

# **COORDINATION COMPOUNDS**

# SOLVED SUBJECTIVE EXERCISE

# Very Short Answer Type Questions (1 mark)

- 1. Write the formulae of the following coordination compounds
  - (i) Tetraamminediaquacobalt (III) chloride
  - (ii) Dichloridobis (ethane-1, 2-diamine) platinum (IV) nitrate
- $\textbf{\textit{Ans.}} \hspace{0.2cm} \text{(i)} \hspace{0.1cm} [\text{Co} \hspace{0.1cm} (\text{NH}_3)_4 \hspace{0.1cm} (\text{H}_2\text{O})_2] \hspace{0.1cm} \text{Cl}_3 \hspace{0.2cm} \text{(ii)} \hspace{0.1cm} [\text{PtCl}_2(\text{en})_2] \hspace{0.1cm} (\text{NO}_3)_2 \hspace{0.1cm} ]$
- 2.  $[NiCl_4]^{2-}$  is paramagnetic while  $[Ni(CO)_4]$  is diamagnetic though both are tetrahedral. Why?
- Ans. In Ni(CO)<sub>4</sub>, Ni is in zero oxidation state whereas in Ni(Cl<sub>4</sub>)<sup>2</sup>, it is in +2 oxidation state. In the presence of CO ligand, the unpaired d-electrons of Ni pair up but Cl<sup>-</sup> being a weak ligand is unable to pair up the unpaired electrons.
- 3. Which compound is used to estimate the hardness of water volumetrically?
- Ans. EDTA
- 4. Square planar complexes with coordination number of four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?
- **Ans.** Tetrahedral complexes do not show geometrical isomerism because the relative positions of the ligands attached to the central metal atom are same with respect to each other.
- 5. What is spectrochemical series?
- Ans. It is a series in which ligands can be arranged in the order of increasing field strength or in order of increasing magnitude of splitting the produce.
  The order is

$$\Gamma < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{\ 2-} < \text{H}_2\text{O} < \text{NCS} < \text{edta}^4 < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}_2\text{O}_4^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{CO}_2\text{O}_3^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{CO}_2\text{O}_3^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{CO}_2\text{O}_3^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{CO}_2\text{O}_3^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{CO}_3^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{CO}_3^{\ 2-} < \text{NCS} < \text{edta}^4 < \text{NCS} < \text{$$

- **6.** Which isomer of [CoCl<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> does not show optical isomerism?
- Ans. Trans isomer does not show optical isomerism.
- 7. Why only transition metals are known to form  $\pi$  complexes?
- **Ans.** Transition metals/ions have empty d-orbitals into which the electron-pairs can be donated by ligands containing  $\pi$  electrons, i.e., electrons in their  $\pi$  molecular orbitals, e.g.,  $C_{5}H_{5}$ ,  $C_{6}H_{6}$  etc.
- **8.** What happens to the colour of coordination compound  $[Ti(H_2O)_6]Cl_3$  when heated gradually?
- Ans. On heating, its colour becomes lighter as  $H_2O$  is gradually lost. When all  $H_2O$  molecules are lost, it becomes colourless because in the absence of ligands, crystal field splitting does not occur.
- 9. When our haemoglobin is low, the deficiency of which metal is caused and why?
- Ans. Deficiency of iron occurs because haemoglobin is a complex compound of iron.
- 10. A coordination compound has the formula, CoCl<sub>3</sub>.4NH<sub>3</sub>. It does not liberate ammonia but precipitates chloride ions as silver chloride. Give the IUPAC name of the complex and write its structural formula.
- **Ans.** Remembering that coordination number of Co is 6, the formula of the complex will be [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl. The name will be tetraamminedichloridocobalt (III) chloride.

# Short Answer Type Questions (2 mark)

- 11. A 0.01 m complex of CoCl<sub>3</sub> and NH<sub>3</sub> (molar ratio 1:4) is found to gives freezing point of 0.0372. Suggest the formula of the complex.
- Ans. Since the depression in freezing point -0.0372°C therefore the effective molality of complex in solution is

$$0.0372 = 1.86 \times m$$
 or  $m = \frac{0.0372}{1.86} = 0.02$ 

Since the molality increases from 0.01 m to 0.02 m therefore the number of ions formed in solution is two. Hence the structure, [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl.

