

# Coordination Compounds

## OBJECTIVE TYPE QUESTIONS

### ➡ Multiple Choice Questions (MCQs)

- The correct IUPAC name of the coordination compound  $K_3[Fe(CN)_5NO]$  is
  - potassium pentacyanonitrosylferrate(II)
  - potassium pentacyanonitroferrate(III)
  - potassium nitritopentacyanoferrate(IV)
  - potassium nitritepentacyanoiron(II).
- Ammonia acts as a very good ligand but ammonium ion does not form complexes because
  - $NH_3$  is a gas while  $NH_4^+$  is in liquid form
  - $NH_3$  undergoes  $sp^3$  hybridisation while  $NH_4^+$  undergoes  $sp^3d$  hybridisation
  - $NH_4^+$  ion does not have any lone pair of electrons
  - $NH_4^+$  ion has one unpaired electron while  $NH_3$  has two unpaired electrons.
- Correct formula of tetraamminechloridonitroplatinum(IV) sulphate can be written as
  - $[Pt(NH_3)_4(ONO)Cl]SO_4$
  - $[Pt(NH_3)_4Cl_2NO_2]_2SO_4$
  - $[Pt(NH_3)_4(NO_2)Cl]SO_4$
  - $[PtCl(ONO)NH_3(SO_4)]$
- The magnitude of magnetic moment (spin only) of  $[NiCl_4]^{2-}$  will be
  - 2.82 B.M.
  - 0
  - 1.23 B.M.
  - 5.64 B.M.
- Consider the following coordination compounds.
  - $[Pt(NH_3)_4Cl_2]Br_2$
  - $[Pt(NH_3)_4Br_2]Cl_2$
  - $[Co(NH_3)_4Cl_2]NO_2$Which of the following observations is correct?
  - (i) will give a pale yellow and (ii) will give a white precipitate with  $AgNO_3$  solution.
  - (iii) will give a white precipitate with  $AgNO_3$  solution.
  - (i), (ii) and (iii) will give white precipitate with  $AgNO_3$  solution.
  - None of the above coordination compounds will give white precipitate with  $AgNO_3$  solution.
- Hexaamminenickel(II) hexanitrocobaltate(III) can be written as
  - $[Ni(NH_3)_6][Co(NO_2)_6]$
  - $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$
  - $[Ni(NH_3)_6][Co(NO_2)_6]$
  - $[Ni(NH_3)_6(NO_2)_6]Co$
- Which of the following is correct?
  - Valence bond theory explains the colour of the coordination compounds.
  - $[NiCl_4]^{2-}$  is diamagnetic in nature.
  - EDTA is a chelating ligand.
  - A bidentate ligand can have four coordination sites.
- Electronic configuration of  $[Cu(NH_3)_6]^{2+}$  on the basis of crystal field splitting theory is
  - $t_{2g}^4 e_g^5$
  - $t_{2g}^6 e_g^3$
  - $t_{2g}^9 e_g^0$
  - $t_{2g}^5 e_g^4$ .
- Which of the following primary and secondary valencies are not correctly marked against the compound?
  - $[Cr(NH_3)_6]Cl_3$   $p = 3, s = 6$
  - $K_2[PtCl_4]$   $p = 2, s = 4$
  - $[Pt(NH_3)_2Cl_2]$   $p = 2, s = 4$
  - $[Cu(NH_3)_4]SO_4$   $p = 4, s = 4$
- What will be the correct order of absorption of wavelength of light in the visible region for the complexes,  $[Co(NH_3)_6]^{3+}$ ,  $[Co(CN)_6]^{3-}$ ,  $[Co(H_2O)_6]^{3+}$ ?
  - $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$
  - $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
  - $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
  - $[Co(CN)_6]^{3-} > [Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+}$
- Which of the following does not depict the correct name of the compound?
  - $K_2[Zn(OH)_4]$  : Potassium tetrahydroxozincate(II)



- (b)  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$  : Pentaammine carbonatochlorocobaltate(III)  
 (c)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  : Sodium hexanitrocobaltate(III)  
 (d)  $\text{K}_3[\text{Cr}(\text{CN})_6]$  : 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)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (ii)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (iii)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (iv)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (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)  $[\text{PdCl}_4]^{2-}$  (b)  $[\text{Pd}(\text{CN})_4]^{2-}$   
 (c)  $[\text{Ni}(\text{CN})_4]^{2-}$  (d)  $[\text{NiCl}_4]^{2-}$

15. The name of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  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)  $\text{Cu}_2\text{O}$  (b)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   
 (c)  $[\text{Cu}(\text{NH}_3)_4]\text{OH}$  (d)  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$

18. When excess of aqueous KCN solution is added to an aqueous solution of copper sulphate, the complex  $[\text{Cu}(\text{CN})_4]^{2-}$  is formed. On passing  $\text{H}_2\text{S}$  gas through this solution no precipitate of  $\text{CuS}$  is formed because

- (a) sulphide ions cannot replace  $\text{CN}^-$  ions  
 (b)  $[\text{Cu}(\text{CN})_4]^{2-}$  does not give  $\text{Cu}^{2+}$  ion in the solution  
 (c) sulphide ions from  $\text{H}_2\text{S}$  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)  $\text{NH}_3 < \text{Cl}^- < \text{CN}^- < \text{F}^- < \text{CO} < \text{H}_2\text{O}$   
 (b)  $\text{F}^- < \text{Cl}^- < \text{NH}_3 < \text{CN}^- < \text{H}_2\text{O} < \text{CO}$   
 (c)  $\text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^- < \text{CO}$   
 (d)  $\text{CO} < \text{CN}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{F}^- < \text{Cl}^-$

21. The number of unpaired electrons in  $[\text{Ni}(\text{CO})_4]$  is

- (a) one (b) two  
 (c) three (d) zero

22.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  show different colours in dilute solution because

- (a)  $\text{CN}^-$  is a strong field ligand and  $\text{H}_2\text{O}$  is a weak field ligand hence magnitude of CFSE is different  
 (b) both  $\text{CN}^-$  and  $\text{H}_2\text{O}$  absorb same wavelength of energy  
 (c) complexes of weak field ligands are generally colourless  
 (d) the sizes of  $\text{CN}^-$  and  $\text{H}_2\text{O}$  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)  $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]$  (b)  $[\text{Ni}(\text{CO})_4]$   
 (c)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$  (d)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

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  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex?

- (a) Electronic configuration =  $3d^7 \rightarrow t_{2g}^5 e_g^2$ , no. of unpaired electrons = 3,  $\mu = 3.87$  B.M.  
 (b) Electronic configuration =  $3d^6 \rightarrow t_{2g}^4 e_g^2$ , no. of unpaired electrons = 2,  $\mu = 2.87$  B.M.  
 (c) Electronic configuration =  $3d^7 \rightarrow t_{2g}^6 e_g^1$ , no. of unpaired electrons = 1,  $\mu = 2.87$  B.M.



