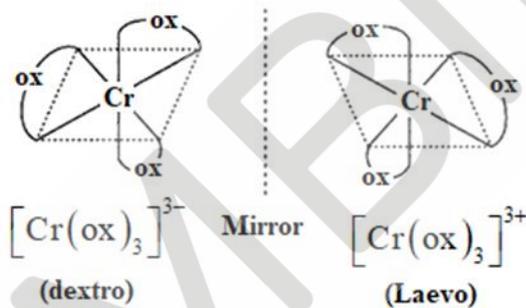


10. Draw the structures of optical isomers of:

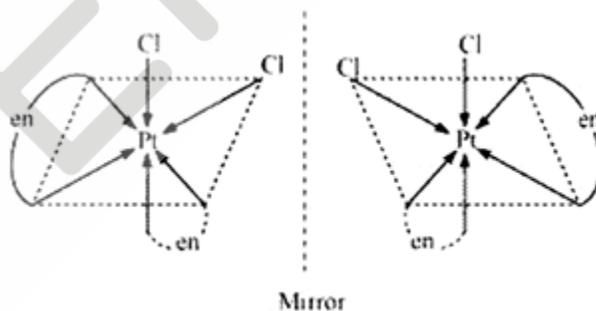
- (i)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (ii)  $[\text{PtCl}_2(\text{en})_2]^{2+}$   
 (iii)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$

**Solution:**

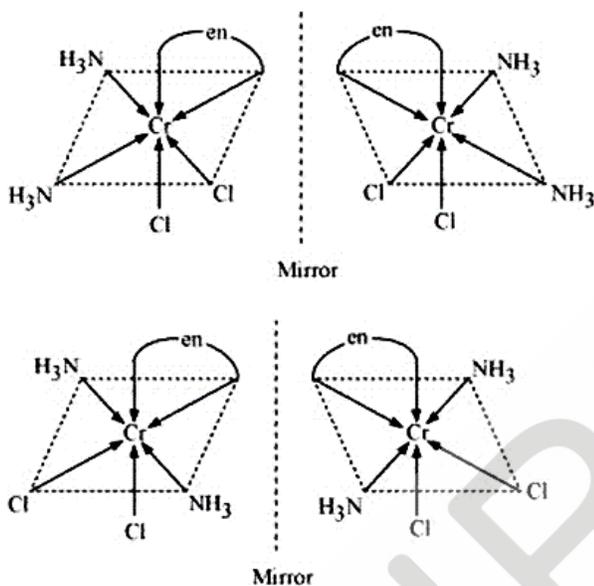
- (i)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$