# Chemistry



- 12. Explain, why the word bis is used while writing the name of ligands like (CH<sub>3</sub>) NH<sub>2</sub> though it is a monodentate ligand.
- Ans. Although methylamine is a monodentate ligand, yet the word bis or tris is used when two or three ligands are present. It is because if the words di or tri are used then dimethylamine or trimethylamine would mean (CH<sub>3</sub>)<sub>2</sub>NH and (CH<sub>3</sub>)<sub>3</sub>N respectively and not CH<sub>3</sub>NH<sub>2</sub>. For example, [Cu(CH<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] is named as Dichloro bis (methylamine) copper (II).
- 13. Explain why  $[Fe(H_2O)_6]^{3+}$  has magnetic moment value of 5.92 BM whereas  $[Fe(CN)_6]^{3-}$  has a value of only 1.74 BM.
- Ans. Both have  $Fe^{3+}$  ( $3d^5 = 3d^1 \ 3d^1 \ 3d^1 \ 3d^1 \ 3d^1$ ).  $H_2O$  is weak ligand. Electrons do not pair up. Hybridisation is  $sp^3d^2$ . As n=5,  $\mu=\sqrt{5(5+2)}=5.92$  BM. CN is a strong ligand. Electrons pair up to give  $3d^2 \ 3d^1 \ 3d^0 \ 3d^0$ . Hybridisation is  $d^2sp^3$ . As n=1,  $\mu=\sqrt{1(1+2)}=1.73$  BM.
- 14. (i) Give the IUPAC name of the ionisation isomer of [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]SO<sub>4</sub>.
  - (ii) Give an example of chelate complex.
- **Ans.** (i)  $[Cr(NH_3)_5 SO_4]$  Cl is the ionisation isomer of  $[Cr(NH_3)_5 Cl]SO_4$ . Its name is pentaammine sulphatochromium (III) chloride.
  - (ii) Bis-(ethylenediamine) copper (II) ion,  $[Cu(en)_2]Cl_2$  is an example of a chelate.

$$\begin{bmatrix} H_2C - NH_2 \\ H_2C - NH_2 \end{bmatrix} Cu \begin{bmatrix} NH_2 - CH_2 \\ NH_2 - CH_2 \end{bmatrix}^{2+1}$$

- 15. What is meant by stability of a coordination compound in solution? State the factors which govern the stability of complexes.
- **Ans.** The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association; quantitative expresses the stability. Thus, in reaction of the type:

$$M + 4L \rightarrow ML_4$$

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

larger the stability constant, the higher is the proportion of  $ML_4$  that exists in solution.

# Factors on which stability of the complex depends:

- (i) Charge on the central metal ion: Greater the charge on the central metal ion, greater is the stability of the
- (ii) Nature of the metal ion: Groups 3 to 6 and inner transition elements form stable complexes when donor atoms of the ligands are N, O and F. The elements after group 6 of the transition metals which have relatively heavier members of N, O and F family.
- (iii) Basic nature of the ligand: Greater the basic strength of the ligand, greater is the stability of the complex. (iv) Presence of chelate rings: In the complex increases its stability.
- (iv)**Presence of chelate rings**: In the complex increases its stability. It is called chelate effect. It is maximum for the 5-and 6-membered rings.
- (v) **Effect of multidentate cyclic ligands**: If the ligands happen to the multidentate and cyclic without any steric effect, the stability of the complex is further increased.



- 16. What is meant by chelate effect? Give an example.
- Ans. When a didentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six membered ring is formed, the effect is called chelate effect.

  Example,

- 17. The hexaaquomanganese (II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using Crystal Field Theory.
- Ans. Mn in the +2 state has the configuration  $3d^5$ . In the presence of  $H_2O$  as ligand, the distribution of these five electrons is  $t_{2g}^3 e_g^2$ , that is, all the electrons remain unpaired. In the presence of CN as ligand, the distribution is  $t_{2g}^5 e_g^0$ , that is, two  $t_{2g}$  orbitals contain paired electrons while the third  $t_{2g}$  orbital contains one unpaired electron.
- 18. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphide is obtained when H<sub>2</sub>S (g) is passed through this solution?
- Ans. K<sub>2</sub>[Cu(CN)<sub>4</sub>] is formed when excess of aqueous KCN is added to an aqueous solution of CuSO<sub>4</sub>.

$$\begin{array}{c} \text{CuSO}_4(\text{aq}) \ + \ 4\text{KCN}(\text{aq}) \\ \text{Copper sulphate} \end{array} \xrightarrow{\text{Potassium cyanide}} \begin{array}{c} K_2[\text{Cu(CN)}_4] \ + \ K_2\text{SO}_4(\text{aq}) \\ \text{Potassium} \\ \text{tetracynocuprate(II)} \\ \text{Soluble} \end{array}$$

As CN ions are strong ligands the complex is very stable. It is not cleared by H<sub>2</sub>S gas when passed through the solution and thus no precipitate of CuS is obtained.

- 19. What is meant by unidentate, and ambidentate ligands? Give two examples for each.
- Ans. A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, e.g., Cl<sup>-</sup> and NH<sub>3</sub>.

  A molecule or an ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called a didentate ligand, e.g., NH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—NH<sub>2</sub> and  $\overline{OOC}$ —CO $\overline{O}$ . A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called ambidentate ligand, e.g., : CN $^-$  or NC $^-$ : and: NO $^-$  or : ONO $^-$ .
- **20.** Explain as to how the two complexes of nickel,  $[Ni (CN)_4]^{2-}$  and  $[Ni(CO)_4]$ , have different structures but do not differ in their magnetic behaviour. (Ni = 28)
- Ans. Structure: Square planar.

