

# Chapter

# Co-ordination Compounds



## Topic-1: Important Terms, Coordination Number, Nomenclature and Isomerism of Coordination Compounds



### 1 MCQs with One Correct Answer

- Among the following options, select the option in which each complex in **Set-I** shows geometrical isomerism and the two complexes in **Set-II** are ionization isomers of each other. [en = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>] [Adv. 2024]
  - Set-I:** [Ni(CO)<sub>4</sub>] and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]  
**Set-II:** [Co(NH<sub>3</sub>)<sub>5</sub>Cl]SO<sub>4</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>(SO<sub>4</sub>)]Cl
  - Set-I:** [Co(en)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]  
**Set-II:** [Co(NH<sub>3</sub>)<sub>6</sub>][Cr(CN)<sub>6</sub>] and [Cr(NH<sub>3</sub>)<sub>6</sub>][Co(CN)<sub>6</sub>]
  - Set-I:** [Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>] and [Co(en)<sub>2</sub>Cl<sub>2</sub>]  
**Set-II:** [Co(NH<sub>3</sub>)<sub>5</sub>Cl]SO<sub>4</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>(SO<sub>4</sub>)]Cl
  - Set-I:** [Cr(NH<sub>3</sub>)<sub>3</sub>Cl]Cl<sub>2</sub> and [Co(en)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]  
**Set-II:** [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> and [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub> · H<sub>2</sub>O
- As per IUPAC nomenclature, the name of the complex [Co(H<sub>2</sub>O)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub> is : [2012]
  - Tetraaquadiamminocobalt (III) chloride
  - Tetraaquadiamminocobalt (III) chloride
  - Diaminetetraaquacobalt (II) chloride
  - Diamminetetraaquacobalt (III) chloride
- The correct structure of ethylenediaminetetraacetic acid (EDTA) is [2010]
  - $$\begin{array}{c} \text{HOOC}-\text{H}_2\text{C} \\ \text{HOOC}-\text{H}_2\text{C} \end{array} \left. \vphantom{\begin{array}{c} \text{HOOC}-\text{H}_2\text{C} \\ \text{HOOC}-\text{H}_2\text{C} \end{array}} \right\} \text{N}-\text{CH}=\text{CH}-\text{N} \left. \vphantom{\begin{array}{c} \text{CH}_2-\text{COOH} \\ \text{CH}_2-\text{COOH} \end{array}} \right\} \begin{array}{c} \text{CH}_2-\text{COOH} \\ \text{CH}_2-\text{COOH} \end{array}$$
  - $$\begin{array}{c} \text{HOOC} \\ \text{HOOC} \end{array} \left. \vphantom{\begin{array}{c} \text{HOOC} \\ \text{HOOC} \end{array}} \right\} \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \left. \vphantom{\begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}} \right\} \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$$
  - $$\begin{array}{c} \text{HOOC}-\text{H}_2\text{C} \\ \text{HOOC}-\text{H}_2\text{C} \end{array} \left. \vphantom{\begin{array}{c} \text{HOOC}-\text{H}_2\text{C} \\ \text{HOOC}-\text{H}_2\text{C} \end{array}} \right\} \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \left. \vphantom{\begin{array}{c} \text{CH}_2-\text{COOH} \\ \text{CH}_2-\text{COOH} \end{array}} \right\} \begin{array}{c} \text{CH}_2-\text{COOH} \\ \text{CH}_2-\text{COOH} \end{array}$$
  - $$\begin{array}{c} \text{COOH} \\ \text{CH}_2 \\ \text{HOOC}-\text{H}_2\text{C} \\ \text{H} \end{array} \left. \vphantom{\begin{array}{c} \text{COOH} \\ \text{CH}_2 \\ \text{HOOC}-\text{H}_2\text{C} \\ \text{H} \end{array}} \right\} \text{N}-\text{CH}-\text{CH}-\text{N} \left. \vphantom{\begin{array}{c} \text{H} \\ \text{CH}_2-\text{COOH} \end{array}} \right\} \begin{array}{c} \text{H} \\ \text{CH}_2-\text{COOH} \end{array}$$
- The ionisation isomer of [Cr(H<sub>2</sub>O)<sub>4</sub>Cl(NO<sub>2</sub>)]Cl is [2010]
  - [Cr(H<sub>2</sub>O)<sub>4</sub>(O<sub>2</sub>N)]Cl<sub>2</sub>
  - [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>](NO<sub>2</sub>)
  - [Cr(H<sub>2</sub>O)<sub>4</sub>Cl(ONO)]Cl
  - [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>(NO<sub>2</sub>)] · H<sub>2</sub>O
- The IUPAC name of [Ni(NH<sub>3</sub>)<sub>4</sub>][NiCl<sub>4</sub>] is [2008]
  - Tetrachloronickel (II) - tetraamminenickel (II)
  - Tetraamminenickel (II) - tetrachloronickel (II)
  - Tetraamminenickel (II) - tetrachloronickelate (II)
  - Tetrachloronickel (II) - tetrachloronickelate (0) Ans. (C)
- Which kind of isomerism is exhibited by octahedral Co(NH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>Cl? [2005S]
  - Geometrical and Ionization
  - Geometrical and Optical
  - Optical and Ionization
  - Geometrical only
- The complex ion which has no 'd' electron in the central metal atom is [2001S]
  - [MnO<sub>4</sub>]<sup>-</sup>
  - [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
  - [Fe(CN)<sub>6</sub>]<sup>3-</sup>
  - [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>
- Which of the following is an organometallic compound? [1997 - 1 Mark]
  - Lithium methoxide
  - Lithium acetate
  - Lithium dimethylamide
  - Methyl lithium



### 2 Integer Value Answer

- Among V(CO)<sub>6</sub>, Cr(CO)<sub>5</sub>, Cu(CO)<sub>3</sub>, Mn(CO)<sub>5</sub>, Fe(CO)<sub>5</sub>, [Co(CO)<sub>3</sub>]<sup>3-</sup>, [Cr(CO)<sub>4</sub>]<sup>4+</sup>, and Ir(CO)<sub>3</sub>, the total number of species isoelectronic with Ni(CO)<sub>4</sub> is \_\_\_\_\_. [Given, atomic number: V = 23, Cr = 24, Mn = 25, Fe = 26, Co = 27, Ni = 28, Cu = 29, Ir = 77] [Adv. 2024]
- The total number of possible isomers for [Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Br<sub>2</sub> is \_\_\_\_\_. [Adv. 2021]
- Total number of *cis* N - Mn - Cl bond angles (that is Mn - N and Mn - Cl bonds in *cis* positions) present in a molecule of *cis* - [Mn(en)<sub>2</sub>Cl<sub>2</sub>] complex is \_\_\_\_\_. (en = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) [Adv. 2019]





12. The number of geometric isomers possible for the complex  $[\text{CoL}_2\text{Cl}_2]^-$  ( $L = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$ ) is [Adv. 2016]
13. Among the complex ions,  $[\text{Co}(\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2)_2\text{Cl}_2]^+$ ,  $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ ,  $[\text{Co}(\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ , the number of complex ion(s) that show(s) *cis-trans* isomerism is [Adv. 2015]
14. In the complex acetyl bromidodicarbonylbis (triethylphosphine) iron (II), the number of Fe-C bond(s) is [Adv. 2015]
15. EDTA<sup>4-</sup> is ethylenediaminetetraacetate ion. The total number of N-Co-O bond angles in  $[\text{Co}(\text{EDTA})]^{1-}$  complex ion is [Adv. 2013]
16. The volume (in mL) of 0.1 M  $\text{AgNO}_3$  required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ , as silver chloride is close to [2011]
17. Total number of geometrical isomers for the complex  $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$  is [2010]
18. The number of water molecule(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is [2009 - 4 Marks]



## 4 Fill in the Blanks

19. The IUPAC name of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is ..... [1994 - 1 Mark]



## 6 MCQs with One or More than One Correct Answer

20. The complex(es), which can exhibit the type of isomerism shown by  $[\text{Pt}(\text{NH}_3)_2\text{Br}_2]$ , is(are)  $[\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2]$  [Adv. 2023]
- (a)  $[\text{Pt}(\text{en})(\text{SCN})_2]$  (b)  $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$   
 (c)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  (d)  $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{SO}_4)]^+$
21. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) [Adv. 2013]
- (a)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$

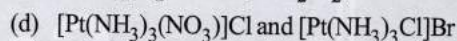
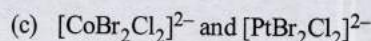


## Topic-2: Bonding, Stability and Application of Coordination Compounds

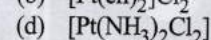
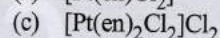
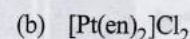
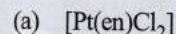


## 1 MCQs with One Correct Answer

1. The reaction of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaCl}$  in water produces a precipitate that dissolves upon the addition of  $\text{HCl}$  of appropriate concentration. The dissolution of the precipitate is due to the formation of [Adv. 2022]
- (a)  $\text{PbCl}_2$  (b)  $\text{PbCl}_4$   
 (c)  $[\text{PbCl}_4]^{2-}$  (d)  $[\text{PbCl}_6]^{2-}$
2. The calculated spin only magnetic moments of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $[\text{CuF}_6]^{3-}$  in BM, respectively, are (Atomic numbers of Cr and Cu are 24 and 29, respectively) [Adv. 2021]
- (a) 3.87 and 2.84 (b) 4.90 and 1.73



22. The compound(s) that exhibit(s) geometrical isomerism is (are) [2009]



## 9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct. Mark your answer as

- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -1.  
 (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.  
 (c) If Statement -1 is correct but Statement -2 is incorrect.  
 (d) If Statement -1 is incorrect but Statement -2 is correct.

23. **Statement-1** : The geometrical isomers of the complex  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  are optically inactive.

**Statement-2** : Both geometrical isomers of the complex  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  possess axis of symmetry. [2008 - 2 Marks]

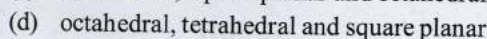
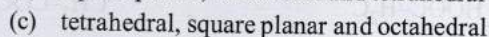
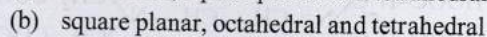
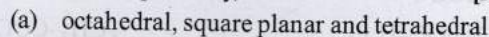


## 10 Subjective Problems

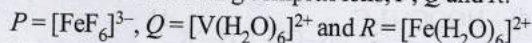
24. *A*, *B*, and *C* are three complexes of chromium (III) with the empirical formula  $\text{H}_2\text{O}_6\text{Cl}_3\text{Cr}$ . All the three complexes have water and chloride ion as ligands. Complex *A* does not react with concentrated  $\text{H}_2\text{SO}_4$ , whereas complexes *B* and *C* lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated  $\text{H}_2\text{SO}_4$ . Identify *A*, *B* and *C*. [1999 - 6 Marks]
25. Write the formulae of the following complexes :
- (i) Pentaamminechlorocobalt(III) [1997 - 1 Mark]  
 (ii) Lithium tetrahydroaluminate(III). [1997 - 1 Mark]
26. Write down the IUPAC names of the following compounds:
- (i)  $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$  [1996 - 1 Mark]  
 (ii)  $\text{K}_3[\text{Cr}(\text{CN})_6]$  [1995 - 1 Mark]  
 (iii)  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  [1995 - 1 Mark]



3. The geometries of the ammonia complexes of  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$  and  $\text{Zn}^{2+}$  respectively, are [Adv. 2016]



4. Consider the following complex ions, *P*, *Q* and *R*.



The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is [Adv. 2013]



