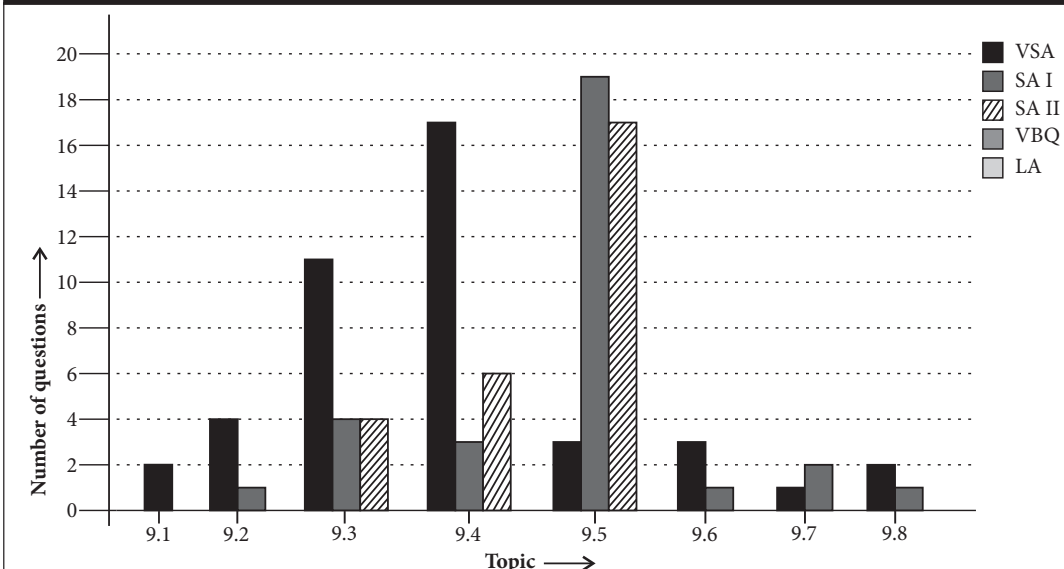


09

Coordination Compounds

9.1 Werner's Theory of Coordination Compounds	9.5 Bonding in Coordination Compounds
9.2 Definition of Some Important Terms Pertaining to Coordination Compounds	9.6 Bonding in Metal Carbonyls
9.3 Nomenclature of Coordination Compounds	9.7 Stability of Coordination Compounds
9.4 Isomerism in Coordination Compounds	9.8 Importance and Applications of Coordination Compounds

Topicwise Analysis of Last 10 Years' CBSE Board Questions



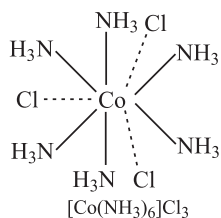
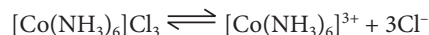
- ▶▶ Maximum total weightage is of *Bonding in Coordination Compounds*.
- ▶▶ Maximum SA I and SA II type questions were asked from *Bonding in Coordination Compounds*.
- ▶▶ Maximum VSA type questions were asked from *Isomerism in Coordination Compounds*.

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 some times by positively charged ligands.

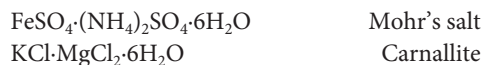
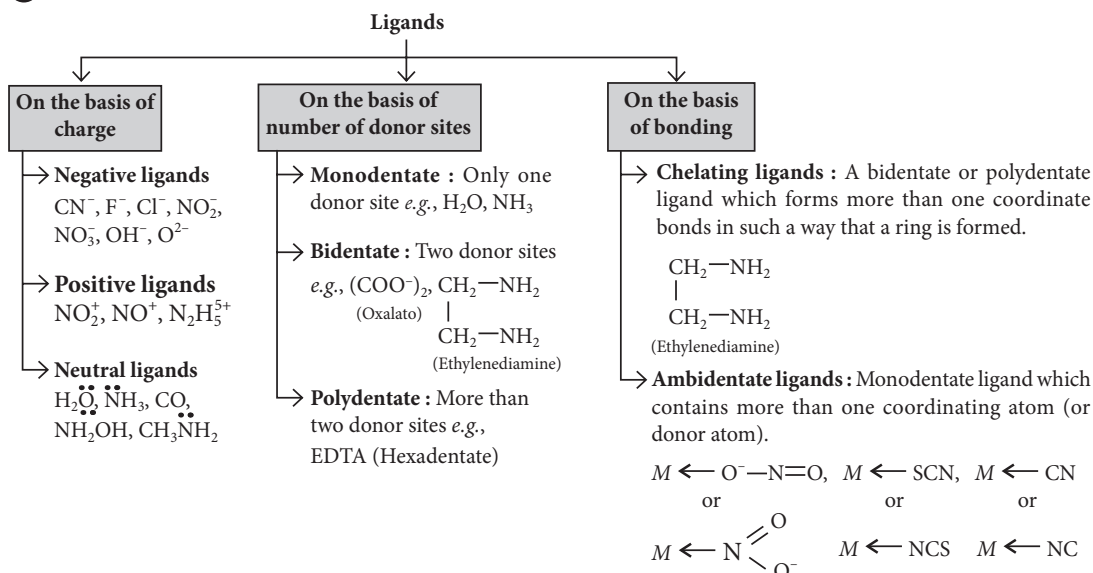
- ▶ The ionisation of the coordination compound is written as :



Representation of $\text{CoCl}_3 \cdot 6\text{NH}_3$ complex according to Werner's theory

- ▶ **Addition compounds** : These are 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.*, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ Potash alum

▶ Classification of ligands :



- ▶ **Complex compound** : A compound formed by combination of two or more simple compounds which retain its identity in solid and solution states both is called *complex compound*.
e.g., $\text{K}_4[\text{Fe}(\text{CN})_6]$ Potassium ferrocyanide
 $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ Cuprammine sulphate

- ▶ The central metal atom or ion and ligand taken together is called *co-ordination entity*. It may be positive, negative or neutral.



- ▶ The atom or ion with which definite number of ligands are attached in a definite geometry are 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).

- ▶ Molecules or ions which are bound to the central atom/ion in the co-ordination 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).

▶▶ **Homoleptic and heteroleptic complexes :**

▶ **Homoleptic complexes :** Complexes in which a metal is bound to only one kind of ligand are called *homoleptic complexes*.

e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cu}(\text{CN})_4]^{3-}$

▶ **Heteroleptic complexes :** Complexes in which the central atom is bound to different type of ligands are called *heteroleptic complexes*.

e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$, $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}]$, $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$

▶▶ **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

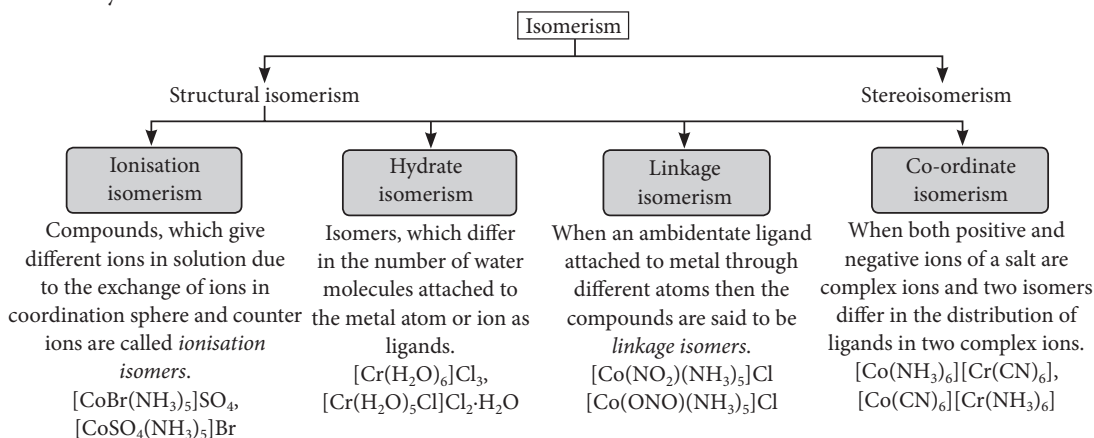
metal by a roman numeral in parentheses.

