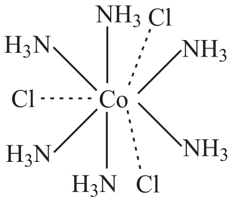
Coordination Compounds

Recap Notes

- **Werner's coordination theory :**
  - ▶ It explains the nature of bonding in complexes. Metals show two different kinds of valencies:
    - – **Primary valency :** Non directional and ionisable. It is equal to the oxidation state of the central metal ion.
    - – **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or sometimes by positively charged ligands.
  - ▶ The ionisation of the coordination compound is written as :
    $[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$



$[Co(NH_3)_6]Cl_3$
Representation of $CoCl_3 \cdot 6NH_3$ complex according to Werner's theory

- **Addition compounds :** The compounds formed by combination of two or more simple compounds are called *addition compounds*. They are of two types :
  - ▶ **Double salt :** A compound formed by combination of two or more simple compounds, which is stable in solid state only is called *double salt*. In solution it breaks into component ions. *e.g.*,

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$;	Potash alum
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$;	Mohr's salt
$KCl \cdot MgCl_2 \cdot 6H_2O$;	Carnallite

  - ▶ **Complex compound :** A compound formed by combination of two or more simple compounds which retain its identity both in solid and solution states is called *complex compound*.
    e.g., $K_4[Fe(CN)_6]$, Potassium ferrocyanide
    $[Cu(NH_3)_4]SO_4$, Cupramine sulphate

- **Some important terms pertaining coordination compound :**
  - ▶ **Coordination entity :** The central metal atom or ion and ligand taken together is called *coordination entity*. It may be positive, negative or neutral.
    e.g., $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$, $[Ni(CO)_4]$
  - ▶ **Central atom :** The atom or ion with which definite number of ligands are attached in a definite geometry is called *central atom/ion*. Any atom/ion which has high positive charge density or vacant orbitals of suitable energy may be central atom or ion, *e.g.,* transition metals, lanthanoids. It is Lewis acid (electron acceptor).
  - ▶ **Ligands :** Molecules or ions which are bound to the central atom/ion in the coordination entity are called *ligands*. A molecule or ion which has high negative charge or dipole or lone pair of electrons may be ligands. It is Lewis base (electron donor).

- **Classification of ligands :**

Ligands

- **On the basis of charge**
  - **Negative ligands** CN^-, F^-, Cl^-, NO_2^-, NO_3^-, OH^-, O^{2-}
  - **Positive ligands** NO_2^+, NO^+, $N_2H_5^+$
  - **Neutral ligands** $H_2\ddot{\underset{\cdot\cdot}{O}}$, $\ddot{N}H_3$, CO, NH_2OH, $CH_3\ddot{N}H_2$
- **On the basis of number of donor sites**
  - **Monodentate :** Only one donor site *e.g.*, H_2O, NH_3
  - **Bidentate :** Two donor sites *e.g.*, $\underset{\text{(Oxalato)}}{(COO^-)_2}$, $\underset{\text{(Ethylenediamine)}}{\begin{array}{l}CH_2—NH_2\\ \;|\\ CH_2—NH_2\end{array}}$
  - **Polydentate :** More than two donor sites *e.g.*, EDTA (Hexadentate)
- **On the basis of bonding**
  - **Chelating ligands :** A bidentate or polydentate ligand which forms more than one coordinate bonds in such a way that a ring is formed. $\underset{\text{(Ethylenediamine)}}{\begin{array}{l}CH_2—NH_2\\ \;|\\ CH_2—NH_2\end{array}}$
  - **Ambidentate ligands :** Monodentate ligand which contains more than one coordinating atom (or donor atom).

$$M \longleftarrow O^-—N{=}O, \quad M \longleftarrow SCN, \quad M \longleftarrow CN$$

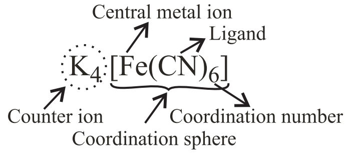
$$\text{or} \qquad\qquad \text{or} \qquad\qquad \text{or}$$

$$M \longleftarrow N\begin{array}{l}\nearrow\!\!{=}O\\ \searrow O^-\end{array} \quad M \longleftarrow NCS \quad M \longleftarrow NC$$

- **Coordination number (C.N.) :** The total number of coordinate bonds through which the central metal atom or ion is attached with ligands is known as coordination number. Examples : $[Ag(CN)_2]^-$: C.N. = 2, $[Cu(NH_3)_4]^{2+}$: C.N. = 4, $[Cr(H_2O)_6]^{3+}$: C.N. = 6
- **Coordination sphere :** The central atom and the ligands which are directly attached are collectively known as coordination sphere. It is non-ionisable and written enclosed in square brackets. The ionisable groups are written outside the brackets.

  Example :

$$\underset{\substack{\text{Coordination}\\\text{sphere}}}{[Cu(NH_3)_4]}\,\underset{\substack{\text{Ionisable}\\\text{group}}}{SO_4} \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$



- **Coordination polyhedron :** The spatial arrangement of the ligand atoms which are directly attached to the central atom defines a coordination polyhedron about the central atom, *e.g.*, $[(Co(NH_3)_6)]^{2+}$ is octahedral $[Ni(CO)_4]$ is tetrahedral. Octahedral is most common coordination polyhedron.

- **Homoleptic and heteroleptic complexes:**
  - **Homoleptic complexes :** Complexes in which a metal is bound to only one kind of ligands are called *homoleptic complexes*. *e.g.,* $[Co(NH_3)_6]^{3+}$, $[Ti(H_2O)_6]^{3+}$, $[Cu(CN)_4]^{3-}$
  - **Heteroleptic complexes :** Complexes in which the central atom is bound to different type of ligands are called *heteroleptic complexes*. *e.g.,* $[Co(NH_3)_4Cl_2]$, $K_2[Fe(CN)_5NO]$, $[Fe(H_2O)_5NO]SO_4$
- **Nomenclature of coordination compounds :**
  - **Rules for writing the formula of coordination compounds :**
  - Formula of the cation whether simple or complex must be written first, followed by anion.
  - The coordination sphere is written in square brackets.
  - Within the coordination sphere the sequence of symbols is, first the metal atom followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.
  - Polyatomic ligands are enclosed in parentheses.
  - The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.

- ▶ **Rules for naming coordination compounds :**
  - The cation is named first then the anion.
  - In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
  - The complex part is written as one word.
  - When the coordination sphere is anionic, name of central metal ends in –*ate*.
- ▶ **Naming of ligands :**
  - Name of anionic ligands end in –*o*.
    e.g., Cl^- : Chlorido
  - Neutral ligands (with a few exceptions) retain their names *e.g.,* NH_3 : Ammine
    Name of cationic ligands end in – *ium*.
    e.g., NO_2^+ : Nitronium
  - Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae.
    e.g., ethylenediamine(*en*).
  - Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
    e.g., —SCN^- (Thiocyanato-S or Thiocyanato), —NCS^- (Thiocyanato-N or Isothiocyanato), —ONO^- (Nitrito-O or Nitrito), —NO_2^- (Nitrito-N or Nitro)
  - The prefixes *di*-, *tri*-, *tetra*-, *penta*- and *hexa*- are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis*-(2), *tris*-(3), *tetrakis*-(4), *pentakis*-(5) and *hexakis*-(6).

- **Bonding in coordination compounds :**
  - ▶ **Valence bond theory :** It was developed by Pauling.
    - A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
    - Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon the total number of ligands.
    - The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

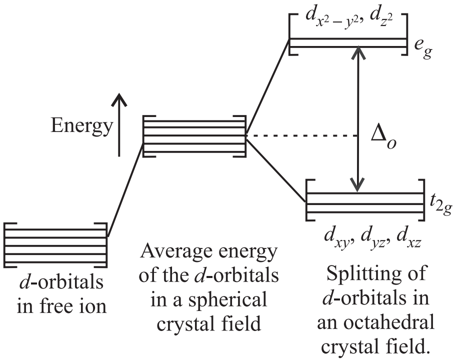
C. No.	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where, $X = Cl^-, Br^-, I^-$
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Inner orbital complexes	Outer orbital complexes
Involves inner *d*-orbitals *i.e.*, $(n-1)d$-orbitals.	Involves outer *d*-orbitals *i.e.*, nd-orbitals.
Low spin complexes	High spin complexes
Have less or no unpaired electrons. *e.g.*, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{4-}$	Have large number of unpaired electrons. *e.g.,* $[MnF_6]^{3-}$, $[CoF_6]^{3-}$

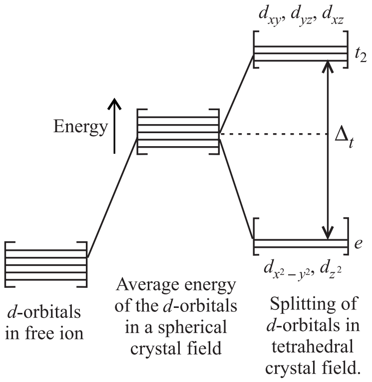
- Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
- Paramagnetism $\propto$ No. of unpaired electrons.
- Magnetic moment $= \sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

▶ **Crystal field theory :** It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength.

- Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.
- Crystal field splitting in octahedral coordination complexes is shown as :



- If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.
- If $\Delta_o > P$, then pairing of electrons takes place and a low spin complex is formed.
- Crystal field splitting in tetrahedral complexes is shown as :



- Difference in energy between e and t_2 level is less in tetrahedral complexes.

$$\Delta_t = \frac{4}{9}\Delta_o$$

- **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength.

$$\text{Weak field ligands} \xrightarrow{\text{Increasing order of CFSE } (\Delta_o)} \text{Strong field ligands}$$

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < \text{edta}^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

● **Colour of coordination compounds :** The magnitude of CFSE (Δ_o) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever *d-d* transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength absorbed.

Practice Time

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. The correct IUPAC name of the coordination compound $K_3[Fe(CN)_5NO]$ is

(a) potassium pentacyanonitrosylferrate(II)
(b) potassium pentacyanonitroferrate(III)
(c) potassium nitritopentacyanoferrate(IV)
(d) potassium nitritepentacyanoiron(II).

2. Ammonia acts as a very good ligand but ammonium ion does not form complexes because

(a) NH_3 is a gas while NH_4^+ is in liquid form
(b) NH_3 undergoes sp^3 hybridisation while NH_4^+ undergoes sp^3d hybridisation
(c) NH_4^+ ion does not have any lone pair of electrons
(d) NH_4^+ ion has one unpaired electron while NH_3 has two unpaired electrons.

3. Correct formula of tetraamminechloridonitroplatinum(IV) sulphate can be written as

(a) $[Pt(NH_3)_4(ONO)Cl]SO_4$
(b) $[Pt(NH_3)_4Cl_2NO_2]_2SO_4$
(c) $[Pt(NH_3)_4(NO_2)Cl]SO_4$
(d) $[PtCl(ONO)NH_3(SO_4)]$

4. The magnitude of magnetic moment (spin only) of $[NiCl_4]^{2-}$ will be

(a) 2.82 B.M. (b) 0
(c) 1.23 B.M. (d) 5.64 B.M.

5. Consider the following coordination compounds.

(i) $[Pt(NH_3)_4Cl_2]Br_2$ (ii) $[Pt(NH_3)_4Br_2]Cl_2$
(iii) $[Co(NH_3)_4Cl_2]NO_2$

Which of the following observations is correct?

(a) (i) will give a pale yellow and (ii) will give a white precipitate with $AgNO_3$ solution.
(b) (iii) will give a white precipitate with $AgNO_3$ solution.
(c) (i), (ii) and (iii) will give white precipitate with $AgNO_3$ solution.
(d) None of the above coordination compounds will give white precipitate with $AgNO_3$ solution.

