CHAPTER

# Coordination Compounds

# 9.1 Werner's Theory of Coordination Compounds

1. The correct order of the stoichiometries of AgCl formed when AgNO<sub>3</sub> in excess is treated with the complexed coll\_3.6NH<sub>3</sub>, CoCl<sub>3</sub>.5NH<sub>3</sub>, CoCl<sub>3</sub>.4NH<sub>3</sub>

(a) 3AgCl, 1AgCl, 2AgCl (b) 3AgCl, 2AgCl, 1AgCl

(c) 2AgCl, 3AgCl, 2AgCl
 (d) 1AgCl, 3AgCl, 2AgCl
 (NEET 2017)

- 2. Cobalt(III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at  $25^{\circ}C$ ?
  - (a)  $CoCl_3 \cdot 5NH_3$  (b) (c)  $CoCl_3 \cdot 3NH_3$  (d)

(b)  $CoCl_3 \cdot 6NH_3$ 

(d)  $CoCl_3 \cdot 4NH_3$ 

(2015, Cancelled)

(1998)

3. An excess of AgNO<sub>3</sub> is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium(III) chloride. The number of moles of AgCl precipitated would be

(a) 0.003	(b) 0.01
() 0.001	

- (c) 0.001 (d) 0.002 (*NEET* 2013)
- 4. Which of the following will exhibit maximum ionic conductivity?

(a) $K_4[Fe(CN)_6]$	(b) $[Co(NH_3)_6]Cl_3$
(c) $[Cu(NH_3)_4]Cl_2(d)$	[Ni(CO) <sub>4</sub> ] (2001)

5. A coordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of AgNO<sub>3</sub> solution, we get two moles of AgCl precipitate. The ionic formula for this complex wouldbe

(a)  $[Co(NH_3)_5(NO_2)]Cl_2$ 

(b)  $[Co(NH_3)_5Cl][Cl(NO_2)]$ 

(c) 
$$[Co(NH_3)_4(NO_2)Cl][(NH_3)Cl]$$

(d)  $(Co(NH_3)_5][(NO_2)_2Cl_2]$ 

- 9.2 Definitions of Some Important Terms Pertaining to Coordination Compounds
- 6. The correct increasing order of *trans*-effect of the following species is

   (a) NH<sub>3</sub> > CN<sup>-</sup>> Br<sup>-</sup>> C<sub>6</sub> H<sup>-</sup>

(b)  $CN > C_6H_5 > Br > NH_3$ (c)  $Br > CN > NH_3 > C_5H - C_5H - C_5H - C_5H - C_5H - C_5H - C_5H_5 > NH_3$ (d)  $CN > Br > C_6H_5 > NH_3$  (NEET-II 2016)

- 7. The sum of coordination number and oxidation number of the metal M in the complex  $[M(en)_2(C_2O_4)]$ Cl (where *en* is ethylenediamine) is (a) 6 (b) 7 (c) 8 (d) 9 (2015)
- 8. The anion of acetylacetone (*acac*) forms  $Co(acac)_3$  chelate with  $Co^{3+}$ . The rings of the chelate are
  - (a) five membered (b) four membered
  - (c) six membered (d) three membered.

(Karnataka NEET 2013)

- 9. Which of the following statements is true?
  - (a) Silicon exhibits 4 coordination number in its compound.
    - (b) Bond energy of  $F_2$  is less than  $Cl_2$ .
    - (c) Mn(III) oxidation state is more stable than Mn(II) in aqueous state.
    - (*d*) Elements of 15<sup>th</sup> gp shows only +3 and +5 oxidation states. (2002)
- **10**. Coordination number of Ni in  $[Ni(C_2O_4)_3]^{4-}$  is

(a) 3	(b) 6	
(c) 4	(d) 2	(2001)

- - (c) 6 and + 3 (d) 4 and + 2 (1995)
- 12. Which of the following ligands is expected to be bidentate?

(a) CH <sub>3</sub> NH <sub>2</sub>	(b) $CH_3C \equiv N$	
(c) Br	(d) $C_2 O_4^{2-}$	(1994)

9.3 Nomenclature Compounds	of C	oordination	20.	The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of which
<ul> <li>13. The name of complex</li> <li>(a) hexacyanitoferrate</li> <li>(b) tricyanoferrate(III)</li> <li>(c) hexacyanidoferrate</li> </ul>	(III) ion ion	<sup>3–</sup> is		<ul> <li>type of isomerism?</li> <li>(a) Linkage isomerism</li> <li>(b) Ionization isomerism</li> <li>(c) Coordination isomerism</li> <li>(d) Geometrical isomerism (2011)</li> </ul>
(d) hexacyanoiron(III)	ion.	(2015)	21.	The complex, $[Pt(py)(NH_3)BrCl]$ will have how
<ul> <li>14. The correct IUPAC national (a) chlorodifluoridoe (III) chloride</li> <li>(1) Life i bli (d bli)</li> </ul>	thylenediamir	nechromium		many geometrical isomers? (a) 3 (b) 4 (c) 0 (d) 2 (2011)
<ul> <li>(b) difluoridobis(ethylechloride</li> <li>(c) difluorobis-(ethylerchloride</li> <li>(d) chlorodifluoridobis</li> </ul>	e diamine)ch	romium (III)	22.	The existence of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to (a) linkage isomerism (b) geometrical isomerism (c) coordination isomerism
chromium (III).	•	a NEET 2013)		( <i>d</i> ) ionization isomerism. (2010)
<ul> <li>15. The hypothetical comprobability of the construction o</li></ul>	be represented $D_{2}$ ]Cl <sub>2</sub>		23.	Which one of the following complexes is not expected to exhibit isomerism?(a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ (b) $[Pt(NH_3)_2Cl_2]$ (c) $[Ni(NH_3)_2Cl_2]$ (d) $[Ni(en)_3]^{2+}$ (2010)
(c) $[Co(NH_2)_3(H_2O)_2]$ (d) $[Co(NH_3)_3(H_2O)_3]$	-	(2002)	24.	Which of the following does not show optical isomerism?
<ul><li>16. IUPAC name of [Pt(NI (a) triamminebromo chloride</li></ul>	$H_3)_3(Br)(NO_2)$	-		<ul> <li>(a) [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]<sup>0</sup></li> <li>(b) [Co(<i>en</i>)Cl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup></li> <li>(c) [Co(<i>en</i>)<sub>3</sub>]<sup>3+</sup></li> </ul>
<ul><li>(b) triamminebromo chloride</li><li>(c) triamminechloro</li></ul>	-		25.	(d) $[Co(en)_2Cl_2]^+(en = \text{ethylenediamine})$ (2009) Which of the following will give a pair of enantiomorphs?
(d) triamminenitroch chloride.	-			(a) $[Cr(NH_3)_6][Co(CN)_6]$ (b) $[Co(en)_2Cl_2]Cl$ (c) $[Pt(NH_3)_4][PtCl_6]$
17. The formula of dichlor (a) [Cu { $O = C(NH_2)$		per(II) is		(d) $[Co(NH_3)_4Cl_2]NO_2$ ( <i>en</i> = NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) (2007)
(d) $[CuCl_2] \{O = C(NH_2) \}$ (b) $[CuCl_2] \{O = C(NH_2) \}$ (c) $[Cu \{O = C(NH_2) \}$ (d) $[CuCl_2 \{O = C(NH_2) \}$	$[H_2)_2$ 2 $Cl_2$	(1997)	26.	<ul> <li>[Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl exhibits</li> <li>(a) linkage isomerism, geometrical isomerism and optical isomerism</li> <li>(b) linkage isomerism, ionization isomerism and</li> </ul>
9.4 Isomerism in Co				<ul><li>(c) linkage isomerism, ionization isomerism and</li><li>(c) linkage isomerism, ionization isomerism and</li></ul>
<ul> <li>18. The type of isomerism s</li> <li>[CoCl<sub>2</sub>(en)<sub>2</sub>] is</li> <li>(a) geometrical isomerical isomeric</li></ul>	rism	mplex		<ul> <li>(c) Initiage isomerism, fonzation isomerism and geometrical isomerism</li> <li>(d) ionization isomerism, geometrical isomerism and optical isomerism. (2006)</li> </ul>
<ul> <li>(c) ionization isomeris</li> <li>(d) linkage isomerism</li> <li>19. Number of possible iso [Co(<i>en</i>)<sub>2</sub>Cl<sub>2</sub>]Cl will be</li> <li>(a) 1</li> </ul>	omers for the co	-	27.	<ul> <li>Which one of the following is expected to exhibit optical isomerism? (<i>en</i> = ethylenediamine)</li> <li>(a) <i>cis</i>-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]</li> <li>(b) <i>trans</i>-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]</li> <li>(c) <i>cis</i>-[Co(<i>en</i>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup></li> </ul>
(c) 4	(d) 2	(2015)		(d) $trans-[Co(en)_2Cl_2]^+$ (2005)