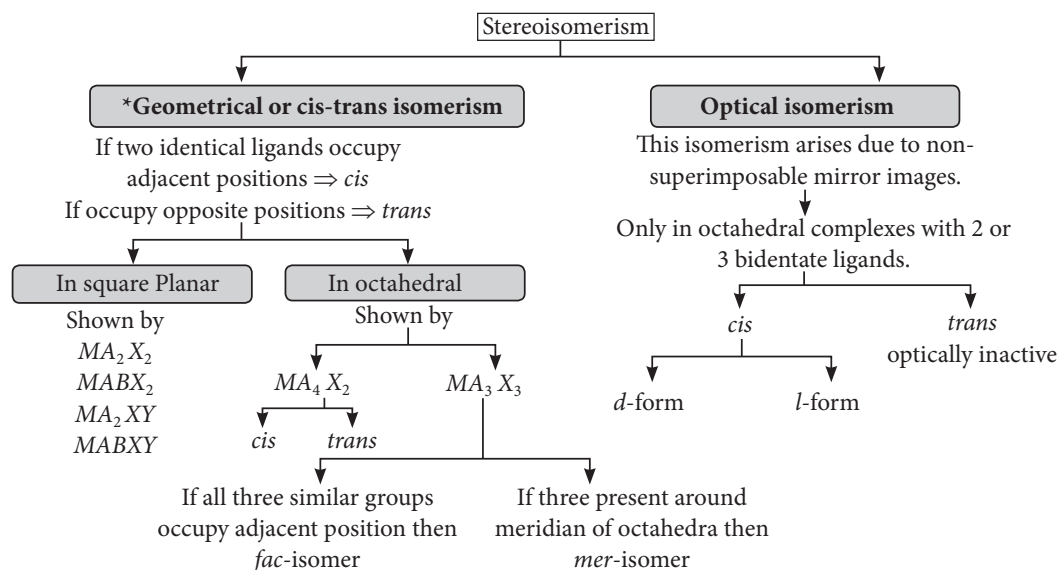
- Name of coordination compounds is started with a small letter and the complex part is written as one word.

▶ **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., $-\text{SCN}^-$ (Thiocyanato-SorThiocyanato), $-\text{NCS}^-$ (Thiocyanato-N or Isothiocyanato), $-\text{ONO}^-$ (Nitrito-O or Nitrito), $-\text{NO}_2^-$ (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).
- When the coordination sphere is anionic, name of central metal ends in *-ate*.

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





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

►► **Bonding in coordination compounds :**

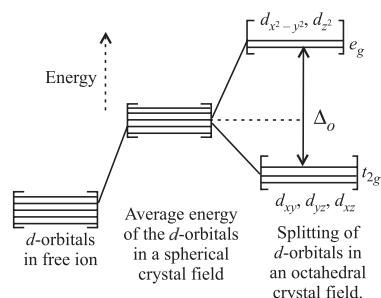
► **Valence bond theory :** It was developed by Pauling.

- 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.

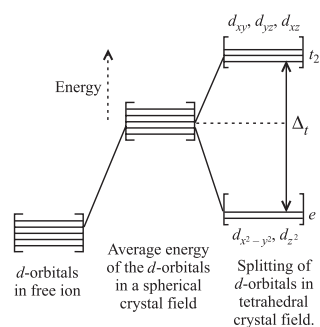
C. No.	Type of hybridisation	Geometry	Examples
2	<i>sp</i>	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	<i>sp</i> ²	Trigonal planar	$[HgI_3]^-$
4	<i>sp</i> ³	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where $X = Cl^-, Br^-, I^-$
	<i>dsp</i> ²	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$
5	<i>dsp</i> ³	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	<i>sp</i> ³ <i>d</i>	Square pyramidal	$[SbF_5]^{2-}$
6	<i>d</i> ² <i>sp</i> ³	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	<i>sp</i> ³ <i>d</i> 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 <i>d</i> -orbitals i.e., $(n - 1)d$ -orbitals.	Involves outer <i>d</i> -orbitals i.e., <i>nd</i> -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 \propto 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 can be shown as :



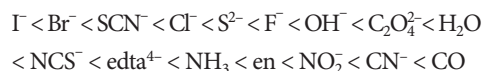
- If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.
- If $\Delta_o > P$ then pairing of electrons takes place and a low spin complex is formed.
- Crystal field splitting in tetrahedral complexes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



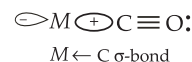
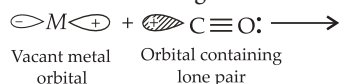
Weak field ligands $\xrightarrow{\text{Increasing order of CFSE } (\Delta_o)}$ Strong field ligands

- **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.

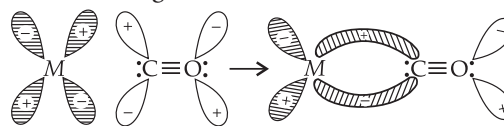
► **Bonding in metal carbonyls** :

- 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.

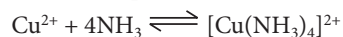


- π -overlap involving filled metal d -orbital with an empty antibonding π^*2p orbital of same CO. This results in formation of $M \rightarrow \text{C } \pi$ -bond. This is also called *back bonding*.



Filled metal d -orbital Empty π^*2p orbital of CO $M \rightarrow \text{C } \pi$ -bond

- **Stability of complexes** : The formation of the complex in a solution is a reversible and exothermic process.



$$K = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

where, K = stability constant

- ▶ Higher the value of stability constant (K), higher will be the stability of complex.
 - ▶ Higher the polarising power of metal ion and basicity of ligand, higher will be the stability of complex.
- ▶▶ **Applications of coordination compounds :**
- ▶ Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, vitamin B₁₂, 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 used as catalyst.
-

Previous Years' CBSE Board Questions

9.1 Werner's Theory of Coordination Compounds

VSA (1 mark)

- When a co-ordination compound $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is mixed with AgNO_3 , 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex.
(1/2, Delhi 2016)
- When a coordination compound $\text{CoCl}_3 \cdot 6\text{NH}_3$ 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)

- What do you understand by 'denticity of a ligand'?
(Foreign 2011)
- Giving a suitable example, explain the following: Ambidentate ligand
(1/3, AI 2009)
- What is meant by chelate effect? (1/3, AI 2009C)
- What is a ligand? Give an example of a bidentate ligand.
(1/3, Delhi 2008)