6. Hexaamminenickel(II) hexanitrocobaltate(III) can be written as

(a) $[Ni(NH_3)_6][Co(NO_2)_6]$
(b) $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$
(c) $[Ni(NH_3)_6]\ [Co(NO_2)_6]$
(d) $[Ni(NH_3)_6(NO_2)_6]Co$

7. Which of the following is correct?

(a) Valence bond theory explains the colour of the coordination compounds.
(b) $[NiCl_4]^{2-}$ is diamagnetic in nature.
(c) EDTA is a chelating ligand.
(d) A bidentate ligand can have four coordination sites.

8. Electronic configuration of $[Cu(NH_3)_6]^{2+}$ on the basis of crystal field splitting theory is

(a) $t_{2g}^4\, e_g^5$ (b) $t_{2g}^6\, e_g^3$
(c) $t_{2g}^9\, e_g^0$ (d) $t_{2g}^5 e_g^4$.

9. Which of the following primary and secondary valencies are not correctly marked against the compound?

(a) $[Cr(NH_3)_6]Cl_3$ $p = 3, s = 6$
(b) $K_2[PtCl_4]$ $p = 2, s = 4$
(c) $[Pt(NH_3)_2Cl_2]$ $p = 2, s = 4$
(d) $[Cu(NH_3)_4]SO_4$ $p = 4, s = 4$

10. What will be the correct order of absorption of wavelength of light in the visible region for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$?

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$
(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
(d) $[Co(CN)_6]^{3-} > [Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+}$

11. Which of the following does not depict the correct name of the compound?

(a) $K_2[Zn(OH)_4]$: Potassium tetrahydroxozincate(II)

(b) $[Co(NH_3)_5CO_3]Cl$: Pentaammine carbonatochlorocobaltate(III)
(c) $Na_3[Co(NO_2)_6]$: Sodium hexanitrocobaltate(III)
(d) $K_3[Cr(CN)_6]$: Potassium hexacyanochromate(III)

12. When excess of ammonia is added to copper sulphate solution, the deep blue coloured complex is formed. The complex is
(a) tetrahedral and paramagnetic
(b) tetrahedral and diamagnetic
(c) square planar and diamagnetic
(d) square planar and paramagnetic.

13. Arrange the following complexes in increasing order of conductivity of their solutions.
(i) $[Co(NH_3)_3Cl_3]$ (ii) $[Co(NH_3)_4Cl_2]Cl$
(iii) $[Co(NH_3)_6]Cl_3$ (iv) $[Co(NH_3)_5Cl]Cl_2$
(a) (i) < (ii) < (iv) < (iii)
(b) (ii) < (i) < (iii) < (iv)
(c) (i) < (iii) < (ii) < (iv)
(d) (iv) < (i) < (ii) < (iii)

14. Which of the following complexes will have tetrahedral shape?
(a) $[PdCl_4]^{2-}$ (b) $[Pd(CN)_4]^{2-}$
(c) $[Ni(CN)_4]^{2-}$ (d) $[NiCl_4]^{2-}$

15. The name of $[Co(NH_3)_5NO_2]Cl_2$ will be
(a) pentaamminonitrocobalt(II) chloride
(b) pentaamminenitrochloridecobaltate(III)
(c) pentaamminenitrito-N-cobalt(III) chloride
(d) pentanitrosoamminechlorocobaltate(III).

16. Which of the following ligands form a chelate?
(a) Acetate (b) Oxalate
(c) Cyanide (d) Ammonia

17. Copper sulphate dissolves in ammonia due to the formation of
(a) Cu_2O (b) $[Cu(NH_3)_4]SO_4$
(c) $[Cu(NH_3)_4]OH$ (d) $[Cu(H_2O)_4]SO_4$

18. When excess of aqueous KCN solution is added to an aqueous solution of copper sulphate, the complex $[Cu(CN)_4]^{2-}$ is formed. On passing H_2S gas through this solution no precipitate of CuS is formed because
(a) sulphide ions cannot replace CN^- ions
(b) $[Cu(CN)_4]^{2-}$ does not give Cu^{2+} ion in the solution
(c) sulphide ions from H_2S do not form complexes
(d) sulphide ions cannot replace sulphate ions from copper sulphate solution.

19. Which of the following shall form an octahedral complex?
(a) d^4(low spin) (b) d^8(high spin)
(c) d^6(low spin) (d) None of these

20. The increasing order of crystal field splitting strength of the given ligands is
(a) $NH_3 < Cl^- < CN^- < F^- < CO < H_2O$
(b) $F^- < Cl^- < NH_3 < CN^- < H_2O < CO$
(c) $Cl^- < F^- < H_2O < NH_3 < CN^- < CO$
(d) $CO < CN^- < NH_3 < H_2O < F^- < Cl^-$

21. The number of unpaired electrons in $[Ni(CO)_4]$ is
(a) one (b) two
(c) three (d) zero

22. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ show different colours in dilute solution because
(a) CN^- is a strong field ligand and H_2O is a weak field ligand hence magnitude of CFSE is different
(b) both CN^- and H_2O absorb same wavelength of energy
(c) complexes of weak field ligands are generally colourless
(d) the sizes of CN^- and H_2O are different hence their colours are also different.

23. In which of the following compounds, the transition metal is in oxidation state of zero?
(a) $[Fe(H_2O)_3(OH)_3]$ (b) $[Ni(CO)_4]$
(c) $[Fe(H_2O)_6]SO_4$ (d) $[Co(NH_3)_6]Cl_3$

24. A substance appears coloured because
(a) it absorbs light at specific wavelength in the visible part and reflects rest of the wavelengths
(b) ligands absorb different wavelengths of light which give colour to the complex
(c) it absorbs white light and shows different colours at different wavelength
(d) it is diamagnetic in nature.

25. Which of the following statements is correct about $[Co(H_2O)_6]^{2+}$ complex?
(a) Electronic configuration = $3d^7 \rightarrow t_{2g}^5 e_g^2$, no. of unpaired electrons = 3, μ = 3.87 B.M.
(b) Electronic configuration = $3d^6 \rightarrow t_{2g}^4 e_g^2$, no. of unpaired electrons = 2, μ = 2.87 B.M.
(c) Electronic configuration = $3d^7 \rightarrow t_{2g}^6 e_g^1$, no. of unpaired electrons = 1, μ = 2.87 B.M.

(d) Electronic configuration = $3d^7 = t_{2g}^3 e_g^4$, no. of unpaired electrons = 3, μ = 3.87 B.M.

26. Hexacyano complexes of metals in their +2 oxidation state are usually yellow while the corresponding hexaaqua compounds are often blue or green. This is so because

(a) hexacyano complexes absorb orange or red light thus appear yellow while hexaaqua complexes absorb indigo thus appear yellow

(b) hexacyano complexes absorb indigo thus appearing yellow while hexaaqua complexes absorb orange or red light thus appear blue or green

(c) hexacyano complexes absorb yellow light while hexaaqua complexes absorb blue light

(d) CN^- ions are yellow in colour while aqua ions are blue or green in colour.

27. Low spin tetrahedral complexes are not formed because

(a) for tetrahedral complexes, the CFSE is lower than pairing energy

(b) for tetrahedral complexes, the CFSE is higher than pairing energy

(c) electrons do not go to e_g in case of tetrahedral complexes

(d) tetrahedral complexes are formed by weak field ligands only.

28. Which of the following sets of examples and geometry of the compounds is not correct?

(a) Octahedral – $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$

(b) Square planar – $[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$

(c) Tetrahedral – $[Ni(CO)_4]$, $[ZnCl_4]^{2-}$

(d) Trigonal bipyramidal – $[Fe(NH_3)_6]^{2+}$, $[CuCl_4]^{2-}$

29. A coordination compound $CrCl_3 \cdot 4H_2O$ gives white precipitate of AgCl with $AgNO_3$. The molar conductance of the compound corresponds to two ions. The structural formula of the compound is

(a) $[Cr(H_2O)_4Cl_3]$ (b) $[Cr(H_2O)_3Cl_3]H_2O$

(c) $[Cr(H_2O)_4Cl_2]Cl$ (d) $[Cr(H_2O)_4Cl]Cl_2$

30. Among the following, which are ambidentate ligands?

(i) SCN^- (ii) NO_3^-

(iii) NO_2^- (iv) $C_2O_4^{2-}$

(a) (i) and (iii) (b) (i) and (iv)

(c) (ii) and (iii) (d) (ii) and (iv)

31. The lowest value of paramagnetism is shown by

(a) $[Co(CN)_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Cr(CN)_6]^{3-}$ (d) $[Mn(CN)_6]^{3-}$

32. Which of the following is a tridentate ligand?

(a) $EDTA^{4-}$ (b) $(COO)_2^{2-}$

(c) dien (d) NO_2^-

33. Which of the following has largest paramagnetism?

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$

(c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_2]^{2+}$

34. Identify the statement which is not correct?

(a) Coordinate compounds are mainly known for transition metals.

(b) Coordination number and oxidation state of a metal are same.

(c) Tetrahedral complexes form low spin complex.

(d) A ligand donates at least one electron pair to the metal atom to form a bond.

35. When aqueous solution of potassium fluoride is added to the blue coloured aqueous $CuSO_4$ solution, a green precipitate is formed. This observation can be explained as follows.

(a) On adding KF, H_2O being weak field ligand is replaced by F^- ions forming $[CuF_4]^{2-}$ which is green in colour.

(b) Potassium is coordinated to $[Cu(H_2O)_4]^{2+}$ ion present in $CuSO_4$ and gives green colour.

(c) On adding KF, Cu^{2+} are replaced by K^+ forming a green complex.

(d) Blue colour of $CuSO_4$ and yellow colour of KI form green colour on mixing.

36. The formula of the complex diamminechlorido (ethylenediamine)nitroplatinum(IV) chloride is

(a) $[Pt(NH_3)_2Cl(en)NO_2]Cl_2$

(b) $Pt[Pt(NH_3)_2(en)Cl_2NO_2]$

(c) $Pt[(NH_3)_2(en)NO_2]Cl_2$

(d) $Pt[(NH_3)_2(en)NO_2Cl_2]$

37. Using valence bond theory, the complex $[Cr(H_2O)_6]^{3+}$ can be described as

(a) sp^3d^2, outer orbital complex, paramagnetic

(b) dsp^2, inner orbital complex, diamagnetic

(c) d^2sp^3, inner orbital complex, paramagnetic

(d) d^2sp^3, outer orbital complex, diamagnetic.

38. The ligand $N(CH_2CH_2NH_2)_3$ is

(a) bidentate (b) tridentate

(c) tetradentate (d) pentadentate.

39. Which of the following is not correctly matched?

(a) Coordination compound containing cationic complex ion : $[Fe(H_2O)_2(C_2O_4)_2]_2SO_4$

(b) Coordination compound containing anionic complex ion : $[Ag(NH_3)_2]Cl$

(c) Non-ionic coordination compound : $[Co(NO_2)_3(NH_3)_3]$

(d) Coordination compound containing cationic and anionic complex ion : $[Pt(NH_3)_4]$ $[CuCl_4]$

40. A coordination compound X gives pale yellow colour with $AgNO_3$ solution while its isomer Y gives white precipitate with $BaCl_2$. Two compounds are isomers of $CoBrSO_4{\cdot}5NH_3$. What could be the possible formula of X and Y?

(a) $X = [Co(NH_3)_5SO_4]Br$, $Y = [Co(NH_3)_5Br]SO_4$

(b) $X = [Co(NH_3)_5Br]SO_4$, $Y = [Co(NH_3)_5SO_4]Br$

(c) $X=[Co(NH_3)_5Br(SO_4)]$, $Y=[CoBr(SO_4)(NH_3)_5]$

(d) $X = [Co(Br)_5NH_3]SO_4$, $Y = [CoBr(SO_4)]NH_3$

41. When one mole of each of the following complexes is treated with excess of $AgNO_3$ which will give maximum amount of AgCl?

(a) $[Co(NH_3)_6]Cl_3$ (b) $[Co(NH_3)_5Cl]Cl_2$

(c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$

42. Which of the following descriptions about $[FeCl_6]^{4-}$ is correct about the complex ion?

(a) sp^3d, inner orbital complex, diamagnetic

(b) sp^3d^2, outer orbital complex, paramagnetic

(c) d^2sp^3, inner orbital complex, paramagnetic

(d) d^2sp^3, outer orbital complex, diamagnetic

43. According to Werner's theory of coordination compounds,

(a) primary valency is ionisable

(b) secondary valency is ionisable

(c) primary and secondary valencies are ionisable

(d) neither primary nor secondary valency is ionisable.