Magnetic behaviour: Diamagnetic due to the absence of unapired electrons.

Orbital of Ni(O)		<b>↑↓</b>
sp <sup>3</sup> hybridised		and the state of t
orbitals of Ni	ou .	sp³ hybrid
Ni(CO) <sub>4</sub>	$ \begin{array}{c c} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\ \hline 3d \end{array} $	Four pairs of electrons from
(Low spin complex)  Structure: Tetrahedral	30	four CO molecules

Magnetic behaviour: Diamagnetic due to the absence of unpaired electrons.

# Chemistry



Differentiate between weak field and strong field coordination entity.

	Weak field coordination entity	Strong field coordination entity	
1	They are formed when the crystal field stabilisation energy ( $\Delta_0$ ) in octahedral complexes is less than the energy required for an electron pairing in a single orbital (P).	They are formed when the crystal field stabilisation energy $(\Delta_0)$ is greater than the	
2	They are also called high spin complexes.	They are called low spin complexes.	
3	They are mostly paramagnetic in nature.	They are mostly diamagnetic or less paramagnetic than weak field.	
4	Never formed by CN <sup>-</sup> ligand.	Formed by CN <sup>-</sup> like ligands.	

- 22. What is crystal field splitting energy? How does the magnitude of  $\Delta_0$  decide the actual configuration of d-orbitals in a coordination entity?
- When ligands approach a transition metal ion, the d-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy  $\Delta_0$  for octahedral field.

If  $\Delta_0 < P$  (pairing energy), the 4th electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$  thereby forming high spin complexes. Such ligands for which  $\Delta_0 < P$  are called weak field ligands. If  $\Delta_0 > P$ , the 4th electron pairs up in one of the  $t_{2g}$  orbitals giving the configuration  $t_{2g}^4$  e°g thus forming low spin complexes. Such ligands for which  $\Delta_0 > P$  are called strong field ligands.

- Aqueous copper sulphate solution (blue in colour) gives (i) a green precipitate with aqueous potassium fluoride, and 23. (ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.
- Aqueous copper sulphate exist as [Cu(H2O)4]SO4. It is labile complex. The blue colour of the solution is due to  $\left[Cu(H_2O)_4\right]^{2+}$  ions.
  - (i) When KF is added, the weak  $H_2O$  ligands are replaced by F ligands forming  $[CuF_4]^{2-}$  ions which is a green

$$[Cu (H2O)4]2+ + 4F- \longrightarrow [CuF4]2- + 4H2O$$
Tetrafluorocuprate (II)
(Green ppt.)

(ii) When KCl is added,  $Cl^-$  ligands replace the weak  $H_2O$  ligands forming  $[CuCl_4)^{2-}$  ion which has bright green

$$[Cu (H2O)4]2+ + 4Cl- \longrightarrow [CuCl4]2- + 4H2O$$
Tetrafluorocuprate (II) (Green solution)

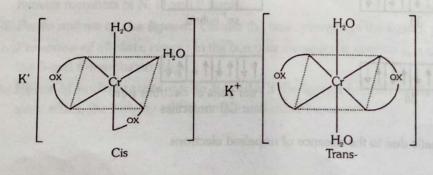
# **Short Answer Type Questions (3 mark)**

Indicate the types of isomerism exhibited by the following complexes and draw the structure for these isomers: 24.

(i) K [Cr 
$$(H_2O)_2 (C_2O_4)_2$$
]

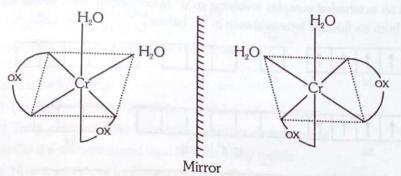
(iii) [Co 
$$(NH_3)_5 (NO_2)$$
]  $(NO_3)_2$ 

Ans. (i) (a) Both geometrical (cis-trans) and optical isomers for cis can exist.





(b) Optical isomers (d-and I-) of cis.



- (ii) Two opticla isomers can exist.
- (iii) There are 10 possible isomers (there are geometrical, ionisation and linkage isomers possible).

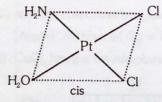
#### **Ionisation isomers:**

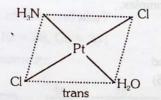
 $[Co(NH_3)_5 (NO_2)] (NO_3)_2, [Co(NH_3)_5 (NO_3)] (NO_2) (NO_3)$ 

### Linkage isomers:

 $[Co(NH_3)_5 (NO_2)] (NO_3)_2, [Co(NH_3)_5 (ONO)] (NO_3)_2$ 

(iv) Geometrical (cis-, trans-) isomers can exist.





Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory: 25.

(i) [Fe(CN)<sub>6</sub>]<sup>4</sup> (ii) [FeF<sub>6</sub>]<sup>3</sup>-

Ans. (i) [Fe(CN), ]4-d2sp3, octahedral, diamagnetic.

