CHAPTER

23

Coordination Compounds

Key Notes and Formulae

Coordination Compounds

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds, the central metal atom or ion is linked by ions or molecules with coordinate bonds. e.g., Potassium ferrycyanide, $K_4[Fe(CN)_6]$.

Double Salts

These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr's salt. $[FeSO_4\ (NH_4)_2SO_4\ 6H_2O]$ get dissociated into Fe^{2+}, NH_4^+ and SO_4^{2-} ions.

Ligands

Ligand is electron donating species (ions or molecules) bound to the central atom in the coordination entity.

(i) Unidentate : It is a ligand, which has one donor site, i.e, the ligand bound to a metal ion through a single donor site, e.g., H_2O, NH_3, etc.

(ii) Didentate: It is the ligand, which have two donor sites.

(iii) Polydentate: It is the ligand, which have several donor sites.

Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g., in $[PtCl_6]^{2-}$, Pt has coordination number

In case of Monodentate Ligands

Coordination number = number of ligands

In polydentate Ligands,

Coordination number = number of ligands x denticity

Werner's Theory

Metals exhibit two types of valencies in the formation of complexes. These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.
2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Inner and Outer Orbital Complexes

When outer d-orbital are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2. They have octahedral shape.

Spectrochemical Series

A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called spectrochemical series.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO.$

Stability of Coordination Compounds

The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).

e.g., $M^+ + nL^{x-} \rightleftharpoons [MLn]y-;$ $\qquad K = \frac{[ML_n)^{y-}]}{[M^+][L^{x-}]^n}$

Previous Years' Questions

NEET

1. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are **[July 2016]**

(a) 4 and 8 (b) 4 and 2

(c) 6 and 6 (d) 8 and 4

2. AlF_3 is soluble in HF only in presence of KF. It is due to the formation of **[July 2016]**

(a) $K[AlF_3H]$ (b) $K_3[AlF_3H_3]$

(c) $K_3[AlF_6]$ (d) AlH_3

3. Among the following, which one is a wrong statement? **[July 2016]**

(a) I^+_3 has bent geometry.

(b) PH_5 and $BiCl_5$ do not exist.

(c) $p\pi - d\pi$ bonds are present in SO_2

(d) SeF_4 and CH_4 have same shape.

4. Which of the following has longest C-O bond length (free C-O bond length in CO is 1.128 A)? **[May 2016]**

(a) $Ni(CO)_4$ (b) $[CO(CO)_4]^-$

(c) $[Fe(CO)_4]^{2-}$ (d) $[Mn(CO)_6]^{6+}$

5. An excess of $AgNO_3$ is added to 100mL of a 0.01 M solution of dichlorotetraaquachromium (111) chloride. The number of moles of AgCl precipitated would be **[2013]**

(a) 0.001 (b) 0.002

(c) 0.003 (d) 0.01

6. A magnetic moment at 1.73 BM will be shown by one among the following **[2013]**

(a) $TiCl_4$ (b) $[CoCl_6]^{4-}$

(c) $[Cu(NH_3)_4]^{2+}$ (d) $[Ni(CN)_4]^{2-}$

AIPMT

7. Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C ? **[2015]**

(a) $COCl_3.5NH_3$ (b) $COCl_3.6NH_3$

(c) $COCl_3.3NH_3$ (d) $COCl_3.4NH_3$

8. Which of these statements about $[Co(Cn)_6]^{3-}$ is true ? **[2015]**

(a) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high-spin configuration.

(b) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high configuration.

(c) $[CO(CN)_6]^{3-}$ has no unpaired electrons and will be in a low spin configuration

(d) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low -spin configuration.

9. Which of the following complexes is used to be as an anticancer agent ? **[2014]**

(a) mer-$[Co(NH_3)_3Cl_3]$

(b) cis-$[PtCl_2(NH_3)_2]$

(c) cis-$K_2[PtCl_2Br_2]$

(d) Na_2CoCl_4

10. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to

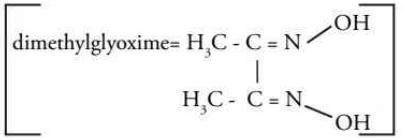
ammoniacal Ni(II). Which of the following statement is not true? **[2012]**

(a) Red complex has a square planar geometry

(b) Complex has symmetrical H- bonding

(c) Red complex has a tetrahedral geometry

(d) Dimetheyl Glyoxime functions as bidentate ligand



11. Low Spin Complex of d^6 Cation in an octahedral field will have the following energy **[2012]**

(a) $\frac{-12}{5}\Delta_0 + p$ (b) $\frac{-12}{5}\Delta_0 + 3p$

(c) $\frac{-2}{5}\Delta_0 + 2p$ (d) $\frac{-2}{5}\Delta_0 + p$

12. The complex, $[Pt(Py)(NH_3)BrCl]$ will have how many geometrical isomers? **[2011]**

(a) 4 (b) 0

(b) 2 (d) 3

13. The d-electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7 respectively. Which one of the following will exhibit minimum paramagnetic behaviour? **[2011]**