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(c)  $[Al(H_2O)_4]^{3+}$ ,  $dsp^2$ Which of the following coordination compounds 28. would exhibit optical isomerism? (a) Pentaamminenitrocobalt(III) iodide 37. (b) Diamminedichloroplatinum(II) (c) *trans*-Dicyanobis(ethylenediamine) chromium(III) chloride (d) tris-(Ethylenediamine)cobalt(III) bromide (2004)Which of the following will give maximum number 29. of isomers? (b)  $[Ni(en)(NH_3)_4]^{2+}$ (a)  $[Co(NH_3)_4Cl_2]$ (c)  $[Ni(C_2O_4)(en)_2]^{2-}$ (d)  $[Cr(SCN)_2(NH_3)_4]^+$ (2001)30. Which complex compound will give four isomers? (a)  $[Fe(en)_3]Cl_3$ (b)  $[Co(en)_2Cl_2]Cl$ (c) [Fe(PPh<sub>3</sub>)<sub>3</sub>NH<sub>3</sub>ClBr]Cl (d)  $[Co(PPh_3)_3Cl]Cl_3$ (2000)The total number of possible isomers for the com-31.  $[Cu^{II}(NH)]$  [Pt<sup>II</sup>Cl], are plex compound (a) 5 (b) 6 (c) 3 (d) 4 (1998)32. The number of geometrical isomers of the complex [Co(NO<sub>2</sub>)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>] is (a) 4 (b) 0 (c) 2 (d) 3 (1997)**33.** The number geometrical isomers for of  $[Pt(NH_3)_2Cl_2]$  is (a) 3 (b) 4 (d) 2 (c) 1 (1995)9.5 Bonding in Coordination Compounds 34. Which of the following is the correct order of increasing field strength of ligands to form *(a* coordination compounds?

(a) 
$$SCN_{-}^{-} < F_{-}^{-} < C_2O_4^{-} < CN_{2_{-}}^{-}$$
  
(a)  $SCN < F < CN_{-}^{-} < C_2O_4$   
(b)  $F^{-} < SCN_{-}^{-} < C_2O_4^{-} < CN_{-}^{-}$   
(c)  $CN < C_2O_4 < SCN < F$  (NEET 2020)

**35.** What is the correct electronic configuration of the central atom in K<sub>4</sub>[Fe(CN)<sub>6</sub>] based on crystal field theory? (a)  $e^{t^2}t^2$ (b)  $t^4 e^2$ 

(c)  $t^{6} \frac{2}{e^{0}}$ (d)  $e^{3g}t^{3g}$ (NEET 2019) 2g g

36. Aluminium chloride in acidified aqueous solution forms a complex 'A', in which hybridisation state of Al is 'B'. What are 'A' and 'B', respectively? (a)  $[Al(H_2O)_6]^{3+}$ ,  $sp^3d^2$ (b)  $[Al(H_2O)_4]^{3+}$ ,  $sp^3$ 

(d) 
$$[Al(H_2O)_6]^{3+}$$
,  $d^2sp^3$  (Odisha NEET 2019)  
The crystal field stabilisation energy (CFSE) for  
 $[CoCl_6]^{4-}$  is 18000 cm<sup>-1</sup>. The CFSE for  $[CoCl_4]^{2-}$   
will be  
(a) 6000 cm<sup>-1</sup> (b) 16000 cm<sup>-1</sup>  
(c) 18000 cm<sup>-1</sup> (d) 8000 cm<sup>-1</sup>  
(Odisha NEET 2019)

- 38. The geometry and magnetic behaviour of the complex [Ni(CO)<sub>4</sub>] are
  - (a) square planar geometry and diamagnetic
  - (b) tetrahedral geometry and diamagnetic
  - (c) square planar geometry and paramagnetic
  - (d) tetrahedral geometry and paramagnetic.

(NEET 2018)

39. Correct increasing order for the wavelengths of absorption in the visible region for the complexes of Co<sup>3+</sup> is

(a)  $[Co(H_2O_6]^{3+}, [Co(en_3)^{3+}, [Co(NH_3)_6]^{3+}]^{3+}$ 

- (b)  $[Co(H_2O)]^{3+}$ ,  $[Co(NH_3)_6]^{3+}$ ,  $[Co(en)_3]^{3+}$
- (c)  $[Co(NH_3)_6]^{3+}$ ,  $[Co(en)_3]^{3+}$ ,  $[Co(H_2O)_6]^{3+}$
- (d)  $[Co(en)_3]^{3+}, [Co(NH_3)_6]^{3+}, [Co(H_2O)_6]^{3+}$

(NEET 2017)

- 40. Pick out the correct statement with respect to  $[Mn(CN)_6]^{3-}$ .
  - (a) It is  $sp^3d^2$  hybridised and tetrahedral.
  - (b) It is  $d^2sp^3$  hybridised and octahedral.
  - (c) It is  $dsp^2$  hybridised and square planar.
  - (d) It is  $sp^3d^2$  hybridised and octahedral.

(NEET 2017)

41. Jahn–Teller effect is not observed in high spin complexes of

a) 
$$d^7$$
 (b)  $d$ 

(c)  $d^4$  (d)  $d^9$  (*NEET-II* 2016) **42.** The hybridization involved in complex [Ni(CN)<sub>4</sub>]<sup>2</sup>

is (At. No. Ni = 28)  
(a) 
$$sp^3$$
 (b)  $d^2sp^2$   
(c)  $d^2sp^3$  (d)  $dsp^2$  (2015)

- **43.** Among the following complexes the one which shows zero crystal field stabilization energy (CFSE)
  - $\begin{array}{l} {}^{1S}\\ (a) \ \left[ Mn(H_2O)_6 \right]_{2+}^{3+} \\ (c) \ \left[ Co(H_2O)_6 \right] \end{array} \begin{array}{l} (b) \ \left[ Fe(H_2O)_6 \right]_{3+}^{3+} \\ (d) \ \left[ Co(H_2O)_6 \right] \end{array} \begin{array}{l} (2014) \end{array}$
- 44. A magnetic moment at 1.73 BM will be shown by one among of the following
  - (b)  $[CoCl_6]^{4-}$ (a) TiCl<sub>4</sub> (c)  $[Cu(NH_3)_4]^{2+}$ (d)  $[Ni(CN)_4]^{2-}$

(NEET 2013)

45. Crystal field splitting energy for high spin d<sup>4</sup> octahedral complex is

(a) -1.2 Δ₀
(b) -0.6 Δ₀
(c) -0.8 Δ₀
(d) -1.6 Δ₀
(*Karnataka NEET2013*)

46. Which among the following is a paramagnetic complex?

(a) [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
(b) [Pt(en)Cl<sub>2</sub>]
(c) [CoBr<sub>4</sub>]<sup>2-</sup>
(d) Mo(CO)<sub>6</sub>
(At. No. Mo = 42, Pt = 78)

**47.** Which is diamagnetic?

(a) $[CoF_6]^{3-}$	(b) $[Ni(CN)_4]^{2-}$
(c) $[NiCl_4]^{2-}$	(d) $[Fe(CN)_6]^{3-}$

- (Karnataka NEET 2013)
- **48.** Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?