[Fe(CN)]4- ion: In this complex ion, the oxidation state of iron is +2.

Electronic configuration of Fe = [Ar]3d<sup>6</sup>4s<sup>2</sup>

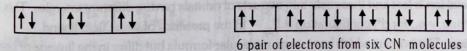
Electronic configuration of  $Fe^{2+} = [Ar]3d^6$ 

To accommodate six pairs of electrons from six cyanide ions, the iron (II) ions must make available six empty orbitals. This can be achieved by the following hybridisation scheme wherein electrons in the d-subshell have been pair up as CN-ions are strong field ligands.

Atomic orbitals of Fe2+ion d<sup>2</sup>sp<sup>3</sup> hybridised orbitals of Fe<sup>2+</sup> ion

Six empty d<sup>2</sup>sp<sup>3</sup> hybridised orbitals

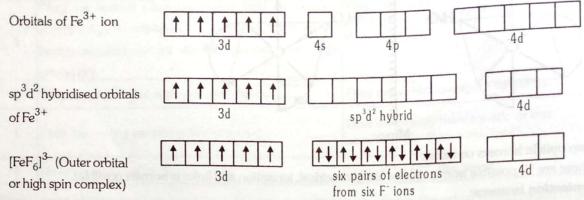
d2sp3 hybridised orbitals of [Fe(CN)6]4 ion



Thus six pairs of electrons from six cyanide ions occupy the six hybridised orbitals of Iron (II) ion. At the same time, we find no orbital which contains unpaired electron. Hence, the iron [Fe (CN)<sub>6</sub>]<sup>4-</sup> shows diamagnetism. Therefore, [Fe (CN)<sub>6</sub>]<sup>4</sup> ion is diamagnetic and octahedral.



(ii) [FeF<sub>6</sub>]<sup>3-</sup>: This complex is high-spin or outer-orbital complex since the central metal ion Fe (III) utilises ndorbitals for hybridisation. It is an octahedral complex involving sp<sup>3</sup>d<sup>2</sup> hybridisation; each orbital accommodates a lone pair of electrons from six fluoride ions as shown in fig. below.



Since this complex contains five unpaired electron, it is paramagnetic.

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

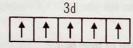
- (i) the oxidation number of iron.
- (ii) the hybrid orbitals and the shape of the complex.
- (iii) the magnetic behaviour of the complex.
- (iv) the number of geometrical isomers.
- (v) whether there is an optical isomer also, and
- (vi) name of the complex. (At. no. of Fe = 26)

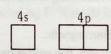
Ans. Given complex is [Fe(en), Cl, ]Cl

(i) Let the oxidation number of iron be x

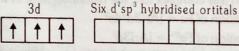
$$\therefore$$
 x + 2×0 + 2 (-1)+1 (-1)=0

(ii) Orbitals of Fe (III)





 $d^2 sp^3$  hybridised orbitals of Fe (III)



Thus, Hybridisation: d<sup>2</sup>sp<sup>3</sup>

Shape of the complex: Octahedral

- (iii) Paramagnetic due to presence of three unpaired electrons
- (iv) Two, cis and trans isomers
- (v) Yes, cis isomer will also show optical isomerism
- (vi) Dichlorido bis (ethane- 1, 2 diamine) iron (III) chloride or Dichloro bis (ethylenediamine) iron (III) chloride.

27. Giving a suitable example for each, explain the following:

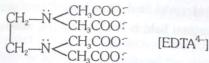
- (i) Crystal field splitting, (ii) Linkage isomerism, (iii) Hexadentate ligand
- Ans. (i) Crystal field splitting: When the ligands approach the central metal ion, the electrons in the d-orbitals of central metal ion will be repelled by the lone pairs of the ligands. Because of these interactions the degeneracy of d orbitals of the metal ion is lost and these split into two sets of orbitals having different energies. This is known as crystal field splitting, e.g., for d<sup>4</sup>, configuration is t<sup>3</sup><sub>2g</sub> e<sup>l</sup><sub>g</sub> in the presence of weak field ligand.

(ii) Linkage isomerism: The isomers which have same molecular formula but differ in the linkage of ligand atom to the central metal atom are called linkage isomers, e.g., [CO(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>ONO]Cl<sub>2</sub>

(iii) **Hexadentate ligand**: Ligands which contain 6 donor atom which can coordinate with C.M.A. are called as Hexadentate Ligand.

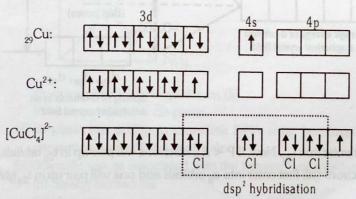
Ex. Ethylenediaminetetracetate



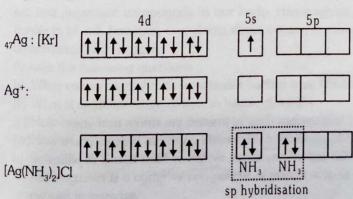


Detection of Ca and Mg ions in hard water.

