CHAPTER
9

Coordination Compounds

- 9.1 Werner's Theory of Coordination Compounds
- 9.2 Definition of Some Important Terms Pertaining to Coordination Compounds
- 9.3 Nomenclature of Coordination Compounds
- 9.4 Isomerism in Coordination Compounds
- 9.5 Bonding in Coordination Compounds
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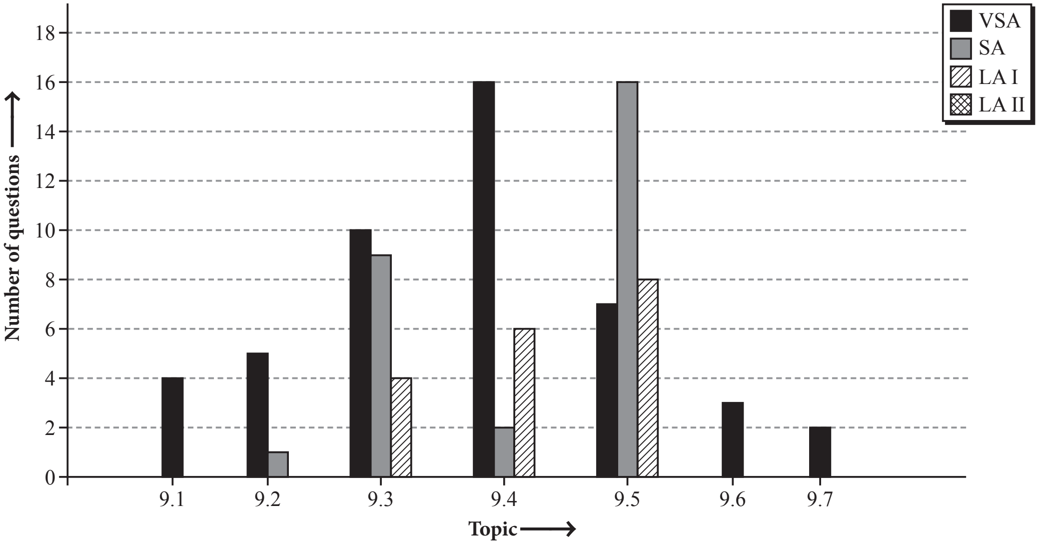
- 9.7 Importance and Applications of Coordination Compounds

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)



- Maximum total weightage is of *Bonding in Coordination Compounds.*
- Maximum VSA type questions were asked from *Isomerism in Coordination Compounds.*
- Maximum SA and LA I type questions were asked from *Bonding in Coordination Compounds.*

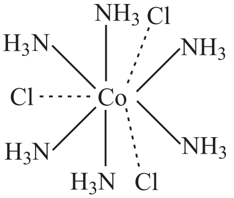
QUICK RECAP

Werner's coordination theory :

- It explains the nature of bonding in complexes. Metals show two different kinds of valencies:
  - **Primary valency :** Non directional and ionisable. It is equal to the oxidation state of the central metal ion.

  - **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or sometimes by positively charged ligands.

- The ionisation of the coordination compound is written as :
  $[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$



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

Addition compounds : The compounds formed by combination of two or more simple compounds are called *addition compounds*. They are of two types :

- **Double salt :** A compound formed by combination of two or more simple compounds, which is stable in solid state only is called *double salt*. In solution it breaks into component ions.

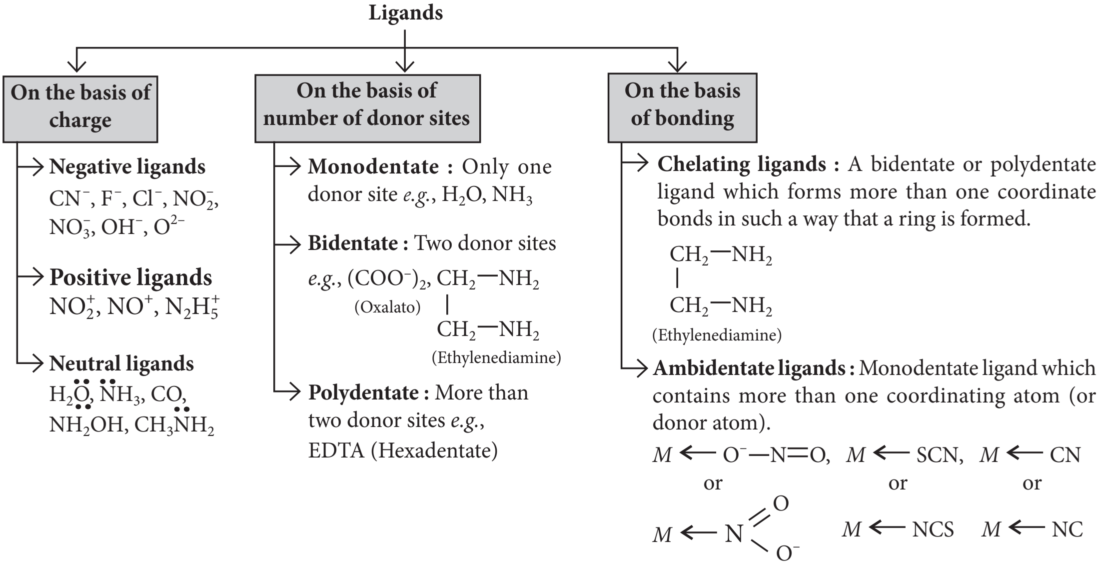
e.g., $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$;	Potash alum
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$;	Mohr's salt
$KCl \cdot MgCl_2 \cdot 6H_2O$;	Carnallite

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

Some important terms pertaining coordination compound :

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

- **Classification of ligands :**



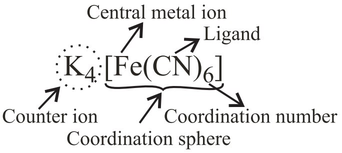
Ligands

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

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

  Example :

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



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

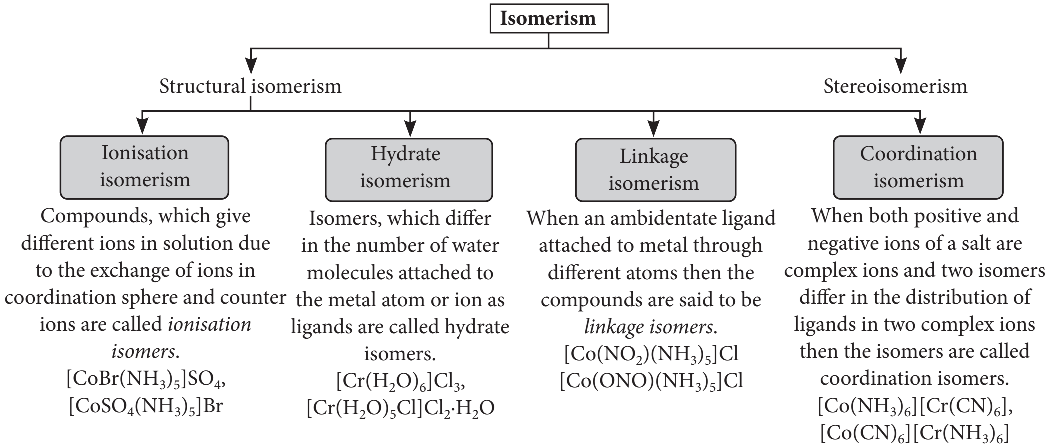
Homoleptic and heteroleptic complexes :