(a) [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>
 (b) [Zn(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>
 (c) [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
 (d) [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> (2012)
 49. Low spin complex of d<sup>6</sup>-cation in an octahedral field

will have the following energy

(a) 
$$\frac{-12}{5}\Delta_o + P$$
 (b)  $\frac{-12}{5}\Delta_o + 3P$   
(c)  $\frac{-2}{5}\Delta_o + 2P$  (d)  $\frac{-2}{5}\Delta_o + P$ 

 $(\Delta_o = \text{crystal field splitting energy in an octahedral field, } P = \text{Electron pairing energy})$  (2012)

- **50.** Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is nottrue?
  - (a) Red complex has a square planar geometry.
  - (b) Complex has symmetrical H-bonding.
  - (c) Red complex has a tetrahedral geometry.
  - (d) Dimethylglyoxime functions as bidentate ligand.

$$\begin{bmatrix} \text{dimethylglyoxime} = \begin{array}{c} H_3C - C = N \\ H_3C - C = N \\ H_3C - C = N \\ OH \end{bmatrix}$$
(Mains 2012)

**51.** Of the following complex ions, which is diamagnetic in nature?

(a)  $[NiCl_4]^{2-}$  (b)  $[Ni(CN)_4]^{2-}$ 

- (c)  $[CuCl_4]^{2-}$  (d)  $[CoF_6]^{3-}$  (2011)
- 52. The *d*-electron configurations of Cr<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup> and Co<sup>2+</sup> are d<sup>4</sup>, d<sup>5</sup>, d<sup>6</sup> and d<sup>7</sup> respectively. Which one of the following will exhibit minimum paramagnetic behaviour?
  (a) [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> (b) [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>

(c)  $[Co(H_2O)_6]^{2+}$  (d)  $[Cr(H_2O)_6]^{2+}$ (At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27) (2011) 53. Which of the following complex compounds will exhibit highest paramagnetic behaviour? (a)  $[Ti(NH_3)_6]^{3+}$ (b)  $[Cr(NH_3)_6]^{3+}$ (c)  $[Co(NH_3)_6]^{3+}$ (d)  $[Zn(NH_3)_6]^{2+}$ (At. No. Ti = 22, Cr = 24, Co = 27, Zn = 30) (2011) 54. Which of the following complex ions is not expected to absorb visible light? (a)  $[Ni(CN)_4]^{2-}$ (b)  $[Cr(NH_3)_6]^{3+}$ (d)  $[Ni(H_2O)_6]^{2+}$ (c)  $[Fe(H_2O)_6]^{2+}$ (2010) **55.** Crystal field stabilization energy for high spin  $d^4$ octahedral complex is (b)  $-1.6 \Delta_0 + P$ (a)  $-1.8 \Delta o$ 56. Out of TiF<sup>2-</sup>,  $CoF^{3-}$ ,  $CuCl and NiCl^{2-}(Z_4 of^{3-})$ (2010) Ti = 22, Co = 27, Cu = 29, Ni = 28) the colourless species are (a)  $\operatorname{Cu_2Cl_2}_{6}$  and  $\operatorname{NiCl_{2^{\perp}}}_{2^{\perp}}$  (b)  $\operatorname{TiF_{2^{-}}}_{2^{-}}$  and  $\operatorname{Cu_2Cl_2}_{6}$  (c)  $\operatorname{CoF_{3^{-2}}}_{6}$  and  $\operatorname{NiCl_{4^{-2}}}_{6}$  (d)  $\operatorname{TiF_{2^{-}}}_{6}$  and  $\operatorname{CoF_{3^{-2}}}_{6}$ 

**57.** Which of the following complex ions is expected to absorb visible light?

(2009)

- (a)  $[Ti(en)_2(NH_3)_2]^{4+}$  (b)  $[Cr(NH_3)_6]^{3+}$ (c)  $[Zn(NH_3)_6]^{2+}$  (d)  $[Sc(H_2O)_3(NH_3)_3]^{3+}$ [At. nos. Zn = 30, Sc = 21, Ti = 22, Cr = 24] (2009)
- **58.** Which of the following complexes exhibits the highest paramagnetic behaviour?
  - (a)  $[Co(ox)_2(OH)_2]^-$  (b)  $[Ti(NH_3)_6]^{3+}$
  - (c)  $[V(gly)_2(OH)_2(NH_3)_2]^+$
  - (d)  $[Fe(en)(bpy)(NH_3)_2]^{2+}$

where gly = glycine, en = ethylenediamine and bpy = bipyridyl moities. (At. nos. Ti = 22, V = 23, Fe = 26, Co = 27) (2008)

**59.** In which of the following coordination entities the magnitude of  $\Delta_0$  (CFSE in octahedral field) will be maximum?

(a) 
$$[Co(CN)_6]^{3-}$$
 (b)  $[Co(C_2O_4)_3]^{3-}$   
(c)  $[Co(H_2O)_6]^{3+}$  (d)  $[Co(NH_3)_6]^{3+}$   
(At. No. Co = 27) (2008)

- **60.** The *d* electron configurations of  $Cr^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Ni^{2+}$  are  $3d^4$ ,  $3d^5$ ,  $3d^6$  and  $3d^8$  respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?
  - (a)  $[Fe(H_2O)_6]^{2+}$  (b)  $[Ni(H_2O)_6]^{2+}$ (c)  $[Cr(H_2O)_6]^{2+}$  (d)  $[Mn(H_2O)_6]^{2+}$ . (At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28) (2007)

66

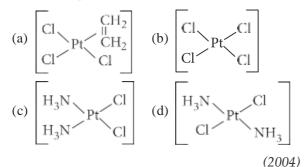
- **61.**  $[Cr(H_2O)_6]Cl_3$  (At. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3delectrons in the chromium of the complex is (a)  $3d^1$ ,  $3d^1$ ,  $3d^1$ ~2 хy уz (b)  $3d^{1}_{(x^{2}-\mu^{2})}, 3d^{1}_{z^{2}}3d^{1}_{xz}$ , 3d<sup>1</sup> (d)  $3d^1$ ,  $3d^1$ ,  $3d^1$ (2006)yzхu 27 62. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? (a)  $[Zn(NH_3)_6]^{2+}$ (b)  $[Cr(NH_3)_6]^{3+}$ (c)  $[Co(NH_3)_6]^{3+}$ (d)  $[Ni(NH_3)_6]^{2+}$ (Atomic number : Zn = 30, Cr = 24, Co = 27, Ni = 28)(2005)63. Among [Ni(CO)<sub>4</sub>], [Ni(CN)<sub>4</sub>]<sup>2-</sup>, [NiCl<sub>4</sub>]<sup>2-</sup> species, the hybridisation states at the Ni atom are, respectively (b)  $sp^3$ ,  $dsp^2$ ,  $sp^3$ (a)  $sp^3$ ,  $dsp^2$ ,  $dsp^2$ (c)  $sp^3$ ,  $sp^3$ ,  $dsp^2$  (d)  $dsp^2$ ,  $sp^3$ ,  $sp^3$ . [Atomic number of Ni = 28] (2004)64. CN<sup>-</sup> is a strong field ligand. This is due to the fact that (a) it carries negative charge (b) it is a pseudohalide (c) it can accept electrons from metal species (d) it forms high spin complexes with metal
- species. (2004)**65.** Considering  $H_2O$  as a weak field ligand, the number of unpaired electrons in  $[Mn(H_2O)_6]^{2+}$  will be (atomic number of Mn = 25)
  - (a) three (b) five (c) two (d) four. (2004)
- 66. In an octahedral structure, the pair of d orbitals involved in  $d^2sp^3$  hybridisation is