- 28. Explain the following:
  - (i) Low spin octahedral complexes of nickel are not known.
  - (ii) The  $\boldsymbol{\pi}$  -complexes are known for transition elements only.
  - (iii) CO is a stronger ligand than  $\mathrm{NH}_{\mathrm{3}}$  for many metals.
- $\pmb{Ans.}$  (i) Ni in its atomic or ionic state can not afford two vacant 3d orbitals hence  $d^2sp^3$  hybridisation is not possible.
  - (ii) Transition metals have vacant d orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing  $\pi$  electrons, e.g.,  $C_6H_6$ ,  $CH_2=CH_2$ , etc. Thus,  $d\pi$ -P $\pi$  bonding is possible.
  - (iii) Because in case of CO back bonding takes place in which the central metal uses its filled d orbital with empty anti bonding  $\pi^*$  molecular orbital of CO.
- **29.** Among  $[Ag(NH_3)_2]$  Cl  $[Ni(CN)_4]^{2-}$  and  $[CuCl_4]^{2-}$  which
  - (i) has square planar geometry?
  - (ii) remains colourless in aqueous solution and why? [Atomic number of  $Ag=47,\,Ni=28,\,Cu=29$ ]
- Ans. (i) CuCl<sub>4</sub> has the square planar geometry:



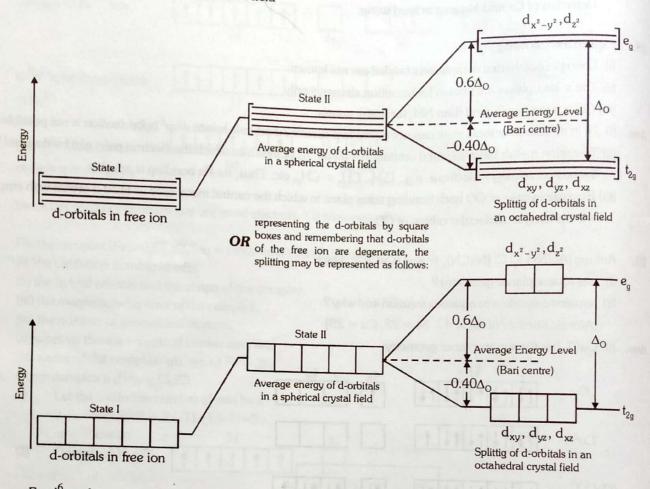
(ii)  $[Ag(NH_3)_2]Cl$  is colourless because there is no unpaired electrons in its d-orbitals hence no d-d transition is possible.





30. Draw a sketch to show the splitting of d-orbitals in an octahedral crystal field. State for a d<sup>6</sup> configuration, how the actual configuration of the split d-orbitals in an octahedral crystal field is decided by the relative values of A and P?

Ans. Splitting of d-orbitals in an octahedral field -



For d<sup>6</sup> configuration, three electrons will first enter into  $t_{2g}$ . Now, if  $P < \Delta_o$ , electrons will pair up in  $t_{2g}$  orbitals, giving the configuration  $t_{2g}^6$  and if  $\Delta_o < P$ , two electrons will first enter into  $e_g$  orbitals and one will pair up in  $t_{2g}$  giving the configuration  $t_{2g}^4$   $e_g^2$ .



# **EXERCISE-1**

# PREVIOUS YEARS BOARD PROBLEMS

### **CBSE 2016**

- When a coordination compound  $NiCl_2.6H_2O$  is mixed with  $AgNO_3$ , 2 moles of AgCl are precipitated per mole of the compound. Write
  - (i) Structural formula of the complex
  - (ii) IUPAC name of the complex
- (a) For the complex [Fe(CN)<sub>6</sub>]<sup>4-</sup>, write the hybridization, magnetic character and spin type of the complex. (At. number : Fe = 26)
  - (b) Draw one of the geometrical isomers of the complex  $[Co(en)_2Cl_2]^+$  which is optically active.

# **CBSE 2015**

- (i) Write down the IUPAC name of the following complex: [Pt(NH<sub>2</sub>)(H<sub>2</sub>O)Cl<sub>2</sub>]
- (ii) Write the formula for the following complex: tris(ethan-1, 2-diamine)chromium(III) chloride
- (i) What type of isomerism is shown by [Co(NH<sub>2</sub>)<sub>5</sub>ONO]Cl<sub>2</sub>?
  - (ii) On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_0 < P$ .
  - (iii) Write the hybridization and shape of [Fe(CN)<sub>6</sub>]<sup>3</sup>. (Atomic number of Fe = 26)