(a) $[Fe(H_2O)_6]^{2+}$ (b) $[CO(H_2O_6)]^{2+}$

(c) $[Cr(H_2O)_6]^{2+}$ (d) $[Mn(H_2O)_6]^{2+}$

14. Which of the following complex ions is not expected to absorb visible light ? **[2010]**

(a) $[Ni(CN)_4]^{2-}$ (b) $[Cr(NH_3)_6]^{3+}$

(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Ni(H_2O)_6]^{2+}$

15. The existance of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to **[2010]**

(a) linkage isomerism

(b) geometrical isomerism

(c) coordination isomerism

(d) ionization isomerism

16. Which of the following complex ions is expected to absorb visible light? **[2009]**

(a) $[Ti(en)_2(NH_3)_2]^{4+}$

(b) $[Cr(NH_3)_6]^{3+}$

(c) $[Zn(NH_3)_6]^{2+}$

(d) $[Co(en)_2Cl_2]^+$

Answer key

1. (d)	2. (c)	3. (d)	4. (c)	5. (a)	6. (c)	7. (c)	8. (c)
9. (b)	10. (c)	11. (b)	12. (d)	13. (b)	14. (a)	15. (d)	16. (b)

Detailed Solutions

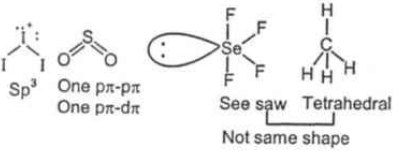
1. **(d).** Ca^{2+} is surrounded by $8F^-$

F^- is surrounded by $4Ca^{+2}$

2. **(c).** $AlF_3 + KF \xrightarrow{HF} K_3[AlF_6]$

(maximum C.N. of Al^{+3} is six so it forms AlF_6^{3-}).

3. **(d).**



4. **(c).** $[Fe(CO)_4]^{2-}$ since metal atom is carrying maximum -ve charge therefore it would show maximum synergic bonding as a resultant C-O bond length would be maximum.

5. **(a).** The formula of dichlorotetradqua chromium (III) chloride is $[Cr(H_2O)_4Cl_2]Cl$

On ionisation it generates only one Cl^- ion

$[Cr(H_2O)_4Cl_2]\ Cl \rightarrow [Cr(H_2O)4Cl_2] + Cl^-$

initial 100 x0.01 0 0

=1mmol

After ionisation 0 1mmol 1mmol

one mole of Cl^- ions react with only 1 mole of $AgNO_3$ molecule and produce 1 mole of AgCl

$\therefore$ 1mmol or 1 x 10^{-3} mole reacts with $AgNO_3$ to give AgCl.

$= \frac{1\times1\times10^{-3}}{1} = 10^{-3}$ or 0.001 mol AgCl

6. **(c).** Oxidation state of Cu in $[Cu(NH_3)_4]^{2+}$ is +2 $Cu^{2+} = 3d^9$

It has one unpaired electron(n = 1)

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

$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM

7. **(c).** For octahedral complexes ,coordination number is 6

Hence, $COCl_3.3NH_3$ ie, $[Co(NH_3)_3Cl]$ will not ionise and will not give test for Cl^{-1} ion with silver nitrate.

8. **(c).** $[Co(CN)_6]^{3-}$, Oxidation no of Co = +3

$Co^{3+} = 3d^6$

As CN^- is a strong field ligand, so all electrons will be paired up and complex will be low spin complex.

9. **(b).** cis-platin is known as anticancer agent, The formula for cis-platin $[PtCl_2(NH_3)_2]$ Here, the word cis refers to cis geometrical isomer of $[PtCl_2(NH_3)_2]$

10. **(c).** $[Ni(dmg)_2]$ is square planar in structure not tetrahedral.

11. **(b).** C.F.S.E = $(-0.4\ x + 0.6\ y)\ \Delta_0 + zP$

where x= number of electrons occupying t_{2g} orbital

y = Number of electrons occupying e_g orbital

z = number of pairs of electron

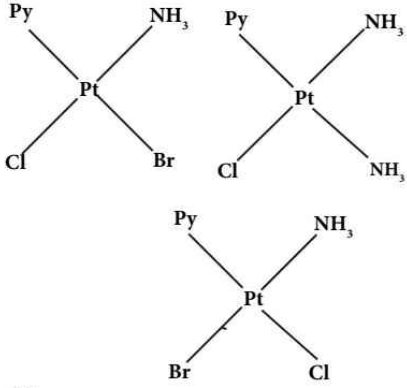
For low spin d^6 complex electronic configuration = $t_{2g}^6\ e_g^0$ or $t_{2g}^{2,2,2}\ e_g^0$

x = 6, y = 0, z = 3

C.F.S.E = $(-0.4 \times 6 + 0 \times 0.6)\ \Delta_0 + 3P$

$= (\frac{-12}{5}\Delta_0 + 3P)$

12. **(d).** The complex is square planar and is of the type [M (abcd)], It has three geometrical isomers.



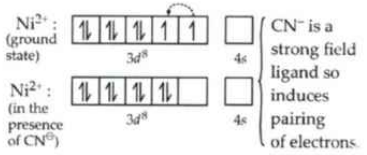
13. **(b).**

$Cr^{2+}: d^4$; $Mn^{2+} d^5$

$Fe^{2+}: d^6$; $Co^{2+}: d^7$

$[Co(H_2O)_6]^{2+}$ has minimum number of unpaired electrons and thus, minimum paramagnetic behaviour.

14. **(a).** A transition metal complex absorbs visible light only if it has unpaired electrons.



No unpaired electron so does not absorb visible light.

15. **(d).**

16. **(b).** $Ti^{4+} \rightarrow 3d^0$, $Cr^{3+} \rightarrow 3d^3$
$Zn^{2+} \rightarrow 3d^{10}$ $Sc^{3+} \rightarrow 3d^0$
Transition metal ions containing completely filled d - orbitals or empty d- orbital are colourless species.