(a) 
$$d_{x^2-y^2}, d_{z^2}$$
 (b)  $d_{xz}, d_{x^2-y^2}$   
(c)  $d_{z^2}, d_{xz}$  (d)  $d_{xy}, d_{yz}$ . (2004)

- 67. The number of unpaired electrons in the complex ion  $[CoF_2]^{3-}$  is (a) 2 (b) 3
  - (c) 4 (d) zero
  - (Atomic no. : Co = 27) (2003)
- 68. Atomic number of Cr and Fe are respectively 24 and 26, which of the following is paramagnetic with the spin of electron?
  - (a)  $[Cr(CO)_6]$ (b)  $[Fe(CO)_5]$ (c)  $[Fe(CN)_6]^{4-}$ (d)  $[Cr(NH_3)_6]^{3+}$  (2002)
- **69.** Which statement is incorrect? (a)  $Ni(CO)_4$  - tetrahedral, paramagnetic (b)  $[Ni(CN)_4]^{2-}$  - square planar, diamagnetic (c)  $Ni(CO)_{-4}$  - tetrahedral, diamagnetic (d)  $[NiCl_4]^{2-}$  - tetrahedral, paramagnetic (2001)**Bonding in Metal Carbonyls** 9.6 **70.** Iron carbonyl,  $Fe(CO)_5$  is (a) tetranuclear (b) mononuclear (c) trinuclear (d) dinuclear. (NEET 2018) 71. An example of a sigma bonded organometallic compound is (a) Grignard's reagent (b) ferrocene (c) cobaltocene (d) ruthenocene. (NEET 2017) 72. Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 Å.) (a)  $[Fe(CO)_4]^{2-}$ (b)  $[Mn(CO)_6]^+$ (c)  $Ni(CO)_4$ (d)  $[Co(CO)_4]^-$ (NEET-I 2016) 73. Which of the following carbonyls will have the strongest C – O bond? (b)  $Cr(CO)_6$ 6 (c)  $V(CO)_{6}^{-}$ (d)  $Fe(CO)_5$ (2011)74. Which of the following does not have a metal carbon bond? (a) Al(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (b)  $C_2H_5MgBr$ (c)  $K[Pt(C_2H_4)Cl_3]$ (d)  $Ni(CO)_4$ (2004)**75.** Among the following which is not the  $\pi$ -bonded organometallic compound? (a) K [PtCl<sub>3</sub>( $\eta^2 - C_2H_4$ )] (b) Fe  $(\eta^5 - C_5 H_5)_2$ (c)  $Cr(\eta^6 - C_6H_6)_2$ (d) (CH<sub>3</sub>)<sub>4</sub>Sn (2003)76. Which of the following organometallic compounds is  $\sigma$  and  $\pi$ -bonded? (a)  $[Fe(\eta^5 - C_5H_5)_2]$ (b) K[PtCl<sub>3</sub>( $\eta^2 - C_2H_4$ )] (c)  $[C_0(CO)_5NH_3]^{2+}$ (d) Fe(CH<sub>3</sub>)<sub>3</sub> (2001)77. Shape of  $Fe(CO)_5$  is (a) octahedral (b) square planar (c) trigonal bipyramidal (d) square pyramidal. (2000)78. In metal carbonyl having general formula  $M(CO)_x$ where M = metal, x = 4 and the metal is bonded to
  - (a) carbon and oxygen (b)  $C \bigcirc$ (c) oxygen (d) carbon. (1995)

### 9.7 Importance and Applications of Coordination Compounds

- 79. Which of the following complexes is used to be as an anticancer agent?
  (a) mer-[Co(NH)) Cl ]
  (b) cis-[PtCl (NH)]
  (c) cis
  - $-K_2[PtCl_2Br_2]$  (d) Na<sub>2</sub>CoCl<sub>4</sub> (2014)
- 80. Copper sulphate dissolves in excess of KCN to give(a) Cu(CN)<sub>2</sub>(b) CuCN
  - (c)  $[Cu(CN)_4]^{3-}$  (d)  $[Cu(CN)_4]^{2-}$  (2006)
- **81.** Which of the following is considered to be an anticancer species?



- (a) a thin layer of Ag is formed on Cu
- (b) more voltage is required
- (c) Ag<sup>+</sup> ions are completely removed from solution
- (d) less availability of  $Ag^+$  ions, as Cu cannot

displace Ag from  $[Ag(CN)_2]^-$  ion. (2002)

- **83.** CuSO<sub>4</sub> when reacts with KCN forms CuCN, which is insoluble in water. It is soluble in excess of KCN, due to formation of the following complex
  - (a)  $K_2[Cu(CN)_4]$
  - (b) K<sub>3</sub>[Cu(CN)<sub>4</sub>]
  - (c)  $CuCN_2$
  - (d)  $Cu[KCu(CN)_4]$  (2002)
- 84. Hypo is used in photography to
  - (a) reduce AgBr grains to metallic silver
  - (b) convert metallic silver to silver salt
  - (c) remove undecomposed silver bromide as a soluble complex
  - (d) remove reduced silver. (1988)

									ANSV		FY								
								C											
1.	(b)	2.	(c)	3.	(c)	4.	(a)	5.	(a)	6.	(b)	7.	(d)	8.	(c)	9.	(b)	10.	(b)
11.	(c)	12.	(d)	13.	(c)	14.	(b)	15.	(a)	16.	(a)	17.	(d)	18.	(a)	19.	(b)	20.	(c)
21.	(a)	22.	(b)	23.	(c)	24.	(a)	25.	(b)	26.	(c)	27.	(c)	28.	(d)	29.	(d)	30.	(c)
31.	(d)	32.	(c)	33.	(d)	34.	(a)	35.	(c)	36.	(a)	37.	(d)	38.	(b)	39.	(d)	40.	(b)
41.	(b)	42.	(d)	43.	(b)	44.	(c)	45.	(b)	46.	(c)	47.	(b)	48.	(a)	49.	(b)	50.	(c)
51.	(b)	52.	(c)	53.	(b)	54.	(a)	55.	(d)	56.	(b)	57.	(b)	58.	(a)	59.	(a)	60.	(b)
61.	(d)	62.	(c)	63.	(b)	64.	(b)	65.	(b)	66.	(a)	67.	(c)	68.	(d)	69.	(a)	70.	(b)
71.	(a)	72.	(a)	73.	(a)	74.	(a)	75.	(d)	76.	(c)	77.	(c)	78.	(d)	79.	(b)	80.	(c)
81.	(c)	82.	(d)	83.	(b)	84.	(c)												

# **Hints & Explanations**

1. (b):  $[Co(NH_3)_6]Cl_3 + 3AgNO_3 \rightarrow 3AgCl\downarrow$ +  $[Co(NH_3)_6](NO_3)_3$  $[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3 \rightarrow 2AgCl\downarrow$ +  $[Co(NH_3)_5Cl](NO_3)_2$  $[Co(NH_3)_4Cl_2]Cl + AgNO_3 \rightarrow AgCl\downarrow$ +  $[Co(NH_3)_4Cl_2]NO_3$ 

2. (c) : For octahedral complexes, coordination number is 6. Hence,  $CoCl_3 \cdot 3NH_3$  *i.e.*,  $[Co(NH_3)_3Cl_3]$  will not ionise and will not give test for  $Cl^-$  ion with silver nitrate.