44. $CuSO_4{\cdot}5H_2O$ is blue in colour while $CuSO_4$ is colourless due to

(a) presence of strong field ligand in $CuSO_4{\cdot}5H_2O$

(b) due to absence of water (ligand), *d-d* transition are not possible in $CuSO_4$

(c) anhydrous $CuSO_4$ undergoes *d-d* transitions due to crystal field splitting

(d) colour is lost due to loss of unpaired electrons.

45. Which of the following complexes will show maximum paramagnetism?

(a) $3d^4$ (b) $3d^5$

(c) $3d^6$ (d) $3d^7$

46. Among the following compounds which is both paramagnetic and coloured?

(a) $K_2Cr_2O_7$ (b) $[Co(SO_4)]$

(c) $(NH_4)_2[TiCl_6]$ (d) $K_3[Cu(CN)_4]$

47. Which of the following rules is not correct regarding IUPAC nomenclature of complex ions?

(a) Cation is named first and then anion.

(b) In coordination sphere, the ligands are named alphabetically.

(c) Positively charged ligands have suffix 'ate'.

(d) More than one ligand of a particular type are indicated by using di, tri, tetra, etc.

48. Mark the correct statements regarding the geometry of complex ions.

(i) The geometry of the complex ion depends upon the coordination number.

(ii) If coordination number is 6, the complex is octahedral.

(iii) If coordination number is 4, the geometry of the complex may be tetrahedral or square planar.

(a) (i), (ii) and (iii) (b) (i) and (ii) only

(c) (i) and (iii) only (d) (ii) and (iii) only

49. Which of the following is not a neutral ligand?

(a) H_2O (b) NH_3

(c) ONO (d) CO

50. In coordination compounds metals show two type of linkages : primary and secondary. Primary valency is ionisable and corresponds to conductivity. Several coordination compounds are formed by Co(III) with ligand NH_3 and Cl^- both.

Conductivity of complex I corresponds to 1 : 3 electrolyte, conductivity of complex II corresponds to 1 : 2 electrolyte while conductivity of complex 3 and 4 corresponds to 1 : 1 electrolyte. So correct option about these complexes is

(a) complex I is $[(Co(NH_3)_6]Cl_3$ with purple colour

(b) complex II is $[(Co(NH_3)_6]Cl_3$ with purple colour

(c) complex III is $[Co(NH_3)_4Cl_2]Cl$ with violet colour

(d) both (b) and (c)

51. Ms. Anjali class 12th chemistry teacher explained IUPAC nomenclature of coordination compounds in her class. Then she asked students to write the names of 5 coordination compounds. Kavya written these five names :

$[Cr(NH_3)_3(H_2O)_3]Cl_3$ - Triamminetriaqua chromium(III)chloride, $[Ag(NH_3)_2][Ag(CN)_2]$ Diamminesilver(I) dicyanidosilver(I)

$[CoCl_2(en)_2]Cl$-Dichloridobis(ethane-1, 2-diammine) cobalt (III) chloride

$K_3[Al(C_2O_4)_3]$ - Potassium trioxalatoaluminium (III)

$[Ni(CO)_4]$-Tetracarbonylnickel(0)

Few names given by her were not correct as she didn't follow one rule while naming these compounds. That one rule is

(a) the ligands are name in an alphabetical order before the name of central atom/ion.

(b) prefixes mono, di, tri etc. are used to indicate the number of individual ligands in the coordination entity.

(c) if the complex ion is cation, the metal is named same as the element.

(d) if the complex ion is anion, the metal ends with suffix – ate.

52. $Fe^{x+} + SCN^- \longrightarrow$ Octahedral complex

$Fe^{y+} + CN^- \longrightarrow$ Octahedral complex

(x and y may or may not be equal)

The difference between the spin-only magnetic moments is 4.2 B.M. approximately. The reason for this difference in magnetic moment is

(a) CN^- is a strong ligand while SCN^- is a weak ligand

(b) Fe is present in O.S. I in complex with SCN^- while in O.S. III in complex with CN^-

(c) SCN^- is a strong ligand while CN^- is a weak ligand

(d) x is 3 while y is 1.

53. If a ligand is weak, the complex will be high spin while if the ligand is strong then the complex will be low spin. Here few complexes are listed:

I. $[Cr(H_2O)_6]^{2+}$	II. $[CoCl_4]^{2-}$
III. $[Fe(H_2O)_6]^{2+}$	IV. $[Mn(H_2O)_6]^{2+}$
V. $[Ni(CO)_4]$	VI. $[Ni(CN)_4]^{2-}$

The complexes which have zero magnetic moment are.

(a) I and V

(b) II and VI only

(c) III and IV

(d) V and VI only

54. Some details of few Nickel complexes are given below:

Complex I : Diamagnetic and square planar

Complex II : Paramagnetic and tetrahedral

Complex III : Diamagnetic and tetrahedral

Complex IV : Paramagnetic and Octahedral

Which is not correct option for the given complexes?

(a) The ligand in complex I is CN^- and it has dsp^2 hybridisation.

(b) The ligand in complex II is Cl^- and it has sp^3 hybridisation.

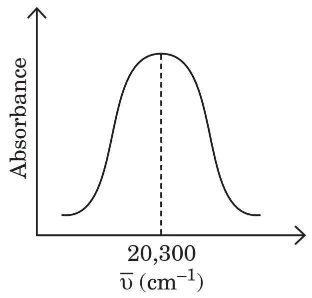
(c) The ligand in complex IV is H_2O and it has d^2sp^3 hybridisation.

(d) The ligand in complex III is CO and it has sp^3 hybridiation.

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 55 to 57.

The extent to which the set of d-orbitals is split in the electrostatic field produced by the ligands depends upon several factors. Two of the most important factors are the nature of the ligands and the nature of the metal ion. In order to see this effect, consider the complex ion $[Ti(H_2O)_6]^{3+}$. The Ti^{3+} ion has a single electron in the $3d$-orbital, and we refer to it as d^1 ion. In the octahedral field generated by six H_2O molecules, the single electron will reside in one of the three degerate t_{2g} orbitals. Under spectral excitation, the electron is promoted to an *e.g.*, orbital giving rise to on absorption spectrum consisting of a single peak that can be represented as shown :



The maximum absorption in the spectrum for $[Ti(H_2O)_6]^{3+}$ occurs at 20,300 cm^{-1} which is equal to 243 kJ mol^{-1}.This gives the value of

Δ_o directly, but only in case of simple d^1 ions. Other complexes containing the Ti^{3+} ion (*e.g.*, $[Ti(NH_3)_6]^{3+}$, $[TiF_6]^{3-}$, etc.) could also be prepared and spectra obtained for these complexes. If this was done, it would be observe that the absorption maximum occurs at a different energy for each complex. Because the maximum corresponds to the splitting of *d*-orbitals, the ligands could be ranked in terms of their ability to cause the splitting of orbital energies. Such a ranking is known as the spectrochemical series and for several common ligands the following order of decreasing energy is observed, $CO > CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^-, Cl^- > Br^-$. In general, the splitting in tetrahedral fields is only about half as large as that in octahedral fields.

55. Which of the following ligands has lowest Δ_o value?

(a) CN^-
(b) CO
(c) F^-
(d) NH_3

56. The visible spectra of salts of the following complexes are measured in aqueous solution for which complex would the spectrum contain absorption with highest E_{max} values?

(a) $[Co(H_2O)_6]^{2+}$
(b) $[Co(H_2O)_6]^{3+}$
(c) $[Co(NH_3)_6]^{3+}$
(d) $[Co(CN)_6]^{3-}$

57. Which of the following statements is incorrect for complex $[Ti(H_2O)_6]^{3+}$?

(a) $[Ti(H_2O)_6]^{3+}$ is violet in colour.
(b) $[Ti(H_2O)_6]^{3+}$ is an octahedral complex.
(c) Exitation of electron in $[Ti(H_2O)_6]^{3+}$ occurs as, $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$
(d) The colour of the complex $[Ti(H_2O)_6]^{3+}$ arises due to *d-d* and *f-f* transition of the electron.

Case II : Read the passage given below and answer the following questions.

Werner, a Swiss chemist in 1892 prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour. He proposed that, in coordination compounds, metals possess two types of valencies, *viz*. primary valencies, which are normally ionisable and secondary valencies which are non-ionisable. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess of $AgNO_3$ solution in cold, but some remained in solution. The number of ions furnished by a complex in a solution can be determined by precipitation reactions. The measurement of molar conductance of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

In the following questions (Q. No. 58-62), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

The following questions are multiple choice questions. Choose the most appropriate answer :

58. Assertion : The complex $[Co(NH_3)_3Cl_3]$ does not give precipitate with silver nitrate solution.

Reason : The given complex is non-ionisable.

59. Assertion : The complex $[Co(NH_3)_4Cl_2]Cl$ gives precipitate corresponding to 2 mol of AgCl with $AgNO_3$ solution.

Reason : It ionises as $[Co(NH_3)_4Cl_2]^+ + Cl^-$.

60. Assertion : $CoCl_3 \cdot 4NH_3$ gives 1 mol of AgCl on reacting with $AgNO_3$, its secondary valency is 6.

Reason : Secondary valency corresponds to coordination number.

61. Assertion : 1 mol of $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ will give 1 mol of AgCl on treating with $AgNO_3$.

Reason : Cl^- ions satisfying secondary valanceis will not be precipitated.

62. Assertion : $CoCl_3 \cdot 3NH_3$ is not conducting while $CoCl_3 \cdot 5NH_3$ is conducting.

Reason : The complex of $CoCl_3 \cdot 3NH_3$ is $[CoCl_3(NH_3)_3]$ while that of $CoCl_3 \cdot 5NH_3$ is $[CoCl(NH_3)_5]Cl_2$.

Case III : Read the passage given below and answer the following questions from 63 to 66.

Valence bond theory considers the bonding between the metal ion and the ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands. In coordination compounds, the interaction between the ligand and the metal ion causes the five *d*-orbitals to split-up. This is called crystal field splitting and the energy difference between the two sets of energy level is called crystal field splitting energy. The crystal field splitting energy (Δ_o) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of Δ_o and P (pairing energy).

If $\Delta_o < P$, then complex will be high spin.

If $\Delta_o > P$, then complex will be low spin.

63. The crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complex is related as

(a) $\Delta_t = \frac{1}{2}\Delta_o$
(b) $\Delta_t = \frac{4}{9}\Delta_o$
(c) $\Delta_t = \frac{3}{5}\Delta_o$
(d) $\Delta_t = \frac{2}{5}\Delta_o$

64. On the basis of crystal field theory, the electronic configuration of d^4 in two situations : (*a*) $\Delta_o > P$ and (*b*) $\Delta_o < P$ are

	(*a*)	**(*b*)**
(a)	$t_{2g}^4 e_g^0$	$t_{2g}^3 e_g^1$
(b)	$t_{2g}^3 e_g^1$	$t_{2g}^4 e_g^0$
(c)	$t_{2g}^3 e_g^1$	$t_{2g}^3 e_g^1$
(d)	$t_{2g}^4 e_g^0$	$t_{2g}^4 e_g^0$

65. Using crystal field theory, calculate magnetic moment of central metal ion of $[FeF_6]^{4-}$.

(a) 1.79 B.M.
(b) 2.83 B.M.
(c) 3.85 B.M.
(d) 4.9 B.M.

66. Electronic configuration of *d*-orbitals in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field is

(a) $t_{2g}^1 e_g^0$
(b) $t_{2g}^2 e_g^0$
(c) $t_{2g}^0 e_g^1$
(d) $t_{2g}^1 e_g^1$

Case IV : Read the passage given below and answer the following questions from 67 to 71.

Coordination compounds are formulated and named according to the IUPAC system.