- **Homoleptic complexes :** Complexes in which a metal is bound to only one kind of ligands are called *homoleptic complexes*.
  e.g., $[Co(NH_3)_6]^{3+}$, $[Ti(H_2O)_6]^{3+}$, $[Cu(CN)_4]^{3-}$
- **Heteroleptic complexes :** Complexes in which the central atom is bound to different type of ligands are called *heteroleptic complexes.*
  e.g., $[Co(NH_3)_4Cl_2]$, $K_2[Fe(CN)_5NO]$, $[Fe(H_2O)_5NO]SO_4$

Nomenclature of coordination compounds :

- **Rules for writing the formula of coordination compounds :**
  - Formula of the cation whether simple or complex must be written first, followed by anion.
  - The coordination sphere is written in square brackets.
  - Within the coordination sphere the sequence of symbols is, first the metal atom followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.
  - Polyatomic ligands are enclosed in parentheses.
  - The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.
- **Rules for naming coordination compounds :**
  - The cation is named first then the anion.
  - In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
  - The complex part is written as one word.
  - When the coordination sphere is anionic, name of central metal ends in –*ate*.
- **Naming of ligands :**
  - Name of anionic ligands end in –*o*.
    e.g., Cl^- : Chlorido
  - Neutral ligands (with a few exceptions) retain their names *e.g.*, NH_3 : Ammine
  - Name of cationic ligands end in – *ium*.
    e.g., NO_2^+ : Nitronium
  - Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. *e.g.*, ethylenediamine(*en*).
  - Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
    e.g., $—SCN^-$ (Thiocyanato-S or Thiocyanato), $—NCS^-$ (Thiocyanato-N or Isothiocyanato), $—ONO^-$ (Nitrito-O or Nitrito), $—NO_2^-$ (Nitrito-N or Nitro)
  - The prefixes *di-*, *tri-*, *tetra-*, *penta-* and *hexa-* are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis-*(2), *tris-*(3), *tetrakis-*(4), *pentakis-*(5) and *hexakis-*(6).

Isomerism : Two or more substances having the same molecular formula but different structural or spatial arrangement are called *isomers* and phenomenon is called *isomerism*.



Isomerism

Structural isomerism

Stereoisomerism

Ionisation isomerism

Compounds, which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called *ionisation isomers*.

$[CoBr(NH_3)_5]SO_4$, $[CoSO_4(NH_3)_5]Br$

Hydrate isomerism

Isomers, which differ in the number of water molecules attached to the metal atom or ion as ligands are called hydrate isomers.

$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

Linkage isomerism

When an ambidentate ligand attached to metal through different atoms then the compounds are said to be *linkage isomers*.

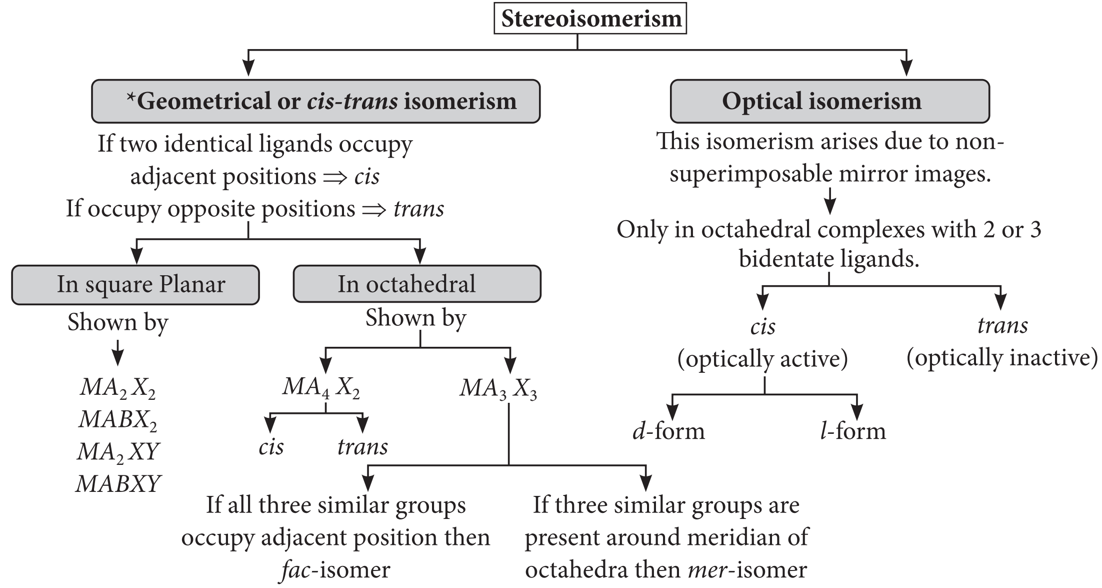
$[Co(NO_2)(NH_3)_5]Cl$

$[Co(ONO)(NH_3)_5]Cl$

Coordination isomerism

When both positive and negative ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complex ions then the isomers are called coordination isomers.

$[Co(NH_3)_6][Cr(CN)_6]$, $[Co(CN)_6][Cr(NH_3)_6]$



Stereoisomerism

***Geometrical or *cis-trans* isomerism**

If two identical ligands occupy adjacent positions ⇒ *cis*

If occupy opposite positions ⇒ *trans*

In square Planar

Shown by

MA_2X_2

$MABX_2$

MA_2XY

$MABXY$

In octahedral

Shown by

MA_4X_2: *cis*, *trans*

MA_3X_3

If all three similar groups occupy adjacent position then *fac*-isomer

If three similar groups are present around meridian of octahedra then *mer*-isomer

Optical isomerism

This isomerism arises due to non-superimposable mirror images.

Only in octahedral complexes with 2 or 3 bidentate ligands.

cis (optically active): *d*-form, *l*-form

trans (optically inactive)

(* Geometrical isomerism is not shown by tetrahedral complexes.)

Bonding in coordination compounds :

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

C. No.	Type of hybridisation	Geometry	Examples
2	*sp*	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$

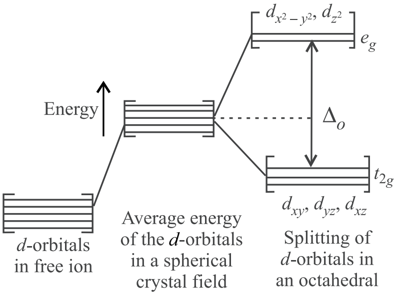
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where, $X = Cl^-, Br^-, I^-$
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

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

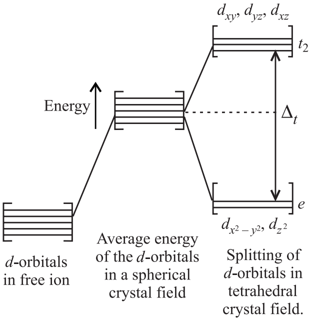
- Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
- Paramagnetism ∝ No. of unpaired electrons.
- Magnetic moment $= \sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

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

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



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



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

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

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

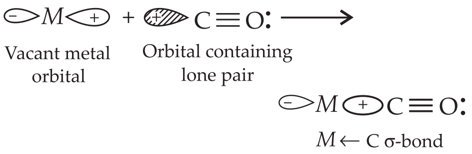
$$\text{Weak field ligands} \xrightarrow{\text{Increasing order of CFSE } (\Delta_o)} \text{Strong field ligands}$$

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

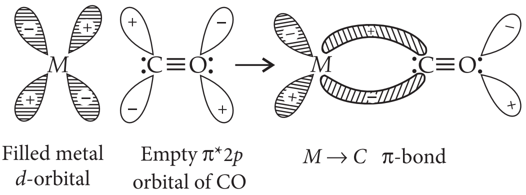
Colour of coordination compounds : The magnitude of CFSE (Δ_o) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever *d-d* transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength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

Bonding in metal carbonyls :

- Metal–carbon bond in metal carbonyls possesses both σ- and π-characters.
- Its formation involves the following steps :
  - Overlap of filled π_{2p} orbital of CO with suitable empty metal *d*-orbital resulting in the formation of sigma bond.