3. (c):  $[Cr(H_2O)_4Cl_2]Cl + AgNO_3 \rightarrow [Cr(H_2O)_4Cl_2]NO_3 + AgCl_{ppt}$ No. of millimoles of solution = 100 mL × 0.01 M - 1 millimole

 $= 10^{-3}$  mole

So, mole of AgCl = 0.001

**4.** (a) : Ionic conductance increases with increasing the number of ions, produced after decomposition.

Compound	No. of ions produced
$K_4[Fe(CN)_6]$	5
[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	4
$[Cu(NH_3)_4]Cl_2$	3
[Ni(CO) <sub>4</sub> ]	0

(a) : As the complex gives two moles of AgCl ppt. 5. with AgNO<sub>3</sub> solution, so the complex must have two ionisable Cl atoms. Hence, the probable complex, which gives three mole ions may be  $[Co(NH_3)_5NO_2]Cl_2$ .  $[Co(NH_3)_5NO_2]Cl_2 \rightarrow [Co(NH_3)_5NO_2]^{2+} + 2Cl^{-1}$ 

one mole  $\rightarrow$  3 mole ions

6. (b): The intensity of the *trans*-effect (as measured by the increase in rate of substitution of the *trans* ligand) follows the sequence : CN > CH > Br > NH6 5 3

(d):  $[M(en)_2(C_2O_4)]Cl$ : 7.

Oxidation number of metal = +3

Coordination number of metal = 6

: Sum of oxidation number and coordination number =3+6=9

(c): The ligand acetylacetone forms six membered 8. chelate ring in the complex  $[Co(acac)_3]$ .

9. (b) : Bond energy of  $F_2$  is less than  $Cl_2$  due to interelectronic repulsions in small sizedF-atoms.

Silicon exhibits coordination number 6.

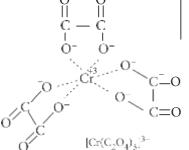
In aqueous state, Mn(II) is more stable.

 $Mn Mn^{2+} + 2e^{-}$ 

The common oxidation states of 15<sup>th</sup> group elements are +3 and +5 (b) : C  $O^{2^-}$  → bidentate ligand.

3 molecules attached from two sides with Ni makes coordination number 6.





As the number of atoms of the ligands that are directly bound to the central metal is known as coordination number. It is six here (see in figure).

Oxidation state : Let oxidation state of Cr be x.

 $\Rightarrow$  3 (+1) + x + 3 (-2) = 0  $\Rightarrow$  3 + x - 6 = 0  $\Rightarrow$  x = + 3

**12.** (d) : When a ligand has two groups that are capable of bonding to the central atom, it is said to be bidentate. Thus, the only ligand, which is expected to be bidentate is  $C_2Q^{2-}$  as

$$O = C - O^{-}$$
  
|  
 $O = C - O^{-}$   
14. (b)

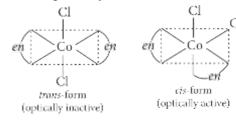
13. (c)

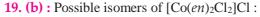
**15.** (a) : Chlorodiaquatriamminecobalt(III) chloride can be represented as  $[CoCl(NH_3)_3(H_2O)_2]Cl_2$ .

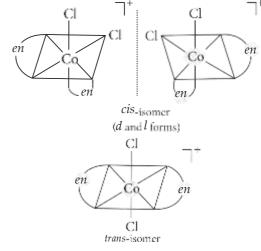
**16.** (a): The ligands are named in the alphabetic order according to latest IUPAC system. So, the name of [Pt(NH<sub>3</sub>)<sub>3</sub>Br(NO<sub>2</sub>)Cl]Cl is triamminebromochloronitro platinum(IV) chloride. (The oxidation no. of 'Pt' is +4).

17. (d) : The formula of dichlorobis(urea)copper(II) is  $[CuCl_2\{(NH_2)_2CO\}_2].$ **18.** (a) :  $[CoCl_2(en)_2]$ , exhibits geometrical isomerism,

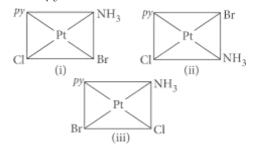
as the coordination number of Co is 6 and this compound has octahedral geometry.



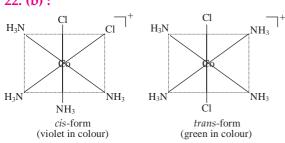




20. (c) : Coordination isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in the complex. e.g.,  $[Co(NH_3)_6][Cr(CN)_6]$  and  $[Cr(NH_3)_6][Co(CN)_6]$ **21.** (a) :  $[Pt(py)(NH_3)BrCl]$  can have three isomers.



### 22. (b) :



**23.** (c) : Compounds having tetrahedral geometry does not exhibit isomerism due to presence of symmetry elements. Here,  $[Ni(NH_3)_2Cl_2]$  has tetrahedral geometry.

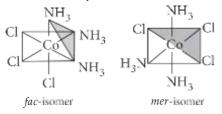
24. (a) : Optical isomerism is shown by :

(i) Complexes of the type  $[M(AA)_2Y_2]$ , containing one symmetrical bidentate ligand *i.e.*,  $[Co(en)Cl_2(NH_3)_2]^+$ .

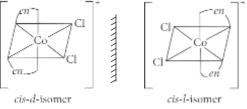
(ii) Complexes of the type  $[M(AA)_3]$ , containing a symmetrical bidentate ligand *i.e.*,  $[Co(en)_3]^{3+}$ .

(iii) Complexes of the type  $[M(AA)_2X_2]$ , *i.e.*,  $[Co(en)_2Cl_2]^+$ . However complexes of the type  $[MA_3B_3]$  show geometrical isomerism, known as *fac-mer* isomerism.

 $\therefore$  [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] exhibits *fac-mer* isomerism.



**25.** (b) : Either a pair of crystals, molecules or compounds that are mirror images of each other but are not identical, and that rotate the plane of polarised light equally, but in opposite directions are called as enantiomorphs.



**26.** (c) : Ionization isomerism arises when the coordination compounds give different ions in solution.

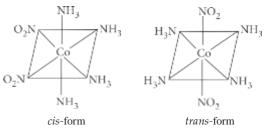
$$\begin{bmatrix} Co(NH_3)_4(NO_2)_2 \\ Co(NH_3)_4(NO_2)_2 \end{bmatrix}^+ + Cl^- \\ \begin{bmatrix} Co(NH_3)_4(NO_2)Cl \end{bmatrix} NO_2 \\ \begin{bmatrix} Co(NH_3)_4(NO_2)Cl \end{bmatrix}^+ + NO_2 \\ \begin{bmatrix} Co(NH_3)_4(NO_2)Cl$$

Linkage isomerism occurs in complex compounds which contain ambidentate ligands like  $NO_2^-$ ,  $SCN^-$ ,  $CN^-$ ,  $S_2O_3^{-2-}$  and CO.

[Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl and [Co(NH<sub>3</sub>)<sub>4</sub>(ONO)<sub>2</sub>]Cl

are linkage isomers as  $NO_2^-$  is linked through N or through O.

Octahedral complexes of the type  $Ma_4b_2$  exhibit geometrical isomerism.