Few rules for naming coordination compounds are :

(I) In ionic complex, the cation is named first and then the anion.
(II) In the coordination entity, the ligands are named first and then the central metal ion.
(III) When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.

67. The IUPAC name of the complex $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ is

(a) triamminechlorobromonitroplatinum(IV) chloride
(b) triamminebromonitrochloroplatinum(IV) chloride
(c) triamminebromidochloridonitroplatinum (IV) chloride
(d) triamminenitrochlorobromoplatinum(IV) chloride.

68. The IUPAC name of $[Ni(CO)_4]$ is

(a) tetracarbonylnickel(II)
(b) tetracarbonylnickel(0)
(c) tetracarbonylnickelate(II)
(d) tetracarbonylnickelate(0).

69. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is

(a) tetraaquadiamminecobalt(II) chloride
(b) tetraaquadiamminecobalt(III) chloride
(c) diamminetetraaquacobalt(II) chloride
(d) diamminetetraaquacobalt(III) chloride.

70. Which of the following represents correct formula of dichlorido*bis*(ethane-1, 2-diamine) cobalt(III) ion?

(a) $[CoCl_2(en)]^{2+}$
(b) $[CoCl_2(en)_2]^{2+}$
(c) $[CoCl_2(en)]^{+}$
(d) $[CoCl_2(en)_2]^{+}$

71. Correct formula of pentaamminenitrito-O-cobalt(III) sulphate is

(a) $[Co(NO_2)(NH_3)_5]SO_4$
(b) $[Co(ONO)(NH_3)_5]SO_4$
(c) $[Co(NO_2)(NH_3)_4](SO_4)_2$
(d) $[Co(ONO)(NH_3)_4](SO_4)_2$

Case V : Read the passage given below and answer the following questions from 72 to 76.

To explain bonding in coordination compounds various theories were proposed. One of the important theory was valence bond theory. According to that, the central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands. The appropriate atomic orbitals of the metal hybridise to give a set of equivalent orbitals of definite geometry.

The *d*-orbitals involved in the hybridisation may be either inner *d*-orbitals *i.e.*, $(n - 1)d$ or outer *d*-orbitals *i.e.*, *nd*.

For example, Co^{3+} forms both inner orbital and outer orbital complexes, with ammonia it forms $[Co(NH_3)_6]^{3+}$ and with fluorine it forms $[CoF_6]^{3-}$ complex ion.

72. Which of the following is not true for $[CoF_6]^{3-}$?

(a) It is paramagnetic.

(b) It has coordination number of 6.

(c) It is outer orbital complex.

(d) It involves d^2sp^3 hybridisation.

73. $[Cr(H_2O)_6]Cl_3$ (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3*d*-electrons in the central metal of the complex is

(a) $3d^1_{xy}, 3d^1_{x^2-y^2}, 3d^1_{yz}$

(b) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}$

(c) $3d^1_{xy}, 3d^1_{zy}, 3d^1_{z^2}$

(d) $3d^1_{x^2-y^2}, 3d^1_{z^2}, 3d^1_{xz}$

74. Which of the following is true for $[Co(NH_3)_6]^{3+}$?

(a) It is an octahedral, dimagnetic and outer orbital complex.

(b) It is an octahedral, paramagnetic and outer orbital complex.

(c) It is an octahedral, paramagnetic and inner orbital complex.

(d) It is an octahedral, dimagnetic and inner orbital complex.

75. The paramagnetism of $[CoF_6]^{3-}$ is due to

(a) 3 electrons

(b) 4 electrons

(c) 2 electrons

(d) 1 electron.

76. Which of the following is an inner orbital or low spin complex?

(a) $[Ni(H_2O)_6]^{3+}$

(b) $[FeF_6]^{3-}$

(c) $[Co(CN)_6]^{3-}$

(d) $[NiCl_4]^{2-}$

Assertion & Reasoning Based MCQs

For question numbers 77-90, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

77. Assertion : The $[Ni(en)_3]Cl_2$ (*en* = ethylenediamine) has lower stability than $[Ni(NH_3)_6]Cl_2$.

Reason : In $[Ni(en)_3]Cl_2$ the geometry of Ni is octahedral.

78. Assertion : Ethylenediaminetetraacetate ion forms an octahedral complex with the metal ion.

Reason : It has six donor atoms which coordinate simultaneously to the metal ion.

79. Assertion : All the octahedral complexes of Ni^{2+} must be outer orbital complexes.

Reason : Outer orbital octahedral complexes are given by weak ligands.

80. Assertion : The second and third transition series elements have lesser tendency to form low spin complex as compared to the first transition series.

Reason : The CFSE (Δ_o) is more for 4*d* and 5*d*.

81. Assertion : $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.

Reason : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

82. Assertion : $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Reason : $d - d$ transition is not possible in $[Sc(H_2O)_6]^{3+}$.

83. Assertion : Thiocarbonyl is a neutral ligand.

Reason : Thiocarbonyl has three donor atoms but behaves as a bidentate ligand.

84. Assertion : The ligand N_3^- is named as nitride.

Reason : N_3^- is derived from HN_3.

85. Assertion : $[CrCl_2(H_2O)_4]NO_3$ is dichlorotetraaquachromium(III) nitrate.

Reason : In writing the name of the complex cation is written first followed by the anion.

86. Assertion : $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Reason : $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.

87. Assertion : $[Al(NH_3)_6]^{3+}$ does not exist in aqueous solution.

Reason : NH_3 is a neutral ligand.

88. Assertion : Low spin complexes have less number of unpaired electrons.

Reason : $[FeF_6]^{3-}$ is a low spin complex.

89. Assertion : $[Pt(NH_3)_2Cl_2]$ is square planar.

Reason : The oxidation state of platinum is + 2.

90. Assertion : $Cu(OH)_2$ is soluble in NH_4OH but not in NaOH.

Reason : $Cu(OH)_2$ forms a soluble complex with NH_3.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27)

2. What do you understand by 'denticity of a ligand'?

3. Explain the term crystal field splitting in an octahedral field.

4. Write the formula of the following coordination compound :
Iron (III) hexacyanoferrate(II)

5. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex.

6. Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At. no. of Ni = 28)

7. Write the IUPAC name of $[Cr(NH_3)_6][Co(CN)_6]$.

8. What is the difference between a complex and a double salt?

9. Chelates are generally more stable than the complexes of unidentate ligands. Explain.

10. Write the coordination number and oxidation state of platinum in the complex $[Pt(en)_2Cl_2]$.

Short Answer Type Questions (SA-I)

11. Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. no. : Cr = 24, Co = 27, Ni = 28)

12. (i) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.
(ii) Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.
(At. no. of Ni =28)

13. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is
(i) diamagnetic (ii) more stable
(iii) outer orbital complex and
(iv) low spin complex ?
(Atomic no. of Co = 27)

14. Using IUPAC norms write the formulae for the following :
(i) Pentaamminenitrito–O–cobalt(III) chloride
(ii) Potassium tetracyanonickelate(II)

15. Explain the following term giving a suitable example : Ambidentate ligand

16. Using valence bond theory, explain the geometry and magnetic behaviour of $[Co(NH_3)_6]^{3+}$.
(At. no. of Co = 27)

17. Why Co^{2+} is easily oxidised to Co^{3+} in presence of a strong ligand?

18. Write down the IUPAC name of the following complex : $[Cr(NH_3)_2Cl_2(en)]Cl$

19. Ravi prepared a complex compound of cobalt with NH_3 and NO_2 as donor ligands. He got a red precipitate. Sohan also prepared the same complex using same metal salt solution and same ligands. He obtained yellow crystals. Sohan complained his teacher that his chemicals were different so he got different product. But their teacher is satisfied with both the results. Now answer the following questions :

(i) What type of ligand is present in the given compounds which is responsible for changing colour?

(ii) Write IUPAC name of both the compounds.

20. Give the formula of each of the following coordination entities :

(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (*en*) molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.

(At. nos. Co = 27, Ni = 28)

Short Answer Type Questions (SA-II)

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

(i) $[Cr(NH_3)_3Cl_3]$ (ii) $K_3[Fe(CN)_6]$

(iii) $[CoBr_2(en)_2]^+$

22. The splitting pattern of *d*-orbitals in octahedral and tetrahedral geometry are reverse of each other. Why?

23. (a) What is *d*-*d* transition?

(b) Tetrahedral complexes are always of high spin. Explain.

24. For the complex $[NiCl_4]^{2-}$, write

(i) the IUPAC name

(ii) the hybridization type

(iii) the shape of the complex.

(Atomic no. of Ni = 28)

25. Write the name, the structure and the magnetic behaviour of each one of the following complexes :

(i) $[Pt(NH_3)_2Cl(NO_2)]$ (ii) $[Co(NH_3)_4Cl_2]Cl$

(iii) $Ni(CO)_4$

(At. nos. Co = 27, Ni = 28, Pt = 78)

26. $[Mn(CN)_6]^{3-}$ has two unpaired electrons whereas $[MnCl_6]^{3-}$ has four unpaired electrons. Why?

27. Write the IUPAC name, deduce the geometry and magnetic behaviour of the complex $K_4[Mn(CN)_6]$.

[Atomic no. of Mn = 25]

28. For the complex $[Fe(en)_2Cl_2]Cl$, identify the following :

(i) Oxidation number of iron

(ii) Hybrid orbitals and shape of the complex

(iii) Magnetic behaviour of the complex

(iv) Name of the complex.

29. Name the following coordination entities and describe their structures.

(i) $[Fe(CN)_6]^{4-}$ (ii) $[Cr(NH_3)_4Cl_2]^+$

(iii) $[Ni(CN)_4]^{2-}$

30. Explain the following :

(i) Anhydrous $CuSO_4$ is white while hydrated $CuSO_4$ is blue in colour.

(ii) $[Ti(H_2O)_6]Cl_3$ is violet in colour but becomes colourless on heating.

31. For the complex $[Fe(CN)_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex. (At. number : Fe = 26)

32. Give reason : $[CoF_6]^{3-}$ is outer orbital but $[Co(NH_3)_6]^{3+}$ is inner orbital complex.

33. Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities :

(i) $[Cr(NH_3)_4Cl_2]Cl$ (ii) $[Co(en)_3]Cl_3$

(iii) $K_2[Ni(CN)_4]$

34. (a) 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) $\Delta_o > P$ (ii) $\Delta_o < P$

(b) Write two limitations of crystal field theory.

35. $[Ni(H_2O)_6]^{2+}$ is green and becomes violet when ethane-1, 2-diamine is added to it. Identify the observation.

Long Answer Type Questions (LA)

36. (i) Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following :
(a) $[CoF_6]^{3-}$, (b) $[FeF_6]^{3-}$, (c) $[Fe(CN)_6]^{4-}$
(ii) $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

37. 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:
(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$
(ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $[CrCl_3(py)_3]$
(iv) $Cs[FeCl_4]$
(v) $K_4[Mn(CN)_6]$

38. (a) What are bidentate ligands? Explain with examples.
(b) Explain the coordination sites of polydentate ligands taking an example of EDTA.
(c) Calculate charge on the central metal in the following complexes:
(i) $[Cu(NH_3)_6]^{2+}$ (ii) $[Ag(CN)_2]^-$

39. Give the oxidation state, *d*-orbital occupation and coordination number of the central metal ion in the following complexes :
(i) $K_3[Co(C_2O_4)_3]$
(ii) $[Cr(en)_2Cl_2]Cl$
(iii) $(NH_4)_2[CoF_4]$
(iv) $[Mn(H_2O)_6]SO_4$

40. (a) Explain hybridisation in the complex which contains hexacyanidoferrate(III) ion.
(b) Based on the valence bond theory describe the formation and nature of hexaamminecobalt(III) chloride.
(c) How will you show that hexafluorocobaltate(III) ion is paramagnetic in nature?

ANSWERS

OBJECTIVE TYPE QUESTIONS

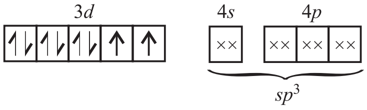
1. (a)

2. (c) : NH_4^+ ion does not have any lone pair of electrons which it can donate to central metal ion hence it does not form complexes.