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



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

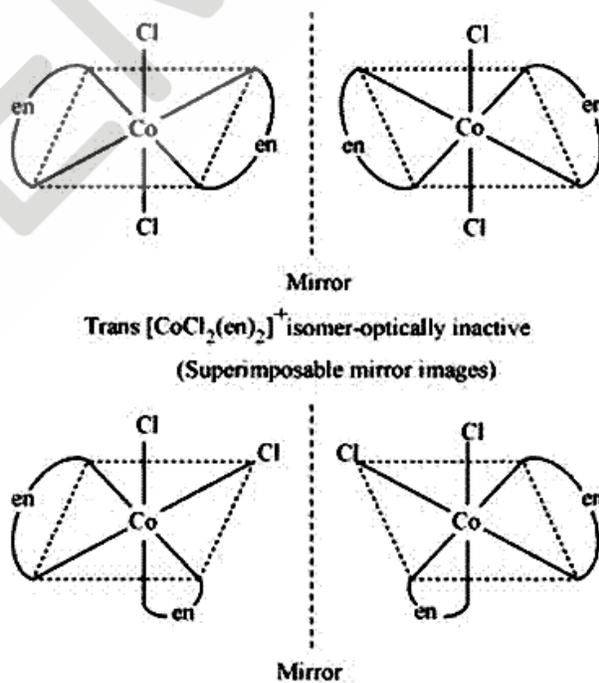


11. Draw all the isomers (geometrical and optical) of:

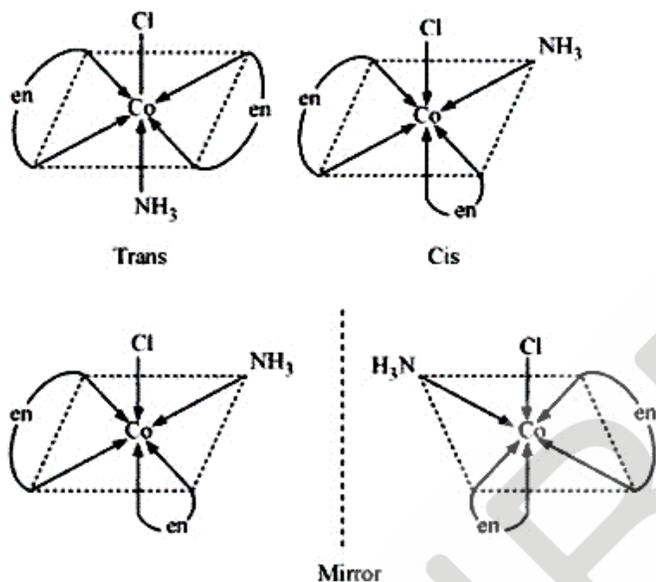
- (i)  $[\text{CoCl}_2(\text{en})_2]^+$
- (ii)  $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$
- (iii)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$

**Solution:**

- (i)  $[\text{CoCl}_2(\text{en})_2]^+$

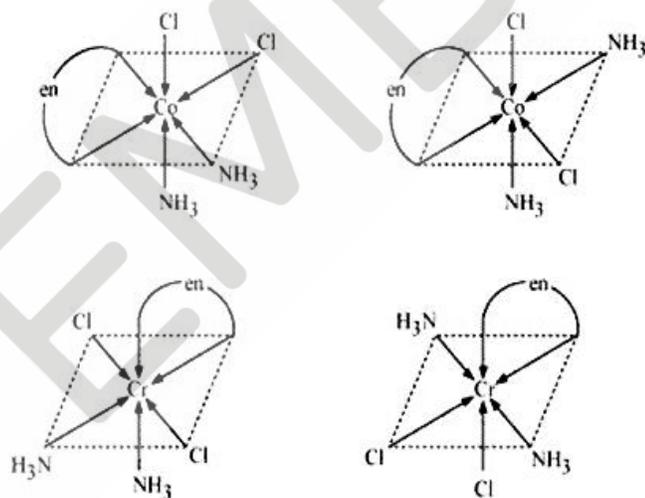


- (ii)  $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$



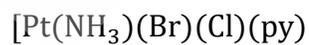
Trans-isomers are optically inactive.

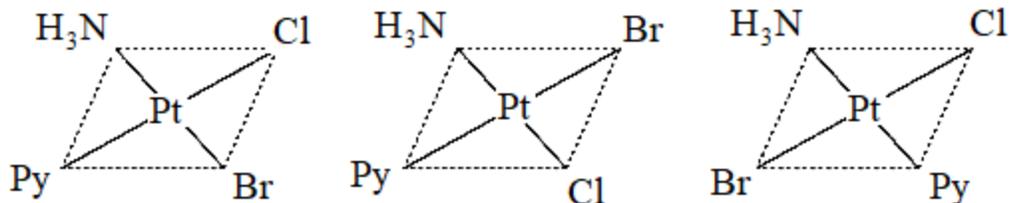
Cis - isomers are optically active



12. Write all the geometrical isomers of  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$  and how many of these will exhibit optical isomers?

**Solution:**





From the above isomers, none will exhibit optical isomerism. Tetrahedral complexes rarely show optical isomerisation. They do so only in the presence of unsymmetrical chelating agents.

13. Aqueous copper sulphate solution (blue in colour) gives:

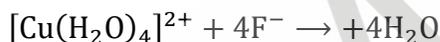
- (i) a green precipitate with aqueous potassium fluoride, and
- (ii) a bright green solution with aqueous potassium chloride

Explain these experimental results.

**Solution:**

Aqueous  $\text{CuSO}_4$  exists as  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$ . It is blue in colour due to the presence of  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  ions.

(i) When KF is added:



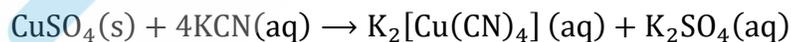
(ii) When KCl is added:



In both these cases, the weak field ligand water is replaced by the  $\text{F}^-$  and  $\text{Cl}^-$  ions.

