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Coordination Compounds

Topic 1 Nomenclature and Isomerism of Coordination Compounds

Objective Questions I (Only one correct option)

1. The coordination numbers of Co and Al in $[CoCl(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$, respectively, are (en = ethane-1, 2-diamine)
   (2019 Main, 12 April II)
   (a) 5 and 3   (b) 3 and 3   (c) 6 and 6   (d) 5 and 6

2. The species that can have a *trans*-isomer is (en = ethane -1, 2-diamine, ox = oxalate) **(2019 Main, 10 April I)**
   (a) $[Pt(en)Cl_2]$ (b) $[Cr(en)_2(ox)]$
   (c) $[Pt(en)_2Cl_2]^2$ (d) $[Zn(en)Cl_2]$

3. The maximum possible denticities of a ligand given below towards a common transition and inner-transition metal ion, respectively, are **(2019 Main, 9 April II)**
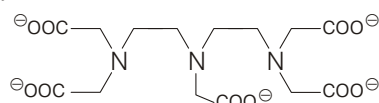
   (a) 8 and 8   (b) 8 and 6   (c) 6 and 6   (d) 6 and 8

4. The one that will show optical activity is (en = ethane-1, 2-diamine) **(2019 Main, 9 April I)**
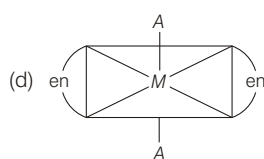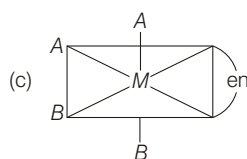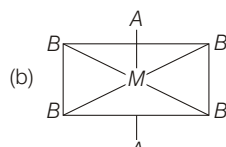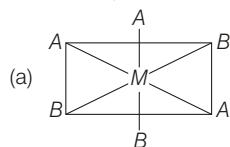
5. The following ligand is
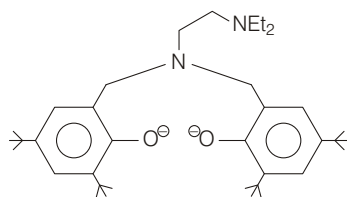
   (2019 Main, 8 April I)
   (a) hexadentate   (b) tetradentate
   (c) bidentate   (d) tridentate

6. The total number of isomers for a square planar complex $[M(F)(Cl)(SCN)(NO_2)]$ is **(2019 Main, 10 Jan I)**
   (a) 12   (b) 16   (c) 4   (d) 8

7. The oxidation states of Cr, in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are **(2018 Main)**
   (a) 3, 4 and 6   (b) 3, 2 and 4
   (c) 3, 0 and 6   (d) 3, 0 and 4

8. Consider the following reaction and statements :
   $$[Co(NH_3)_4Br_2]^+ + Br^- \rightarrow [Co(NH_3)_3Br_3] + NH_3$$

   I. Two isomers are produces if the reactant complex ion is a *cis*-isomer.

   II. Two isomers are produced if the reactant complex ion is a *trans*-isomer.

   III. Only one isomer is produced if the reactant complex ion is a *trans*-isomer.

   IV. Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

   The correct statements are **(2018 Main)**
   (a) (I) and (II)   (b) (I) and (III)
   (c) (III) and (IV)   (d) (II) and (IV)

9. Which one of the following complexes shows optical isomerism? **(2016 Main)**
   (a) *cis* $[Co(en)_2Cl_2]Cl$ (b) *trans* $[Co(en)_2Cl_2]Cl$
   (c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$

10. The number of geometric isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]$ is (py = pyridine). **(2015 Main)**
    (a) 2   (b) 3   (c) 4   (d) 6

11. Which of the following complex species is not expected to exhibit optical isomerism? **(2013 Main)**
    (a) $[Co(en)_3]^3$ (b) $[Co(en)_2Cl_2]$
    (c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)Cl_2]$

12. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is **(2012)**
    (a) tetraaquadiaminecobalt (III) chloride
    (b) tetraaquadiamminecobalt (III) chloride

(c) diaminetetraaquacobalt (III) chloride

(d) diamminetetraaquacobalt (III) chloride

13. Geometrical shapes of the complexes formed by the reaction of Ni^2 with Cl^-, CN^- and H_2O, 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

14. The correct structure of ethylenediaminetetraacetic acid (EDTA) is **(2010)**

(a) $\begin{array}{l} HOOCCH_2 \\ HOOCCH_2 \end{array} \hspace{-2mm} N-CH=CH-N \hspace{-2mm} \begin{array}{l} CH_2COOH \\ CH_2COOH \end{array}$

(b) $\begin{array}{l} HOOC \\ HOOC \end{array} \hspace{-2mm} N-CH-CH-N \hspace{-2mm} \begin{array}{l} COOH \\ COOH \end{array}$

(c) $\begin{array}{l} HOOCCH_2 \\ HOOCCH_2 \end{array} \hspace{-2mm} N-CH_2-CH_2-N \hspace{-2mm} \begin{array}{l} CH_2COOH \\ CH_2COOH \end{array}$

(d)
$$\begin{array}{c} H_2C \overset{\displaystyle COOH}{\underset{|}{}} \\ HOOC-H_2C \\ N-CH-CH-N \\ H \\ HOOC^{CH_2} \end{array} \quad \begin{array}{c} H \\ CH_2-COOH \\ CH_2 \end{array}$$

15. The ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is **(2010)**

(a) $[Cr(H_2O)_4(O_2N)]Cl_2$ (b) $[Cr(H_2O)_4Cl_2](NO_2)$

(c) $[Cr(H_2O)_4Cl(ONO)]Cl$ (d) $[Cr(H_2O)_4Cl_2(NO_2)]\,H_2O$

16. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is **(2008, 3M)**

(a) Tetrachloronickel (II)-tetraamminenickel (II)

(b) Tetraamminenickel (II)-tetrachloronickel (II)

(c) Tetraamminenickel (II)-tetrachloronickelate (II)

(d) Tetrachloronickel (II)-tetraamminenickelate (0)

17. Which kind of isomerism is shown by $Co(NH_3)_4Br_2Cl$? **(2005, 1M)**

(a) Geometrical and ionisation (b) Optical and ionisation

(c) Geometrical and optical (d) Geometrical only

Objective Questions II
(One or more than one correct option)

18. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is/are **(2013 Adv.)**

(a) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$

(b) $[Co(NH_3)_4Cl_2]$ and $[Pt(NH_3)_2(H_2O)Cl]$

(c) $[CoBr_2Cl_2]^2$ and $[PtBr_2Cl_2]^2$

(d) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

19. The compound(s) that exhibit(s) geometrical isomerism is/are **(2009)**

(a) $[Pt(en)Cl_2]$ (b) $[Pt(en)_2]Cl_2$

(c) $[Pt(en)_2Cl_2]Cl_2$ (d) $[Pt(NH_3)_2]Cl_2$

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

20. Statement I The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.
Statement II Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. **(2008, 3M)**

Passage Based Question

Passage

The coordination number of Ni^2 is 4.

$NiCl_2 \quad KCN \text{ (excess)} \quad A \text{ (cyano complex)}$

$NiCl_2 \quad \text{conc. HCl (excess)} \quad B \text{ (chloro complex)}$

21. The IUPAC name of A and B are **(2006,3 4M =12M)**

(a) potassium tetracyanonickelate (II), potassium tetrachloronickelate (II)

(b) tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II)

(c) tetracyanonickel (II), tetrachloronickel (II)

(d) potassium tetracyanonickel (II), potassium tetrachloronickel (II)

Fill in the Blank

22. The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is … **(1994, 1M)**

Integer Answer Type Questions

23. The possible number of geometrical isomers for the complex $[CoL_2Cl_2]$ $(L \quad H_2NCH_2CH_2O^-)$ is (are) … **(2016 Adv.)**

24. Among the complex ions,
$[Co(NH_2CH_2CH_2 \quad NH_2)_2Cl_2]^+, [CrCl_2(C_2O_4)_2]^3$,
$[Fe(H_2O)_4(OH)_2]$, $[Fe(NH_3)_2(CN)_4]^-$,
$[Co(NH_2 \quad CH_2 \quad CH_2 \quad NH_2)_2 (NH_3)Cl]^2$ and
$[Co(NH_3)_4(H_2O)Cl]^2$ the number of complex ion(s) that show(s) *cis-trans* isomerism is **(2015 Adv.)**

25. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to **(2011)**

26. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is **(2010)**
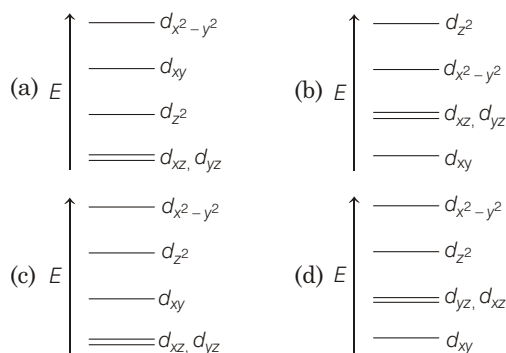
Subjective Questions

27. Write the formulae of the following complexes :
(i) Pentamminechlorocobalt (III) ion
(ii) Lithium tetrahydridoaluminate (III) **(1997, 2M)**

28. Write the IUPAC name for $[Cr(NH_3)_5CO_3]Cl$. **(1996, 1M)**

29. Write the IUPAC name of the following compounds :
(i) $[Co(NH_3)_5ONO]Cl_2$
(ii) $K_3[Cr(CN)_6]$ **(1995, 2M)**

Topic 2 Bonding and Important Property of Coordination Compounds

Objective Questions I (Only one correct option)

1. The compound used in the treatment of lead poisoning is

(2019 Main, 12 April II)

(a) D-penicillamine (b) desferrioxime-B
(c) *cis*-platin (d) EDTA

2. Complete removal of both the axial ligands (along the *z*-axis) from an octahedral complex leads to which of the following splitting patterns? (relative orbital energies not on scale).

(2019 Main, 12 April I)

(a) E | $d_{x^2-y^2}$ / d_{xy} / d_{z^2} / d_{xz}, d_{yz}

(b) E | d_{z^2} / $d_{x^2-y^2}$ / d_{xz}, d_{yz} / d_{xy}

(c) E | $d_{x^2-y^2}$ / d_{z^2} / d_{xy} / d_{xz}, d_{yz}

(d) E | $d_{x^2-y^2}$ / d_{z^2} / d_{yz}, d_{xz} / d_{xy}

3. The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to 3 state is

(Phen = [phenanthroline structure with two N atoms])
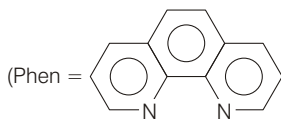
Ignore pairing energy **(2019 Main, 12 April I)**
(a) $[Co(phen)_3]^2$ (b) $[Ni(phen)_3]^2$
(c) $[Zn(phen)_3]^2$ (d) $[Fe(phen)_3]^2$

4. The crystal field stabilisation energy (CFSE) of $[Fe(H_2O)_6]Cl_2$ and $K_2[NiCl_4]$, respectively, are

(2019 Main, 10 April II)

(a) $0.4 \Delta_o$ and $1.2 \Delta_t$ (b) $0.4 \Delta_o$ and $0.8 \Delta_t$
(c) $2.4 \Delta_o$ and $1.2 \Delta_t$ (d) $0.6 \Delta_o$ and $0.8 \Delta_t$

5. The incorrect statement is **(2019 Main, 10 April II)**

(a) the gemstone, ruby, has Cr^3 ions occupying the octahedral sites of beryl

(b) the color of $[CoCl(NH_3)_5]^2$ is violet as it absorbs the yellow light

(c) the spin only magnetic moments of $Fe(H_2O)_6]^2$ and $[Cr(H_2O)_6]^2$ are nearly similar

(d) the spin only magnetic moment of $[Ni(NH_3)_4(H_2O)_2]^2$ is 2.83 BM

6. Three complexes,

$[CoCl(NH_3)_5]^2$ (I), $[Co(NH_3)_5 H_2O]^3$ (II) and
$[Co(NH_3)_6]^3$ (III)

absorb light in the visible region. The correct order of the wavelength of light absorbed by them is **(2019 Main, 10 April I)**

(a) II > I > III (b) I > II > III
(c) III > I > II (d) III > II > I

7. The degenerate orbitals of $[Cr(H_2O)_6]^3$ are

(2019 Main, 9 April I)

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

8. The calculated spin only magnetic moments (BM) of the anionic and cationic species of $[Fe(H_2O)_6]_2$ and $[Fe(CN)_6]$, respectively, are **(2019 Main, 8 April II)**

(a) 0 and 4.9 (b) 2.84 and 5.92
(c) 0 and 5.92 (d) 4.9 and 0

9. The compound that inhibits the growth of tumors is

(2019 Main, 8 April II)

(a) *trans*-$[Pt(Cl)_2(NH_3)_2]$ (b) *cis*-$[Pd(Cl)_2(NH_3)_2]$
(c) *cis*-$[Pt(Cl)_2(NH_3)_2]$ (d) *trans*-$[Pd(Cl)_2(NH_3)_2]$

10. The correct order of the spin only magnetic moment of metal ions in the following low spin complexes, $[V(CN)_6]^4$, $[Fe(CN)_6]^4$, $[Ru(NH_3)_6]^3$, and $[Cr(NH_3)_6]^2$, is

(2019 Main, 8 April I)

(a) $Cr^{2+} > Ru^{3+} > Fe^{2+} > V^{2+}$
(b) $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$
(c) $V^{2+} > Ru^{3+} > Cr^{2+} > Fe^{2+}$
(d) $Cr^{2+} > V^{2+} > Ru^{3+} > Fe^{2+}$

11. The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is

(a) CN (b) ethylenediamine
(c) NCS (d) CO

12. The pair of metal ions that can given a spin-only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$, is

(2019 Main, 12 Jan I)

(a) Co^2 and Fe^{2+} (b) Cr^{2+} and Mn^{2+}
(c) V^{2+} and Co^{2+} (d) V^{2+} and Fe^{2+}

13. The metal *d*-orbitals that are directly facing the ligands in $K_3[Co(CN)_6]$ are **(2019 Main, 12 Jan I)**

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

14. $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of **(2019 Main, 12 Jan I)**