- (a)  $R < Q < P$  (b)  $Q < R < P$   
 (c)  $R < P < Q$  (d)  $Q < P < R$
5.  $\text{NiCl}_2 \cdot \text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2$  exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of  $\text{Ni}^{2+}$  in the paramagnetic and diamagnetic states are respectively [2012]  
 (a) tetrahedral and tetrahedral  
 (b) square planar and square planar  
 (c) tetrahedral and square planar  
 (d) square planar and tetrahedral
6. Among the following complexes (K-P)  
 $\text{K}_3[\text{Fe}(\text{CN})_6]$  (K),  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (L),  $\text{Na}_3[\text{Co}(\text{oxalate})_3]$  (M),  
 the  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  (N),  $\text{K}_2[\text{Pt}(\text{CN})_4]$  (O) and  
 $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  (P) the diamagnetic complexes are [2011]  
 (a) K, L, M, N (b) K, M, O, P  
 (c) L, M, O, P (d) L, M, N, O
7. Geometrical shapes of the complexes formed by the reaction of  $\text{Ni}^{2+}$  with  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{H}_2\text{O}$ , respectively, are [2011]  
 (a) octahedral, tetrahedral and square planar  
 (b) tetrahedral, square planar and octahedral  
 (c) square planar, tetrahedral and octahedral  
 (d) octahedral, square planar and octahedral
8. The complex showing a spin-only magnetic moment of 2.82 B.M. is: [2010]  
 (a)  $[\text{Ni}(\text{CO})_4]$  (b)  $[\text{NiCl}_4]^{2-}$   
 (c)  $[\text{Ni}(\text{PPh}_3)_4]$  (d)  $[\text{Ni}(\text{CN})_4]^{2-}$
9. The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is [2009]  
 (a) 0 (b) 2.84 (c) 4.90 (d) 5.92
10. Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridisations of nickel in these complexes, respectively, are [2008]  
 (a)  $sp^3, sp^3$  (b)  $sp^3, dsp^2$   
 (c)  $dsp^2, sp^3$  (d)  $dsp^2, sp^2$
11. Among the following metal carbonyls, the C–O bond order is lowest in [2007]  
 (a)  $[\text{Mn}(\text{CO})_6]^+$  (b)  $[\text{Fe}(\text{CO})_5]$   
 (c)  $[\text{Cr}(\text{CO})_6]$  (d)  $[\text{V}(\text{CO})_6]^-$
12.  $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+; k_1 = 6.8 \times 10^{-3}$   
 $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+; k_2 = 1.6 \times 10^{-3}$   
 then the formation constant of  $[\text{Ag}(\text{NH}_3)_2]^+$  is [2006 - 3M, -1]  
 (a)  $6.8 \times 10^{-6}$  (b)  $1.08 \times 10^{-5}$   
 (c)  $1.08 \times 10^{-6}$  (d)  $6.8 \times 10^{-5}$
13. The spin magnetic moment of cobalt in the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [2004S]  
 (a)  $\sqrt{3}$  (b)  $\sqrt{8}$  (c)  $\sqrt{15}$  (d)  $\sqrt{24}$
14. The species having tetrahedral shape is [2004S]  
 (a)  $[\text{PdCl}_4]^{2-}$  (b)  $[\text{Ni}(\text{CN})_4]^{2-}$   
 (c)  $[\text{Pd}(\text{CN})_4]^{2-}$  (d)  $[\text{NiCl}_4]^{2-}$
15. The geometry of  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  are [1999 - 2 Marks]  
 (a) both square planar  
 (b) tetrahedral and square planar, respectively  
 (c) both tetrahedral  
 (d) square planar and tetrahedral, respectively
16. Amongst  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$  [1991 - 1 Mark]  
 (a)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{NiCl}_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic  
 (b)  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CO})_4]$  is paramagnetic  
 (c)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{NiCl}_4]^{2-}$  is paramagnetic  
 (d)  $[\text{Ni}(\text{CO})_4]$  is diamagnetic and  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic
17. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by [1988 - 1 Mark]  
 (a)  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  (b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
 (c)  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  (d)  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$



## 2 Integer Value Answer

18. Among  $[\text{Co}(\text{CN})_4]^{4-}$ ,  $[\text{Co}(\text{CO})_3(\text{NO})]$ ,  $\text{XeF}_4$ ,  $[\text{PCl}_4]^+$ ,  $[\text{PdCl}_4]^{2-}$ ,  $[\text{ICl}_4]^-$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $\text{P}_4$  the total number of species with tetrahedral geometry is \_\_\_\_\_. [Adv. 2024]
19. Among the following complexes, the total number of diamagnetic species is \_\_\_\_\_. [Adv. 2024]  
 $[\text{Mn}(\text{NH}_3)_6]^{3+}$ ,  $[\text{MnCl}_6]^{3-}$ ,  $[\text{FeF}_6]^{3-}$ ,  $[\text{CoF}_6]^{3-}$ ,  $[\text{Fe}(\text{NH}_3)_6]^{3+}$ ,  
 and  $[\text{Co}(\text{en})_3]^{3+}$   
 [Given, atomic number: Mn = 25, Fe = 26, Co = 27;  
 en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ]
20. Among the species given below, the total number of diamagnetic species is \_\_\_\_\_.  
 H atom,  $\text{NO}_2$  monomer,  $\text{O}_2^-$  (superoxide), dimeric sulphur in vapour phase,  $\text{Mn}_3\text{O}_4$ ,  $(\text{NH}_4)_2[\text{FeCl}_4]$ ,  $(\text{NH}_4)_2[\text{NiCl}_4]$ ,  
 $\text{K}_2\text{MnO}_4$ ,  $\text{K}_2\text{CrO}_4$  [Adv. 2018]
21. For the octahedral complexes of  $\text{Fe}^{3+}$  in  $\text{SCN}^-$  (thiocyanato-S) and in  $\text{CN}^-$  ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [Atomic number of Fe = 26] [Adv. 2015]



## 4 Fill in the Blanks

22. The type of magnetism exhibited by  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ion is ..... [1994 - 1 Mark]



## 5 True / False

23. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. [1989 - 1 Mark]



## 6 MCQs with One or More than One Correct Answer

24. The pair(s) of complexes wherein both exhibit tetrahedral geometry is(are)  
 (Note: py = pyridine)  
 Given: Atomic numbers of Fe, Co, Ni and Cu are 26, 27, 28 and 29, respectively) [Adv. 2021]



- (a)  $[\text{FeCl}_4]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$   
 (b)  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{CoCl}_4]^{2-}$   
 (c)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$   
 (d)  $[\text{Cu}(\text{py})_4]^+$  and  $[\text{Cu}(\text{CN})_4]^{3-}$
25. Choose the correct statement(s) among the following:  
 (a)  $[\text{FeCl}_4]^-$  has tetrahedral geometry. [Adv. 2020]  
 (b)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$  has 2 geometrical isomers.  
 (c)  $[\text{FeCl}_4]^-$  has higher spin-only magnetic moment than  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ .  
 (d) The cobalt ion in  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$  has  $sp^3d^2$  hybridization.
26. The correct option(s) regarding the complex  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  (en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) is (are)  
 (a) It has two geometrical isomers [Adv. 2018]  
 (b) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands  
 (c) It is paramagnetic  
 (d) It absorbs light at longer wavelength as compared to  $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$
27. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28) [Adv. 2018]  
 (a) Total number of valence shell electrons at metal centre in  $\text{Fe}(\text{CO})_5$  or  $\text{Ni}(\text{CO})_4$  is 16  
 (b) These are predominantly low spin in nature  
 (c) Metal-carbon bond strengthens when the oxidation state of the metal is lowered  
 (d) The carbonyl C-O bond weakens when the oxidation state of the metal is increased
28. Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $\text{MCl}_2 \cdot 6\text{H}_2\text{O}(\text{X})$  and  $\text{NH}_4\text{Cl}$  gives an octahedral complex  $\text{Y}$  in the presence of air. In aqueous solution, complex  $\text{Y}$  behaves as 1:3 electrolyte. The reaction of  $\text{X}$  with excess  $\text{HCl}$  at room temperature results in the formation of a blue coloured complex  $\text{Z}$ . The calculated spin only magnetic moment of  $\text{X}$  and  $\text{Z}$  is 3.87 B.M., whereas it is zero for complex  $\text{Y}$ . Among the following options, which statement(s) is (are) correct? [Adv. 2017]  
 (a) Addition of silver nitrate to  $\text{Y}$  gives only two equivalents of silver chloride  
 (b) The hybridization of the central metal ion in  $\text{Y}$  is  $d^2sp^3$   
 (c)  $\text{Z}$  is a tetrahedral complex  
 (d) When  $\text{X}$  and  $\text{Z}$  are in equilibrium at  $0^\circ\text{C}$ , the colour of the solution is pink
29. If the bond length of CO bond in carbon monoxide is  $1.128\text{Å}$ , then what is the value of CO bond length in  $\text{Fe}(\text{CO})_5$ ? [2006 - 5M, -1]  
 (a)  $1.15\text{Å}$  (b)  $1.128\text{Å}$  (c)  $1.13\text{Å}$  (d)  $1.118\text{Å}$
30. In nitroprusside ion the iron and NO exist as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and NO. These forms can be differentiated by [1998 - 2 Marks]  
 (a) estimating the concentration of iron  
 (b) measuring the concentration of  $\text{CN}^-$   
 (c) measuring the solid state magnetic moment  
 (d) thermally decomposing the compound.
31. Among the following ions which one has the highest paramagnetism? [1993 - 1 Mark]  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- 7 Match the Following
32. Match the electronic configurations in List-I with appropriate metal complex ions in List-II and choose the correct option. [Adv. 2023]  
 [Atomic number: Fe = 26, Mn = 25, Co = 27]
- | List-I               | List-II                                      |
|----------------------|--|
| (P) $t_{2g}^6 e_g^0$ | (1) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ |
| (Q) $t_{2g}^3 e_g^2$ | (2) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ |
| (R) $e^2 t_2^3$      | (3) $[\text{Co}(\text{NH}_3)_6]^{3+}$        |
| (S) $t_{2g}^4 e_g^2$ | (4) $[\text{FeCl}_4]^-$                      |
|                      | (5) $[\text{CoCl}_4]^{2-}$                   |
- (a) P  $\rightarrow$  1; Q  $\rightarrow$  4; R  $\rightarrow$  2; S  $\rightarrow$  3  
 (b) P  $\rightarrow$  1; Q  $\rightarrow$  2; R  $\rightarrow$  4; S  $\rightarrow$  5  
 (c) P  $\rightarrow$  3; Q  $\rightarrow$  2; R  $\rightarrow$  5; S  $\rightarrow$  1  
 (d) P  $\rightarrow$  3; Q  $\rightarrow$  2; R  $\rightarrow$  4; S  $\rightarrow$  1
33. List-I contains metal species and List-II contains their properties. [Adv. 2022]
- | List-I   | List-II                                      |
|--|--|
| (I) $[\text{Cr}(\text{CN})_6]^{4-}$            | (P) $t_{2g}$ orbitals contain 4 electrons    |
| (II) $[\text{RuCl}_6]^{2-}$                    | (Q) $\mu(\text{spin-only}) = 4.9 \text{ BM}$ |
| (III) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | (R) low spin complex ion                     |
| (IV) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  | (S) metal ion in 4+ oxidation state          |
|  | (T) $d^4$ species                            |
- [Given: Atomic number of Cr = 24, Ru = 44, Fe = 26]  
 Match each metal species in LIST-I with their properties in LIST-II, and choose the correct option  
 (a) I  $\rightarrow$  R, T; II  $\rightarrow$  P, S; III  $\rightarrow$  Q, T; IV  $\rightarrow$  P, Q  
 (b) I  $\rightarrow$  R, S; II  $\rightarrow$  P, T; III  $\rightarrow$  P, Q; IV  $\rightarrow$  Q, T  
 (c) I  $\rightarrow$  P, R; II  $\rightarrow$  R, S; III  $\rightarrow$  R, T; IV  $\rightarrow$  P, T  
 (d) I  $\rightarrow$  Q, T; II  $\rightarrow$  S, T; III  $\rightarrow$  P, T; IV  $\rightarrow$  Q, R
34. Match each set of hybrid orbitals from List-I with complex(es) given in List-II [Adv. 2018]
- | List-I        | List-II  |
|---------------|--|
| (A) $dsp^2$   | (p) $[\text{FeF}_6]^{4-}$                          |
| (B) $sp^3$    | (q) $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$ |
| (C) $sp^3d^2$ | (r) $[\text{Cr}(\text{NH}_3)_6]^{3+}$              |
| (D) $d^2sp^3$ | (s) $[\text{FeCl}_4]^{2-}$                         |
|               | (t) $[\text{Ni}(\text{CO})_4]$                     |
|               | (w) $[\text{Ni}(\text{CN})_4]^{2-}$                |
- The correct option is  
 (a) A-t; B-s, w; C-q, r; D-p  
 (b) A-t, w; B-s; C-q; D-p, q  
 (c) A-w; B-s, t; C-p; D-q, r  
 (d) A-s, w; B-t, w; C-p, q; D-r



35. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.