14. What is the coordination entity formed when an excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when  $\text{H}_2\text{S}(\text{g})$  is passed through this solution?

**Solution:**



Thus, the coordination entity formed in the process is  $\text{K}_2[\text{Cu}(\text{CN})_4]$ . It is a very stable complex, which does not ionise to give  $\text{Cu}^{2+}$  ions when added to water. Hence,  $\text{Cu}^{2+}$  ions do not precipitate when  $\text{H}_2\text{S}(\text{g})$  is passed through the solution.

15. Discuss the nature of bonding in the following coordination entities based on valence bond theory:

- (i)  $[\text{Fe}(\text{CN})_6]^{4-}$

- (ii)  $[\text{FeF}_6]^{3-}$   
 (iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (iv)  $[\text{CoF}_6]^{3-}$

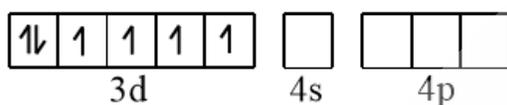
**Solution:**

- (i)
- $[\text{Fe}(\text{CN})_6]^{4-}$

In the coordination complex  $[\text{Fe}(\text{CN})_6]^{4-}$ , iron exists in the (+II) oxidation state.

Electronic configuration of  $\text{Fe}^{2+}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$

Orbitals of  $\text{Fe}^{2+}$  ion:

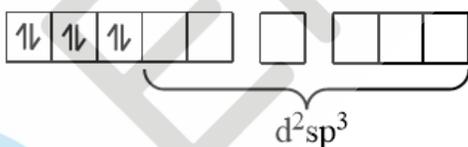


As  $\text{CN}^-$  is a strong field ligand, so the pairing of the unpaired 3d electrons occurs



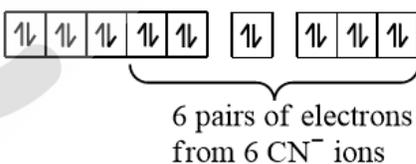
Since there are six ligands around the central metal ion, the hybridisation is  $d^2sp^3$ .

$d^2sp^3$  hybridised orbitals of  $\text{Fe}^{2+}$  are:



6 electron pairs from  $\text{CN}^-$  ions occupy the six hybrid  $d^2sp^3$  orbitals.

Then,



Hence, the geometry of the complex is octahedral.

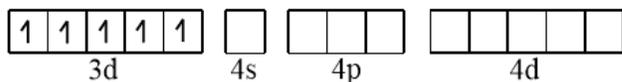
The compound does not have unpaired electrons, so the complex is diamagnetic.

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

In this complex, the oxidation state of Fe is +3.

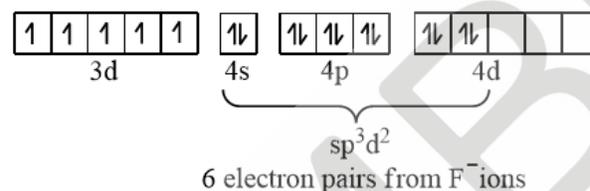
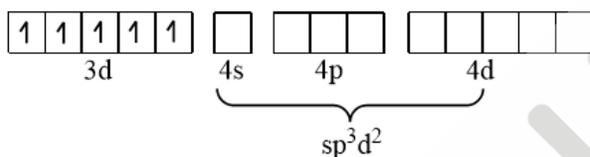
Electronic configuration of  $\text{Fe}^{3+}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$

Orbitals of  $\text{Fe}^{3+}$  ion:



There are 6  $\text{F}^-$  ions. As  $\text{F}^-$  is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the hybridisation is  $sp^3d^2$ .

$sp^3d^2$  hybridised orbitals of Fe are:



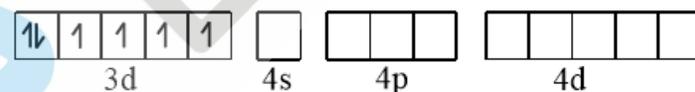
Hence, the geometry of the complex is found to be octahedral.

(iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

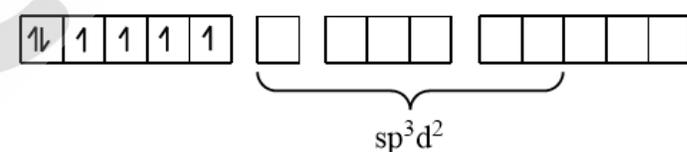
Cobalt exists in the +3 oxidation state in the given complex.