(a) Mn C bond (b) Mn O bond
(c) C O bond (d) Mn Mn

15 The number of bridging CO ligand(s) and Co Co bond(s) in $Co_2(CO)_8$, respectively are **(2019 Main, 11 Jan II)**
(a) 2 and 0 (b) 0 and 2 (c) 4 and 0 (d) 2 and 1

16. The coordination number of Th in $K_4[Th(C_2O_4)_4(OH_2)_2]$ is

$(C_2O_4^2$ Oxalato) **(2019 Main, 11 Jan II)**
(a) 14 (b) 10 (c) 8 (d) 6

17. Match the metals (Column I) with the coordination compound(s)/enzyme(s) (Column II).   **(2019 Main, 11 Jan I)**

Column I		Column II	
(A)	Co	(i)	Wilkinson catalyst
(B)	Zn	(ii	Chlorophyll
(C)	Rh	(iii)	Vitamin B_{12}
(D)	Mg	(iv)	Carbonic anhydrase

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(iii)	(i)	(ii)
(c)	(iii)	(iv)	(i)	(ii)
(d)	(ii)	(i)	(iv)	(iii)

18. The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is   **(2019 Main, 10 Jan II)**
(a) Mn^2 (b) Fe^2 (c) Ni^2 (d) Co^2

19. A reaction of cobalt (III) chloride and ethylene diamine in a $1:2$ mole ratio generates two isomeric products A (violet coloured) and B (green coloured). A can show optical activity, but B is optically inactive. What type of isomers does A and B represent ?   **(2019 Main, 10 Jan II)**
(a) Ionisation isomers   (b) Coordination isomers
(c) Geometrical isomers   (d) Linkage isomers

20. Wilkinson catalyst is   **(2019 Main, 10 Jan I)**
(a) $[(Et_3P)_3RhCl]$ (b) $[(Et_3P)_3IrCl](Et = C_2H_5)$
(c) $[(Ph_3P)_3RhCl]$ (d) $[(Ph_3P)_3IrCl]$

21. Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is   **(2019 Main, 9 Jan II)**
(a) $L_1 < L_2 < L_3$ (b) $L_2 < L_1 < L_3$
(c) $L_3 < L_1 < L_2$ (d) $L_3 < L_2 < L_1$

22. The complex that has highest crystal field splitting energy ( ), is   **(2019 Main, 9 Jan II)**
(a) $[Co(NH_3)_5Cl] Cl_2$ (b) $[Co(NH_3)_5(H_2O)]Cl_3$
(c) $K_3[Co(CN)_6]$ (d) $K_2[CoCl_4]$

23. The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complexes is   **(2019 Main, 9 Jan I)**
(a) 5.92   (b) 3.87   (c) 6.93   (d) 4.90

24. Two complexes $[Cr(H_2O)_6]Cl_3$ (A) and $[Cr(NH_3)_6]Cl_3$ (B) are violet and yellow coloured, respectively. The incorrect statement regarding them is   **(2019 Main, 9 Jan I)**
(a) $_o$ value for (A) is less than that of (B)
(b) both absorb energies corresponding to their complementary colours
(c) $_o$ values of (A) and (B) are calculated from the energies of violet and yellow light, respectively
(d) both are paramagnetic with three unpaired electrons

25. The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harder by converting $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ to :   **(2018 Main)**
(a) $[CaF_2]$ (b) $[3(CaF_2) \cdot Ca(OH)_2]$
(c) $[3Ca_3(PO_4)_2 \cdot CaF_2]$ (d) $[3\{Ca_3(PO_4)_2\} \cdot CaF_2]$

26. On treatment of 100 mL of 0.1 M solution of $CoCl_3 \cdot 6H_2O$ with excess of $AgNO_3; 1.2 \times 10^{22}$ ions are precipitated. The complex is   **(2017 Main)**
(a) $[Co(H_2O)_4Cl_2] Cl \cdot 2H_2O$ (b) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$
(c) $[Co(H_2O)_6]Cl_3$ (d) $[Co(H_2O)_5Cl] Cl_2 \cdot H_2O$

27. The pair having the same magnetic moment is [at. no. Cr = 24, Mn = 25, Fe = 26 and Co = 27]   **(2016 Main)**
(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^2$
(c) $[CoCl_4]^2$ and $[Fe(H_2O)_6]^2$
(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^2$

28. Among $[Ni(CO)_4]$, $[NiCl_4]^2$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is   **(2016 Adv.)**
(a) 2   (b) 3   (c) 4   (d) 5

29. The colour of $KMnO_4$ is due to   **(2015 Main)**
(a) $M \quad L$ charge transfer transition
(b) $d \quad d$ transition
(c) $L \quad M$ charge transfer transition
(d)   transition

30. The equation which is balanced and represents the correct product(s) is   **(2014 Main)**
(a) $Li_2O + 2KCl \quad 2LiCl + K_2O$
(b) $[CoCl(NH_3)_5] + 5H^+ \quad Co^{2+} \quad 5NH_4 + Cl$
(c) $[Mg(H_2O)_6]^{2+} + (EDTA)^4 \xrightarrow{\text{Excess NaOH}}$
$[Mg(EDTA)]^{2+} + 6H_2O$
(d) $CuSO_4 + 4KCN \quad K_2[Cu(CN)_4] + K_2SO_4$

31. The octahedral complex of a metal ion M^3 with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is   **(2014 Main)**
(a) $L_4 < L_3 , L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$
(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

32. Consider the following complex ions, P, Q and R. $P = [FeF_6]^3, Q = [V(H_2O)_6]^2$ and $R = [Fe(H_2O)_6]^2$ The correct order of the complex ions, according to their spin-only magnetic moment values (in BM) is   **(2013 Adv.)**
(a) $R < Q < P$ (b) $Q < R < P$
(c) $R < P < Q$ (d) $Q < P < R$

33. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic) the coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states respectively, are   **(2012)**
(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

34. Among the following complexes (K-P), **(2011)**

$K_3[Fe(CN)_6]$ (K), $[Co(NH_3)_6]Cl_3$ (L),

$Na_3[Co(ox)_3]$ (M), $[Ni(H_2O)_6]Cl_2$ (N),

$K_2[Pt(CN)_4]$ (O), $[Zn(H_2O)_6](NO_3)_2$ (P)

the diamagnetic complexes are

(a) K, L, M, N
(b) K, M, O, P
(c) L, M, O, P
(d) L, M, N, O

35. The complex showing a spin only magnetic moment of 2.82 BM is **(2010)**

(a) $Ni(CO)_4$
(b) $[NiCl_4]^2$
(c) $Ni(PPh_3)_4$
(d) $[Ni(CN)_4]^2$

36. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is **(2009)**

(a) 0
(b) 2.84
(c) 4.90
(d) 5.92

37. Among the following, the coloured compound is **(2008, 3M)**

(a) CuCl
(b) $K_3[Cu(CN)_4]$
(c) CuF_2
(d) $[Cu(CH_3CN)_4]BF_4$

38. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^2$ are diamagnetic. The hybridisations of nickel in these complexes respectively, are

(a) sp^3, sp^3
(b) sp^3, dsp^2 **(2008, 3M)**
(c) dsp^2, sp^3
(d) dsp^2, dsp^2

39. Among the following metal carbonyls, the C—O bond order is lowest in **(2007, 3M)**

(a) $[Mn(CO)_6]$
(b) $[Fe(CO)_5]$
(c) $[Cr(CO)_6]$
(d) $[V(CO)_6]$

40. If the bond length of CO bond in carbon monoxide is 1.128 Å, then what is the value of CO bond length in $Fe(CO)_5$? **(2006)**

(a) 1.15 Å
(b) 1.128 Å
(c) 1.72 Å
(d) 1.118 Å

41. Spin only magnetic moment of the compound $Hg[Co(SCN)_4]$ is **(2004, 1M)**

(a) $\sqrt{3}$
(b) $\sqrt{15}$
(c) $\sqrt{24}$
(d) $\sqrt{8}$

42. The compound having tetrahedral geometry is **(2004, 1M)**

(a) $[Ni(CN)_4]^{2-}$
(b) $[Pd(CN)_4]^{2-}$
(c) $[PdCl_4]^{2-}$
(d) $[NiCl_4]^{2-}$

43. Mixture X = 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L of solution.

1 L of mixture X + excess $AgNO_3$ Y

1 L of mixture X + excess $BaCl_2$ Z

Number of moles of Y and Z are **(2003)**

(a) 0.01, 0.01
(b) 0.02, 0.01
(c) 0.01, 0.02
(d) 0.02, 0.02

44. The complex ion which has no 'd'-electrons in the central metal atom is **(2001, 1M)**

(a) $[MnO_4]^-$
(b) $[Co(NH_3)_6]^{3+}$
(c) $[Fe(CN)_6]^{3-}$
(d) $[Cr(H_2O)_6]^{3+}$

45. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are **(1999, 2M)**

(a) both square planar
(b) tetrahedral and square planar, respectively
(c) both tetrahedral
(d) square planar and tetrahedral, respectively

46. Which of the following is formed when excess of KCN is added to aqueous solution of copper sulphate? **(1996, 1M)**

(a) $Cu(CN)_2$
(b) $K_2[Cu(CN)_4]$
(c) $K[Cu(CN)_2]$
(d) $K_3[Cu(CN)_4]$

47. Among the following ions, which one has the highest paramagnetism? **(1993, 1M)**

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

48. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$ **(1991, 1M)**

(a) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(b) $[NiCl_4]^2$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic
(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^2$ is paramagnetic
(d) $Ni(CO)_4$ is diamagnetic and $[NiCl_4]^2$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

49. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by **(1988, 2M)**

(a) $MnSO_4 \cdot 4H_2O$
(b) $CuSO_4 \cdot 5H_2O$
(c) $FeSO_4 \cdot 6H_2O$
(d) $NiSO_4 \cdot 6H_2O$

Objective Question II

(One or more than one correct option)

50. The correct statement (s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers : Fe = 26, Ni = 28) **(2018 Adv.)**

(a) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ 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

51. The correct option(s) regarding the complex
$[Co(en)(NH_3)_3(H_2O)]^3$ (en $H_2NCH_2CH_2NH_2$) is (are)

(2018 Adv.)

(a) It has two geometrical isomers

(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 $[Co(en)(NH_3)_4]^3$

52. Addition of excess aqueous ammonia to a pink coloured aqueous solution of MCl_2 $6H_2O(X)$ and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue colured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whersas it is zero for complex Y.

Among the following options, which statement(s) is (are) correct? **(2017 Adv.)**

(a) The hybridisation of the central metal ion in Y is d^2sp^3

(b) Addition of silver nitrate to Y given only two equivalents of silver chloride

(c) When X and Y are in equilibrium at 0°C, the colour of the solution is pink

(d) Z is a tetrahedral complex

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

53. **Statement I** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.

Statement II The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. **(2008, 3M)**

Passage Based Questions

The coordination number of Ni^2 is 4.

$NiCl_2$ KCN (excess) A (cyano complex)
$NiCl_2$ conc. HCl (excess) B (chloro complex)

54. Predict the magnetic nature of A and B.

(a) Both are diamagnetic

(b) A is diamagnetic and B is paramagnetic with one unpaired electron

(c) A is diamagnetic and B is paramagnetic with two unpaired electrons

(d) Both are paramagnetic

55. The hybridisation of A and B are

(a) dsp^2, sp^3

(b) sp^3, sp^3

(c) dsp^2, dsp^2

(d) sp^3d^2, d^2sp^3

Match the Columns

56. Match each set of hybrid orbitals from List–I with complexes given in List-II.

	List–I		List–II
P.	dsp^2	1.	$[FeF_6]^4$
Q.	sp^3	2.	$[Ti(H_2O)_3Cl_3]$
R.	sp^3d^2	3.	$[Cr(NH_3)_6]^3$
S.	d^2sp^3	4.	$[FeCl_4]^2$
		5.	$[Ni(CO)_4]$
		6.	$[Ni(CN)_4]^2$

The correct option is **(2018 Adv.)**

(a) P 5; Q 4, 6; R 2, 3; S 1

(b) P 5,6; Q 4; R 3; S 1,2

(c) P 6; Q 4, 5; R 1; S 2, 3

(d) P 4,6; Q 5, 6; R 1,2; S 3

57. Match each coordination compound in Column I with an appropriate pair of characteristics from Column II and select the correct answer using the codes given below the Columns (en $H_2NCH_2CH_2NH_2$; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78) **(2014 Adv.)**

	Column I		Column II
(A)	$[Cr(NH_3)_4Cl_2]Cl$	1.	Paramagnetic and exhibits ionisation isomerism
(B)	$[Ti(H_2O)_5Cl](NO_3)_2$	2.	Diamagnetic and exhibits *cis-trans* isomerism
(C)	$[Pt(en)(NH_3)Cl]NO_3$	3.	Paramagnetic and exhibits *cis-trans* isomerism
(D)	$[Co(NH_3)_4(NO_3)_2]NO_3$	4.	Diamagnetic and exhibits ionisation isomerism

Codes

	A	B	C	D			A	B	C	D
(a)	4	2	3	1		(b)	3	1	4	2
(c)	2	1	3	4		(d)	1	3	4	2

58. Match the complexes in Column I with their properties listed in Column II. **(2007, 6M)**

	Column I		Column II
(A)	$[Co(NH_3)_4(H_2O)_2]Cl_2$	p.	Geometrical isomers
(B)	$[Pt(NH_3)_2Cl_2]$	q.	Paramagnetic
(C)	$[Co(H_2O)_5Cl]Cl$	r.	Diamagnetic
(D)	$[Ni(H_2O)_6]Cl_2$	s.	Metal ion with +2 oxidation state

Fill in the Blanks

59. The IUPAC name of $[Co(NH_3)_6]Cl_3$ is …… **(1994, 1M)**

True/False

60. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. **(1989, 1M)**

61. The electron density in the xy plane in $3d_{x^2-y^2}$ orbital is zero. **(1986, 1M)**

Integer Answer Type Questions

62. For the octahedral complexes of Fe^{3+} in SCN (thiocyanato-S) and in 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] **(2015 Adv.)**

63. In the complex acetylbromidodicarbonylbis (triethylphosphine) iron (II), the number of Fe C bond (s) is **(2015 Adv.)**