SA I (2 marks)

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

9.3 Nomenclature of Coordination Compounds

VSA (1 mark)

- When a co-ordination compound $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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)

- Write the IUPAC name of the complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.
(1/3, AI 2014)
- Write down the formula of : Tetraammineaquachloridocobalt(III)chloride.
(AI 2012C)
- Name the following coordination compound : $\text{K}_3[\text{CrF}_6]$
(Foreign 2011)
- Write the IUPAC name of $[\text{PtCl}(\text{NH}_2\text{CH}_3)(\text{NH}_3)_2]\text{Cl}$.
(Delhi 2011C, 2010C)
- Write the IUPAC name of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$.
(AI 2011C)
- Write the IUPAC name of $[\text{Cr}(\text{NH}_3)_6[\text{Co}(\text{CN})_6]]$.
(AI 2011C)
- Write the IUPAC name of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. (Atomic no. of Co = 27)
(Delhi 2010C)
- Using the IUPAC norms, write the systematic name of following : $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$
(Delhi 2008C)
- Using the IUPAC norms, write the systematic name of the following : $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$
(Delhi 2008C)

SA I (2 marks)

- (i) Write down the IUPAC name of the following complex : $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]\text{Cl}$ (en = ethylenediamine)
(ii) Write the formula for the following complex : Pentaamminenitrito-O-cobalt (III).
(Delhi 2015)
- Using IUPAC norms write the formulae for the following coordination compounds :
(i) Hexaamminecobalt(III)chloride
(ii) Potassiumtetrachloridonickelate(II)
(AI 2015)
- (i) Write down the IUPAC name of the following complex. $[\text{Cr}(\text{en})_3]\text{Cl}_3$
(ii) Write the formula for the following complex. Potassium trioxalato chromate (III)
(Foreign 2015)

21. Name the following coordination compounds according to IUPAC system of nomenclature :

- (i) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
 (ii) $[\text{CrCl}_2(\text{en})_2]\text{Cl}$, (*en* = ethane - 1,2-diamine)
 (Delhi 2010)

SA II (3 marks)

22. Write the IUPAC name of the following :

- (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (ii) $[\text{NiCl}_4]^{2-}$
 (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (AI 2015C)

23. Write down the IUPAC name for each of the following complexes :

- (i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (ii) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (iii) $[\text{NiCl}_4]^{2-}$ (Delhi 2014C)

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

- (i) $\left[\text{Co} \left(\begin{array}{c} \text{COO} \\ | \\ \text{COO} \end{array} \right)_3 \right]^{3-}$ (ii) $[\text{Cr}(\text{CO})_6]$
 (iii) $[\text{PtCl}_3(\text{C}_2\text{H}_4)]$
 (At. nos. Cr = 25, Co = 27, Pt = 78) (AI 2014C)

25. Write the IUPAC names of the following coordination compounds :

- (i) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$
 (ii) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (iii) $[\text{CoBr}_2(\text{en})_2]^+$, (*en* = ethylenediamine)
 (Delhi 2013)

9.4 Isomerism in Coordination Compounds

VSA (1 mark)

26. Draw one of the geometrical isomers of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ which is optically active.

(1/3, Delhi 2016)

27. Draw one of the geometrical isomers of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ which is optically inactive.

(AI 2016)

28. Draw the geometrical isomers of complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

(1/3, Delhi 2015, 2007)

29. Write down the IUPAC name of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$. What type of isomerism is shown by this complex?

(AI 2015)

30. Draw the geometrical isomers of complex $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$.

(1/3, Foreign 2015)

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

(1/3, AI 2014)

32. What type of isomerism is shown by the following complex :



33. What type of isomerism is exhibited by the following complex :



34. What type of isomerism is exhibited by the complex $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$?

(Foreign 2014)

35. Indicate the types of isomerisms exhibited by the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$. (At no. Co = 27)

(AI 2012C)

36. Give IUPAC name of ionisation isomer of $[\text{Ni}(\text{NH}_3)_3\text{NO}_3]\text{Cl}$.

(AI 2012C)

37. Give an example of linkage isomerism.

(Delhi 2010)

38. Give an example of coordination isomerism.

(Delhi 2010)

39. Give an example of ionization isomerism.

(Delhi 2010)

40. Giving a suitable example, explain the following: Linkage isomerism

(1/3, AI 2009)

41. Square planar complexes (of MX_2L_2 type) with coordination number of 4 exhibit geometrical isomerism whereas tetrahedral complexes with similar composition, do not. Why?

(1/3, Delhi 2009C)

SA I (2 marks)

42. Name the following coordination compounds and draw their structures.

- (i) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
 (ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
 (At. No. Co = 27, Pt = 78) (Foreign 2011)

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

- (i) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$
 (ii) $[\text{Co}(\text{en})_3]^{3+}$ (Foreign 2011)

44. Write the name and draw the structures of each of the following complex compounds :

- (i) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$
 (ii) $[\text{Pt}(\text{NH}_3)_4][\text{NiCl}_4]$ (2/5, Delhi 2007)

SA II (3 marks)

45. Indicate the types of isomerism exhibited by the following complexes :
- $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$
 - $[\text{Co}(\text{en})_3]\text{Cl}_3$ (*en* = ethylene diamine)
 - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (Delhi 2015C)
46. Write the IUPAC name of the complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$. What type of isomerism does it exhibit? (Delhi 2014)
47. Draw the structures of optical isomers of each of the following complex ions :
 $[\text{Cr}(\text{C}_2\text{O}_4)]^{3-}$, $[\text{PtCl}_2(\text{en})_2]^{2+}$, $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$ (Delhi 2014C)
48. Write the types of isomerism exhibited by the following complexes :
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$
 - $[\text{Co}(\text{en})_3]^{3+}$
 - $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ (Delhi 2013)
49. Name the following coordination entities and draw the structures of their stereoisomers :
- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (*en* = ethane-1,2-diamine)
 - $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$
 - $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
- (Atomic numbers Cr = 24, Co = 27) (AI 2012)
50. Write the structures and names of all the stereoisomers of the following compounds :
- $[\text{Co}(\text{en})_3]\text{Cl}_3$
 - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 - $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (AI 2011)

9.5 Bonding in Coordination Compounds

VSA (1 mark)

51. Why is $[\text{NiCl}_4]^{2-}$ paramagnetic but $[\text{Ni}(\text{CO})_4]$ is diamagnetic? (At. no. : Cr = 24, Co = 27, Ni = 28) (1/3, AI 2014)
52. Explain the following term giving a suitable example :
Crystal field splitting in an octahedral field. (1/3, AI 2011)
53. Giving a suitable example, explain the following :
Crystal field splitting (1/3, AI 2009)

SA I (2 marks)