  - π-overlap involving filled metal *d*-orbital with an empty antibonding π*2*p* orbital of same CO. This results in formation of *M* → C π-bond. This is also called *back bonding*.



Applications of coordination compounds :

- Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, vitamin B_{12}, etc. are coordinate compounds of Mg, Fe and Co respectively.
- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography and as dyes.
- *cis*-Platin is used in cancer treatment, EDTA is often used for treatment of lead poisoning.
- Coordination compounds are also used as catalyst.

Previous Years' CBSE Board Questions

9.1 Werner's Theory of Coordination Compounds

VSA (1 mark)

1. One mole of $CrCl_3 \cdot 6H_2O$ compound reacts with excess $AgNO_3$ solution to yield two moles of $AgCl_{(s)}$. The structural formula of the compound is
(a) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
(b) $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$
(c) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
(d) $[Cr(H_2O)_6Cl_3]$ *(2020)*

2. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex. *(AI 2019, 1/2, Delhi 2016)*

3. What is the difference between a complex and a double salt? *(AI 2019)*

4. When a coordination compound $CoCl_3 \cdot 6NH_3$ is mixed with $AgNO_3$, 3 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex. *(1/2, AI 2016)*

9.2 Definition of Some Important Terms Pertaining to Coordination Compounds

VSA (1 mark)

5. The coordination number of 'Co' in the complex $[Co(en)_3]^{3+}$ is
(a) 3 (b) 6
(c) 4 (d) 5 *(2020)*

6. **Assertion (A) :** $[Pt(en)_2Cl_2]^{2+}$ complex is less stable than $[Pt(NH_3)_4Cl_2]^{2+}$ complex.

Reason (R) : $[Pt(en)_2Cl_2]^{2+}$ complex shows chelate effect.

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

7. Write the coordination number and oxidation state of platinum in the complex $[Pt(en)_2Cl_2]$. *(2018)*

8. Which of the following is more stable complex and why?
$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ *(Delhi 2014)*

9. What do you understand by 'denticity of a ligand'? *(Foreign 2011)*

SA (2 marks)

10. Explain the following terms giving a suitable example in each case :
(i) Ambidenate ligand
(ii) Denticity of a ligand *(2/3, AI 2011)*

9.3 Nomenclature of Coordination Compounds

VSA (1 mark)

11. Write the formula of the following coordination compound :
Iron (III) hexacyanidoferrate(II) *(1/3, 2018)*

12. Write the IUPAC name of the following complex : $[Cr(NH_3)_3Cl_3]$. *(1/3, Delhi 2017)*

13. Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$. *(1/3, Delhi 2017)*

14. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write IUPAC name of the complex. *(1/2, Delhi 2016)*

15. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$. *(1/3, AI 2014)*

16. Write down the formula of : Tetrammineaquachloridocobalt(III)chloride. *(AI 2012C)*

17. Name the following coordination compound : $K_3[CrF_6]$. *(Foreign 2011)*

18. Write the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$. *(Delhi 2011C)*

19. Write the IUPAC name of $[Pt(NH_3)_4Cl_2]Cl_2$. *(AI 2011C)*

20. Write the IUPAC name of $[Cr(NH_3)_6][Co(CN)_6]$. *(AI 2011C)*

SA (2 marks)

21. Give the formulae of the following compounds :
(a) Potassium tetrahydroxidozincate(II)
(b) Hexaammineplatinum(IV) chloride
(2020)

22. Using IUPAC norms write the formulae for the following :
(i) Pentaamminenitrito–O–cobalt(III) chloride
(ii) Potassium tetracyanidonickelate(II)
(Delhi 2019)

23. Using IUPAC norms write the formulae for the following :
(a) Sodium dicyanidoaurate(I)
(b) Tetraamminechloridonitrito-N-platinum(IV) sulphate *(AI 2017)*

24. Using IUPAC norms write the formulae for the following :
(a) *Tris*(ethane-1,2,diamine)chromium(III) chloride
(b) Potassium tetrahydroxozincate(II)
(AI 2017)

25. Using IUPAC norms write the formulae for the following :
(a) Potassium trioxalatoaluminate(III)
(b) Dichlorido*bis*(ethane-1,2-diamine) cobalt(III) *(AI 2017)*

26. (i) Write down the IUPAC name of the following complex : $[Cr(NH_3)_2Cl_2(\textit{en})]Cl$ (*en*=ethylenediamine)
(ii) Write the formula for the following complex: Pentaamminenitrito-O-cobalt (III).
(Delhi 2015)

27. Using IUPAC norms write the formulae for the following coordination compounds :
(i) Hexaamminecobalt(III) chloride
(ii) Potassium tetrachloridonickelate(II)
(AI 2015)

28. (i) Write down the IUPAC name of the following complex : $[Cr(\textit{en})_3]Cl_3$.
(ii) Write the formula for the following complex : Potassium trioxalatochromate (III).
(Foreign 2015)

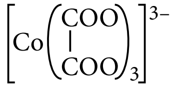
29. Name the following coordination compounds and draw their structures :
(i) $[CoCl_2(\textit{en})_2]Cl$
(ii) $[Pt(NH_3)_2Cl(NO_2)]$
(At. No. Co = 27, Pt = 78)
(Foreign 2011)

LA I (3 marks)

30. Write the IUPAC name of the following :
(i) $[Co(NH_3)_6]Cl_3$ (ii) $[NiCl_4]^{2-}$
(iii) $K_3[Fe(CN)_6]$ *(AI 2015C)*

31. Write down the IUPAC name for each of the following complexes :
(i) $[Co(NH_3)_5Cl]Cl_2$ (ii) $K_3[Fe(CN)_6]$
(iii) $[NiCl_4]^{2-}$ *(Delhi 2014C)*

32. Write the IUPAC name and draw the structure of each of the following complex entities :

(i) 

$$\left[Co\begin{pmatrix}COO\\ |\\ COO\end{pmatrix}_3\right]^{3-}$$

(ii) $[Cr(CO)_6]$

(iii) $[PtCl_3(C_2H_4)]^-$
(At. nos. Cr = 25, Co = 27, Pt = 78)
(AI 2014C)

33. Write the IUPAC names of the following coordination compounds :
(i) $[Cr(NH_3)_3Cl_3]$
(ii) $K_3[Fe(CN)_6]$
(iii) $[CoBr_2(\textit{en})_2]^+$, (*en* = ethylenediamine)
(Delhi 2013)

9.4 Isomerism in Coordination Compounds

VSA (1 mark)

34. **Assertion (A) :** Linkage isomerism arises in coordination compounds because of ambidentate ligand.

Reason (R) : Ambidentate ligand like NO_2 has two different donor atoms *i.e.*, N and O.