64. $EDTA^{4}$ is ethylenediaminetetraacetate ion. The total number of N Co O bond angles in [Co(EDTA)] complex ion is **(2013 Adv.)**

Subjective Questions

65. $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH, giving a bright red colour.
(a) Draw its structure and show H-bonding
(b) Give oxidation state of Ni and its hybridisation
(c) Predict whether it is paramagnetic or diamagnetic **(2004, 4M)**

66. Write the IUPAC name of the compound $K_2[Cr(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex $= 1.73$ BM. Give the structure of anion. **(2003, 4M)**

67. Deduce the structures of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. **(2002, 5M)**

68. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ 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 hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). **(2001, 5M)**

69. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. **(2000, 4M)**

70. A, B and C are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands.

Complex A does not react with concentrated H_2SO_4, whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4. Identify A, B and C. **(1999, 2M)**

71. Identify the complexes which are expected to be coloured. Explain **(1994, 2M)**
(i) $[Ti(NO_3)_4]$ (ii) $[Cu(NCCH_3)]^+ BF_4$
(iii) $[Cr(NH_3)_6] Cl_3$ (iv) $K_3[VF_6]$

72. Give reasons in two or three sentences only for the following :

"The species $[CuCl_4]^{2-}$ exists, while $[CuI_4]^{2-}$ does not exist." **(1992, 1M)**

Answers

Topic 1

1. (d)	**2.** (c)	**3.** (d)	**4.** (c)
5. (b)	**6.** (a)	**7.** (c)	**8.** (b)
9. (a)	**10.** (b)	**11.** (c)	**12.** (d)
13. (b)	**14.** (c)	**15.** (b)	**16.** (c)
17. (a)	**18.** (b,d)	**19.** (c,d)	**20.** (b)
21. (a)	**22.** paramagnetism		**23.** (5)
24. (6)	**25.** (6)	**26.** (3)	

Topic 2

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

17. (c)	**18.** (d)	**19.** (c)	**20.** (c)
21. (c)	**22.** (c)	**23.** (a)	**24.** (c)
25. (c)	**26.** (d)	**27.** (a)	**28.** (b)
29. (c)	**30.** (b)	**31.** (b)	**32.** (b)
33. (c)	**34.** (c)	**35.** (b)	**36.** (a)
37. (c)	**38.** (b)	**39.** (b)	**40.** (a)
41. (b)	**42.** (d)	**43.** (a)	**44.** (a)
45. (c)	**46.** (d)	**47.** (b)	**48.** (c)
49. (b)	**50.** (b, c)	**51.** (a, b, d)	**52.** (a, b, d)
53. (a)	**54.** (c)	**55.** (a)	**56.** (c)
57. (b)	**58.** A p, q, s B p, r, s C q, s D q, s		
59. hexaammine cobalt (III) chloride		**60.** F	
61. F	**62.** (4)	**63.** (3)	**64.** (8)

Hints & Solutions

Topic 1 Nomenclature and Isomerism of Coordination Compounds

1.

> **Key Idea** The total number of ligands to which the metal is directly attached is called coordination number.

The coordination numbers of Co and Al in $[Co(Cl)(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$ are 5 and 6 respectively.

In first complex, 'en' is a didentate ligand and 'Cl' is a unidentate ligand.

$[Co(Cl)(en)_2]Cl$, coordination number $= 1 \times 2 \times 2 \times 1 \times 4 = 5$

So, the coordination number is 5.

For $K_3[Al(C_2O_4)_3]$, '$C_2O_4^{2-}$' is a didentate ligand.

Coordination number $= 3 \times 2 = 6$.

Hence, coordination number is 6.

2.

> **Key Idea** Square planar complexes of general formulae : $[M(a\ \ a)b_2]$ and $[M(a\ \ a)\ (b\ \ b)]$ do not show geometrical isomerism. Whereas, an octahedral complex of general formula $[M(a\ \ a)_2b_2]$ can show geometrical (*cis-trans*) isomerism.

$[Pt(en)_2(Cl_2)]^{2+}$ with formula $[M(a\ \ a)_2b_2]$ will show geometrical isomerism as follows:

cis-
(optically active)
(I)

trans-
(optically inactive)
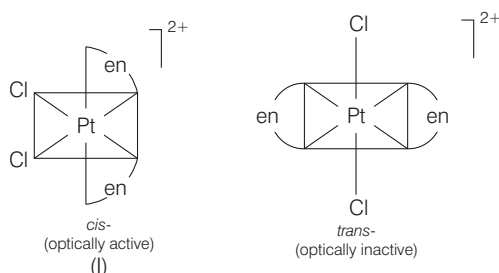
3. The maximum possible denticities of given ligand towards a common transition and inner transition metal ion, are 6 and 8 respectively.
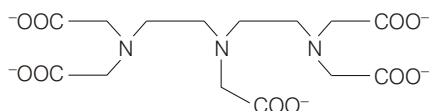
The given ligand act as hexadentate ligand in transition metal ion because the common oxidation state shown by them is $+3$. Whereas in case of inner transition metal ion, its denticity is 8 because their common oxidation state is $+4$.

4. Optical activity is the ability of a chiral molecule to rotate the plane of polarised light, measured by a polarimeter. A chiral molecule does not have any plane of symmetry. If a molecule possess any plane of symmetry, then it is an achiral molecule. Given options (a), (b) and (d) possess plane of symmetry.

(b)

(d)

(a)
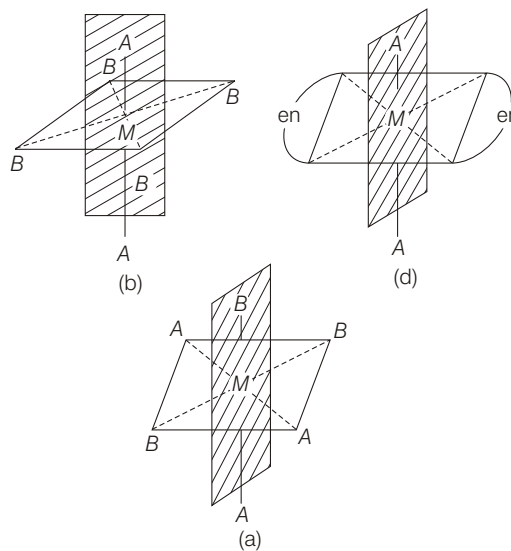
Only molecule (c) does not possess any plane of symmetry. Hence, it is a chiral molecule and shows optical activity.

5.

> **Key Idea** Denticity of ligand is defined as donor sites or number of ligating groups.

The given ligand is tetradentate. It contains four donor atoms. It can bind through two nitrogen and two oxygen atom to the central metal ion.

Ligand bound to the central atom or ion through coordinate bond in the coordination entity. It act as a Lewis base. The attacking site of the given ligand is given in bold.
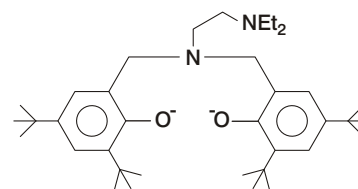
6. A square planar complex of general formula, M_{abcd} gives three geometrical isomers only.

Let, $a = F^-$, $b = Cl^-$, $c = SCN^-$, $d = NO_2^-$

SCN^- and NO_2^- are ambidentate ligands and they also show linkage isomerism (structural). Considering both linkage and geometrical isomerism.

Total number of possible isomers given by the complex,
$$= 3 \times (2 \times 2) = 12$$

7. Let the oxidation state of Cr in all cases is 'x'

(i) Oxidation state of Cr in $[Cr(H_2O)_6]Cl_3$
$$x + (0 \times 6) + (-1 \times 3) = 0$$
or $x + 0 - 3 = 0$ or $x = 3$

(ii) Oxidation state of Cr in $[Cr(C_6H_6)_2]$
$$x + (2 \times 0) = 0 \text{ or } x = 0$$

(iii) Oxidation state of Cr in

$$K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$$

1 2 x (−1 ×2) (−2 ×2) (−2) 0 0

or   2 x − 2 − 4 − 2 0 or x − 6 − 0

hence x = 6
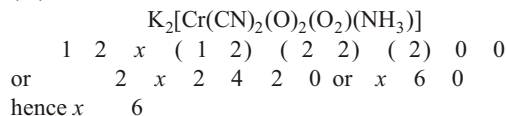
Thus, −3, 0 and +6 is the answer.

8. If the reactant is *cis* isomer than following reaction takes place.

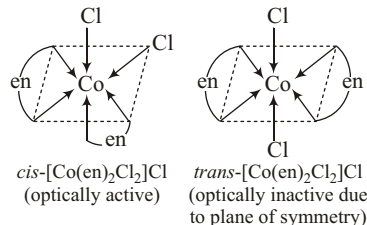*Cis*-isomer   Facial   Meridonial
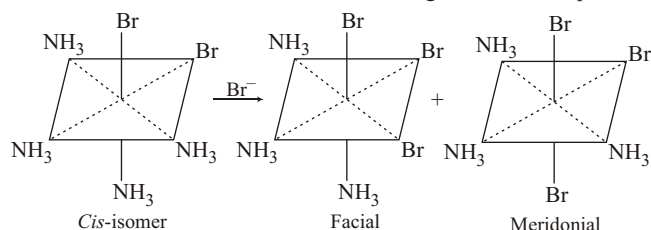
i.e. two isomers are produced. If the reactant is *trans* isomer than following reaction takes place.

Trans   Meridonial
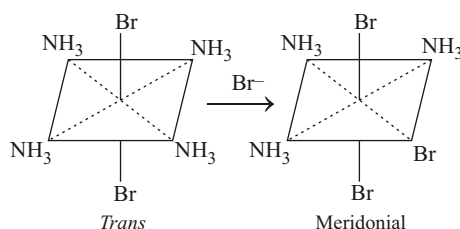
i.e. only 1 isomer is produced. Thus, statement (I) and (III) are correct resulting to option (b) as the correct answer.

9.

cis-[Co(en)$_2$Cl$_2$]Cl   trans-[Co(en)$_2$Cl$_2$]Cl
(optically active)   (optically inactive due to plane of symmetry)

$[Co(NH_3)_4Cl_2]Cl$ can exist in both *cis* and *trans* forms that are given below:

trans-[Co(NH$_3$)$_4$Cl$_2$]Cl   cis-[Co(NH$_3$)$_4$Cl$_2$]Cl
(optically inactive)   (optically inactive)
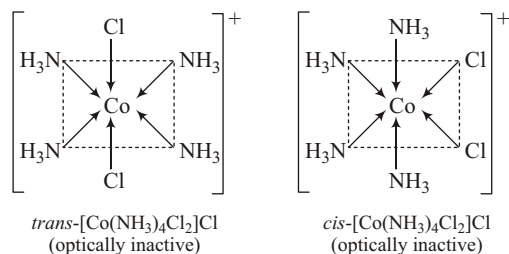
$[Co(NH_3)_3Cl_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.

fac-isomer   mer-isomer
(optically inactive)   (optically inactive)
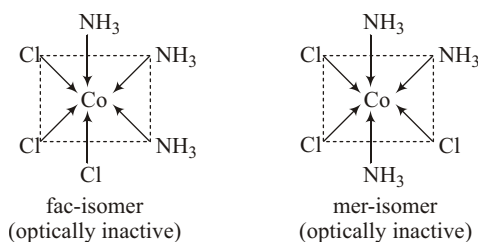
10. $[Pt(Cl)(py)(NH_3)(NH_2OH)]$ is square planar complex. The structures are formed by fixing a group and then arranging all the groups.
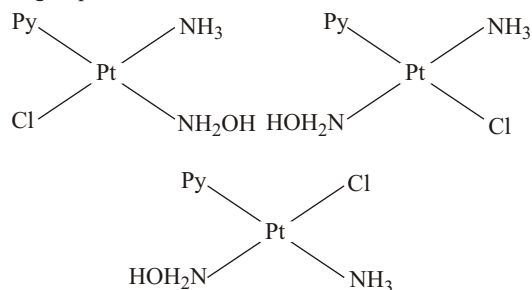
Hence, this complex shows three geometrical isomers.

11. Optical isomerism is exhibited by only those complexes which lacks elements of symmetry. $[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

12. First of all, the compound has complex positive part "$[Co(H_2O)_4(NH_3)_2]^{3+}$" therefore, according to IUPAC conventions, positive part will be named first. Secondly, in writing name of complex, ligands are named first in alphabetical order, irrespective of its charge, hence "ammine" will be written prior to "aqua". Therefore, name of the complex is $[Co(H_2O)_4(NH_3)_2]Cl_3$. Diamminetetraaqua cobalt (III) chloride.

NOTE In alphabetical order, original name of ligands are considered not the initials of prefixes. Also, special precaution should be taken in spelling name of NH_3 ligand as it is ammine.

13. $Ni^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-}$

Here, Ni^2 has d^8-configuration with CN^- as strong ligand.
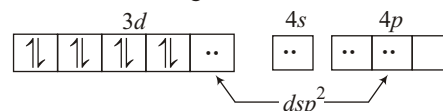
d^8-configuration in strong ligand field gives dsp^2-hybridisation, hence square planar geometry.

$$Ni^{2+} + 4Cl^- \longrightarrow [NiCl_4]^{2-}$$
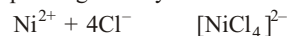
Here, Ni^2 has d^8-configuration with Cl^- as weak ligand.
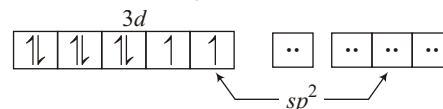
d^8-configuration in weak ligand field gives sp^3-hybridisation, hence tetrahedral geometry. Ni^2 with H_2O forms $[Ni(H_2O)_6]^2$ complex and H_2O is a weak ligand.
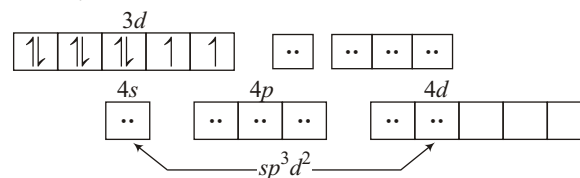
Therefore, $[Ni(H_2O)_6]^2$ has octahedral geometry.