3. (c) : Tetraamminechloridonitroplatinum(IV) sulphate can be written as $[Pt(NH_3)_4(NO_2)Cl]SO_4$.

4. (a) : In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state.

In $[NiCl_4]^{2-}$:



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

[$\because$ n = number of unpaired electrons]

$= \sqrt{2(2+2)}$ = 2.82 B.M.

5. (a) : $[Pt(NH_3)_4Cl_2]Br_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Br^-$

$Br^- + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr} + NO_3^-$

$[Pt(NH_3)_4Br_2]Cl_2 \longrightarrow [Pt(NH_3)_4Br_2]^{2+} + 2Cl^-$

$Cl^- + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl} + NO_3^-$

6. (b) : $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$
Hexaamminenickel(II) hexanitrocobaltate(III)

7. (c)

8. (b) : In $[Cu(NH_3)_6]^{2+}$, oxidation state of Cu = +2, $Cu^{2+} = 3d^9$
$3d^9 = t_{2g}^6 e_g^3$

9. (d) : In $[Cu(NH_3)_4]SO_4$ primary valency is 2 and secondary valency is 4.

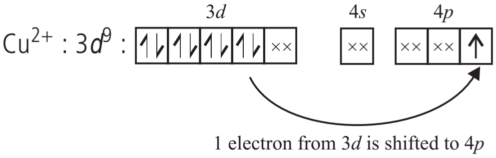
10. (c) : The CFSE of the ligands is in the order :
$H_2O < NH_3 < CN^-$
Hence, excitation energies is in the order:
$[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$
From the relation $E = \dfrac{hc}{\lambda} \Rightarrow E \propto \dfrac{1}{\lambda}$

The order of absorption of wavelength of light in the visible region : $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

11. (b) : $[Co(NH_3)_5CO_3]Cl$
Pentaamminecarbonatocobalt(III) chloride

12. (d) : $CuSO_4 + 4NH_3 \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}} + SO_4^{2-}$

In $[Cu(NH_3)_4]^{2+}$, oxidation state of Cu = +2



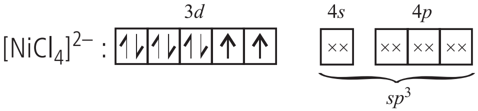
Hybridisation is dsp^2 hence geometry is square planar and paramagnetic due to presence of one unpaired electron.

13. (a) : Higher the number of ions in the solution, higher is the conductivity.

No. of ions : $[Co(NH_3)_3Cl_3] = 0$; $[Co(NH_3)_4Cl_2]Cl = 2$

$[Co(NH_3)_5Cl]Cl_2 = 3$; $[Co(NH_3)_6]Cl_3 = 4$

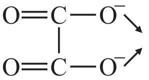
14. (d) : In $[NiCl_4]^{2-}$, oxidation state of Ni = + 2



sp^3 hybridisation and tetrahedral shape.

15. (c) : The name of $[Co(NH_3)_5NO_2]Cl_2$ is pentaamminenitrito-N-cobalt(III) chloride.

16. (b) : Oxalate is a bidentate ligand hence forms a chelate.



17. (b) : $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$

18. (b) : When excess of aqueous KCN solution is added to aqueous $CuSO_4$ solution, highly stable $[Cu(CN)_4]^{2-}$ is formed which does not give Cu^{2+} ion in the solution, hence copper sulphide, is not formed.

$[Cu(H_2O)_4]^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-} + 4H_2O$

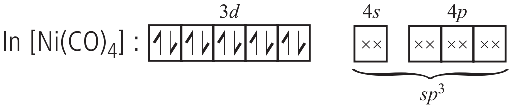
19. (c) : In d^6 (low spin), electrons get paired up to make two empty *d*-orbitals. Hybridisation is d^2sp^3 (octahedral) and the complex is low spin.

20. (c) : In general, the ligands can be arranged in a series in the order of increasing field strength as

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O <$ $NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

21. (d) : Ni (Z = 28) : $3d^8\,4s^2$

Oxidation state of Ni in $[Ni(CO)_4] = 0$



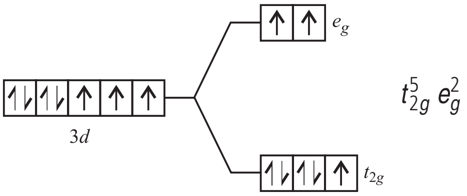
No. of unpaired electrons = 0

22. (a) : CN^- is a strong field ligand hence pairing of electrons takes place while in case of H_2O pairing does not take place. Both ligands show different magnitude of crystal field splitting energy hence absorb different wavelengths and show different colours.

23. (b) : In metal carbonyls, metal is in zero oxidation state.

24. (a) : A substance absorbs light at specific wavelength in the visible part of the spectrum and reflects the rest of the wavelengths. Each wavelength represents a different colour hence corresponding colour is observed.

25. (a) : In $[Co(H_2O)_6]^{2+}$, oxidation state of Co = +2, $Co^{2+} = 3d^7$



$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$ = 3.87 B.M. $[\because n = 3]$

26. (b) : The ligand CN^- absorbs indigo, the high energy radiation and thus appears yellow. The aqua complexes have much smaller CFSE, they absorb orange or red light and thus appear blue or green.

27. (a) : Crystal field stabilisation energy for tetrahedral complexes is less than pairing energy hence they do not pair up to form low spin complexes.

28. (d) : $[CuCl_4]^{2-}$ – Tetrahedral

$[Fe(NH_3)_6]^{2+}$ – Octahedral

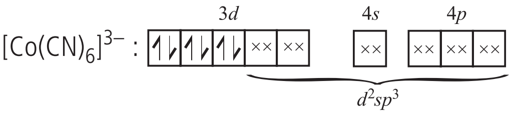
29. (c) : It gives precipitate with $AgNO_3$ it means it gives Cl^- ions in the solution. Since conductivity corresponds to two ions, it shows one Cl^- is outside the coordination sphere. The structure will be

$[Cr(H_2O)_4Cl_2]Cl \longrightarrow [Cr(H_2O)_4Cl_2]^+ + Cl^-$

$AgNO_3 + Cl^- \longrightarrow \underset{\text{white ppt.}}{AgCl} + NO_3^-$

30. (a) : SCN^- and NO_2^- are ambidentate ligands since they have more than one donor atoms to attach to the central metal atom.

31. (a) : Electronic configuration of $Co^{3+} = 3d^6$



No. of unpaired electrons = 0, hence, shows no paramagnetism.

32. (c) : Dien (Diethylenetriamine) has the following structure

$H_2\ddot{N} — CH_2 — CH_2 — \ddot{N}H — CH_2 — CH_2 — \ddot{N}H_2$

33. (b) : More the number of unpaired electrons, higher is its paramagnetism.

$Cr^{3+} : 3d^3$, $Fe^{2+} : 3d^6$, $Cu^{2+} : 3d^9$, $Zn^{2+} : 3d^{10}$

Fe^{2+} has four unpaired electrons hence it shows highest paramagnetism.

34. (b) : Coordination number is the number of ligands that are directly bound to the central metal atom by coordinate bonds. Oxidation state is the residual charge on the central metal atom left after removing all ions.

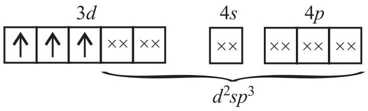
35. (a) : Aqueous $CuSO_4$ solution contains $[Cu(H_2O)_4]^{2+}$ ions which are blue in colour. When aqueous solution of KF is added, H_2O being weak field ligand can be replaced by F^- ions forming $[CuF_4]^{2-}$ which is green in colour.

$$[Cu(H_2O)_4]^{2+} + \underset{\text{(from KF)}}{4F^-} \longrightarrow \underset{\text{green}}{[CuF_4]^{2-}} + 4H_2O$$

36. (a) : $[Pt(NH_3)_2Cl(en)NO_2]Cl_2$:
Diamminechlorido(ethylenediamine)nitroplatinum(IV) chloride

37. (c) : In $[Cr(H_2O)_6]^{3+}$, oxidation state of Cr = + 3,
$Cr^{3+} = 3d^3$

$[Cr(H_2O)_6]^{3+}$:



It is an inner orbital ($3d - 4p$) complex. Due to presence of three unpaired electrons, it is paramagnetic.

38. (c) : Number of donor atoms in $N(CH_2CH_2NH_2)_3$ is four hence it is a tetradentate ligand.

39. (b) : $[Ag(NH_3)_2]Cl$ is a coordination compound containing cationic complex ion.

40. (a) : $\underset{X}{[Co(NH_3)_5SO_4]Br} \longrightarrow [Co(NH_3)_5SO_4]^+ + Br^-$

$AgNO_3 + Br^- \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr} + NO_3^-$

$\underset{Y}{[Co(NH_3)_5Br]SO_4} \longrightarrow [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$

$BaCl_2 + SO_4^{2-} \longrightarrow \underset{\text{white ppt.}}{BaSO_4} + 2Cl^-$

41. (a) : $[Co(NH_3)_6]Cl_3$ gives 3 moles of AgCl.

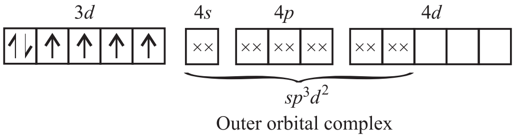
$[Co(NH_3)_5Cl]Cl_2$ gives 2 moles of AgCl.

$[Co(NH_3)_4Cl_2]Cl$ gives 1 mole of AgCl.

$[Co(NH_3)_3Cl_3]$ will not give AgCl.

42. (b) : In $[FeCl_6]^{4-}$, oxidation state of Fe = +2, $Fe^{2+} = 3d^6$

$[FeCl_6]^{4-}$:



Paramagnetic due to presence of four unpaired electrons.

43. (a) : Primary valency is ionisable according to Werner's theory of coordination compounds.

44. (b) : In $CuSO_4 \cdot 5H_2O$, water acts as ligand and as a result it causes crystal field splitting making *d-d* transition possible in $CuSO_4 \cdot 5H_2O$. Hence, it is coloured. In anhydrous $CuSO_4$ due to absence of ligand, crystal field splitting is not possible hence no colour is observed.

45. (b) : $3d^5$ has maximum number of unpaired electrons.

46. (b) : In $[Co(SO_4)]$, the oxidation state of Co is +2. Configuration of $Co^{2+} = 3d^7$, it has unpaired electrons in 3*d*-orbitals so it is paramagnetic. Because of incompletely filled *d*-orbitals it is coloured.

47. (c) : Positively charged ligands have suffix 'ium'.

48. (a) : All the statements are correct with respect to the geometry of complex ions.

49. (c) : ONO is an anionic ligand (ONO^-).

50. (c) :

Colour	Formation	Solution conductivity corresponds to
Yellow	$[Co(NH_3)_6]^{3+}3Cl^-$	1 : 3 electrolyte
Purple	$[CoCl(NH_3)_5]^{2+}2Cl^-$	1 : 2 electrolyte
Green	$[CoCl_2(NH_3)_4]^+Cl^-$	1 : 1 electrolyte
Violet	$[CoCl_2(NH_3)_4]^+Cl^-$	1 : 1 electrolyte

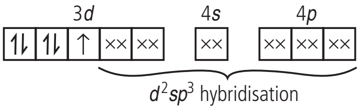
51. (d) : $[Ag(NH_3)_2]$ $[Ag(CN)_2]$: Diamminesilver(I) dicyanidoargentite(I)

$K_3[Al(C_2O_4)_3]$ Potassium trioxalatoaluminate(III)

52. (a) : Fe (26) : $3d^6 4s^2$

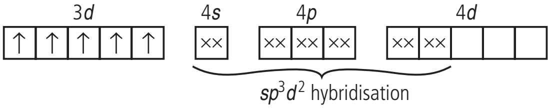
Fe^{3+} : $3d^5$

In $[Fe(CN)_6]^{3-}$, CN^- is a strong field ligand which causes pairing of electrons.