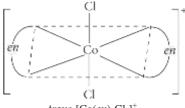


**27.** (c) : Optical isomerism is not shown by square planar complexes.

Octahedral complexes of general formulae,

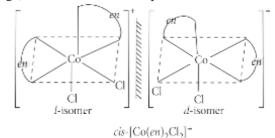
 $[Ma_2b_2c_2]^{n\pm}$ , [Mabcdef],  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$  (where AA = symmetrical bidentate ligand),  $[M(AA)_2ab]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$ 

(where AB = unsymmetrical ligands) show optical isomerism.

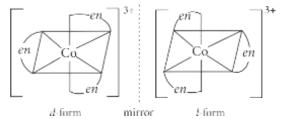


 $trans-[Co(en)_2Cl_2]^+$ 

does not show optical isomerism (superimposable mirror image). But *cis*-form shows optical isomerism.



**28. (d) :**  $[Co(en)_3]^{3+}$ :



**29.** (d) :  $[Cr(SCN)_2(NH_3)_4]^+$  shows linkage, geometrical and optical isomerism.

30. (c) : [Fe(PPh)] NH ClBr]Cl can give two optical

and two geometrical isomers. While other complexes do not form geometrical isomers.

**31.** (d) : The isomers of the complex compound  $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$  are :

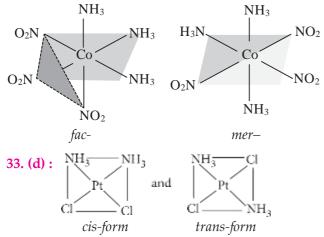
(i) [Cu(NH<sub>3</sub>)<sub>3</sub>Cl] [Pt(NH<sub>3</sub>)Cl<sub>3</sub>]

(ii)  $[Pt(NH_3)_3Cl][Cu(NH_3)Cl_3]$ 

(iii) [Pt(NH<sub>3</sub>)<sub>4</sub>][CuCl<sub>4</sub>]

So, the total no. of isomers are = 4

**32.** (c) : Possible geometrical isomers are :



34. (a) : According to spectrochemical series, order of increasing field strength is :  $SCN < F < CO^{2} < CN^{-}$ 

**35.** (c) : In  $K_4[Fe(CN)_6]$  complex, Fe is in +2 oxidation state.

 $Fe^{2+}: 1$ 

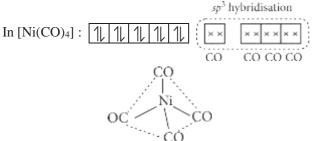
As  $CN^-$  is a strong field ligand, it causes pairing of electrons therefore, electronic configuration of  $Fe^{2+}$  in K<sub>4</sub>[Fe(CN)<sub>6</sub>] is  $t_{2g}^{\ 6} e^{0}$ .

36. (a)

**37.** (d) : 
$$\Delta_t = \frac{4}{9} \Delta_0 = \frac{4}{9} \times 18000 = 8000 \text{ cm}^{-1}$$

**38. (b) :** Ni(28) :  $[Ar]3d^84s^2$ 

: CO is a strong field ligand, so, unpaired electrons get paired.



Thus, the complex is  $sp^3$  hybridised with tetrahedral

geometry and diamagnetic in nature.

**39.** (d) : Increasing order of crystal field splitting energy is :  $H_2O < NH_3 < en$ 

Thus, increasing order of crystal field splitting energy for the given complexes is :

 $[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(en)_3]^{3+}$ As,  $E = \frac{hc}{2}$ 

Thus, increasing order of wavelength of absorption is :  $[Co(en)_3]^{3+} < [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$ 

40. (b):  $[Mn(CN)_6]^3$ : Let oxidation state of Mn be x.  $x + 6 \times (-1) = -3 \Rightarrow x = +3$ 

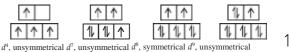
Electronic configuration of Mn :  $[Ar]4s^2 3d^5$ Electronic configuration of Mn<sup>3+</sup> :  $[Ar]3d^4$ CN<sup>-</sup> is a strong field ligand thus, it causes pairing of electrons in 3*d*-orbital.

 $d^2sp^3$  hybridisation Thus,  $[Mn(CN)_6]^{3-}$  has  $d^2sp^3$  hybridisation and has octahedral geometry.

**41.** (b) : Jahn–Teller distortion is usually significant for asymmetrically occupied  $e_8$  orbitals since they are directed towards the ligands and the energy gain is considerably more.

In case of unevenly occupied  $t_{2g}$  orbitals, the Jahn–Teller distortion is very weak since the  $t_{2g}$  set does not point directly at the ligands and therefore, the energy gain is much less.

High spin complexes :



**42.** (d) :  $[Ni(CN)_4]^{2-}$ : Oxidation number of Ni = +2 Electronic configuration of Ni<sup>2+</sup>:  $3d^84s^0$ 

$$[Ni(CN)_{4}]^{2-} = \underbrace{\boxed{11}111}_{3d} \underbrace{4s}_{4s} \underbrace{4p}_{4p}_{4s} \underbrace{4s}_{4p}_{4s} \underbrace{4p}_{5}_{4s} \underbrace{4s}_{4s} \underbrace{4p}_{5}_{5} \underbrace{1111111}_{5} \underbrace{5s}_{5s} \underbrace{5s}_$$

Pairing of electrons in *d*-orbital takes place due to the presence of strong field ligand ( $CN^{-}$ ).

**43.** (b) :  $H_2O$  is a weak field ligand, hence  $\Delta_0 <$  pairing energy.

 $CFSE = (-0.4x + 0.6y)\Delta_0$ 

where, x and y are no. of electrons occupying  $t_{2g}$  and  $e_g$  orbitals respectively.

For 
$$[Fe(H_2O)_6]^{3+}$$
 complex ion,  
 $Fe^{3+}(3d^5) = t^3 e^2 = -0.4 \times 3 + 0.6 \times 2 = 0.0 \text{ or } 0 \Delta$   
28 g  
44. (c) : Oxidation state of Cu in  $[Cu(NH_3)_4]^{2+}$  is + 2  
 $Cu^{2+} = 3d^9 [4\nu |4\nu |4\nu |4\nu|]$ 

It has one unpaired electron (n = 1).

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

**45. (b)** : CFSE =  $(-0.4 x + 0.6 y) \Delta_0$ where,  $x = \text{No. of electrons occupying } t_{2g}$  orbitals  $y = \text{no. of electrons occupying } e_g$  orbitals =  $(-0.4 \times 3 + 0.6 \times 1)\Delta_0$  [ $\because$  High spin  $d^4 = t^3 e_g^1$ ] =  $(-1.2 + 0.6)\Delta_0 = -0.6 \Delta_0$  **46.** (c) :  $Co^{2+}$  in  $[CoBr_4]^{2-}$  has  $3d^74s^0$  configuration and Br<sup>-</sup> is a weak field ligand. Thus, it has 3 unpaired electrons and hence, paramagnetic.

**47.** (b): In  $[Ni(CN)_4]^{2-}$  all orbitals are doubly occupied, hence, it is diamagnetic.

$$Ni^{2+} = 3d^{8}$$

$$[Ni(CN)_{4}]^{2-} = \underbrace{1 \downarrow 1 \downarrow 1 \downarrow 1 \downarrow 1 \downarrow}_{dep^{2}} \underbrace{4s}_{dep^{2}} \underbrace{4p}_{dep^{2}}$$

 $CN^-$  is a strong field ligand and causes pairing of 3*d*-electrons of Ni<sup>2+</sup>.