14.

$$HOOCH_2C \diagdown N-CH_2CH_2-N \diagup CH_2COOH$$
$$HOOCH_2C \diagup \qquad\qquad \diagdown CH_2COOH$$
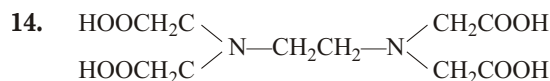
15. Ionisation isomers are the complexes that produces different ions in solution, i.e. they have ions interchanged inside and outside the coordination sphere.

$[Cr(H_2O)_4Cl(NO_2)]Cl$ and $[Cr(H_2O)_4Cl_2](NO_2)$ have different ions inside and outside the coordinate sphere and they are isomers.
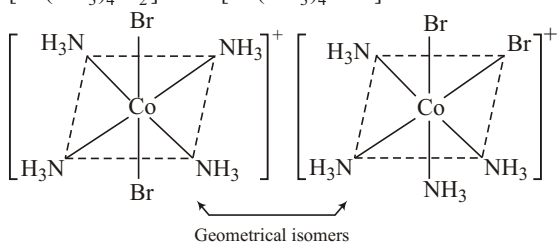
Therefore, they are ionisation isomers.

16. $[Ni(NH_3)_4]^{2+}$ tetraamminenickel (II)

$[NiCl_4]^{2-}$ tetrachloronickelate (II)

Cationic part is named first, hence :
tetraamminenickel (II)-tetrachloronickelate(II)

17. $[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4BrCl]Br$ are ionisation isomers.

Geometrical isomers

18. PLAN Depending on the structure of the complex,different types of isomerism are shown.

Complex	Isomerism
A. $[Cr(NH_3)_5 Cl]Cl_2$ $[Cr(NH_3)_4Cl_2] Cl$	Neither of structural nor stereoisomerism
B. $[Co (NH_3)_4 Cl_2]$	*trans w.r.t.* Cl *cis w.r.t.* Cl
$[Pt(H_2O) (NH_3)_2Cl]$	*cis* *trans*
C. $[Co Br_2Cl_2]^{2-}$ $[PtBr_2Cl_2]^{2-}$	sp^3 tetrahedral dsp^2 square planar
D. $[Pt (NH_3)_3 (NO_3)]Cl$ $[Pt(NH_3)_3 Cl]Br$	$[Pt(NH_3)_3(NO_3)Cl]$ $[Pt(NH_3)_3Cl] NO_3]$ ionisation $[Pt(NH_3)_3Cl]Br$ $[Pt(NH_3)_3 Br]$ ionisation

19. Both $[Pt(en)_2Cl_2]Cl_2$ and $[Pt(NH_3)_2Cl_2]$ are capable of showing geometrical isomerism.

trans   *cis*

cis   *trans*

Square planar complex
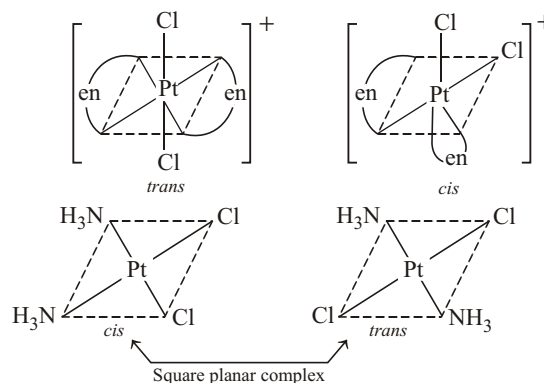
20. Both statements are true. However, axis of symmetry is not a criteria of optical isomerism. Optical inactivity of the two geometrical isomers of $[M(NH_3)_4Cl_2]$ is due to the presence of plane of symmetry.

Trans   *Cis*
Both have several planes of symmetry
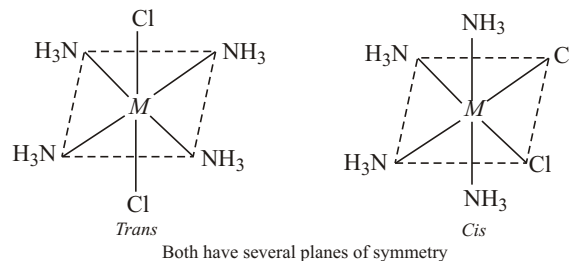
21. A $K_2[Ni(CN)_4]$; B $K_2[NiCl_4]$

A : Potassium tetracyanonickelate (II)

B : Potassium tetrachloronickelate (II)

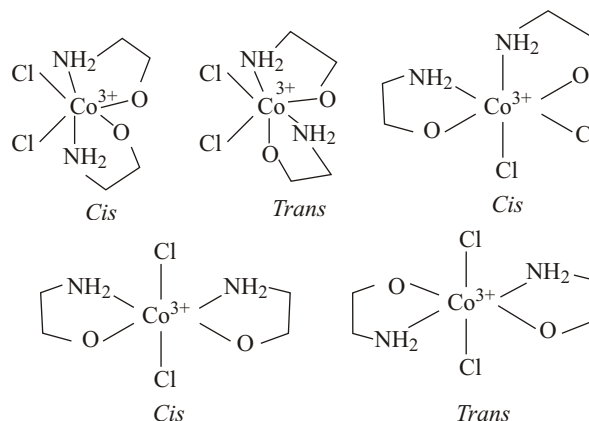**22.** Paramagnetism : In $[Mn(H_2O)_6]^{2+}$, Mn(II) has $3d^5$ configuration.
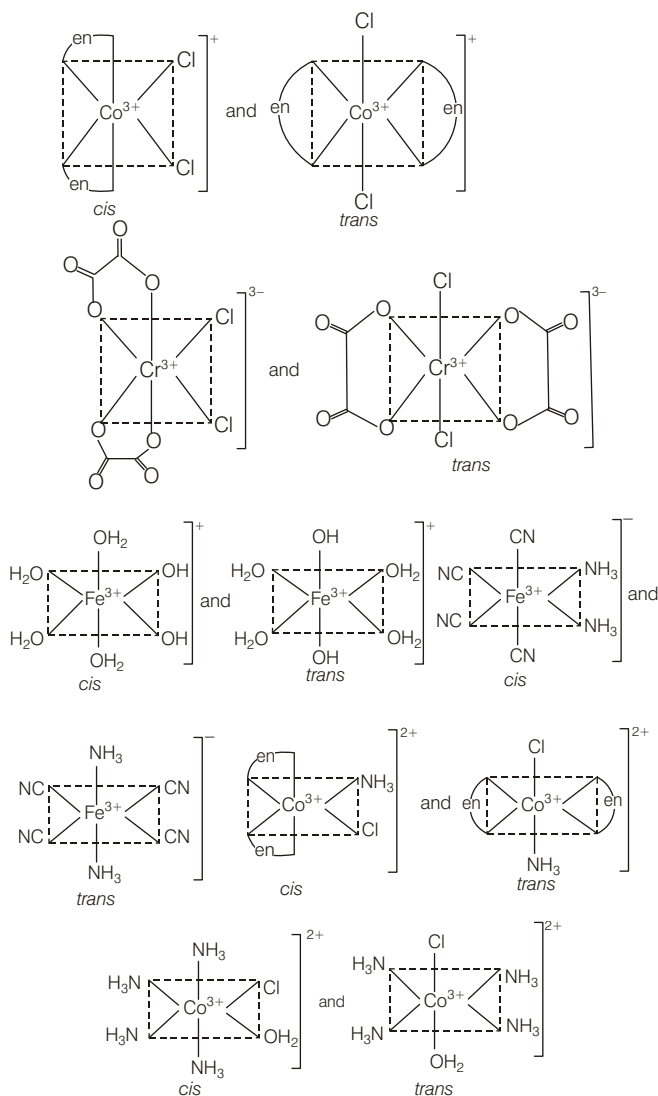Since, H_2O is a weak ligand, all five d-electrons are unpaired :

23. Ligand is $CH_2 - NH_2$
$\qquad\qquad CH_2\bar{O}$
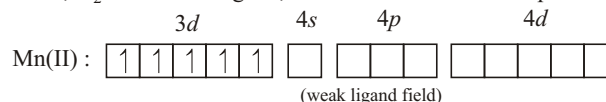
Geometrical isomers are

Cis   *Trans*   *Cis*

Cis   *Trans*

24. All six complex will show *cis-trans* isomerism

cis   trans

and   trans

cis   trans   cis

trans   cis   trans

cis   trans

25. mmol of complex = $30 \times 0.01 = 0.3$

Also, 1 mole of complex $[Cr(H_2O)_5Cl]Cl_2$ gives only two moles of chloride ion when dissolved in solution

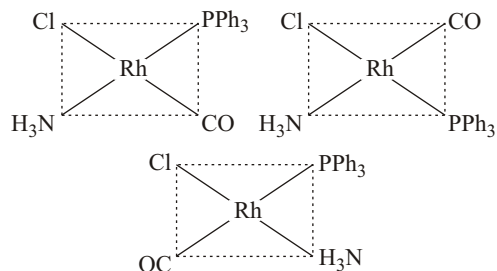$$[Cr(H_2O)_5Cl]Cl_2 \longrightarrow [Cr(H_2O)_5Cl]^{2+} + 2Cl^-$$

mmol of Cl^- ion produced from its 0.3 mmol = 0.6

Hence, 0.6 mmol of Ag^+ would be required for precipitation.

0.60 mmol of $Ag^+ = 0.1M \times V$ (in mL) $V = 6$ mL

26.

27. (i) $[Co(NH_3)_5Cl]^{2+}$ (ii) $Li[AlH_4]$

28. $[Cr(NH_3)_5CO_3]Cl$
: pentaamminecarbonatochromium (III) chloride.

29. (i) $[Co(NH_3)_5ONO]Cl_2$
: pentaamminenitritocobalt (III) chloride.
(ii) $K_3[Cr(CN)_6]$: potassium hexacyanochromate (III)

Topic 2 Bonding and Important Property of Coordination Compounds

1. The compound used in the treatment of lead poisoning is EDTA. Medication occurs through chelation therapy. Calcium disodium ethylenediamine tetraacetic acid chelates divalent metal ion such as Pb^{2+} from plasma and interstitial body fluids.

The metal displaces Ca and is chelated, mobilised and usually excreted. Less then 5% $CaNa_2EDTA$ is absorbed in the gastrointestinal tract and it possibly increases the absorption of Pb present in the tract. Therefore, it is not recommended for oral use. It is usually given intravenously.

2. Complete removal of both the axial ligands (along the *z*-axis) from an octahedral complex leads to the following splitting pattern.
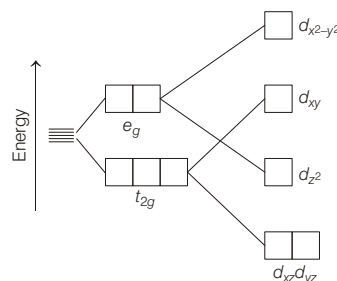
The single electron in the $d_{x^2-y^2}$ orbital is being repelled by four ligands, while the electron in the d_{z^2} orbital is only being repelled by two ligands. Thus, the energy of the $d_{x^2-y^2}$ increases relative to that of d_{z^2}. A more stable arrangement arises when both the e_g electrons pair up and occupy the lower energy d_{z^2} orbital. This leaves the $d_{x^2-y^2}$ orbital empty.

Thus, four ligands can now approach along $+x$, $-x$, $+y$ and $-y$ directions without any difficulty as $d_{x^2-y^2}$ orbital is empty. However, ligands approaching along $+z$ and $-z$ directions meet very strong repulsive forces from filled d_{z^2} orbitals. Thus, only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.
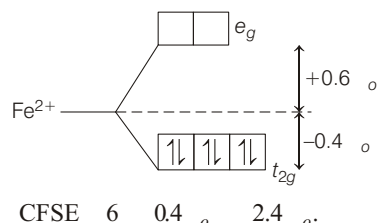
3. **Key Idea** Crystal field splitting occurs due to the presence of ligands in a definite geometry. In octahedral complexes the energy of two, e_g orbitals will increase by (0.6) Δ_o and that of three t_{2g} will decrease by (0.4) Δ_o.

The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is $[Fe(phen)_3]^{2+}$.
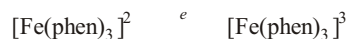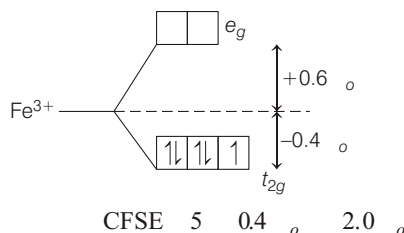
$$[Fe(phen)_3]^{2+} \xrightarrow{-e} [Fe(phen)_3]^{3+}$$

In $[Fe(phen)_3]^{2+}$, electronic configuration of Fe^{2+} is $3d^6 4s^0$. Phenanthrene is a strong field symmetrical bidentate ligand. The splitting of orbital in Fe^{2+} is as follows:

$$CFSE = 6 \times 0.4\Delta_o = 2.4\Delta_o.$$

The splitting of orbital and arrangement of electrons in Fe^{3+} is as follows :

$$CFSE = 5 \times 0.4\Delta_o = 2.0\Delta_o$$

Fe^{2+} upon oxidation of its metal to $+3$ state lose its CFSE from $2.4\Delta_o$ to $2.0\Delta_o$.

4.
> **Key Idea** Crystal field stabilisation energy (CFSE) for octahedral complexes $= (-0.4x + 0.6y)\Delta_o$
> where, $x =$ number of electrons occupying t_{2g} orbital.
> $y =$ number of electrons occupying e_g orbital.
> CFSE for tetrahedral complexes
> $= (-0.6x + 0.4y)\Delta_t$
> where, $x =$ number of electrons occupying e orbital.
> $y =$ number of electrons occupying t orbital.