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

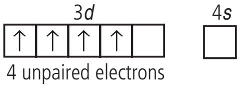
In $[Fe(SCN)_6]^{3-}$, SCN^- being a weak field ligand does not cause pairing of electrons.



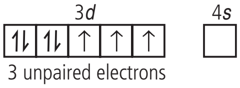
$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.916 \text{ BM}$$

Difference = 5.916 – 1.732 = 4.184 ≈ 4.2 BM

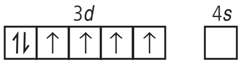
53. (d) : $[Cr(H_2O)_6]^{2+}$: $Cr^{2+} \rightarrow [Ar]3d^4 4s^0$



$[CoCl_4]^{2-}$: $Co^{2+} \rightarrow [Ar]3d^7 4s^0$

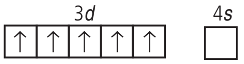


$[Fe(H_2O)_6]^{2+}$: $Fe^{2+} \rightarrow [Ar]3d^6 4s^0$



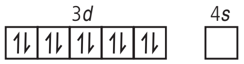
4 unpaired electrons

$[Mn(H_2O)_6]^{2+}$: $Mn^{2+} \rightarrow [Ar]3d^5 4s^0$



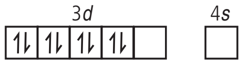
5 unpaired electrons

$[Ni(CO)_4]$: $Ni^0 \rightarrow [Ar]3d^8 4s^2$



Zero unpaired electrons

$[Ni(CN)_4]^{2-}$: $Ni^{2+} \rightarrow [Ar]3d^8 4s^0$



Zero unpaired electrons

Hence, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ have zero unpaired electrons *i.e.*, zero magnetic moment.

54. (c) : $[Ni(CN)_4]^{2-}$: dsp^2 hybridisation (square planar complex) and have zero unpaired electrons (diamagnetic)

$[NiCl_4]^{2-}$: sp^3 hybridisation (tetrahedral) and have two unpaired electrons (paramagnetic)

$[Ni(H_2O)_6]^{2+}$: sp^3d^2 hybridisation (octahedral) and have two unpaired electrons (paramagnetic)

$[Ni(CO)_4]$: sp^3 hybridisation (tetrahedral) and have zero unpaired electrons (diamagnetic)

55. (c) : Because F^- is a weak field ligand.

56. (d) : $[Co(CN)_6]^{3-}$ complex would contain absorption with highest E_{max} value because according to spectrochemical series, the crystal field splitting energy of CN^- ion is very high.

57. (d) **58. (a)**

59. (d) : $[Co(NH_3)_4Cl_2]Cl + AgNO_3 \longrightarrow [Co(NH_3)_4Cl_2]^+ + AgCl\downarrow$

Thus it gives precipitate of 1 mol of AgCl.

60. (b) : $CoCl_3 \cdot 4NH_3$ gives 1 mol AgCl on reaction with $AgNO_3$, hence the complex can be represented as $[CoCl_2(NH_3)_4]Cl$.

61. (a) : The Cl^- ions outside the coordination sphere can only be precipitated.

62. (a) **63. (b)**

64. (a) : When $\Delta_o > P$, the electrons paired up in the t_{2g} level rather than going to the e_g level, so

when $\Delta_o > P : t_{2g}^4 e_g^0$

and $\Delta_o < P : t_{2g}^3 \; e_g^1$

65. (d) : $Fe^{2+} : 3d^6 \Rightarrow t_{2g}^4 \; e_g^2$

(Since, F^- is a weak field ligand)

Hence four unpaired electrons are present.

Magnetic moment $(\mu) = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9$ B.M.

66. (a) : In $[Ti(H_2O)_6]^{3+}$, Ti is in +3 oxidation state and there is only one electron in *d*-orbital.

67. (c) : Ligands are named in alphabetical order irrespective of their charge.

68. (b) **69. (d)** **70. (d)**

71. (b) : Ligand NO_2^- is ambidentate ligand as it can donate electrons through either nitrogen (NO_2) or oxygen (ONO).

72. (d) : It involves sp^3d^2 hybridisation and not d^2sp^3.

73. (b) : Magnetic moment of 3.83 B.M. suggests that it has 3 unpaired electrons,

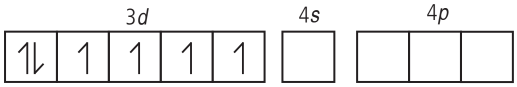
$\therefore \quad n = 3$ *i.e.*, $Cr^{3+} : 3d^3$

It involves d^2sp^3 hybridisation so correct distribution of electrons is $3d_{xy}^1$, $3d_{yz}^1$, $3d_{zx}^1$.

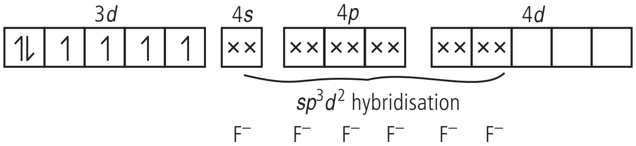
74. (d) : $[Co(NH_3)_6]^{3+}$ is d^2sp^3 hybridised with all electrons paired hence, it is diamagnetic and inner orbital complex.

75. (b) :

Co^{3+} :



$[CoF_6]^{3-}$:



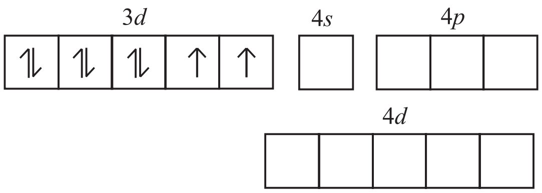
76. (c) : Inner orbital complexes are formed with strong ligands as they force electrons to pair up and hence the complex will be either diamagnetic or will have less number of unpaired electrons.

77. (d) : $[Ni(en)_3]Cl_2$ is a chelating compound and chelated complexes are more stable than similar complexes with unidentate ligands as dissociation of the complex involves breaking of two bonds rather than one.

In $[Ni(en)_3]Cl_2$, Ni with d^8 configuration shows octahedral geometry.

78. (a)

79. (b) : Ni^{2+} configuration



During rearrangement only one 3*d*-orbital may be made available by pairing the electrons. Thus, inner d^2sp^3 hybridisation is not possible. So, only sp^3d^2 (outer) hybridisation can occur.

80. (d) : 4*d* and 5*d* elements have greater tendency to form low spin complex (allows better pairing of electrons) in comparison to 3*d* because the difference in energy of t_{2g} and e_g (CFSE, Δ_o) increases in 4*d* and 5*d*.

81. (c) : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

82. (a) : $[Sc(H_2O)_6]^{3+}$ has no unpaired electron in its *d* subshell and thus *d* – *d* transition is not possible whereas $[Ti(H_2O)_6]^{3+}$ has one unpaired electron in its *d*-subshell which gives rise to *d* – *d* transition to impart colour.

83. (c) : Thiocarbonyl (CS) has one donor atom.

84. (d) : N_3^- is named as azido. It is derived from HN_3.

85. (d) : Correct IUPAC name is tetraaquadichloridochromium(III) nitrate.

86. (b) : $[Fe(CN)_6]^{3-}$ has one unpaired electron, hence it shows paramagnetic nature while $[Fe(CN)_6]^{4-}$ possesses no unpaired electron and thus shows diamagnetic nature.

87. (b) : The complex ion $[Al(NH_3)_6]^{3+}$ undergoes the change into new complex ion $[Al(H_2O)_6]^{3+}$ in aqueous medium due to higher heat of hydration of aluminium ion on account of its small size.

$[Al(NH_3)_6]^{3+} + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 6NH_3$

88. (c) : $[FeF_6]^{3-}$ is a high spin complex since F^- is a weak field ligand.

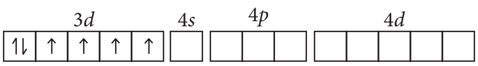
89. (b) : The outer electronic configuration of platinum in ground state is $5d^96s^1$. The Pt^{2+} ion formed by the loss of two electrons has outer electronic configuration of $5d^8$. In the presence of strong ligands (NH_3) two unpaired electrons in the 5*d*-subshell pair up. This is followed by dsp^2 hybridisation resulting in the formation of four hybridised vacant orbitals which accommodate four pairs of electrons from four ligands (two from ammonia and two from Cl^-). As such the resulting complex is square planar.

90. (a)

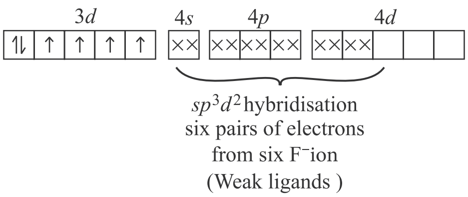
SUBJECTIVE TYPE QUESTIONS

1. Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

Co^{3+} :



Co^{3+} in $[CoF_6]^{3-}$:



No. of unpaired electrons = 4

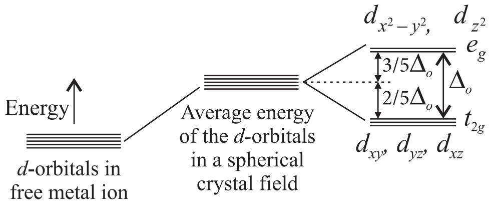
2. Denticity : The number of coordinating groups present in a ligand is called the denticity of ligand.

For example, bidentate ligand ethane-1, 2-diamine has two donor nitrogen atoms which can link to central metal atom.

$$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$$

Ethane-1, 2-diamine

3. The splitting of the degenerate *d*-orbitals into three orbitals of lower energy, t_{2g} set and two orbitals of higher energy e_g set due to the interaction of ligand in an octahedral crystal field is known as crystal field splitting in an octahedral field.



d-orbital splitting in an octahedral crystal field

4. $Fe_4[Fe(CN)_6]_3$

5. For one mole of the compound, two moles of AgCl are precipitated which indicates that two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

6. $[Ni(H_2O)_6]^{2+}$ is a high spin complex (Δ_o small) while $[Ni(CN)_4]^{2-}$ is a low spin square planar complex.

In $[Ni(H_2O)_6]^{2+}$ complex, *d-d* transitions are taking place on absorbing low energy radiation (red component of spectrum) from visible region showing green as the complementary colour.

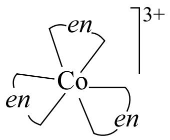
In $[Ni(CN)_4]^{2-}$ complex, *d-d* transitions do not take place in the visible region of spectrum, *d-d* transitions take place in the UV region and hence, complex is colourless.

7. Hexaamminechromium(III) hexacyanocobaltate(III).

8. Double salts dissociate into ions completely when dissolved in water. On the other hand, in complexes, the complex ion does not dissociate.

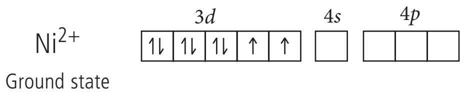
9. Chelates are cyclic compounds so they are more stable than normal complexes. In chelates ligands are held by two or more bonds with the transition metals. *e.g.,*

$[Co(en)_3]^{3+}$ or

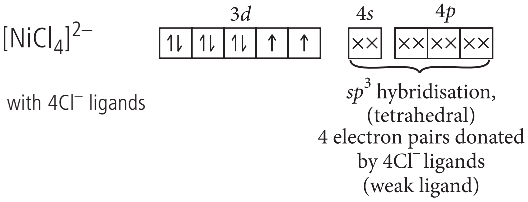


10. Coordination number and oxidation state of Pt in the complex $[Pt(en)_2Cl_2]$ are 6 and +2 because *en* is a bidentate and neutral ligand.

11. $[NiCl_4]^{2-}$ contains Ni^{2+} ion with $3d^8$ configuration.

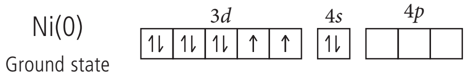


Cl^- is a weak field ligand. Hence, outer 4*s* and 4*p*-orbitals are used in hybridisation.