- (d) Electronic configuration =  $3d^7 = t_{2g}^3 e_g^4$ , no. of unpaired electrons = 3,  $\mu = 3.87$  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
- hexacyano complexes absorb orange or red light thus appear yellow while hexaaqua complexes absorb indigo thus appear yellow
  - hexacyano complexes absorb indigo thus appearing yellow while hexaaqua complexes absorb orange or red light thus appear blue or green
  - hexacyano complexes absorb yellow light while hexaaqua complexes absorb blue light
  - $\text{CN}^-$  ions are yellow in colour while aqua ions are blue or green in colour.
- 27.** Low spin tetrahedral complexes are not formed because
- for tetrahedral complexes, the CFSE is lower than pairing energy
  - for tetrahedral complexes, the CFSE is higher than pairing energy
  - electrons do not go to  $e_g$  in case of tetrahedral complexes
  - 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?
- Octahedral –  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$
  - Square planar –  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$
  - Tetrahedral –  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{ZnCl}_4]^{2-}$
  - Trigonal bipyramidal –  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ ,  $[\text{CuCl}_4]^{2-}$
- 29.** A coordination compound  $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$  gives white precipitate of  $\text{AgCl}$  with  $\text{AgNO}_3$ . The molar conductance of the compound corresponds to two ions. The structural formula of the compound is
- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_3]$
  - $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]\text{H}_2\text{O}$
  - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$
  - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}]\text{Cl}_2$
- 30.** Among the following, which are ambidentate ligands?
- $\text{SCN}^-$
  - $\text{NO}_3^-$
  - $\text{NO}_2^-$
  - $\text{C}_2\text{O}_4^{2-}$
- (i) and (iii)
  - (i) and (iv)
  - (ii) and (iii)
  - (ii) and (iv)
- 31.** The lowest value of paramagnetism is shown by
- $[\text{Co}(\text{CN})_6]^{3-}$
  - $[\text{Fe}(\text{CN})_6]^{3-}$
  - $[\text{Cr}(\text{CN})_6]^{3-}$
  - $[\text{Mn}(\text{CN})_6]^{3-}$
- 32.** Which of the following is a tridentate ligand?
- $\text{EDTA}^{4-}$
  - $(\text{COO})_2^{2-}$
  - dien
  - $\text{NO}_2^-$
- 33.** Which of the following has largest paramagnetism?
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- 34.** Identify the statement which is not correct?
- Coordinate compounds are mainly known for transition metals.
  - Coordination number and oxidation state of a metal are same.
  - Tetrahedral complexes form low spin complex.
  - 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  $\text{CuSO}_4$  solution, a green precipitate is formed. This observation can be explained as follows.
- On adding  $\text{KF}$ ,  $\text{H}_2\text{O}$  being weak field ligand is replaced by  $\text{F}^-$  ions forming  $[\text{CuF}_4]^{2-}$  which is green in colour.
  - Potassium is coordinated to  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  ion present in  $\text{CuSO}_4$  and gives green colour.
  - On adding  $\text{KF}$ ,  $\text{Cu}^{2+}$  are replaced by  $\text{K}^+$  forming a green complex.
  - Blue colour of  $\text{CuSO}_4$  and yellow colour of  $\text{KI}$  form green colour on mixing.
- 36.** The formula of the complex diamminechlorido (ethylenediamine)nitroplatinum(IV) chloride is
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{en})\text{NO}_2]\text{Cl}_2$
  - $\text{Pt}[\text{Pt}(\text{NH}_3)_2(\text{en})\text{Cl}_2\text{NO}_2]$
  - $\text{Pt}[(\text{NH}_3)_2(\text{en})\text{NO}_2]\text{Cl}_2$
  - $\text{Pt}[(\text{NH}_3)_2(\text{en})\text{NO}_2\text{Cl}_2]$
- 37.** Using valence bond theory, the complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  can be described as
- $sp^3d^2$ , outer orbital complex, paramagnetic
  - $dsp^2$ , inner orbital complex, diamagnetic
  - $d^2sp^3$ , inner orbital complex, paramagnetic
  - $d^2sp^3$ , outer orbital complex, diamagnetic.

38. The ligand  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$  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 :  $[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]_2\text{SO}_4$   
 (b) Coordination compound containing anionic complex ion :  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$   
 (c) Non-ionic coordination compound :  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$   
 (d) Coordination compound containing cationic and anionic complex ion :  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
40. A coordination compound  $X$  gives pale yellow colour with  $\text{AgNO}_3$  solution while its isomer  $Y$  gives white precipitate with  $\text{BaCl}_2$ . Two compounds are isomers of  $\text{CoBrSO}_4 \cdot 5\text{NH}_3$ . What could be the possible formula of  $X$  and  $Y$ ?  
 (a)  $X = [\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ ,  $Y = [\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$   
 (b)  $X = [\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ ,  $Y = [\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
 (c)  $X = [\text{Co}(\text{NH}_3)_5\text{Br}(\text{SO}_4)]$ ,  $Y = [\text{CoBr}(\text{SO}_4)(\text{NH}_3)_5]$   
 (d)  $X = [\text{Co}(\text{Br})_5\text{NH}_3]\text{SO}_4$ ,  $Y = [\text{CoBr}(\text{SO}_4)]\text{NH}_3$
41. When one mole of each of the following complexes is treated with excess of  $\text{AgNO}_3$  which will give maximum amount of  $\text{AgCl}$ ?  
 (a)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (d)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
42. Which of the following descriptions about  $[\text{FeCl}_6]^{4-}$  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.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour while  $\text{CuSO}_4$  is colourless due to  
 (a) presence of strong field ligand in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
 (b) due to absence of water (ligand),  $d-d$  transition are not possible in  $\text{CuSO}_4$   
 (c) anhydrous  $\text{CuSO}_4$  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)  $\text{K}_2\text{Cr}_2\text{O}_7$  (b)  $[\text{Co}(\text{SO}_4)]$   
 (c)  $(\text{NH}_4)_2[\text{TiCl}_6]$  (d)  $\text{K}_3[\text{Cu}(\text{CN})_4]$
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)  $\text{H}_2\text{O}$  (b)  $\text{NH}_3$   
 (c)  $\text{ONO}$  (d)  $\text{CO}$
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  $\text{Co}(\text{III})$  with ligand  $\text{NH}_3$  and  $\text{Cl}^-$  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  $[(\text{Co}(\text{NH}_3)_6)\text{Cl}_3]$  with purple colour  
 (b) complex II is  $[(\text{Co}(\text{NH}_3)_6)\text{Cl}_3]$  with purple colour  
 (c) complex III is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  with violet colour  
 (d) both (b) and (c)



51. Ms. Anjali class 12<sup>th</sup> 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<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl<sub>3</sub> - Triamminetriaqua chromium(III)chloride, [Ag(NH<sub>3</sub>)<sub>2</sub>][Ag(CN)<sub>2</sub>] Diamminesilver(I) dicyanidosilver(I)

[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl-Dichloridobis(ethane-1, 2-diammine) cobalt (III) chloride

K<sub>3</sub>[Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]-Potassium trioxalatoaluminium(III) [Ni(CO)<sub>4</sub>]-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

- the ligands are name in an alphabetical order before the name of central atom/ion.
- prefixes mono, di, tri etc. are used to indicate the number of individual ligands in the coordination entity.
- if the complex ion is cation, the metal is named same as the element.
- if the complex ion is anion, the metal ends with suffix -ate.

52. Fe<sup>x+</sup> + SCN<sup>-</sup> → Octahedral complex

Fe<sup>y+</sup> + CN<sup>-</sup> → 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

- CN<sup>-</sup> is a strong ligand while SCN<sup>-</sup> is a weak ligand

(b) Fe is present in O.S. I in complex with SCN<sup>-</sup> while in O.S. III in complex with CN<sup>-</sup>

(c) SCN<sup>-</sup> is a strong ligand while CN<sup>-</sup> 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<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>

II. [CoCl<sub>4</sub>]<sup>2-</sup>

III. [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>

IV. [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>

V. [Ni(CO)<sub>4</sub>]

VI. [Ni(CN)<sub>4</sub>]<sup>2-</sup>

The complexes which have zero magnetic moment are.