In $[Fe(H_2O)_6]Cl_2$, H_2O is a weak field ligand, so it is a high spin (outer orbital) octahedral complex of Fe^{2+}.

$$Fe^{2+}(3d^6) =$$
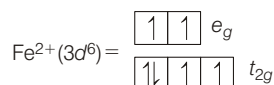
$$CFSE = (-0.4x + 0.6y)\Delta_o$$
$$= [-0.4 \times 4 + 0.6 \times 2]\Delta_o = -0.4\Delta_o$$

In $K_2[NiCl_4]$, Cl^- is a weak field ligand, so it is a high spin tetrahedral complex of Ni^{2+}.

$$Ni^{2+}(3d^6) =$$
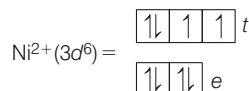
$$CFSE = (-0.6 \times 4 + 0.4 \times 4)\Delta_t = -0.8\Delta_t$$

5. The explanation of given statements are as follows :
(a) Ruby, a pink or blood-red coloured gemstone belongs to corundum (Al_2O_3, alumina) system which has trigonal crystalline lattice containing the repeating unit of $Al_2O_3 - Cr^{3+}$. So, ruby does not belong to beryl lattice $(Be_3Al_2Si_6O_{18})$.
Thus, statement (a) is incorrect.

(b) $[Co(Cl)(NH_3)_5]^{2+}$ is a low spin octahedral complex of Co^{3+}. It absorbs low energy yellow light and high energy complementary violet light will be shown off. Thus, statement (b) is correct.

(c) $[Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ are the high-spin octahedral complexes of Fe^{2+} $(3d^6, n = 4)$ and Cr^{2+} $(3d^5, n = 5)$ ions and weak field ligand, H_2O respectively. So, spin-only magnetic moment $= \sqrt{n(n+2)}$ of the complexes.

$$[Fe(H_2O)_6]^{2+}, \quad \mu_1 = \sqrt{4(4+2)}$$
$$(n = 4), \quad = \sqrt{24} = 4.89 \, BM$$
$$[Cr(H_2O)_6]^{2+}, \quad \mu_2 = \sqrt{5(5+2)}$$
$$(n = 5), \quad = \sqrt{35} = 5.92 \, BM$$

So, $\mu_1 < \mu_2$. Thus, statement (c) is correct.

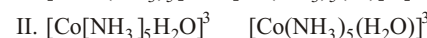(d) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ is also a high-spin octahedral complex of Ni^{2+} $(3d^8, n = 2)$
$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \, BM$$
Thus, statement (d) is correct.

6.
> **Key Idea** The wavelength (λ) of light absorbed by the complexes is inversely proportional to its Δ_0 CFSE (magnitude). Δ_0(CFSE) $\propto 1/\lambda$

The complexes can be written as:
I. $[CoCl(NH_3)_5]^{2+} = [Co(NH_3)_5(Cl)]^{2+}$
II. $[Co[NH_3]_5H_2O]^{3+} = [Co(NH_3)_5(H_2O)]^{3+}$
III. $[Co(NH_3)_6]^{3+} = [Co(NH_3)_5(NH_3)]^{3+}$

So, the differentiating ligands in the octahedral complexes of Co (III) in I, II and III are $Cl^{\ominus}$, H_2O and NH_3 respectively. In the spectrochemical series, the order of this power for crystal field splitting is $Cl^- < H_2O < NH_3$.

So, the crystal field splitting energy (magnitude) order will be
$$\Delta_0^{CFSE} (I) < \Delta_0^{CFSE} (II) < \Delta_0^{CFSE} (III)$$
and the order of wavelength (λ) of light absorbed by the complexes will be
$$\lambda(I) > \lambda(II) > \lambda(III) \qquad \because Energy \, (\Delta_0^{CFSE}) \propto \frac{1}{\lambda}$$

7. The degenerate orbitals of $[Cr(H_2O)_6]^{3+}$ are d_{xz} and d_{yz}. Electronic configuration of Cr^{3+} is $3d^5 4s^1$. The five d-orbitals in an isolated gaseous atom or ion have same energy, i.e. they are degenerate. This degeneracy has been removed due to the ligand electron–metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.
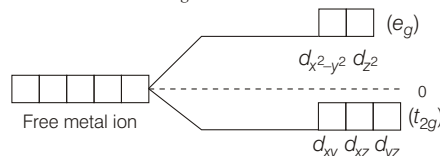
8. $[Fe(H_2O)_6]_2$ It will form 2 cationic species. i.e.
I. (i) As $[\overset{II}{Fe}(H_2O)_6]^{2+}$ High spin octahedral complex of Fe^{2+}.
$Fe^{2+} : 3d^6, x = 4$ (unpaired electrons)
$$\mu = \sqrt{4(4+2)} \, BM = 4.9 \, BM$$

or (ii) as $[\overset{III}{Fe}(H_2O)_6]^{3+}$ High spin octahedral complex of Fe^{3+}.

$Fe^{3+} : 3d^5, x = 5, \sqrt{5(5+2)} = 5.92\,BM$

[H_2O is a neutral weak field ligand]
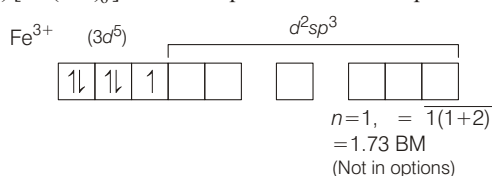
So, $[Fe(H_2O)_6]^{2+}$ will be the cationic specie, $= 4.9\,BM$.

$[Fe(CN)_6]$ will have two anionic complexes

II. (i) $[\overset{II}{Fe}(CN)_6]^{4-}$ Low spin, octahedral complex of Fe^{2+}.

As CN^- is a strong ligand it will pair up the electrons.

$Fe^{2+}(3d^6)$ d^2sp^3

| ⇅ | ⇅ | ⇅ | | | | | | | | |

$n=0, \ \mu=0$
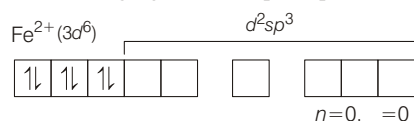
or, (ii) $[\overset{III}{Fe}(CN)_6]^{3-}$ Low spin octahedral complex of Fe^{3+}.

Fe^{3+} $(3d^5)$ d^2sp^3

| ⇅ | ⇅ | ↑ | | | | | | | | |

$n=1, \ \mu = \sqrt{1(1+2)}$
$= 1.73\,BM$
(Not in options)

[CN^- is an anionic strong field ligand]

So, the anionic species is $[Fe(CN)_6]^{4-}$, $\mu = 0$

Thus, the calculated spin only magnetic moments (BM) of the anionic and cationic species of $[Fe(H_2O)_6]_2$ and $[Fe(CN)_6]$ respectively are 4.9 and 0.

9. cis-$[Pt(Cl)_2(NH_3)_2]$ is known as cis-platin. It is a σ-bonded organo-metallic compound and is used as an anti-tumor agent in the treatment of cancer.

$$\begin{bmatrix} H_3N & & Cl \\ & \overset{II}{Pt} & \\ H_3N & & Cl \end{bmatrix}$$
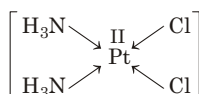
10.

> **Key Idea** In presence of strong field ligands, $\Delta_0 > P$, for fourth electron it is more energetically favourable to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^0$ and form low spin complexes.

The correct order of the spin only magnetic moment of metal ions in the given low-spin complexes is $V^2 > Cr^2 > Ru^3 > Fe^2$. All the given complexes possess strong field ligands (CN, NH_3). Hence, readily form low spin complexes.

Complex	Oxidation state	Configuration	Orbital splitting	No. of unpaired electrons
$[V(CN)_6]^{4-}$	V^{2+}	$t_{2g}^3 e_g^0$		3
$[Cr(NH_3)_6]^{2+}$	Cr^{2+}	$t_{2g}^4 e_g^0$		2
$[Ru(NH_3)_6]^{3+}$	Ru^{3+}	$t_{2g}^5 e_g^0$		1
$[Fe(CN)_6]^{4-}$	Fe^{2+}	$t_{2g}^6 e_g^0$		0

11. The magnetic moment of the magnitude 5.9 BM suggest the presence of 5 unpaired electrons in Mn(II). This can be cross verified by putting the value (5) of unpaired electrons in the formula, $\sqrt{n(n+2)}$ BM

Thus, the valence electronic configuration of Mn(II) in the complex is

$Mn^{2+} =$ | ↑ | ↑ | ↑ | ↑ | ↑ | | | | | | | | | | | |
      $3d$ $4s$ $4p$ $4d$

The octahedral homoleptic complex suggests sp^3d^2-hybridisation in the complex, i.e.

sp^3d^2-hybridisation

$Mn^{2+} =$ | ↑ | ↑ | ↑ | ↑ | ↑ | | | | | | | | | | | |
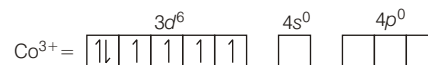 $3d$ $4s$ $4p$ $4d$
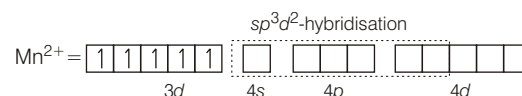
Thus, 5 unpaired electrons are present in the complex which suggest the presence of a weak ligand like NCS^-.

12. As H_2O is a weak field ligand. It readily forms high spin complexes. In $[M(H_2O)_6]Cl_2$, M exist in $+2$ oxidation state. The arrangement of electrons in the given metal ions are as follows:

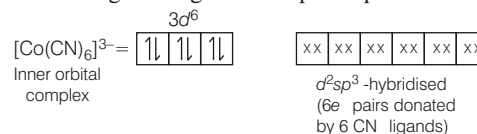| Metal ions	Configuration	Number of unpaired electrons	Spin only Magnetic moment (in BM) $\sqrt{n(n+2)}$
Co^{2+}	$(d^7) = t_{2g}^5 e_g^2$	3	3.9
Fe^{2+}	$(d^6) = t_{2g}^4 e_g^2$	4	4.9
Cr^{2+}	$(d^4) = t_{2g}^3 e_g^1$	4	4.9
Mn^{2+}	$(d^5) = t_{2g}^3 e_g^2$	5	5.9
V^{2+}	$(d^3) = t_{2g}^3 e_g^0$	3	3.9

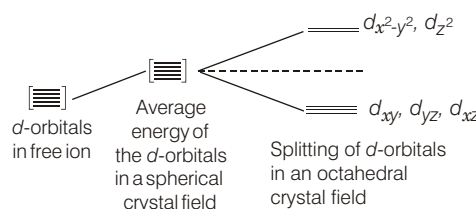Therefore, Co^2 and V^2 contains same value of magnetic moment (3.9 BM).

13. In $K_3[Co(CN)_6]$, Co have $+3$ oxidation state and electronic configuration of Co^{3+} is $[Ar]_{18}\,3d^6$.

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

$Co^{3+} =$ | ⇅ | ↑ | ↑ | ↑ | ↑ | | | | | |

As, CN^- is a strong field ligands so it pairs up the $d\,e^-s$

     $3d^6$

$[Co(CN)_6]^{3-} =$ | ⇅ | ⇅ | ⇅ | | xx | xx | xx | xx | xx | xx |

Inner orbital complex d^2sp^3-hybridised (6e^- pairs donated by 6 CN^- ligands)

In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x, y and z under the influence of an octahedral field, the d-orbitals split as follow.
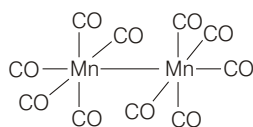
                   $d_{x^2-y^2}, d_{z^2}$

                   d_{xy}, d_{yz}, d_{xz}

d-orbitals in free ion   Average energy of the d-orbitals in a spherical crystal field   Splitting of d-orbitals in an octahedral crystal field
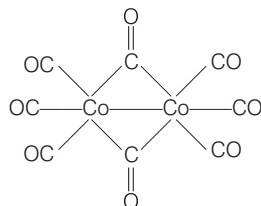
As the d-orbitals, i.e. $d_{x^2-y^2}$ and d_{z^2} are vacant. Hence, these both orbitals are directly facing the ligands in $K_3[Co(CN)_6]$.

14. $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of $Mn-C$ bond. The metal-carbon bond in organometallic compounds possess both σ- and π- character. The $M-C$ σ bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The $M-C$ π-bond is formed by the donation of pair of electrons from a filled d-orbital of metal into vacant antibonding π^* orbital of CO. The $M \to L$ bonding creates a synergic effect which strengthens the bond between CO and the metal.

The structure of $Mn_2(CO)_{10}$ is shown below :

15. The structure of $Co_2(CO)_8$ (a polynuclear metal carbonyl) can be written as:

Total number of bridging CO ligands $= 2$ and the Co$-$Co bond $= 1$

16. Coordination number is defined as the total number of ligands to which the metal is directly attached.
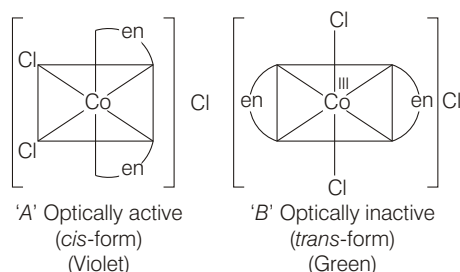
Here, $C_2O_4^{2-}$ is a bidentate ligand,
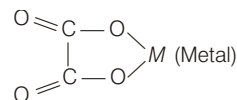
and H_2O is a monodentate ligand, $H_2\ddot{O}: \longrightarrow M$

So, total number of sites offered by $C_2O_4^{2-}$ and H_2O ligands around Th(IV) = Coordination number of Th (IV)

$= 4 \times 2(\text{by } C_2O_4^{2-}) + 2 \times 1(\text{by } H_2O) = 10$

17. (A) Co is present in vitamin B_{12} (iii) having molecular formula, $C_{63}H_{88}\overset{II}{Co}N_{14}O_{14}P$.

(B) Zn is present in carbonic anhydrase (iv) in which three histidine units and the —OH group coordinate with one Zn (II) ion.

(C) Rh is present in Wilkinson catalyst (i) having molecular formula $[(Ph_3P)_3RhCl]$.