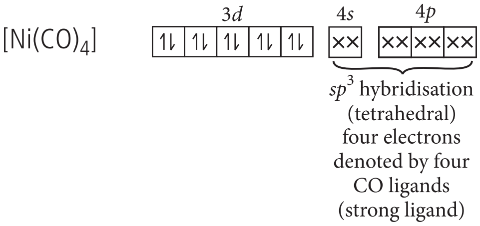


It has two unpaired electrons hence, it is paramagnetic.

$[Ni(CO)_4]$ contains Ni(0) – $3d^8 4s^2$ configuration.



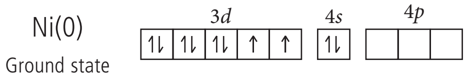
CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.



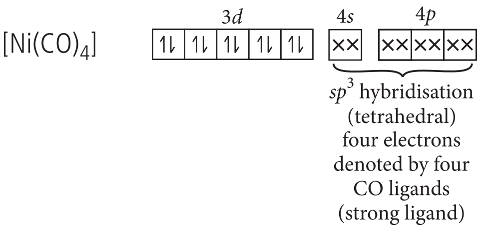
The complex has all paired electrons hence, it is diamagnetic.

12. (i) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

(ii) $[Ni(CO)_4]$ contains Ni(0) – $3d^8 4s^2$ configuration.

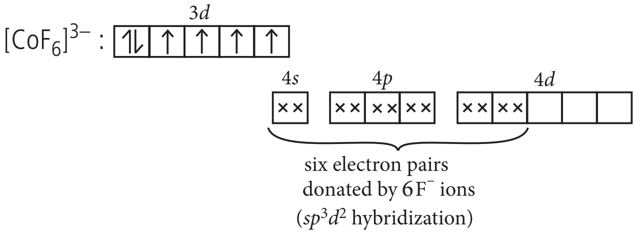


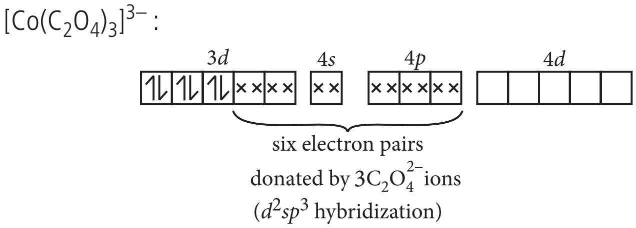
CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.



The complex has all paired electrons hence, it is diamagnetic.

13. Formation of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ can be represented as :





(i) $[Co(C_2O_4)_3]^{3-}$ is diamagnetic as all electrons are paired.

(ii) $[Co(C_2O_4)_3]^{3-}$ is more stable as $C_2O_4^{2-}$ is a chelating ligand and forms chelate rings.

(iii) $[CoF_6]^{3-}$ is an outer orbital complex as it undergoes sp^3d^2 hybridization using the outer 4*d*-orbital.

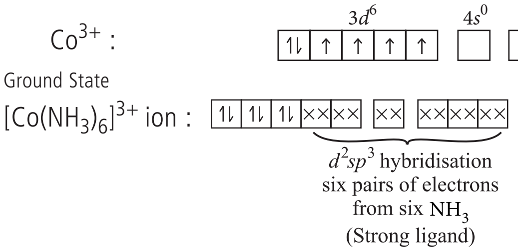
(iv) $[Co(C_2O_4)_3]^{3-}$ is low spin complex due to absence of any unpaired electron.

14. (i) $[Co(NH_3)_5(ONO)]Cl_2$ (ii) $K_2[Ni(CN)_4]$

15. Ambidentate ligand : A unidentate ligand which can coordinate to central metal atom through two different atoms is called ambidentate ligand.

For example, NO_2^- ion can coordinate either through nitrogen or through oxygen to the central metal atom/ion.

16. Oxidation state of cobalt in $[Co(NH_3)_6]^{3+}$ is +3.

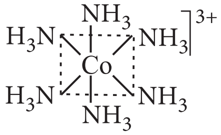


Hybridisation – d^2sp^3

Structure – Octahedral

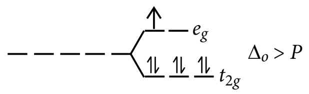
(low spin)

Nature – Diamagnetic



IUPAC name : Hexaamminecobalt(III) ion

17. In presence of strong field ligand, Co(II) has electronic configuration $t_{2g}^6 e_g^1$.



It can easily lose one electron present in e_g orbital to give stable t_{2g}^6 configuration. This is why Co^{2+} is easily oxidised to Co^{3+} in the presence of strong field ligand.

18. Diamminedichlorido(ethane-1,2-diamine)chromium(III) chloride.

19. (i) Ambindent ligands (NO_2, ONO) present in the given compounds.

(ii) $[Co(NH_3)_5(NO_2)]Cl_2$ (Yellow)
Pentaamminenitrito-N-cobalt(III) chloride
$[Co(NH_3)_5(ONO)]Cl_2$ (Red)
Pentaamminenitrito-O-cobalt(III) chloride

20. (i) $[Co(en)_2Cl(NH_3)]^{2+}$

Amminechlorido*bis*(ethane-1,2-diamine)cobalt(III) ion

In presence of strong NH_3 and *en* ligand, Co^{3+} ($3d^6$) forms low spin complex. Hence, complex is diamagnetic.

(ii) $[Ni(ox)_2(H_2O)_2]^{2-}$: Diaquadioxalatonickelate(II) ion

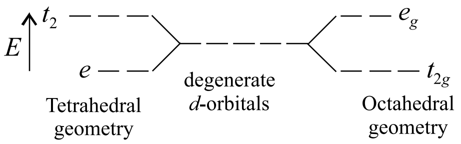
In the presence of weak *ox* and H_2O ligand, Ni(II) forms high spin complex (sp^3d^2 hybridisation). It is paramagnetic.

21. (i) Triamminetrichloridochromium(III)

(ii) Potassium hexacyanoferrate(III)

(iii) Dibromido*bis*(ethane-1,2-diamine)cobalt(III) ion

22. In octahedral complex ligands approach along the axes. So axial orbitals ($d_{x^2-y^2}$, d_{z^2}) lie directly in the path of ligand and experience greater repulsion than the non-axial orbitals. Whereas in tetrahedral complex ligands are closer to non-axial orbitals (*i.e.* d_{xy}, d_{xz} and d_{yz}). So, non-axial orbitals experience greater force of repulsion than the axial orbitals. *i.e.* approach of ligands in octahedral and tetrahedral fields is opposite of each other. This is why splitting pattern of *d*-orbitals in octahedral and tetrahedral geometry is reverse of each other.



23. (a) When ligands approach the central metal, atom or ion of complex its *d*-orbital breaks into two parts t_{2g} and e_g levels. When light falls on the complex the complex absorbs light of suitable frequency for transfer of electron from lower level to higher level. This jump of electron from one *d*-level to another is called *d-d* transition.

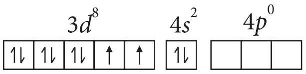
Before absorption After absorption

(b) For tetrahedral complexes crystal field splitting energy Δ_t is always less than pairing energy. So, tetrahedral complexes are always high spin.

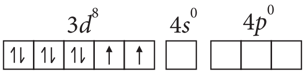
24. Tetrachloridonickelate(II) ion

Ni atom ($Z = 28$)

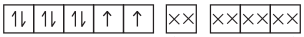
Ground state :



Ni^{2+} ion :



$[NiCl_4]^{2-}$:



sp^3 hybridisation
four pairs of electrons
from four Cl^- ligands
(weak ligands)

The complex ion has tetrahedral geometry and is paramagnetic due to the presence of unpaired electrons.

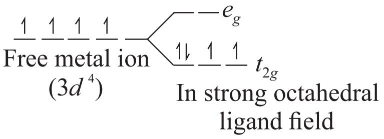
25. (i) $[Pt(NH_3)_2Cl(NO_2)]$:
Diamminechloridonitrito-N-platinum(II)
It is square planar and diamagnetic.

(ii) $[Co(NH_3)_4Cl_2]Cl$:
Tetraamminedichloridocobalt(III) chloride
It is octahedral and diamagnetic.

(iii) $Ni(CO)_4$: Tetracarbonylnickel(0)
It is tetrahedral and diamagnetic.

26. In $[Mn(CN)_6]^{3-}$, Mn is in +3 state so, it has configuration of $3d^4$.

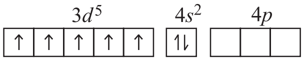
Since CN^- is a strong field ligand hence pairing of electrons in 3*d*-orbital takes place.



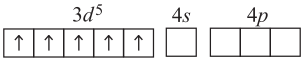
So, $[Mn(CN)_6]^{3-}$ has two unpaired electrons. But in $[MnCl_6]^{3-}$, Cl^- is a weak field ligand, so no pairing takes place and it has 4 unpaired electrons.

27. Mn ($Z = 25$)

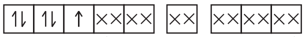
Ground state :



Mn^{2+} ion :



$[Mn(CN)_6]^{4-}$:



d^2sp^3 hybridisation
six pairs of electrons
from six CN^- ions
(Strong ligand)

IUPAC name : Potassium hexacyanomanganate(II)

Geometry : Octahedral

No. of unpaired electrons, $n = 1$

Magnetic behaviour : paramagnetic

28. (i) $[Fe(en)_2Cl_2]Cl$

$x + 0 \times 2 + (-1) \times 2 + (-1) \times 1 = 0 \quad \therefore \; x = +3$

Oxidation number of iron = +3

(ii) d^2sp^3 hybridisation and octahedral shape.

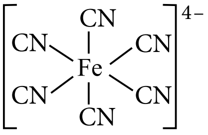
(iii) Paramagnetic due to presence of one unpaired electron.

(iv) dichlorido*bis*(ethane-1,2-diamine)iron(III) chloride

29. (i) $[Fe(CN)_6]^{4-}$: Hexacyanidoferrate(II) ion

Hybridisation - d^2sp^3

Structure : Inner orbital octahedral complex



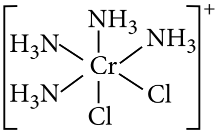
Octahedral

(ii) $[Cr(NH_3)_4Cl_2]^+$:

Tetraamminedichloridochromium(III) ion

Hybridisation - d^2sp^3

Structure : Inner orbital octahedral complex

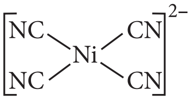


Octahedral

(iii) $[Ni(CN)_4]^{2-}$: Tetracyanidonickelate(II) ion

Hybridisation - dsp^2

Structure - Square planar

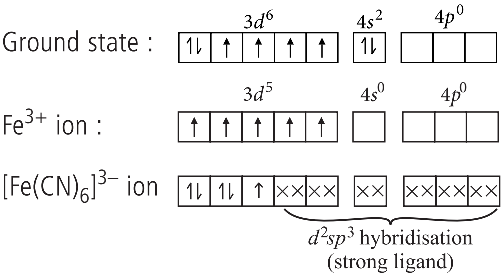


Square planar

30. (i) Anhydrous $CuSO_4$ has no ligand. So, crystal field splitting does not occur so, it does not show any colour but in hydrated form it is linked with H_2O ligand so, it shows colour due to *d-d* transition.

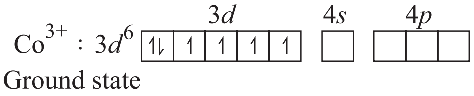
(ii) $[Ti(H_2O)_6]Cl_3$ is a complex compound. In presence of 6 H_2O molecules the *d*-orbitals of Ti^{3+} undergo splitting. The compound is coloured (violet) due to *d-d* transition. On heating water molecules escape, *d*-orbitals become degenerate. There is no *d-d* transition. Hence compound becomes colourless.

31. Fe atom (*Z* = 26)

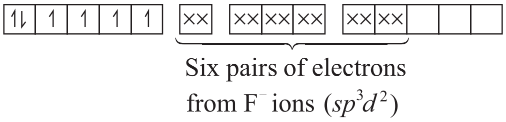


The complex ion has inner orbital octahedral geometry (low spin) and is paramagnetic due to the presence of one unpaired electron.