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

35. What type of isomerism is shown by the complex $[Co(en)_2\ Cl_2]^{2+}$? Name the structure of an isomer of this complex which is optically active. *(1/2, 2020)*

36. What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$? *(1/3, 2018)*

37. What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$? *(1/3, Delhi 2017, Foreign 2014)*

38. What type of isomerism is shown by the complex $[Co(en)_3]Cl_3$? *(1/3, Delhi 2017)*

39. What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$? *(1/3, AI 2017)*

40. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically active. *(1/3, Delhi 2016)*

41. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive. *(AI 2016)*

42. Draw the geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$. *(1/3, Delhi 2015)*

43. Write down the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. What type of isomerism is shown by this complex? *(AI 2015)*

44. Draw the geometrical isomers of complex $[Pt(en)_2Cl_2]^{2+}$. *(1/3, Foreign 2015)*

45. What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (*en* = ethane-1,2-diamine) *(1/3, AI 2014)*

46. What type of isomerism is exhibited by the following complex :
$[Co(NH_3)_5SO_4]Cl$ *(Foreign 2014)*

47. What type of isomerism is exhibited by the complex $[Co(NH_3)_5NO_2]^{2+}$? *(Foreign 2014)*

48. Indicate the types of isomerism exhibited by the complex $[Co(NH_3)_5(NO_2)](NO_3)_2$. (At no. Co = 27) *(AI 2012C)*

49. Give IUPAC name of ionisation isomer of $[Ni(NH_3)_3NO_3]Cl$. *(AI 2012C)*

SA (2 marks)

50. Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex. *(Delhi 2019)*

51. Draw the structure of isomers, if any and write the name of the following complexes :

(i) $[Cr(NH_3)_4Cl_2]^+$

(ii) $[Co(en)_3]^{3+}$ *(Foreign 2011)*

LA I (3 marks)

52. Indicate the types of isomerism exhibited by the following complexes :

(i) $[Co(NH_3)_5(NO_2)]^{2+}$

(ii) $[Co(en)_3]Cl_3$ (*en* = ethylene diamine)

(iii) $[Pt(NH_3)_2Cl_2]$ *(Delhi 2015C)*

53. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? *(Delhi 2014)*

54. Draw the structures of optical isomers of each of the following complex ions :
$[Cr(C_2O_4)]^{3-}$, $[PtCl_2(en)_2]^{2+}$, $[Cr(NH_3)_2Cl_2(en)]^+$ *(Delhi 2014C)*

55. Write the types of isomerism exhibited by the following complexes :

(i) $[Co(NH_3)_5Cl]SO_4$

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

(iii) $[Co(NH_3)_6]\ [Cr(CN)_6]$ *(Delhi 2013)*

56. Name the following coordination entities and draw the structures of their stereoisomers :

(i) $[Co(en)_2Cl_2]^+$ (*en* = ethane-1,2-diamine)

(ii) $[Cr(C_2O_4)_3]^{3-}$

(iii) $[Co(NH_3)_3Cl_3]$

(Atomic numbers Cr = 24, Co = 27) *(AI 2012)*

57. Write the structures and names of all the stereoisomers of the following compounds :

(i) $[Co(en)_3]Cl_3$ (ii) $[Pt(NH_3)_2Cl_2]$

(iii) $[Fe(NH_3)_4Cl_2]Cl$ *(AI 2011)*

9.5 Bonding in Coordination Compounds

VSA (1 mark)

58. The crystal field splitting energy for octahedral (Δ_0) and tetrahedral (Δ_t) complexes is related as

(a) $\Delta_t = \frac{2}{9}\Delta_0$ (b) $\Delta_t = \frac{5}{9}\Delta_0$

(c) $\Delta_t = \frac{4}{9}\Delta_0$ (d) $\Delta_t = 2\,\Delta_0$ *(2020)*

59. Write the IUPAC name and hybridisation of the complex $[CoF_6]^{3-}$ (Given : Atomic number of Co = 27) *(1/2, 2020)*

60. Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) *(1/3, 2018)*

61. Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At. no. of Ni = 28) *(1/3, Delhi 2017)*

62. Write the hybridisation and magnetic character of $[Co(C_2O_4)_3]^{3-}$. (At. no. of Co = 27) *(1/3, Delhi 2017)*

63. Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. no. : Cr = 24, Co = 27, Ni = 28) *(1/3, AI 2014)*

64. Explain the following term giving a suitable example :
Crystal field splitting in an octahedral field. *(1/3, AI 2011)*

SA (2 marks)

65. Write IUPAC name and hybridization of the following complexes :

(i) $[Ni(CO)_4]$ (ii) $[CoF_6]^{3-}$

(Atomic number Ni = 28, Co = 27) *(2020)*

66. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is

(i) diamagnetic (ii) more stable

(iii) outer orbital complex and

(iv) low spin complex ?

(Atomic no. of Co = 27) *(Delhi 2019)*

67. (a) Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic?

(Atomic number of Ni = 28)

(b) Why are low spin tetrahedral complexes rarely observed? *(2/3, AI 2017)*

68. For the complex $[Fe(CN)_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex.
(At. number : Fe = 26). *(2/3, Delhi 2016)*

69. For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number Fe = 26) *(2/3,AI 2016)*

70. (i) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.

(ii) Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.
(At. no. of Ni =28) *(2/3, Delhi 2015)*

71. Write the hybridization and shape of the following complexes :

(i) $[CoF_6]^{3-}$ (ii) $[Ni(CN)_4]^{2-}$

(Atomic number : Co = 27, Ni = 28) *(AI 2015)*

72. Write the state of hybridization, shape and IUPAC name of the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) *(Foreign 2014)*

73. Write the state of hybridization, shape and IUPAC name of the complex $[Ni(CN)_4]^{2-}$. (Atomic no. of Ni = 28) *(Foreign 2014)*

74. Write the state of hybridization, shape and IUPAC name of the complex $[Co(NH_3)_6]^{3+}$. (Atomic no. of Co = 27) *(Foreign 2014)*

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

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

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

Write the name and magnetic behaviour of each of the above coordination entities.
(At. nos. Co = 27, Ni = 28) *(2/3, Delhi 2012)*

76. State a reason for each of the following situations :

(i) Co^{2+} is easily oxidised to Co^{3+} in presence of a strong ligand.

(ii) The molecular shape of $Ni(CO)_4$ is not the same as that of $[Ni(CN)_4]^{2-}$.

(2/3, Delhi 2012)

77. Using valence bond theory, explain the geometry and magnetic behaviour of $[Co(NH_3)_6]^{3+}$.

(At. no. of Co = 27) *(2/3, Delhi 2012C)*

78. Using valence bond theory of complexes, explain the geometry and magnetic nature of $[Ni(CN)_4]^{2-}$. (At. no. of Ni = 28)

(2/3, Delhi 2012C)

79. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain (At. no. Fe = 26] *(Delhi 2012C)*

80. Give the name, the stereochemistry and the magnetic behaviour of the following complexes:

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

(ii) $K_2[Ni(CN)_4]$ *(Foreign 2011)*

LA I (3 marks)

81. Write the hybridisation and magnetic character of the following complexes:

(i) $[Fe(H_2O)_6]^{2+}$ (ii) $[Ni(CN)_4]^{2-}$

[Atomic number : Fe = 26, Ni = 28]

(AI 2019)

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

(i) the IUPAC name

(ii) the hybridization type

(iii) the shape of the complex.