- I and V
- II and VI only
- III and IV
- 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?

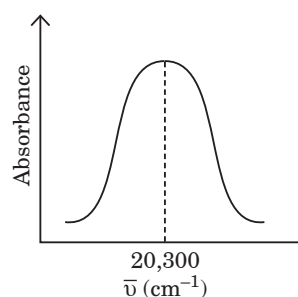
- The ligand in complex I is CN<sup>-</sup> and it has dsp<sup>2</sup> hybridisation.
- The ligand in complex II is Cl<sup>-</sup> and it has sp<sup>3</sup> hybridisation.
- The ligand in complex IV is H<sub>2</sub>O and it has d<sup>2</sup>sp<sup>3</sup> hybridisation.
- The ligand in complex III is CO and it has sp<sup>3</sup> hybridisation.

## ➡ 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<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. The Ti<sup>3+</sup> ion has a single electron in the 3d-orbital, and we refer to it as d<sup>1</sup> ion. In the octahedral field generated by six H<sub>2</sub>O molecules, the single electron will reside in one of the three degenerate t<sub>2g</sub> orbitals. Under spectral excitation, the electron is promoted to an e.g., orbital giving

rise to an absorption spectrum consisting of a single peak that can be represented as shown :



The maximum absorption in the spectrum for [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> occurs at 20,300 cm<sup>-1</sup> which is equal to 243 kJ mol<sup>-1</sup>. This gives the value of

$\Delta_o$  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 observed 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  $\Delta_o$  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) Excitation 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 valence 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 ( $\Delta_o$ ) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of  $\Delta_o$  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 ( $\Delta_o$ ) and tetrahedral ( $\Delta_t$ ) 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  $[\text{FeF}_6]^{4-}$ .

- |               |               |
|---------------|---------------|
| (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  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  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  $[\text{Pt}(\text{NH}_3)_3\text{Br}(\text{NO}_2)\text{Cl}]\text{Cl}$  is

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

68. The IUPAC name of  $[\text{Ni}(\text{CO})_4]$  is

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

69. As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  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 dichloridobis(ethane-1, 2-diamine) cobalt(III) ion?

- |                                       |   |
|---------------------------------------|---|
| (a) $[\text{CoCl}_2(\text{en})]^{2+}$ | (b) $[\text{CoCl}_2(\text{en})_2]^{2+}$ |
| (c) $[\text{CoCl}_2(\text{en})]^+$    | (d) $[\text{CoCl}_2(\text{en})_2]^+$    |

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

- (a)  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{SO}_4$
- (b)  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{SO}_4$
- (c)  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_4](\text{SO}_4)_2$
- (d)  $[\text{Co}(\text{ONO})(\text{NH}_3)_4](\text{SO}_4)_2$

**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,  $\text{Co}^{3+}$  forms both inner orbital and outer orbital complexes, with ammonia it forms  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and with fluorine it forms  $[\text{CoF}_6]^{3-}$  complex ion.

**72.** Which of the following is not true for  $[\text{CoF}_6]^{3-}$ ?

- (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.**  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of  $3d$ -electrons in the central metal of the complex is

- (a)  $3d_{xy}^1, 3d_{x^2-y^2}^1, 3d_{yz}^1$     (b)  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$
- (c)  $3d_{xy}^1, 3d_{zy}^1, 3d_{z^2}^1$     (d)  $3d_{x^2-y^2}^1, 3d_{z^2}^1, 3d_{xz}^1$

**74.** Which of the following is true for  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ?

- (a) It is an octahedral, diamagnetic 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, diamagnetic and inner orbital complex.

**75.** The paramagnetism of  $[\text{CoF}_6]^{3-}$  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)  $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$     (b)  $[\text{FeF}_6]^{3-}$
- (c)  $[\text{Co}(\text{CN})_6]^{3-}$     (d)  $[\text{NiCl}_4]^{2-}$

## ➡ 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  $[\text{Ni}(\text{en})_3]\text{Cl}_2$  ( $\text{en}$  = ethylenediamine) has lower stability than  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ .

**Reason :** In  $[\text{Ni}(\text{en})_3]\text{Cl}_2$  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  $\text{Ni}^{2+}$  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 ( $\Delta_o$ ) is more for  $4d$  and  $5d$ .

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

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

**82. Assertion :**  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless.

**Reason :**  $d-d$  transition is not possible in  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ .

**83. Assertion :** Thiocarbonyl is a neutral ligand.

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



**84. Assertion :** The ligand  $\text{N}_3^-$  is named as nitride.

**Reason :**  $\text{N}_3^-$  is derived from  $\text{HN}_3$ .

**85. Assertion :**  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{NO}_3$  is dichlorotetraaquachromium(III) nitrate.

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

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

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

**87. Assertion :**  $[\text{Al}(\text{NH}_3)_6]^{3+}$  does not exist in aqueous solution.

**Reason :**  $\text{NH}_3$  is a neutral ligand.

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

**Reason :**  $[\text{FeF}_6]^{3-}$  is a low spin complex.

**89. Assertion :**  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is square planar.

**Reason :** The oxidation state of platinum is + 2.

**90. Assertion :**  $\text{Cu}(\text{OH})_2$  is soluble in  $\text{NH}_4\text{OH}$  but not in  $\text{NaOH}$ .

**Reason :**  $\text{Cu}(\text{OH})_2$  forms a soluble complex with  $\text{NH}_3$ .

## SUBJECTIVE TYPE QUESTIONS

### ➡ Very Short Answer Type Questions (VSA)

1. Write the hybridisation and number of unpaired electrons in the complex  $[\text{CoF}_6]^{3-}$ . (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  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is mixed with  $\text{AgNO}_3$ , 2 moles of  $\text{AgCl}$  are

precipitated per mole of the compound. Write structural formula of the complex.

6. Why a solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green while a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless? (At. no. of Ni = 28)

7. Write the IUPAC name of  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ .

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  $[\text{Pt}(\text{en})_2\text{Cl}_2]$ .

### ➡ Short Answer Type Questions (SA-I)

11. Why is  $[\text{NiCl}_4]^{2-}$  paramagnetic but  $[\text{Ni}(\text{CO})_4]$  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  $[\text{Ni}(\text{CO})_4]$ . (At. no. of Ni = 28)

13. Out of  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ , 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  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . (At. no. of Co = 27)

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



18. Write down the IUPAC name of the following complex :  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]\text{Cl}$

19. Ravi prepared a complex compound of cobalt with  $\text{NH}_3$  and  $\text{NO}_2$  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)  $\text{Co}^{3+}$  ion is bound to one  $\text{Cl}^-$ , one  $\text{NH}_3$  molecule and two bidentate ethylene diamine (*en*) molecules.

(ii)  $\text{Ni}^{2+}$  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)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$  (ii)  $\text{K}_3[\text{Fe}(\text{CN})_6]$

(iii)  $[\text{CoBr}_2(\text{en})_2]^+$

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  $[\text{NiCl}_4]^{2-}$ , 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)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$  (ii)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

(iii)  $\text{Ni}(\text{CO})_4$

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

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

27. Write the IUPAC name, deduce the geometry and magnetic behaviour of the complex  $\text{K}_4[\text{Mn}(\text{CN})_6]$ .