54. For the complex $[\text{Fe}(\text{CN})_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex. (At. number : Fe = 26). (2/3, Delhi 2016)
55. For the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, write the hybridization magnetic character and spin of the complex. (At number Fe = 26) (2/3, AI 2016)
56. (i) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.
 (ii) Write the hybridization and magnetic behaviour of the complex $[\text{Ni}(\text{CO})_4]$. (At. no. of Ni = 28) (2/3, Delhi 2015)
57. Write the hybridization and shape of the following complexes :
 (i) $[\text{CoF}_6]^{3-}$ (ii) $[\text{Ni}(\text{CN})_4]^{2-}$
 (Atomic number : Co = 27, Ni = 28) (AI 2015)
58. Write the state of hybridization, shape and IUPAC name of the complex $[\text{CoF}_6]^{3-}$. (Atomic no. of Co = 27) (Foreign 2014)
59. Write the state of hybridization, shape and IUPAC name of the complex $[\text{Ni}(\text{CN})_4]^{2-}$. (Atomic no. of Ni = 28) (Foreign 2014)
60. Write the state of hybridization, shape and IUPAC name of the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$. (Atomic no. of Co = 27) (Foreign 2014)
61. Give the formula of each of the following coordination entities :
- Co^{3+} ion is bound to one Cl^- , one NH_3 molecule and two bidentate ethylene diamine (*en*) molecules.
 - 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)
62. State a reason for each of the following situations :
- Co^{2+} is easily oxidised to Co^{3+} in presence of a strong ligand.
 - The molecular shape of $\text{Ni}(\text{CO})_4$ is not the same as that of $[\text{Ni}(\text{CN})_4]^{2-}$. (2/3, Delhi 2012)
63. Using valence bond theory, explain the geometry and magnetic behaviour of $[\text{Co}(\text{NH}_3)_6]^{3+}$. (At. no. of Co = 27) (2/3, Delhi 2012C)
64. Using valence bond theory of complexes, explain the geometry and magnetic nature of $[\text{Ni}(\text{CN})_4]^{2-}$. (At. no. of Ni = 28) (2/3, Delhi 2012C)

65. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic. Explain (At. no. Fe = 26) (Delhi 2012C)
66. Give the name, the stereochemistry and the magnetic behaviour of the following complexes :
(i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (ii) $\text{K}_2[\text{Ni}(\text{CN})_4]$
(Foreign 2011)
67. Describe the shape and magnetic behaviour of following complexes :
(i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (ii) $[\text{Ni}(\text{CN})_4]^{2-}$.
(At. no. Co = 27, Ni = 28) (Delhi 2010)
68. Using the valence bond theory predict the geometry and magnetic behaviour of $[\text{CoF}_6]^{3-}$.
[At. no. of Co = 27] (Delhi 2010C)
69. Describe the type of hybridization, shape and magnetic property of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.
[Given : At. no. of Co = 27] (2/3, Delhi 2009C)
70. Write the IUPAC name and indicate the shape of the complex ion $[\text{Co}(\text{en})_2\text{Cl}(\text{ONO})]^+$.
[At. no. Co = 27] (2/3, Delhi 2009C)
71. Using the valence bond approach, deduce the shape and magnetic character of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion.
[Given : Atomic no. of Co = 27] (Delhi 2008C)
72. Explain as to how the two complexes of nickel, $[\text{Ni}(\text{CN})_4]^{2-}$ but $\text{Ni}(\text{CO})_4$ have different structures but do not differ in their magnetic behaviour. (Ni = 28) (2/3, Delhi 2008)
- SA II (3 marks)**
73. For the complex $[\text{NiCl}_4]^{2-}$, write
(i) the IUPAC name
(ii) the hybridization type
(iii) the shape of the complex.
(Atomic no. of Ni = 28) (AI 2013)
74. 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)
75. Write the name, the structure and the magnetic behaviour of each one of the following complexes :
(i) $[\text{Pt}(\text{NH}_3)\text{Cl}(\text{NO}_2)]$ (ii) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
(iii) $\text{Ni}(\text{CO})_4$
(At. nos. Co = 27, Ni = 28, Pt = 78)
(Delhi 2012)
76. Name the following coordination entities and describe their structures.
(i) $[\text{Fe}(\text{CN})_6]^{4-}$ (ii) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$
(iii) $[\text{Ni}(\text{CN})_4]^{2-}$ (AI 2012)
77. Write the name, stereochemistry and magnetic behaviour of the following : (At. nos. Mn = 25, Co = 27, Ni = 28)
(i) $\text{K}_4[\text{Mn}(\text{CN})_6]$ (ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
(iii) $\text{K}_2[\text{Ni}(\text{CN})_4]$ (Delhi 2011)
78. For the complex $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$, identify the following :
(i) Oxidation number of iron
(ii) Hybrid orbitals and shape of the complex
(iii) Magnetic behaviour of the complex
(iv) Number of its geometrical isomers
(v) Whether there may be optical isomer also.
(vi) Name of the complex. (Delhi 2011, 2009)
79. Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities :
(i) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (ii) $[\text{Co}(\text{en})_3]\text{Cl}_3$
(iii) $\text{K}_2[\text{Ni}(\text{CN})_4]$ (AI 2011)
80. Write the name, the state of hybridization, the shape and the magnetic behaviour of the following complexes :
 $[\text{CoCl}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$
(At. no. : Co = 27, Ni = 28, Cr = 24) (AI 2010)
81. Write the IUPAC name, deduce the geometry and magnetic behaviour of the complex $\text{K}_4[\text{Mn}(\text{CN})_6]$.
[Atomic no. of Mn = 25] (AI 2010C)
82. Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved :
(i) $[\text{CoF}_4]^{2-}$
(ii) $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$
(iii) $[\text{Ni}(\text{CO})_4]$
(Atomic number : Co = 27, Cr = 24, Ni = 28)
(Delhi 2009)
83. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :
 $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $\text{Ni}(\text{CO})_4$
(At. nos. : Co = 27, Cr = 24, Ni = 28) (AI 2009)

84. Explain the following :

- Low spin octahedral complexes of nickel are not known.
- The π -complexes are known for transition elements only.
- CO is a stronger ligand than NH_3 for many metals. (AI 2009)

85. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :

- $[\text{Ni}(\text{CN})_4]^{2-}$ (ii) $[\text{NiCl}_4]^{2-}$
 - $[\text{CoF}_6]^{3-}$
- [At. nos. : Ni = 28; Co = 27] (AI 2009)

86. What will be the correct order for the wave lengths of absorption in the visible region for the following :

- $$[\text{Ni}(\text{NO}_2)_6]^{4+}, [\text{Ni}(\text{NH}_3)_6]^{2+}, [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$$
- (AI 2008)

87. (a) What is the basis of formation of the spectrochemical series?

- (b) Draw the structures of geometrical isomers of the following coordination complexes :
 $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ and $[\text{CoCl}_2(\text{en})_2]^+$
 (en = ethylenediamine and atomic number of Co is 27) (AI 2008)

88. Describe for any two of the following complex ions, the type of hybridization, shape and magnetic property :

- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{NiCl}_4]^{2-}$
- [At. Nos. Fe = 26, Co = 27, Ni = 28] (AI 2007)

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)

SA I (2 marks)

92. Draw the structures of :

- $\text{Ni}(\text{CO})_4$ (ii) $\text{Fe}(\text{CO})_5$
- (AI 2007)

9.7 Stability of Coordination Compounds

VSA (1 mark)

93. Which of the following is more stable complex and why?

- $$[\text{Co}(\text{NH}_3)_6]^{3+} \text{ and } [\text{Co}(\text{en})_3]^{3+}$$
- (Delhi 2014)

SA I (2 marks)

94. How is the stability of a co-ordination compound in solution decided? How is the dissociation constant of a complex defined? (AI 2012C)

95. What do you understand by stepwise stability constant and overall stability constant of a coordination compound? How are these two constants related? (AI 2011C)

9.8 Importance and Applications of Coordination Compounds

VSA (1 mark)

96. Give two examples of coordination compounds used in industries. (1/3, Delhi 2012C)

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

SA I (2 marks)

98. Describe with an example of each, the role of coordination compounds in :

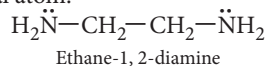
- Biological systems
- Analytical chemistry
- Medicinal chemistry (Delhi 2009C)

Detailed Solutions

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

2. Structural formula : $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

3. **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.