(Atomic no. of Ni = 28) *(AI 2013)*

83. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when

(i) $\Delta_o > P$

(ii) $\Delta_o < P$ *(AI 2013)*

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

(i) $[Pt(NH_3)_2Cl(NO_2)]$

(ii) $[Co(NH_3)_4Cl_2]Cl$ (iii) $Ni(CO)_4$

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

(Delhi 2012)

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

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

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

(iii) $[Ni(CN)_4]^{2-}$ *(AI 2012)*

86. Write the name, stereochemistry and magnetic behaviour of the following :

(At. nos. Mn = 25, Co = 27, Ni = 28)

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

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

(iii) $K_2[Ni(CN)_4]$ *(Delhi 2011)*

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

(i) Oxidation number of iron

(ii) Hybrid orbitals and shape of the complex

(iii) Magnetic behaviour of the complex

(iv) Number of its geometrical isomers

(v) Whether there may be optical isomer also.

(vi) Name of the complex. *(Delhi 2011)*

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

(i) $[Cr(NH_3)_4Cl_2]Cl$

(ii) $[Co(en)_3]Cl_3$

(iii) $K_2[Ni(CN)_4]$ *(AI 2011)*

9.6 Bonding in Metal Carbonyls

VSA (1 mark)

89. Out of NH_3 and CO, which ligand forms a more stable complex with a transition metal and why? *(1/3, AI 2015)*

90. State a reason for the following situation :
CO is a stronger complexing reagent than NH_3. *(1/3, Delhi 2012)*

91. Why is CO a stronger ligand than Cl^-?

(Foreign 2011)

9.7 Importance and Applications of Coordination Compounds

VSA (1 mark)

92. Give two examples of coordination compounds used in industries.

(1/3, Delhi 2012C)

93. Give names of two complexes which are used in medicines. *(1/3, Delhi 2012C)*

Detailed Solutions

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

2. *Refer to answer 1.*

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

4. Structural formula : $[Co(NH_3)_6]Cl_3$

5. **(b) :** Ethane-1, 2-diamine (*en*) is a bidendate ligand.

6. **(d) :** Formation of chelate rings increases the stability of the complex.

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

8. $[Co(en)_3]^{3+}$ is more stable complex than $[Co(NH_3)_6]^{3+}$ due to chelate effect as it forms rings.

9. **Denticity :** The number of coordinating groups present in a ligand is called the denticity of ligand. For example, bidentate ligand ethane-1, 2-diamine has two donor nitrogen atoms which can link to central metal atom.

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

Ethane-1, 2-diamine

10. (i) **Ambidentate ligand :** A unidentate ligand which can coordinate to central metal atom through two different atoms is called ambidentate ligand. For example, NO_2^- ion can coordinate either through nitrogen or through oxygen to the central metal atom/ion.

(ii) *Refer to answer 9.*

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

12. IUPAC name of the complex $[Cr(NH_3)_3Cl_3]$ is triamminetrichloridochromium(III).

13. Pentaamminecarbonatocobalt(III) chloride

14. IUPAC name of the complex $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ is : pentaaquachloridochromium (III) chloride.

15. IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$ is tetraamminedichloridochromium(III) chloride.

16. $[Co(NH_3)_4(H_2O)(Cl)]Cl_2$

17. Potassium hexafluoridochromate(III).

18. Diamminechlorido(methylamine)platinum(II) chloride.

19. Tetraamminedichloridoplatinum(IV) chloride.

20. Hexaamminechromium(III) hexacyanidocobaltate(III).

21. (a) $K_2[Zn(OH)_4]$
Potassium tetrahydroxidozincate(II)

(b) $[Pt(NH_3)_6]Cl_4$
Hexaammineplatinum(IV) chloride

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

23. (a) $Na[Au(CN)_2]$
Sodium dicyanidoaurate(I)

(b) $[Pt(NH_3)_4(Cl)(NO_2)]SO_4$
Tetraamminechloridonitrito-N-platinum(IV) sulphate

24. (a) $[Cr(en)_3]Cl_3$
Tris(ethane-1,2-diamine)chromium(III) chloride

(b) $K_2[Zn(OH)_4]$
Potassium tetrahydroxidozincate(II)

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

(b) $[CoCl_2(en)_2]^+$
Dichlorido*bis*(ethane–1,2-diamine)cobalt(III) ion

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

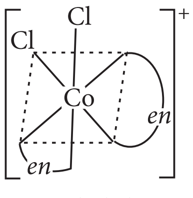
(ii) $[Co(NH_3)_5(ONO)]^{2+}$

27. (i) $[Co(NH_3)_6]Cl_3$ (ii) $K_2[NiCl_4]$

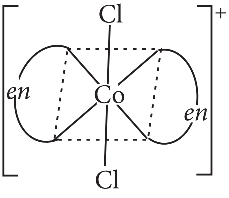
28. (i) *Tris*(ethylenediammine)chromium(III) chloride

(ii) $K_3[Cr(ox)_3]$

29. (i) Dichlorido*bis* (ethane-1, 2-diamine) cobalt(III) chloride.

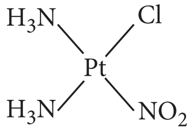


Octahedral
cis-$[CoCl_2(en)_2]^+$



Octahedral
trans-$[CoCl_2(en)_2]^+$

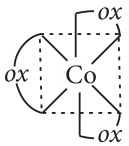
(ii) Diamminechloridonitrito-N-platinum(II)



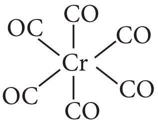
30. (i) Hexaamminecobalt(III) chloride
(ii) Tetrachloridonickelate(II) ion
(iii) Potassium hexacyanidoferrate(III)

31. (i) Pentaamminechloridocobalt(III) chloride
(ii) *Refer to answer 30(iii).*
(iii) *Refer to answer 30(ii).*

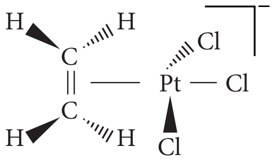
32. (i) Trioxalatocobaltate(III)



(ii) Hexacarbonylchromium(0)



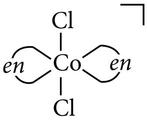
(iii) Trichloridoetheneplatinum(III)



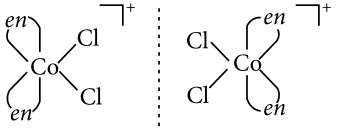
33. (i) Triamminetrichloridochromium(III)
(ii) *Refer to answser 30(iii)*
(iii) Dibromido*bis*(ethane-1,2-diamine) cobalt(III) ion

34. **(a)**

35. $[CoCl_2(en)_2]^+$: Dichlorido*bis*(ethane-1, 2-diamine)cobalt(III) ion
This complex exhibit both optical and geometrical isomerism and *cis* isomer is optically active.



trans-form



cis-form exists in two enantiomeric forms (*d* and *l*)

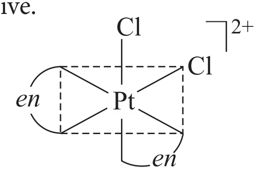
36. Ionisation isomerism : $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$

37. Coordination isomerism

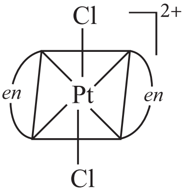
38. The complex, $[Co(en)_3]Cl_3$ shows optical isomerism.