48. (a):  $[Ni(NH_3)_6]^{2+}$ :  $sp^3d^2$  (outer), octahedral, paramagnetic  $[Zn(NH_3)_6]^{2+}$ :  $sp^3d^2$  (outer), octahedral, diamagnetic  $[Cr(NH_3)_6]^{3+}$ :  $d^2sp^3$  (inner), octahedral, paramagnetic  $[Co(NH_3)_6]$  : dsp (inner), octahedral, diamagnetic 49. (b): CFSE =  $(-0.4x + 0.6y)\Delta_0 + zP$ where x = number of electrons occupying  $t_{28}$  orbital y = number of electrons occupying  $e_8$  orbital z = number of pairs of electrons For low spin  $d^6$  complex electronic configuration  $= t_{28}^{6} e_{8}^{0}$  or  $t_{28}^{2,2,2} e_{8}^{0}$  $\therefore x = 6, y = 0, z = 3$ CFSE =  $(-0.4 \times 6 + 0 \times 0.6)\Delta_0 + 3P$  $= \frac{-12}{5}\Delta_0 + 3P$ 

**50.** (c) : [Ni(dmg)<sub>2</sub>] is square planar in structure not tetrahedral.

Number of unpaired electrons = 2

Hence, [NiCl<sub>4</sub>]<sup>2-</sup> is paramagnetic.

$$[\operatorname{Ni}(\operatorname{CN})_4]^{2-:} \underbrace{1 \hspace{-0.1cm} 1 \hspace$$

Number of unpaired electrons = 0, so it is diamagnetic in nature.

No. of unpaired electron = 1, so it is paramagnetic.  $[CoF_6]^{3-}$ :

$$\begin{array}{c|c} 3d \\ \hline 1 & \uparrow \uparrow \uparrow \uparrow \\ \hline sp^3d^2 \end{array} \xrightarrow{4s} \begin{array}{c} 4p \\ \hline \times & \times & \times \\ sp^3d^2 \end{array} \xrightarrow{4d} \\ \hline \end{array}$$

No. of unpaired electrons = 4, so it is paramagnetic.

**52.** (c) : 
$$[Mn(H_2O)_6]^{2+}$$
 :  $Mn^{2+} = 3d^5$ 

:. Number of unpaired electrons = 5  $[Fe(H_2O)_6]^{2+}$ :  $Fe^{2+} = 3d^6$ 

- :. Number of unpaired electrons = 4  $[Co(H_2O)_6]^{2+}: Co^{2+} = 3d^7$
- :. Number of unpaired electrons = 3  $[Cr(H_2O)_6]^{2+}: Cr^{2+} = 3d^4$

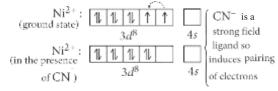
:. Number of unpaired electrons = 4 Minimum paramagnetic behaviour is shown by  $[Co(H_2O)_6]^{2+}$ .

**53. (b) :** Ti : [Ar] 
$$3d^{2}4s^{2}$$
, Ti<sup>3+</sup> : [Ar]  $3d^{1}4s^{0}$   
<sup>4</sup> <sup>2</sup> <sup>3+</sup> <sup>3</sup> (1 unpaired electron)  
Cr : [Ar]  $3d^{4}4s^{2}$ , Cr <sup>3+</sup> : [Ar]  $3d^{4}s^{0}$   
(3 unpaired electrons)  
Co : [Ar]  $3d^{7}4s^{2}$ , Co<sup>3+</sup> : [Ar]  $3d^{6}4s^{0}$   
Zn + [An] 2d (No unpaired electrons because of pairing)

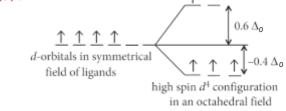
Zn : [Ar] 3d (No unpaired electrons because of pairing)  ${}^{10}4s^2$ , Zn<sup>2+</sup> : [Ar]  $3d^{10}$ (No unpaired electrons)

 $[Cr(NH_3)_6]^{3+}$  exhibits highest paramagnetic behaviour as it contains 3 unpaired electrons.

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



No unpaired electron so does not absorb visible light. **55.** (d) :  $\uparrow$ 



 $CFSE = 3(-0.4)\Delta_0 + 0.6\Delta_0 = -1.2\Delta_0 + 0.6\Delta_0 = -0.6\Delta_0$ 

56. (b) : A species is coloured when it contains unpaired d-electrons which are capable of undergoing d-d transition on adsorption of light of a particular wavelength.

In TiF<sub>6</sub><sup>2-</sup>, Ti<sup>4+</sup>: 
$$3d^0$$
, colourless  
In CoF<sub>6</sub><sup>3-</sup>, Co<sup>3+</sup>:  $3d^6$ , coloured  
In Cu<sub>2</sub>Cl<sub>2</sub>, Cu<sup>+</sup>:  $3d^{10}$ , colourless  
In NiCl<sub>4</sub><sup>2-</sup>, Ni<sup>2+</sup>,  $3d^8$ , coloured

Thus, TiF<sub>6</sub> (3*d*) and Cu<sub>2</sub>Cl<sub>2</sub> (3*d*) with empty and fully filled *d*-orbitals appear colourless as they are not capable of undergoing *d*-*d* transition.

**57.** (b) : 
$$\text{Ti}^{4+} \to 3d^0$$
,  $\text{Cr}^{3+} \to 3d^3$   
 $\text{Zn}^{2+} \to 3d^{10}$ ,  $\text{Sc}^{3+} \to 3d^0$ 

Transition metal ions containing completely filled *d*-orbitals or empty *d*-orbitals are colourless species. Thus, only  $[Cr(NH_3)_6]^{3+}$  having unpaired electron absorb visible light and is coloured.

### Coordination Compounds

**58.** (a) : O.S. of Ti in the complex  $[Ti(NH_3)_6]^{3+}$  is +3. Ti<sup>3+</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ No. of unpaired electrons in *d* orbital is one. Let O.S. of V in complex  $[V(gly)_2(OH)_2(NH_3)_2]^+$  is *x*.  $x + 2 \times 0 + 2 \times (-1) + 2 \times 0 = +1$ 

 $\therefore \quad x = +3$ 

 $V^{3+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ 

No. of unpaired electrons in *d* orbital is two. O.S. of Fe in complex  $[Fe(en)(bpy)(NH_3)_2]^{2+}$  is +2.

:.  $Fe^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ 

As all are strong ligands so, pairing of electrons takes place.

No. of unpaired electron in d orbital is zero.

Let O.S. of Co in the given complex  $[Co(ox)_2(OH)_2]^-$  is x. x + 2 × (-2) + 2 × (-1) = -1  $\Rightarrow$  x - 4 - 2 = -1

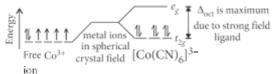
 $\therefore x = +5$ 

 $Co^{5+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$ 

As ox and OH<sup>-</sup> are weak field ligands so no pairing of electrons takes place,  $\frac{b_g^3}{c_g^3}e_g^1$ so, it has 4 unpaired electrons and has highest paramagnetic behaviour.

**59.** (a) : When the ligands are arranged in order of the magnitude of crystal field splitting, the arrangement, thus, obtained is called spectrochemical series.

It has been observed that ligands before  $H_2O$  are weak field ligands while ligands after  $H_2O$  are strong field ligands.



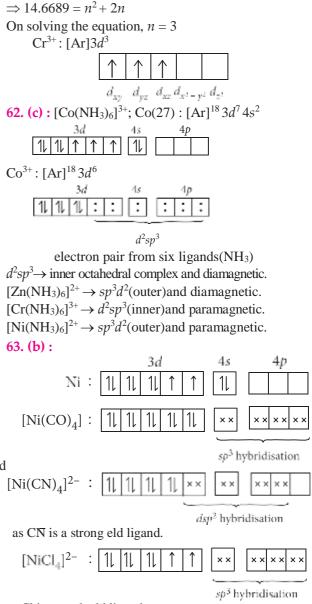
CFSE in octahedral field depends upon the nature of ligands. Stronger the ligands larger will be the value of  $\Delta_{oct}$ .