# **CBSE 2014**

- Write the IUPAC name of the complex [Cr(NH<sub>3</sub>)<sub>4</sub> Cl<sub>2</sub>]Cl. 1.
- What type of isomerism is exhibited by the complex  $[Co(en)_3]^{3+}$ ? 2. (en = ethane-1, 2-diamine)
- Why is  $[NiCl_4]^{2-}$  paramagnetic but  $[Ni(Co)_4]$  is diamagnetic? (At. nos. : Cr = 24, Co = 27, Ni = 28)

#### **CBSE 2013**

- For the complex [NiCl<sub>4</sub>]<sup>2-</sup>, write
  - (i) The IUPAC name.
  - (ii) The hybridization type.
  - (iii) The shape of the complex. (Atomic number of Ni = 28)

What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of  $d^4$  in terms of  $t_{2g}$  and  $e_g$  in an octahedral field when (i)  $\Delta_0 > P$  (ii)  $\Delta_0 < P$ 

#### **CBSE 2012**

- Name the following coordination entities and describe their structures (At. No. of Fe = 26, Cr = 24, Ni = 28) (ii)  $[C_{J}(NH_{3})_{4}Cl_{2}]^{+}$  (iii)  $[Ni(CN)_{4}]^{2-}$ 
  - (i) [Fe(CN)<sub>6</sub>]<sup>4</sup>

- Name the following coordination entities and draw the structures of their stereo isomers.
  - (i)  $[Co(en)_2Cl_2]^+$  (en = ethane, 2-diamine)
- (ii) [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3</sup>-
- (iii) [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]

(At. No. of Cr = 24, Co = 27)

- Write the IUPAC name of  $[Pt(NH_3)_4Cl_2]Cl_2$ .
- Write the IUPAc name of [Cr(NH<sub>3</sub>)<sub>6</sub>][Co(CN)<sub>6</sub>].
- **3**. Write the IUPAC name of  $[Cr(NH_3)_5(NCS)][ZnCl_4]$ .
- What do you understand by stepwise stability constant and overall stability constant of a coordination compound How are these two constants related?
- Explain the following terms giving a suitable example in each case.
  - (i) Ambidentate ligand
  - (ii) Denticity of ligand
  - (iii) Crystal field splitting in an octahedral field.
- Write the structures and names of all the stereo isomers of the following compounds.
  - (i) [Co(en)<sub>3</sub>]Cl<sub>2</sub>
- (ii) [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]
- (iii) [Fe(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl
- Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities.
  - (i) [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl
- (ii) [Co(en)<sub>3</sub>]Cl<sub>3</sub>
- (iii) K<sub>2</sub>[Ni(CN)<sub>4</sub>]

# **CBSE 2010**

- Explain the following cases giving appropriate reasons.
  - (i) Nickel does not form low spin octahedral complexes.
  - (ii) The  $\pi\mbox{-complexes}$  are known for the transition metals only.
  - (iii)  $Co^{2+}$  is easily oxidised to  $Co^{3+}$  in the presence of a strong ligand.
- Write the name, the state of hybridization, the shape and magnetic behaviour of the following complexes.  $\begin{array}{l} [\text{CoCl}_4]^{2-}, [\text{Ni}(\text{CN})_4]^{2-}, [\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^{-} \\ (\text{At. No. of Co} = 27, \, \text{Ni} = 28, \, \text{Cr} = 24) \end{array}$
- Write the IUPAC name and deduce the geometry and magnetic behaviour of the complex  $K_4[Mn(CN)_6]$ . (Atomic number of Mn = 25)

# **CBSE 2009**

- Giving a suitable example for each explain the following:
  - (i) Crystal field splitting
- (ii) Linkage isomerism
- (iii) Ambidentate ligand
- Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbital  $[Co(NH_3)_6]^{3+}$ ,  $[Cr(NH_3)_6]^{3+}$ ,  $Ni(CO)_4$ (Atomic number of Co = 27, Cr = 24, Ni = 28)
- Explain the following
  - (i) Low spin octahedral complexes of nickel are not known.
  - (ii) The  $\pi$ -complexes are known for transition elements only.
  - (iii) CO is a stronger ligand than NH<sub>3</sub> for many metals.
- Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbital shapes of units, magnetic behaviour and hybrid orbital shapes of units.
  - (i) [Ni(CN)<sub>4</sub>]<sup>2-</sup>,
  - (Atomic number of Ni = 28, Co = 27)
- (iii) [CoF<sub>6</sub>]<sup>3</sup>-
- (i) Write the IUPAC name and indicate the shape of the complex ion [Co(en)<sub>2</sub>Cl(ONO)]<sup>+</sup>.
  - (ii) What is meant by chelate effect?
- Describe with an example of each, the role of coordination compounds in (i) biological system (ii) analytical characteristic (iii) medicinal chemistry.