{en = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78} [Adv. 2014]

List-I	List-II
(A) [Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl	(p) Paramagnetic and exhibits ionisation isomerism
(B) [Ti(H <sub>2</sub> O) <sub>5</sub> Cl](NO <sub>3</sub> ) <sub>2</sub>	(q) Diamagnetic and exhibits <i>cis-trans</i> isomerism
(C) [Pt(en)(NH <sub>3</sub> )Cl]NO <sub>3</sub>	(r) Paramagnetic and exhibits <i>cis-trans</i> isomerism
(D) [Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	(s) Diamagnetic and exhibits ionisation isomerism

Code:

	A	B	C	D
(a)	(s)	(q)	(r)	(p)
(b)	(r)	(p)	(s)	(q)
(c)	(q)	(p)	(r)	(s)
(d)	(p)	(r)	(s)	(q)

36. Match the complexes in **Column-I** with their properties listed in **Column-II**. [2007]

Column-I	Column-II
(A) [Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	(p) geometrical isomers
(B) [Pt(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	(q) paramagnetic
(C) [Co(H <sub>2</sub> O) <sub>5</sub> Cl]Cl	(r) diamagnetic
(D) [Ni(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>2</sub>	(s) metal ion with +2 oxidation state



### 8 Comprehension/Passage Based Questions

The coordination number of Ni<sup>2+</sup> is 4.

NiCl<sub>2</sub> + KCN(excess) → A (cyano complex)

NiCl<sub>2</sub> + Conc. HCl(excess) → B (chloro complex)

37. The IUPAC name of A and B are [2006 - 5M, -2]
- Potassium tetracyanonickelate (II), potassium tetrachloronickelate (II)
  - Tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II)
  - Tetracyanonickel (II), tetrachloronickel (II)
  - Potassium tetracyanonickel (II), potassium tetrachloronickel (II)
38. Predict the magnetic nature of A and B [2006 - 5M, -2]
- Both are diamagnetic
  - A is diamagnetic and B is paramagnetic with one unpaired electron
  - A is diamagnetic and B is paramagnetic with two unpaired electrons
  - Both are paramagnetic
39. The hybridization of A and B are [2006 - 5M, -2]
- dsp<sup>2</sup>, sp<sup>3</sup>
  - sp<sup>3</sup>, sp<sup>3</sup>
  - dsp<sup>2</sup>, dsp<sup>2</sup>
  - sp<sup>3</sup>d<sup>2</sup>, d<sup>2</sup>sp<sup>3</sup>



### 9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

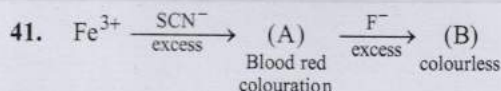
- If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -1.
- If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- If Statement -1 is correct but Statement -2 is incorrect.
- If Statement -1 is incorrect but Statement -2 is correct.

40. **Statement-1** : [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> is paramagnetic.

**Statement-2** : The Fe in [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> has three unpaired electrons. [2008]



### 10 Subjective Problems



What are (A) and (B)? Give IUPAC name of (A). Find the spin only magnetic moment of (B). [2005 - 4 Marks]

42. Nickel chloride, when treated with dimethylglyoxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following. [2004 - 4 Marks]
- Draw the structure of the complex showing H-bonds
  - Give oxidation state of nickel and its hybridisation
  - Predict the magnetic behaviour of the complex
43. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.  
K<sub>2</sub>[Cr(NO)(NH<sub>3</sub>)(CN)<sub>4</sub>], μ = 1.73 BM [2003 - 4 Marks]
44. Deduce the structure of [NiCl<sub>4</sub>]<sup>2-</sup> and [Ni(CN)<sub>4</sub>]<sup>2-</sup> considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species. [2002 - 5 Marks]
45. A metal complex having composition Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>Br has been isolated in two forms (A) and (B). The form (A) reacts with AgNO<sub>3</sub> to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate their magnetic moments (spin-only value). [2001 - 5 Marks]
46. Draw the structures of [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [Ni(CN)<sub>4</sub>]<sup>2-</sup> and [Ni(CO)<sub>4</sub>]. Write the hybridisation of atomic orbitals of the transition metal in each case. [2000 - 4 Marks]
47. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. [1997 - 2 Marks]
48. Identify the complexes which are expected to be coloured. Explain [1994 - 2 Marks]
- [Ti(NO<sub>3</sub>)<sub>4</sub>]
  - [Cu(NCCH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> BF<sub>4</sub><sup>-</sup>
  - [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> 3Cl<sup>-</sup>
  - K<sub>3</sub>[VF<sub>6</sub>]



**AnswerKey**

**Topic-1 : Important Terms Coordination Number, Nomenclature and Isomerism of Coordination Compounds**

1. (c)    2. (d)    3. (c)    4. (b)    5. (c)    6. (a)    7. (a)    8. (d)    9. (3)    10. (6)  
 11. (6)    12. (5)    13. (6)    14. (3)    15. (8)    16. (6)    17. (3)    18. (4)  
 19. (Hexamine cobalt (III) chloride)    20. (c, d)    21. (b, d)    22. (c, d)    23. (b)

**Topic-2 : Bonding, Stability and Application of Coordination Compounds**

1. (c)    2. (a)    3. (a)    4. (b)    5. (c)    6. (c)    7. (b)    8. (b)    9. (a)    10. (b)  
 11. (d)    12. (b)    13. (c)    14. (d)    15. (c)    16. (c)    17. (b)    18. (5)    19. (1)    20. (1)  
 21. (4)    22. (Paramagnetism)    23. (False)    24. (a, b, d)    25. (a, c)    26. (a,b,d)    27. (b, c)    28. (b,c,d)  
 29. (a, c)    30. (c)    31. (b)    32. (d)    33. (a)    34. (c)    35. (b)  
 36. (A): (p), (q) and (s); (B): (p), (r) and (s); (C): (q) and (s); (D): (q) and (s)    37. (a)    38. (c)    39. (a)    40. (a)



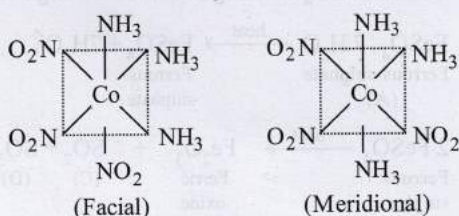
# Hints & Solutions



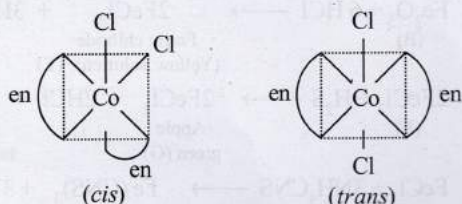
## Topic-1: Important Terms, Coordination Number, Nomenclature and Isomerism of Coordination Compounds

1. (c) Complexes of type  $[Ma_3b_3]^{h+}$  form facial and meridional isomers.

Set-I:

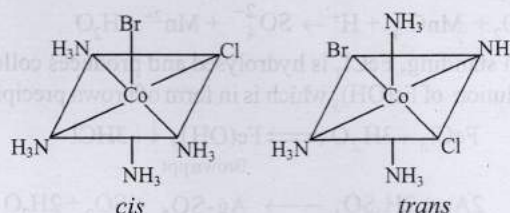
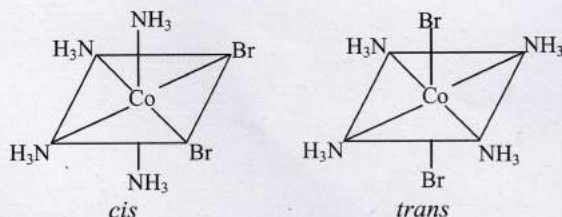


Complexes of type  $[MX_2(L-L)_2]^\pm$  give *cis* and *trans* isomers.



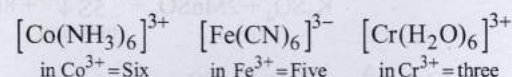
Set-II:  $[Co(NH_3)_5Cl]SO_4$  and  $[Co(NH_3)_5SO_4]Cl$  are ionisation isomers.

2. (d)  $[Co(H_2O)_4(NH_3)_2]Cl_3$   
= Diamminetetraaquacobalt (III) chloride.
3. (c) The correct structure of EDTA is
- $$\begin{array}{c} \text{HOOC-H}_2\text{C} \\ \text{HOOC-H}_2\text{C} \end{array} \rangle \text{N-CH}_2\text{-CH}_2\text{-N} \begin{array}{c} \text{CH}_2\text{-COOH} \\ \text{CH}_2\text{-COOH} \end{array}$$
4. (b) Ionisation isomer of  $[Cr(H_2O)_4Cl(NO_2)]Cl$  is  $[Cr(H_2O)_4Cl_2]NO_2$ .
5. (c) The correct IUPAC name of the given compound is tetraamminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.
6. (a)  $Co(NH_3)_4Br_2Cl$  will show both geometrical and ionization isomerism.  
 $[Co(NH_3)_4Br_2Cl]$  and  $[Co(NH_3)_4BrCl]Br$  are ionization isomers and geometrical isomers are



7. (a) In  $[MnO_4]^-$ , Mn is in +7 oxidation state.  
Electronic configuration of Mn ( $Z = 25$ ):  $[Ar] 3d^5 4s^2$   
Electronic configuration of  $Mn^{7+}$ :  $[Ar] 3d^0 4s^0$   
Central atom in other ions have definite number of *d* electrons.

No. of electrons



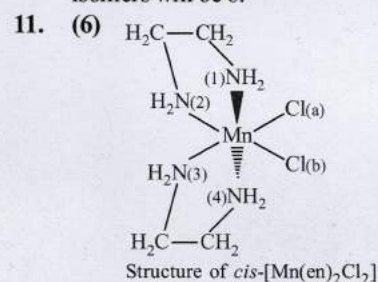
8. (d) Organometallic compounds are those compounds in which metal atom is directly bonded with C-atom.  $H_3C-Li$ .
9. (3) Species having the equal number of valence shell electron are considered as isoelectronic species.

Valence electron in  $Ni(CO)_4 = 18$

Species	Total valence electrons in species
$V(CO)_6$	17
$Cr(CO)_5$	16
$Cu(CO)_3$	17
$Mn(CO)_5$	17
$Fe(CO)_5$	18
$[Co(CO)_3]^{3-}$	18
$[Cr(CO)_4]^{4-}$	18
$Ir(CO)_3$	15

Note: Total valence electrons = Valence electron of metal + Electron donated by ligand.

10. (6) Possible isomers are  
(I)  $[Pt(NH_3)_4Cl_2]Br_2 \Rightarrow G.I. = 2$   
(II)  $[Pt(NH_3)_4Br_2]Cl_2 \Rightarrow G.I. = 2$   
(III)  $[Pt(NH_3)_4BrCl]Br.Cl \Rightarrow G.I. = 2$   
I, II, III are ionisation isomers of given complex and each exhibits two geometrical isomers. Therefore total possible isomers will be 6.