### **60. (b) :** 3*d*

$$Cr^{2+} \Rightarrow \boxed{\uparrow \uparrow \uparrow \uparrow} \\ 4 \text{ unpaired electrons} \\ Mn^{2+} \Rightarrow \boxed{\uparrow \uparrow \uparrow \uparrow \uparrow} \\ 5 \text{ unpaired electrons} \\ Fe^{2+} \Rightarrow \boxed{1 \uparrow \uparrow \uparrow \uparrow} \\ 4 \text{ unpaired electrons} \\ Ni^{2+} \Rightarrow \boxed{1 \downarrow 1 \downarrow \downarrow \uparrow \uparrow} \\ 2 \text{ unpaired electrons} \\ \end{cases}$$

Greater the number of unpaired electrons, higher is the paramagnetism. Hence,  $[Ni(H_2O)_6]^{2+}$  will exhibit the minimum paramagnetic behaviour.

61. (d) : Magnetic moment = 
$$\sqrt{n(n+2)}$$
  
3.83 =  $\sqrt{n(n+2)} \implies (3.83)^2 = n(n+2)$ 



as Clīis a weak eld ligand.

**64.** (b) : Cyanide ion is strong field ligand because it is a pseudohalide ion. Pseudohalide ions are stronger coordinating ligands and they have the ability to form  $\sigma$ -bond (from the pseudohalide to the metal) and  $\pi$  bond (from the metal to pseudohalide).

65. (b) : Mn (25) : 
$$3d^54s^2$$
  
 $3d^5$   
Mn<sup>2+</sup> :  $\uparrow \uparrow \uparrow \uparrow \uparrow$ 

In presence of weak field ligand, there will be no pairing of electrons. So, it will form a high spin complex, *i.e.*, the number of unpaired electrons =5.

**66.** (a) : In the formation of  $d^2sp^3$  hybrid orbitals, two (n-1)d orbitals of  $e_s$  set [*i.e.*  $(n-1)d_z^2$  and  $(n-1)d_{\frac{3}{2}2y}$  orbitals)], one *ns* and three  $np(np_x, np_y \text{ and } np_z)$  orbitals combine together and form six  $d^2sp^3$  hybrid orbitals.

67. (c) :  $[\operatorname{CoF}_6]^{3-}$ : 3d 4s  $27^{\text{Co}}$  : 11 11  $\uparrow$   $\uparrow$  11  $Co^{3+}$  : 11  $\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$  1  $(weak field ligand F^-)$ 

Thus, the number of unpaired electrons = 4.

**68.** (d) : Odd electrons, ions and molecules are paramagnetic.

In  $Cr(CO)_6$  molecule 12 electrons are contributed by CO group and it contains no odd electron.

 $Cr: 3d^54s^1$ 

Fe(CO)<sub>5</sub> molecule also does not contain odd electron. Fe :  $3d^6 4s^2$ 

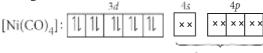
In  $[Fe(CN)_6]^{4-}$  ion  $Fe(+2) : 3d^6 4s^0$ 

.: No odd electrons.

In  $[Cr(NH_3)_6]^{3+}$  ion  $Cr(+3) : 3d^3 4s^0$ 

This ion contains odd electron so it is paramagnetic.

**69.** (a) : In Ni(CO)<sub>4</sub> complex, Ni(0) will have  $3d^{10}$  configuration.



sp3 hybridisation

Hence, [Ni(CO)<sub>4</sub>] will have tetrahedral geometry and diamagnetic as there are no unpaired electrons.

**70.** (b): Based on the number of metal atoms present in a complex, they are classified as :

*e.g.*, : Fe(CO)<sub>5</sub> : mononuclear

 $Co_2(CO)_8$ : dinuclear;  $Fe_3(CO)_{12}$ : trinuclear

**71.** (a) : In sigma bonded organometallic complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, *i.e.*, ligand contributes one electron and is therefore, called one electrons donor, *e.g.*, Grignard's reagent *R*-Mg-*X*.

**72.** (a) : The greater the negative charge on the carbonyl complex, the more easy it would be for the metal to permit its electrons to participate in the back bonding, the higher would be the M—C bond order and simultaneously there would be larger reduction in the C—O bond order. Thus,  $[Fe(CO)_4]^{2-}$  has the lowest C—O bond order means the longest bond length.

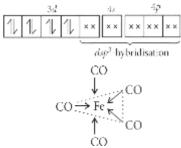
73. (a) : The presence of positive charge on the metal carbonyl would resist the flow of the metal electron charge to  $\pi^*$  orbitals of CO. This would increase the CO bond order and hence, CO in a metal carbonyl cation would absorb at a higher frequency compared to its absorption in a neutral metal carbonyl.

74. (a) :  $Al(OC_2H_5)_3$  contains bonding through O and thus it does not have metal - carbon bond.

**75.** (d) :  $\pi$ -bonded organometallic compound includes organometallic compounds of alkenes, alkynes and some other carbon containing compounds having electrons in their *p*-orbitals.

76. (c) :  $[Co(CO)_5NH_3]^{2+}$  : In this complex, Co-atom is attached with NH<sub>3</sub> through  $\sigma$  bonding and with CO through dative  $\pi$ -bond.

**77.** (c) : In Fe(CO)<sub>5</sub>, the 'Fe' atom is  $dsp^3$  hybridised, therefore, shape of the molecule is trigonal bipyramidal. Fe atom in Fe(CO)<sub>5</sub>



78. (d) : In  $M(CO)_4$ , metal is bonded to the ligands via carbon atoms with both  $\sigma$  and  $\pi$ -bond character. Both metal to ligand and ligand to metal bonding are possible.

## 79. (b)

**80.** (c) : First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cyanide  $[K_3Cu(CN)_4]$ .

 $[CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4] \times 2$ 

 $2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$  $Cu_2(CN)_2 + 6KCN \rightarrow 2K_3Cu(CN)_4$ 

 $Cu_2(CIN)_2 + 0KCIN \rightarrow 2K_3Cu(CIN)_4$ 

 $2CuSO_4 + 10KCN \rightarrow 2K_3Cu(CN)_4 + 2K_2SO_4 + (CN)_2$ 81. (c) : cis-platin, is cis-[PtCl (NH)] is used as an

anticancer agent.

82. (d) : Copper being more electropositive readily precipitate silver from their salt  $(Ag^+)$  solution.  $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + Ag$ 

In K[Ag(CN)<sub>2</sub>] solution, a complex anion [Ag(CN)<sub>2</sub>] is formed so  $Ag^+$  ions are less available in the solution and Cu cannot displace Ag from this complex ion.

83. (b) : Copper sulphate reacts with potassium cyanide giving a white precipitate of cuprous cyanide and cyanogen gas. The cuprous cyanide dissolves in excess of KCN forming potassium cuprocyanide  $K_3[Cu(CN)_4]$ . 2CuSO<sub>4</sub> + 4KCN  $\rightarrow$  2CuCN + (CN)<sub>2</sub> + 2K<sub>2</sub>SO<sub>4</sub>

 $CuCN + 3KCN \rightarrow K_3[Cu(CN)_4]$ 

**84.** (c) : Undecomposed AgBr forms a soluble complex with hypo and the reaction is given as :

 $\begin{array}{l} AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr\\ Soluble \ complex \end{array}$