4. **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.

5. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion. It is said to be a chelate ligand. Chelating ligands form more stable complexes than monodentate analogs. This is called chelating effect.

6. The ions or molecules bonded to the central atom in the coordination entity are called ligands. Ethylene diammine is a bidentate ligand.

7. (i) Refer to answer 4.
(ii) Refer to answer 3.

8. IUPAC name of the complex $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ is : pentaquachloridochromium (III) chloride.

9. IUPAC name of the complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is tetraamminedichloridochromium (III) chloride.

10. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{Cl})]\text{Cl}_2$

11. Potassium hexafluoridochromate(III).

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

13. Tetraamminedichloridoplatinum (IV) chloride.

14. Hexaamminechromium(III) hexacyanocobaltate(III).

15. Pentaamminechloridocobalt(III) chloride.

16. Tetraamminechloridonitrito-N-cobalt(III) chloride.

17. Hexaamminecobalt(III)hexacyanochromate(III)

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

(ii) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

19. (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

(ii) $\text{K}_2[\text{NiCl}_4]$

20. Tris(ethylenediamine)chromium(III) chloride

(ii) $\text{K}_3[\text{Cr}(\text{ox})_3]$

21. (i) Hexaamminecobalt(III) chloride

(ii) Tetrachloridonickelate(II)ion

(iii) Potassiumhexacyanoferrate(III)

22. (i) Tetraammineaquachloridocobalt(III) chloride

(ii) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride

23. (i) Pentaamminechloridocobalt(III)chloride

(ii) Refer to answer 22(iii).

(iii) Refer to answer 22(ii).

24. (i) Trioxalatocobaltate (III)

(ii) Hexacarbonylchromium (0)

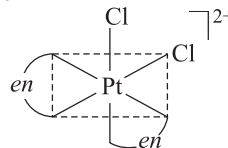
(iii) Trichloroetheneplatinum (III)

25. (i) Triamminetrichloridochromium (III)

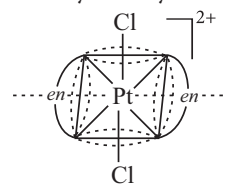
(ii) Refer to answer 22(iii).

(iii) Dibromidobis(ethane-1,2-diamine)cobalt (III) ion

26. *cis*-isomer of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ is optically active

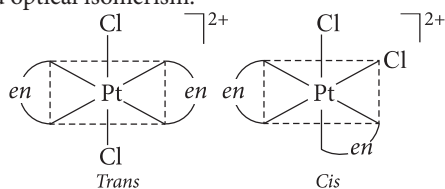


27. *Trans*-isomer is optically inactive due to the presence of plane of symmetry.

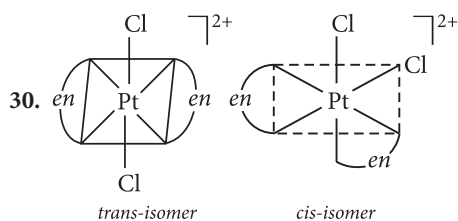
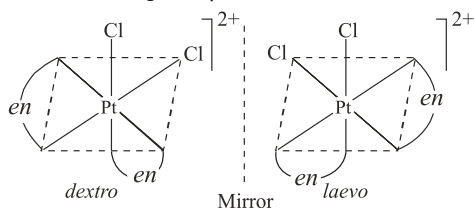


28.

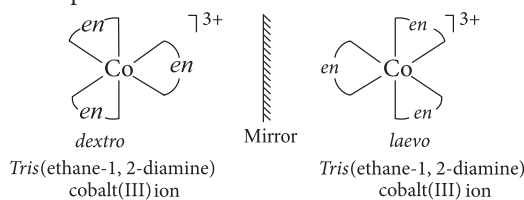
29. IUPAC name - Dichloridobis(ethane-1,2-diamine) platinum(IV) ion. This complex shows geometrical and optical isomerism.



cis-isomer is optically active.



31. Optical isomerism :



32. **Coordination isomerism** : Its coordination isomer $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, in which NH_3 ligands are bound to Cr^{3+} and CN ligands to Co^{3+} .

33. Ionisation isomerism : $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

34. Linkage isomerism : $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ and $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$

35. (i) Ionisation isomers :

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ and $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_2)(\text{NO}_3)$

(ii) Linkage isomers :

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{NO}_3)_2$

36. Ionisation isomer of $[(\text{Ni}(\text{NH}_3)_3\text{NO}_3)\text{Cl}]$ is $[\text{Ni}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$. The IUPAC name of this complex is triamminechloridonickel(II) nitrate.

37. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$

38. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

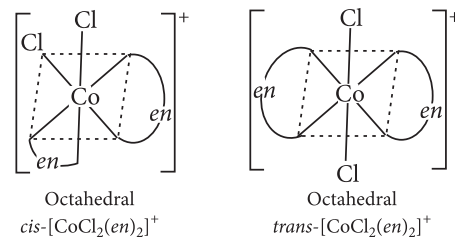
39. $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$

40. **Linkage isomerism** : Linkage isomerism arises in a coordination compound containing ambidentate ligand.

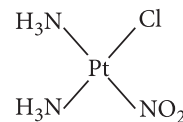
A simple example is provided by complexes containing the thiocyanate ligand, NCS^- which may bind through the nitrogen to give $M\text{-NCS}$ or through sulphur to give $M\text{-SCN}$. This behaviour was seen in the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen ($-\text{ONO}$), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-\text{NO}_2$).

41. The tetrahedral complexes do not show geometrical isomerism because the relative positions of the atoms with respect to each other will be the same.

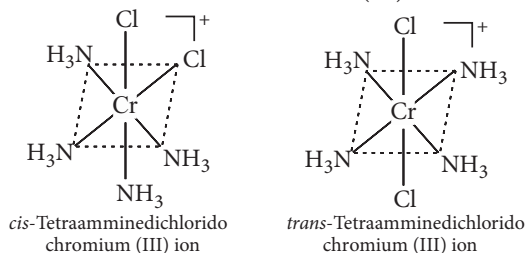
42. (i) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride.



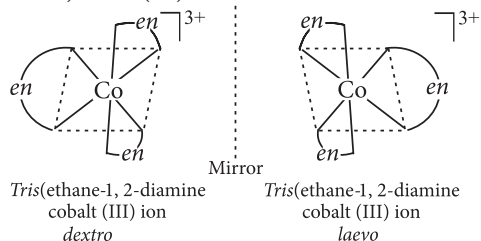
(ii) Diamminechloridonitrito-N-platinum (II)



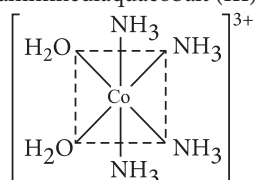
43. (i) Geometrical isomers of $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ - Tetraamminedichloridochromium (III) ion



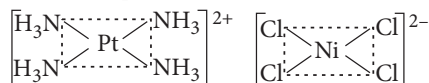
(ii) Optical isomers of $[\text{Co}(\text{en})_3]^{3+}$ - Tris(ethane-1,2-diamine)cobalt (III) ion.