Number of *cis* N – Mn – Cl bonds, i.e. Mn – N and Mn – Cl bonds are in adjacent positions.

- 1 – Cl (a) – Mn – N (1)      2 – Cl (a) – Mn – N (2)  
 3 – Cl (a) – Mn – N (4)      4 – Cl (b) – Mn – N (4)  
 5 – Cl (b) – Mn – N (3)      6 – Cl (b) – Mn – N (1)

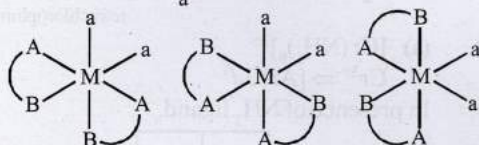
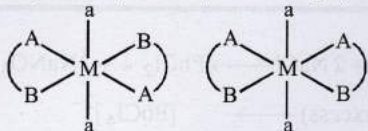
Hence, the answer is 6.

**Note :** All adjacent positions (at 90°) are *cis* to each other.

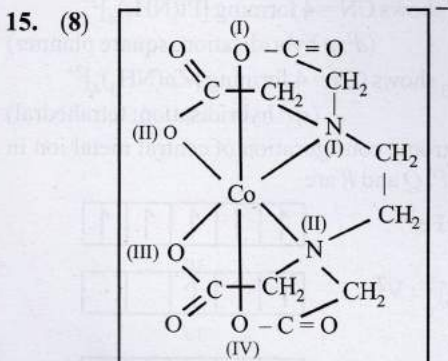
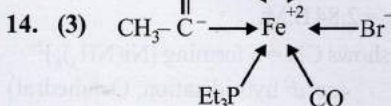
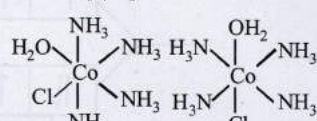
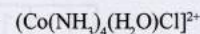
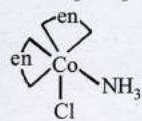
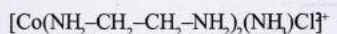
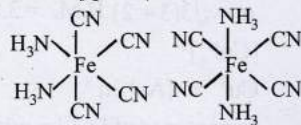
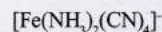
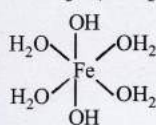
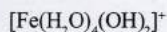
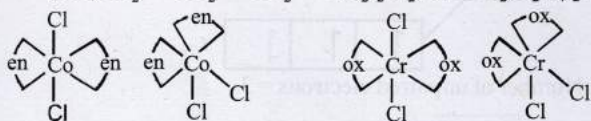
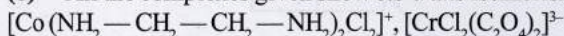
12. (5)  $[\text{CoL}_2\text{Cl}_2]^-$  ( $L = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$ )

*L* is unsymmetrical didentate ligand.

So, the complete is equivalent to  $[M(AB)_2a_2]$  Possible G.I. are



13. (6) All the complexes given show *cis-trans* isomerism



Total no. of N – Co – O bonds are 8.

16. (6)  $m$  moles of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 = 0.01 \times 30 = 0.3$

$m$  moles of  $\text{Cl}^- = 0.3 \times 2 = 0.6$

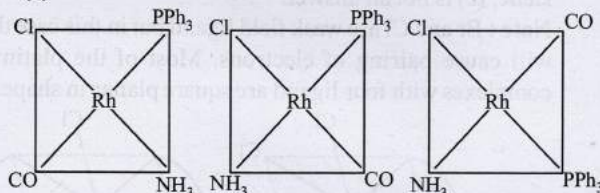
[1 mole of complex gives 2  $\text{Cl}^-$  ions]

$m$  moles of  $\text{Ag}^+ = m$  moles of  $\text{Cl}^-$

$0.1 \times V = 0.6$

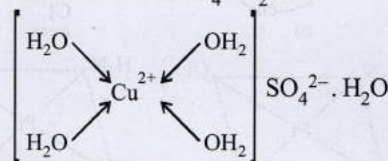
$V = 6 \text{ mL}$

17. (3)



The number of geometrical isomers is 3.

18. (4) The number of water molecules directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is 4.



19. Hexammine cobalt (III) chloride

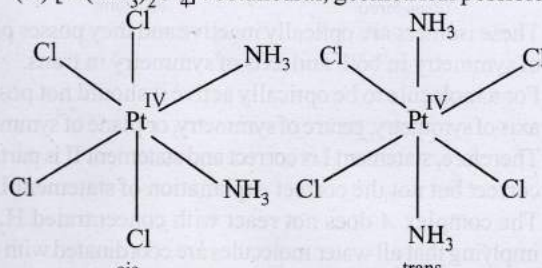
20. (c, d)  $[\text{Pt}(\text{NH}_3)_2\text{Br}_2]^{+2}$

Hybridisation :  $dsp^2$ , geometry : square planar, show geometrical isomerism

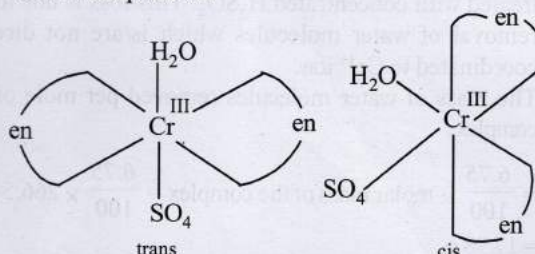
(A)  $[\text{Pt}(\text{en})(\text{SCN})_2]$  : square planar, geometrical not possible

(B)  $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$  : tetrahedral, geometrical not possible

(C)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  : octahedral, geometrical possible



(D)  $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{SO}_4]^{+}$  : Octahedral, geometrical isomerism possible.



21. (b, d) The pair of complex ions  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$  show geometrical isomerism. The pair of complexes  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$  show ionisation isomerism. The other pairs

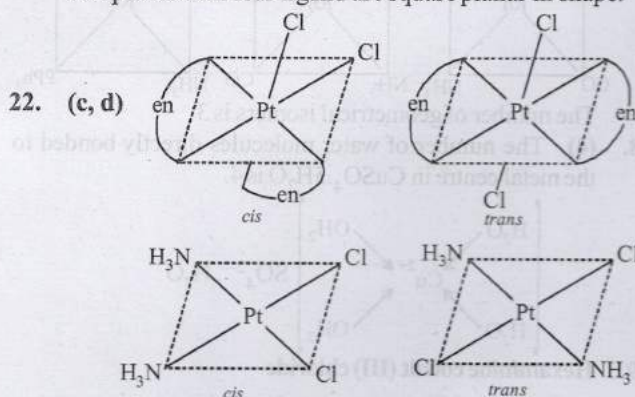


given do not have same type of isomerism.  
The complex  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  will show  $sp^3$  hybridisation. The tetrahedral shape will not show any kind of isomerism.

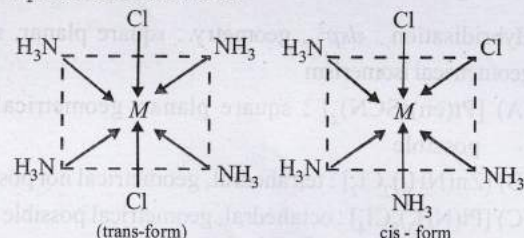
(c) The complex  $[\text{PtBr}_2\text{Cl}_2]^{2-}$  will show  $dsp^2$  hybridisation. The square planar shape will show geometrical isomerism.

Hence, (c) is not an answer.

**Note :** Br and Cl are weak field ligand but in this case they will cause pairing of electrons. Most of the platinum complexes with four ligand are square planar in shape.



23. (b) The geometrical isomers of  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  can be represented as follows:-



These isomers are optically inactive and they possess plane of symmetry in both and axis of symmetry in trans.

For a molecule to be optically active it should not possess axis of symmetry, centre of symmetry, or plane of symmetry. Therefore, statement I is correct and statement II is partially correct but not the correct explanation of statement I.

24. The complex *A* does not react with concentrated  $\text{H}_2\text{SO}_4$  implying that all water molecules are coordinated with  $\text{Cr}^{3+}$  ion. Hence, its structure would be  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ . The compound *B* loses 6.75% of its original mass when treated with concentrated  $\text{H}_2\text{SO}_4$ . This loss is due to the removal of water molecules which is/are not directly coordinated to  $\text{Cr}^{3+}$  ion.

The mass of water molecules removed per mole of the complex

$$= \frac{6.75}{100} \times \text{molar mass of the complex} = \frac{6.75}{100} \times 266.5 \text{ g} = 17.98 \text{ g}$$

This corresponds to one mole of water. Hence, the structure of the compound *B* will be  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}](\text{H}_2\text{O})\text{Cl}_2$ . The compound *C* loses 13.5% of its mass when treated with concentrated  $\text{H}_2\text{SO}_4$  which is twice of the mass lost

by the compound *B*. Hence, the structure of the compound *C* will be  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{H}_2\text{O})_2\text{Cl}$ .

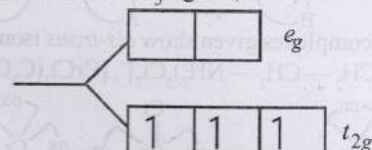
25. (i)  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  Formula of pentaamminechlorocobalt (III)  
(ii)  $\text{LiAlH}_4$  Formula of lithium tetrahydroaluminate (III)
26. (i) Pentaamminecarbonatochromium (III) chloride.  
(ii) Potassium hexacyanochromate (III)  
(iii) Pentaamminenitrito-*o*-cobalt (III) chloride



### Topic-2: Bonding, Stability and Application of Coordination Compounds

1. (c)  $\text{Pb}(\text{NO}_3)_2 + 2 \text{NaCl} \longrightarrow \text{PbCl}_2 \downarrow + 2 \text{NaNO}_3$   
 $\text{PbCl}_2 + 2 \text{Cl}^- (\text{excess}) \longrightarrow [\text{PbCl}_4]^{2-}$   
tetrachloroplumbate(II) ion

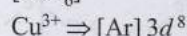
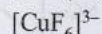
2. (a)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 $\text{Cr}^{3+} \Rightarrow [\text{Ar}] 3d^3$   
In presence of  $\text{NH}_3$  ligand,



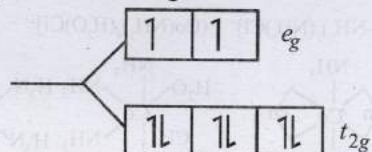
Number of unpaired electrons = 3

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

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



In presence of  $\text{F}^-$  Ligand



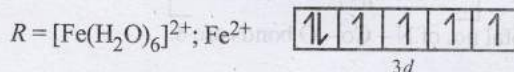
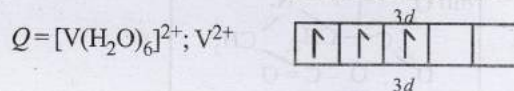
Number of unpaired electrons = 2

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

$$\mu = \sqrt{2(2+2)} \text{ B.M.} = 2.84 \text{ B.M.}$$

3. (a)  $\text{Ni}^{2+}$  with  $\text{NH}_3$  shows CN = 6 forming  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   
( $sp^3d^2$  hybridisation, Octahedral)  
 $\text{Pt}^{2+}$  with  $\text{NH}_3$  shows CN = 4 forming  $[\text{Pt}(\text{NH}_3)_4]^{2+}$   
( $d^2sp$  hybridisation, square planar)  
 $\text{Zn}^{2+}$  with  $\text{NH}_3$  shows CN = 4 forming  $[\text{Zn}(\text{NH}_3)_4]^{2+}$   
( $sp^3$  hybridisation, tetrahedral)

4. (b) The electronic configuration of central metal ion in complex ions *P*, *Q* and *R* are

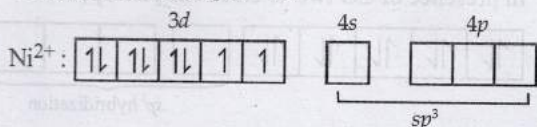




Higher the no. of unpaired electron(s), higher will be magnetic moment.