[Atomic no. of Mn = 25]

28. For the complex  $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$ , 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)  $[\text{Fe}(\text{CN})_6]^{4-}$  (ii)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$

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

30. Explain the following :

(i) Anhydrous  $\text{CuSO}_4$  is white while hydrated  $\text{CuSO}_4$  is blue in colour.

(ii)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  is violet in colour but becomes colourless on heating.

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

32. Give reason :  $[\text{CoF}_6]^{3-}$  is outer orbital but  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is inner orbital complex.

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

(i)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (ii)  $[\text{Co}(\text{en})_3]\text{Cl}_3$

(iii)  $\text{K}_2[\text{Ni}(\text{CN})_4]$

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.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  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)  $[\text{CoF}_6]^{3-}$ , (b)  $[\text{FeF}_6]^{3-}$ , (c)  $[\text{Fe}(\text{CN})_6]^{4-}$   
 (ii)  $\text{FeSO}_4$  solution mixed with  $(\text{NH}_4)_2\text{SO}_4$  solution in 1:1 molar ratio gives the test of  $\text{Fe}^{2+}$  ion but  $\text{CuSO}_4$  solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of  $\text{Cu}^{2+}$  ion. Explain why?

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:

- $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- $[\text{CrCl}_3(\text{py})_3]$
- $\text{Cs}[\text{FeCl}_4]$
- $\text{K}_4[\text{Mn}(\text{CN})_6]$

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:

- $[\text{Cu}(\text{NH}_3)_6]^{2+}$  (ii)  $[\text{Ag}(\text{CN})_2]^-$

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

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

40. (a) Explain hybridisation in the complex which contains hexacyanidoferrate(III) ion.

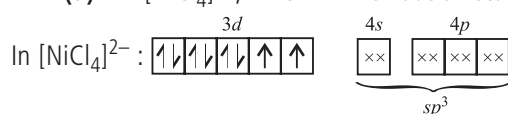
(b) Based on the valence bond theory describe the formation and nature of hexamminecobalt(III) chloride.

(c) How will you show that hexafluorocobaltate(III) ion is paramagnetic in nature?

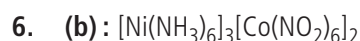
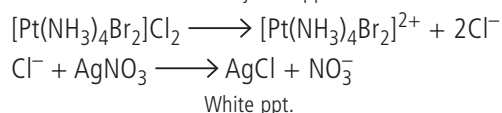
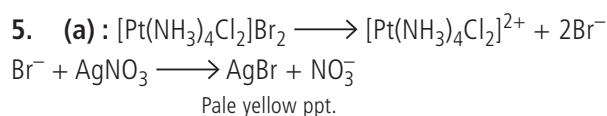
## ANSWERS

### OBJECTIVE TYPE QUESTIONS

- (a)
- (c) :  $\text{NH}_4^+$  ion does not have any lone pair of electrons which it can donate to central metal ion hence it does not form complexes.
- (c) : Tetraamminechloridonitroplatinum(IV) sulphate can be written as  $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{SO}_4$ .
- (a) : In  $[\text{NiCl}_4]^{2-}$ , Ni is in +2 oxidation state.



Magnetic moment,  $\mu = \sqrt{n(n+2)}$   
 [∵ *n* = number of unpaired electrons]  
 $= \sqrt{2(2+2)} = 2.82 \text{ B.M.}$



Hexaamminenickel(II) hexanitrocobaltate(III)

7. (c)

8. (b) : In  $[\text{Cu}(\text{NH}_3)_6]^{2+}$ , oxidation state of Cu = +2,  $\text{Cu}^{2+} = 3d^9$

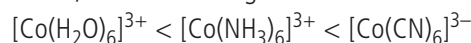
$$3d^9 = t_{2g}^6 e_g^3$$

9. (d) : In  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  primary valency is 2 and secondary valency is 4.

10. (c) : The CFSE of the ligands is in the order :



Hence, excitation energies is in the order:

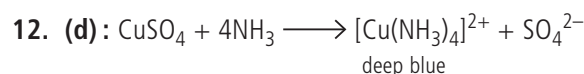


From the relation  $E = \frac{hc}{\lambda} \Rightarrow E \propto \frac{1}{\lambda}$

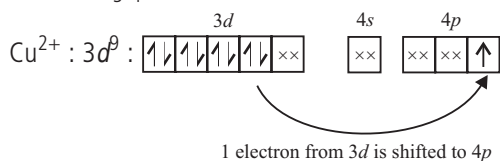
The order of absorption of wavelength of light in the visible region :  $[\text{Co}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{CN})_6]^{3-}$



Pentaamminecarbonatocobalt(III) chloride



In  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , oxidation state of Cu = +2

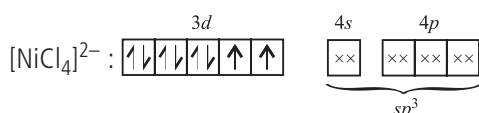


Hybridisation is  $dsp^2$  hence geometry is square planar and paramagnetic due to presence of one unpaired electron.

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

No. of ions :  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] = 0$ ;  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} = 2$   
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 = 3$ ;  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = 4$

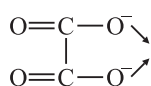
**14. (d) :** In  $[\text{NiCl}_4]^{2-}$ , oxidation state of Ni = +2



$sp^3$  hybridisation and tetrahedral shape.

**15. (c) :** The name of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  is pentaamminenitrito-N-cobalt(III) chloride.

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



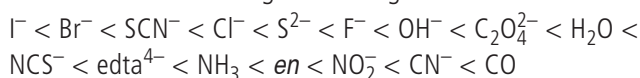
**17. (b) :**  $\text{CuSO}_4 + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

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



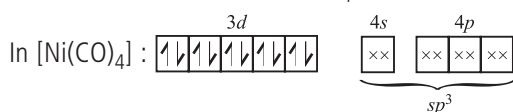
**19. (c) :** In  $d^6$  (low spin), electrons get paired up to make two empty  $d$ -orbitals. Hybridisation is  $d^2sp^3$  (octahedral) and the complex is low spin.

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



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

Oxidation state of Ni in  $[\text{Ni}(\text{CO})_4] = 0$



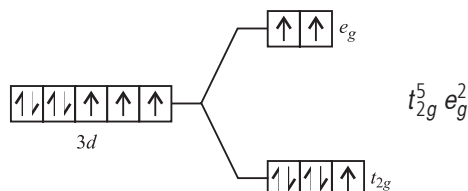
No. of unpaired electrons = 0

**22. (a) :**  $\text{CN}^-$  is a strong field ligand hence pairing of electrons takes place while in case of  $\text{H}_2\text{O}$  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  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , oxidation state of Co = +2,  $\text{Co}^{2+} = 3d^7$



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

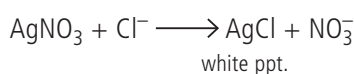
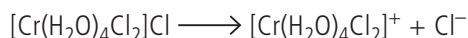
**26. (b) :** The ligand  $\text{CN}^-$  absorbs indigo, the high energy radiation and thus appears yellow. The aqua complexes have much smaller CFSE, they absorb orange or red light and thus appear blue or green.