(D) Mg is present in chlorophyll (ii) having molecular formula $C_{55}H_{70}O_6N_4\overset{II}{Mg}$ (chlorophyll-b).
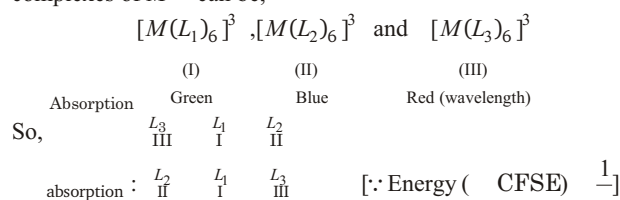
18. The difference in the number of unpaired electrons of different metal ions in their high spin and low spin octahedral complexes are given in the table below :

Metal ion	Number of e^- in high spin complex (n_1)			Number of e^- in low spin complax (n_2)			n_2	n_1
Mn^{2-}	$n_1=5$			$n_2=1$			5	1	4
Fe^{2-}	$n_1=4$			$n_2=0$			4	0	4
Ni^{2-}	$n_1=2$			Ni^{2-} does not form low spin octahedral complexes.				
Co^{2-}	$n_1=3$			$n_1=1$			3	1	2

19. According to the situation given in question, reactions are as follows:

$$\overset{III}{CoCl_3} + 2en \longrightarrow [\overset{III}{Co}(en)_2Cl_2]Cl$$

en $\rightarrow$ ethylene-1, 2-diamine,
$$\begin{array}{c} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array}$$

'A' Optically active   'B' Optically inactive
(cis-form)   (trans-form)
(Violet)   (Green)

20. Wilkinson's catalyst is a σ-bonded organometallic compound $[(Ph_3P)_3RhCl]$. It is commercially used for hydrogenation of alkenes and vegetable oils (unsaturated).

IUPAC name Chloridotris (triphenylphosphene) rhodium (I).

21. In homoleptic complexes, the metal atom/ion is linked to only one type of ligand. Assuming, ligands are neutral, the octahedral complexes of M^{3+} can be,

$$\underset{\text{(I)}}{[M(L_1)_6]^{3+}}, \underset{\text{(II)}}{[M(L_2)_6]^{3+}} \text{ and } \underset{\text{(III)}}{[M(L_3)_6]^{3+}}$$

	Green	Blue	Red (wavelength)
Absorption	L_3	L_1	L_2
So,	III	I	II

$$\lambda_{absorption} : \underset{II}{L_2} > \underset{I}{L_1} > \underset{III}{L_3} \quad [\because \text{Energy} (\propto CFSE) \propto \frac{1}{\lambda}]$$

We know, ligand strength $\propto \frac{1}{\lambda_{absorption}}$

So, the increasing order of the ligand strength will be,
$$L_3 < L_1 < L_2$$

22. All of the complex given are the octahedral complexes of Co (III) except $K_2[CoCl_4]$, which is a tetrahedral complex of Co (II) (sp^3-hybridised).

We know, $\Delta_t < \Delta_o \quad [\because \Delta_t = \frac{4}{9}\Delta_o]$

So, the octahedral complexes (a, b, c) have higher Δ_o values than that of tetrahedral, $K_2[CoCl_4]$.

Now, for the complexes, a, b and c,

the magnitude of $\Delta_o \propto$ ligand strength, which is based on their positions in the spectrochemical series.

$$Cl^- < H_2O < NH_3 < CN^-$$

Hence, $K_3[Co(CN)_6]$ will have the highest Δ_o value.

23. The spin only magnetic moment (μ in BM) is given by
$$\mu \text{ (in BM)} = \sqrt{n(n+2)}$$
where, $n =$ number of unpaired electrons

The highest value of n in transition metal complex is 5 in its d^5-configuration.
$$\mu = \sqrt{5(5+2)}\,BM = 5.916\,BM$$

24. 'A' absorbs yellow light of less energy and emits violet light of high energy (complementary colour) because H_2O is a weak field ligand. But in case of 'B', due to presence of strong field ligand (NH_3), it absorbs high energy violet light and emits low energy complementary yellow colour.

(CFSE) is measured with help of wavelength of the colour absorbed by the given coordination compound, as
$$\Delta_o = h\nu = h \times \frac{c}{\lambda}$$

Both the complexes contain three unpaired electrons. Therefore, both are paramagnetic.

25. Fluoride ions help in making teeth enamel harder by converting $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ i.e. Hydroxy apatite to $[3Ca_3(PO_4)_2 \cdot CaF_2]$ i.e., Fluorapatite (Harder teeth enamel) *via* following reaction:

$$[3Ca_3(PO_4)_2 \cdot Ca(OH)_2] + \underset{\substack{\text{From}\\\text{drinking}\\\text{water}}}{2F^-} \longrightarrow [3Ca_3(PO_4)_2 \cdot CaF_2] + 2OH^-$$

26. Molarity $(M) = \dfrac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$

Number of moles of complex
$$= \frac{\text{Molarity} \times \text{volume (in mL)}}{1000}$$
$$= \frac{0.1 \times 100}{1000} = 0.01\,\text{mole}$$

Number of moles of ions precipitate
$$= \frac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02\,\text{moles}$$

Number of Cl^- present in ionisation sphere
$$= \frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}} = \frac{0.02}{0.01} = 2$$

2 Cl^- are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is
$$[Co(H_2O)_5Cl]Cl_2 \cdot H_2O.$$

27.

Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (n)	
$[Cr(H_2O)_6]^{2+}$	Cr^{2+} ; [Ar] $3d^4$	↑ ↑ ↑ ↑ ☐	; 4
$[Fe(H_2O)_6]^{2+}$	Fe^{2+} ; [Ar] $3d^6$	↑↓ ↑ ↑ ↑ ↑	; 4
$[Mn(H_2O)_6]^{2+}$	Mn^{2+} ; [Ar] $3d^5$	↑ ↑ ↑ ↑ ↑	; 5
$[CoCl_4]^{2-}$	Co^{2+} ; [Ar] $3d^7$	↑↓ ↑↓ ↑ ↑ ↑	; 3

28.

Compounds	Hybridisation	Unpaired electron(s)	Magnetic character
$Ni(CO)_4$	sp^3	No	Diamagnetic
$[NiCl_4]^2$	sp^3	two	Paramagnetic
$[Co(NH_3)_4Cl_2]Cl$	sp^3d^2	No	Diamagnetic
$Na_3[CoF_6]$	sp^3d^2	three	Paramagnetic
Na_2O_2	—	No	Diamagnetic (O_2^2)
CsO_2	—	One	Paramagnetic O_2 (superoxide ion is paramagnetic)

29. $KMnO_4 \quad K^+ + MnO_4$

In MnO_4, Mn has $+ 7$ oxidation state having no electron in d-orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur $L \quad M$ charge transfer, because ligand is able to donate the electron into the vacant d-orbital of metal.

Since, charge transfer is laporate as well as spin allowed, therefore, it shows colour.

Time saving Technique There is no need to check all the four options. Just find out the oxidation state of metal ion. If oxidation state is highest and ligand present there is of electron donating nature, gives LMCT, which shows more intense colour.

30. This problem is based on conceptual mixing of properties of lithium oxide and preparation, properties of coordination compounds. To answer this question, keep in mind that on adding acid, ammine complexes get destroyed.

(a) $Li_2O + KCl \quad 2LiCl + K_2O$

This is wrong equation, since a stronger base K_2O cannot be generated by a weaker base Li_2O.

(b) $[CoCl(NH_3)_5] + 5H^+ \quad Co^2 (aq) \quad 5NH_4 + Cl$

This is correct. All ammine complexes can be destroyed by adding H . Hence, on adding acid to $[CoCl(NH_3)_5]$, it gets converted to $Co^2 (aq)^+ NH_4$ and Cl .

(c) $[Mg(H_2O)_6]^2 \quad EDTA^4 \xrightarrow{OH}_{\text{Excess}} [Mg(EDTA)]^2 \quad 6H_2O$

This is wrong, since the formula of complex must be $[Mg(EDTA)]^{2+}$ as EDT.

(d) The 4th reaction is incorrect. It can be correctly represented as
$$2CuSO_4 + 10KCN \quad 2K_3[Cu(CN)_4] + 2K_2SO_4 \quad (CN)_2$$

31. Arrange the complex formed by different ligands L_1, L_2, L_3 and L_4, according to wavelength of their absorbed light, then use of the following relation to answer the question.

Ligand field strength Energy of light absorbed

$$\frac{1}{\text{Wavelength of light absorbed}}$$

	L_1	L_2	L_3	L_4
Absorbed light	Red	Green	Yellow	Blue

Wavelength of absorbed light decreases.

Increasing order of energy of wavelengths absorbed reflect greater extent of crystal field splitting, hence, higher field strength of the ligand.

Energy blue $(L_4) \quad$ green $(L_2) \quad$ yellow $(L_3) \quad$ red (L_1)

$L_4 \quad L_2 \quad L_3 \quad L_1$ in field strength of ligands.

32. PLAN Spin only magnetic moment have the formula $\sqrt{n(n \quad 2)}$ BM, where N is the number of unpaired electrons. In the presence of weak ligand (as H_2O, Cl , F) there is no pairing of electrons, and electrons donated by ligands are filled in outer vacant orbitals.

In the presence of strong ligand (as CN , CO, NH_3, en) electrons are paired and electrons from ligands are filled in available inner orbitals

Complex	Atomic number of	O.N.	E.C.	Unpaired electrons	Magnetic moment
$P : [FeF_6]^3$ weak ligand	26	3	$[Ar]3d^5$	5	$\sqrt{35}$ BM
$Q : [V(H_2O)_6]^2$ weak ligand	23	2	$[Ar]$	3	$\sqrt{15}$ BM
$R : [Fe(H_2O)_6]^2$	26	2	$[Ar]3d^6$	4	$\sqrt{24}$ BM

Thus, order of spin-only magnetic moment $Q < R < P$

33. In the given complex, $NiCl_2 \{P(C_2H_5)_2(C_6H_5)\}_2$ nickel is in 2 oxidation state and the ground state electronic configuration of Ni^{2+} ions in free gaseous state is

Ni^{2+} $3d^8$ $4s^0$ $4p^0$
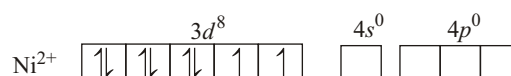
For the given four coordinated complex to be paramagnetic, it must possess unpaired electrons in the valence shell. To satisfy this condition, four lone pairs from the four ligands occupies the four sp^3-hybrid orbitals as :

Ni^{2+} sp^3
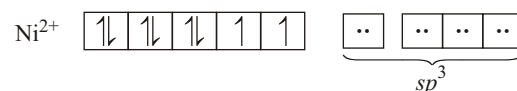
Therefore, geometry of paramagnetic complex must be **tetrahedral**. On the otherhand, for complex to be diamagnetic, there should not be any unpaired electrons in the valence shell.

This condition can be fulfilled by pairing electrons of $3d$-orbitals against Hund's rule as

Ni^{2+} $3d^8$ dsp^2
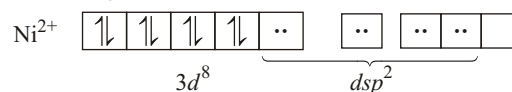
The above electronic arrangement gives dsp^2-hybridisation and therefore, **square planar** geometry to the complex.

**34.** For a diamagnetic complex, there should not be any unpaired electron in the valence shell of central metal.

In $K_3[Fe(CN)_6]$, Fe (III) has d^5-configuration (odd electrons), hence it is paramagnetic.

In $[Co(NH_3)_6]Cl_3$, Co (III) has d^6-configuration in a strong ligand field, hence all the electrons are paired and the complex is diamagnetic.

In $Na_3[Co(ox)_3]$, Co (III) has d^6-configuration and oxalate being a chelating ligand, very strong ligand and all the six electrons remains paired in lower t_{2g} level, diamagnetic.

In $[Ni(H_2O)_6]Cl_2$, Ni (II) has $3d^8$-configuration and H_2O is a weak ligand, hence
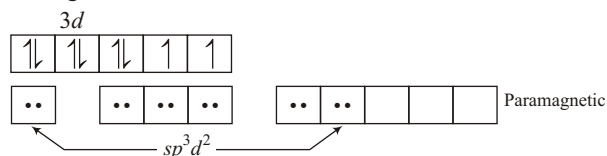
In $K_2[Pt(CN)_4]$, Pt(II) has d^8-configuration and CN^- is a strong ligand, hence all the eight electrons are spin paired. Therefore, complex is diamagnetic.

In $[Zn(H_2O)_6](NO_3)_2$, Zn (II) has $3d^{10}$ configuration with all the ten electrons spin paired, hence diamagnetic.

35. Magnetic moment 2.83 BM indicates that there is two unpaired electrons.

$$u = \sqrt{n(n+2)} \text{ BM} = \sqrt{8} \text{ BM} = 2.82 \text{ BM}$$

In $[NiCl_4]^2$, Ni has d^8 configuration and Cl^- is a weak ligand :
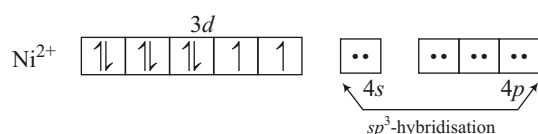
36. In $Cr(CO)_6 : 3d^6$, has no unpaired electrons, zero magnetic moment.

37. $CuF_2 : Cu^{2+}$ has $3d^9$-configuration, allowed d-d transition, hence, coloured.

38. In $Ni(CO)_4$, Ni is sp^3-hybridised while in $[Ni(CN)_4]^{2-}$, Ni^{2+} is dsp^2-hybridised.

39. Greater the extent of d - p back bonding, smaller will be the bond order of CO bond in metal carbonyls. In $Fe(CO)_5$, there is maximum number of valence shell electrons (d-electrons), greatest chances of p - d back bonding, lowest bond order of CO bond.

40. In CO, bond order = 3. In metal carbonyls like $Fe(CO)_5$, due to d - p back-bonding, bond order of CO decreases slightly therefore, bond length increases slightly.

41. In $Hg[Co(SCN)_4]$, Co^{2+} has $3d^7$ configuration. SCN^- produces weak ligand field, no pairing of electrons in d-orbitals occurs against Hund's rule, hence :


$$\sqrt{3(3+2)} \text{ BM} = \sqrt{15} \text{ BM}$$
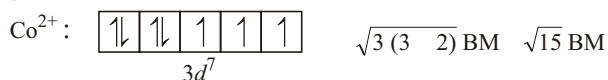
42. $[NiCl_4]^2 : Ni^{2+}(3d^8)$
Tetrahedral
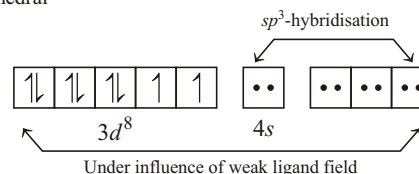
In all other complexes, hybridisation at central metal is dsp^2 and complexes have square planar geometries.