Electronic configuration of  $\text{Co}^{3+}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$

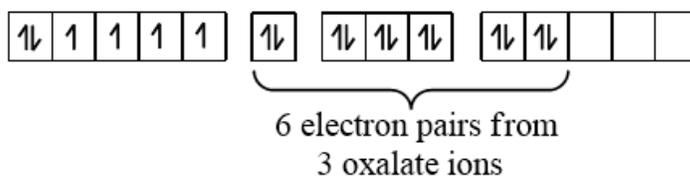
Orbitals of  $\text{Co}^{3+}$  ion:



Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridisation is  $sp^3d^2$



The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these  $sp^3d^2$  orbitals.



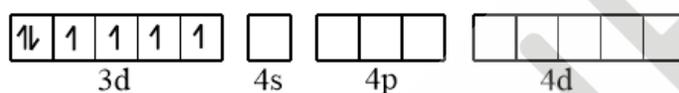
Hence, the geometry of the complex is found to be octahedral.



Cobalt exists in the +3 oxidation state.

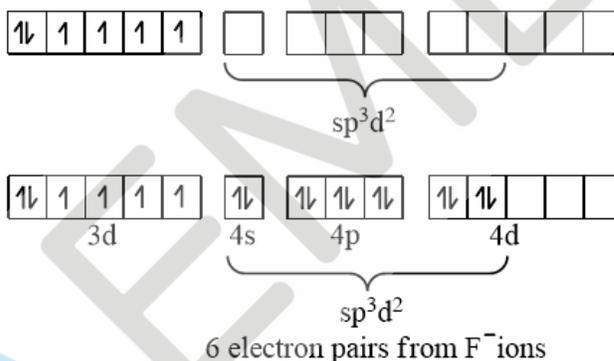
Electronic configuration of  $\text{Co}^{3+}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$

Orbitals of  $\text{Co}^{3+}$  ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the  $\text{Co}^{3+}$  ion will undergo  $sp^3d^2$  hybridization.

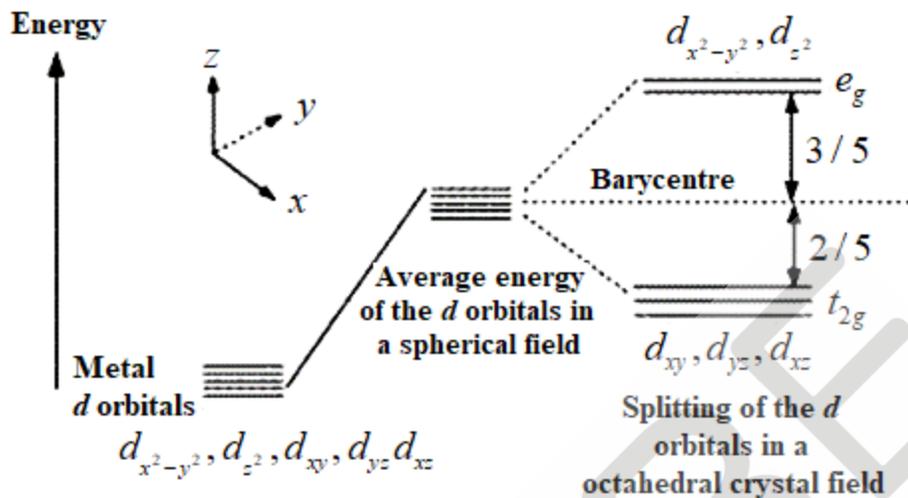
$sp^3d^2$  hybridized orbitals of  $\text{Co}^{3+}$  ion are:



Hence, the geometry of the complex is octahedral and paramagnetic.

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

**Solution:**

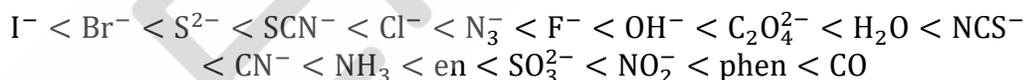


The splitting of the d orbitals in an octahedral field takes place in such a way that  $d_{x^2-y^2}$ ,  $d_{z^2}$  experience a rise in energy and form the  $e_g$  level, while  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  experience a fall in energy and form the  $t_{2g}$  level.