**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) :**  $[\text{CuCl}_4]^{2-}$  – Tetrahedral

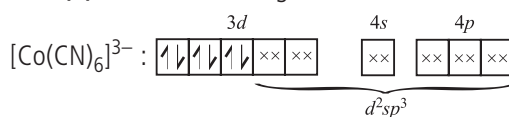
$[\text{Fe}(\text{NH}_3)_6]^{2+}$  – Octahedral

**29. (c) :** It gives precipitate with  $\text{AgNO}_3$  it means it gives  $\text{Cl}^-$  ions in the solution. Since conductivity corresponds to two ions, it shows one  $\text{Cl}^-$  is outside the coordination sphere. The structure will be



**30. (a) :**  $\text{SCN}^-$  and  $\text{NO}_2^-$  are ambidentate ligands since they have more than one donor atoms to attach to the central metal atom.

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

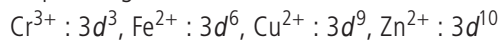


No. of unpaired electrons = 0, hence, shows no paramagnetism.

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



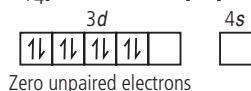
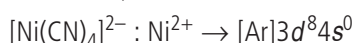
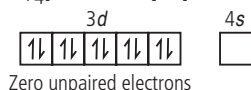
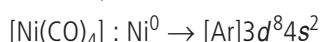
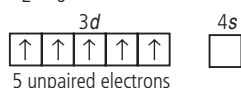
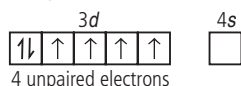
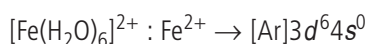
**33. (b) :** More the number of unpaired electrons, higher is its paramagnetism.



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



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

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

$[\text{NiCl}_4]^{2-} : sp^3$  hybridisation (tetrahedral) and have two unpaired electrons (paramagnetic)

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} : sp^3 d^2$  hybridisation (octahedral) and have two unpaired electrons (paramagnetic)

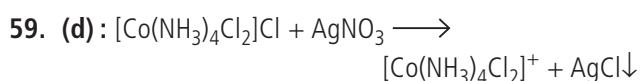
$[\text{Ni}(\text{CO})_4] : sp^3$  hybridisation (tetrahedral) and have zero unpaired electrons (diamagnetic)

**55. (c) :** Because  $\text{F}^-$  is a weak field ligand.

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

**57. (d)**

**58. (a)**



Thus it gives precipitate of 1 mol of AgCl.

**60. (b) :**  $\text{CoCl}_3 \cdot 4\text{NH}_3$  gives 1 mol AgCl on reaction with  $\text{AgNO}_3$ , hence the complex can be represented as  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ .

**61. (a) :** The  $\text{Cl}^-$  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) :**  $\text{Fe}^{2+} : 3d^6 \Rightarrow t_{2g}^4 e_g^2$

(Since,  $\text{F}^-$  is a weak field ligand)

Hence four unpaired electrons are present.

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

**66. (a) :** In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , 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  $\text{NO}_2^-$  is ambidentate ligand as it can donate electrons through either nitrogen ( $\text{NO}_2$ ) or oxygen ( $\text{ONO}$ ).

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

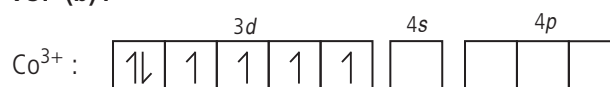
**73. (b) :** Magnetic moment of 3.83 B.M. suggests that it has 3 unpaired electrons,

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

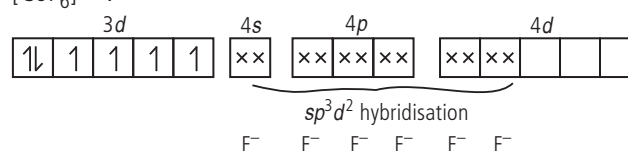
It involves  $d^2 sp^3$  hybridisation so correct distribution of electrons is  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$ .

**74. (d) :**  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is  $d^2 sp^3$  hybridised with all electrons paired hence, it is diamagnetic and inner orbital complex.

**75. (b) :**



$[\text{CoF}_6]^{3-}$  :



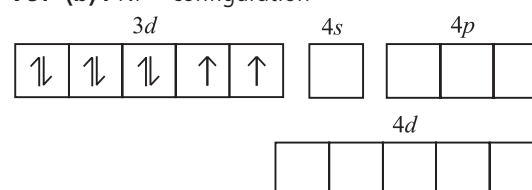
**76. (c) :** Inner orbital complexes are formed with strong ligands as they force electrons to pair up and hence the complex will be either diamagnetic or will have less number of unpaired electrons.

**77. (d) :**  $[\text{Ni}(\text{en})_3]\text{Cl}_2$  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  $[\text{Ni}(\text{en})_3]\text{Cl}_2$ , Ni with  $d^8$  configuration shows octahedral geometry.

**78. (a)**

**79. (b) :**  $\text{Ni}^{2+}$  configuration



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

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

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

82. (a) :  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  has no unpaired electron in its  $d$  subshell and thus  $d-d$  transition is not possible whereas  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  has one unpaired electron in its  $d$ -subshell which gives rise to  $d-d$  transition to impart colour.

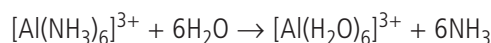
83. (c) : Thiocarbonyl (CS) has one donor atom.

84. (d) :  $\text{N}_3^-$  is named as azido. It is derived from  $\text{HN}_3$ .

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

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

87. (b) : The complex ion  $[\text{Al}(\text{NH}_3)_6]^{3+}$  undergoes the change into new complex ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in aqueous medium due to higher heat of hydration of aluminium ion on account of its small size.



88. (c) :  $[\text{FeF}_6]^{3-}$  is a high spin complex since  $\text{F}^-$  is a weak field ligand.

89. (b) : The outer electronic configuration of platinum in ground state is  $5d^9 6s^1$ . The  $\text{Pt}^{2+}$  ion formed by the loss of two electrons has outer electronic configuration of  $5d^8$ . In the presence of strong ligands ( $\text{NH}_3$ ) two unpaired electrons in the  $5d$ -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  $\text{Cl}^-$ ). As such the resulting complex is square planar.

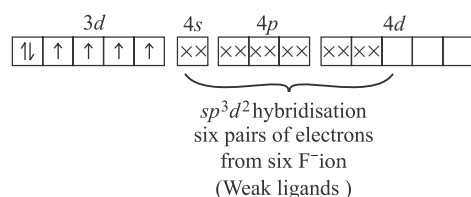
90. (a)

### SUBJECTIVE TYPE QUESTIONS

1. Oxidation state of Co ion in  $[\text{CoF}_6]^{3-}$  is +3.



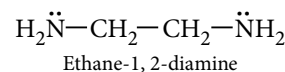
$\text{Co}^{3+}$  in  $[\text{CoF}_6]^{3-}$  :



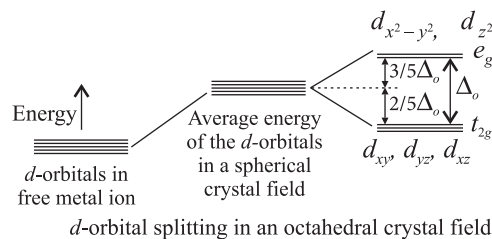
No. of unpaired electrons = 4

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.



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.