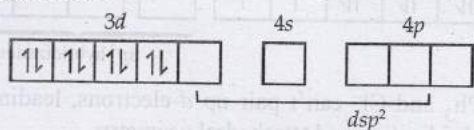
Thus, the correct order of spin only magnetic moment is  $Q < R < P$

5. (c) In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as  $Ni^{2+}$  whose electronic configuration is  $[Ar] 3d^8 4s^0$ .



In the above paramagnetic state, the geometry of the complex is  $sp^3$  giving tetrahedral geometry.

The diamagnetic state is achieved by pairing of electrons in  $3d$  orbital.



Thus, the geometry of the complex will be  $dsp^2$  giving square planar geometry.

6. (c)

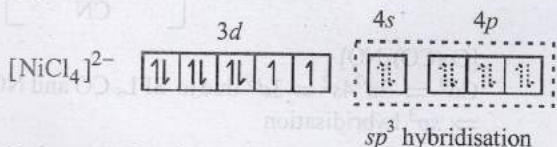
Complex	No. of electrons in outer $d$ orbital	No. of unpaired electron (s)
$[Fe(CN)_6]^{3-}$ (K)	$3d^5$	1 (CN <sup>-</sup> causes pairing of electrons)
$[Co(NH_3)_6]^{3+}$ (L)	$3d^6$	0 (NH <sub>3</sub> causes pairing of electrons)
$[Co(oxal.)_3]^{3-}$ (M)	$3d^6$	0 (oxalate causes pairing of electrons)
$[Ni(H_2O)_6]^{2+}$ (N)	$3d^8$	2
$[Pt(CN)_4]^{2-}$ (O)	$5d^8$	0 (CN <sup>-</sup> causes pairing of electrons)
$[Zn(H_2O)_6]^{2+}$ (P)	$3d^{10}$	—

Thus L, M, O and P are diamagnetic.

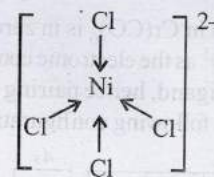
7. (b)  $Ni^{+2} + 4Cl^- \longrightarrow [NiCl_4]^{2-}$

$[NiCl_4]^{2-}$ , =  $3d^8$  configuration with nickel in + 2 oxidation state,  $Cl^-$  being weak field ligand does not compel for pairing of electrons.

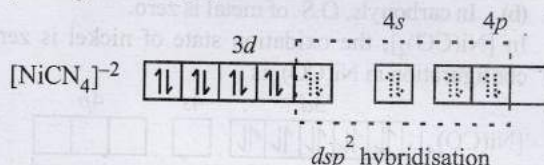
So,



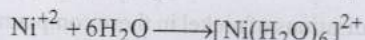
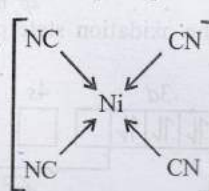
Hence, complex has tetrahedral geometry



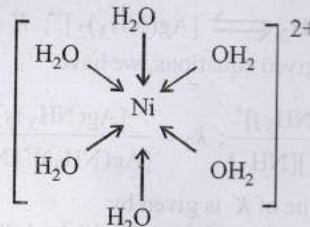
$[Ni(CN)_4]^{2-}$  =  $3d^8$  configuration with nickel in + 2 oxidation state,  $CN^-$  being strong field ligand compels for pairing of electrons.



Hence, complex has square planar geometry.

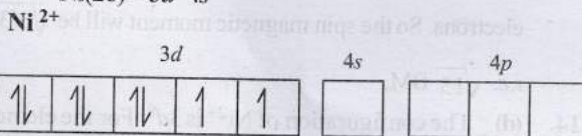


$[Ni(H_2O)_6]^{2+}$  =  $3d^8$  configuration with nickel in + 2 oxidation state. As with  $3d^8$  configuration two  $d$ -orbitals are not available for  $d^2sp^3$  hybridisation. So, hybridisation of Ni (II) is  $sp^3d^2$  and Ni (II) with six co-ordination will have octahedral geometry.

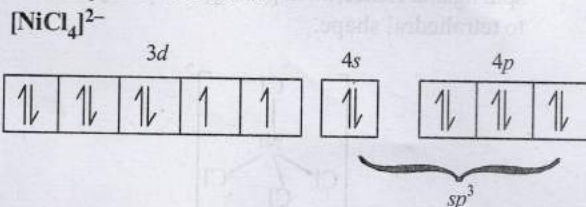


Note : With water as ligand, Ni (II) forms octahedral complexes.

8. (b)  $[NiCl_4]^{2-}$ , O.S. of Ni = +2  
Ni(28) =  $3d^8 4s^2$



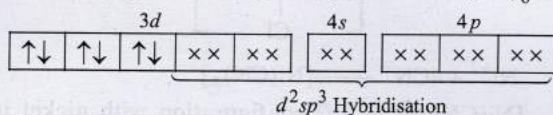
$Cl^-$  being weak ligand it cannot pair up the two electrons present in  $3d$  orbital



No. of unpaired electrons = 2  
Magnetic moment,  $\mu = 2.82$  BM.

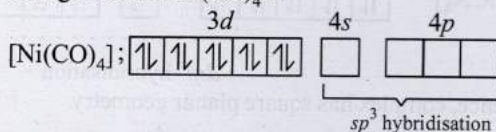


9. (a) Chromium in  $\text{Cr}(\text{CO})_6$  is in zero oxidation state and has  $[\text{Ar}]^{18} 3d^5 4s^1$  as the electronic configuration. However, CO is a strong ligand, hence pairing up of electrons takes place leading to following configuration in  $\text{Cr}(\text{CO})_6$ .

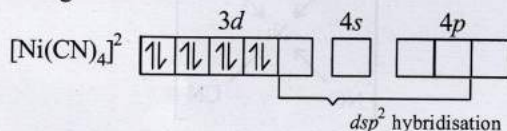


Since, the complex has no unpaired electron, its magnetic moment is zero.

10. (b) In carbonyls, O.S. of metal is zero. In  $[\text{Ni}(\text{CO})_4]$ , the oxidation state of nickel is zero. Its configuration in  $[\text{Ni}(\text{CO})_4]$  is

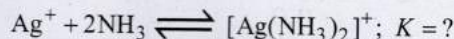


In  $[\text{Ni}(\text{CN})_4]^{2-}$  the oxidation state of Ni is  $2+$  and its configuration is



Thus, the hybridisations of nickel in these compounds are  $sp^3$  and  $dsp^2$  respectively.

11. (d) An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.
12. (b) The required reaction is



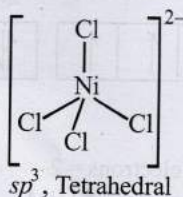
From the given equations, we have

$$k_1 = \frac{[\text{Ag}(\text{NH}_3)]^+}{[\text{Ag}^+][\text{NH}_3]}; k_2 = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}(\text{NH}_3)]^+[\text{NH}_3]}$$

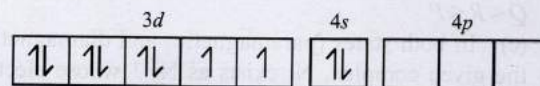
$\therefore$  The value of  $K$  is given by

$$K = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5}$$

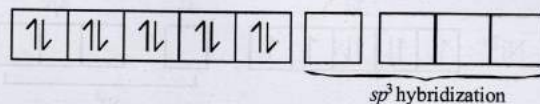
13. (c)  $\mu = \sqrt{n(n+2)} \text{ BM}$  ( $\mu$  = spin magnetic moment)  
Here Co is present as  $\text{Co}^{2+}$  ion which has 3 unpaired electrons. So the spin magnetic moment will be  $\sqrt{3(3+2)}$ ,  
i.e.  $\sqrt{15} \text{ BM}$ .
14. (d) The configuration of  $\text{Ni}^{2+}$  is  $3d^8$ . For the elements of the first transition series,  $\text{Cl}^-$  behaves as a weak field/high spin ligand. Hence, Ni in  $[\text{NiCl}_4]^{2-}$  is  $sp^3$  hybridised leading to tetrahedral shape.



15. (c) In metal carbonyl the metal is in zero oxidation state. In  $\text{Ni}(\text{CO})_4$ , O.N. of Ni = 0  
For Ni ( $Z = 28$ )

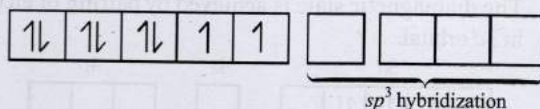


In presence of CO two 4s electrons pair up, thus



In  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ , O.N. of Ni =  $+2$

For  $\text{Ni}^{2+}$



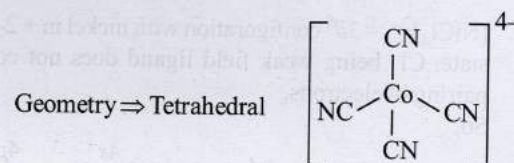
$\text{PPh}_3$  and  $\text{Cl}^-$  can't pair up  $d$ -electrons, leading to  $sp^3$  hybridization and tetrahedral geometry.

16. (c)

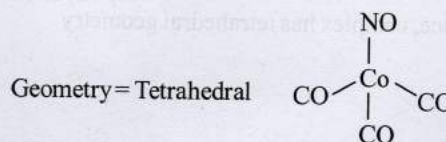
Atom/Ion Complex	Configuration	No. of unpaired electrons	Magnetic nature
$\text{Ni}^{2+} (d^8)$		2	Paramagnetic
$[\text{NiCl}_4]^{2-}$		2	Paramagnetic
$[\text{Ni}(\text{CN})_4]^{2-}$		0	Diamagnetic
$\text{Ni} (d^8 s^2)$		2	Paramagnetic
$[\text{Ni}(\text{CO})_4]$		0	Diamagnetic

17. (b)  $\text{Mn}^{2+}$  in  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  has  $d^5$  configuration (five unpaired electrons);  $\text{Cu}^{2+}$  in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has  $d^9$  configuration (one unpaired electron);  $\text{Fe}^{2+}$  in  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  has  $d^6$  configuration (four unpaired electron); and  $\text{Ni}^{2+}$  in  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  has  $d^8$  configuration (two unpaired electron). Thus,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has lowest degree of paramagnetism.

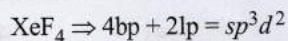
18. (5)  $[\text{Co}(\text{CN})_4]^{4-} \Rightarrow \text{Co}^0 \quad 3d^7 4s^2 \Rightarrow 3d^9$   
Due to SFL,  $\text{CN}^-$  pairing and transference of electron takes place and hybridisation is  $sp^3$ .