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

**Solution:**

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 right-hand side of the series are strong field ligands while that on the light hand side are weak field ligands. Also, strong-field ligands cause higher splitting in the d orbitals than weak field ligands.



18. What is crystal field splitting energy? How does the magnitude of  $\Delta_0$  decide the actual configuration of d-orbitals in a coordination entity?

**Solution:**

The degenerate d-orbitals (having same energy) split into two energy levels i.e.,  $e_g$  and  $t_{2g}$  in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels ( $e_g$  and  $t_{2g}$ ) is called the crystal-field splitting energy. It is denoted by  $\Delta_0$ .

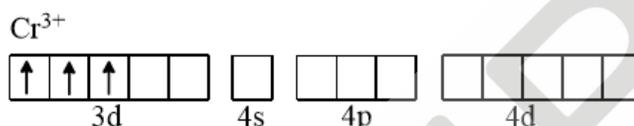
After the orbitals have split, the filling of the electrons takes place. After 1 electron (each) has been filled in the three  $t_{2g}$  orbitals, the filling of the fourth electron takes place in two ways. It can enter the  $e_g$  orbital (giving rise to  $t_{2g}^3 e_g^1$  like electronic configuration) or the pairing of the electrons can take place in the  $t_{2g}$  orbitals

(giving rise to  $t_{2g}^4 e_g^0$  like electronic configuration). If the  $\Delta_o$  value of a ligand is less than the pairing energy (P), then the electrons enter the  $e_g$  orbital. On the other hand, if the  $\Delta_o$  value of a ligand is more than the pairing energy (P), then the electrons enter the  $t_{2g}$  orbital.

19.  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain why?

**Solution:**

Cr is in the +3 oxidation state i.e.,  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^0$  electronic configuration.  $\text{NH}_3$  act as a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

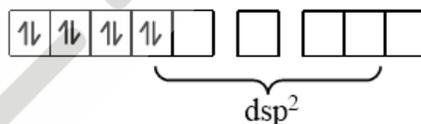


Therefore, it undergoes  $d^2sp^3$  hybridization and the three electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.

In  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni exists in the +2 oxidation state i.e.,  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^0$  configuration.



$\text{CN}^-$  is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then,  $\text{Ni}^{2+}$  undergoes  $dsp^2$  hybridization.



As there are no unpaired electrons, it is diamagnetic.

20. A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green but a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless. Explain.

**Solution:**

In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{H}_2\text{O}$  acts as a weak field ligand. Therefore, there are unpaired electrons in  $\text{Ni}^{2+}$ . In this complex, the d electrons from the lower energy level can be excited to the higher energy level, i.e., the possibility of d-d transition is present. Hence,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is coloured.

In  $[\text{Ni}(\text{CN})_4]^{2-}$ , all the electrons are paired as  $\text{CN}^-$  is a strong field ligand. Therefore, a d-d transition is not possible in  $[\text{Ni}(\text{CN})_4]^{2-}$ . Hence, it is colourless.

21.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. Why?

**Solution:**

The colour of a particular coordination compound depends on the magnitude of the Crystal-Field Splitting Energy ( $\Delta_o$ ). This CFSE, in turn, depends on the nature of the ligand. In the case of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , the colour differs because there is a difference in the CFSE. Now,  $\text{CN}^-$  is a strong field ligand having a higher CFSE value as compared to the CFSE value of water, This means that the absorption of energy for the intra d-d transition also differs.

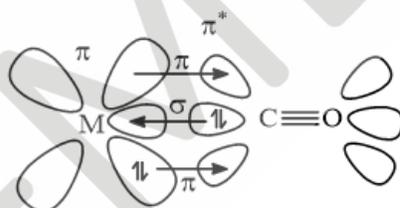
Hence, the transmitted colour also differs.

22. Discuss the nature of bonding in metal carbonyls.

**Solution:**

The metal-carbon bonds in metal carbonyls have both  $\sigma$  and  $\pi$  characters. A  $\sigma$  bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal. A  $\pi$  bond is formed by the donation of a pair of electrons from the filled metal d orbital into vacant anti-bonding  $\pi^*$  orbital (also known as back bonding of the carbonyl group). The  $\sigma$  bond strengthens the  $\pi$  bond and vice-versa.

Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.



Synergic bonding in metal carbonyls

23. Give the oxidation state, d-orbital occupation and coordination number of the central metal ion in the following complexes:

- $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$
- cis -  $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$
- $(\text{NH}_4)_2[\text{CoF}_4]$
- $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$

**Solution:**

- $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$

The central metal ion is Co. Let its oxidation state = x

$\text{C}_2\text{O}_4^{2-}$  oxalate ion is negative ligand its oxidation state = -2

Oxidation state of potassium = +1

The  $\text{C}_2\text{O}_4^{2-}$  oxalate ion is a bidentate ligand.

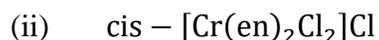
Oxidation state can be given as:

$$x - 6 = -3$$

$$x = +3$$

$\text{C}_2\text{O}_4^{2-}$  oxalate ion is bidentate ligand and there are three in the complex. So, the coordination number of the complex is 6.

$\text{C}_2\text{O}_4^{2-}$  oxalate ion is weak field ligand so the d orbital occupation for  $\text{Co}^{3+}$  is  $t_{2g}^6 e_g^0$ .



The central metal ion is Cr

Let its oxidation state of Cr = x

Cl chloride ion is negatively charged ligand and its oxidation state = -1

en is neutral ligand and its oxidation state = 0

The oxidation state can be given as:

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

$$x - 2 = +1$$

$$x = +3$$

chloride ion monodentate ligand and en is a bidentate ligand, so the coordination number is 6.

The d orbital occupation for  $\text{Cr}^{3+}$  is  $t_{2g}^3$ .



The central metal ion is Co.

Let its oxidation state of Cr = x

F fluoride ion is negatively charged ligand and its oxidation state = -1

Ammonium ( $\text{NH}_4^{+1}$ ) is positively charged ion and its oxidation state = 0

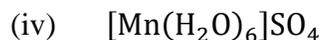
The oxidation state can be given as:

$$x - 4 = -2$$

$$x = +2$$

chloride ion is a mono-dentate ligand, so the coordination number is 4.

The d orbital occupation for  $\text{Co}^{2+}$  is  $e_g^4 t_{2g}^3$ .



The central metal ion is Mn.

Let its oxidation state of Mn = x

Water ( $\text{H}_2\text{O}$ ) is neutral ligand and its oxidation state = 0

Sulphate ( $\text{SO}_4$ ) is negatively charged ion and its oxidation state = -2

Water ( $\text{H}_2\text{O}$ ) is a monodentate ligand so the coordination number of compound is 6.

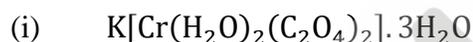
The oxidation state can be given as:

$$x + 6(0) = +2$$

$$x = +2$$

The d orbital occupation for Mn is  $t_{2g}^3 e_g^2$ .

24. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also, give stereochemistry and magnetic moment of the complex:



**Solution:**

Rules to write the IUPAC name of coordination compound :

- (i) Calculate the oxidation number of the central atom involved.
- (ii) The cation is named first as is the case with other ionic compounds. This rule applies to both positively and negatively charged coordination entities.
- (iii) Usually, the number of free cation or anions is not given as can easily be calculated by charge
- (iv) For writing the names of complex cation use the following rule.

Names of the ligand in english alphabetical order with their quantity as prefix (but do not use mono for one and do not consider first letters of these number denoting prefixes in alphabetisation). This is followed by the name of metal followed by its oxidation number (in Roman numeral) in a bracket like (0) (I), (II), (III), (-I), (-II) etc.

- (v) For writing the names of complex anion use the following rule.

Names of the ligand in english alphabetical order with their quantity as prefix (but do not use mono for one and do not consider first letters of these number denoting prefixes in alphabetisation). This is followed by the name of metal(modified as per rule already specified) followed by its oxidation number (in Roman numeral) in a bracket. (I), (II), (III), (0), (-I), (-II), etc.

- (vi) The neutral complex molecule is named similar to that of the complex cation.

Following the above rules we get the IUPAC names as follows:

- (i) Potassium diaquadioxalatochromate (III) trihydrate.