43. In 1 L solution, there will be 0.01 mole of each $[Co(NH_3)_5SO_4]$ Br and $[Co(NH_3)_5Br]SO_4$. Addition of excess of $AgNO_3$ will give 0.01 mole of AgBr. Addition of excess of $BaCl_2$ will give 0.01 mole of $BaSO_4$.

44. In MnO_4, Mn^{+7} has $3d^0$ configuration.

45. In $Ni(CO)_4$, Ni is in $3d^{10}$ state due to strong ligand field produced by CO. Hence, Ni is sp^3-hybridised and complex is tetrahedral. In $NiCl_2(PPh_3)_2$, Ni^2 has $3d^8$-configuration. Due to weak ligand field, Ni is sp^3-hybridised and complex is tetrahedral.

46. $Cu^{2+} + CN \longrightarrow CuCN$
$CuCN + 3CN \longrightarrow [Cu(CN)_4]^3$

47. Fe in $[Fe(H_2O)_6]^{2+}$ has maximum (four) unpaired electrons, has highest paramagnetism.

48. In $Ni(CO)_4$, Ni has $3d^{10}$-configuration, diamagnetic. In $Ni(CN)_4]^2$, Ni has $3d^8$-configuration but due to strong ligand field, all the d-electrons are spin paired giving dsp^2-hybridisation, diamagnetic.

In $[NiCl_4]^2$, Ni has $3d^8$-configuration and there is two unpaired electrons (weak chloride ligand do not pair up d - electrons), hence paramagnetic.

49. Salt with least number of unpaired electrons in d- orbital of central metal will show lowest degree of paramagnetism
Mn^2 ($3d^5$, 5 unpaired electrons)
Cu^2 ($3d^9$, 1 unpaired electrons)
Fe^2 ($3d^6$, 4 unpaired electrons)
Ni^2 ($3d^8$, 2 unpaired electrons)

Hence, $CuSO_4 \cdot 5H_2O$ has lowest degree of paramagnetism.

50. Statement wise explanation is
(i) **Statement (a)** The total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 8 instead of 16 as shown below
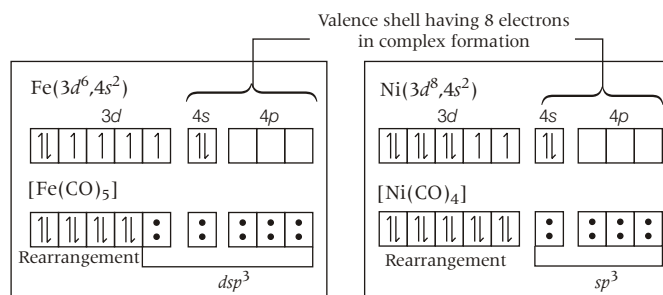
Hence, this statement is incorrect.

(ii) **Statement (b)** Carbonyl complexes are predominantly low spin complexes due to strong ligand fields. Hence, this statement is correct.

(iii) **Statement (c)** For central metal lowering of oxidation state results to increase in electron density on it. This in turn results to increase in extent of synergic bonding. Thus, we can say ''metal carbonyl bond strengthens, when oxidation state of metal is lowered''.
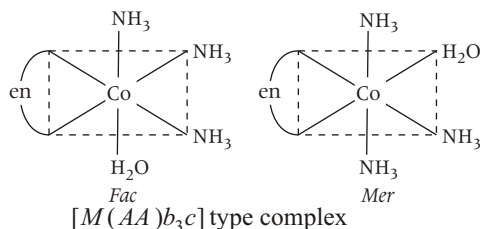
Hence, it is a correct statement.

(iv) **Statement (d)** Increase in positive charge on metal (i.e., increase in oxidation state) results to decrease in synergic bonding strength.

This in turn makes C—O bond stronger instead of weaker. Hence this statement is also incorrect.

51. Statement wise explanation is

Statement (a) $[Co(en)(NH_3)_3H_2O]^3$ have following 2 geometrical isomers.

Fac   *Mer*

$[M(AA)b_3c]$ type complex

Hence, this is correct statement.

Statement (b) If bidentate ligand 'en' is replaced by two cyanide ligands then $[Co(NH_3)_3(H_2O)(CN)_2]$ is formed.

It is $[Ma_3b_2c]$ type complex which has following 3 geometrical isomers.

(*Fac*)   *Fac* with respect to NH_3 and *Mer* with respect to —CN

(*Mer*)
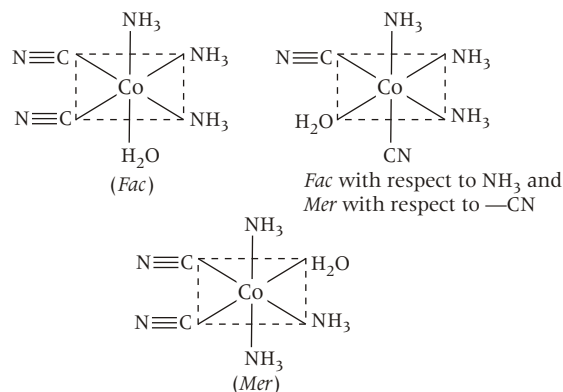
Hence, this statement is also correct.

Statement (c) Co metal has $[Ar]3d^7 4s^2$ configuration while in $[Co(en)(NH_3)_3(H_2O)]^3$ it is in +3 oxidation state. Thus, Co^{3+} has $[Ar]3d^6$ configuration.
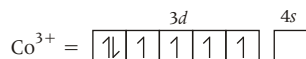
As *en* is a strong ligand, so pairing will occur
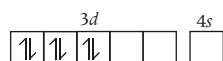
Due to the presence of all paired electrons it show diamagnetic behaviour rather than paramagnetic.

Hence, this statement is incorrect.

Statement (d) According to CFT, absorption of light by coordination complexes depends upon CFSE i.e., crystal field splitting energy ( )as

$$\frac{1}{_0}$$

Among the complexes given $[Co(en)(NH_3)_4]^3$ has more $_0$ value as compared to complex $[Co(en)(NH_3)_3(H_2O)]^3$. Thus, $[Co(en)(NH_3)_3(H_2O)]^3$ absorbs the light at longer wavelength for *d-d* transition.

Hence, this statement is also correct.

Note : For any complex, the value of $_0$ can be calculated via the difference or gap between e_g and t_{2g} values.
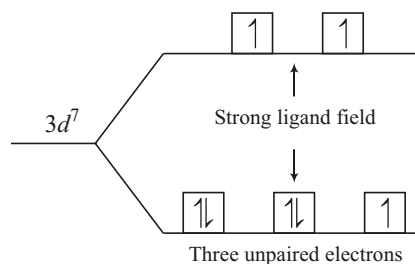
52.
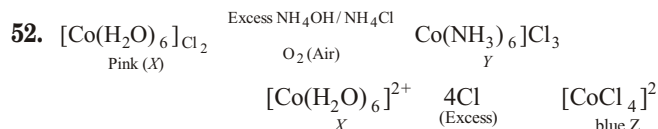
(a) Since NH_3 is moderately strong ligand, hybridisation of cobalt in Y is d^2sp^3.
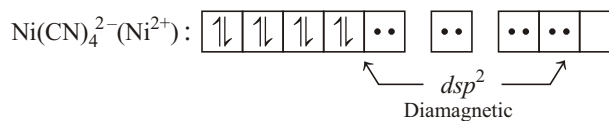
(b) Cobalt is sp^3-hybridised in $[CoCl_4]^2$.

(c) $[Co(NH_3)_6]Cl_3 + 3AgNO_3(aq) \quad 3AgCl$
    Y

(d) $[CoCl_4]^2 + 6H_2O \rightleftharpoons [Co(H_2O)_6]^{2+} + 4Cl$; $\quad H \quad 0$
  Blue   Pink

53. In the complex $[Fe(H_2O)_5NO]SO_4$, Fe is in +1 oxidation state because NO is in +1 state. Also NO is a strong ligand, complex has $3d^7$-configuration at Fe(I) as :

Three unpaired electrons

54. A is diamagnetic, square planar complex because of strong ligand field of CN .

$Ni(CN)_4^{2-}(Ni^{2+})$:

dsp^2
Diamagnetic

B is paramagnetic, tetrahedral complex because of weak ligand field of Cl .

$NiCl_4^{2-}(Ni^{2+})$:

sp^3
Paramagnetic
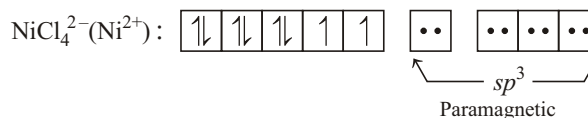
55. Described in 2, A has dsp^2 hybridisation while B has sp^3-hybridisation of Ni.

56. **For, P i.e. dsp^2,** It is seen in $[Ni(CN)_4]^2$

Ni $[Ar]3d^8 4s^2$

Ni^{2+} $[Ar]3d^8$

Ni^{2+} — [3d: ⇅|⇅|⇅|↑|↑] [4s: ☐] [4p: ☐☐☐]

as CN⁻ is a strong ligand so when it approaches towards central metal pairing of unpaired electrons takes place.
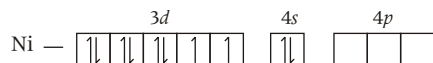
Thus, in $[Ni(CN)_4]^{2-}$

Ni^{2+} — dsp^2-hybridisation [3d: ⇅|⇅|⇅|⇅|••] [4s: ••] [4p: ••|••]
CN⁻ CN⁻ CN⁻ CN⁻
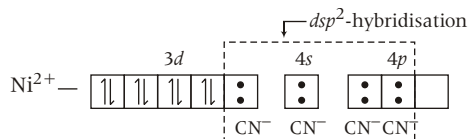
Structure : Square planar

So correct match for P is 6.

For Q i.e., sp^3

It is seen in $[FeCl_4]^{2-}$ and $Ni(CO)_4$

Fe [Ar]$3d^6 4s^2$

Fe^{2+} [Ar]$3d^6$

Fe^{2+} — [3d: ⇅|↑|↑|↑|↑] [4s: ☐] [4p: ☐☐☐]

As Cl⁻ is a weak ligand so when it approaches towards central metal pairing of unpaired electrons does not take place.

Thus, in $[FeCl_4]^{2-}$

Fe^{2+} — [3d: ⇅|↑|↑|↑|↑] sp^3 hybridisation [4s: ••] [4p: ••|••|••]
Cl⁻ Cl⁻ Cl⁻ Cl⁻
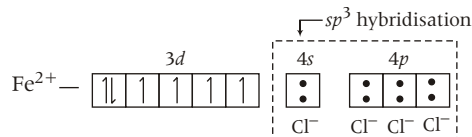
Structure-Tetrahedral

Likewise in $Ni(CO)_4$

Ni [Ar]$3d^8 4s^2$

Ni — [3d: ⇅|⇅|⇅|↑|↑] [4s: ⇅] [4p: ☐☐☐]

As CO is a strong ligand, hence when it approaches towards central metal atom pairing of unpaired electron of central atom takes place.

Thus, in $Ni(CO)_4$

Ni — [3d: ⇅|⇅|⇅|⇅|⇅] sp^3 hybridisation [4s: ••] [4p: ••|••|••]
CO CO CO CO
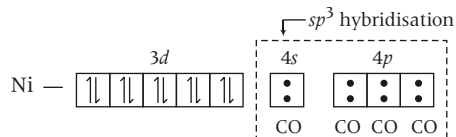
Structure Tetrahedral

So, for Q-4 and 5 are correct match.

For R i.e., $sp^3 d^2$

It is seen in $[FeF_6]^{4-}$

Fe [Ar]$3d^6 4s^2$

Fe^{2+} [Ar]$3d^6$

Fe^{2+} — [3d: ⇅|↑|↑|↑|↑] [4s: ☐] [4p: ☐☐☐] [4d: ☐☐☐☐☐]
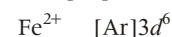
As F⁻ is a weak field ligand hence, when it approaches towards central metal atom, pairing of its electrons does not take place.

Thus, in $[FeF_6]^{4-}$

Fe^{2+} — [3d: ⇅|↑|↑|↑|↑] $sp^3 d^2$ hybridisation [4s: ••] [4p: ••|••|••] [4d: ••|••] ☐☐☐
F⁻ F⁻ F⁻ F⁻ F⁻ F⁻
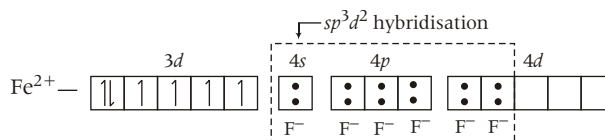
Structure : Octahedral

So, 1 is the correct match for R.

For S i.e., $d^2 sp^3$

It is seen in $[Ti(H_2O)_3 Cl_3]$ and $[Cr(NH_3)_6]^{3+}$

Ti [Ar]$3d^2 4s^2$

Ti^{3+} [Ar]$3d^1$

Ti^{3+} — [3d: ↑|☐☐☐☐] [4s: ☐] [4p: ☐☐☐]

Here, both H_2O and Cl⁻ are weak ligands

So, in $[Ti(H_2O)_3 Cl_3]$

Ti^{3+} — $d^2 sp^3$ hybridisation [3d: ↑|••|••] [4s: ••] [4p: ••|••|••]
H₂O H₂O H₂O Cl⁻ Cl⁻ Cl⁻
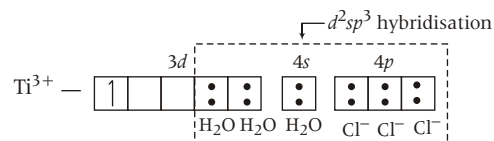
Structure Octahedral

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

Cr [Ar]$3d^5 4s^1$

Cr^{3+} [Ar]$3d^3 4s^0$

Cr^{3+} — [3d: ↑|↑|↑|☐☐] [4s: ☐] [4p: ☐☐☐]

Here, NH_3 is also a weak field ligand so due to its approach no pairing takes place in Cr.