39. The complex $[Co(NH_3)_5(SCN)]^{2+}$ shows linkage isomerism as SCN^- is an ambidentate ligand.

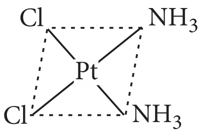
40. *cis*-isomer of the complex $[Pt(en)_2Cl_2]^{2+}$ is optically active.



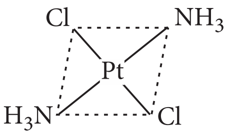
41. *Trans*-isomer is optically inactive due to the presence of plane of symmetry.



42. Geometrical isomers

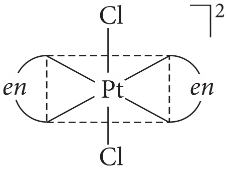


cis-Diamminedichlorido platinum(II)

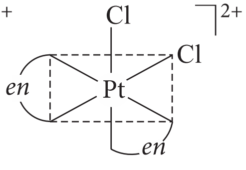


trans-Diamminedichlorido platinum(II)

43. IUPAC name - Dichlorido*bis*(ethane-1,2-diamine)platinum(IV) ion. This complex shows geometrical and optical isomerism.

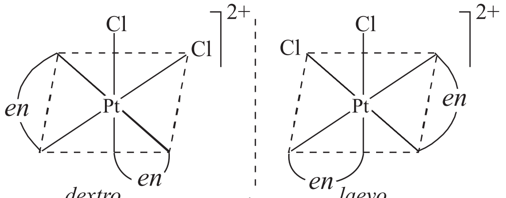


trans



cis

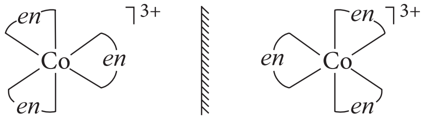
cis-isomer is optically active.



dextro Mirror *laevo*

44. *Refer to answer 43.*

45. Optical isomerism :



dextro Mirror *laevo*

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

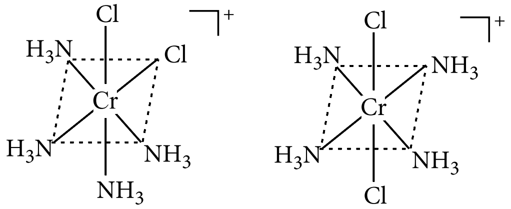
46. *Refer to answer 36.*

47. Linkage isomerism : $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(ONO)(NH_3)_5]^{2+}$

48. (i) Ionisation isomers :
$[Co(NH_3)_5(NO_2)](NO_3)_2$ and
$[Co(NH_3)_5(NO_3)](NO_2)(NO_3)$
(ii) Linkage isomers : $[Co(NH_3)_5(NO_2)](NO_3)_2$ and $[Co(NH_3)_5(ONO)](NO_3)_2$

49. Ionisation isomer of $[Ni(NH_3)_3NO_3]Cl$ is $[Ni(NH_3)_3Cl]NO_3$. The IUPAC name of this complex is triamminechloridonickel(II) nitrate.

50. *Tetra*amminedichloridochromium(III) ion
Geometrical isomers of $[Cr(NH_3)_4Cl_2]^+$;



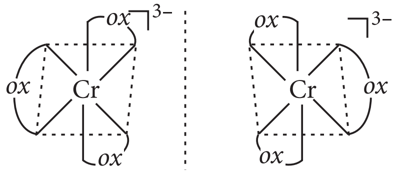
cis-Tetraamminedichlorido chromium(III) ion *trans*-Tetraamminedichlorido chromium(III) ion

51. (i) *Refer to answer 50.*
(ii) *Refer to answer 45.*

52. (i) *Refer to answer 47.*
(ii) *Refer to answer 45.*
(iii) *Refer to answer 42.*

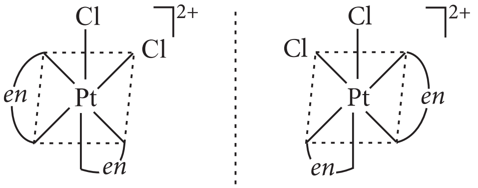
53. *Refer to answer 50.*

54. $[Cr(C_2O_4)]^{3-}$:



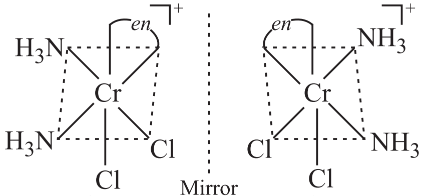
$[Cr(ox)_3]^{3-}$ *dextro* Mirror $[Cr(ox)_3]^{3-}$ *laevo*

$[PtCl_2(en)_2]^{2+}$:



dextro Mirror *laevo*

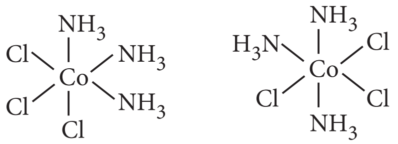
$[Cr(NH_3)_2Cl_2(en)]^+$:



dextro Mirror *laevo*

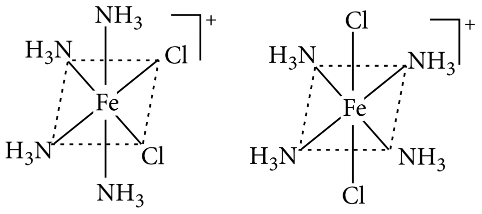
55. (i) *Refer to answer 36.*
(ii) *Refer to answer 45.*
(iii) *Refer to answer 37.*

56. (i) *Refer to answer 35.*
(ii) $[Cr(C_2O_4)_3]^{3-}$: Trioxalatochromate(III) ion
It will show optical isomerism.
Refer to answer 54.
(iii) $[Co(NH_3)_3Cl_3]$: Triamminetrichloridocobalt(III)
It will exist in two geometrical isomeric forms :



Facial (*fac*) *Meridional* (*mer*)

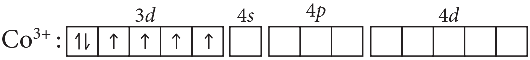
57. (i) *tris*(ethane-1,2-diamine) cobalt(III) chloride : *Refer to answer 45.*
(ii) *Refer to answer 42.*
(iii) $[Fe(NH_3)_4Cl_2]Cl$



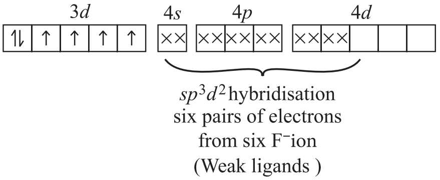
cis-tetraamminedichlorido iron (III) *trans*-tetraamminedichlorido iron (III)

58. **(c)**

59. The IUPAC name of $[CoF_6]^{3-}$ is hexafluoridocobaltate(III).
Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.



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



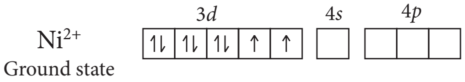
No. of unpaired electrons = 4

60. *Refer to answer 59.*

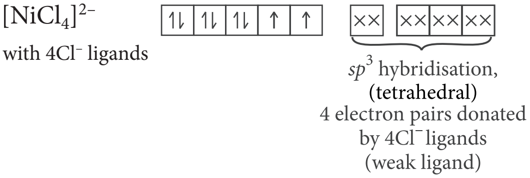
61. $[Ni(H_2O)_6]^{2+}$ is a high spin complex (Δ_o small) while $[Ni(CN)_4]^{2-}$ is a low spin square planar complex.
In $[Ni(H_2O)_6]^{2+}$ complex, *d-d* transitions are taking place on absorbing low energy radiation (red component of spectrum) from visible region showing green as the complementary colour.
In $[Ni(CN)_4]^{2-}$ complex, *d-d* transitions do not take place because there is no unpaired electron present hence, complex is colourless.