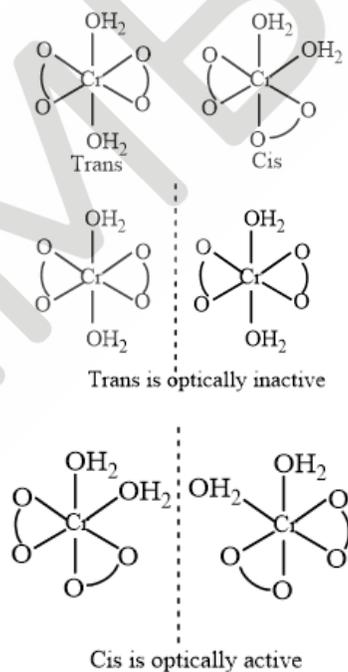
Oxidation state of chromium = 3

Electronic configuration:  $3d^3: t_{2g}^3$

Coordination number = 6

Shape: octahedral

Stereochemistry:



$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}$$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

$$= 4 \text{ BM}$$

- (ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

IUPAC name: Pentaamminechloridocobalt (III) chloride

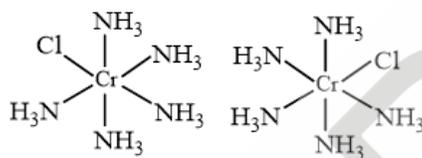
Oxidation state of Co = +3

Coordination number = 6

Shape: octahedral

Electronic configuration:  $3d^6; t_{2g}^6$ .

Stereochemistry:



2 isomers

Magnetic Moment = 0

(iii)  $\text{CrCl}_3(\text{py})_3$

IUPAC name: Trichloridotripyridinechromium (III)

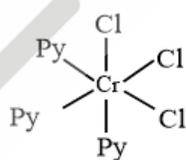
Oxidation state of chromium = +3

Electronic configuration for  $d^3 = t_{2g}^3$

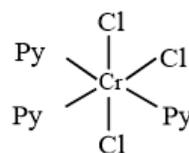
Coordination number = 6

Shape: octahedral.

Stereochemistry:



Facial isomer



Meridional isomer

Both isomers are optically active. Therefore, a total of 4 isomers exist.

Magnetic moment,  $\mu = \sqrt{n(n+2)}$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

$$= 4 \text{ BM}$$

(iv)  $\text{Cs}[\text{FeCl}_4]$

IUPAC name: Caesium tetrachloroferrate (III)

Oxidation state of Fe = +3

Electronic configuration of  $d^5 = e_g^2 t_{2g}^3$

Coordination number = 4

Shape: tetrahedral

Stereochemistry: optically inactive

Magnetic moment:

$$\mu = \sqrt{n(n+2)}$$

$$= \sqrt{5(5+2)}$$

$$= \sqrt{35} \sim 6 \text{ BM}$$

(v)  $K_4[Mn(CN)_6]$

Potassium hexacyanomanganate (II)

The oxidation state of manganese = +2

Electronic configuration:  $d^{5+}; t_{2g}^5$

Coordination number = 6

Shape: octahedral

Stereochemistry: optically inactive

Magnetic moment,  $\mu = \sqrt{n(n+2)}$

$$= \sqrt{1(1+2)}$$

$$= \sqrt{3}$$

$$= 1.732 \text{ BM}$$

**25.** What is meant by the stability of a coordination compound in solution? State the factors which govern the stability of complexes.

**Solution:**

The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.



$$\text{Stability constant } (k_{\text{stability}}) = \frac{[ML_3]}{[M][L]^3}$$

For this reaction, the higher the value of the stability constant, the greater is the proportion of  $ML_3$  in the solution.

Stability can be of two types:

(a) Thermodynamic stability:

The extent to which the complex will be formed or will be transformed into another species at the point of equilibrium is determined by thermodynamic stability.

(b) Kinetic stability:

This helps in determining the speed with which the transformation will occur to attain the state of equilibrium.

Factors that affect the stability of a complex are:

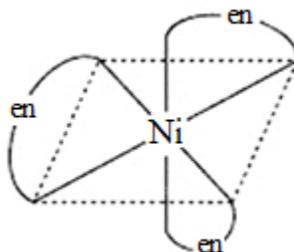
1. Charge on the central metal ion: The greater the charge on the central metal ion, the higher is the stability of the complex.
2. Basic nature of the ligand: A more basic ligand will form a more stable complex.
3. Presence of chelate rings: Chelation increases the stability of complexes.