4.  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

5. For one mole of the compound, two moles of  $\text{AgCl}$  are precipitated which indicates that two ionisable chloride ions in the complex. Hence, its structural formula is  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$

6.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is a high spin complex ( $\Delta_o$  small) while  $[\text{Ni}(\text{CN})_4]^{2-}$  is a low spin square planar complex.

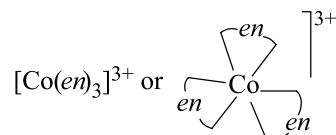
In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  complex,  $d-d$  transitions are taking place on absorbing low energy radiation (red component of spectrum) from visible region showing green as the complementary colour.

In  $[\text{Ni}(\text{CN})_4]^{2-}$  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).

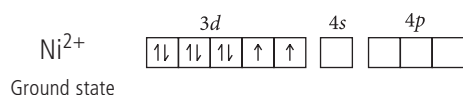
8. Double salts dissociate into ions completely when dissolved in water. On the other hand, in complexes, the complex ion does not dissociate.

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.,

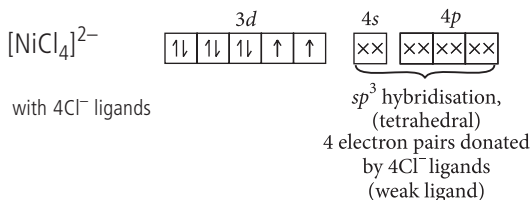


10. Coordination number and oxidation state of Pt in the complex  $[\text{Pt}(\text{en})_2\text{Cl}_2]$  are 6 and +2 because  $\text{en}$  is a bidentate and neutral ligand.

11.  $[\text{NiCl}_4]^{2-}$  contains  $\text{Ni}^{2+}$  ion with  $3d^8$  configuration.

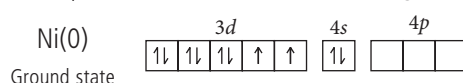


$\text{Cl}^-$  is a weak field ligand. Hence, outer 4s and 4p-orbitals are used in hybridisation.

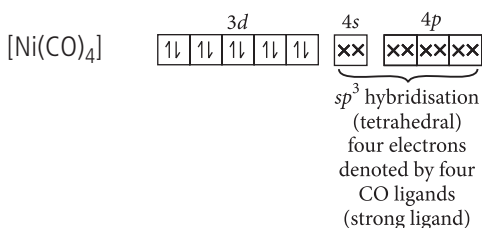


It has two unpaired electrons hence, it is paramagnetic.

$[\text{Ni}(\text{CO})_4]$  contains  $\text{Ni}(0) - 3d^8 4s^2$  configuration.



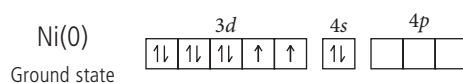
CO is a strong field ligand hence, 4s-electrons will shift to 3d-orbital making 4s-orbital vacant.



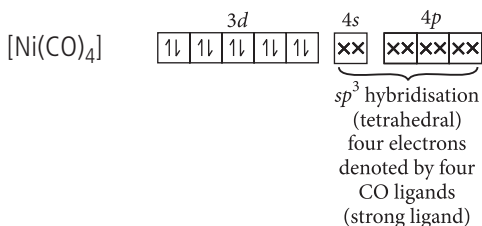
The complex has all paired electrons hence, it is diamagnetic.

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)  $[\text{Ni}(\text{CO})_4]$  contains  $\text{Ni}(0) - 3d^8 4s^2$  configuration.

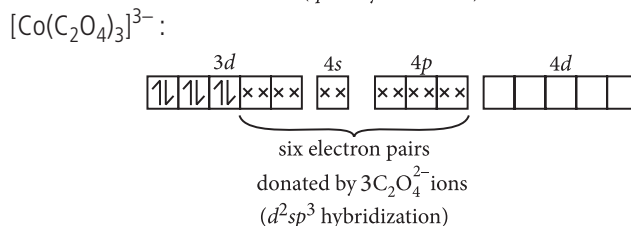
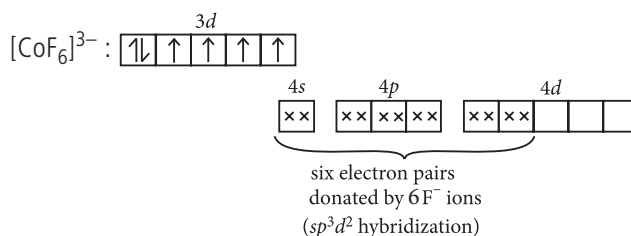


CO is a strong field ligand hence, 4s-electrons will shift to 3d-orbital making 4s-orbital vacant.



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

13. Formation of  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  can be represented as :



(i)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is diamagnetic as all electrons are paired.

(ii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is more stable as  $\text{C}_2\text{O}_4^{2-}$  is a chelating ligand and forms chelate rings.

(iii)  $[\text{CoF}_6]^{3-}$  is an outer orbital complex as it undergoes  $sp^3d^2$  hybridization using the outer 4d-orbital.

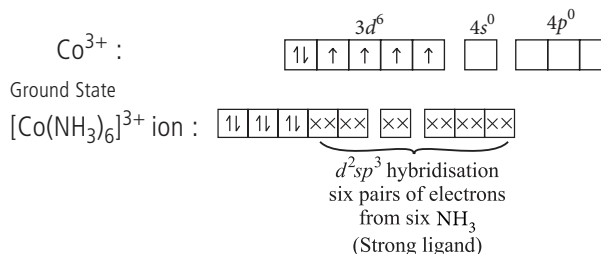
(iv)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is low spin complex due to absence of any unpaired electron.

14. (i)  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$  (ii)  $\text{K}_2[\text{Ni}(\text{CN})_4]$

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

For example,  $\text{NO}_2^-$  ion can coordinate either through nitrogen or through oxygen to the central metal atom/ion.

16. Oxidation state of cobalt in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is +3.

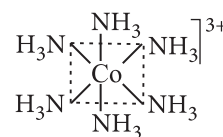


Hybridisation –  $d^2sp^3$

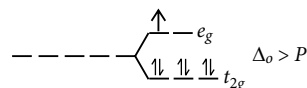
Structure – Octahedral (low spin)

Nature – Diamagnetic

IUPAC name : Hexaamminecobalt(III) ion



17. In presence of strong field ligand,  $\text{Co}(\text{II})$  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  $\text{Co}^{2+}$  is easily oxidised to  $\text{Co}^{3+}$  in the presence of strong field ligand.



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

19. (i) Ambident ligands ( $\text{NO}_2$ ,  $\text{ONO}$ ) present in the given compounds.

(ii)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  (Yellow)

Pentaamminenitrito-N-cobalt(III) chloride

$[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$  (Red)

Pentaamminenitrito-O-cobalt(III) chloride

20. (i)  $[\text{Co}(\text{en})_2\text{Cl}(\text{NH}_3)]^{2+}$

Aminechloridobis(ethane-1,2-diamine)cobalt(III) ion

In presence of strong  $\text{NH}_3$  and  $\text{en}$  ligand,  $\text{Co}^{3+}$  ( $3d^6$ ) forms low spin complex. Hence, complex is diamagnetic.