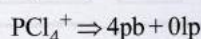
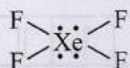
$[\text{Co}(\text{CO})_3\text{NO}]$   
 $\text{Co}^0 \Rightarrow 3d^7 4s^2 \Rightarrow 3d^9$  due to SFL, CO and NO  
 $\Rightarrow sp^3$  hybridisation



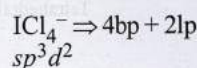
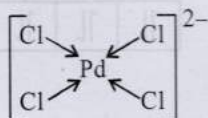
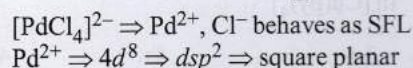
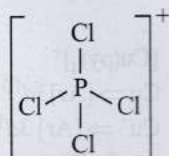




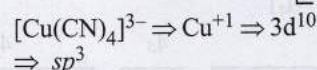
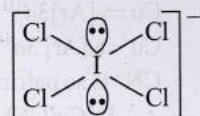
Square planar



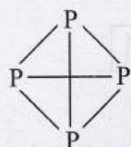
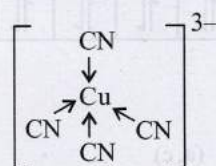
$sp^3 \Rightarrow$  tetrahedral



square planar



Tetrahedral



Tetrahedral

19. (1)  $[\text{Mn}(\text{NH}_3)_6]^{3+} \Rightarrow d^4$  system :  $\uparrow\downarrow \uparrow \uparrow \times \times \times \times$ ,  $\text{NH}_3$  strong field, ligand. Paramagnetic

$[\text{MnCl}_6]^{3-} \Rightarrow d^4$  system :  $\uparrow \uparrow \uparrow \uparrow$ ,  $\text{Cl}^-$  a weak field ligand. Paramagnetic

$[\text{FeF}_6]^{3-} \Rightarrow d^5$  system :  $\uparrow \uparrow \uparrow \uparrow \uparrow$ ,  $\text{F}^-$  a weak field ligand. Paramagnetic

$[\text{CoF}_6]^{3-} \Rightarrow d^6$  system :  $\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$ ,  $\text{F}^-$  a weak field ligand. Paramagnetic

$[\text{Fe}(\text{NH}_3)_6]^{3+} \Rightarrow d^5$  system :  $\uparrow\downarrow \uparrow \uparrow \uparrow \times \times$ ,  $\text{NH}_3$  a strong field ligand. Paramagnetic

$[\text{Co}(\text{en})_3]^{3+} \Rightarrow d^6$  system :  $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \times \times \times \times$ , en a strong field ligand. Diamagnetic  
 Only 1 complex is diamagnetic.

20. (1)

• H-atom =  $1s^1$  Paramagnetic

•  $\text{NO}_2 = \text{odd electron species}$  Paramagnetic

•  $\text{O}_2^-$  (superoxide) = One unpaired electron in  $\pi^*$  M.O. Paramagnetic

•  $\text{S}_2$  (in vapour phase) = same as  $\text{O}_2$ , two unpaired e<sup>-</sup>s are present in  $\pi^*$  M.O. Paramagnetic

•  $\text{Mn}_3\text{O}_4 = 2\text{MnO} \cdot \text{MnO}_2$  Paramagnetic

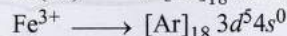
•  $(\text{NH}_4)_2[\text{FeCl}_4] = \text{Fe}^{2+} = 3d^6 4s^0$  Paramagnetic

•  $(\text{NH}_4)_2[\text{NiCl}_4] = \text{Ni} = 3d^8 4s^2$  Paramagnetic

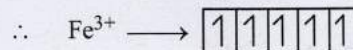
•  $\text{K}_2\text{MnO}_4 = 2\text{K}^+ [\text{MnO}_4]^{2-}$ ,  $\text{Mn}^{6+} = [\text{Ar}] 3d^1$  Paramagnetic

•  $\text{K}_2\text{CrO}_4 = 2\text{K}^+ [\text{CrO}_4]^{2-}$ ,  $\text{Cr}^{6+} = [\text{Ar}] 3d^0$  Diamagnetic

21. (4)  $\text{Fe}(26) \longrightarrow [\text{Ar}]_{18} 3d^6 4s^2$



$\text{SCN}^-$  is weak field ligand hence pairing will not occur.

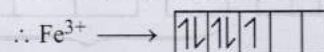


Unpaired electrons = 5

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

=  $\sqrt{35}$  B.M. = 5.92 B.M.

$\text{CN}^-$  is strong field ligand hence pairing will take place.



Unpaired electrons = 1

Magnetic moment =  $\sqrt{1(1+2)}$  B.M. =  $\sqrt{3}$  B.M. = 1.732

Difference = 5.92 - 1.732 = 4.188

Hence, answer is (4).

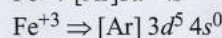
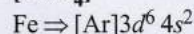
22. Paramagnetism;

$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  shows paramagnetism because of presence of 5 unpaired electrons in the outer most orbital ( $3d^5$ ) of  $\text{Mn}^{2+}$ .

23. False : Octahedral complexes of Fe(III) like  $[\text{Fe}(\text{CN})_6]^{3-}$  are low spin ( $d^2sp^3$  hybridization) with one unpaired electron and have magnetic moment of about 1.9 BM. On the other hand, complexes of Fe(II) like  $[\text{Fe}(\text{CN})_6]^{2-}$  are low spin complex ( $d^2sp^3$ ) with no unpaired electron and thus diamagnetic.

24. (a, b, d)

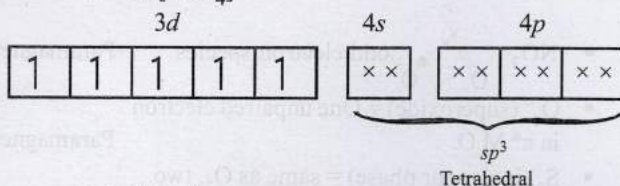
(a)  $[\text{FeCl}_4]^-$





$\text{Cl}^-$  is weak field ligand, So pairing does not take place.

$\therefore$  In  $[\text{FeCl}_4]^-$

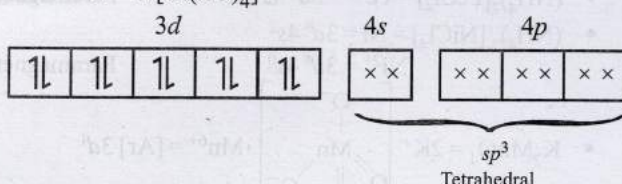


$[\text{Fe}(\text{CO})_4]^{2-}$

$\text{Fe} \Rightarrow [\text{Ar}]3d^6 4s^2$

$\text{Fe}^{2-} \Rightarrow [\text{Ar}]3d^8 4s^2$

$\therefore$  In  $[\text{Fe}(\text{CO})_4]^{2-}$

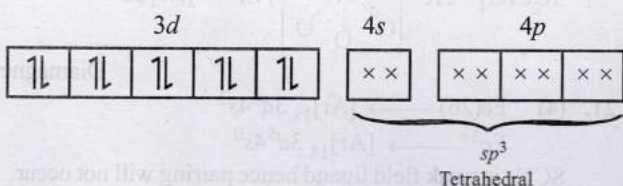


(b)  $[\text{Co}(\text{CO})_4]^-$

$\text{Co} \Rightarrow [\text{Ar}]3d^7 4s^2$

$\text{Co}^{-1} \Rightarrow [\text{Ar}]3d^8 4s^2$

$\therefore$  In  $[\text{Co}(\text{CO})_4]^-$

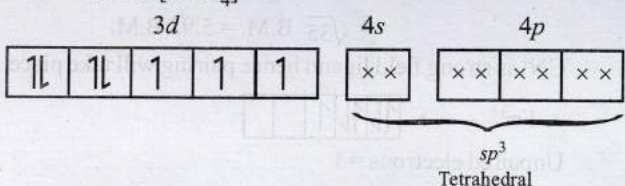


$[\text{CoCl}_4]^{2-}$

$\text{Co} \Rightarrow [\text{Ar}]3d^7 4s^2$

$\text{Co}^{+2} \Rightarrow [\text{Ar}]3d^7 4s^0$

$\therefore$  In  $[\text{CoCl}_4]^{2-}$

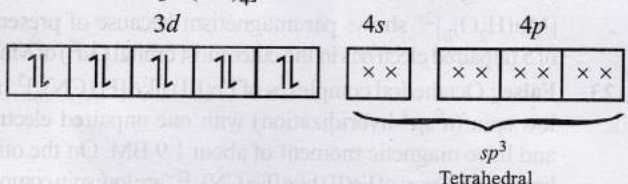


(c)  $[\text{Ni}(\text{CO})_4]$

$\text{Ni} \Rightarrow [\text{Ar}]3d^8 4s^2$

$\text{Ni}^0 \Rightarrow [\text{Ar}]3d^8 4s^0$

$\therefore$  In  $[\text{Ni}(\text{CO})_4]$

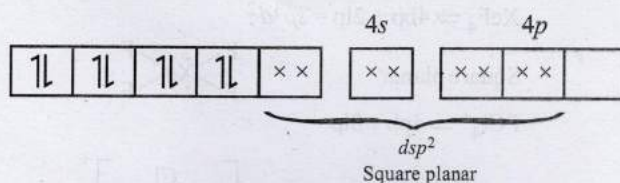


$[\text{Ni}(\text{CN})_4]^{2-}$

$\text{Ni} \Rightarrow [\text{Ar}]3d^8 4s^2$

$\text{Ni}^{+2} \Rightarrow [\text{Ar}]3d^8 4s^0$

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

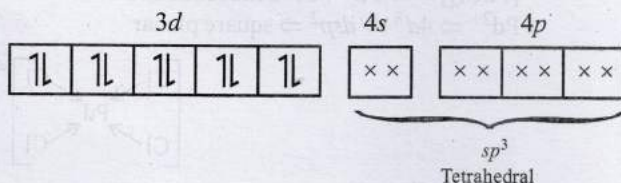


(d)  $[\text{Cu}(\text{py})_4]^+$

$\text{Cu} \Rightarrow [\text{Ar}]3d^{10} 4s^1$

$\text{Cu}^+ \Rightarrow [\text{Ar}]3d^{10} 4s^0$

$\therefore$  In  $[\text{Cu}(\text{py})_4]^+$



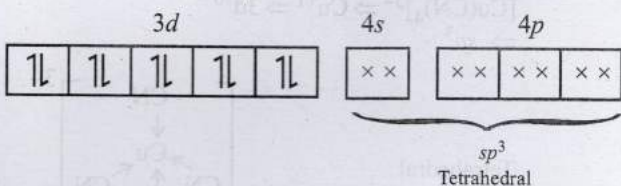
$[\text{Cu}(\text{CN})_4]^{3-}$

$\text{Cu} \Rightarrow [\text{Ar}]3d^{10} 4s^1$

$\text{Cu}^+ \Rightarrow [\text{Ar}]3d^{10} 4s^0$

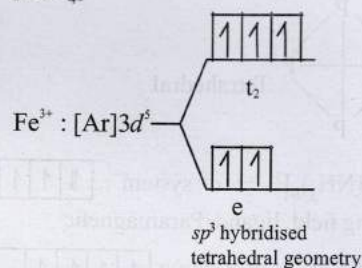
$\text{CN}^-$  is so pairing occurs.

$\therefore$  In  $[\text{Cu}(\text{CN})_4]^{3-}$

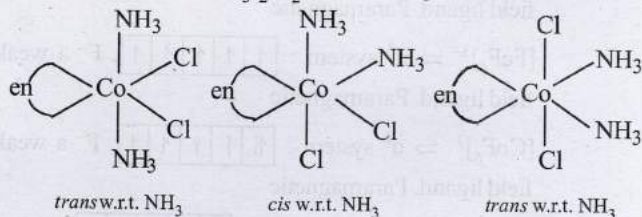


25. (a, c)

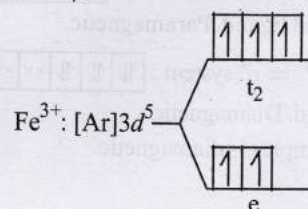
(a)  $[\text{FeCl}_4]^-$



(b)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$  has three geometrical isomers.