26. What is meant by the chelate effect? Give an example.

Solution:

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

For example:



27. 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

**Solution:**

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

Photosynthesis is made possible by the presence of the chlorophyll pigment and 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:

Coordination compounds of platinum such as cis-platin is used for inhibiting the growth of tumours.

- (iii) Role of coordination compounds in analytical chemistry:

During the analysis of salt, when different reagents containing ligands are added to different basic radicals they form coordination compounds. These coordination compounds exhibit different colours associated with each of the basic radicals. Thus some coordination compounds can be used in the detection of various radicals.

- (iii) Role of coordination compounds in extraction or metallurgy of metals:

In metallurgy, 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  $[\text{Au}(\text{CN})_2]$ . From this solution, gold is later extracted by the addition of zinc metal.

28. How many ions are produced from the complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  in solution?

- (i) 6
- (ii) 4
- (iii) 3
- (iv) 2

**Solution:** (iii)

The given complex can be written as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$

Thus,  $[\text{Co}(\text{NH}_3)_6]^{+2}$  along with two  $\text{Cl}^-$  ions are produced. So, a total of 3 ions are produced.

29. Amongst the following ions which one has the highest magnetic moment value?

- (i)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- (ii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- (iii)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

**Solution:**

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  :  $\text{H}_2\text{O}$  is a weak field ligand.

oxidation state of Cr = +3

Electronic configuration of  $\text{Cr}^{+3} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^0$

Number of unpaired electrons in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} = 3$

Then,  $\mu = \sqrt{n(n+2)}$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

~4BM

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  :  $\text{H}_2\text{O}$  is a weak field ligand

The oxidation state of Fe = +2

Electronic configuration of  $\text{Fe}^{+2} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$

Coordination number = 6

Number of unpaired electrons in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} = 4$

Then,  $\mu = \sqrt{4(4+2)}$

$$= \sqrt{24}$$

~5 BM

$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  :  $\text{H}_2\text{O}$  is a weak field ligand

The oxidation state of Zn = +2

Electronic configuration of  $\text{Zn}^{+2} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$

Number of unpaired electrons in  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+} = 0$

Hence,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  has the highest magnetic moment value.

30. The oxidation number of cobalt in  $\text{K}[\text{Co}(\text{CO})_4]$  is

- (i) +1
- (ii) +3

(iii) -1

(iv) -3

**Solution:** (iii)

We know that CO is a neutral ligand and K carries a charge of +1.

Let the oxidation number of Co =  $x$

Oxidation number =  $1(+1) + x + 4(0) = 0$

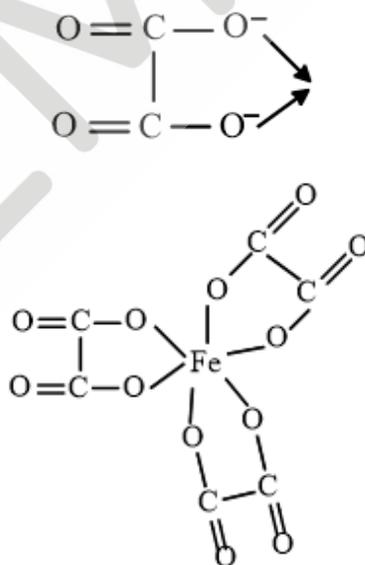
$x = -1$

Hence, the option (iii) is correct.

**31.** Amongst the following, the most stable complex is

(i)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (ii)  $[\text{Fe}(\text{NH}_3)_6]^{3+}$ (iii)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ (iv)  $[\text{FeCl}_6]^{3-}$ **Solution:**

Since the stability of a complex increases by chelation, the most stable complex is  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ .



**32.** What will be the correct order for the wavelengths of absorption in the visible region for the following:

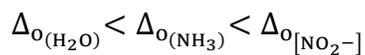
$[\text{Ni}(\text{NO}_2)_6]^{4-}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

**Solution:**

Since the central metal ion in all the three complexes is the same, the absorption in the visible region depends on the ligands. The order in which the CFSE values of the ligands increases in the spectrochemical series is as follows:



Hence, the amount of crystal-field splitting observed will be in the following order:



Therefore, the wavelengths of absorption in the visible region will be in the order:



◆◆◆