# **EXERCISE-1**

# SOLUTION PREVIOUS YEARS BOARD PROBLEMS

# COORDINATION COMPOUND

### **CBSE 2016**

Sol.1. (i) [Ni(H<sub>2</sub>O)<sub>6</sub>] Cl<sub>2</sub>

(ii) Hexaaquanickel(II) chloride

Sol.2 (a)  $d^2sp^3$ ,

Diamagnetic,

low'spin

# **CBSE 2015**

- Sol.1 (i) Ammineaquadichloridoplatinum(II)
  - (ii) [Cr(en)<sub>3</sub>]Cl<sub>3</sub>
- Sol.2 (i) Linkage isomerism
  - (ii) t<sub>2</sub>g<sup>3</sup> eg<sup>1</sup> / Diagrammatic representation
  - (iii) d<sup>2</sup>sp<sup>3</sup>, Octahedral

### **CBSE 2014**

Tetraamminedichloridochromium(III) chloride Sol.1

Sol.2

# **Optical Isomer**

In Ni(CO)<sub>4</sub>, Ni is in zero oxidation state whereas in NiCl<sub>4</sub><sup>2-</sup>, it is in +2 oxidation state. In the presence Sol.3 of CO ligand, the unpaired d electrons of Ni pair up but Cl being a weak ligand is unable to pair up the unpaired electrons.



Sol.1 [NiCl<sub>4</sub>]2-

- (1) Tetrachlorido nickelate (II) ion
- $(2) sp^3$
- (3) tetrahedral

OR

The difference of energy two sets of d-orbitals (which are no longer degenerate under different kinds of electric fields).

Is called crystal field stabilization energy or (CFSE) represented by symbol  $\Delta_0$ .

 $d^4$  when  $\Delta_0 > P$ 

t4 eg°.

 $d^4$  when  $\Delta_0 < P$ 

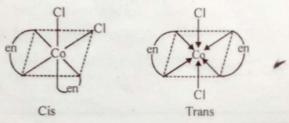
t3 eg1.

### **CBSE 2012**

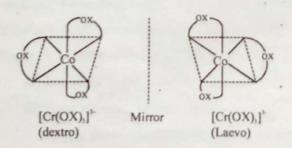
Sol.1 (i) Hexa cyanido Ferrete(II) d<sup>2</sup>sp<sup>3</sup>

- (ii) Tetraamminedichlorido chromium(II) ion, d2sp3
- (iii) Tetracynidonickelt(II) dsp2

Sol.2 (i) Dichlorido bis ethylenediamine cobalt (III) ion



(ii) Trioxalato chromate (III) ion



(iii) Triamine trichlorido cobalt (III)



- Sol.1 Tetra aminedichloridoplatinum(IV) chloride
- Sol.2 Hexaaminechromium(III) hexacynido coboltate(III)
- Sol.3 Pentaammineiso thiocyanats chromium
- Sol.4 The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association; quantitative expresses the stability. Thus, in reaction of the type:

$$M + 4L \rightarrow ML_4$$

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

larger the stability constant, the higher is the proportion of ML4 that exists in solution.

# Factors on which stability of the complex depends:

- Charge on the central metal ion: Greater the charge on the central metal ion, greater is the stability of the complex.
- . (ii) Nature of the metal ion: Groups 3 to 6 and inner transition elements form stable complexes when donor atoms of the ligands are N, O and F. The elements after group 6 of the transition metals which have relatively d-orbitals (e.g., Rh, Pd, Ag, Au, Hg etc.) form stable complexes when the donor atoms of the ligands are heavier members of N, O and F family.
  - (iii) Basic nature of the ligand: Greater the basic strength of the ligand, greater is the stability of the complex.
  - (iv) Presence of chelate rings: In the complex increases its stability. It is called chelate effect. It is maximum for the 5-and 6-membered rings.
  - (v) Effect of multidentate cyclic ligands: If the ligands happen to the multidentate and cyclic without any steric effect, the stability of the complex is further increased.
- Sol.5 (i) Ambidentate ligand: Ligand which can link through two different atoms is called ambident ligand.

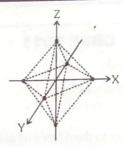
  Example SCN, CNO, CN, NO<sub>2</sub> can link through 'N' as well as O while SCN can link through 'S' as well 'N' atom.
  - (ii) Denticity of a ligand: Total number of lone pair donated by a ligand when it is bonded with metal is called denticity or number of doner sites on a ligand is called denticity.

(iii) Crystal field spliting in an octahedral field: In a octahedral complex, the co-ordination number is
 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

We know that two orbitals,  $d_{x^2-y^2}$  and  $d_{z^2}$  are oriented along the axis while the remaining three orbitals, viz.,  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  are oriented in between the axis.

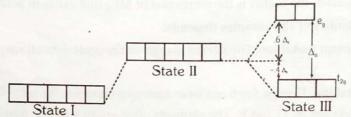
The two orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$  are designated as  $e_g$  orbitals while the three orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  are designated as  $t_{2g}$  orbitals. As the six ligands approach the central ion along the axis,  $e_g$  orbitals, is repelled more by the ligand than the  $t_{2g}$  orbitals.