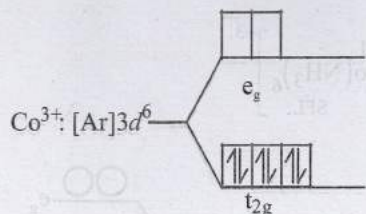
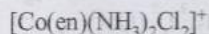
(c)  $[\text{FeCl}_4]^-$





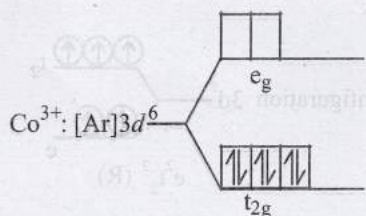
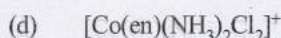
Number of unpaired electrons ( $n$ ) = 5

$$\text{Spin only magnetic moment} = \sqrt{n(n+2)} \text{ B.M.} \\ = 5.92 \text{ B.M.}$$



Number of unpaired electrons ( $n$ ) = 0

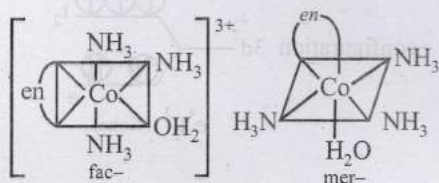
$$\text{Spin only magnetic moment} = \sqrt{n(n+2)} \text{ B.M.} \\ = 0$$



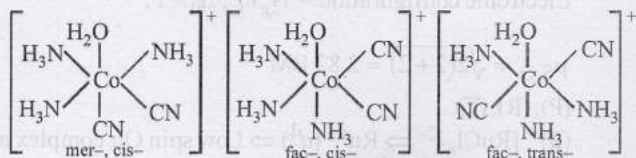
$d^2sp^3$  hybridisation, octahedral geometry

26. (a, b, d)

(a)  $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  has 2 geometrical isomers.



(b) Compound  $[\text{Co}(\text{CN})_2(\text{NH}_3)_3(\text{H}_2\text{O})]^+$  will have three geometrical isomers.



[Note: fac- and mer- w.r.t.  $\text{NH}_3$ , cis- and trans- w.r.t.  $-\text{CN}$ ]

(c)  $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  is diamagnetic

Due to the presence of strong field ligand 'en'  $d^6$  system ( $\text{Co}^{3+}$ ) forms low spin (l.s) complex in Oh splitting of d-orbitals.

(d)  $[\text{Co(en)}(\text{NH}_3)_4]^{3+}$  has larger gap between  $e_g$  and  $t_{2g}$  than  $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ .

So,  $[\text{Co(en)}(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  absorbs light at longer wavelength as compared to  $[\text{Co(en)}(\text{NH}_3)_4]^{3+}$ .

27. (b, c)

(a)  $[(\text{Fe}(\text{CO})_5)]$  &  $[\text{Ni}(\text{CO})_4]$  complexes have 18-electrons in their valence shell.

For transition elements of 3d-series, the valence shells are 3d- and 4s.

(b) Due to strong ligand field, carbonyl complexes are predominantly low spin complexes.

(c) As electron density increases on metals (with lowering oxidation state on metals), the extent of synergic bonding increases. Hence, M-C bond strength increases.

(d) While positive charge on metals increases and the extent of synergic bond decreases and hence, C-O bond becomes stronger.

28. (b, c, d) Magnetic moment,  $\mu = \sqrt{n(n+2)}$  B.M.

where,  $n$  = No. of unpaired electrons

Given for X and Z,  $\mu = 3.87$  B.M.

$$\text{i.e. } \sqrt{n(n+2)} = 3.87$$

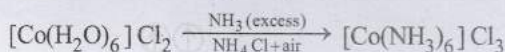
$$n^2 + 2n - 15 = 0 \quad \therefore n = 3$$

For complex Y (1 : 3 electrolyte) given  $\mu = 0$

$$\text{i.e. } \sqrt{n(n+2)} = 0 \Rightarrow n = 0$$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $[\text{Co}(\text{H}_2\text{O})_6] \text{Cl}_2$  (X) is pink coloured compound and octahedral in structure.

On adding excess of HCl at room temperature,  $[\text{Co}(\text{H}_2\text{O})_6] \text{Cl}_2$  (X) changes into tetrahedral,  $[\text{CoCl}_4]^{2-}$  (Z) and on adding excess of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  in the presence of air forms  $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$  (Y).



(X) Pink

( $\mu = 3.87$  B.M)

(Y)

( $\mu = 0$ )

29. (a, c) The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fe).

As the bond strength  $\text{Fe} \leftarrow \text{C} \equiv \text{O}$

between Fe - C increases, the bond order between C - O decreases and the effective bonding can be represented as  $\text{Fe} = \text{C} = \text{O}$ .

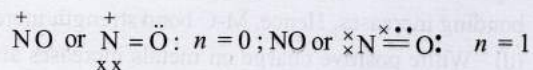
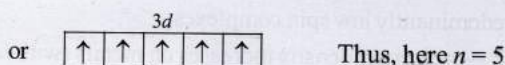
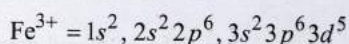
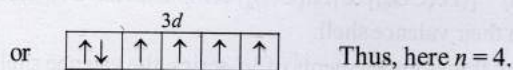
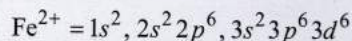
This will increase the C - O bond length. Thus, the answers can be 1.13 Å or 1.15 Å.



30. (c) The magnetic moment ( $\mu$ ) of a species is related to its number of unpaired electrons ( $n$ ) in form of following expressions.

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

The number of unpaired electrons in the given pairs are as follows:



The given combinations differ in the number of unpaired electrons. Hence, these can be differentiated by the measurement on the solid state magnetic moment of nitropusside ion.

31. (b) Highest paramagnetic character will be shown by the ion having maximum number of unpaired electrons in their  $d$ -subshells.

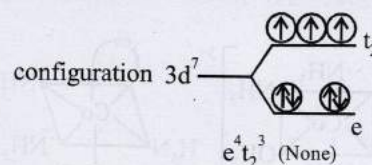
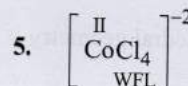
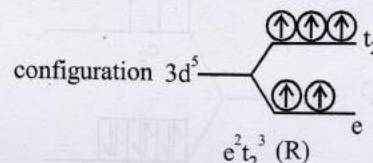
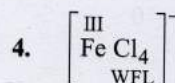
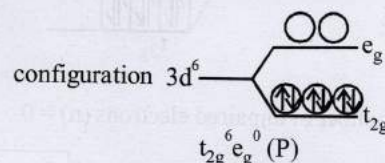
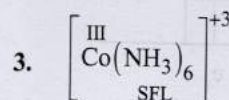
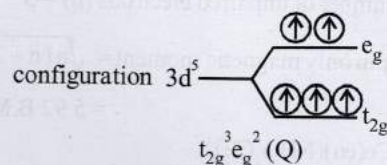
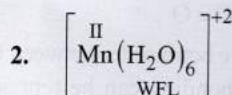
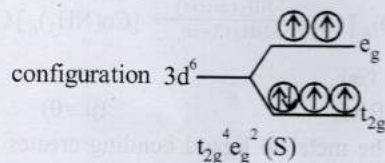
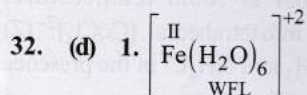
${}_{25}\text{Cr}^{3+}$  has 3 unpaired electrons ;

${}_{26}\text{Fe}^{2+}$  has 4 unpaired electrons

${}_{29}\text{Cu}^{2+}$  has 1 unpaired electrons ;

${}_{30}\text{Zn}^{2+}$  has no unpaired electrons

So (a), (b) & (c) show paramagnetism. Out of which (b) has the highest paramagnetism.



33. (a) (I)  $[\text{Cr}(\text{CN})_6]^{4-} \Rightarrow \text{Cr}^{2+} (d^4) \Rightarrow$  low spin Oh complex as  $\text{CN}^-$  is strong field ligand.

$$\text{Electronic configuration} = t_{2g}^4 e_g^0; \Delta_0 > P;$$

$$\mu_{\text{S.O.}} = \sqrt{2(2+2)} = 2.82 \text{ BM}$$

(P), (R), (T)

(II)  $[\text{RuCl}_6]^{2-} \Rightarrow \text{Ru}^{4+} (d^4) \Rightarrow$  Low spin Oh complex as Ru is of large size.

$$\text{Electronic configuration} = t_{2g}^4 e_g^0; \Delta_0 > P;$$



$$\mu_{S.O.} = \sqrt{2(2+2)} = 2.82 \text{ BM}$$

(P), (R), (S), (T)

(III)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} \Rightarrow \text{Cr}^{2+} (d^4) \Rightarrow$  high spin Oh complex as  $\text{H}_2\text{O}$  is weak field ligand.Electronic configuration =  $t_{2g}^3 e_g^1$ ;  $\Delta_0 < P$ ;

$$\mu_{S.O.} = \sqrt{4(4+2)} = 4.89 \text{ BM}$$

(Q), (T)

(IV)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \Rightarrow \text{Fe}^{2+} (d^6) \Rightarrow$  high spin Oh complexElectronic configuration =  $t_{2g}^4 e_g^2$ ;  $\Delta_0 < P$ ;

$$\mu_{S.O.} = \sqrt{4(4+2)} = 4.89 \text{ BM}$$

(P), (Q)

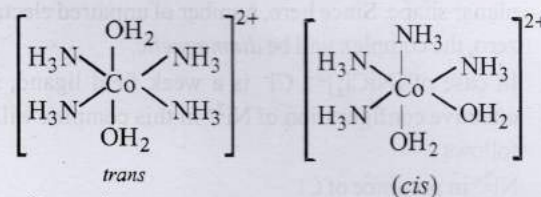
34. (c)

(p)  $[\text{FeF}_6]^{4-}$ ,  $\text{Fe}^{2+} = 3d^6$  and  $\text{F}^-$  is weak field ligand $\therefore$  Hybridization is  $sp^3d^2$  (high spin complex)(q)  $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$ ,  $\text{Ti}^{3+} = 3d^1$  (No effect of ligand field strength) $\therefore$  Hybridization is  $d^2sp^3$ (r)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $\text{Cr}^{3+} = 3d^3$  (No effect of ligand field strength) $\therefore$  Hybridization is  $d^2sp^3$ (s)  $[\text{FeCl}_4]^{2-}$ ,  $3d^6$  and  $\text{Cl}^-$  is weak field ligand $\therefore$  Hybridization is  $sp^3$ (t)  $[\text{Ni}(\text{CO})_4]$ ,  $\text{Ni} = 3d^{10}$  and  $\text{CO}$  is strong field ligand $\therefore$  Hybridization is  $sp^3$ (w)  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{Ni}^{2+} = 3d^8$  and  $\text{CN}$  is strong field ligand $\therefore$  Hybridization is  $dsp^2$ 

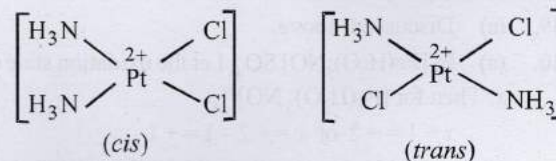
35. (b)

Complex	Magnetic character	Isomerism
A, $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$\text{Cr}^{3+}$ is $d^3$ , hence paramagnetic	cis-trans
B, $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$	$\text{Ti}^{3+}$ is $d^1$ , hence paramagnetic.	ionization
C, $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$	$\text{Pt}^{2+}$ is $d^8$ , complex is square planar, all electrons are paired, hence diamagnetic	ionization
D, $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$	$\text{Co}^{3+}$ is $d^6$ , all electrons are paired due to strong ligands, hence diamagnetic	cis-trans

36. (A): (p), (q) and (s)

In  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ , Co is in +2 state having  $3d^7$  configuration, which makes it paramagnetic due to odd electrons. Moreover, it is an octahedral complex showing cis-trans isomerism w.r.t.,  $\text{H}_2\text{O}$ . $\text{Co}^{2+} = 3d^7$  (Paramagnetic)

(B): (p), (r) and (s)

In  $[\text{Pt}(\text{NH}_3)\text{Cl}_2]$ , Pt is in +2 state with configuration  $5d^8$ . Since  $\text{NH}_3$  is a strong field ligand, it will pair all the electrons making the complex diamagnetic. Moreover, it is a square planar complex showing cis-trans isomerism. $\text{Pt}^{2+} = 5d^8 4s^0$  (diamagnetic)

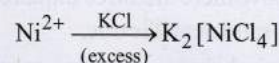
(C): (q) and (s)

In  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$ , Co is in +2 state with  $3d^7$  configuration making it paramagnetic.