(ii)  $[\text{Ni}(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$ : Diaquadioxalatonicelate(II) ion

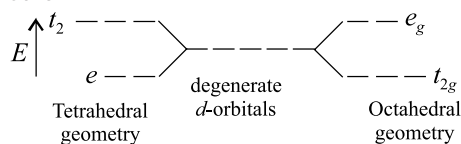
In the presence of weak  $\text{ox}$  and  $\text{H}_2\text{O}$  ligand,  $\text{Ni}(\text{II})$  forms high spin complex ( $sp^3d^2$  hybridisation). It is paramagnetic.

21. (i) Triamminetrichloridochromium(III)

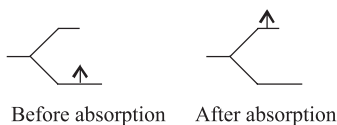
(ii) Potassium hexacyanoferrate(III)

(iii) Dibromidobis(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.



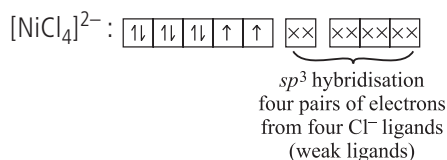
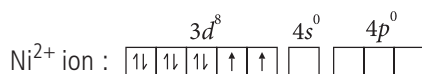
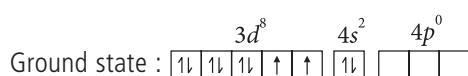
23. (a) When ligands approach the central metal, atom or ion of complex its  $d$ -orbital breaks into two parts  $t_{2g}$  and  $e_g$  levels. When light falls on the complex the complex absorbs light of suitable frequency for transfer of electron from lower level to higher level. This jump of electron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



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

24. Tetrachloridonickelate(II) ion

Ni atom ( $Z = 28$ )



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

25. (i)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$  :

Diamminechloridonitrito-N-platinum(II)

It is square planar and diamagnetic.

(ii)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  :

Tetraamminedichloridocobalt(III) chloride

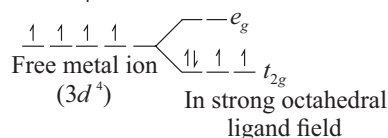
It is octahedral and diamagnetic.

(iii)  $\text{Ni}(\text{CO})_4$  : Tetracarbonylnickel(0)

It is tetrahedral and diamagnetic.

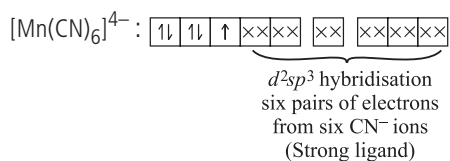
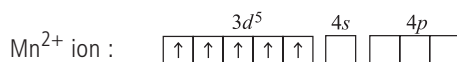
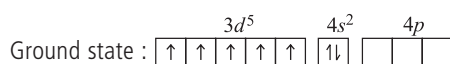
26. In  $[\text{Mn}(\text{CN})_6]^{3-}$ , Mn is in +3 state so, it has configuration of  $3d^4$ .

Since  $\text{CN}^-$  is a strong field ligand hence pairing of electrons in  $3d$ -orbital takes place.



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

27. Mn ( $Z = 25$ )



IUPAC name : Potassium hexacyanomanganate(II)

Geometry : Octahedral

No. of unpaired electrons,  $n = 1$

Magnetic behaviour : paramagnetic

28. (i)  $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$

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

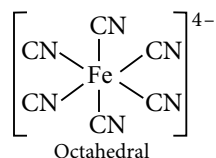
Oxidation number of iron = +3

- (ii)  $d^2sp^3$  hybridisation and octahedral shape.  
 (iii) Paramagnetic due to presence of one unpaired electron.  
 (iv) dichloridobis(ethane-1,2-diamine)iron(III) chloride

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

Hybridisation -  $d^2sp^3$

Structure : Inner orbital octahedral complex

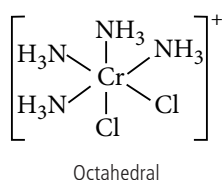


(ii)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$  :

Tetraamminedichloridochromium(III) ion

Hybridisation -  $d^2sp^3$

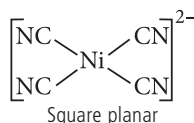
Structure : Inner orbital octahedral complex



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

Hybridisation -  $dsp^2$

Structure - Square planar



30. (i) Anhydrous  $\text{CuSO}_4$  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  $\text{H}_2\text{O}$  ligand so, it shows colour due to  $d-d$  transition.

(ii)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  is a complex compound. In presence of 6  $\text{H}_2\text{O}$  molecules the  $d$ -orbitals of  $\text{Ti}^{3+}$  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 ( $Z = 26$ )

Ground state :  $3d^6 4s^2 4p^0$

$\text{Fe}^{3+}$  ion :  $3d^5 4s^0 4p^0$

$[\text{Fe}(\text{CN})_6]^{3-}$  ion :  $d^2sp^3$  hybridisation (strong ligand)

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

32. In  $[\text{CoF}_6]^{3-}$ , Co is in +3 state and has  $3d^6$  configuration.

$\text{Co}^{3+} : 3d^6 4s^0 4p^0$

Ground state

Since  $\text{F}^-$  is a weak field ligand. So, outer  $d$ -orbitals will be used.

$3d^6 4s^0 4p^0$

Six pairs of electrons from  $\text{F}^-$  ions ( $sp^3d^2$ )

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

In  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , Co is in +3 state.

$\text{Co}^{3+} : 3d^6 4s^0 4p^0$

Ground state

Since  $\text{NH}_3$  is a strong field ligand pairing of electrons in  $3d$ -orbital takes place to make two  $3d$  orbitals vacant.

$d^2sp^3$  hybridised orbital of  $\text{Co}^{3+}$

$d^2sp^3$

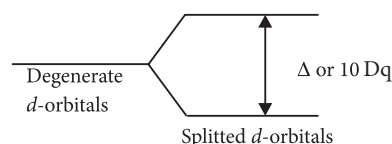
Since it uses inner  $d$ -orbital for its hybridisation so, it is inner orbital complex.

33.

Complex	Central metal ion/atom	Hybridisation of metal ion involved	Geometry of complex	Magnetic behaviour
$[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$\text{Cr}^{3+}$	$d^2sp^3$	Octahedral	Paramagnetic
$[\text{Co}(\text{en})_3]\text{Cl}_3$	$\text{Co}^{3+}$	$d^2sp^3$	Octahedral	Diamagnetic
$\text{K}_2[\text{Ni}(\text{CN})_4]$	$\text{Ni}^{2+}$	$dsp^2$	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  $\Delta$  or  $10 \text{ Dq}$ .

For octahedral  $\Delta_o$ , for tetrahedral it is  $\Delta_t$  and for square planar  $\Delta_{sp}$ .

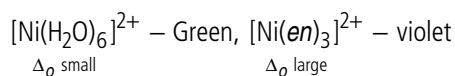


(i) When  $\Delta_o > P$ ,  $t_{2g}^4 e_g^0$  (ii) When  $\Delta_o < P$ ,  $t_{2g}^3 e_g^1$

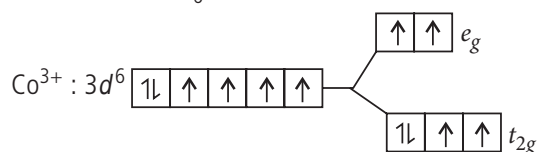
(b) (i) It assumes ligand to be point charges.

(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  $\text{H}_2\text{O}$ . When  $\text{H}_2\text{O}$  molecule is replaced by ethane-1,2-diamine (*en*) the crystal field splitting energy ( $\Delta$ ) increases. Complex absorbs light of higher frequency for *d-d* transition. This is why colour of complex changes from green to violet.