32. In $[CoF_6]^{3-}$, Co is in +3 state and has $3d^6$ configuration.

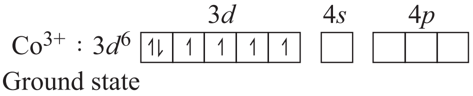


Since F^- is a weak field ligand. So, outer *d*-orbitals will be used.

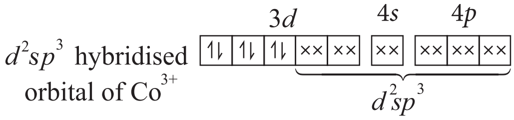


Since, outer *d*-orbital is used for hybridisation. So, it is outer orbital complex.

In $[Co(NH_3)_6]^{3+}$, Co is in +3 state.



Since NH_3 is a strong field ligand pairing of electrons in 3*d*-orbital takes place to make two 3*d* orbitals vacant.



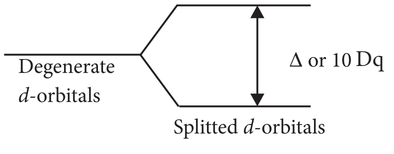
Since it uses inner *d*-orbital for its hybridisation so, it is inner orbital complex.

33.

Complex	Central metal ion/ atom	Hybridi-sation of metal ion involved	Geometry of complex	Magnetic behaviour
$[Cr(NH_3)_4Cl_2]Cl$	Cr^{3+}	d^2sp^3	Octahedral	Paramagnetic
$[Co(en)_3]Cl_3$	Co^{3+}	d^2sp^3	Octahedral	Diamagnetic
$K_2[Ni(CN)_4]$	Ni^{2+}	dsp^2	Square planar	Diamagnetic

34. (a) The difference of energy between two splitted levels of *d*-orbitals is called crystal field splitting energy. It is denoted by Δ or 10 Dq.

For octahedral Δ_o, for tetrahedral it is Δ_t and for square planar Δ_{sp}.



(i) When $\Delta_o > P$, $t_{2g}^4 e_g^0$ (ii) When $\Delta_o < P$, $t_{2g}^3 e_g^1$

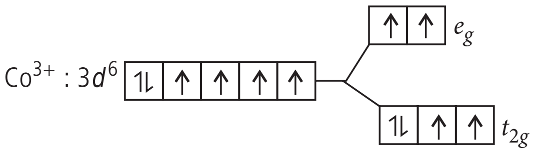
(b) (i) It assumes ligand to be point charges.

(ii) It does not take into account the covalent character of bonding between the ligand and the central atom.

35. Ethane-1,2-diamine is stronger ligand than H_2O. When H_2O molecule is replaced by ethane-1,2-diamine (*en*) the crystal field splitting energy (Δ) increases. Complex absorbs light of higher frequency for *d-d* transition. This is why colour of complex changes from green to violet.

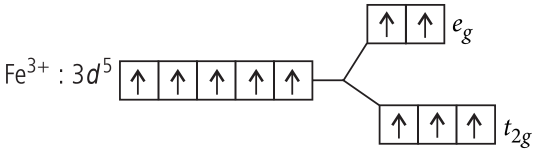
$$\underset{\Delta_o \text{ small}}{[Ni(H_2O)_6]^{2+}} \text{ – Green, } \underset{\Delta_o \text{ large}}{[Ni(en)_3]^{2+}} \text{ – violet}$$

36. (i) (a) $[CoF_6]^{3-}$:



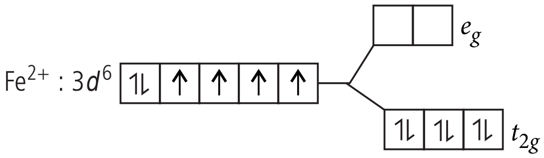
No. of unpaired electrons = 4, $\mu = \sqrt{4(4+2)} = 4.9$ B.M.

(b) $[FeF_6]^{3-}$:



No. of unpaired electrons = 5, $\mu = \sqrt{5(5+2)} = 5.92$ B.M.

(c) $[Fe(CN)_6]^{4-}$:



No. of unpaired electrons = 0, $\mu = 0$

(ii) When $FeSO_4$ and $(NH_4)_2SO_4$ solutions are mixed in 1 : 1 molar ratio, Mohr's salt (a double salt) is formed.

$FeSO_{4(aq)} + (NH_4)_2SO_{4(aq)} \rightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightleftharpoons Fe^{2+}_{(aq)} + 2NH^+_{4(aq)} + 2SO^{2-}_{4(aq)} + 6H_2O$

Because Fe^{2+} ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of Fe^{2+} ions.

When $CuSO_4$ is mixed with ammonia, following reaction occurs :

$CuSO_{4(aq)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]SO_4$

This complex does not produce Cu^{2+} ion, so the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion.

$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

37. (i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$

Potassium diaquadioxalatochromate(III) trihydrate

Oxidation state of Cr = +3; coordination number = 6

Stereochemistry : octahedral

E.C. of Cr^{3+}, $3d^3 = (t_{2g})^3, (e_g)^0$

Magnetic moment $(\mu) = \sqrt{n(n+2)}$ B.M.

$= \sqrt{3(3+2)} = \sqrt{15}$ B.M. = 3.87 B.M.

(ii) $[Co(NH_3)_5Cl]Cl_2$

Pentaamminechloridocobalt(III) chloride

Oxidation state of Co = +3, coordination number = 6

Stereochemistry = octahedral

E.C. of Co^{3+}, $3d^6 = (t_{2g})^6, (e_g)^0$

Magnetic moment $(\mu) = 0$

(iii) $[CrCl_3(py)_3]$

Trichloridotripyridinechromium(III)

Oxidation state of Cr = +3, coordination number = 6

Stereochemistry : octahedral

E.C. of Cr^{3+}, $3d^3 = (t_{2g})^3, (e_g)^0$

Magnetic moment = 3.87 B.M.

(iv) $Cs[FeCl_4]$

Caesium tetrachloridoferrate(III)

Oxidation state of Fe = +3; coordination number = 4

Stereochemistry = Tetrahedral

E.C. of Fe^{3+}, $3d^5 = (e)^2, (t_2)^3$

Magnetic moment $= \sqrt{5(5+2)}$ B.M. $= \sqrt{35}$ B.M. = 5.92B.M.

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

Potassium hexacyanomanganate(II)

Oxidation state of Mn = +2, coordination number = 6

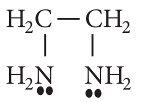
Stereochemistry = octahedral

E.C. of Mn^{2+}, $3d^5 = (t_{2g})^5 (e_g)^0$

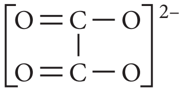
Magnetic moment

$(\mu) = \sqrt{1(1+2)}$ B.M. $= \sqrt{3}$ B.M. = 1.73B.M.

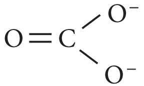
38. (a) Ligands which can coordinate with the central metal atom or ion through two donor atoms are known as bidentate ligands. Examples of bidentate ligands are:



Ethylene diamine (*en*)

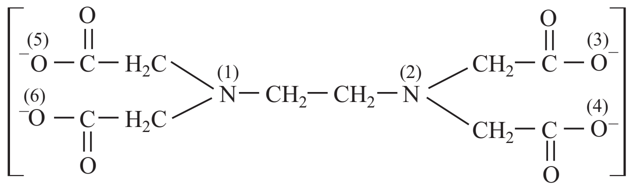


Oxalate anion



Carbonate ion

(b) Ligands which coordinate with the central ion through more than two donor atoms present in the molecule are called polydentate ligands. These are called tridentate (three), tetradentate (four), pentadentate (five) and hexadentate (six) ligands depending upon the number of coordinating donor atoms present in their molecules. A common example of hexadentate ligand is ethylenediamminetetraacetate ion as shown below:



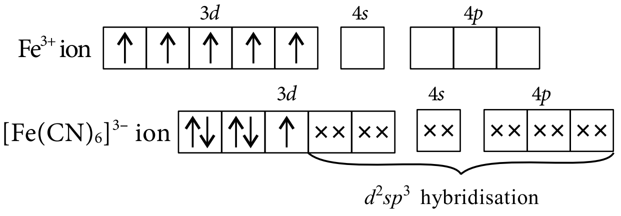
Structure of ethylenediamminetetraacetate ion

(c) The charge carried by a complex ion is the algebraic sum of charges carried by the central ion and the ligands coordinated to it. Thus $[Cu(NH_3)_6]^{2+}$ carries a charge of +2 and because ammonia molecule is neutral therefore, Cu^{2+} carries a charge of +2. $[Ag(CN)_2]^-$, ion carries a charge of –1 and two cyanide ions coordinated to it carry a charge of –1 each. So, Ag^+ carries a charge of +1.

39.

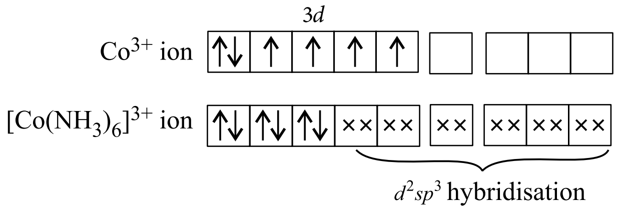
S.No.	Complex	Oxidation state of metal atom	Coordination number of central metal atom	*d*-orbital occupation
(i)	$K_3[Co(C_2O_4)_3]$	+3	6	$Co^{3+} = 3d^6; (t_{2g})^6, (e_g)^0$
(ii)	$[Cr(en)_2Cl_2]Cl$	+3	6	$Cr^{3+} = 3d^3; (t_{2g})^3$
(iii)	$(NH_4)_2[CoF_4]$	+2	4	$Co^{2+} = 3d^7; (e)^4, (t_2)^3$
(iv)	$[Mn(H_2O)_6]SO_4$	+2	6	$Mn^{2+} = 3d^5; (t_{2g})^3, (e_g)^2$

40. (a) Formation of hexacyanidoferrate(III) ion; $[Fe(CN)_6]^{3-}$: Electronic configuration of iron in the ground state is $3d^6 4s^2$. The oxidation state of iron is +3 in this complex. Iron (III) has outer electronic configuration $3d^5 4s^0$. It has been experimentally observed that this complex has one unpaired electron. To account for this, two unpaired electrons in 3*d* subshell pair up, thus leaving two 3*d*-orbitals empty. These two vacant 3*d*-orbitals, alongwith one 4*s*-orbital and three 4*p*-orbitals hybridise to give six equivalent d^2sp^3 hybridised orbitals. Six pairs of electrons, one from each cyanide ion, occupy the six vacant hybrid orbitals so produced. The complex has octahedral geometry and is paramagnetic due to the presence of one unpaired electron.



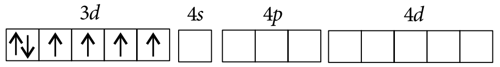
The complex evidently involves $(n-1)d^2nsnp^3$ hybridisation and is, therefore, called inner orbital or low spin complex.

(b) The outer electronic configuration of cobalt (III) ion is $3d^6$. According to Hund's rule, four of the 3*d*-orbitals are singly filled and one 3*d*-orbital has a pair of electrons. Octahedral complexes are formed through d^2sp^3 hybridisation for which the metal atom must have two of its 3*d*-orbitals empty. This is achieved by the pairing of the two 3*d*-electrons as a result of the energy released due to the approach of the ligands. This results in the formation of an octahedral complex. As is evident from the figure, the complex does not contain any unpaired electron and is, therefore, diamagnetic.

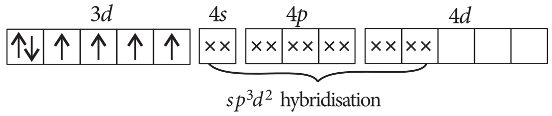


(c) In $[CoF_6]^{3-}$ complex, the 3*d*-orbitals remain undisturbed while the outer 4*d*-orbitals are used for hybridisation, as

Co^{3+} ion



$[CoF_6]^{3-}$ ion



The complex is paramagnetic since it contains four unpaired electrons.

☺☺☺