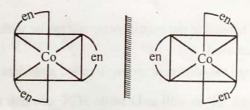
In other words, the energy of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals increases much more than the energy of the  $d_{xy}$   $d_{yz}$  and  $d_{zx}$  orbitals.

Thus, in octahedral complexes, the five d-orbitals split up into two sets: one set consisting of two orbitals  $(d_{x^2-y^2} \text{ and } d_{z^2})$  of higher energy  $(e_g \text{ orbitals})$  and the other set consisting of three orbitals  $(d_{xy}, d_{yz} \text{ and } d_{zx})$  of lower energy  $(t_{2g} \text{ orbitals})$ .



The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting discussed above.

Sol.6 (i) Trisethan-1,2-diamminecobalt(II) chloride



### (ii) Diamminedichlorido phtinum (II)

# (iii) Tetraammine dichloridoison(III) chloride

E



- Sol.7 (i) d<sup>2</sup>sp<sup>3</sup> / octahedral / paramagnetic
  - (ii) d<sup>2</sup>sp<sup>3</sup> / octahedral / Diamagnetic
  - (iii) dsp2 / square planner / Diamagnetic

- Sol.1 (i) Since nickel in zero oxidation state contain no unpaired electron.
  - (ii) The transition metal/ions have electrons in d- orbitals which can be shared to  $\pi$  -acid ligands through synergic bonding.

For example :  $CH_2 = CH_2$  and  $C_6 H_6$  etc.

- (iii) Co3+ can from very stable low spin octahedral complex.
- Sol.2 (i) sp<sup>3</sup> / Tetrahedral / paramagnetic
  - (ii) dsp<sup>2</sup> / squareplanner / Diamagnetic
  - (iii) d<sup>2</sup>sp<sup>3</sup> / octahedral/ Diamagnetic
- Sol.3 d<sup>2</sup>sp<sup>3</sup> / octahedral / Diamagnetic

Potassium hexa cynomengnate(II)

# **CBSE 2009**

- Sol.1 (i) Crystal field splitting: In a free transition metal ion, all the five orbitals are degenerate, but when it is involved in a complex formation, the degeneracy split. This is called crystal field splitting.
  - (ii) Linkage isomerism: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS.
  - (iii) Ambidentate ligand: Unidentate ligands containing more than one coordinating atoms are called ambidentate ligands. For example,

NO<sub>2</sub>, CN, SCN are all ambidentate ligands.

Sol.2	,
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S. No.	Complexes	Magnetic behaviour	Hybridisation	Shape
1	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	Diamagnetic	d <sup>2</sup> sp <sup>3</sup>	Octahedral
2	$[Cr(NH_3)_6]^{3+}$	Paramagnetic	d <sup>2</sup> sp <sup>3</sup>	Octahedral
3	[Ni(CO) <sub>4</sub> ]	Diamagnetic	sp <sup>3</sup>	Tetrahedral

- Sol.3 (i) Ni in its atomic or ionic state can not afford two vacant 3d orbitals hence d<sup>2</sup>sp<sup>3</sup> hybridisation is not possible.
  - (ii) Transition metals have vacant d orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing p electrons, e.g., C<sub>6</sub>H<sub>6</sub>, CH<sub>2</sub> = CH<sub>2</sub>, etc. Thus, dp-Pp bonding is possible.
  - (iii) Because in case of CO back bonding takes place in which the central metal uses its filled d orbital with empty anti bonding p\* molecular orbital of CO.



Sol.4 (i) dsp2 / squareplanner / Diamagnetic

- (ii) sp1 / Tetrahedral / paramagnetic
- (iii) Sp3d2 / octahedral / paramagnetic

# Sol.5 (i) Octahedral

bisethan-1,2-diaminechloridonitrito-0-Calalt(III) ion

(ii) When a didentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six membered ring is formed, the effect is called chelate effect. Example,

## Sol.6 Biological System :-

- (i) Haemoglobin, the oxygen carrier in blood, is a coordination compound of Fe2\* with parptyrin.
- (ii) The pigment chlorophyl in plants, responsible for photosynthesis, is a coordination compound of megnisium.
- (iii) Vitamin B, also called cobalamin, is a coordination compound of cobalt.

### Analytical Chemistry :-

- (i) Deptection of Cu2+
- (ii) Estimation of hardness of water
- (iii) Ni2+ is detected by the formation of a red complex with dimethyl glyoxime (DMG).
- (iv) The separation of Ag\* and Hg2\* in group I is based on the fact that AgCl dissolves in NH3, while Hg.Cl, makes a insoluble black substance with it.

## Medicinal Chemistry :-

- (i) The platinum complex cis-[Pt (NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], commonly known as cis- platin, is ased in the treatment of cancer.
- (ii) EDTA complex of calcium is used in the treatement of lead posioning.
- (iii) The excess of copper and iron presentg in animal system are removed by the chelating ligands

  D-penicillamine and desferrioxine B via the formation of complexes.