44. (i) Tetraamminediaquacobalt (III) chloride.



(ii) Tetraammineplatinum(II)tetrachloridonickelate(II)



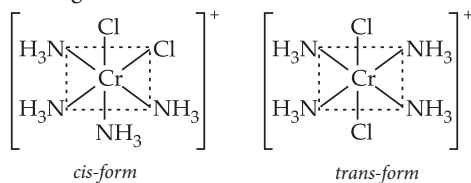
45. (i) Refer to answer 34.

(ii) Refer to answer 43 (ii).

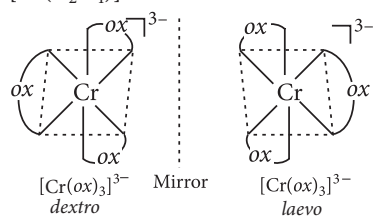
(iii) Refer to answer 28.

46. Tetraamminedichloridochromium(III) ion.

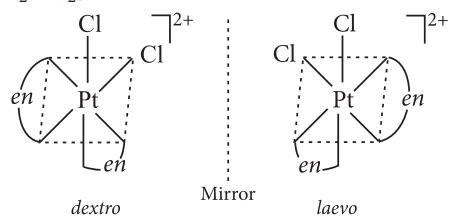
It exhibits geometrical isomerism.



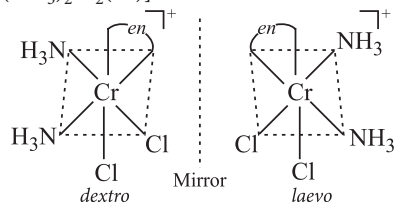
47. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$:



$[\text{PtCl}_2(\text{en})_2]^{2+}$:



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



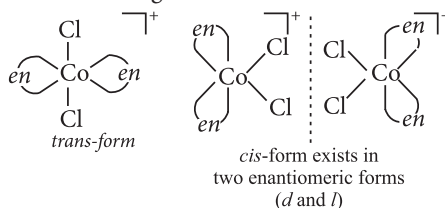
48. (i) Refer to answer 33.

(ii) Refer to answer 31.

(iii) Refer to answer 32.

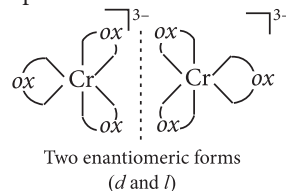
49. (i) $[\text{CoCl}_2(\text{en})_2]^+$: Dichloridobis(ethane-1,2-diamine)cobalt(III) ion

It will exist in two geometrical isomeric forms :



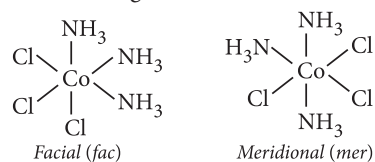
(ii) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$: Trioxalatochromium(III) ion

It will show optical isomerism.



(iii) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$: Triamminetrichloridocobalt(III)

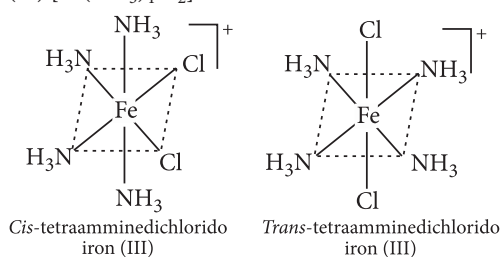
It will exist in two geometrical isomeric forms:



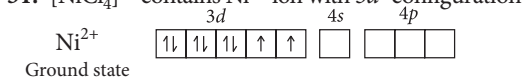
50. (i) $[\text{Co}(\text{en})_3]\text{Cl}_3$: Refer to answer 43(ii).

(ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$: Refer to answer 28.

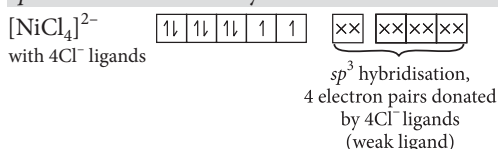
(iii) $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$



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

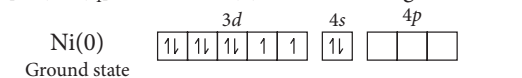


Cl^- is a weak field ligand. Hence, outer 4s and 4p-orbitals are used in hybridisation.

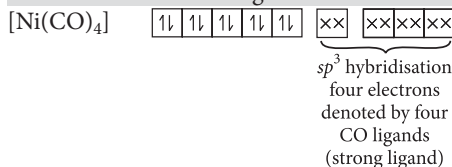


It has two unpaired electrons hence, it is paramagnetic.

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

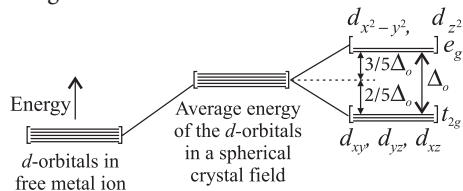


CO is a strong field ligand hence, 4s-electrons will shift to 3d-orbital making 4s-orbital vacant.



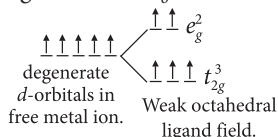
The complex has all paired electrons hence, it is diamagnetic.

52. 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.

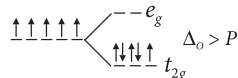
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ contains $\text{Mn}^{2+} - 3d^5$ configuration
C.N. = 6, octahedral structure, H_2O is a weak field ligand, hence $\Delta_o < P$



Electrons enter into e_g orbital before pairing. It has five unpaired electrons.

$[\text{Mn}(\text{CN})_6]^{4-}$ contains Mn^{2+} ion $3d^5$ configuration.

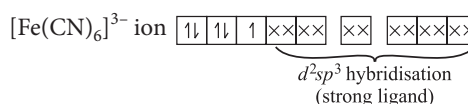
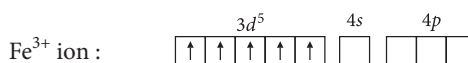
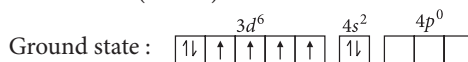
C.N. = 6, octahedral geometry, CN^- is strong field ligand, $\Delta_o > P$



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

53. Refer to answer 52.

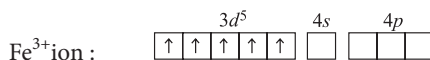
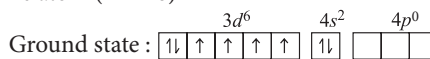
54. Fe atom ($Z = 26$)



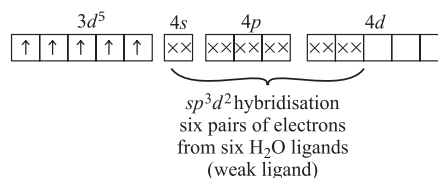
The complex ion has inner orbital octahedral geometry (low spin) and is paramagnetic due to the presence of one unpaired electron.

55. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$:

Fe atom ($Z = 26$)



$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$:

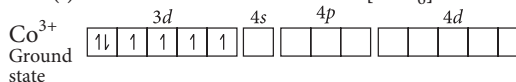


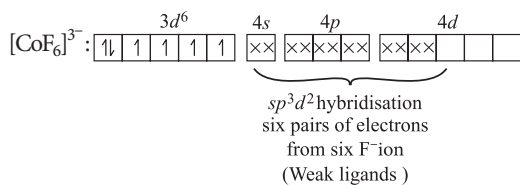
The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

56. (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.

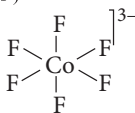
(ii) Refer to answer 51.

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



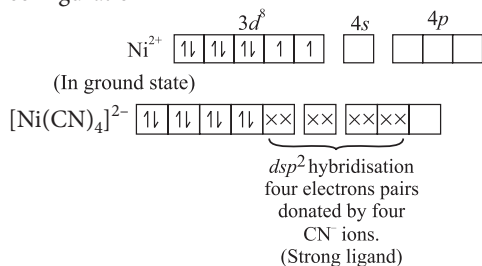


Structure – Outer orbital octahedral complex



Nature – Paramagnetic

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



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

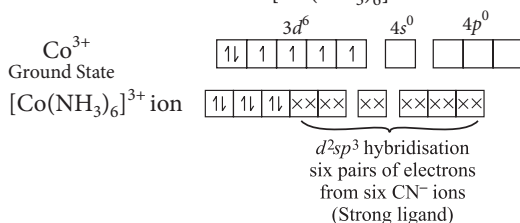
58. Refer to answer 57(i).

IUPAC Name : Hexafluoridocobaltate(III) ion

59. Refer to answer 57(ii).

IUPAC name : Tetracyanonickelate(II) ion

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



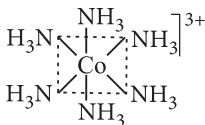
Hybridisation – d^2sp^3

Structure – Octahedral

(low spin)

Nature – Diamagnetic

IUPAC name : Hexaamminecobalt(III) ion



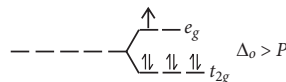
61. (i) $[\text{Co}(\text{en})_2\text{Cl}(\text{NH}_3)]^{2+}$

Amminechloridobis(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) $[\text{Ni}(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$: Diaquadioxalato nickelate(II) ion
In the presence of weak *ox* and H_2O ligand, Ni(II) forms high spin complex (sp^3d^2 hybridisation). It is paramagnetic.

62. (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 57(ii) and 51.

63. Refer to answer 60.

64. Refer to answer 57 (ii).

65. In presence of CN^- , the $3d$ 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 , $3d$ electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital octahedral complex containing five unpaired electrons. Hence, it is strongly paramagnetic.

66. (i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$: Pentaamminechlorido cobalt (III) chloride.

$\text{Co}(\text{III})$: $[\text{Ar}]3d^64s^0$: d^2sp^3 hybridisation leads to octahedral shape.

Magnetic behaviour : Diamagnetic.

Stereochemistry : Complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ do not exhibit geometrical and optical isomerism.

(ii) $\text{K}_2[\text{Ni}(\text{CN})_4]$: Potassiumtetracyanonickelate(II)
 $\text{Ni}(\text{II})$: $[\text{Ar}]3d^84s^0$ – dsp^2 hybridisation leads to square planar shape.

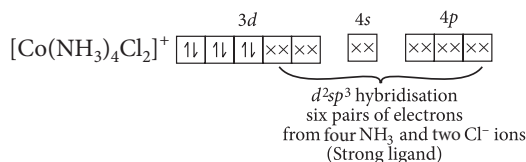
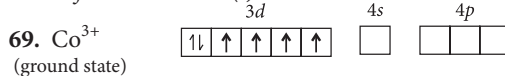
Magnetic behaviour : Diamagnetic.

Stereochemistry : Complex $[\text{Ni}(\text{CN})_4]$ do not exhibit geometrical isomerism and optical isomerism because all the possible arrangement are equivalent.

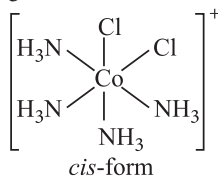
67. (i) Refer to answer 60.

(ii) Refer to answer 57(ii).

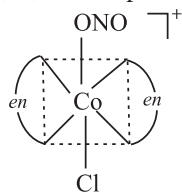
68. Refer to answer 57(i).



In this complex, Co is d^2sp^3 hybridised because NH_3 is strong field ligand.



70. IUPAC name : Chloridobis(ethylenediamine) nitrito-O-cobalt(III) ion. Shape is octahedral.

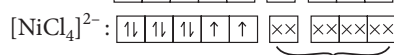
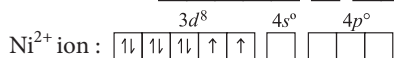
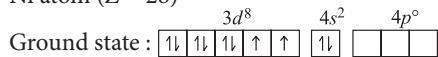


71. Refer to answer 60.

72. Refer to answers 57 (ii) and 56 (ii).

Thus, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ have different structures but same magnetic behaviour.

73. (i) Tetrachloridonickelate(II) ion
Ni atom ($Z = 28$)



sp^3 hybridisation
four pairs of electrons
from four Cl^- ligands
(weak ligands)

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

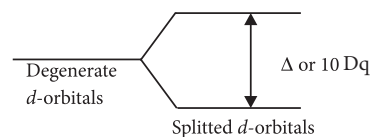
74. (i) The difference of energy between two states of splitted d -orbitals is called crystal field splitting energy. It is denoted by Δ or $10 Dq$.

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

77.

Formulae	Name of the Complex	Hybridisation of metal ion involved	Geometry of complex (stereochemistry)	Magnetic behaviour
$\text{K}_4[\text{Mn}(\text{CN})_6]$	Potassium hexacyanomanganate(II)	d^2sp^3	Octahedral	Paramagnetic
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Pentaamminechloridocobalt(III) chloride	d^2sp^3	Octahedral	Diamagnetic
$\text{K}_2[\text{Ni}(\text{CN})_4]$	Potassiumtetracyanonickelate (II)	dsp^2	Square planar	Diamagnetic

None of these complexes will show stereoisomerism.



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

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

Diamminechloridonitrito-N-platinum(II)

It is square planar and diamagnetic.

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

It is octahedral and diamagnetic.