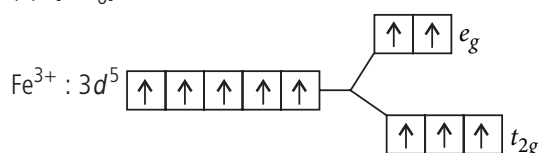


**36.** (i) (a)  $[\text{CoF}_6]^{3-}$  :



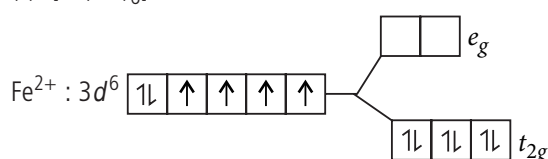
No. of unpaired electrons = 4,  $\mu = \sqrt{4(4+2)} = 4.9 \text{ B.M.}$

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



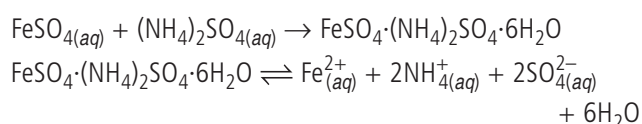
No. of unpaired electrons = 5,  $\mu = \sqrt{5(5+2)} = 5.92 \text{ B.M.}$

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



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

(ii) When  $\text{FeSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  solutions are mixed in 1 : 1 molar ratio, Mohr's salt (a double salt) is formed.

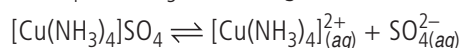


Because  $\text{Fe}^{2+}$  ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of  $\text{Fe}^{2+}$  ions.

When  $\text{CuSO}_4$  is mixed with ammonia, following reaction occurs :



This complex does not produce  $\text{Cu}^{2+}$  ion, so the solution of  $\text{CuSO}_4$  and  $\text{NH}_3$  does not give the test of  $\text{Cu}^{2+}$  ion.



**37.** (i)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$

Potassium diaquadioxalatochromate(III) trihydrate

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

Stereochemistry : octahedral

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

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

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

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

Pentaamminechloridocobalt(III) chloride

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

Stereochemistry = octahedral

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

Magnetic moment ( $\mu$ ) = 0

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

Trichloridotripyridinechromium(III)

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

Stereochemistry : octahedral

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

Magnetic moment = 3.87 B.M.

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

Caesium tetrachloridoferrate(III)

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

Stereochemistry = Tetrahedral

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

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

(v)  $\text{K}_4[\text{Mn}(\text{CN})_6]$

Potassium hexacyanomanganate(II)

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

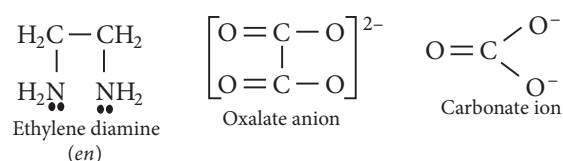
Stereochemistry = octahedral

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

Magnetic moment

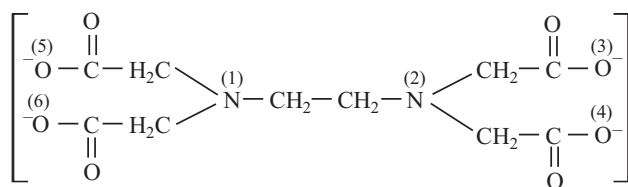
$$(\mu) = \sqrt{1(1+2)} \text{ B.M.} = \sqrt{3} \text{ B.M.} = 1.73 \text{ B.M.}$$

**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:



(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 ethylenediaminetetraacetate ion as

shown below:



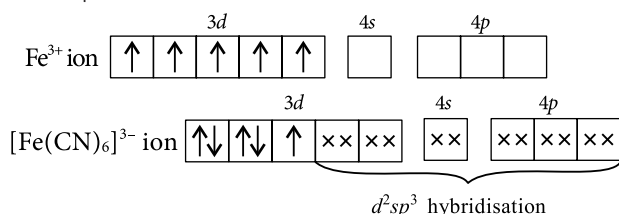
Structure of ethylenediaminetetraacetate ion

(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  $[\text{Cu}(\text{NH}_3)_6]^{2+}$  carries a charge of +2 and because ammonia molecule is neutral therefore,  $\text{Cu}^{2+}$  carries a charge of +2.  $[\text{Ag}(\text{CN})_2]^-$  ion carries a charge of -1 and two cyanide ions coordinated to it carry a charge of -1 each. So,  $\text{Ag}^+$  carries a charge of +1.

39.

S.No.	Complex	Oxidation state of metal atom	Coordination number of central metal atom	d-orbital occupation
(i)	$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$	+3	6	$\text{Co}^{3+} = 3d^6; (t_{2g})^6, (e_g)^0$
(ii)	$[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	+3	6	$\text{Cr}^{3+} = 3d^3; (t_{2g})^3$
(iii)	$(\text{NH}_4)_2[\text{CoF}_4]$	+2	4	$\text{Co}^{2+} = 3d^7; (e)^4, (t_2)^3$
(iv)	$[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$	+2	6	$\text{Mn}^{2+} = 3d^5; (t_{2g})^3, (e_g)^2$

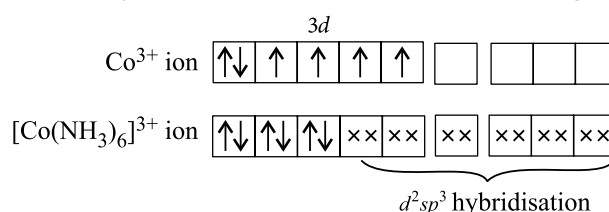
40. (a) Formation of hexacyanidoferrate(III) ion;  $[\text{Fe}(\text{CN})_6]^{3-}$ : Electronic configuration of iron in the ground state is  $3d^6 4s^2$ . The oxidation state of iron is +3 in this complex. Iron (III) has outer electronic configuration  $3d^5 4s^0$ . It has been experimentally observed that this complex has one unpaired electron. To account for this, two unpaired electrons in 3d subshell pair up, thus leaving two 3d-orbitals empty. These two vacant 3d-orbitals, along with one 4s-orbital and three 4p-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.



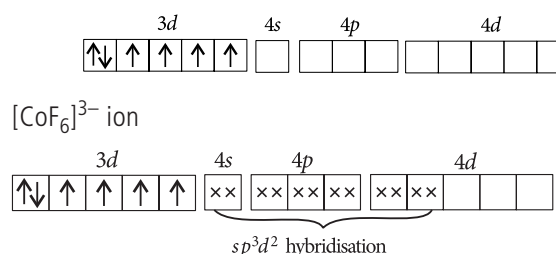
The complex evidently involves  $(n-1)d^2nsnp^3$  hybridisation and is, therefore, called inner orbital or low spin complex.

(b) The outer electronic configuration of cobalt (III) ion is  $3d^6$ . According to Hund's rule, four of the 3d-orbitals are singly filled and one 3d-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 3d-orbitals empty. This is achieved by the pairing of the two 3d-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  $[\text{CoF}_6]^{3-}$  complex, the 3d-orbitals remain undisturbed while the outer 4d-orbitals are used for hybridisation, as  $\text{Co}^{3+}$  ion



The complex is paramagnetic since it contains four unpaired electrons.