62. The complex $[Co(C_2O_4)_3]^{3-}$ has d^2sp^3-hybridisation and it is diamagnetic in nature due to the absence of unpaired electrons.

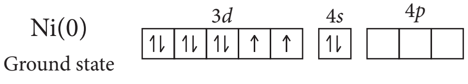
63. $[NiCl_4]^{2-}$ contains Ni^{2+} ion with $3d^8$ configuration.



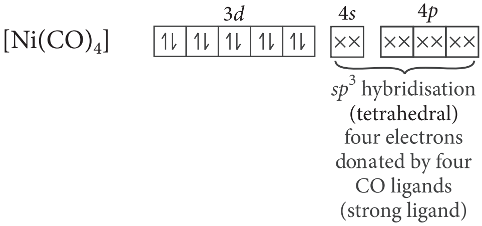
Cl^- is a weak field ligand. Hence, outer 4*s* and 4*p*-orbitals are used in hybridisation.



It has two unpaired electrons hence, it is paramagnetic.
$[Ni(CO)_4]$ contains Ni(0) – $3d^84s^2$ configuration.

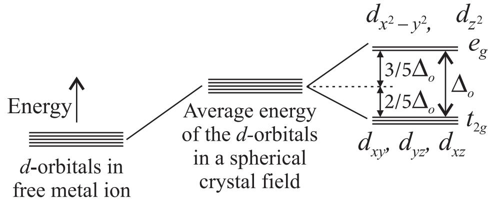


CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.



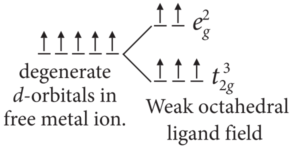
The complex has all paired electrons hence, it is diamagnetic.

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

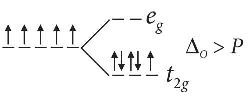


d-orbital splitting in an octahedral crystal field

$[Mn(H_2O)_6]^{2+}$ contains : Mn^{2+} – $3d^5$ configuration, C.N. = 6, octahedral structure, H_2O (weak field ligand) hence $\Delta_o < P$.



Electrons enter into e_g orbital before pairing. It has five unpaired electrons.
$[Mn(CN)_6]^{4-}$ contains : Mn^{2+} ion-$3d^5$ configuration, C.N. = 6, octahedral geometry, CN^- (strong field ligand) hence, $\Delta_o > P$.

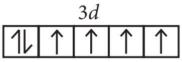


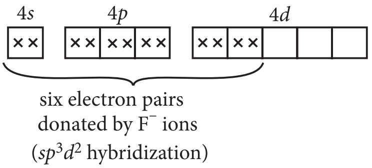
Hence, pairing of electrons in t_{2g} orbitals takes place. It has only one unpaired electron.

65. (i) Name; Tetracarbonylnickel (0)
For hybridisation; *Refer to answer 63.*
(ii) *Refer to answer 59.*

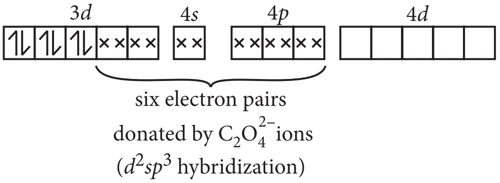
66. Formation of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ can be represented as :

$[CoF_6]^{3-}$:





$[Co(C_2O_4)_3]^{3-}$:



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

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

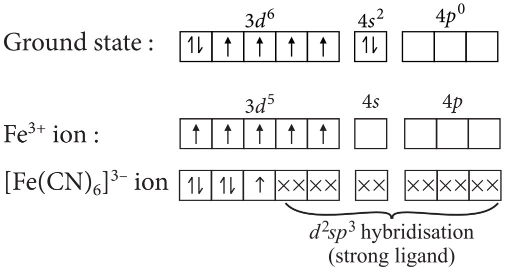
(iii) $[CoF_6]^{3-}$ is outer orbital complex as it undergoes sp^3d^2 hybridization using the outer 4*d*-orbital.

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

67. (a) Due to the presence of weak field ligand, *i.e.*, Cl^- in the complex $[NiCl_4]^{2-}$ two unpaired electrons are present in 3*d*-orbitals of Ni-atom hence, this complex is paramagnetic in nature. On the other hand, due to the presence of strong field ligand *i.e.*, CN^- in the complex $[Ni(CN)_4]^{2-}$, no unpaired electron is present in 3*d*-orbitals of Ni-atom (as strong field ligand causes pairing of electrons), hence, it is diamagnetic in nature.

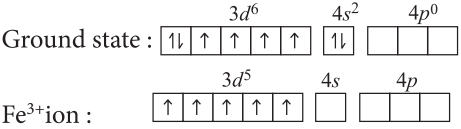
(b) In tetrahedral coordination entity formation, the *d*-orbital splitting is smaller. Consequently, the orbital splitting energies are not sufficiently large to force pairing and therefore, low spin configurations are rarely observed.

68. Fe atom ($Z = 26$)

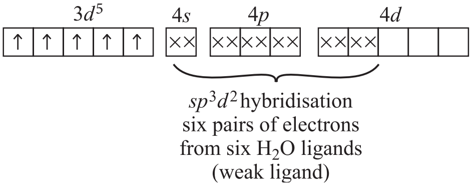


The complex ion has inner orbital octahedral geometry (low spin) and is paramagnetic due to the presence of one unpaired electron.

69. $[Fe(H_2O)_6]^{3+}$:
Fe atom ($Z = 26$)



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

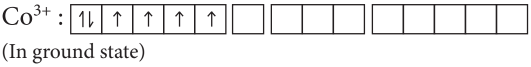


The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

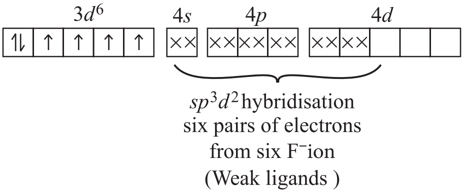
70. (i) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\, e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

(ii) *Refer to answer 63.*

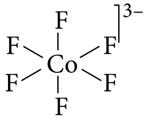
71. (i) Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.



$[CoF_6]^{3-}$:

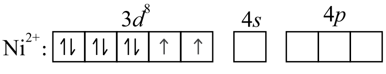


Structure – Outer orbital octahedral complex



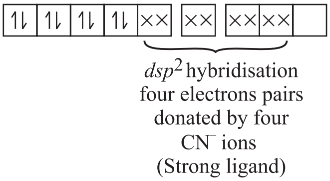
Nature – Paramagnetic

(ii) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.



(In ground state)

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



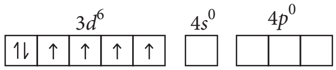
The complex ion has square planar geometry and is diamagnetic in nature.