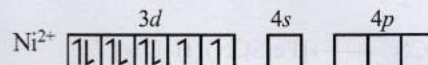
(D): (q) and (s)

In  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ , Ni is in +2 state with  $3d^8$  configuration. It is attached with weak field ligands, therefore it is paramagnetic.37. (a)  $\text{Ni}^{2+} \xrightarrow[\text{excess}]{\text{KCN}} \text{K}_2[\text{Ni}(\text{CN})_4]$ ;

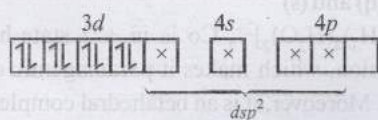
potassium tetracyano nickete (II)



potassium tetrachloro nichelate (II)

38. (c) For  $[\text{Ni}(\text{CN})_4]^{2-}$ ;  $\text{Ni} = [\text{Ar}]3d^8 4s^2$ ;  $\text{Ni}^{2+} = [\text{Ar}]3d^8$ However,  $\text{CN}^-$  is a strong field ligand so it forces the  $3d$  electrons to pair up and hence the effective configuration in this case will be: $\text{Ni}^{2+}$  in presence of  $\text{CN}^-$ 

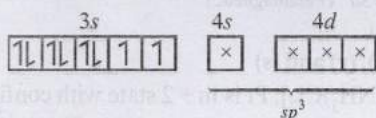




Thus,  $[\text{Ni}(\text{CN})_4]^{2-}$  exhibits  $dsp^2$  hybridization and square planar shape. Since here, number of unpaired electrons is zero, the complex will be *diamagnetic*.

In case of  $[\text{NiCl}_4]^{2-}$ ,  $\text{Cl}^-$  is a weak field ligand, so the effective configuration of  $\text{Ni}^{2+}$  in this complex will be as follows:

$\text{Ni}^{2+}$  in presence of  $\text{Cl}^-$



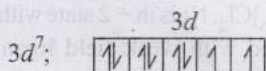
So here,  $\text{Ni}^{2+}$  is  $sp^3$  hybridised and thus, tetrahedral in shape. Since, the complex has two unpaired electrons, it will be *paramagnetic*.

39. (a) Discussed above.

40. (a) In  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ , Let the oxidation state of Fe be  $x$ . Then for  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ ,  
 $x + 1 = +2$  or  $x = +2 - 1 = +1$

Hence, in this complex the oxidation state of Fe is +1  
 Electronic configuration of  $\text{Fe}^+$  can be represented as  $\text{Fe}^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ . This unexpected configuration is due to presence of  $\text{NO}^+$ . Due to which 1 electron from  $4s^1$  gets shifted to  $3d$ - orbitals.

The  $3d^7$  electrons in five  $3d$ - orbitals can be shown as

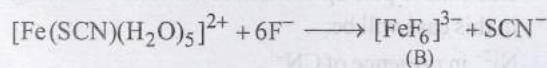
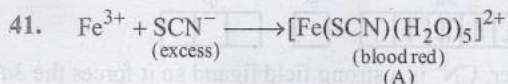


In it, we find 3 unpaired electrons.

Because of the presence of unpaired electrons the complex is paramagnetic *i.e.* statement 1 is true.

As is clear from above there are three unpaired electrons in this complex *i.e.* statement 2 is true.

Since, paramagnetic behaviour is due to presence of unpaired electrons in it so statement 2 is correct explanation of statement 1.



IUPAC name of (A) is pentaquathiocyanatoferrate (III) ion  
 IUPAC name of (B) is hexafluoroferrate (III)

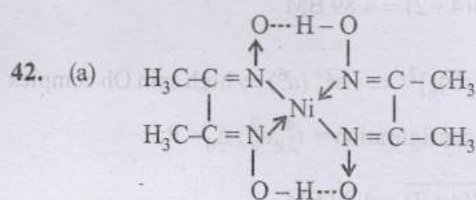
In  $[\text{FeF}_6]^{3-}$  coordination no. of Fe = 6

In  $[\text{FeF}_6]^{3-}$  oxidation state of Fe = +3

$\therefore$  It has 5 unpaired electrons,  $n = 5$ ,  $\text{Fe}^{3+}$  is  $3d^5$

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

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



Bis(dimethylglyoximate) nickel (II)

(b) Charge on Ni in the complex is +2 and it is  $dsp^2$  hybridised

(c) Since number of unpaired electrons in  $\text{Ni}^{2+}$  is zero, the complex is diamagnetic.

43. The spin magnetic moment,  $m$  of the complex is 1.73 BM.

$\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$

It means that nucleus of the complex, chromium ion has one unpaired electron. So the ligand NO is unit positively charged.

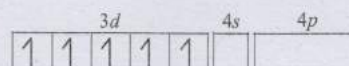
$\text{Cr} (z = 24) = 3d^5 4s^2$ , after pairing up of electrons, there shall be one unpaired electron left.

Thus, chromium can be in  $\text{Cr}^+$  state.

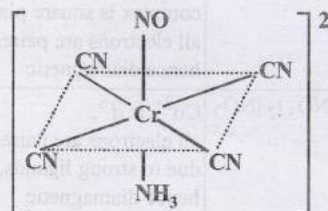
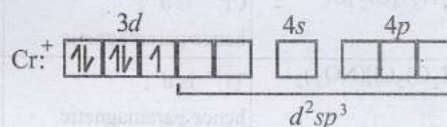
IUPAC name:

Potassium amminetetracyanonitrosochromate (I).

(a) Electronic configuration of  $\text{Cr}^+$ :



(b) Electronic configuration of  $\text{Cr}^+$  under the influence of strong field ligand  $\text{CN}^-$

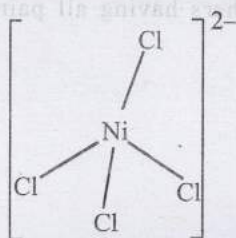
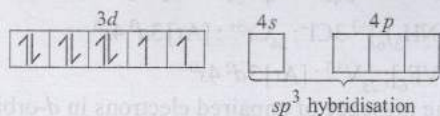


So, Hybridization :  $d^2sp^3$ ; Shape : Octahedral



44.  $\text{Cl}^-$  is a weak ligand which is unable to pair the electrons of  $\text{Ni}^{2+}$ . Therefore, here hybridisation is  $sp^3$  and shape will be tetrahedral.

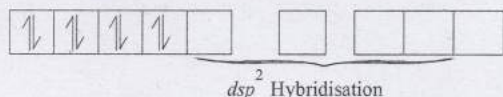
Electronic configuration of  $\text{Ni}^{2+}$  (No. of electrons = 26) in presence of  $\text{Cl}^-$  ion, a weak ligand.



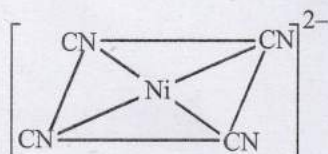
Magnetic moment of  $[\text{NiCl}_4]^{2-} = \sqrt{2(2+2)} = 2.82 \text{ BM}$

On the other hand,  $\text{CN}^-$  is a strong ligand which pairs the electrons of  $\text{Ni}^{2+}$ . Therefore, here hybridisation is  $dsp^2$  and shape will be square planar.

Electronic configuration of  $\text{Ni}^{2+}$  in presence of  $\text{CN}^-$  ion, a strong ligand.



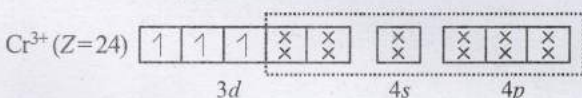
Magnetic moment of  $[\text{Ni}(\text{CN})_4]^{2-} = \sqrt{0(0+2)} = 0.0 \text{ BM}$



Square planar  $dsp^2$  hybridisation

45. Compound (A) on treatment with  $\text{AgNO}_3$  gives white precipitate of  $\text{AgCl}$ , which is readily soluble in dil. aq.  $\text{NH}_3$ . Therefore it has at least one  $\text{Cl}^-$  ion in the ionization sphere. Furthermore, chromium has coordination number equal to 6. So, its formula is  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$ .

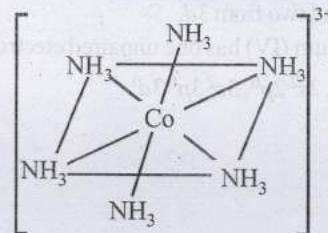
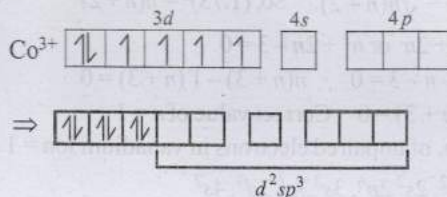
Compound (B) on treatment with  $\text{AgNO}_3$  gives pale yellow precipitate of  $\text{AgBr}$  soluble in conc.  $\text{NH}_3$ . Therefore it has  $\text{Br}^-$  in the ionization sphere. So, its formula is  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ .



State of hybridization of chromium in both (A) and (B) is  $d^2sp^3$ . Spin magnetic moment of (A) or (B),

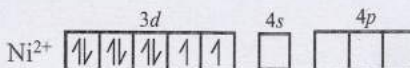
$$\mu_{\text{spin}} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

46.  $[\text{Co}(\text{NH}_3)_6]^{3+}$

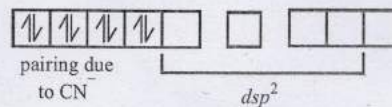


Octahedral complex,  $d^2sp^3$  hybridisation

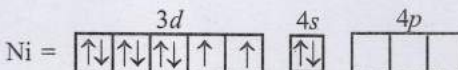
$[\text{Ni}(\text{CN})_4]^{2-}$



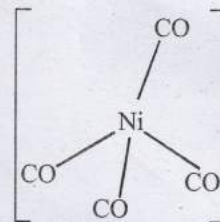
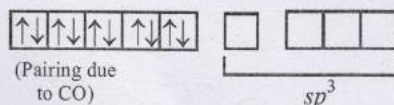
$\text{Ni}^{2+}$  (after rearrangement)



$[\text{Ni}(\text{CO})_4]$



$\text{Ni}$  (after rearrangement)



Tetrahedral ( $sp^3$  hybridisation)



47. Magnetic moment ( $\mu$ ) =  $\sqrt{n(n+2)}$  BM

where  $n \rightarrow$  number of unpaired electrons

$\mu = 1.73$  BM for vanadium ion

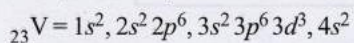
$$1.73 \text{ BM} = \sqrt{n(n+2)} \quad \text{So, } (1.73)^2 = n(n+2)$$

$$3.0 = n^2 + 2n \quad \text{or } n^2 + 2n - 3 = 0$$

$$n^2 + 3n - n - 3 = 0 \quad \therefore n(n+3) - 1(n+3) = 0$$

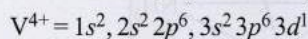
$$(n-1)(n+3) = 0 \quad \text{Correct value of } n = 1$$

Thus, no. of unpaired electrons in vanadium ion = 1

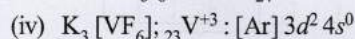
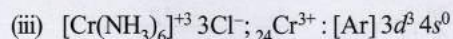
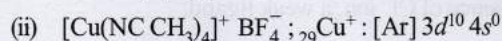
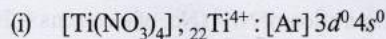


It will have one unpaired electron if it will lose two electrons from  $4s$  and two from  $3d$ .

$\therefore$  Vanadium (IV) has one unpaired electron.



48. For the explanation of colouration of complexes, first of all find out the number of unpaired electrons present in outer available  $d$ -orbitals



Due to the presence of unpaired electrons in  $d$ -orbitals, two complexes *i.e.*,  $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$  and  $\text{K}_3[\text{VF}_6]$  are coloured. Others having all paired electrons are colourless.