Thus, In $[Cr(NH_3)_6]^{3+}$

Cr^{3+} — [3d: ↑|↑|↑|••|••] [4s: ••] [4p: ••|••|••] $d^2 sp^3$ hybridisation
NH₃ NH₃ NH₃ NH₃ NH₃ NH₃
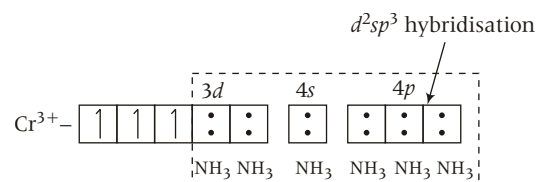
So for, S-2 and 3 are the correct match.

57. PLAN This problem is based on concept of VBT and magnetic properties of coordination compound.
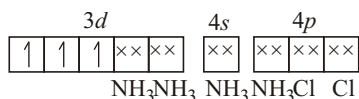
Draw VBT for each coordination compound.

If unpaired electron is present then coordination compound will be paramagnetic otherwise diamagnetic.

Coordination compounds of $[MA_4 B_2]$ type show geometrical isomerism. Molecular orbital electronic configuration (MOEC) for various coordination compound can be drawn using VBT as

A. MO EC for $[Cr(NH_3)_4Cl_2]Cl$ is
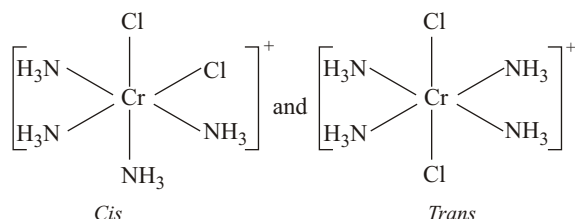

Number of unpaired electrons (n) 3
Magnetic properties paramagnetic
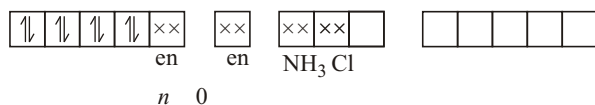Geometrical isomers of $[Cr(NH_3)_4Cl_2]^+$ are

Cis   *Trans*

B. n 1
Magnetic properties paramagnetic
Ionisation isomers of $[Ti(H_2O)_5Cl](NO_3)_2$ are
$[Ti(H_2O)_5Cl](NO_3)_2$ and $[Ti(H_2O)_5(NO_3)]Cl(NO_3)$

C. MOEC of $[Pt(en)(NH_3)Cl]NO_3$ is

en   en   NH$_3$ Cl
n 0
Magnetic property diamagnetic
Ionisation isomers are $[Pt(en)_2(NH_3)Cl]NO_3$
and $[Pt(en)_2NH_3(NO_3)]Cl$

D. MOEC of $[Co(NH_3)_4(NO_3)_2]NO_3$
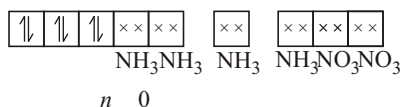
NH_3NH_3 NH_3 $NH_3NO_3NO_3$
n 0
Magnetic property Diamagnetic
Geometrical isomers are
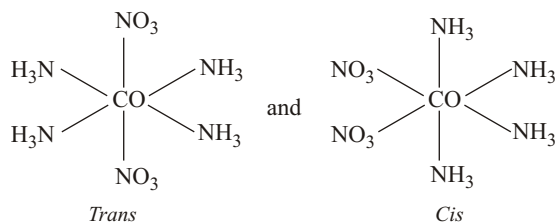
Trans   *Cis*

Thus, magnetic property and isomerism in given coordination compound can be summarised as
 (P) $[Cr(NH_3)_4Cl_2]Cl$ Paramagnetic and exhibits *cis-trans* isomerism (3)
 (Q) $[Ti(H_2O)_5Cl](NO_3)_2$ Paramagnetic and exhibits ionisation isomerism (1)
 (R) $[Pt(en)(NH_3)Cl]NO_3$ Diamagnetic and exhibits ionisation isomerism (4)
 (S) $[Co(NH_3)_4(NO_3)_2]NO_3$ Diamagnetic and exhibits *cis-trans* isomerism (2)
    P 3, Q 1, R 4, S 2
    Hence, (b) is the correct choice.

58. (A) $[Co(NH_3)_4(H_2O)_2]Cl_2:Co^2$, $3d^7$ show geometrical isomerism, paramagnetic.
 (B) $Pt(NH_3)_2Cl_2:Pt^2$ has d^8-configuration with all paired electrons. Show geometrical isomerism, diamagnetic.
 (C) $[Co(H_2O)_5Cl]Cl : Co^2$, $3d^7$ Cannot show geometrical isomerism, paramagnetic.
 (D) $[Ni(H_2O)_6]Cl_2: Ni^2$, $3d^8$, weak ligand, has two unpaired electrons. Paramagnetic but cannot show geometrical isomerism.

59. Complex part is cationic, named first : $[Co(NH_3)_6]Cl_3$: hexaammine cobalt (III) chloride.

60. False : Cyanide (CN) is a strong ligand, brings about pairing of $3d$ electrons.

$K_4[Fe(CN)_6]$ Fe
Potassium ferrocyanide

$Fe(CN)_6^{4-}$

No unpaired electron, diamagnetic

$K_3[Fe(CN)_6]$: Fe
Potassium ferricyanide

$[Fe(CN)_6]^3$:

Has one unpaired electron, paramagnetic
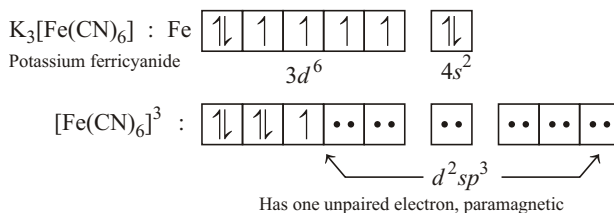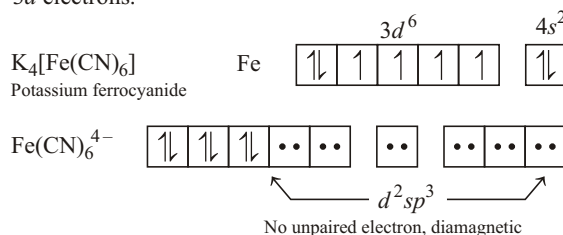
61. False : Lobes of $3d_{x^2 y^2}$ orbitals lies in XY plane on the X and Y coordinate axes, therefore electron density of $d_{x^2 y^2}$ orbital in XY plane is non-zero.

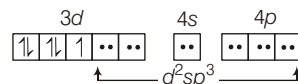62. When S is donor atom of SCN , it produces weak ligand field and forms high spin complex as
$[Fe(SCN)_6]^3$: $Fe^{3+} (3d^5)$

$3d^5(n$-5) sp^3d^2
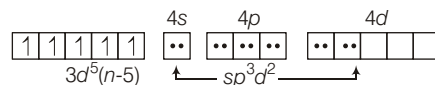
Spin only magnetic moment ($_s$) $\sqrt{5(5 \; 2)}$ BM $\sqrt{35}$ BM

In case of CN ligand, carbon is the donor atom , it produces strong ligand field and forms low spin complex as
$[Fe(CN)_6]^3$: $Fe^{3+} (3d^5)$

d^2sp^3

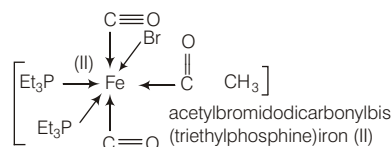Spin only magnetic moment ($_s$) $\sqrt{1(1 \; 2)}$ BM $\sqrt{3}$ BM

Hence, difference in spin only magnetic moment
$\sqrt{35}$ $\sqrt{3}$ 4 BM

63.

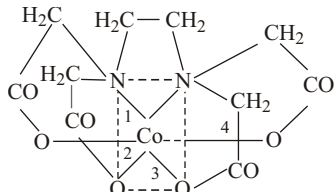

acetylbromidodicarbonylbis
(triethylphosphine)iron (II)

64. **PLAN** EDTA is a multidentate ligand as it can donate six pairs of electrons – two pair from the two nitrogen atoms and four pair from the four terminal oxygens of the COO^- groups.
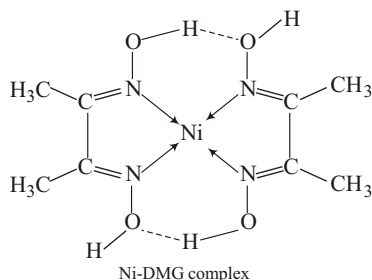
$$^-OOCCH_2 \diagdown \overset{..}{N}-CH_2CH_2-\overset{..}{N} \diagup CH_2COO^-$$
$$^-OOCCH_2 \diagup \qquad \diagdown CH_2COO^-$$
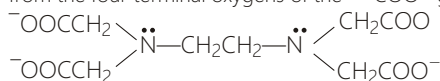
The structure of a chelate of a divalent Co^{2+} with EDTA is shown as

Each N has four N—Co—O bonds thus total eight N—Co—O bonds.

65.

Ni-DMG complex

Oxidation state of Ni is +2 and hybridisation is dsp^2.
$\mu = 0$ (no unpaired electron) hence, diamagnetic.

66. The spin-only magnetic moment (μ) of the complex is 1.73 BM. It indicates that nucleus of complex, chromium ion has one unpaired electron. So, the ligand NO is unit positively charged.
$K_2[Cr(NO)(CN)_4(NH_3)]$
potassium amminetetracyanonitrosoniumchromate (I)

$$Cr^{+1} : \boxed{\uparrow\,|\,\uparrow\,|\,\uparrow\,|\,\uparrow\,|\,\uparrow} \quad \boxed{}$$
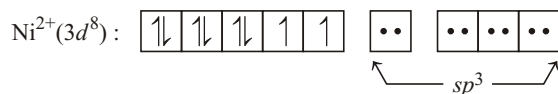$$\underset{3d^5}{} \qquad \underset{4s^0}{}$$
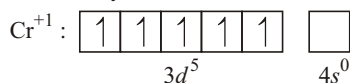
Cr(I) "under influence of strong ligand field".
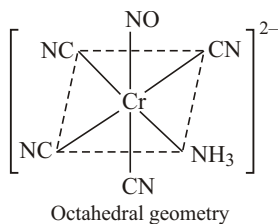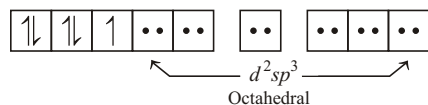
Octahedral

Octahedral geometry

67. $[NiCl_4]^{2-}$: Ni^{2+} ($3d^8$), weak ligand field.

$$Ni^{2+}(3d^8) : \boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow} \quad \boxed{..} \; \boxed{..\,|\,..\,|\,..}$$
$$\underbrace{\qquad\qquad}_{sp^3}$$

$\sqrt{n\,(n+2)} = \sqrt{8} = M$
$[Ni(CN)_4]^{2-}$: Ni^{2+} ($3d^8$), strong ligand field.

$$Ni^{2+}(3d^8) : \boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,..} \; \boxed{..} \; \boxed{..\,|\,..}$$
$$\underbrace{\qquad\qquad}_{dsp^2}$$
Square planar
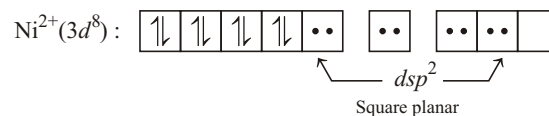
$\mu = 0$ (no unpaired electron)

68. In complexes A and B, one halide (Cl or Br) is outside coordination sphere, i.e. complexes are :
$[Cr(NH_3)_4Br_2]Cl$ and $[Cr(NH_3)_4BrCl]Br$

A gives white precipitate AgCl with excess of $AgNO_3$ which dissolve in excess ammonia. Therefore, A must be $[Cr(NH_3)_4Br_2]Cl$.
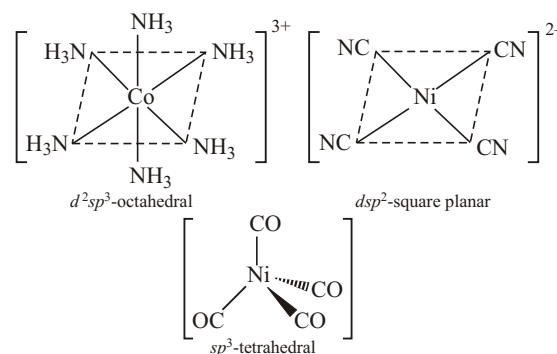
B gives a pale yellow precipitate with excess of $AgNO_3$, which dissolve in concentrated ammonia solution. Therefore, precipitate is AgBr and complex B is $[Cr(NH_3)_4ClBr]Br$.

In both A and B, hybridisation of chromium is d^2sp^3 and magnetic moment : $\mu = \sqrt{n\,(n+2)}$ BM $= 0$
($3d^6$, strong ligand, no unpaired electron)

69.

d^2sp^3-octahedral dsp^2-square planar

sp^3-tetrahedral

70. A has no water molecules of crystallisation.
Hence, A is $[Cr(H_2O)_6]Cl_3$.

Both B and C loses weight with concentrated H_2SO_4, therefore, both B and C have some water molecules of crystallisation.

Moreover, weight loss with C is just double of the same with B indicates that number of water molecules of crystallisation of C is double of the same for B. Therefore, B has one and C has two water molecules of crystallisation.

$B = [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O, C = [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

71. (i) $[Ti(NO_3)_4]$: Ti^{4+} ($3d^0$) No d-electron, no d-d transition possible, colourless.
(ii) $[Cu(NCCH_3)]BF_4$: Cu^+ ($3d^{10}$) All d-orbitals are completely filled, no d-d transition possible, colourless.
(iii) $[Cr(NH_3)_6]Cl_3$: Cr^{3+} ($3d^3$) Complex has allowed d-d-transitions from t_{2g} to e_g level, hence coloured.
(iv) $K_3[VF_6]$: V^{3+} ($3d^2$) Complex has allowed d-d-transitions from t_{2g} to e_g level, hence coloured.

72. I^- is a strong reducing agent, reduces Cu^{2+} to Cu^+ and precipitate out as stable CuI.