72. *Refer to answer 71(i).*
IUPAC Name : Hexafluoridocobaltate(III) ion

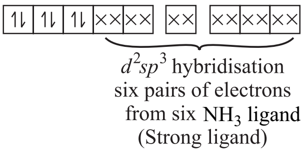
73. *Refer to answer 71(ii).*
IUPAC name : Tetracyanidonickelate(II) ion

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

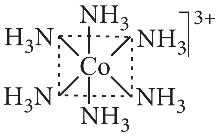
Co^{3+} :
Ground State



$[Co(NH_3)_6]^{3+}$ ion :



Hybridisation – d^2sp^3
Structure – Octahedral
(low spin)
Nature – Diamagnetic

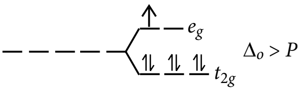


IUPAC name : Hexaamminecobalt(III) ion

75. (i) $[Co(en)_2Cl(NH_3)]^{2+}$
Amminechlorido*bis*(ethane-1,2-diamine)cobalt(III) ion
In presence of strong NH_3 and *en* ligand, Co^{3+} ($3d^6$) forms low spin complex. Hence, complex is diamagnetic.

(ii) $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$:
Diaquadioxalatonickelate(II) ion
In the presence of weak H_2O and *ox* ligand, Ni(II) forms high spin complex (sp^3d^2 hybridisation). It is paramagnetic.

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



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

(ii) *Refer to answers 71(ii) and 63.*

77. *Refer to answer 74.*

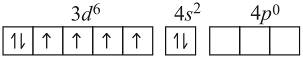
78. *Refer to answer 71(ii).*

79. In presence of CN^-, the 3*d* electrons pair up leaving only one unpaired electron, the hybridisation is d^2sp^3 forming an inner orbital octahedral complex whereas in the presence of H_2O, 3*d* electrons do not pair up. The hydridisation is sp^3d^2 forming an outer orbital octahedral complex containing five unpaired electrons. Hence, it is strongly paramagnetic.

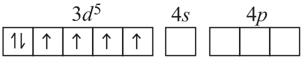
80. (i) $[Co(NH_3)_5Cl]Cl_2$: Pentaamminechloridocobalt (III) chloride.
Co(III) : $[Ar]3d^64s^0$: d^2sp^3 hybridisation leads to octahedral shape.
Magnetic behaviour : Diamagnetic.
Stereochemistry : Complex $[Co(NH_3)_5Cl]Cl_2$ do not exhibit geometrical and optical isomerism.
(ii) $K_2[Ni(CN)_4]$: Potassium tetracyanidonickelate(II)
Ni(II) : [Ar] $3d^84s^0$ – dsp^2 hybridisation leads to square planar shape.
Magnetic behaviour : Diamagnetic.
Stereochemistry : Complex $[Ni(CN)_4]$ do not exhibit geometrical isomerism and optical isomerism because all the possible arrangement are equivalent.

81. (i) $[Fe(H_2O)_6]^{2+}$:
Fe atom (Z = 26)

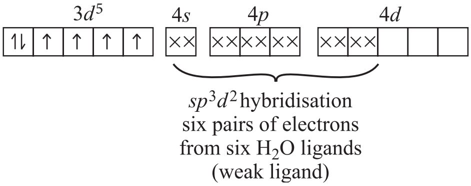
Ground state :



Fe^{2+}ion :



$[Fe(H_2O)_6]^{2+}$:

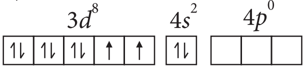


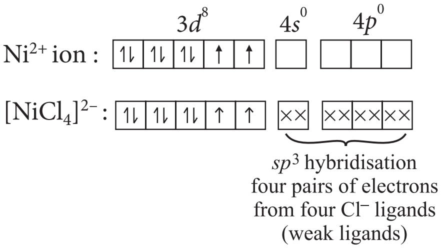
The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of four unpaired electrons.

(ii) *Refer to answer 71(ii).*

82. Tetrachloridonickelate(II) ion
Ni atom (Z = 28)

Ground state :

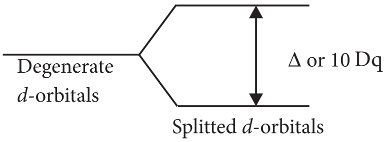




The complex ion has tetrahedral geometry and is paramagnetic due to the presence of unpaired electrons.

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

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



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

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

84. (i) $[Pt(NH_3)_2Cl(NO_2)]$:

Diamminechloridonitrito-N-platinum(II)

It is square planar and diamagnetic.

(ii) $[Co(NH_3)_4Cl_2]Cl$:

Tetraamminedichloridocobalt (III) chloride

It is octahedral and diamagnetic.

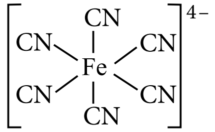
(iii) $Ni(CO)_4$: Tetracarbonylnickel(0)

It is tetrahedral and diamagnetic.

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

Hybridisation - d^2sp^3

Structure : Inner orbital octahedral complex



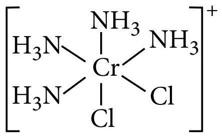
Octahedral

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

Tetraamminedichloridochromium(III) ion

Hybridisation - d^2sp^3

Structure : Inner orbital octahedral complex

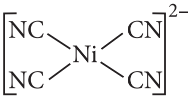


Octahedral

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

Hybridisation - dsp^2

Structure - Square planar



Square planar

86.

	Formulae	**Name of the Complex**	**Hybridisation of metal ion involved**	**Geometry of complex (stereochemistry)**	**Magnetic behaviour**
(i)	$K_4[Mn(CN)_6]$	Potassium hexacyanidomanganate(II)	d^2sp^3	Octahedral	Paramagnetic
(ii)	$[Co(NH_3)_5Cl]Cl_2$	Pentaamminechloridocobalt(III) chloride	d^2sp^3	Octahedral	Diamagnetic
(iii)	$K_2[Ni(CN)_4]$	Potassiumtetracyanidonikelate (II)	dsp^2	Square planar	Diamagnetic

None of these complexes will show stereoisomerism.

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

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

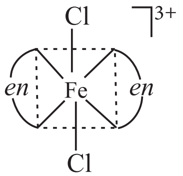
$\therefore$ $x = +3$

Oxidation number of iron = +3

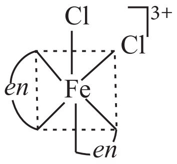
(ii) d^2sp^3 hybridisation and octahedral shape.

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

(iv) 2, *cis*- and *trans*-isomers.

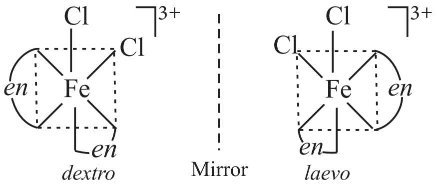


trans-bis(ethane-1,2-diamine) dichloridoiron(III) chloride



cis-bis(ethane-1,2-diamine) dichloridoiron(III) chloride

(v) *cis*-$[Fe(en)_2Cl_2]$ has optical isomer.



dextro Mirror *laevo*

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

88.

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

89. In CO both lone pair of electrons and vacant π^* orbitals are present. Hence, it acts as electron pair σ donor as well as π acceptor by back bonding. Hence, M—CO bond is stronger.

$$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} \text{CO}$$

NH_3 is electron pair donor only. Accumulation of negative charge on the metal ion takes place, hence M—NH_3 bond is weaker.

$M \leftarrow NH_3$

90. *Refer to answer 89.*

91. Because CO has vacant molecular orbitals with which it can form π-bond with metal through back donation.

92. (i) Na_2EDTA is used for estimation of hardness of water.

(ii) Wilkinson's catalyst is used as catalyst for hydrogenation.

93. *cis*-Platin is used in the treatment of cancer. EDTA is used in lead poisoning.