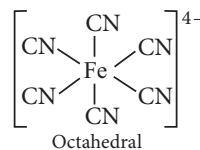
(iii) $\text{Ni}(\text{CO})_4$: Tetracarbonylnickel(0)

It is tetrahedral and diamagnetic

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

Hybridisation - d^2sp^3

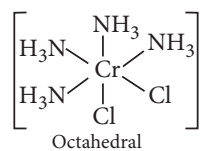
Structure : Inner orbital octahedral complex



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

Hybridisation - d^2sp^3

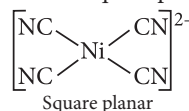
Structure : Inner orbital octahedral complex



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

Hybridisation - dsp^2

Structure - Square planar



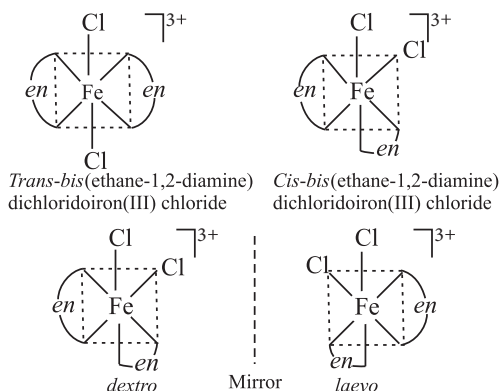
78. (i) $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$

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

Oxidation number of iron = 3

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

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

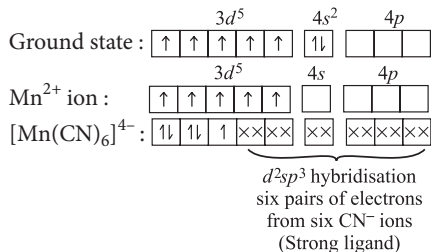
(iv) 2, *cis* and *trans* isomers.(v) *cis*- $[\text{Fe}(\text{en})_2\text{Cl}_2]$ has optical isomer.(vi) dichlorido*bis*(ethane-1,2-diamine)iron(III) chloride

79.

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

80. $[\text{CoCl}_4]^{2-}$ Tetrachloridocobaltate(II) ion $[\text{Ni}(\text{CN})_4]^{2-}$ Tetracyanonickelate(II) ion $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$ Diaquadioxalatochromate(III) ion

Complexes	Hybridisation	Shape	Magnetic behaviour
$[\text{CoCl}_4]^{2-}$	sp^3	Tetrahedral	Paramagnetic
$[\text{Ni}(\text{CN})_4]^{2-}$	dsp^2	Square planar	Diamagnetic
$[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$	d^2sp^3	Octahedral	Paramagnetic

81. Mn atom ($Z = 25$)

IUPAC name : Potassium hexacyanomanganate (II)

Geometry : Octahedral

No. of unpaired electrons, $n = 1$

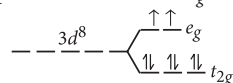
Magnetic behaviour : paramagnetic.

82.

Complexes	Shape	Magnetic behaviour	Hybridisation
$[\text{CoF}_4]^{2-}$	Tetrahedral	Paramagnetic	sp^3
$[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$	Octahedral	Paramagnetic	d^2sp^3
$[\text{Ni}(\text{CO})_4]$	Tetrahedral	Diamagnetic	sp^3

83.

Complexes	Magnetic behaviour	Hybridisation	Shape
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Diamagnetic	d^2sp^3	Octahedral
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Paramagnetic	d^2sp^3	Octahedral
$[\text{Ni}(\text{CO})_4]$	Diamagnetic	sp^3	Tetrahedral

84. (i) Nickel forms octahedral complexes mainly in +2 oxidation state which has $3d^8$ configuration. In presence of strong field ligand also it has two unpaired electrons in e_g orbital.

Hence, it does not form low spin octahedral complexes.

(ii) The transition metals/ions have empty d orbitals into which the electron pairs can be donated by ligands containing π electrons.For example : $\text{CH}_2=\text{CH}_2$ and C_6H_6 , C_5H_5^- .(iii) Co is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π -bond with metal through back donation.

85.

Complexes	Magnetic behaviour	Hybridisation	Shape
$[\text{Ni}(\text{CN})_4]^{2-}$	Diamagnetic	dsp^2	Square planar
$[\text{NiCl}_4]^{2-}$	Paramagnetic	sp^3	Tetrahedral
$[\text{CoF}_6]^{3-}$	Paramagnetic	sp^3d^2	Octahedral

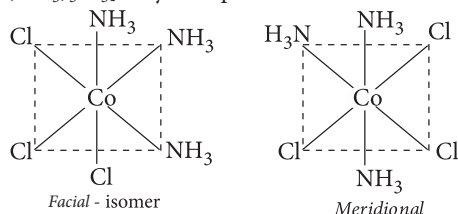
86. All the complex ions are derived from Ni^{2+} ion with different ligands. From the position of the ligands in the spectrochemical series the order of field strength is $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$

That means Δ_o for NO_2^- is maximum and so it would absorb the radiation of shorter wavelength having high energy. So, the order of absorption of the correct wavelengths is

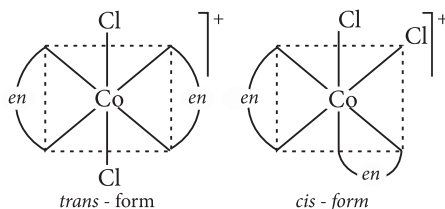


87. (a) The arrangement of ligands in order of their increasing field strength *i.e.* increasing crystal field splitting energy (CFSE) value is called spectrochemical series.

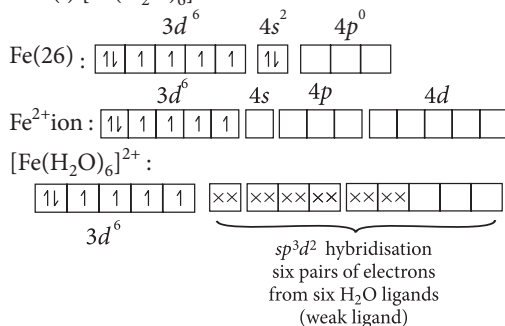
(b) (i) The facial and meridional isomers of $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ may be represented as



(ii) $[\text{CoCl}_2(\text{en})_2]^+$ ion exists in two geometrical isomers as shown below :



88. (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



Hybridization - sp^3d^2

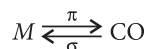
Shape - Octahedral.

Magnetic property - Paramagnetic.

(ii) Refer to answer 60.

(iii) $[\text{NiCl}_4]^{2-}$: Refer to answer 51.

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, $M-\text{CO}$ bond is stronger.



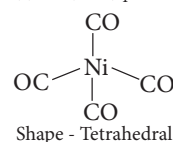
NH_3 is electron pair donor only. Accumulation of negative charge on the metal ion takes place, hence $M-\text{NH}_3$ bond is weaker.

$M \leftarrow \text{NH}_3$

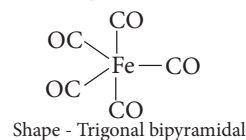
90. Refer to answer 89.

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

92. (i) $\text{Ni}(\text{CO})_4$:



(ii) $\text{Fe}(\text{CO})_5$:



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

94. The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant for the association, quantitatively expresses the stability.

The instability constant or dissociation constant of coordination compound is defined as the reciprocal of the formation constant.

95. Stability constant of each step of complex formation reaction is called stepwise stability constant. It is denoted by K . Stability constant of overall complex formation reaction is called overall stability constant. It is denoted by β .

The stepwise and overall stability constant are therefore related as follows:

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \text{ or more generally,}$$

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots K_n$$

96. (i) EDTA is used for water softening and in purification of metals.

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

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

98.(a) **Biological systems** : Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which act as oxygen carrier is a coordination compound of iron. Vitamin B₁₂, cyanocobalamine, the anti-pernicious anaemia factor, is a coordination compound of cobalt.

(b) **Analytical Chemistry** : Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour

reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α -nitroso- β -naphthol, cupron, etc.

(c) **Medicinal Chemistry** : There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/ animal system. Thus, excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime-B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are : *cis*-platin and related compounds.

